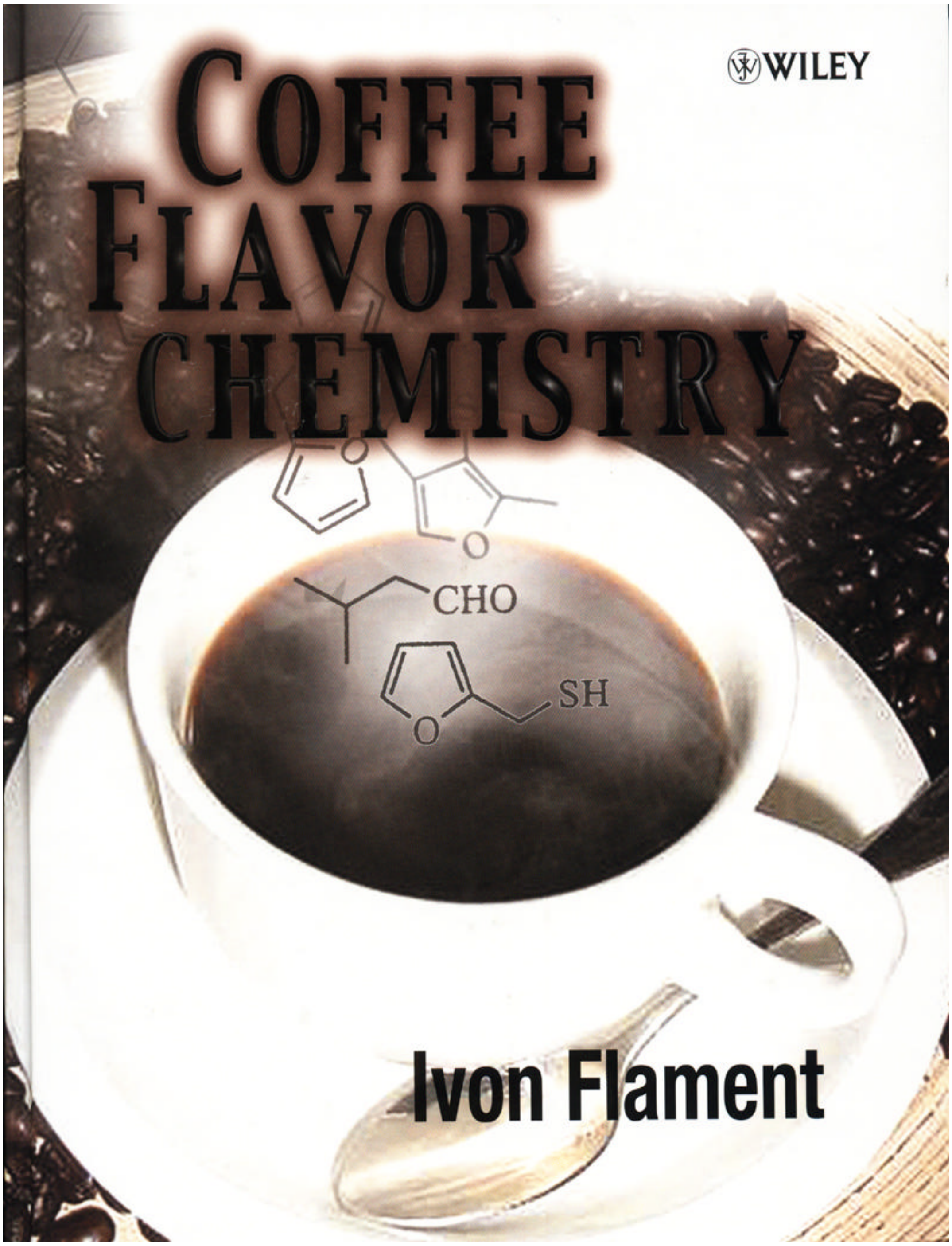

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COFFEE FLAVOR CHEMISTRY

Ivon Flament

Coffee Flavor Chemistry

Ivon Flament
Formerly of Firmenich SA, Geneva, Switzerland

With the collaboration of
Yvonne Bessière-Thomas

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Dedication

To the memory of Dr Roger Firmenich
who was convinced that research is the critical, if not the unique, key of progress and success.

To all the scientists
who perseveringly contributed to the development of the savory world of flavor chemistry

To Annie

Contents

Foreword

The distinctive flavor of coffee is certainly the principal reason for the high acceptability of the beverage prepared from roasted coffee. Even before the introduction of gas chromatography coupled with mass spectrometry Reichstein and Staudinger made an outstanding contribution by characterizing more than 70 flavor compounds (among them several key odorants) in roasted coffee. Since 1960 the list of constituents increased to 300 in green coffee, and to 850 in roasted coffee, respectively. Many natural flavor compounds were first identified in roasted coffee and were later characterized as key compounds in certain processed foods. Due to the high selectivity of the olfactory system, bioactive compounds must be evaluated by determination of odor activity values or by gas chromatography olfactory methods. Comparable to other foods the number of key odorants of roasted coffee is drastically reduced by these methods. Sensory properties of individual compounds may be changed by interaction, generating new aroma qualities or might lead to suppression of odorants. Green coffee beans contain compounds with extremely low sensory thresholds obviously formed by microorganisms during fermentation and processing. To some extent these contaminants are transferred to roasted coffee influencing flavor and quality. During roasting more than 500 compounds are formed by Strecker and Maillard reactions as predominant reactions. Specific precursors, pathways and a better insight into the fundamental chemistry leading to key flavor compounds may be elucidated by new analytical techniques in the future.

It was a great pleasure for me to read this comprehensive review on Coffee Flavor Chemistry. In my opinion it is an excellent data base for coffee flavor chemistry.

Prof. Dr. Roland Tressl
Technischen Universität, Berlin

Preface

After nearly 40 years of activity in perfume and flavor research, the author has considered that a detailed description of coffee flavor volatile constituents could make people concretely acquainted with the identity and the organoleptic properties of the hundreds of constituents they unconsciously swallow every day. From the simple to the more complex structures, each compound brings a contribution to the pleasure felt when drinking a cup of good coffee. Through this book, organic and analytical chemists, quality control specialists and flavorists, will have at their disposal information on the nearly 300 and 850 volatile constituents which have been respectively identified in green and roast coffee.

This monograph deals essentially with the relatively volatile constituents contributing to the smell of green coffee and to the flavor of roasted coffee. As the term flavor means a combination of the smell and of the taste sensations, it was logical to mention some non-volatile constituents that resist the roasting conditions and consequently participate more or less to the organoleptic qualities of the final beverage. This is particularly true for multifunctional acids and phenols. Many other constituents of green coffee such as alkaloids, amino acids, oligopeptides, proteins, glycerides, mono- and oligosaccharides, are more or less resistant to heat treatment but they will be considered here more as flavor precursors than as taste contributors to the beverage. The complex transformations, for instance the Strecker degradations and the Maillard reactions that occur during roasting, have been the subject of thousands of publications and of numerous meetings. They will not, therefore, be exhaustively reviewed but will be mentioned, as far as possible, when they are responsible for the formation of volatile flavor constituents or when they explain some original structures. In Chapter 1, we present a very short historical recall of the discovery of coffee as a beverage and we give a sketch of health concerns. We will mention a list of books and reviews on coffee and coffee chemistry. Chapter 2 is devoted to the constituents of green coffee, the non-volatiles being particularly considered as flavor precursors, and the volatiles as being responsible for the smell, a very important property allowing the detection of defective elements before roasting. The results obtained by specialized groups are commented upon. The tremendous transformations produced by roasting, the development of analytical techniques and the more recent systematic use of sensory-analysis methods are developed in Chapter 3. Chapter 4 deals with the progressive discovery of the individual components of roasted coffee aroma during the last two centuries, concentrating particularly on the difficulties encountered by the pioneers who tackled the analysis of roasted coffee extracts well before the advent of gas chromatography. More recently, and within a quarter of a century, from 1965 to 1990, the number of coffee flavor volatile compounds identified was sextupled, from 130 to 780. At the end of the twentieth century this number had reached approximately 850. A figure of more than 1000 has been suspected. In Chapter 5, we list the coffee flavor constituents according to their function, from hydrocarbons (Section 5.A) to miscellaneous sulfur-containing compounds (Section 5.Q), each compound being mentioned with its structure and nomenclature, the discoverer (as far as we know), some qualitative and/or quantitative data, and some information about formation mechanisms, synthesis and the organoleptic properties.

I.F.

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The following illustrations which serve to introduce each chapter are reproduced by permission of *The Johann Jacobs Museum Collection*, Zürich, Switzerland:

Chapter 1: A coffee-house in Albania, R. Caton Woodwille (1893)
Chapter 2: Vendor of coffee in the streets, G.J.B. Scotin (in about 1700)
Chapter 3: View of a roasting workshop in a coffee factory (New York, in about 1880)
Chapter 4: The lover of coffee (Honoré Daumier, Paris 1841)
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References A 'patented' percolator (J.P. Moynet, Paris, in about 1850)
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A coffee-house in Albania, R. Caton Woodwille (1893)

1

Introduction

1.1 A SHORT HISTORY OF COFFEE

Is it possible to start a book about coffee without tracing some of the history (and legend) of this beverage, even though many people know it? The word 'coffee' is a story in itself. Does it derive from *Kaffa* where the plant grew wild, or from *kawah* (*kahweh*) which means strength and is also a poetic name for wine? Whatever its origins, it became coffee.

It all began, it is said, because of some excited goats which stayed awake all night, prompting a shepherd somewhere in Yemen to ask advice of the priests in the vicinity. The priests soon observed that the animals were eating red berries from a bush, so they tried these berries themselves and found that they could attend their prayers without the problem of falling asleep. It appears, therefore, that it is not because of a compound responsible for the taste that the whole story started.

In fact, it was in Ethiopia (or was it Abyssinia?) that coffee was first grown and a beverage made from it. It was exported to the other side of the Red Sea in Aden in the Fifteenth century. As its property of preventing drowsiness was taken advantage of as a devotional antisoporific, there was fierce opposition from the strictly orthodox Muslims. The supposed intoxicant beverage was prohibited by the Koran. Notwithstanding the threat of divine penalties, the use of the beverage spread rapidly among the Arabians.

A hundred years later, in the middle of the sixteenth century, the first coffee houses were established in Constantinople, where the new habit also provoked the ire of the religious orders. As a result of complaints to the Sultan, heavy taxes were imposed on the coffee houses but this did not prevent them from flourishing. After another century, a coffee house opened in London. Here also it encountered hostility, but more for political reasons as coffee houses were thought to be seditious meeting places. After an attempt to suppress them, the most effective way of reducing coffee consumption here too, was to introduce heavy taxes. However, this had no obvious effect.

At around the same period coffee was introduced into France where wine merchants feared that the new beverage would compete with wine. Anyway after the tribulations at the beginning, coffee drinking became an established custom in Europe.

For two centuries the only source of coffee was Yemen (Arabia). To keep their monopoly, the Yemeni rulers ordered that the seeds should be roasted or steamed before being exported. The sources vary concerning the smuggling of raw seeds or plants but agree that the Dutch were at the origin of cultivation of coffee outside Arabia. The town of Mokha (Mocha) on the Red Sea was a flourishing town even before the coffee trade was introduced, because of all the boats and caravans meeting there for trade in incense, myrrh, mother of pearl, etc. It became even more prosperous after the introduction of coffee into European countries, being the center of the new trade. This golden age came to an end near the middle of the Eighteenth century when the quantities of coffee grown in other countries such as Indonesia, West Indies, etc., were important enough to lower the price. The first largely cultivated species was what Linné called *Coffea arabica* which grows well on hilly, well-watered and drained slopes. Nowadays, the 'robust' *Coffea canephora*, var. *robusta* which has fewer needs and different characteristics, is mainly produced in Africa, and hybrids are also cultivated.

Great care has to be taken concerning all the steps from the plant to the cup: collecting, pulping, drying, freeing from the husk, storage, roasting and further storage. Small scale operations may not be successful as complete control of cultivation and production is essential to high quality. Bad storage and bad drying of the berries may be at the origin of 'stinking' green beans, as observed in Yemen (Vincent *et al.*, 1976), even though some of the very primitively treated crops will certainly not reach the international trade (see the picture taken in February 2000, Figure 1.1, plate 2).

Economy always being an important factor, it has to be noted that in Yemen, coffee at first replaced (although never completely) a beverage made with 'qat' (*Caltha edulis*), by bringing in more money. However, cultivation, collection and treatment of coffee are time-consuming. Nowadays coffee is hardly cultivated at all in this part of the world and has been replaced by 'qat' which is consumed (leaves are chewed) on a large scale for a purpose similar to that of coffee, becoming again economically important for the growers if not for the country. [Some of the preceding information has been taken from the *Encyclopaedia Britannica*, 1878, Ninth edition.]

For all that, the history of coffee has not come to an end. People liked the social atmosphere of coffee drinking but did not want the possible effect of caffeine, hence the decaffeination process, or of some acids, hence the steam-treatment. For others, making coffee from the roasted beans was too much trouble, hence the preparation of soluble coffees, decaffeinated or not. All these treatments alter the content, and therefore the taste of the beverage. There is now a trend to new products (iced coffee, iced cappuccino for example). There are also 'gourmet' people who buy specialty roasted coffee and increase the side-market for coffee-pots or espresso makers by brewing coffee according to their taste.

Now, to drink or not to drink coffee? That is the question... Something has been said and has to be said on both sides. Coffee has been alternatively hell and heaven, source of all the diseases or a universal panacea. A French song dating from the beginning of the Eighteenth century (reported in 'Remèdes d'autrefois' par le Docteur Cabanès, A.Maloine, Ed., 1910) said *inter alia*:

'Si vous voulez sans peine
Vivre en bonne santé
Sept jours par semaine
Prenez de bon café'.

The truth lies somewhere between the two (see also Section 4.1). During recent decades, the concern about health and food has increased so much that many publications can be found about coffee in this respect. Pharmacology is certainly not the purpose of this book, but nevertheless, we estimate that these studies are part of the new history of coffee, as the conclusions will encourage or discourage coffee drinking. We will try to summarize (without quoting any special work, but the results are from recent years) what could be of some interest to a reader not specialized in this field.

Caffeine is certainly the best known of all the compounds extracted from the beverage. The stimulating effect had already been studied at the beginning of the Nineteenth century and is still under examination.

One need only read titles of conferences in a 'workshop' at the Eighteenth meeting of the Association Scientifique Internationale du Café in 1999: 'Effects of caffeine on attention', 'Effects of caffeine on memory and aging', etc. Caffeine certainly has a positive effect on attention, it reduces the sensation of tiredness, consequently gives a lighter sleep. There is also a question of habit and every individual has to adapt his consumption to his own reactions.

Of the mycotoxins which may arise in food products, **ochratoxin A** is under careful scrutiny. It is a secondary metabolite produced by fungi of the *Aspergillus* and *Penicillium* genera, especially *Aspergillus niger* and *Aspergillus ochraceus* in coffee. It is ubiquitous and can contaminate cereals, dried fruit, beans, cocoa, beer, wine, poultry, eggs, pork, milk . . . and coffee. This isocoumarin derivative is 'nephrotoxic, hepatotoxic, teratogenic, carcinogenic, immunosuppressive' and in humans, of all the species examined, it shows the longest half-life time for elimination. There is some controversy about its disappearance by roasting, and it passes nearly completely into the brew. However, there is also good news. Preventive means of colonization by the moulds, careful picking, good processing (drying, dehulling), good storage (for example drying to a moisture content lower than 15%) and good transport conditions minimize the contamination. The content, higher in the husks, will therefore be higher in soluble coffees adulterated by husks and/or parchments. Several European countries have proposed regulations for the level of ochratoxin A in foods, and coffee is well within the safety limits. Moreover, coffee is not the major dietary source of this toxin, the consumption of which, by drinking four cups a day (ca 25 g) of a brew made with roasted coffee containing 0.8 part per billion, will be equivalent to about 2% of the intake allowed by official international organizations.

Two mechanisms of action have been recognized for ochratoxin A: inhibition of protein synthesis and enhancement of oxygen reactive radical production with lipid peroxidation. The first effect can be counteracted by the presence of amino acids in the diet (the sweetener aspartame may be one source), the second by the presence in the diet of antioxidants, and coffee itself contains such compounds.

In fact coffee generates hydrogen hydroperoxide. On the other hand, it contains **phenolic acids**, known to have anticarcinogenic properties. Fruit and coffee (mainly with caffeic acid (**H.86**)) are the major sources of phenolic acids in the diet. Besides this type of compound, coffee contains other good antioxidants. Therefore, like other beverages, it shows a complex mixture of oxidant and antioxidant activities. Some studies have shown that not only is coffee not carcinogenic *in vivo* but that it could even protect against colon and breast cancers. Possible mechanisms include the effects of antioxidants in blocking mutations and carcinogen metabolites.

Other compounds, the **diterpenes** cafestol and kahweol (see Section 2.1.3), have been shown to increase cholesterol levels, this effect being drastically reduced by drinking filtered coffee. Anyway, they have also been recognized as chemoprotective agents.

In conclusion, a reasonable consumption of coffee is certainly harmless for most people and we will quote the 'Mémoire sur le café' of Payen (1846c), in the original, beautiful language used at that time in scientific publications: '. . . l'expérience de chaque jour . . . confirme que le café, tout différent des boissons fortement alcooliques et des vapeurs narcotiques qui enivrent et engourdissent les sens, semble réunir ce qu'on peut trouver d'agréable dans les sensations des deux ordres, tout en excitant les facultés de l'intelligence au lieu de les assoupir'. We do not know if the author was a great coffee drinker!

1.2 BOOKS, REVIEWS AND MEETINGS ON COFFEE FLAVOR

The research on coffee chemistry has been particularly active during the last 50 years and the scientific literature on the subject is extensive. The content of this monograph is limited to the identification and the characteristics of the compounds present in the volatiles of green and roasted coffees. The mechanisms of formation of the flavor during roasting will not be extensively developed, the browning reactions having been the subject of numerous publications and meetings mentioned in the text and in the References. The reader will find hereafter a list of books and reviews on the subject.

Books

Coffee Processing Technology. Sivetz, M.S. and Foote, H.E. (Eds.), The AVI Pub. Co., Inc., Westport, Conn. (1963).
Kaffee und Coffein. Eichler, O. (Ed.), Springer Verlag (1975).
Kaffee. Maier, H.G. Verlag Paul Parey. Berlin, Hamburg (1981). Series: Grundlagen und Fortschritte der Lebensm. Unters.und Lebensm.Technol., Volume **18**.
Coffee. Vol.1. *Chemistry*. Clarke, R.J. and Macrae, R. (Eds.), Elsevier Applied Science Ltd (1985).
Coffee. Botany, Biochemistry and Production of Beans and Beverages. Clifford, M.N. and Wilson, K.C. (Eds.) Croom Helm & AVI (1985).
Caffeine, Coffee and Health. Garattini, S. (Ed.), Raven Press (1993).
Espresso Coffee. Illy, E. and Viani, R. (Eds.), Academic Press (1995).

Reviews

Moncrieff R.W. (1950a), Part 1.: 3 pp., 18 ref.; Part 2: 4 pp., 61 ref.: The aroma of coffee.
Gautschi F. *et al.* (1968), 9 pp., 24 ref.: The chemistry of coffee aroma. A survey of present knowledge.
Smith R.F. (1968), 20 pp., 258 ref.: Tea and coffee.
Walter W. and Weidemann H.L. (1969), 24 pp., 32 ref.: Coffee flavor compounds.
Smith R.F. (1970, 1973, 1974a, 1976, 1979, 1981, 1983, 1986b): Recent reports on the chemistry and technology of coffee: a review. (Periodical reports on the Chemistry and Technology of Coffee, ASIC meetings).
Weidemann H.L. and Mohr W. (1970), 9 pp., 143 ref.: Specificity of roasted coffee aroma.
Streuli H. (1974), 12 pp., 23 ref.: Der heutige Stand der Kaffeechemie.
Clifford M.N. (1975b), 4 pp., 73 ref.: The composition of green and roasted coffee beans.
Vitzthum O.G. and Werkhoff P. (1976a), 11 pp., 18 ref.: Les constituants volatils du café torréfié.
Vitzthum *et al.* (1976), 8 pp., 14 ref.: Flüchtige Inhaltsstoffe des Rohkaffees.
Wurziger J. (1977), 11 pp., 15 ref.: Kaffee
Reymond D. (1977), 6 pp., 55 ref., (1978), 17 pp., 54 ref.: Flavor chemistry—coffee, cocoa and tea.
Heyns K. (1979), 7 pp., no ref.: Aspects scientifiques de la recherche sur le café.
Flament I. (1982a), 23 pp., 90 ref.: Coffee, cocoa and tea flavors: a review of present knowledge.
Maier H.G. (1983), 5 pp., 47 ref.: Chemistry and technology of coffee.
Smith R.F. (1984, 1985a, 1986a): New aspects on chemistry of coffee.
Spiller M.A. (1984), 56 pp., 161 ref.: The chemical components of coffee.
Clarke R.J. (1986a), 47 pp., 69 ref.: The flavour of coffee.
Viani R. (1986), 24 pp., 59 ref.: Coffee.
Viani R. (1989), 60 pp., 76 ref.: Coffee.
Flament I. (1989), 97 pp., 507 ref.: Coffee, cocoa and tea.
Clarke R.J. (1990), 9 pp., 20 ref.: The volatile compounds of roasted coffee.
Flament I. (1991), 52 pp., 314 ref.: Coffee, cocoa and tea.
Shibamoto T. (1991), 10 pp., 39 ref.: An overview of coffee aroma and flavor chemistry.
Viani R. (1993) 24 pp., 89 ref.: The composition of coffee.
Holscher W. and Steinhart H. (1995), 19 pp., 39 ref.: Aroma compounds in green coffee.
Suwabe H. and Kumazawa K. (1998), 16 pp., 20 ref.: Coffee. (in Japanese)
Grosch W. (1998b), 7 pp., 59 ref.: Flavor of coffee.
Maier H.G. (1999), 8 pp., 113 ref.: Progress in the fields of coffee chemistry, analysis and pharmacology.
de Maria *et al.* (1999), 9 pp., 119 ref.: Volatile components in roasted coffee. Part I. Heterocyclic compounds.
Vitzthum O.G. (1999), 17 pp., no ref. Thirty years of coffee chemistry research.

List of IFCC and Asic symposiums

First International Colloquium on the Chemistry of Coffee (Paris, 20–22.5.1963) (IFCC) Café Cacao Thé, **7**, 173–265 (1963)

Second International Colloquium on the Chemistry of Coffee (Paris, 3–7.5.1965) (IFCC) (1966)
Third International Colloquium on the Chemistry of Coffee (Trieste, 2–9.6.1967) (ASIC) (1968)
Fourth International Colloquium on the Chemistry of Coffee (Amsterdam, 2–6.6.1969)(ASIC)(1970)
Fifth International Colloquium on the Chemistry of Coffee (Lisbon, 14–19.6.1971) (ASIC) (1973)
Sixth International Colloquium on the Chemistry of Coffee (Bogota, 4–9.6.1973) (ASIC) (1974)
Seventh International Colloquium on the Chemistry of Coffee (Hamburg, 9–14.6.1975) (ASIC) (1976)
Eighth International Colloquium on the Chemistry of Coffee (Abidjan, 28.11–3.12.1977) (ASIC) (1979)
Ninth International Colloquium on the Chemistry of Coffee (London, 16–20.6.1980) (ASIC) (1981)
Tenth International Colloquium on the Chemistry of Coffee (Salvador, Bahia 11–14.10.82) (ASIC) (1983)
Eleventh International Colloquium on the Chemistry of Coffee (Lomé, 11–15.2.1985) (ASIC) (1986)
Twelfth International Colloquium on the Chemistry of Coffee (Montreux, 29.6–3.7.1987) (ASIC) (1988)
Thirteenth International Colloquium on the Chemistry of Coffee (Paipa, Colombia, 21–25.8.1989) (ASIC) (1990)
Fourteenth International Colloquium on the Chemistry of Coffee (San Francisco, 14–19.7.1991) (ASIC) (1992)
Fifteenth International Colloquium on the Chemistry of Coffee (Montpellier, 6–11.6.1993) (ASIC) (1993)
Sixteenth International Colloquium on the Chemistry of Coffee (Kyoto, 9–14.4.1995) (ASIC) (1995)
Seventeenth International Colloquium on the Chemistry of Coffee (Nairobi, 20–25.7.1997) (ASIC) (1998)
Eighteenth International Colloquium on the Chemistry of Coffee (Helsinki, 2–6.8.1999) (ASIC) (2000)

Numerous articles on coffee flavor chemistry have been published in the Proceedings of the symposiums on the Maillard reaction and in the Weurman Flavor Research meetings. References for the corresponding books can be found in the References at the end of this book under 'Maillard reactions' and 'Weurman Flav.Res.Symp'.

1.3 ABBREVIATIONS

AOAC	Association of Official Agricultural Chemists
ASIC	Association Scientifique Internationale du Café
FEMA	Flavor and Extract Manufacturers Association
GRAS	Generally Recognized As Safe
ICO	International Coffee Organization
IFCC	Institut Français du Café, du Cacao et autres plantes stimulantes
IOFI	International Organization of Flavor Industries
IUPAC	International Union of Pure and Applied Chemistry
TNO	Nutrition and Food Research Institute, Zeist, The Netherlands

Methods

AECA	Aroma Extract Concentration Analysis
AEDA	Aroma Extract Dilution Analysis or Assay (or ADA)
CHARM®	Combined Hedonic Aroma Response Measurements. (Gas chromatography-sniffing or GCO)
DAD	Diode Array Detection
FD	Flavor Dilution factor
FID, FPD	Flame Ionization Detector, Flame Photometric Detector
FTIR	Fourier Transform InfraRed spectrometry
GC–O	Gas chromatography–Olfactometry
GC–O–H or H–GCO	Gas chromatography–Olfactometry–Headspace
GLC	Gas–Liquid Chromatography
GLPC	Gas–Liquid Partition Chromatography
HPGF	High Performance Gel Filtration
HPLC	High Performance Liquid Chromatography
HRGC	High Resolution (capillary) Gas Chromatography
HS	Headspace
IDA	Isotope Dilution Assay

IRMS	Stable Isotope Ratio Mass Spectrometry
LC	Liquid Chromatography
MDGC	MultiDimensional Gas Chromatography
MS	Mass Spectrometry
MSA	Multivariate Sensory Analysis
NIF	Nasal Impact Frequency
NMR	Nuclear Magnetic Resonance spectroscopy
OAV	Odor Activity value
OSV	Odor Spectrum Value
PCA	Principal Component Analysis
RAS	Retronasal Stimulation
RP	Reversed Phase
SDE	Simultaneous steam Distillation Extraction
SFE	Supercritical Fluid Extraction
SIM	Selected Ion Monitoring
SNIF	Surface of Nasal Impact Frequency
SPME	Solid Phase Micro Extraction
TIC	Total Ion Current
TLC	Thin Layer Chromatography

db, dm, dmb	dry basis, dry matter, dry matter basis
µg	Microgram
ng	Nanogram
pg	Picogram
ppb	Part per billion (10^{-9})
ppm	Part per million (10^{-6})
ppt	Part per trillion (10^{-12})

The non-exhaustive list summarizes for the reader the main acronyms found in the literature, but we will use abbreviations as little as possible.

Vendor of coffee in the streets, G.J.B. Scotin (in about 1700)

2

Green Coffee

Before starting the description of green coffee content, we will follow very succinctly the steps leading from the berries, usually called cherries, to the seeds, usually called beans (normally two in one berry). The care taken in all the operations will ensure the quality of the coffee and later of the beverage (for details see Clarke, 1985, Illy *et al.*, 1995).

There are several modes of **harvesting**. Picking is the most time-consuming method, requiring several passages, but only the ripe cherries are collected. It needs good weather conditions. Mechanical harvesting is done by shaking the trees which may be more or less damaged, or a kind of flexible comb is passed through the twigs so that the ripe cherries fall and are collected. Finally, the whole twigs can be stripped (stripping). This method gives bad results, as unripe and overripe cherries are collected and a first classification is necessary.

The seeds then have to be released from the layers that surround them. The **dry processing** starts by **drying**, sun drying which is dependent on weather conditions with the possibility of growth of micro-organisms, or well-controlled mechanical drying. Then by the **husking** (or dehulling), the dried husks are removed (dried skin, pulp and parchment), leaving the silverskin still adhering to the bean.

Wet processing is much more complex but gives better quality coffee. Only the ripe fruit have to be used and usually a selection is made by flotation. The **pulping** must be completed quickly after the harvest (not more than 24 h). A mucilaginous layer is left which will be removed by **fermentation**, with or without water, sometimes with addition of enzymes. After 6–40 h during which time the acidity increases (final point at pH ca 4.5), the seeds are washed extensively. The now so-called 'parchment coffee' is dried by sun or hot-air **drying**, or a mixture of the two methods. Great care has to be taken to avoid absorption and desorption of moisture and the breaking of the parchment. Next, **hulling** (or peeling, shelling) will remove the dry parchment, or a combined hulling/**polishing** will also remove the silverskin.

The green coffee, from dry or wet processing, is submitted to **size grading** and **sorting** to eliminate the defective beans. A mechanical sorting with air lifting (specially useful when the harvest has been done by stripping) will not separate insect-damaged beans. Manual sorting involves considerable labor so electronic sorters have now been developed. Schematically, the beans pass at high speed in front of light beams, and those with undesired colors are ejected. Sophisticated programs allow separation not only of the black beans but of a range of discolored beans. This may be followed by sorting with UV excitation, the 'stinker' beans, that can be produced during wet processing and which show special fluorescence.

Finally the **polishing** will remove the silverskin, specially for the dry-processed beans. What is left will be removed as chaff after roasting.

2.1 THE NON-VOLATILE CONSTITUENTS AND THEIR CONTRIBUTION AS PRECURSORS OF THE FLAVOR OF ROASTED COFFEE

A review of the chemical and biological aspects of raw coffee composition was published by Poisson in 1979. In the introduction, the author noted that correct evaluation of the content of green coffee is not easy, the fresh coffee seed being a living material and therefore subject to variability. Moreover, the analytical methods remained, at that time, very imprecise, particularly for categories of constituents with high molecular weights, such as proteins, polypeptides and oligopeptides, which were very difficult to separate. The performances of analytical techniques have evidently made great progress during the last two decades, for instance with the development of HPLC/MS coupling. The purpose of this book being essentially limited to the formation and the structures of flavor constituents, the analytical aspects of these non-volatile potential flavor precursors will not be specially discussed. As early as 1961, Navellier gave a mean composition of green coffee: glucides (58 %), lignine (2 %), lipids (13 %), proteins (13 %), ash (4 %), non-volatile acids (8 %), trigonelline (1 %), caffeine (1 %). A chemical study of Angola coffees was performed by Derbesy *et al.* (1969) for green beans, and by Roffi *et al.* (1973) for green and roasted beans on 40 samples (eight arabicas).

Smith (1963a) and Feldman *et al.* (1969) underlined the importance of non-volatile compounds to the flavor of coffee. The comparison between the composition of green and of roasted coffee showed an important decrease in the content of proteins, chlorogenic acid and sucrose on roasting. Fractionation and analysis of the aroma precursors in green coffee have also been studied by Russwurm (1970) who considers that the non-volatile constituents of green coffee that may be involved in flavor formation are carbohydrates, proteins, peptides and free amino acids, polyamines and tryptamines, lipids, phenolic acids, trigonelline and various non-volatile acids.

At the same time, Merritt *et al.* (1970) published one of the first studies insisting on the relationship of volatile compounds in roasted flavor to their precursors in the green beans. Thaler and Arneth (1970) discussed the transformation of highly-polymerized carbohydrates in the roasting of arabica coffee. Amorim *et al.* (1974) studied the relationship between some organic compounds of Brazilian green coffee and the quality of the beverage. Water-soluble protein and non-protein components of Brazilian green coffee beans were studied by Amorim and Josephson (1975), and Baltes (1976, 1979b) reviewed the precursors and origin of coffee color and flavor, and the effect of roasting, discussing the contribution of monosaccharides, amino acids and chlorogenic acids. More references on the transformation of the non-volatile components will be given in Section 3.1.

Clifford (1985b) reviewed the chemical and physical aspects of green coffee, discussing particularly the properties of its non-volatile constituents and Clifford and Kazi (1987) were interested in the changes in the contents of chlorogenic acids (Section 2.1.4), caffeine (in 2.1.1.1) and trigonelline (2.1.1.2) during the fruit maturity. Guyot *et al.* (1988a) also investigated physical and chemical changes as a function of the maturity for a robusta [fatty acids, amino acids (Section 2.1.1.3), mono- and disaccharides (2.1.2), chlorogenic acids, caffeine, trigonelline] and the influence on the organoleptic characteristics of the corresponding brews. They concluded that high contents of chlorogenic acids, caffeine, trigonelline, and arabinose are the result of a high proportion of immature beans, the color of the cherry not being always characteristic of the best stage of maturity.

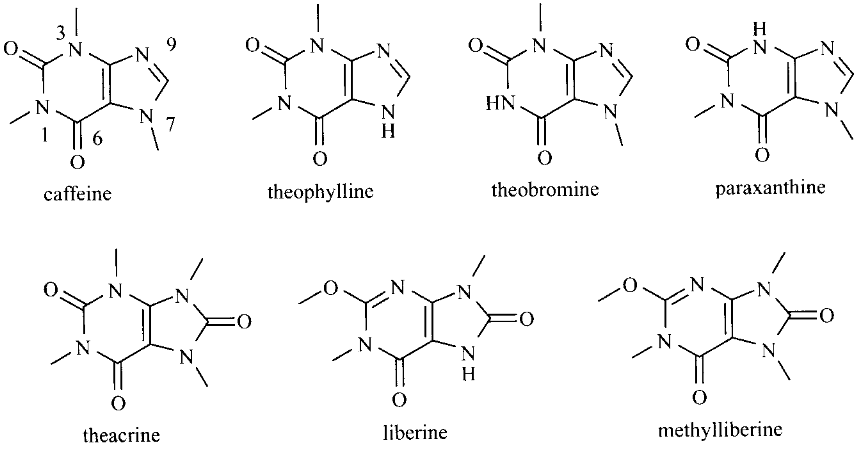
De Maria *et al.* (1995, 1996c) have described a simultaneous determination of total chlorogenic acids, trigonelline and caffeine in green coffee by high-performance gel filtration chromatography. They also analyzed (de Maria *et al.*, 1996a) the roasting of the water-soluble fractions of a defatted green coffee. Martin *et al.* (1998) examined 41 samples of green arabicas and robustas. They analyzed chlorogenic acid, caffeine, trigonelline, amino acids, polyphenols and aqueous extract, which they used as chemical descriptors. They concluded that the contents of caffeine and total amino acids allow an easy differentiation between the two varieties.

King and Solms (1981) have shown that caffeine–chlorogenic complex, i.e. caffeine, chlorogenic acids and also phenols, are effective solubilizers of flavor compounds. This property could be of interest for modifications of the flavor quality.

2.1.1 Nitrogenous components

2.1.1.1 Alkaloids

By far the most important constituent with a purine ring system (Figure 2.1) is caffeine (**1*H*-purine-2,6-dione, 3,7-dihydro-1,3,7-trimethyl-**, 1,3,7-trimethylxanthine (xanthine is a trivial name not to be confused with xanthene which is the name of another heterocyclic system) **[58-08-2]**. Smaller quantities of the caffeine metabolites, theophylline (**1*H*-purine-2,6-dione, 3,7-dihydro-1,3-dimethyl-**, 1,3-dimethylxanthine) **[58-55-9]** and theobromine (**1*H*-purine-2,6-dione, 3,7-dihydro-3,7-dimethyl-**, 3,7-dimethylxanthine) **[83-67-0]** are also present. Other metabolites have been found in small amounts by Kappeler and Baumann (1986): paraxanthine (**1*H*-purine-2,6-dione, 3,7-dihydro-1,7-dimethyl-**, 1,7-dimethylxanthine) **[611-59-6]**, theacrine (**1*H*-purine-2,6,8(3*H*)-trione, 7,9-dihydro-1,3,7,9-tetramethyl-**, 1,3,7,9-tetramethyluric acid) **[2309-49-1]**, liberine (**1*H*-purine-6,8-dione, 7,9-dihydro-2-methoxy-1,9-dimethyl-**) **[56119-16-5]** and methylliberine (**1*H*-purine-6,8-dione, 7,9-dihydro-2-methoxy-1,7,9-trimethyl-**) **[51168-26-4]**. Theacrine and methylliberine were not detected in arabica. Kappeler and Baumann (1986) found that beans considered as harvested when unripe have higher contents of theophylline, theobromine, liberine and theacrine. For differentiation between green arabicas and robustas, they evaluated ratios of alkaloids and concluded that the ratio of theobromine to theophylline is a reliable measure that is not affected by the stage of ripeness. Liberine and methylliberine were previously discovered in the leaves of some *Coffea* species by Wanner *et al.* (1975) (synthesis, UV and NMR data of purine derivatives), and Petermann *et al.* (1977) who consider the latter alkaloid to be an intermediate between theacrine and liberine. Weidner and Maier (1999) also identified paraxanthine and theacrine. They found that at different degrees of



caffeine theophylline theobromine paraxanthine

theacrine liberine methylliberine

Fig. 2.1 Alkaloids of coffee (purine skeleton) roasting *Coffea robusta*, the contents of paraxanthine and of theobromine remains unchanged but that of theacrine and theophylline decrease with increasing roasting. In wild coffees of Madagascar, Rakotomalala *et al.* (1993a) identified caffeine in two taxa, with contents up to 0.8 %, the same coffees also containing theobromine (0.03–0.08 %) and one containing theacrine (1.46 %). Some wild plants also contain theophylline.

The first discoveries in this domain are due to Friedlieb Ferdinand Runge (1795–1867) who, in 1820 (Runge, 1820) isolated caffeine, a crystalline and sublimable product, and to Pierre Jean Robiquet (1780–1840) who studied its stimulating, cardiotonic and diuretic properties (Robiquet and Boutron, 1837a,b,c). The raw formula of caffeine was determined by Pfaff and Liebig (1832), and the exact formula proposed by Medicus (1875), but the structure was only confirmed by total synthesis by Fischer and Asch (1895) after a tedious period of intensive work. The caffeine content of green coffee is relatively limited (1–2.5 % of dry matter) and changes little with seed development (Clifford and Kazi, 1987). It is known to be lower in arabicas than in robustas, for example 1.32 and 2.18–2.61 % respectively for Angola coffees (Roffi *et al.*, 1973). In Madagascar, most of the wild coffees belong to the group of caffeine-free coffee trees (*Mascarocoffea*) (Rakotomalala *et al.*, 1993a). Stennert and Maier (1994) did not find appreciable differences between steam-treated or untreated coffees, either green or roasted.

As mentioned by Macrae (1985) the losses of caffeine during roasting are relatively modest, rarely amounting to more than a few percent under normal roasting conditions. In fact the actual percentage of caffeine present may increase by up to 10 % on a dry roasted basis, taking into account the weight loss of the beans. The loss is limited by the increase of the sublimation point of caffeine during roasting (by increase of the pressure within the bean) and by a poor rate of diffusion through the outer layers. The content in instant coffee powders is about twice that of green coffee as a consequence of extraction with hot water, the solubility of caffeine increasing more than 10 times between room temperature and 80 °C. Caffeine, which is odorless, has a bitter taste but contributes only ca 10 % of the perceived bitterness of the beverage. This sensory characteristic is difficult to distinguish, even by a trained panel of assessors, from the astringency caused simultaneously by phenolic compounds. The stability of the purine ring skeleton to heat treatment is confirmed by the fact that pyrimidines or imidazoles have rarely been found in volatile flavor components. To our knowledge, only one publication mentions pyrimidines in a coffee brew (T.A. Lee *et al.*, 1992).

Prodolliet *et al.* (1998) tried to determine the geographic origin of coffee using the isotope ratios (C, N, H) in samples of caffeine extracted from green arabicas and robustas from 16 countries. Neither univariate nor multivariate analysis allowed the determination of the species or of the country of origin.

Pathways of caffeine metabolism are described and discussed by Waller and Suzuki (1990). One methyl source is *S*-adenosylmethionine synthesized from methionine. In *Coffea arabica*, caffeine is synthesized in the pericarp and transported to the seeds where it accumulates.

The physiological effects are difficult to evaluate. The well-known stimulant effect varies greatly, according to individuals. The certain fact is that it is quickly absorbed and metabolized as methylxanthines. The other toxic effects which have been often discussed are not proven.

2.1.1.2 Trigonelline

Trigonelline (**pyridinium, 3-carboxy-1-methyl-, inner salt,** (*1-methyl-3-pyridinio*) *carboxylate*, *N*-methylnicotinate, betaïne nicotinate) **[535-83-1]** was isolated from an arabica coffee in 1909 by Polstorff, quoted by Gorter (1910) who identified the same compound in a Liberia coffee. It is identical to the compound from *Trigonella foenum-graecum*. The content in green coffee is 0.6–1 % according to Hughes and Smith (1946) who observed a very rapid degradation, the content decreasing to 0.25–0.63 % for a medium roast. At 230 °C for 15 min, only 15 % of the trigonelline initially present is surviving. The decomposition gives

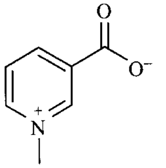


Fig. 2.2 Trigonelline

some nicotinic acid (Section 5,**N.24**) which is found in green coffee at low levels, 16–44 ppm. The increase in the content of nicotinic acid (150–200 ppm for medium roast) represents only a small part of the loss in trigonelline (see Section 5,**N.24**). The thermal fragmentation of trigonelline has been carefully studied by Viani and Horman (1974), using GC/MS and TLC analytical methods. Important aroma constituents, such as pyridines, pyrroles, methyl nicotinate (Section 5,**N.25**), are actually formed and the presence of other active species as trace constituents is suggested. A mechanism of pyridine formation from trigonelline under coffee roasting conditions has been proposed by Rizzi and Sanders (1996). This is very important as pyridine affects the overall aroma of a brewed coffee. The non-decarboxylative mechanism leads to the ester by a methyl migration and the decarboxylation involves 1-methylpyridinium hydroxide leading to pyridine. From their results, De Maria *et al.* (1996a) conclude that trigonelline is not the only source of pyridine in roasted coffee to be formed by protein pyrolysis.

Mazzafera (1991) examined 28 coffee species for their trigonelline content. For the arabicas it is mainly around 2%, the extremes in other varieties being ca 0.8 and 3.0%, higher than the values generally reported. The differences are probably due to different methods of determination. Stennert and Maier (1994) reported literature values in agreement with their own values of 0.88% (average) for seven green arabicas and 0.67% for three robustas.

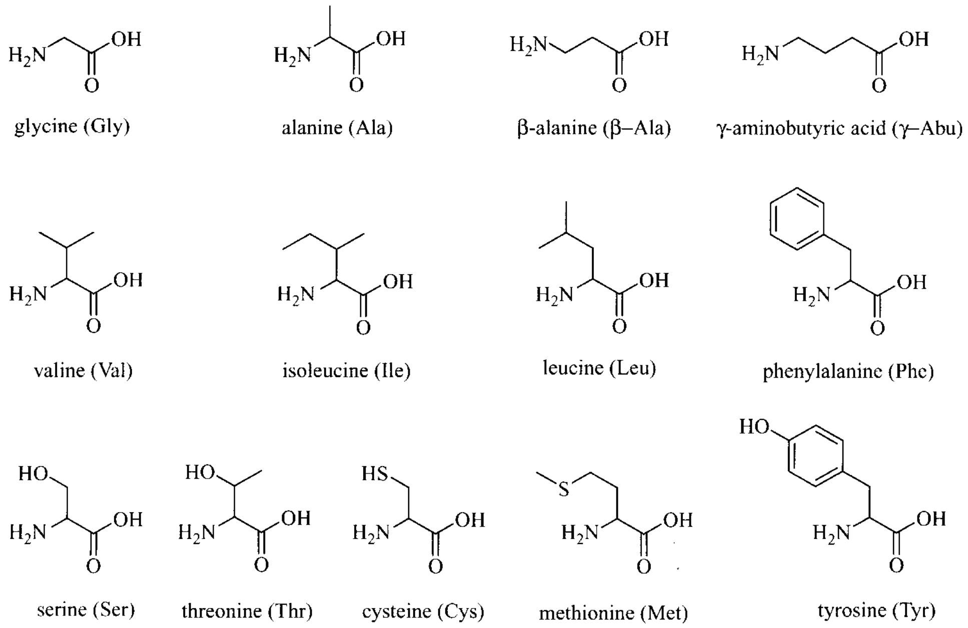
According to Macrae (1985) and many other authors, trigonelline has little direct influence on the quality of coffee brew, having a bitter taste approximately a quarter the strength of that of caffeine, but its thermal degradation products have sensory and nutritional importance. It has relatively little pharmacological activity although mutagenic activity has been detected (Wu *et al.*, 1997). Anyway the amount of trigonelline ingested by drinking coffee is too small to induce toxicity.

Nakabayashi and Masano (1986a) proposed using the ratio of trigonelline to caffeine as an indication of the degree of roasting, the content of trigonelline decreasing suddenly after medium roasting and that of caffeine increasing slightly. This ratio decreases from 0.86 for green beans to 0.15 for 'Italian' roast beans. Using a new GLC method for the determination of nicotinic acid (Section 5,**N.24**), Stennert and Maier (1996) proposed using the trigonelline/nicotinic acid ratio for calculating the degree of roast. They had previously found (1994) that steaming does not lead to appreciable changes in the content of trigonelline.

Trigonelline is biogenetically derived from nicotinic acid by an enzymatic methylation, at the expense of the methyl group coming from methionine (Poisson, 1979).

2.1.1.3 Proteins and free amino acids

The nature of the proteins present in coffee (Figure 2.3) did not receive much attention in the past as complex and difficult analyses were required, the majority of the proteins having molecular weights above 150 000 and there being many other nitrogenous components present. The protein content is evaluated from total nitrogen determination, with corrections for trigonelline and caffeine contents, and is close to 10% in arabica and robusta coffees. Determining the amino-acid composition requires



glycine (Gly) alanine (Ala) β-alanine (β-Ala) γ-aminobutyric acid (γ-Abu)

valine (Val) isoleucine (Ile) leucine (Leu) phenylalanine (Phe)

serine (Ser) threonine (Thr) cysteine (Cys) methionine (Met) tyrosine (Tyr)

Fig. 2.3 Amino acids

hydrolysis of the protein prior to separation, and quantification of the resulting amino acids. Total protein and albumin (water-soluble part) have been particularly studied by Thaler and Gaigl (1962). The major constituents are glutamic acid (19% of total protein), aspartic acid (10%) and leucine (9%). The major difference between the composition of albumin and of total protein is the methionine content which is much lower in albumin, histidine being slightly less abundant in albumin (1.9 vs 2.5% of the amino acids). The chemical study of 40 samples of Angola green coffees by Roffi *et al.* (1973) gave analogous figures for the main amino acids, 13.1–19.9, 8.2–10.8 and 6.2–8.9% respectively for glutamic, aspartic acids and leucine. Previously, the same group (Derbesy *et al.*, 1969) had quantified tryptophan (0.9–1.0% of protein) after alkaline hydrolysis. Amino-acid composition in green and roasted coffee after acid hydrolysis was also determined by Feldman *et al.* (1969), and their figures are similar for the three main components, but they quoted asparagine instead of aspartic acid. In green and roasted coffees, Macdonald and Macrae (1986) determined free (after water extraction), total (after acid hydrolysis) amino acids, sulfur-containing amino acids after oxidation (cysteine as cysteic acid, methionine as methionine sulfone which they could not quantify) and tryptophan by HPLC after alkaline hydrolysis and fluorescence detection. They observed similarity between arabica and robusta for the total amino-acid content except for alanine, phenylalanine and tryptophan (alanine being more abundant in arabica). The total sum of amino acids is slightly higher for mature than for immature beans, this trend being reversed when the corresponding arabica beans were roasted. The content in free amino acids did not vary appreciably with species or with maturity (see below), and had only a very slight tendency to a higher content in mature beans. Mazzafera (1999) also found a higher protein content in mature beans than in the immature but a lower content of free amino acids, with asparagine as the main component.

The free amino acids, although representing only ca 1% of green coffee, probably form the most important group of compounds in relation to the final flavor of roasted coffee, although recently Ludwig *et al.* (1997) showed that peptides and proteins are probably also aroma precursors. According to Walter *et al.* (1970) and Maier (1981), they are present only at levels of 0.15–0.25% and are destroyed to a very high extent by pyrolysis, only traces being found in the roasted beans. Tressl *et al.* (1983) measured ca 0.5% in arabica and ca 0.8% in robusta species, a result somewhat different to that of Macdonald and Macrae (1986) who found ca 0.45 and 0.4% respectively in arabicas and robustas, with little difference between mature and immature beans. Contrary to this last result, Guyot *et al.* (1988a) found a global decrease in free amino acids with increasing maturity of a robusta. Asparagine, glutamine, glycine, and cystine were not detected at any stage. In beans from cherries which could be qualified as 'really unripe', the content of serine, γ-aminobutyric acid, valine, leucine, isoleucine and methionine is clearly more important than in other samples (red cherries or even green late pickings).

After extraction of green coffee with a solution of 5-sulfosalicylic acid, Arnold *et al.* (1994) used derivatization with 9-fluorenylmethyl chloroformate followed by HPLC for separation and quantification of the free amino acids in 17 arabicas and seven robustas: 20 were quantified, six other were eluted and quantified as pairs [glutamine/asparagine, histidine/1-(or 3-)methylhistidine, phenylalanine/tryptophan]. Cysteine could be derivatized only after oxidation. Minor acids were quantified for the first time: ornithine (which in fact had been quantified by Guyot *et al.*,1988a, in immature and mature beans of a robusta), β-alanine and pipecolic acid in arabicas and robustas, hydroxyproline in arabicas, the total amount of these acids being 1.9 (robustas) to 2.8% (arabicas) of the free acids. [*Remark*: the other methylhistidine, 3- (or 1-) was also quantified in the same work, but the numbering used by biochemists (the first quoted in the table of structures) is different from the numbering adopted by organic chemists and as used in *Chemical Abstracts*. In the absence of structures we do not know what is used there.] β-Alanine, hydroxyproline and pipecolic acid were mentioned by Pereira and Pereira (1973) and by Campos and Rodrigues (1973), and 3- (or 1-)methylhistidine by Tressl *et al.* (1983) who also found cystathionine in only one coffee blend. Using 'free flow field step' electrophoresis, Bähre and Maier (1996) identified an important series of acids (see Section 5,E), among them pyroglutamic acid (5-oxoproline) (Figure 2.4).

Pipecolic acid has also been detected in pericarps and seeds of some *Coffea* species, specially in unripe fruits, together with proline (also more abundant in unripe fruits) and hydroxyproline by Higuchi *et al.* (1995). With the method that they described previously (Arnold *et al.*, 1994), Arnold and Ludwig (1996) investigated the changes in free amino acids with post-harvest treatments for eight samples of arabica berries. The sum of the concentrations of the amino acids does not show clear changes after drying at 40 °C. The individual contents change for some acids, especially glutamic acid which shows an increase of about 50% and aspartic acid which mainly decreases. The hydrophobic acids (valine, phenylalanine, leucine, isoleucine) generally increase. Drying at 80 °C decreases the content of amino acids, but fermentation-drying does not bring significant changes as compared with drying alone (40 °C).

Decaffeinated samples are clearly poorer in free amino acids than are the corresponding samples with caffeine, and occasionally contain less-attractive flavor compounds after roasting, as amino acids react easily with reducing carbohydrates in the Maillard reaction (Tressl, 1981). On the other hand, the same author has shown that decaffeination increases the level of reducing sugar content from 0.53 to 2.9%.

Steinhart and Luger (1995) studied the effect of steam-treatment on green coffee, a treatment developed for people with a sensitive stomach. They analyzed the contents of amino acids (and also carbohydrates and chlorogenic acids in other publications). There is a significant decrease during the treatment with differences between the acids, arabicas being more sensitive to the treatment than robustas. Generally, pretreated coffees contain about half the original amount of free amino acids. There is also a decrease in the sum of protein-bound amino acids, normally by about 10%. The values differ with the duration and the pressure applied during the treatment. After roasting, the free amino acids are not detected. The initial decrease in content of bound amino acids is followed by a slight increase. The pretreated roasted arabicas contain more (ca 150%) protein-bound amino acids than the untreated, but the difference is not significant in the robustas.

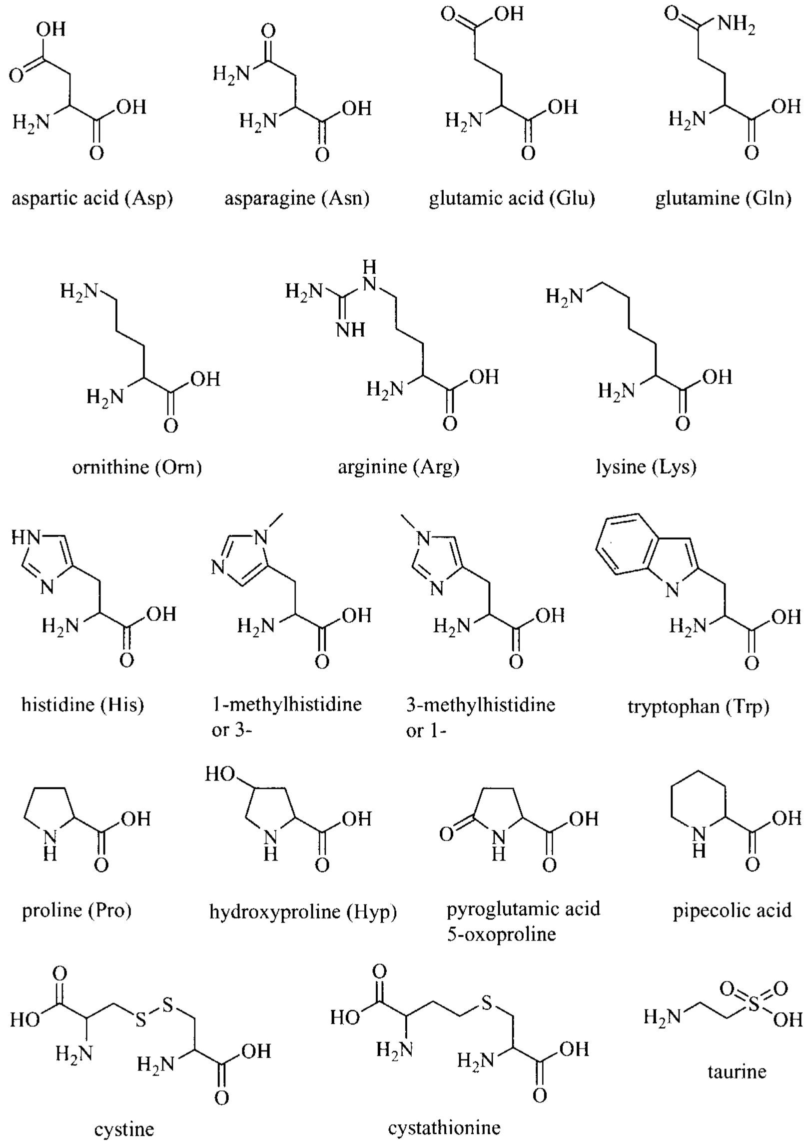


Fig. 2.4 Amino acids (continued)

Clinton (1986) lists, in decreasing quantitative order, the amino acids and peptides present in a coffee beverage: glutamic acid, glycine, aspartic acid, alanine, leucine, valine, isoleucine, serine, phenylalanine, threonine, tyrosine, histidine and γ-aminobutyric acid.

Recently, Ginz and Engelhardt (1999) studied water-soluble proteins of raw coffee as a source of bitterings. After roasting, by using gel chromatography and HPLC they identified diketopiperazines: cyclo(Pro-Pro), cyclo(Pro-Leu), cyclo(Pro-Phe) and isolated cyclo(Pro-Val). These and similar diketopiperazines are known as bitter principles in foodstuffs, but the authors have not yet drawn any conclusions as to the importance of their participation in the bitterness of roasted coffee.

We will quote here the identification of the amides of tyrosine and tryptophan with caffeic (Section 5,**H.86**) and *p*-coumaric acids (Section 5,**H.84**) (see in Section 5,H, hydroxycinnamic acids).

2.1.2 CARBOHYDRATES

This is an essential class for the formation of aroma compounds, mainly by caramelization of the low-molecular-weight sugars and by Maillard reaction with the amino acids (see Section 3.1).

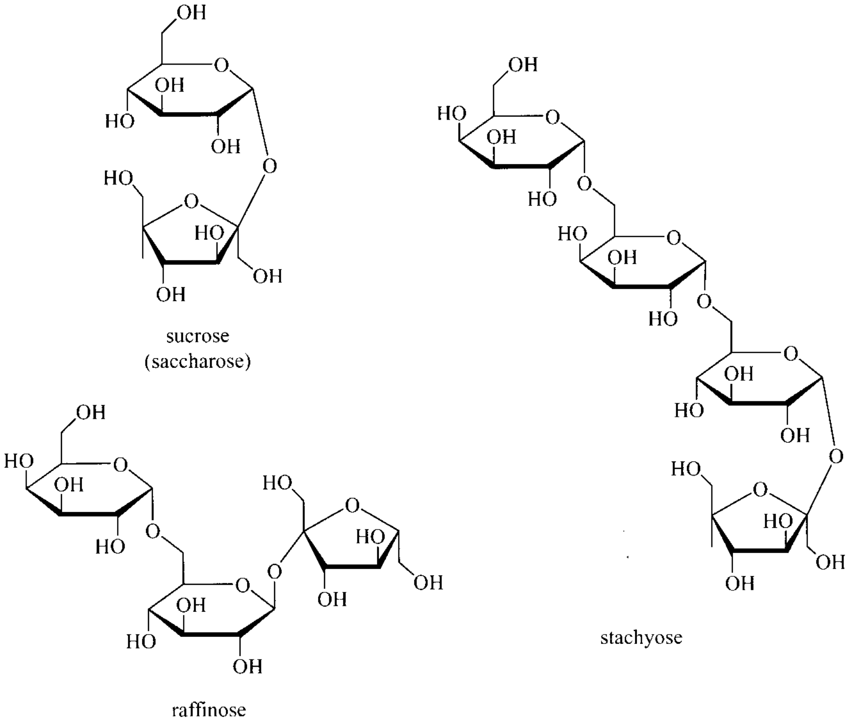
The total amount of carbohydrates represents about 50% dry basis (d.b.) of green coffee. The composition is complex with a range of different poly-, oligo- and monosaccharides, subdivided into reducing and non-reducing sugars (Trugo, 1985). According to Hadorn and Sutter (quoted by Courtois *et al.*, 1963) there are no free reducing sugars in green beans if the enzymatic hydrolysis of sucrose is avoided during the extractions. Courtois *et al.* (1963) and Glomaud *et al.* (1966) studied water extraction of oligo- and polysaccharides of green coffee. Pictet and Moreau (1970) extracted green coffees with water from 80 to 180 °C. The extracted carbohydrates (ca 20% d.b.) consisted of equal proportions of oligo- and polysaccharides.

As already said, the quantification becomes complicated and the results are somewhat conflicting, the extraction techniques being rendered difficult owing to the low permeability of the bean tissues and the formation of artefacts. Results are not always easy to compare. The transformations arising during treatments, steam treatment, decaffeination of green coffee, roasting, affect the contents and hence the taste of the final beverage and, as we will not treat carbohydrates separately as components of roasted coffee, we include here some results obtained on roasted coffees.

2.1.2.1 Polysaccharides (glycans)

Polysaccharides, by far the most abundant class of carbohydrates in coffee and representing almost 50% of dry matter in green beans, are identified after hydrolysis by their monosaccharide units. In the 10% potassium hydroxide insoluble 'holocellulose', Wolfrom *et al.*(1960) quantified the units as D-mannose, D-galactose, D-glucose and L-arabinose in the ratios 6:2:2:1. Later (Wolfrom *et al.*, 1961) they isolated a mannan, corresponding to 5% (d.b.) of the green coffee bean, then an arabinogalactan (Wolfrom and Patin, 1965) and cellulose (Wolfrom and Patin, 1964). They also isolated mannan and arabinogalactan from an instant coffee powder (Wolfrom and Anderson, 1967), but the heteroglucan contained a different arabinose:galactose ratio from that found in green coffee. In the water-soluble polysaccharides of green coffee, Courtois *et al.* (1963) and Glomaud *et al.* (1966) identified heteroglycans, glucogalactomannan (cold-water extract) and arabinogalactan (hot-water extract). Pictet and Moreau (1970) also examined the water-soluble polysaccharides of green coffee up to 180 °C and found arabinogalactans, galactomannans, xylans and traces of glucans. The highly-polymerized carbohydrates of green and roasted coffee were studied by Thaler and Arneth (1968c) and in other publications of the same group. From the figures given, Trugo (1985) obtained the following amounts of monosaccharide units present in the 'pure polysaccharides' of green arabica coffee: mannose (20.8% d.b.), galactose (9.3%), glucose (6.8%), arabinose (1.8%). This is in good agreement with the work of Wolfrom (see above). Thaler (1976) mentioned that the content and properties of arabica and robusta polysaccharides are not significantly different, although Clifford (1985b) suggested that the mannose–galactose ratio is ca 4:1 for arabicas and 2:1 for the robustas.

More recently, Bradbury and Halliday (1988, 1990) investigated the whole polysaccharide fraction in green coffee by the type of linkage of the units. The monosaccharides obtained after hydrolysis are mannose (22.4% d.b.), galactose (12.4%), glucose (8.7%), and arabinose (4.0%), with minor contents of rhamnose (0.3%) and xylose (0.2%). The values are in agreement with the previous findings. The glucose



sucrose (saccharose)

raffinose

stachyose

Fig. 2.5 Polysaccharides

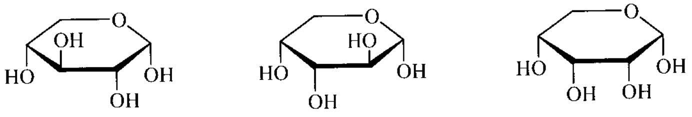
is entirely in an unbranched 1–4 linked form, but the glucan component being resistant to amylase hydrolysis and inert to strong-alkali extraction, the authors concluded that starch (α-glucans) was absent and cellulose (β-glucans) was present in green coffee, a result previously suggested. Fischer *et al.* (2000) analyzed the structure and content of total polysaccharides in arabica coffee beans, finding a content of 56 %, with more than 50 % mannan and galactomannan, 22 % being arabinogalactan and 20 % cellulose. In the early stages of growth, cellulose and arabinogalactan predominate (high percentages of the corresponding monosaccharide units), while later in the development, mannan and galactomannan increase.

Polysaccharides are partially lost (ca 30 %) by roasting, via various and not well-known mechanisms, dehydration, formation of condensation complexes linked, for example, with polysaccharides, protein or protein fragments, and chlorogenic acids (Trugo, 1985).

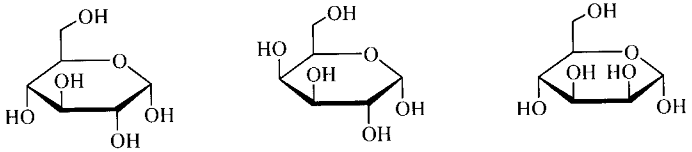
Contrary to low molecular-weight sugars, polysaccharides (celluloses, pectins, starch), do not specially contribute to flavor formation during the roasting of coffee, but they are the most important aroma-binding agents in the beverage (Maier, 1976; Maier and Krause, 1977).

2.1.2.2 Low molecular-weight sugars

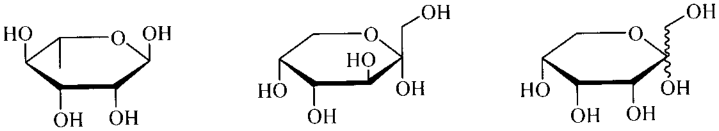
A good analysis of **monosaccharides** (Figure 2.6) was realized by Kröplien (1973, 1974) who listed some previous and contradictory results on monosaccharides in green and roasted coffee. Using column ('combination column') and thin-layer chromatography, he analyzed green, roasted and soluble coffees. He found glucose and occasionally fructose in green coffee (0.02 % d.b.), glucose (0.18 %) and fructose (0.28 %) in steam-treated green coffee, and glucose (0.21 %) and fructose (0.20 %) in decaffeinated green coffee, which shows a partial hydrolysis of sucrose. In roasted coffee, Kröplien also detected arabinose



xylose (α-D-) arabinose (α-D-) ribose (α-D-)



glucose (α-D-) galactose (α-D-) mannose (α-D-)



rhamnose

fructose (α-D-)
(D-*arabino*hexulose)

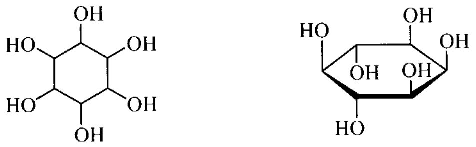
psicose
(pseudofructose)
(*ribo*hexulose)

Fig. 2.6 Monosaccharides

and occasionally galactose, but the total content was very low (0.04–0.08 %) with no detectable difference between steam-treated or untreated samples. In instant coffees, glucose and fructose are only present in traces, usually arabinose predominates (0.45–2.5 %), followed by galactose (0.20–0.93 %) and mannose (0.12–1.05 %); ribose and xylose are also present. Trugo and Macrae (1983) give similar figures, using high-performance liquid chromatography (HPLC).

Tressl *et al.* (1983), using a GC method after trimethylsilylation, reported total reducing sugar contents of 0.1 % for two green arabicas and 0.45 % for two green robustas with mainly glucose (0.030–0.038 and 0.16–0.18 % respectively), fructose (0.023–0.030 and 0.19–0.21 %) and galactose (0.035 and 0.07–0.08 %), ribose and mannose being also present in smaller amounts. Upon roasting, glucose, fructose and ribose disappear nearly completely, while galactose and mannose are transformed to the extent of 40–80 %. Small amounts of arabinose and rhamnose appear. Pokorny *et al.* (1974) (reported by Trugo, 1985) observed that enzymatic hydrolysis, i.e. during one year of storage, produces an increase of reducing sugars (mainly glucose) to a level of 0.5 % but that this content fell sharply on subsequent storage at high temperature (60 °C) and high humidity by Maillard reaction with the free amino acids also present. Bucheli *et al.* (1998 and previous publications) have shown that poor storage generates glucose by sucrose hydrolysis and demonstrated that glucose could be a sensitive marker for green coffee quality. Studying industrial storage of green robusta under tropical conditions, with air conditioning, aeration or not, in bags, they observed that at 28–30 °C, the glucose levels increased under all the conditions examined, with an average of 0.06 % at month 0 and reaching 0.10 % after 8 months. The increase occurs mainly during the rainy season, third to sixth month, when there is also an increase in the moisture content of the beans. Over the same period, there is an increase in the woody/rubbery note linked to the marked increase in glucose.

Mannitol (Figure 2.7), a polyhydric sugar alcohol, has been identified in dried coffee husks by Davis *et al.* (1990) with a content of 1.61–2.03 % and only 0.05 % in green coffee. The other polyol identified in



inositol

myo-inositol (*meso*-inositol)
(1α,2α,3α,4β,5α,6β-cyclohexanehexol)

mannitol

sorbitol (glucitol)

Fig. 2.7 Sugars

husks (0.20–1.03%) and roasted coffee (0.21–0.31%) is inositol. Mishkin *et al.* (1970) isolated and characterized the *meso*-form, *myo*-inositol, from a soluble coffee powder and from a roasted arabica. Xylose occurs only in traces as a free carbohydrate, the content being higher in the total carbohydrates of green (0.18–0.35%) and roasted (0.15–0.33%) coffees and much higher in the total carbohydrates of husks and parchments (Blanc *et al.*, 1989; Prodolliet *et al.*, 1995a,b). The latter authors used anion-exchange chromatography with pulsed amperometric detection for quantifying the main carbohydrates in soluble coffees and consequently determining adulterations. High levels of free mannitol and total xylose are a clear indication of presence of husks or parchments in the process. Addition of cereals or caramelized sugar leads to a high level of total glucose. Noyes *et al.* (1992) also related the levels of mannitol, total xylose, and free sugars with the contents of husks in soluble coffees. A high level of fructose (of the order of 4–5% instead of 0.3–0.5%) in a soluble coffee mixture indicates adulteration by chicory (White, 1995). Mannitol is known to be a selective hydroxy radical scavenger (Morishita and Kido, 1995).

Psicose has been identified and quantified by Blanc and Parchet (1990) after HPLC, derivatization and GC. The level of this sugar, practically absent in green beans, increases upon roasting with a maximum well before complete roast. It is present only in traces in roasted pure coffee. In husks, the level also reaches a maximum during roasting experiments, but is higher than in the beans for a degree of roasting corresponding to a commercial coffee. Therefore this sugar was also proposed as a marker for adulteration by husks of soluble coffees.

Luger and Steinhart (1995) examined the changes in carbohydrate content in green coffee in relation with duration and pressure of steam-treatment. For a robusta, fructose and glucose increased considerably, to 0.15% (1500 ppm) and 0.05% (500 ppm) respectively, after 4-hour treatment at 0.8 bar (in the laboratory). Mannose also clearly increased as did psicose (see previous paragraph). Galactose seems to be destroyed when it is liberated from oligo- or polysaccharides by this treatment. The general behavior is the same with arabicas and robustas, but the increase is dependent upon the species and upon the applied pressure. Sucrose decreased significantly during steam treatment.

In an extract (ethanol:water, 80:20) of a Brazilian coffee, Wolfrom *et al.* (1960) found 5.5% sucrose in the green coffee, and only traces after roasting. A study of the water-soluble **oligosaccharides** of green coffee was presented by Courtois *et al.* (1963) who found, besides the most abundant sucrose, two higher oligosaccharides, raffinose and stachyose. Tressl *et al.* (1983), in the work mentioned above, observed that arabica contains more than double the content of robusta (8.2–8.3% vs 3.3–4.1%) but some differences may be due to variety, maturity stage, processing and storage conditions. The proportion of oligosaccharides can reach 10%, depending on the different varieties.

Trugo and Macrae (1983) confirmed the higher level of sucrose in arabica than in robusta (6.1 vs 3.4%) using HPLC, but did not detect the raffinose and stachyose announced by Courtois *et al.* (1963). Silwar and Lüllmann (1988), using the same method, confirmed the higher content of mono- and disaccharides in green arabicas as compared to robustas (6.5–8.5 vs 1.5–5.5% d.b.) with sucrose as the main component, often constituting 90% or more of this fraction. In the 20 green coffees that they analyzed, the authors did not identify some other low molecular-weight sugars, stachyose, raffinose, galactose, xylose and ribose, that had been reported as being present in traces. Arabinose was identified in all the samples examined, mannose and rhamnose in some of them, maltose in only one robusta.

Guyot *et al.* (1988a) measured the contents in mono- and disaccharides as a function of maturity in a green robusta. They observed that the saccharose content increases while the arabinose content decreases, and that the ratio sucrose:arabinose (from 0 to 0.7 and 5.4) can characterize the stage of maturity. They found 3–3.5% sucrose for ripe beans when the content in arabinose was ca 0.9%.

According to Clinton (1986), the carbohydrates present in a coffee beverage can be listed in the decreasing quantitative order: sucrose, inositol, glucose, arabinose, sorbitol, mannose, mannitol and fructose.

We will mention in this section the results of Zuluaga Vasco and Tabacchi (1981) on the sugar content of lyophilized or sun-dried coffee pulp. The sucrose content decreases during sun drying (3.2 to 1.8%), as does the small value for inositol (0.28 to 0.1%). Glucose (6.8 to 7.6%) and galactose (2.4 to 1.9%) maintain nearly the same level, but the amount of fructose increases notably (9.9 to 15.2%).

2.1.3 LIPIDS

As summarized in the review by Clifford (1985b), the terms 'crude' and 'total' lipid refer to substances extracted by a non-polar solvent and may include non-lipid substances such as caffeine. The yield is a function of the extraction method as much as of the composition of the beans. The crude lipid includes the wax coating the coffee bean (0.2–0.3%), the main constituents of which are the C_{20} and C_{22} amides of 5-hydroxytryptamine [1*H*-indol-5-ol, 3-(2-aminoethyl-), serotonine]. These amides have their importance. As they are possible antioxidants, it has been suggested that premature dewaxing leads to a fall in the bean quality during storage. The major part of the crude lipid is a typical seed oil, with triglycerides of fatty acids, some other esters and unsaponifiable matter.

According to Carisano and Gariboldi (1964) the main free fatty acids (FFA) in the oil (see Section 5,E) are linoleic acid (43–46% of the acids) and palmitic acid (30–35%). Oleic, stearic, arachidic and linolenic acids are also present in lower proportions. The presence of free fatty acids is evidently the most important factor affecting flavor formation during roasting. Carisano and Gariboldi found 0.50–1.89% FFA in petroleum ether extracts obtained from samples of green coffee of different geographical origin. Speer *et al.* (1993) separated the free fatty acids from the total lipids, extracted with *tert*-butyl methyl ether, by means of gel permeation chromatography. They determined the individual acids by capillary GC of the methyl esters. Although they observed variations between coffees of various origins, they found that generally the arabicas (four samples) have a lower free-acid content (1–1.5% of the lipids) than do the robustas (eight samples, 1–2.7%) with similar profiles (see Section 5.E).

Studying Angola green and roasted coffees (eight arabicas, 32 robustas, after dry or wet processing), Derbesy *et al.* (1969) and Roffi *et al.* (1973) measured for total lipids (ether extraction, 24 h) 11.7–14% (d.b.) of fatty acids with 1.6–2.3% unsaponifiable in the arabicas, and 7.6–9.5% acids with 1.0–2.4%

unsaponifiable in the robustas. The fatty acids are mainly palmitic acid, C_{16} (25–34.5% of fatty acids), linoleic acid, $C_{18:2}$ (30–46.5%), oleic acid, $C_{18:1}$ (8.8–17.2%) and stearic acid, C_{18} (6.4–10.9%). Three of the robustas growing in the same location show slightly different results, with 7.3–7.5% acids (less than the average), 16.8–18.1 palmitic acid (less) and 46.4–48 linoleic acid (more). On roasting there is some loss in the lipid content (11–11.5% acids, 1.2–1.7% unsaponifiable for the arabicas and 6.3–7.8% acids, 0.9–1.5% unsaponifiable for the robustas) but the profile is similar.

The composition of fatty acids in coffee oil and coffee wax has been extensively studied by Folstar *et al.* (1975a,b, 1976; Folstar, 1985) who observed large differences in the composition of free fatty acids between the wax (surface layer) and the wax-free oil (underlying cells). The wax contains a rather high percentage of the C_{18}–C_{24} saturated acids, 45.3% of the fatty acids vs 14.6% in the oil. On the contrary, the unsaturated $C_{18:2}$ represents 23.8% in the wax vs 43.1% in the oil. In the triglycerides, the main differences were a lower value for $C_{18:2}$ and higher values for the saturated C_{20}, C_{22}, C_{24} in the wax than in the wax-free oil. The acids of the triglycerides are mainly $C_{18:2}$ (47%) and C_{16} (33%) in the wax-free oil. Later, we will see that this is different for the diterpene esters. The unsaturated acids are mainly esterified with the secondary hydroxyl group of glycerol, a fact common to most vegetable oils (Folstar *et al.*, 1975b).

The list of crude lipid contents of green coffee beans, measured by different authors and published in Clifford (1985b), confirms that arabicas have a higher lipid content (13.5–17.4%) than do robustas (9.8–10.7%), with variations within a species depending upon the location at which the bean is grown.

The effect of lipids in the Maillard reaction has been studied by many authors who cooked or roasted mixtures of amino acids and reducing sugars in various vegetable oils. The thermal oxidative degradation of lipids generates lower molecules, for instance aldehydes, that contribute to the formation of heterocyclic volatile compounds.

The total **diterpene** (Figure 2.8) content in the lipids is about 20%. Cafestol is the main constituent of the unsaponifiable portion of coffee oil. It has been known for a long time but the purification was rendered difficult by the presence of kahweol, which is more unsaturated and therefore more sensitive to light, oxygen, heat, and acids (see references in Haworth *et al.*, 1955). The structure of cafestol was established by Djerassi *et al.* (1958), but the structure proposed (Djerassi *et al.*, 1959) for kahweol had one double bond in excess. It was corrected by Kaufmann and Sen Gupta (1963) to the formula shown in Figure 2.8. In coffee oil diterpenes occur preponderantly as esters of saturated fatty acids. For Kaufmann and Hamsagar (1962) the terpenic esters represent 18% of the coffee lipids which are mainly triglycerides (75%). The proportions of the main fatty acids are reversed for the diterpene esters (linoleic ca 20%, palmitic ca 40%) compared with the triglycerides. They are followed by stearic (ca 18%) and oleic (ca 11%) esters, the proportions also being reversed in the triglycerides. Minor amounts of the C_{20} and C_{22} esters are present. The saturated esters of the diterpenes are clearly more abundant than the unsaturated. These results are globally confirmed by Folstar *et al.* (1975b) who also examined the composition of the esters in the wax (extraction of whole beans) as a function of extracting time. The authors observed an increase for C_{16}, and sharp decreases for C_{20}, C_{22} and C_{24} until the values were similar to those in the wax-free oil (extraction of ground beans). This might be an interpretation of inconsistency in the results. The diterpene content decreases during storage. They are partially removed during dewaxing and extensively destroyed during roasting (Clifford, 1985b). Gautschi *et al.* (1968) suggested that diterpene degradation may probably be the origin of volatile terpenes, and possibly of naphthalenes.

Speer (1989) identified 16-*O*-methylcafestol in green robustas, and Speer *et al.* (1991) quantified it using HPLC with detection in UV at 220 nm. In 10 samples from different countries, they found total contents of 0.07–0.15% with only 1.0–3.4% of this as unbound alcohol. The same authors (Speer *et al.*, 1992a) did not detect it in any of the green arabicas analyzed. Finding that this diterpene is even more stable than cafestol during roasting, they considered that it could be an ideal indicator for characterizing

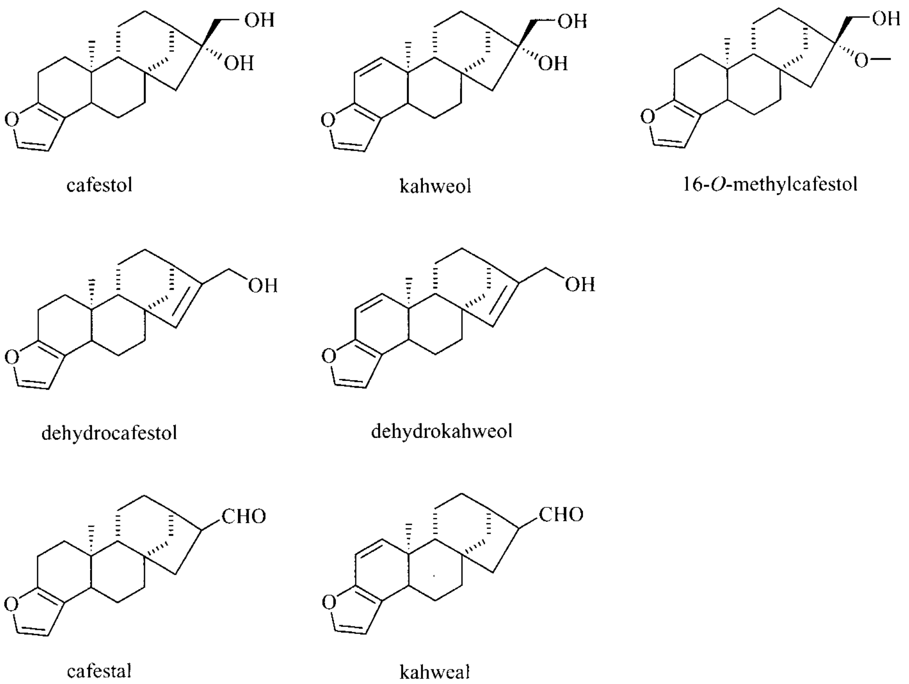


Fig. 2.8 Diterpenes

coffee blends. They succeeded in detecting 2% robusta in mixtures and found it in the ppm range in soluble coffees. The same group (Kölling-Speer *et al.*, 2000) devised a new method for quicker determination of 16-*O*-methylcafestol in roasted coffee. Using gel permeation chromatography, they separated the free fatty acids (see above), triglycerides and diterpene esters (Speer, 1995; Kurzrock and Speer, 1998). After solid phase extraction and semi-preparative HPLC they identified the esters of cafestol and 16-*O*-methylcafestol. At first sight, the most striking differences were higher proportions of C_{18} and $C_{18:2}$ and a lower proportion of C_{20} for the cafestol esters than for the 16-*O*-methylcafestol esters. The distribution does not change upon roasting or in an espresso brew. The same authors (Speer *et al.*, 1992b; Tewis *et al.*, 1993) also identified two dehydration products formed during roasting, dehydrocafestol and dehydrokahweol. Finding a relationship between roasting temperature and the cafestol/dehydrocafestol ratio for arabicas and robustas, they proposed using this ratio as an objective criterion for organoleptic estimation of roasted coffees (Kölling-Speer *et al.*, 1998). Suspecting the presence of other diterpene degradation products, Speer *et al.* (2000b) analyzed the thermal behavior of cafestol itself and proposed the name of cafestal for a new compound also found in roasted coffee. At 270 °C the proportions of dehydrocafestol and cafestal first increase and then decrease after 60 min, when the content of cafestol decreases continuously. These authors apparently also identified kahweal but there is no comment.

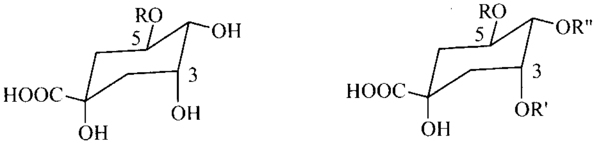
The extraction of lipids from the roasted coffee into the brew has received special attention because of the tendency of cafestol, and possibly also kahweol, to increase the (total and low-density lipoprotein) cholesterol level (the intake of 16-*O*-methylcafestol is too low to be taken into account). This effect of the coffee beverage, already suspected in 1963 (reference quoted in Katan and Urgert, 1995), was later confirmed (for example Thelle, 1992, and earlier work; many publications appeared on the subject) and the brewing method was especially examined. The conclusion was that there is no problem when the brew is filtered and not boiled as it is (or at least was) in the Scandinavian countries. Sehat *et al.* (1993) compared the lipid contents in ground coffee, boiled, espresso and filter coffee beverages, and also examined the influence of the grinding grade. The content is much higher in boiled (2.2 % relative to ground coffee) than in espresso (0.4 %) and filter coffee (0.2 %). More lipids are extracted with fine than with coarse grade for boiled coffee contrary to what is found for espresso. From the data of Katan and Urgert (1995), with the same coffee consumption (five cups/day), the cholesterol level increases in order from filter to instant, percolator, mocha (Neapolitan), espresso, Scandinavian, French press ('cafetiere') and Turkish coffee. Diterpenes are extracted by hot water but retained by a paper filter. Even if some cafestol and kahweol is left in the coffee brew, it is not dramatic. Effectively, the two alcohols have been recognized to have chemoprotective effects and could serve as specific protective agents against benzo[*a*]pyrene (see Section 5.A) and aflatoxin B1, two well-known carcinogens. Mechanisms are proposed for their actions (Huggett *et al.*, 1998).

Sterols are also present in free and esterified forms. We will take the review of Folstar (1985) as the reference. Free sterols constitute on average 2.2 % of the total lipids and the esters with fatty acids 3.2 %. In the sterolic fraction, 92.7 % are 4-desmethylsterols, 2 % are 4-methylsterols and 5.1 % are 4,4-dimethylsterols. The three major components belong to the first category: sitosterol (53–54 % of the sterolic fraction), stigmasterol (20–22 %) and campesterol (18–19 %). The qualitative composition has been reported to be independent of the geographical origin.

2.1.4 CHLOROGENIC ACIDS

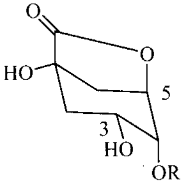
Besides caffeine, Payen (1846b) isolated another crystallized compound from coffee. From his observations, he deduced that it was a mixed salt which he named 'chloroginate de potasse et de caféine' (Chlorogensaures Kali-Kaffeïn', Payen, 1846d), the colorless corresponding acid developing a green coloration. The acid was also isolated from the salt by Gorter (1908a) who prepared several salts and found that upon hydrolysis, chlorogenic acid was split into caffeic and quinic acids. The structure was established as 3-caffeoylquinic acid by Fischer and Dangschat in 1932 [although there is no stereochemistry given, it is certainly the most abundant 5-CQA according to the present IUPAC nomenclature for cyclitols (IUPAC, 1976)]. Mabrouk and Deatherage (1956) estimated the content of chlorogenic acid as 4.3 % by weight of roasted coffee beans. They confirmed that in the presence of a strong acid, chlorogenic acid was hydrolyzed to one molecule of caffeic acid and a molecule of quinic acid. Quantitative determination of chlorogenic acid and trigonelline in coffee was proposed by Lehmann and Hahn (1968). Determination of and changes in chlorogenic acids during roasting were presented by Feldman *et al.* (1969) in a more general review on the importance of non-volatile compounds to coffee flavor. Horman and Viani (1973) studied the caffeine–chlorogenate complex, as such or in coffee brews, by NMR.

The chlorogenic acids (CGA) are ubiquitous in the plant kingdom (Figure 2.9). They are a family of esters of quinic acid (QA) (Section 5,**E.62**) with several hydroxycinnamic acids, particularly caffeic (Section 5,**H.86**), ferulic (Section 5,**H.87**), *p*-coumaric (Section 5,**H.84**) acids. In coffee they are essentially mono- and diesters and by far the prevailing acids (Maier, 1993). Other esters may occur but generally only in small amounts. The higher total content of the CGAs in robustas (mean content 9 %) than in arabicas (6.5 %) could be responsible for the inferior quality of brews made with robustas (Clifford, 1985a). Effectively, CGAs constitute an important class of compounds by virtue of their taste, said to be astringent (especially the diesters of caffeic acid), which can be easily recognized in a coffee brew and be objectionable at too high a concentration (Ohiokpehai *et al.*, 1983). According to these authors, the mono/diester molar ratio is very important for the sensation, low ratios being undesirable The astringency of diCQA is reduced by 5-CQA. Castle de Menezes and Clifford (1988, also Clifford, 1985a) studied the influence of maturity and of the processing method (see beginning of this chapter) on the



5-CQA R = caffeoyl,
5-FQA feruloyl,
5-CoQA *p*-coumaroyl

3,5-di-CQA R = R' = caffeoyl, R" = H,
etc.



R = caffeoyl

4-caffeoyl-γ-quinide

Fig. 2.9 Chlorogenic acids

caffeoyl and dicaffeoylquinic acid contents and on their ratio. The monoesters decrease first from unripe (green/hard cherries) to semi-ripe stage (half-green/half-pink) then increase to the ripe stage. This is followed by a decrease in the slightly overripe (almost black cherries), more important with wet than with dry processing. The diesters decrease throughout maturation, although not regularly. If the mono/diester ratio is important for the final coffee taste, cherries with some green have to be avoided or discarded, and dry processing has to be used if the cherries are harvested by stripping. Effectively, with almost ripe (light red) to slightly overripe cherries and dry processing, the ratio is relatively constant. Clifford and Kazi (1987), who studied the influence of maturity on the content of chlorogenic acids, caffeine and trigonelline, concluded that the two latter compounds are not responsible for any change in beverage acceptability. The changes in their content during maturation are small and they have a minor contribution to the beverage bitterness. Clifford's group, always interested in the organoleptic properties of the CGAs, found for 5-CQA, the most abundant of all, a taste threshold of 50 ppm in distilled water, this being a bitter recognition theshold. At 500 ppm a metallic note appears, and at 1 g/L (1000 ppm) sourness and other notes appear. More limited studies on 3-CQA give a bitter threshold similar to that of 5-CQA (Kellard *et al.*, 1988). In the same publication, chemical syntheses were proposed.

Van der Stegen and Van Duijn (1981) used HPLC for the analysis of green arabica, arabusta and robusta. They examined the influence of steaming, decaffeination and roasting on the caffeoylquinic (CQA), feruloylquinic (FQA) and dicaffeoylquinic (diCQA) acids (in their publication, the present IUPAC nomenclature for cyclitols is not used, therefore all '3-' have to be 'translated' as '5-', and vice versa). For the arabusta the figures are between those of the other species. The mono CQAs are predominant (70% of total CGA in robusta, 80% in arabica), with the FQAs representing only 5.5% in arabica and 12% in robusta. In each group the 5-isomer is predominant (ca 75% of the CQAs and 85% of the FQAs). The diCQAs represent 15% of the total CGA in arabica and 20% in robusta. From the figures given, the differences between the 4,5-, 3,5- and 3,4-diCQA do not look very significant. There is a tendency for the decreasing order to be 3,5-, 4,5-, 3,4- in arabicas. With steaming and decaffeination there is a slight decrease in the total CGA, but essentially the 5-monoesters clearly decrease when the 3- and 4-isomers increase. This might be explained by acyl migration. The effect of roasting is much more important, the total CGA content dropping to ca 3 %. The 5-monoesters and diesters content is reduced when that of 3- and 4-CQA does not change appreciably. After roasting at 205 °C of arabicas and robustas, Trugo and Macrae (1984) obtained similar results. After a very dark roast (19 min), there were more CGAs left in a Guatemala arabica (2.4 % d.b.) than in a Uganda robusta (1.75 %) consisting mainly of CQAs. Besides, 5-FQA degrades at a slower rate than do CQA and diCQA, and degradation rates are faster in robustas than in arabicas.

Iwahashi *et al.* (1985) identified a mixed diester in a green robusta, the 5-feruloyl-4-caffeoylquinic acid (5-F,4-CQA) using NMR and MS (the publication does not use the present IUPAC nomenclature for cyclitols), then Morishita *et al.* (1989) identified the isomer 4-F,5-CQA (IUPAC nomenclature). They found the two isomers in arabicas and a robusta, with concentrations of 40–80 ppm (d.b.) in arabicas and 10-times higher in a robusta. Bicchi *et al.* (1995), in the HPLC/UV pattern of a green robusta, identified three peaks as being those of feruloyl-caffeoylquinic acids without attributing one peak to one isomer. The results of Morishita *et al.* for the other acids are consistent with those of Van der Stegen and Van Duijn (1981), with high contents of 5-CQA and 5-FQA, higher in robusta than in the arabicas. The content of 5-FQA reached 20 % of the total CGA in the robusta examined. Upon roasting, the mixed diesters disappear completely, and the diCQA contents decrease and even disappear in several arabicas, with 5–8 % of the starting diCQA surviving in the robusta. As reported above, 5-CQA and 5-FQA are clearly reduced when 3-CQA, 4-CQA and 4-FQA increase or are slightly reduced. For a Brazil arabica, the authors found a maximum for 3- and 4-CQA after 40 min at 177 °C, and after 45 min at 205 °C the total CGA content is only 1.1 % (6.7 % when green).

Lactones corresponding to CGA have been detected in roasted coffee, but Bennat *et al.* (1994) were able to isolate, identify and quantify the 3- and 4-cafeoylquinic lactones (3-, 4-CQL) not present in green coffee. They used HPLC with diode array detection and HPLC–thermospray-MS (MS and NMR data are given). The 3-CQL is slightly more abundant than the 4-isomer (ratio 60:40), the total mean content being 0.23 % (d.b.). The formation of the lactones reaches a maximum with a medium roast (ca 6 % organic roasting loss), then the lactones decompose. A very low content was found in a soluble coffee probably because of hydrolysis during the extraction process.

Leloup *et al.* (1995) focused their attention on the degradation kinetics of the CGAs and the behavior of the quinic and hydroxycinnamic moieties during roasting of a Columbia coffee at 240 °C for up to 10 min. The main lines are similar to previous descriptions, and they proposed the following mechanisms. At the beginning of roasting, in the presence of water, 3,5-diCQA (for example) undergoes rapid hydrolysis, and 5-CQA, probably the most reactive, is esterified on the quinic acid site with carbohydrates or proteins. Then after 2 min, the hydrolysis of the esterified 5-CQA starts, giving caffeic acid and esterified quinic acid. Owing to steric hindrance, the 3-CQA is not esterified but is directly hydrolyzed. All caffeic acid units, from diCQA, esterified 5-CQA, and 3-CQA are not freed but decompose rapidly, mainly to 4-ethylcatechol (Section 5,**H.29**) and catechol (Section 5,**H.23**). During this time, free or freed quinic acid degrades slowly, mainly to hydroquinone, catechol, phenol, and pyrogallol. A similar scheme would be valid for ferulic acid derivatives, with degradation mainly to 4-ethylguaiacol (Section 5,**H.35**) and guaiacol (Section 5,**H.33**).

Bicchi *et al.* (1995) envisaged the possibility of characterizing green and roasted coffee by the CGA fraction, using the results of HPLC with UV detection and principal component analysis (PCA), and comparing them with the results from sensory evaluation. A direct relationship is not yet fully demonstrated.

Chlorogenic acids can be either beneficial or detrimental to biological processes depending on the conditions. *In vitro*, they have scavenging activities and an inhibitory effect on conjugated diene formation in the first stage of linoleic acid oxidation (Morishita and Kido, 1995). 3,5-DiCQA, 5-CQA and caffeic acid are more effective than ascorbic acid and much more so than mannitol, which is a selective hydroxy-radical scavenger. This suggests that they are also peroxy-radical scavengers, thus inhibiting lipid peroxidation and the next step. The authors proposed a mechanism for this antioxidant activity and considered these CQA to be potentially important biological antioxidants.

2.2 THE VOLATILE COMPOUNDS IDENTIFIED IN GREEN COFFEE BEANS

In spite of careful examination of the published results, the number of chemicals identified in the volatiles of green coffee beans is difficult to calculate exactly. Figure 2.10 lists the four research groups that have been particularly active in the analysis of raw beans.

Green coffee, which has a relatively faint but characteristic odor, has mainly been studied in order to appreciate the quality of the cultivated product and to detect, before roasting, any off-flavors present in defective beans. One of the first studies of volatile green coffee constituents (headspace) by gas chromatography is due to Rhoades (1960). With some modifications of the procedure and equipment described two years before (Rhoades, 1958), he obtained quantitative data on volatile constituents and, for the first time, on green beans. The analysis of 13 retail brands of coffee was performed and the data presented for comparative purposes. Mass spectrometry not yet being at the disposal of Rhoades, the identifications were based on retention times and, for some typical compounds, on their distinctive odors. Of the 19 compounds found in roasted coffee, 16 were also detected in the green beans of one or more of the varieties analyzed. The differences observed were suggested to be helpful in typing or grading coffee. The author concluded that only a statistical analysis of green coffee data and organoleptic tests on roasted coffee could show if there were a relationship between the two. Rhoades positively identified and quantified relatively volatile constituents, aldehydes, ketones, furans and sulfur compounds. During the same period, Clements and Deatherage (1957) and Lentner and Deatherage (1959) identified acetic, propanoic, butanoic, pentanoic, malic, citric and quinic acids in green coffee (Section 5.E). They also isolated caffeic (Section 5,H.86) and several chlorogenic acids (Section 2.1.4). In 1960, Zlatkis and Sivetz identified pentanal (valeraldehyde) which contributes to the penetrating odor of green coffee. Carisano and Gariboldi (1964) confirmed the presence of palmitic acid in green beans, both free and esterified as glyceride (see Lipids, Section 2.1.3).

Rodriguez *et al.* (1969) studied the concentrations of several volatile components in different lots of Kona (Hawaii) coffee demucilaged experimentally by various methods (mechanical, enzymic, chemical or natural fermentation). The concentrations of four volatile components, acetaldehyde, dimethyl sulfide, acetone and isobutyraldehyde, varied depending on the treatment, but the relative concentrations of these compounds did not vary appreciably except for acetaldehyde following over

(1) **Hag AG, Jacobs-Suchard Corporate R&D, Kraft Jacobs Suchard, Bremen, Germany**
Vitzthum O.G., Werkhoff P., Holscher W., Steinhart H., Bade-Wegner H., Gutmann W., Barthels M., Boosfeld J. and Ablanque E **(Federation Nacional de Cafeteros de Colombia, Bogota).**

(2) **Nestlé Techn. Assist. Co., Nestec Ltd, Lausanne, Switzerland**
Liardon R., Spadone J.C., Takeoka G., Blanc M., Cantergiani E., Brevard H., Krebs Y., Feria-Morales A., Amado R. and Yerantsian C.

(3) **US Army Natick Laboratories, Natick, Mass., USA**
Merritt C.Jr., Robertson D.H., McAdoo D.J.

(4) **IRCC-CIRAD, Montpellier, France**
Vincent J.C., Barel M., Challot F., Guyot B., Cros E.

Fig. 2.10 Research groups which have identified 83.5% of the raw coffee volatile constituents.

fermentation. Therefore, they suggest, acetaldehyde could serve as an indicator of spoilage in Hawaiian coffee.

Merritt *et al.* (1970) having in the meantime at their disposal a more efficient GC/MS system, identified 45 volatile compounds in the headspace of green beans and tried to relate, as did Rhoades in 1960, the constituents of the roasted aroma to the volatiles already present in the raw material. Their opinion is that it is safe to postulate that most of the hydrocarbons present in green coffee are formed by oxidation of fats during all the operations happening before roasting. This work can be considered as the first performant analysis of green coffee volatile constituents: among the 30 newly identified compounds figure 12 hydrocarbons and 10 esters. Unfortunately the nomenclature of the hydrocarbons mentioned in their list is not clear, particularly concerning the *normal* or *iso* structures.

Barel *et al.* (1974, 1976) analyzed the defect origin of 'stinker' beans by headspace gas chromatography. Gibson (1974a) compared the composition of the volatiles of a Colombian coffee (data from Rhoades, 1960) with two distinct hybrid species of mild East African arabica coffee and studied the quality characteristics associated with green coffee volatiles. He observed a strong correlation between the concentration of dimethyl sulfide (Section 5,**Q.11**) and the acidity of coffee beverage. Dimethyl sulfide has antioxidant properties and it could react with hydroperoxides or peracids to give at first dimethyl sulfoxide, then methylsulfenic acid. In fact, coffees with a high content of the sulfide, when stored under ventilated conditions, are better than those with a low content. However, Gibson did not conclude that there was a causal relationship because the presence of dimethyl sulfoxide, intermediate to acidic compounds, was not proven. Different hybrids grown in the same geographical conditions, or the same hybrid grown in different geographical conditions, show different concentrations. Besides, high concentrations of dimethyl sulfide correspond to the appearance of a desirable bluish color of the beans. In the second part of his work, Gibson (1974b) especially studied the ethanol content and the ethanol/methanol ratio in East African green coffee possessing a special flavor known in Kenya as the 'Solai' or 'up-country' flavor, desirable if not excessive. Such coffees present high contents of ethanol which do not vary appreciably with different types of fermentation. The high contents and high ratios are attributed to the special climate and geographical situation of the Solai area. In this particular area, the ethanol/methanol ratio increases with altitude, up to 13.5 at 2100 m (7000 ft). The flavor quality of the corresponding roasted coffee could be explained by organoleptic differences between the ethyl and methyl derivatives formed during roasting.

Amorim *et al.* (1976, 1977) using thin-layer chromatography isolated and identified polyamines from green coffee beans: putrescine and spermine. These products are degraded during roasting, except putrescine which could be detected in the light roasted coffee.

A second significant step in the knowledge of green-coffee flavor constituents (Figure 2.11) was made by Vitzthum *et al.* (1976) who described the identification of 53 volatile compounds including numerous heterocycles, 15 of which not previously found in roasted coffee. The particular 'green' smell of unroasted beans was discovered to be due to the presence of methoxypyrazines in concentrations of about 10 ppb. The most potent and typical member of this family, 2-isobutyl-3-methoxypyrazine (Section 5,**O.77**), has a perception threshold of 0.002 ppb and had been found to be responsible for the typical flavor of green bell pepper *Capsicum annuum* (Buttery *et al.*, 1969b,c) and green peas (Murray *et al.*, 1970). A mechanism for the biogenesis of these methoxypyrazines has been proposed by the latter authors (Murray and Whitfield, 1975). Moreover, Vitzthum *et al.* (1976) confirmed that the basic fraction of green coffee contains various pyridines, quinolines, aromatic amines, and alkylpyrazines while the neutral fraction mainly consists of furans, aromatic aldehydes, and alcohols. Two years later, the same research group (Gutmann *et al.*, 1979) compared the headspace aroma profiles of the hybrid arabusta with various samples of arabica and robusta. They observed that arabusta contains more aromatic compounds (alkylbenzenes and naphthalene) and that arabica is definitely richer in terpenic constituents and poorer in furans and pyrazines. In these two important analytical works, about 90 new volatile compounds were identified in green coffee.

Rahn *et al.* (1979) measured the effect of steam treatment on the green beans by quantifying their content of catechol and 4-vinylcatechol.

Vincent *et al.* (1976) and Guyot *et al.* (1982, 1983) mention that a few defective 'stinking' beans can contaminate an entire lot in spite of careful manual, mechanical or colorimetric control. Their analytical studies concerned the identification of off-flavors (foul smelling and 'stinking') constituents in green beans by comparing the volatile constituents of good and rejectable arabica coffees. Vincent *et al.* (1976) observed the presence of butanol, 2-methylpropanol, 1,2-butanediol and 3-hydroxy-2-butanone (acetoin) in the defective beans. Butanol and 1,2-butanediol have effectively only been identified in green coffee, and the excessive and undesirable creamy, buttery note of acetoin has been underlined by other authors (see Section 5,D). Moreover, Guyot *et al.* (1982, 1983) detected the acrid and powerful odor of 2-isobutyl-3-methoxypyrazine (Section 5.**O.77**) previously discovered by Vitzthum *et al.* (1976), and also discovered the negative effect of six esters, two diketones and a terpenic alcohol (linalool, Section 5,**B.35**). Surprisingly, none of these compounds individually present the foul smell that characterizes the stinking beans, but they do possess mainly fruity, pear, apricot, pine cone, silage-like, green, rotten or potato-like flavor notes. Their detection thresholds are, on the other hand, so low that a little excess can probably explain their offensive and undesirable effect.

Dyszel (1985) performed a thermogravimetric analysis/atmospheric-pressure chemical-ionization mass spectrometry (TGA/APCIMS) on green coffee beans. Using various combinations of 14 ($M+1$) ions, the author concluded that unknown coffees can be matched, with varying degrees of certainty, to known coffees for their country of origin.

At the Twelfth ASIC colloquium at Montreux, Spadone and Liardon (1988) published the fact that the musty note of certain Brazilian coffees is due to the presence of 2,4,6-trichloroanisole (2,4,6-TCA, Section 5,**H.82**) and geosmin (Section 5,**B.46**). The same research group (Spadone *et al.*, 1990) performed an extensive analytical investigation of 'Rio' off-flavor (musty, cellar-like odor) in green coffee, adding to the number of identified volatile compounds (Figure 2.11). The authors asserted that about 20% of Brazil coffee production presents the so-called 'Rio' defect which is characterized by a strong medicinal, phenolic or iodine-like note. More details on this defect were given by Liardon *et al.* (1990) and the study was completed with the analysis of a Puerto Rico coffee possessing a particularly pronounced off-flavor (Spadone *et al.*, 1990). Among the original identifications figured phenolic compounds including vanillin (Section 5,**H.56**), while salicylates, trichlorophenol (Section 5,**H.81**), geosmin and trichloroanisole had been mentioned eariler. Geosmin has a disagreeable earthy–musty odor. As opposited to vanillin, which has a pleasant and desirable flavor, methyl (Section 5,**H.77**) and ethyl (Section 5,**H.78**) salicylates have an undesirable sweet and rooty–fruity odor. The presence of 2,4,6-trichloroanisole would explain the earthy and musty notes detected in 'Rio' green coffees. Holscher *et al.* (1995) calculated that 10–25 contaminated beans/kg could negatively affect a coffee beverage. They suggested a hypothetical degradation pathway of the pesticide (Prochloraz) which already contains the trichlorophenol moiety (see Section 5.H).

Spadone *et al.* (1990) also identified aliphatic unsaturated aldehydes, long-chain 2-alkanones, lactones and esters which are only present in green coffee and would give the beans the characteristic soapy, fatty and fruity (coconut, peach, apricot) notes. They were the first authors to find β-damascenone (Section 5,**D.38**) in raw coffee, a compound that resists roasting and contributes highly to the tea-like and fruity flavor of the beverage.

2-Methylisoborneol (MIB, Section 5,**B.44**), which could be responsible for the earthy, musty smell of roasted robustas (Vitzthum *et al.*, 1990) has been found by Grosch *et al.* (1993) and Rouge *et al.* (1993) in green robustas and, at lower levels, in arabicas. It is not really characteristic of robustas according to the latter authors.

In Colombian green coffee, Boosfeld *et al.* (1994) and Boosfeld and Vitzthum (1995) elucidated the structure of two pairs of unsaturated aldehydes, (*E*,*E*)-2,4- and (2*E*,4*Z*)-2,4-nonadienal as well as (*E*,*E*)-2,4- and (2*E*,4*Z*)-2,4-decadienal, probably generated via autoxidation of unsaturated fatty acids and contributing particularly to the typical green-coffee odor. The products were identified by mass spectrometry, GC-FTIR and NMR spectroscopy. The authors used particularly mild extraction techniques in order to avoid artifact formation and isomerization of the conjugated double bonds. The sensory impressions of these aldehydes at the sniffing port varied from metallic, fried, and flowery to oily notes.

The aroma compounds in green coffee were reviewed by Holscher and Steinhart (1995) with an exhaustive bibliography of the 230 identified volatile compounds, ten of them being mentioned for the first time (Figure 2.11). Among them figured decanal, (*E*)-2-hexenal and (*E*,*E*)-2,4-heptadienal which have not yet been identified in the roasted beans and which have characteristic fatty and soapy notes. On the other hand, the authors mentioned that a large number of green-coffee volatiles survive roasting and contribute to the final roasted-coffee flavor.

Bade-Wegner *et al.* (1998) studied the volatile compounds associated with the 'over-fermented' flavor defect, considered to be one of the most objectionable organoleptic defects in coffee. They examined two defective samples of arabica and one sample of robusta green coffees, comparing them to reference products with a neutral flavor. As the off-flavor can be due to overfermentation of green coffee or to the presence of so-called 'stinker' beans, the authors considered that the previous studies and identifications were more indicative than causative. By GC-olfactometry, three *fruity* odor notes were perceived, at different intensities, that were attributed to ethyl 2-methylbutanoate (Section 5,**F.40**), ethyl 3-methylbutanoate (Section 5,**F.41**) and ethyl cyclohexanecarboxylate (Section 5,**F.46**). The three esters were considered to be the most important contributors to the 'over-fermented' flavor defect.

Mathieu *et al.* (1996, 1998) identified the volatile components released by fresh coffee berries at different stages of ripeness. Among 45 compounds, two esters, 2-pentyl acetate (Section 5,**F.13**) and 2-heptyl acetate (Section 5,**F.15**), have not been found in green beans and many terpenic hydrocarbons have been identified (see in Section **H5.1**).

Procida *et al.* (1997) used dynamic headspace GC-MS to characterize the aroma volatiles of green arabica and robusta coffees (six varieties of each). They declared that robusta varieties have a higher content of methanol, acetone, pyridine, methylpyrazine and furfural, and that methyl formate, *tert*-butyl alcohol, and furfuryl alcohol are almost exclusively found in robustas. When looking at the figures, the conclusions are not as clear-cut. They identified 12 original constituents, mainly hydrocarbons and alcohols.

The contents of volatile acids of green and roasted coffee were studied by Wöhrmann *et al.* (1997a). By means of simultaneous distillation/extraction (SDE), ion exchange and GC/FID, they identified and quantified 12 acids, including volatile saturated and unsaturated aliphatic acids which have a rancid and sweaty character.

In 1999, Vitzthum reviewed the last 30 years of coffee chemistry research and, among others, the off-flavors to be found in some green coffees. He gives an odor description of the individual compounds of a green coffee aroma extract separated by GC.

Very recently, Cantergiani *et al.* (2001) (Figure 2.11) investigated the composition of the volatile fraction of a Mexican green coffee with a pronounced earthy/mouldy off-flavor. The three components responsible were determined by GC-olfactometry, isolated, concentrated and finally characterized by GC/MS as geosmin (Section 5,**B.46**), 2-methylisoborneol (Section 5,**B.44**) and 2,4,6-trichloroanisole (Section 5,**H.82**). The concentrations were lower in the reference than in the defective samples. The authors attributed the formation of the three compounds to post-harvest treatments. The methoxypyrazines, isopropyl- (Section 5,**O.75**), 1-methylpropyl- (Section 5,**O.76**) and isobutyl- (Section 5,**O.77**), present in only slightly higher concentrations in the defective sample than in the reference, could contribute only marginally to the defect. The isobutyl compound, present at approximately 1000-times its odor threshold, is probably important but its mouldy/earthy note is weak. Among the compounds identified, 56 were not in the literature lists. The most interesting of these were the peculiar acetals in Section 5,**I.118** and **I.119**, a pyrazine (Section 5,**O.76**) and a substituted maleimide (Section 5,**K.63**).

Non-volatile multifunctional acids present in green coffee are not mentioned here. Their contribution to the flavor and taste qualities essentially concerns the roasted coffee beverage. Their structures and properties are partly discussed in Section 5.E. Similarly, free acid-phenols present in small amounts, mainly decomposition products of chlorogenic acids and depsides, will be discussed in Section 5.H.

2.3 RESULTS

Figure 2.11 illustrates the identification, between 1958 and 2001, of 300 volatile constituents given off by green coffee beans. The curve shows that the first significant contribution was realized by Merritt *et al.* (1970) (Group 3 in Figure 2.10) who identified 33 compounds, including 15 hydrocarbons and 10 esters. The next remarkable step was due to Vitzthum *et al.* (1976) and Gutmann *et al.* (1979) (Group 1) who, respectively, discovered 49 and 47 volatiles, mainly hydrocarbons, alcohols, pyrazines, ketones and furans. Twenty years later, members of the same laboratory (Holscher and Steinhart, 1995) added ten new constituents, mainly aldehydes, raising the total number of original identifications by this research group to 111. In the meantime, Spadone *et al.* (1990) (Group 2) identified 27 volatiles, mainly phenols, aldehydes, ketones and esters. Very recently, thanks to the discovery of 56 original constituents (Cantergiani, 2001), this group raised the number to 87 identifications. Vincent *et al.* (1976) and Guyot *et al.* (1982, 1983) (Group 4) contributed by adding a further 16 compounds.

Figure 2.12 shows that hydrocarbons, alcohols, aldehydes and esters represent the majority of the identified compounds. Thiophenes, oxazoles and thiazoles are absent, an observation confirming that they are formed exclusively during the roasting of coffee, as will be discussed in Sections 5.J, 5.L and 5.M.

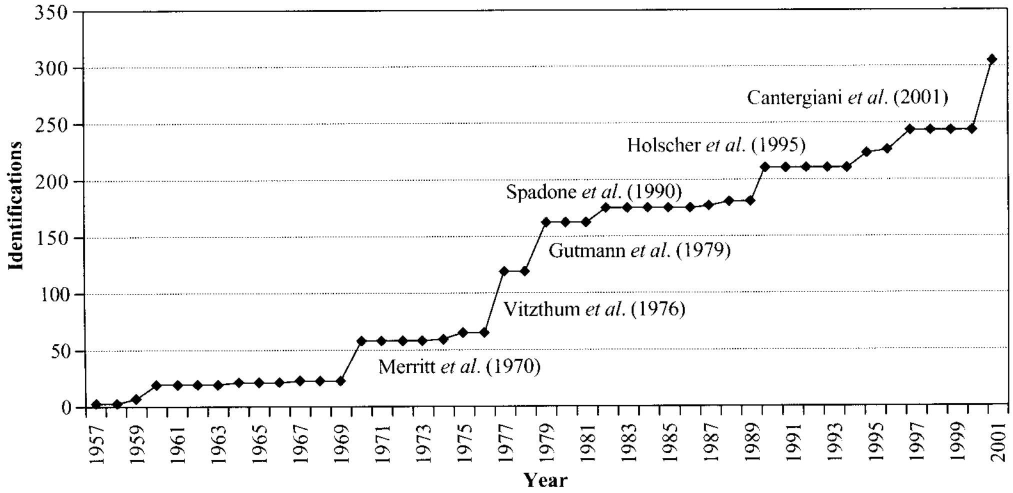


Fig. 2.11 Progressive identification of green coffee volatile constituents

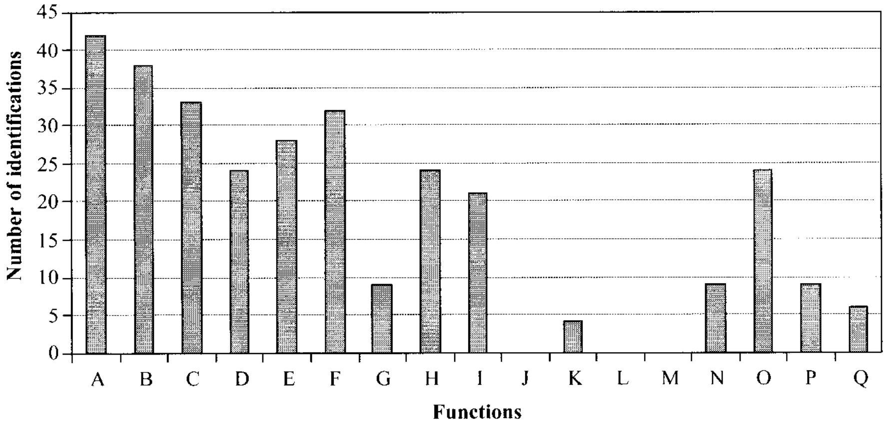
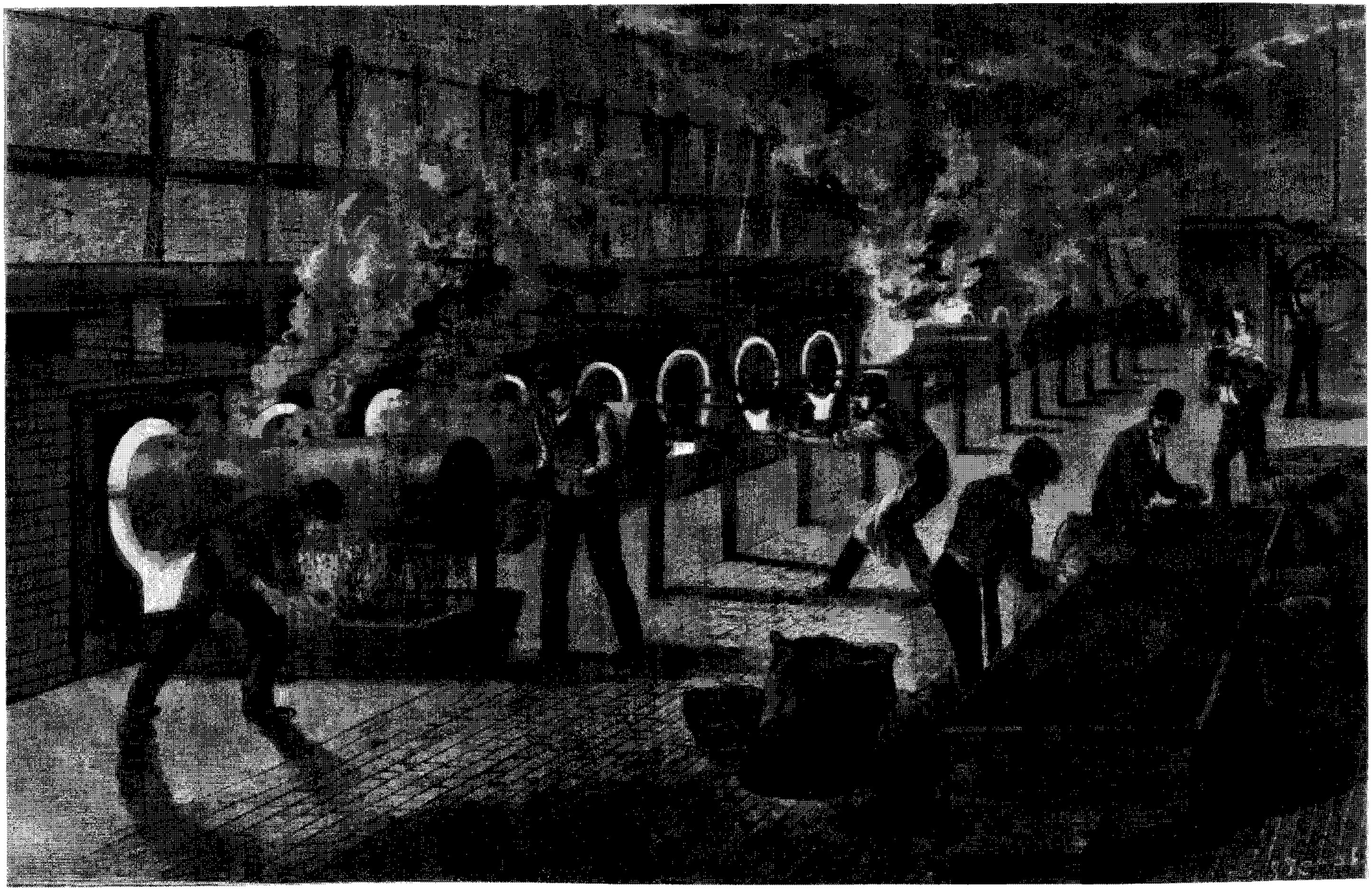


Fig. 2.12 Distribution of the volatile constituents of green coffee



View of a roasting workshop in a coffee factory (New York, in about 1880)

3

From the Raw Bean to the Roasted Coffee

3.1 THE ROASTING PROCESS: STRECKER AND MAILLARD REACTIONS

As early as 1862, Strecker observed that alloxan [5-oxobarbituric acid, 2,4,5,6(1*H*,3*H*)-pyrimidinetetrone] reacts with alanine to give carbon dioxide and acetaldehyde, a number of other compounds producing the same result. Schönberg *et al.* (1948) proposed the name 'Strecker degradation' for all degradations of α-amino acids by carbonyl compounds to give aldehydes and ketones containing one carbon fewer, whatever the degrading agent may be. Schönberg and Moubacher (1952) reviewed the various conditions contributing to this reaction. A recent review of Strecker degradation is due to Rizzi (1999).

Camille Maillard (1878–1936) is recognized as being the first chemist to observe that free amino acids, most commonly from peptides and proteins, interact with reducing sugars to form nitrogenous heterocycles and brown melanoidins (1912). A biography of this chemist was published by Adrian (1991) and numerous scientific publications, reviews and meetings have been devoted to the reaction bearing his name (see in the reference list: Maillard Reactions, Meetings of 1979, 1983, 1985, 1989, 1993, 1997). Without depriving Maillard of the credit for this discovery, we will mention that Erdmann (1902b) had already observed empirically a similar non-enzymatic browning reaction resulting from the heating of sugars with amino acids, peptides and other nitrogenous components.

The desired flavor of coffee is produced during roasting, green coffee having no desirable flavor of its own. Kaufman (1951) observed that the pressure formed in the beans during roasting is necessary to the proper development of coffee flavor. He also noticed the change in pH during roasting. The initial pH of 5.8 in green coffee drops at first to about 4.8, and rises again, the optimum roast being shortly after the minimum pH value. The proposed explanations are the formation and volatilization of acetic acid from sugar decomposition, decarboxylation of acids formed by rearrangement of the sugar molecule, and the decarboxylation of chlorogenic acid. In summary, the conclusions were that chlorogenic acid contributes to body and astringency; sucrose contributes to the color, aroma, bitterness and sourness, and proteins remain perfectly stable, but minor protein components such as free amino acids, are highly reactive. Trigonelline generates pyridine and may consequently be responsible for some objectionable flavors. Caffeine has no function other than a contribution to the bitterness.

Thaler and Gaigl (1963) compared the content of amino acids (after hydrolysis) in roasted coffee with their content in green coffee (Thaler and Gaigl, 1962). Serine, cystine and lysine are clearly reduced, arginine disappears. Glutamic acid, the most abundant of the amino acids, proportionally increases. Later, Thaler and Arneth (1968c) and Thaler (1976) observed the partial destruction of the glucides, except cellulose, during roasting. Oligosaccharides and arabans disappear nearly totally, galactans are strongly degraded, but mannans remain particularly resistant. Monosaccharides, conjointly with amino acids and amines, are at the origin of the formation of melanoidins, pyrazines and other nitrogen-containing heterocycles, resulting mainly from the Strecker and Maillard reactions.

Radtke *et al.* (1966b) suggested that the less-volatile aroma fraction contains the most important flavor constituents, but they failed to detect any new compound in the non-volatile aroma of stale coffee. The influence of the degree of roasting (ca 230 °C, increasing time) on the chemical composition of an arabica coffee was studied by Fobé *et al.* (1968) who determined the content of total sugars, caffeine, proteins and lipids. Sugars at first increased, then decreased. Caffeine followed the same scheme with smaller variations (+8 to −20% of the original 1.4% value). The proteins decreased regularly. The free fatty acids increased from 1.1% to >3% after 1 h roasting when the unsaponifiable component decreased from 11 to 9.3%.

The importance of the less-volatile compounds to the flavor was also studied by Feldman *et al.* (1969) in their review on the changes in chemical composition between green and roasted coffees. They summarized the data on the behavior of proteins, carbohydrates and acids (volatile, non-volatile and phenolic) during roasting. They observed that the content of chlorogenic acid could be used to measure the degree of roast. Pypker and Brouwer (1970) tried to apply the headspace analysis to the less volatile constituents of coffee, by collecting them in a short auxiliary column. The results were somewhat disappointing, but the technique allowed the observation of the considerable higher content of some phenolic compounds in robusta versus arabica coffee. Maier *et al.* (1968) and Maier and Buttle (1973) isolated and characterized the brown compounds in roasted coffee. They hydrolyzed the oligosaccharides and oligopeptides with mineral acids and some enzymes, and identified some sugars and amino acids. Borralho da Graca an Pereira (1973) hydrolyzed coffee grounds and identified numerous amino acids.

Roffi *et al.* (1973) analyzed 41 samples of green and roasted coffees, again observing that the most interesting changes during roasting affect carbohydrates, amino acids, trigonelline and chlorogenic acid. Fatty acids were not significantly changed. Clifford (1975a,b) reviewed these compositional changes. Pokorny *et al.* (1975) mentioned that the Maillard reaction can sometimes start in green coffees stored at relatively high temperatures and humid medium, producing a browning reaction. The reaction is subsequently maintained by the increased quantities of sugars and amino acids simultaneously and progressively liberated by hydrolysis.

The composition of the caramel-color polymers present in roasted coffee has been studied by Casier *et al.* (1978) and by Tressl *et al.* (1978a). As pointed out by Heyns (1979), the substantial modifications produced by the thermal treatment of green beans at 180–220 °C result from two principal modes of reaction. (i) The caramelization, which consists essentially of pyrolysis of mono-, di-, oligo- and polysaccharides, forming reactive intermediates under dehydration (mainly of furanic type) that condense into more complex molecules to give soluble caramel compounds or insoluble high molecular weight black particles. (ii) The Maillard reaction, which involves the interaction between reducing sugars and amino acids or low molecular-weight peptides, leading logically to the formation of nitrogen- and sulfur-containing molecules, in particular heterocyclic compounds such as pyrroles, thiophenes, oxazoles, and thiazoles.

Tressl *et al.* (1983) described the formation of aromatic substances in roasted coffee in relation to the levels of free amino acids and reducing sugars. They observed that over 99% of sucrose, glucose and fructose are degraded during roasting.

According to Macdonald and Macrae (1986), proteins will be denatured upon roasting and further degraded to yield low-molecular-weight fragments. Some of the proteins will react with carbohydrates and with phenolic compounds. From the analysis conducted by these authors, the sum of the total amino acids was clearly reduced, by about 30% for a robusta and slightly for an arabica. The thermally-labile amino acids are evidently more involved; serine and cysteine (determined after oxidation) are reduced by more than 50%, arginine disappears. The most stable are alanine, glutamic acid, glycine, leucine and valine.

Coffee aroma formation has been summarized by Ho *et al.* (1993). The authors insist on the deamidation of glutamine and asparagine which give more pyrazines than do the corresponding acids when heated with reducing sugars. The amide nitrogen would contribute to the amino/carbonyl reactions. Holscher and Steinhart (1994) reviewed the formation pathways for roasted-coffee aroma-relevant compounds. They considered that the majority of the volatiles identified in roasted coffee are formed by Maillard reactions. However, recent sensory-specific investigations have shown that many odorants with a strong flavor impact are also generated by other formation pathways besides the Maillard reaction.

Gretsch *et al.* (2000) studied the evolution of coffee aroma characteristics during roasting, by correlating the global aroma quality of ground coffee with the relative composition of its odorous components for various roast levels, ranging from green to dark roast coffee. According to these authors, only sparse information is available on the evolution of odorous volatiles during roasting, except for the works of Silwar and Lüllmann (1993b), Kawakami *et al.* (1995) and Hashim and Chaveron (1996).

A remarkable scheme of the Maillard reactions has been proposed by Hodge (1953, 1967) who gives clear information on the mechanisms of this non-enzymatic browning reaction. Nursten (1981) proposed a classification system of the Maillard reaction products: (i) 'simple' sugar dehydration/fragmentation products (furans, pyrones, cyclopentenes, carbonyl compounds, acids); (ii) 'simple' amino-acid degradation products (aldehydes, sulfur compounds); (iii) volatiles produced by further interactions (pyrroles, pyridines, imidazoles, pyrazines, oxazoles, thiazoles, compounds from aldol condensations). The role of sugar fragmentation in the Maillard reaction has been studied by Hayashi and Namiki (1986) and an overview of the thermal degradation of carbohydrates has been published by Maga (1989).

Studies of the behavior of Maillard reaction products analyzed by solid-phase microextraction (SPME)–GC/MS selective detection have been realized by Coleman (1996, 1997). A concerted procedure for the generation, concentration, fractionation, and sensory evaluation of Maillard reaction products has recently been published by Parliment (1999).

Within the scope of this chapter, it would be unrealistic and irrelevant to cover the scientific literature on non-enzymic browning reactions. The quoted references are restricted, but the articles mentioned have been chosen mainly for their connection with the generation of coffee aroma during roasting. There were several reviews by Vernin on the Maillard reaction and heterocyclic compounds in food flavors (Vernin, 1980a, 1981; Vernin and Parkanyi, 1982; Vernin *et al.*, 1983). The parameters influencing the browning reaction are indicated: temperature, pH, humidity of the medium and relative concentration of the precursors. Although the heterocycles are essentially formed by heat treatment of sugars, amino acids and fatty acids, some compounds can result from the degradation of minor constituents such as vitamins, trigonelline and uric acid. Vernin comments on the seven distinct steps of the Maillard reaction previously proposed by Hodge (1953, 1967) and also details the formation of furaneol, isomaltol and maltol from Amadori intermediates.

Reviews have been published by Baltes (1980, 1982, 1990), Angrick and Rewicki (1980), Hurrell (1982), Danehy (1983), Ames (1987, 1988) and Reineccius (1995). The chemical pathways of the Maillard reaction have also been reviewed by Ledl (1990).

The role of the Maillard reaction in foods and medicine has been the subject of the Sixth International Symposium on the Maillard Reaction (Mlotkiewicz, 1998). Other recent reviews on this reaction are by Tressl and Rewicki (1999), Ho and Chen (1999) and Reineccius (1999).

Through model reactions, the mechanisms of formation of the minor products are easier to understand. This helpful and efficient approach allows the prediction of structures and, after the syntheses of most of the original compounds, the measurement of the organoleptic properties by focusing the analytical effort on the appropriate fractions. Ledl and Severin (1982) studied the browning reactions involving hexoses. Through labeling experiments involving the reaction of ^{13}C-labeled hexoses, pentoses and D-lactose, Tressl *et al.* (1993a,b, 1995, 1998d) gave an insight into the formation pathways of fragments of the sugar skeletons and their polycondensation into Maillard polymers. The formation of melanoidin-like polymers from pentoses and hexoses has been intensively studied by Tressl *et al.* (1998a,b,c).

Numerous model reactions based on the thermal interaction of amino acids and sugars have been studied and reviewed. We will only mention a series of works done by Baltes and his team (Berlin). After the publication of 'Model studies on aroma formation in coffee' (Herrmann and Baltes, 1981), many other articles appeared: Mevissen and Baltes (1983) on the reaction of D-glucose with phenylalanine, Baltes and Bochmann (1986a) on the volatiles formed in a model reaction between serine and threonine with sucrose (this reaction was extensively developed in several publications), Baltes and Bochmann (1986b) on the interaction of hydroxyamino acids with sucrose, Bohnenstengel and Baltes (1992) on the reaction of glucose with aspartic acid or asparagine, Baltes and Knoch (1993) on the reaction of tryptophan with reducing sugars and sugar degradation products. Farmer *et al.* (1989) identified 152 compounds in the headspace analysis of the cysteine/ribose reaction, with or without the presence of a phospholipid, a model reaction that is also involved in the formation of meat flavor.

In a survey, Fors (1983) compiled the sensory properties of nearly 450 Maillard reaction products classified according to their chemical structure. The review includes qualitative aroma and flavor descriptions as well as sensory threshold values in different media.

3.2 IDENTIFICATION AND CHARACTERIZATION OF FLAVOR CONSTITUENTS: EXTRACTION, ISOLATION, IDENTIFICATION AND QUANTIFICATION

In a patent on the 'Improvements in a method for isolating the aromatic principle contained in roasted coffee', Reichstein and Staudinger (1926a) reviewed and commented on the work previously done with a view to isolating the aromatic principle from roasted coffee along the following lines. Early in the Nineteenth century, Lampadius (1832) heated the ground coffee beans directly, but the aromatic substances were destroyed to a great extent at the high temperatures used and were contaminated by decomposition products. Robiquet and Boutron (1837a), and later Cech (1880), extracted the roasted and ground coffee beans with different solvents but some of the very volatile aromatic substances were lost by the elimination of large quantities of solvent. On the other hand, numerous products, such as fats and oils, were extracted together with the aromatic substances and could not be separated. Payen (1846a,b,c, 1849) in fact used steam-distillation. He distilled a coffee infusion containing a great deal of water and described the aromatic principle thus obtained to be an oil. Erdmann (1902a) realized a steam-distillation with roasted coffee, a method later used by Grafe (1912) and Bertrand and Weisweiler (1913). For Reichstein and Staudinger (1926a), the excessive quantities of steam necessary made this method inconvenient for economic production of coffee aroma. Moreover, the subsequent separation of the very small quantities of aromatic substances was unsuccessful. Other works on the roasted product of coffee did not contain any information about the proper composition of the aroma. Bernheimer (1880a), for example, described the identification of some simple substances contained in the gases obtained by roasting and believed he had discovered the 'bearer' of the aroma in the coffee oil. This result was not confirmed by Padé (1887) or by Jaeckle (1898) in spite of exhaustive research. The British patent specifications of Barotte (1889) and Meyer (1891), as well as the French patent specification of Forot and Pélissier (1902), described the condensation, in receivers cooled to about −20 °C, of the vapors of a ground roasted coffee heated under vacuum. Reichstein and Staudinger (1926a) considered that the substances particularly responsible for the pleasing aroma of coffee were far too volatile to be recovered under these conditions and they recommended the use of much lower condensation temperatures (−80 °C and even down to −180 °C). Some of the essential parts of the aroma have a relatively low volatility. Erdmann (1902a), for example (work quoted above), had isolated from the 'coffee oil' a fraction with a pleasant coffee odor, having a boiling point of 93 °C under 12 mm pressure and containing nitrogen. Therefore, according to Reichstein and Staudinger (1926a) the use of extremely low condensation temperatures should make it possible to obtain all the substances essential for the aroma, even the very volatile compounds such as diacetyl or aliphatic aldehydes, substances which contribute undeniably to the aroma.

The publication by Dimick and Corse (1956) was one of the first to describe the use of gas chromatography for the separation and identification of volatile materials in foods. The authors estimate that for the flavor chemist, most of the volatile material is of low flavor intensity and contributes little, if anything, to the characteristic aroma of the food! They refer for example to a study by Nelson and Curl (1939) who reported that the composition of the volatiles from Montmorency cherries is 97 % methyl and ethyl alcohols, 3 % benzaldehyde, and a trace of geraniol, other substances being in amounts too small to be determined. They also mention the difficulties they encountered when from 100 lb of strawberries one might only expect to obtain 0.1 to 0.4 g of the aromatic oil. They pragmatically observe that the isolation of total volatiles from a food yielded little information in regard to the total flavor of the food, and that separation by distillation usually resulted only in group separation, with the risk of thermal damage. They commented on gas–liquid partition chromatography (GLPC) recently developed by James and Martin (1952) and by James *et al.* (1952) for the separation of volatile acids and amines (the retention times on the columns were then called 'residence times'). Dimick and Corse also quote what is in fact headspace analysis: adsorption of emanations from food material onto activated charcoal or sweeping the food with a gas stream and condensation with dry ice or liquid air. They do not forget to mention the work of Reichstein and Staudinger (1926a) on coffee (published later, 1955a). Rhoades (1958) describes the use of gas chromatography (GC) for analyzing coffee volatiles and emphasizes the extraordinary advantages of the technique: the short time necessary to quantify a rather large number of constituents, the rapid information on the effects of time and temperature on roasting, the accelerated measurements on staling, storing and packaging, and evidently the characterization of the large number of coffee varieties. Rhoades proposes a sampling procedure based on the sweeping of volatile materials (the headspace) from the heated, ground coffee by a stream of warm, moist helium. Kaiser (1974) presented the use of low-temperature GC separation for the analysis of trace constituents of coffee aroma.

Methods used in the chemistry of natural substances, particularly in the coffee field, were reviewed by Reymond (1974), and the techniques for flavor analysis by Merritt and Robertson (1982) and by Adda and Jounela-Eriksson (1979).

Roboz (1974) commented, without giving any original result, on GC/MS techniques in use at that time, and which progressively replaced gas chromatography using packed columns. They combined highly efficient capillary columns with sensitive mass spectrometers. Other quick and smooth techniques, such as combined extraction and chromatography using supercritical fluids, introduction of new combinations such as GC/FTIR or headspace enrichment (multidimensional GC), and multidetection, progressively brought exceptional development in aroma knowledge. The efficiency of GC/MS and of GC/FTIR is related essentially to the copiousness of their data banks and original structures cannot easily be inferred from their information alone. However, when there is neither an isomer nor a homologue, nuclear magnetic resonance remains the practically universal identification method suitable for small quantities, but the isolation of trace components in a pure state is still an almost insuperable problem, especially if the starting material is scarce or if the preenrichment techniques are not selective enough. A study of the sample preparation techniques for GLC analysis of biologically derived aromas has been published by Parliment (1986).

Flavor characterization using adsorbent-trapping/thermal desorption and GC/MS has been reviewed by Hartman *et al.* (1993). This method was developed after the introduction of the porous polymer Tenax as a GC stationary phase. Tenax was used to isolate and concentrate volatile compounds in food (Zlatkis *et al.*, 1973). Solid phase microextraction (SPME/GC) introduced by Arthur and Pawliszyn (1990) and developed by Pawliszyn's research group (Eisert and Pawliszyn, 1997; Pawliszyn, 1997) used coated fibers. Yang and Peppard (1994) reported the HS-SPME/GC of espresso-roast coffee and found that conventional headspace sampling was more sensitive for the highly volatile compounds, SPME detecting more of the less volatile compounds. Wang *et al.* (1996) tested SPME coupled with microwave assisted extraction in several matrices including coffee beverages. They described the determination of maltol (Section 5,**I.146**) and ethylmaltol (2-ethyl-3-hydroxy-4*H*-pyran-4-one), which they call Veltol® and Veltol-Plus®. Only the first of these compounds occurs naturally, but they are often added to food products. Recently, Bicchi *et al.* (1997) applied solid-phase microextraction to the vapor phase in equilibrium with ground coffee and coffee brews (HS-SPME) and to the brews (LS-SPME) and found that, with both samplings (HS, LS), SPME could be used for routine analysis of coffees. Combined with principal component analysis (PCA), the method allowed the differentiation between coffee samples (arabicas, robustas and blends). Nevertheless, according to the authors, an increase in peak area reproducibility with LS-SPME is desirable in order to improve PCA effectiveness. Ramos *et al.* (1998) used GC/MS to compare the extracts of a brewed coffee obtained by liquid–liquid extraction with two solvents, headspace–solid phase microextraction and supercritical-fluid extraction (SFE). To simplify, the volatile compounds are preferentially extracted with supercritical CO_2, the less-volatile compounds by HS-SPME (this is in agreement with the work of Yang and Peppard), liquid–liquid extraction lies between the two other methods, but pentane extracts slightly more compounds than does methylene chloride. The authors found a high olfactory resemblance between the brewed coffee and the extract with supercritical CO_2. Blank *et al.* (1999) underlined some of the difficulties encountered when quantification is desired. The amount of compound adsorbed on the fiber depends on the partitioning coefficients and on the sampling time. The time required for equilibrium between the phases depends on the chemical and physical properties of the compounds and on the presence of other volatile compounds. A difficulty with coffee, and other food aromas, is the wide concentration range of the aroma-active compounds.

Quantification of aroma-impact components by isotope dilution assays (IDA) was introduced in food flavor research by Schieberle and Grosch (1987), when trying to take into account losses of analytes due to isolation procedures. The labeled compounds have to be synthesized, the suitable fragments have to be chosen, and calibration has to be effected. A quantitative determination of ppb levels of β-damascenone (Section 5,**D.38**) in foods, particularly in roasted coffee (powder and brew), was developed by Sen *et al.* (1991a). Semmelroch *et al.* (1995) quantified the potent odorants in roasted coffee by IDA. Hawthorne *et al.* (1992) directly determined caffeine concentration in coffee beverages with reproducibility of about 5% using solid-phase microextraction combined with IDA. Blank *et al.* (1999) applied this combined method to potent coffee odorants and found it to be a rapid and accurate quantification method. They also concluded that the efficiency of IDA could be improved by optimizing the MS conditions.

Chirospecific analysis can only be applied to a minority of coffee flavor constituents, most of them being aromatic and planar heterocyclic compounds. Nevertheless, Werkhoff *et al.* (1993) published a review on chirospecificity in essential oil, fragrance and flavor research.

To date, approximately 850 compounds have been identified in roasted coffee. The components most frequently identified in the aroma (Figure 4.2) are furans (16.1%), pyrazines (11.8%), pyrroles (11.0%) and ketones (10.5%). Let us however remind ourselves that the most abundant families are not necessarily those which contain the most characteristic or powerful components.

3.3 SENSORY ANALYSIS: DETERMINATION OF QUALITIES AND DEFECTS

Food flavors do not generally consist of a single key compound. This is particularly true for roasted coffee, one of the most complex aromas. Analytical chemists wanted to bring their stones to the building in the hope of isolating the key compound(s) as the philosopher's stone but, as the French mathematician Henri Poincaré (1854–1912) said: '*une accumulation de faits n'est pas plus une science qu'un tas de pierre n'est une maison*' (an accumulation of facts is no more a science than a heap of stones is a house), and an exact reconstitution of a coffee flavor, which has evidently no economical interest, should remain a utopia. Since the isolation by von Reichenbach in 1844, of the pseudo-key compound which he named 'assamar' (see Section 4.1), numerous scientists have claimed to have identified the character impact compounds. A great step forward is certainly due to Reichstein and Staudinger in 1926 with the discovery of furfuryl mercaptan (furfurylthiol, Section 5,**I.128**), α-diketones and alkylpyrazines. In the sixties the advent of gas chromatography allowed the rapid identification of several hundreds of constituents, a great number of them contributing substantially to the richness and originality of the flavor. Nevertheless the long lists of chemicals detected in foods 'have created the illusion that we understand their flavor chemistry better than we do' (Acree *et al.*, 1984).

In 1966, Le Magnen proposed a designation of the organoleptic qualities of coffee. A choice of tests for the organoleptic valuation of coffee has been presented by Depledt (1968) and a sensory analysis of coffees and instant coffees has also been published by Van Roekel (1976). Vitzthum *et al.* (1976) were the first to use the 'sniffing'-technique in the analysis of coffee volatiles.

After an avalanche of analytical results, mainly with a view to discover a maximum number of new and typical constituents, some research groups focused their attention on the 'key constituents', arranging them in order of decreasing flavor contribution. This approach has been particularly conducted during the last two decades, thanks to the development of new concepts in sensory analysis and to the general tendency to improve the quality of foodstuffs. Moreover, the application of sensory analysis allowed, in collaboration with chemical methods, the identification of the compounds responsible for the aroma and, notably, determination of the intensity of individual odors of the fractions separated by chromatography.

Reviews of the association of chemical and sensory aspects were published as early as 1965 by Wick and later, for instance, by Vernin (1981), who gave examples of odor–structure relationship. Different structures can be related to similar odors, similar structures to different odors, and similar structures to similar odors. A statistical treatment of data became necessary to correlate analytical results with those obtained by sensory analysis, as stated by Adda and Jounela-Eriksson (1979). Since then, correlation between sensory analysis and instrumental analysis has been the subject of important sessions of the Weurman Flavor Research Symposia, for instance in the chapters on 'Sensory science in flavor research' (Weurman 5th Meeting, 1987) or 'Correlation between sensory and instrumental analysis' (Weurman 7th meeting, 1993).

In addition to the book by Arctander (1967), exhaustive reviews on flavor descriptions and threshold values of aroma volatiles have been published, for instance, by Meilgaard (1975), Maga and Sizer (1973a,b), Maga (1975a,b,c, 1976, 1978a,b,c, 1979, 1981a,b,c, 1982a), Calabretta (1978), Vernin (1979) and Fors (1983). The chemistry of odor stimuli has been studied by Ohloff (1986) and a survey of molecular structure and sensory attributes has been published by Heath (1986). In a recent retrospective, Rothe and Kruse (1999) described how to solve flavor problems by sensory methods.

3.3.1 ODOR THRESHOLD, FLAVOR THRESHOLD

In 1957, Patton and Josephson proposed that the odor thresholds of the identified compounds should be systematically determined in order to ascertain their significance in the total perception of a food flavor. Guadagni, Buttery, Teranishi and their colleagues at the Western Regional Research Center (Albany, CA, USA) began measuring odor thresholds of various compounds from the 1960s (Guadagni *et al.*, 1963a,b) and have compiled numerous lists of odor thresholds for many interesting compounds (Teranishi *et al.*, 1991; Buttery, 1999). Unfortunately, sensory methods being based on physiological perception (of more or less trained panelists) and on numerous important physical parameters (partition coefficients in various solvents, temperature, exact concentrations in controlled air flows, etc.), the measured values fluctuate and are sometimes imprecise. We nevertheless report some of the published thresholds of individual constituents in Chapter 5 with brief mention of the experimental conditions used by the various authors.

3.3.2 ODOR ACTIVITY VALUE (OAV) OR ODOR UNIT OR AROMA VALUE OR FLAVOR UNIT

The importance of minor components in flavors and fragrances has been emphasized and discussed by Ohloff (1977), the author referring to the concept of 'odor value', a first approach to bringing to light the contribution of a compound to the flavor of a particular food. The 'aroma value' was proposed in 1963 by Rothe and Thomas as the ratio of the concentration of a volatile compound to its odor threshold. The concept was also used by Guadagni *et al.* (1966) and Mulders (1973b), and expanded in newly developed GC variants by Grosch and Acree (see below). Although it has been successfully used, it must nevertheless be considered with a critical eye: odor thresholds are, in fact, 'monodimensional' values; they are only one point on the Stevens' curve which represents the variations of the perceived intensity of an ingredient according to its concentration. Consequently OAVs have a somewhat restricted significance owing to the fact that they neglect the slopes of the olfactometric curves. In any case, it is important to have thresholds measured in a medium similar to the medium under analysis.

Using odor units, Tressl (1989) found that some of the compounds that contribute the most are furfurylthiol (Section 5,**I.128**, sulfury), 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (Furaneol®, Section 5, **I.100**, caramel), 2-isobutyl-3-methoxypyrazine (Section 5,**O.77**, green), 2- and 3-methylbutanal (Section 5,**C.12** and 5,**C.13**, malty, burnt), guaiacol (Section 5,**H.33**), and 4-vinylguaiacol (Section 5,**H.36**, smoky burnt).

On the basis of the odor activity value (OAV) concept, only a limited number of volatile components are sensorially relevant in a given foodstuff (Grosch, 1994). Teranishi *et al.* (1996) also presented a computer-assisted correlation of chromatographic and sensory data in food aromas. In a bar graph were shown the logarithms of the concentrations and of the odor units of the individual constituents of the aroma. The representation shows clearly the constituents present above the threshold values and therefore the most useful for the aroma.

3.3.3 GAS CHROMATOGRAPHY–OLFACTOMETRY (GC-O)

This method was at first used empirically and then only to detect the smell of effluents at the exit of a chromatograph using, in fact, the human nose as a detector. Qualities were attributed to the various 'odorant peaks' which were also characterized by their retention indexes. One evaluation was not sufficient, hence the development of the following techniques.

3.3.4 DILUTION ANALYSIS: CHARM® ANALYSIS AND AROMA EXTRACT DILUTION ANALYSIS (AEDA)

A procedure based on the relative odor thresholds of volatile compounds with known GC retention indexes was proposed by Acree *et al.* (1984), thus transforming the qualitative GC-O to a quantitative method by computerizing the observations. The concept of CHARM® analysis was systematically constructed from the idea of 'odor values'. It is a dilution-to-threshold technique. A flavor extract is injected into the chromatograph, and during the entire chromatogram, the tester presses a button each time he notices a smell and again when he does not detect any smell. This gives a diagram with square signals. Then the extract is diluted by a known factor and another run is effected. This is continued till there is no more response. The different diagrams are then combined.

Acree (1993, 1997) summarized the history of GC-O, giving examples of its application in natural product chemistry. He speculated about its future, using it as a method to bridge the gap between sensory science and analytical chemistry. Acree emphasized the fact that none of the detectors used in gas chromatography is as sensitive as the human nose for many of the odorants found in foods. He noted that splitting devices can be altered by casual obstructions and, in all cases, reduce the dose of the odorant delivered to the 'sniffer'. Deibler *et al.* (1999) reviewed the characteristics of the GC-O technique.

Also based on the OAV concept, the aroma extract dilution analysis (AEDA), was developed by Grosch and his team and was first published in 1986 by Schmid and Grosch. A series of articles followed (Ullrich and Grosch, 1987; Grosch, 1993; Guth and Grosch, 1994; Grosch, 1995). As obviously stated by Grosch (1994), distinguishing between the more potent odorants and those volatiles having low or no odor activity is the first task to be solved in flavor analysis. Like CHARM® analysis, AEDA is based on the progressive dilution of an extract obtained from the food, each diluted sample being analyzed by GC-olfactometry. In this case, an odorant is noted when smelled. The highest dilution at which it is perceivable gives the flavor dilution (FD) factor, that is to say, the ratio of the concentration of the odorant in the initial extract to its concentration in the most dilute extract in which the odor is detected by GC-olfactometry. The FD factor is therefore a relative measure and is proportional to the odor activity value (OAV) of the compound in air. The graph (log FD vs retention indexes), called an aromagram or olfactogram, is formed of bars. Odorants with high FDs are important contributors to the characteristic flavors or off-flavors and are suitable as indicator substances for an objective determination of flavor differences in foods. The big advantage of the method is that it does not need sophisticated equipment.

Applying this technique to roasted coffee extracts, Grosch (1996) determined the significant constituents of ground coffee powder to be 3-mercapto-3-methylbutyl formate (Section 5,**Q.20**) (FD 2048), 2-ethyl-3,5-dimethylpyrazine (Section 5,**O.24**) (FD 2048), and (*E*)-β-damascenone (Section 5,**D.38**) (FD 2048). For the beverage, the main contributing constituents are 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolon, Section 5,**G.12**) (FD 2048), 5-ethyl-3-hydroxy-4-methyl-2[5*H*]-furanone (Section 5,**G.13**) (FD 1024), and 2-ethyl-3,5-dimethylpyrazine (FD 1024). In this publication furfurylthiol is mentioned with a rather low FD of 256. In other articles (Semmelroch *et al.*, 1995; Semmelroch and Grosch, 1996), furfurylthiol is noted as having the highest OAV of the compounds (quantified by isotope dilution assays, see Section 3.2) examined in roasted coffee and in brews prepared from arabica and robusta varieties. However, this thiol is known to be unstable (Grosch *et al.*, 1993). 4-Vinylguaiacol (Section 5,

H.36) and 4-ethylguaiacol (Section 5,**H.35**) have high flavor dilution factors and are important in the flavor. They have also high concentrations and high thresholds, therefore the OAVs are weak. Some compounds having a typical earthy character are 2-ethenyl-3,5-dimethylpyrazine (Section 5,**O.46**) and 2-ethenyl-3-ethyl-5-methylpyrazine (Section 5,**O.47**, Grosch *et al.*, 1996) which were identified by Goldman *et al.* (1967) and recognized as having a roasted, intense nutty smell. Unfortunately vinylpyrazines have a short lifetime. They rapidly polymerize in the presence of air, forming a brown sticky compound.

The study of the valuation, release and formation of key odorants of roasted coffee was continued by Grosch (2000) who confirmed that the roasty-sulfurous smelling furfurylthiol is undoubtedly the outstanding odorant of coffee.

The CHARM® and AEDA analyses based on odor detection thresholds (measurement of the odor potency) have been criticized. The conclusions as to the relative contribution of odorants to a flavor may be limited, the responses for a given compound being dependent on the concentration. The relative intensity of two odorants with the same threshold does not necessarily correspond to their relative concentrations in a mixture (Abbott *et al.*, 1993). For these authors, the contribution of a compound to an odor is probably better determined by CHARM® analysis than by AEDA, which does not take into account the duration of the smell. Other methods have been proposed for a better determination of potent odorants.

3.3.5 OSME ANALYSIS

The name of the method is not an acronym but the Greek word meaning odor. Osme was developed to take into account psychophysical laws (De Maria *et al.*, 1994). The odor intensities of the eluted compounds are followed by trained panelists moving a cursor with a scale (from none = 0 to extreme = 15) and recorded. This gives an aromagram called an 'osmegram' (odor intensity vs retention indexes) representing odor significance of the compounds in a flavor. At the same time, the qualities are described. The subjects' capability for establishing a good relationship between both the odor intensity and the area under the odor peak and physical stimuli has first to be established.

3.3.6 GC-SNIF ANALYSIS

This sensorial analysis (headspace-GC–sniffing) has been developed by Pollien *et al.* (1997). It is realized with panels of eight (six as a minimum) to ten members. Only one concentration level is needed. As in CHARM® analysis, the panelist presses a button as long as he can perceive the odor of a GC effluent. The time-dependent signal is continuously recorded by the computer. The individual aromagrams (square signals) are averaged. The mean aromagram is normalized. Independent panels generate similar aromagrams. The height of a signal represents the number of panelists who have detected an odor at the corresponding retention time, not the odor intensity. The peak height is called NIF (nasal impact frequency), the peak area is SNIF (surface of nasal impact frequency). If a 'NIF' is smaller than 100%, it means that the concentration of the compound is below the odor threshold for one panelist or more. Without a direct measure of odor intensity, NIF and SNIF increase with concentration, consequently with odor intensity, allowing olfactogram comparisons. The method does not require trained panelists or dilutions, and is therefore quicker and easier than the dilution methods or 'osme' analysis (Chaintreau, 2001).

Pollien *et al.* (1998) have thus compared headspaces of a brew and of an instant coffee and could detect a new key compound, 1-nonen-3-one (Section 5,**D.36**) and confirm the aroma impact of other compounds.

3.3.7 MULTIVARIATE SENSORY ANALYSIS (MSA) AND STATISTICAL TREATMENTS

Over the years, many attempts have been made to represent food volatile profiles. In order to find an objective method for evaluating food flavors, multivariate analysis has been widely used. In one of the earliest studies, Powers and Keith (1968) examined steam distillates of coffees with different flavors. They used stepwise discriminant analysis of the chromatograms to select the most critical peak ratios to be correlated with flavor. Although they recognized that the method has the advantage of being objective, it will 'at best complement organoleptic evaluation, not replace it'. Similarly, Biggers *et al.* (1969) differentiated arabica and robusta coffees by evaluation of GC profiles, comparing numerically derived quality predictions with organoleptic evaluations. Powers (1984) used statistical programs to evaluate sensory data. An analysis of headspace profiles of freshly brewed coffee by multivariate statistics has been published by Liardon *et al.* (1984) and Liardon and Spadone (1986). They discriminated varieties and/or roasting degrees, showing that a technique like canonical analysis provides, in a single treatment, a complete overview of the influence of the two parameters on the coffee composition. Trying to correlate chemical and sensory data, they first realized the canonical analysis of a quantitative descriptive analysis (12 trained tasters, 12 sensory descriptors, seven-point scale). The descriptors were roughly distributed along two axes (roasting, quality). Using a specialized program (Procrustes analysis), they superposed the headspace and sensory canonical configurations. The roasting descriptors were related to a fairly large number of components, but the quality descriptors did not seem to be related to any component. The authors conclude that the evaluation of coffee quality, being subjective, cannot be determined by just a few components, and that it would also be necessary to take into account interaction effects between the components.

Schlich *et al.* (1987) proposed a new approach to selecting variables in principal component analysis (PCA) and getting correlations between sensory and instrumental data. Among other studies, Wada *et al.* (1987a,b) evaluated 39 trade varieties of coffee by coupling gas chromatographic data with two kinds of multivariate analysis. The objective classification was compared with the sensory data (cup test), directly or after statistical treatment. The results were concordant. Murota (1993) used qualitative sensory data to interpret further the results of GC data and canonical discriminant analysis. He could thus suggest which were the components responsible for the flavor characteristics in different coffee cultivars.

White (1995), not for a sensory analysis but mainly with a view to determining coffee adulterations, used the data of combined headspace GC and high-performance LC for multivariate analysis. Principal component analysis visualized the relationship between samples, and the outlying samples could be identified. The method could be an additional tool for classification and quality control of coffee products.

According to Ennis (1988), the application of the various multivariate analysis techniques (factor, cluster, discriminant analysis, multidimensional scaling) to classification in sensory analysis has been very valuable but is of little help for understanding the modes of perception. Mathematical models are proposed for predicting human sensory responses and the author concludes that they need development before they are able to improve the understanding of the 'complex perceptions associated with foods and beverages'.

Deibler *et al.* (1998) propose the Flavornet database ('a new tool available on the Worldwide web', Cornell University) which contains data for over 500 compounds sorted by their chromatographic and sensory properties, the non-active odor compounds being excluded. This tool is especially useful for tentative identification of odorants found in GC-olfactometry analyses.

3.3.8 THE 'FIELD OF ODORS' (CHAMP DES ODEURS®)

This procedure for odor descriptions, proposed by Jaubert *et al.* (1987a,b, 1995), differs from the conventional approach in that it provides 45 stable compounds as flavor references to cover the whole odor spectrum rather than the usual real food references. The references are defined by their chemical name and organized in a two-dimensional field to provide easier representation and to facilitate memorization. The use of chemical names as odor descriptors does not imply that these compounds have been identified in the samples. Nevertheless, Sarrazin *et al.* (2000) and Gretsch *et al.* (2000) found that, with 15 trained panelists, certain notes present in coffee could not be described by the basic set proposed by Jaubert. Nine further references (to cover amine, sulfur, pyrogenic and woody notes) were added, raising the reference number to 54. However, from the 54 references, some did not correspond to notes in coffee, and 26 references were retained by the assessors, who were in good agreement, for describing the odor of ground coffees ranging from green to over-roast levels. From the 26 descriptors, 16 were found to be relevant for differentiating the samples. It was observed, nothing new, that fatty, green, lactonic and terpenic notes are representative of green coffee and that sweet notes, pyrogenic, sulfurous, and finally amino odors develop during roasting. These sensory intensities were compared with the composition of the odorous components, located by the CHARM® method, then identified and quantified. If the concentration of the volatiles associated with green, earthy notes remained unchanged or increased during roasting, the sensory intensities were equal or lower, probably masked by the sulfurous and smoky notes. For the sweet notes, the maximum in the sensory evaluation was reached before the maximum of concentration of the corresponding components. There was a good correlation between the two evaluations for the sulfurous and smoky notes. Nevertheless, the authors concluded that the method provides a useful training tool for general olfactive analysis and hope that it will allow the establishment of a potential correlation between sensory and analytical data.

Numerous other chemicals will certainly be necessary to cover the description of special food flavors. For instance, this new concept will probably not replace the traditional precise descriptors used by panelists in the dairy products industry.

3.3.9 THE STALING OF ROASTED COFFEE

Clifford (1985b) defines staling as the deterioration in taste and odor that occurs when roasted coffee and coffee products are stored prior to the preparation of the beverage by the consumer. This phenomenon has been studied extensively since it determines the commercial shelf life. To study the staling of coffee, Prescott *et al.* (1937a,b) examined roasted coffee extracts. They considered that oxidation and the loss of volatiles are inadequate to explain all the changes, and that no experimental data are given in the literature to provide a satisfactory explanation. Indeed, they only had at their disposal gravimetric or titration methods such as acid values, saponification number, percentage of unsaponifiable matter, iodine value and peroxide content. Some details of the results of these authors are given in the following chapter (Section 4.1).

Johnston and Frey (1938) mentioned that coffee staling is probably concerned with changes in the volatile aroma and flavor substances and does not involve fat rancidity. The stability of coffee flavor constituents, which imparts to coffee the sensation of taste, as opposed to the aroma which is detected by the sensation of smell, has intrigued numerous analytical chemists. Hughes and Smith (1949), for instance, considered that the continuous sweeping with an inert gas for a period of days, does not appreciably impair the 'cup value' although a considerable loss of aroma takes place. On the other hand, they affirmed that the tarry products formed during roasting, probably result from the combination of phenols and aldehydes, accounting for part of the flavor, and that these substances undergo partial oxidation during staling of coffee. They also observed that during staling there was neither loss of pyridine nor of furfural, and only small losses of aldehydes, acetone and volatile phenols. The small amounts of hydrogen sulfide found in freshly roasted coffee were rapidly lost during the first two weeks of storage and the diacetyl originally present was reduced to acetylmethyl carbinol (3-hydroxy-2-butanone, Section 5,**D.41**). They concluded that these observations would partly account for a loss of aroma. Reymond *et al.* (1962) examined the changes in roasted coffee aroma induced by staling and observed that the ratio 2-methylfuran/2-butanone (Sections 5,**I.2** and 5,**D.2**) measured from an aqueous suspension of ground coffee decreases from 2.6 to 0.1 within 4 days.

To understand the aroma changes occurring during storage, Radtke (1964) and Radtke *et al.* (1966a) measured the concentration variations of the roasted coffee components of 'medium' volatility i.e. with a boiling point between 100 and 220 °C. They used extraction techniques with petroleum ether, methylene chloride or aqueous methanol, then methylene chloride, enfleurage with glycol, paraffin or olive oil, or concentration by gas-sweeping with a nitrogen stream saturated with methanol or water, followed by thin-layer distillation techniques. The constituents were chemically fractionated into monoacids, phenols, nitrogen-containing bases, and a neutral fraction further separated by gas chromatography. The carbonyl compounds were isolated as 2,4-dinitrophenylhydrazones. The authors observed that when the coffee extracts were spread on a paper filter they first diffused an agreeable perfume, but within a few hours the odor became pungent, fishy and perspiration like, and even, after a few days, absolutely repulsive. Extraction of the impregnated paper with hot water revealed the effects of evaporation and oxidation. The residual odor, considered by the authors to be the fundamental aroma of coffee, was characterized by leather, malt and tobacco-like notes due to phenols and carbonyl compounds. This experience confirmed that the coffee aroma is a complex mixture of compounds with a wide range of volatility, stability and odor complementarity.

Selected volatiles can be used as indicators of the staling of roasted coffee. In order to get quality data for measuring the freshness of roasted coffee, Kwasny and Werkhoff (1979) used the 'aroma-index' 2-methylfuran/2-butanone (Sections 5,**I.2** and **D.2**; 'aroma index MB'), previously proposed by Reymond *et al.* (1962), as an indicator of the changes occurring in the headspace under the influence of oxygen in the surrounding atmosphere. The index was dependent upon the degree of roasting and grinding, the origin and, particularly, upon the storage, having a neat decrease with a dark roasted coffee. Arackal and Lehmann (1979) observed that the staling of roasted coffee becomes noticeable after 10–11 days, leading to a clearly recognizable stale taste and smell after 6–8 weeks and to rancidity after 4–5 months, but did not specify the storage conditions. However, in airtight packages or cans sealed under vacuum, the coffee will keep its fresh aroma at least 12 months. Grinding liberates a substantial part of the protective carbon dioxide entrapped in the beans, which explains why roast and ground coffee are less stable. Arackal and Lehmann use the same 'aroma index'(MB) as a measure for assessing the degree of freshness of roasted coffee. A similar method had been proposed by Vitzthum and Werkhoff (1978, 1979) who applied a headspace technique with enrichment on a cooled GC capillary column for measuring coffee staleness. They observed that its chemical mechanism was not yet known and that typical staleness compounds had not been discovered. They confirm the validity of the index MB but, as the methanol content increases directly with the staleness of coffee, they proposed using the methanol/2-methylfuran ratio (Sections 5,**B.1** and **I.2**; 'aroma index MM') as a measure of the freshness of whole or ground roast coffee beans.

With the same intention of establishing a relationship between a quality sensorial test and the concentrations of some volatile substances in roasted coffee, Radtke-Granzer and Piringer (1981) proposed measuring and summing the absolute concentrations of 2-methylpropanal (Section 5,**C.11**), 3-methylbutanal (Section 5,**C.13**), diacetyl (Section 5,**D.44**) and 2-methylfuran (Section 5,**I.2**) in commercial coffees. For freshly roasted qualities this value amounts to 110 ± 21 mg/kg, but during storage under different conditions, the concentration can drop to 89 mg/kg, corresponding to a degradation of the sample with an easily detectable variation of the organoleptic qualities. Clifford (1985a,b) gives a list of volatiles which can explain the undesirable odors detected in stale coffee, for instance those due to an excess of *N*-furfurylpyrrole (Section 5,**K.67**) or furfurylmercaptan (Section 5,**I.128**).

According to Leino *et al.* (1992), the preceding aroma indices are only valid for the treatment of defined coffee mixtures, but they are unfortunately impracticable for unknown roasted coffee varieties. After studying the changes in headspace volatiles of some Finnish coffee blends during storage and the relative proportions of 43 compounds over a one-year period, they concluded that, in their work, none of the previously proposed ratios were good indicators of the staling of coffee. Several components were useful indicators of the ageing for an 'Espresso' blend [butanal, Section 5,**C.4**; 2-butanone, Section 5, **D.2**, and 5-methyl-2-furaldehyde, Section 5,**I.66**, for example). For this blend, the ratio 2-methylfuran/propanal (Sections 5,**I.2** and **C.3**) could not be used. The ratios acetone/propanal (Sections 5,**D.1** and **C.3**), thiophene/propanal (Sections 5,**D.1** and **C.3**), thiophene/butanedione (Section 5,**D.1** and **D.44**) and butanedione/2-methylfuran (Sections 5,**D.44** and **I.2**) were preferred and proposed by the authors as useful indicators of the ageing of coffee.

Hinman (1992) points to the fact that the staling of coffee due to the consumption of oxygen, normally slow, might be potentiated by reactions taking place before packaging. Lower coffee density, which depends on roasting and also on grinding techniques, increases the oxygen exposure after packaging. Temperature and moisture have more important effects. Nicoli *et al.* (1993) showed parallelism between the release of carbon dioxide and of volatile compounds from roasted coffee. The slow lipid oxidation, strictly depending on oxygen availability, can enhance the staling of coffee but only after package opening. These results are in agreement with very early observations.

The lover of coffee (Honoré Daumier, Paris 1841)

4

A Historical Survey of Coffee Aroma Research

4.1 THE PIONEERS (FROM 1800 TO 1956)

For about two hundred years attempts have been made to isolate and identify the constituents of coffee flavor or, at least, by the end of the Eighteenth century, to prepare extracts for the purpose of identifying its 'principes immédiats' (fundamental principles). In his *Système de Chimie*, Thomson (1807) wrote that 'chemists have performed many experiments to ascertain the constituent parts of coffee and its qualities'. He mentions the work, now only accessible with difficulty and of pure historical interest, carried out by such scientists as Neuman, Geoffroi, Dufour, Kruger, Westfeld and Herman. The state of knowledge in the early Nineteenth century was summed up as follows:

> when one roasts coffee, a small portion of tannin is formed by the action of heat. It can be observed that another substance develops with a particular, pleasant odor; however, the nature of this new principle has not yet been determined. This principle also occurs when one roasts barley, beans, and a large number of other plant varieties which for this reason are used where necessary to replace coffee.

The approach at that time was thus chiefly based on the search for relatively simple general 'principles' common to all roasted products. A few other precursors, Payssé, Chenevix, Cadet de Vaux or Cadet de Gassicourt, are mentioned by Payen (1846a). These workers also made many attempts to investigate the content of coffee, but without much success. They merely demonstrated the presence of a 'bitter principle' (Chenevix) and an 'aromatic principle' (Cadet). Apart from these 'principles', constituent parts 'identified' at that time in coffee consisted merely of 'a little oil, an acid, mucilage, extractif [*sic*], aluminum sulfate, lime, potassium chloride and a little albumin which separates from the decoction in the form of froth'. In view of the limited number of reference products known at that time, the proposed identifications are often questionable. Thus, Robiquet and Boutron (1837a), without giving the source of their predecessors' publications, think, like Cadet, that the 'acid principle' is gallic acid, Grindel claims it is quinic acid, Payssé describes it as a particular, as yet unknown acid, and Pfaff regards it simply as the cause of coffee's aromatic odor. Gallic acid, also called 'gallnut acid' by Scheele who had isolated it from the gallnut and crystallized it in 1786, was in fact one of the first known vegetal aromatic acids. It possesses an acid and astringent flavor (Thénard, 1818a) and it continued for decades to be considered as one of the 'principles' because, like the numerous phenolic acids of roasted coffee, it gives a green pigment with ferric chloride. This somewhat doubtful identification must nevertheless be quoted because it constitutes a first original and significant step in the chemistry of coffee constituents.

At the beginning of the Nineteenth century, in the heroic and romantic age that saw the birth of 'The Chemistry of Nature' initiated by Wöhler and Liebig, enthusiastic scientists were convinced that identification of the essential and general 'principles of organic materials' should progress rapidly and confer on mankind a period of exceptional health and prosperity. However, it was natural—but also admirable, in view of the rudimentary analytical resources available at the time and the stage to which organic chemistry, still in its infancy, had progressed—that only a few non-volatile products, such as acids, lipids and carbohydrates, had been isolated if not identified. Although the discovery and isolation of caffeine by Runge (1820) and the ground breaking work of Robiquet, Pelletier, Caventou and Pfaff date from the period 1820–1830, it was not until the end of the Nineteenth century that the exact formula of this alkaloid was proposed by Medicus (1875) and its total synthesis carried out by Fischer and Ach (1895).

If we wish to pay tribute to the pioneers and take due note of their perspicacity and perseverance, though without citing their work exhaustively, we cannot do better than start this historical review with the first observations on the volatile components of coffee, jointly made in 1832 by Weiss and Lampadius. In the *Leipziger Zeitung* of 9 January 1832, Dr Christian Conrad Weiss (1832) wrote an article entitled '*Coffea arabica*, nach seiner zerstörenden Wirkung auf animalische Dünste, als Schutzmittel gegen Contagien' (*Coffea arabica*, its destructive effect on animal emanations as a protective agent against contagion), which confirms the interest already shown by some at the time in the physiological action of natural extracts. Weiss claims to have observed that the effect of roast coffee on the organism was not confined simply to odorous principles; he notes that it is possible to deodorize or effectively neutralize rapidly, sometimes instantly, and even lastingly, premises contaminated by plant or animal effluvia such as the stench of rotten meat or eggs, ammonia, musk, castoreum and even *Assa foetida*, a foetid and alliaceous gum resin previously described and analyzed by Pelletier and described by Thénard (1818b). To explain this action Weiss quotes the very recent discoveries of Pfaff and Lampadius who reported that they had identified a component of green coffee which, when roasted, releases an acid and an 'empyreumatic' oil which account for the burnt flavor of coffee. In his view these products readily became fixed on objects and clothes and impregnated them lastingly. Weiss therefore advances the hypothesis that these substances could act as disinfectants, protect against contagion and thus preserve health by replacing the foul-smelling processes used at the time to disperse noxious emanations. The very simple procedure was to burn a few pinches of finely powdered coffee in a simple lamp. The odor released is pleasant, persistent and, above all, not discomforting. He even held that a drop of the empyreumatic extract, which he called 'Caffeesaüre' (a complex mixture different from the later identified coffeic acid), was sufficient to purify and perfume an average-sized living room for several days. It is arguable that this observation was not unfounded, since many phenols with disinfectant properties were later to be identified among the volatile components of roasted coffee.

An article describing the work of Lampadius, published on 7 April 1832, confirms Weiss's observations: the fragrance of roasted coffee is an excellent substitute for vinegar, which, with its unpleasant odor, was commonly used to disinfect insanitary premises. Lampadius attributed this disinfectant effect to the 'volatile acids which are understood to be released by roasting of an aromatic oil of hitherto unknown nature'. He does indeed observe that dry distillation of green coffee generates water, acetic acid and an empyreumatic oil representing 8.3% of the green coffee. This oil is of an 'organic' nature since its combustion produces a residue of black soot. In the light of combustion tests in chambers of various sizes and for varying periods, Lampadius was able to confirm the deodorizing power of his extract. Despite more intensive analysis of the aromatic acid which he called, as has been mentioned, 'Caffeesaüre' (caffeic acid), and of the oil he terms 'brenzliche Caffeefett' (burnt coffee fat), Lampadius failed to identify any volatile component other than acetic acid, one of the first positively identified volatile constituents of green and roasted coffee flavor. Radius (1832) made a few additions to the observations of Weiss and Lampadius in the form of reports on roasting tests with various qualities of coffee in sickrooms.

Robiquet and Boutron (1837a,b,c) also considered the question of whether the characteristics of coffee are due to one 'principle' or a set of components. While everything remained to be discovered, they display an alarming pessimism in observing:

> on several occasions coffee has been the subject of research projects but, so far, no clear-cut result has emerged from this work and we still do not know whether its remarkable effect is a result of a particular constituent or of a compounded action of all the constituents. In the hope of solving this problem for the second time, we had decided not to give up our efforts until we had succeeded but we had presumed on our perseverance and have thus regretfully abandoned a project which was not really satisfying. However, to assist those who, more skilful or persevering than we, may undertake new attempts, we have decided to publish our results, however imperfect, to avoid always treading the same paths and, if possible, take a better direction.

Robiquet and Boutron did no more than confirm the presence among the volatile components of acetic acid, already mentioned by Lampadius in 1832. Additionally, they isolated from coffee 'small bright yellow crystals, though few in number, which, when burned on a platinum plate, gave off a bluish flame and an extremely pronounced odor of sulphurous acid'. They conclude that coffee contains a small quantity of sulfur, another element known for its disinfectant properties. They further extracted a whitish, granular substance which, when heated on a platinum plate, gave off an odor of fish oil. Apart from caffeine which, as has been mentioned, is easily separable by crystallization, they isolated an aroma and an oil which seemed to them to form an indissociable whole which they called 'huile fixe' (stable oil). Robiquet and Boutron also mentioned two fatty substances in coffee, one akin to resins and having a pungent flavor and the other sweet, with a balsamic odor. Moreover, in view of the formation of a green coloring in the presence of ferric chloride, they make various assumptions regarding the presence of gallic, quinic acid or other ill-defined products previously isolated by Scheele, Cadet, Grindel, Payssé and Pfaff. They realized that the problem was complex, since they pose an essential question which sums up all the issues surrounding research into the aromatic components of roasted coffee:

> We will pass rapidly over all these facts because, there being nothing in them which suggests to us the solution we seek to the problem, it becomes pointless to look any further. We also tried, with just as little success, some other avenues it is necessary to know to save our successors from treading them. It was claimed that roasting developed new principles, and it has often been repeated that heat releases an essential oil which is the real source of the entire coffee fragrance.

In conclusion, these authors modestly assert that both roasted and green coffee still guard their secrets. They succeeded in extracting from coffee neither the roasting oil nor the flavor or the odor, still less coffee's aromatic properties. In their view the 'fixed principle' remains irrevocably imprisoned in the fatty oil. The only salient facts to emerge from this study were that about one-eighth of the weight of green coffee consists of 'stable oil', and that after roasting this oil becomes highly charged with the aromatic principle and even the flavor of burnt coffee. Moreover, caffeine is found in all the products of coffee, irrespective of the treatment it has undergone.

To open a parenthesis in an anecdotal vein, a scientifically questionable and somewhat naïve communication on the roasting of organic bodies was published in 1844 by Freiherr von Reichenbach, an independent researcher working in his castle at Reisenberg near Vienna. In his preamble, the author does show some modesty in declaring:

> 'The investigations undertaken here are in all probability far-reaching and difficult, and it is with trepidation that I set foot on, and take the first steps in, unexplored territory'.

He started by distinguishing the different degrees of heating applied to organic bodies: grilling (das Braten)—meat, chestnuts on the grill, potatoes in the ashes; roasting (das Rösten) for coffee roasting or caramelization of sugar, and finally, baking (das Backen), to describe ordinary culinary operations as well as bread making and confectionery. Naïve questions sum up the modest state of scientific knowledge at the time:

> We do not know the process that takes place in malt-drying—Indeed, do we even know what bread really is?—Let us confess our surprise that, strictly speaking, we do not.

The author observed that the action of temperature on organic bodies, foods particularly, radically alters their color, odor and taste by the formation of new bodies, which 'simply' need to be identified. Reichenbach set out from the observation that the main organoleptic characteristic of grilled foods is their bitter taste. He will therefore endeavor to isolate the 'bitter principle' of these products, which he baptized 'assamar', a neologism derived from the Latin *assare* (roast) and *amarus* (bitter). In his view, any organic product—albumin, glue, gum, starch, sugar, meat, bread, blood or coffee—produces, after prolonged heating, a solid residue of brown-black color consisting for the most part of 'assamar' and to a lesser extent of various foreign bodies. This residue, macerated in alcohol, filtered and then concentrated, was, he believed, a relatively simple body. Describing its chemical and physical properties in terms of the criteria prevailing at the time, he claimed to have isolated a solid, transparent, amorphous, hygroscopic body of amber color, with a mild odor but a very bitter taste, impervious to the action of hydrochloric acid, chlorine and ammonia. There is another explanation 'the author considers logical': 'assamar' is the hygroscopic principle of all grilled foodstuffs, and it is that which softens caramel and almond cakes and makes them sticky. Hence it is quite naturally and unwittingly consumed all over the world since it is present in nearly all foodstuffs. He believed it to be particularly present in roast coffee since it is more bitter than caffeine! Prepared from other plants such as chicory or peanuts, it could even readily replace the bitter principle of coffee. Ending on a somewhat ambitious note, the author even expresses the hope that if 'assamar' could be produced industrially it would be used as a condiment, a dietetic product and above all as a tonic and medicine.

At the same time, in 1844, Rochleder noted that knowledge of the composition and extraction of foodstuffs was of prime importance, particularly since von Liebig had initiated and encouraged this type of research. The authority of Liebig's scientific name could give the impression that coffee infusions chiefly exerted a physiological activity but were devoid of nutritive properties, the active principle—caffeine—being similar in composition to alloxane, a pyrimidine analogous to the six-membered cycle of caffeine and also containing a fragment of urea. Hence, in the author's view, the best way of settling the question of whether the future of coffee lay in nutrition or medicinal use was to study it in depth. After elementary analyses that were highly aggressive but common at the time, Rochleder distinguished four main components in green coffee: lignous vegetable fiber, fat, crystalline caffeine, and a nitrogenous component susceptible to fermentation which he compares to casein. A more concrete scientific result came with his success in identifying palmitic acid in the lipid phase. He was probably one of the first researchers to observe the association of caffeine with a relatively complex acid. Continuing his investigations two years later Rochleder, in 1846, confirmed the protein nature of 'légumine' and the isolation of a sugar, a 'tannic' acid, caffeic acid already mentioned by Pfaff (around 1832), glycerine and oleic acid. Unfortunately, in view of the non-volatile nature of these products, their imperfect purification and the imprecision of their elementary analyses, their isolation cannot be considered as a contribution to knowledge of coffee aroma.

Between 1846 and 1849, a number of studies were published by Payen. In the first (1846a), he focused interest on a crystalline substance, white in the natural state, present in the perisperm of coffee and that, in an ammoniac solution, turns bright green and even blue. He even proposed using these colorants as a safe means of modifying liqueurs and other edible products. After experiments at different roasting temperatures, he observed that too profound a change in organic nitrogenous substances other than caffeine develops unpleasant-smelling empyreumatic oils. He concludes:

> It can probably be accepted that coffee possesses nutritive properties; but its chief value derives from its flavor, its pleasant aroma and the stimulant properties it may develop in twenty times its weight of liquid and transmit to as large a volume of solid nutritive substance but little savory.

Economic considerations also enter into this study as it mentions the major interests that would be served by the spread of coffee-drinking, since wider consumption would inevitably spur parallel growth in the big metropolitan and colonial sugar industries.

In a second publication, Payen (1846b) resumed in-depth study of the greenish, viscous substance he had previously described (1846a) and announced that none of the learned experimenters who had preceded him had succeeded in extracting from coffee the crystallizable substances he is about to describe. For, having extracted caffeine with ether and purified it, he treated the powdery residue of green coffee with alcohol and isolated 'abundant prismatic crystals grouped in spheroids'. Thus, for the first time, he had isolated a complex of 'double chloroginate of potash and caffein' which he calls the 'natural salt of coffee' and its component the 'chloroginic' acid, later to be called 'chlorogenic' acid (see Section 2.1.4). Identification of the chlorogenic acids was to take almost another hundred years, their exact composition being elucidated only by Gorter (1908a,b) and their structure by Fischer and Dangschat (1932).

Lastly, in his third publication on coffee, Payen (1846c) draws attention to:

> the aroma... which alerts our senses and, however evanescent and diversified it may be, nevertheless leaves us a memory capable of making a choice among several foodstuffs. Such a possibility which, by the pleasure it awakens, urges us to satisfy a need and acts as its guide, must obviously count as one of the chief guarantees of existence; this it is which directs, in an even more assured manner, the instinct of self-preservation which is more constant and better developed in a large number of animals than in man. We shall shortly show that substances endowed with the power to excite such sensations in us are of great importance, from a variety of viewpoints, for science and its applications; and that thus, when we succeed in extracting them and determining their ponderal quality, we shall be able to deduce their value which will consequently appear enormous. Unfortunately, on these latter points positive data are lacking and work has barely begun.

Payen reaffirms, according to an already familiar precept, that it is in the various substances carried by the vapors, i.e. in the essential oils, that the more-or-less complex causes of odors, and in particular the aroma specific to food components, are to be found. Regrettably, he observed once again that coffee contains aromatic essences that imprison the volatile components. No distillation, infusion, extraction, refrigeration, precipitation or evaporation enabled him to isolate any definite aromatic principle whatever. The author is reduced to performing a first analysis of the (composition by weight) ponderal composition of coffee in which 'the concrete insoluble essential oil' represents 0.001 % and an 'aromatic, fluid essence with a sweet smell, and a less soluble, pungent aromatic essence' represent only 0.002 %. This is probably the first quantification to indicate that the aromatic essence constitutes only a few parts per million (ppm) of roasted coffee (Table 4.1).

On the basis of his analysis, Payen proposed an elementary but highly valid mechanism for the effects of roasting:

> ... at approx. 250 degrees water vapor is given off, the double chloroginate tumefies... and releases the caffeine it held in combination; cellulose and its like, undergo slight caramelisation and give acid and pyrogenated dying products. The fatty oils spread into the now porous mass and keep with them the slightly modified essences. These oils, fixed and volatile, then appear on very large surfaces by the action of water... In an infusion obtained rapidly by hot filtration and consumed at once, one discovers and appreciates in particular the aroma, which contributes so powerfully to rendering the flavor pleasant and is chiefly due to the most soluble essential oil.

The author also observes that coffee, unlike hard liquor or narcotics which intoxicate and numb the senses, appears to combine the pleasant sensations of the two kinds while stimulating the intelligence instead of dulling it. Economic considerations reappear in the conclusions to this study:

> If one assigned only two thirds of its value to the weight of essence which appears to be the source of these effects, the price of coffee's main essential oil would have to be set at the enormous sum of 10 000 francs a kilogram!.

In 1849, Payen again performed an isolation, a purification and an elementary analysis of caffeine, but the formula he proposed was wrong. He also attempted, unsuccessfully, to analyze 'chloroginic' acid which he had isolated two years before. In addition, he resumed study of the 'aromatic essence of coffee'. In the products of roasting he detected the presence of highly volatile hydrocarbons with an unpleasant empyreumatic odor. The aromatic essence isolated by Payen is also mentioned in the book of Pelouze and Fremy (1861) under the name of '*caféone*'.

In 1853, Völckel published an article on dry distillation of organic materials. His main subject of study was caramelization of sugar; he attempted once again to isolate, purify and describe von Reichenbach's

Table 4.1 The content of roasted coffee (Payen, 1847–49)

Constituent	Content (%)
Cellulose	34
Hygroscopic water	12
Fats	10–13
Glucose, dextrine, unknown vegetal acid	15.5
Legumin, casein (glutin)?	10
Potassium and caffeine chloroginate	3.5–5.0
Nitrogenous organism	3
Free caffeine	0.8
Insoluble concrete essential oil	0.001
Aromatic essence, fluid with pleasant odor and less soluble, acrid, aromatic essence	0.002
Mineral substances: potash, lime, magnesia, phosphoric, sulfuric, silicic acids and chlorine traces	6.697

(1844) assamar but 'got stuck' without success in an unbelievable series of analyses of caramels of various shades of brown and difficult to identify.

In 1858, Vlaanderen and Mulder claimed to have isolated from Jara coffees 'Kaffeesäure' ($C_{14}H_8O_7$) and acids from its transformations [one 'Kaffeansäure' ($C_{14}H_8O_8$) and two 'Coerulinsäuren' ($C_{14}H_8O_9$, $C_{14}H_7O_8$], and 'Kaffeëlsäure' ($C_{14}H_8O_{12}$). Since these substances were relatively impure, no subsequent study proved possible on the basis of their results. Hlasiwetz (1867) published a study on the tannic acids of coffee and reviewed the previous studies.

Bernheimer (1880a,b) observed with sober realism that, apart from non-volatile components such as caffeine, the famous 'assamar', oleic and palmitic acids, 'chloroginic' acid and its decomposition products, as well as various phenolic compounds, all that had really been identified as a volatile and aromatic component of roast coffee was acetic acid. He embarked on the first genuine study of the roasting products of coffee by constructing special apparatus and applying thermal treatment to 50 kg of green coffee which unfortunately, no doubt for reasons of economy, he describes as damaged. He first observed that roasting caused a 25% loss in the weight of the mass treated. The release of carbon dioxide and formation of pyrrole are clearly observed. He isolated 5 liters of liquid condensate and 680 g of solid extract. For the first time he isolated an ethereal extract with a very pleasant odor but which, on distillation, gave only water, acetic acid and a liquid whose odor was strongly reminiscent of acetone. By progressive heating he obtained, around 190–200 °C, a relatively characteristic liquid fraction, but at 300 °C a fatty mass started to distil having the consistency of butter and an odor of rancid fat. Without further ado he successively treated part of the distillate—a brownish oil insoluble in hot water, alcohol or ether—with caustic soda and then sulfuric acid, thus irreparably destroying the particularly delicate components. From the more or less pyrolized mass he nevertheless succeeded in extracting, crystallizing and identifying hydroquinone. Since at this stage there remained only 100 mg of extract, he gave up all hope of any subsequent elementary analysis. He continued the analysis of the fraction of distillate collected between 195 and 197 °C, which he called 'caffeol', in the hope either of identifying it simply as a component or of isolating a known substance from it. By elementary analysis he characterized this extract as a compound with the formula $C_8H_{10}O_2$, which recalls creosol or veratrol, and for which he proposed the structure of a methyl derivative of saligenin, either 2-methoxybenzyl alcohol, or 2-(methoxymethyl)phenol. Having isolated only 20 g of this substance from the initial 50 kg of coffee, he decided to forsake the analysis. He does however indicate that the batch of coffee yielded 140 g of caffeine, a proportion of 0.28% of the roasted beans. To sum up, the results of this analysis, though modest, indicate that the main components of coffee are palmitic acid, caffeine, 'caffeol' (an as yet undefined substance), acetic acid and carbonic acid. His most original discoveries are rather the identification of hydroquinone, methylamine, pyrrole and perhaps acetone.

Cech (1880) published a short and unsubstantial article on the preparation of a roasted coffee oil. He obtained yields between 8 and 13% from the roasted beans, mentioned the possibility of using it as a liquor ingredient and simply observed the slow formation of fine caffeine needles.

In 1887, Padé described a piece of apparatus that enabled researchers to determine precisely the absolute densities of coffees and to detect coffee frauds involving manipulation of green coffees and watering of roast coffees. In this connection he mentions and comments on a fraudulent method whereby products released during roasting are condensed and reinserted into the coffee beans. After a summary analysis he deduces that this concentrated liquid contains caffeine, ammonia, amines, ammonia salts, acrid bases near pyridinic compounds and fatty acids. By watering down the still-hot coffee with this mixture, 14 to 15% of the lost weight can be fraudulently restored to it.

In 1895, Monari and Scoccianti demonstrated the formation of pyridine by roasting coffee; they could not confirm the presence of methylamine and trimethylamine in the volatile components.

In 1898 Jaeckle resumed study of the 'caffeol' to which Bernheimer (1880a) had assigned the formula $C_8H_{10}O_2$. At that time the complex mixture of organic compounds produced by the decomposition of larger molecules during roasting was still considered to be a single constituent called 'caffeol'. He analyzed the volatile components supplied to him by a company whose roaster blow-off pipes were provided with a snow-cooled condensation system. The extract thus obtained appeared representative, with a good aromatic odor, but sour and bitter in taste. Using vapor distillation, Jaeckle isolated an oil which was fairly representative but which had a relatively pronounced acetic odor. During this analysis, he lengthened the list of identified components by the addition of furfurol (in fact furfural), trimethylamine, formic acid and resorcinol, but did not find Bernheimer's 'caffeol'.

Nineteenth century research into coffee aroma ends with the laborious and somewhat doubtful identification of some ten volatile components: carbonic, formic and acetic acids, methylamine, trimethylamine, acetone, furfural, furfurylic alcohol, pyrrole and pyridine, as well as a few ill-defined phenolic components.

At a time when organic nomenclature was neither codified nor scrupulously respected, and still highly empirical, risks of confusion abounded in the naming of aromatic extracts, their more or less purified components, and synthetic products. Thus, the aromatic distillate isolated by Bernheimer in 1880, and which he called 'caffeol', is changed to 'kaffeol' by Erdmann (1902a). This researcher takes over Bernheimer's assumptions regarding the presence of methylated derivatives of saligenin (2-hydroxybenzyl alcohol) and denies their presence in this 'caffeol'. This is because 2-methoxybenzyl alcohol, already synthesized by Cannizzaro and Körner (1872), possesses markedly different physical and organoleptic characteristics; this incompatibility of structure had, indeed, already been mentioned by Bötsch (1880), who supported the second assumption, of the methyl ether of saligenin [2-(methoxymethyl)phenol]. Unfortunately, this product, prepared subsequently by Thiele and Dimroth (1899), presented no coffee odor whatsoever. The contents of the article by Erdmann (1902a) exemplified the new approach to the search for, and confirmation of, volatile aromatic components; through developments in organic synthesis, reference products were used systematically to check the validity of an identification. Erdmann thus invalidated the elucidation of a principle allegedly olfactively characteristic of roast coffee. In the course of his research he prepared and carefully studied an extract, which he now called Kaffeeöl, obtained by hydrodistillation of 225 kg powdered roast coffee. By extraction with ether, he obtained a yield of only 228 mg/kg, which he felt portended difficulties in conducting an effective study with the analytical resources then available. He undertook distillation under atmospheric pressure and obtained a clear acid distillate between 150 and 190 °C and a few brownish drops up to 230 °C. The residue took the form of a thick, brownish mass. He also performed a careful distillation of the neutral fraction under reduced pressure (12–13 mm and 9.5 mm). He observed that a major portion of this extract, i.e. 43% of the total with a boiling point of between 70 and 80 °C, chiefly consisted of furfurylic alcohol. Erdmann (1902b) confirmed the nature of this product by treating it with diphenylurea chloride and preparing a crystalline carbamate. He also drew attention to its formation by degradation of sugars and pyrolysis of lignous fibers. At the cost of laborious extractions, fractionations and derivatizations of the aromatic oily extract, he isolated methyl ethyl acetic acid, the structure of which was at first contested by Reichstein and Staudinger (1926b) (in 1955, they refer to Erdmann and quote 'methyl ethyl acetic acid'). In the less volatile fractions of the distillation under reduced pressure (b.p.: 93–150 °C/12–13 mm), he freed the phenol components that possess the characteristic odor of coffee. Thus, in the acid fraction he demonstrated a pronounced flavor of guaiacol and creosol, and suggested that several other phenol components were present. This discovery thus supports observations mentioned earlier on coffee's antiseptic properties and its action on certain lower organisms; they also echo the empiric observations of Weiss (1832) seventy years earlier. Erdmann also made an interesting observation: roasting equal weights of cane sugar, green coffee extract—prepared by Rochleder's (1844, 1846) technique—and caffeine produced, after percolation, a beverage with the flavor and aroma of coffee, whereas binary mixtures of these components produce by no means the same flavor. From these observations we may deduce that ten years before Maillard (1912), Erdmann had discovered empirically the non-enzymatic browning reaction resulting from the heating of sugars with amino acids, peptides and other nitrogenous components.

The publications of Gorter (1908a,b) review and take stock of work on the non-volatile components of coffee over the previous 70 years. These studies show *inter alia* that the chlorogenic acid isolated by Payen is indeed split by alkaline hydrolysis into caffeic acid ($C_9H_8O_4$) and quinic acid ($C_7H_{12}O_6$). They also recall the isolation of quinic acid by Payen (1846a) and by Zwenger and Siebert (1861).

In 1912, Grafe takes over the confused nomenclature of previous studies in regarding 'Kaffeol', 'Kaffeon', 'Caféone' and 'Kaffeeöl' as the group of aromatic substances obtained with a yield of 0.3–0.45% by hydrodistillation of roast coffee powder and ether extraction. He contributes no notable advance in mentioning that 38% of the extract consists of acetic and valerianic acid, that 50% is furfurylic alcohol and other furans, and that the rest is a mixture of phenols with the odor of creosote and a pyridinic derivative that could be responsible for coffee's specific aroma. His article includes a comparative analysis of the components of normal coffee and decaffeinated coffee, the method for which had recently been patented.

In 1913, Bertrand and Weisweiller, unaware of the previous discovery by Monari and Scoccianti, claimed to have identified pyridine in coffee for the first time. They considered that the proportion of this volatile base is larger than the total of all the other bodies thus far reported in coffee. In several freshly roasted commercial samples they found quantities of 200–250 mg/kg, and proposed investigating whether pyridine plays an appreciable role in the physiological action of coffee infusion.

In a bizarre twist, Sethness, in 1924, unaware of Erdmann's (1902a) previous invalidation of Bernheimer's (1880a,b) results and having himself conducted no tests on the product he isolates, again asserts that the methyl ether of saligenin is the major component of the aromatic oil of coffee. He cites the work of Lehmann and Wilhelm (1898), whom he wrongly quotes 'as having also found caffeol, or chemically speaking the methyl ether of saligenin to be the principal ingredient of the fraction possessing the powerful coffee aroma' (Table 4.2)

In the years 1921–30, Reichstein and Staudinger started exhaustive research on the aroma of coffee. The work was sponsored by the Swiss Confederate Foundation for the Promotion of National Economics through Scientific Research and, later, by Internationale Nahrungs und Genussmittel AG, Schaffhausen,

Table 4.2 The aroma constituents of roasted coffee identified before 1902

Discoverers	Compounds suspected or (tentatively) identified
Lampadius (1832)	Acetic acid
Robiquet and Boutron (1837)	Sulfur-containing compounds, gallic acid
Rochleder (1844)	Palmitic acid
Rochleder (1846)	Oleic acid
Payen (1846)	Quinic acid
Payen (1849)	Volatile hydrocarbons
Bernheimer (1880)	Methylamine, pyrrole, acetone, carbonic acid, hydroquinone
Padé (1887)	Ammonia, amines
Monari and Scoccianti (1895)	Pyridine
Jaeckle (1898)	Furfurol (furfuraldehyde), trimethylamine, formic acid, resorcinol
Erdmann (1902)	Methylethylacetic acid (or valerianic acid), furfuryl alcohol, phenolic compounds

Switzerland. In fact this research was economically motivated since, during and after the First World War, the effects of coffee shortage were keenly felt in Europe. With this grant, Reichstein and Staudinger conducted a particularly brilliant study and, using classic derivatizing techniques and measurements of physical constants, succeeded in identifying ca 30 new components. Since their results are only to be found in patents, they have often escaped the scientific community's notice. Particularly worthy of mention is British Patent 246454 (Reichstein and Staudinger, 1926a), describing the method of isolating the 'aromatic principle' of roast coffee, and British Patent 260960 (Reichstein and Staudinger, 1926b), describing the components identified and 'a new or improved method of producing artificial coffee oil'. These results were to be published again only in the years 1950–55 (Reichstein and Staudinger, 1950b, 1955a,b), when the authors wished to gain acceptance for the priority of their discovery of particularly original components. It was then universally admitted that not one of the substances isolated from roasted coffee possessed in itself the characteristic flavor aimed at. Nevertheless, there was little awareness that specific compounds were of paramount importance. This applied particularly to furfuryl mercaptan, a chemical unknown in the twenties when the authors detected and synthesized it for purposes of comparison. Pure furfuryl mercaptan has a persistent, obtrusive odor. Highly thinned, however, it exhales a pleasant note indicative of coffee. Marketing of this component under the name 'coffee-captan', announced in 1950 as an innovation by Cargill Scientific, Inc., New York in 1950, prompted Reichstein and Staudinger to redirect attention to their work (1950b) and the priority of all their studies between 1921 and 1930, as well as their patents filed between 1925 and 1929 (see References). They emphasize that furfuryl mercaptan does not in itself possess the aromatic qualities of coffee but is one of its most characteristic components. This product was, moreover, already contained in a more elaborate formula marketed under the name 'Cofarom' for many years by the company Haarmann & Reimer (Holzminden). Their article, designed to set the record straight, likewise includes a list of the many patents attesting to the priority and validity of their work. In a more detailed publication (Reichstein and Staudinger, 1955a), they reviewed a century of research into the aromatic components of coffee. They pointed out the difficulties and failures—inevitable for most of the time—of their predecessors. To recover the aromatic substances, large quantities of freshly roasted and ground coffee were first heated to 100 °C under a good vacuum, at about 3 torr. The rising gases were collected after gradual cooling down to −180 °C. Thus it became possible to concentrate strongly all the aromatics present, and to maintain their structure unchanged, avoiding the formation of undesirable by-products. By distillation a highly unstable yellow-colored oil was recovered and stored at −80 °C.

> Through exerting separation procedures, over 70 characteristic substances could be isolated from this source and each of them identified beyond doubt by the presence of crystalline derivatives, and by chemical analysis.

The authors observed that an exhaustive list of all the chemicals present in coffee flavor had not yet been compiled, but they believed they had identified the components that are present at the higher ratio of weight, and those which principally control the odor note. Most of the substances identified were well-known compounds present in other roasted products as well, for instance in caramel sugar, cocoa, baked bread and—partially—even in wood tar. However, some of the chemicals detected were new and, obviously, characteristic of roasted coffee. Traces of methyl mercaptan, which was already known at that time and which smells even worse, were also detected in coffee aroma. Commenting on this observation, Reichstein and Staudinger note that it is generally known that many popular raw materials and synthetic perfume compounds owe their characteristic note, which is extremely pleasant to the olfactory sense, to their content of small quantities in additives which carry a rather unpleasant odor in themselves but prove very attractive in thinned solutions and in admixture with other oils. The authors tried to reconstitute coffee aroma, and only by combining over 40 of the substances extracted from coffee oil did it become possible to develop compound mixtures which, upon adequate thinning, held a typical coffee aroma, though this was not up to par in quality with the natural product. Reichstein and Staudinger (1955a) also compared the most important components of raw and roasted coffee. They observed that sugars and tannic acid are dramatically reduced in quantity while the caffeine content remains constant. Finally, they observed that the fats do not undergo degradation but play a role through their capacity to adsorb and protect the volatile aromas of evaporation, oxidation and deterioration. In conclusion, the authors identified numerous new constituents mentioned in the Table 4.3.

Schmalfuss and Barthmeyer (1929), still unaware of the results of the analytical work of Reichstein and Staudinger, studied the presence of diacetyl in foods. They noticed the caramel and buttery note of this compound that results from the oxidation of acetylmethylcarbinol (3-hydroxy-2-butanone) and quantified its presence in butter, tobacco, coffee, cocoa, beer and honey.

Under the title 'The staling of coffee', Prescott *et al.* (1937a,b) drew attention to the fragility of the volatile components of roasted coffee to preservation and to the modification of flavor known variously as 'flatness, staleness or rancidity'. It was generally assumed that oxidation or saturation of fats was the principal cause of this rancidity. Prescott *et al.* (1937a) considered that there were reasons for believing that the oxidation theory was inadequate to explain all the changes that were brought about. Deterioration is also due to hydrolysis, alteration and volatilization of the aromatic principles. After

Table 4.3 Volatile compounds identified by Reichstein and Staudinger (1926)

Hydrogen sulfide
Methylmercaptan
Furfurylmercaptan
Higher mercaptans
Dimethyl sulfide
Higher sulfides
Acetaldehyde
Methylethylacetaldehyde (2-methylbutanal)
Furfurol
Methylfurfurol
2-Acetylfuran
Acetone
Higher aliphatic aldehydes and ketones
Ketones of the furan series
Diacetyl
Acetylpropionyl
Oxysulfides and mercaptans of carbonyl compounds with the above mentioned mercaptans
Methyl alcohol
Higher aliphatic alcohols
Acetol
Furfuryl alcohol
Acetic acid
Isovaleric acid
Higher fatty acids
Palmitic acid
Esters of the former two acids with the above mentioned alcohols
Methyl acetate
Methyl 3-methylbutanoate
Phenol
Catechol
Guaiacol
p-Vinylguaiacol
2,3-Dihydroxyacetophenone
Further phenols and phenol ethers of a higher valency
Maltol
Pyridine
Pyrazine
Methylpyrazine
2,5-Dimethylpyrazine
2,6-Dimethylpyrazine
Higher homologues of pyrazine
N-Methylpyrrole
N-Furfurylpyrrole
Further higher pyrroles
Higher derivatives of furan
Furfuryl acetate
Furfuryl 3-methylbutanoate
Naphthalene

summarizing previous work on the volatile constituents of coffee, the authors performed different extractions of volatile constituents. Having observed that the percentage of volatile oil in roasted coffee is always very small, since Erdmann (1902a) obtained only 83.3 g of volatile oil from 150 kg of roasted coffee (0.05%), four different methods of isolation were used. The authors were only able to identify furfuryl alcohol, furfuraldehyde and acetic acid from the volatile oil.

Prescott *et al.* (1937a) finally preferred to extract a coffee brew with ether. The results were again very disappointing, the identified constituents being ethyl alcohol, acetic acid, furfuraldehyde, furfuryl acetate, furfuryl alcohol, probably furfuryl formate and a small amount of phenol. In the discussion of their results the authors agreed with the results of previous investigators: furfuryl alcohol is the chief neutral constituent of aromatic oils of coffee, as ascertained by Erdmann (1902a) and Grafe (1912). However, they disputed the preponderance of valerianic (or methylethyl acetic) acid for which Erdmann argued, since in their view acetic acid was the principal volatile acid present in roasted coffee. Everything suggests that Prescott *et al.* were then unaware of the content of the patent of Reichstein and Staudinger applied for 10 years earlier. They suspected the presence and olfactory contribution of nitrogenous components present in the 'caffeol' of Sethness (1924). They also remained intrigued by the hypothetical discovery of a methyl derivative of saligenin by Bernheimer (1880a) nearly 60 years before. In fact, since Prescott *et al.* really only demonstrated in their analysis the relative abundance of furfuryl alcohol and acetic acid in coffee essence, they ascribed the rancidity of coffee either to the presence of or the interaction of these two components. Furfuryl alcohol, its formate and its acetate, preserved in sealed test tubes in the presence of damp air, exhibit a marked tendency towards polymerization and resinification in 8 weeks' standing. However, the authors did not rule out the contribution of degradation phenomena due to the presence of other unstable products such as certain phenolic components or the decomposition of volatile constituents. They wished to point out the possibility of any group of compounds other than the fat being responsible for the staleness of coffee and concluded that this statement is based on experimental observations and not on pure speculation.

In a second study on the staling of coffee, Prescott *et al.* (1937b) observed that furfuraldehyde, the oxidation product of furfuryl alcohol, is an odoriferous liquid which promptly undergoes decomposition with the formation of tarry materials. They identify diacetyl, diethyl ketone, *n*-heptacosane, *p*-vinylguaiacol and guaiacol (two phenols already identified by Reichstein and Staudinger, 1926b). They suspected, without really being able to confirm it, the presence of *p*-vinyl catechol. They identified for the first time eugenol and vanillone (4-hydroxy-3-methoxyacetophenone) and isolated the 'kahweol' (the name was used later for a diterpene, see Section 2.1.3) previously reported by Bengis and Anderson (1932a). Prescott *et al.* (1937b) have the merit of being the first to isolate a terpenic fraction and of identifying sylvestrene in it, i.e. limonene, which was only to be confirmed 30 years later by Stoll *et al.* (1967). They also mentioned that the terpenes of this fraction are volatile substances possessing taste and odor but sensitive in the highest degree to heat, light, air, and chemical reagents. They predicted that their identification would be a matter of great importance where the flavor and aroma of coffee are in question. In view of the hydrocarbon nature of the terpenes they decided to substitute benzene for ether as extractive. For Prescott *et al.* (1937a,b), unlike their predecessors in the Nineteenth century, the evidence indicated that the fats were not responsible for either flavor or aroma, since fat-free coffee extracts also possess a rich full coffee odor. This prompted them to put the question yet again: 'What types of chemical reaction must occur on roasting?' They suggested three different mechanisms. The oxidation of the fats, however, is not in itself responsible for the staleness as distinguished from the rancidity of coffee. It is worth noting that Prescott *et al.* (1937b), when they published the second part of their work, knew of the English patent of Reichstein and Staudinger, 'two of the best organic chemists of the present time. Staudinger is noted for his work in organic qualitative analysis and highly polymerized substances, while Reichstein first synthesized vitamin C'.

The results of an analysis of the volatile constituents was published by Johnson and Frey (1938), the aim of their study being to prevent or retard the staling of roasted coffee. The authors declared that this effort would have been undertaken with better prospects of success if the identity and nature of the substances responsible for coffee flavor and aroma had been more completely ascertained. Johnson and Frey believed that the treatment used by Reichstein and Staudinger was not ideal because previous work on staling had shown that very small amounts of oxygen and moisture were sufficient to cause and accelerate deterioration. They decided to use a high-vacuum apparatus and to avoid using water during distillation. They were merely able to isolate, as actual constituents of coffee, several of the substances reported by Reichstein and Staudinger, and to detect acetylmethylcarbinol (3-hydroxy-2-butanone), a constituent of roasted coffee previously identified by Schmalfuss and Barthmeyer (1929). From Prescott's results and their own work they concluded that most, if not all, the compounds previously identified by Reichstein and Staudinger (1926b), suggested by these authors to be split products formed during the analytical treatment, were in fact actually present in coffee. They are in complete agreement with Prescott *et al.* (1937a,b) with respect to the probable changes occurring during the staling process, which probably involves volatilization, oxidation, hydrolysis, and polymerization of the various flavor and aroma constituents, and has little if anything to do with the fat of coffee. Johnson and Frey (1938) identified furan. In 1948, Neu identified nonacosane after extraction and column chromatography.

A study on the volatile constituents of roasted coffee was published by Hughes and Smith (1949) but without the identification of any original component. The authors considered that the substance, or substances, giving the characteristic aroma to roasted coffee was as yet unidentified and that it was probable that less volatile and readily oxidizable substances, were involved in the flavor of roasted coffee. Their main problem was to investigate the changes that take place during staling. With the relatively poor analytical tools then available, essentially colorimetric methods, they tried to quantify the main—already identified—volatile constituents which they considered to be typical. They particularly observed the evolution of pyridine, furfural, aldehydes, diacetyl, acetylmethylcarbinol, acetone, volatile phenols and hydrogen sulfide.

In the first part of his review on the aroma of coffee, Moncrieff (1950a) did not reveal the identification of any new flavor constituent, but summarized 120 years of research. He reminded us obviously that the oily substance, the lighter fraction of the distillate which gives much aroma to roasted coffee, initially named 'caffeol' and whose identification had been the dream of generations of chemists, is in fact a complex mixture of substances.

Kaufman (1951) summarized some recent developments in fundamental research on coffee flavor, reviewing the evolution of knowledge in the fields of green coffee production, roasted coffee processing, methods of control and packaging. He reviewed the developments of the powdered or soluble coffee extracts technology and made some general comments on the fundamental analytical research into coffee aroma, insisting that the sulfur compounds in coffee were the most important contributors to the flavor.

After the identification of pyruvic acid by Mabrouk and Deatherage (1956), Clements and Deatherage (1957) proposed a chromatographic study of some compounds of roasted coffee but their results are somewhat ambiguous because the lists of oxo acids characterized as 2,4-dinitrophenylhydrazones are given as reference compounds with the risk of persuading the reader that they are effectively present in coffee. In fact, only trivial compounds were tentatively identified, and propionic and butyric acids mentioned for the first time as being present in roasted coffee flavor. Lockhart (1957) identified ethanol and furfuryl formate. Högl (1958) analyzed by paper chromatography an extract of non-volatile constituents of roasted coffee. He identified hydroxymethylfurfurol, pyrogallol, and rediscovered hydroquinone (Bernheimer, 1880a,b), as well as maltol and catechol previously identified by Reichstein and Staudinger (1926b).

4.2 MODERN TIMES: THE ADVENT OF GAS CHROMATOGRAPHY

From 1956, gas chromatography (GC) was introduced as a separation technique, and throughout the sixties, identification systems like mass spectrometry (MS) and nuclear magnetic resonance (NMR) progressively equipped analytical laboratories. The use of these instruments has dramatically accelerated the identification of volatile food constituents.

Including the previous noteworthy contribution of Reichstein and Staudinger (1926a,b), 10 outstanding research groups have actively participated, mainly between 1965 and 1985, in the development of roasted coffee flavor chemistry, by discovering more than 600 original constituents (Table 4.4). The identification of original characteristic compounds is becoming more and more difficult, but thanks to very sensitive detectors, typical trace constituents continue to be discovered, as will be discussed later.

Dimick and Corse (1956) were probably among the first authors to analyze food flavor volatiles by GC. They published an article entitled: 'Gas chromatography. A new method for the separation and identification of volatile materials in foods'. Unfortunately, lacking a satisfactory identification device, the authors did not discover any new constituents. Using a home-made chromatograph, constructed by his colleague E.Palluy, for the analysis of coffee flavor, Gautschi (1958) separated, within 35 min, and identified seven volatile aliphatic acids: formic, acetic, propionic, isobutyric, butyric, isovaleric and valeric acids. The less polar and more volatile corresponding methyl esters were prepared by the action of diazomethane and separated within 25 min.

Table 4.4 The ten research groups having identified 77% of the roasted coffee flavor constiuents

(1) **Firmenich et Cie, Geneva, Switzerland**
Stoll M., Winter M., Gautschi F., Willhalm B., Flament I. and Goldman I. M., Seibl J. (Massachusetts Institute of Technology, Cambridge, USA): 149 identifications (1958–67).

(2) **Hag AG, Jacobs-Suchard Corporate R&D, Kraft Jacobs Suchard, Bremen, Germany**
Vitzthum O.G., Werkhoff P., Holscher W., Becker R., Weisemann C., Köhler H.S., Steinhart H., Bade-Wegner H., Gutmann W., Barthels M., Bendig I., Wollmann R. and Nitz S., Doehla B. (Technische Universität Munchen, Freising-Weihenstephan, Germany): 145 identifications (1974–97).

(3) **Res. Inst. Chem. Tech. Anal., Technische Universität, Berlin, Germany**
Tressl R., Silwar R., Köppler H., Grünewald K.G., Bahri D., Jensen A., Kamperschroer and Rewicki D. (Inst. for Org. Chem., Free University, Berlin): 99 identifications (1978–87).

(4) **The Coca-Cola Company, Atlanta, Ga., USA**
Gianturco M.A., Friedel P., Giammarino A.S., Renner J.A., Shephard F.W., Krampl V., Radford T., Bondarovich H.A., Flanagan V., Pitcher R.G.: 61 identifications (1963–71).

(5) **Institute for Food Chemistry, Technical University, Berlin, Germany**
Baltes W., Bochmann G., Heinrich L.: 56 identifications (1986–87).

(6) **US Army Natick Laboratories, Natick, Mass., USA**
Merritt C. Jr., Robertson D.H., McAdoo D.J., Bazinet C., Sullivan J.H.: 38 identifications (1963–70).

(7) **International Nahrungs-und Genussmittel A.G., Schaffausen, Switzerland**
Reichstein, T., Staudinger H.: 31 identifications (1926).

(8) **Polak's frutal Works N. V., Amersfoort, Holland**
Stoffelsma J., Sipma G., Kettenes D.K. and **Pypker J.** (Douwe Egberts Koninklijke Tabaksfabriek-Koffiebranderijen-Theehandel N.V., Utrecht, Holland): 30 identifications (1968).

(9) **Nestlé Techn. Assist. Co., Nestec Ltd, Lausanne, Switzerland**
Reymond D., Egli R.H., Liardon R., Viani R., Müggler-Chavan F., Vuataz L., Ott U., Aeschbacher H.U., Wolleb U., Löliger J., Spadone J.C., Woodman J.S., Giddey A., Pollien P., Krebs. Y., Chaintreau A., Takeoka G.: 25 identifications (1963–98)

(10) **University of Houston, Texas, USA**
Zlatkis A., Sivetz M., Wang T.H., Shanfield H.: 18 identifications (1960–83)

Another innovative GC application is due to Rhoades (1958). He used, in isothermal conditions at 45 °C, one of the first commercial chromatographs (Vapor Fractometer Perkin-Elmer, Model 154), equipped with an external gas sampling valve and 2-meters of copper tubing filled with dried fire brick coated with 20% Carbowax 1500. The sampling procedure consisted in sweeping heated ground coffee with a stream of warm and moist helium. The chromatogram of the volatiles exhibited 16 distinct peaks and the author identified acetaldehyde, acetone and methanol, compounds which were unfortunately already known coffee components. Dimethyl sulfide, propionaldehyde, ethyl methyl ketone and diacetyl were also tentatively identified. Though the results were somewhat meager, they where promising. Two years later, Rhoades (1960) compared seven varieties of coffee and noted the modifications of volatile concentrations with roasting. He observed, for example, that hydrogen sulfide reaches a maximum concentration at ca 175 °C, methyl formate near 200 °C and acetyl propionyl (2,3-pentanedione) near 220 °C usually the final roast temperature. He identified and quantified 18 volatile compounds and confirmed, for the first time, the presence of isoprene, propanal, butanal, isobutyraldehyde, isovaleraldehyde, 2-butanone, methyl formate and 2-methylfuran. He observed that the ratio of diacetyl to acetyl propionyl increases with roasting, a value which he proposes be used for measuring the roasting degree of trade coffee varieties.

Zlatkis and Sivetz (1960) (University of Houston, Texas, USA, see Table 4.4) isolated and analyzed two types of extract: the very volatile 'coffee aroma essence' (CAE), collected from commercial percolator vent gases (200 ppm from roasted coffee) and the less volatile 'dry vacuum aroma' (DVA) fraction, prepared by steam distillation and ether extraction. Using packed columns mounted with a catharometer, the classical equipment at that time, the authors observed that the CAE, which has an extremely powerful odor and gives the true coffee aroma when sufficiently diluted in the air, is largely composed of aldehydes and sulfides, the main constituents being acetaldehyde, acetone, diacetyl, valeraldehyde and 2- and 3-methylbutyraldehydes. In spite of the low resolution of the GC columns then available, the authors obtained an outstanding chromatogram of coffee aroma essence. MS helped them to characterize 30 volatile components, some of them not yet identified in coffee, such as 1,3-pentadiene, valeraldehyde, ethyl formate, thiophene and carbon disulfide. More than 20 years later, a group from the same laboratory analyzed the trace volatile compounds in coffee by headspace concentration, heart cutting separations, Tenax adsorption and GC-MS identification. Wang *et al.* (1983) identified 13 other constituents and observed, that the characteristic compounds of coffee aroma formed a complex mixture including esters, ketones, alcohols, phenols, sulfur-containing compounds, pyrazines, furans and pyrroles.

Schormüller *et al.* (1961) identified and quantified organic acids in a commercial instant coffee powder whose origin was not revealed. To be noted particularly were lactic, succinic, fumaric and 2-oxoglutaric acids.

In 1963, the Institut Français du Café, du Cacao et autres Plantes Stimulantes (IFCC) organized in Paris the first 'International Colloquium on the Chemistry of Green and Roasted Coffee and other Stimulant Plants'. A biennial frequency was planned. The second meeting was again held in Paris in 1965. Then from 1967, in Trieste, the name became 'International Colloquium on the Chemistry of Coffee' organized by the Association Scientifique Internationale du Café (see Section 1.2).

Analyzing low-boiling volatiles of cooked foods, Self *et al.* (1963) observed that, after boiling, a number of foods contained at least six of the 13 components of the volatile fraction from boiled potatoes. The authors concluded that most cooked foods probably produce a similar pattern of low-boiling volatiles varying only in the relative quantities present. This suggested the formation of the common volatiles by degradation of metabolites that are normally present in all biological material. Most of them were indeed produced from amino acids in model systems. The authors concluded that the differences in flavor among certain foods, do not lie in the presence of one or more unique components, but in the relative quantitative pattern of low-boiling substances. In an instant coffee powder, Self *et al.* (1963) identified ethanethiol.

In 1963 appeared the publications of a second group actively involved in coffee aroma research (Merritt *et al.*, US Army Natick Laboratories, Natick, Mass., USA, see Table 4.4). Merritt *et al.* (1963) applied more or less routinely the 'modern technique' of GC/MS coupling as an identification tool. After having discussed the possibility of chemical changes or contamination of the volatile components, by the use of heat, steam, water or solvent extraction, they considered that the most typical compounds may be sampled by an entirely static transfer procedure, that is to say by distillation under vacuum at room temperature from dry and ground roasted coffee, with condensation into a receiver at liquid nitrogen temperature. Merritt *et al.* (1963) give a table summarizing the functions of coffee aroma constituents: aldehydes (50.7 %), ketones (21.5 %), esters (10.3 %), heterocyclic compounds (7.0 %), sulfur compounds (4.3 %), alcohols (2.4 %), and nitriles (1.7 %). According to these authors, the occurrence of 12 compounds previously reported was confirmed and 18 additional compound were identified, six of these tentatively. In fact, eight products were really original: propenal, 2,4-pentanedione, 2,5-dimethylfuran, 2-propenenitrile and 3-butenenitrile, ethyl methyl sulfide, dimethyl disulfide and ethyl methyl disulfide. The criterion for an identification was the concordance of the mass spectrum of the sample component with that of a pure reference compound. This method of confirmation had, in effect, been too often neglected by authors, complicating the validity of numerous 'identifications'. Merritt and Robertson (1966) presented the continuation of this study at the Second International Colloquium on the Chemistry of Coffee in Paris in 1965. They described in detail a special headspace-sampling device and a combined gas chromatograph–rapid scanning mass spectrometer analysis system which looked very impressive and was evidently only available to a restricted number of analytical laboratories. The mass spectra of eluted components were monitored visually with an oscilloscope and recorded, when appropriate, on an oscillograph recorder. Of the 56 compounds identified, 14 were original, particularly the hydrocarbons. The authors had already insisted that the investigation of natural flavors must incorporate organoleptic evaluation with the analytical methods employed, otherwise there is no assurance that what is detectable is significant for the aroma. It is therefore neither presumed that each compound is flavor significant nor that the analytical results allow the establishing of quality control for the finished market products, the target of these studies being, among other things, to improve the acceptability of soluble coffee products.

In 1969, at the 4th ASIC symposium in Amsterdam, Merritt *et al.* (1970) asserted that the object of research on the composition of the constituents of coffee aroma is not the mere compilation of lists, but the relationship of the compounds to their precursors, in order to establish a mechanism for their formation, and ultimately for controlling the quality of the product. Merritt *et al.* (1970) tried to correlate the composition of green and roasted coffees and gave a list of some pyrolysis products of various amino acids, observing that proteins containing the same amino acids produce the same pyrolysates. After having identified 16 other constituents, the authors hoped that new techniques will lead to more direct correlations between the aroma and their precursors, providing a more secure basis to evaluate and control the quality of coffee.

Gianturco *et al.* (Coca-Cola Company Laboratories, Atlanta, Ga, USA, see Table 4.4) elucidated, in 1963, the structure of five cyclic diketones isolated from a coffee oil obtained by extrusion-pressing of whole roasted coffee beans. They prepared an 'aroma complex', with a yield of 0.025 % based on the weight of roasted coffee, by stripping the volatile fraction, at room temperature and at a pressure of 0.1–0.2 micrometers, from the mixture of glycerides. The separations and identifications were made by repeated gas chromatography, measurement of the retention times on a polar and a non-polar column, together with the pertinent UV data. The syntheses of the original compounds were published by Gianturco and Friedel (1963). In 1964, Gianturco *et al.* (1964a) described the structures of two heterocyclic compounds and the synthesis of some tetrahydrofuranones. They pointed out that the instability and complexity of the 'aroma complex' mixture and the very low concentration of many of its constituents caused some difficulty in the analysis of the aromatic fraction. They isolated by gas chromatography and identified by IR and MS, 2-methyltetrahydrofuran-3-one and confirmed the structure of *N*-furfurylpyrrole, a substance previously found in roasted coffee by Reichstein and Staudinger (1926b) and synthesized by Reichstein (1930a). Gianturco *et al.* (1964b) reported the isolation from roasted coffee of 25 simple furanic and pyrrolic compounds, all identified by IR spectroscopy. They considered that the recent investigations had been focused exclusively on the very volatile constituents of the 'aroma complex', that this choice was somewhat arbitrary, and that this approach had too narrow a base. They intended to go deeper into the identification results by focusing on only the furanic and the pyrrolic compounds. Through this specific approach, the authors obtained efficient results with the new identifications of six furans and eight pyrroles. In a short article, Gianturco *et al.* (1966) gave a list of 85 compounds including 12 new identifications. Bondarovich *et al.* (1967), recalling the results of their previous investigations (Gianturco *et al.*, 1966; Gianturco, 1967), realized that continuation of the analysis of the complex roasted coffee flavor became futile without the aid of mass spectrometry. They estimated the total number of reported volatile components to be 284 but considered rightly that although it could not be claimed that all of the constituents had already been identified, the information collected so far should be sufficient to attempt to determine the relative organoleptic significance of the various compounds. They particularly insisted on the fact that the pyrazines might contribute in an important way to the flavor of a variety of roasted, or otherwise cooked, foods. The article includes the IR spectra, MS and UV data of 22 alkyl- and alkenylpyrazines present in coffee, five of them being new identifications: 2,3-diethyl-5-methylpyrazine, 2,6-diethyl-3-methylpyrazine, 2-(*trans*-1-propenyl)pyrazine, 2-methyl-5-(*trans*-1-propenyl)pyrazine and 2-methyl-6-(*trans*-1-propenyl)pyrazine. Twelve other identifications of constituents were mentioned: tetradecane, pentadecane, four cyclopentenones, two cyclohexenones, 1-hydroxy-2-butanone acetate, acetol propionate, 2,4,5-trimethyl-2*H*-furan-3-one and *N*-amylpyrrole. Friedel *et al.* (1971) reported 12 new identifications: one ketone, two furans, eight pyrazines and butyraldoxime.

Reymond *et al.* (1963) (Nestlé Technical Assistance Co, Nestec, Lausanne, Switzerland. See Table 4.4) inaugurated a series of articles by publishing the results obtained by the separation on a steel capillary column (with a sensitive β-ionization ^{90}Sr detector) of samples obtained by the gas sweeping method, from the gas surrounding roasted coffee, from an aqueous suspension and from an aqueous extract of ground coffee. The identifications were made by measurement of the retention times relative to acetone, chosen as an internal standard, and for 13 of the 23 constituents detected the structures were elucidated by IR spectroscopy. Among the highly volatile constituents were methane, ethylene and acetaldehyde dimethyl acetal. The authors also measured the changes occurring during the staling of coffee and observed, following extraction of roasted coffee by means of hot water, the variations in the equilibrium of the aroma constituents. The relative amounts of methyl acetate, acetaldehyde, propionaldehyde, isobutyraldehyde, butyraldehyde, isovaleraldehyde and methyl ethyl acetaldehyde increase and the relative amounts of (2-?)methylfuran, methyl formate, methyl ethyl ketone and diacetyl decrease. Viani *et al.* (1965) enumerated the previous analytical works on coffee flavor. Using preparative gas chromatography on several stationary phases, measurement of Kovats indices and IR spectrography, they identified 38 compounds and confirmed the structures of four new substances: 2,3-dimethylpyrazine, γ-butyrolactone, acetol acetate and 2,3-hexanedione. With high resolution mass spectrometry they explained the fragmentation of 2-methyltetrahydrofuran-3-one, previously isolated by Gianturco *et al.* (1964a), and confirmed the structure. In order to enrich the samples in higher boiling components not detected by the classical head-space procedure, Reymond *et al.* (1966b) proceeded to a steam distillation of an aqueous beverage under reduced pressure, followed by extraction of the condensate with dichloromethane. Using ethyl butyrate as internal standard, they converted head-space data into liquid-composition data and calculated the approximate composition of an aqueous solution from the composition of the head space. 3,4-Dimethoxystyrene was among the 18 steam-volatile constituents of a Nicaragua coffee. At the 3rd ASIC symposium in Trieste in 1967, Woodman *et al.* (1968) presented a work on the carboxylic acids of brewed coffee with the identification of non-volatile acids such as fumaric, citraconic, mesaconic and itaconic acids. An exhaustive review of the role and quantification of carboxylic acids in green and roasted coffee, their origin and their changes on roasting and storage was published by Woodman (1985). Liardon and Ott (1984) analyzed 15 coffees from three different origins and attempted, with the help of multivariate statistics, to classify the headspace profiles into coffee variety and/or roasting categories. A success rate of 98% was obtained using 18 components. Profile assignment appeared to result from the combined information provided by components belonging to four families: aliphatic aldehydes, furans, pyrroles or pyrazines, and thiophenes. GC/MS analysis led to 92 identifications, of which five were new: 2-hexanone, 3-ethylfuran, 3,4-dimethylfuran, acetonitrile and *S*-methyl ethanethioate. Spadone and Liardon (1988) identified specific volatile components in 'Rio' green coffee beans. They quantified particularly 2,4,6-trichloranisole which is responsible for the phenolic, medicinal and musty off-flavor of green coffee beans, originating mainly from Brazil and Puerto Rico. Although this compound is destroyed at 50% by roasting, it remains perceptible in the final beverage. Aeschbacher *et al.* (1989) studied the contribution of 40 coffee aroma constituents to the mutagenicity of coffee. They mention, for the first time, the presence of glyoxal in coffee and observed that only aliphatic dicarbonyl compounds showed notable direct mutagenic activity. Pollien *et al.* (1997, 1998) developed a new GC-olfactometric method (SNIF-analysis) for tracking the key components of coffee. They compared a brew and an instant coffee and observed that 3-methyl-2-butenal (erroneously described as the 2-methyl isomer), never previously mentioned in coffee, has a high aroma impact in the brew; however it could be an artifact. They also identified 1-nonen-3-one, a compound exhibiting a typical mushroom odor and a very potent odorant.

Among numerous already known components, Radtke (1964) identified two phenols (2- and 4-methylphenol) and two picolines (2- and 3-methylpyridine).

In 1965, at the Second International Colloquium on the Chemistry of Green and Roasted Coffees, Heesterman and Weurman (1966) presented a 'preliminary report on the tentative organization of an international cooperation in the field of research into the aroma of coffee and especially by gas chromatography' and 'on coffee-odor research methods'. It was good advice from a scientific point of view, but utopian on an economical basis. The coffee market presents such an enormous capacity that coffee and flavor companies involved in the field were not enthusiastic about sharing the results of the considerable investments in their own research laboratories in order to improve the quality of their products. The use of the indices proposed by Kovats in 1958 was timidly applied by Chassevent *et al.* (1966) who recognized that they were not able at that time to analyze 'very complex mixtures containing 24 to 28 constituents'! At the same meeting, Gianturco and Giammarino (1966) report that the 'aroma complex' of coffee may be made up of approximately 250 components and one of the chromatograms that he had shown presented 150 peaks. Joking during his presentation, the first author affirms that he 'would be only too happy if someone will be able to show that, under certain chromatographic conditions, one can indeed achieve complete—or almost complete—resolution of the "aroma complex", even if this involves the use of up-to-one-mile long capillary columns!'

The 11 polycyclic aromatic hydrocarbons identified by Grimmer and Hildebrandt (1966), will be discussed in Section 5.A.

For the first time, Heins *et al.* (1966) analyzed the head-space vapors by their direct injection on a GC capillary column coupled to a mass spectrometer, eliminating by this procedure the danger of artifact formation occasionally due to concentration procedures. Unfortunately a number of technical imperfections had to be worked on, particularly the blocking of the capillary by dry ice during the injection.

The results were indeed relatively mediocre. Of the 56 peaks present in the chromatogram only 31 were indubitably identified, among them 12 new identifications: benzene, styrene, 1-hexanol, 2-butenal, methyl propionate, butyl acetate, 3-methylfuran, 3-propylfuran, tetrahydrofuran, 2-thiophenemethanol, 2-ethylpyrrole and diethyl disulfide.

Walter *et al.* (1967) recommended the use of derivatization techniques, as a complement to gas chromatography, for the identification of less volatile compounds, in spite of the danger of producing artifacts. They characterized 1,2-propanedione (methylglyoxal) and 1,2-cyclopentanedione, already identified by Gianturco *et al.* (1963), through the 2,4-dinitrophenylhydrazones using IR spectroscopy and thin-layer chromatography.

Volatile acids in the beverages of three varieties of coffee (Columbia, Santos and robusta) were determined by Kung *et al.* (1967), formic acid by NMR, the remainder by gas chromatography. Heptanoic, nonanoic and decanoic acids were identified. Parliment *et al.* (1973) discovered the presence of *trans*-2-nonenal, a compound which imparts 'a fresh-brewed woody character to roasted and ground coffee'. Kung (1974) described the identification of 3-hydroxy-3-penten-2-one with a pleasant, buttery caramel aroma. This 'compound' [Section 5, **D.45B**] is, in fact, the tautomer form of the already found 2,3-pentanedione [Section 5, **D.45A**].

Chronologically, the results for the research team (1) of the 'modern period' appeared only in 1967. As reminded in the publication of Stoll *et al.* (1967) (Firmenich et Cie, Geneva, Switzerland, see Table 4.4, the analytical project on coffee flavor started in 1957 but, for commercial reasons, the publication of results already obtained in 1965 was postponed to 1967. In the meantime, first results on the GC separation of acids were published by Gautschi (1958). At the 3rd International Colloquium on Coffee Chemistry (Trieste, 1967), Gautschi *et al.* (1968) presented a survey of the research of coffee aroma, discussing the concentration steps, the separation procedures and the identification techniques. An original, simple and efficient analytical method coupling gas chromatography with thin-layer chromatography (Flament *et al.*, 1967b) was also mentioned. Flament *et al.* (1968a) developed some chemical and spectroscopical aspects of the furanic components. The various origins of the furanic cycle were considered, as well as its transformation into other heterocyclic substances already identified or still undefined. Two complementary papers published successively by Gautschi *et al.* (1967) and by Stoll *et al.* (1967), mention the identification of 203 coffee constituents, nearly 150 being identified for the first time. The most represented classes were hydrocarbons (13), ketones (22), phenols (10), furans (37), thiophenes (17) and pyrroles (9). The same research team (Goldman *et al.*, 1967) found 18 pyridines and pyrazines. The publications of Stoll and Goldman, which revealed the results of intensive analytical work carried out over more than 7 years, were immediately followed by the disclosure of numerous other identifications obtained during the same period by other research groups. The syntheses, the physicochemical and spectroscopic characteristics, as well as the organoleptic properties of identified and potentially active constituents of coffee flavor have been published in 42 patents between 1968 and 1980 under the names of Winter *et al.* or Firmenich & Cie (see References). Büchi *et al.* (1971) confirmed by synthesis the structure of kahweofuran, a key constituent of coffee flavor discovered by Stoll *et al.* (1967).

For Broderick (1968) a new approach was needed in spite of the very promising results obtained at that time. Considering that attempts to reproduce coffee aroma synthetically had failed, the author rightly affirmed that isolation and separation techniques could alter, modify, or inactivate the key aroma compounds. He assumed that some unknown constituents, particularly among the highly volatiles, are probably extremely unstable and rapidly deteriorate. He refered to other fugacious components probably present in onion and meat and gives, as an example, the identification of propanethial (propyl thioaldehyde) in fresh onion flavor. This compound, which is particularly unstable, polymerizes rapidly and cannot be isolated or used by flavorists. By analogy he deduces and feels that 2-furancarbothialdehyde (improperly named furfuryl thioaldehyde) has all the *theoretical* flavor properties of a freshly brewed coffee flavor. He does not minimize the difficulty in preparing and stabilizing 2-furancarbothialdehyde and recognizes that it may be impossible. He concludes that the production of an instant coffee with a full fresh roasted flavor is a practical impossibility without added complementary flavors.

In two publications, Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968) (Polak's Frutal Works, Amersfoort & Douwe Egberts, Utrecht, Holland. See Table 4.4) give a list of 158 compounds, 30 being reported for the first time in coffee. Among them figure five esters, five lactones and five furans. The aroma compounds were isolated from a solvent extract of the steam condensate of roasted and ground coffee. They were identified by comparison of their IR spectra, of their retention times on two GC columns and, in a number of cases of their mass spectra, with those of reference samples.

Other contributions were published by Feldmann *et al.* (1969) who added two esters, and by Haberer (1970) and Klöcking *et al.* (1971) who added five phenols to the lists.

From the seventies, Hag AG, Jacobs-Suchard Corp. R&D, Kraft Jacobs Suchard, Bremen, Germany (Table 4.4) shared in the knowledge of coffee aroma. In their important work, Vitzthum and Werkhoff (1974a,b) enriched, by adsorption on Porapak Q, and analyzed, by combination of glass capillary GC-MS, the basic and neutral components of a steam-volatile extract of roasted coffee. The number of identified components increased by 80, among which were 7 pyrroles, 20 oxazoles, 25 thiazoles, 6 pyridines and 20 pyrazines. These publications point to the role played by oxazoles and thiazoles in food flavors. Nevertheless, the authors realized that, although the number of volatile components of coffee reported until then was relatively high, they only represented the tip of the iceberg. Also in 1975, the same authors identified 17 alkylated cyclopenta- and cyclohexapyrazines (tetrahydroquinoxalines) in the basic fraction of a normal pressure steam-distilled coffee extract. Possible precursors of these heterocycles were discussed and the principal MS fragmentation pathways were demonstrated. Among the 120 components identified by Vitzthum and Werkhoff (1976b) in the neutral fraction, 29 were not yet known components. Methylated vinylfurans, alkenylfurans and *N*-acylated pyrroles, which had not been previously found in roasted foodstuffs, are specially mentioned. Mass-spectral data for the newly identified substances were tabulated and discussed. An exhaustive table of the constituents or raw and roasted coffee identified 25 years ago was published by Vitzthum (1976). Gutmann *et al.* (1979) compared the volatile components of roasted arabusta (hybrid from the Ivory Coast) coffee with arabica and robusta by enrichment of the headspace volatiles on Tenax polymers and GC/MS identification. The aroma profile of arabusta is very similar to that of arabica, confirming the close relationship of their flavors. Moreover, the robusta shows more GC peaks than the other varieties. The authors mentioned 11 furanic compounds which are more abundant in arabica and arabusta and four sulfur constituents which predominate in roasted robusta. Becker *et al.* (1988) investigated the origin of a 'peasy' off-flavor note present in Central African coffees, defective green beans impairing considerably the flavor of the final roasted product. They used a cryogenic headspace enrichment device coupled with a double-oven GC/MS system. They located two peaks, one having a 'peasy' note, the other a 'bell pepper' character, which they respectively identified as 3-methoxy-2-isopropylpyrazine and 3-methoxy-2-isobutylpyrazine. Both compounds resist roasting conditions and are present, although in lower concentration, in ordinary 'non-peasy' Colombian coffee. Holscher *et al.* (1990) investigated aroma extracts from roasted Colombian coffee, by means of a HRGC-sniffing technique recently introduced by Grosch *et al.* (Ullrich and Grosch, 1988a; Gasser and Grosch, 1988, Blank *et al.*, 1989). Of the 61 peaks present in the GC, 49 constituents were characterized by an odor description and a flavor dilution factor. This technique confirmed that only a comparatively small proportion of the volatiles is significant for coffee flavor. In fact, only nine compounds have a very powerful impact, some not yet having been reported in the literature. Among them figure 2-methyl-3-furanthiol and methional which exhibit a strong meat-like flavor, and 3-mercapto-3-methylbutyl formate which is described as having a 'catty' or black-currant-like odor. 2-Furanmethanethiol, discovered by Reichstein and Staudinger (1926b), was again recognized as one of the most typical constituents of roasted coffee. Furaneol, β-damascenone and, surprisingly, 2- and 3-methylbutanoic acids were recognized as contributing remarkably to the flavor. Typical 3 methoxy-2-isopropyl- and -isobutylpyrazines, previously mentioned as being present in green beans by Vitzthum *et al.* (1976) and by Becker *et al.* (1988), were easily located. Holscher *et al.* (1990) also observed the presence, at the GC-sniffing port, of several other interesting spicy and catty odors whose nature remained unidentified. Vitzthum *et al.* (1990) compared the GC profiles and the sensorial differences of arabica versus robusta. They observed that robustas have a typical harsh, rubbery, often earthy and mouldy character, whereas arabicas exhibit a milder, finer and more aromatic flavor. The authors reviewed the analytical studies which had shown that robusta coffees contain higher concentrations of phenols, pyrroles and sulfur compounds. A GC peak corresponding to the very typical earthy musty note of robusta varieties was located and identified as that of 2-methylisoborneol. This key compound has an exceedingly low threshold, corresponds to the descriptor 'robusta' in sensorial profile tests and is present at higher concentrations in robustas than in arabicas by a factor of at least 3. Bade-Wegner *et al.* (1998) tracked the 'stinker' constituents of over-fermented green coffee which are associated with an intolerable 'fruity, silage-like, rotten' flavor. Their work revealed that three ethyl esters of short chain or alicyclic acid, ethyl 2- and 3-methylbutanoates (2-MBEE, 3-MBEE) and ethyl cyclohexanecarboxylate acid ester (CHEE, improperly named cyclohexanoic acid ethyl ester), are the actual or potential key aroma compounds responsible for the over-fermented flavor defect. Critical factors, such as elevated moisture levels and temperatures, might support growth of microbes that generate the off-flavor during shipping or storage. The roasting of the spoiled beans reduces but does not eliminate the light volatile 3-MBEE, and it does not affect the levels of CHEE. The threshold value of CHEE is particularly low (0.005–$0.01\,\mu g/L = 5$–$10\,ppb$). Consequently its aroma value in the beverage is relatively high and it may be directly related to the 'stinker' bean phenomenon. Boosfeld and Vitzthum (1995) identified four aldehydes from green coffee, some also being present in roasted coffee.

Singer and Lijinsky (1976), Neurath *et al.* (1977) and Amorim *et al.* (1977) identified some amines and polyamines, Rahn and König (1978, 1980a,b) and Rahn *et al.* (1979) some original phenols and acids. Heyns (1979) reviewed the scientific aspects of coffee research.

Tressl *et al.* (1978a,b) and Tressl (1979a) (Institute for Biotechnology, Technical University, Berlin, Germany. See Table 4.4) isolated 30 phenols from roasted coffee by distillation–extraction. Separation from the other constituents was carried out by adsorption chromatography on aluminum oxide and the identification by capillary GC/MS. The authors observed that the robusta contains the largest amount of phenols (mainly phenol, guaiacol and 4-ethylguaiacol) and maltol, followed by arabusta and arabica varieties. They also note that the quantity and the types of phenols depend on the coffee variety as well as on the roasting conditions. New identified components comprised 15 phenols, three furans and two pyrans. Arabica contained higher amounts of these heterocycles than the other varieties. 4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone (Furaneol®), the 2- or 5-ethylhomologue (ambiguously called ethylfuraneol), isomaltol (2-acetyl-3-hydroxyfuran), 5-hydroxymaltol (3,5-dihydroxy-2-methyl-4-pyrone) and 5-hydroxy -5,6-dihydromaltol (2,3-dihydro-3,5-dihydroxy-6-methyl-4-pyrone) have an agreeable and characteristic caramel note (see Section 5.I).

The presence of pyrroles in roasted coffee was studied by Tressl *et al.* (1981a) who added a list of 27 coffee components. After a special separation process involving distillation–extraction of freshly roasted coffees, adsorption chromatography on silica gel, and capillary GC/MS, more than 20 *N*-alkylpyrroles and 15 furfurylpyrroles were identified and (semi)quantified. Robusta coffees contain higher amounts of alkylpyrroles and lower amounts of furfurylpyrroles than arabica varieties. The authors proposed a possible formation mechanism by reaction of furfurylamine with sugar fragmentation products.

Tressl and Silwar (1981) investigated the sulfur-containing components of roasted coffee. Twenty-three mercaptans, sulfides, di- and trisulfides were characterized, 15 of these products being newcomers.

The structures were confirmed by synthesis. Among the most original compounds figure homokahweofuran (2,4-dimethyl-3-oxa-8-thiabicyclo[3.3.0]-1,4-octadiene), a homologue of the typical kahweofuran identified by Stoll *et al.* (1967), 3,3-dimethyl-1,2-dithiolane and 3,3-dimethyl-4-oxo-1,2-dithiolane.

Silwar (1982) identified numerous components which have been published with Tressl in various quoted references.

Baltes and Bochmann (1986a, 1987b,c,d,e) (Institute Food Chemistry, Technical University, Berlin, Germany. See Table 4.4) intensively studied model reactions on roast aroma formation. They particularly reported the reaction of serine and threonine with sucrose, which are present in green coffee, under the conditions of coffee roasting. From the reaction mixture they identified about 350 compounds including furans, pyrroles, pyrazines, pyridines and oxazoles. By comparison of the compounds with the components of an original coffee aroma, they identified 53 aroma components. Among them were present, sometimes in very low concentrations, 12 furans, 9 pyridines, 15 pyrazines (alkyl- and alkenylpyrazines, pyrrolo[1,2-*a*]pyrazines and furfurylpyrazines) and 2 oxazoles. Heinrich and Baltes (1987a,b) identified 14 phenolic constituents in four commercial coffee samples and particularly in robusta varieties.

Nishimura and Mihara (1990) investigated 2-hydroxy-2-cyclopenten-1-ones in a steam-distilled coffee extract and identified ten compounds of this class, seven of them being reported for the first time in a natural flavor and some even being original chemicals. Procedures used for their syntheses are described. All the 2-hydroxy-2-cyclopenten-1-ones were also identified in a model reaction, when sucrose, the major component of green coffee, was heated with alkali in aqueous solution. Some had been previously found in maple syrup or tobacco. We are reminded that Gianturco *et al.* (1963) mentioned for the first time the presence of these typical, sweet, caramel-like and burnt compounds in a roasted coffee extract.

Other analytical works including original identifications have been published by Maier (1987, 1988), Guyot *et al.* (1988b), Kallio *et al.* (1989) and Shimoda and Shibamoto (1990a). Hills *et al.* (1991), Blank *et al.* (1992a), and Leino *et al.* (1992) have also contributed to the identification of roasted coffee constituents.

Lee *et al.* (1992) monitored by GC-MS the compositional changes in 44 volatile components of a coffee beverage as a function of brewing time, concluding that the maximum time should be 10–11 min. Ho *et al.* (1993) reviewed the relationship of Maillard reactions with aroma generation in coffee. Ten constituents, mainly furans, were identified for the first time. Wöhrmann *et al.* (1997a,b), particularly interested in the rancid and sweaty smelling notes, identified five volatile minor acids in raw and roasted coffees. Ramos *et al.* (1998) compared supercritical fluid extraction (SFE) of a brewed coffee with other extraction techniques, liquid–liquid extraction and headspace–solid-phase microextraction (HS-SPME). There was a high olfactory resemblance of the supercritical-CO_2 extract to the original brewed coffee. Fifteen components were identified.

For about 15 years, analytical research has turned to more selective approaches, essentially based on sensory methods. The research group of Grosch (Garching, Germany) has been particularly active in this field by turning the attention to the qualitative aspects of the already identified and most-contributing constituents. The Nestlé group has also been very much involved in this field. More details are given in Section 3.3.

This overview of the most recent studies on coffee aroma chemistry is inevitably full of matter and tediously enumerative. The reader will find more specific details and discussions in Chapter 5.

4.3 RESULTS

Figure 4.1 illustrates the progressive identification of the nearly 850 volatile constituents discovered in roasted coffee flavor. It shows that at the advent of chromatography (1956) 60 compounds were already known thanks to the remarkable contribution of Reichstein and Staudinger (1926) (see Table 4.4).

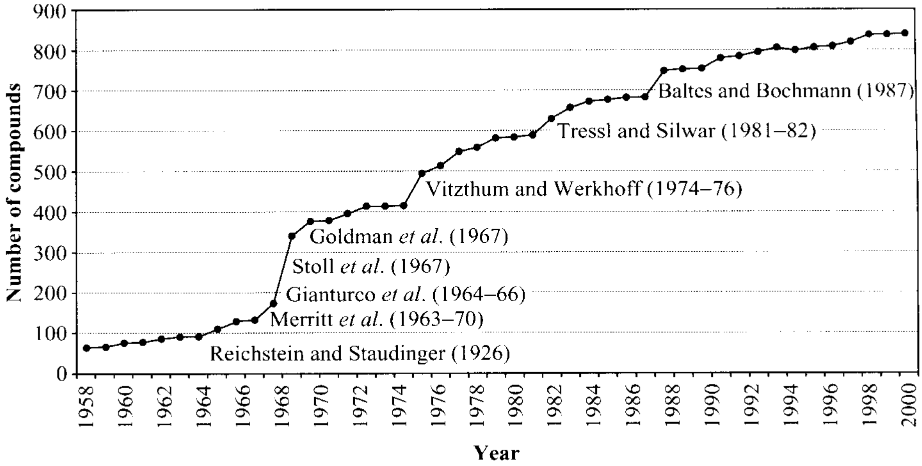


Fig. 4.1 Identification of roasted coffee flavor constituents

Nearly 100 scientific papers mentioning original structure discoveries have been published during the last 40 years.

Table 4.4 showed the research groups who, during the last half century, found the structures of nearly 80% of the volatile constituents identified up to now. Table 4.5 details the functions of the constituents identified by these groups. Under reserve of possible statistical omissions or errors, five each discovered more than 50 volatiles.

Group 1 (Stoll *et al.*, Firmenich) found a wide variety of ketones and of numerous furans, pyrazines and thiophenes.

Table 4.5 Functions of the compounds identified by the different research groups

	Function	1	2	3	4	5	6	7	8	9	10	Total/Function
A	Hydrocarbons	13	0	7	2	0	16	2	0	2	3	45
B	Alcohols	8	2	1	0	0	3	0	1	0	4	19
C	Aldehydes	4	3	1	1	0	4	2	0	3	3	21
D	Ketones	22	4	5	16	1	3	3	3	3	2	62
E	Acids	1	0	0	2	0	0	1	3	7	0	14
F	Esters	5	1	1	3	0	2	2	5	1	1	21
G	Lactones	0	0	0	1	1	0	0	5	1	0	8
H	Phenols	10	1	15	2	14	0	5	0	2	0	49
I	Furans and pyrans	37	20	29	10	12	2	7	5	3	1	126
J	Thiophenes	17	5	0	1	0	0	0	2	0	1	26
K	Pyrroles	9	14	28	8	2	3	2	2	0	1	69
L	Oxazoles	0	20	0	0	2	0	0	1	0	0	23
M	Thiazoles	2	25	0	0	0	0	0	0	0	0	27
N	Pyridines	1	8	0	1	9	0	0	0	0	0	19
O	Pyrazines	17	39	0	13	15	0	4	2	1	0	91
P	N-Compounds	0	0	0	1	0	2	0	0	1	1	5
Q	S-Compounds	3	3	8	0	0	3	3	1	1	1	23
	Total/Group	**149**	**145**	**95**	**61**	**56**	**38**	**31**	**30**	**25**	**18**	**648**

Group 2 (Vitzthum *et al.*, Hag-Kraft-Jacobs-Suchard) identified numerous heterocyclic compounds, mainly pyrazines, thiazoles, oxazoles and furans.

Group 3 (Tressl *et al.*, Berlin) identified mainly furans, pyrroles, phenols and sulfur-containing compounds, emphasizing particularly their formation pathways.

Group 4 (Gianturco *et al.*, Coca-Cola) was the first to identify caramel compounds such as cyclic ketones and to reveal the organoleptic interest of pyrazines, furans and pyrroles.

Group 5 (Baltes *et al.*, Berlin) contributed to the isolation of many pyrazines, phenols, furans and pyridines by the systematic study of model reactions.

Figure 4.2 shows the distribution according to their functions or structure of the constituents of roasted coffee flavor. Furanic compounds are predominant. The other main constituents are pyrazines, ketones, pyrroles, phenols and hydrocarbons.

Figure 4.3 compares the number of compounds identified in green and in roasted coffee beans. Green coffee contains a larger number of identified alcohols (B) and nearly the same number of identified aldehydes (C) and esters (F) than roasted beans. On the contrary, the latter are richer in furans (I), pyrazines (O), ketones (D) and phenols (H). Thiophenes (J), oxazoles (L) and thiazoles (M) have only been identified in roasted coffee. The roasting effect is also revealed by the increased number of pyrroles (K) and sulfur-containing compounds. The distribution of aroma volatiles is shown in Figure 4.4.

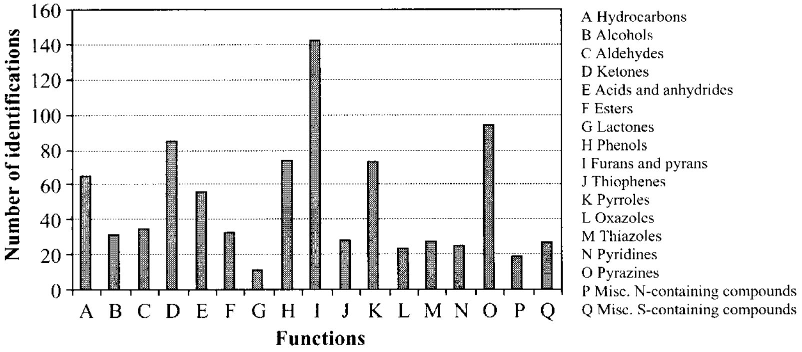


Fig. 4.2 Volatile constituents of roasted coffee flavor

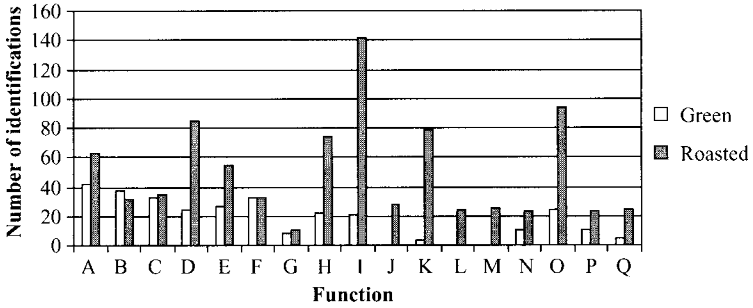


Fig. 4.3 Green and roasted coffee volatiles

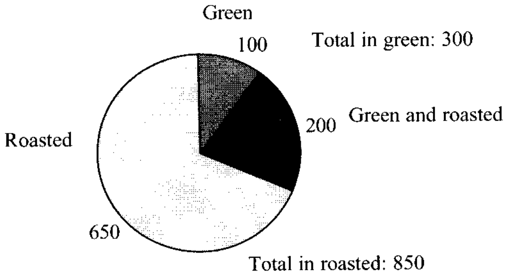


Fig. 4.4 Distribution of aroma constituents in green and roasted coffee

A coffee-fountain in the streets of London (in about 1860)

5

The Individual Constituents: Structure, Nomenclature, Origin, Chemical and Organoleptic Properties

In the following sections, 5A to 5Q, of this chapter, the compounds will be identified by a letter corresponding to the section followed by a digit for the individual structures. The compounds identified in roasted coffee are given upright **bold** characters and are in ***bold italics*** when identified in green coffee. Each identification number will be followed by the name with which it is indexed in *Chemical Abstracts*, in **bold** characters, then one or more of the names more generally accepted by IUPAC (International Union of Pure and Applied Chemistry) rules with the 1993 recommendations, in *italics*, together with other synonyms and trivial names under which the compounds can be found in literature and which may be sometimes confusing. The Register Number in *Chemical Abstracts* will follow (very few have not been found), in **bold** characters and, where possible, the FEMA number in ***bold italics***. We remind readers that the IUPAC agrees that indexes, like *Chemical Abstracts* or *Beilstein*, need more 'stringent requirements' than are usually necessary. Moreover the application of the principles 'will not necessarily lead to a unique name, but the name obtained should be unambiguous'.

For each compound, we have tried to identify the original discoverer in coffee and we also give, in a non-exhaustive manner, a list of some other references, sometimes with methods of identification, concentration in coffee and thresholds. Some of the model reactions in which the compounds are formed will be quoted, then some syntheses, and eventually the organoleptic properties.

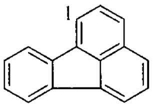
We will avoid acronyms as much as possible. Anyway a list is given in Chapter 1.

5.A HYDROCARBONS

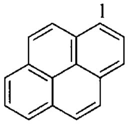
Lower alkanes and alkenes with straight or branched chains have been found in coffee volatiles. For example, Zlatkis and Sivetz (1960) drew attention to the presence of low molecular weight hydrocarbons in a coffee aroma essence (C_4–C_7 paraffins and olefins), but propane and heptane, which have not yet been identified in coffee, are probably also present. These small molecules are certainly produced during the roasting of the beans, an operation generally conducted at temperatures near 200 °C, relatively higher than those used for the thermal treatment of cocoa beans and tea leaves that are, consequently, poorer in hydrocarbons. Other mechanisms can be suggested since a few hydrocarbons are actually present in flavors as primary metabolites (in green tea, for instance), and others can be formed enzymatically (in black tea and cocoa) or by various pyrolysis transformations. According to the observations of Merritt *et al.* (1970), hydrocarbons could be formed by oxidation of fats before roasting, the process itself having little effect, although some compounds may disappear and some olefins may be produced.

The organoleptic character of hydrocarbons has received little attention in spite of the fact that compounds such as hexane or cyclohexane have a detectable odor. Boelens (1974) reported that the members of a panel could not make any distinction between C_{11}- to C_{15}-alkanes and the corresponding aliphatic alcohols. On the contrary, polyunsaturated hydrocarbons possess typical odor qualities and may therefore be important contributors to food flavors (Ohloff, 1978a) but their presence in coffee is limited to aliphatic volatile compounds, such as pentadiene (**A.41**) and isoprene (**A.44**), and to 5-methyl-1,3-cyclohexadiene (**A.47**), not forgetting the terpenes mentioned later. Nevertheless the flavoring power of these paraffins is certainly negligible as compared with the most characteristic constituents of coffee, cocoa, and tea.

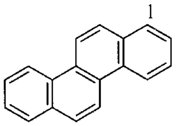
Monoterpenes, on the other hand, possess particularly desirable flavor notes. Three of them, β-myrcene (**A.45**), limonene (**A.46**) and *p*-cymene (**A.59**) are common to coffee, cocoa and tea, and to numerous plant families: β-myrcene for example constitutes 63 % of hop oils. It is worth remembering that they particularly contribute to the flavor of spices. In a study of the effluvia of fresh red coffee berries, Mathieu *et al.* (1996) identified, in two varieties of robusta, a series of mono- and sesquiterpenes, a blend also present in cold pressed oil from pommelos. In fact, the effluvia of red berries attracts the females of the coffee berry borer, a very important pest. Without giving a list of the hydrocarbons identified in this study, let us note that limonene is the most abundant of them, caryophyllene (4,11,11-trimethyl-8-methylenebicyclo[7.2.0]undec-4-ene), followed by humulene (2,6,6,9-tetramethylundeca-1,4,8-triene) and α-pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene), are rather important in two robusta



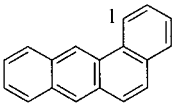
fluoranthene



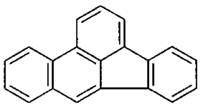
pyrene

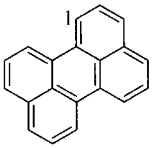


chrysene

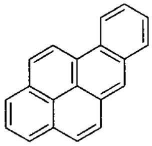


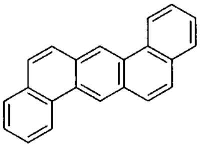
benz[*a*]anthracene

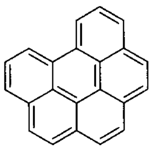

benz[*e*]acephenanthrylene



perylene


benzo[*a*]pyrene


dibenz[*a,h*]anthracene


benzo[*g,h,i*]perylene

varieties. In one arabica variety, only caryophyllene and humulene are identified and no monoterpenes. The amount of terpenic hydrocarbons decreases drastically when the berries are left on the tree after the red stage (Mathieu *et al.*, 1998), and only limonene is still emitted in appreciable quantity by a robusta, accompanied mainly by *p*-cymene and pinenes and the two sesquiterpenes quoted above. With an arabica (grown in a greenhouse) some limonene was detectable after longer ripening on the tree but no sesquiterpene was identified. Parallel to the decrease in these hydrocarbons is the increase in oxygenated compounds by ripening. Recently, Cantergiani *et al.* (2001) identified kaur-16-ene, a tetracyclic diterpene, in the volatiles of a green Mexican arabica coffee.

Being interested here in the volatile components of coffee aroma, we shall arbitrarily limit the list of the aromatic hydrocarbons to tricyclic structures. The higher fused polycyclic hydrocarbons (fluoranthene **[206-44-0]**, pyrene **[129-00-0]**, chrysene **[218-01-9]**, benz[*a*]anthracene (1,2-benzanthracene) **[56-55-3]**, benz[*e*]acephenanthrylene (3,4-benzofluoranthene) **[205-99-2]**, benzo[*a*]pyrene (3,4-benzopyrene, 3,4-BP) **[50-32-8]**, benzo[*e*]pyrene (1,2-benzopyrene) **[192-97-2]**, perylene **[198-55-0]**, benzo[*g,h,i*]perylene (1,12-benzopyrene) **[191-24-2]**, and dibenz[*a,h*]anthracene (1,2,5,6-dibenzanthracene) **[53-70-3]**) cannot be considered as a part of the aroma. However, as some of these, specially benzo[*a*]pyrene, are known for carcinogenic properties, they have been particularly analyzed in food subject to roasting or smoke-curing.

A work of Kuratsune and Hueper (1958) quotes concentrations of benzo[*a*]pyrene as high as 0.44 ppm in soots of torrefaction but the same authors (1960) identified (by extraction and chromatography) nine hydrocarbons including benzo[*a*]pyrene (with a large predominance of pyrene and fluoranthene) only in a very dark roasted coffee that was nearly black at the surface. In other commercial brands only pyrene and fluoranthene were identified. Chassevent and Héros (1963) found no benzo[*a*]-pyrene or concentrations lower than 0.1 ppb in arabica and robusta coffees from New Caledonia, green, or light to dark roasted. After grinding, they extracted with petroleum ether, and used chromatography and the fluorescence spectra. The concentrations are higher in the endosperm of roasted beans (0.15 ppm) and in soots of industrial torrefaction (0.26–0.28 ppm). After analyses of brewed coffee, Grimmer and Hildebrandt (1966) found that the main aromatic polycyclic hydrocarbons were phenanthrene (**A.77**), pyrene and fluoranthene but that the concentration of benzo[*a*]pyrene was less than 0.4 ppb, ten times lower than in Indian black tea. These concentrations were similar to those found in other food, like bread or smoked products. Calzolari and Pertoldi-Marletta (1968) also analyzed the aromatic hydrocarbons (extraction with petroleum ether and separation of unsaponifiable matter) in roasted coffee at different temperatures, and in the fumes. The concentrations were similar in Columbian, Haiti and Santos samples. At 180 °C, they only detected the 3,4-benzofluoranthene (0.4 ppb) but, for the seven of the eight hydrocarbons studied, the concentrations increased at 210 °C and even more so at the over-roasting temperature of 240 °C, benzofluoranthene being still preponderant (ca 5 ppm at 210 °C). Benzo[*a*]pyrene (3,4-BP) was only detected at 240 °C (ca 5 ppb) and in the fumes of the corresponding roasting (ca 0.5 ppb). Decaffeination apparently brings a diminution in the concentration in hydrocarbons (of the order of 50%). Baltes (1979b), in a publication on the effect of roasting on coffee composition, noted an increase of polycyclic hydrocarbons with roasting. At medium roast, phenanthrene (**A.77**) is by far the most important (28–30 ppb), when benzo[*a*]pyrene is only present at 0.3–0.5 ppb; at extremely dark roast, phenanthrene is still the most abundant (ca 70 ppb), followed by fluoranthene (ca 35 ppb) and pyrene (ca 30 ppb), the concentration of benzo[*a*]pyrene being about 6 ppb; other hydrocarbons are in the range of 0.6–15 ppb. Strobel (1974) proposed a method for the determination of benzo[*a*]pyrene in coffee products (brew, oils and commercial extracts) and other foodstuffs. A combination of extraction, paper chromatography and fluorometry enabled the detection of less than 10^{-10} g of benzo[*a*]pyrene and measurement of 10^{-9} g. Such a sensitive method demands special attention for possible contaminations. Strobel measured 0.003 ppb in a brewed roasted coffee, 0.02–0.06 ppb in commercial coffee extracts and 0.5 ppb in coffee oil. The amount is relatively low compared to other foodstuffs. It is suggested that the reason could be that coffee is grown in places where there is not too much pollution, and also that the roasting process does not involve severe pyrolysis. Van der Stegen and van Overbruggen (1983) also studied coffee roasting and benzo[*a*]pyrene. They concluded that if burning is avoided, the content is about 0.2 ppb. The 47 commercial samples analyzed were all under 1 ppb. Husks which are left or added contain more benzopyrene, therefore that should be avoided. Eventually, consumption of coffee could contribute to less than 0.4% of total daily consumption, including other food and drinks without even taking pollution into account.

Holscher and Steinhart (1995) considered a surprising amount of a great number of hydrocarbons in roasted coffee and attributed this to contamination by the bags used for storing and transportation of the beans, the jute or sisal being treated with batching oils before spinning in order to make the fibers more elastic. The work of Grob *et al.* (1992) shows that this contamination is not negligible, coffee beans sometimes containing about 100 mg of oil/kg (using jute bags). Nevertheless it depends on the oil used. Some raw mineral oils contain more aromatics (>10%), with aliphatic hydrocarbons, nearly exclusively isoalkanes, from C_{17} to at least C_{35} (mainly C_{25}–C_{30}). Other oils contain mainly isoalkanes and about 3% of aromatics and others are in fact waxes consisting of alkanes, mainly C_{23} to C_{40}. The authors made several recommendations: reduction of the batching oil on the bags, use of oils free of aromatics and use of oils not containing alkanes with fewer than 25 carbon atoms, the transfer to the packed food being more efficient for volatile compounds. In analysis of a brew, Ramos *et al.* (1998) detected an appreciable amount of hydrocarbons in a liquid–liquid extract with pentane, and in an extract with supercritical CO_2. They agreed that this presence was probably due to contact with materials used for transportation or storage. In any case, these compounds do not contribute to the genuine coffee aroma.

Remarks concerning the validity of some identifications

The following lists are deliberately limited to confirmed identifications, the compounds mentioned in the literature with the mention 'T' (tentatively identified), '?' (questionable identification) or 'unkn.str.' (unknown structure) being usually commented on but the structures deliberately omitted from the illustrations. Sometimes, nevertheless, doubts remain concerning the actual structures of many compounds which have been somewhat misunderstood or considered by subsequent authors or reviewers as definitely identified. It is, for instance, the case for aliphatic alkanes and alkenes mentioned in the following paragraph. Some hypothetical identifications were made by Merritt and Robertson (1966) and

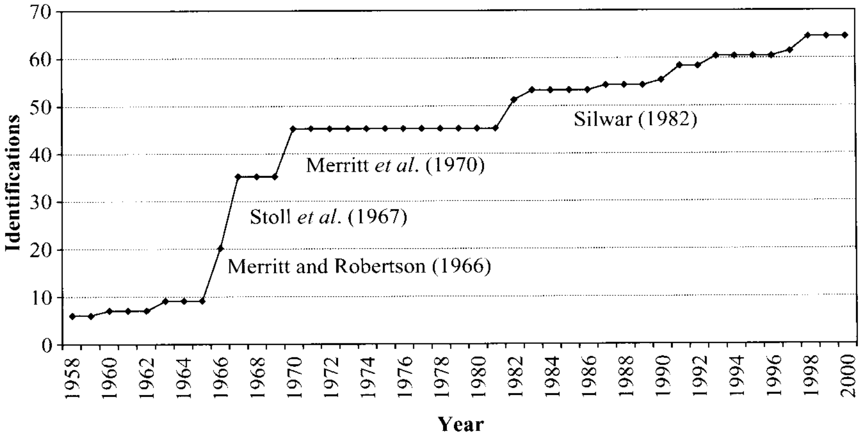


Fig. 5.1 Progressive identification of hydrocarbons in roasted coffee volatiles

listed as 'an octane, an octene, an octyne...' In such a case the identification cannot be considered as definitive, but, in a subsequent publication, Merritt *et al.* (1970) listed saturated and unsaturated homologues from C_6 to C_{11} in such a manner that the reader cannot deduce the actual structure, doubt existing concerning the 'normal' or the 'iso' nature of the molecular skeleton, the prefix 'i' (iso) being not repeated in front of '-hexane, -heptane...'. Consequently TNO lists (1996) consider these hydrocarbons to be 2-methyl-substituted homologues. On the other hand, in an exhaustive review of aroma compounds in green coffee, Holscher and Steinhart (1995) were more prudent and restricted the number of identifications to the certified compounds and considered all the doubtful cases as 'unknown structures'. We choose to give both interpretations mentioning the actual risks of confusion.

Saturated straight chains and 2-methyl-substituted alkanes

$R-H$

$R = CH_3$ **(A·1)**, C_2H_5 *(A·2)*, C_4H_9 **(A·3)** *(A·3)*,

C_5H_{11} **(A·4)** *(A·4)*, C_6H_{13} **(A·5)** *(A·5)*, C_8H_{17} **(A·6)**,

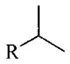
C_9H_{19} **(A·7)** *(A·7)*, $C_{10}H_{21}$ **(A·8)** *(A·8)*, $C_{11}H_{23}$ **(A·9)**,

$C_{12}H_{25}$ **(A·10)**, $C_{13}H_{27}$ **(A·11)**, $C_{14}H_{29}$ **(A·12)**,

$C_{15}H_{31}$ **(A·13)**, $C_{16}H_{33}$ **(A·14)**, $C_{17}H_{35}$ **(A·15)**,

$C_{18}H_{37}$ **(A·16)**, $C_{22}H_{45}$ **(A·17)** *(A·17)*, $C_{24}H_{49}$ *(A·18)*,

$C_{25}H_{51}$ *(A·19)*, $C_{26}H_{53}$ *(A·20)*, $C_{27}H_{55}$ **(A·21)**, $C_{29}H_{59}$ **(A·22)**



$R = CH_3$ **(A·23)** *(A·23)*, C_2H_5 **(A·24)** *(A·24)*,

C_3H_7 **(A·25)** *(A·25)*, C_4H_9 **(A·26)** *(A·26)*,

C_5H_{11} **(A·27)** *(A·27)*, C_6H_{13} **(A·28)** *(A·28)*,

C_7H_{15} **(A·29)** *(A·29)*, C_8H_{17} *(A·30)*

(A.1) Methane [74-82-8]

Methane was identified as one of three products more volatile than acetaldehyde in one the first head-space analyses of roasted coffee, that of a suspension of roasted coffee heated at 80 °C and of an extract by Reymond *et al.* (1963). The identification was confirmed by Merritt and Robertson (1966).

Methane is an odorless gas.

(A.2) Ethane [74-84-0]

Identified in green coffee by Merritt *et al.* (1970).

Ethane is an odorless gas.

(A.3) *(A.3)* **Butane [106-97-8]**

Identified in roasted coffee by Merritt *et al.* (1970) and in 'stinking' green beans by Vincent *et al.* (1976).

Butane has a sweet-nauseating odor, perceptible only in relative high concentration (Arctander, 1967).

(A.4) *(A.4)* **Pentane [109-66-0]**

Identified in roasted coffee by Merritt and Robertson (1966) and in green coffee by Merritt *et al.* (1970).

It is a well-known product of autoxidation of linoleic acid ($C_{18:2}$), but it is not a flavor substance (Ullrich and Grosch, 1987). As the other volatile alkanes, it can eventually be present as a residual trace of solvent after a petroleum ether extraction of ground coffee samples.

Pentane has a gasoline, petroleum-ether odor.

(A.5) *(A.5)* **Hexane [110-54-3]**

Identified in roasted coffee by Wang *et al.* (1983) and in green arabicas and robustas (each of six origins) by Procida *et al.* (1997).

Hexane has a faint, peculiar petroleum-ether odor.

(A.6) **Octane [111-65-9]**

Identified in roasted coffee as 'an' octane by Merritt and Robertson (1966) (see **A.23**). Ramos *et al.* (1998) found it in a brewed arabica (liquid–liquid extraction or supercritical-fluid extraction).

Octane has a petroleum odor.

(A.7) *(A.7)* **Nonane [111-84-2]**

Identified in roasted coffee by Merritt and Robertson (1966) and in a brewed arabica (after liquid–liquid extraction with pentane or supercritical-fluid extraction) by Ramos *et al.* (1998). It has been found in the headspaces of six green arabicas and six green robustas by Procida *et al.* (1997).

(A.8) *(A.8)* **Decane [124-18-5]**

Identified as *n*-decane in roasted coffee by Merritt *et al.* (1970) (see **A.25**); found later by Spadone *et al.* (1990) in a Puerto Rico 'Rio' green coffee and not in healthy beans, and by Ramos *et al.* (1998) in a brewed arabica (liquid–liquid extraction with pentane).

(A.9) **Undecane [1120-21-4]**

Identified in roasted coffee by Silwar (1982) and in a brewed arabica by Ramos *et al.* (1998) (after liquid–liquid extraction with pentane).

(A.10) Dodecane [112-40-3]
(A.11) Tridecane [629-50-5]
(A.12) Tetradecane [629-59-4]
(A.13) Pentadecane [629-62-9]
(A.14) Hexadecane [544-76-3],
(A.15) Heptadecane [629-78-7] and
(A.16) Octadecane [593-45-3]

These were identified in roasted coffee by Silwar (1982). (**A.12**) and (**A.13**) were first found by Bondarovich *et al.* (1967). (**A.10**) was also identified in a supercritical-fluid extract of brewed coffee by Ramos *et al.* (1998).

(A.17) ***(A.17)*** **Docosane [629-97-0]**

(A.18) **Tetracosane [646-31-1]**

(A.19) **Pentacosane [629-99-2]** and

(A.20) **Hexacosane [630-01-3]**

These were identified in a green Mexican arabica coffee by Cantergiani *et al.* (2001), after hydrodistillation at room temperature, extraction and concentration. The peak areas on a polar GC-column range from 0.09–0.22%. (**A.17**) was also identified in a brewed arabica (liquid–liquid extraction with pentane) by Ramos *et al.* (1998).

(A.21) ***(A.21)*** **Heptacosane [593-49-7]**

Identified in roasted coffee, isolated by Prescott *et al.* (1937b) and found in green Mexican coffee by Cantergiani *et al.* (2001) (peak area 0.13%, see above).

(A.22) Nonacosane [630-03-5]

Identified in roasted coffee by Neu (1948) and by Hills *et al.* (1991) (simultaneous supercritical fluid derivatization and extraction).

(A.23) ***(A.23)*** **Propane, 2-methyl-**, *isobutane, 2-methylpropane, i*-butane **[75-28-5]**

(A.24) ***(A.24)*** **Butane, 2-methyl-**, *isopentane, 2-methylbutane, i*-pentane **[78-78-4]**

These were identified by Merritt *et al.* (1970) in headspace analysis of green and roasted arabica and robusta coffees.

(A.25) ***(A.25)*** **Pentane, 2-methyl-**, *2-methylpentane, i*-hexane **[107-83-5]**

(A.26) ***(A.26)*** **Hexane, 2-methyl-**, *2-methylhexane, i*-heptane **[591-76-4]**

These were identified, with a lack of structural precision, by Merritt *et al.* (1970) in green and roasted coffee, confirmed as 2-methylpentane and 2-methylhexane in the TNO lists (1996) but as 'unkn.str.' by Holscher and Steinhart (1995). (**A.25**) has been identified in green arabica and robusta, each of six origins by Procida *et al.* (1997), who also found it in a Guatemala arabica at different roasting times.

(A.27) ***(A.27)*** **Heptane, 2-methyl-**, *2-methylheptane, i*-octane **[592-27-8]**

Identified in green and roasted coffees, with a lack of structural precision, by Merritt *et al.* (1970), confirmed as 2-methylheptane in the TNO lists (1996). 2-Methylheptane was identified by Guyot *et al.* (1982, 1983) in stinking but not in healthy green beans and considered as 'unkn. str.' by Holscher and Steinhart (1995). It was found by Ramos *et al.* (1998) in a supercritical fluid extract of a brewed arabica coffee.

(A.28) ***(A.28)*** **Octane, 2-methyl-**, *2-methyloctane, i*-nonane **[3221-61-2]**

Identified in green and roasted coffee, with a lack of structural precision, by Merritt *et al.* (1970), confirmed as 2-methyloctane in the TNO lists (1996–97) and considered with 'unkn. str.' by Holscher and Steinhart (1995) as present in green coffee. It was identified in a brewed arabica by Ramos *et al.* (1998).

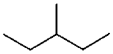
(A.29) *(A.29)* **Nonane, 2-methyl-,** *2-methylnonane, i*-decane **[871-83-0]**

(A.30) **Decane, 2-methyl-,** *2-methyldecane, i*-undecane **[6975-98-0]**

These were identified in headspace of green coffee, with a lack of structural precision, by Merritt *et al.* (1970), confirmed as 2-methylnonane and 2-methyldecane in the TNO lists (1996) but considered as 'unkn. str.' by Holscher and Steinhart (1995).

(**A.29**) was found in a brewed arabica by Ramos *et al.* (1998) after liquid–liquid extraction with pentane.

Saturated substituted alkanes: Cyclohexanes



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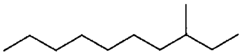

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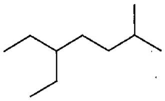

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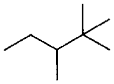

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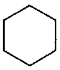

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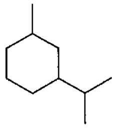

(A·36)

(A.31) *(A.31)* **Pentane, 3-methyl-,** *3-methylpentane* **[96-14-0]**

Identified in the headspace of green coffee (four arabicas and six robustas) by Procida *et al.* (1997) who also found it in a roasted arabica.

(A.32) Decane, 3-methyl-, *3-methyldecane,* 2-ethylnonane **[13151-34-3]**

Identified in a brewed arabica after liquid-liquid extraction with pentane by Ramos *et al.* (1998).

(A.33) **Heptane, 5-ethyl-2-methyl-,** *5-ethyl-2-methylheptane* **[13475-78-0]**

Identified by Guyot *et al.* (1982, 1983) in stinking but not in healthy green beans.

(A.34) Pentane, 2,2,3-trimethyl-, *2,2,3-trimethylpentane* **[564-02-3]**

Identified by Ho *et al.* (1993) in a roasted Columbian coffee (headspace analysis by combined adsorbent trapping/short path thermal desorption and GC/MS), with a concentration of 0.05 ppm.

(A.35) Cyclohexane, *cyclohexane,* hexahydrobenzene **[110-82-7]**

Identified in roasted coffee by Wang *et al.* (1983).

Cyclohexane has a 'solvent' odor.

(A.36) Cyclohexane, 1-methyl-3-(1-methylethyl)-, *1-isopropyl-3-methylcyclohexane*, m-*menthane* **[16580-24-8]; *cis*- [17066-65-8]; *trans*- [17066-66-9];** (1***R*-*trans***)- **[13837-67-7];** (1***S*-*cis***)- **[13837-66-6]**

Identified by Ho *et al.* (1993) in a roasted Columbian coffee (see **A.34**) with a concentration of 0.14 ppm. The name given is 1-methyl-3-(1-isopropyl)cyclohexane.

A hydrocarbon with an interesting skeleton, *1,1-dimethylcyclopropane* **[1630–94–0]**, has been identified by Mathieu *et al.* (1998) in the effluvia of the berries of a robusta left on the tree for several days after the red stage. No other compound with a structure related to chrysanthemic acid has been found in coffee. It is probably very hazardous to relate the presence of this hydrocarbon to that of 3-methyl-3-buten-1-ol **(B.28)** which Mathieu *et al.* found in the dried berries (left on the tree for two months after the red stage). An enzymatic-catalyzed oxygenation of the hydrocarbon proceeds via the (1-methylcyclopropyl)carbinyl radical which could undergo ring opening and rearrangement to the 3-methyl-3-buten-1-yl radical oxygenated to the alcohol (Ruzicka *et al.*, 1990). The normal oxidation product is (1-methylcyclopropyl)methanol which has not been identified at any stage in coffee.

Alkenes: Unsaturated alicyclic hydrocarbons

$CH_2{=}CH_2$

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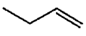
(A.37)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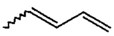
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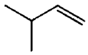
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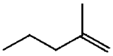
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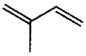
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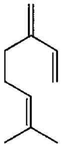
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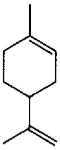
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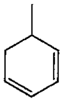

(A.47)

(A.37) *(A.37)* **Ethylene,** *ethylene*, ethene **[74-85-1]**

Identified in roasted coffee by Reymond *et al.* (1963) (see comment on **A.1**); identified in green coffee by Merritt *et al.* (1970).

Ethylene is a gas with faint sweet odor.

(A.38) 1-Butene, *but-1-ene*, α-butene, ethylethylene **[106-98-9]**

Mentioned in roasted coffee by Merritt and Robertson (1966) as 'a' butene, then by Merritt *et al.* (1970) as 'butene'. Wang *et al.* (1983) mentioned 1-butene in a headspace analysis of roasted coffee, but they referred to the review of Vitzthum (1976) quoting 'butene' with Merritt's references.

1-Butene is a narcotic gas in high concentrations.

(A.39) 2-Butene, *but-2-ene*, β-butene **[107-01-7]; (*E*)- [624-64-6]; (*Z*)- [590-18-1]**

Identified by Shimoda and Shibamoto (1990a) in a headspace analysis of brewed coffee (peak area 5.2 %).

(A.40) 3-Octene, *oct-3-ene* **[592-98-3]; (*E*)- [14919-01-8]; (*Z*)- [14850-22-7]**

Identified in a brewed arabica by Ramos *et al.* (1998) (after supercritical-fluid extraction).

(A.41) 1,3-Pentadiene, *penta-1,3-diene*, piperylene, 1-methylbutadiene **[504-60-9]; (*E*)- [2004-70-8], (*Z*)- [1574-41-0]**

Identified by Zlatkis and Sivetz (1960), called 'pentadiene' without any specification. Merritt and Robertson (1966) identified 'a' pentadiene. Quoting these two publications, Vitzthum (1976) referred to 1,4-pentadiene and TNO lists (1996) a pentadiene of unknown structure. It is very probably 1,3-pentadiene. In a later work, Merritt *et al.* (1970) did not quote pentadiene in an analysis of ground coffee beans, green and roasted, but Shimoda and Shibamoto (1990a) identified two isomers of 1,3-pentadiene in a headspace analysis of brewed coffee (peak areas 1.0 and 0.79% of the volatiles). Murota (1993) finds also 1,3-pentadiene in headspace of arabica.

(A.42) 1-Butene, 3-methyl-, *3-methylbut-1-ene*, isopentene, 2-methyl-3-butene, isopropylethylene **[563-45-1]**

Identified in headspace of roasted coffee by Merritt *et al.* (1970) as *i*-pentene and noted 3-methyl-1-butene by TNO lists (1996) referring to Merritt *et al.* The name *i*-pentene could also correspond to 2-methyl-2-butene.

(A.43) **1-Pentene, 2-methyl-, *2-methylpent-2-ene*,** 4-methyl-4-pentene **[763-29-1]**

Identified in green arabica (of three origins over six) and robusta (six origins) by Procida *et al.* (1997). It did not appear after various roasting times of the arabica which had the highest proportion when green.

In the headspace (with GC/MS) of four green arabicas and six green robustas, Procida *et al.* (1997) found 'diisobuthylene' which could be 2,4,4-trimethyl-2-pentene or 2,4,4-trimethyl-1-pentene.

(A.44) *(A.44)* **1,3-Butadiene, 2-methyl-,** *isoprene*, isopropylethylene, isoamylene **[78-79-5]**

Identified in roasted coffee by Rhoades (1958), by Reymond *et al.* (1963) in the highly volatile constituents of roasted coffee, by Gianturco *et al.* (1966) and Stoffelsma *et al.* (1968); identified and quantified in two hybrid species of arabica green coffee by Gibson (1974a). Holscher and Steinhart (1992a) found it by GC/MS also when investigating over-roasted coffee freshness using the headspace technique. The ion $M + 1$ ($m/z = 69$) is one of the ions used by Dyszel (1985) when trying to differentiate green coffees of various origins.

(A.45) 1,6-Octadiene, 7-methyl-3-methylene-, *7-methyl-3-methyleneocta-1,6-diene*, 2-methyl-6-methylene-2,7-octadiene, β-myrcene **[123-35-3]** ***FEMA 2762***

Identified in coffee flavor by Stoll *et al.* (1967) and by Friedel *et al.* (1971). Silwar (1982) quantified it.

Myrcene could be formed by degradation of higher terpenoids during roasting (Yamanishi, 1981 as quoted by Dart and Nursten, 1985b). It is produced industrially by pyrolysis of β-pinene.

It has a sweet-balsamic-resinous 'gum' odor of poor tenacity (Arctander, 1967), an earthy, metallic, orange flavor (Chemisis, 1988). Purified myrcene is refreshing, almost citrusy, but warm-balsamic and ethereal-sweet. The odor threshold is reported to be 13 ppb in water by Guadagni *et al.* (1966) and probably 36 ppb according to Ahmed *et al.* (1978) who gave a flavor threshold concentration of about 42 ppb, a very low value for a hydrocarbon.

(A.46) Cyclohexene, 1-methyl-4-(1-methylethenyl)-, *4-isopropenyl-1-methyl-1-cyclohexene*, p-*mentha-1,8-diene*, limonene, dipentene **[138-86-3]; (±)- [7705-14-8]; (±)-(*R*)- [5989-27-5]** ***FEMA 2633;*** **(−)-(*S*)- [5989-54-8]**

Limonene (unspecified) has been identified in coffee flavor by Stoll *et al.* (1967). It is probably the 'sylvestrene' previously isolated by Prescott *et al.* (1937b). Silwar *et al.* (1987) found a concentration of 0.03 ppm.

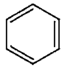
With its citrusy, lemon-like, fresh and sweet odor, it is the most widely distributed monoterpenic hydrocarbon; it has been detected in varying amounts in several hundred essential oils.

The (+)-enantiomer, main constituent of cold-pressed citrus peel oils, has a remarkably low odor threshold value of 10 ppb in water (Buttery *et al.*, 1969b). This figure has been corrected to 200 ppb for the (*R*)-(+)-isomer and 500 ppb for the (*S*)-(−)-isomer, the error being due to impurities, very important for these low values (Buttery, 1999). Ahmed *et al.* (1978) estimated a probable odor threshold of 60 ppb and flavor threshold of 210 ppb, but these were measured on a sample 96.5% pure.

(A.47) 1,3-Cyclohexadiene, 5-methyl-, *5-methylcyclohexa-1,3-diene*, 1-methyl-2,4-cyclohexadiene; 1,2-dihydrotoluene **[19656-98-5]; (±)- [116781-86-3]**

Identified by Merritt and Robertson (1966), although it was not quoted in a later work by Merritt *et al.* (1970).

Aromatic hydrocarbons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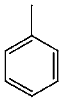
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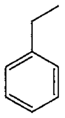
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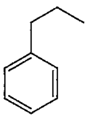
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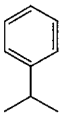
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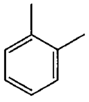
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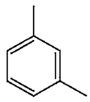
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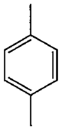
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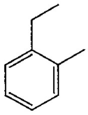
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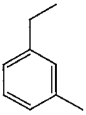
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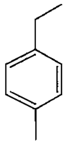
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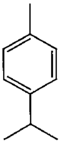
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(A.48) ***(A.48)*** **Benzene,** *benzene*, benzol, cyclohexatriene **[71-43-2]**

Identified by Heins *et al.* (1966) in a headspace analysis of commercial roasted beans and by Merritt *et al.* (1970) in green and roasted (400–430 °F, ca 205–240 °C) beans. Silwar *et al.* (1987) gave a concentration of 0.10–0.15 ppm in roasted coffee. It is present in the analysis of Puerto Rico 'Rio' and healthy green beans (simultaneous distillation-extraction, GC/MS) by Spadone *et al.* (1990) and in the green Mexican coffee analyzed by Cantergiani *et al.* (2001).

It is one of the products formed in the pyrolysis of phenylalanine (Merritt *et al.*, 1970).

Arctander (1967) mentions gassy, hydrocarbon, choking, diffusive and warm odor.

(A.49) *(A.49)* **Benzene, methyl-,** *toluene*, phenylmethane **[108-88-3]**

Identified by Heins *et al.* (1966), Gianturco *et al.* (1966) and in green as well as in roasted beans by Merritt *et al.* (1970). Silwar *et al.* (1987) gave a concentration of 0.3–0.35 ppm in roasted coffee. Spadone and Liardon (1988) and Spadone *et al.* (1990) found it in their analysis (see **A.48**). Toluene was identified in a headspace of brewed coffee (peak area 0.16%) by Shimoda and Shibamoto (1990a), in six green arabicas and six green robustas by Procida *et al.* (1997) and in a green Mexican arabica (peak area 0.16%) by Cantergiani *et al.* (2001) (see **A.17–20**).

It is formed in the pyrolysis of tyrosine (Merritt *et al.*, 1970).

Pure toluene has a sweet-gassy odor, milder than that of benzene (Arctander, 1967).

(A.50) *(A.50)* **Benzene, ethyl-,** *ethylbenzene*, phenylethane, α-methyltoluene **[100-41-4]**

Identified by Merritt and Robertson (1966) and by Merritt *et al.* (1970) in green and roasted beans. It was only tentatively identified by Spadone *et al.* (1990) in a Puerto Rico 'Rio' but not in a healthy green coffee. Procida *et al.* (1997) identified it in headspace of green arabica and robusta (each of six origins), in about the same proportion, without any mention of off-flavor. Ramos *et al.* (1998) found it in extract of brewed arabica (liquid–liquid or supercritical-fluid extraction).

It is one of the pyrolysis products of phenylalanine (Merritt *et al.*, 1970).

The odor is sweet but somewhat 'gassy'. If at all reminiscent of any natural material, it would be a hyacinth-type of gassy sweetness (Arctander, 1967).

(A.51) **Benzene, propyl-,** *propylbenzene*, isocumene, 1-phenylpropane **[103-65-1]**

(A.52) **Benzene, 1-methylethyl-,** *cumene, isopropylbenzene*, cumol, 2-phenylpropane **[98-82-8]**

These were identified in raw coffee by Gutmann *et al.* (1979).

They have a solvent flavor, slightly floral for **A.51** and chemical for **A.52**.

(A.53) **Benzene, 1,2-dimethyl-,** o-*xylene*, o-xylol, 1,2-xylene, 3,4-xylene, *o*-methyltoluene **[95-47-6]**

A xylene, without specification, was found by Heins *et al.* (1966) and also in green and roasted coffee by Merritt *et al.* (1970). Procida *et al.* (1997) found *o*-xylene in headspace of green arabica and robusta (each of six origins) but not in an arabica after different roasting times.

Identified as *o*-xylene in raw coffee by Gutmann *et al.* (1979) and in a brew (see **A.50**) by Ramos *et al.* (1998).

(A.54) *(A.54)* **Benzene, 1,3-dimethyl-,** m-*xylene*, *m*-xylol, 1,3-xylene, 2,4-xylene, *m*-methyltoluene **[108-38-3]**

Identified in raw coffee by Gutmann *et al.* (1979). It was also found by Cros *et al.* (1980) by trapping the headspace components of roasted coffee on Tenax GC (polymer of 2,6-diphenyl-*p*-phenylene oxide) followed by heat desorption. Studying 'Rio' off-flavor, Spadone and Liardon (1988) found *m*-xylene in green beans, healthy or not (after simultaneous distillation–extraction). Procida *et al.* (1997) identified it in headspace of green coffee (six arabicas and six robustas) but not of roasted coffee (one arabica). After extraction of a brewed arabica (see **A.50**), it was identified by Ramos *et al.* (1998).

(A.55) *(A.55)* **Benzene, 1,4-dimethyl-,** p-*xylene*, *p*-xylol, *p*-methyltoluene **[106-42-3]**

Identified in raw coffee by Gutmann et *al.* (1979), in roasted coffee by Silwar *et al.* (1987) who gave a concentration of 0.02–0.05 ppm and in a brew (see **A.50**) by Ramos *et al.* (1998).

It has a pungent, gassy, kerosene-like odor, but not nearly as powerful as that of toluene, or as nauseating as benzene. Overall sweeter and milder than the two (Arctander, 1967).

(A.56) **Benzene, 1-ethyl-2-methyl-,** *2-ethyltoluene*, *o*-ethylmethylbenzene **[611-14-3]**

Identified in raw coffee by Gutmann *et al.* (1979).

It has an earthy, green flavor (Chemisis, 1979).

(A.57) *(A.57)* **Benzene, 1-ethyl-3-methyl-,** *3-ethyltoluene*, *m*-ethylmethylbenzene **[620-14-4]**

(A.58) *(A.58)* **Benzene, 1-ethyl-4-methyl-,** *4-ethyltoluene*, *p*-ethylmethylbenzene **[622-96-8]**

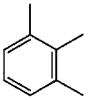
These were identified by Hills *et al.* (1991) in roasted beans by means of supercritical fluid derivatization and extraction, and by Gutmann *et al.* (1979) in green beans.

A.57 is described as having a weak, earthy flavor (Chemisis, 1978).

(A.59) Benzene, 1-methyl-4-(1-methylethyl)-, p-*cymene*, *1-isopropyl-4-methylbenzene*, *p*-isopropyltoluene, 2-*p*-tolylpropane, *p*-methylcumene **[99-87-6]** ***FEMA 2356***

Identified by Stoll *et al.* (1967).

In high concentration *p*-cymene displays a typical kerosene-like odor (Arctander, 1967). Ahmed *et al.* (1978) gave a probable odor threshold of 11.4 ppb in water and a probable flavor threshold of 13.3 ppb. It contributes to the 'reverted' flavor of citrus peel oils (Slater and Watkins, 1964).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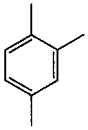
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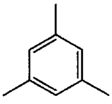
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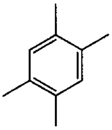
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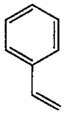
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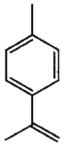
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(A.60) **Benzene, 1,2,3-trimethyl-,** *1,2,3-trimethylbenzene*, hemimellitene **[526-73-8]**

Identified in raw coffee by Gutmann *et al.* (1979).

The flavor is metallic, mouldy, dirty (Chemisis, 1986).

(A.61) *(A.61)* **Benzene, 1,2,4-trimethyl-,** *1,2,4-trimethylbenzene*, 1,2,5-trimethylbenzene, *as*-trimethylbenzene, pseudocumene, pseudocumol **[95-63-6]**

Identified in roasted coffee by Stoll *et al.* (1967) and in raw coffee by Gutmann *et al.* (1979).

The flavor is mouldy, the odor hazelnut (Chemisis, 1962).

(A.62) *(A.62)* **Benzene, 1,3,5-trimethyl-,** *mesitylene*, *1,3,5-trimethylbenzene*, *sym*-trimethylbenzene **[108-67-8]**

Identified in raw coffee by Gutmann *et al.* (1979) and in roasted coffee by Hills *et al.* (1991) (simultaneous supercritical fluid derivatization and extraction).

The odor is aromatic–herbaceous, ethereal, comparatively diffusive, reminiscent of thyme, overall pleasant, not as gassy as cymene (Arctander, 1967). It is also described as naphthalenic with a weak, gassy, naphthalenic flavor (Chemisis, 1962).

(A.63) Benzene, 1,2,4,5-tetramethyl-, *1,2,4,5-tetramethylbenzene*, durene, durol **[95-93-2]**

Identified by Stoll *et al.* (1967).

The flavor is chemical, phenolic, gassy and the odor weak, hazelnut (Chemisis, 1965).

A tetramethylbenzene was found by Ho *et al.* (1993) with a concentration of 0.28 ppm in a roasted Columbian coffee.

(A.64) *(A.64)* **Benzene, ethenyl-,** *styrene*, *vinylbenzene*, phenylethylene, cinnamene **[100-42-5]** ***FEMA 3233***

Identified by Heins *et al.* (1966) and in raw coffee by Gutmann *et al.* (1979). In roasted coffee, Silwar *et al.* (1987) found a concentration of 0.02–0.05 ppm. Again found in green coffee (Mexican arabica) by Cantergiani *et al.* (2001).

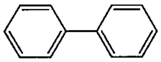
It is formed in the pyrolysis of phenylalanine (Merritt *et al.*, 1970).

Styrene has an extremely diffusive, sweet-gassy, in dilution balsamic and almost floral odor of poor tenacity; overall a rather chemical odor, often described as prototype of 'hydrocarbon' odor (Arctander, 1967).

(A.65) Benzene, 1-methyl-4-(1-methylethenyl)-, *1-isopropenyl-4-methylbenzene*, *p*,α-dimethylstyrene, *p*-isopropenyltoluene, dehydro-*p*-cymene **[1195-32-0]** ***FEMA 3144***

Identified by Stoll *et al.* (1967).

The odor is citrusy-lemon-like, but rather gassy, styrene-like when undiluted. It bears some resemblance to the odor of phellandrene (Arctander, 1967). It is also described as solvent, hydrocarbon (Chemisis, 1983).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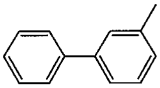
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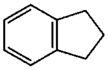
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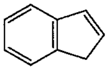
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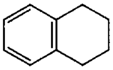
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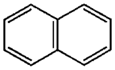
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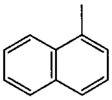
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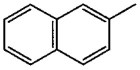
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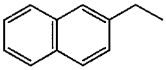
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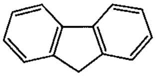
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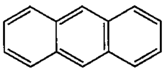
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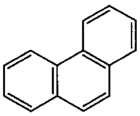
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(A.66) *(A.66)* **1,1′-Biphenyl,** *biphenyl*, diphenyl, bibenzene, phenylbenzene **[92-52-4]**

Identified in roasted coffee by Stoll *et al.* (1967) and in raw coffee by Gutmann *et al.* (1979).

The note is neroli and bergamot- and cinnamon-like (Winter *et al.*, 1975a), peculiar odor, gassy-green, remotely reminiscent of geranium, but overall mild and rather nondescript, choking in high concentration. Sometimes described as metallic odor (Arctander, 1967).

(A.67) 1,1′-Biphenyl, 3-methyl-, *3-methylbiphenyl*, 3-phenyltoluene **[643-93-6]**

Identified by Stoll *et al.* (1967).
It has a green, rose-like note (Winter *et al.*, 1975a).

(A.68) **1*H*-Indene, 2,3-dihydro-,** *indane*, indan, 2,3-dihydroindene, hydrindene, benzocyclopentane **[496-11-7]**

Identified in raw coffee by Gutmann *et al.* (1979) (who also found 'methylindan' without any precision).
It has an earthy, woody flavor (Chemisis, 1979).

(A.69) 1*H*-Indene, *indene*, indonaphthene **[95-13-6]**

Identified by Stoll *et al.* (1967).
It is formed in the pyrolysis of phenylalanine (Merritt *et al.*, 1970).

(A.70) *(A.70)* **Naphthalene, 1,2,3,4-tetrahydro-,** *1,2,3,4-tetrahydronaphthalene*, tetralin **[119-64-2]**

Identified in raw coffee by Gutmann *et al.* (1979). It was found by Andrade-Aispuro and Crouzet (1983) in volatile compounds recovered during roasting, identified by MS.

(A.71) *(A.71)* **Naphthalene,** *naphthalene*, naphthalin, naphthene **[91-20-3]**

Identified in roasted flavor by Reichstein and Staudinger (1926b) and in raw coffee by Gutmann *et al.* (1979).
It has a pungent, choking dry-tarry odor of moderate to poor tenacity (Arctander, 1967).

(A.72) *(A.72)* **Naphthalene, 1-methyl-,** *1-methylnaphthalene*, α-methylnaphthalene **[90-12-0]** ***FEMA 3193***

(A.73) *(A.73)* **Naphthalene, 2-methyl-,** *2-methylnaphthalene*, β-methylnaphthalene **[91-57-6]**

These were identified by Stoll *et al.* (1967) and in raw coffee by Gutmann *et al.* (1979).
A.72 has a green, musty flavor and **A.73** an oily character (Winter *et al.*, 1975a). **A.73** is also described as having a naphthalenic, chemical flavor (Chemisis, 1999).

(A.74) Naphthalene, 2-ethyl-, *2-ethylnaphthalene*, β-ethylnaphthalene **[939-27-5]**

Identified by Stoll *et al.* (1967).
The flavor is described as machine oil (Chemisis, 1963).

A dimethylnaphthalene was found by Gutmann *et al.* (1979), by Spadone *et al.* (1990) in green coffee; a trimethyl and a tetramethylnaphthalene were also isolated by Stoll *et al.* (1967).

(A.75) 9*H*-fluorene, *fluorene*, diphenylenemethane; *o*-biphenylenemethane, 2,2′-methylenebiphenyl, 2,3-benzindene **[86-73-7]**

Identified by Stoll *et al.* (1967). Grimmer and Hildebrandt (1966) found concentrations of 4–10 ppb in various coffees roasted at different temperatures.
It has a naphthalenic, mouldy flavor (Chemisis, 1965).

(A.76) Anthracene, *anthracene*, paranaphthalene **[120-12-7]**

(A.77) Phenanthrene, *phenanthrene* **[85-01-8]**

These were identified by Grimmer and Hildebrandt (1966) who found concentrations of 1–2.3 ppb for **A.76** and 10–50 ppb for **A.77**, the most abundant polycyclic aromatic hydrocarbon that they identified in roasted coffee.

5.B ALCOHOLS

When looking at various analyses of green and roasted coffee, differences observed in the detection of the volatile alcohols are seen to be certainly due to the various methods of extraction and identification, and also to the different origins and the degree of roasting of the beans under study. Even in headspace analyses of roasted coffee, methanol and ethanol were not regularly found. We will give some examples: Merritt *et al.* (1970) did not quote any alcohol in headspace analysis of green or roasted coffee although Merritt and Robertson (1966) identified several low-molecular-weight alcohols in the total analysis when using a subambient temperature for GC. In the headspace of roasted coffee with trapping on Tenax GC followed by heat desorption, Cros *et al.* (1980) only identified 3-methyl-2-buten-1-ol (**B.27**) and 1-octen-3-ol (**B.31**) although in 'gases above roasted coffee' Reymond *et al.* (1963) were able to identify methanol and ethanol, also found by Shimoda and Shibamoto (1990a) in a headspace of brewed coffee with a direct on-column injection. Ho *et al.* (1993) did not find any straight-chain alcohols but 2-methyl-3-buten-2-ol (**B.34**) and 3-methyl-1-butanol (**B.13**) besides linalool (**B.35**), α-terpineol (**B.43**) and 2-furanmethanol (**I-52**) in a headspace analysis (combined adsorbent-trapping/short-path thermal desorption). There is no alcohol in headspace GC profiles examined by Murota (1993). On the other hand, the light alcohols were sometimes identified in a roasted-coffee extract (Gianturco *et al.*, 1966; Stoll *et al.*, 1967) or even after steam distillation and fractionation (for example Stoffelsma *et al.*, 1968). In a comparison of green coffees of various origins (six arabicas and six robustas) using a headspace technique, Procida *et al.* (1997) found the proportion of methanol varying from 9–32% of the aroma compounds and for ethanol from 2 to 36%. As the low-molecular-weight alcohols are not potent odorants, they are of no use in GC-olfactometry of headspace components of roasted coffee and brews (Holscher *et al.*, 1990; Semmelroch and Grosch, 1995). Only linalool (**B.35**) (Blank *et al.*, 1992a) and 2-phenylethanol (**B.49**) (Holscher *et al.*, 1990) are listed with the important odorants of arabica coffee.

Merritt *et al.* (1963) distilled dry ground roasted coffee under high vacuum at room temperature, with a receiver at liquid nitrogen temperature and, after fractionation of the condensate, obtained a 'center cut', products volatile between −145 and −78 °C under a pressure of about 1 μm. Alcohols (methanol, **B.1**, about 80% of the alcohols) represented only 2.4% of this fraction, which they called 'coffee aroma'. Later Merritt and Robertson (1966) identified several alcohols in the complete analysis of the headspace (see above) among them three new compounds: isobutyl alcohol (**B.11**), *tert*-butyl alcohol (**B.24**) and 2-methyl-2-butanol (**B.25**).

In a recent analysis of a Mexican arabica green coffee, looking for the compounds responsible for the earthy/mouldy defect, Cantergiani *et al.* (2001), identified 25 alcohols in their extract (hydrodistillation at room temperature, extraction) and found that this was the most important class in their extract representing 31% of total ion current. Among them 2-phenylethanol (**B.49**) and 3-methyl-1-butanol (**B.13**) represented more than half of the alcohol content.

Methanol and ethanol were found by Sugisawa (1966) when heating glucose for 2.5 h at 150 °C but no alcohol was found by Heyns *et al.* (1966a) in a similar reaction but at higher temperature. Alcohols are not significantly formed either when glucose is heated with serine and threonine, only one simple alcohol 'methylcyclopentanol' was identified by Baltes and Bochmann (1987d).

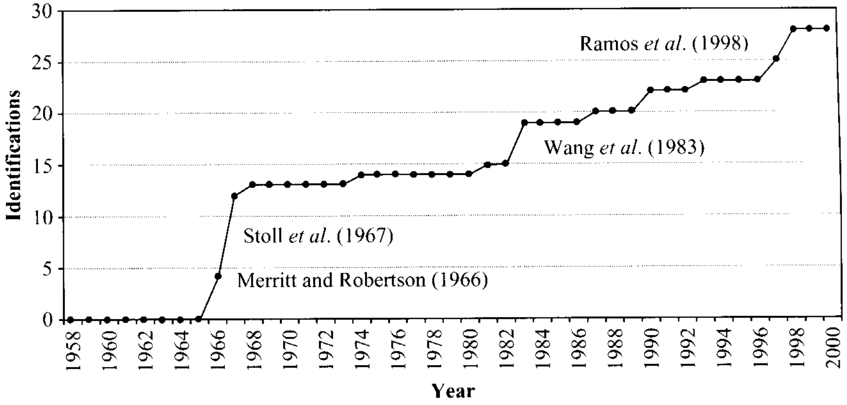


Fig. 5.2 Progressive identification of alcohols in roasted coffee volatiles

Saturated alcohols

R – OH

R = CH_3 **(B·1)** ***(B·1)***, C_2H_5 **(B·2)** ***(B·2)***, C_3H_7 ***(B·3)***,

C_4H_9 ***(B·4)***, C_5H_{11} **(B·5)** ***(B·5)***, C_6H_{13} **(B·6)** ***(B·6)***,

C_7H_{15} ***(B·7)***, C_8H_{17} ***(B·8)***, $C_{12}H_{25}$ **(B·9)**, $C_{18}H_{37}$ ***(B·10)***

(B.1) *(B.1)* **Methanol,** *methanol, methyl alcohol,* carbinol **[67-56-1]**

Identified by Reichstein and Staudinger (1926b), and with GC/MS of the volatiles (headspace), by Rhoades (1958, 1960) who estimated concentrations of 5.0–15.0 ppm in green, 60–100 ppm in roasted beans (given as unreliable data), and 0.83 ppm in brewed coffee. It constitutes 2% of the 'coffee aroma' according to Merritt *et al.* (1963), is present in the analysis of the total headspace of ground coffee (Merritt and Robertson, 1966). It was also quantified by Gibson (1974a) in green beans of two hybrid species of arabica. Found in headspace analyses of brewed coffee by Shimoda and Shibamoto (1990a) (0.09% peak area) and of freshly roasted coffee by Holscher and Steinhart (1992a). Leino *et al.* (1992) noticed that the content (by headspace analysis) of methanol was higher in ground than in whole freshly roasted beans, but increased with storage of whole beans to the level of ground beans. Procida *et al.* (1997) who identified (headspace) methanol in six green arabicas (8.9–15.7% of the aroma compounds) and six green robustas (12.1–32.3%) did not find it in a roasted arabica.

Very pure methanol has only a mild odor (Arctander, 1967). An odor threshold of 8 g/m^3 of air is quoted by Maier (1970c).

(B.2) *(B.2)* **Ethanol,** *ethanol, ethyl alcohol,* methyl carbinol **[64-17-5]** ***FEMA 2419***

Identified by Prescott *et al.* (1937a,b) through a naphthyl carbamate derivative and by Lockhart (1957). Rhoades (1960) with GC/MS measures a concentration of 0.2–4.0 ppm in green and 0.6–4 ppm in roasted beans (given also as unreliable data). It constitutes only 0.4% of the 'coffee aroma' according to Merritt *et al.* (1963) and is one of the alcohols found by Merritt and Robertson (1966) in the analysis of the total headspace of ground coffee. It was also quantified by Gibson (1974a) who found (1974b) an apparent correlation between a high ethanol content in green coffee and the special flavor of the beverage made with coffee grown in a restricted Kenya area (Solai). The flavor could be a consequence of the high ethanol/methanol ratio, the ethyl and methyl derivatives formed during roasting having different organoleptic properties (see Section 2.2). It is present in the headspace of a brewed coffee (0.17% of the volatiles, GC) (Shimoda and Shibamoto, 1990a). Procida *et al.* (1997) found ethanol in six green arabicas (4.7–35.8% of the headspace components) and in six green robustas (2.2–16.6%), the proportion decreasing quickly upon roasting.

An odor threshold of 100 ppm in water is given by Flath *et al.* (1967), of 900 ppm by Mulders (1973b), and a flavor threshold of 53 ppm by Keith and Powers (1968).

(B.3) **1-Propanol,** *propan-1-ol, propyl alcohol, n*-propanol, 1-hydroxypropane **[71-23-8]** ***FEMA 2928***

Identified by Guyot *et al.* (1982, 1983) at about the same level in healthy and 'stinking' green beans (headspace).

It is characterized by a fruity, alcoholic note. An odor threshold of 9 ppm in water is given by Flath *et al.* (1967) and of 40 ppm by Mulders (1973b).

(B.4) ***(B.4)*** **1-Butanol,** *butan-1-ol, butyl alcohol, n*-propyl carbinol, 1-hydroxybutane **[71-36-3]** ***FEMA 2178***

Identified by Gutmann *et al.* (1979) in green coffee and in unhealthy beans by Vincent *et al.* (1976). The same group, Guyot *et al.* (1982, 1983), found it in healthy and tentatively in 'stinking' green beans. It was detected in a green Puerto Rico 'Rio' coffee and in a Santos coffee by Spadone and Liardon (1988) and Spadone *et al.* (1990), and also by Cantergiani *et al.* (2001) in a green Mexican arabica. Ramos *et al.* (1998) found it at a low concentration in a brewed arabica after supercritical-fluid extraction.

It has an alcoholic note. The odor threshold in water is 0.5 ppm (Flath *et al.*, 1967).

(B.5) ***(B.5)*** **1-Pentanol,** *pentan-1-ol, pentyl alcohol,* amyl alcohol, *n*-butyl carbinol **[71-41-0]** ***FEMA 2056***

Identified by Stoll *et al.* (1967) in a coffee aroma and by Merritt and Robertson (1966); Gutmann *et al.* (1979) identified it in green coffee. It was found by Guyot *et al.* (1982, 1983) in healthy and 'stinking' green beans at the same concentration level, by Spadone and Liardon (1988) in a green 'Rio' coffee and a Santos reference, and also by Cantergiani *et al.* (2001) in a green Mexican arabica (0.82% of the volatiles, GC). Ramos *et al.* (1998) identified it in an extract (supercritical fluid) of a brewed arabica.

Somewhat harsh, chemical odor, reminiscent of fusel oil, but not as heavy, however, more penetrating, nauseating, cough-provoking (Arctander, 1967). An odor threshold of 0.5 ppm is given by Flath *et al.* (1967).

(B.6) ***(B.6)*** **1-Hexanol,** *hexan-1-ol, hexyl alcohol,* pentyl carbinol, alcohol C-6, caproic alcohol **[111-27-3]** ***FEMA 2567***

Identified by Heins *et al.* (1966) and by Merritt and Robertson (1966) with GC/MS in headspace of roasted coffee, and by Gutmann *et al.* (1979) in green coffee; found by Guyot *et al.* (1982, 1983) in healthy and 'stinking' green beans with a slighly lower concentration in the latter. On the other hand, Spadone *et al.* (1990) identified it in a Puerto Rico 'Rio' coffee and not in a healthy reference. Procida *et al.* (1997) find it in headspaces of green arabica and robusta (each of six different origins), representing 0.05–1% of the aroma components, but not after roasting of one of the arabicas. According to

Cantergiani *et al.* (2001), it represents 2.55% of the volatiles (GC) in a Mexican green coffee, after vacuum hydrodistillation/extraction.

The odor is somewhat chemical, winey, slightly fatty and fruity, weaker than 1-pentanol, resembling that material, but fattier and fruiter (Arctander, 1967), the flavor is green, fatty (Chemisis, 1999). An odor threshold of 0.5 ppm in water is given by Flath *et al.* (1967).

(B.7) **1-Heptanol,** *heptan-1-ol, heptyl alcohol,* 1-hydroxyheptane, enanthic alcohol **[111-70-6]** ***FEMA 2548***

Identified by Gutmann *et al.* (1979) in green coffee and also mentioned by Cantergiani *et al.* (2001).

The flavor is described as green, fatty, dairy, lactonic (Chemisis, 1991). Siek *et al.* (1969) gave a taste threshold in water of 2.4 ppm.

(B.8) **1-Octanol,** *octan-1-ol, octyl alcohol,* caprylic alcohol, capryl alcohol, 1-hydroxyheptane **[111-87-5]** ***FEMA 2800***

Identified by Gutmann *et al.* (1979) in green coffee.

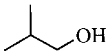
The flavor is green, fatty, coconut (Chemisis, 1991). Ahmed *et al.* (1978) give a probable odor threshold in water of 190 ppb (confidence limits 95–370) and a probable flavor threshold of 54 ppb (confidence limits 12–230).

(B.9) 1-Dodecanol, *dodecan-1-ol, dodecyl alcohol,* lauric alcohol **[112-53-8]** *FEMA 2617*

Identified by Ramos *et al.* (1998) from a brewed arabica (headspace/solid-phase microextraction).

(B.10) **1-Octadecanol, *octadecan-1-ol, octadecyl alcohol* [112-82-5]**

Identified in a Mexican green coffee by Cantergiani *et al.* (2001) (0.18% of the volatiles, GC).



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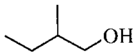

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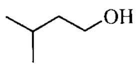

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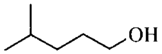

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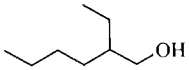

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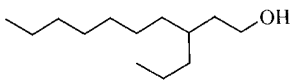


(B·16)

(B.11) *(B.11)* **1-Propanol, 2-methyl,** *2-methylpropan-1-ol, isobutanol, isobutyl alcohol,* isopropyl carbinol **[78-83-1]** *FEMA 2179*

Identified by Merritt and Robertson (1966) and by Vincent *et al.* (1976) in green unhealthy beans; found by Guyot *et al.* (1982, 1983) in healthy as well as stinking green coffee (headspace analysis) and also by Cantergiani *et al.* (2001) (0.61% of the volatiles, GC) in a green Mexican coffee. It is one of the headspace components identified by Liardon and Ott (1984). Ramos *et al.* (1998) found it in a brewed arabica (liquid–liquid extraction with methylene chloride).

It is described as having an unpleasant note. An odor threshold of 3.2 ppm in water was given by Mulders (1973b).

(B.12) *(B.12)* **1-Butanol, 2-methyl-,** *2-methylbutan-1-ol, 2-methylbutyl alcohol, sec*-butylcarbinol **[137-32-6]; (±)- [34713-94-5]; (*R*)- [616-16-0]; (*S*)- [1565-80-6]**

Identified in green coffee by Gutmann *et al.* (1979) and found by Guyot *et al.* (1982, 1983), together with the 3-methyl isomer, at high concentration level in healthy green coffee and to a lesser extent in 'stinking' green beans. Spadone *et al.* (1990) identified it in a Puerto Rico 'Rio' green coffee and in a healthy variety, and Procida *et al.* (1997) in green arabicas of six origins (0.26–4.35% of the volatiles) and green robustas of six origins (0.80–3.41%). According to the data of the latter authors, the proportion of this alcohol decreases quickly on roasting. It is found also in small quantities in the effluvia of berries left on the tree after the red stage (Mathieu *et al.*, 1998).

The odor description of the 3-methyl isomer is acrid, penetrating, pungent. Karl *et al.* (1992) describe the (*R*)-isomer as pleasant, earthy-musty and the (*S*)-isomer as pleasant, ethereal-fruity.

(B.13) *(B.13)* **1-Butanol, 3-methyl-,** *3-methylbutan-1-ol, isopentyl alcohol,* isopentanol, isoamyl alcohol **[123-51-3]** *FEMA 2057*

Identified by Stoll *et al.* (1967) in roasted coffee. Silwar *et al.* (1987) found a concentration of 0.10–0.20 ppm by analysis of a coffee aroma obtained after simultaneous distillation–extraction. Ho *et al.* (1993) found 0.43 ppm in headspace of a roasted Columbian coffee. It was found by Gutmann *et al.* (1979) in green coffee with a higher concentration in arabica than in robusta and arabusta, by Guyot *et al.* (1982, 1983) (with the 2-methyl isomer) in both healthy and 'stinking' green coffee beans, by Spadone and Liardon (1988), Spadone *et al.* (1990) in green 'Rio' coffee and a Santos reference. It is present in the headspaces of six green arabicas and six green robustas (the proportions, 0.20 to 5.7% of the volatiles, depending as much on the origins than on the species) according to Procida *et al.* (1997) and, in a green Mexican arabica, it represents 6.24% (GC) of the volatiles obtained after vacuum hydrodistillation and extraction (Cantergiani *et al.*, 2001). It is one of the compounds emitted by two varieties of fresh red arabica berries (Mathieu *et al.*, 1996), the concentration seeming to increase in the effluvia when the berries are left on the tree after the red stage (Mathieu *et al.*, 1998).

For Ho *et al.* (1993), it is generated from the Maillard reaction.

3-Methylbutanol is a common constituent of plant oils. The odor is choking, disagreeable, cough provoking, somewhat alcoholic, only in high dilution becoming pleasant, fruity-winey (Arctander, 1967). The odor threshold in water is 0.25 ppm for Buttery *et al.* (1971), 0.77 ppm for Mulders (1973b).

(B.14) 1-Pentanol, 4-methyl-, *4-methylpentan-1-ol, 4-methylpentyl alcoho,* 2-methyl-5-pentanol, isohexyl alcohol **[626-89-1]**

Identified by Wang *et al.* (1983) in headspace analysis of ground coffee heated at 100 °C.

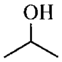
(B.15) **1-Hexanol, 2-ethyl-,** *2-ethylhexan-1-ol, 2-ethylhexyl alcohol* **[104-76-7]** *FEMA 3151*

Identified in a green Mexican arabica by Cantergiani *et al.* (2001).

The flavor is described as fermented, yeast, fusel, ethereal (Chemisis, 1998).

(B.16) 1-Decanol, 2-propyl-, *2-propyldecan-1-ol* **[60671-35-4]; (*R*)- [174848-65-8]; (*S*)- [174848-66-9]**

Identified by Hills *et al.* (1991) after simultaneous supercritical fluid derivatization and extraction



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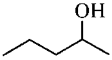

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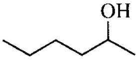

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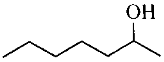

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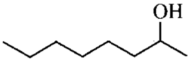

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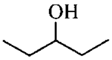

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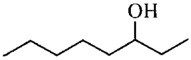

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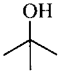

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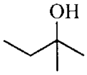

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(B.17) ***(B.17)*** **2-Propanol,** *propan-2-ol, isopropyl alcohol,* isopropanol, *sec*-propyl alcohol, dimethyl carbinol **[67-63-0]** ***FEMA 2929***

Identified by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968). It is one of the headspace components of roasted coffee identified by Liardon and Ott (1984). Procida *et al.* (1997) found it in the headspace of six green arabicas and six green robustas, but not in the roasted Guatemala arabica, with a mean proportion of 1% of the volatile compounds (headspace).

It has an alcoholic-ethereal, acetone-like odor, the similarity to acetone being characteristic of 2-propanol, not of 1-propanol (Arctander, 1967).

(B.18) **2-Pentanol,** *pentan-2-ol, sec*-pentanol, *sec*-amyl alcohol, 2-pentyl alcohol, 1-methyl-1-butanol **[6032-29-7]** ***FEMA 3316;*** **(±)- [13403-73-1]; (*R*)- [31087-44-2]; (*S*)- [26184-62-3]**

Identified in green coffee by Gutmann *et al.* (1979) (headspace) and by Cantergiani *et al.* (2001) in a green Mexican arabica after vacuum-hydrodistillation/extraction (0.18% of the volatiles, GC). It is emitted by the fresh red coffee berries of one variety of robusta coffee (Mathieu *et al.*, 1996).

It has a weak flavor (Chemisis, 1995).

(B.19) ***(B.19)*** **2-Hexanol,** *hexan-2-ol, sec*-hexyl alcohol, *n*-butyl methyl carbinol **[626-93-7]; (±)- [20281-86-1]; (*R*)- [26549-24-6]; (*S*)- [52019-78-0]**

Identified by Procida *et al.* (1997) in headspace of a roasted Guatemala arabica (not in green coffees) and by Cantergiani *et al.* (2001) in a green Mexican arabica (0.15% of the volatiles, GC).

The flavor is described as fusel, mouldy (Chemisis, 1970).

(B.20) ***(B.20)*** **2-Heptanol,** *heptan-2-ol, sec*-heptyl alcohol, amyl methyl carbinol, 2-hydroxyheptane **[543-49-7]** ***FEMA 3288;*** **(±)- [52390-72-4]; (*R*)- [6033-24-5]; (*S*)- [6033-23-4]**

Identified by Stoll *et al.* (1967) in roasted, and by Gutmann *et al.* (1979) in green coffee headspace. It was found by Spadone *et al.* (1990) in green Puerto Rico 'Rio' coffee but not in healthy beans, and by Cantergiani *et al.* (2001) in green Mexican beans (1.14% of the volatiles by GC).

The odor is described as fresh, lemon-like, grassy-herbaceous, with a sweet-floral undertone. The overall 'lift' is primarily fruity-green (Arctander, 1967). The flavor is green, fatty, nutty, sweet (Chemisis, 1995).

(B.21) **2-Octanol,** *octan-2-ol*, *sec*-octyl alcohol, 1-methyl-1-heptanol, capryl alcohol, 2-hydroxyoctane **[123-96-6]** ***FEMA 2801;*** **(±)- [4128-31-8]; (*R*)- [5978-70-1]; (*S*)- [6169-06-8]**

(B.22) ***(B.22)*** 3-Pentanol, *pentan-3-ol*, 3-pentyl alcohol **[584–02–1]**

These were identified by Cantergiani *et al.* (2001) in green coffee, their peak areas in GC representing 0.04 and 0.25% respectively of the volatiles. **B.22** had previously been found in the headspace of a roasted Guatemala arabica by Procida *et al.* (1997) who did not characterize it in green arabicas and robustas.

(B.23) ***(B.23)*** **3-Octanol,** ***octan-3-ol***, amyl ethyl carbinol **[589-98-0]** ***FEMA 3581***; **(±)- [20296-29-1]; (*R*)- [70492-66-9]; (*S*)- [22658-92-0]**

Identified by Stoll *et al.* (1967), in green coffee by Gutmann *et al.* (1979) (headspace) and by Cantergiani *et al.* (2001) (vacuum hydrodistillation), representing 0.14% of the volatiles (GC).

The odor is described as sweet and powerful herbaceous, oily-nutty and warm, milder and not as harsh as that of 2-octanol, much warmer than 1-octanol with moderate to poor tenacity (Arctander, 1967). The flavor is fatty, cheesy, ketonic, mushroom (Chemisis, 1982).

(B.24) ***(B.24)*** **2-Propanol, 2-methyl-,** *2-methylpropan-2-ol*, tert-*butyl alcohol*, *tert*-butanol, 1,1-dimethylethanol **[75-65-0]**

Identified by Merritt and Robertson (1966) in the total analysis of dry, ground, roasted-coffee headspace. Procida *et al.* (1997) find it in the headspace of four (out of six) green robustas and of only one green arabica (out of six) where it was absent after roasting.

The odor is camphoraceous and somewhat minty, the dryness being characteristic of the other isomers (Arctander, 1967).

(B.25) ***(B.25)*** **2-Butanol, 2-methyl-,** *2-methylbutan-2-ol*, tert-*pentyl alcohol*, *tert*-amyl alcohol, 1,1-dimethyl-1-propanol, dimethylethylcarbinol, amylene hydrate **[75-85-4]**

Identified by Merritt and Robertson (1966) in the total headspace of dry ground roasted coffee. In the analysis of a green coffee by Cantergiani *et al.* (2001), it represents 0.69% of the volatiles (GC).

The flavor is described as weak, fermented, cocoa (Chemisis, 1988).

Unsaturated aliphatic alcohols

(B.26) **2-Buten-1-ol, 2-methyl-,** *2-methylbut-2-en-1-ol* **[4675-87-0]**, tiglic alcohol, **(*E*)- [497-02-9]; (*Z*)- [19319-26-7]**

Identified by Shimoda and Shibamoto (1990a) in the headspace of brewed coffee (peak area in GC 0.16% of the area of the volatiles).

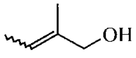
(B.27) ***(B.27)*** **2-Buten-1-ol, 3-methyl-,** *3-methylbut-2-en-1-ol*, 3,3-dimethylallyl alcohol, prenol, prenyl alcohol **[556-82-1]** ***FEMA 3647***

Identified by Stoll *et al.* (1967) in a coffee aroma, by Stoffelsma *et al.* (1968) (steam distillation and distillation, then GC) and by Cros *et al.* (1980) in the headspace of ground roasted coffee heated at 65 °C.

It was found also by Silwar (1982). Silwar *et al.*(1987) give a concentration of 0.20–0.30 ppm (steam distillation then simultaneous distillation–extraction). Holscher and Steinhart (1995) identified this alcohol in green coffee with a concentration of 0.53 ppm.

The pyrophosphate is a key compound in the biosynthesis of isoprenoids. This alcohol could be a source for odorants in roasted coffee (Holscher *et al.*, 1992).

The odor is fresh, herbaceous-fruity-green, somewhat lavender-like, of poor tenacity (Arctander, 1967), the flavor green, fruity, fermented (Chemisis, 1998).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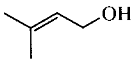
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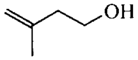
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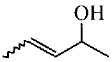
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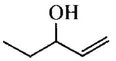
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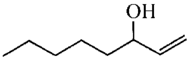
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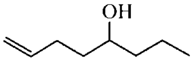
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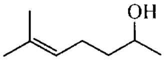
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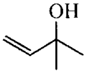
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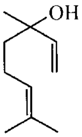
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(B.28) ***(B.28)*** **3-Buten-1-ol, 3-methyl-,** *3-methylbut-3-en-1-ol*, 2-methyl-1-buten-4-ol, isobutenyl carbinol, methallyl carbinol **[763-32-6]**

Identified in the headspace of a roasted Guatemala arabica by Procida *et al.* (1997). It is present among the compounds emitted by fresh red berries of only one variety of robusta studied by Mathieu *et al.* (1996). The same team (Mathieu *et al.*, 1998) also found it in the effluvia of an arabica (grown in a greenhouse), with an important increase when the berries are left on the trees after the red stage.

It is an important compound, its pyrophosphate sometimes called 'active isoprene' being a major key compound in the biosynthesis of isoprenoids.

3-Hexen-1-ol, (*Z*)-, leaf alcohol **[928-96-1]** *FEMA 2563*

This has been tentatively identified by Cantergiani *et al.* (2001) in a green Mexican arabica.

(B.29) 3-Penten-2-ol, *pent-3-en-2-ol* **[1569-50-2]; (±)- [42569-16-4]; (±)-(*E*)- [60102-79-6]; (±)- (*Z*)- [60102-80-9]; (*S*)-(*E*)- [926-58-9]; (*S*)-(*Z*)- [31001-81-7]**

Identified in a brewed arabica after supercritical-fluid extraction by Ramos *et al.* (1998).

(B.30) **1-Penten-3-ol,** *pent-1-en-3-ol*, ethyl vinyl carbinol, ethyl allyl alcohol **[616-25-1]** *FEMA 3584*; **(±)- [67928-92-1]; (*R*)- [93222-01-6]; (*S*)- [93222-00-5]**

Identified in a green Mexican arabica by Cantergiani *et al.* (2001) (0.13 % of the area of the volatiles, GC).

This alcohol has been identified as a degradation product of sotolone (**G.12**) in the presence of UV light (Martin *et al.*, 1990).

The flavor is fusel, solvent, estery, leafy (Chemisis, 1999)

(B.31) ***(B.31)*** **1-Octen-3-ol,** *oct-1-en-3-ol,* amyl vinyl carbinol, pentyl vinyl carbinol, 3-hydroxy-1-octene, Matsutake alcohol **[3391-86-4]** ***FEMA 2805*****; (±)- [50999-79-6]; (*R*)-(-)- [3687-48-7]; (*S*)-(+)- [24587–53–9]**

Identified by Stoll *et al.* (1967) in roasted coffee, by Cros *et al.* (1980) (headspace analysis) and in green coffee by Gutmann *et al.* (1979). In green coffee, the concentration is 0.03 ppm for Holscher and Steinhart (1995) and the peak area in GC represents 0.60% of the volatiles for Cantergiani *et al.* (2001) (vacuum hydrodistillation).

It is one of the most intense flavor compounds formed by autoxidation of linoleic acid ($C_{18:2}$) (Ullrich and Grosch, 1987). As an aside, it is interesting to note that in mushrooms, an enzymic oxidative breakdown of linoleic acid gives the (*R*)-isomer by the intermediate of 10(*S*)-hydroperoxy-8(*E*),12(*Z*)-octadienoic acid (Grosch and Wurzenberger, 1985).

These authors mention a mushroom aroma and give an odor threshold range of 2.3–5.3 ppb determined by high-resolution GC olfactometry. The (*S*)-isomer is described with a green, vegetable mouldy flavor (Chemisis, 1999) and the (*R*)-isomer with a green, mushroom meaty flavor (Chemisis, 1992).

(B.32) **7-Octen-4-ol,** *oct-7-en-4-ol,* 1-octen-5-ol **[53907-72-5]; (±)- [87830-31-7]**

Identified in green coffee by Gutmann *et al.* (1979) and found by Guyot *et al.* (1982, 1983) in healthy as well as 'stinking' green coffee.

It is characterized by a powerful, earthy note.

(B.33) **5-Hepten-2-ol,** 6-methyl-, *6-methylhept-5-en-2-ol* **[1569-60-4]; (±)- [4630-06-2]; (*R*)- [58917-27-4]; (*S*)- [58917-26-3]**

Identified by Cantergiani *et al.* (2001) in a green Mexican coffee (0.25% of the volatiles by GC). The corresponding ketone (**D.33**) has been identified but only in roasted coffee.

The racemic mixture has a green, fatty odor (Chemisis, 1981).

(B.34) ***(B.34)*** **3-Buten-2-ol, 2-methyl-,** *2-methylbut-3-en-2-ol,* 1,1-dimethyl-2-propenol, 1,1-dimethylallyl alcohol, dimethyl vinyl carbinol, 3-hydroxy-3-methyl-1-butene **[115-18-4]**

Identified by Silwar (1982). Silwar *et al.* (1987) give a concentration of 0.20–0.35 ppm in roasted coffee (steam distillation and distillation–extraction) and Ho *et al.* (1993) of 0.06 ppm in a Columbian coffee (headspace). Procida *et al.* (1997) found it only in a roasted arabica, disappearing upon prolonged roasting, and not in the various green arabicas and robustas that they examined. Cantergiani *et al.* (2001) identified it in a green Mexican coffee where it represents 0.13% of the volatiles by GC (after vacuum hydrodistillation).

The odor and flavor are described as solvent (Chemisis, 1972).

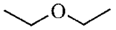
(B.35) ***(B.35)*** **1,6-Octadien-3-ol, 3,7-dimethyl-,** *3,7-dimethylocta-1,6-dien-3-ol,* 2,6-dimethyl-2,7-octadien-6-ol, linalool **[78–70–6]** ***FEMA 2635*****; (±)- [22564-99-4];** licareol, **(*R*)-(-)- [126-91-0];** coriandrol, **(*S*)-(+)- [126-90-9]**

Identified by Stoll *et al.* (1967), Stoffelsma *et al.* (1968), and Friedel *et al.* (1971) (IR, MS data given) in roasted coffee. Ho *et al.* (1993) gave a concentration of 0.73 ppm in a roasted Columbian coffee (headspace). Linalool was found by Guyot *et al.* (1982, 1983) in 'stinking' green coffee, but not in a healthy variety. On the contrary Spadone *et al.* (1990) found it in green beans of a Puerto Rico 'Rio' and of a healthy variety. Holscher and Steinhart (1995) give a concentration of 0.175 ppm in green coffee (distillation–extraction at room temperature then at 70 °C). It represents 1.16% (GC) of the volatiles (vacuum hydrodistillation at room temperature) in the analysis of a green Mexican arabica by Cantergiani *et al.* (2001). Linalool has also been identified in red berries of an arabica (grown in a greenhouse), the amount decreasing with time with a concomitant increase of linalool oxides (see **I.56**, **I.57**, **I.144** and **I.145**).

Linalool has a light and refreshing, floral-woody odor with a faintly citrusy note (Arctander, 1967). The flavor of the racemic is woody, floral, green, bergamot (Chemisis, 1991). The typical floral character can explain a somewhat undesirable note in disharmony with the notes of a roasted coffee. It is among the potent odorants of roasted powder of arabica coffee but not of the brew (Blank *et al.*, 1992b) and also of raw arabica coffee (Czerny and Grosch, 2000). Buttery *et al.* (1969b) give an odor threshold of 6 ppb in water, and Ahmed *et al.* (1978) of 5.3 ppb in water (confidence limits 1.9–15) with a flavor threshold in water of 3.8 ppb (confidence limits 1.4–10).

Diols and ethers


(B·36)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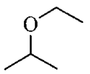
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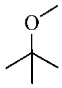
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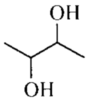
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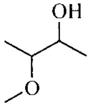
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(B.36) Ethane, methoxy-, *methoxyethane, ethyl methyl ether* **[540-67-0]**

Identified in headspace analysis of roasted coffee by Wang *et al.* (1983).

(B.37) **Ethane, 1,1′-oxybis-,** *ethoxyethane, diethyl ether*, ethylether, diethyl oxide **[60-29-7]**

Identified in four green arabicas (out of six) and in five green robustas (out of six) by Procida *et al.* (1997) who did not find it in a roasted arabica (headspace, GC/MS).

(B.38) Propane, 2-ethoxy-, *2-ethoxypropane, ethyl isopropyl ether* **[625-54-7]**

Identified by Ho *et al.* (1993) in a headspace of roasted Columbian coffee, with a concentration of 3.8 ppm

(B.39) Propane, 2-methoxy-2-methyl-, *2-methoxy-2-methylpropane*, tert-*butyl methyl ether*, 1,1-dimethylethyl methyl ether **[1634-04-4]**

Identified in headspace analysis of roasted coffee by Wang *et al.* (1983).
Guyot *et al.* (1983) mention the presence of dimethoxycyclohexane, without any structural precision , in stinking as well as in healthy green beans.

(B.40) **2,3-Butanediol,** *butane-2,3-diol*, dimethylethyleneglycol, 2,3-butyleneglycol **[513-85-9]; (R*,R*)- [35007-63-7]; (2R,3R)-** (or {R-(R*,R*)}-) (or levo, or threo, **2R,3R**) **[24347-58-8]; (2S,3S)-** (or {S-(R*,R*)}-) (or dextro, or threo, 2S,3S) **[19132-06-0]; (R*,S*)-** (or meso, or erythro, 2R,3S) **[5341-95-7]**

Identified by Vincent *et al.* (1976) in stinking green beans. It was noted as butane diol-2, in the text and in the summary, but with the presence of the corresponding diketone and hydroxyketone in the same analysis, it is safe to assume that it is butanediol-2,3 (in French) or 2,3-butanediol. Moreover a monoether (**B.41**) has also been found in green coffee.

Its formation could be due to an undesired fermentation.

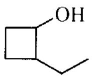
(B.41) **2-Butanol, 3-methoxy-,** *3-methoxybutan-2-ol* **[53778-72-6]; (*R**,*R**)- [54389-81-0]; (*R**,*S**)-[54389-82-1]**

Identified in green coffee (headspace) by Gutmann *et al.* (1979).

2-Propanol, 1-methoxy-, [107-98-2]; (±)- [58769-19-0]; (*R*)- [4984-22-9]; (*S*)- [26550-55-0]

This has been found in the effluvia of berries left on the tree after the red stage in an arabica coffee (grown in a greenhouse) and to a lesser extent in a robusta (Mathieu *et al.*, 1998).

Alicyclic, cyclic and aromatic alcohols



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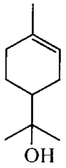

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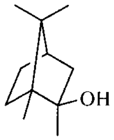

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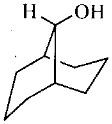

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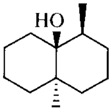

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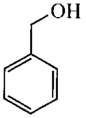

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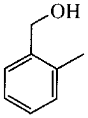

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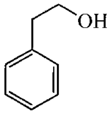


(B·49)
(B·49)

(B.42) Cyclobutanol, 2-ethyl-, *2-ethylcyclobutan-1-ol* **[35301-43-0]**

Identified by Wang *et al.* (1983) in a headspace analysis of ground coffee heated at 100 °C.

(B.43) ***(B.43)*** **3-cyclohexene-1-methanol,** α,α-4-trimethyl-, *2-(4-methyl-3-cyclohexen-1-yl)propan-2-ol, p*-menth-1-en-8-ol, α-terpineol **[98-55-5]** ***FEMA 3045*; (±)- [2438-12-2]; (*R*)- [7785-53-7]; (*S*)- [10482-56-1]**

Identified by Stoll *et al.* (1967) and found in green 'Rio' coffee and a Santos reference (in a lower concentration) by Spadone and Liardon (1988). The same group (Spadone *et al.*, 1990) could identify this compound (simultaneous distillation–extraction) in green beans of a Puerto Rico 'Rio' coffee but not in a healthy variety. By headspace analysis of a roasted Columbian coffee, Ho *et al.* (1993) found a concentration of 0.12 ppm.

The odor is floral, lilac (Chemisis, 1989). Buttery *et al.* (1971) gave an odor threshold in water of 350 ppb. With α-terpineol 97% pure, Ahmed *et al.* (1978) give a probable odor threshold of 280 ppb (confidence limits 31–2000) and a probable flavor threshold of 300 ppb in water (confidence limits 120–890).

(B.44) ***(B.44)*** **Bicyclo[2.2.1]heptan-2-ol, 1,2,7,7-tetramethyl-, *exo-*,** *1,2,7,7-tetramethylbicyclo [2.2.1]heptan-2-*exo-*ol,* 2-methylisoborneol (MIB) **[2371-42-8]; (1*R*)-(−)- [68330-43-8]** (structure shown); **(1*S*)-(+)- [68330-44-9]**

Identified by Vitzthum *et al.* (1990) (simultaneous distillation–extraction). The quantification was improved by Bade-Wegner *et al.* (1993) by use of deuterated internal standard combined with high-resolution MS, the concentration being in the range from 0.12–0.43 ppb of dry matter for roasted robusta of various origins, and < or ≪ 0.02 ppb for various arabica coffees. This could be due to the fact that robusta coffees grow at lower and more humid altitudes than do the arabica coffees (Holscher and Steinhart, 1995). For Rouge *et al.* (1993), 2-methylisoborneol is not really specific of robusta coffees; they found 0.02–0.30 ppb in green robustas, and < 0.005 ppb in one batch of green Columbian arabica but 2.2 in another batch (steam distillation, extraction). They could not detect this alcohol after steam treatment or medium roasting. Grosch *et al.* (1993) determined the concentrations in various samples of green coffee by stable isotope dilution assays: they found 1.28 and 0.74 ppb in robustas, respectively from Ivory Coast and Indonesia, 0.42 and 0.08 ppb in arabicas, respectively from Columbia and Santos.

2-Methylisoborneol is very likely of microbiological origin.

The pure substance has a camphor-like odor, which becomes musty, earthy, tarry and mouldy on dilution. The flavor is woody, camphoraceous, earthy, mouldy, borneol-like for the (1*R*)- isomer and more fenchol-like for the (1*S*)-isomer (Chemisis, 1994). For Vitzthum *et al.* (1990), it is responsible for the earthy, musty smell of robusta coffee, with an odor threshold of 0.005 ppb in coffee beverages and 0.0025 ppb in water. Other thresholds in water quoted by these authors vary from 0.0014–0.1 ppb. For Rouge *et al.* (1993, see above) 2-methylisoborneol is not responsible for the robusta flavor character in a brew.

(B.45) Bicyclo[3.3.1]nonan-9-ol, *bicyclo[3.3.1]nonan-9-ol* **[15598-80-8]**

Identified in a brew by T.A. Lee *et al.* (1992) and qualified as 'fast extractor', that is 70–80% of the maximum is extracted after 5 min brewing (see B.49).

(B.46) **4a(2*H*)-Naphthalenol, octahydro-4,8a-dimethyl-, [(4*S*)-(4α,4aα,8aβ)]-** or **(4*S*,4a*S*,8a*R*)-,** *(4*S*,4a*S*,8a*R*)-decahydro-4,8a-dimethyl- 4a-naphthol,* 1,10-dimethyl-*trans*-9-decalol, geosmin **[19700-21-1]**

Identified by Spadone *et al.* (1990) in green beans of a Puerto Rico 'Rio' coffee and not in a healthy variety. Cantergiani *et al.* (2001) found a concentration of 0.05% of the volatiles (GC) in a green Mexican arabica.

This compound, probably derived from an eudesmane sesquiterpene, is a metabolite of many actinomycetes and of several blue-green algae.

Geosmin was previously found in red beets (*Beta vulgaris* L.) by Murray *et al.* (1975) and Tyler *et al.* (1978) and is known as a contaminant of water supplies. A very low aroma threshold of 0.021 ppb is found by Buttery *et al.* (1976a). By GC-sniffing, Spadone *et al.* (1990) characterized it as an important contributor to the 'Rio' off-odor, with its earthy-musty odor typical of freshly-ploughed soil.

(B.47) **Benzenemethanol,** *phenylmethanol, benzyl alcohol,* hydroxymethylbenzene, phenylcarbinol, α-hydroxytoluene **[100-51-6]** ***FEMA 2137***

Identified by Vitzthum *et al.* (1976) in green coffee. It was found by Spadone and Liardon (1988), in 'Rio' green coffee as well as in a Santos reference, but Spadone *et al.* (1990) did not find it in a healthy variety.

In a green Mexican arabica, Cantergiani *et al.* (2001) found that it represented 2.61 % of the volatiles by GC.

It is a weak constituent with a light floral note. A flavor threshold of 5.5 ppm in water is given by Keith and Powers (1968).

(B.48) **Benzenemethanol, 2-methyl-,** *2-methylbenzenemethanol, 2-methylbenzyl alcohol, o*-tolyl carbinol **[89-95-2]**

Identified by Cantergiani *et al.* (2001) in the analysis of a green Mexican arabica, where it represents 0.26 % of the volatiles (GC).

(B.49) ***(B.49)*** **Benzeneethanol,** *phenylethyl alcohol, 2-phenylethan-1-ol, β*-phenylethanol, benzyl carbinol **[60-12-8]** ***FEMA 2858***

Identified by Vitzthum and Werkhoff (1974b) in steam volatiles of roasted coffee and by Vitzthum *et al.* (1976) in green coffee. Silwar *et al.* (1987) found a concentration of 0.40–0.60 ppm in roasted coffee (simultaneous distillation–extraction). Spadone and Liardon (1988) and Spadone *et al.* (1990) found it in green 'Rio' coffee as well as in a healthy reference. Silwar *et al.* (1987) gave a concentration of 0.4–0.6 ppm; its content in steam-volatile components greatly increases with roasting temperature, from 0.22 ppm at 170 °C to about 0.9 ppm at 230 °C and nearly 1.4 ppm at over-roasting temperature of 270 °C (Silwar and Lüllmann, 1993b). Like **B.45**, phenylethanol is a 'fast extractor', quickly extracted under rapid brewing conditions, for T.A. Lee *et al.* (1992), who identified only two alcohols (excepting 2-furanmethanol, **I.52**) in the brews (basic and acid fractions being extracted and analyzed with GC/MS). It is the most important compound of the volatiles (11.17 %, GC) in the analysis of Cantergiani *et al.* (2001) (vacuum hydrodistillation/extraction).

Phenylethanol is derived from phenylalanine.

It has a mild and warm, rose-honey-like odor of moderate to poor tenacity (Arctander, 1967). In spite of its pleasant floral-woody, honey-like character, its presence at an excessive concentration could be undesired.

Other compounds containing alcohol function(s) are present In section 5.D (ketones), 5.E (acids and anhydrides), 5.F (esters), 5.G (lactones), 5.I (furans and pyrans), 5.J (thiophenes), 5.K (pyrroles), 5.N (pyridines) and 5.Q (sulfur compounds).1

5.C ALDEHYDES

Volatile aldehydes that play an important role in black tea aroma, in fermented or roasted cocoa beans, in the wine bouquet and certainly in coffee aroma, are formed partially by Strecker degradation of amino acids. Aldehydes are formed by the oxidative degradation of amino acids during their interaction with sugars at high temperatures and during the interaction of amino acids and polyphenols in the presence of polyphenol oxidase at normal temperatures (see Motoda, 1979 and references therein). Motoda used a microbial polyphenol oxidase from *Alternaria tenuis* strain A-2. The mechanism involves two steps: formation of quinones from polyphenols by polyphenol oxidase, then Strecker degradation catalyzed by the quinones. Of the various polyphenols tested on the formation of 3-methylbutanal (**C.13**) from leucine, Motoda observed that *o*-diphenols such as 4-methylcatechol (**H.27**) and chlorogenic acids are excellent substrates but that gallic acid (**H.75**) formed almost no 3-methylbutanal. Coffee extracts liberate 3-methylbutanal (**C.13**) by incubation at 30 °C for 2 h with the oxidase. A mechanism of formation of phenyl alkenyl aldehydes by Strecker degradation of leucine and phenylalanine then aldol condensation of 3-methylbutanal (**C.13**) and phenyacetaldehyde (**C.42**) has been proposed by Manley *et al.* (1974).

The formation of various aldehydes and ketones by autoxidation of unsaturated fatty acids via breakdown of hydroperoxide intermediates is well established in the literature. Therefore their presence is not surprising considering that green coffee beans contain lipids and proteins. Total lipids amount to about 13 % in arabica coffee, 10 % in robusta, and of this nearly half is linoleic acid ($C_{18:2}$). In the volatile flavor compounds formed by autoxidation of linoleic acid and methyl linoleate, Ullrich and Grosch (1987, 1988a) identified mainly aldehydes ranging from saturated pentanal and hexanal to monounsaturated aldehydes and the diunsaturated decadienals (**C.30**, **C.31**). The aldehydes participate in the staling of roasted coffee in oxygen-containing atmospheres. Stale notes in roasted coffee could be correlated with the generation of hexanal (**C.6**) after 7 weeks of storage in air (Spadone and Liardon, 1990). Whether hexanal (**C.6**) arises from autoxidation of the lipid complex or from volatile roasting products is not yet clear (Holscher and Steinhart, 1994).

Maier (1973) studied the physical sorption of volatile aroma constituents by foods using IR spectroscopy. He observed that aliphatic aldehydes such as propanal (**C.3**), hexanal (**C.6**), acrolein (**C.16**) were also reacting chemically with some amino compounds, specially with cysteine (formation of thiazolidine carboxylic acids), with other amino acids, with glutathione and with urea. The bound aldehydes are nevertheless, in most cases, released by heating with water, especially during the percolation of the coffee beverage.

In a review on the volatile products formed by heating glucose, Fagerson (1969) quotes 12 aliphatic aldehydes. Only two of them, 2-pentenal and '1,3-pentadienal' (= 2,4-pentadienal) have not been identified in coffee.

Flavor thresholds of the saturated aldehydes were found by Lea and Swoboda (1958) to decrease from C_3 to C_{12}. Ullrich and Grosch (1988b) also found a decrease in the odor thresholds from C_6 to C_8 and C_9, and even lower thresholds for the unsaturated aldehydes. Hexanal (**C.6**), (*Z*)-2-nonenal (**C.24**), (*E*)-2-nonenal (**C.23**), (2*E*,6*Z*)-2,6-nonadienal (**C.29**), (*E*,*E*)-2,4-nonadienal (**C.27**) and (*E*,*E*)-2,4-decadienal (**C.30**) contribute significantly to roasted coffee flavor. Nevertheless Holscher *et al.* (1990)did not mention any aldehyde in the eight most contributing constituents of an aromagram obtained from roasted Colombian coffee. They considered that their contribution to coffee flavor is low in regard to the flavor-dilution (FD) factor, sensorial evaluation carried out by means of aroma dilution analysis (see Section 3.3.4), a useful tool in estimation of character-impact compounds of several flavors (Gasser and Grosch, 1988). In a list of important odorants of roasted arabica coffee, Blank *et al.* (1992a) included only 3-methylbutanal (**C.13**), (*E*)-2-nonenal (**C.23**) and phenylacetaldehyde (**C.42**) as simple aldehydes. Holscher *et al.* (1990), listing aroma-impact compounds in roasted Columbian coffee (the aroma extract being obtained by simultaneous distillation–extraction, then analyzed by high-resolution GC),

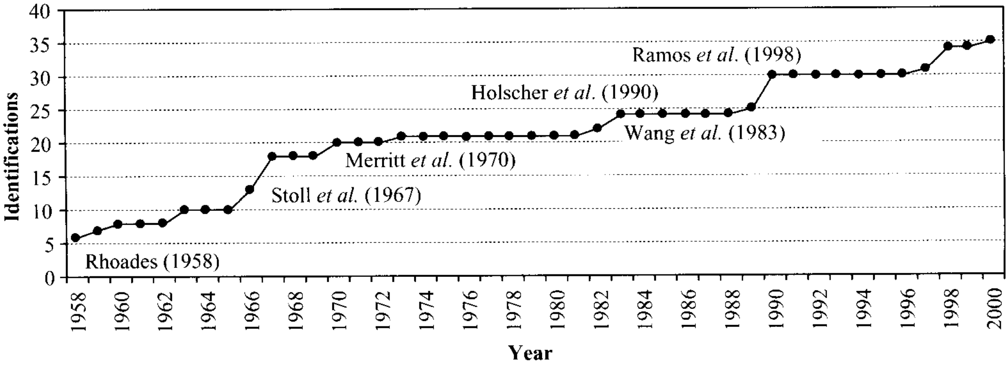


Fig. 5.3 Progressive identification of aldehydes in roasted coffee volatiles

included hexanal (**C.6**)—with a low flavor-dilution factor—, 2-methylpropanal (**C.11**), 2- and 3-methylbutanal (**C.12** and **C.13**). By GC-olfactometry of headspace of arabica and robusta coffee brews, Semmelroch and Grosch (1996) determined the potent odorants, among them **C.11**, **C.12**, **C.13** and propanal (**C.3**) to a lower extent. Previously the same authors (1995) also included acetaldehyde (**C.2**) in the list of odorants of powders and brews. **C.11**, **C.12** and **C.13** are some of the aroma-intense Strecker aldehydes. In a literature review, Fors (1983) summarizes the sensory properties of volatile Maillard-reaction products, among them several aldehydes, with their odor and flavor thresholds. These estimations and values vary from one investigator to the other and have to be taken as an order of magnitude.

Merritt *et al.* (1963) estimated that aldehydes constitute 50.7% of the 'coffee aroma' (see section 5.B), half of this being acetaldehyde.

Some aldehydes have been identified in green coffee by Guyot *et al.* (1983). These authors mention the presence in green coffee of 2,4-dimethylpentanal (**C.15**), a compound which has not been identified in the roasted beans. Some volatile unsaturated aldehydes contribute to the typical green coffee odor and may impact the cultivar-related flavor or off-flavor characteristics in corresponding roasted coffee.

Saturated aldehydes

$R{-}CHO$

R = H **(C·1)**, CH_3 **(C·2)** ***(C·2)***, C_2H_5 **(C·3)** ***(C·3)***, C_3H_7 **(C·4)** ***(C·4)***,
C_4H_9 **(C·5)** ***(C·5)***, C_5H_{11} **(C·6)** ***(C·6)***, C_6H_{13} **(C·7)** ***(C·7)***,
C_7H_{15} **(C·8)** ***(C·8)***, C_8H_{17} **(C·9)** ***(C·9)***, C_9H_{19} ***(C·10)***

(C.1) Formaldehyde, *formaldehyde, methanal,* formic aldehyde, formal, methylaldehyde **[50-00-0]**

Identified by Gianturco *et al.*(1966). Finding rather scarce reports on formaldehyde in coffee, Hayashi *et al.* (1986) and Shibamoto (1988) suggested that the partitioning of formaldehyde between water and solvents was a factor responsible for the analytical difficulty, as well as its high volatility. They proposed GC determination via thiazolidine derivative (see in Section 5.M). Cysteamine (2-aminoethanethiol) is added to freshly brewed coffee and instant coffees. The amounts found vary from 3.4 ppm (decaffeinated coffee), 4.5 ppm (regular) to 10.0–16.3 ppm (coffee extracts). Baltes (1990) has shown that serine decomposes into formaldehyde and glycine.

(C.2) ***(C.2)*** **Acetaldehyde,** *acetaldehyde, ethanal,* acetic aldehyde, ethylaldehyde **[75-07-0]** ***FEMA 2003***

Identified by Reichstein and Staudinger (1926b), it was confirmed through a dinitrophenylhydrazone derivative by Johnston and Frey (1938). As the main aliphatic aldehyde present in roasted coffee, Hughes and Smith (1949) followed its behavior during roasting and staling. They observed that its content increases with the extent of roasting and more rapidly with over-roasting, the aldehyde content—mainly acetaldehyde— varying from 27 to 124 ppm. By staling there is some loss of aldehydes. Rhoades (1960) found a concentration of 1.6–5.0 ppm in volatile compounds (headspace) of green beans, increasing to 45–70 ppm at the final roast (400–430 °F, 200–220 °C). Later acetaldehyde was isolated by numerous authors thanks to the introduction of higher performance GC/MS techniques. According to Merritt *et al.* (1963) it constitutes 26.4% of a 'coffee aroma'. Rodriguez *et al.* (1969) considered that it could be used as an indicator of spoilage in a green Hawaiian (Kona) arabica coffee during demucilaging. Its presence in the volatiles of green and roasted (400–430 °F, about 200–220 °C) robusta, Columbian and Santos coffees was confirmed by Merritt *et al.* (1970), and in two hybrid species of arabica by Gibson (1974a). Found with GC/MS in the headspace of roasted brewed coffee (peak area 2.5% of the volatiles) by Shimoda and Shibamoto (1990a); in this case it is less important than 2-methylpropanal (**C.11**), 2- and 3-methylbutanal (**C.12** and **C.13**). The same conclusion was drawn from the results of Procida *et al.* (1997) with a roasted Guatemala arabica. In the headspace profile of a freshly roasted coffee on a GC-capillary column, acetaldehyde was apparently slightly less important than **C.11** and of the same order as **C.12** and **C.13** (Holscher and Steinhart, 1992a). However the concentration of 139 ppm (Columbia arabica) or 141 ppm (Kenya arabica) given by Grosch *et al.* (1996) is distinctly higher than those of the three quoted aldehydes.

It is formed in the pyrolysis of alanine (Merritt *et al.*, 1970) and in the reaction of alanine with a polyphenol oxidase (Motoda, 1979). In coffee, it comes from sugar pyrolysis (Liardon *et al.*, 1984).

Acetaldehyde has a pungent ethereal-nauseating odor, which in high dilution, is reminiscent of coffee or wine (Arctander, 1967). The odor description at a sniffing port is pungent, fruity, given as malt by Motoda (1979). Fors (1983) mentions other odor descriptions as sour, greenhouse, caramel at 100 °C, burnt sugar at 180 °C and even green and sweet. The flavor is green, ethereal, fresh, fruity (Chemisis, 1998).

Rhoades (1960) quotes a taste threshold of 1.3 ppm. Mulders (1973b) found an odor threshold as low as 0.12 ppm in water. Quoted odor thresholds vary from 0.005 to 0.12 mg/m^3 air; from 15 to 120 ppb in water. Ahmed *et al.* (1978) quoted odor thresholds in water of 4–21 ppb and gave a probable value of 17 ppb, their probable flavor threshold being 22 ppb.

(C.3) *(C.3)* **Propanal,** *propionaldehyde, propanal,* propionic aldehyde, propylaldehyde, methylacetaldehyde **[123-38-6]** ***FEMA 2923***

Identified by Rhoades (1958, 1960) in the volatiles of green (0.05–0.4 ppm) and roasted (6–11 ppm) coffee; found also by Zlatkis and Sivetz (1960), Reymond *et al.* (1963) and other authors. For Merritt *et al.* (1963) it constituted 8.9% of the 'coffee aroma' and the same group (1970) identified it in roasted but not in green coffee (headspace). It was quantified by Gibson (1974a) in green beans of two hybrid species of arabica. It is characterized in GC-olfactometry of headspace of arabica and robusta coffees, powders and brews, by Semmelroch and Grosch (1995b). Grosch *et al.* (1996) gave a concentration of about 17 ppm in ground roasted arabica (Columbia or Kenya) coffee. Ramos *et al.* (1998) extracted it (with supercritical fluid) from a brewed arabica.

It is formed in the pyrolysis of serine (Merritt *et al.*, 1970) but in coffee it is said to originate from sugar pyrolysis (Liardon *et al.*, 1984).

The odor is very diffusive and penetrating, suffocating, with choking effect upon the respiratory system. At extreme dilutions an odor of roasted coffee appears (Arctander, 1967). It is described as fruity by GC-olfactometry (Semmelroch and Grosch, 1995). The flavor is fresh, green, aggressive (Chemisis, 1995).

The flavor threshold found by Lea and Swoboda (1958) is 0.17 ppm in water. An odor threshold of 10 ppb in water is given by Grosch (1995).

(C.4) *(C.4)* **Butanal,** *butyraldehyde, butanal,* butyric aldehyde, butylaldehyde **[123-72-8]** ***FEMA 2219***

Identified by Rhoades (1958, 1960) in the volatiles of green (0.02–0.07 ppm), roasted (0.3–1 ppm) and brewed coffee. It has also been found by Zlatkis and Sivetz (1960), Reymond *et al.* (1963), and Heins *et al.* (1966). Merritt *et al.* (1970) characterized it in roasted but not in green coffee. Gibson (1974a) quantified butanal in the volatiles of green beans of two hybrid species of arabica. and Gutmann *et al.* (1979) also found this aldehyde in green coffee. Leino *et al.* (1992) noted a decrease in the concentration of butanal during storage (headspace). Procida *et al.* (1997) identified it in headspace of a roasted Guatemala arabica, but not in various green coffees. It is also identified (see **C.3**) in a brew by Ramos *et al.* (1998).

It is formed in the pyrolysis of norvaline (Merritt *et al.*, 1970).

The odor is very diffusive, penetrating, pungent-irritating. Only in extreme dilution will truly a fruity, banana-like, green-fresh odor become perceptible (Arctander, 1967). As a GC eluate it is described with a burnt, green and nasty odor (Persson and von Sydow, 1973). The flavor is described as fatty, dairy, green, cocoa, fermented (Chemisis, 1998). Lea and Swoboda (1958) find a flavor threshold of 70 ppb.

Odor thresholds quoted by Fors (1983) vary from 0.013 to 0.042 mg/m^3 air; the odor thresholds in water are between 9.0 and 37.3 ppb. Ahmed *et al.* (1978) quoted odor thresholds in water from 4 to 21 ppb, their probable value being 15.9 ppb (confidence limits: 4.2–60.2) and a probable flavor threshold of 5.3 ppb in water.

(C.5) ***(C.5)*** **Pentanal,** *pentanal*, valeraldehyde; valerianic aldehyde, amyl aldehyde **[110-62-3]** ***FEMA 3098***

Identified by Zlatkis and Sivetz (1960) and by Merritt *et al.* (1970) in green and roasted coffee; found also in Puerto Rico 'Rio' and healthy green coffee by Spadone *et al.* (1990). Procida *et al.* (1997) characterize it in headspaces of six green arabicas and six green robustas; they also list it with the components of a roasted Guatemala arabica, but there is some discrepancy in the figure given for the retention time compared with the figure given for the green-coffee samples. It was also identified in a brew by Ramos *et al.* (1998) (see **C.3**).

Pentanal has a very powerful and diffusive, penetrating, acrid-pungent odor, in the concentrated form repulsively shocking, cough-provoking. In extreme dilution dry-fruity, musty, nut-like (Arctander 1967).

The mean odor threshold given by Guadagni *et al.* (1963a) is 12 ppb in water and the flavor threshold found by Siek *et al.* (1969) is 70 ppb in water.

(C.6) ***(C.6)*** **Hexanal,** *hexanal*, caproic aldehyde, caproaldehyde, capronaldehyde, caproylaldehyde **[66-25-1]** ***FEMA 2557***

Identified by Merritt and Robertson (1966), by Stoll *et al.* (1967), and by Silwar (1982); also identified in healthy and in stinking green coffee beans by Guyot *et al.* (1982, 1983). Spadone and Liardon (1988) found a significant increase of hexanal content in all extracts of 'Rio' green coffee. Ho *et al.* (1993) gave a concentration of 0.53 ppm in a roasted Columbian coffee and Holscher and Steinhart (1995) of 0.775 ppm in green coffee (distillation–extraction). For Procida *et al.* (1997) it represented 1.05–18.9% of the headspace of six green arabicas and 1.8–13.2% for six green robustas, the proportion decreasing after roasting (one arabica sample). Ramos *et al.* (1998) found an important proportion of hexanal in the extract (supercritical CO$_2$) of a brewed arabica (about 10% normalized area). It was also identified by Cantergiani *et al.* (2001) in a green Mexican arabica (0.24% of the volatiles). Czerny and Grosch (2000) put it in the list of potent odorants in green arabica coffee (extraction, distillation, then analysis of basic and acidic fractions).

Being formed, at least partially, by oxidation of lipids, hexanal is involved in the staling of coffee in the presence of oxygen. Spadone and Liardon (1988, 1990) related the increase of hexanal in 'Rio' coffee to the damage of cell membranes after massive invasion by mold species. Lipids, being not protected, are more susceptible to oxidation.

The odor is very powerful, penetrating, fatty-green, grassy. In extreme dilution it becomes more reminiscent of freshly cut grass and unripe fruit (apple and plum). The acrid note of the concentrated material resembles that of rancid butter (Arctander, 1967). Holscher and Steinhart (1995) gave a green oily odor description (GC-olfactometry of green coffee aroma extract) but with a low flavor-dilution factor (Holscher *et al.*, 1990). According to Guyot *et al.* (1983) the fruity character is more perceptible in stinking than in healthy beans. The flavor is described as leafy, green, fatty, fruity (Chemisis, 1999).

The odor threshold range in air is 65–98 μg/m^3 (Ullrich and Grosch, 1988b). The mean odor threshold is of 4.5 ppb in water for Guadagni *et al.* (1963a) and 9.2 (confidence limits 1.4–58.9) for Ahmed *et al.* (1978). The last authors gave a probable flavor threshold in water of 3.7 ppb, the quoted values varying from 5 to 30 ppb; Lea and Swoboda (1958) gave 30 ppb and Siek *et al.* (1969) 16 ppb.

(C.7) *(C.7)* **Heptanal,** *heptanal*, heptylaldehyde, enanthal, enanthic aldehyde **[111-71-7]** ***FEMA 2540***

Identified by Wang *et al.* (1983) (headspace) and in green Columbian coffee by Holscher and Steinhart (1995) who gave a concentration of 0.104 ppm (simultaneous distillation–extraction). It was found in the extract of a brew with supercritical CO_2 by Ramos *et al.* (1998) (see **C.3**).

Very powerful and diffusive oily-fatty, 'rancid odor. Penetrating and pungent at high concentration, almost fruity, 'fermented-fruit'-like in extreme dilution (Arctander, 1967).

The mean odor threshold in water is 3 ppb (Guadagni *et al.*, 1963a), the flavor threshold in water 31 ppb (Siek *et al.*, 1969).

(C.8) *(C.8)* **Octanal,** *octanal*, octanoic aldehyde, capryl aldehyde **[124-13-0]** ***FEMA 2797***

Identified in headspace (and GC/MS) of six green arabicas and six green robustas by Procida *et al.* (1997) but not in the roasted arabica sample. It was found in the extract of a brewed arabica with supercritical CO_2 by Ramos *et al.* (1998) (see **C.3**,**C.7**).

The flavor is described as green fatty, orange, juicy.

A flavor threshold of 5 ppb is given by Lea and Swoboda (1958). An odor threshold of 5.8–13.6 μg m^{-3} air is measured by Ullrich and Grosch (1988b).

(C.9) *(C.9)* **Nonanal,** *nonanal*, nonanoic aldehyde, nonylaldehyde, pelargonaldehyde **[124-19-6]** ***FEMA 2782***

Identified in green beans by Spadone *et al.* (1990) in a Puerto Rico 'Rio' coffee as well as in a healthy variety. Holscher and Steinhart (1995) gave a concentration of 75 ppb in green coffee. As for the lower homologue, Procida *et al.* (1997) found nonanal in all the green coffees that they studied, but not in the roasted sample. It was found in a brewed arabica (see **C.3**) by Ramos *et al.* (1998).

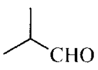
Described as strong, soap-like, metallic by GC-olfactometry (Holscher and Steinhart, 1995). The odor threshold is 1 ppb in water for Guadagni *et al.* (1972), 2.5 for Ahmed *et al.* (1978) with a flavor threshold of 4.25 ppb. In air 5.2–12.1 μg/m^3 is the range given by Ullrich and Grosch (1988b).

(C.10) **Decanal,** *decanal*, decaldehyde, capric aldehyde, caprinaldehyde, caprinic aldehyde, capraldehyde (this name causes confusion with the C_6 and C_8 aldehydes) **[112-31-2]** ***FEMA 2362***

Identified in green coffee by Holscher and Steinhart (1995) who found a concentration of 45 ppb (simultaneous distillation–extraction). For Cantergiani *et al.* (2001), it represents 0.25% (GC) of the volatiles in a green Mexican coffee (vacuum hydrodistillation/extraction).

A mean odor threshold of 0.1 ppb in water was found by Guadagni *et al.* (1963a) and a flavor threshold of 7 ppb by Lea and Swoboda (1958). Ahmed *et al.* (1978) gave a probable odor threshold of

1.97 ppb (confidence limits: 0.79–4.90) and a probable flavor threshold of 3.02 ppb (confidence limits: 2.67–3.41).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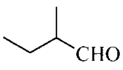
(C·11)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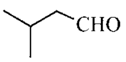
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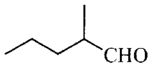
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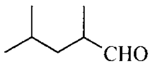

(C·15)

(C.11) ***(C.11)*** **Propanal, 2-methyl-,** *isobutyraldehyde, 2-methylpropanal* **[78-84-2]** ***FEMA 2220***

Identified by Rhoades (1958, 1960) in the volatiles of green (0.2–1.2 ppm), roasted (15–20 ppm) and brewed (0.47 ppm) coffee. Found by Zlatkis and Sivetz (1960) in a 'coffee aroma essence', and in green and roasted coffee by Merritt *et al.* (1970). It is very often quoted in coffee analyses. It was quantified by Gibson (1974a) in the volatiles of green beans of two species of arabica. Gutmann *et al.* (1979) found a more important concentration in green robusta and arabusta than arabica. Shimoda and Shibamoto (1990a) gave an area peak (GC) of 5.5% in the headspace analysis of brewed coffee. Holscher and Steinhart (1992a) found a decrease with the degree of roasting in the headspace aroma of freshly roasted coffee. Leino *et al.* (1992) note that the level is higher in roasted ground coffee than in the whole beans, without a big change during storage. From the figures given by Procida *et al.* (1997), the proportion of 2-methylpropanal, present in the headspace of all the green coffees examined (six arabicas, six robustas), seems to increase first by roasting, decreasing with a prolonged roasting time. Grosch *et al.* (1996) gave a concentration of 34.2 ppm for a ground roasted Columbia arabica and 21.7 for a Kenya arabica.

Isobutanal is formed in the pyrolysis of alanine, valine or leucine (Merritt *et al.*, 1970) and also from valine by polyphenol oxidase (Motoda, 1979).

It has an extremely diffusive, penetrating odor, pungent, and unpleasant, sour, repulsive when undiluted. In extreme dilution it becomes almost pleasant, fruity, banana-like, overripe fruit-like and overall is more pleasant than butanal (Arctander, 1967). It has an apple odor for Motoda (1979). This compound is considered to be a potent odorant in brews of arabica and robusta coffees. In a coffee headspace analysis, at the GC/sniffing port, the odor description is pungent, fruity, malty (Holscher and Steinhart, 1992a). It is also considered by Pollien *et al.* (1998) to be a key component in a brew (80% arabica, 20% robusta) with a high aroma impact (SNIF method, see Section 3.C). Some other odor descriptions mentioned by Fors (1983) are green, harsh, grain and baked potatoes, rye bread at 100 °C, penetrating chocolate at 180 °C. The flavor is described as fermented, green, chocolate, slightly cereal (Chemisis, 1988).

The odor thresholds quoted are between 0.015 and 0.14 mg/m^3 air, Blank *et al.* (1992b) gave an even lower value: 0.002–0.004 mg/m^3 air measured by GC-olfactometry). Thresholds in water were 0.9 ppb for Guadagni *et al.* (1963a), 10 ppb for Mulders (1973b), 0.7 ppb for Grosch (1995).

(C.12) ***(C.12)*** **Butanal, 2-methyl-,** *2-methylbutanal,* 2-methylbutyraldehyde, methylethylacetaldehyde, 2-formylbutane **[96-17-3]** ***FEMA 2691*****; (±)- [57456-98-1]; (*R*)- [33204-48-7]; (*S*)- [1730-97-8]**

Identified by Reichstein and Staudinger (1926b), and by Merritt *et al.* (1970) in green and roasted coffee; found also in headspace of green coffee (with a more important concentration for robusta and arabusta than arabica) by Gutmann *et al.* (1979), of ground roasted coffee by Wang *et al.* (1983) and of brewed coffee by Shimoda and Shibamoto (1990a) (17.7% of the volatiles by GC). Guyot *et al.* (1988a) observe a decreasing formation of 2-methylbutanal during roasting as the maturity of the cherries increases (see also 2,3-butanedione, **D.44**, contrary to 2-furaldehyde, **I.63**). Spadone *et al.* (1990) identified it in a Puerto Rico 'Rio' and a healthy green coffee. In the headspace analysis of freshly roasted coffee, Holscher and Steinhart (1992a) noted a decrease with the degree of roasting. For Procida *et al.* (1997), who found it in the headspace of green coffee (six arabicas, six robustas), it was apparently more important after roasting (for one arabica studied). Ho *et al.* (1993) found 0.46 ppm in the headspace of a roasted Columbian coffee. Higher values of 20.2 ppm in a roasted Columbia arabica and 11.6 in a Kenya arabica were found by Grosch *et al.* (1996) after extraction of medium-roasted ground coffee, quantification was by isotope dilution assays. Ramos *et al.* (1998) extracted 2-methylbutanal from a brewed arabica with supercritical CO_2.

Formed in the pyrolysis of isoleucine (Merritt *et al.*, 1970) and from isoleucine by polyphenol oxidase (Motoda, 1979). For Ho *et al.* (1993) it is also generated by a Maillard reaction.

The odor is powerful, choking when undiluted, but becomes tolerable in extreme dilution, almost pleasant fruity, 'fermented' with a peculiar note resembling that of roasted cocoa or coffee (Arctander, 1967). For Motoda (1979), it is apple or malt. Fors (1983) mentions other odor descriptions as burnt, sickly for GC eluates, musty, fruity aromatic at 100 °C becoming 'burnt cheese' at 180 °C. It is described as fermented, pungent, fruity at a sniffing port in a headspace/GC analysis of freshly roasted coffee (Holscher and Steinhart, 1992a). Like **C.11**, it is a key component in a brew with a high aroma impact (Pollien *et al.*, 1998). The flavor of the (*R*)-isomer is chocolate-like (Chemisis, 1971).

Odor thresholds in water are 0.9 ppb (Guadagni *et al.*, 1963a), 1.3 ppb (Grosch, 1995).

(C.13) *(C.13)* **Butanal, 3-methyl-**, *3-methylbutanal*, 3-methylbutyraldehyde, isopentananal, isoamylaldehyde, isovaleraldehyde **[590-86-3]** ***FEMA 2692***

Identified by Rhoades (1958, 1960) in the volatiles of green (0.2–2.0 ppm), roasted (2.0–4.0 ppm) and brewed (0.073 ppm) coffee. It is considered by Zlatkis and Sivetz (1960) to be one of the important volatile aldehydes present in coffee. and represents 13.7% of a 'coffee aroma' for Merritt *et al.* (1963). It was also identified and quantified by Gibson (1974a) in green beans of two hybrid species of arabica. Stofberg and Stoffelsma (1981) reported a concentration of 6.7 ppm in roasted coffee and Grosch (1998b) of 18.6 ppm in a roasted arabica coffee. It has been found in green coffee by Gutmann *et al.* (1979), who found a concentration more important in green robusta and arabusta than in arabica, and by Guyot *et al.* (1982, 1983) in healthy and stinking green coffee beans, conferring a powerful acrid and rancid flavor in both varieties. In a headspace analysis of brewed coffee, the peak area in GC is 9.7% (Shimoda and Shibamoto, 1990a). In headspace of freshly roasted coffee, Holscher and Steinhart (1992a) noted a slight decrease with the degree of roasting. Ho *et al.* (1993) found 0.27 ppm in a roasted Columbian (headspace), value less important than for the 2-methyl isomer (**C.12**) and again smaller than the values given by Grosch *et al.* (1996) in their work on the potent odorants of roasted coffee (see **C.12**): 17.8 ppm in a Columbia arabica and 10.4 in a Kenya arabica which showed also smaller concentrations than the Columbian in **C.11** and **C.12**. Looking at the figures given by Procida *et al.* (1997), the proportion of 3-methylbutanal in the aroma (headspace) components also varied with the origin of the sample: 3.8–21.3% for six green arabicas and 3.4–14.9% for six green robustas. For one arabica studied, the proportion first increases by roasting and decreases slowly with a prolonged roasting time. This aldehyde was identified by Ramos *et al.* (1998) in the extract of a brewed arabica with supercritical CO_2. Leino *et al.* (1992) remarked that, contrary to acetone (**D.1**) and 2-methylpropanal (**C.11**), the level of 3-methylbutanal is lower in ground than in whole beans.

It is formed in the pyrolysis of leucine (Merritt *et al.*, 1970) and from leucine by polyphenol oxidase (Motoda, 1979).

This aldehyde has a very powerful, penetrating, acrid-pungent odor, causing cough-reflexes unless highly diluted. In extreme dilution, the odor becomes fruity, rather pleasant, and the flavor is peach-like, heavy-fruity below 10 ppm (Arctander, 1967). The odor description is chocolate (Motoda, 1979), burnt, sickly for GC eluates of canned beef (Persson and von Sydow, 1973) and sweaty, pungent, fruity for GC eluates of freshly roasted coffee (Holscher and Steinhart, 1992a). Fors (1983) mentions other odor descriptions, sweet, chocolate and toasted bready at 100 °C , burnt cheese at 180 °C. It is a more potent odorant than the 2-methyl isomer (**C.12**) in brews of arabica and robusta coffees (Semmelroch and Grosch, 1996). Pollien *et al.* (1998) considered it to be a key component in a brew (see also **C.11** and **C.12**). The flavor description is malt, chocolate, slightly cheesy (Chemisis, 1988).

Odor thresholds in water vary from 0.15–0.2 ppb, Guadagni *et al.* (1963a, 1972), 0.35 ppb (Grosch, 1995) to 7 ppb (Mulders, 1973b). An odor threshold of 2–4 $\mu g/m^3$ air was given by Blank *et al.* (1992b). The flavor threshold in water is 0.17 ppm according to Keith and Powers (1968).

(C.14) Pentanal, 2-methyl-, *2-methylpentanal,* 2-methylvaleraldehyde, 2-formylpentane **[123-15-9]** *FEMA 3413*; **(±)- [69685-10-5]; (*R*)- [53531-14-9]; (*S*)- [82043-22-9]**

Identified by Merritt *et al.* (1970) in roasted coffee.

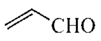
The racemic aldehyde has a fruity, cereal, cocoa, meaty flavor (Chemisis, 1994).

(C.15) **Pentanal, 2,4-dimethyl-,** *2,4-dimethylpentanal,* 2,4-dimethylvaleraldehyde **[24944-79-2]**

Found by Guyot *et al.* (1982, 1983) in healthy and stinking green coffee beans.

The flavor of the racemic compound is green, fruity, apple-like (Chemisis, 1984).

Unsaturated aldehydes



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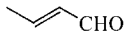

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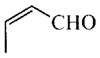

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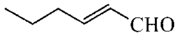

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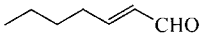

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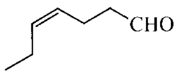

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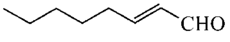

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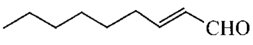

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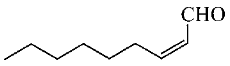

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(C·24)

(C.16) 2-Propenal, *acrylaldehyde, prop-2-enal,* acrolein, acrylic aldehyde, allyl aldehyde **[107-02-8]**

Identified by Merritt *et al.* (1963), representing 0.8 % of a 'coffee aroma'(see Section 5.B).

The odor is pungent, irritating (lachrymatory), acrid, resembling an extinguished stearin candle. Daylight enhances polymerization and formation of a plastic solid (Arctander, 1967).

(C.17) ***(C.17)*** **2-Butenal, (*E*)-,** *(E)-but-2-enal*, crotonaldehyde, crotonic aldehyde, β-methylacrolein **[123-73-9]**; no stereochemistry **[4170-30-3]**

Tentatively identified by Heins *et al.* (1966). Found in green coffee by Gutmann *et al.* (1979) as 'crotonaldehyde', very probably the (*E*)-isomer. As (*E*)-isomer, it was found in headspace extracts of ground roasted coffee and of commercial extracts by Elmore and Nursten (1990).

This unsaturated aldehyde is produced by aldol condensation of acetaldehyde, followed by dehydration.

(C.18) 2-Butenal, (*Z*)-, *(Z)-but-2-enal* **[15798-64-8]**

Identified in headspace of ground roasted coffee and of commercial extracts by Elmore and Nursten (1990).

(C.19) **2-Hexenal, (*E*)-,** *(E)-hex-2-enal*, hexylenic aldehyde, leaf aldehyde **[6728-26-3]** ***FEMA 2560***; **(*Z*)- [16635-54-4]**; no stereochemistry **[505-57-7]**

Identified by Holscher and Steinhart (1995) who gave a concentration of 20 ppb in green coffee, and by Vitzthum (1999) using GC-olfactometry of a green coffee aroma extract.

The flavor is described as green, fatty, fruity (Chemisis, 1996).

An odor threshold of 17 ppb in water was given by Buttery *et al.* (1971). Ahmed *et al.* (1978) found a probable odor threshold in water of 24.2 ppb (confidence limits: 19.9–29.9), and 49.3 ppb for the flavor threshold (confidence limits: 31.0–78.4).

(C.20) **2-Heptenal,** *hept-2-enal*, 3-butylacrolein **[2463-63-0]** ***FEMA 3165***; **(*E*)- [18829-55-5]**; **(*Z*)- [57266-86-1]**

Identified in green 'Rio' and healthy coffee by Spadone *et al.* (1990) and, as the (*E*)-isomer, in an extract of green Columbian coffee by Holscher and Steinhart (1995) who found a concentration of 75 ppb (simultaneous distillation/extraction).

The flavor description of (*E*)-2-heptenal is green, fatty, apple-like (Chemisis, 1969).

An odor threshold of 13 ppb in water was given by Buttery *et al.* (1971) for this isomer.

(C.21) **4-Heptenal, (*Z*)-,** *(Z)-hept-4-enal* **[6728-31-0]** ***FEMA 3289***

Identified in immature green beans by Full *et al.* (2000). The concentration could be about 10 times higher in immature than in normal beans. The sorting of the beans was done electronically.

This aldehyde is a product of autoxidation of linolenic acid (Grosch, 1998a), not linoleic as quoted in the publication by Full *et al.*, which is present in green coffee, representing 1.1–1.5% of the total acid content of immature or mature beans (Guyot *et al.*, 1988a).

It is described as fishy, sardine-like and could be responsible for the rotten fish flavor and astringency accompanying immature beans.

The odor threshold is 0.4 ppb.

(C.22) **2-Octenal,** *oct-2-enal* **[2363-89-5]** ***FEMA 3215***; **(*E*)- [2548-87-0]**; **(*Z*)- [20664-46-4]**

Identified in 'Rio' green coffee (off-flavor) by Spadone *et al.* (1990) but not in a Santos coffee; given as (*E*)-isomer in green coffee by Holscher and Steinhart (1995) with a concentration of 75 ppb.

The two isomers are formed in the autoxidation of linoleic acid and of its methyl ester (Ullrich and Grosch, 1987).

For the (*E*)-isomer, the aroma description is fatty-nutty, and for the (*Z*) fatty-fruity-slight and green (Ullrich and Grosch).

The odor threshold is 3 ppb in water for the (*E*)-isomer (Buttery *et al.*, 1971) and 0.9–2.5 μg/m^3 air for the (*Z*) (Ullrich and Grosch, 1988b).

(C.23) *(C.23)* **2-Nonenal, (*E*)-,** *(E)-non-2-enal, trans*-2-nonenal **[18829-56-6];** no stereochemistry **[2463-53-8]** *FEMA 3213*

After steam-distillation at atmospheric pressure of ground roasted arabica coffee beans, extraction and multiple GC, this unsaturated aldehyde was isolated and identified by mass spectrometry and IR spectroscopy (Parliment *et al.*, 1973). 2-Nonenal without specification of stereochemistry was identified in green coffee ('Rio' off-flavor and Santos) by Spadone *et al.* (1990). As the (*E*)-isomer, it was found in green Columbian coffee by Holscher and Steinhart (1995) who gave a concentration of 280 ppb (simultaneous distillation/extraction, column chromatography, GCMS with use of an internal standard). Lower concentrations of 12 ppb in green and 19 ppb in medium-roasted arabica coffee are given by Czerny and Grosch (2000) (using multidimensional high- resolution GC/MS after extraction).

(*E*)-2-Nonenal is easily formed from unsaturated fatty acids (Feenstra and Meijboom, 1971, Parliment *et al.*, 1973). The precursor at the origin and formation of 2-nonenal (producing an intense papery to heated beer flavor) was studied by Stenroos *et al.* (1976). Linoleic acid ($C_{18:2}$, the most important acid in the lipids of coffee, see Section 5.E) is oxidized enzymatically to mono-, di- and trihydroxy octadecenoic and octadecadienoic acids, the degradation of which is at the origin of many unsaturated aliphatic aldehydes characterized by green notes.

2-Nonenal contributes very likely to the flavor of numerous natural products. It imparts, at a concentration of 1 ppb in a soluble coffee, a fresh-brewed woody character of roasted and ground coffee, lacking otherwise, but it is also related to a cardboard-like off-flavor note in some coffee beverages. Its organoleptic effect was evaluated at various levels, showing that at progressive concentrations from 8 to 40 ppb, the flavor changes from fatty to unpleasant fatty in water at room temperature, becoming even strongly cucumber at a concentration of 1 ppm; in a soluble coffee at 140–160 °F (60–70 °C), it turns from high woody impact at 8 ppb to burnt, fatty, rancid at 40 ppb (Parliment *et al.*, 1973). It exhibits synergistic effects and may influence the sour taste perception without changing the pH. It helps significantly to balance other flavor notes, specifically the acid or sour, caramel, and winey buttery notes. (*E*)-2-Nonenal is, with (*Z*)-2-octenal, the most potent odorant formed by autoxidation of linoleic acid and its methyl ester (Ullrich and Grosch, 1987). It is in the list of the potent odorants in green coffee with a better flavor-dilution factor than the (*Z*)-isomer (Czerny and Grosch, 2000) with an odor threshold of 15 μg/kg cellulose.

The odor threshold was 0.5–1 ppb in water for Forss *et al.* (1962), 0.08 ppb for Buttery *et al.* (1968), the precision for stereochemistry being given in Buttery *et al.* (1971). A value of 0.5 μg/m^3 air was quoted by Ullrich and Grosch (1988b).

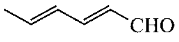
(C.24) *(C.24)* **2-Nonenal, (*Z*)-,** *(Z)-non-2-enal* **[60784-31-8]**

Identified by Holscher *et al.* (1990) in Columbian green coffee extract where the MS could be measured, the chromatogram being less complex than that of the roasted coffee where it was confirmed only by retention data and sniffing. Holscher and Steinhart (1995) gave a concentration of 8 ppb in green coffee, but Czerny and Grosch (2000) found less than 0.3 ppb in green as well as in roasted arabica coffee (see (*E*)-isomer **C.23**).

(*Z*)-2-Nonenal is also formed during autoxidation of linoleic acid.

It has been prepared (Ullrich and Grosch, 1988b) by oxidation of 2-nonynol with pyridinium chlorochromate, followed by hydrogenation in the presence of palladium on calcium carbonate. The formed aldehydes were separated, the (*Z*)-isomer being eluted before the (*E*)-, by column chromatography then with high performance LC (NMR, MS data).

Extremely powerful and diffusive, penetrating, fatty-orrisy odor in higher concentrations. In dilutions below 0.1 % the odor becomes more orris-like, waxy, less fatty, slightly green and in extreme dilutions quite pleasant (Arctander, 1967). The aroma description is green-cucumber for Ullrich and Grosch (1987), the odor description fatty, green, slightly rancid with an odor threshold at 0.08–0.23 μg/m^3 air for Ullrich and Grosch (1988b). It is in the list of potent odorants of green arabica coffee with a lower flavor-dilution factor than the (*E*)-isomer and an odor description also fatty, cardboard-like (Czerny and Grosch, 2000).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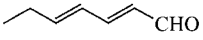
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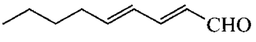
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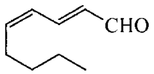
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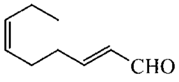
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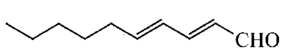
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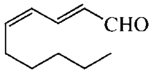
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(C.25) *(C.25)* **2,4-Hexadienal, (2*E*,4*E*)-,** *(E,E)-hexa-2,4-dienal,* 1,3-pentadienecarboxaldehyde, 3-propyleneacrolein, sorbaldehyde **[142-83-6]; (*E,Z*)- [53398-76-8]; (*Z,E*)- [54716-12-0]; (*Z,Z*)- [4488-47-5];** no stereochemistry **[80466-34-8].** (In the TNO, *FEMA 3429* is given with the first register number but without mention of stereochemistry, the last register number being given with (*E,E*) stereochemistry).

Identified in green coffee by Holscher and Steinhart (1995) who found a concentration of 10 ppb (distillation–extraction). Procida *et al.* (1997) characterized it in the headspace of a roasted Guatemala arabica, although they did not find it in the various green coffees that they analyzed.

The (*E,E*)-isomer is described with green, fatty, fruity flavor (Chemisis, 1972).

(C.26) **2,4-Heptadienal, (2*E*,4*E*)-,** *(*E,E*)*-hepta-2,4-dienal **[4313-03-5]** *FEMA 3164*; **(*E,Z*)- [4313-02-4]; (*Z,E*)- [59121-26-5]; (*Z,Z*)- [108793-60-8];** no stereochemistry **[5910-85-0]**

Identified in an extract (distillation–extraction) of green Columbian coffee by Holscher and Steinhart (1995) who found a concentration of 20 ppb.

The (*E,E*)-isomer has a fatty, woody, herbal flavor (Chemisis, 1968).

(C.27) *(C.27)* **2,4-Nonadienal, (2*E*,4*E*)-,** *(E,E)-nona-2,4-dienal, trans,trans -2,4-nonadienal* **[5910-87-2];** no stereochemistry **[6750-03-4]** *FEMA 3212*

2,4-Nonadienal without specified stereochemistry was identified by Spadone and Liardon (1988) in green 'Rio' coffee and in the reference Santos coffee (although not mentioned in a later publication, Spadone *et al.*, 1990). Identified as the (*E,E*)-isomer in roasted Columbian coffee by Holscher *et al.* (1990) and the structure confirmed by Boosfeld and Vitzthum (1995) who gave the complete IR and MS data. Holscher and Steinhart (1995) found a concentration of 35 ppb in green coffee.

The odor perception is fatty-soapy (Ullrich and Grosch, 1987), geranium-like, metallic (Holscher *et al.*, 1990), strong and geranium-like (Holscher and Steinhart, 1995). The flavor is oily, green, very fatty (Chemisis, 1969).

(C.28) **2,4-Nonadienal, (2*E*,4*Z*)-,** *(*2E,*4Z)-nona-2,4-dienal, trans,cis*-2,4-nonadienal **[21661-99-4]; (2*Z*,4*E*)- [5910-86-1]**

Identified for the first time in green coffee by Boosfeld and Vitzthum (1995) who present complete IR and MS data.

(C.29) *(C.29)* **2,6-Nonadienal, (2*E*, 6*Z*)-,** (2E,6Z)-nona-2,6-dienal; trans,cis-2,6-nonadienal, violet leaf aldehyde, cucumber aldehyde **[557-48-2]** ***FEMA 3377;* (*E,E*)- [17587-33-6]; (2*Z*,6*E*)- [23313-79-3]; (*Z,Z*)- [134998-58-6];** no stereochemistry **[27370-28-5]** ***FEMA 3766***

Identified in Columbian green coffee and suspected (retention data and sniffing) in the roasted flavor (Holscher *et al.*, 1990). The confirmation in the latter was possible by comparison with the green extract giving a less complex chromatogram and where the MS could be taken.

It is formed during autoxidation of methyl linolenate ($C_{18:3}$) (Ullrich and Grosch, 1988b).

The (2*E*,6*Z*)-isomer has an extremely powerful and very diffusive green-vegetable odor, only in dilution becoming reminiscent of cucumber or violet leaf. (Arctander, 1967). The flavor is described as green, fatty, fruity, perfumy (Chemisis, 1995).

An odor threshold of 0.1 ppb in water is determined by Forss *et al.* (1962) and of 0.01 ppb by Buttery *et al.* (1969b). The odor description is green, cucumber- like and the odor threshold is 0.6–1.6 $\mu g\ m^{-3}$ air (Ullrich and Grosch, 1988b).

(C.30) *(C.30)* **2,4-Decadienal, (2*E*,4*E*)-,** *(*E,E*)-deca-2,4-dienal, trans,trans*-2,4-decadienal **[25152-84-5]** ***FEMA 3135*; (2*Z*,4*E*)- [5910-88-3]; (*Z,Z*)- [65909-91-3];** no stereochemistry **[2363-88-4]**

Identified in a roasted Columbian coffee by Holscher *et al.* (1990) and in a Columbian green coffee by Boosfeld *et al.* (1994) (complete IR, MS data). Spadone *et al.* (1990) mentioned the presence of 2,4-decadienal (without specifying stereochemistry) in 'Rio' green coffee beans and a Santos reference coffee. Holscher and Steinhart (1995) find a concentration of 0.105 ppm in green coffee (simultaneous distillation/extraction).

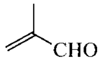
The odor of the (*E,E*)-isomer is extremely powerful, orange-like, sweet and fresh-citrusy, diffusive, yet quite tenacious. The orange character is more attractive and natural at dilutions below 0.1 %, while higher concentrations display fatty-green notes (Arctander, 1967). For Ullrich and Grosch (1987) the odor description was deep fried and for Holscher *et al* (1990) it is fried, oily. The flavor is meaty, cereal (Chemisis, 1973).

Buttery *et al.* (1969b) measured an odor threshold of 0.07 ppb in water, Gasser and Grosch (1990) measure 0.04–0.16 $\mu g\,m^{-3}$ air.

(C.31) *(C.31)* **2,4-Decadienal, (2*E*,4*Z*)-,** *(2E,4Z)-deca-2,4-dienal, trans,cis*-2,4-decadienal **[25152-83-4]**

Identified in roasted Columbian coffee by Holscher *et al.* (1990) and in green coffee by Boosfeld *et al.* (1994) who presented complete IR and MS data. Holscher and Steinhart (1995) found a concentration of 20 ppb in green coffee.

The odor perception at the sniffing port, weak, is metallic, tallowy (Holscher *et al.*, 1990). The flavor is cereal, meaty like the previous isomer (Chemisis, 1973).



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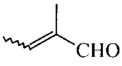

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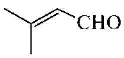

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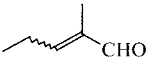

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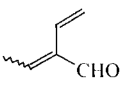


(C.36)

(C.32) ***(C.32)*** **2-Propenal, 2-methyl-,** *2-methylacrylaldehyde, 2-methylprop-2-enal,* isobutenal, 2-methylenepropanal, methacrylaldehyde, α-methylacrolein, methacrolein **[78-85-3]**

Identified by Merritt *et al.* (1970) in roasted coffee and in green coffee by Gutmann *et al.* (1979).

It is formed in the pyrolysis of serine (Merritt *et al.*, 1969).

Extremely diffusive, gassy, sweet odor, in high concentration pungent and irritating, only in extreme dilution fairly pleasant herbaceous-balsamic and remotely orange-like (Arctander, 1967).

(C.33) ***(C.33)*** **2-Butenal, 2-methyl-,** *2-methylbut-2-enal,* 2-methylcrotonaldehyde, 2,3-dimethylacrolein **[1115–11-3]; (*E*)-,** tiglaldehyde, tiglinaldehyde **[497-03-0]** ***FEMA 3407*; (*Z*)- [6038-09-1]**

Identified by Stoll *et al.* (1967), Stoffelsma *et al.* (1968) (who quoted an older reference: Sullivan *et al.*, 1959). Merritt *et al.* (1970) found it in green and roasted coffee and Cros *et al.* (1980) in the headspace of brewed coffee. For Cantergiani *et al.* (2001) it represents 0.09 % (GC) of the volatiles of a green Mexican coffee.

According to Vitzthum (1999), unsaturated aldehydes contribute to the 'old crop' off-flavor of certain green coffees. The flavor of the (*E*)-isomer is described as fruity-apple, estery, benzaldehyde, banana, pear (Chemisis, 1999).

(C.34) ***(C.34)*** **2-Butenal, 3-methyl-,** *3-methylbut-2-enal,* 3-methylcrotonaldehyde, 3,3-dimethylacrolein, senecialdehyde, prenal **[107-86-8]** ***FEMA 3646***

Identified by Pollien *et al.* (1998) who mention it as one of the key components with high aroma impact in a brew made with a blend of 80% arabica and 20% robusta (see also **C.11–13**), however the authors consider that it could be an artifact. Cantergiani *et al.* (2001) found this aldehyde in a green Mexican arabica (0.23 % of the volatiles by GC).

The flavor is green, bitter almond, furfurylic (Chemisis, 1970).

(C.35) 2-Pentenal, 2-methyl-, *2-methylpent-2-enal,* 2-methyl-2-pentenoic aldehyde, α-methyl-β-ethylacrolein **[623-36-9]** ***FEMA 3194*; (*E*)- [14250-96-5]; (*Z*)-, [16958-22-8]**

Identified by Sullivan *et al.* (1959) and by Merritt *et al.* (1963) as representing 0.9% of their 'coffee aroma' (see Section 5.B).

The odor is powerful and diffusive, gassy-green and slightly fruity of poor tenacity (Arctander, 1967). The flavor was described as green, fruity, cooked, cranberry (Chemisis,1973), and for the (*E*)-isomer, animal, fruity, musty, sweet (Chemisis, 1999).

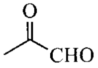
(C.36) 2-Butenal, 2-ethenyl-, *2-vinylbut-2-enal,* 2-vinylcrotonaldehyde **[20521-42-0]; (*E*)- [13061-87-5]**

Identified by Wang *et al.* (1983) in roasted coffee by headspace concentration and GC/MS.

Bifunctional aldehydes: Aromatic aldehydes; Acetal

OHC — CHO

(C.37)



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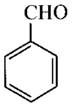

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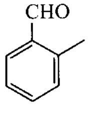

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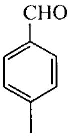

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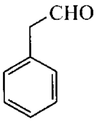

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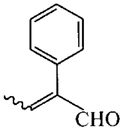

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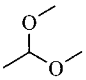


(C.44)

(C.37) **Ethanedial,** ***glyoxal,*** glyoxaldehyde, ethanedione, oxalaldehyde, biformal **[107-22-2]**

Identified by Aeschbacher *et al.* (1989) in roasted coffee aroma.

According to Hayashi and Namiki (1986), glyoxal and methylglyoxal (**C.38**) result from sugar fragmentation and are formed in the initial stages of browning.

(C.38) **Propanal, 2-oxo-,** *2-oxopropanal, pyruvaldehyde,* 1,2-propanedione, acetylformaldehyde, methylglyoxal, pyruvic aldehyde **[78-98-8]** ***FEMA 2969***

Identified by Walter *et al.* (1967) as the bis-2,4-dinitrophenylhydrazone. It was also found by Aeschbacher *et al.* (1989).

It is one of the main components of coffee responsible for mutagenic activity *in vitro*, not observed *in vivo*, therefore an effect which is not relevant for humans (Aeschbacher *et al.*, 1989, Adamson, 2000).

The odor is pungent, stinking, very diffusive and of poor tenacity (Arctander, 1967).

(C.39) *(C.39)* **Benzaldehyde,** *benzaldehyde,* benzoic aldehyde, benzenecarboxaldehyde, phenylmethanal **[100-52-7]** ***FEMA 2127***

Identified by Stoll *et al.* (1967) and Merritt *et al.* (1970) in roasted coffee; also identified in green coffee by Vitzthum *et al.* (1976), by Guyot *et al.* (1983) and Spadone *et al.* (1990) in healthy and 'stinking' green arabica. In a headspace analysis of brewed coffee (Shimoda and Shibamoto, 1990a), its peak area represented 0.11 % of the volatiles. Silwar *et al.* (1987) found a concentration of 0.7–1.1 ppm in roasted coffee, Ho *et al.* (1993) of 1.26 ppm and Holscher and Steinhart (1995) of 0.63 ppm in a green Columbian coffee. Its content in steam-volatile components increases slightly with temperature, from 0.3 ppm at 170 °C to 0.5 ppm at a normal roasting temperature of 230 °C, reaching more than 1.4 ppm with over-roasting, 260 °C (Silwar and Lüllmann, 1993b). Procida *et al.* (1997) identified benzaldehyde in six green arabicas and six green robustas (headspace, GC/MS) but not in a roasted arabica sample.

It is a phenylalanine-derived product (Silwar and Lüllmann, 1993b). Ho *et al.* (1993) did not confirm the formation by a Maillard reaction.

Benzaldehyde has a powerful sweet odor, reminiscent of freshly crushed bitter almonds. The taste is burning, but sweet in proper dilution (Arctander, 1967). It is described with cherry, pistachio flavor (Chemisis, 1962).

The odor threshold in water is 350 ppb (Buttery *et al.*, 1969b) and the flavor threshold 1.5 ppm (Keith and Powers, 1968).

(C.40) Benzaldehyde, 2-methyl-, *2-methylbenzaldehyde, o*-tolualdehyde, *o*-toluic aldehyde, 2-formyltoluene **[529-20-4]**

Identified by Stoll *et al.* (1967).

Warm and sweet benzaldehyde-type odor of moderate tenacity (Arctander, 1967).

Benzaldehyde, 3-methyl-, (*m*-tolualdehyde) **[620-23-5]**

This was tentatively identified by Stoffelsma *et al.* (1968).

(C.41) Benzaldehyde, 4-methyl-, *4-methylbenzaldehyde, p*-tolualdehyde, *p*-formyltoluene **[107-87-0]**

Identified in green coffee by Gutmann *et al.* (1979).

(C.42) *(C.42)* **Benzeneacetaldehyde,** *phenylacetaldehyde*, α-tolualdehyde, hyacinthin **[122-78-1]** ***FEMA 2874***

Identified by Stoll *et al.* (1967) in an extract and in green coffee by Vitzthum *et al.* (1976). Spadone and Liardon (1988) found it in green Rio coffee beans as well as in a reference Santos green coffee. Silwar *et al.* (1987) measured a concentration of 1.5–2.0 ppm in roasted coffee and Holscher and Steinhart (1995) of 0.445 ppm in green coffee. Its content in steam-volatile components increases greatly with temperature (after 5 min), from 0.3 ppm at 170 °C to 1 ppm at 230 °C and nearly 1.6 ppm with over-roasting temperature of 260 °C (Silwar and Lüllmann, 1993b). In a green Mexican coffee (vacuum-hydrodistillation/extraction), it represents 0.46% of the volatiles by GC (Cantergiani *et al.*, 2001).

It is formed from phenylalanine by polyphenol oxidase (Motoda, 1979).

Phenylacetaldehyde has a very powerful and penetrating, pungent-green, floral and sweet odor of hyacinth-type (Arctander, 1967), which is lilac or rose for Motoda (1979), honey-like for Holscher *et al.* (1990). The flavor is described as green, floral, sweet, honey (Chemisis, 1996). A threshold of 4 ppb in water is given by Buttery *et al.* (1969b).

(C.43) *(C.43)* **Benzeneacetaldehyde, α-ethylidene-,** *2-phenylbut-2-enal* **[4411-89-6]** ***FEMA 3224***; **(*E*)- [54075-09-1]; (*Z*)- [54075-10-4]**

Identified by Silwar (1982) in roasted coffee. Silwar *et al.* (1987) found a concentration of 0.1–0.2 ppm, Ho *et al.* (1993) the similar value of 0.18 ppm in a roasted Columbian coffee. It is present in steam-volatile components at a lower concentration than the previous aldehydes, noticeable with less than 1 ppm after 5 min at 230 °C and about 1.5 ppm after 5 min at 260 °C (Silwar and Lüllmann, 1993b). For Cantergiani *et al.* (2001), it represents 0.27% of the volatiles (GC) in the analysis of a green Mexican arabica.

Like benzaldehyde (**C.39**) and phenylacetaldehyde (**C.42**), it is a phenylalanine-derived product. A scheme for the formation of phenylalkenyl aldehydes was given by Manley *et al.* (1974): Strecker degradation of phenylalanine and glycine give phenylacetaldehyde and acetaldehyde, which then undergo aldol condensation.

The flavor is described with green, floral, fruity (Chemisis, 1968).

(C.44) Ethane, 1,1-dimethoxy-, *1,1-dimethoxyethane, acetaldehyde dimethyl acetal* **[534-15-6]** ***FEMA 3426***
Identified by Reymond *et al.* (1963).

Other compounds containing aldehydic function(s) are present in Sections 5.H (phenols), 5.I (furans), 5.J (thiophenes), 5.K (pyrroles) and 5.Q (sulfur compounds).

5.D KETONES

Ketones constitute an important part of the volatile compounds. They represent 21.5% of the components of a 'coffee aroma' (the 'center-cut' of the fractionation, see in Alcohols, Section 5.B) described by Merritt *et al.* (1963), more than half being 2-butanone.

An analysis of the less volatile carbonyl compounds of a roasted coffee has been realized by Radtke *et al.* (1966b) by column and paper chromatography separation of 2,4-dinitrophenylhydrazones, or by GC of the carbonyl compounds after treatment of the derivatives with levulinic acid (4-oxopentanoic acid), (**E.41**). This technique allows separation and characterization of aldehydes, ketones, conjugated and diconjugated aldehydes, α-dicarbonyls isolated or conjugated with a double bond and α-hydroxydicarbonyl compounds by the UV spectra of their derivatives. Unfortunately this classical and somewhat tedious analytical technique did not yield any original results, GC having in the meantime made considerable progress.

Many cyclic ketones are associated with food aromas and may be formed in coffee from carbohydrates. Among the volatile compounds from heated glucose, Heyns *et al.* (1966a) could identify 12 aliphatic ketones and diketones that have also been (except one: 3-methyl-3-buten-2-one) identified in coffee and also cyclopentanone (**D.58**) and 2-cyclopenten-1-one (**D.60**). From the same reaction Walter and Fagerson (1968) identified also 2-hydroxy-3-methyl-2-cyclopenten-1-one (**D.68**), the important 'cyclotene'. In the base-catalyzed degradation of fructose, Shaw *et al.* (1968) identified five of the cyclic α-diketones of coffee, (**D.68**, **D.69**, **D.72**, **D.73** and **D.87**), along with aliphatic hydroxyketones **D.39**, **D.40** and **D.41**, and 2,5-hexanedione (**D.56**). Nishimura and Mihara (1990) suggested that sucrose (saccharose), a major component in green coffee and mainly destroyed by roasting (Feldman *et al.*, 1969), was a precursor of the diketones **D.68**–**D.81** which they identified by GC/MS after treating

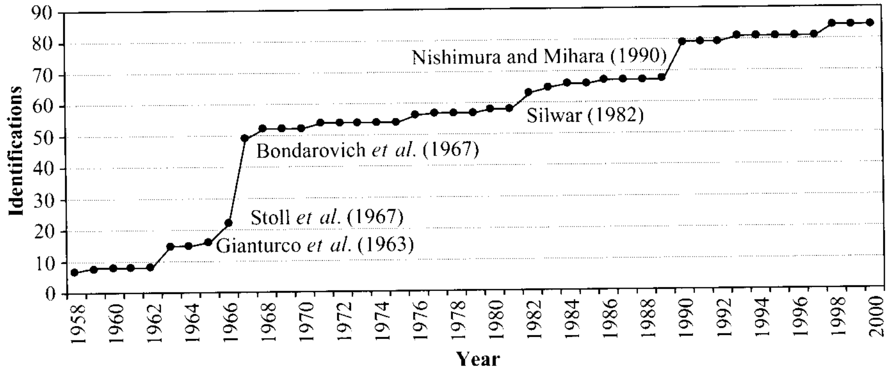
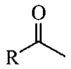


Fig. 5.4 Progressive identification of ketones in roasted coffee volatiles

sucrose with alkali. Hollnagel and Kroh (1998) studied the formation of α-dicarbonyl fragments from mono- and disaccharides under caramelization and Maillard reaction conditions. When studying reaction of threonine and serine with sucrose under coffee-roasting conditions, Baltes and Bochmann (1987d) were able to identify, among heterocyclic compounds, some cyclic ketones, (**D.58**, **D.60** and **D.61**) and diketones, (**D.68**, **D.69** and **D.87**, the last one only tentatively), which they compared with products from coffee. Some of these could come from carbohydrate pyrolysis. They attributed the presence of phenols and aliphatic compounds to the degradation of sucrose. Zhang and Ho (1991) also studied the thermal reaction of serine and glucose and identified eight carbonyl compounds (among them ethyl acetate), all of which are present in coffee.

Saturated aliphatic ketones



R = CH_3 **(D.1)** ***(D.1)***, C_2H_5 **(D.2)** ***(D.2)***, C_3H_7 **(D.3)** ***(D.3)***,

C_4H_9 **(D.4)**, C_5H_{11} **(D.5)** ***(D.5)***, C_6H_{13} **(D.6)** ***(D.6)***, C_7H_{15} **(D.7)** ***(D.7)***,

C_8H_{17} **(D.8)**, C_9H_{19} **(D.9)**, $C_{11}H_{23}$ **(D.10)** ***(D.10)***, $C_{13}H_{27}$ **(D.11)**

(D.1) ***(D.1)*** **2-Propanone,** *acetone, propan-2-one, dimethyl ketone* **[67-64-1]** ***FEMA 3326***

Identified by Bernheimer (1880a) and by Jaeckle (1898) but Hughes and Smith (1949) claimed its first identification by a salicylaldehyde reaction which produces a red color. The authors observed that the acetone content increased during the roasting process, the highest value obtained being 8.3 mg/100 g and decreases with staling. Identified by GC/IR by Rhoades (1958, 1960) who found 0.6–5.0 ppm in the volatiles (headspace) of green coffee, 40–100 ppm in those of roasted coffee, and 1.95 ppm with a brew of fresh coffee. According to Merritt *et al.* (1963) it constitutes 0.5 % of the 'coffee aroma'. Merritt *et al.* (1970) found it in green and roasted coffee (headspace) and Gibson (1974a) determined the content in the green beans of two hybrid species of East African arabica coffee. In headspace of different roasted coffee blends, Leino *et al.* (1992) found that the content in acetone varied little with storage, but the content was significantly higher in ground than in whole beans. Acetone was the only simple ketone identified in the headspace of different green coffees (six arabicas, six robustas) by Procida *et al.* (1997), and it was also present in the roasted arabica studied.

It is formed in the pyrolysis of glycine (Merritt *et al.*, 1970).

Acetone has a light ethereal-nauseating and powerful odor of very poor tenacity. Irritant at high concentration, rather pleasant in dilution (Arctander, 1967).

An odor threshold of 300 ppm in water is given by Mulders (1973b) and of 500 ppm quoted by Persson and von Sydow (1973).

(D.2) ***(D.2)*** **2-Butanone,** *butan-2-one, ethyl methyl ketone* **[78-93-3]** ***FEMA 2170***

Identified by GC/IR by Rhoades (1958, 1960) at a concentration of 0.2–1.3 ppm in green, 15–25 ppm in roasted coffee (headspace) and by Zlatkis and Sivetz (1960) in a 'coffee aroma essence'. It constitutes 12.7 % of the 'coffee aroma' according to Merritt *et al.* (1963) (see Section 5.B). Merritt *et al.* (1970) found it in green and roasted coffee (headspace). It was also identified and quantified by Gibson (1974a) in two hybrid species of arabica. The GC-peak area in a headspace of a brew is 3.1 % (Shimoda and Shibamoto, 1990a). For Procida *et al.* (1997), 2-butanone, not found in green coffee (six arabicas, six robustas), is present in the headspace of a roasted arabica after 18 min at 218 °C, but was no longer dectectable after 20 min. Ramos *et al.* (1998) found it in brewed arabica (liquid–liquid extraction with pentane or supercritical-CO_2 extraction).

It is formed when heating glucose (Heyns *et al.*, 1966a) and is one of the main aliphatic volatile compounds identified after thermal interaction of glucose and cysteine (Zhang and Ho, 1991).

Ethereal, slightly nauseating odor, not exactly pleasant (Arctander, 1967).

An odor threshold of 50 ppm is quoted by Persson and von Sydow (1973).

(D.3) *(D.3)* **2-Pentanone,** *pentan-2-one, methyl propyl ketone* **[107-87-9]** ***FEMA 2842***

Identified by Merritt and Robertson (1966), by Stoll *et al.* (1967), by Silwar (1982). Found in headspace of green coffee by Gutmann *et al.* (1979), in extracts (simultaneous distillation–extraction) of green 'Rio' coffee and a Santos reference by Spadone *et al.* (1990). Procida *et al.* (1997), who did not find 2-pentanone in green coffee of various origins, found it in headspace of a roasted arabica, the proportion increasing slightly with roasting time. Ramos *et al.* (1998) identified it only with supercritical-CO_2 extraction of a brew. It was also present in the compounds emitted by fresh red coffee berries of one robusta and one arabica varieties (Mathieu *et al.*, 1996).

The odor is powerful and very diffusive, ethereal-fruity of heavy type, pungent but not lasting (Arctander, 1967).

(D.4) **2-Hexanone,** *hexan-2-one, butyl methyl ketone* **[591-78-6]**

Identified as a headspace component by Liardon and Ott (1984).

It is formed in the pyrolysis of threonine (Merritt *et al.*, 1970).

The flavor is fruity, blue cheese (Chemisis, 1992).

(D.5) *(D.5)* **2-Heptanone,** *heptan-2-one, pentyl methyl ketone*, amyl methyl ketone **[110-43-0]** ***FEMA 2544***

Identified by Stoll *et al.* (1967). Merritt *et al.* (1970) found it in roasted but not in green coffee (headspace), but Gutmann *et al.* (1979) identified it in headspace of green coffee (more in robusta and arabusta than in arabica). For Cantergiani *et al.* (2001), it represents 0.25 % (GC) of the volatiles in a green Mexican arabica. It is one of the compounds emitted by fresh red coffee berries of one robusta variety (Mathieu *et al.*, 1996).

An odor threshold of 140 ppb in water was given by Buttery *et al.* (1969b).

(D.6) *(D.6)* **2-Octanone,** *octan-2-one, hexyl methyl ketone* **[111-13-7]** ***FEMA 2802***

Identified by Stoll *et al.* (1967) and found in green coffee (headspace) by Gutmann *et al.* (1979), more in arabica than robusta and arabusta.

It has a pleasant, floral, but bitter-green, slightly musty-herbaceous and unripe-apple fruity odor of moderate to poor tenacity (Arctander, 1967).

A flavor threshold in water of 1.6 ppm (for a C_8 methyl ketone) is given by Lea and Swoboda (1958) and of 0.15 ppm by Siek *et al.* (1969).

(D.7) *(D.7)* **2-Nonanone,** *nonan-2-one, heptyl methyl ketone* **[821-55-6]** ***FEMA 2785***

Identified by Stoll *et al.* (1967) in a coffee aroma and by Cantergiani *et al.* (2001) in a green Mexican arabica (0.05 % of the volatiles by GC).

The odor is fruity-floral, slightly fatty and herbaceous of moderate to poor tenacity and the flavor is described as green, fatty, herbal, parsley (Chemisis, 1989).

(D.8) 2-Decanone, *decan-2-one, methyl octyl ketone* [693-54-9]

Identified by Stoll *et al.* (1967).

It has an aromatic, floral, lavender, fruity odor and a fatty, sweet flavor (Chemisis, 1981).

A flavor threshold of 0.19 ppm in water was given by Siek *et al.* (1969).

(D.9) 2-Undecanone, *undecan-2-one, methyl nonyl ketone* [112-12-9] *FEMA 3093*

Identified by Stoll *et al.* (1967).

2-Undecanone has a fruity-rosy, orange-like odor, slightly herbaceous and orrisy on its oily notes (Arctander, 1967) and a fatty cheesy ketonic flavor (Chemisis, 1988).

An odor threshold of 7 ppb is given by Guadagni *et al.* (1966).

(D.10) *(D.10)* 2-Tridecanone, *tridecan-2-one, methyl undecyl ketone* [593-08-8] *FEMA 3388*

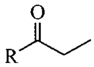
Identified by Stoll *et al.* (1967) and found by Spadone *et al.* (1990) in a green 'Rio' coffee after simultaneous distillation–extraction and GC/MS.

The odor is warm-oily, herbaceous and delicately spicy, nut-like, of considerable tenacity (Arctander, 1967).

(D.11) 2-Pentadecanone, *pentadecan-2-one, methyl tridecyl ketone* [2345-28-0] *FEMA 3724*

Identified in roasted-coffee aroma (steam-volatile constituents, then simultaneous distillation–extraction, preparative chromatography and analysis by GC/MS) by Silwar (1982). Silwar *et al.* (1987) gave a concentration of 0.10–0.15 ppm.

The odor is waxy and the flavor fatty, palmitic (Chemisis, 1974).



R = C_2H_5 **(D·12)** *(D·12)*, C_3H_7 **(D·13)** *(D·13)*,

C_4H_9 **(D·14)** *(D·14)*, C_5H_{11} **(D·15)** *(D·15)*

(D.12) *(D.12)* 3-Pentanone, *pentan-3-one, diethyl ketone,* propione [96-22-0]

Identified by Prescott *et al.* (1937b) through its 2,4-dinitrophenylhydrazone and by Merritt and Robertson (1966) in roasted coffee (headspace); it is present in the volatiles obtained by steam-distillation of roasted coffee and GC/MS of the neutral fraction (Vitzthum and Werkhoff, 1976b). Gutmann *et al.* (1979) found it also in a headspace analysis of green coffee. 3-Pentanone is in the list of coffee-headspace components identified by GC/MS by Liardon and Ott (1984). It is not present in the analyses of green coffees of various origins described by Procida *et al.* (1997) but was present in a roasted arabica.

The odor is pleasant, ethereal-warm, diffusive, milder than that of acetone, but similar in character (Arctander, 1967).

(D.13) *(D.13)* 3-Hexanone, *hexan-3-one, ethyl propyl ketone* [589-38-8] *FEMA 3290*

Identified by Heins *et al.* (1966), by Stoll *et al.* (1967), with confirmation by Stoffelsma *et al.* (1968) after steam distillation, then distillation and preparative GC of the neutral fraction. Vitzthum and Werkhoff

(1976b) used a similar method but with analysis by GC/MS of the neutral fraction. Gutmann *et al.* (1979) found it in a headspace analysis of green coffee. In their list of products identified in the headspace of freshly ground roasted coffee, Wang *et al.* (1983) gave it as not being previously identified. Liardon and Ott (1984) included it in their list of coffee-headspace components. Procida *et al.* (1997) did not find it in green coffee (six arabicas, six robustas) but in a roasted arabica.

(D.14) *(D.14)* **3-Heptanone,** *heptan-3-one, butyl ethyl ketone* **[106-35-4]** *FEMA 2545*

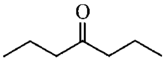
Identified by Silwar (1982) (simultaneous distillation–extraction) in roasted coffee (MS data given) and by Gutmann *et al.* (1979) in headspace analysis of green coffee (more in robusta and arabusta than in arabica).

3-Heptanone has a powerful, green-fatty, somewhat fruity odor (Arctander, 1967).

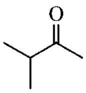
(D.15) *(D.15)* **3-Octanone,** *octan-3-one, ethyl pentyl ketone*, amyl ethyl ketone **[106-68-3]** *FEMA 2803*

Identified by Stoll *et al.* (1967) in roasted coffee, by Gutmann *et al.* (1979) in the headspace of green coffee (more in arabica than robusta and arabusta) and by Cantergiani *et al.* (2001) in a green Mexican arabica.

The odor is pungent, herbaceous-fruity, warm, somewhat spicy-buttery with distinct resemblance to the top notes in lavender oil (Arctander, 1967).



(D·16)



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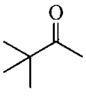

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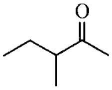

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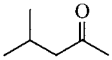

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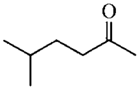

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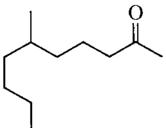

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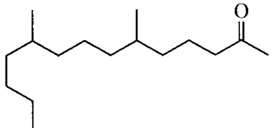

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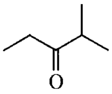

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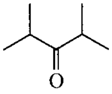


(D·25)

(D.16) 4-Heptanone, *heptan-4-one, dipropyl ketone* **[123-19-3]** *FEMA 2546*

Identified by Silwar (1982) (MS data given).

It has a powerful and diffusive ethereal-fruity, pungent odor, in dilution reminiscent of pineapple and strawberry (Arctander, 1967).

(D.17) 2-Butanone, 3-methyl-, *3-methylbutan-2-one, isopropyl methyl ketone* **[563-80-4]**

Identified by Merritt and Robertson (1966) in their 'coffee aroma' (see Section 5.B), by Ho *et al.* (1993) in the volatile compounds of a roasted Colombian coffee (headspace trapping with short-path thermal desorption GC/MS), the concentration given is 0.1 ppm.

The odor is diffusive, ethereal-camphoraceous, pleasant in dilution, somewhat pungent-choking when concentrated (Arctander, 1967).

(D.18) 2-Butanone, 3,3-dimethyl-, *3,3-dimethylbutan-2-one*, tert-*butyl methyl ketone*, 2,2-dimethylbutanone, trimethylacetone, pinacoline, pinacolone **[75-97-8]**

Identified in a brewed arabica by Ramos *et al.* (1998), after liquid–liquid extraction with methylene chloride.

(D.19) 2-Pentanone, 3-methyl-, *3-methylpentan-2-one, methyl 1-methylpropyl ketone*, sec-*butyl methyl ketone* **[565-61-7]; (*S*)- [2695-53-6]**

Identified by Ho *et al.* (1993) in a roasted Columbian coffee, with a concentration of 0.61 ppm (see **D.17**).

(D.20) 2-Pentanone, 4-methyl-, *4-methylbutan-2-one, isobutyl methyl ketone* **[108-10-1]** ***FEMA 2731***

Identified by Silwar (1982). Liardon and Ott (1984) gave it in the list of headspace components of roasted coffee.

The odor is powerful and diffusive ethereal-fruity, of poor tenacity (Arctander, 1967). The flavor is fruity, lactonic, slightly cuminic (Chemisis, 1986).

(D.21) 2-Hexanone, 5-methyl-, *5-methylhexan-2-one, isopentyl methyl ketone*, isoamyl methyl ketone **[110-12-3]**

Identified by Silwar (1982) in roasted coffee.

The flavor is fruity-red fruit, gooseberry, slightly blue cheese (Chemisis, 1993).

(D.22) 2-Undecanone, 6,10-dimethyl-, *6,10-dimethylundecan-2-one*, hexahydropseudoionone tetrahydrogeranylacetone **[1604-34-8]**

Identified by Stoll *et al.* (1967) and found by Spadone *et al.* (1990) in analysis of green coffee by GC/MS after simultaneous distillation–extraction.

It has citronella, soapy flavor (Chemisis, 1963).

(D.23) ***(D.23)*** **2-Pentadecanone, 6,10,14-trimethyl-,** *6,10,14-trimethylpentadecan-2one*, hexahydrofarnesylacetone **[502-69-2]; [*R*- (*R**,*R**)]- [16825-16-4]**

Identified by Stoll *et al.* (1967). For Cantergiani *et al.* (2001), it represents 0.06% of the volatiles by GC (after vacuum hydrodistillation and extraction) in a green Mexican arabica.

(D.24) 3-Pentanone, 2-methyl-, *4-methylpentan-2-one, ethyl isopropyl ketone* **[565-69-5]**

Identified by Wang *et al.* (1983) in headspace of roasted coffee.

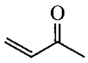
It has acetone odor and ketonic, solvent flavor (Chemisis, 1970).

(D.25) 3-Pentanone, 2,4-dimethyl-, *2,4-dimethylpentan-3-one, diisopropyl ketone* **[565-80-0]**

Identified by Wang *et al.* (1983) in the headspace of roasted coffee and by Shimoda and Shibamoto (1990a) in the headspace of brewed coffee (peak area: 0.25% of the volatiles).

It has a chemical, minty, solvent flavor (Chemisis, 1999).

Unsaturated aliphatic ketones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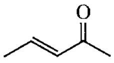
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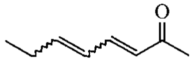
(D·28)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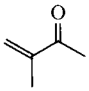
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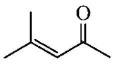
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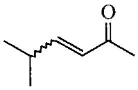
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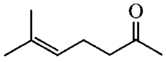
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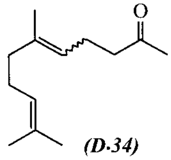
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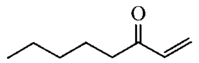
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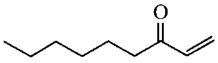
(D·35)


(D·36)

(D.26) 3-Buten-2-one, *but-3-en-2-one, methyl vinyl ketone,* 1-buten-3-one **[78-94-4]**

Identified by Sullivan *et al.* (1959) and by Merritt *et al.* (1963) who gave a concentration of 0.4% in their 'coffee aroma' (see Section 5.B). Ramos *et al.* (1998) found it after extraction of a brewed arabica with supercritical CO_2.

The odor is very sharp and pungent, rather irritating and penetrating, becoming sweet-ethereal, not unpleasant in extreme dilution (Arctander, 1967).

(D.27) 3-Penten-2-one, (*E*)-, *(E)-pent-3-en-2-one, methyl propenyl ketone, trans-*2-penten-4-one, ethylidene acetone **[3102-33-8]; (*Z*)- [3102-32-7];** no stereochemistry **[625-33-2]** ***FEMA 3417***

Identified by Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968) in roasted coffee and by Vitzthum and Werkhoff (1976b) in the volatiles of green coffee obtained by steam-distillation. (*E*)- and (*Z*)-3-Penten-2-one have been tentatively identified by Elmore and Nursten (1990) (noted (*E*)- 4-penten-2-one, which can only be a printing error!).

It is formed when heating glucose (Heyns *et al.*, 1966a), and is one of the aliphatic compounds identified (only in a small proportion) in the thermal interaction of cysteine and glucose (Zhang and Ho, 1991).

The (*E*)/(*Z*) mixture has a nutty, fruity, green-leafy and floral flavor (Chemisis, 1999).

(D.28) **3-Octen-2-one,** *oct-3-en-2-one* **[1669-44-9]** ***FEMA 3416*; (*E*)- [18402-82-9]; (*Z*)- [51193-77-2]**

(D.29) **3,5-Octadien-2-one,** *octa-3,5-dien-2-one* **[38284-27-4]; (*E,E*)- [30086-02-3]; (*E,Z*)- [4173-41-5]; (*Z,E*)- [78468-46-9]; (*Z,Z*)- [108793-59-5]**

These were identified by Gutmann *et al.* (1979) in headspace of green coffee.

The (*E*)-isomer of **D.28** has fruity, ketonic, estery, amylic flavor (Chemisis, 1962) and the (*E,E*)-isomer of **D.29** a milky, sweet, lactonic, coconut flavor (Chemisis, 1995), the (*E,Z*)-isomer being green, herbal, weak (Chemisis, 1999).

(D.30) 3-Buten-2-one, 3-methyl-, *3-methylbut-3-en-2-one, isopropenyl methyl ketone* **[814-78-8]**

Identified by Ho *et al.* (1993) in a Columbian roasted coffee (see D.17) with a concentration of 0.07 ppm.

It has a green, earthy, fermented flavor (Chemisis, 1985).

(D.31) ***(D.31)*** **3-Penten-2-one, 4- methyl-,** *4-methylpent-3-en-2-one*, isopropylidene acetone, mesityl oxide **[141-79-7]** ***FEMA 3368***

Identified by Stoll *et al.* (1967) and also found by Vitzthum and Werkhoff (1976b) in the neutral volatile compounds obtained from roasted coffee after steam distillation. It has been recently identified in a green Mexican arabica by Cantergiani *et al.* (2001), where it represented 0.03% of the volatiles (GC).

The flavor is described as pyrazines, roasted, musty, cocoa and fatty-waxy (Chemisis, 2000).

(D.32) 3-Hexen-2-one, 5-methyl-, *5-methylhex-3-en-2-one*, 2-oxo-5-methyl-3-hexene **[5166-53-0]** ***FEMA 3409***

Identified by Cros *et al.* (1980) in headspace of roasted coffee.

The odor is unpleasant with a nutty, blue-cheese, plastic, machine oil and raw mushroom flavor (Chemisis, 1998).

(D.33) 5-Hepten-2-one, 6-methyl-, *6-methylhept-5-en-2-one*, 2-methyl-2-hepten-6-one, methyl heptenone **[110-93-0]** ***FEMA 2707***

Identified by Stoll *et al.* (1967). Ramos *et al.* (1998) found it, in a low concentration, only after extraction of a brewed arabica with supercritical CO_2 (other methods, see **D.45A**).

It has a green, fresh fruity flavor (Chemisis, 1996).

An odor threshold of 50 ppb in water was given by Buttery *et al.* (1971).

(D.34) **5,9-Undecadien-2-one, 6,10-dimethyl-,** *6,10-dimethylundeca-5,9-dien-2-one* **[689-67-8]; (*E*)- [3796-70-1]** ***FEMA 3542*****; (*Z*)- [3879-26-3]**

Identified after simultaneous distillation–extraction of green beans by Spadone *et al.* (1990).

It has a fatty, somewhat metallic flavor (Chemisis, 1968).

(D.35) ***(D.35)*** **1-Octen-3-one,** *oct-1-en-3-one, pentyl vinyl ketone*, amyl vinyl ketone **[4312-99-6]** ***FEMA 3515***

Identified in roasted Columbian coffee by Holscher *et al.* (1990) after distillation–extraction and in green coffee by Holscher and Steinhart (1995) who found a concentration of 10 ppb, but only detected by Semmelroch and Grosch (1995b) in brews of arabica and robusta and not in powders or in a soluble coffee. It was identified by Pollien *et al.* (1998) in a brew and in instant coffee beverage using a new GC-olfactometric method (Surface of Nasal Impact Frequency, see Section 3.3). They were able to quantify 1-octen-3-one with this method (Pollien *et al.*, 1999) although they estimated that the value of about 0.5 ppb could be an overestimate, because of partial overlapping of other effluents.

It is formed in a very small amount (but as a predominant odor compound) during autoxidation of linoleic acid ($C_{18:2}$) and methyl linoleate (Ullrich and Grosch, 1987).

The flavor is described as green, earthy, mushroom (Chemisis, 1986). The odor perception at the sniffing port is mushroom-like (Semmelroch and Grosch, 1995b).

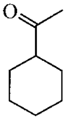
1-Octen-3-one is in the list of potent odorants of green arabica coffee (Czerny and Grosch, 2000). The range for the odor threshold in air is 0.3–0.6 $\mu g/m^3$ (Ullrich and Grosch, 1988b), who considered this ketone to be an impact compound in the odor of spoiled soybean oil).

(D.36) 1-Nonen-3-one, *non-1-en-3-one* **[24415-26-7]**

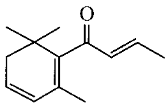
Identified by Pollien *et al.* (1998) in a headspace-GC-olfactometric analysis (see **D.35**) of brewed coffee (80% arabica–20% robusta) where it is present in too low a concentration for spectral confirmation (but the authors had previously identified it in yogurt aroma, making a comparison possible).

It has a mushroom, ketonic, plastic flavor (Chemisis, 1986). It exhibits a mushroom odor, like **D.35**. It has one of the lowest known odor thresholds, 8 pg/kg (8×10^{-15}) in water (Ott *et al.*, 1997).

Alicyclic saturated and unsaturated ketones



(D.37)



(D.38)
(D.38)

(D.37) Ethanone, 1-cyclohexyl-, *1-cyclohexylethan-1-one, cyclohexyl methyl ketone*, acetylcyclohexane, hexahydroacetophenone **[823-76-7]**

Identified by Vitzthum and Werkhoff (1976b) among the neutral volatile components of roasted coffee, isolated by steam-distillation at normal pressure (MS data given).

The odor is camphoraceous, minty, isopropanol-like (Chemisis, 1993).

(D.38) *(D.38)* **2-Buten-1-one, 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-, (*E*)-,** *(E)-1-(2,6,6-trimethylcyclohexa-1,3-dien-1-yl)but-2-en-1-one*, β-damascenone **[23726-93-4]** ***FEMA 3420***

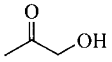
Identified by Gautschi and Willhalm (unpublished results mentioned by Flament, 1989) and later by Holscher *et al.* (1990) after simultaneous distillation–extraction of roasted coffee. With a similar technique, it was found by Spadone *et al.* (1990) in green coffee and also by Blank *et al.* (1992b) after extraction and distillation, then GC/MS, of roasted arabica coffee and brew. Concentrations of 0.26 ppb in arabica and of 0.293 ppb in robusta roasted beans and of 3.8 ppt in a robusta coffee brew were measured by stable isotope dilution assay by Sen *et al.* (1991a). The robusta sample contains approximately 10% more β-damascenone than the arabica. However, when a coffee brew was prepared from the robusta, only 18% of the β-damascenone was extracted. Semmelroch *et al.* (1995), using also stable isotope dilution assays (see Section 3.2), gave higher concentrations of about 0.20 ppm in Columbian arabica and Indonesian robusta roasted coffees, and placed it in the list of potent odorants of ground roasted coffee. Holscher and Steinhart (1995) found a concentration of 90 ppb in a green Columbian arabica. but Czerny and Grosch (2000) found that (*E*)-β-damascenone is below the detection limit of 0.3 ppb in green coffee but with an increase after roasting (255 ppb). These authors did not believe that it was one of the intense odorants of green coffee.

A suggested formation pathway is the degradation of carotenoids by heating, via oxidation and isomerization (Holscher and Steinhart, 1995).

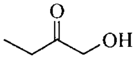
The flavor of β-damascenone is described as fruity-juicy, red-fruit, woody, sweet (Chemisis, 1999). By GC-olfactometry, the odor is described as tea-like, fruity (Holscher *et al.*, 1990) or honey-like, fruity (Blank *et al.*, 1992b). The latter authors found that the contribution to the flavor was stronger with the powder than with the brew; they gave a threshold of 0.002 – 0.004 $\mu g/m^3$ air. Ohloff (1978b) reported a new value of 9 ppt for the odor threshold in water, 1000-times lower than previous values. Semmelroch *et al.* (1995) gave the even lower value of 0.75 ppt. Czerny and Grosch (2000) found a threshold of 0.15 μg/kg cellulose.

The (*Z*)-isomer is described with saffron, pepper, rosy, fruity odor and fruity, sweet floral flavor Chemisis, 1998).

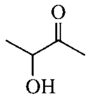
Aliphatic hydroxyketones



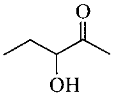
(D.39)



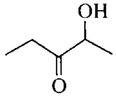
(D.40)



(D.41)
(D.41)



(D.42)



(D.43)

(D.39) 2-Propanone, 1-hydroxy-, *1-hydroxypropan-2-one*, hydroxyacetone, acetyl carbinol, 2-oxo-1-propanol, 1-propanol-2-one, acetol, pyruvic alcohol (it has to be noted that the name acetol has also been used for diethyl acetal and for acetylsalicylic acid = aspirin) **[116-09-6]**

Identified by Reichstein and Staudinger (1926b), Viani *et al.* (1965), and by Gianturco *et al.* (1966) in an 'aroma complex' from roasted coffee. Cros *et al.* (1980) found it in headspace of brewed Columbian coffee. Silwar *et al.* (1987) gave concentrations of 0.25–0.30 ppm (simultaneous distillation–extraction of steam-volatile constituents, preparative GC). In headspace after a solid-phase microextraction of a brew, it was identified by Ramos *et al.* (1998).

The odor is pungent, sweet-caramellic, somewhat choking-ethereal and the taste is sweet, slightly burning (Arctander, 1967).

(D.40) 2-Butanone, 1-hydroxy-, *1-hydroxybutan-2-one* **[5077-67-8]** *FEMA 3173*

Identified by Stoll *et al.* (1967).

(D.41) ***(D.41)*** **2-Butanone, 3-hydroxy-,** *3-hydroxybutan-2-one*, 2-hydroxybutan-3-one, acetoin, acetyl methyl carbinol, 2-butanol-3-one **[513-86-0]; (±)- [52217-02-4]; (*R*)- [53584-56-8]; (*S*)- [78183-56-9]** *FEMA 2008*

Identified by Schmalfuss and Barthmeyer (1929) and by Johnston and Frey (1938) and also tentatively by Clements and Deatherage (1957) by paper chromatography of the 2,4-dinitrophenylhydrazine derivative. It was mentioned by Gianturco *et al.* (1966), Stoffelsma *et al.* (1968) and found by Cros *et al.* (1980) in headspace of roasted coffee. Vincent *et al.* (1976) identified it in unhealthy green beans. Silwar *et al.* (1987) obtained concentrations of 0.25–0.35 ppm (see method for **D.39**). In investigations of off-flavor in green coffee, Spadone *et al.* (1990) found it in the 'Rio' and in the Santos coffee used as a reference (simultaneous distillation–extraction), and Cantergiani *et al.* (2001) in a green Mexican arabica (0.36% of the volatiles by GC). However, this hydroxyketone was not identified by Procida *et al.* (1997) in any of the aroma (headspace) of green coffees (six arabicas, six robustas), although the authors found it in a roasted arabica. Ramos *et al.* (1998) identified it only in the liquid–liquid extraction of a brew with methylene chloride (see **D.45A**). 3-Hydroxy-2-butanone is one of the components emitted by fresh red coffee berries of one arabica variety as described by Mathieu *et al.* (1996).

In coffee, it could result from a fermentation similar to that produced by Enterobacterias or by other paths, such as condensation of two molecules of acetaldehyde activated by carboxydase (Vincent *et al.*, 1976).

It is formed when glucose is heated (Heyns *et al.*, 1966a) and was one of the aliphatic compounds identified in the thermal interaction of glucose and cysteine (Zhang and Ho, 1991)

The odor is intensively creamy-fatty-buttery, penetrating, yet milder and less 'quinone-like' than diacetyl, not as sharp or volatile; it is pleasant in extreme dilution (Arctander, 1967).

(D.42) 2-Pentanone, 3-hydroxy-, *3-hydroxypentan-2-one*, acetyl ethyl carbinol, 1-acetyl-1-propanol **[3142-66-3]** *FEMA 3550;* **(±)- [118712-30-4; (*S*)- [132881-72-2]**

Identified by Gianturco *et al.* (1966).

The racemic compound has a buttery, creamy flavor (Chemisis, 1993).

(D.43) 3-Pentanone, 2-hydroxy-, *2-hydroxypentan-3-one* **[5704-20-1]; (±)-[118712-31-5]; (*S*)- [125948-63-2]**

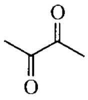
Identified by Gianturco *et al.* (1966). Silwar *et al.* (1987) measured concentrations of 0.05–0.15 ppm (see method for **D.39**).

The flavor is milky, buttery (Chemisis, 2000).

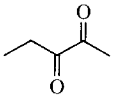
Aliphatic diketones

Kung (1974) mentioned that numerous reports appear in the literature on the study of keto–enol tautomerism of carbonyl compounds, triacylmethanes and cyclodiketones depending on the state as pure liquid, diluted in an organic solvent or in a gas phase. Except for compound **D.45**, which will be discussed, the aliphatic structures are represented as α-diketones and the cyclic structures under the keto-enolic form.

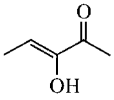
α-Dicarbonyl compounds are widespread in foods and in heated fats (Cobb and Day, 1965).



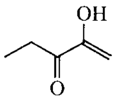
(D·44)
(D·44)



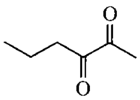
(D·45A)
(D·45A)



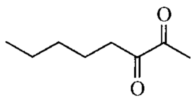
(D·45B)



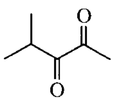
(D·45C)



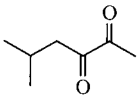
(D·46)



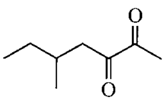
(D·47)



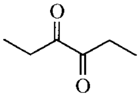
(D·48)



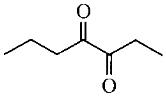
(D·49)



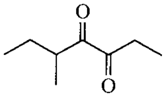
(D·50)



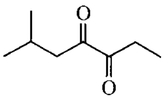
(D·51)



(D·52)



(D·53)



(D·54)

(D.44) *(D.44)* 2,3-Butanedione, *butane-2,3-dione, biacetyl, dimethyl diketone*, diacetyl **[431-03-8]** ***FEMA 2370***

Identified by Reichstein and Staudinger (1926b), then as a nickel dimethylglyoxime precipitate by Schmalfuss and Barthmeyer (1929) and Prescott *et al* (1937a,b), and as a bis-semicarbazone by Johnston and Frey (1938). Hughes and Smith (1949) estimate its concentration as 11 ppm in normally roasted coffee, but in smaller amounts in over-roasted coffee. As they estimated the threshold as 1 or 2 ppm, they confirmed the definite contribution of biacetyl on flavor, but observed that upon staling it is relatively rapidly converted to 3-hydroxybutan-2-one (**D.41**), a clearly weaker constituent. Biacetyl in roasted coffee flavor has also been tentatively identified as a 2,4-dinitrophenylhydrazone by Clements and Deatherage (1957), then by GC/IR by Rhoades (1958, 1960). In the latter publication, the author mentioned concentrations of 0.07–0.3 ppm in green, 16–20 ppm in roasted coffee. He even proposed measuring the degree of roasting by the ratio of biacetyl to 2,3-pentanedione. Afterwards this compound was described by numerous authors using more sophisticated GC/MS techniques. According to Merritt *et al.* (1963) it represented 1.67% of a 'coffee aroma' (see Section 5.B). Merritt *et al.* (1970) found it in green and roasted coffee, Vincent *et al.* (1976) in green unhealthy beans and Guyot *et al.* (1983) in stinking but not in healthy green coffee beans. Guyot *et al.* (1988a) observed a decrease in the formation of 2,3-butanedione by roasting with the increase of the maturity of the cherries (see also C.12). During roasting, the concentration in the headspace of this potent odorant rapidly increases then decreases with further thermal treatment, staying higher in arabica than in robusta coffee. The changes (with those of D.45) were accompanied by an aroma shifting from mild buttery notes to a more burnt or sulfurous character (Holscher and Steinhart, 1992a). Biacetyl is present in the headspace of brewed coffee with a peak area of 2.2% of the volatiles (Shimoda and Shibamoto, 1990a). Ho *et al.* (1993) find a concentration of 1.78 ppm in a roasted Columbian coffee (adsorbent trapping/short-path thermal desorption GC/MS), Silwar *et al.* (1987) of 0.05–0.15 ppm (simultaneous distillation-extraction of steam-volatile constituents) but Grosch (1995) gives a value of ca 50 ppm for an Indonesian robusta coffee ('stable isotope dilution assays'). Grosch *et al.* (1996) again gave a concentration of about 50 ppm in Columbia roasted arabica and 58.7 in a Kenya arabica. Procida *et al.* (1997) found this compound in headspace of green coffees of various species and origins, and in the Guatemala arabica that they studied at different roasting times, the proportion still increasing after 22 min at 218 °C, and then decreasing.

It is formed when heating glucose (Heyns *et al.*, 1966a; Walter and Fagerson, 1968) and was one of the aliphatic compounds identified in thermal interaction of glucose and cysteine (Zhang and Ho, 1991).

Having a very powerful and diffusive, pungent, buttery odor, biacetyl is described as being a chlorine–quinone-like in high concentration, becoming oily-buttery in extreme dilution (Arctander, 1967). The odor perception is buttery at the sniffing port of a chromatograph (Holscher *et al.*, 1990; Blank *et al.*, 1992b). For Pollien *et al.* (1998) it was a key component in a brew (blend of 80% arabica and 20% robusta). This α-diketone brings to coffee a very pleasant note.

The odor threshold was 6.5 ppb in water for Mulders (1973b). Blank *et al.* (1992b) gave an odor threshold of 10 – 20 $\mu g/m^3$ air and (1992b) of 15 ppb in water. A flavor threshold of 5.4 ppb in water was found by Siek *et al.* (1969).

(D.45A) *(D.45A)* 2,3-Pentanedione, *pentane-2,3-dione, ethyl methyl diketone*, acetyl propionyl **[600-14-6]** ***FEMA 2841***

Identified by Reichstein and Staudinger (1926b). Rhoades (1960) did not find it in headspace of crushed green beans, but found concentrations of 10–19 ppm in ground roasted beans. The concentration appears to reach a maximum at a roasting temperature of 425 °F (~ 220 °C). Merritt *et al.* (1970) confirmed its absence in green beans. Vincent *et al.* (1976) found this diketone in unhealthy green beans and Guyot *et* *al.* (1983) did not find it in healthy green beans. A maximum in concentration (higher in arabica than in robusta) was reached under slight roasting conditions with changes in the aroma, see **D.44** (Holscher and Steinhart, 1992a). In headspace analysis of brewed coffee, it represented 3.6% of the volatiles in GC (Shimoda and Shibamoto, 1990a). The concentration in roasted coffee is estimated at 4.0 ppm by Stofberg and Stoffelsma (1981) and at 1–3 ppm by Silwar *et al.* (1987). Concentrations of about 40 and 20 ppm were found by Grosch (1995) and Grosch *et al.* (1996), for arabica and robusta coffees respectively ('stable isotope dilution assays'). Procida *et al.* (1997) identified 2,3-pentanedione in a roasted arabica but not in green coffees of various origins; the proportion in the headspace decreased after 20 min at 218 °C. Ramos *et al.* (1998) identified it in the different extracts of a brewed arabica: liquid–liquid extraction with pentane or methylene chloride, solid-phase microextraction, supercritical-CO_2 extraction.

Heyns *et al.* (1966a) identified it in the products formed when heating glucose. 2,3-Pentanedione is the main volatile compound formed by thermal degradation of Furaneol® (**I.100**): after $\frac{1}{2}$h at 160 °C in water at pH 5.1, it represents nearly half of the volatiles (GC). It is one of the aliphatic compounds identified in the thermal interaction of glucose and cysteine (Zhang and Ho, 1991).

2,3-Pentanedione has an oily-buttery odor, pungent and somewhat 'quinone-like', less sharp and volatile than biacetyl (Arctander, 1967). Like biacetyl (**D.44**) it has a high aroma impact in a brew (Pollien *et al.*, 1998).

Blank *et al.* (1992a,b) gave an odor threshold of 30 ppb in water and of $10 - 20\,\mu g/m^3$ air with a buttery perception in a GC-olfactometry of roasted-coffee headspace.

(D.45B) 3-Penten-2-one, 3-hydroxy-, *3-hydroxypent-3-en-2-one* [52704-36-6]

Kung (1974) isolated a compound responsible for a pleasant, buttery caramel aroma during GC of a coffee aroma. The MS corresponded to that of 2,3-pentanedione, but the retention time and odor did not. IR and NMR spectra of the trapped compound were more likely those of an enol form which could effectively be produced by injection at 300 °C of the dione or by action of a concentrated acid at lower temperature. The free enol form is not stable and reverts to the keto form at room temperature. This observation does not entirely exclude the occasional organoleptic contribution of enolized forms in certain states of the coffee beverage, but contrary to 2,4-pentanedione (**D.55**) which is enolized to a significant extent, the α-diketones are not discussed here under their enolic forms.

(D.45C) 1-Penten-3-one, 2-hydroxy-, *2-hydroxypent-1-en-3-one*

This second enolic form of 2,3-pentanedione is noted by Ho *et al.* (1993) in the volatile compounds of a roasted Columbian coffee (see **D.44**), with a concentration of 1.43 ppm. The other enolic form **D.45B** is also present (1.66 ppm) as well as the diketone **D.45A** (0.73 ppm). There is no comment about the presence of the three tautomeric forms.

(D.46) 2,3-Hexanedione, *hexane-2,3-dione, methyl propyl diketone*, acetyl-*n*-butyryl [3848-24-6] *FEMA 2558*

Identified by Viani *et al.* (1965) after steam distillation of a roasted Brazilian coffee, preparative chromatography and characterization by IR spectrum of the product and UV of its monohydrazone. Merritt *et al.* (1970) found it in headspace of several varieties of roasted but not green beans. The concentration in roasted coffee is estimated at 0.33 ppm by Stofberg and Stoffelsma (1981), at 0.30–0.50 ppm by Silwar *et al.* (1987) (simultaneous distillation–extraction of the steam-volatile components and preparative GC). Procida *et al.* (1997) characterized this diketone only in the headspace of a roasted arabica and not in any of the green coffees studied.

2,3-Hexanedione has a powerful, creamy-sweet, heavy-buttery, oily odor, yet somewhat milder than diacetyl. The odor is often classified as 'quinone-like'. The taste is buttery-cheesy, particularly in acid medium (Arctander, 1967). The flavor is fatty, fruity, pear-like (Chemisis, 1961).

(D.47) 2,3-Octanedione, *octane-2,3-dione, methyl pentyl diketone,* acetylcaproyl **[585-25-1]**

Identified by Stoll *et al.* (1967).

It has a creamy-cheesy taste, mildly buttery in dilutions near 10 ppm (Arctander, 1967).

(D.48) 2,3-Pentanedione, 4-methyl-, *4-methylpentane-2,4-dione,* acetyl isobutyryl **[7493-58-5]** *FEMA 2730*

Identified by Stoll *et al.* (1967), and by Cros *et al.* (1980) in headspace of ground roasted Columbian coffee. The peak area represents 0.14% of the GC-area of the volatiles in a headspace of brewed coffee (Shimoda and Shibamoto, 1990a). In the various extracts (see **D.45A**) of a brewed arabica, Ramos *et al.* (1998) found it only in supercritical-CO_2 extract.

The odor is heavy creamy-sweet, fruity-buttery, often described as 'quinone-like', milder and weaker than biacetyl (Arctander, 1967).

(D.49) 2,3-Hexanedione, 5-methyl-, *5-methylhexane-2,3-dione, isobutyl methyl diketone,* acetyl isovaleryl **[13706-86-0]** *FEMA 3190*

(D.50) 2,3-Heptanedione, 5-methyl-, *5-methylheptane-2,3-dione*

(D.51) 3,4-Hexanedione, *hexane-3,4-dione, diethyl diketone,* bipropionyl, dipropionyl **[4437-51-8]** *FEMA 3168*

(D.52) 3,4-Heptanedione, *heptane-3,4-dione, ethyl propyl diketone* **[13706-89-3]**

(D.53) 3,4-Heptanedione, 5-methyl-, *5-methyl-3,4-heptanedione* **[13678-56-3]**

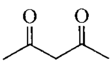
(D.54) 3,4-Heptanedione, 6-methyl-, ***6-methylheptane-3,4-dione, ethyl isobutyl diketone*** **[3131-90-6]**

These were identified by Stoll *et al.* (1967).

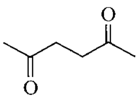
For **D.51**, Merritt and Robertson (1966) mentioned 'dimethyldiketone' as first identified in coffee. They also mentioned 'diacetyl' in their list. The product could be diethyl diketone.

D.49 has a powerful oily-buttery, somewhat fruity odor, 'quinone-like', rather pungent and mild animal, cheesy (Arctander, 1967). The flavor is caramel, fruity, creamy, valerianic (Chemisis, 1999)

D.51 has a pungent buttery odor, resembling biacetyl but not as diffusive or penetrating (Arctander, 1967). Flavors are described as fruity, buttery, horse stable for **D.50**, fruity, chemical for **D.53** (Chemisis, 1963) and fruity, buttery, burnt for **D.54.**



(D-55)



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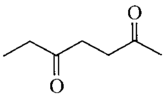


(D-57)

(D.55) 2,4-Pentanedione, *pentane-2,4-dione,* acetylacetone, diacetylmethane **[123-54-6]**

Identified by Merritt *et al.* (1963), representing 0.1% of their 'coffee aroma' (see Section 5.B).

It has an ethereal-minty odor, somewhat metallic or 'chemical'. In high dilution, the flavor in aqueous medium is sweet, remotely reminiscent of peppermint sweetness (Arctander, 1967).

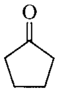
(D.56) 2,5-Hexanedione, *hexane-2,5-dione*, acetonyl acetone, diacetonyl **[110-13-4]**

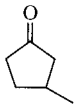
(D.57) 2,5-Heptanedione, *heptane-2,5-dione* **[1703-51-1]**

These were identified by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968). Ho *et al.* (1993) found **D.56** in a roasted Columbian coffee with a concentration of 0.74 ppm (see **D.44**).

D.56 has a pleasant, sweet-ethereal odor (Arctander, 1967).

Cyclopentanones and cyclopentenones


(D·58)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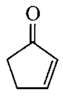
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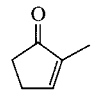
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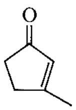
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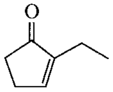
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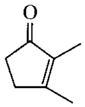
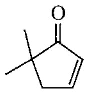

(D·64)
(D·64)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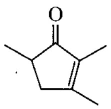

(D·66)

(D.58) Cyclopentanone, *cyclopentanone*, adipic ketone **[120-92-3]**

Identified by Gianturco *et al.* (1966) and found also by Merritt *et al.* (1970) in headspace of roasted but not of green coffee.

It is formed during the heating of glucose (Heyns *et al.*, 1966a).

(D.59) Cyclopentanone, 3-methyl-, *3-methylcyclopentan-1-one* **[1757-42-2]; (±)- [6195-92-2]; (*R*)- [6672-30-6]; (*S*)- [6672-24-8]**

Identified by Vitzthum and Werkhoff (1976b) in the neutral volatile compounds obtained by steam distillation at room temperature.

The odor description is roasted beef (Nishimura *et al.*, 1980).

(D.60) 2-Cyclopenten-1-one, *cyclopent-2-en-1-one* **[930-30-3]**,

(D.61) 2-Cyclopenten-1-one, 2-methyl-, *2-methylcyclopent-2-en-1-one* **[1120-73-6]**

These were identified by Bondarovich *et al.* (1967) (UV data). Ramos *et al.* (1998) found **D.61** in extract of a brew with supercritical CO_2.

D.60 is one of the compounds formed when heating glucose (Heyns *et al.*, 1966a) and **D.61** has been identified in reaction of sucrose with serine or threonine under coffee-roasting conditions (Baltes and Bochmann, 1987d).

(D.62) 2-Cyclopenten-1-one, 3-methyl-, *3-methylcyclopent-1-en-2-one*, 1-methyl-1-cyclopenten-3-one **[2758-18-1]** *FEMA 3435*

Identified by Ho *et al.* (1993) in a roasted coffee.

The flavor is burnt, rubbery, mouldy, earthy (Chemisis, 1980).

(D.63) 2-Cyclopenten-1-one, 2-ethyl-, *2-ethylcyclopent-2-en-1-one* **[2931-10-4]**

Identified by Bondarovich *et al.* (1967).

(D.64) ***(D.64)*** **2-Cyclopenten-1-one, 2,3-dimethyl-,** *2,3-dimethylcyclopent-2-en-1-one* **[1121-05-7]**

Identified by Friedel *et al.* (1971) (MS and IR data given) and by Vitzthum and Werkhoff (1976b) after steam distillation at normal pressure and analysis by GC/MS of the neutral fraction. Cantergiani *et al.* (2001) found it in the volatile compounds of a green Mexican arabica (0.17% of the volatiles, GC-area).

The flavor is described as mouldy, dirty, weak (Chemisis, 1986).

(D.65) 2-Cyclopenten-1-one, 5,5-dimethyl-, *5,5-dimethylcyclopent-2-en-1-one* **[17197-84-1]**

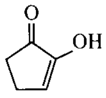
Identified by Ramos *et al.* (1998) only in their extract with supercritical CO_2 of a brewed arabica (other methods, see **D.45A**).

(D.66) 2-Cyclopenten-1-one, 2,3,5-trimethyl-, *2,3,5-trimethylcyclopent-2-en-1-one* **[54562-24-2]**

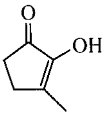
Identified by Bondarovich *et al.* (1967).

α-Cyclopentanediones

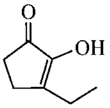
These compounds exist normally under the enol form, as shown by IR spectroscopy. Gianturco *et al.* (1963). Gianturco and Friedel (1963) published the identification and synthesis of some of these cyclic diketones. Nishimura and Mihara (1990) found ten other compounds of the series (identified also when heating glucose with alkali) in analysis of a roasted Columbian arabica coffee: steam distillation, extraction, separation of the concentrate in basic, acidic, weakly acidic and neutral fractions, the weakly acidic being further fractionated by TLC.



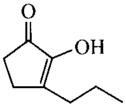
(D·67)



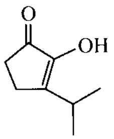
(D·68)



(D·69)



(D·70)



(D·71)

(D.67) 2-Cyclopenten-1-one, 2-hydroxy-, *2-hydroxycyclopent-2-en-1-one* **[10493-98-8]; 1,2-cyclopentanedione,** *cyclopentane-1,2-dione* **[3008-40-0]**

Identified by Gianturco *et al.* (1963), confirmed by Walter *et al.* (1967) through the 2,4-dinitrophenylhydrazone derivative.

It is prepared by the method of Hesse and Bücking (1949).

The flavor is maple, caramel like (Chemisis, 1972).

(D.68) 2-Cyclopenten-1-one, 2-hydroxy-3-methyl-, *2-hydroxy-3-methylcyclopent-2-en-1-one*, 3-methylcyclopent-2-en-2-ol-1-one **[80-71-7]; 1,2-cyclopentanedione, 3-methyl-,** *3-methylcyclopentane-1,2-dione*, cyclotene, corylone, maple lactone, nussol **[765-70-8]** ***FEMA 2700***

Identified by GC/IR by Gianturco *et al.* (1963); also by Vitzthum and Werkhoff (1976b) after steam distillation at normal pressure and analysis of the neutral fraction by GC/MS. Nishimura and Mihara (1990) found a concentration of 9.8 ppm (MS data given). It is one of the non-volatile caramel compounds, whose concentration increases strongly with temperature (after 5 min): from <5 ppm at 170 °C to 37 ppm at 230 °C and ca 80 ppm with the over-roasting temperature of 260 °C (Silwar and Lüllmann, 1993b). It was identified in a brew after liquid–liquid extraction with methylene chloride (other methods, see **D.45A**) by Ramos *et al.* (1998).

Shaw *et al.* (1968) proposed a formation pathway via the dehydration of two molecules of hydroxyacetone (acetol) between the hydroxy group of one and the methyl group of the other, followed by a second dehydration between the methylene hydrogens of the remaining hydroxymethyl group and the carbonyl group near the other end of the molecule. This mechanism has been questioned by Nursten (1998) who also proposed the condensation of acetol, but through an aldol reaction taking place between the hydroxymethyl group of one molecule with the keto group of the other. The product would be able to lose water and the vinyl alcohol would tautomerize to an aldehyde. Another aldol condensation could then take place between the aldehyde group and the methyl group at the other end of the molecule. The dehydration of the intermediate obtained results in one of the 12 tautomers of cyclotene. Nursten (1998) recalled that acetol is formed by degradation of many sugars, particularly from glucose and xylose.

Cyclotene is a commercially available product, frequently used as flavoring ingredient. It has a sweet and very powerful, caramellic-spicy odor, often described as walnut, maple, licorice, celery, tobacco, *etc.* (Arctander, 1967). It is spicy for Holscher *et al.* (1990). At 1 ppm in water, the odor is maple-like, burnt for Nishimura and Mihara (1990) with an odor threshold of 0.3 ppm in water. Brulé *et al.* (1971) find a flavor threshold of 2 ppm in water.

(D.69) 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-, *3-ethyl-2-hydroxycyclopent-2-en-1-one*, 3-ethylcyclopenten-2-en-2-ol-1-one [21835-01-8]; 1,2-cyclopentanedione, 3-ethyl-, *3-ethylcyclopentane-1, 2-dione* [13494-08-1]

Identified by GC/IR by Gianturco *et al.* (1963). Nishimura and Mihara (1990) found a concentration of 57 ppm (MS data given). Under the name of ethylcyclopentenolone or ethylcyclotene, Ramos *et al.* (1998) observed its presence in a brewed arabica and, like the lower homologue **D.68**, only after liquid-liquid extraction with methylene chloride.

Gianturco and Friedel (1963) synthesized it by alkylation of diethyl 4,5-dioxocyclopentane-1,3-dicarboxylate, followed by hydrolysis and decarboxylation of the resulting diethyl 1-ethyl-4,5-dioxocyclopentane-1,3-dicarboxylate.

It has a strong caramel-like odor (Shaw *et al.*, 1968), sweet, sugary at 1 ppm in water (Nishimura and Mihara, 1990). The flavor is maple, caramel, weak (Chemisis, 1967). Fors (1983) reported enhancing flavor characteristics.

(D.70) 2-Cyclopenten-1-one, 2-hydroxy-3-propyl-, *2-hydroxy-3-propylcyclopent-2-en-1-one* [25684-04-2]; 1,2-cyclopentanedione, 3-propyl-, *3-propylcyclopentane-1,2-dione*

Identified by Nishimura and Mihara (1990) who give a concentration of 42 ppm (MS data given).

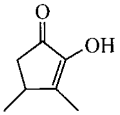
The synthesis was described by Arnap *et al.* (1986) in a work on tobacco smoke using the method described for **D.69**.

The odor description is sweet, burnt at 1 ppm in water (Nishimura and Mihara, 1990).

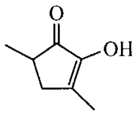
(D.71) 2-Cyclopenten-1-one, 2-hydroxy-3-(1-methylethyl)-, *2-hydroxy-3-isopropylcyclopent-2-en-1-one* [55277-47-9]; 1,2-cyclopentanedione, 3-isopropyl-, *3-isopropylcyclopentane-1,2-dione*

Identified with a concentration of 0.02 ppm by Nishimura and Mihara (1990) (MS data given).

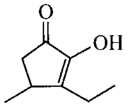
Synthesis and odor description as for **D.70.**



(D.72)



(D.73)



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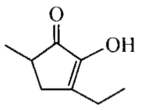

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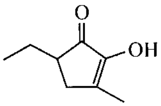

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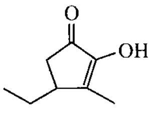

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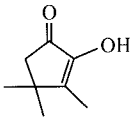

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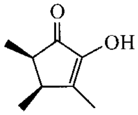

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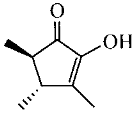
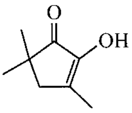
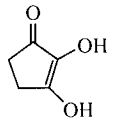


(D.80)



(D.81)



(D.82)

(D.72) 2-Cyclopenten-1-one, 2-hydroxy-3,4-dimethyl-, *2-hydroxy-3,4-dimethylcyclopent-2-en-1-one*, 3,4-dimethylcyclopenten-2-en-2-ol-1-one **[21835-00-7]; (±)- [147770-82-9]; 1,2-cyclopentanedione, 3,4-dimethyl-,** *3,4-dimethylcyclopentane-1,2-dione* **[13494-06-9]** ***FEMA 3268***

Identified by GC/IR by Gianturco *et al.* (1963). Nishimura and Mihara (1990) found a concentration of 0.73 ppm (MS data given).

It was prepared by Gianturco and Friedel (1963) by alkylation of diethyl 2-methyl-4,5-dioxocyclopentane-1,3-dicarboxylate followed by hydrolysis and decarboxylation.

The flavor description is maple, fenugreek, burnt (Chemisis, 1968). The odor description is very strong caramel-like, stronger than **D.68**, **D.69**, **D.73** and **D.87** (Shaw *et al.*, 1968); sweet, burnt at 1 ppm in water, with an odor threshold of 0.02 ppm in water (Nishimura and Mihara, 1990).

It is an important odorant of ground and brewed coffee, more potent in powder than in brew, and more in arabica than in robusta; it has a threshold of 0.05–1 $\mu g/m^3$ air (Blank *et al.*, 1992b).

(D.73) 2-Cyclopenten-1-one, 2-hydroxy-3,5-dimethyl-, *2-hydroxy-3,5-dimethylcyclopent-2-en-1-one*, 3,5-dimethylcyclopenten-2-en-2-ol-1-one **[21834-98-0]; 1,2-cyclopentanedione, 3,5-dimethyl-,** *3,5-dimethylcyclopentane-1,2-dione* **[13494-07-0]** ***FEMA 3269***

Identified by GC/IR by Gianturco *et al.* (1963), and also found by Nishimura and Mihara (1990) in a concentration of 2.2 ppm (MS data given).

The synthesis starts with formylation of the methyl ether of **D.68** (Gianturco and Friedel, 1963). An improvement is probably the use of Mannich reaction on **D.68** (Tonari *et al.*, 1970).

The odor description is strong caramel-like (Shaw *et al.*, 1968), caramel-like, sweet at 1 ppm in water (Nishimura and Mihara, 1990). The flavor is sweet, caramel, nussol (**D.68**) (Chemisis, 1998).

(D.74) 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-4-methyl-, *3-ethyl-2-hydroxy-4-methylcyclopent-2-en-1-one* **[42348-12-9]** ***FEMA 3453;*** 1,2-cyclopentanedione, 3-ethyl-4-methyl-, *3-ethyl-4-methylcyclopentane-1,2-dione*

Identified by Nishimura and Mihara (1990) who gave a concentration of 1 ppm (MS data); sweet, maple-like.

The synthesis is described by Arnap *et al.* (1986) with the same method as for **D.72**.

(D.75) 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-5-methyl-, *3-ethyl-2-hydroxy-5-methylcyclopent-2-en-1-one* **[58228-72-1]; 1,2-cyclopentanedione, 3-ethyl-5-methyl-,** *3-ethyl-5-methylcyclopentane-1,2-dione* **[71608-11-2]**

(D.76) 2-Cyclopenten-1-one, 5-ethyl-2-hydroxy-3-methyl-, *5-ethyl-2-hydroxy-5-methylcyclopent-2-en-1-one* **[53263-58-4]** ***FEMA 3454;*** (tautomeric form of **D.75**)

These were identified in concentrations of 0.06 and 0.21 ppm respectively (MS data given) by Nishimura and Mihara (1990) who were apparently able to separate them by preparative TLC of the weakly acidic fraction of their steam distillate.

The synthesis was realized with the method used for **D.73** by Arnap *et al.* (1986) who could not separate the tautomers by HPLC.

Their odor description is sweet, malty at 1 ppm in water (Nishimura and Mihara, 1990).

(D.77) 2-Cyclopenten-1-one, 4-ethyl-2-hydroxy-3-methyl-, *4-ethyl-2-hydroxy-3-methylcyclopent-2-en-1-one* **[71387-71-8]; 1,2-cyclopentanedione, 4-ethyl-3-methyl-,** *4-ethyl-3-methylcyclopentane-1,2-dione*

0.21 ppm; sweet, malty

(D.78) 2-Cyclopenten-1-one, 2-hydroxy-3,4,4-trimethyl-, *2-hydroxy-3,4,4-trimethylcyclopent-2-en-1-one* **[86702-81-0]; 1,2-cyclopentanedione, 3,4,4-trimethyl-,** *3,4,4-trimethylcyclopentane-1,2-dione*

0.02 ppm; sweet, burnt.

(D.79) 2-Cyclopenten-1-one, 2-hydroxy-3,4,5-trimethyl-, *cis-*, cis-*2-hydroxy-3,4,5-trimethylcyclopent-2-en-1-one* **[125476-24-6]; (±)- [147770-78-3]; 1,2-cyclopentanedione, 3,4,5-trimethyl-,** *3,4,5-trimethylcyclopentane-1,2-dione*

0.01 ppm (IR and NMR data); sweet, maple-like; odor threshold 0.015 ppm in water.

(D.80) 2-Cyclopenten-1-one, 2-hydroxy-3,4,5- trimethyl-, *trans-*, trans-*2-hydroxy-3,4,5-trimethylcyclopent-2-en-1-one* **[125476-23-5]; (±)- [147770-84-1]; 1,2-cyclopentanedione, 3,4,5-trimethyl-,** *3,4,5-trimethylcyclopentane-1,2-dione*

0.1 ppm (IR and NMR data); sweet, milky; odor threshold 0.4 ppm in water.

(D.81) 2-Cyclopenten-1-one, 2-hydroxy-3,5,5-trimethyl-, *2-hydroxy-3,5,5-trimethylcyclopent-2-en-1-one* **[53263-56-2]; 1,2-cyclopentanedione, 3,5,5-trimethyl-,** *3,5,5-trimethylcyclopentane-1,2-dione*

0.21 ppm; sweet, caramel-like.

D.77 to **D.81** were identified (MS data given) by Nishimura and Mihara (1990) with the concentrations and odor descriptions at 1 ppm in water as indicated.

D.77 was prepared like **D.72** using diethyl 2-ethyl-4,5-dioxocyclopentane-1,3-dicarboxylate by Arnap *et al.* (1986). Nishimura and Mihara (1990) prepared **D.79** and **D.80** by formylation then reduction of **D.72**, followed by TLC and preparative GLC.

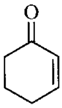
D.81 was obtained by selenium oxidation of 2,4,4-trimethyl-1-cyclopentanone (Gianturco and Friedel, 1963).

(D.82) 2-Cyclopenten-1-one, 2,3-dihydroxy-, *2,3-dihydroxy-cyclopent-2-en-1-one*, reductic acid **[80-72-8]**

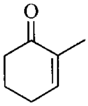
Identified in roasted coffee by Tillack and Maier (1999) while investigating reducing agents in roasted coffee.

It is one of the products formed in pyrolysis of cellulose, sugar, ascorbic acid (Kimoto *et al.*, 1993).

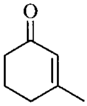
Cyclohexenones, cyclohexanedione and cyclohexenedione



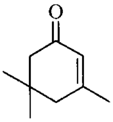
(D·83)



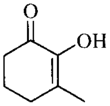
(D·84)



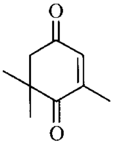
(D·85)



(D·86)



(D·87)



(D·88)

(D.83) 2-Cyclohexen-1-one, *cyclohex-2-en-1-one* **[930-68-7]**

Identified by Friedel *et al.* (1971) (MS and IR data given). Silwar *et al.* (1987) gave a concentration of 1.2–1.6 ppm.

The odor is powerful and diffusive, somewhat gassy-minty (Arctander, 1967).

(D.84) 2-Cyclohexen-1-one, 2-methyl-, *2-methylcyclohex-2-en-1-one* **[1121-18-2]**

Identified by Bondarovich *et al.* (1967) (UV data).

The flavor is green, camphoraceous, naphthalenic (Chemisis, 1968).

(D.85) 2-Cyclohexen-1-one, 3-methyl-, *3-methylcyclohex-2-en-1-one* **[1193-18-6]** *FEMA 3360*

Identified by Gianturco *et al.* (1963), then by Vitzthum and Werkhoff (1976b) in the neutral volatile compounds obtained after steam distillation at normal pressure.

It has a strong caramel-like odor (Shaw *et al.*, 1968). The flavor is described as shellfish-shrimp, iodine, phenolic, vanilla (Chemisis, 1998).

2-Cyclohexen-1-one, 4,5-dimethyl-, *4,5-dimethylcyclohex-2-en-1-one* **(*cis*- [194606-60-5]; *trans*- [194606-61-6])**

Tentatively identified by Elmore and Nursten (1990).

(D.86) **2-Cyclohexen-1-one, 3,5,5-trimethyl-,** *3,5,5-trimethylcyclohex-2-en-1-one*, 1,1,3-trimethyl-3-cyclohexen-5-one, isophorone **[78-59-1]**

Identified by Cantergiani *et al.* (2001) in a green Mexican arabica, representing 0.35% of the volatiles (GC).

(D.87) 2-Cyclohexen-1-one, 2-hydroxy-3-methyl-, *2-hydroxy-3-methylcyclohex-2-en-1-one* **[3400-78-0]; 1,2-cyclohexanedione, 3-methyl-,** *3-methylcyclohexane-1,2-dione* **[3008-43-3]** *FEMA 3305*

Identified by GC/IR by Gianturco *et al.* (1963) (UV data given).

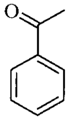
Prepared by the method of Wallach (1916) (1924).

The flavor is saffron, burnt, chemical (Chemisis, 1967).

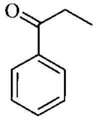
(D.88) **2-Cyclohexene-1,4-dione, 2,6,6-trimethyl-,** *2,6,6-trimethylcyclohex-2-ene-1,4-dione*, 3,5,5-trimethyl-2-cyclohexene-1,4-dione, 4-oxoisophorone **[1125-21-9]**

Identified by Cantergiani *et al.* (2001) in a green Mexican arabica, representing 0.25 % of the volatiles (GC). It has a floral, slightly oily flavor (Chemisis, 1974).

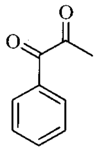
Aromatic ketones



(D·89)
(D·89)



(D·90)



(D·91)

(D.89) ***(D.89)*** 1-Ethanone, 1-phenyl-, *acetophenone, methyl phenyl ketone*, acetylbenzene, hypnone **[98-86-2]** ***FEMA 2009***

Identified in headspace of green coffee by Gutmann *et al.* (1979), in ground and instant commercial coffees by Elmore and Nursten (1990) (headspace after 5 min at 65 °C), in a brewed arabica by Ramos *et al.* (1998) only after their extraction with supercritical CO_2 (other extractions, see **D.45A**). For Cantergiani *et al.* (2001), it represented by GC 0.29 % of the volatiles (vacuum hydrodistillation, extraction) in a green Mexican arabica.

(D.90) 1-Propanone, 1-phenyl-, *1-phenylpropan-1-one, ethyl phenyl ketone*, propiophenone, propenoylbenzene **[93-55-0]** ***FEMA 3469***

Identified by Stoll *et al.* (1967).

(D.91) 1,2-Propanedione, 1-phenyl-, *1-phenylpropane-1,2-dione, methyl phenyl diketone*, benzoyl methyl ketone, acetylbenzoyl **[579-07-7]** ***FEMA 3226***

Identified by Stoll *et al.* (1967).

The odor is powerful, warm-floral, moderately pungent-herbaceous of rather poor tenacity (Arctander, 1967), and the flavor buttery, fatty fried (Chemisis, 2000).

Compounds containing ketone and other functions are described in Sections 5.E (acids), 5.H (phenols), 5.I (furans), 5.J (thiophenes), 5.K (pyrroles), 5.L (oxazoles), 5.M (thiazoles), 5.N (pyridines), 5.O (pyrazines), 5.P (amines), 5.Q (sulfur compounds).

5.E ACIDS AND ANHYDRIDES

Acids present in coffee can be divided into two classes:

(i) The volatile flavor constituents which can be identified, without derivatization, by GC, and are indexed in reference tables of the TNO-CIVO type. The data of TNO-tables show that acids are present in relatively high concentrations, of the same order as furfuryl alcohol, furfuraldehyde and 5-methylfurfuraldehyde. The acids are essentially aliphatic, arbitrarily limited to a C_{16}-chain length (free fatty acids with chains up to C_{24} have also been identified). Two lower aromatic acids (benzoic and phenylacetic acids) are also included in this class. In this review, we limit the number of 'volatile acids' to 28 structures. In fact, the analytical results concerning this group are relatively restricted compared with the literature on non-volatile acids.

(ii) The less volatile, or non-volatile, acids which are not considered or mentioned as aroma constituents. They contribute more to the quality of the taste than to the smell part of the 'flavor'.

For this functional group we will mention the non-volatile members, nevertheless excluding the chlorogenic acids (Section 2.1.4) and the phenolic compounds resulting from their degradation during roasting (Section 5.H).

The pioneers, such as Lampadius (1832) and Robiquet and Boutron (1837a), suspected the presence and identity of volatile acids by smell and by simple intuition. The early isolation and identification of non-volatile crystalline members, such as quinic acid (**E.62**), was indeed facilitated by their crystallization (Payen, 1846a). At the end of the Nineteenth century the precipitation techniques as in the formation of mercury, silver, calcium or barium salts, were used, for instance by Hlasivetz (1867) for caffeic acid (**H.86**), Bernheimer (1880a), Jaeckle (1898) and Erdmann (1902a). Later, Reichstein and Staudinger (1926a,b) systematically and very efficiently applied the measurement of the melting points of crystalline derivatives (quoted in Reichstein and Staudinger, 1955a). After a somewhat lean period of 30 years, LC and GC techniques appeared and in 1956 the 'Golden Age' of flavor chemistry began, marked by an increase in the number of original identifications, particularly in the coffee domain.

Using partition chromatography on a silicic acid column, Mabrouk and Deatherage (1956) determined the organic acids in five coffee extracts. Such a column does not normally separate the volatile acids, nevertheless, acetic acid was found to represent 0.59% of the total acid content, far away from the predominant non-volatile acid, chlorogenic acid, which represents 66.7% of the total organic acids. Also present in higher proportions than acetic acid were the non-volatile citric acid (**E.57**), 7.7%, malic acid (**E.53**), 7.2%, and tartaric acid (**E.55**), 6.2%. Oxalic acid (**E.42**) and pyruvic acid (**E.38**) were quantified.

Clements and Deatherage (1957) pointed out that the presence of volatile acids would be of particular significance, since they exhibit characteristic flavors in addition to their acidic properties, and contribute significantly to the characteristic coffee aroma. The titration curves, similar for acids from roasted and green coffee (obtained by chromatography on buffered silicic acid), compared with curves obtained for known acids confirmed the identification of acetic acid (**E.2**), propanoic acid (**E.3**), butanoic acid (**E.4**), and pentanoic acid (**E.5**). The presence of these simple compounds seems to be necessary to ensure the stability and the particular flavor of some other important constituents, presumably because of salt or ester formation. After treatment with diazomethane and using one of the first gas chromatographs constructed by Dr E.Palluy, in the Firmenich laboratories, Gautschi (1958) confirmed, probably for the first time with a GC technique, the identification of nine lower aliphatic acids. This approach followed the invention of James and Martin (1952) who had applied this revolutionary and efficient technique to the separation and micro-estimation of volatile fatty acids from formic to dodecanoic acids.

Lentner and Deatherage (1959) used partition chromatography on silica gel for quantitative evaluation of organic acids during roasting. They mentioned the suggestion by Kaufman (1951) that the changes in acid content were due to the formation and volatilization of acetic acid from the decomposition of sugars, decarboxylation of acids formed by rearrangement of sugars and decarboxylation of chlorogenic acid, thus explaining why the pH of coffee brews reaches a minimum with a light roasted coffee. The optimum roast is often considered to terminate shortly after the pH of the water extract begins to increase. In a heavy roast, approximately 50% of the original chlorogenic acid is destroyed.

Schormüller *et al.* (1961) reviewed the literature of acids identified in some coffee substitutes (raw and roasted rye, barley and chicory) and coffee. They quantified the lower aliphatic acids (C_1–C_6 and C_8) and also the non-volatile acids in a commercial coffee extract: lactic acid (**E.30**), succinic acid (**E.44**), malic acid (**E.53**), tartaric acid (**E.55**), citric acid (**E.57**), fumaric acid (**E.47**), α-oxoglutaric (**E.56**) and pyruvic acid (**E.38**), finding citric acid in a much higher proportion than the other non-volatile acids. Apparently, lactic, succinic, fumaric and α-oxoglutaric acids were found for the first time (lactic acid was in fact identified by Gorter in 1910, in the fermentation products of coffee). However, they mentioned as certain the identification of non-volatiles, such as oxalsuccinic acid, hydroxypyruvic acid, phenylpyruvic acid, α-oxovaleric acid, α-oxocaproic acid, oxalacetic acid, mesoxalic acid and β-mercaptopyruvic acid in green or roasted coffees, while these acids had only be used as reference compounds. In fact, the study by paper chromatography of the 2,4-dinitrophenylhydrazine derivatives of the acidic carbonyl compounds in roasted coffee (Clements and Deatherage, 1957) is somewhat confusing and the authors could not draw definite conclusions from their results. Radtke *et al.* (1966b) identified low volatile carbonyl constituents by paper chromatography and the most volatile fatty acids of roasted coffee (up to C_6) by a remarkable GC separation, but without any new identifications.

Analytical work on the acid content of raw and roasted coffees was published by von Werner and Kohley (1965a,b,c), but mainly on the chlorogenic acids.

By NMR and GC, Kung *et al.* (1967) determined the volatile acids (C_1 to C_{10}) in coffee beverages. They examined the difference in acid concentration between medium- and dark-roasted coffees (Columbian, Santos, robusta) and observed that, in general, the dark roasts were lower in volatile acids than were the medium roasts, and robusta coffee had the highest volatile acid content. They confirmed the predominance of the non-volatile acids.

Woodman *et al.* (1968) developed a gravimetric method (by means of the sodium salts) for determining the total carboxylic acids present in infusions of Santos coffee. This quantity increased with the degree of roasting, a consequence of the destruction of phenolic acids. From the 12 identified acids, eight were said to be reported for the first time in coffee: 2-furoic acid (**I.103**) (see Section 5.I), mesaconic acid (**E.50**), fumaric acid (**E.47**), citraconic acid (**E.51**), itaconic acid (**E.52**), lactic acid (**E.30**), succinic acid (**E.44**) and maleic acid (**E.48**). In fact, fumaric, lactic and succinic acids were mentioned by Schormüller *et al.* (1961) (see above).

In an attempt to correlate the chemical changes that occur during roasting with the formation of non-volatile flavors, Feldman *et al.* (1969) reviewed the chemical composition of green and roasted coffee. Generally, all acids decreased with increased roasting time. The differences in concentration of volatile acids were relatively low and the differences between varieties were slight. In any case, these lower acids are not the major contributors to the acidity in the coffee brew. Their total represents only 0.39–0.45% of the dry roasted coffee beans.

Sivetz (1972) examined how acidity affects coffee flavor. He estimated that very little data, and that of doubtful accuracy, have been published relating pH of coffee beverages to acid taste and reviewed the factors affecting acidity: botany, altitude, processing, age of the beans and degree of roasting. From the concentrations in the beverage and the respective dissociation constants of acids, he calculated the hydrogen ion dissociations. The fact that acetic acid (**E.2**) is only 7% dissociated, whereas the corresponding value is 98% for tartaric acid (**E.55**), 95% for citric acid (**E.57**) and 50% for malic acid (**E.53**) explains the organoleptically important contribution of non-volatile acids: to increase the hydrogen ion concentration by 25% or to reduce the pH by 0.10, either four times the calculated amount of acetic acid or much less of a more highly dissociated acid must be used. The author measured the pH of beverages prepared from various commercial brands of coffee extract: for spray-dried extracts it varied between 4.77 and 5.05; for freeze-dried types it fluctuated between 4.75 and 5.22. Professional tasters could distinguish 0.025 pH units between cups of coffee beverage, considering that those below pH 4.90 were too acid-tasting and those above pH 5.20 were too flat-tasting.

In a review of components of green and roasted coffee, Vitzthum (1976) gave a list of the 33 carboxylic acids (purely aliphatic) identified at that time.

Blanc (1979) considered that the organoleptic influence of carboxylic acids in coffee was undeniable but that numerous difficulties continue to exist concerning their quantitative evaluation. He used specific enzymic methods to determine the contents of citric acid (**E.57**), malic acid (**E.53**), lactic acid (**E.30**), pyruvic acid (**E.38**) and acetic acid in aqueous extracts of roasted coffees over a range of different degrees of roasting. He asserted that the assembly of these five acids represented the main part of the aliphatic carboxylic acid fraction.

Maier *et al.* (1984) and Engelhardt and Maier (1985b) studied the contribution of individual acids to the sour taste of coffee beverages: 22 acids contributed 93% (roast coffee) and 75% (coffee extract) to the titratable acidity of the beverage, the main contributors being acetic and citric acids. Only citric acid is present above its threshold value for sour taste in roast-coffee beverages, while acetic acid nearly reaches its threshold value. The high-molecular-weight acids and malic acid also participate appreciably as contributors to acidity. All other acids are present in small amounts (below 3% each) but they probably also contribute to the sour taste of coffee beverages.

In Chapter 8 of Volume 1 of *Coffee Chemistry*, edited by Clarke and Macrae (1985), Woodman (1985) reviewed the role of carboxylic acids in coffee infusions and the importance of acidity to taste and flavor. The acid content of green coffee, roasted coffee and dried coffee extracts were also discussed. The author observed that lightly roasted samples developed a 'fine' acidity which is 'clean' and 'quick off' the palate, but darkly roasted qualities show little or no acidity so that the desirable bitterness is perceived as a pure state, thus confirming that, in general, the darker the roast, the lower the acid content. Woodman considered that the aliphatic carboxylic acids, which are present only in very small or trace amounts, have not been exactly quantified whereas they contribute significantly to the quality of the beverage. Non-volatile acids are, on the contrary, reported by most workers as being present in more significant amounts. They play an important role in the very complex organoleptic mechanisms: undissociated acids contribute to the aroma, the aroma to the flavor, and the hydrogen ions to the acidity. The patent literature showed that there was interest within the industry in modifying the acidity in order to improve some of the finest flavor notes. Woodman also mentioned that a number of acids reported to be present in coffee have characteristic flavors, most of the lower aliphatic acids having thresholds in aqueous solutions of 4 to 8 ppm, such as 2-methylbutanoic acid (**E.16**), 2-methylpentanoic acid (**E.19**) and 2-ethylbutanoic (**E.18**) acid.

According to Clinton (1986), the acids present in a coffee beverage can be classified in the following decreasing quantitative order: quinic, acetic, citric, malic, phosphoric, formic, glycolic, lactic and oxalic. Van der Stegen and van Duijn (1988) presented a simple routine analysis for aliphatic ('normal') acids (those previously quoted, without phosphoric and oxalic, and plus succinic). The three predominant acids are citric (**E.57**), malic (**E.53**) and quinic (**E.62**), the first two decreasing upon roasting. The authors found that a brew turned acid when it was kept at a high temperature, and that there is a parallel between the increase in titratable acidity and the increase in the content of eight of these acids.

Hughes and Thorpe (1987) used capillary GC to obtain high-resolution profiles of 27 organic acids in roasted and ground coffee. Nanogram detection limits were achieved, but volatile aliphatics, such as formic and acetic acids could not even be determined, the method being more efficient for the quantification of quinic acid (**E.62**), C_{16} and C_{18} fatty acids, sucrose and caffeoylquinic (chlorogenic) acids (3-, 4-, and 5-CQA). Nevertheless, from the given qualitative organic acid profile, they identified heptanedioic acid (pimelic acid) in small amounts, among the aliphatic acids in addition to the already known diacids.

A summary of results on acids of coffee has been done by Maier (1987, 1988). Acids are responsible for about 11 % of the weight of green coffee, for 6 % of that of roasted coffee and for 16 % of that of coffee extracts. A good scheme for the determination of the various types of acids was given. During roasting the content of minor acids and of fumaric (**E.47**) and mesaconic (**E.50**) acids first increased, but content of citraconic (**E.51**), itaconic (**E.52**), maleic (**E.48**) and succinic (**E.44**) acids decreased (possibly because of isomerization for the three unsaturated acids). In coffee infusions, the acids content increased with temperature and time, a phenomenon explained by the hydrolysis of the esters and lactone (G.15) of quinic acid (**E.62**), (−)-isomer shown). As a rule, the acid-rich arabicas are considered to be specially valuable in contrast to the low-acid robustas, but the sum of acids in green beans is a little higher in robustas than in arabicas, in contrast to the taste of the beverage made of the roasted coffees. The greater intensity of acid taste in arabicas could be due to three factors: the higher content of acids in roasted beans, the somewhat higher proportion of free acid groups, and the greater sensory effectiveness of the prevailing individual acids. Maier calculated the sensory effective part of acids in several samples of robusta and arabica commercial blends and coffee extracts. In all groups, acetic, citric and malic acids were the most important for the acid taste. It is astonishing that quinic, formic and chlorogenic acids, present in relatively large amounts, do not contribute much to the acid taste. The concentrations of acetic and citric acid in coffee are near their threshold values, those of malic and phosphoric acid at one-half of these, the concentrations of the other acids even lower. In a very interesting series of publications, Maier's group (Scholz and Maier, 1990; Scholz-Böttcher and Maier, 1992; Scholz-Böttcher *et al.*, 1991) described the identification of six quinic acids (five new in coffee) and seven lactones (six new) at different degrees of roast. They show that if the isomer (**E.62**), already present in green coffee, kept a rather constant concentration decreasing only slightly at dark roast, the content of the other isomers increased constantly, although remaining well below that of (**E.62**). They found similar evolution for the lactones (except that the lactone corresponding to the main acid first increased quickly, being absent in green coffee) and tried to establish a relationship between isomerization and degree of roast.

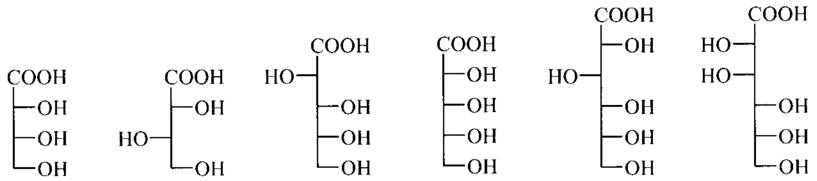
According to Holscher *et al.* (1990), volatile aliphatic acids are potent aroma compounds which contribute to the sweaty, fermented notes of roasted Colombian coffee, but among the 72 volatile compounds identified in the headspace gas of brewed coffee, Shimoda and Shibamoto (1990a) did not detect any acid.

Hills *et al.* (1991) applied simultaneous supercritical fluid extraction to roasted coffee beans. This technique can be used with or without a derivatizing reagent: 'In a dissociative mechanism, the adsorbed analyte must first desorb from a matrix active site and be dissolved in the supercritical fluid and then react to form the less polar derivative, which favors solvation in the supercritical carbon dioxide. In the associative mechanism, derivatization occurs while the analyte is adsorbed on the active site of the matrix. Reaction with the adsorbed analyte results in the desorption of the non-polar derivative into the supercritical fluid'. Thus 2-hexenedioic acid (**E.49**) was identified for the first time as a native compound (without the use of a derivatizing agent). Benzenic and furanic compounds and caffeine were also identified.

In 1997, Clark and Bunch quantified the short-chain volatile acids in tobacco, tea and coffee, using derivatization, purge and trap gas chromatography, and selected ion monitoring mass spectrometry (SIMMS). The authors estimated that these $C_1 - C_8$ organic acids contributed significantly to the aroma and taste. In the headspace analyses of green coffees of various origins (six arabicas and six robustas) and of a roasted arabica, Procida *et al.* (1997) did not find any acid. Ramos *et al.* (1998) compared several methods with a view to obtaining an extract with an aroma similar to original brewed coffee: liquid–liquid extraction with pentane or methylene chloride, headspace after solid-phase microextraction, extraction with supercritical CO_2. C_6, C_7, C_8 and C_{10}-acids were only identified after solid-phase microextraction.

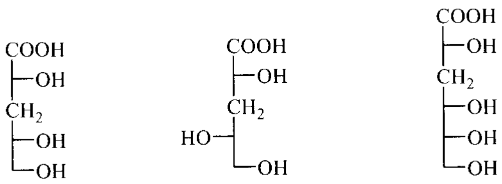
Maier (1993) quoted the work of Hughes and Thorpe (1987) (see above) on the identification of non-volatile acids, among them ascorbic acid which was in fact only a reference compound in this publication. In 1997, Maier's research group published a series of articles on the volatile minor acids in green and roasted coffee (Wöhrmann *et al.*, 1997a), in steam-treated coffee (Schröder *et al.*, 1997), and in chicory roots and barley malt (Wöhrmann *et al.*, 1997b). They confirmed (Wöhrmann *et al.*, 1997a) that the most abundant volatile acids in coffee were acetic and formic acids, but were especially interested in the rancid/sweaty smelling compounds previously mentioned by Schnabel *et al.* (1988), Karl *et al.* (1992) and Holscher *et al.* (1990). They determined the content of volatile acids by means of simultaneous distillation/extraction, ion exchange and GC/FID, the identification of the compounds being made with GC/MS using electron impact (EI) and chemical ionization (CI). By this method they identified 15 aliphatic acids for the first time in green coffee (see Section 3.1) and five in roasted coffee, *inter alia* 3-methylpentanoic (**E.20**) and 2-ethylhexanoic (**E.22**) acids. The authors also observed that the figures they found for the concentrations were much lower than most of the literature values. Most of the contents increase with the degree of roasting, particularly propanoic (**E.3**), 3-methyl-2-butenoic (**E.28**), 3-methylbutanoic (**E.17**), butanoic (**E.4**) and (*E*)-2-butenoic (**E.23**) acids. Higher aliphatic acids (apart from decanoic acid) are less affected by the heating treatment. During storage at higher temperatures or/and high water content the quantities also increase. Schröder *et al.* (1997) started their procedure with water extraction and freeze drying of the alkaline solution. The values found for the volatile acids were higher than those of their colleagues starting with diethyl ether extraction. After roasting, steamed green coffee produced lower quantities of the volatile acids than unsteamed coffee, 3-methyl- (**E.17**) followed by (*S*)-2-methylbutanoic (**E.16**) acids being the best for detecting steam treatment. More recently, the same group (Maier *et al.*, 1999) tested the validity of this conclusion on instant coffees prepared from steam-treated (or decaffeinated) or untreated coffees. The content of 2- and 3-methylbutanoic acids in the treated samples were only 40–80 % of those of the untreated samples, and losses by the extraction amounted to 65–75 %.

Aldonic acids



erythronic threonic arabinonic (arabonic) ribonic gluconic mannonic

Deoxyaldonic acids



erythro-3-deoxypentonic *threo*-3-deoxypentonic 3-deoxyhexonic (3-deoxy-D-ribohexonic shown) (metasaccharinic)

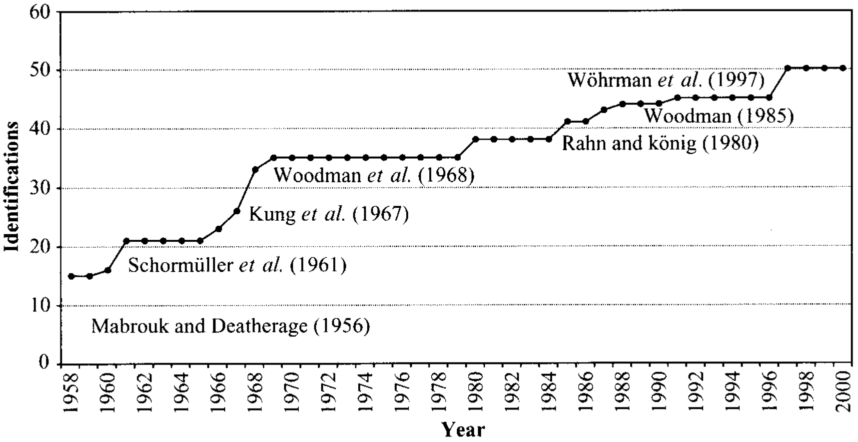


Fig. 5.5 Progressive identification of acids and anhydrides in roasted coffee volatiles

Using a new method of preseparation of acids, 'free flow field step electrophoresis', followed by GC of the trimethylsilyl derivatives, Bähre and Maier (1996, 1999) identified an impressive series of new non-volatile acids (including 5-hydroxymethyl-2-furancarboxylic acid, **I.104**). They analyzed steamed and unsteamed, green and roasted arabica coffees, as well as an espresso blend and an instant coffee. The lower members will be mentioned in our list but we give the names and structures of the higher carbohydrate-derived acids in a separate illustration (see p.149). On average, the contents of the acids increased slightly in green coffee by steam treatment and increased strongly by roasting even more in espresso quality) except for the aldonic acids after C_3, which are probably destroyed in the process. The content of deoxyaldonic acids ($> C_4$, the C_3 and C_4 will be treated with the other acids) increased drastically during roasting, from about 10 ppm in the green arabicas, steamed or not, to 160–190 ppm in the unsteamed roasted and 140–160 in the steamed roasted. However the authors concluded that a distinction between treated and untreated roasted coffees by analysis of the acids is not possible.

Volatile acids can be formed during the thermal degradation of sugars. After heating glucose, Heyns *et al.* (1966a) identified in particular formic and acetic acids, but also small quantities of the non-volatile levulinic (**E.41**) and pyruvic (**E.38**) acids. In the same reaction, Sugisawa (1966) also identified volatile acids and the non-volatile succinic (**E.44**), fumaric (**E.47**) and levulinic (**E.41**) acids. Some aliphatic acids (C_5 to C_{10}) can be formed by thermal oxidation of the long-chain fatty acids (Watanabe and Sato, 1971).

Long-chain fatty acids present in coffee flavor

It is often difficult to affirm that the presence of these fatty acids in the free state is due to roasting or to extraction techniques.

By 1844 Rochleder had already identified the acids C_{16} (palmitic, **E.14**) and $C_{18:1}$ (oleic) after saponification. Bengis and Anderson (1932b), after a study of the unsaponifiable matter of coffee-bean oil (Bengis and Anderson, 1932a) reviewed the work on fat from both raw and roasted coffee, finding that the available information was 'not only meager but in some cases conflicting'. They separated and quantified the fatty acids in green, fresh and stale-roasted coffee: $C_{18:2}$ (linoleic), 28–33 % of the total fatty-acid content, more important than $C_{18:1}$ (oleic), 23–26 %; in the saturated fatty acids, C_{16} (**E.14**) represents 31–37 % of the total fatty-acid content, well before C_{18} (stearic), 5–8 %,and C_{14} (myristic, **E.12**) about 2 %.

As coffee grounds are produced in enormous amounts by the soluble-coffee industry, they have presented a problem for industrial disposal. They have been considered as a potential source of protein, carbohydrate and also of oil with possible edible or other uses. Khan and Brown (1953) also presented a review of the previous work on coffee oil that they considered, like Bengis and Anderson (1932b) before them, to be 'meager and conflicting'. Their conclusion was that coffee oil contained excessive amounts of unusual unsaponifiables, which make the oil unfit for most uses. They separated and quantified the main fatty acids in coffee oil: $C_{18:2}$, 46%; C_{16}, 32%; $C_{18:1}$, 8%; C_{18} (stearic), 7.5%; $C_{16:1}$ (palmitoleic), 0.9%. Wohlers and Amato (1962) made a spectrophotometric determination of unsaturated fatty acids in two coffee oils. The percentages are rather in agreement with the preceding ones: 40% of $C_{18:2}$, 12–17% $C_{18:1}$, 0.8–1.4% $C_{18:3}$, the saturated acids representing 34% of the total. The fatty acids combined as glycerides in coffee oil were examined by Carisano and Gariboldi (1964) who measured the decreasing order of importance of $C_{18:2}$, C_{16} (**E.14**), much more important than $C_{18:1}$, C_{18}, C_{20}, (arachidic), $C_{18:3}$ (linolenic) and C_{22} (behenic) acids; traces of C_{14} (**E.12**), $C_{16:1}$, C_{17}. (margaric) and $C_{20:1}$ (gadoleic) acids were found as traces. These authors considered that the oil extracted from coffee grounds may be recommended for human nutrition but that it would be advisable, however, to eliminate first some of the saturated members, particularly hexadecanoic acid, by fractional crystallization.

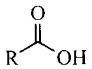
Rahn *et al.* (1979) and Rahn and König (1980a) identified C_{16}, C_{18}, C_{20} and C_{22} fatty acids, in the free state, in an arabica Nicaragua green coffee, by GC/MS after silylation. A review of the composition of lipids in green beans, including the fatty acids of triglycerides and other esters, was published by Folstar (1985) (see Section 2.1.3). Guyot *et al.* (1988a) examined a robusta coffee at different stages of ripeness. They concluded that the ratio $C_{18:1}$:C_{18}, increasing from 0.8–1.4–1.5, could constitute an important criterion of immaturity.

Speer *et al.* (1993) studied the fatty acids present in green and roasted coffees. Using gel permeation chromatography, they separated free and linked (triglycerides, diterpene esters) fatty acids, the content of the free acids in the lipids being slightly lower in arabica than in robusta green coffees, (respectively 1–1.5 and 1–2.7% of the lipid content). After GC of the methyl esters, the authors determined that nine fatty acids, from C_{14} to C_{24}, were similarly distributed in the two species, only oleic acid was in a higher proportion in robusta than in arabica (ratio oleic : stearic = about 2 and 1 respectively). The content decreased by about 20% during roasting. Roasting temperatures did not have a significant effect, and there were scarcely any changes in the distribution of the individual fatty acids. The decreasing order of the acids from C_{14} to C_{24} is very similar to the order given by Carisano and Gariboldi (1964). Only the $C_{18:2}$ (linoleic acid) content decreased slightly with the increase in the roasting temperature. After transesterification of the triglycerides and GC, the same fatty acids were found (with a similar distribution) and, as traces, $C_{16:1}$ (palmitoleic) and $C_{20:1}$. The odd-numbered acids, from C_{15} to C_{23}, were detected (C_{19} and C_{21} for the first time). The distribution was somewhat different in the esters linked to the diterpenes cafestol and 16-*O*-methylcafestol (Speer, 1995; Kurzrock and Speer, 1998, see Section 2.1.3). Palmitic acid (45–50%) is clearly dominant over oleic acid (20–30%).

Saturated aliphatic acids

(E.1) Methanoic acid, *formic acid* [64-18-6] *FEMA 2487*

Identified by Jaeckle (1898); confirmation by Prescott *et al.* (1937b) through the *p*-bromophenacyl ester. Found only in roasted coffee by Lentner and Deatherage (1959): from 0 mg per 100 beans at 300 °F (ca 150 °C) to nearly 40 mg per 100 beans at 425 °F (ca 220 °C). Woodman *et al.* (1968), then Feldman *et al.* (1969) reported a decrease from medium roast to dark roast: from 0.09–0.08% to 0.065–0.070% (in arabica Columbian and Santos respectively) and from 0.14 to 0.12% (in robusta), calculated on dry coffee basis. Van der Stegen and van Duijn (1988) found up to 0.14% (dry matter) in green arabicas, up to 0.39 in robustas, and 0.18–0.25 in commercial roasted coffee.



R = H **(E·1)**, CH_3 **(E·2)** ***(E·2)***, C_2H_5 **(E·3)** ***(E·3)***, C_3H_7 **(E·4)** ***(E·4)***,

C_4H_9 **(E·5)** ***(E·5)***, C_5H_{11} **(E·6)** ***(E·6)***, C_6H_{13} **(E·7)** ***(E·7)***, C_7H_{15} **(E·8)** ***(E·8)***,

C_8H_{17} **(E·9)** ***(E·9)***, C_9H_{19} **(E·10)** ***(E·10)***, $C_{11}H_{23}$ **(E·11)** ***(E·11)***,

$C_{13}H_{27}$ **(E·12)** ***(E·12)***, $C_{14}H_{29}$ **(E·13)** ***(E.13)***, $C_{15}H_{31}$ **(E·14)** ***(E·14)***

Estimated by Schormüller *et al.* (1961) at 1% (46 mg per 100 g) of the total acid content of an instant commercial coffee powder.

The odor is pungent with a stinging sensation on the mucous membranes. At dilutions below 50 ppm, the taste is sour without stinging or burning (Arctander, 1967).

(E.2) ***(E.2)*** **Ethanoic acid,** *acetic acid* **[64-19-7]** ***FEMA 2006***

Positively identified by Bernheimer (1880a) with confirmation by Prescott *et al.* (1937b) through the *p*-bromophenacyl ester. Mabrouk and Deatherage (1956) estimated its content at only 0.04% by weight of roasted coffee beans (0.59% of the total organic acids recovered from coffee extracts). Using chromatography with a column of buffered silicic acid, Clements and Deatherage (1957) gave an estimation of at least 0.3% by weight of the roasted coffee beans, approximately the same estimation being found by Kung *et al.* (1967) and Feldman *et al.* (1969) for medium and dark roast, arabica and robusta coffees. Lentner and Deatherage (1959) showed that the content of acetic acid, already present in green beans, increased by a factor of 3 during roasting, from 300 °F (about 150 °C) to 425 °F (about 220 °C). Vincent *et al.* (1976) noted a neat increase (headspace) in the concentration of acetic acid in unhealthy green beans compared with the healthy quality. Blanc (1979) observed that the formation of acetic acid, only present in trace quantities in green coffee, largely depends on the conditions of roasting. The content decreased with a high roasting, the maximum largely depending on the conditions of roasting (Woodman *et al.*, 1968), an observation also made by Scholze (1983). Van der Stegen and van Duijn (1988) found only traces in green arabicas, up to 0.2% (dry matter) in robustas, increasing to 0.36–0.55 in commercial roasted coffee. Acetic acid could be extracted from a brewed arabica by Ramos *et al.* (1998) using liquid–liquid extraction with methylene chloride, solid-phase microextraction or supercritical-CO_2 extraction.

In a commercial coffee extract, Schormüller *et al.* (1961) found that acetic acid represented 0.95% of the dry extract (20% of the total acid content).

The odor is pungent, stinging sour, unpleasant when concentrated, less repulsive below 15% in water (Arctander, 1967). Flavor threshold in water is 54 ppm for Patton (1964) and 22 ppm for Siek *et al.* (1969).

(E.3) ***(E.3)*** **Propanoic acid,** *propionic acid, propanoic acid* **[79-09-4]** ***FEMA 2924***

Identified after chromatography on buffered silicic acid and titration by Clements and Deatherage (1957) who estimated its concentration to 0.02% of their *standard* roasted coffee. Separated as free acid and methyl ester, by Gautschi (1958) using one of the first GC techniques. Identification confirmed by Zlatkis and Sivetz (1960). The estimations by Kung *et al.* (1967) and Feldman *et al.* (1969) were very similar for medium and dark roast, 0.005–0.01 % calculated on dry coffee beans for robusta and arabica coffees respectively. Found also in green coffee (Lentner and Deatherage, 1959), although said to be under the detection limit by Wöhrmann *et al.* (1997a) in green coffee and present at a mean concentration of 1.8 mg per 100 g (18 ppm) in roasted coffee.

Estimated by Schormüller *et al.* (1961) at 0.05% (22.2 mg per 100 g) of the total acid content in a commercial coffee extract.

The odor is reminiscent of sour milk, cheese or butter; the taste is sour in aqueous solution, pleasant at concentrations below 100 ppm in water and cheesy-sour at higher concentrations. (Arctander, 1967).

(E.4) *(E.4)* **Butanoic acid,** *butyric acid, butanoic acid,* *n*-butyric acid **[107-92-6]** ***FEMA 2221***

Identified together with the lower homologs by Clements and Deatherage (1957) who estimated its concentration as 0.01 % of roasted coffee; later identified by Meyer (1960) and quantified by Kung *et al.* (1967) and Feldman *et al.* (1969) as representing 0.005–0.0075 % calculated on dry coffee beans (medium to dark roast, arabica and robusta). Clark and Bunch (1997) measured its concentration in a 'commercial' coffee (ca 8 ppm) by derivatization (methyl ester) and GC/MS. Mentioned by Lentner and Deatherage (1959) as also being present in green beans, with a concentration increasing during roasting, from 2 mg per 100 beans at 300 °F (ca 150 °C) to 15 mg per 100 beans at 425 °F (ca 220 °C). Schröder *et al.* (1997) found 7 and 9 ppm respectively in a Kenya arabica coffee, steam-treated or not before roasting. Wöhrmann *et al.* (1997a) measured the mean concentrations in raw coffees at 0.45 ppm and at 3.5 ppm in roasted coffees, figures again much lower than most of the literature values. Ramos *et al.* (1998) found it only after extraction of a brew with supercritical CO_2 (compare with **E.2**). For Cantergiani *et al.* (2001), butanoic acid represented 0.19 % of the volatiles by GC after vacuum hydrodistillation and extraction of a green Mexican arabica.

Schormüller *et al.* (1961) estimated that butanoic acid constituted 0.7 % (350 ppm) of the total acid content of an commercial instant coffee powder.

Butanoic acid has a powerful, penetrating, diffusive sour odor, reminiscent of rancid butter (Arctander, 1967). It is in the list of potent odorants in raw arabica with a sweaty odor description (Czerny and Grosch, 2000). An odor threshold of 240 μg/l (0.24 ppm) in water is quoted by Teranishi (1971). A flavor threshold of 6.8 ppm in water is given by Patton (1964), and 6.2 ppm by Siek *et al.* (1969).

(E.5) *(E.5)* **Pentanoic acid,** *pentanoic acid,* valeric acid, *n*-valeric acid valerianic acid, propylacetic acid **[109-52-4]** ***FEMA 3101***

According to Reichstein and Staudinger (1926b) the acid identified by Erdmann (1902a) as 2-methylbutanoic acid was in fact pentanoic acid (in a later publication, 1955a, referring to Erdmann, they quote 'methyl ethyl acetic acid'). Clements and Deatherage (1957) estimated its concentration as 0.02 % of roasted coffee and also found it in green beans (see also Lentner and Deatherage, 1959). It was later confirmed in roasted coffee by Meyer (1960). Feldman *et al.* (1969) found only traces of pentanoic acid in arabica or in robusta. Ho *et al.* (1993) measured a concentration of 0.47 ppm in a roasted Columbian coffee and Clark and Bunch (1997) 0.7 ppm in a 'commercial' sample. Schröder *et al.* (1997) found 2.5 and 3 ppm in a Kenya arabica, steamed or not before roasting. Wöhrmann *et al.* (1997a) measured mean concentration of 0.45 ppm in raw and 0.6 ppm in roasted coffee, values close to previous results. Cantergiani *et al.* (2001) also identified it in a green Mexican arabica extract (0.36 % of the volatiles by GC).

Pentanoic acid constitutes 0.9 % (40.8 mg per 100 g) of the total acid content of an instant commercial coffee powder (Schormüller *et al.*, 1961).

It has a very powerful and penetrating, diffusive, acid odor, pungent when undiluted, but more unpleasant when diluted. In fact it becomes more animal- and perspiration-like in dilution. Only in extreme dilution does the odor become again more pleasant, fruity, warm. Below 10 ppm, the taste is rather fruity, but at higher concentrations, the odor develops and it becomes more unpleasant (Arctander, 1967). For Czerny and Grosch (2000), it is one of the potent odorants in green coffee with a sweaty odor description.

(E.6) *(E.6)* **Hexanoic acid,** *hexanoic acid*, hexylic acid, caproic acid **[142-62-1]** ***FEMA 2559***

Identified by Meyer (1960). For Kung *et al.* (1967) and Feldman *et al.* (1969), the concentration varied between 7 and 19 ppm in medium and dark-roasted arabicas, being slightly higher for robusta. Clark and Bunch (1997) measured 1.5 ppm, a value similar to that of Wöhrmann *et al.* (1997a) who found mean concentrations of 1.6 ppm in raw coffee and 1.5 in roasted coffee. Ramos *et al.* (1998) found hexanoic acid only after solid-phase microextraction of a brew (compare with **E.2**). For Cantergiani *et al.* (2001), this acid represented 2.71 % of the volatiles (GC) in a green Mexican arabica (vacuum hydrodistillation and extraction)

Schormüller *et al.* (1961) found that the total acid content of a commercial coffee extract contained 1 % (46.4 mg per 100 g) of hexanoic acid.

Hexanoic acid has an heavy, acrid-acid, fatty-rancid odor, often described as sweat-like (Arctander, 1967).

Patton (1964) gives a flavor threshold of 5.4 ppm in water and Siek *et al.* (1969) of 15 ppm.

(E.7) *(E.7)* **Heptanoic acid,** *heptanoic acid*, heptylic acid, enanthic acid, oenanthic acid **[111-14-8]** ***FEMA 3348***

Identified by Kung *et al.* (1967) and its concentration evaluated on a dry coffee basis at 60–100 ppm in roasted Columbian and Santos coffees, 30–40 ppm in a robusta. Also identified in green coffee by Wöhrmann *et al.* (1997a) who measured mean concentrations of 0.34 ppm in green and 0.45 in roasted coffee but it was not detected by Clark and Bunch (1997). Ramos *et al.* (1998) found it in a brewed arabica after solid-phase microextraction (see **E.2**) and Cantergiani *et al.* (2001) in a green Mexican arabica (0.61 % of the volatiles by GC).

Purified heptanoic acid has a fatty odor (Arctander, 1967). The flavor is fatty, nutty, fruity, weak (Chemisis, 1991).

(E.8) *(E.8)* **Octanoic acid,** *octanoic acid*, octylic acid, caprylic acid (2-ethylhexanoic acid is sometimes also called caprylic acid) **[124-07-2]** ***FEMA 2799***

Found by Kung *et al.* (1967) at concentrations of 2.2 and 2.8 ppm respectively in medium and roasted Columbian coffee, 16 and 32 in a Santos, 6 and 8 in a robusta. Clark and Bunch (1997) gave a concentration of 6.75 ppm. Wöhrmann *et al.* (1997a) measured mean concentrations of 0.55 in raw and 0.64 ppm in roasted coffee. It was found by Ramos *et al.* (1998) in a brew only after the solid-phase microextraction (see **E.2**) and by Cantergiani *et al.* (2000) in a green Mexican arabica (by GC, 0.24 % of the volatiles).

Schormüller *et al.* (1961) had previously identified octanoic acid in a commercial coffee powder (28.8 mg per 100 g = 0.6 % of the total acid content).

The odor is oily-rancid, sweat-like, repulsive even in dilution of less than 0.1 % acid. Below 50 ppm the taste is burning, rancid, but cheesy-sour at lower concentrations (Arctander, 1967).

Patton (1964) gives a flavor threshold of 5.8 ppm in water.

(E.9) ***(E.9)*** **Nonanoic acid,** *nonanoic acid,* nonylic acid, pelargonic acid **[112-05-0]** ***FEMA 2784***

Identified by Kung *et al.* (1967) who gave concentrations of the order of 10 ppm in roasted coffee. Wöhrmann *et al.* (1997a) measured mean concentrations of 0.75 ppm in green coffee and 0.51 in roasted coffee. It is mentioned by Cantergiani *et al.* (2001) in a green Mexican arabica (0.12 % of the volatiles by GC).

Nonanoic acid has a mild nut-like, fatty and acid odor. The taste is waxy-nut like, and slightly brandy-like, not sour in extreme dilution (Arctander, 1967).

(E.10) ***(E.10)*** **Decanoic acid,** *decanoic acid,* decylic acid, capric acid, caprinic acid **[334-48-5]** ***FEMA 2364***

Identified by Kung *et al.* (1967) who found concentrations of the order of 10 ppm. It was identified in green coffee by Wöhrmann *et al.* (1997a) who measured mean concentrations of 0.27 ppm in green and 0.55 in roasted coffee. Ramos *et al.* (1998) found it in the brew of an arabica only after the solid-phase micro-extraction (see **E.2**) and Cantergiani *et al.* (2001) in a green Mexican coffee (0.09 % of the volatiles by GC).

Decanoic acid is rather unpleasant and has a sour-fatty, rancid odor (Arctander, 1967).

Patton (1964) finds a flavor threshold of 3.5 ppm in water.

(E.11) ***(E.11)*** **Dodecanoic acid,** *dodecanoic acid,* dodecylic acid, lauric acid, **[143-07-7]** ***FEMA 2614***

(E.12) ***(E.12)*** **Tetradecanoic acid,** *tetradecanoic acid,* 1-tridecanecarboxylic acid, myristic acid **[544-63-8]** ***FEMA 2764***

(E.13) ***(E.13)*** **Pentadecanoic acid,** *pentadecanoic acid,* pentadecylic acid **[1002-84-2]**

These three acids were identified by Wöhrmann *et al.* (1997a) who measured the concentrations in green and roasted coffees, respectively 0.33, 6.9, 0.38 ppm in green and 0.45, 7, 2.7 in roasted coffee. Tetra- and pentadecanoic acid were also found by Cantergiani *et al.* (2001) in a green Mexican arabica, after vacuum hydrodistillation and extraction (0.64 and 0.58 % of the volatiles by GC).

Dodecanoic and tetradecanoic acids are almost odorless when purified. The flavor is fatty, weak for (**E.11**) (Chemisis, 1998).

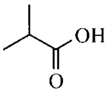
(E.14) ***(E.14)*** **Hexadecanoic acid,** *hexadecanoic acid, palmitic acid,* cetylic acid **[57-10-3]** ***FEMA 2832***

Identified probably as glyceride, after saponification by Rochleder (1844). Identified by Reichstein and Staudinger (1926b). It is the second main fatty acid (after $C_{18:2}$) found in oil of green and roasted coffee, free and combined as glyceride (Carisano and Gariboldi, 1964; Speer *et al.*, 1993). It is the main acid in coffee wax (Folstar, 1985, in *Coffee* Volume 1, *Chemistry*, 1985). Its proportion was about $\frac{1}{3}$ of the fatty acids present. Palmitic acid was found by Cantergiani *et al.* (2001) in the analysis of green Mexican coffee (2.59 % of the extract by GC).

It is virtually odorless and has a bland taste (Arctander, 1967).

(E.15) ***(E.15)*** **Propanoic acid, 2- methyl-,** *isobutyric acid, 2-methylpropanoic acid,* isobutanoic acid **[79-31-2]** ***FEMA 2222***

Identified by Gautschi (1958) as the methyl ester, by Radtke (1964) and by Gianturco *et al.* (1966). With efficient GC conditions, Radtke *et al.* (1966b) found its presence more important than that of butanoic acid in a roasted Costa Rica coffee. For Clark and Bunch (1997), its concentration was 5.11 ppm. Schröder *et al.* (1997) found values of approx. 1–5 ppm in roasted coffee whether it had been steam treated or not, depending on the extraction method. Wöhrmann *et al.* (1997a) measured mean concentrations of 0.88 ppm in green and 1.17 ppm in roasted coffee. This acid represents 0.36 % (by GC) of the volatiles in the analysis of green Mexican arabica by Cantergiani *et al.* (2001).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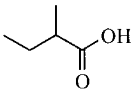
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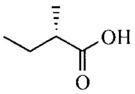
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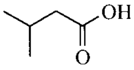
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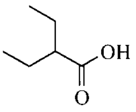
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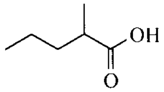
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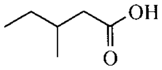
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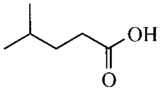
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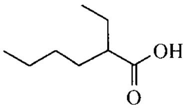

(E·22)

This product has a powerful, diffusive sour, acid odor, slightly less repulsive, and also less buttery than butanoic acid. In extreme dilution the odor becomes almost pleasant, fruity. The taste has a buttery-cheesy note (Arctander, 1967).

(E.16) ***(E.16)*** **Butanoic acid, 2-methyl-,** *2-methylbutanoic acid,* 2-methylbutyric acid, α-methylbutyric acid, methylethylacetic acid **[116-53-0]** ***FEMA 2695*****; (±)- [600-07-7]; (*R*)- [32231-50-8]; (*S*)- [1730-91-2]**

Identified probably by Erdmann (1902a) (see **E.5**). Gianturco *et al.* (1966) and Stoll *et al.* (1967) confirmed its identification. Silwar *et al.* (1987) gave a concentration of 2.5–4 ppm in a roasted arabica and Ho *et al.* (1993) gave 1.15 ppm in a Columbian coffee. Holscher and Steinhart(1995) found it in a green Columbian coffee, the sum of the 2- and 3-methyl isomers representing 3.2 ppm. (*R*)- and (*S*)-2-Methylbutanoic acids have been identified in green and in roasted coffee by Wöhrmann *et al.* (1997a) who estimated the mean concentration of the *(S)*-enantiomer in green coffee at 2.75 ppm and in roasted coffee at 4.5 ppm. Schröder *et al.* (1997) found concentrations of 3.17 or 7.2 ppm (depending on the extraction method) in a Kenya arabica steamed before roasting and 5.35 or 9.1 ppm in unsteamed sample.

This acid is formed by oxidation of the corresponding Strecker aldehyde (**C.12**). For Ho *et al.* (1993), it is generated by a Maillard reaction.

This acid has a particularly pungent and acrid odor reminiscent of Roquefort cheese and of other cheeses. The taste is acrid-acid but becomes fruity-sour below 10 ppm (Arctander, 1967). By GC-olfactometry, the odor perception, in the evaluation of the aroma of a roasted Columbian coffee, is sweaty, fermented; together with the 3-methyl isomer, the contribution to coffee flavor is very important (Holscher *et al.*, 1990). In the aroma of a green coffee, it is described as weak, fermented (Holscher and Steinhart, 1995). Karl *et al.* (1992) showed that the enantiomers have different odors, the (*R*)-isomer being cheesy and the (*S*)-isomer fruity.

(E.17) ***(E.17)*** **Butanoic acid, 3-methyl-,** *3-methylbutanoic acid,* 3-methylbutyric acid, *iso*-valerianic acid, *iso*-valeric acid **[503-74-2]** ***FEMA 3102***

Identified by Reichstein and Staudinger (1926b). Its presence (at a concentration more important than that of the other volatile acids) was unequivocally confirmed by Radtke *et al.* (1966b) and also mentioned by Maier (1987,1988). In a roasted Columbian coffee (adsorbent trapping/short-path heat desorption GC/MS), Ho *et al.* (1993) found a concentration of 0.96 ppm, much lower than the concentration of 113 ppm measured by Clark and Bunch (1997) in a 'commercial' coffee. 3-Methylbutanoic acid was identified in green coffee by Holscher and Steinhart (1995). According to Wöhrmann *et al.* (1997a) the mean concentration was 13 ppm in green and 21 ppm in roasted coffee. Schröder *et al.* (1997) found 16 or 34 ppm (depending on the extraction method) for an arabica steamed before roasting, and 26 or 41 ppm for an unsteamed sample. Cantergiani *et al.* (2001) found that it is the most abundant of the acids in the analysis of a green Mexican arabica, 6.83% of the volatiles by GC, after vacuum hydrodistillation and extraction (it has to be noted that in this analysis, the corresponding alcohol, **B.13**, is the most abundant of the aliphatic alcohols).

It is formed by oxidation of the corresponding Strecker aldehyde (**C.13**). For Ho *et al.* (1993), it is generated by Maillard reaction.

This compound is very diffusive, acid-acrid; in moderate dilution it has a cheesy, unpleasant odor. In extreme dilution the odor becomes more agreeable, herbaceous (Arctander, 1967). The odor perception by GC-olfactometry is strong, sweaty in roasted (Holscher *et al.*, 1990) and green Columbian coffee (Holscher and Steinhart, 1995). Together with the 2-methyl isomer, it makes an important contribution in coffee flavor.

Keith and Powers (1968) gave a threshold of 1.6 ppm in water.

(E.18) Butanoic acid, 2-ethyl-, *2-ethylbutanoic acid*, 2-ethylbutyric acid, diethylacetic acid **[88-09-5]** *FEMA 2429*

(E.19) Pentanoic acid, 2-methyl-, *2-methylpentanoic acid*, 2-methylvaleric acid **[97-61-0]** *FEMA 2754*; **(±)- [22160-39-0]; (*R*)- [49642-47-9]; (*S*)- [1187-82-2]**

These acids (without stereochemistry) were mentioned by Woodman (1985) as present in coffee but without reference of the discoverer.

E.18 has a oily-fruity odor and a fruity-earthy taste. (**E.19**) has an oily, herbaceous odor in extreme dilution; below 10 ppm the taste is pleasantly sour, and less pleasant at higher concentrations, with bite and acid (Arctander, 1967).

(E.20) *(E.20)* **Pentanoic acid, 3-methyl-,** *3-methylpentanoic acid*, 3-methylvaleric acid **[105-43-1]** *FEMA 3437*; **(±)- [22160-40- 3]; (*R*)- [16958-25-1]; (*S*)- [1730-92-3]**

Identified in green and roasted coffees by Wöhrmann *et al.* (1997a) who measured mean concentrations of 0.46 ppm in green and 1.1 in roasted coffee. For Clark and Bunch (1997) it represented 7.1 ppm in 'commercial' coffee.

This acid has a sour-pungent odor, in dilution sour herbaceous, slightly green. The taste is warm-herbaceous, pleasantly sour below 1 ppm (Arctander, 1967), also described as valerianic, apple, strawberry (Chemisis, 1973).

(E.21) Pentanoic acid, 4-methyl-, *4-methylpentanoic acid*, 4-methylvaleric acid, isohexanoic acid, isocaproic acid **[646-07-1]** *FEMA 3463*

This acid has been mentioned by Maier (1987) with oligo-acids non-detectable in all coffee samples.

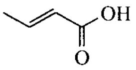
Unpleasant sour and penetrating odor; sour taste, slightly fruity at very low concentrations (Arctander, 1967). The flavor is also described as fruity-tropical, jam and berry (Chemisis, 1998).

(E.22) Hexanoic acid, 2-ethyl-, *2-ethylhexanoic acid* **[149-57-5]; (±)- [83829- 68-9]; (*R*)- [56006-48-5]; (*S*)- [72377-05-0]**

Identified in roasted coffee by Wöhrmann *et al.* (1997a) with a mean concentration of 0.17 ppm in roasted coffees, being below the detection threshold in green coffees.

The flavor is weak, fatty, herbal, green (Chemisis, 1976).

Unsaturated aliphatic acids



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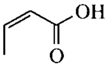

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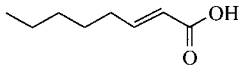

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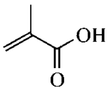

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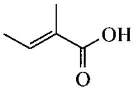

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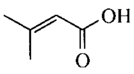

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(E.23) 2-Butenoic acid, (*E*)-, *(*E*)-but-2-enoic acid*, crotonic acid, *trans*-crotonic acid, *(E)*-crotonic acid, **[107-93-7]**; no stereochemistry **[3724-65-0]**

Identified by Gianturco *et al.* (1966). Wöhrmann *et al.* (1997a) found mean concentrations of 2.76 ppm in roasted coffees and below the detection limit in green coffees.

The flavor is very weak, mild, milky (Chemisis, 1991).

(E.24) 2-Butenoic acid, (*Z*)-, *(*Z*)-but-2-enoic acid*, isocrotonic acid, *cis*-crotonic acid, *(Z)*-crotonic acid **[503-64-0]**

Identified by Stoffelsma *et al.* (1968) (IR and MS data given).

(E.25) **2-Octenoic acid, (*E*)-,** *(*E*)oct-2-enoic acid* **[1871-67-6]; (Z)- [1577-96-4];** no stereochemistry **[1470-50-4]**

Identified by Cantergiani *et al.* (2001) in a green Mexican arabica (0.08 % of the volatiles by GC, after vacuum hydrodistillation and extraction).

The odor is green, fatty (Chemisis, 1986).

(E.26) *(E.26)* **2-Propenoic acid, 2-methyl-,** *methacrylic acid, prop-2-enoic acid*, 2-methylacrylic acid **[79-41-4]**

Identified by Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968) and in green coffee by Wöhrmann *et al.* (1997a) who measured mean concentrations of 1.52 ppm in roasted coffees and a maximum of 0.14 in green coffees.

(E.27) *(E.27)* **2-Butenoic acid, 2-methyl, (*E*)-,** *(*E*)-2-methylbut-2-enoic acid*, tiglic acid, *trans*-tiglic acid, 2,3-dimethylacrylic acid, (*E*)-2-methylcrotonic acid **[80-59-1]** *FEMA 3599*; undefined stereochemistry **[13201-46-2]**

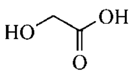
Identified in roasted coffee by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968). Wöhrmann *et al.* (1997a) found it in green coffee and measured mean concentrations of 1.95 ppm in roasted and 0.59 in green coffees.

It has a spicy-rooty odor; at about 50 ppm the taste is spicy-warm, slightly sour and only spicy-rooty below this concentration (Arctander, 1967).

(E.28) ***(E.28)*** 2-Butenoic acid, 3-methyl-, *3-methylbut-2-enoic acid*, 3,3-dimethylacrylic acid, senecioic acid **[541-47-9]** ***FEMA 3187***

Identified in roasted coffee by Gianturco *et al.* (1966). Maier (1987) did not find a reliable method and gave an approximate concentration of 500 ppm in roasted coffee, but Wöhrmann *et al* (1997a) measured mean concentrations of 7.25 ppm in green and 18.3 ppm in roasted coffees. Cantergiani *et al.* (2001) identified this acid in a green Mexican arabica (1.48 % of the volatiles by GC).

Hydroxy aliphatic acids



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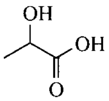

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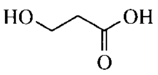

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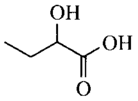

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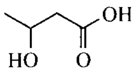

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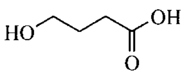

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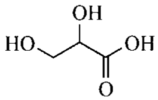

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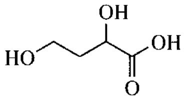

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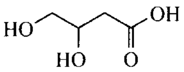

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(E.29) ***(E.29)*** **Acetic acid, hydroxy-,** *glycolic acid* **[79-14-1]**

Identified by Rahn and König (1980b) in arabica roasted coffees. The concentration increases at the beginning of the torrefaction as observed by Scholze (1983) and by Scholze and Maier (1984). It also increased if brews were maintained for 3 days at temperatures from 20 to 80 °C (Maier *et al.*, 1984) and it was estimated at 0.1–0.3 % of dry material (d.m.) in roasted coffee, but was not found in green coffee by Maier (1987). Van der Stegen and van Duijn (1988) had the same results, finding the presence of glycolic acid only in roasted coffee (0.17–0.49 % d.m.) with a slow increase if a brew was maintained at high temperature. In their analysis of steam-treated or untreated arabicas, Bähre and Maier (1996, 1999) found 4–5 ppm in untreated and 30–50 ppm in treated green arabicas, the content reaching 1100 and 870 ppm respectively after roasting. They used a preseparation of the acids by 'free flow field step electrophoresis' before GC of the trimethylsilyl esters.

It is carbohydrate derived.

(E.30) ***(E.30)*** **Propanoic acid, 2-hydroxy-,** *lactic acid* **[50-21-5]; (±)- [598-82-3]** ***FEMA 2611*** (the FEMA number corresponds to this RN but does not specify (±); **(+)-(*S*)- [79-33-4]**

Gorter (1910) observed the formation of lactic acid in the fermentation of a Liberia coffee. The acid was identified by Schormüller *et al.* (1961) in a commercial coffee extract (0.45 %, 9 % of the acid content), and the presence confirmed by Woodman *et al.* (1968). Feldman *et al.* (1969) mentioned a content of 0.055–0.09 % based on the dry coffee basis, for medium to dark roast arabica and robusta coffees. Blanc (1979) considered that the content of this acid, low in green beans (0.08–0.09 % of the dry material), only slowly increased to 0.10–0.16 % during roasting for Tanzania and Kenya arabicas. Van der Stegen and van Duijn (1988) could measure the content of lactic acid only in roasted coffee (0.0–0.18 % d.m.) with an increase if a brew was maintained at high temperature. Maier (1987) similarly found 0.1% in roasted coffee only. Bähre and Maier (1999), with their new method (see E.29), found 42–75 and 82–93 ppm respectively in untreated and steamed green arabicas (the higher level for the Kenyan, the lower for the Columbian), this content increasing to about 670 ppm in the roasted Kenyan arabica.

It is carbohydrate-derived.

Pure lactic acid is odorless; the taste is pleasantly acid in proper dilution (Arctander, 1967).

(E.31) *(E.31)* **Propanoic acid, 3-hydroxy-,** *3-hydroxypropanoic acid* **[503-66-2]**

Identified by Bähre and Maier (1996, 1999) (see **E.29**). The content increased from 4 (untreated) and 15 ppm (steamed) to 32–34 ppm after roasting of a Kenyan arabica.

Like the two previous hydroxy acids, it is derived from carbohydrates.

(E.32) *(E.32)* **Butanoic acid, 2-hydroxy-,** 2-hydroxybutyric acid **[565-70-8]**

Identified by Maier (1987, 1988) who measured a concentration of 0.1% in roasted coffee. Bähre and Maier (1999) detected it in traces in a green Kenyan arabica (steam treated or not), but found ca 50 ppm after roasting (see **E.29**).

(E.33) *(E.33)* **Butanoic acid, 3-hydroxy-,** *3-hydroxybutanoic acid,* 3-hydroxybutyric acid **[300-85-6]; (*R*)-[625-72-5]; (*S*)-[6168-83-8]**

Identified by Bähre and Maier (1999) (see **E.29**) with a content of 2–3 ppm in green arabicas and 5–7 after roasting.

(E.34) *(E.34)* **Butanoic acid, 4-hydroxy-,** *4-hydroxybutanoic acid,* 4-hydroxybutyric acid **[591-81-1]**

Identified by Bähre and Maier (1999) (see **E.29**). The low content of 2–5 ppm in green coffees increases by roasting to about 20 ppm, slightly more than that of the 3-hydroxy isomer (**E.33**).

(E.35) *(E.35)* **Propanoic acid, 2,3-dihydroxy-,** *2,3-dihydroxypropanoic acid,* glyceric acid **[473-81-4];** (R)-**[6000-40-4];** (S)-**[28305-26-2]**

Identified by Bähre and Maier (1996, 1999) who found 7 and 20–30 ppm respectively in untreated and steamed green arabicas, and about 155 ppm in the two qualities after roasting (see **E.29**).

It is derived from carbohydrates, as are the two following isomers.

(E.36) *(E.36)* **Butanoic acid, 2,4-dihydroxy-,** *2,4-dihydroxybutanoic acid* **[1518-62-3]; (*R*)-[157543-57-2]; (*S*)-[62445-25-4]**

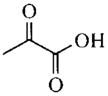
Identified by Bähre and Maier (1996, 1999) (see **E.29**). The content of 1 ppm in a green Kenya arabica (steamed) reaches 32 ppm after roasting.

(E.37) *(E.37)* **Butanoic acid, 3,4-dihydroxy-,** *3,4-dihydroxybutanoic acid,* 3-deoxytetrose **[1518-61-2]; (*R*)-[158800-76-1]; (*S*)-[51267-44-8]**

Identified by Bähre and Maier (1999) (see **E.29**) in green and roasted coffees. Contrary to the previous hydroxy acids (**E.29–36**), the content decreased slightly upon roasting.

The presence of **acetic acid, oxo-,** *oxoacetic acid, glyoxylic acid,* glyoxalic acid **[298-12-4]** in roasted coffee has been suggested by Van der Stegen and Van Duijn (1988).

Keto aliphatic acids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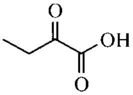
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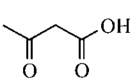
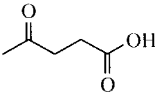

(E.40)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(E.41)

(E.38) ***(E.38)*** **Propanoic acid, 2-oxo-,** *pyruvic acid,* acetylformic acid; 'Brenztraubensaüre' **[127-17-3]** ***FEMA 2970***

Identified by Mabrouk and Deatherage (1956) who estimated its content at 0.056% by weight of roasted beans and only 0.87% of the total acids recovered from extracts. Schormüller *et al.* (1961) found ca 0.08% of a commercial extract (1.7% of the acid content). Blanc (1979) observed few changes from 0.17 to 0.14% of the dry material during roasting of a Tanzania arabica for example. Bähre and Maier (1999) (see E.29) found a slight increase in the concentration after roasting but not with prolonged heating and the content was only 24 ppm in a roasted untreated arabica.

It has a sour-acetic odor; the taste gives an impression of caramellic sweetness (Arctander, 1967).

(E.39) ***(E.39)*** **Butanoic acid, 2-oxo-,** *2-oxobutanoic acid,* 2-oxobutyric acid, α-ketobutyric acid, methylpyruvic acid **[600-18-0]** ***FEMA 3733***

Identified by Bähre and Maier (1996, 1999) (see **E.29**) in traces in a green Kenya arabica. The content rose only to 4–5 ppm after roasting.

It is a degradation product of carbohydrates, like pyruvic acid.

(E.40) **Butanoic acid, 3-oxo-,** *acetoacetic acid,* acetylacetic acid

Present in traces, but not detectable in all coffee samples (Maier, 1988).

(E.41) ***(E.41)*** **Pentanoic acid, 4-oxo-,** *4-oxopentanoic acid,* levulinic acid, levulic acid, γ-acetylpropionic acid **[123-76-2]** ***FEMA 2627***

This acid is mentioned as present in coffee by Woodman (1985) and by Maier (1988). Found by Bähre and Maier (1999) (see **E.29**) in a steam-treated green arabica (4 ppm), its content increased to ca 60 ppm after roasting.

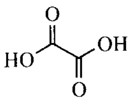
Levulinic acid is derived from carbohydrates.

It has a sweet, caramel, acid flavor (Arctander, 1967).

Saturated aliphatic diacids

(E.42) Ethanedioic acid, *oxalic acid* [144-62-7]

Identified by Arbenz (1917) who reported the presence of 0.08% in roasted coffee. Mabrouk and Deatherage (1956) estimated its content at 0.20% by weight of roasted coffee beans (3.1% of the total acids present in coffee extracts). Lentner and Deatherage (1959) did not detect it and deduced that it may be present as the water-insoluble calcium salt. Feldman *et al.* (1969) found 250–500 ppm (0.025–0.05%) in roasted arabica and robusta, the content being slightly lower for a medium than for a dark roast. Maier (1987) did not find a reliable method and gave an approximate content <100 ppm in roasted beans. Hills *et al.* (1991) identified the trimethylsilyl ester by GC/MS after supercritical carbon dioxide extraction at 200 atm. and 80 °C.



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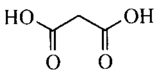

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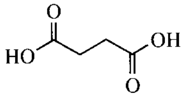

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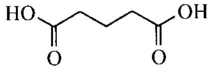

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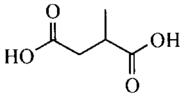


(E.46)
(E.46)

(E.43) Propanedioic acid, *malonic acid* [141-82-2]

Identified by Feldman *et al.* (1969) with mean concentrations of about 60 ppm based on dry coffee. According to Maier (1987, 1988), its content was <0.020 % in roasted coffee and <0.024 % in extracts.

It is practically odorless. The taste is acid, somewhat acrid-astringent, not very pleasant (Arctander, 1967).

(E.44) *(E.44)* Butanedioic acid, *succinic acid*, 'Bernsteinsaüre' [110-15-6]

Identified by Schormüller *et al.* (1961) in a commercial coffee extract (0.28 %, 6 % of the acid content) and later by Woodman *et al.* (1968) in a Santos roasted coffee. It was also found by Feldman *et al.* (1969) in concentrations of 55–160 ppm in medium and dark-roasted arabica and robusta coffees. Van der Stegen and van Duijn (1988) found higher values for which they did not have a definite explanation: up to 0.15 % in green arabicas, 0.05–0.35 % in robustas and 0.19–0.8 % (d.m.) in commercial roasted coffee. The quantity increased in a brew left at high temperature. Maier (1987, 1988) mentioned the presence of succinic acid in a Santos green arabica (180 ppm) and with other minor acids in roasted coffee (50–100 ppm). Bähre and Maier (1999) (see **E.29**) found only 40–50 ppm in green arabicas and about 80 ppm after roasting.

Succinic acid derives from citric acid.

It is odorless. The taste is tart-acid, almost astringent, mouthfeel at concentrations >2000 ppm in water (Arctander, 1967).

(E.45) *(E.45)* Pentanedioic acid, *glutaric acid* [110-94-1]

Identified by Feldman *et al.* (1969) in concentrations of 80–130 ppm on a dry coffee basis for Columbian and Santos coffee, 180–370 ppm for a robusta, the higher concentrations being for the dark-roasted coffees. Bähre and Maier (1999) (see **E.29**), who found 2–4 ppm in a green arabica, found only 22–24 ppm after roasting without a tendency to increase after prolonged heating.

This acid is also derived from citric acid.

(E.46) *(E.46)* Butanedioic acid, methyl-, *methylbutane dioic acid, methylsuccinic acid*, 1,2-propanedicarboxylic acid [498-21-5]; (±)-[636-60-2]; (*R*)-[3641-51-8]; (*S*)-[2174-58-5]

Identified by Bähre and Maier (1996, 1999) (see **E.29**) who found 3 ppm in a green Kenya arabica (steam-treated or not), content increasing to ca 40 ppm after roasting.

It is derived from carbohydrates.

A method of synthesis is given in a Japanese patent (Saito and Tokito, 1995), by hydroformylation of methyl methacrylate, followed by oxidation and hydrolysis.

Heptanedioic acid, *heptanedioic acid,* 1,5-pentanedicarboxylic acid, pimelic acid **[111-16-0]**

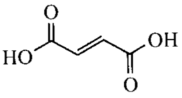
Octanedioic acid, *octanedioic acid,* 1,6-hexanedicarboxylic acid, hexamethylenedicarboxylic acid, suberic acid, cork acid **[505-48-6]**

Decanedioic acid, *decanedioic acid,* 1,8-octanedicarboxylic acid, sebacic acid **[111-20-6]**

Dodecanedioic acid, *dodecanedioic acid,* 1,10-decanedicarboxylic acid, decamethylenedicarboxylic acid **[693-23-2]**

These non-volatile acids were mentioned by Maier (1993) as being identified by Hughes and Thorpe (1987) in roasted coffee. In fact only **heptanedioic acid** had been identified. The others were standard compounds.

Unsaturated aliphatic diacids



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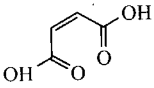

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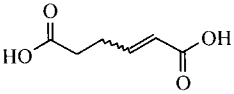

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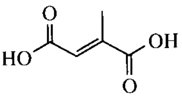

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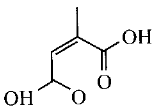

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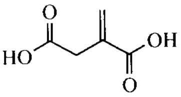


(E.52)
(E.52)

(E.47) ***(E.47)*** **2-Butenedioic acid (*E*)-,** *fumaric acid* **[110-17-8]** ***FEMA 2488***

Identified by Schormüller *et al.* (1961) in a commercial coffee extract (4 mg per 100 g, 0.1 % of the acid content), and by Woodman *et al.* (1968) who found a constant increase during roasting of a Santos coffee. For the latter authors, part of the identified methyl fumarate was accounted for by dehydration of the methyl malate during GC separation of the esters. Feldman *et al.* (1969) find 48–72 ppm in medium roasted arabicas, with an increase to 120–140 ppm in dark-roasted; for a robusta the concentration more important with a medium roast (230 ppm) does not increase as much (280 ppm). According to Maier (1987, 1988) the content is 100–160 ppm in roasted coffee and 440–500 ppm in extracts. Bähre and Maier (1999) with a new method (see **E.29**) found 15 and 20 ppm respectively in a green arabica (steam treated or not), the contents reaching 175 and 200 ppm after roasting.

Rahn and König (1978) suggested that the acid is a metabolite of malic acid.

Virtually odorless; clean, slightly tart, acid taste in aqueous solution (Arctander, 1967).

(E.48) ***(E.48)*** **2-Butenedioic acid (*Z*)-,** *maleic acid* **[110-16-7]**

Identified by Woodman *et al.* (1968). Feldman *et al.* (1969) found increasing concentrations by roasting in arabica coffees (38–85 ppm, or 200–380 ppm) but a decrease for a robusta (540–85 ppm). Maier (1987,

1988) finds contents of 60–160 ppm in roasted coffee and < 300 ppm in extracts with a tendency to decrease with long roasting times. Bähre and Maier (1999) (see **E.29**) detected maleic acid in a green Kenya arabica (6–7 ppm) but not in a Columbia. The content increased to 85 ppm after roasting but did not vary appreciably with prolonged heating (espresso quality).

Like fumaric acid, it probably comes from malic acid.

The odor is faintly caramellic, the taste is acid-astringent and mouthfeel (Arctander, 1967).

(E.49) 2-Hexenedioic acid, *hex-2-enedioic acid* **[4440-68-0]**; **(*E*)-[2583-24-6]; (*Z*)-[87080-01-1]**

Identified by Hills *et al.* (1991) after repeated extractions of roasted coffee beans with pure supercritical carbon dioxide at 200 atm and 80 °C and GC/MS separation of trimethylsilyl derivatives.

(E.50) ***(E.50)*** **2-Butenedioic acid, 2-methyl-, (*E*)-,** *(*E*)-2-methylbut-2-enedioic acid*, mesaconic acid, methylfumaric acid **[498-24-8]**

Identified by Woodman *et al.* (1968) who find increasing amounts during roasting According to Maier (1987, 1988), the content was 50–130 ppm in roasted coffee and 130–280 ppm in extracts and did not tend to decrease with long roasting times. For Bähre and Maier (1999) (see **E.29**), the content of 2–3 ppm in a green arabica reaches ca 110 ppm after roasting.

Woodman *et al.* (1967) suggest the formation by degradation of citric acid for mesaconic (**E.50**), citraconic (**E. 51**) and itaconic (**E.52**) acids, an interpretation followed by Feldman *et al.* (1969) and Rahn and König (1978).

(E.51) ***(E.51)*** **2-Butenedioic acid, 2-methyl-, (*Z*)-,** *(*Z*)-2-methylbut-2-enedioic acid*, citraconic acid, methylmaleic acid **[498-23-7]**

Identified by Woodman *et al.* (1967) who found increasing amounts during roasting. For Maier (1987, 1988) the content of 480–700 ppm in roasted coffee (610–1360 ppm in extracts) tended to decrease with long roasting times. Bähre and Maier (1999) (see **E.29**) detected only traces in a green Kenya arabica (not in a Columbia) but a content of 240 ppm after roasting, even more after prolonged heating (espresso quality).

(E.52) ***(E.52)*** **Butanedioic acid, 2-methylene-,** *2-methylenebutanedioic acid*, itaconic acid, methylenesuccinic acid **[97-65-4]**

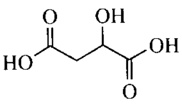
Identified, in increased amounts during roasting, by Woodman *et al.* (1968). Maier (1987, 1988) found concentrations of 130–200 ppm in roasted coffees (320–450 in commercial extracts), which tended to decrease with long roasting times. From 3–4 ppm in a green arabica, the content increased to 130–140 ppm after roasting but did not seem to increase after prolonged heating in the results of Bähre and Maier (1999) (see **E.29**).

Hydroxy and keto diacids and triacid

(E.53) ***(E.53)*** **Butanedioic acid, 2-hydroxy-,** *2-hydroxybutanedioic acid*, malic acid, α-hydroxysuccinic acid, 'Apfelsäure' **[6915-15-7]** ***FEMA 2655*****; (±)-[617-48-1]; (*R*)-[636-61-3]; (*S*)-[97-67-6]**

Identified by Mabrouk and Deatherage (1956) who estimated that malic acid represented 0.46% by weight of roasted beans and 7.2% of the total acids of extracts. Also mentioned by Lentner and Deatherage (1959) as being present in green and roasted coffee. In this study, malic acid started decomposing at 350 °F (ca 175 °C) and its concentration decreased from 73 mg per 100 beans at

300 °F (ca 150 °C) to 53 mg per 100 beans at 425 °F (ca 220 °C). Its presence is confirmed by Feldman *et al.* (1969) who estimated its concentration at 150–390 ppm, calculated on dry coffee basis, slightly higher for dark than for medium roast. Blanc (1977) found that the content in malic acid falls during roasting in a proportion of 33–50 % (from 0.30 % to 0.19 % for a Kenya coffee). Maier *et al.* (1984) found an increase in the concentration (15 % of the starting value) by maintaining brews during three days at temperatures from 20 to 80 °C. Van der Stegen and van Duijn (1988) found contents of 0.26–0.67 % (d.m) in green arabicas, 0.18–0.73 % in green robustas, decreasing on roasting (0.1–0.39 % in a roasted commercial sample) but did not measure an increase if a brew was maintained at high temperature.



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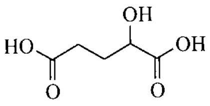

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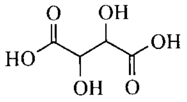

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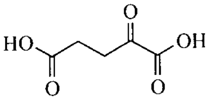

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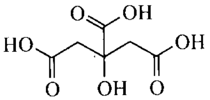

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Schormüller *et al.* (1961) found a concentration of 0.5 % (10.5 % of the acid content) in a commercial extract.

Malic acid is considered to be odorless or sometimes having a very faint, caramellic-acrid odor (Arctander, 1967).

(E.54) ***(E.54)*** **Pentanedioic acid, 2-hydroxy-,** *2-hydroxypentanedioic acid,* 2-hydroxyglutaric acid **[2889-31-8]; (±)- [636-67-9]; (*R*)-[13095-47-1]; (*S*)-[13095-48-2]**

Identified by Bähre and Maier (1996, 1999) (see **E.29**). The contents did not vary significantly on roasting: 15–25 ppm in green and roasted arabicas.

(E.55) ***(E.55)*** **Butanedioic acid, 2,3-dihydroxy-,** *tartaric acid,* tartric acid, (+)-'Weinsäure', (±)-'Traubensäure'; **(+)-(*R*,*R*)- [87-69-4]; (±)- [133-37-9]**

Identified by Mabrouk and Deatherage (1956), estimated at 0.4 % by weight of roasted beans and 6.2 % of total acids recovered from powdered extracts. Schormüller *et al.* (1961) found a much smaller amount: 40 ppm (0.2 % of the acid content) in a commercial powder, near the values given later by Maier (1987, 1988): 10–60 ppm in roasted coffee and 30–60 ppm in commercial extracts. Feldman *et al.* (1969) found decreasing values from medium to dark roast, from 460–1000 ppm of dry material to 350–790 ppm, with various species. Different values were given by Bähre and Maier (1999) (see **E.29**): 4 ppm in a green and roasted arabica, not even detectable in a coffee of espresso quality or in an instant coffee.

Tartaric acid is odorless, the taste is refreshing, strongly acid, pleasant below 5000 ppm. Its perception depends upon sweeteners and other additives (Arctander, 1967). A flavor threshold of 10 ppm in water is given by Maga and Lorenz (1973).

(E.56) *(E.56)* **Pentanedioic acid, 2-oxo-,** *2-oxopentanedioic acid*, 2-oxoglutaric acid, α-ketoglutaric acid **[328-50-7]**

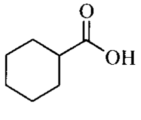
Identified by Schormüller *et al.* (1961) in a commercial extract at the extent of 200 ppm (0.4 % of the acid content). Bähre and Maier (1999) (see **E.29**) found 12–15 ppm in steamed arabicas (not detected in untreated coffees) and ca 50 ppm after roasting.

(E.57) *(E.57)* **1,2,3-Propanetricarboxylic acid, 2-hydroxy-,** *citric acid* **[77-92-9]** ***FEMA 2306***

Identified by.Gorter (1910) in Liberia coffee beans. Mabrouk and Deatherage (1956) estimated the concentration at 0.5 % by weight of roasted beans (7.7 % of the total acids recovered from coffee extracts), values not very far from the values for tartaric and malic acids. For Lentner and Deatherage (1959), citric acid, present in green coffee, started decomposing at 300 °F (ca 150 °C), the content falling from 170 mg per 100 beans at 300 °F (150 °C) to 80 mg per 100 beans at 425 °F (220 °C). Schormüller *et al.* (1961) found a higher concentration in a commercial extract than for the other non-volatile acids: 2.2 g per 100 g of the extract (47 % of the acid content). Using a colorimetric method (pentabromacetone procedure), Schormüller and Rubach (1964) determined the content of citric acid 0.62–1.15 % (d.m) in raw coffee, 0.44–0.85 in normal roasted coffee, 0.26–0.73 in espresso-roasted coffee and 2.07–2.28 in two extracts. This quantification technique has the advantage to be specific for citric acid and to avoid interference with the other multifunctional acids. Woodman *et al.* (1968) estimated its proportion at 0.27–0.37 % depending on the degree of roast of a Santos coffee and they did not find a real decrease of the concentration during roasting. Feldman *et al.* (1969) gave lower values of 350–750 ppm calculated on dry coffee basis for medium-roasted coffees (the highest value for robusta) with a decrease to 180–690 ppm after dark-roast. Blanc (1979) confirmed a neat decrease during roasting reaching only 50 % of the initial content in the green beans. The same observation was made by Scholze (1983). Van der Stegen and van Duijn (1988) found 0.50–1.29 % (d.m.) in green arabicas, 0.33–1 % in green robustas and 0.43–0.70 % in a in roasted commercial sample, and a slight increase if a brew is maintained at high temperature.

Citric acid is virtually odorless. The aqueous solution has a clean acid taste, pleasant at concentrations of 0.02 to 0.08 % (Arctander, 1967).

Alicyclic and aromatic acids



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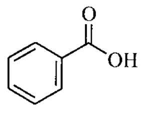

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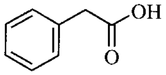

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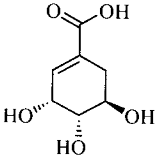

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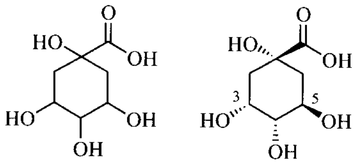

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(E.58) **Cyclohexanecarboxylic acid,** *cyclohexanecarboxylic acid,* hexahydrobenzoic acid, cyclohexylmethanoic acid, carboxycyclohexane **[98-89-5]**

Identified by Cantergiani *et al.* (2001) in a green Mexican arabica, 1.47% (GC) of the components extracted after vacuum hydrodistillation. (the ethyl ester, **F.46**, was previously identified and associated with the over-fermented flavor defect of green beans, Bade-Wegner *et al.*, 1997).

The flavor is described as ripe, tropical fruit, green, valerianic and grape (Chemisis, 1999).

(E.59) ***(E.59)*** **Benzoic acid,** *benzoic acid* **[65-85-0]** ***FEMA 2131***

(E.60) ***(E.60)*** **Benzeneacetic acid,** *phenylacetic acid* **[103-82-2]** ***FEMA 2878***

These were identified by Rahn and König (1980a) from an arabica Nicaragua extract by GC/MS separation, after silylation with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide. **E.60** was also identified in 'Rio' green coffee by Spadone *et al.* (1990). The two acids were found in a green Mexican arabica by Cantergiani *et al.* (2001), respectively 0.15 and 0.32% (GC) of the compounds extracted after vacuum hydrodistillation.

The flavor is honey, sweet at 50 ppm in water, becoming floral when more diluted (10 ppm) (Chemisis, 1999). Maga and Lorenz (1973) gave a flavor threshold of 10 ppm for (**E.60**).

1,2-Benzenedicarboxylic acid, *phthalic acid, benzene-1,2-dicarboxylic acid* **[88-99-3]**

Mentioned by Maier (1993) as identified by Hughes and Thorpe (1987) and was only a standard compound in this article.

(E.61) ***(E.61)*** **1-Cyclohexene-1-carboxylic acid, 3,4,5-trihydroxy-, (3α,4α, 5β)-,** r-*3*,c-*4*,t-*5*-*3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid,* shikimic acid **[15271-51-9]; [3*R*-(3α,4α, 5β)]-,** recently **(3*R*,4*S*,5*R*)-[138-59-0]**

Identified by Bähre and Maier (1999) (see **E.29**) in a green steam-treated Kenya arabica (10 ppm, traces only when untreated). The content increases to 35–40 ppm after roasting.

This polyhydroxy acid is formed from the chlorogenic acids (Section 2.1.4).

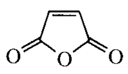
(E.62) ***(E.62)*** **Cyclohexanecarboxylic acid, 1,3,4,5-tetrahydroxy-, [(1*R*)-(1α,3α, 4α,5β)],** recently **(1α,3*R*,4α,5*R*)-,** *(1R, 3S, 4R, 5R)-1,3,4,5-tetrahydroxycyclohexanecarboxylic acid,* or according to IUPAC Commission for Nomenclature for cyclitols (1976): *1L-1(OH),3,4/5-tetrahydroxycyclohexanecarboxylic acid, L-quinic acid,* quininic acid **[77-95-2]**

First isolated from coffee by Zwenger and Siebert in 1907 (quoted by Gorter, 1908a). Its presence could only be due to decomposition of chlorogenic acid during acid treatments of extracts. (Mabrouk and Deatherage, 1956). Lentner and Deatherage (1959) found it in traces in the extract of green coffee, with an increase during roasting, however this is only a small fraction of the amount of quinic acid calculated from the decomposition of chlorogenic acid, probably because of decomposition and/or formation of the γ-lactone (quinide). Blanc (1979) measured the content in the free state of this quantitatively minor acid by GC of the trimethylsilyl derivative. In spite of the degradation of quinic acid, he observed a relatively good linearity between the disappearance of chlorogenic acid and the formation of quinic acid during roasting. According to Ohiokpehai (1982) and Ohiokpehai *et al.* (1983) free quinic acid is commonly found at levels in the range 0.4–0.7% in green coffee but may be as high as 1.5% in discolored green beans. Van der Stegen and van Duijn (1988) found contents in the range of 0.33–0.61% (d.m.) in green arabicas, 0.16–0.86 in robustas with an increase to 0.89–1.5 in a roasted commercial sample, and they observed an increase if a brew was maintained at high temperature. Hucke and Maier (1985) and Maier (1987) noted that quinic acid, present in steamed green coffee, increased during roasting together with its lactone (**G.15**). The content of these two compounds decreases only with a high roast. Maier's group (Scholz and Maier, 1990; Scholz-Böttcher and Maier, 1992; Scholz-Böttcher *et al.*, 1991) carefully examined the isomerization of the isomer (**E.62**). In a Kenya robusta, the concentration of 0.55 % when green, increased to 0.75 % for a low roast then decreased; at the same time the contents in the five isomers increased.

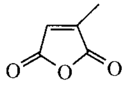
Maga and Lorenz (1973) measured a flavor threshold of 10 ppm in water.

Phenol(s) and/or phenol ether(s) with a carboxylic acid function are treated under 5.H (phenols). Other compounds containing a carboxylic acid function are present in the sections 5.I (furans), and 5.K (pyrroles).

Anhydrides



(E.63)



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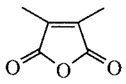

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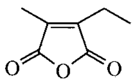

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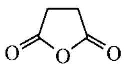


(E.67)

(E.63) 2,5-Furandione, *2,5-dihydrofuran-2,5-dione, maleic anhydride,* maleic acid anhydride **[108-31-6]**

Identified by Kallio *et al.* (1989) among 41 constituents of a coffee headspace. The authors measured the changes of some volatiles of coffee during aging at 39 °C and observed that the concentration of maleic anhydride diminished rapidly with time and that it had almost disappeared after 120 days of storage. Ramos *et al.* (1998) could identify it after liquid–liquid extraction of a brewed arabica with methylene chloride

(E.64) 2,5-Furandione, 3-methyl-, *2,5-dihydro-3-methylfuran-2,5-dione, methylmaleic anhydride,* methyl-2,5-furandione, citraconic anhydride **[616-02-4]**

Identified by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968) among the 30 new structures of the 140 constituents isolated after extraction of a steam distillate of roasted ground coffee (IR, MS data).

(E.65) 2,5-Furandione, 3,4-dimethyl-, *2,5-dihydro-3,4-dimethylfuran-2,5-dione, dimethylmaleic anhydride,* dimethyl-2,5-furandione, pyrocinchonic anhydride **[766-39-2]**

Identified by Gianturco *et al.* (1966) in an 'aroma complex' of coffee, and by Stoffelsma *et al.* (1968) after steam-distillation and extraction. Found also by Ho *et al.* (1993) in headspace of roasted coffee (0.17 ppm).

(E.66) 2,5-Furandione, 3-ethyl-4-methyl-, *3-ethyl-2,5-dihydro-4-methylfuran-2, 5-dione, 2-ethyl-3-methylmaleic anhydride,* ethylmethylmaleic anhydride **[3552-33-8]**

Identified by Gianturco *et al.* (1966).

The flavor is described as burnt, maple (Chemisis, 1970).

(E.67) 2,5-Furandione, dihydro-, *tetrahydrofuran-2,5-dione, succinic anhydride,* butanedioic anhydride, 'bernsteinsaüre anhydrid' **[108-30-5]**

Identified by Ho *et al.* (1993) in headspace of a ground roasted Columbian coffee, with a concentration of 0.49 ppm.

5.F ESTERS

Contrary to their abundance and essential contribution in fruit flavors, aliphatic and aromatic monofunctional esters are less represented in roasted coffee volatiles. For example methyl formate (**F.1**) and methyl acetate (**F.7**) were the only esters identified in a 'coffee aroma' (see Alcohols, Section 5.B) by Merritt *et al.* (1963), representing 10.3% of the aroma in nearly equal proportions. They do not significantly contribute to the character of the beverage (apart from a few, particularly **F.40**, **F.42** and **F.46** which contribute to an off-flavor produced by unhealthy green beans (Bade-Wegner *et al.*, 1998, Full *et al.*, 2000). By way of compensation, when esters are associated, for instance, with heterocyclic rings, thiols or phenols, they can sometimes afford original flavor notes. In this chapter, only relatively simple esters are enumerated and discussed. Some esters with a function either on the acid part or the alcohol part are also mentioned.

Most of the volatile esters were identified during the period 1967–69 by Stoll *et al.* (1967), Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968) and Merritt *et al.* (1970). The latter authors commented on the ester composition of coffee volatiles. They observed that more esters are present in the green beans than in the roasted beans. Consequently they considered that the esters were produced in connection with the metabolic processes in the fruit and were not associated with pyrolysis. Some of the esters (**F.10**, **F.26**, **F.29**, and **F.31**) were identified only in Columbian green beans, and it was suggested that this information could be used for the qualitative determination of a variety. Furfuryl acetate (**I.109**) is an exception: it has only been identified in roasted coffee as furfuryl alcohol (**I.52**) only appears during roasting by caramelization of sugars. In their investigation on 'stinking' green coffee, Guyot *et al.* (1982, 1983) mentioned that the differences between 'stinking' and healthy green beans were essentially due to the presence of a greater number of esters in the former. (A review, with comments, of the literature on green-bean constituents is included in Chapter 2)

Mathieu *et al.* (1996, 1998) studied the red berries of robusta and arabica varieties. They identified a number of esters, two of which, 2-pentyl (**F.13**) and 2-heptyl (**F.15**) acetates, have not yet been found in the beans themselves.

The saturated long-chain fatty acids are discussed in Section 5.E, therefore we include some corresponding esters, but not, for example, linoleic esters or esters of long-chain alcohols that are not in Section 5.B. For example, ethyl linoleate and farnesyl acetate have been identified in green Mexican arabica by Cantergiani *et al.* (2001).

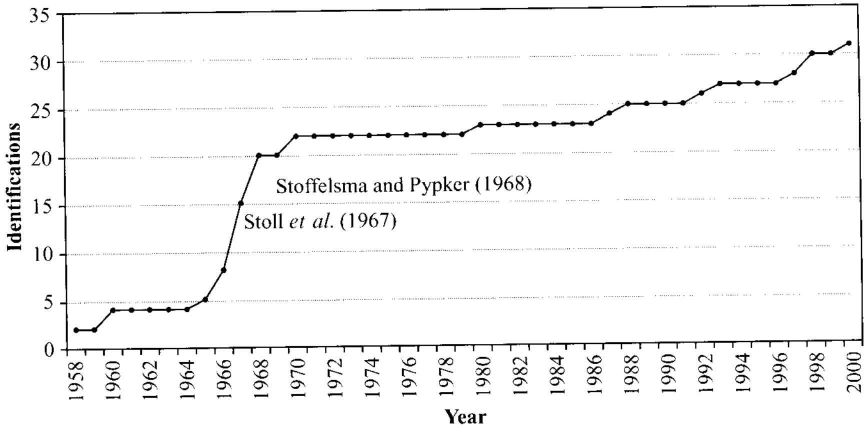
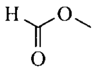


Fig. 5.6 Progressive identification of esters in roasted coffee volatiles

Odor thresholds of saturated and unsaturated branched esters were determined by Takeoka *et al.* (1995, 1998). Generally, unsaturated branched esters have higher odor thresholds than their saturated counterparts. Double-bond position and configuration have a marked influence on the odor threshold. Ethyl 2-methylbutanoate (**F.40**) has a threshold 10 times lower than the (*Z*)-2-methyl-2-butenoate and 10^4 lower than the (*E*)-ester (**F.44**). Ethyl esters seem to have lower odor thresholds than the corresponding methyl esters.

Formates



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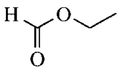

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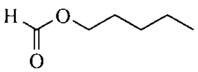

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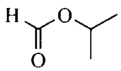

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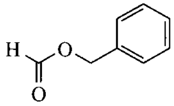

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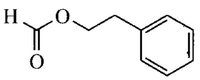


(F·6)

(F.1) *(F.1)* Formic acid, methyl ester, *methyl formate, methyl methanoate* [107-31-3]

Rhoades (1960) identified methyl formate in headspace of roasted coffee, but did not detect it in green beans; the concentration of this ester reaches a maximum at about 400 °F (200 °C), being 9.0–13.5 ppm after roasting at 400–430 °F (ca 200–220 °C). This increase is in good correlation with the subsequent observations of Woodman (1968) and Feldman *et al.* (1969), who noticed a decrease in the concentration of formic acid with the degree of roasting, possibly due to the formation of some formates. Zlatkis and Sivetz (1960) were among the first authors to succeed in performing efficient GC separation of a 'coffee-aroma essence' using an original packing composed of ethylene carbonate and propylene carbonate on aqua regia treated C-22 firebrick. The essence represented about 200 ppm of the roasted coffee beans and the estimated concentration was 8 ppm in roasted beans (4 % of the aroma), a value in good correlation with the results of Rhoades. Methyl formate was also identified in green beans by Merritt *et al.* (1970), and quantified by Gibson (1974a) in headspace of green beans of two arabica hybrids. It was also one of the headspace components identified with GC/MS by Liardon and Ott (1984). Analyzing headspaces of six green arabicas and six green robustas, Procida *et al.* (1997) only found it in one robusta, but also in a roasted arabica.

Methyl formate is a colorless flammable liquid with a very ethereal-diffusive odor of winey chloroform type (Arctander, 1967). Over-exposure irritates nose and eyes (*Merck Index*).

(F.2) Formic acid, ethyl ester, *ethyl formate, ethyl methanoate* [109-94-4] *FEMA 2434*

Identified by Zlatkis and Sivetz (1960) in a 'coffee aroma essence' (see **F.1**) representing about 200 ppm of a roasted coffee. The concentration was approximately 0.6 ppm of the roasted beans (0.3 % of the essence).

It is a mobile, narcotic, flammable liquid whose over-exposure irritates eyes and upper respiratory system (*Merck Index*). It has a sweet-ethereal, fruity taste in water (Arctander, 1967). An odor threshold of 17 ppm in water was given by Mulders (1973b).

(F.3) **Formic acid, pentyl ester,** *pentyl formate, pentyl methanoate,* amyl formate **[638-49-3]**

Identified in the headspace of green coffees of various origins (six arabicas and five robustas out of six) by Procida *et al.* (1997), but not in a roasted coffee.

(F.4) Formic acid, 1-methylethyl ester, *isopropyl formate, isopropyl methanoate* **[625-55-8]** *FEMA 2944*

Identified after steam distillation, fractionation and analysis, by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968).

Isopropyl formate has a sweet-ethereal, very diffusive odor, fresher than chloroform, not as pungent as propyl formate (Arctander, 1967).

(F.5) Formic acid, phenylmethyl ester, *benzyl formate,* benzyl alcohol formate **[104-57-4]** *FEMA 2145*

Identified by Stoll *et al.* (1967).

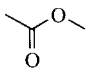
It has a powerful, fruity-green, herbaceous-earthy, yet somewhat floral, heavy, but not very tenacious odor (Arctander, 1967).

(F.6) Formic acid, 2-phenylethyl ester, *phenethyl formate, 2-phenylethyl formate* **[104-62-1]** *FEMA 2864*

Identified by Stoll *et al.* (1967) and also by Stoffelsma *et al.* (1968) after steam-distillation, fractionation and GC.

It has a powerful, green-herbaceous, rosy odor with some similarity to chrysanthemum, hyacinth and watercress foliage. It has a moderate to poor tenacity (Arctander, 1967).

Acetates



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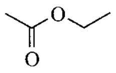

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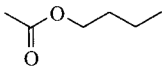

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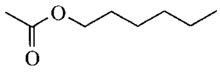

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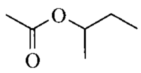

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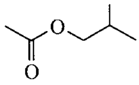

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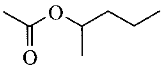

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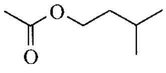

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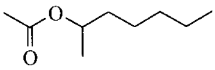

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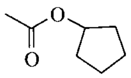

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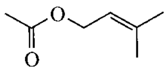


(F.17)

(F.7) *(F.7)* **Acetic acid, methyl ester,** *methyl acetate, methyl ethanoate* **[79-20-9]** *FEMA 2676*

Identified in roasted coffee by Reichstein and Staudinger (1926b) and later by Rhoades (1960). Zlatkis and Sivetz (1960) estimated the concentration as 3.4 ppm in roasted beans (1.7% of a 'coffee aroma essence' representing 200 ppm of the roasted beans, see **F.1**). Merritt *et al.* (1963, 1970) identified the ester in green and in roasted coffee. Methyl acetate was given as newly identified by Wang *et al.* (1983) in a headspace analysis of roasted coffee; it was also found by Liardon and Ott (1984). It was the only aliphatic ester positively identified by Shimoda and Shibamoto (1990a) in the headspace of a brewed coffee (peak area 1.7% of the volatiles). According to Holscher and Steinhart (1992a), the concentration increased slightly but significantly with the degree of roasting.

Over-exposure to this colorless liquid can irritate nose and throat (*Merck Index*). Methyl acetate has a sweet, and extremely diffusive, ethereal-fruity odor of very poor tenacity (Arctander, 1967).

(F.8) *(F.8)* Acetic acid, ethyl ester, *ethyl acetate, ethyl ethanoate*, acetic ether [141-78-6] *FEMA 2414*

Its presence in roasted coffee is mentioned for the first time by Gianturco *et al.* (1966). It was also identified in green beans by Merritt *et al.* (1970). It was the only aliphatic ester identified by Vitzthum and Werkhoff (1976b) (steam distillation and analysis of the neutral fraction), and by Silwar (1982) in a roasted-coffee aroma. Spadone *et al.* (1990) identified it in a Puerto Rico ('Rio') green coffee extract (simultaneous distillation–extraction) and in a healthy green coffee. Ethyl acetate was also the only simple ester extracted from a brewed arabica by Ramos *et al.* (1998) with supercritical CO_2.

Ethyl acetate is (with 2-butanone) one of the main aliphatic volatile compounds that Zhang and Ho (1991) identified after thermal interaction of cysteine and glucose.

When pure, it is a clear, volatile, narcotic, flammable liquid, overexposure to which can irritate eyes, nose and throat; it has a pleasant, ethereal-fruity, brandy-like odor, somewhat nauseating in high concentration (Arctander, 1967). The odor threshold given by Flath *et al.* (1967) was 5 ppm (probably in water), and by Mulders (1973b) 6.2 ppm in water. The flavor threshold given by Keith and Powers (1968) was 3 ppm in water and by Siek *et al.* (1969) 6.6 ppm.

(F.9) *(F.9)* Acetic acid, butyl ester, *butyl acetate, butyl ethanoate* [123-86-4] *FEMA 2174*

Identified by Heins *et al.* (1966) in the headspace over coffee beans by one of the first capillary-GC/MS coupling. The ion $M + 1 (m/z = 117)$ was one of the ions used by Dyszel (1985) when using thermogravimetric analysis/atmospheric pressure chemical ionization mass spectrometry (TGA/APCIMS) for determining the origin of green coffee. It was found after simultaneous distillation–extraction and analysis by GC/MS by Spadone *et al.* (1990) in a Puerto Rico 'Rio' coffee, but not in a healthy variety. It was one of the compounds emitted by fresh red coffee berries in two robusta varieties (Mathieu *et al.*, 1996), and was found to decrease if the berries were left on the plant after the red stage (Mathieu *et al.*, 1998).

The odor is often described as resembling that of pear, banana, strawberry, etc. but it may be closer to pear than to any other single fruit (Arctander, 1967). It has a very diffusive, ethereal-fruity, pungent odor, reminiscent of many kinds of ripe and over-ripe fruits, but with a very poor tenacity. An odor threshold of 66 ppb was given by Flath *et al.* (1967).

(F.10) Acetic acid, hexyl ester, *hexyl acetate, hexyl ethanoate* [142-92-7] *FEMA 2565*

Identified in green beans volatiles by Merritt *et al.* (1970). It was also found by Guyot *et al.* (1982, 1983) in stinking green coffee but not in healthy beans.

It is characterized by a pear note contributing to the undesirable off-flavor. It is also described with apple, melon green flavor notes (Chemisis, 1999).

(F.11) Acetic acid, 1-methylpropyl ester; *1-methylpropyl acetate*, sec-*butyl acetate*, 2-butyl acetate, 2-butanol acetate, *sec*-butanol acetate **[105-46-4]**

This ester has been identified by Leino *et al.* (1992) in headspace when observing the changes of the volatiles during storage of commercial blends of Finnish roasted coffee samples.

The flavor is described as green, burnt, coffee (Chemisis, 1963).

(F.12) **Acetic acid, 2-methylpropyl ester,** *isobutyl acetate, 2-methylpropyl acetate*, β-methylpropyl ethanoate **[110-19-0]** ***FEMA 2175***

Identified by Guyot *et al.* (1982, 1983) in stinking not in healthy green coffee beans. It is one of the compounds emitted by fresh red berries of one robusta variety (of the three examined) and of one arabica (of three examined) (Mathieu *et al.*, 1996).

An excess of concentration in the later variety provokes the too fruity character.

(F.13) **2-Pentanol, acetate,** *1-methylbutyl acetate*, 2-pentyl acetate, *sec*-amyl acetate, 2-acetoxypentane **[626-38-0]; (±)-[116783-17-6]; (*R*)-[54638-10-7]; (*S*)-[55621-90-4]**

Identified in fresh red coffee berries of two varieties of robusta and one of arabica coffee by Mathieu *et al.* (1996), who studied three varieties of each. The quantity apparently increased when berries were left drying on the tree after the red stage (Mathieu *et al.*, 1998).

(F.14) ***(F.14)*** **1-Butanol, 3-methyl-, acetate,** *isopentyl acetate, 3-methylbutyl acetate*, isoamyl acetate, isopentyl alcohol acetate, pear oil, banana oil **[123-92-2]** ***FEMA 2055***

This ester was isolated (steam-distillation, distillation, preparative GC) by Stoffelsma and Pypker (1968) and by Stoffelsma *et al.* (1968). It was found by Guyot *et al.* (1982, 1983) in stinking green coffee (only tentatively in healthy beans). In the GC of a green Mexican arabica, after vacuum hydrodistillation and extraction, it represented 0.09% (Cantergiani *et al.*, 2001). Mathieu *et al.* (1996), examining fresh red berries of three robustas and three arabicas, found this ester only in one variety of robusta.

It has a pronounced fruity-fresh odor, sweet but slightly nauseating. In dilution it is reminiscent of over-ripe banana and apple (Arctander, 1967). Its excessive concentration produces a fruity, pear character in stinking beans. The flavor is described as flat, earthy, fusel (Chemisis, 1988).

(F.15) **2-Heptanol, acetate,** *1-methylhexyl acetate*, 2-heptyl acetate **[5921-82-4]; (±)-[145840-85-3]; (*R*)-[54638-12-9]; (*S*)-[3540-06-5]**

Identified in fresh red berries of one robusta variety (of three robustas and three arabicas examined) by Mathieu *et al.* (1996).

It has a fatty, green, fruity flavor with a fenugreek, fruity odor (Chemisis, 1974).

(F.16) Cyclopentanol, acetate, *cyclopentyl acetate* **[933-05-1]**

Identified by Cros *et al.* (1980) in a headspace of roasted coffee.

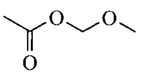
(F.17) 2-Buten-1-ol, 3-methyl-, acetate, *3-methyl-2-butenyl acetate*, isopentenyl acetate, prenyl acetate **[1191-16-8]**

Identified by Stoll *et al.* (1967).

It has a fresh and very diffusive, fruity, banana-like and bergamot-like odor of poor tenacity (Arctander, 1967).

Acetic acid, ethenyl ester, *vinyl acetate* **[108-05-4]**

This has been tentatively identified by Wang *et al.* (1983) in the headspace of roasted coffee.



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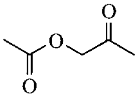

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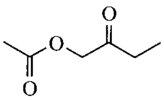

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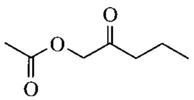

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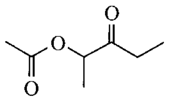

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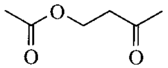

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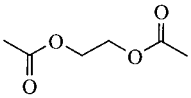


(F.24)

(F.18) **Methanol, methoxy-, acetate,** *methoxymethyl acetate*, 'acétate de méthylméthoxy' **[4382-76-7]**

Identified by Guyot *et al.* (1982, 1983) with a low concentration in stinking green coffee and and even lower concentration in healthy green beans.

(F.19) 2-Propanone, 1-(acetyloxy)-, *2-oxopropyl acetate*, 1-acetoxy-2-propanone, 1-hydroxy-2-propanone acetate, acetylmethyl acetate, acetol acetate, *O*-acetylacetol, acetoxyacetone **[592-20-1]**

Identified by Viani *et al.* (1965), the structure was confirmed by IR-spectroscopy comparison with a commercially available sample; found also by Gianturco *et al.* (1966), Stoffelsma *et al.* (1968) and by Silwar *et al.* (1987) in the analysis of a coffee-aroma extract obtained by distillation–extraction and concentration (2.0–5.0 ppm in coffee). Procida *et al.* (1987) detected this ketoester in a roasted arabica but in none of the green coffees that they studied. Ramos *et al.* (1998) found it in a brew only after liquid–liquid extraction with pentane or methylene chloride.

It has a peculiar fruity-buttery, somewhat sour odor (Arctander, 1967).

(F.20) 2-Butanone, 1-(acetyloxy)-, *2-oxobutyl acetate*, 1-acetoxy-2-butanone, 1-hydroxy-2-butanone acetate **[1575-57-1]**

Identified in an 'aroma complex' of roasted coffee by Bondarovich *et al.* (1967) and a little later by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968), after steam distillation, fractionation and preparative GC for identification by IR spectroscopy, and comparison with authentic samples. Silwar *et al.* (1987) estimated its concentration at 2.0–3.0 ppm (see **F.19**), and Ho *et al.* (1993) at 4.58 ppm in a roasted Columbian coffee. The latter authors identified only two purely aliphatic esters in their analysis (see **F.24**). Ramos *et al.* (1998) identified it in a brewed arabica only after liquid–liquid extraction with methylene chloride (compare with **F.8**).

This ester is described with a coffee odor (Chemisis, 1966).

(F.21) 2-Pentanone, 1-(acetyloxy)-, *2-oxopentyl acetate*, 1-acetoxypentan-2-one **[68113-53-1]**

(F.22) 3-Pentanone, 2-(acetyloxy)-, *1-methyl-2-oxobutyl acetate*, 2-acetoxypentan-3-one, 2-hydroxy-3-pentanone acetate **[2983-05-3]**

These were identified by Stoffelsma and Pypker (1968) and by Stoffelsma *et al.* (1968), after steam distillation, distillation and GC, by IR spectroscopy and comparison with authentic samples.

(F.23) 2-Butanone, 4-(acetyloxy)-, *3-oxobutyl acetate,* 1-acetoxy-3-butanone, 2-butanone, 4-hydroxy-, acetate **[10150-87-5]**

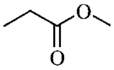
Identified by Silwar *et al.* (1987) who estimated its concentration at 2.0–4.0 ppm (see **F.19**).

(F.24) 1,2-Ethanediol, diacetate, *1,2-ethanediyl diacetate,* glycol diacetate, ethyleneglycol diacetate, 1,2-diacetoxyethane, ethylene acetate **[111-55-7]**

Identified in the headspace of a roasted Columbian arabica by Cros *et al.* (1980), and by Ho *et al.* (1993). In the headspace analysis (combined adsorbent trapping/short-path thermal desorption GC/MS), the latter authors found very few esters, and glycol diacetate was one of the main compounds with 19.53 ppm, only surpassed by four furan derivatives.

The odor is described with green, floral, esters notes (Chemisis, 1988).

Other esters of straight-chain aliphatic saturated acids



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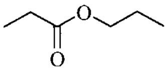

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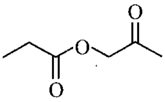

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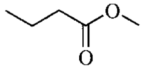

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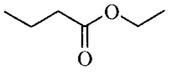

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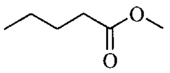

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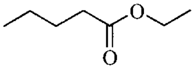

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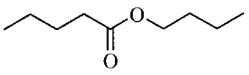

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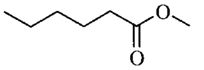

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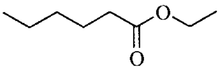

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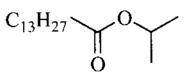

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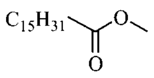

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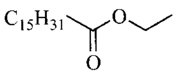

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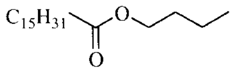


(F.38)

(F.25) ***(F.25)*** **Propanoic acid, methyl ester,** *methyl propionate, methyl propanoate* **[554-12-1]**
FEMA 2742

Identified by Heins *et al.* (1966) in the headspace of coffee beans by one of the first capillary–GC/MS coupling, in spite of the fact that the experimental conditions and the resolution were still of relatively poor quality. The number of certified identifications was consequently strongly reduced. Merritt *et al.* (1970) found it in headspace of green and of roasted coffee. Wang *et al.* (1983) mentioned it as a new identification in a headspace analysis of roasted coffee; it was also identified by Liardon and Ott (1984).

Methyl propanoate has a very diffusive, ethereal-rum-like odor, sweet and fruity of very poor tenacity (Arctander, 1967). The flavor is fruity, green, chemical (Chemisis, 1999). Ahmed *et al.* (1978) gave a probable odor threshold in water of 100 ppb and a probable flavor threshold in water of 58 ppb.

(F.26) **Propanoic acid, propyl ester,** *propyl propionate, propyl propanoate* **[106-36-5]** ***FEMA 2958***

Identified in a green coffee headspace analysis by Merritt *et al.* (1970), only in a Columbian arabica and not in a Santos arabica and a robusta.

Fresh-ethereal, fruity-floral odor of very poor tenacity. The fruity notes being apple-pineapple-like, while the floral character is more of a general lift of sweetness (Arctander, 1967). The flavor is ethereal, fruity, rum, weak (Chemisis, 1998). The odor threshold given by Flath *et al.* (1967) was 57 ppb.

(F.27) 2-Propanone, 1-(1-oxopropoxy)-, *2-oxopropyl propionate, 2-oxopropyl propanoate,* hydroxyacetone propionate, acetol propionate, acetonyl propanoate **[72845-79-5]**

Identified by Bondarovich *et al.* (1967) in an 'aroma complex' of roasted coffee.

(F.28) Butanoic acid, methyl ester, *methyl butyrate, methyl butanoate* **[623-42-7]** ***FEMA 2693***

Identified in roasted coffee but absent from green beans according to Merritt *et al.* (1970).

This ester has a very diffusive and penetrating, sweet-ethereal, fruity odor. In extreme dilution it is reminiscent of apple peel with a slightly fatty peach-like undertone (Arctander, 1967). It has a fruity, over-ripe, cheesy flavor (Chemisis, 1999). The probable threshold would be 43 ppb in water (confidence limits: 15–120 ppb) according to Ahmed *et al.* (1978) and the probable flavor threshold 59 ppb (confidence limits: 23–150).

(F.29) **Butanoic acid, ethyl ester,** *ethyl butyrate, ethyl butanoate* **[105-54-4]** ***FEMA 2427***

Identified by Merritt *et al.* (1970) in a green coffee headspace of a Columbian arabica but not in a Santos arabica and a robusta coffee. It has also been found by Guyot *et al.* (1982, 1983) in stinking green coffee, and in a very low concentration in healthy beans of a Cameroon arabica.

Its pine-cone character can contribute to the defective off-flavor. Powerful, ethereal-fruity odor suggestive of banana and pineapple and very diffusive (Arctander, 1967). The flavor is fruity, fresh (Chemisis, 2000).

An odor threshold of 1 ppb is given by Flath *et al.* (1967). The flavor threshold was 0.45 ppm in water for Keith and Powers (1968) and 15 ppb for Siek *et al.* (1969). Ahmed *et al.* (1978) gave lower values: probable odor threshold in water 0.13 ppb (but with confidence limits 0.003–4.6) and flavor threshold of 0.13 ppb (with confidence limits 0.0008–2).

Butanoic acid, ethenyl ester, *vinyl butanoate* **[123-20-6]**

This was tentatively identified in headspace of roasted coffee by Wang *et al.* (1983).

(F.30) **Pentanoic acid, methyl ester,** *methyl pentanoate*, methyl valerate **[624-24-8]** ***FEMA 2752***

Its presence in headspace of green coffee, but not of roasted beans, was mentioned by Merritt *et al.* (1970).

It is described as having a pungent-ethereal, green-fruity apple-like odor of poor tenacity (Arctander, 1967).

(F.31) **Pentanoic acid, ethyl ester,** *ethyl pentanoate*, ethyl valerate, ethyl valerianate **[539-82-2]** ***FEMA 2462***

Identified by Merritt *et al.* (1970) in the headspace of green beans of a Columbian arabica (not in a Santos arabica or a robusta).

The odor is powerful and diffusive, ethereal-fruity, apple-like with a remote resemblance to pineapple (Arctander, 1967). The flavor is described as juicy, estery, blueberry, tropical and apple (Chemisis, 1999). An odor threshold of 5 ppb was given by Flath *et al.* (1967) and a flavor threshold of 94 ppb by Keith and Powers (1968).

(F.32) **Pentanoic acid, butyl ester,** *butyl pentanoate*, butyl valerate, butyl valerianate **[591-68-4]** ***FEMA 2217***

Identified in green beans volatiles (simultaneous distillation–extraction and GC of the concentrate) by Spadone and Liardon (1988), only in Puerto Rico 'Rio' coffee and not in other 'Rio' and healthy beans.

The flavor is fruity, apricot-like (Chemisis, 1978).

(F.33) *(F.33)* **Hexanoic acid, methyl ester,** *methyl hexanoate*, methyl caproate **[106-70-7]** ***FEMA 2708***

Identified by Merritt *et al.* (1970) in green and roasted beans.

It is described as having a powerful ethereal and diffusive, sweet odor of pineapple-apricot type (Arctander, 1967).

(F.34) **Hexanoic acid, ethyl ester,** *ethyl hexanoate*, ethyl caproate **[123-66-0]** ***FEMA 2439***

Identified in green immature beans by Full *et al.* (2000), after electronic sorting of the beans followed by simultaneous distillation–extraction.

It is described as pineapple, banana, fruity. The odor threshold in water was 1 ppb according to Takeoka *et al.* (1995).

(F.35) Tetradecanoic acid, 1-methylethyl ester, *isopropyl tetradecanoate*, isopropyl myristate **[110-27-0]** ***FEMA 3556***

Identified by Ramos *et al.* (1998) in headspace after solid-phase microextraction of a brewed arabica (compare with **F.8** and **F.19**).

(F.36) *(F.36)* **Hexadecanoic acid, methyl ester,** *methyl palmitate, methyl hexadecanoate* **[112-39-0]**

Identified by Stoll *et al.* (1967) in a roasted coffee extract and by Cantergiani *et al.* (2001) in a green Mexican arabica extract (after vacuum hydrodistillation) where it represents 0.04% (GC).

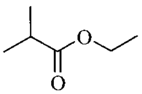
(F.37) **Hexadecanoic acid, ethyl ester,** *ethyl palmitate, ethyl hexadecanoate* **[698-97-7]**

(F.38) **Hexadecanoic acid, butyl ester,** *butyl palmitate, butyl hexadecanoate* **[111-06-8]**

These have been found, like the lower homolog (see **F.36**), by Cantergiani *et al.* (2001) in a green Mexican coffee (respectively 0.12 and 0.05% of the extract in GC). **F.37** had previously been tentatively identified by Spadone and Liardon (1988) in 'Rio' and healthy green beans.

The flavor of **F.38** is described as fatty, waxy, mouthfeel (Chemisis, 1989).

Esters of saturated and unsaturated branched-chain and alicyclic acids



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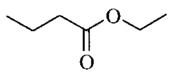

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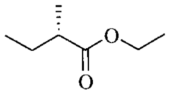

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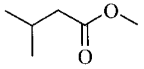

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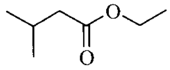

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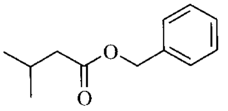

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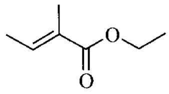

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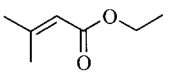

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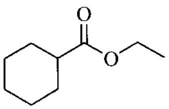


(F.46)

(F.39) **Propanoic acid, 2-methyl-, ethyl ester,** *ethyl isobutyrate, ethyl 2-methylpropanoate*, isobutanoic acid ethyl ester, ethyl 2-methylpropionate **[97-62-1]** ***FEMA 2428***

Identified by Guyot *et al.* (1982, 1983) with low concentration in stinking green coffee and not in healthy beans. This ester is emitted by fresh red berries of two robusta varieties (Mathieu *et al.*, 1996).

The flavor is ethereal, fruity, sweet (Chemisis, 1995). Its pine-cone note can contribute to the defective off-flavor.

(F.40) *(F.40)* **Butanoic acid, 2- methyl-, ethyl ester,** *ethyl 2-methylbutanoate*, ethyl α-methylbutyrate **[7452-79-1]** ***FEMA 2443*; ($\pm$)-[53956-13-1]; (*R*)- [40917-00-8]; (*S*)- [10307-61-6]**

It was identified by Guyot *et al.* (1982, 1983) with a rather high concentration in stinking green coffee, but not in healthy beans. It was also found (said to be a new identification) by Bade-Wegner *et al.* (1998) to contribute to the fruity, over-fermented, flavor defect of certain green coffee beans. While controls only contained 0.15–2.5 ppb, the most contaminated samples contained 37.4 ppb. From aroma values (concentration divided by the threshold value in the matrix), this ester does not contribute to an off-flavor in a roasted coffee when the concentration is only 1.8 ppb.

For Czerny and Grosch (2000), it was one of the potent odorants in green coffee, with a concentration of 2.4 ppb increasing to 3.9 ppb after medium roasting in a Columbian arabica coffee (using multidimensional high-resolution GC/MS). After enantioselective analysis, the authors found that the ester is 95% (*S*)-enantiomer, in agreement with the result of Wöhrmann *et al.* (1997b) for the corresponding acid (**E.16**). Cantergiani *et al.* (2001) found 0.06% (GC) of the volatiles in a green Mexican arabica (see **F.36**).

Its excessive concentration contributes to the perception of a fruity, apricot off-flavor character. For the (*S*)- enantiomer, Karl *et al.* (1992) gave the description of ethereal, sweet, non-specific, becoming pleasantly apple-like when diluted. The flavor of this isomer was described as fruity, ethereal, strawberry, similar to that of the racemic compound (Chemisis, 1995). The odor threshold given by Flath *et al.* (1967) was 0.1 ppb, 0.006 ppb [(+)-(*S*)-] by Takeoka *et al.* (1995) and 0.5 μg/kg cellulose by Czerny and Grosch (2000).

(F.41) *(F.41)* **Butanoic acid, 3-methyl-, methyl ester,** *methyl 3-methylbutanoate*, methyl isopentanoate, methyl isovalerate, methyl isovalerianate **[556-24-1]** ***FEMA 2753***

Its presence was suspected in roasted coffee by Reichstein and Staudinger (1926b) and confirmed later as a headspace component identified by GC/MS (Liardon and Ott, 1984). Procida *et al.* (1997) characterized it in the headspace of a roasted arabica but in none of the green coffees examined. Cantergiani *et al.* (2001) found 0.25% (GC) of the volatiles in a green Mexican arabica extract (see **F.36**).

This ester has a pungent, ethereal, valerian, fruity-apple-like odor of poor tenacity (Arctander, 1967).

(F.42) *(F.42)* **Butanoic acid, 3-methyl-, ethyl ester,** *ethyl 3-methylbutanoate*, ethyl isopentanoate, ethyl isovalerate **[108-64-5]** ***FEMA 2463***

It has been identified by Bade-Wegner *et al.* (1998) as contributing to the over-fermented flavor defect of certain green coffee beans. It was described as fruity, and quantified by the use of stable isotopes as internal standard. While controls only contain 2.3–13.3 ppb, the most contaminated samples contained 345 ppb. The sensory impact is important in green beans, but roasting significantly reduces and nearly eliminates this ester, annihilating its negative contribution. Considering that the threshold value of this ester is only of 0.2–0.5 ppb in coffee beverage, the impact is questionable with a concentration of 13.9 ppb in a roasted coffee, but becomes important with more contaminated samples. Contrary to the results for **F.41**, Procida *et al.* (1997) detected this ester in five green arabicas (out of six) and five green robustas (out of six) but not in the roasted Guatemala arabica. For Cantergiani *et al.* (2001), it represented 0.34% (GC) of a green arabica extract (see **F.36**). Czerny and Grosch (2000) considered it to be a potent odorant in green coffee with an impact of the same order as some pyrazines; they found concentrations of 22 and 14 ppb in green and roasted coffee respectively (see **F.40**).

The odor threshold of 0.6 ppb (cellulose) is given by the latter authors. The flavor is blueberry, fruity, woody, animal (Chemisis, 1995). The threshold in water is 0.01 ppb (Takeoka *et al.*, 1995).

(F.43) **Butanoic acid, 3-methyl-, phenylmethyl ester,** *benzyl 3-methylbutanoate*, benzyl isovalerate **[103-38-8]** ***FEMA 2152***

Identified by Spadone *et al.* (1990) in green coffee volatiles (simultaneous distillation–extraction and analysis by GC/MS).

The flavor is fruity, valerianic (Chemisis, 1970).

(F.44) **2-Butenoic acid, 2-methyl-, ethyl ester, (2*E*)-,** *ethyl (*E*)-2-methylbut-2-enoate*, ethyl tiglate, ethyl α-methylcrotonate **[5837-78-5]** ***FEMA 2460***

Identified in immature green beans by Full *et al.* (2000) (see **F.34**).

Described with a caramel-note, it has an odor threshold of 65 ppb in water, more than 10^4 times that of **F.40** (Takeoka *et al.*, 1998).

(F.45) **2-Butenoic acid, 3-methyl-, ethyl ester,** *ethyl 3-methylbut-2-enoate*, ethyl 3-methylcrotonate, ethyl 3,3-dimethylacrylate, ethyl isobutenoate, ethyl senecioate **[638-10-8]**

Identified by Cantergiani *et al.* (2001) in the extract of a green Mexican arabica: 0.15% in GC (see **F.36**).

The flavor is fruity, pineapple, green, apple skin (Chemisis, 1998). The odor threshold given by Takeoka *et al.* (1998) is 25 ppb in water.

(F.46) **Cyclohexanecarboxylic acid, ethyl ester,** *ethyl cyclohexanecarboxylate*, ethyl cyclohexylmethanoate **[3289-28-9]** ***FEMA 3544***

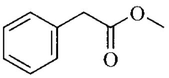
Identified (simultaneous distillation–extraction, GC/MS) by Bade-Wegner *et al.* (1998) as contributing to the over-fermented flavor defect of certain green coffee beans, and quantified by using stable isotopes as internal standard. While controls only contained 0.1–0.7 ppb, the contaminated samples contained

10.4–19.8 ppb. Cantergiani *et al.* (2001), who also found the corresponding acid **E.49**, identified the ethyl ester in their green arabica extract (see **F.36**). It represented 0.05 % by GC.

Bade-Wegner *et al.* (1998) suggested that specific microbes play a role in the the generation of this ester, also found in milk contaminated by certain bacteria.

It is described as fruity, silage-like. Considering that the threshold value of this ester is only 0.005–0.01 ppb in the beverage, its sensory impact is unquestionable.

Esters of benzene-containing acids: Hydroxy and keto esters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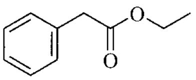
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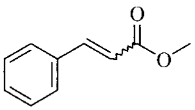
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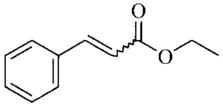
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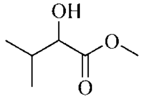
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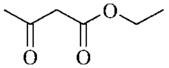
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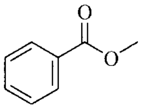
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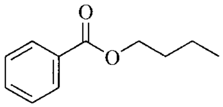

(F.54)
(F.54)

(F.47) Benzeneacetic acid, methyl ester, *methyl phenylacetate* **[101-41-7]** ***FEMA 2733***

Identified by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968) (MS data given).

It has a powerful and quite diffusive honey-musky odor with traces of jasmine-floral notes and moderate to poor tenacity (Arctander, 1967). The flavor is fruity, honey-like (Chemisis, 1999).

(F.48) **Benzeneacetic acid, ethyl ester,** *ethyl phenylacetate*, ethyl phenylethanoate, α-toluic acid, ethyl ester **[101-97-3]** ***FEMA 2452***

(F.50) 2-Propenoic acid, 3-phenyl-, ethyl ester, *ethyl 3-phenylprop-2-enoate*, *ethyl cinnamate*, ethyl β-phenylacrylate **[103-36-6]** ***FEMA 2430***; **(*E*)- [4192-77-2]**; **(*Z*)- [4610-69-9]**

These were identified by Cantergiani *et al.* (2001) in a green Mexican arabica (0.15 and 0.05 % respectively by GC, see **F.36**).

For **F.50**, a flavor threshold of 16 ppb in water was given by Keith and Powers (1968) and the flavor notes are balsamic, fruity, not very different for the two isomers (Chemisis, 1970, 2000).

(F.49) 2-Propenoic acid, 3-phenyl-, methyl ester, *methyl 3-phenylprop-2-enoate*, *methyl cinnamate*, methyl β-phenylacrylate **[103-26-4]** ***FEMA 2698***; **(*E*)- [1754-62-7]**; **(*Z*)- [19713-73-6]**

Identified by Lee *et al.* (1992), when studying extracts as a function of brewing time. It is qualified as 'slow extractor' (low concentration under rapid brewing conditions).

(F.51) **Butanoic acid, 2-hydroxy-3-methyl-, methyl ester,** *methyl 2-hydroxy-3-methylbutanoate* **[17417-00-4]; (±)- [21632-23-5]; (*R*)- [90244-32-9]; (*S*)- [24347-63-5]**

It has been identified by Spadone *et al.* (1990) in Puerto Rico 'Rio' green coffee volatiles (simultaneous distillation–extraction, capillary GC, GC/MS).

(F.52) Butanoic acid, 3-oxo-, ethyl ester, *ethyl acetoacetate, ethyl 3-oxobutanoate*, ethyl acetylacetate, acetoacetic acid ethyl ester, diacetic ether **[141-97-9]** ***FEMA 2415***

Identified by Guyot *et al.* (1988a) by a GC/MS analysis of headspace of a roasted robusta coffee, in a study of the influence of berry ripeness on the final quality of roasted coffee. The concentration of this compound seemed to be higher with red berries collected at the end of harvesting.

(F.53) Benzoic acid, methyl ester, *methyl benzoate* **[93-58-3]** ***FEMA 2683***

Identified by Stoll *et al.* (1967) in roasted coffee flavor.

It is a colorless liquid, with a pleasant odor, having a sweet, berry-like, somewhat spicy, slightly nutmeg-like taste in dilutions below 20 ppm. It is pungent at higher concentrations (Arctander, 1967). The flavor is floral, jasmine, balsamic, fruity (Chemisis, 1991).

(F.54) ***(F.54)*** **Benzoic acid, butyl ester,** *butyl benzoate* **[136-60-7]**

Identified by Spadone *et al* (1990) in green coffee volatiles during investigation of Rio off-flavor. Ramos *et al.* (1998) found it in a brew, in the headspace after solid-phase microextraction (compare with **F.8** and **F.19**).

The flavor is fruity, chemical, strong (Chemisis, 1983).

Other compounds containing ester functions are present in sections 5.H (phenols), 5.I (furans), 5.J (thiophenes), 5.N (pyridines), 5.P (nitrogen compounds) and 5.Q (sulfur compounds).

5.G LACTONES

Lactones are widely distributed in foods and beverages, and confer on them a wide variety of very odorant and tenacious qualities. Saturated and unsaturated aliphatic γ-lactones are widely distributed in the aromas of fruits, meats, dairy products and beverages. Their importance in food flavors (structure, distribution, sensory properties and biosynthesis) has been reviewed by many authors and recently by Dufossé *et al.* (1994) who also showed the frequencies of distribution of saturated γ- and δ-lactones for 100 different foodstuffs. The saturated γ-lactones (**G.1** to **G.6**) which have a strong buttery, fruity character, reminiscent of apricot, peach and coconut, are mainly found in green coffee beans. The α, β-unsaturated γ-lactones, such as **G.7** to **G.13**, which have a stronger roasted and spicy character, are more frequently found in roasted coffee flavor. They are closely related to the tobacco, wood smoke, fried onions, white bread or roasted filberts aromas in which they have also been identified (TNO-CIVO, 1997). The first confirmation of the presence of lactones in roasted coffee were published by Viani *et al.* (1965) for **G.1**, Gianturco *et al.* (1966) for **G.7**, Stoffelsma *et al.* (1968), and by Stoffelsma and Pypker (1968) who identified **G.2**, **G.3**, **G.8**, **G.10**, **G.11**. Latif and Salib (1975b) particularly studied the lactones and the corresponding hydroxy acids present in green and roasted coffee. They observed that the odor of roasted coffee disappeared on treatment with strong alkalis, and reappeared only when the neutralized alkali extract was treated with a dehydrating agent. They concluded that lactones present in coffee clearly contributed to its flavor and that their precursors were hydroxy acids. The characteristic odor of roasted coffee did not appear when the green coffee had previously been extracted with alkali. As for the roasted coffee, the acidification of this alkaline extract with cold concentrated sulfuric acid liberated the typical odor. The authors isolated the hydroxy acids and lactonized them, observing that the residue contained the most characteristic odor of roasted coffee. The authors probably overestimated the contribution of lactones by considering them to be principal odoriferous constituents. Moreover they did not identify any compound, limiting their conclusion to the fact that 'we are dealing with a

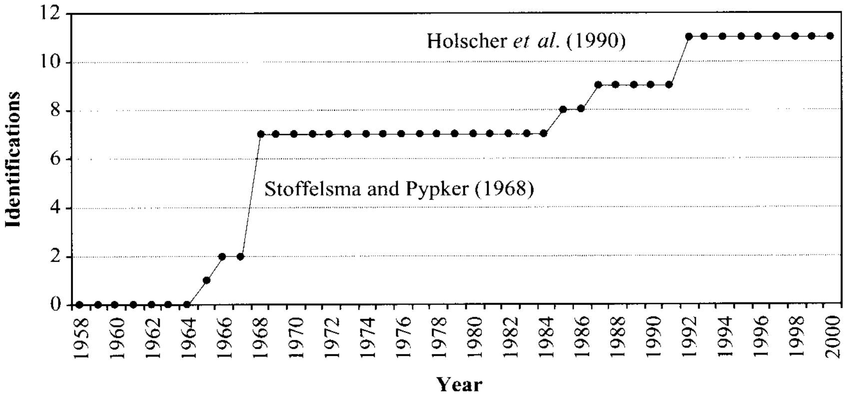


Fig. 5.7 Progressive identification of lactones in roasted coffee volatiles

material containing four carbon atoms or their multiples'. The validity of another study by these authors (Latif and Salib, 1975a) is seriously questionable when they affirm that the qualitative analysis of the odor extract of both roasted and green coffees showed the absence of nitrogen and sulfur compounds!

The γ-quinide **G.15**, the lactone of the main quinic acid (**E.52**) formed during roasting was identified in roasted coffee (chlorogenic lactones have been found in green coffee, see Section 2.1.4). The identification of isomers of this lactone was described by Maier's group (Scholz and Maier, 1990; Scholz-Böttcher *et al.*, 1991; Scholz-Böttcher and Maier, 1992). The formation of the main lactone reached a maximum with a medium roast, whereas the minor isomers increased regularly.

In the volatile fraction of heated glucose, Walter and Fagerson (1968) identified the unsaturated lactone, 2-buten-4-olide (**G.7**) for the first time in this reaction. In a study of model reactions (see Maillard reaction in Section 3.1), Baltes and Bochmann (1987a) identified **G.1**, **G.7**, **G.8**, **G.9** and **G.11** (MS data given), among more than 100 monocyclic furans (and ca 350 volatile compounds) in the reactions of serine and threonine with sucrose under conditions similar to coffee roasting.

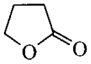
Formation of γ- and δ-lactones by thermal oxidation of saturated fatty acids has been studied by Watanabe and Sato (1971).

In a review, Dufossé *et al.* (1994) mentioned the flavor thresholds of some lactones, particularly the olfactory perception after dispersion in water and the perception 'in mouth' after dispersion in aqueous or deodorized oily solution. They also insist on the different sensory properties of γ-lactone enantiomers isolated by Mosandl and Günther (1989). Guichard *et al.* (1990) studied the lactones in apricot cultivars and found that the (*R*)-enantiomer is always predominant for the γ-C_6 to γ-C_{12} lactones (C_6, C_9 and C_{10} lactones have been identified in green coffee). Certainly because of the small amount present, no study has been conducted in coffee, to our knowledge, on the enantiomeric distribution of the lactones.

Saturated γ-lactones

(G.1) *(G.1)* **2(3*H*)-Furanone dihydro-**, *butano-4-lactone, tetrahydrofuran-2-one*, 4-butanolide, 4-hydroxybutanoic acid lactone, γ-butyrolactone **[96-48-0]** ***FEMA 3291***

Identified in roasted coffee after steam distillation and preparative GC by Viani *et al.* (1965), Gianturco *et al.* (1966), and Stoffelsma *et al.* (1968), also by Gutmann *et al.* (1979) in headspace of green coffee and by Cros *et al.* (1980) in headspace of ground roasted Colombian coffee. Its concentration in roasted coffee was estimated at 4.7 ppm by Stofberg and Stoffelsma (1981). For Shibamoto *et al.* (1982), the formation increased with roasting time at 230 °C (between 25 and 30 min). Cantergiani *et al.* (2001) identified the lactone in an extract (1.53 % by GC) after vacuum hydrodistillation of a green Mexican arabica.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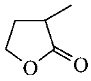
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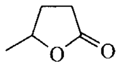
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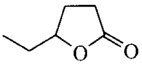
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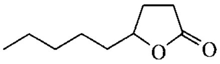
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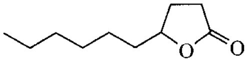

(G.6)

Formation of γ-butyrolactone from glutamic acid has been proposed by Tressl *et al.* (1978d).

This widely distributed and common aroma constituent has a faint, sweet-aromatic odor (Arctander, 1967). The sensory properties mentioned by Dufossé *et al.* (1994) are slightly buttery, acrid, rubbery.

(G.2) 2(3*H*)-Furanone, dihydro-3-methyl-, *2-methylbutano-4-lactone, tetrahydro-3-methylfuran-2-one,* 2-methyl-4-butanolide, 4-hydroxy-2-methylbutanoic acid lactone, α-methyl-γ-butyrolactone **[1679-47-6]; (±)- [69010-09-9]; (*R*)- [55254-35-8]; (*S*)- [65527-79-9]**

Identified by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968) (IR and MS data given).

The flavor is described as solvent, hydrocarbons (Chemisis, 1967).

(G.3) ***(G.3)*** **2(3*H*)-Furanone, dihydro-5-methyl-,** *pentano-4-lactone, tetrahydro-5-methylfuran-2-one,* 4-pentanolide, 4-hydroxypentanoic acid lactone, γ-methyl-γ-butyrolactone, γ-pentalactone, γ-valerolactone **[108-29-2]** ***FEMA 3103;*** **(±)- [57129-69-8]; (*R*)- [58917-25-2]; (*S*)- [19041-15-7]**

Identified by Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968), also by Wang *et al.* (1983) in headspace of roasted coffee. In headspace of brewed coffee, Shimoda and Shibamoto (1990a) found that it represented 0.07 % (peak area) of the volatiles. For Cantergiani *et al.* (2001), it represented 0.85 % of the volatiles in the extract of a green Mexican arabica.

Formation of γ-pentalactone from levulinic acid has been proposed by Tressl *et al.* (1978d).

Warm, sweet, hay- and tobacco-like, herbaceous odor of moderate tenacity (Arctander, 1967). The sensory properties mentioned by Dufossé *et al.* (1994) are sweet, herbaceous, fatty, coconut-like, woody, resinous. The (*R*)- enantiomer has a faint, sweet odor, and the (*S*) is nearly odorless according to Mosandl and Günther (1989). The flavor is milky, fatty, weak for the racemic lactone (Chemisis, 1996).

(G.4) **2(3*H*)-Furanone, 5-ethyldihydro-,** *hexano-4-lactone, 5-ethyltetrahydrofuran-2-one,* γ-hexalactone, 4-hexanolide, 4-hydroxyhexanoic acid lactone, γ-caprolactone **[695-06-7]** ***FEMA 2556;*** **(±)- [57129-70-1]; (*R*)- [63357-95-9]; (*S*)- [41035-07-8]**

Identified by Cantergiani *et al.* (2001) in the extract of a green arabica (see **G.1**), representing 0.54 % (GC).

The sensory properties mentioned by Dufossé *et al.* (1994) are warm, sweet, powerful, herbaceous, caramelic, coumarinic. Mosandl and Günther (1989) found for the (*R*)-enantiomer a faint, sweet coconut with herbaceous note, and for the (*S*) a sweet, creamy coconut odor with some woody aspects. The flavor is weak, sweet for the racemic compound (Chemisis, 1979).

(G.5) **2(3*H*)-Furanone, dihydro-5-pentyl-,** *nonano-4-lactone, tetrahydro-5-pentylfuran-2-one,* 1,4-nonanolide, γ-nonalactone, 4-hydroxynonanoic acid lactone, amylbutyrolactone **[104-61-0]** ***FEMA 2781,*** **[82373-92-0]; (±)- [57084-16-9]; (*R*)- [63357-96-0]; (*S*)- [63357-97-1]**

Identified in Puerto Rico 'Rio' and healthy green coffee (simultaneous distillation extraction, GC/MS) by Spadone *et al.* (1990). It represented 0.5% (GC) of the extract after hydrodistillation in a green Mexican arabica (Cantergiani *et al.*, 2001).

Formation of γ-nonalactone from linoleic acid has been proposed by Tressl *et al.* (1978d).

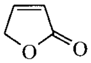
This lactone has an odor reminiscent of coconut; it is one of the flavor constituents of fruits, distilled beverages and wine. The sensory properties, mentioned by Dufossé *et al.* (1994) are strongly coconut, fatty, anise, liquorice, fruity, almond. Mosandl and Günther (1989) described the odor as strong, sweet, soft-coconut with fatty-milky aspects for the (*R*)-enantiomer and fatty moldy, with a weak coconut note for the (*S*), less intense than the (*R*). The flavor of the (*R*)-lactone is herbal, coumarinic, coconut and of the (*S*) coconut, creamy, dairy, mouthfeel (Chemisis, 1993). The threshold is supposed to be very low (estimated at 30 ppb in wine by Nakamura *et al.*, 1988).

(G.6) **2(3*H*)-Furanone, 5-hexyldihydro-,** *decano-4-lactone, 5-hexyltetrahydrofuran-2-one,* 4-decanolide, 4-hydroxydecanoic acid, γ-lactone, 4-hexylbutyrolactone, γ-decalactone **[706-14-9]** ***FEMA 2360;*** **(±)- [2825-92-5]; (*R*)- [107797-26-2]; (*S*)- [107797-27-3]**

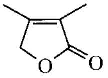
Identified in a Puerto Rico 'Rio' green coffee by Spadone *et al.* (1990).

The sensory properties mentioned by Dufossé *et al.* (1994) are an agreeable fruity odor, typically peach and apricot. For the (*R*)-enantiomer, Mosandl and Günther (1989) found a strong, fatty-sweet, fruity note, with reminiscent of coconut, and for the (*S*) a soft, sweet coconut note, with fruity-fatty aspects. The flavor is fruity, milky, peach (Chemisis, 1988). A flavor threshold of 0.09 ppm was given by Keith and Powers (1968).

Unsaturated alkyl- and hydroxy-substituted γ-lactones



(G·7)



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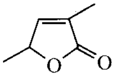
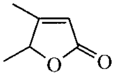


(G·9)



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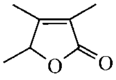

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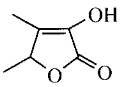

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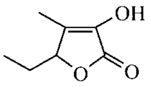


(G·13)

(G.7) 2(5*H*)-Furanone, *but-2-eno-4-lactone, 2,5-dihydrofuran-2-one,* 2-buten-4-olide, 2-butenoic acid, γ-lactone, 4-hydroxy-2-butenoic acid, γ-lactone, crotonolactone, isocrotonolactone **[497-23-4]**

Identified by Gianturco *et al.* (1966), also by Baltes and Bochmann (1987a) (MS data given). Hills *et al.* (1991) extracted and identified it (GC/MS) in roasted coffee, after supercritical fluid derivatization, not as a derivative but rather as the native compound.

(G.8) 2(5*H*)-Furanone, 3,4-dimethyl-, *2,3-dimethylbut-2-eno-4-lactone, 2,5-dihydro-3,4-dimethylfuran-2-one*, 2,3-dimethyl-2-buten-4-olide, 2,3-dimethyl-4-hydroxy-2-butenoic acid, γ-lactone **[1575-46-8]**

Identified by Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968) (IR and MS data given), and also by Baltes and Bochmann (1987a).

(G.9) 2(5*H*)-Furanone, 3,5-dimethyl-, *2-methylpent-2-eno-4-lactone, 2,5-dihydro-3,5-dimethylfuran-2-one*, 2,4-dimethyl-2-buten-4-olide **[5584-69-0]; (*S*)- [127418-12-6]**

Identified by Baltes and Bochmann (1987a) (MS data given).

It has a strong odor of freshly baked bread (Ohloff and Flament, 1979).

(G.10) 2(5*H*)-Furanone, 4,5-dimethyl-, *3-methylpent-2-eno-4-lactone, 2,5-dihydro-4,5-dimethylfuran-2-one*, 3,4-dimethyl-2-buten-4-olide **[10547-85-0]**

(G.11) 2(5*H*)-Furanone, 3,4,5-trimethyl-, *2,3-dimethylpent-2-eno-4-lactone, 2,5-dihydro-3,4,5-trimethylfuran-2-one*, 2,3,4-trimethyl-2-buten-4-olide **[33488-51-6]**

These were identified by Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968) (IR and MS data). **G.11** was also mentioned by Baltes and Bochmann (1987a).

(G.12) *(G.12)* **2(5*H*)-Furanone, 3-hydroxy-4,5-dimethyl-,** *2-hydroxy-3-methylpent-2-eno-4- lactone, 2,5-dihydro-3-hydroxy-4,5-dimethylfuran-2-one*, 2-hydroxy-3,4-dimethyl-2-buten-4-olide, sotolon(e) **[28664-35-9]** ***FEMA 3634***

Identified by Blank *et al.* (1992a) in powder and brew of roasted arabica and robusta (with a lower concentration) coffees. Concentrations of 1.36–1.47 ppm in arabica (1.7 in a Kenya arabica by Grosch *et al.*, 1996), 0.63 ppm in robusta were measured by Semmelroch *et al.* (1995) using stable isotope dilution assays. It was found in raw and medium-roasted arabica coffee (extraction, distillation, separation of acids) by Czerny and Grosch (2000) who gave concentrations of 0.7 ppb in green and 1.870 ppm in roasted coffee.

Hofmann and Schieberle (1996) suggested hydroxyacetaldehyde and 2,3-butanedione as possible precursors of this odorant lactone. A mechanism of formation (in 'vin jaune') has been proposed by Guichard *et al.* (1998) by transformation of threonine (present in coffee) into 2-oxobutyric acid (which can also be derived from carbohydrates), condensation with acetaldehyde and cyclization.

The synthesis described by Sulser *et al.* (1972) starts by condensation of diethyl oxalate with ethyl propanoate, which is followed by condensation with acetaldehyde and acidic decarboxylation. Martin *et al.* (1990) used this synthesis but with aqueous thermal decarboxylation, the sample thus obtained proved to be stable (three years in a freezer). They studied the equilibrium between the enolic sotolone and the ketolactonic form. The enol was unstable at high pH values and the transformation was irreversible by lowering the pH. Only the enol was observed in UV and NMR spectra. Moreover the degradation by UV light led the authors to suspect the intervention of a UV-induced radical. One of the degradation product was 1-penten-3-ol (**B.30**). Both the enantiomers have been synthesized by Okada *et al.* (1983) from the enantiomers of tartaric acid.

This compound was identified in a French flor sherry wine by Dubois *et al.* (1976) and was characterized by Etievant (1991) as having a 'typical vin jaune du Jura', nutty, sweet and sugared flavor. For Sulser *et al.* (1972) it had a strong, spicy, walnut aroma at a concentration of 0.1 ppb and a taste threshold of 1–5 ppb. It has a burnt flavor and a typically caramel odor (Manley *et al.*, 1980). Okada *et al.* (1983) found that the two enantiomers had the identical sugary flavor and the same insect attractant properties as the racemic sotolone. It was considered by Blank *et al.* (1992a,b) to be a potent odorant in roasted arabica with a seasoning-like odor (GC-olfactometry) becoming caramel-like in higher dilution with an odor threshold of 0.01–0.020 $\mu g/m^3$ air, and 20 ppb in water for Semmelroch *et al.* (1995). It was considered also to be a potent odorant in raw coffee with a spicy odor description and an odor threshold of 2.1 ppb (cellulose) by Czerny and Grosch (2000).

(G.13) 2(5*H*)-Furanone, 5-ethyl-3-hydroxy-4-methyl-, *2-hydroxy-3-methylhex-2-eno-4-lactone, 5-ethyl-2,5-dihydro-3-hydroxy-4-methylfuran-2-one*, 4-ethyl-2-hydroxy-3-methyl-2-buten-4-olide, 2,4-dihydroxy-3-methyl-2-hexenoic acid, γ-lactone, α-hydroxy-β-methyl-$\Delta^{\alpha,\beta}$-γ-hexenolactone, abhexone **[698-10-2]** ***FEMA 3153;*** **(±)- [144810-13-9]; (*R*)- [144831-60-7]; (*S*)- [144831-61-8]**

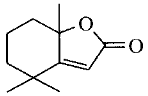
Identified by Blank *et al.* (1992a) in roasted arabica coffee and with a very low concentration in robusta coffee. Concentrations of 0.160 ppm in arabica and 0.085 ppm in robusta roasted coffees are given by Semmelroch *et al.* (1995) and Grosch *et al.* (1996) using stable isotope dilution assays.

The synthesis was identical to that of **G.12**, using propanal instead of acetaldehyde (Sulser *et al.*, 1972). The same group (Sulser *et al.*, 1967) previously achieved the synthesis by aldol condensation of α-ketobutyric acid followed by decarboxylation.

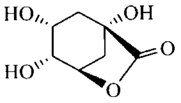
The same authors described a formation pathway from threonine starting by the degradation to α-ketobutyric acid.

This lactone is the flavoring compound formed by the aging of α-ketobutyric acid (Sulser *et al.*, 1967). The flavor is described as malt, molasses, maple, burnt sugar (Chemisis, 1965), with a strong seasoning-like aroma at a concentration of 0.1 ppm and a taste threshold of 1–5 ppb for Sulser *et al.* (1972). Manley *et al.* (1980) reported a maple-like, remarkably persistent curry-like odor and wondered if the enolization or the instability of the compound could be responsible for the two notes. It is a potent odorant of roasted powder and brew of arabica coffee with odor descriptions similar to those of **G.12**, and an odor threshold of 2–4 ng/m^3 air (Blank *et al.*, 1992a,b), of 7.5 ppb in water (Semmelroch *et al.*, 1995).

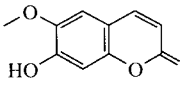
Bicyclic lactones



(G·14)



(G·15)



(G·16)

(G.14) **2(4*H*)-Benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-,** *2,4,5,6,7,7a-hexahydro-4,4,7a-trimethylbenzofuran-2-one*, dihydroactinidiolide, **[15356-74-8]; (*R*)- [17092-92-1]**

Identified in green coffee by Vitzthum *et al.* (1976), and by Cantergiani *et al.* (2001) in a green Mexican arabica where it represented 0.10% (GC) of the volatiles obtained after vacuum hydrodistillation and extraction.

It may be formed *in vivo* from β-carotene by a mechanism similar to photooxygenation, according to Isoe *et al.* (1969). It has been found in black tea aroma and is formed probably from β-carotene as secondary oxidation product during fermentation (Sanderson *et al.*, 1971).

Demole and Enggist (1968) synthesized (±)-dihydroactinidiolide from β-cyclohomogeranic acid (2,6,6-trimethyl-1-cyclohexene-1-acetic acid) with two variants. Cyclization of the epoxide gave a hydroxylactone which was dehydrated, or the acid was transformed into the iodolactone which was dehydrohalogenated. A similar synthesis with bromine was carried out by Sakan *et al.* (1967).

The flavor is weak, woody, floral (Chemisis, 1974).

(G.15) 6-Oxabicyclo[3.2.1]octan-7-one, 1,3,4-trihydroxy-, *endo*, *endo*-(±)-, (±)-*3endo, 4endo-1,3,4-trihydroxy-6-oxabicyclo[3.2.1]octan-7-one*, γ-quinide **[770-67-2]**

Identified with certainty in roasted coffee by Sturm (1983 thesis, quoted by Hucke and Maier, 1985); it could only be detected after a roasting loss of 6.5% and the concentration reached a maximum (ca 1%). Maier's group (Scholz and Maier, 1990; Scholz-Böttcher *et al.*, 1991; Scholz-Böttcher and Maier, 1992) identified the isomers of quinide (γ-and δ-lactones), the concentrations of which increased regularly with roasting.

(G.16) **2*H*-1-Benzopyran-2-one, 7-hydroxy-6-methoxy-,** *7-hydroxy-6-methoxy-2*H*-chromen-2-one, 7-hydroxy-6-methoxy-2*H*-1-benzopyran-2-one*, 7-hydroxy-6-methoxycoumarin, scopoletin, β-methylesculetin **[92-61-5]**

Identified in green coffee by Thier *et al.* (1968). The content in arabicas (Columbia, Santos) was about 0.1 ppm, 3 to 4 times lower than in African robustas.

This lactone, related to ferulic acid, could be formed by degradation of its glucoside, scopolin, or by direct cyclization of ferulic acid (**H.87**). It was noted that esculetin, the lactone corresponding to caffeic acid (**H.86**) has not been reported (Clifford, 1975a).

2*H*-1-benzopyran-2-one, coumarin, (*o*-hydroxycinnamic acid lactone) **[91-64-5]**

This was mentioned by Dyszel (1985) as found to be present in green coffee when trying to find a way for differentiating coffees of various origins. One of the ions (M+1) studied by thermogravimetric analysis/atmospheric pressure chemical ionization mass spectrometry is 149 but the molecular weight of coumarin is 146. It is therefore difficult to determine where the error is.

5.H PHENOLS

Phenols are widespread in nature and as such are consumed in most diets. They are present in nature in bound or conjugated form, but flavor analysts generally limit their interest to the most significant free forms and to the relatively low-molecular-weight constituents. Nearly 140 simple phenols have been identified in a multitude of food systems, including alcoholic and non-alcoholic beverages, meat and poultry products, milk and cheese, nuts, vegetables, fruits and cereals (Maga, 1978a). Phenols are essential contributors to the typical quality of coffee flavor, with their ca 80 representatives discussed in this chapter. They are often qualified as having a somewhat negative character as tarry, smoky, woody, spicy, leathery or medicinal. Nevertheless most of them, at low concentrations, are described as having a sweeter, warm, floral, balsamic with pleasant vanilla, clove, carnation or anisic character. On account of their low volatility and crystalline state, polyphenols were among the first aromatic compounds identified in food flavors. Gallic acid (**H.75**) isolated by Scheele in 1786 (Thénard, 1818a), was indeed among the first constituents considered to be a coffee constituent. Robiquet and Boutron (1837a) suggested that a free acid present in green coffee would be effectively gallic acid, considering its reaction with ferric chloride, but a caffeic acid residue would have given the same result (Clifford, 1985a). As rightly observed by Scheele, gallic acid (**H.75**) only exists linked to tannins and it was at that time, in this form, frequently used as a dying agent. Later, Bernheimer (1880a) proposed that the unidentified 'caffeol' was a phenolic compound since it has a smell reminiscent of creosol (2-methoxy-4-methylphenol, 4 methylguaiacol) (**H.34**) or veratrole (1,2-dimethoxybenzene) (**H.40**). He confirmed the presence of hydroquinone (**H.25**) and Jaeckle (1898) identified resorcinol (**H.24**). Erdmann (1902a) mentions that certain distillation fractions probably contain a high proportion of phenolic compounds since they smell like creosote and guaiacol. Phenol (**H.1**), catechol (**H.23**), guaiacol (**H.33**), vinylguaiacol (**H.36**) and 2,3-dihydroxyacetophenone (**H.64**) as well as 'further phenols and phenol ethers of a higher valency' were only discovered by Reichstein and Staudinger (1926b) but considered to be 'split products obtained by analysis, the real products being themselves unstable and not capable of being isolated'.

The transition period preceding the advent of gas chromatography and the use of efficient identification methods, was relatively sterile. We will mention the works of Prescott *et al.* (1937b) and Högl (1958). Surprisingly, the latter author seemed to ignore the previous works, claiming the first identification of catechol (**H.23**) or hydroquinone (**H.25**) that had been mentioned by Bernheimer (1880a). Nevertheless he is credited of the identification of 1,2,3-trihydroxybenzene (pyrogallol, **H.45**). When studying the constituents of roasted coffee and their behavior during staling, Hughes and Smith (1949) tried to quantify the volatile phenol content using Folin reagent and measuring the resulting blue color with a photometer. The results were arbitrarily recorded as guaiacol, since the exact composition of the phenols was not known. The method was difficult, phenols being continuously produced by decomposition of the chlorogenic acids during boiling. Nevertheless the results showed that the total volatile phenol content increased proportionally with the extent of roasting. The Sixties, with the works of Radtke (1964), Gianturco *et al.* (1966), Reymond *et al.* (1966a,b,c) and Stoll *et al.* (1967) were, by way of compensation, a prolific period for original identifications. Pypker and Brouwer (1970) showed by headspace analysis of less volatile constituents of coffee that robusta is richer than arabica coffee in phenolic constituents.

During the next decade, Tressl *et al.* (1978a,b, 1979a) described the identification of mono-, di-, and triphenols and derivatives in roasted coffees: arabica, robusta and the hybrid arabusta. By distillation–extraction, extraction at various pH, separation by adsorption chromatography, and characterization by GC/MS, they isolated 30 phenols, 11 of them being new in coffee [three having undetermined positions for the substituents; in the eight well-defined phenols, 2,3- and 3,4-dimethylphenols, **H.10** and **H.14**, were designated as new but had in fact already been identified by Stoll *et al.* (1967); it is probably question of 2,4-and 3,5-dimethylphenols **H.11** and **H.15**]. The authors observed that robusta coffee had the highest content of monophenols and guaiacols, followed by arabusta (Ivory Coast) then arabica. Quantities and types of phenols depend on the varieties as well as on the roasting conditions, in particular dimethyl- and trimethylphenols were detected in over-roasted coffee. From the figures, the content in diphenols was less important in the hybrid arabusta than in the two other varieties. Heinrich and Baltes (1987a) also quantified phenols in roasted and over-roasted robusta coffee (Cameroon); the coffee extract treated at pH 6.5–6.8 was steam distilled and, after various extractions and treatment by trimethylsilane, the phenols were identified (GC/MS). Among them, 16 were newly identified in roasted coffee (two dimethyl-1,2-diphenols having undetermined positions of the substituents). Although the figures may differ from those of Tressl (see references above) there is a certain agreement that phenol (**H.1**) is the only relatively important monophenol, and that among the diphenols and derivatives, 1,2-benzenediol (**H.23**) is the most important, followed by the 4-ethyl-derivative (**H.29**) and 2-methoxy-4-vinylphenol (**H.36**) (4-vinylguaiacol). Silwar and Lüllmann (1993b) studied the formation of aroma during roasting (of a robusta from Philippines) and determined concentrations every 10 °C, from 170 up to 260 °C, after a constant roasting time (5 min) confirming the increase in content of phenols during roasting and over-roasting with only few exceptions '4-vinylbrenzcatechin' (**H.30**) and vanillin (**H.56**). Even (**H.36**), found by Tressl *et al.* (1978b) to decrease upon over-roasting, apparently starts with a rapid increase.

Coffee, like tea and cocoa, contains polyhydroxyphenols with antioxidative effects *in vitro* and *in vivo* which are related to reducing and radical scavenging properties. Catechol (**H.23**) is one of the most effective, followed by the cinnamic derivatives, ferulic (**H.87**), sinapic (**H.90**) and caffeic (**H.86**) acids. The benzoic acids are less effective (Bungert and Eichner, 2000).

It must be remembered that some phenols mentioned in this chapter do not necessarily exist in the free state in ground coffee or beverages. They are often present in so-called condensation products or complexes that are covalently linked with proteins or protein fragments, also with unchanged polysaccharides and with some components such as chlorogenic acids and their breakdown products. Such brown-colored complexes have been variously referred to as 'humic acids' or 'coffee-melanoidins', caramel compounds or just 'Maillard products' (Trugo, 1985). Some phenols have only been identified after alkaline pressure hydrolysis of the humic substances, as described by Klöcking *et al.* (1971), but their presence is convenient for explaining the origin of certain simple phenolic acids from chlorogenic acids. Stadler *et al.* (1996) identified two tetraoxygenated phenylindan isomers alter mild pyrolysis (225–226 °C) of caffeic acid: they are the *cis*-and *trans*-isomers of 2,3-dihydro-3-(3,4-dihydroxyphenyl)-1*H*-indene-5,6-diol. The proposed mechanism for their formation is the dimerization of 4-ethenyl-1,2-benzenediol (**H.30**). These phenols are probably involved in hydrogen peroxide formation in coffee.

Formation pathways

The phenolic compounds present in smoke and partly in roasted coffee are derived from the lignin portion of wood. The presence of ferulic acid (**H.87**), a primary thermal decomposition product of lignin, and its decomposition appear to be the source of other phenolic compounds. Fiddler *et al.* (1967) described the isolation and identification of the degradation products and their possible mode of formation. They submitted ferulic acid to higher temperatures than those generally used during coffee roasting, in presence or absence of air. Guaiacol (**H.33**), and its 4-vinyl- (**H.36**), 4-ethyl- (**H.35**) and 4-methyl- (**H.34**) derivatives are formed even in absence of air, contrary to vanillin (**H.56**), acetovanillone (**H.66**) and vanillic acid (**H.74**) formed only in presence of air. '*cis*'-Isoeugenol (*Z*-?) (**H.38**) was also identified. Although the conclusion was that the first stage of the decomposition occurred at 245 °C, all derived phenolic components are present in roasted coffee flavor constituents.

Later, Tressl *et al.* (1976) also proceeded to the thermic degradation (2 h, 200 °C) of ferulic acid (**H.87**) and identified the same phenols as Fiddler *et al.*, plus 4-isopropylguaiacol and vanillin alcohol (4-hydroxy-3-methoxybenzenemethanol) which have not been found in coffee. For isoeugenol (**H.38**), the formula is written as the (*E*)-('*trans*'-) isomer, but nothing was specified in the text. Tressl *et al.* (1976) also published the results of thermal decomposition of cinnamic, *p*-coumaric (**H.84**) and sinapic (**H.90**) acids. Many of the simple phenols (and other aromatic compounds) formed have also been identified in roasted coffee volatiles. A thermic fragmentation of quinic acid (**E.62**) has shown that simple acids, phenols and polyphenols originate from this precursor (Tressl *et al.*, 1978a).

A scheme for the formation of guaiacols from ferulic acid has also been proposed by Manley *et al.* (1974). The biosynthesis of various phenolic acids from *p*-coumaric acid (**H.84**) was studied by Friedrich (1976). Formation pathways for simple phenols in food flavors have been reviewed (Maga, 1978a). The two primary pathways could be the decarboxylation of phenolic carboxylic acids and the thermal degradation of lignin. Secondary pathways include bacterial, fungal, yeast enzymic and glycosidic reactions.

Clifford and Hole (1977) published a review dealing with the natural occurrence, biosynthesis, applications and syntheses of cinnamaldehydes. In fact, many cinnamoylquinic conjugates are widespread in the plant kingdom. Clifford (1985a) also reviewed the chlorogenic acids of coffee, detailing their extraction and analysis, their content in soluble powders, in green and roasted beans, and organoleptic properties contributing to the beverage quality. The author gave a list of low-molecular-weight phenols in coffee pigment hydrolysates: **H.55**, **H.69–70**, **H.72–75**, **H.86–87** (the 3,4,5-trihydroxybenzene also mentioned could be 1,2,3-trihydroxybenzene, **H.45**) which had been identified by himself, by Klöcking *et al.* (1971) and by Tressl *et al.* (1978a,b). If guaiacols (**H.33–36**) were derived from the ferulic acid residue (**H.87**), catechol (**H.23**) and pyrogallol (**H.45**) probably derived mainly from the quinic acid residue (**E.62**). Ethyl- (**H.29**), vinylcatechol (**H.30**) and

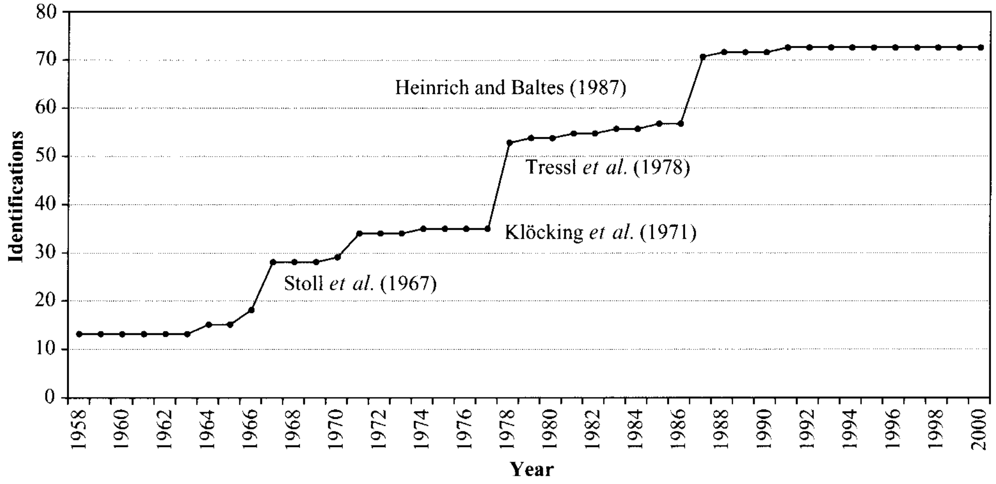


Fig. 5.8 Progressive identification of phenols in roasted coffee volatiles

3,4-dihydroxycinnamaldehyde (**H.58**) resulted from the degradation of the caffeic acid residue (**H.86**) (Clifford, 1979).

According to Silwar and Lüllmann (1993a), roasted robustas show significantly higher contents in phenols and phenols ethers than roasted arabicas because of the corresponding high contents in chlorogenic acids and 3-feruloylquinic acid in the green coffees (see 2.1.4).

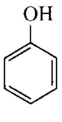
Organoleptic qualities and threshold values

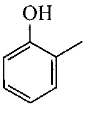
Rahn and König (1978) recalled previous findings suggesting that phenols and other moderately acidic organic components could be responsible for the frequently observed nauseous symptoms of sensitive coffee drinkers. It was not known whether there is a specific component that is responsible for nausea. This was why they analyzed an ether extract of a coffee infusion, analysis of which allowed the identification of three new coffee constituents: 3-methyl- (**H.26**), 4-ethyl- (**H.29**) 1,2-benzenediols and 1,2,4-benzenetriol (**H.46**) (these three were identified in the same year by Tressl *et al.*, 1978a). Nevertheless, the authors did not comment on the physiological properties of these phenolic compounds. Apparently contradictory facts have also been observed concerning the influence of phenolic compounds in foods. Maga and Lorenz (1973) and Maga (1978a) reported the synergistic lowering of flavor threshold values when certain phenols were mixed, whereas King and Solms (1981) have shown that chlorogenic acids raise the threshold values of some odor volatiles. Taste threshold values in aqueous solution for more than 30 phenolic acids and ethers have been evaluated by Maga and Lorenz (1973). The odor or taste thresholds of numerous simple phenols have also been measured by Winter *et al.* (1976o) in a syrup base and in two soluble coffee bases.

Monophenols and ether

(**H.1**) *(H.1)* **Phenol,** *phenol*, phenyl alcohol, phenic acid, benzenol, hydroxybenzene **[108-95-2]** ***FEMA 3223***

Identified by Reichstein and Staudinger (1926b) and Heins *et al.* (1966). Tressl *et al.* (1978b) found concentrations of 13.0 (arabica) to 17.0 ppm (robusta) (9.5 for arabusta) in normally roasted coffee with an increase up to 60 ppm (arabica) after over-roasting. Silwar and Lüllmann (1993b) found $\ll 1$ ppb at 170 °C (5 min), 1.55 ppm at 230 °C (5 min) for a robusta. Heinrich and Baltes (1987a) gave somewhat higher concentrations than Tressl, 53.7 for normally roasted and 141 ppm for over-roasted robusta (Cameroon) coffee. Ho *et al.* (1993) found only 0.20 ppm in a roasted Columbian coffee. Phenol has also been identified in green coffee volatiles (steam distillation) by Vitzthum *et al.* (1976). The ion $M+1$ ($m/z = 95$) was one of the ions used for trying to differentiate green coffees of various origins and determine unknown origins by Dyszel (1985), with thermogravimetric analysis/atmospheric pressure CI-MS. The corresponding peak area represented 0.18 % in an extract of a Mexican arabica obtained after hydrodistillation at ambient temperature, extraction and GC (polar)/MS (Cantergiani *et al.*, 2001).


(H·1)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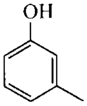
(H·3)
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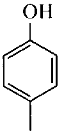
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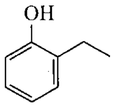
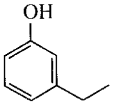
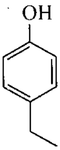

(H·5)


(H·6)


(H·7)
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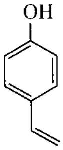
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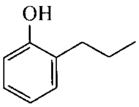

(H·9)

Phenol is characterized by a smoky aroma (Maga, 1978a). Odor thresholds quoted by Maga are 5.9 ppm in water, 47 ppb in air. Characteristics reported by Kim Ha and Lindsay (1991) are: medicinal, smokey, shoe-polish-like (neat), a taste threshold of 250 ppb in water.

(H.2) Phenol, 2-methyl-, *2-methylphenol, o-cresol,* 1-hydroxy-2-methylbenzene, 2-hydroxytoluene, *o*-cresylic acid **[95-48-7]** ***FEMA 3480***

Identified by Radtke (1964), Radtke *et al.* (1966a), Stoll *et al.* (1967) and Stoffelsma *et al.* (1968). Tressl *et al.* (1978b) found concentrations of 1.1 (robusta) to 1.2 ppm (arabica) (0.7 for arabusta) with normal roasting and 12.4 ppm with over-roasting (arabica). Values from Silwar *et al.* (1987) were in the same range: 0.7–1.1 ppm. Heinrich and Baltes (1987a) gave 1.8 and 2.8 ppm respectively for a robusta normally and over-roasted. Silwar and Lüllmann (1993b) find $\ll 1$ ppb at 170 °C (5 min), and 0.45 ppm at 230 °C (5 min) for a robusta.

The odor threshold in water quoted by Maga (1978a) was 0.065 ppm. As reported by Kim Ha and Lindsay (1991), 2-methylphenol is phenol-like, indole-like, medicinal (neat) with odor thresholds varying from 65 to 260 ppb in water.

(H.3) ***(H.3)*** **Phenol, 3-methyl-,** *3-methylphenol, m-cresol,* 3-hydroxytoluene, 3-methyl-1-hydroxybenzene, *m*-cresylic acid **[108-39-4]** ***FEMA 3530***

Identified by Gianturco *et al.* (1966). In this publication the name used is '*m*-creosol' but it is meant to be *m*-cresol (the name creosol has been used for **H.34**). The concentration in coffee is 0.7 (arabica) to 1.2 ppm (robusta) for Tressl *et al.* (1978b) (1.0 for arabusta) and 7.4 ppm by over-roasting. The values of

Silwar *et al.* (1987) were in the same range: 0.15–0.50 ppm and those of Heinrich and Baltes (1987a) were 3.6 and 5.5 ppm respectively for normally and over-roasted robusta. Silwar and Lüllmann (1993b) found ≪1 ppb at 170 °C (5 min), 0.20 ppm at 230 °C (5 min) for a robusta. This phenol has also been found in headspace of brewed coffee by Cros *et al.* (1980), in headspace of a freshly ground roasted coffee heated at 100 °C by Wang *et al.* (1983). In a green Mexican arabica it was recently identified by Cantergiani *et al.* (2001).

The odor is dry-tarry, medicinal-leathery (Arctander, 1967). The flavor is described as phenolic, medicinal, barn-yard, dirty (Chemisis, 1999). Maga (1978a) reports a an odor threshold in water of 68 ppb. Kim Ha and Lindsay (1991) report phenol-like, fresh hot asphalt-like, wood preservative-like, indole-like (neat) characteristics with odor thresholds ranging from 68 to 200 ppb in water.

(H.4) Phenol, 4-methyl-, *4-methylphenol, p-cresol*, 4-hydroxytoluene, *p*-cresylic acid [106-44-5] *FEMA 2337*

Identified by Radtke (1964) and Radtke *et al.* (1966a). For Tressl *et al.* (1978b), the concentration in coffee was 1.0 (robusta) to 1.3 ppm (arabica) (0.3 for arabusta) with an increase to 13.2 ppm by over-roasting. Silwar *et al.* (1987) mentioned 0.30–0.50 ppm, Heinrich and Baltes (1987a) 0.5 and 2.1 ppm for normally and over-roasted robusta. Silwar and Lüllmann (1993b) found ≪1 ppb at 170 °C (5 min), 1.50 ppm at 230 °C (5 min) for a robusta.

The odor is tarry-smoky, medicinal type, and sweeter, almost floral in extreme dilution (Arctander, 1967). The flavor is solvent, medicinal, animal, rum and fruity (Chemisis, 1999).

An odor threshold of 8×10^{-3} in ethanol–water 9.4% was given by Adda and Jounela-Eriksson (1979). Maga (1978a) reported an odor threshold of 1 ppb in air with a phenol-like aroma, and Kim Ha and Lindsay (1991) reported odor characteristics similar to those of *m*-cresol (**H.3**) with odor thresholds from 2 to 550 ppb in water.

(H.5) Phenol, 2-ethyl-, *2-ethylphenol*, *o*-ethylphenol, phlorol [90-00-6]

Identified by Stoll *et al.* (1967). Tressl *et al.* (1978b) determined a concentration of 1.7 ppm in an over-roasted arabica coffee.

It has a semi-sweet, tarry-medicinal odor, tar-like, smokey (Arctander, 1967); burnt, guaiacol-like (from Kim Ha and Lindsay, 1991). The flavor is chemical, phenolic, disinfectant (Chemisis, 1963).

(H.6) Phenol, 3-ethyl-, *3-ethylphenol* [620-17-7]

Identified by Tressl *et al.* (1978b) who found a concentration of 0.4 ppm in normally roasted arabusta coffee and 1.3 ppm in an over-roasted arabica.

It has a burnt taste (Winter *et al.*, 1976o). It is phenolic for Holscher *et al.* (1990), phenolic, sheepy, medicinal when neat, as reported in Kim Ha and Lindsay (1991).

(H.7) *(H.7)* Phenol, 4-ethyl-, *4-ethylphenol* [123-07-9] *FEMA 3156*

Identified by Stoll *et al.* (1967), noted also by Tressl *et al.* (1978b) in arabica coffee. Heinrich and Baltes (1987a) found 0.8–0.9 ppm for normal and over-roasting of a robusta coffee. Cantergiani *et al.* (2001) identified it in green Mexican arabica coffee.

Formed by reduction of *p*-vinylphenol (**H.8**).

Powerful, woody-phenolic, medicinal, yet rather sweet odor, somewhat to the anisic type (Arctander, 1967). In a wine it recalls horse manure (Dubois, 1983). Kim Ha and Lindsay (1991) report phenolic, sheep pen-like descriptions when neat, with odor threshold in water of 600 ppb and taste threshold of 100 ppb.

(H.8) *(H.8)* Phenol, 4-ethenyl-, *4-vinylphenol* [2628-17-3] *FEMA 3739*

Identified in green coffee beans volatiles by Vitzthum *et al.* (1976). The concentration for Tressl *et al.* (1978b) is 0.02 ppm in roasted arabica, robusta as well as in arabusta coffees, 0.6 ppm in an over-roasted arabica; it is less than to 0.1 ppm in roasted or over-roasted robusta, for Heinrich and Baltes (1987a).

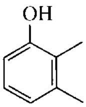
It is formed by decarboxylation of *p*-coumaric acid (**H.84**).

The flavor is described as phenolic, smoky, medicinal (Chemisis, 1999).

(H.9) Phenol, 2-propyl-, *2-propylphenol* [644-35-9] *FEMA 3522*

Identified by Tressl *et al.* (1978b) in an over-roasted arabica.

It has a smoky, fatty, meaty flavor (Chemisis, 1974).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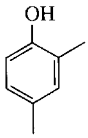
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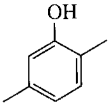
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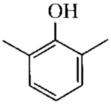
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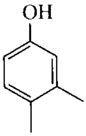
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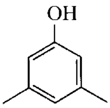
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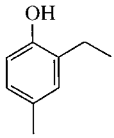
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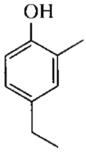
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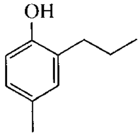
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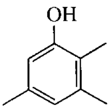
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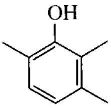
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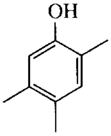
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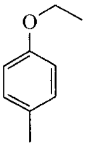

(H·22)

(H.10) Phenol, 2,3-dimethyl-, *2,3-dimethylphenol*, 2,3-xylenol, *o*-xylenol, 1-hydroxy-2,3-dimethylbenzene [526-75-0]

Identified by Stoll *et al.* (1967). Its presence in coffee, at a concentration of 2.1 ppm in an over-roasted arabica, has been confirmed by Tressl *et al.* (1978b).

o-Xylenol has a cresolic taste (Winter *et al.*, 1976o). Odor characteristics are chemical, phenolic, stale, musty (neat) as quoted by Kim Ha and Lindsay (1991).

(H.11) Phenol, 2,4-dimethyl-, *2,4-dimethylphenol*, 1,2,4-xylenol, *m*-xylenol [105-67-9]

Identified by Tressl *et al.* (1978b) who found a concentration of 2.0 ppm.

The flavor is described as burnt, roasted, animal, cresolic (Chemisis, 1994). According to Kim Ha and Lindsay (1991) odor characteristics are similar to those of the 2,3-isomer **H.10**.

(H.12) Phenol, 2,5-dimethyl-, *2,5-dimethylphenol*, 2,5-xylenol, *p*-xylenol **[95-87-4]** ***FEMA 3595***

Identified by Stoll *et al.* (1967). Tressl *et al.* (1978b) found 1.5 ppm in an over-roasted arabica.

It has a smoky, sweet, guaiacol flavor (Chemisis, 1994).

(H.13) Phenol, 2,6-dimethyl-, *2,6-dimethylphenol*, 2,6-xylenol, cresylic acid (this last name causes confusion with the monomethylphenols) **[576-26-1]** ***FEMA 3249***

Identified by Stoll *et al.* (1967), Stoffelsma *et al.* (1968) and Silwar (1982). A concentration of 0.2 ppm was given by Tressl *et al.* (1978b).

This phenol has a ground-coffee note, sweet and burnt taste (Winter *et al.*, 1976o). Odor perception at the sniffing port is simply phenolic (Holscher *et al.*, 1990).

(H.14) Phenol, 3,4-dimethyl-, *3,4-dimethylphenol*, 3,4-xylenol **[95-65-8]** ***FEMA 3596***

Identified by Stoll *et al.* (1967). Tressl *et al.* (1978b) found 0.8 ppm in an over-roasted arabica coffee.

The flavor description is smoky, sweet, earthy (Chemisis, 1994). The odor perception is phenolic at the sniffing port for Holscher *et al.* (1990). Kim Ha and Lindsay (1991) reported the odor as being chemical, phenolic, indole-like, animal-like (neat).

(H.15) Phenol, 3,5-dimethyl-, *3,5-dimethylphenol*, 3,5-xylenol **[108-68-9]**

Identified by Tressl *et al.* (1978b).

The odor is sweet, phenolic, slightly medicinal (neat), as quoted in Kim Ha and Lindsay (1991), and the flavor weak, metallic (Chemisis, 1994).

(H.16) Phenol, 2-ethyl-4-methyl-, *2-ethyl-4-methylphenol*, 2-ethyl-*p*-cresol **[3855-26-3],**

(H.17) Phenol, 4-ethyl-2-methyl-, *4-ethyl-2-methylphenol* **[2219-73-0]**

(H.18) Phenol, 4-methyl-2-propyl-, *4-methyl-2-propylphenol*, 2-propyl-*p*-cresol **[4074-46-8]**

These were identified by Tressl *et al.* (1978b), who found 1.0, 0.9 and 0.2 ppm respectively, in an over-roasted arabica. Ho *et al.* (1993) found a concentration of 0.32 ppm for **(H.16)** in a roasted Columbian coffee.

(H.19) Phenol, 2,3,5-trimethyl-, *2,3,5-trimethylphenol*, 1-hydroxy-2,3,5-trimethylbenzene, isopseudocumenol **[697-82-5]**

Identified by Stoll *et al.* (1967). Tressl *et al.* (1978b) gave a concentration of 0.3 ppm in an over-roasted arabica.

It has a woody note (Winter *et al.*, 1976o).

(H.20) Phenol, 2,3,6-trimethyl-, *2,3,6-trimethylphenol* **[2416-94-6]**

(H.21) Phenol, 2,4,5-trimethyl-, *2,4,5-trimethylphenol*, pseudocumenol **[496-78-6]**

These were identified by Tressl *et al.* (1978b), who found concentrations in an over-roasted arabica. of 0.2 ppm for **H.20** and 0.3 ppm for **H.21**.

H.21 has a phenolic, chemical flavor (Chemisis, 1965).

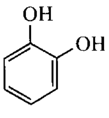
Two **ethylmethylphenols**, without specification of the positions of the substituents are mentioned by Tressl *et al.* (1978b).

(H.22) Benzene, 1-ethoxy-4-methyl-, *1-ethoxy-4-methylbenzene*, 4-ethoxytoluene, *p*-methylphenetole **[622-60-6]**

Identified by Vitzthum and Werkhoff (1974b) in the neutral fraction of the coffee aroma (steam-volatiles).

The odor is phenol/cresol type, somewhat salicylate like (Chemisis, 1984).

Diphenols



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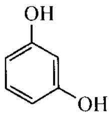

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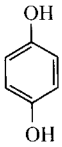

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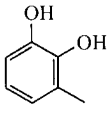

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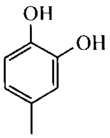

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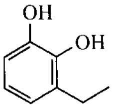

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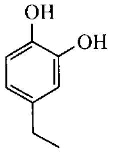

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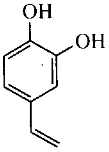

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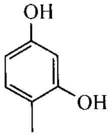
(H·30)



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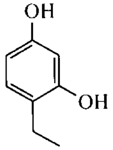


(H·32)

(H.23) ***(H.23)*** **1,2-Benzenediol,** *pyrocatechol*, pyrocatechin, 'brenzcatechin', catechol (this name is also used for a tetrahydroxyflavanol), 1,2-dihydroxybenzene **[120-80-9]**

Identified by Reichstein and Staudinger (1926b), and by Rahn and König (1978) in brewed coffee. Rahn *et al.* (1979) found 60 ppm in an unsteamed roasted arabica with a decrease of ca 25% when the green coffee was steam-treated. Tressl *et al.* (1978a) and Tressl (1979a) found concentrations of 80–137 ppm in arabica and 115–120 ppm in robusta (95 in arabusta). Heinrich and Baltes (1987a) found even 207 and 667 ppm respectively in normal and over-roasted robusta (Cameroon). Silwar and Lüllmann (1993b), after 5 min at a determined temperature, found a concentration of ca 20 ppm at 170 °C, increasing to ca 90 ppm at 230 °C, and to more than 300 ppm at 260 °C (robusta from Philippines).The ion M+1 ($m/z = 111$) was one of the ions used by Dyszel (1985) when trying to differentiate green coffees of various origins (see **H.1**).

Formed by pyrolysis of caffeic acid, itself resulting from the decomposition of chlorogenic acid (Högl, 1958), probably partly from a caffeic acid residue (Clifford, 1979) or from quinic acid (Clifford, 1979, Tressl, 1978a).

(H.24) 1,3-Benzenediol, *resorcinol*, resorcin, 1,3-dihydroxybenzene, *m*-hydroquinone **[108-46-3]** ***FEMA 3589***

Identified only tentatively by Jaeckle (1898). Tressl *et al.* (1978a) could identify it after extraction at pH 2 with ether, silylation and GC.

It is one of the thermal degradation products of quinic acid (**E.62**) (Tressl *et al.*, 1978a).

It is practically odorless when pure and has a tar-sweet taste in proper dilution in water (Arctander, 1967).

(H.25) 1,4-Benzenediol, *hydroquinone*, quinol, hydroquinol, 1,4-dihydroxybenzene, *p*-hydroxyphenol **[123-31-9]**

Identified in coffee by Bernheimer (1880a) in the oil obtained from an over-roasted coffee (25% weight loss). The concentration in coffee amounted to 30 (robusta) to 40 ppm (arabica) (25 for arabusta) according to Tressl *et al.* (1978a). An increase in concentration with increase of the roasting temperature (after 5 min) was shown by Silwar and Lüllmann (1993b), from 0.25 ppm at 170 °C to 1.25 at 230 °C and 4.20 at 260 °C.

Hydroquinone was formed by pyrolysis of quinic acid (Högl, 1958), a fact already mentioned by Bernheimer (1880a).

The pure chemical is virtually odorless. Its taste is sweet in concentrations near 50 ppm, but the sweetness is accompanied by an astringent mouthfeel at higher concentrations of the material (Arctander, 1967).

(H.26) 1,2-Benzenediol, 3-methyl-, *3-methyl-1,2-benzenediol*, 2,3-dihydroxytoluene, 3-methyl-1,2-dihydroxybenzene, 3-methylpyrocatechol, 3-methylcatechol, '3-methylbrenzcatechin' **[488-17-5]**

Identified by Rahn and König (1978) (9 ppm in an unsteamed Salvador arabica according to Rahn *et al.*, 1979), Tressl *et al.* (1978a), and Heinrich and Baltes (1987a). The concentration increased strongly from 1.40 ppm at 170 °C (5 min) to 32.50 ppm at 230 °C (5 min), 40 ppm were reached after 5 min at 260 °C (Silwar and Lüllmann, 1993b).

It is a potential emetic constituent of coffee. It has a chemical, phenolic taste (Chemisis, 1969).

(H.27) 1,2-Benzenediol, 4-methyl-, *4-methyl-1,2-benzenediol*, 4-methyl-1,2-dihydroxybenzene, 4-methylcatechol, 4-methylpyrocatechol, homopyrocatechol, '4-methylbrenzcatechin' **[452-86-8]**

Identified by Tressl *et al.* (1978a) who estimated the concentration at 13 (robusta) to 16 ppm (arabica) (10 for arabusta). Heinrich and Baltes (1987a) found a similar figure of 16.7 ppm for a robusta, increasing to 24.6 by over-roasting. From 0.85 ppm after 5 min at 170 °C, the concentration increased to 8.50 after 5 min at 230 °C and 14.0 after 5 min at 260 °C (Silwar and Lüllmann, 1993b).

(H.28) 1,2-Benzenediol, 3-ethyl-, *3-ethyl-1,2-benzenediol*, 3-ethyl-1,2-dihydroxybenzene, '3-ethylbrenzcatechin' **[933-99-3]**

Identified by Heinrich and Baltes (1987a) who found 1.1 ppm in normally roasted robusta, apparently with a small decrease on over-roasting (0.9 ppm).

(H.29) 1,2-Benzenediol, 4-ethyl-, *4-ethyl-1,2-benzenediol*, 4-ethyl-1,2-dihydroxybenzene, 1-ethyl-3,4-dihydroxybenzene, 4-ethylcatechol, '4-ethylbrenzcaztechin' **[1124-39-6]**

Identified by Rahn and König (1978). Rahn *et al.* (1979) found 9 ppm in an unsteamed Salvador arabica and noted a decrease of ca 20% when the green coffee was steam-treated. Tressl *et al.* (1978a) gave values of 37 ppm in roasted arabica and 80 in robusta (20 in arabusta). Heinrich and Baltes (1987a) found 106 ppm in roasted robusta (179 in over-roasted). After 5 min at 170 or 230 °C, the concentrations varied from 25 to 40 ppm (Silwar and Lüllmann, 1993b).

It is a degradation product of the chlorogenic acids and produced from the two moieties, caffeic acid (**H.86**) (Clifford, 1979) and quinic acid (**E.62**) (Leloup *et al.*, 1995) (see Section 2.1.4).

The structure was proved by synthesis of a reference sample obtained by catalytic hydrogenation of dihydroxystyrene, itself prepared by decarboxylation of 3,4-dihydroxycinnamic acid (caffeic acid) according to Reichstein (1932).

This compound has possible emetic properties (Rahn and König, 1978). The odor is phenolic, leather, thymol (Chemisis, 1996).

Two dimethyl-1,2-benzenediols without specification of positions of the substituents were found by Heinrich and Baltes (1987a).

(H.30) ***(H.30)*** **1,2-Benzenediol, 4-ethenyl-,** *4-vinyl-1,2-benzenediol,* 4-vinyl-1,2-dihydroxybenzene, 4-vinylcatechol, 3,4-dihydroxystyrene (3,4-DHS), '4-vinylbrenzcatechin' **[6053-02-7]**

Identified by Prescott *et al.* (1937b). Rahn *et al.* (1979) found it in green arabica coffees of several sources with a much higher concentration (3–6 times) when the coffee had been steam-treated, the increase being dependent on the coffee origin, and gave a concentration of 16 ppm in an unsteamed roasted Salvador arabica. Tressl *et al.* (1978a) found 25 ppm in arabica and robusta coffees (15 in arabusta), and Heinrich and Baltes (1987a) 6.0 ppm in a robusta with a decrease to 4.4 after over-roasting. Silwar and Lüllmann (1993b) noted that after 5 min at a given temperature the concentration first increased (ca 20 ppm at 170 °C and ca 40 ppm at 230 °C) then decreased (ca 20 ppm at 260 °C).

This diphenol was formed by decomposition of chlorogenic acids (Rahn and König, 1979) and probably produced from the caffeic acid residue, like ethylcatechol (**H.29**) and a part of catechol (**H.23**) (Clifford, 1979).

A synthesis based on decarboxylation of 3,4-dihydroxycinnamic acid (caffeic acid, **H.86**), according to Reichstein (1932), has been repeated by Rahn and König (1978).

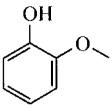
(H.31) 1,3-Benzenediol, 4-methyl-, *4-methyl-1,3-benzenediol,* 4-methyl-1,3-dihydroxybenzene, 4-methylresorcin **[496-73-1]**

Identified by Heinrich and Baltes (1987a) in a normally and an over-roasted robusta, but at a low concentration (< 0.1 ppm).

(H.32) 1,3-Benzenediol, 4-ethyl-, *4-ethyl-1,3-benzenediol,* 4-ethylcatechol, 4-ethyl-1,3-dihydroxybenzene **[2896-60-8]**

Identified by Heinrich and Baltes (1987a) in a normally and over-roasted robusta, at a low concentration (< 0.1 ppm), like the 4-methyl homologue (**H.31**).

Ethers of diphenols



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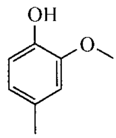
(H·33)



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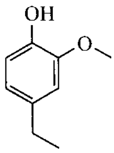

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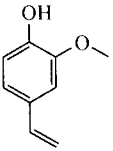

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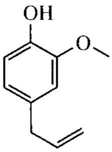
(H·36)



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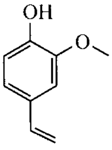

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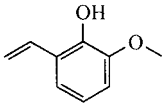


(H·39)

(H.33) *(H.33)* **Phenol, 2-methoxy-,** *2-methoxyphenol,* *o*-methylcatechol, *o*-hydroxyanisole, 1-hydroxy-2-methoxybenzene, guaiacol (the name guajol has even been used, rather confusing with the sesquiterpenic alcohol guaiol) **[90-05-1]** ***FEMA 2532***

Identified by Reichstein and Staudinger (1926b). Hughes and Smith (1949) have shown that the total volatile phenol content, particularly guaiacol, increases with roasting. The evolution during staling of coffee is more difficult to measure, some loss occurring when the samples were stored for six weeks, but a very stale sample of about 3 years of age contained a nearly permanent content. The authors concluded that there is a possibility that although a loss of aroma was due to polymerization, the phenols may be liberated again in the course of the determination and so count as volatile. These results must be regarded with caution, as the measure was made on a complex mixture of phenolic constituents. Tressl *et al.* (1978b) found 2.7 ppm in arabica to 8.4 in robusta (3.9 in arabusta), with an increase to 10.6 in an over-roasted arabica and Silwar *et al.* (1987) 2–3 ppm (arabica). Ho *et al.* (1993) found 2.11 ppm in a roasted Columbian coffee. Not too different were the results of Semmelroch *et al.* (1995) who used isotope dilution assays (IDA) for the quantification, with 4.2 ppm for an arabica (see also Grosch *et al.*, 1996) and 28.2 for a robusta. According to Silwar and Lüllmann (1993b) the increase in guaiacol content is strong when a robusta coffee is heated 5 min at a given temperature: from < 1 ppb at 170 °C, to 1.60 ppm at 230 °C and 11.5 at 260 °C. Heinrich and Baltes (1987a) gave the higher figures of 35.8 ppm in a robusta increasing to 95.5 by over-roasting. The ion M+1 ($m/z = 125$) was one of the ions used by Dyszel (1985) when trying to differentiate green coffees of various origins (see **H.1**). Ramos *et al.* (1998) identified this phenol in a brewed arabica after liquid–liquid extraction with pentane or methylene chloride. Very recently it was identified in a green Mexican arabica coffee by Cantergiani *et al.* (2001), representing 0.32% (GC, polar) of the extract after vacuum hydrodistillation.

Tressl *et al.* (1976) and Fiddler *et al.* (1967) identified it as a thermal decomposition product of ferulic acid (**H.87**). This phenolic compound was probably formed by oxidation of vanillin (H.56) and decarboxylation of the resulting vanillic acid (**H.74**).

Guaiacol has a powerful smoke-like, somewhat medicinal odor (Arctander, 1967); it is described as phenolic, burnt by Blank *et al.* (1992b), phenolic, spicy (1992a), and perceived as phenolic, aromatic by Holscher *et al.* (1990). The flavor is described as smoky, woody, phenolic, meaty (Chemisis, 1996). Wasserman (1966) found an odor threshold in water of 21 ppb with a flavor threshold of 13 ppb. According to Buttery *et al.* (1971) the odor threshold in water is 3 ppb, 2.5 ppb for Semmelroch *et al.* (1995). For Pollien *et al.* (1998), guaiacol has a high aroma impact in a brew and even more in an instant coffee prepared with the same blend (GC-olfactometry, SNIF method, see Section 3.3).

(H.34) **Phenol, 2-methoxy-4-methyl-,** *2-methoxy-4-methylphenol,* 2-methoxy-*p*-cresol, creosol, 4-methylguaiacol, homoguaiacol, 3-methoxy-4-hydroxytoluene, 4-hydroxy-3-methoxy-1-methylbenzene **[93-51-6]** ***FEMA 2671***

Stofberg and Stoffelsma (1981) mentioned a concentration of 0.1 ppm and Silwar *et al.* (1987) of 0.01–0.02 ppm.

It is produced in the thermal degradation of ferulic acid (**H.87**) (Tressl *et al.*, 1976; Fiddler *et al.*, 1967).

4-Methylguaiacol has a sweet-spicy, phenolic-leathery odor with distinctly vanilla-like undertones, balsamic-warm sweetness, but overall too medicinal to become classified as a versatile, floral-balsamic ingredient (Arctander, 1967). Wasserman (1966) noted smoky, phenolic, sweet odor and smoky, phenolic, bitter taste with an odor threshold in water 90 ppb and a taste threshold of 65 ppb.

(H.35) ***(H.35)*** **Phenol, 4-ethyl-2-methoxy-,** *4-ethyl-2-methoxyphenol,* 4-ethylguaiacol **[2785-89-9]** ***FEMA 2436***

Identified by Gianturco *et al.* (1966). Its concentration in coffee was estimated to be 0.3 (arabica) to 5.6 ppm (robusta) and 1.2 (arabusta), by Tressl *et al.* (1978b). Silwar *et al.* (1987) found 0.80–1.50 ppm in roasted arabica, Czerny and Grosch (2000) 21 ppb in raw and 4.06 ppm in medium-roasted arabica. By isotope dilution assays, Semmelroch *et al.* (1995) previously found 1.63 ppm for an arabica and 18.1 for a robusta. Cantergiani *et al.* (2001) found it in green Mexican arabica (1.05 % of the extract, see **H.33**).

It is formed by reduction of 4-vinylguaiacol (**H.36**). Fiddler *et al.* (1967) and Tressl *et al.* (1976) identified it in the thermal decomposition of ferulic acid (**H.87**). Ethylguaiacol was also produced from *p*-coumaric acid (**H.84**) by yeasts and lactic bacteria (Dubois, 1983).

4-Ethylguaiacol has a smoky and roasted flavor, burnt taste for Winter *et al.* (1976o), a typical soy sauce flavor for Maga (1978a). The very complex odor is described as smoky, clove-like, spicy, medicinal, burnt and vanilla-like (Dubois, 1983). Blank *et al.* (1992b), with a spicy description, give an odor threshold of 10–30 ng/m^3 air. It is described as phenolic, spicy by Semmelroch and Grosch (1995b), sweet with an odor threshold of 35 μg/kg^1 cellulose by Czerny and Grosch (2000), of 50 ppb in water by Semmelroch *et al.* (1995).

(H.36) ***(H.36)*** **Phenol, 4-ethenyl-2-methoxy-,** *2-methoxy-4-vinylphenol,* *p*-vinylguaiacol, 4-hydroxy-3-methoxystyrene (3-MHS) **[7786-61-0]** ***FEMA 2675***

Identified by Reichstein and Staudinger (1926b) and confirmed by Reichstein (1932). It was also identified by Prescott *et al.* (1937b) through its benzoate derivative and in green coffee volatiles (steam distillation) by Vitzthum *et al.* (1976). Spadone and Liardon (1988) noted that the largest peak in the GC profile in 'Rio' green coffee is that of vinylguaiacol, and it was up to three times more abundant than in normal green beans (simultaneous distillation–extraction, GC/MS). The concentration in coffee was estimated to be 9.5 (arabica) to 19.5 ppm (robusta) (18.4 for arabusta) by Tressl *et al.* (1978b) who also found (1979b) that the content in this phenol reaches a maximum after storage of 4–5 weeks at 25 °C in package permeable to air. Similar values of 8.00–20.00 ppm in roasted arabica coffee were given by Silwar *et al.* (1987). Measurements by Silwar and Lüllmann (1993b) after 5 min at a given temperature were 6, 8.7 and 20 ppm for 170, 230 and 260 °C respectively. Higher values (ca 115 ppm in normally and over-roasted robusta) were given by Heinrich and Baltes (1987a) and also by Semmelroch *et al.* (1995), and Grosch *et al.* (1996) with 64.8 (arabica)–177.7 ppm (robusta). Czerny and Grosch (2000) found low values with 117 ppb in raw and 39 ppm in a medium-roasted arabica. 4-Vinylguaiacol has also been found in a green Mexican arabica by Cantergiani *et al.* (2001) (0.61 % of the extract, see **H.33**).

Reichstein (1932) prepared it by decarboxylation of ferulic acid (**H.87**) and by Grignard reaction from vanillin (**H.56**). It was produced from ferulic acid by yeasts and lactic bacteria (Dubois, 1983). Tressl *et al.* (1976) and Fiddler *et al.* (1967) identified it as a thermal decomposition product of ferulic acid.

p-Vinylguaiacol has a powerful, spicy, clove-like odor with a penetrating, warm, but also somewhat tarry undertone and good tenacity (Arctander, 1967). The flavor is smoky, sweet, spicy (Chemisis, 1997). The odor threshold in water was 3 ppb for Buttery *et al.* (1976c), 5 ppb for Tressl *et al.* (1979b), 20 ppb for Semmelroch *et al.* (1995) with phenolic, spicy description (Semmelroch and Grosch, 1995b), 0.4 – 0.8 μg/m^3 air with a spicy description for Blank *et al.* (1992b). Czerny and Grosch (2000) gave a clove-like odor description and an odor threshold of 80 μg/kg cellulose.

(H.37) **Phenol, 2-methoxy-4-(2-propenyl)-,** *4-allyl-2-methoxyphenol,* eugenol, eugenic acid, *p*-allylguaiacol, caryophyllic acid (this name induces confusion with sesquiterpenes) **[97-53-0]** ***FEMA 2467***

Identified by Prescott *et al.* (1937b) through its benzoate derivative.

The odor is powerful, warm-spicy, rather dry and almost sharp, drier and harder than that of clove bud oil, less peppery-woody than that of clove leaf oil (Arctander, 1967). An odor threshold of 6 ppb in water was given by Buttery *et al.* (1971).

(H.38) Phenol, 2-methoxy-4-(1-propenyl)-, *2-methoxy-4-(prop-1-enyl)phenol*, isoeugenol, 4-propenylguaiacol, 4-hydroxy-3-methoxy-1-propenylbenzene **[97-54-1]** ***FEMA 2468;*** **(*E*)- [5932-68-3]; (*Z*)- [5912-86-7]**

Identified by Haberer (1970). Tressl *et al.* (1978b), and Ho *et al.* (1993) found it in a roasted Columbian coffee in a concentration of 0.12 ppm.

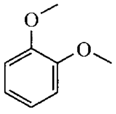
Tressl *et al.* (1976) and Fiddler *et al.* (1967) identified it as a decomposition product of ferulic acid (**H.87**).

The odor is mild and sweet, deep-floral, very tenacious with great warmth and resemblance to carnation, sweet william or wallflower (Arctander, 1967). The (*E*)-isomer has a smoky, phenolic flavor and the (*Z*)- sweet, eugenol-like (Chemisis, 1965).

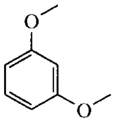
(H.39) Phenol, 2-methoxy-6-(1-propenyl)-, *2-methoxy-6-(prop-1-enyl)phenol*, 2-(1-propenyl)-6-methoxyphenol, *o*-isoeugenol **[1076-55-7]; (*E*)- [29275-83-0]; (*Z*)- [29275-82-9]**

Identified by Andrade-Aispuro and Crouzet (1983) when they studied the condensation products recuperated during the torrefaction.

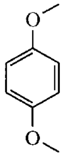
Diethers of diphenols



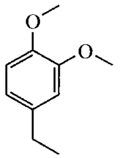
(H·40)



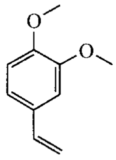
(H·41)



(H·42)



(H·43)



(H·44)
(H·44)

(H.40) **Benzene, 1,2-dimethoxy-**, *1,2-dimethoxybenzene*, *O*,*O*-dimethylcatechol, veratrole **[91-16-7]** ***FEMA 3799***

Identified in a green Mexican arabica coffee by Cantergiani *et al.* (2001), representing 1.24% of the volatiles (GC on a polar column after vacuum hydrodistillation and extraction).

The flavor is described as sweet, phenolic, musty and earthy (Chemisis, 2000).

(H.41) **Benzene, 1,3-dimethoxy-**, *1,3-dimethoxybenzene*, resorcinol dimethyl ether, 3-methoxyanisole **[151-10-0]** ***FEMA 2385***

Identified in green coffee by Gutmann *et al.* (1979) when comparing the headspace profiles of arabusta, arabica and robusta varieties of coffee.

(H.42) **Benzene, 1,4-dimethoxy-**, *1,4-dimethoxybenzene*, hydroquinone dimethyl ether, quinol dimethyl ether, *p*-methoxyanisole **[150-78-7]** ***FEMA 2386***

Identified in a green Mexican arabica coffee by Cantergiani *et al.* (2001), representing 0.13% of the volatiles (see **H.40**).

(H.43) **Benzene, 4-ethyl-1,2-dimethoxy-,** *4-ethyl-1,2-dimethoxybenzene* **[5888-51-7]**

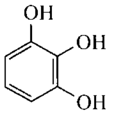
Identified by Spadone *et al.* (1990) during an analytical investigation of 'Rio' off-flavor in green coffee, by sequential cuts and injections of a GC a region where musty and earthy odors had been detected.

(H.44) ***(H.44)*** **Benzene, 4-ethenyl-1,2-dimethoxy-,** *1,2-dimethoxy-4-vinylbenzene*, 3,4-dimethoxystyrene **[6380-23-0]** ***FEMA 3138***

Identified by Reymond *et al.* (1966b). Silwar *et al.* (1987) gave a concentration of 0.40–0.80 ppm in roasted coffee. Cantergiani *et al.* (2001) found it in a green Mexican arabica (0.17% of the volatiles, see H.40).

The flavor is smoky, meaty, phenolic, burnt (Chemisis, 1964).

Triphenols and ethers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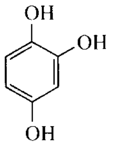
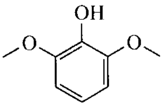

(H.46)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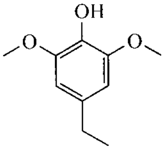
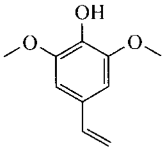

(H.48)


(H.49)

(H.45) 1,2,3-Benzenetriol, *1,2,3-benzenetriol*, 1,2,3-trihydroxybenzene, pyrogallol, pyrogallic acid **[87-66-1]**

Identified by Högl (1958). Rahn and König (1978) estimated the concentration at 40–60 ppm in a Nicaragua arabica after acidification at pH 1.5 of a coffee infusion, and ether extraction for 12 h. The same group (Rahn *et al.*, 1979) obtained a similar value of 35 ppm in the ether extract of an unsteamed roasted Salvador arabica. Tressl *et al.* (1978b) found 45 ppm in arabica, 54 ppm in robusta (25 in arabusta) and Clifford (1985a) 25–45 ppm in coffee aroma. Smaller values are given by Heinrich and Baltes (1987a) with less than 0.1 ppm in normally and over-roasted robusta (aqueous extract treated at pH 6.5–6.8, extraction, steam distillation and further extraction). Silwar and Lüllmann (1993b) found an increase from 1.55 ppm to 2.0 and 4.85 when treating a robusta for 5 min at 170, 230 or 260 °C.

It is formed in the pyrolysis of quinic acid (**E.62**) (Högl, 1958).

(H.46) 1,2,4-Benzenetriol, *1,2,4-benzenetriol*, 2,5-dihydroxyphenol, 1,2,4-trihydroxybenzene, 2-hydroxy-1,4-hydroquinone, hydroxyhydroquinone (HHQ), hydroxyquinol **[533-73-3]**

Identified by Rahn and König (1978). The study was conducted in order to identify phenols or other moderately acidic components responsible for the frequently observed nauseous symptoms of sensitive coffee drinkers. After ether extraction of an acidified (pH 1.5) roasted-coffee infusion, the authors measured a concentration of 50 to 70 ppm. This compound was one of the main phenolic constituents together with pyrocatechol (**H.23**) and pyrogallol (**H.45**). Concentrations given the same year by Tressl *et al.* (1978a) were 20, 13 and 6 ppm respectively for arabica robusta and arabusta (steam distillation and extraction). Silwar and Lüllmann (1993b) determined 0.05, 0.15 and 0.75 ppm after 5 min at 170, 230 and 260 °C respectively, for a robusta.

Hydroxyhydroquinone was formed in the thermal degradation of quinic acid (**E.62**) (Tressl *et al.*, 1978a). It is a possible emetic constituent of coffee. It has been identified in instant coffee by Hiramoto *et al.* (1998) as the major source of hydrogen peroxide and as such, responsible for the genotoxic activity of coffee, with a higher activity in coffee than the Maillard-reaction products, Furaneol® (**I.100**), 3,5-dihydroxy 4*H*-pyran-4-one and 5-hydroxy-5,6-dihydromaltol (**I.148**).

(H.47) Phenol, 2,6-dimethoxy-, *2,6-dimethoxyphenol*, pyrogallol 1,3-dimethyl ether, 1,3-dimethyl pyrogallate, syringol **[91-10-1]** ***FEMA 3137***

Identified by Heinrich and Baltes (1987a), who gave a concentration of 0.8 ppm in a normally roasted and 1.1 in an over-roasted robusta.

According to Wasserman (1966), aroma and taste are smoky, phenolic, the odor threshold in water being 1.85 ppm and the flavor threshold 1.65 ppm.

(H.48) Phenol, 4-ethyl-2,6-dimethoxy-, *4-ethyl-2,6-dimethoxyphenol*, 4-ethylsyringol **[14059-92-8]** ***FEMA 3671***

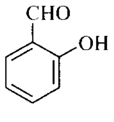
(H.49) Phenol, 4-ethenyl-2,6-dimethoxy-, *2,6-dimethoxy-4-vinylphenol*, 4-vinylsyringol **[28343-22-8]**

These were identified by Heinrich and Baltes (1987a). The concentrations are 1.4 and 1.7 ppm respectively in a normally roasted robusta, 4.3 and 1.8 in the over-roasted quality.

H.48 has a phenolic, leather, animal flavor (Chemisis, 1968).

A **trimethoxybenzene** without any precision was found by Spadone *et al.* (1990) in a 'Rio' green coffee.

Phenols and phenol ethers with aldehyde function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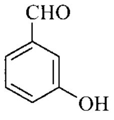
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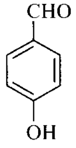
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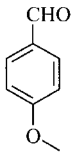
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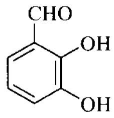
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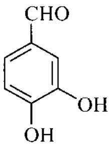
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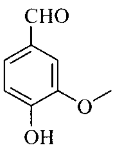
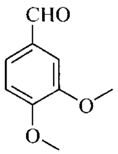

(H-56)
(H-56)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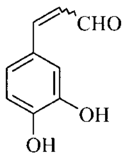
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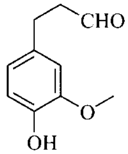

(H-59)

(H.50) Benzaldehyde, 2-hydroxy-, *2-hydroxybenzaldehyde*, salicylaldehyde, salicylal, *o*-formylphenol **[90-02-8]** ***FEMA 3004***

Identified by Stoll *et al.* (1967).

The odor is pungent, irritating, reminiscent of benzaldehyde, acetophenone and nitrobenzene. In extreme dilution, the odor is warm, herbaceous, spicy-floral but the phenolic note remains perceptible (Arctander, 1967)

(H.51) Benzaldehyde, 3-hydroxy-, *3-hydroxybenzaldehyde*, *m*-formylphenol **[100-83-4]**

Identified by Heinrich and Baltes (1987a), concentration varying from 1.1 ppm in normally roasted to 1.6 in over-roasted robusta.

(H.52) Benzaldehyde, 4-hydroxy-, *4-hydroxybenzaldehyde*, *p*-formylphenol **[123-08-0]**

Identified by Heinrich and Baltes (1987a), who found 0.5 and less than 0.1 ppm respectively in normally and over-roasted robusta coffee.

A possible way of formation is by oxidation of *p*-coumaric acid (**H.84**) (Friedrich, 1976).

This aldehyde has a very faint, sweet-woody-balsamic odor, and is virtually odorless when chemically pure (Arctander, 1967).

(H.53) Benzaldehyde, 4-methoxy-, *4-methoxybenzaldehyde*, *p*-anisaldehyde, *p*-formylanisole **[123-11-5]** ***FEMA 2670***

Identified by Blank *et al.* (1992a).

Results from the methylation of *p*-hydroxybenzaldehyde (Friedrich, 1976).

The odor is intensively sweet floral, yet somewhat 'hay-like', generally described as hawthorne-like (Arctander, 1967). At the sniffing port of a chromatograph, the odor perception is sweet, minty with a dilution factor more important with the powder than with the brew of an arabica (Blank *et al.*, 1992b). The flavor is described as sweet, anisic, coumarinic (Chemisis, 1989).

(H.54) Benzaldehyde, 2,3-dihydroxy-, *2,3-dihydroxybenzaldehyde*, 5,6-dihydroxybenzaldehyde, pyrocatechualdehyde **[24677-78-9]**

Identified by Heinrich and Baltes (1987a) in a roasted 'Mocca type' coffee.

(H.55) Benzaldehyde, 3,4-dihydroxy-, *3,4-dihydroxybenzaldehyde*, 1,2-dihydroxy-4-formylbenzene, protocatechuic aldehyde **[139-85-5]**

Identified by Tressl *et al.* (1978a) who found 20 ppm in roasted arabica and only 9 ppm in robusta (8 in arabusta). Heinrich and Baltes (1987a) found less than 0.1 ppm in a roasted 'Mocca type' coffee.

It could be formed by the oxidation of caffeic acid (**H.86**) (Friedrich, 1976).

(H.56) ***(H.56)*** **Benzaldehyde, 4-hydroxy-3-methoxy-**, *4-hydroxy-3-methoxybenzaldehyde*, 4-formyl-2-methoxyphenol, vanillin, *p*-vanillin **[121-33-5]** ***FEMA 3107***

Identified by Tressl *et al.* (1978a) with concentrations of 2–3 ppm in roasted coffees of various species. Heinrich and Baltes (1987a) found 5.9 and 4.4 ppm in a normally and over-roasted robusta coffee, but ca 40 ppm in a 'type Mocca' coffee. Semmelroch *et al.* (1995) gave 4.8 ppm for a Columbia arabica and 16.1 for an Indonesian robusta by quantification with stable isotope dilution assays. The concentration after

5 min at 230 °C (ca 40 ppm) was higher than after 5 min either at 170 or 260 °C (ca 20 ppm). It was found in green coffee by Spadone *et al.* (1990).

Friedrich (1976) suggested formation by methylation of protocatechuic aldehyde (**H.55**), the corresponding glycoside being the immediate precursor. Tressl *et al.* (1976, 1979b) identified vanillin as a thermal decomposition product of ferulic acid (**H.87**), formed by oxidation of 4-vinylguaiacol (**H.36**).

The odor is intensively sweet and very tenacious creamy-vanilla-like (Arctander, 1967). It is considered to be an important odorant in roasted coffee with an odor threshold of 0.6 – 1.2 $\mu g/m^3$ air (Blank *et al.*, 1992b), and 25 ppb in water (Semmelroch *et al.*, 1995).

(H.57) **Benzaldehyde, 3,4-dimethoxy-,** *3,4-dimethoxybenzaldehyde*, veratraldehyde, methylvanillin, protocatechualdehyde dimethyl ether **[120-14-9]** ***FEMA 3109***

Identified in green coffee by Vitzthum *et al.* (1976).

(H.58) 2-Propenal, -3-(3,4-dihydroxyphenyl)-, *3,4-dihydroxyprop-2-enal*, 3,4-dihydroxycinnamaldehyde **[68149-78-0]; (*E*)- [141632-15-7]**

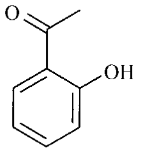
Identified by Tressl *et al.* (1978a) who gave concentrations of 10 ppm in roasted arabica, 12 in robusta and 5 in arabusta.

(H.59) Benzenepropanal, 4-hydroxy-3-methoxy-, *3-(4-hydroxy-3-methoxyphenyl)propanal* **[80638-48-8]**

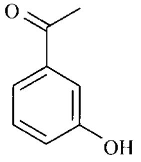
Identified by Heinrich and Baltes (1987a) who gave a concentration < 0.1 ppm in normally roasted robusta increasing to 0.8 ppm after over-roasting.

The flavor is sweet, caramel, cinnamon, celery (Chemisis, 1973).

Phenols and phenol ethers with a ketone function



(H·60)



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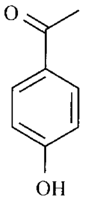

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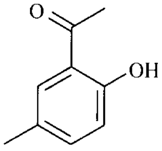
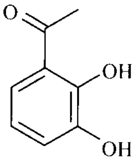
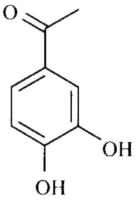


(H·63)

(H·63)



(H·64)



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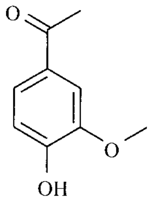

(H·66)

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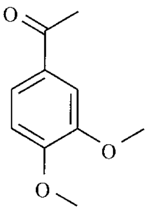
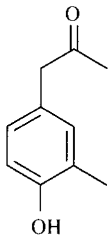


(H·67)



(H·68)

(H.60) Ethanone, 1-(2-hydroxyphenyl)-, *1-(2-hydroxyphenyl)-1-ethanone*, *o*-hydroxyphenyl methyl ketone, 2′-hydroxyacetophenone (at least, 2′-avoid confusion on the site of the substitution), *o*-hydroxyacetophenone, *o*-acetylphenol **[118-93-4]** ***FEMA 3548***

Identified by Stoll *et al.* (1967), by Stoffelsma *et al.* (1968) after steam distillation, by Vitzthum and Werkhoff (1976b) after steam distillation and separation of neutral and basic fractions.

The odor is sweet, rather heavy-floral, also somewhat herbaceous, reminiscent of new-mown hay or hawthorne in higher concentration, almost mimosa-like in extreme dilution (Arctander, 1967).

(H.61) Ethanone, 1-(3-hydroxyphenyl)-, *1-(3-hydroxyphenyl)-1-ethanone*, 3-hydroxyacetophenone, 3-acetylphenol **[121-71-1]**

Identified by Heinrich and Baltes (1987a), the concentrations being 0.4 and 0.5 ppm in normally and over-roasted robusta coffee.

(H.62) Ethanone, 1-(4-hydroxyphenyl)-, *1-(4-hydroxyphenyl)-1-ethanone*, 4-hydroxyacetophenone, *p*-oxyacetophenone, 4-acetylphenol **[99-93-4]**

Identified by Heinrich and Baltes (1987a), the concentrations being 2.2 and 3.2 ppm in a normally and over-roasted robusta.

It has a heavy-floral, somewhat herbaceous or woody-hay-like odor of considerable tenacity, slightly more floral than the *o*-isomer, also more tenacious and overall more pleasant (Arctander, 1967).

(H.63) ***(H.63)*** **Ethanone, 1-(2-hydroxy-5-methylphenyl)-,** *1-(2-hydroxy-5-methylphenyl)-1-ethanone*, 2′-hydroxy-5′-methylacetophenone, 2-acetyl-4-methylphenol, *o*-acetyl-*p*-cresol, 1-hydroxy-2-acetyl-4-methylbenzene **[1450-72-2]**

Identified in roasted coffee flavor by Stoll *et al.* (1967), tentatively by Vitzthum and Werkhoff (1976b) in the neutral fraction of steam volatiles of roasted coffee, and in green coffee volatiles (same method) by Vitzthum *et al.* (1976). Ho *et al.* (1993) gave a concentration of 1.2 ppm in a roasted Columbian coffee. Ramos *et al.* (1998) found it in extracts of a brewed arabica, by liquid–liquid extraction with pentane or solid-phase microextraction.

The flavor is described as anthranilate-type (Chemisis, 1976).

(H.64) Ethanone, 1-(2,3-dihydroxyphenyl)-, *1-(2,3-dihydroxyphenyl)-1-ethanone*, 2′,3′-dihydroxyacetophenone **[13494-10-5]**

Identified by Reichstein and Staudinger (1926b).

(H.65) Ethanone, 1-(3,4-dihydroxyphenyl)-, *1-(3,4-dihydroxyphenyl)-1-ethanone*, 3,4-dihydroxyacetophenone **[1197-09-7]**

Identified by Heinrich and Baltes (1987a) who found concentrations of 1.5 and 2.6 ppm respectively, in a normally and an over-roasted robusta.

(H.66) ***(H.66)*** **Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-,** *1-(4-hydroxy-3-methoxyphenyl)-1-ethanone*, acetovanillone (not to be confused with acetovanillin which is *O*-acetylvanillin), vanillone, acetoguaiacone, 4-hydroxy-3-methoxyacetophenone **[498-02-2]**

Identified by Prescott *et al.* (1937b) through its benzoate derivative. For Silwar and Lüllmann (1993b), the concentration increased with roasting (from ca 10 ppm at 170 °C to ca 50 ppm at 230 °C) and over-roasting (ca 100 ppm after 5 min at 260 °C). Cantergiani *et al.* (2001) found it in a small proportion (0.04% by GC on a polar column) in the volatiles of a green Mexican arabica, after vacuum hydro-distillation and extraction.

Tressl *et al.* (1976) have identified it as a thermal decomposition product of ferulic acid (**H.87**).

The odor is very faint, sweet, remotely reminiscent of vanillin, but less spicy, somewhat fresher (Arctander, 1967).

(H.67) Ethanone, 1-(3,4-dimethoxyphenyl)-, *1-(3,4-dimethoxyphenyl)-1-ethanone,* 3,4-dimethoxyphenyl methyl ketone, 3,4-dimethoxyacetophenone, acetoveratrone, 4-acetylveratrole **[1131-62-0]**

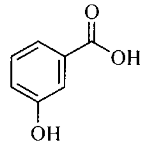
Identified by Andrade-Aispuro and Crouzet (1983), see (**H.39**).

It has a sweet-woody, very tenacious odor with a pleasant, floral undertone (Arctander, 1967). The flavor is weak, floral-flowery, musky (Chemisis, 1980).

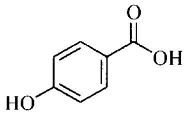
(H.68) **2-Propanone, 1-(4-hydroxy-3-methylphenyl)-**, *1-(4-hydroxy-3-methylphenyl)propan-2-one* **[88659-81-8]**

Identified by Spadone *et al.* (1990) in a Puerto Rico 'Rio' green coffee, in the fraction obtained after simultaneous distillation–extraction, where the chromatogram gave an earthy-musty odor.

Phenols and phenol ethers with a carboxylic acid function



(H·69)
(H·69)



(H·70)
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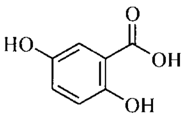
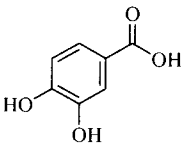
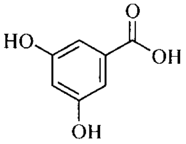


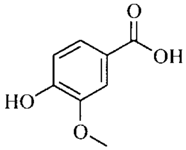
(H·71)



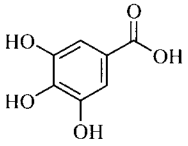
(H·72)



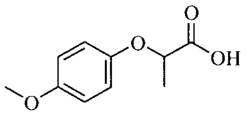
(H·73)



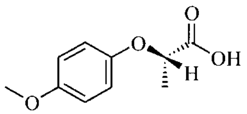
(H·74)



(H·75)



(H·76)



(*S*)-**(H·76)**

(H.69) ***(H.69)*** **Benzoic acid, 3-hydroxy-**, *3-hydroxybenzoic acid, m*-salicylic acid, 3-carboxyphenol **[99-06-9]**

(H.70) ***(H.70)*** **Benzoic acid, 4-hydroxy-**, *4-hydroxybenzoic acid, p*-salicylic acid **[99-96-7]**

These were identified (two-dimensional paper chromatography) by Klöcking *et al.* (1971), but only after alkaline pressure hydrolysis of the humic acids isolated from a commercial coffee extract. They have recently been identified by Bähre and Maier (1996, 1999) (see Section 5.E) using their new method for the preseparation of the acids. In a green Kenya arabica, steam-treated or untreated, they amounted to 7–10 ppm (undetected in a Columbia). After roasting, the content of the 3-hydroxy is 25–30 ppm and of the 4-hydroxy acid 10 ppm. This did not tend to increase with prolonged heating (espresso quality).

They are formed in the thermal degradation of quinic acid (**E.62**) (Tressl *et al.*, 1978a) and of chlorogenic acids (Heinrich and Baltes, 1987b).

The flavor thresholds in water according to Maga and Lorenz (1973) are 20 and 40 ppm respectively for **H.69** and **H.70**.

(H.71) Benzoic acid, 2,5-dihydroxy-, *2,5-dihydroxybenzoic acid*, 5-hydroxysalicylic acid, gentisic acid, hydroquinonecarboxylic acid **[490-79-9]**

Identified by Rahn *et al.* (1979) who found 15 ppm in a roasted unsteamed Salvador arabica. Engelhardt and Maier (1985a,b) found the higher value of 240 ppm in roasted coffee. Maier (1987) gave a content of 170–280 ppm in roasted coffee and 210–1330 ppm in commercial coffee extracts.

Maga and Lorenz (1973) gave a flavor threshold of 90 ppm in water.

(H.72) Benzoic acid, 3,4-dihydroxy-, *3,4-dihydroxybenzoic acid*, protocatechuic acid, 4-carboxy-1,2-dihydroxybenzene **[99-50-3]**

Identified by Engelhardt and Maier (1985a,b), who found a concentration of 80 ppm in roasted coffee. Maier (1987) gave a content of 30–130 ppm in roasted coffee and 0–230 ppm in commercial coffee extracts.

The taste threshold in aqueous solution is 30 ppm (Maga and Lorenz, 1973).

(H.73) Benzoic acid, 3,5-dihydroxy-, *3,5-dihydroxybenzoic acid*, α-resorcylic acid, 5-carboxyresorcinol **[99-10-5]**

Identified by Klöcking *et al.* (1971), like **H.69** and **H.70**.

The taste threshold given by Maga and Lorenz (1973) is 90 ppm in water.

(H.74) Benzoic acid, 4-hydroxy-3-methoxy-, *4-hydroxy-3-methoxybenzoic acid*, *p*-vanillic acid, vanillic acid, 4-hydroxy-*m*-anisic acid **[121-34-6]**

Identified by Klöcking *et al.* (1971), like **H.69**, **H.70** and **H.73**.

It also results from the oxidation of vanillin (Friedrich, 1976).

The flavor threshold given by Maga and Lorenz (1973) is 30 ppm in water.

(H.75) Benzoic acid, 3,4,5-trihydroxy-, *3,4,5-trihydroxybenzoic acid*, gallic acid **[149-91-7]**

Considered very early to be constituent of coffee (see Robiquet and Boutron, 1837a).

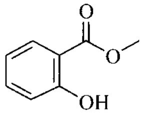
The flavor threshold given by Maga and Lorenz (1973) is 40 ppm in water.

(H.76) Propanoic acid, 2-(4-methoxyphenoxy)-, *2-(4-methoxyphenoxy)propanoic acid*, lactisol(e) **[13794-15-5]; (±)- [4276-73-7]; (*R*)- [4276-75-9]; (*S*)- [4276-74-8]**

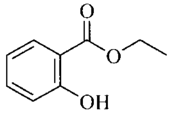
Identified in a roasted Columbia arabica by Rathbone *et al.* (1989a,b) who suspected its presence in green coffee. The aqueous coffee extract was extracted with dichloromethane and, after TLC, the acid was analyzed by HPLC or the methyl ester by GC/MS. The level of the acid was 0.55–1.2 ppm in roasted coffee. In the second publication, the authors performed a chiral HPLC analysis of the ester and found the (*S*)-enantiomer to be predominant (ca 80%).

This compound has been patented (Tate & Lyle PLC) as a flavoring agent. It has only an acid taste but could be used to modify high sweetness. The sodium salt is a selective inhibitor of the sweetness of sucrose and has been used in aqueous solution to elucidate the mechanism of this inhibition (Mathlouthi *et al.*, 1994).

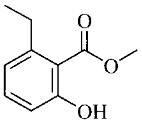
Hydroxybenzoates



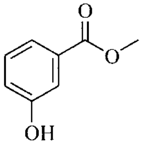
(H·77)
(H·77)



(H·78)



(H·79)



(H·80)

(H.77) ***(H.77)*** **Benzoic acid, 2-hydroxy-, methyl ester,** *methyl 2-hydroxybenzoate*, methyl salicylate, salicylic acid methyl ester **[119-36-8]** ***FEMA 2745***

Identified by Stoll *et al.* (1967) in roasted coffee, by Spadone and Liardon (1988) and Spadone *et al* (1990) in volatiles of green Puerto Rico 'Rio' and healthy beans, and also by Silwar (1982) in roasted coffee. Ho *et al.* (1993) found 0.26 ppm in a roasted Columbian coffee. For Cantergiani *et al.* (2001) this ester represented 1.60% (GC, polar) of the volatiles in an extract of a green Mexican arabica obtained after vacuum hydrodistillation. A rather high quantity of methyl salicylate was released by berries of a robusta, left on the tree after the red stage (Mathieu *et al.*, 1998).

This ester has a warm, sweet, rooty-fruity odor, of moderate to poor tenacity (Arctander, 1967). It has an odor threshold of 40 ppb in water (Buttery *et al.*, 1969b). Maier (1970c) quoted an odor threshold of 100 mg/m^3 air.

(H.78) **Benzoic acid, 2-hydroxy-, ethyl ester,** *ethyl 2-hydroxybenzoate*, ethyl salicylate, salicylic acid ethyl ester **[118-61-6]** ***FEMA 2458***

Identified by Spadone *et al.* (1990) in volatiles of Puerto Rico 'Rio' green beans but not in healthy beans. Cantergiani *et al.* (2001) also found it (0.6% of the extract by GC) in a green Mexican coffee (see **H.77**). Ethyl salicylate is, like the methyl ester **H.77** and to a small extent, released by berries of a robusta left on the tree after the red stage (Mathieu *et al.*, 1998).

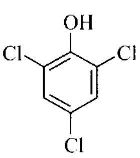
(H.79) **Benzoic acid, 2-ethyl-6-hydroxy-, methyl ester,** *methyl 2-ethyl-6-hydroxybenzoate* **[55836-64-1]**

Identified by Spadone *et al.* (1990) in volatiles of a Puerto Rico 'Rio' green coffee.

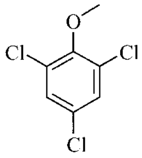
(H.80) Benzoic acid, 3-hydroxy-, methyl ester, *methyl 3-hydroxybenzoate* **[19438-10-9]**

Identified by Heinrich and Baltes (1987a) with a concentration <0.1 ppm in a normally and over-roasted robusta.

The same authors (1987b) found it, together with the 4-hydroxy isomer, after pyrolysis of the melanoidins of roasted coffee.



(H·81)



(H·82)
(H·82)

2,4,6-Trichlorophenol and ether

(H.81) **Phenol, 2,4,6-trichloro-,** *2,4,6-trichlorophenol,* (TCP) **[88-06-2]**

Identified in six 'Rio' green coffees examined by Spadone *et al.* (1990) but not in healthy beans.

For these authors, it is the probable precursor of trichloroanisole (**H.82**) by biomethylation, some molds isolated from 'Rio' coffee being able to transform chlorophenols into chloroanisoles. They seemed to exclude the possibility that trichlorophenol is derived from an industrial contaminant. It could be a natural metabolite of the molds present in the 'Rio' beans.

Unlike the ether, 2,4,6-trichlorophenol does not give a 'musty' odor at the sniffing-port of a chromatograph (Holscher *et al.*, 1995).

(H.82) ***(H.82)*** **Benzene, 1,3,5-trichloro-2-methoxy-,** *1,3,5-trichloro-2-methoxybenzene, methyl 2,4,6-trichlorophenyl ether,* 2,4,6-trichloroanisole (TCA, but this abbreviation is also used for 2,3,6-trichloroanisole) **[87-40-1]**

Identified by Spadone and Liardon (1988). Its presence was discussed by Liardon *et al.* (1990) and Spadone *et al.* (1990) who found it in the nine 'Rio' green coffees examined (106 ppb in Puerto Rico and 24 in Santos 'Rio'). Roasting reduced the content only by half. Holscher *et al.* (1995) found about 16 ppb in a Kenya coffee with a 'hardish' off-flavor, after simultaneous distillation/extraction for 3 h.

Trichloroanisole plays an important role in off-flavors. Holscher *et al.* (1995) followed the suggestion by Kenyan authors that its presence in Kenyan crops could be related to the use of the fungicide 'prochloraz-Mn' containing the ether unit. They studied the stability of this compound in hydrolytic and oxidative media, at various pH, and suggested a degradation pathway. They concluded that the formation of 2,4,6-trichloroanisole from the fungicide could be favored by wet weather and damp environment. Since abandoning 'prochloraz-Mn' the 'hardish' off-flavor has not been observed in crops of Kenyan coffee.

In coffee brew, the odor threshold value is 0.008 ppb [only 0.03 ppt in water was found by Curtis *et al.*, (1972) but this is probably questionable as the value of 0.0003 ppt given in the same publication for the 2,3,6-isomer has been corrected to 7.4 ppt by Guadagni and Buttery, (1978)] and the flavor threshold value is 0.001–0.002 ppb (Spadone *et al.*, 1990).

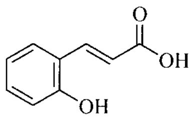
Some of the odor descriptions noted by the same authors are dusty, musty, earthy, wine cork taint, iodine, phenolic.

A **methyltrichloroanisole** and two isomers of **dichlorodimethoxybenzene** were also detected by the latter authors.

Hydroxy(alkoxy) cinnamic acids

Except perhaps for caffeic acid (**H.86**), these acids were mainly identified after hydrolysis of extracts, which means after degradation of the chlorogenic acids, CGA (See Section 2.1.4). In commercial roasted coffee, Hughes and Thorpe (1987) identified, by comparison with standard compounds, coumaric acid (without specification, probably *p*-), isoferulic acid (**H.88**) but surprisingly not ferulic acid (**H.87**), caffeic acid (**H.86**) and its dimethyl ether (**H.89**) as well as sinapic acid (**H.90**). They used capillary GC for the separation and identification of these phenolic acids and other carboxylic acids. The cinnamic acids are generally linked to quinic acid, but in robusta coffee caffeic and *p*-coumaric (**H.84**) acids have also been identified as derivatives of tryptophan (see Section 2.1.2) (Morishita *et al.*, 1987; Murata *et al.*, 1995) and caffeic acid as a derivative of tyrosine (Clifford *et al.*, 1989). All the cinnamic acids mentioned here have been identified in wild coffees from Madagascar by Rakotomalala *et al.* (1993a,b) who proposed using them as taxonomic markers. Andrade *et al.* (1997, 1998) developed an accurate method for the determination of seven of these acids (sinapic acid, **H.90**, not being included) in green coffee, separated by HPLC, with detection at 320 nm. The method is similar to that used by Murata *et al.* for the chlorogenic acids. These authors found caffeic (**H.86**) and ferulic (**H.87**) acids in all the samples examined, but sinapic acid (**H.90**) and its methyl ether (**H.91**) only in one sample each.

The hydroxycinnamic (like the hydroxybenzoic) acids have antioxidant and anticarcinogenic activities *in vitro* and in animal experiments (see History, Section 1.1).



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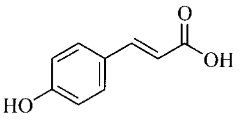

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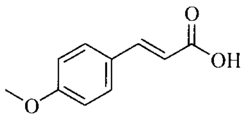

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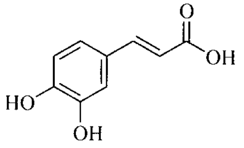

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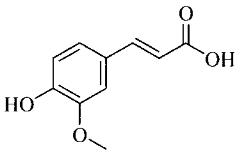

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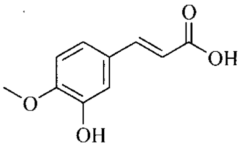

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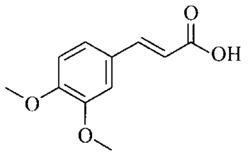

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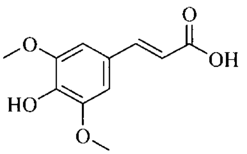

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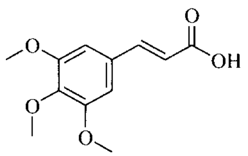


(H·91)

(H.83) 2-Propenoic acid, 3-(2-hydroxyphenyl)-, *3-(2-hydroxyphenyl)prop-2-enoic acid,* *o*-hydroxycinnamic acid, *o*-coumaric acid **[583-17-5]; (*E*)- [614-60-8]; (*Z*)- [495-79-4]**

Estimated at 200 ppm in arabica and 165 in robusta by Andrade *et al.* (1997), after hydrolysis of green coffee extracts. The same group (1998) confirmed these values with 120–210 ppm in six arabicas and 140–280 ppm in ten robustas.

Maga and Lorenz (1973) gave a flavor threshold of 25 ppm in water.

(H.84) 2-Propenoic acid, 3-(4-hydroxyphenyl)-, *3-(4-hydroxyphenyl)prop-2-enoic acid,* *p*-hydroxycinnamic acid, *p*-coumaric acid **[7400-08-0]; (*E*)- [501-98-4]; (*Z*)- [4501-31-9]**

A coumaric acid (probably *p*-) was identified by Hughes and Thorpe (1987) in one commercial roasted coffee with GC/MS and GC/IR using reference compounds. Estimated at 340 ppm in green arabica and 300 in green robusta by Andrade *et al.* (1997). More precisely, they found (1998) 260–340 ppm in five arabicas and values from 190–510 ppm in 13 robustas.

p-Coumaroyl-L-tryptophan was isolated and identified by Murata *et al.* (1995) in a green robusta (NMR data). It was detected only in robusta beans and in instant coffees made of robusta and could serve as an indicator (Okada *et al.*, 1997).

Maga and Lorenz (1973) gave a flavor threshold of 40 ppm in water.

(H.85) 2-Propenoic acid, 3-(4-methoxyphenyl)-, *3-(4-methoxyphenyl)prop-2-enoic acid*, 4-methoxycinnamic acid [830-09-1]; (*E*)- [943-89-5]; (*Z*)- [5676-64-2]

Detected, but not quantified, only in a green arabica from Honduras by Andrade *et al.* (1997, 1998) after analysis of seven green arabicas and 13 robustas.

(H.86) 2-Propenoic acid, 3-(3,4-dihydroxyphenyl)-, *3-(3,4-dihydroxyphenyl)-2-propenoic acid*, 3,4-dihydroxycinnamic acid, caffeic acid [331-39-5]; (*E*)- [501-16-6]; (*Z*)- [4361-87-9]

Mabrouk and Deatherage (1956) estimated that the content of caffeic acid represented 0.492% by weight of roasted beans and 7.63% of the total acids recovered from coffee extracts. However, according to Engelhardt (1984, thesis, quoted by Maier, 1987), caffeic acid is present only in traces after roasting. It was found in commercial roasted coffee, apparently in more than traces from the chromatogram, by Hughes and Thorpe (1987). It was the main degradation product identified by Klöcking *et al.* (1971) from humic acids of coffee extracts (see **H.69**). Andrade *et al.* (1997, 1998) after hydrolysis of green coffee extracts, found ca 1000 ppm in the seven arabicas and 13 robustas analyzed, the highest values being 1120 and 1510 respectively for an arabica and a robusta.

Caffeic acid can result from the hydroxylation of *p*-coumaric acid (Friedrich, 1976). In coffee, it is mainly linked as 5-caffeoylquinic acid (5-CQA), which is the main chlorogenic acid (ca 50%), but it is also present as caffeoyltryptophan (Morishita *et al.*, 1987, NMR data) and caffeoyltyrosine (Clifford *et al.*, 1989, NMR data). According to Casal *et al.* (1999), it is the most sensitive of all the hydroxycinnamic acids of coffee to heat degradation.

Caffeoyltryptophan has a strong antioxidant activity (Ohnishi *et al.*, 1998).

The taste threshold of the acid measured by Maga and Lorenz (1973) is 90 ppm in water.

(H.87) 2-Propenoic acid, (4-hydroxy-3-methoxyphenyl)-, *3-(4-hydroxy-3-methoxyphenyl)-2-propenoic acid*, 4-hydroxy-3-methoxycinnamic acid, ferulic acid [1135-24-6]; (*E*)- [537-98-4]; (*Z*)- [1014-83-1]

Identified by Klöcking *et al.* (1971) from the humic acids together with other acid phenols (see, for example, **H.69** and **H.86**). After hydrolysis of green coffee extracts, Andrade *et al.* (1997) found a clearly lower content in an arabica than in a robusta (840 vs 1150 ppm), and identified it in all the samples analyzed, seven arabicas (550–840 ppm) and 13 robustas (840–1230 ppm) (Andrade *et al.*, 1998).

Tressl *et al.* (1976) identified the simple phenols formed by thermal fragmentation of ferulic acid.

Maga and Lorenz (1973) gave a flavor threshold of 90 ppm in water.

(H.88) 2-Propenoic acid, 3-(3-hydroxy-4-methoxyphenyl)-, *3-(3-hydroxy-4-methoxyphenyl)prop-2-enoic acid*, 3-hydroxy-4-methoxycinnamic acid, isoferulic acid [537-73-5]; (*E*)- [25522-33-2]; (*Z*)- [1135-16-6]

Identified by Hughes and Thorpe (1987) in commercial roasted coffees, with GC/MS, GC/IR and reference compounds (they did not find ferulic acid).

(H.89) 2-Propenoic acid, 3-(3,4-dimethoxyphenyl)-, *3-(3,4-dimethoxyphenyl)prop-2-enoic acid*, 3,4-dimethoxycinnamic acid [2316-26-9]; (*E*)- [14737-89-4]; (*Z*)- [14737-88-3]

Identified in commercial roasted coffees by Hughes and Thorpe (1987), by means of GC/MS, GC/IR with reference compounds. The content after hydrolysis of green coffee extracts was nearly 10 times lower in an arabica (55 ppm) than in a robusta (490 ppm) for Andrade *et al.* (1997). After analysis of seven arabicas and 13 robustas, giving ranges of 20–100 and 240–690 ppm respectively, Andrade *et al.* (1998) proposed using the content of this acid as a tool for differentiating the species.

(H.90) 2-Propenoic acid, 3-(4-hydroxy-3,5-dimethoxyphenyl)-, *3-(4-hydroxy-3,5-dimethoxyphenyl) prop-2-enoic acid*, sinapic acid, sinapinic acid **[530-59-6]; (*E*)- [7362-37-0]; (*Z*)- [7361-90-2]**

Identified by Hughes and Thorpe (1987) in commercial roasted coffees (GC/MS, GC/IR, with reference compounds) and in low amounts by Rakotomalala *et al.* (1993a,b) in one of the wild Madagascar (caffeine-free, *Mascarocoffea*) coffees (after hydrolysis). It was found only in one sample of green Mexican arabica by Andrade *et al.* (1998) from the more than 20 samples analyzed.

(H.91) 2-Propenoic acid, 3-(3,4,5-trimethoxyphenyl)-, *3-(3,4,5-trimethoxyphenyl)prop-2-enoic acid*, **[90-50-6]; (*E*)- [20329-98-0]; (*Z*)- [20329-99-1]**

Identified (after hydrolysis) in one Uganda green robusta extract (730 ppm) by Andrade *et al.* (1997), and in one green Brazil arabica extract (70 ppm) by Andrade *et al.* (1998).

It was the most resistant to heat degradation of all the hydroxycinnamic acids present in coffee (Casal *et al.*, 1999).

Phenol or phenol ethers with other functional groups are listed in Sections 5.P (amines) and 5.Q (sulfur compounds).

5.I FURANS AND PYRANS

Furans are, in fact, cyclic ethers that are mainly found in condensates from carbohydrates subjected to browning reactions. Since green coffee contains large quantities of sucrose and other sugars, it was normally postulated that furan compounds were formed during the roasting process (Gianturco *et al.*, 1964b). This observation was rapidly confirmed by the identification of caramelization products. In the thermal degradation of D-glucose and sugar polymers, Heyns *et al.* (1966a) demonstrated that furanic compounds were the principal decomposition products, and Fagerson (1969) identified 28 furans after pyrolysis of D-glucose. In model reactions involving mixtures of serine, threonine and sucrose, Baltes and Bochmann (1986a, 1987a) identified about 350 compounds (heterocycles), among them more than 100 simple furans, 13 furanones (including γ-lactones) and eight compounds with two furan rings, many of these compounds also being present in coffee. The furan derivatives were not formed in the absence of sucrose. In this work the authors characterized 53 new components of coffee. Generally, roasted arabicas show higher contents of steam-volatile furans than do robustas, corresponding to a high-sucrose content (see 2.1.2.1) (Silwar and Lüllmann, 1993a).

In reality, the presence of furans in heated or roasted foods has various origins. According to Mottram (1991), they are indeed typical Maillard-reaction compounds of carbohydrates, but they also result from thermal oxidation of lipids, from degradation of thiamine, and from breakdown of nucleotides. Sometimes they result from terpenic precursors already present in the green beans; for instance, Gautschi *et al.* (1967) observed that the furanic linalool oxides (**I.56** and **I.57**) were formed during roasting by thermal breakdown of the higher terpenes that occur among the lipids of green coffee, such as cafestol, kahweol or squalene. However, these two linalool oxides (as well as the two pyranic forms (**I.144** and **I.145**) were found by Cantergiani *et al.* (2001) in a green Mexican coffee. In addition to the identification of 49 furans in roasted coffee by Stoll *et al.* (1967), Flament *et al.* (1968a) described and discussed their chemical and spectroscopic aspects. An important analytical work was also carried out by Vitzthum and Werkhoff

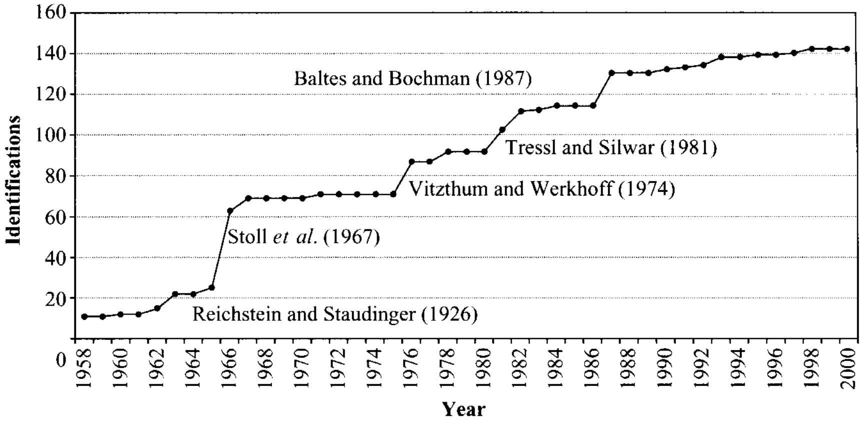
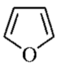


Fig. 5.9 Progressive identification of furan derivatives in roasted coffee volatiles

(1976b) who identified 50 furanic compounds, among which 15 were new for coffee, particularly 2-vinylfuran (**I.19**) and a series of its higher homologs (eight alkenyl- and methylvinyl furans) which had not been previously reported in heat-processed foodstuffs. The syntheses of the new constituents and comparison of their chromatographic and mass spectral properties with the substances obtained from coffee confirmed this assumption. The authors also presented a detailed study of the MS-fragmentation pathway of vinylfurans.

As a rule, furan derivatives are considered to be important aroma constituents from a sensory point of view. Merritt *et al.* (1963) considered that furan (**I.1**) and 2-methylfuran (**I.2**) were among the main components responsible for the typical coffee aroma. Vitzthum and Werkhoff (1976b) mentioned that furan compounds with an unsaturated substituent possessed strong odors ranging from unpleasant to food like. According to Ohloff and Flament (1978), furans that do not contain sulfur are mainly associated with sweet, fruity, nutty or caramel-like odor impressions, but with introduction of functional groups they have increased sensory values. The syntheses and organoleptic properties of furans have been described in a series of patents by Firmenich *et al.* (1969 g,k,m) and by Winter *et al.* (1972a) (1975h) (1976e,f,g,m,n,o) (1978d).

Alkylfurans



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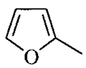

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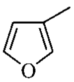

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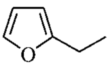

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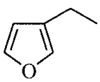

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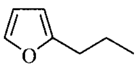

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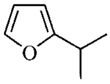

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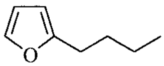

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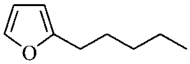

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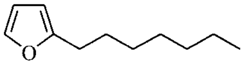


(I·10)

(I.1) *(I.1)* **Furan,** *furan, oxole* **[110-00-9]**

Identified in roasted coffee flavor by Johnston and Frey (1938) through a green pine splinter reaction and brown precipitate with concentrated HCl, then confirmed by Rhoades (1960) by GC/IR. It has also been identified in green coffee volatiles by Rhoades (1960) who found a concentration of 0.03 ppm. For Merritt *et al.* (1963), furan represented 2.3% of their 'coffee aroma' (see Section 5.B) and has an important impact on the typical aroma. The same team, Merritt *et al.* (1970), also found it in green arabicas and robusta, and Gibson (1974a) identified it in green beans of two hybrid species of East African arabica coffee. In the headspace of a brew analyzed by Shimoda and Shibamoto (1990a), furan represented 13.8% (GC), second after 2-methylbutanal.

As with many other furans, it is formed simply by heating glucose (Heyns *et al.*, 1966a; Fagerson, 1969), but many other complex pathways can explain its presence in roasted coffee.

It is characterized by a peculiar spicy-smokey, slightly cinnamon-like odor (Arctander, 1967). It has a threshold value of 4.5 ppm in water (Mulders, 1973b).

(I.2) *(I.2)* **Furan, 2-methyl-,** *2-methylfuran,* sylvan, silvan **[534-22-5]**

Identified in roasted coffee by Rhoades (1960) with GC/IR, Zlatkis and Sivetz (1960) with GC/MS, Merritt *et al.* (1963) (4% of the volatiles of their 'coffee aroma', see Section 5.B), Gianturco *et al.* (1966) and Stoffelsma *et al.* (1968). It was identified in green coffee volatiles by Rhoades (1960) at a concentration of 0.2 ppm and by Merritt *et al.* (1970). It was also (as methylfuran) quantified by Gibson (1974a). Silwar *et al.* (1987) gave a concentration of 0.05–0.15 ppm (simultaneous distillation–extraction) in a roasted arabica. Cros *et al.* (1980) found it in the headspace of ground roasted coffee. For Leino *et al.* (1992), it was a major headspace component of a dark-roasted blend, representing about 17% of the volatiles against 4–6% for lighter roasts, the proportion being nearly constant during one-year's storage. 2-Methylfuran was identified in headspace of five (out of six) ground green arabicas and six green robustas, also in a roasted Guatemala arabica by Procida *et al.* (1997). It was present in headspace of a brew (0.48% by GC, Shimoda and Shibamoto, 1990a) and in a supercritical CO_2 extract of a brewed arabica with (Ramos *et al.*, 1998).

It was identified in the products of thermal degradation of glucose (Heyns *et al.*, 1966a; Walter and Fagerson, 1968), in the model reaction cysteine–xylose (Ledl and Severin, 1973), and in model reactions of serine and threonine with sucrose (as well as in coffee) by Baltes and Bochmann (1987a).

The odor is ethereal, sickly. The odor threshold in water is 3.5 ppm (Mulders, 1973b) and 27 ppm in a bland edible (cottonseed) oil (Evans *et al.*, 1971).

(I.3) *(I.3)* **Furan, 3-methyl-,** *3-methylfuran* **[930-27-8]**

Doubtfully identified by Heins *et al.* (1966) in the headspace over roasted coffee beans by one of the first capillary GC/MS couplings but confirmed later by Liardon and Ott (1984) in an analytical study applying multivariate statistics for the classification of coffee headspace profiles. For Shimoda and Shibamoto (1990a), 3-methylfuran represented 9.7% (GC) in the headspace of a brew (equal to 3-methylbutanal, compare with (**I.1**). Leino *et al.* (1992) found it as a minor component in headspace of various blends, with a constant proportion during one-year storage, but more important in a blend with long roasting time like 2-methylfuran (**I.2**). In headspace of green coffee, it was identified by Gutmann *et al.* (1979), and by Procida *et al.* (1997) in six green arabicas and five (out of six) robustas with concentrations lower than those of the 2-methyl isomer.

It is formed by thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969).

(I.4) *(I.4)* **Furan, 2-ethyl-,** *2-ethylfuran* **[3208-16-0]** ***FEMA 3673***

Identified by Vitzthum and Werkhoff (1976b). It has been identified in green coffee volatiles by Gutmann *et al.* (1979) and in volatiles of a brew (0.07%, GC) by Shimoda and Shibamoto (1990a).

It is formed by thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969). It was found (as well as in coffee) by Baltes and Bochmann (1987a) in model reactions, heating serine and threonine with sucrose.

Powerful and diffusive, sweet-ethereal, burnt odor, in extreme dilution rather pleasant, warm and sweet (Arctander, 1967). The flavor is described as alliaceous, dirty, musty, phenolic and medicinal (Chemisis, 1998). An odor threshold of 8.0 ppm in cottonseed oil is given by Evans *et al.* (1971).

(I.5) **Furan, 3-ethyl-,** *3-ethylfuran* **[67363-95-5]**

Identified by Liardon and Ott (1984) when classifying coffee headspace profiles, and in headspace of a brew (0.04%, GC) by Shimoda and Shibamoto (1990a).

(I.6) **Furan, 2-propyl-,** *2-propylfuran* **[4229-91-8]**

Identified by Merritt *et al.* (1963) as propylfuran, probably the 2-isomer, as noted by Gianturco *et al.* (1964b, footnote 14) which could not confirm its presence in coffee volatiles. It was still later noted as 'a' propylfuran by Merritt and Robertson (1966). The identification was finally confirmed by Vitzthum and Werkhoff (1976b) by comparison of the MS spectrum with the data of Heyns *et al.* (1966b).

It is formed in the thermal degradation of glucose (Heyns *et al.*, 1966a; Walter and Fagerson, 1968).

The flavor is described as green, mustard, radish, buttery (Chemisis, 1980). The threshold in cottonseed oil is 8 ppm (Evans *et al.*, 1971).

Furan, 3-propyl-, *3-propylfuran* **[42908-61-2]**

Two propylfurans, therefore the 2-and 3-isomers were identified but only tentatively by Heins *et al.* (1966) in the headspace over coffee beans by one of the first capillary GC/MS coupling.

(I.7) **Furan, 2-(1-methylethyl)-,** *2-isopropylfuran* **[10599-59-4]**

Identified by Vitzthum and Werkhoff (1976b) in the neutral extract of the steam-distillate; the MS data were compared with those of Heyns *et al.* (1966b).

It is formed in the thermal degradation of glucose (Fagerson, 1969).

(I.8) *(I.8)* **Furan, 2-butyl-,** *2-butylfuran* **[4466-24-4]**

Identified in roasted coffee flavor by Merritt *et al.* (1963) as butylfuran (same remark as for 2-propylfuran, **I.6**). The identification was also confirmed in the same way by Vitzthum and Werkhoff (1976b). It was identified in green coffee volatiles by Gutmann *et al.* (1979). Baltes and Bochmann (1987a) found it in coffee but not in model reactions when heating serine and threonine with sucrose.

At a concentration of 5 ppm the flavor is weak, woody, herbal, fennel (Chemisis, 1980). The odor is weak, non-characteristic and the threshold in cottonseed oil is 10 ppm (Evans *et al.*, 1971).

The 2-isobutylfuran quoted by Maga (1979) is not in the reference quoted (Stoffelsma *et al.*, 1968); it is more probably the '2-isobutyrylfuran' (**I.78**) which has been effectively identified by these authors.

(I.9) *(I.9)* **Furan, 2-pentyl-,** *2-pentylfuran*, 2-amylfuran **[3777-69-3]** ***FEMA 3317***

Identified by Stoll *et al.* (1967), by Vitzthum and Werkhoff (1976b), and by Silwar *et al.* (1987) who gave a concentration of 0.05–0.1 ppm in roasted coffee (see **I.2**). It was also identified in green coffee volatiles (headspace) by Vitzthum *et al.* (1976) and by Spadone and Liardon (1988) in 'Rio' as well as in healthy green beans (simultaneous distillation–extraction). As for 2-butylfuran (**I.8**), Baltes and Bochmann (1987a) found it in coffee but not in model reactions involving heating of serine and threonine with sucrose. For Cantergiani *et al.* (2001), 2-pentylfuran represented 0.03% of the volatiles (GC polar) obtained after vacuum hydrodistillation and extraction.

2-Pentylfuran may originate from linoleic acid, $C_{18:2}$ (Krishnamurthy and Chang, 1967).

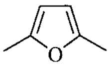
Stoll *et al.* (1967) prepared it by dehydration of 1-(2-furyl)-1-pentanol, then catalytic hydrogenation of the unsaturated hydrocarbons.

The flavor is perceived as earthy, mouldy, oily anisic (Chemisis, 1994). Krishnamurthy and Chang (1967) considered that it could be responsible for reversion flavor in fats and gave a flavor threshold of 1 ppm in oil. Its odor threshold is 6 ppb in water (Buttery *et al.*, 1969b) and 2 ppm in cottonseed oil (Evans *et al.*, 1971).

(I.10) Furan, 2-heptyl-, *2-heptylfuran* **[3777-71-7]** ***FEMA 3401***

Identified by Ho *et al.* (1993) in roasted Columbian arabica (adsorbent trapping/short-path thermal desorption = headspace, GC/MS; concentration 1.18 ppm).

The flavor is sweet, fatty (Chemisis, 1978).



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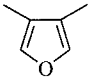

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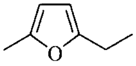

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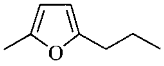

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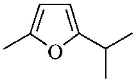

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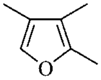

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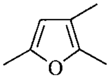

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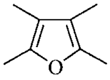


(I·18)

(I.11) *(I.11)* **Furan, 2,5-dimethyl-,** *2,5-dimethylfuran* **[625-86-5]**

Identified in roasted coffee by Merritt *et al.* (1963) (0.2% of their 'coffee aroma', see in Section 5.B), by Stoffelsma *et al.* (1968), by Wang *et al.* (1983) (headspace concentration, GC/MS) and in volatiles of green beans by Merritt *et al.* (1970). Silwar *et al.* (1987) gave a concentration of 0.15–0.25 ppm in a roasted arabica (see **I.2**). It represented 0.54% (GC) in a headspace of a brew (Shimoda and Shibamoto, 1990a). As for **I.2** and **I.3**, the concentration is more important in a dark-roasted coffee (Leino *et al.*, 1992). Procida *et al.* (1997) identified this furan in headspace of a roasted Guatemala arabica but not in the green coffees examined.

It is formed in the thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969). Baltes and Bochmann (1987a) found it in reactions of serine and threonine with sucrose (as well as in coffee; the 2,3- and 2,4-dimethyl isomers were only identified in the model reactions).

It has an ethereal odor (Sakaguchi and Shibamoto, 1978 a,b).

(I.12) Furan, 3,4-dimethyl-, *3,4-dimethylfuran* [20843-07-6]

Identified by Liardon and Ott (1984), when studying a classification of coffees by their headspace profiles.

Furan, 2,3-dimethyl-, [14920-89-9]

Furan, 2,4-dimethyl-, [3710-43-8]

These been tentatively identified by Liardon and Ott (1984). In a roasted arabica, Procida *et al.* (1997) identified two dimethylfurans besides 2,5-dimethylfuran (**I.11**), but as the printed version twice gave '2,4-dimethylfuran', they could be the 2,3-, 2,4-or 3,4-isomers.

(I.13) Furan, 2-ethyl-5-methyl-, *2-ethyl-5-methylfuran* [1703-52-2]

Identified in roasted coffee flavor by Baltes and Bochmann (1987a) (MS data compared with those discussed by Heyns *et al.*, 1966b).

It was formed in the thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969). It was identified in the products of thermal degradation of cysteine and xylose in tributyrin (Ledl and Severin, 1973) and in a heated cysteine–glucose model system (Sheldon *et al.*, 1986). In the same type of reaction, with serine, threonine and sucrose, Baltes and Bochmann (1987a) identified this isomer and the two other 2-ethylmethylfurans.

(I.14) Furan, 2-methyl-5-propyl-, *2-methyl-5-propylfuran*, 5-methyl-2-propylfuran [1456-16-2]

Identified by Baltes and Bochmann (1987e) (extraction of the condensates of roasting).

It was formed by thermal degradation of glucose (Fagerson, 1969). This isomer was formed in reactions of serine and threonine with sucrose (Baltes and Bochmann, 1987a).

Another **methyl-2-propylfuran** was found by the latter authors in coffee and in their model reactions.

(I.15) Furan, 2-methyl-5-(1-methylethyl)-, *2-isopropyl-5-methylfuran* [10504-05-9]

Identified by Vitzthum and Werkhoff (1976b) in the neutral extract after steam distillation (MS data compared with those discussed by Heyns *et al.*, 1966b).

It is formed by thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969).

(I.16) Furan, 2,3,4-trimethyl-, *2,3,4-trimethylfuran* [10599-57-2]

Identified by Baltes and Bochmann (1987e) (MS data compared with those of Heyns *et al.*, 1966b).

(I.17) Furan, 2,3,5-trimethyl-, *2,3,5-trimethylfuran* [10504-04-8]

Identified by Vitzthum and Werkhoff (1976b) (see **I.15**), and by Baltes and Bochmann (1987a), the two publications referring to the MS data of Heyns *et al.* (1966b). Shimoda and Shibamoto (1990a) found it in headspace of a brewed Columbia arabica (0.11%, GC), and Procida *et al.* (1997) in headspace of ground roasted Guatemala arabica.

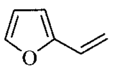
It is formed by thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969). Contrary to the 2,3,4-trimethyl isomer (**I.16**), this compound was found by Baltes and Bochmann (1987a) when heating serine and threonine with sucrose.

(I.18) Furan, tetramethyl-, *tetramethylfuran, 2,3,4,5-tetramethylfuran* [10599-58-3]

Identified in a roasted arabica by Ho *et al.* (1993) (see under **I.10**); concentration 1.34 ppm).

It is a product of Maillard reaction.

Alkenylfurans



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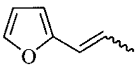

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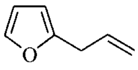

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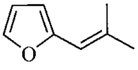

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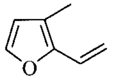

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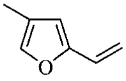

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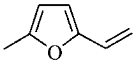

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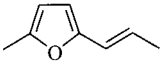

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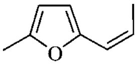

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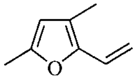

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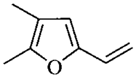


(I.29)

(I.19) Furan, 2-ethenyl-, *2-vinylfuran* [1487-18-9]

Identified (see **I.15**) by Vitzthum and Werkhoff (1976b) (MS data), and by Silwar *et al.* (1987) who found a concentration of 0.02–0.05 ppm in a roasted arabica (see **I.2**). It represented 0.17% in GC) of the headspace of roasted coffee for Shimoda and Shibamoto (1990a).

It was formed from the thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969). Baltes and Bochmann (1987a) found 2-and 3-vinylfurans in model reactions involving serine, threonine and sucrose. Only the 2-vinyl isomer was present in coffee.

According to Winter *et al.* (1976e), at a concentration of 5 ppm in a syrup base, it has a phenolic, ground-coffee taste, becoming groundsy, cereal-like and enhancing the roasted note when tasted in a neutral, soluble coffee base. The threshold value is of 1 ppm in a bland edible oil (Evans *et al.*, 1971).

(I.20) Furan, 2-(1-propenyl)-, *2-(prop-1-enyl)furan* [10599-55-0]; (*E*)- [10504-08-2]; (*Z*)- [10504-07-1]

Identified (see **I.15**) by Vitzthum and Werkhoff (1976b) (MS data) and by Baltes and Bochmann (1987a), the stereochemistry not being specified (named 2-propenylfuran).

Heyns *et al.* (1966a) and Fagerson (1969) identified the two isomers in the pyrolysis of D-glucose. Propenylfuran was not formed when serine and threonine were heated without sucrose (Baltes and Bochmann).

(I.21) Furan, 2-(2-propenyl)-, *2-allylfuran, 2-(prop-2-enyl)furan* [75135-41-0]

Identified in headspace of a roasted Guatemala arabica by Procida *et al.* (1997).

(I.22) Furan, 2-(2-methyl-1-propenyl)-, *2-(2-methylprop-1-enyl)furan*, 2-isobutenylfuran, 2-methyl-3-(2-furyl)-2-propene [10504-11-7]

Identified (see **I.15**) by Vitzthum and Werkhoff (1976b) (MS data), confirmed by Silwar (1982), Silwar *et al.* (1987) (0.03–0.05 ppm) and by Baltes and Bochmann (1987a). The name 2-isobutenylfuran, used in some of the references quoted, is slightly ambiguous: it could correspond to 2-methyl-2-propenyl- or 2-methyl-1-propenyl-, although more probably to the last radical as specified by Baltes and Bochmann.

It was formed upon thermal degradation of glucose (Heyns *et al.*, 1966a). It was not found in the reactions of serine and threonine with sucrose (Baltes and Bochmann, 1987a).

(I.23) Furan, 2-ethenyl-3-methyl-, *3-methyl-2-vinylfuran* **[52559-01-0]**

(I.24) Furan, 2-ethenyl-4-methyl-, *4-methyl-2-vinylfuran* **[59417-61-7]**

These were identified (see **I.15**) by Vitzthum and Werkhoff (1976b) (MS data), and by Baltes and Bochmann (1987a). **I.23** represented 0.13% (GC) in the headspace of a brew for Shimoda and Shibamoto (1990a).

I.23 has a burnt, acrylic, ethereal flavor (Chemisis, 1996).

(I.25) Furan, 2-ethenyl-5-methyl-, *2-methyl-5-vinylfuran* **[10504-13-9]**

Identified (see **I.15**) by Vitzthum and Werkhoff (1976b) (MS data), and by Baltes and Bochmann (1987a). Silwar *et al.* (1987) gave a concentration of 0.05–0.10 ppm in a roasted arabica (see **I.2**). Shimoda and Shibamoto (1990a) found 0.37% (GC) in headspace of a brew, Procida *et al.* (1997) identified it in headspace of a roasted arabica.

I.25 is formed by thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969). Of the three isomers **I.23** to **25**, only **I.24** is not formed by heating serine or threonine with sucrose (Baltes and Bochmann, 1987a).

(I.26) Furan, 2-methyl-5-(1-propenyl)-, (*E*)-, *(*E*)-2-methyl-5-(prop-1-enyl)furan* **[10504-10-6]**; no stereochemistry **[5555-95-3]**

Identified (see **I.15**) by Vitzthum and Werkhoff (1976b) without precision of the stereochemistry. The (*E*)-isomer was identified by Silwar (1982) and Silwar *et al.* (1987) gave a concentration of 0.05–0.10 ppm ('*trans*-2-methyl-5-*n*-propenylfuran') in a roasted arabica (see **I.2**). It was also found by Baltes and Bochmann (1987a), and by Shimoda and Shibamoto (1990a) (0.08% of the volatiles by GC).

The latter authors characterized this furan when heating serine and threonine with sucrose. It is formed by thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969).

(I.27) Furan, 2-methyl-5-(1-propenyl)-, (*Z*)-, *(*Z*)-2-methyl-5-(prop-1-enyl)furan* **[10504-12-8]**

Identified by Silwar (1982), and Silwar *et al.* (1987) gave a concentration of 0.15–0.20 ppm ('*cis*-2-methyl-5-*n*-propenylfuran') in a roasted arabica (see **I.2**). This (*Z*)-isomer was also found by Baltes and Bochmann (1987a).

It is formed in the same model reactions as the (*E*)-isomer **I.26**.

(I.28) Furan, 2-ethenyl-3,5-dimethyl-, *3,5-dimethyl-2-vinylfuran* **[59417-62-8]**

(I.29) Furan, 5-ethenyl-2,3-dimethyl-, *2,3-dimethyl-5-vinylfuran* **[59417-63-9]**

These were identified (see **I.15**) by Vitzthum and Werkhoff (1976b) (MS data).

The flavor of I.28 is described as burnt, cereal, beany (Chemisis, 1996).

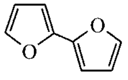
Bifurans and methylenebifurans

(I.30) 2,2′-Bifuran, *2,2′-bifuryl, 2,2′-bifuran*, 2-(2-furanyl)furan, 2,2′-difuryl **[5905-00-0]**

Identified by Stoll *et al.* (1967), by Baltes and Bochmann (1987a) (MS data given), and by Ho *et al.* (1993) (0.17 ppm, see **I.10**). The 3,3′-bifuran (peak No. 173) mentioned by Silwar *et al.* (1987) was probably the 2,2′-isomer (concentration 0.01–0.02 ppm), otherwise there would not be the alternative **I.31** and **I.32**.

2,2′-Bifuran was present in reactions of serine and threonine with sucrose (Baltes and Bochmann, 1987a).

According to Winter *et al.* (1976e), at a concentration of 10 ppm in a syrup base, it has an aromatic taste, becoming medicinal, camphor and ricy when tasted in a neutral, soluble coffee base.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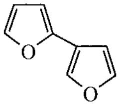
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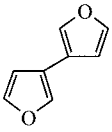
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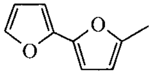
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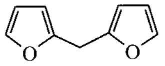
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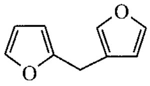
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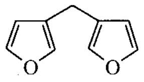
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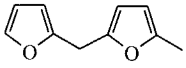
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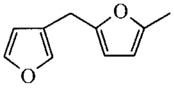
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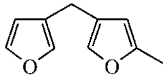
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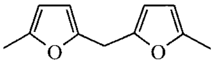

(I·40)

(I.31) 2,3′-Bifuran, *2,3′-bifuryl, 2,3′-bifuran* **[27521-86-4] or**

(I.32) 3,3′-Bifuran, *3,3′-bifuryl, 3,3′-bifuran* **[13803-57-1]**

This was identified by Silwar (1982), and Silwar *et al.* (1987) found a concentration of 0.01–0.02 ppm.

(I.33) 2,2′-Bifuran, 5-methyl-, *5-methyl-2,2′-bifuran, 2-(2-furyl)-5-methylfuran* **[16303-61-0]**

Identified by Baltes and Bochmann (1987a) (MS data given).

It was found by these authors only in reaction of serine (and not threonine) with sucrose.

(I.34) Furan, 2,2′-methylenebis-, *2-furfurylfuran, 2,2′-difurylmethane* **[1197-40-6]**

Identified by Gianturco *et al.* (1964b) using MS and IR-spectroscopy, and also by Stoffelsma *et al.* (1968), by Baltes and Bochmann (1987a) (MS data given), and Shibamoto *et al.* (1982) who found an increasing proportion with increasing roasting time: 0.13 to 0.40% of the volatiles (simultaneous distillation–extraction and high performance LC) after 27 and 30 min respectively at 230 °C. Shimoda and Shibamoto (1990a) found 0.11% (GC) in the volatiles of a brew. Silwar *et al.* (1987) gave a concentration of 0.50–1 ppm (simultaneous distillation–extraction) and Ho *et al.* (1993) 0.97 ppm (headspace, see **I.10**).

For some brief comments on the mass spectrum see Biemann (1963).

It was identified in the products of thermal degradation of cysteine and xylose in tributyrin (Ledl and Severin, 1973), in reaction of serine (but not threonine) with sucrose (Baltes and Bochmann, 1987a).

It is described as having a caramellic odor (Shibamoto, 1977) and an alliaceous, earthy and mushroom flavor (Chemisis, 1996).

(I.35) Furan, 2-(3-furanylmethyl)-, *3-furfurylfuran, 2-(3-furylmethyl)furan* **[107716-11-0]** or

(I.36) Furan, 3,3′-methylenebis-, *3-(3-furylmethyl)furan, 3,3′-difurylmethane* **[146699-68-5]**

Identified by Silwar (1982). Silwar *et al.* (1987) found a concentration of 0.02-0.05 ppm.

(I.37) Furan, 2-(2-furanylmethyl)-5-methyl-, *2-furfuryl-5-methylfuran*, 2-furyl-(2′-methyl-5′-furyl)methane **[13678-51-8]**

Identified by Stoll *et al.* (1967) (with a synthesis), and by Stoffelsma *et al.* (1968). Shibamoto *et al.* (1982) could characterize it only in a strong-roasted arabica (230 °C, 30 min) after simultaneous distillation–extraction (peak area 0.24% in high performance LC).

Baltes and Bochmann (1987a) found it (as well as in coffee) when heating serine and threonine with sucrose (MS data).

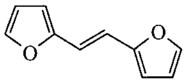
According to Winter *et al.* (1976e), at a concentration of 10 ppm in a sugar syrup it has a green-cooked taste and, at a concentration of 1 ppm, it imparts to a neutral soluble coffee beverage a liquorice-like note. At a concentration of 2 ppm it was described as having an alliaceous, earthy, mushroom flavor (Chemisis, 1996).

A **3- or 4-methyl isomer** was also found by Baltes and Bochmann (1987a) (MS data) in coffee as well as in their model reactions.

(I.38) Furan, 2-(3-furanylmethyl)-5-methyl-, *2-(3-furylmethyl)-5-methylfuran*, (3-furyl)(5-methyl-2-furyl)methane **[107716-12-1]** or

(I.39) Furan, 4-(3-furanylmethyl)-2-methyl-, *4-(3-furylmethyl)-2-methylfuran*, (3-furyl)(5-methyl-3-furyl)methane

Identified by Silwar *et al.* (1987), who found a concentration of 0.03–0.06 ppm.



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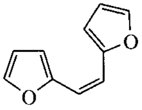

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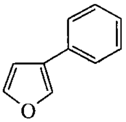

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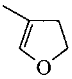

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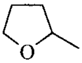

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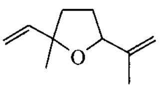

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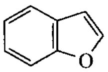

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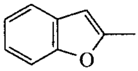

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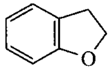


(I·51)

(I.40) Furan, 2,2′-methylenebis[5-methyl-, *2,2′-methylenebis(5-methylfuran)*, bis(5-methyl-2-furyl)methane **[13679-43-1]**

Identified by Stoll *et al.* (1967) and Silwar (1982). Silwar *et al.* (1987) gave a concentration of 0.10–0.15 ppm. This compound was also found by Baltes and Bochmann (1987a) (MS data).

The latter authors identified it in the heated mixture of serine and threonine with sucrose.

At a concentration of 20 ppm in a sugar syrup, it has a green, powdery taste and, at a concentration of 0.7 ppm, it imparts to a neutral soluble coffee beverage a bitter, wintergreen note and a mouthfeel sensation (Winter *et al.*, 1976e).

Other non functional furanic compounds

(I.41) Furan, 2,2′-(1,2-ethenediyl)bis-, (*E*)-, *(*E*)-2,2′-vinylenebis(furan)*, 2-[2E-*(2-furyl)ethenyl]furan*, *trans*-di-(2-furyl)ethylene **[1439-19-6]**; no stereochemistry **[5416-79-5]**

(I.42) Furan, 2,2′-(1,2-ethenediyl)bis-, (*Z*)-, *(*Z*)-2,2′-vinylenebis(furan)*, *cis*-di-(2-furyl)ethylene **[18266-93-8]**

These were identified by Silwar (1982). The concentrations found by Silwar *et al.* (1987) were, respectively, 0.02–0-06 and 0.05–0.10 ppm.

(I.43) *(I.43)* **Furan, 3-phenyl-,** *3-phenylfuran* **[13679-41-9]**

Identified in roasted coffee volatiles by Stoll *et al.* (1967), by Stoffelsma *et al.* (1968), by Vitzthum and Werkhoff (1976b), and in green coffee volatiles by Gutmann *et al.* (1979). Silwar *et al.* (1987) found a concentration of 0.20–0.30 ppm in roasted coffee.

It is characterized by a naphthalenic flavor and a jasmine odor (Chemisis, 1963).

(I.44) Furan, 2,5-dihydro-, *2,5-dihydrofuran, 2,5-dihydrooxole*, 3-oxolene **[1708-29-8]**

(I.45) Furan, 2,3-dihydro-4-methyl-, *2,3-dihydro-4-methylfuran* **[34314-83-5]**

These were identified by Ramos *et al.* (1998) after supercritical-CO_2 extraction of a brewed arabica. Ho *et al.* (1993) found for (**I.45**) a concentration of 0.39 ppm (see **I.10**).

(I.46) *(I.46)* **Furan, tetrahydro-,** *tetrahydrofuran, oxolane*, 1,4-epoxybutane, butylene oxide **[109-99-9]**

Identified by Heins *et al.* (1966) in the headspace over coffee beans by one of the first capillary GC/MS couplings; also identified by Stoffelsma and Pypker (1968). It has been identified in green coffee volatiles by Gutmann *et al.* (1979).

The odor is penetrating, sweet-gassy and warm, bread-like, unpleasant in its diffusive power and pungency (Arctander, 1967).

(I.47) Furan, tetrahydro-2-methyl-, *tetrahydro-2-methylfuran* **[96-47-9]**

Identified by Stoffelsma and Pypker (1968).

(I.48) Furan, 2-ethenyltetrahydro-2-methyl-5-(1-methylethenyl)-, *tetrahydro-5-isopropenyl-2-methyl-2-vinylfuran*, anhydrolinalool oxide **[13679-86-2]** ***FEMA 3759***; ***cis*-** **[54750-69-5]**; ***trans*-** **[54750-70-8]**

Identified by Stoll *et al.* (1967).

The flavor is described as green, solvent, fatty at 10 ppm, and celery, dill, spicy, anise, citrus, etc., at 5 ppm (Chemisis, 1998).

(I.49) Benzofuran, *benzo[*b*] furan, 1-benzofuran,* 2,3-benzofuran, 1-oxindene **[271-89-6]**

Identified by Stoll *et al.* (1967), it has also been found (see **I.15**) by Vitzthum and Werkhoff (1976b), and by Silwar *et al.* (1987) the concentration given being 0.02–0.05 ppm.

According to Winter *et al.* (1976e), at a concentration of 0.5 ppm in a syrup base, it has a styrene-like, aromatic taste.

(I.50) Benzofuran, 2-methyl-, *2-methylbenzo[*b*] furan* **[4265-25-2]**

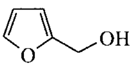
Identified by Stoll *et al.* (1967), and by Vitzthum and Werkhoff (1976b). Silwar *et al.* (1987) found a concentration of 0.01–0.04 ppm.

According to Winter *et al.* (1976e), at a concentration of 10 ppm in a syrup base, it has a slightly phenolic, burnt taste, and it enhances the bitter note of a neutral, soluble coffee base.

(I.51) Benzofuran, 2,3-dihydro-, *2,3-dihydrobenzo*[b]*furan,* coumaran (!) **[496-16-2]**

Identified by Stoll *et al.* (1967) and tentatively by Vitzthum and Werkhoff (1976b). Silwar *et al.* (1987) gave a concentration of 0.05–0.1 ppm.

Furans with an alcohol function



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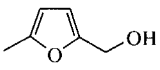

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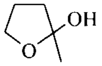

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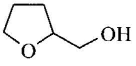

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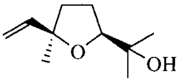

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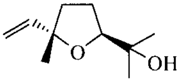

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(I.52) ***(I.52)*** **2-Furanmethanol,** *furan-2-methanol, (2-furyl)methanol, furfuryl alcohol,* 2-furylcarbinol, 2-hydroxymethylfuran **[98-00-0]** ***FEMA 2491***

Identified by Erdmann (1902a) in the 'coffee oil' obtained after steam distillation of ground roasted coffee, followed by ether extraction and distillation. Prescott *et al.* (1937b) confirmed its structure through the α-naphthyl isocyanate. They characterized it as a colorless liquid having a fragrant odor and which exhibits a marked tendency towards polymerization and resinification on standing, especially in aqueous solution. It was also found by Viani *et al.* (1965). Its concentration in roasted coffee was estimated at 226 ppm by Stofberg and Stoffelsma (1981); it was 300 ppm in arabica and 520 ppm in robusta (150 in arabusta) for Tressl *et al.* (1978a), and 90–135 ppm (the highest concentration of all the heterocyclic compounds that they identified) for Silwar *et al.* (1987). It has been identified by Vitzthum *et al.* (1976) in green beans volatiles. Shibamoto *et al.* (1982) mentioned the increase in this furan during roasting of a Columbian arabica (peak area of the volatiles): from 16.6 % after 25 min at 230 °C to 25.4 % after 30 min at the same temperature (simultaneous distillation–extraction, high performance LC). A similar increase was noted by Silwar and Lüllmann (1993b): after 5 min at a given temperature, formation started at 170 °C and increased until 260 °C, unlike the aldehydes **I.63**, **I.66** and **I.72**. In a headspace of a brew, it represented 0.66 % (Shimoda and Shibamoto, 1990a). For Ho *et al.* (1993) the concentration was 63.5 ppm, and it was also the main product (followed by three furancarbaldehydes) in headspace of a roasted Columbian coffee (see **I.10**). Procida *et al.* (1997) found this alcohol in the volatiles of two green arabicas (out of six) and five green robustas (out of six); in the roasted Guatemala arabica studied, the concentration first increased, then decreased after 22 min at 218 °C. Ramos *et al.* (1998) extracted the alcohol from a brewed arabica by various methods (liquid–liquid extraction with pentane or methylene chloride, solid-phase microextraction, supercritical CO_2), and it represented ca 40 % (GC) of the compounds extracted with methylene chloride (other methods giving ca 1–7 %).

It has been identified in the products of thermal degradation of cysteine and xylose in tributyrin (Ledl and Severin, 1973). It was found in a heated cysteine/glucose model system by Sheldon *et al.* (1986) and in serine/threonine/sucrose model systems (as well as in coffee) by Baltes and Bochmann (1987a). Silwar and Tressl (1989) studied a model reaction involving heating cysteine and methionine with 2-furaldehyde (**I.63**) under roasting conditions and they found that an important part of the aldehyde is reduced to furfuryl alcohol.

It has a very mild, slightly caramellic, warm-oily odor (Arctander, 1967) and is well correlated with the undesirable burnt and bitter note of dark-roasted coffees. Its flavor threshold in water was 5 ppm for Brulé *et al.* (1971) who found a slight taste of smoked meat.

(I.53) 2-Furanmethanol, 5-methyl-, *5-methylfuran-2-methanol, 5-methylfurfuryl alcohol* **[3857-25-8]**

Identified by Vitzthum and Werkhoff (1976b) (MS data). Silwar *et al.* (1987) found a concentration of 1.20–1.80 ppm.

Baltes and Bochmann (1987a) found it in their model reactions (see **I.52**) as well as in coffee.

The flavor is described as weak, resinous, myrrh, woody (Chemisis, 2000).

2-Furanmethanol, 3(4)-methyl-, *3(4)-methylfuran-2-methanol*; **3-methyl- [20416-16-4]; 4-methyl- [33845-39-5]**

Found by Baltes and Bochmann (1987e) (MS data) in coffee as well as in their model reactions.

(I.54) 2-Furanol, tetrahydro-2-methyl-, *tetrahydro-2-methylfuran-2-ol* **[7326-46-7]**

Identified by Ho *et al.* (1993) in a roasted Columbian coffee with a concentration of 0.25 ppm (see under **I.10**).

(I.55) 2-Furanmethanol, tetrahydro-, *tetrahydrofuran-2-methanol, tetrahydrofurfuryl alcohol,* tetrahydro-2-furancarbinol, hydroxymethyltetrahydrofuran **[97-99-4]** ***FEMA 3056***

Identified by Hills *et al.* (1991) after simultaneous supercritical-fluid derivatization and extraction.

(I.56) *(I.56)* **2-Furanmethanol, 5-ethenyltetrahydro-α, α, 5-trimethyl-, (*cis*)-,** *2-(tetrahydro-*t*-5-methyl-5-vinyl-*r*-2-furyl)propan-2-ol, tetrahydro-*c*-5-(1-hydroxy-1-methylethyl)-*r*-2-vinyl-2-methylfuran, cis-linalool oxide* **[5989–33–3]; (±)-*cis*- [128441-08-7]; 2*R,cis*- [4031-48-5]; 2*S,cis*- [23007-29-6]**; no stereochemistry **[60047-17-8]**

Identified by Stoll *et al.* (1967), and by Stoffelsma *et al.* (1968) in roasted coffee flavor. This isomer was found by Cantergiani *et al.* (2001) in a green Mexican arabica (vacuum hydrodistillation and extraction), representing 1.54 % of the volatiles (GC polar).

'Linalool oxide' was found by Shibamoto *et al.* (1982) only in a strongly roasted coffee (230 °C, 30 min). A stereochemically undefined linalool oxide was identified by Spadone *et al.* (1990) in a green coffee characterized by a 'Rio' off-flavor.

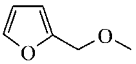
Powerful sweet-woody, penetrating odor with floral-woody-earthy undertones. Almost pungent when undiluted, it reveals more pleasant floral woody character upon dilution. The camphoraceous notes bear some resemblance to those of cineol and eucalyptol (Arctander, 1967).

(I.57) *(I.57)* **2-Furanmethanol, 5-ethenyltetrahydro-α, α,5-trimethyl-, (*trans*)-,** *2-(tetrahydro-*c*-5-methyl-5-vinyl-*r*-2-furyl)propan-2-ol, tetrahydro-*t*-5-(1-hydroxy-1-methylethyl)-*r*-2-vinyl-2-methylfuran, trans-linalool oxide* **[34995-77-2]; (±)-*trans*- [128441-10-1];** ***2R,trans*- [41720-55-2]; 2*S*, *trans*- [41720-60-9]**

Identified by Stoffelsma *et al.* (1968) in roasted coffee flavor. In fact, the authors did not specify the furanic structure but, as they referred to Stoll *et al.* (1967) for the *cis*-isomer, there is little doubt about the identification. Friedel *et al.* (1971) confirmed the identification for the *trans*-isomer in an 'aroma complex' of coffee (method in Gianturco *et al.*, 1963). Cantergiani *et al.* (2001) found it in a green Mexican arabica (1.56% of the volatiles by GC on a polar column).

cis- and *trans*-Linalool oxides, without precision of furanic or pyranic structure, have been identified by Mathieu *et al.* (1998) in berries of an arabica plant (grown in a green house) left on the tree after the first stage of ripeness. The amount increases when that of linalool decreases.

Furan ethers



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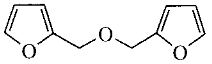

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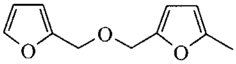

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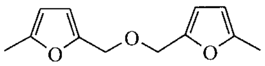

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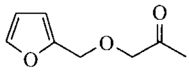


(I·62)

(I.58) Furan, 2-(methoxymethyl)-, *2-(methoxymethyl)furan, furfuryl methyl ether* **[13679-46-4]** ***FEMA 3159***

Identified by Stoll *et al.* (1967) (synthesis), Stoffelsma *et al.* (1968), Vitzthum and Werkhoff (1976b) (see **I.15**), Cros *et al.* (1980) (headspace of a brew), and by Wang *et al.* (1983) (headspace concentration) who did not quote it as having been previously identified in coffee. It was found by Shibamoto *et al.* (1982), after simultaneous distillation–extraction (0.17% of the volatiles, high performance LC), only in a strong-roasted arabica (30 min at 230 °C). Using a similar method, Silwar *et al.* (1987) gave a concentration of 0.10–0.30 ppm. Shimoda and Shibamoto (1990a) found it in the headspace of a brew (0.12%, GC) and Ramos *et al.* (1998) only in the extract of a brew with supercritical CO_2 (see under **I.52**).

According to Winter *et al.* (1976e), at a concentration of 10 ppm in a syrup base, it has a strong mustard taste, becoming nutty, coffee grounds-like, ricy and phenolic when tasted, at the same concentration, in a neutral soluble coffee base.

(I.59) Furan, 2,2′-[oxybis(methylene)]bis-, *2,2′-(oxydimethylene)bis(furan), 2-[(2-furylmethoxy) methyl]furan, 2-[(furfuryloxy)methyl]furan, difurfuryl ether* **[4437-22-3]** ***FEMA 3337***

Identified by Stoll *et al.* (1967) (with a synthesis), and by Stoffelsma *et al.* (1968). Shibamoto *et al.* (1982) found an increase with increasing roasting time: 0.14 to 0.54% of the volatiles (high performance

LC) after 27 and 30 min respectively at 230 °C. Silwar *et al.* (1987) found a concentration of 0.60–1.40 ppm.

According to Winter *et al.* (1976e), at a concentration of 10 ppm in a syrup base, it has a salicylate, coffee-like note; a mushroom note being perceived, when tasted, at 1.5 ppm in a neutral soluble coffee base.

(I.60) Furan, 2-[(2-furanylmethoxy)methyl]-5-methyl-, *2-[(2-furylmethoxy)methyl]-5-methylfuran, 2-[(furfuryloxy)methyl]-5-methylfuran, furfuryl 5-methylfurfuryl ether* **[13678-72-3]**

Identified and synthesized by Stoll *et al.* (1967). Silwar *et al.* (1987) found a concentration of 0.05–0.10 ppm.

It is prepared by condensation of 2-bromomethyl-5-methylfuran, obtained by action of *N*-bromosuccinimide on 2,5-dimethylfuran with furfuryl alcohol (**I.52**).

This ether has a typical mushroom odor. According to Winter *et al.* (1976e), at a concentration of 10 ppm in a syrup base, it has a green, water-cress like flavor; an earthy, mushroom note being perceived, when tasted, at 0.7 ppm in a neutral soluble coffee base.

(I.61) Furan, 2,2′-[oxybis(methylene)]bis(5-methyl-, *2,2′-(oxydimethylene)bis(5-methylfuran), bis(5-methylfurfuryl) ether*

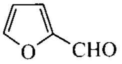
Identified and synthesized by Stoll *et al.* (1967).

The synthesis is similar to that of **I.60**, but using 5-methylfurfuryl alcohol (**I.53**).

(I.62) 2-Propanone, 1-(2-furanylmethoxy)-, *1-(furfuryloxy)propan-2-one, 1-(2-furylmethoxy)propan-2-one, furfuryloxyacetone*, acetonyl furfuryl ether **[147380-69-6]**

Identified by Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968) (MS data).

Furans with an aldehyde function



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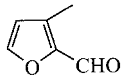

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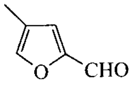

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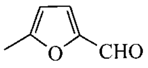

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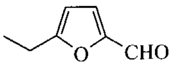

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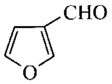

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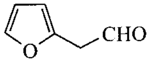

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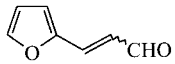

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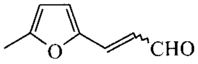

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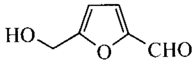


(I·72)

(I.63) ***(I.63)*** **2-Furancarboxaldehyde,** *2-furaldehyde, furan-2-carbaldehyde*, furfural, furfurol, furanal, 2-formylfuran, pyromucic aldehyde **[98-01-1]** ***FEMA 2489***

Identified by Jaeckle (1898). Its presence was also reported by Reichstein and Staudinger (1926b). Prescott *et al.* (1937a,b) identified it as its dimethyl dihydroresorcinol condensation product and observed that it promptly underwent decomposition with the formation of tarry materials. The presence of 2-furaldehyde has also been confirmed by Johnston and Frey (1938) by determining the melting point of the phenylhydrazone. Hughes and Smith (1949) have shown that the coffee content was high (ca 85 ppm) in the early stages of roasting, and then fell rapidly as the extent of roasting increased. They did not observe appreciable losses during storage, despite the volatility and chemical instability of the compound. Shibamoto *et al.* (1982) also noted a drastic fall in the concentration of 2-furaldehyde with increasing roasting intensity from 19.9% (high performance LC) after 25 min at 230 °C (weak) to 2% after 30 min (strong). Silwar and Lüllmann (1993b) underlined the decomposition of furfural, which is fully formed after 5 min at 230 °C, but decomposes at a higher temperature. Guyot *et al.* (1988a), roasting green coffee of different degrees of maturity (cherries collected from green to red, at various periods), observed an increase in the formation of furfural with the increase of maturity (see **C.12** and **D.44**). In the headspace of a brew, this aldehyde represented 1.3% (GC) for Shimoda and Shibamoto (1990a). The concentration in roasted coffee was estimated at 60 ppm by Stofberg and Stoffelsma (1981), 55–80 ppm by Silwar *et al.* (1987), 22.5 ppm by Ho *et al.* (1993) (see under **I.10**). It was identified by Vitzthum *et al.* (1976) in green beans volatiles. Procida *et al.* (1997) found furfural in headspaces of 11 out of the 12 green coffees (six arabicas and six robustas) examined, the proportion in the volatiles being 0.04–0.5% but reaching 3.3% in an Angola robusta; the concentration reached a maximum after roasting for 21 min at 218 °C for a Guatemala arabica. Ramos *et al.* (1998) extracted it from a brewed arabica (see under **I.52**) but the proportion in the volatiles was more important in the extraction with supercritical CO_2 (23%).

It results from the oxidation of furfuryl alcohol and is also formed by the decomposition of pentosans, for instance by dehydration of the furanose form of arabinose (Smith, 1963a), and is a feature of lightly roasted coffee to which it imparts a flavor like that of roasted cereals. It is formed by thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969). It has been identified in the products of thermal degradation of cysteine and xylose in tributyrin (Ledl and Severin, 1973) and in a heated cysteine/glucose model system (Sheldon *et al.*, 1986). Mottram (1991) has shown that it is formed from the Amadori compound of a pentose and an intermediate 3-deoxyosone.

Furfural has been described as pungent, but sweet, bread-like, caramellic, cinnamon-almond-like odor of poor tenacity (Arctander, 1967). Its flavor is sweet bread-like, caramellic in proper dilution and bitter (Fors, 1983). The odor threshold, determined by Buttery *et al.* (1969b), is 3 ppm in water and the flavor threshold determined by Brulé *et al.* (1971) is 5 ppm in water.

(I.64) 2-Furancarboxaldehyde, 3-methyl-, *3-methylfuran-2-carbaldehyde, 3-methyl-2-furaldehyde,* 3-methyl-2-furfural **[33342-48-2]**

Identified by Baltes and Bochmann (1987e) (MS data), and the same year by Silwar *et al.* (1987) who gave a concentration of 70–90 ppm.

It is formed in the thermal degradation of glucose (Fagerson, 1969) and also in reactions of serine and threonine with sucrose (Baltes and Bochmann, 1987a).

(I.65) 2-Furancarboxaldehyde, 4-methyl-, *4-methylfuran-2-carbaldehyde, 4-methyl-2-furaldehyde,* 4-methyl-2-furfural **[33342-49-3]**

Identified by Baltes and Bochmann (1987e) (MS data).

These authors (1987a) characterized it when heating serine and threonine with sucrose.

(I.66) *(I.66)* **2-Furancarboxaldehyde, 5-methyl-,** *5-methylfuran-2-carbaldehyde, 5-methyl-2-furaldehyde,* 5-methylfurfurol **[620-02-0]** ***FEMA 2702***

Identified by Reichstein and Staudinger (1926b), Viani *et al.* (1965) ('méthyl-5-furanne-2-carbonal'), Stoffelsma *et al.* (1968), Cros *et al.* (1980), and Baltes and Bochmann (1987a) (MS data). As for 2-furaldehyde, Shibamoto *et al.* (1982) noted an important decrease with increasing roasting time: 9.3% of the volatiles (high performance LC) after 25 min at 230 °C (weak), 9% after 27 min (normal) and 2.3% after 30 min (strong). The decrease with strong roasting was also noted by Silwar and Lüllmann (1993b). Similarly to 2-furaldehyde (**I.63**) and 5-hydroxymethyl-2-furaldehyde (**I.72**), the concentration of 5-methyl-2-furaldehyde after 5 min roasting increases until 230 °C then decreases quickly. For Shimoda and Shibamoto (1990a) it represented 0.69% (GC) of the volatiles of a brew. The concentration in roasted coffee is estimated at 39 ppm by Stofberg and Stoffelsma (1981), 50–70 ppm by Silwar *et al.* (1987), and 26.6 ppm by Ho *et al.* (1993). It has been identified by Vitzthum *et al.* (1976) in volatiles of green beans and by Procida *et al.* (1997) in volatiles of 12 green coffees examined (six arabicas, six robustas) and of a roasted Guatemala arabica. It has also been extracted from a brewed arabica (Ramos *et al.*, 1998) by several methods (see under **I.52**).

It is formed in the thermal degradation of glucose (Heyns *et al.*, 1966a, Fagerson, 1969). Mottram (1991) has shown that it is formed from the Amadori compound of a hexose and an intermediate 3-deoxyosone. Baltes and Bochmann (1987a) identified it in model reactions of serine/threonine/sucrose (as well as in coffee).

The odor is described as sweet-spicy, warm, and slightly caramellic (Arctander, 1967). The flavor threshold in beer is 20 ppm (Meilgaard, 1975).

A **dimethylfurfural** has been identified by Baltes and Bochmann (1987a,e) in coffee and in their model reactions.

(I.67) 2-Furancarboxaldehyde, 5-ethyl-, *5-ethylfuran-2-carbaldehyde, 5-ethylfuraldehyde* **[23074-10-4]**

Identified by Baltes and Bochmann. (1987a) (MS data) in coffee and in their model reactions (see **I.66**).

(I.68) 3-Furancarboxaldehyde, *furan-3-carbaldehyde, 3-furaldehyde*, 3-formylfuran **[498-60-2]**

Identified by Ho *et al.* (1993) in a roasted Columbian coffee (see **1.10**) with a concentration of 33.50 ppm, even higher than that of the 2-isomer (**I.63**) and only surpassed by furfuryl alcohol (**I.52**).

It has been found in the pyrolysis of D-glucose (Heyns *et al.*, 1966a).

(I.69) 2-Furanacetaldehyde, *furan-2-acetaldehyde, 2-(2-furyl)acetaldehyde* **[15022-16-9]**

Identified by Silwar (1982); Silwar *et al.* (1987) gave a concentration of 0.25–0.40 ppm.

The odor is rather sharp, but warm, green-spicy, pungent (Arctander, 1967).

2-Furanpropanal, *3-(2-furyl)propanal* **[4543-51-5]**

Identified only tentatively by Stoffelsma *et al.* (1968).

(I.70) 2-Propenal, 3-(2-furanyl)-, *3-(2-furyl)prop-2-enal*, furylacrolein, 1-(2-furanyl)-1-propen-3-al, 2-(β-propenal)furan **[623-30-3]** ***FEMA 2494;*** **(*E*)- [39511-08-5]; (*Z*)- [71277-14-0]**

Identified by Merritt and Robertson (1966) and also tentatively by Stoffelsma *et al.* (1968).

It was found by Baltes and Bochmann (1987a) in model reactions of serine and threonine with sucrose (MS data).

The odor is warm, sweet, woody-cinnamon-like, remotely reminiscent of coffee (Arctander, 1967).

(I.71) 3-Propenal, 3-(5-methyl-2-furanyl)-, *3-(5-methyl-2-furyl)prop-2-enal,* 1-(5-methyl-2-furanyl)-1-propen-3-al **[5555-90-8]**

Identified by Baltes and Bochmann (1987a,e) (MS data).

The same authors found it in model reactions of serine and threonine with sucrose.

(I.72) 2-Furancarboxaldehyde, 5-(hydroxymethyl)-, *5-(hydroxymethyl)-2-furaldehyde, 5-(hydroxymethyl)furan-2-carbaldehyde,* hydroxymethylfurfural (HMF) **[67-47-0]**

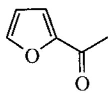
Identified by Högl (1958), by Vitzthum and Werkhoff (1976b) (see **I.15**), and by Baltes and Bochmann (1987a). Ramos *et al.* (1998) found it in a brewed arabica only after liquid–liquid extraction with pentane (other methods, see in **I.52**).

It is formed in the dehydration of levulose (furanose form) (Smith, 1963a), and in the heating of serine and threonine with sucrose (Baltes and Bochmann, 1987a). A mechanism of formation from a sugar with an amino acid was proposed by Feather and Huang (1986). The formation of hydroxymethylfurfural parallels the degradation of sucrose during coffee roasting (see also **I.63** and **I.66**): it started at 170 °C, and reached a maximum at ca 230 °C. There was rapid decomposition at over-roasting temperature (Silwar and Lüllmann, 1993b).

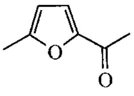
Hydroxymethylfurfural was studied (with maltol **I.146**) for antioxidative activity. It inhibits the formation of C_5 and C_6 acids from the corresponding aldehydes, showing for this system an activity comparable to those of 2,6-di-*tert*-butyl-4-methylphenol and α-tocopherol (Singhara *et al.*, 1998).

The odor is warm-herbaceous, winey-ethereal, remotely resembling that of Hungarian chamomile (matricaria oil). The flavor is sweet, herbaceous, hay-like, mildly tobacco-like (Arctander, 1967). The flavor threshold is 100 ppm in water as determined by Brulé *et al.* (1971) who found that it gave a mouldy, bitter taste depending on the concentration.

Furans with ketone(s) function (on a chain)



(I.73)
(I.73)



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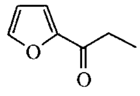

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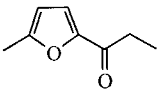

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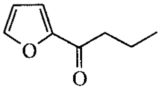

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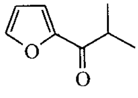


(I.78)

(I.73) *(I.73)* **Ethanone, 1-(2-furanyl)-,** *1-(2-furyl)ethan-1-one, 2-furyl methyl ketone,* 2-acetylfuran **[1192-62-7]** *FEMA 3163*

Identified by Reichstein and Staudinger (1926b). The product was also found by Gianturco *et al.* (1964b) in an 'aroma complex' (method in Gianturco *et al.*, 1963), by Viani *et al.* (1965), Stoffelsma *et al.* (1968), Vitzthum and Werkhoff (1976b) (see **I.15**), Cros *et al.* (1980) (headspace), and Baltes and

Bochmann (1987a). Its concentration in roasted coffee was estimated at 10 ppm by Stofberg and Stoffelsma (1981), 6–12 ppm by Silwar *et al.* (1987). It was identified by Vitzthum *et al.* (1976) in green beans volatiles. It represented 0.20% (GC) of the volatiles of a brew (Shimoda and Shibamoto, 1990a) and was extracted from a brewed arabica by Ramos *et al.* (1998) (but not with supercritical CO_2, see in **I.52**).

2-Acetylfuran was prepared by Reichstein (1930b) by acetylation of furan with acetyl chloride.

It is formed in the thermal degradation of glucose (Heyns *et al.*, 1966a; Fagerson, 1969). It has been found in a heated proline/glucose system by Brulé *et al.* (1971), in a cysteine/glucose model system by Sheldon *et al.* (1986), and in threonine/serine/sucrose models by Baltes and Bochmann (1987a).

2-Furylethanone has a powerful balsamic-sweet odor with a tobacco-like, almost narcotic pungency and floral undertones of balsamic-cinnamic character (Arctander, 1967). At 70 ppm in a syrup base, it has a slight caramel-like taste (Winter *et al.*, 1976e), at 15 ppm it has a sweet, grape flavor (Chemisis, 1998). The flavor threshold in water is 80 ppm and like I.72 it gives a moldy, bitter taste depending on the concentration according to Brulé *et al.* (1971).

(I.74) Ethanone, 1-(5-methyl-2-furanyl)-, *1-(5-methyl-2-furyl)ethan-1-one, 5-methyl-2-furyl methyl ketone*, 2-acetyl-5-methylfuran **[1193-79-9]** ***FEMA 3609***

Identified by Gianturco *et al.* (1964b) in an 'aroma complex' (see **I.73**), Stoffelsma *et al.* (1968), Vitzthum and Werkhoff (1976e), and Baltes and Bochmann (1987a). Silwar *et al.* (1987) gave a concentration of 0.5–1 ppm.

It is formed in the thermal degradation of glucose (Fagerson, 1969), in serine/threonine/sucrose models (Baltes and Bochmann, 1987a).

The compound was prepared by Reichstein (1930b) by acetylation of 2-methylfuran (**I.2**) with acetyl chloride.

For Sakaguchi and Shibamoto (1978b), the odor is caramel-like. At a concentration of 40 ppm in a syrup base, it has a light burnt taste (Winter *et al.*, 1976e), at 20 ppm a sweet, nutty, weak flavor (Chemisis, 1998).

(I.75) 1-Propanone, 1-(2-furanyl)-, *1-(2-furyl)propan-1-one, ethyl 2-furyl ketone,* 2-propanoylfuran, 2-propionylfuran **[3194-15-8]**

Identified by Stoll *et al.* (1967), it was also found by Stoffelsma *et al.* (1968), Vitzthum and Werkhoff (1976b), and by Andrade-Aispuro and Crouzet (1983) in the gases recovered during roasting. Silwar *et al.* (1987) gave a concentration of 1.10–1.50 ppm.

Baltes and Bochmann (1987a) found this ketone in model reactions of serine and threonine with sucrose (as well as in coffee).

According to Winter *et al.* (1976e), at a concentration of 40 ppm in a syrup base, it has a slight fruity taste. Sakaguchi and Shibamoto (1978b) characterized it as having a sweet and caramellic odor.

(I.76) 1-Propanone, 1-(5-methyl-2-furanyl)-, *1-(5-methyl-2-furyl)propan-1-one, ethyl 5-methyl-2-furyl ketone,* 2-methyl-5-propanoylfuran, 2-propionyl-5-methylfuran **[10599-69-6]**

Identified by Stoll *et al.* (1967), it was also found by Stoffelsma *et al.* (1968), and Silwar (1982). Silwar *et al.* (1987) gave a concentration of 0.15–0.25 ppm.

Baltes and Bochmann (1987a) identify this ketone in model reactions of serine and threonine with sucrose, as well as in coffee.

At a concentration of 10 ppm in a syrup base, it has a green, hazelnut-like taste (Winter *et al.*, 1976e).

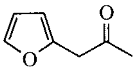
(I.77) 1-Butanone, 1-(2-furanyl)-, *1-(2-furyl)butan-1-one, 2-furyl propyl ketone,* 2-butanoylfuran, 2-n-butyrylfuran **[4208-57-5]**

Identified by Stoll *et al.* (1967), and by Stoffelsma *et al.* (1968). Silwar *et al.* (1987) found a concentration of 0.05–0.10 ppm.

According to Winter *et al.* (1976e), at a concentration of 40 ppm in a syrup base, it has a fruity taste.

(I.78) 1-Propanone, 1-(2-furanyl)-2-methyl-, *1-(2-furyl)-2-methylpropan-1-one, 2-furyl isopropyl ketone,* 2-isobutyrylfuran **[4208-53-1]**

Identified by Stoffelsma *et al.* (1968).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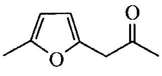
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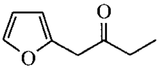
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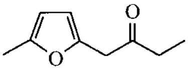
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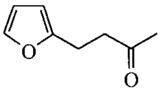
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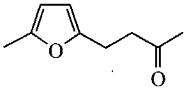
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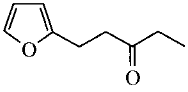
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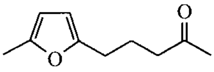
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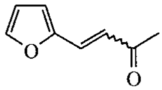
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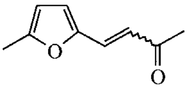

(I·88)

(I.79) 2-Propanone, 1-(2-furanyl)-, *1-(2-furyl)propan-2-one, furfuryl methyl ketone,* 2-furylacetone, 2-acetonylfuran **[6975-60-6]** ***FEMA 2496***

Identified by Stoll *et al.* (1967), and by Stoffelsma *et al.* (1968). Silwar *et al.* (1987) found a concentration of 2.5–4.0 ppm and Shimoda and Shibamoto (1990a) 0.06% (GC) in the volatiles of a brew.

Baltes and Bochmann (1987a) found this ketone in model reactions when heating serine and threonine with sucrose, as well as in coffee.

2-Furylacetone has been described as having a mild, sweet, fruity-caramellic, somewhat spicy odor (Arctander, 1967) and a sweet, fruity-spicy, slightly nut-like flavor suggesting radish (Fors, 1983). According to Winter *et al.* (1976e), at a concentration of 20 ppm in a syrup base, it has a green, burnt taste; an astringent, peachpit, almond-note being perceived when tasted, at 40 ppm, in a neutral soluble coffee base.

(I.80) 2-Propanone, 1-(5-methyl-2-furanyl)-, *1-(5-methyl-2-furyl)propan-2-one, methyl 5-methylfurfuryl ketone,* 2-acetonyl-5-methylfuran **[13678-74-5]**

Identified by Stoll *et al.* (1967), it was also found by Baltes and Bochmann (1987a) (MS data). Silwar *et al.* (1987) gave a concentration of 0.6–1.1 ppm.

Baltes and Bochmann (1987a) found this ketone in model reactions of serine and threonine with sucrose.

Stoll *et al.* (1967) prepared this ketone by condensation of 5-methyl-2-furaldehyde **(I.66)** with nitroethane followed by acid hydrolysis of the resulting oxime.

(I.81) 2-Butanone-1-(2-furanyl)-, *1-(2-furyl)butan-2-one, ethyl furfuryl ketone* **[4208-63-3]**

Identified and synthesized by Stoll *et al.* (1967). Silwar *et al.* (1987) gave a concentration of 0.10–0.20 ppm.

Baltes and Bochmann (1987a) characterized the ketone in serine/threonine/sucrose systems (as well as in coffee).

According to Winter *et al.* (1976e), at a concentration of 60 ppm in a syrup base, it has a slight rum-like taste.

(I.82) 2-Butanone, 1-(5-methyl-2-furanyl)-, *1-(5-methyl-2-furyl)butan-2-one* **[13678-70-1]**

Identified by Stoll *et al.* (1967). Silwar *et al.* (1987) found a concentration of 0.25–0.35 ppm.

The ketone is identified in model reactions involving serine, threonine and sucrose (and in coffee) by Baltes and Bochmann (1987a).

The preparation by Stoll *et al.* is similar to that of **I.80** but with 1-nitropropane.

According to Winter *et al.* (1976e), at a concentration of 30 ppm in a syrup base, it has a green taste.

(I.83) 2-Butanone, 4-(2-furanyl)-, *4-(2-furyl)butan-2-one,* 1-(2-furyl)-3-butanone **[699-17-2]**

Identified by Stoll *et al* (1967), and by Stoffelsma *et al.* (1968). Silwar *et al.* (1987) gave a concentration of 0.10–0.15 ppm.

Baltes and Bochmann (1987a) found it when heating serine and threonine with sucrose (and in coffee).

According to Winter *et al.* (1976e), at a concentration of 50 ppm in a syrup base, it has a weak furanic note; a fruity, banana flavor note being perceived when tasted in a neutral, soluble coffee base at a concentration of 6 ppm.

(I.84) 2-Butanone, 4-(5-methyl-2-furanyl)-, *4-(5-methyl-2-furyl)butan-2-one* **[13679-56-6]**

Identified by Stoll *et al.* (1967), and by Stoffelsma *et al.* (1968). Silwar *et al.* (1987) found a concentration of 0.25–0.30 ppm.

Baltes and Bochmann (1987a) identified it in their model reactions (above) as well as in coffee.

According to Winter *et al.* (1976e), at a concentration of 50 ppm in a syrup base, it has a weak furanic note; a bitter, roasted, acid and flowery note being perceived when tasted in a neutral, soluble coffee base at a concentration of 10 ppm.

(I.85) 3-Pentanone, 1-(2-furanyl)-, *1-(2-furyl)pentan-3-one* **[69978-21-8]**

(I.86) 2-Pentanone, 5-(5-methyl-2-furanyl)-, *5-(5-methyl-2-furyl)pentan-2-one,* 1-(5-methyl-2-furyl)-4-pentanone **[106060-94-0]**

These were identified by Baltes and Bochmann (1987e) (MS data) who did not find them in the serine/threonine/sucrose systems (1987a).

(I.87) 3-Buten-2-one, 4-(2-furanyl)-, *4-(2-furyl)but-3-en-2-one,* furfural acetone, furfurylidene acetone, 1-(2-furyl)-1-buten-3-one **[623-15-4]** ***FEMA 2495;*** **(*E*)- [41438-24-8]; (*Z*)- [108811-61-6]**

Identified by Stoffelsma *et al.* (1968) and Stoffelsma and Pypker (1968), probably as the (*E*)-isomer. Baltes and Bochmann (1987a) specified the presence of the (*E*)-isomer. On the other hand, Elmore and Nursten (1990) identified the (*Z*)-isomer in headspace of ground coffee.

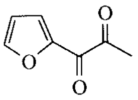
Baltes and Bochmann found the two isomers (MS data) in model reactions (see **I.86**) but did not find the (*Z*)-isomer in coffee.

The odor is mild, warm, spicy-woody, sweet, somewhat reminiscent of cinnamon (Arctander, 1967). At 7.5 ppm the flavor is described as ethereal, solvent, caramel, green (Chemisis, 1999).

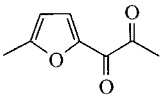
(I.88) 3-Buten-2-one, 4-(5-methyl-2-furanyl)-, *4-(5-methyl-2-furyl)but-3-en-2-one*, 1-(5-methyl-2-furanyl)-1-buten-3-one [23120-57-2]; (*E*)- [66434-99-9]

Identified by Baltes and Bochmann (1987e) (MS data), the stereochemistry not being specified.

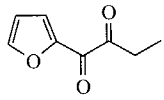
The same authors (1987a) found this compound in their model reactions (see **I.86**).



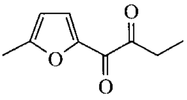
(I.89)



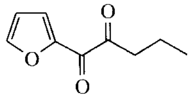
(I.90)



(I.91)



(I.92)



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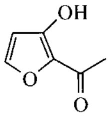
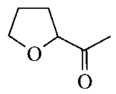


(I.94)



(I.95)

(I.89) 1,2-Propanedione, 1-(2-furanyl)-, *1-(2-furyl)propane-1,2-dione* [1438-92-2]

Identified by Gianturco *et al.* (1964b) (IR data), Stoll *et al.* (1967), and Stoffelsma *et al.* (1968). Silwar *et al.* (1987) gave a concentration of 0.10–0.15 ppm.

It is formed in the thermal degradation of glucose (Fagerson, 1969). It was also identified (as well as in coffee) by Baltes and Bochmann (1987a) in model systems (see **I.86**).

This diketone was obtained by selenium dioxide oxidation of 1-(2-furyl)-2-propanone (**I.79**) (17% yield) or of 1-(2-furyl)-1-propanone (**I.75**) (4% yield) (Cosgrove *et al.*, 1952). It was prepared by Gianturco *et al.* (1964b), in 60% overall yield, by acid-catalyzed hydrolysis (or by transoximation) of 1-(2-furyl)-2-oximino-1-propanone, obtained in turn by nitrosation of 1-(2-furyl)-1-propanone. The same method was used by Stoll *et al.* (1967) as well as the oxidation of the keto alcohol obtained by a Grignard reaction on the cyanhydrin of 2-furaldehyde.

The flavor is weak, burnt (Chemisis, 1963).

(I.90) 1,2-Propanedione, 1-(5-methyl-2-furanyl)-, *1-(5-methyl-2-furyl)propane-1,2-dione*, 2-(1,2-dioxopropyl)-5-methylfuran [1197-20-2]

Identified by Gianturco *et al.* (1964b), by Stoll *et al.* (1967), and by Stoffelsma *et al.* (1968). The concentration given by Silwar *et al.* (1987) was 0.25–0.30 ppm.

Baltes and Bochmann (1987a) found this diketone in their model systems (see **I.86**), as well as in coffee.

The syntheses are analogous to those of **I.89**. Stoll *et al.* (1967) also obtained it by oxidation of the keto alcohol formed by a Grignard reaction on 5-methyl-2-furaldehyde (**I.66**).

It has a caramel odor and a flavor threshold of 2 ppm in water according to Brulé *et al.* (1971).

Another **1-(methyl-2-furyl)-1,2-propanedione** (3 or 4-methyl) was found in coffee by Baltes and Bochmann (1987a).

(I.91) 1,2-Butanedione, 1-(2-furanyl)-, *1-(2-furyl)butane-1,2-dione* **[1438-90-0]**

Identified by Gianturco *et al.* (1964b), Stoll *et al.* (1967), and Stoffelsma *et al.* (1968). Silwar *et al.*(1987) found 0.10–0.15 ppm.

Stoll *et al.* (1967) obtained it as described for the homolog **I.89** and by the oxidation of the keto alcohol prepared by a Grignard reaction on 2-furaldehyde.

The flavor is weak, chemical (Chemisis, 1964).

(I.92) 1,2-Butanedione, 1-(5-methyl-2-furanyl)-, *1-(5-methyl-2-furyl)butane-1,2-dione* **[13678-76-7]**

Identified by Stoll *et al.* (1967). The concentration given by Silwar *et al.* (1987) was 0.05–0.10 ppm.

This compound was found in coffee and in serine/threonine/sucrose systems (but not **I.91**) by Baltes and Bochmann (1987a).

It was prepared (Stoll *et al.*,1967) either by oxidation of the corresponding monoketone with selenium dioxide, by its nitrosation followed by acid hydrolysis, or by a Grignard reaction with the cyanhydrin of 5-methylfurfural (**I.66**). The yellow crystals obtained had an agreeable fruity, buttery odor.

(I.93) 1,2-Pentanedione, 1-(2-furanyl)-, *1-(2-furyl)pentane-1,2-dione* **[20894-91-1]**

Identified by Silwar (1982) and Silwar *et al.* (1987) who found a concentration of 0.05–0.10 ppm.

The synthesis can be achieved by oxidation with selenium dioxide of the corresponding 1-(2-furyl)-1-pentanone (to our knowledge not yet identified in coffee).

(I.94) Ethanone, 1-(3-hydroxy-2-furanyl)-, *1-(3-hydroxy-2-furyl)ethan-1-one, 3-hydroxy-2-furyl methyl ketone,* 2-acetyl-3-hydroxyfuran, isomaltol **[3420-59-5]**

Identified by Tressl *et al.* (1978a) who found 8 ppm in roasted arabica, 1.5 in robusta and 2 in arabusta.

The formation of isomaltol and its synthesis from lactose by action of piperidine acetate have been described by Hodge *et al.* (1963). The formation from Amadori intermediates was described by Vernin (1981).

The odor is caramellic-sweet, but rather pungent, of good tenacity. It is described as having a sweet, fruity, cooked and maple flavor (Chemisis, 1964). The flavor is first sour, then sweet, caramellic-fruity, bread-like, depending on the concentration used. A sour taste is mostly noticed at high concentration (Arctander, 1967).

(I.95) Ethanone, 1-(tetrahydro-2-furanyl)-, *1-(tetrahydro-2-furyl)ethan-1-one,* 2-acetyltetrahydrofuran **[25252-64-6]**

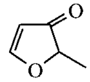
Identified by Friedel *et al.* (1971) in an 'aroma complex' of coffee (method in Gianturco *et al.*, 1963).

The structure has been confirmed by synthesis (IR and MS data).

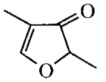
3-Furanones

(I.96) 3(2*H*)-Furanone, 2-methyl-, *2,3-dihydro-2-methylfuran-3-one* **[41763-99-9]**

Identified by Silwar *et al.* (1987) who found a concentration of 1.20–1.80 ppm (steam distillation, then simultaneous distillation–extraction), by Ho *et al.* (1993) who gave a concentration of 9.7 ppm (see **I.10**). Ramos *et al.* (1998) extracted it from a brewed arabica only with supercritical CO_2 (see **I.52**).



(I·96)



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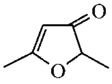

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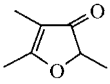

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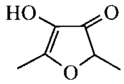

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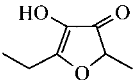
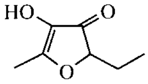
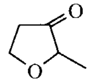


(I·101a)



(I·101b)



(I·102)
(I-102)

Baltes and Bochmann (1987a) proposed this structure for a furanone, not identified in coffee, but present in model reactions, heating serine and threonine with sucrose (MS data).

(I.97) 3(2*H*)-Furanone, 2,4-dimethyl-, *2,3-dihydro-2,4-dimethylfuran-3-one* **[37713-48-7]**

Identified by Silwar *et al.* (1987) who gave a concentration of 0.50–0.60 ppm.(It has to be noted that, in this publication, only the 2,4-dimethyl isomer is mentioned, although Silwar (1982) only mentioned the 2,5-dimethyl-isomer **I.98**, see below).

(I.98) 3(2*H*)-Furanone, 2,5-dimethyl-, *2,3-dihydro-2,5-dimethylfuran-3-one* **[14400-67-0]**

Identified by Friedel *et al.* (1971), by Silwar (1982) and by Baltes and Bochmann (1987a) (MS data).

This structure was proposed by Baltes and Bochmann for a compound present in coffee and in serine/threonine/sucrose systems.

Its formation has been described by Ledl (1990).

The racemic compound has a green, cheesy, ketonic, weak flavor (Chemisis, 1996).

(I.99) 3(2*H*)-Furanone, 2,4,5-trimethyl-, *2,3-dihydro-2,4,5-trimethylfuran-3-one*, 2,4,5-trimethyl-2*H*-furan-3-one **[64880-73-5]**

Identified by Bondarovich *et al.* (1967).

The flavor is described as burnt, weak at 5 ppm, nutty, musty, caramel, fruity, etc., but weak, at 30 ppm (Chemisis, 1999).

(I.100) 3(2*H*)-Furanone, 4-hydroxy-2,5-dimethyl-, *2,3-dihydro-4-hydroxy-2,5-dimethylfuran-3-one*, Furaneol®, furonol, (HDF or HDMF) **[3658-77-3]** ***FEMA 3174*; (*R*)- [131222-82-7]; (*S*)- [131222-81-6]**

Identified by Tressl *et al.* (1978a) who estimated its content at 50 ppm in roasted arabica, 25 in robusta and 35 in arabusta. Semmelroch *et al.* (1995) found concentrations of 109 ppm in arabica and 57 in robusta using stable isotope dilution assays. Silwar and Lüllmann (1993b) noted that after 5 min of roasting, the concentration was higher at 230 °C than at 170 or 260 °C (ca 35 ppm).

Its formation from rhamnose heated with piperidine acetate in ethanol, under the same conditions that produced amino-hexose-reductones from glucose and other hexoses, was described as early as 1963 by Hodge *et al.*, who confirmed the structure by IR and NMR data and proposed a formation pathway. The formation from Amadori intermediates was been reviewed by Vernin (1981). Numerous model systems have confirmed that it is one of the main Maillard-reaction products. For instance we will mention the formation from L-rhamnose and ethylamine (Kato *et al.*, 1972) and from pentose/glycine or alanine, whose mechanism was proposed by Blank and Fay (1996) and Blank *et al.* (1998), from the intermediate Amadori compound, *N*-(1-deoxy-D-pentos-1-yl)glycine. Furaneol is also formed by recombination of sugar degradation products, as demonstrated by Blank *et al.* (1996) using reactions of xylose with labeled amino acids.

Several syntheses have been proposed with 2,5-dihydroxy-3,4-hexanedione as intermediate (Büchi *et al.*, 1973; Re *et al.*, 1973). A conversion of deoxyhexoses, obtained chemically or enzymically from dihydroxyacetone and lactaldehyde, to Furaneol® by action of piperidine/acetic acid has also been published (Wong *et al.*, 1983).

It has an intensively caramellic-fruity and jam-like odor reminiscent of that of cooked pineapple with some resemblance to the odor of 'maltol' (Arctander, 1967). Buttery *et al.* (1969a) gave an odor threshold of 0.1 ppm in water but Ohloff (1978b) reported a value of 0.04 ppb and Semmelroch and Grosch (1996) of 10 ppm. The latter authors found Furaneol® to be the major compound extracted from brewed arabicas and robustas and estimated that it participates (together with the homolog **I.101a,b**) in the sweetish-caramel quality that is more intense in arabica than in robusta brews. Another value of 60 ppb for the odor threshold was given by Buttery (1999) who concluded that this relatively high threshold was compensated for by a rather high concentration (in foods). Brulé *et al.* (1971) found a flavor threshold of 1 ppm in water and Huber (1992) quoted a value of 160 ppb.

Bruche *et al.* (1995) achieved an enantioselective separation and found, by sniffing at the port of a chromatograph, that the (−)-isomer had the intensive caramel-note, sweet. The odor of the (+)-isomer is reminiscent of the (−)-, but faint, sweet, roasty.

(I.101a) (I.101b) 3(2*H*)-Furanone, 2 (or 5)-ethyl-4-hydroxy-5 (or 2)-methyl-, *2 (or 5)-ethyl-2,3-dihydro-5 (or 2)-methylfuran-3-one*, homofuraneol, homofuronol, (HEMF), ethylfuraneol (a rather confusing name!) **[110516-60-4]; (a): 2-ethyl-5-methyl- [27538-10-9]; (*R*)- [131222-80-5]; (*S*)- [131222-79-2]; (b): 5-ethyl-2-methyl- [27538-09-6]** ***FEMA 3623;*** **(*R*)- [131222-78-1]; (*S*)- [131222-77-0]**

Identified by Tressl *et al.* (1978a) as ethylfuraneol (a rather misleading name) with concentrations of 8 ppm in a roasted arabica, 2 in a robusta and 4 in an arabusta. Semmelroch *et al.* (1995) identified it as the 5-ethyl-2-methyl compound (**I.101**), with a concentration of 17.3 ppm in a roasted arabica and 14.3 ppm in a robusta (stable isotope dilution assay); it was later noted under the tautomeric forms, 2(5)-ethyl-5(2)-methyl (**I.101a,b**), by Grosch (1998b). Until 1991, it was said to exist only in soy sauce (shoyu) by Sasaki *et al.* (1991), the error perhaps arising from the trivial name 'ethylfuraneol'.

The tautomeric forms exist in a ratio of 3:1 to 2:1; the pure, more abundant, tautomer **I.101a** could be crystallized after storage for years in a freezer but it returns to equilibrium mixture by melting or dissolution (Huber, 1992).

Using labeled precursors, Blank *et al.* (1996) explained the formation of homofuraneol in reactions of xylose with alanine (preferentially to glycine). The proposed mechanism suggested the incorporation of the Strecker degradation product, acetaldehyde. This mode of formation is preferred to sugar fragmentation.

Syntheses similar to those of **I.100** have been carried out: by ozonization of 3-heptyne-2,5-diol without isolation of the intermediate (Re *et al.*, 1973), by conversion of deoxyheptoses, obtained chemically or enzymacally from dihydroxyacetone and 2-hydroxybutanal (Wong *et al.*, 1983).

The flavor of the tautomer mixture is perceived as burnt sugar, maple, cereal, chicory (Chemisis, 1978). The odor threshold reported by Semmelroch *et al.* (1995) was 1.15 ppm in water with a caramel-like quality. The odor threshold in air given by Blank *et al.* (1992b) was 0.5–1.5 $\mu g/m^3$. A flavor threshold of 21 ppb was reported by Huber (1992). By their enantioselective separation (see in **I.100**), Bruche *et al.* (1995) determined that only one isomer of the less abundant tautomer **I.101b** had a very intensive 'roasted almonds' odor, the other isomer being less intensive; of the two other tautomers, one is odorless, and the other reminiscent of the odorant **I.101b**, is nearly odorless. Therefore ca 85 % of the mixture have no influence on the aroma.

3(2*H*)-Furanone, 4-ethoxy-2,5-dimethyl-, *4-ethoxy-2,3-dihydro-2,5-dimethylfuran-3-one* **[65330-49-6]**, which is *O*-ethylfuraneol, has been interpreted as ethylfuraneol with identification attributed to Tressl *et al.* (1978a) (TNO-CIVO).

(I.102) *(I.102)* **3(2*H*)-Furanone, dihydro-2-methyl-,** *tetrahydro-2-methylfuran-3-one,* 2-methyl-3-oxotetrahydrofuran **[3188-00-9]** *FEMA 3373*

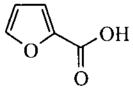
Identified by Gianturco *et al.* (1964a) who found approximately 0.3 ppm in a commercial blend of roasted coffee, by Viani *et al.* (1965) and Wang *et al.* (1983) (headspace). Silwar *et al.* (1987) gave a concentration of 10–16 ppm. Shimoda and Shibamoto (1990a) found 0.33% (GC) in the volatiles of a brew. It has been identified by Vitzthum *et al.* (1976) in the volatiles of green beans. Procida *et al.* (1997) found this compound only in a roasted Guatemala arabica but not in the green coffees examined (six arabicas, six robustas).

It was formed from the thermal degradation of glucose (Fagerson, 1969). Baltes and Bochmann (1987a) characterized this furanone when heating serine/threonine/sucrose systems (and in coffee).

The synthesis was achieved (Gianturco *et al.*, 1964a) by reaction of methyl acrylate with methyl lactate, followed by decarboxylative acid hydrolysis of the resulting β-ketoester. The product was characterized by the elemental analysis of its 2,4-dinitrophenylhydrazone and by the IR spectrum. The IR spectrum and the MS fragmentation of this substance have been discussed by Viani *et al.* (1965).

It has a sweet, roasted odor (Sakaguchi and Shibamoto, 1978b). At a concentration of 30 ppm it was perceived as having a caramel, sweet, creamy, fruity flavor (Chemisis, 1998).

Furoic acids and esters



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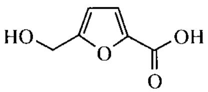
(I·103)



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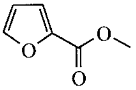

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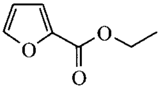

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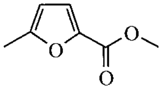


(I·107)

(I.103) *(I.103)* **2-Furancarboxylic acid,** *furan-2-carboxylic acid, 2-furoic acid,* furanoic acid, pyromucic acid, 'brenzschleimsaüre' **[88-14-2]**

Identified by Woodman *et al.* (1968) and later (as furancarboxylic acid, certainly in the 2-position) by Tressl *et al.* (1978a) who gave a concentration of 80 ppm in roasted arabica, 55 in robusta and only 50 in arabusta. According to Maier (1987, 1988), the content was 90–250 ppm in roasted coffee and can reach 310–390 ppm in commercial coffee extracts. Using 'free flow field step electrophoresis' Bähre and Maier (1999) identified a series of non-volatile acids (see Section 5.E), among them furoic acid, detectable in traces in an unsteamed Columbia arabica and with a content of 2 ppm in Kenya and Colombia steam-treated arabicas. This content increased to ca 110 ppm after roasting.

Furoic acid is formed in the thermal degradation of glucose (Fagerson, 1969). It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

This compound is practically odorless, with a clear acid, mildly caramellic flavor (Arctander, 1967), or earthy, weak flavor (Chemisis, 1991). A threshold of 37 ppm in water (0.33 mmol/L) was given by Engelhardt and Maier (1985b).

(I.104) *(I.104)* **2-Furancarboxylic acid, 5-hydroxymethyl-,** *5-hydroxymethyl-2-furoic acid,* 5-hydroxymethyl-2-furanoic acid **[6338-41-6]**

Identified by Bähre and Maier (1996, 1999) (see I.103). The content of 1–3 ppm in steam-treated arabicas (not detectable in the untreated qualities) increased to ca 40 ppm upon roasting.

(I.105) 2-Furancarboxylic acid, methyl ester, *methyl furan-2-carboxylate, methyl 2-furoate* **[611-13-2]** ***FEMA 2703***

Identified (see **I.15**) by Vitzthum and Werkhoff (1976b) (MS data), by Silwar (1982), by Baltes and Bochmann (1987a). Silwar *et al.* (1987) gave a concentration of 0.05–0.10 ppm.

Baltes and Bochmann found this ester in model reactions, heating serine and threonine with sucrose.

The odor is berry-like fruity, winey, rather heavy, of moderate to poor tenacity. Some observers found a nauseating or fungus-like tobacco odor (Arctander, 1967). The flavor is malt, fruity, cereal (Chemisis, 1992).

(I.106) 2-Furancarboxylic acid, ethyl ester, *ethyl furan-2-carboxylate, ethyl 2-furoate* **[614-99-3]**

Identified (see **I.15**) by Vitzthum and Werkhoff (1976b) (MS data), and by Baltes and Bochmann (1987a).

The latter authors also found this ester in model reactions (see **I.105**).

It is described as having a warm, fruity-floral odor, slightly more pungent than that of ethyl benzoate; moreover it has very pleasant over-ripe fruit or plum-raisin-like undertones. It is also characterized by a burnt, buttery, vanilla-like odor (Ohloff and Flament, 1978).

(I.107) 2-Furancarboxylic acid, 5-methyl-, methyl ester, *methyl 5-methylfuran-2-carboxylate, methyl 5-methyl-2-furoate* **[2527-96-0]**

Identified by Baltes and Bochmann (1987e) (MS data).

The same authors (1987a) also identified it in their model reactions (see I.104).

Furfuryl esters

(I.108) 2-Furanmethanol, formate, *furfuryl formate,* furfuryl alcohol formate **[13493-97-5]**

Identified by Gianturco *et al.* (1964b), Stoll *et al.* (1967), and Stoffelsma *et al.* (1968). Vitzthum and Werkhoff (1976b) found it in the neutral fraction of a steam distillate of roasted coffee. Silwar *et al.* (1987) gave a concentration of 0.10–0.15 ppm. For Shimoda and Shibamoto (1990a) furfuryl formate represented 0.06% (GC) of the volatiles of a brew. Procida *et al.* (1997) identified this ester only in a roasted arabica but in none of the green coffees they examined (six arabicas, six robustas). Ramos *et al.* (1998) found it after liquid–liquid extraction of a brewed arabica with pentane or methylene chloride.

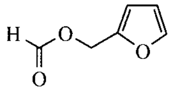
Baltes and Bochmann (1987a) identified furfuryl formate in model reactions (see **I.105**) as well as in coffee.

(I.109) *(I.109)* **2-Furanmethanol, acetate,** *furfuryl acetate,* furfuryl alcohol acetate **[623-17-6]** ***FEMA 2490***

Identified by Reichstein and Staudinger (1926b), Gianturco *et al.* (1964b), Viani *et al.* (1965) ('acétate de furanne-2-carbinyle'), Stoll *et al.* (1967), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b) (see I.108). Its concentration in roasted coffee was estimated at 5.4 ppm by Stofberg and Stoffelsma (1981), 3.50–5.50 ppm by Silwar *et al.* (1987) (see **I.96**), higher than for the formate. Shimoda and Shibamoto (1990a) also found a higher proportion than for the formate in headspace of a brew (0.92%, GC). Ho *et al.* (1993) found 9.7 ppm in a roasted Columbian arabica (see **I.10**). It has been identified by Vitzthum *et al.* (1976) in volatiles of green beans, by Procida *et al.* (1997) in headspaces of six green arabicas and six green robustas, also in the roasted Guatemala arabica that they studied. With various extraction methods (see under **I.52**), it was found by Ramos *et al.* (1998) in a brewed arabica.

Baltes and Bochmann (1987a) characterized this ester in coffee and in their model reactions (see **I.105**). The odor is mild, ethereal-floral, somewhat reminiscent of ethyl acetoacetate, benzyl acetate and the glycol acetates, with an herbal-spicy undertone (Arctander, 1967).

The following esters, **I.110** to **I.114**, were interpreted by Maga (1979) as furoates and not as the 2-furylmethyl (furfuryl) esters present in the two references quoted. Elsewhere in the review, the esters **I.108** to **I.110** and **I.112** were quoted correctly with another reference. In the same line, the thioester **I.139** was interpreted as a derivative of furoic acid instead of ethanethioic (thioacetic) acid.



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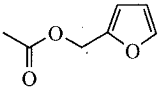

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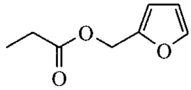

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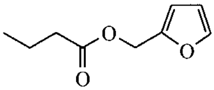

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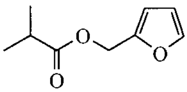

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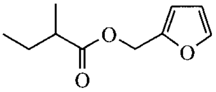

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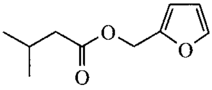

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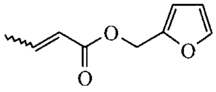

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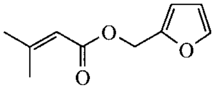


(I·116)

(I.110) 2-Furanmethanol, propanoate, *furfuryl propanoate, furfuryl propionate* **[623-19-8]** ***FEMA 3346***

Identified by Stoll *et al.* (1967) (MS data), Stoffelsma *et al.* (1968), Vitzthum and Werkhoff (1976b) (see I.108), and Silwar (1982). Silwar *et al.* (1987) found a concentration of 0.40–0.70 ppm. The ester represented 0.04% (GC) of the volatiles of a brew for Shimoda and Shibamoto (1990a).

Like the lower homologs **I.108** and **109**, this ester was identified by Baltes and Bochmann (1987a).

According to Winter *et al.* (1976e), at a concentration of 10 ppm in a syrup base, it has a pear-like taste; a bitter, nutty note being perceived when tasted, at 7 ppm, in a neutral soluble coffee base. The flavor is also described as fruity, green, pear, fresh-refreshing (Chemisis, 1998).

(I.111) Butanoic acid, 2-furanylmethyl ester, *furfuryl butanoate, furfuryl butyrate* **[623-21-2]**

Identified by Stoll *et al.* (1967) (MS data), and by Silwar (1982). Silwar *et al.* (1987) gave a concentration of 0.02–0.08 ppm.

The flavor is described as fruity, green, berry, tutti-frutti (Chemisis, 1992).

(I.112) Propanoic acid, 2-methyl-, 2-furanylmethyl ester, *furfuryl 2-methylpropanoate, furfuryl isobutyrate,* furfuryl isobutyric ester **[6270-55-9]**

Identified by Stoll *et al.* (1967) (MS data).

According to Winter *et al.* (1976e), at a concentration of 20 ppm in a syrup base, it has a fruity, quince-like taste.

(I.113) Butanoic acid, 2-methyl-, 2-furanylmethyl ester, *furfuryl 2-methylbutanoate*, furfuryl 2-methylbutyrate **[13678-61-0]**

Identified by Stoll *et al.* (1967) (MS and IR data), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b).

According to Winter *et al.* (1976e), at a concentration of 10 ppm in a syrup base, it has an agreeable fruity odor and taste.

(I.114) Butanoic acid, 3-methyl-, 2-furanylmethyl ester, *furfuryl 3-methylbutanoate*; furfuryl isovalerianate, furfuryl isovalerate **[13678-60-9]** ***FEMA 3283***

Identified by Reichstein and Staudinger (1926b), Stoll *et al.* (1967) (MS and IR data), and Silwar (1982). Silwar *et al.* (1987) estimated a concentration of 0.01–0.03 ppm.

According to Winter *et al.* (1976e), at a concentration of 20 ppm in a sugar syrup base, it has fruity odor and taste.

(I.115) 2-Butenoic acid, 2-furanylmethyl ester, *furfuryl but-2-enoate*, furfuryl crotonate **[59020-84-7];** (*E*)- **[13678-63-2]**

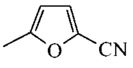
Identified by Stoll *et al.* (1967) (IR, MS data). Silwar *et al.* (1987) found a concentration of 0.10–0.20 ppm.

Stoll *et al.* described it as having an agreeable fruity odor. According to Winter *et al.* (1976e), it has a mushroom-like note at 20 ppm in a syrup base; an earthy note is also perceived when tasted at 0.7 ppm in a neutral soluble coffee base.

(I.116) 2-Butenoic acid, 3-methyl-, 2-furanylmethyl ester, *furfuryl 3-methylbut-2-enoate*, furfuryl β, β-dimethylacrylate, furfuryl senecioate **[13678-62-1]**

Identified by Stoll *et al.* (1967) (MS and IR data), and described with an agreeable fruity odor. According to Winter *et al.* (1976e), it has a mushroom-like taste at 20 ppm in a syrup base.

Nitrile and acetals



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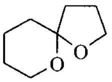

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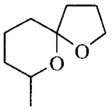


(I·119)

(I.117) 2-Furancarbonitrile, 5-methyl-, *5-methylfuran-2-carbonitrile, 5-methyl-2-furonitrile,* 2-cyano-5-methylfuran **[13714-86-8]**

Identified by Stoll *et al.* (1967) (MS data; quoted as 5-methyl-2-furfurylnitrile by Maga, 1979).

It has a nut-like, bitter almond-like odor according to Baltes (1979a), and a caramel, coumarinic, cherry, tobacco flavor (Chemisis, 1962).

(I.118) 1,6-Dioxaspiro[4.5]decane, *1,6-dioxaspiro[4.5]decane* **[177-23-1]**

(I.119) 1,6-Dioxaspiro[4.5]decane, 7-methyl-, *7-methyl-1,6-dioxaspiro[4.5]decane* **[73046-13-6]**; (±)-***cis*- [68108-89-4]**; ***trans*- [75354-36-8]**; (±)-***trans*- [68108-90-7]**; **5*R*, *cis*- [89576-31-8]**; **5*R*, *trans*- [77715-03-8]**

These were identified in a green Mexican arabica by Cantergiani *et al.* (2001) after vacuum hydrodistillation and extraction (**I.119** represented 0.71 % of the extract, GC polar).

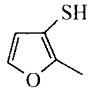
The authors reported that these spiroacetals had been found in insect pheromones.

Furanic sulfur compounds

Since Reichstein and Staudinger, we have been aware that furan compounds containing one or more sulfur atoms play an essential role in the aroma of roasted coffee. A review of the sulfur volatile constituents of coffee, showing the importance for coffee flavor of furans substituted on the 3-position by a sulfur atom, has been published by Flament and Chevallier (1988). As can be seen in the values given for the furfuryl sulfur compounds, the concentrations are higher in robustas than in arabicas when there is no methyl substituent on the ring. When there is a 5-methyl the concentrations are lower overall but higher in the arabicas than in the robustas (compare for example **I.128** and **I.129**).

Remark. In the publication by Tressl (1989), figures 7, 8 and 10, concerning sulfur compounds in coffee, are mentioned with units in ppm. The units are very probably ppb, the sulfur-containing compounds being announced in the text as amounting to 5–15 ppm depending on the variety, roasting and storing. Comparisons with other publications confirm this assertion. The remark is valid for sections 5.I (furans with sulfur), 5.J (thiophenes), 5.M (thiazoles) and 5.Q (miscellaneous sulfur compounds).

According to Rizzi (2000) furfuryl mercaptan (**I.128**) and related compounds are readily formed by reactions of furfuryl alcohols, formed in Maillard reaction, and sulfur-containing amino acids at acid pH.



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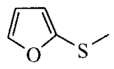

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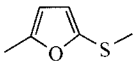

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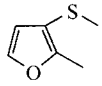

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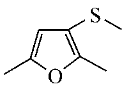

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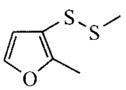

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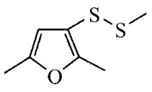

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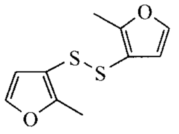


(I.127)

(I.120) 3-Furanthiol, 2-methyl-, *2-methylfuran-3-thiol*, 3-mercapto-2-methylfuran **[28588-74-1]** ***FEMA 3188***

Identified in coffee flavor by Holscher *et al.* (1990). Grosch *et al.* (1996) found 0.148 ppm in a Columbia arabica and 0.195 in a Kenya arabica.

Evers *et al.* (1976) had already isolated and identified it in among the products of a model reaction involving cysteine, thiamine and a vegetable protein hydrolysate. Its formation had also been explained by the degradation of ribose phosphate and reaction of hydrogen sulfide on the formed 4-hydroxy-5-methyl-3(2*H*)-furanone (van den Ouweland and Peer, 1975). 2-Methyl-3-furanthiol was identified in the thermal degradation products of thiamin (van der Linde *et al.*, 1979). It is one of the two major components (with 2-furanmethanethiol, **I.128**, see also the thiophenone **J.25**) formed in the Maillard reaction mixture cysteine/ribose (Whitfield *et al.*, 1988). It has been reported in numerous roast model reactions (Werkhoff *et al.*, 1990). Hofmann and Schieberle (1996) obtained substantial amounts of 2-methyl-3-furanthiol by heating cysteine with carbohydrates (mainly with ribose). They proposed a pathway by reaction of hydroxyacetaldehyde with mercaptoacetone, dry heating of which give high amounts of the thiol. None of these compounds has been identified as such in coffee (to our knowledge) but mercaptoacetone can be generated from 2-oxopropanal (**C.38**) and SH_2, and hydroxyacetaldehyde is a carbohydrate degradation product.

This thiol exhibits an intense meat-like aroma and, as with other furans substituted by a sulfur atom in the 3-position, it contributes undeniably to the character of roasted coffee (Holscher and Steinhart, 1994). Its flavor is described as sweetish, fried meat, beef broth (Golovnya and Rothe, 1980), burnt, meaty, onion, thiol at a concentration of 0.5 ppm (Chemisis, 1982). Gasser and Grosch (1988, 1990) gave an odor threshold of 0.005–0.01 ppb and of 2.5–10 $\mu g/m^3$ air (probably a printing error gave 0.0025–0.001 ng/L).

(I.121) Furan, 2-(methylthio)-, *2-(methylsulfanyl)furan, 2-furyl(methyl)sulfane, 2-furyl methyl sulfide,* 2-(methylthio)furan **[13129-38-9]**

Identified by Holscher *et al.* (1990); characterized by a weak, garlic-like odor.

(I.122) Furan, 2-methyl-5-(methylthio)-, *2-methyl-5-(methylsulfanyl)furan, methyl (5-methyl-2-furyl)sulfane, methyl 5-methyl-2-furyl sulfide,* 2-methyl-5-(methylthio)furan **[13678-59-6]** ***FEMA 3366***

Identified by Stoll *et al.* (1967).

The authors prepared this compound by reaction of 2-methylfuran with methanesulfenyl chloride (MS and IR data).

It is characterized by a very strong sulfurated odor, reminiscent of coffee (Chemisis, 1962).

(I.123) Furan, 2-methyl-3-(methylthio)-, *2-methyl-3-(methylsulfanyl)furan, methyl (2-methyl-3-furyl)sulfane, methyl 2-methyl-3-furyl sulfide,* 2-methyl-3-(methylthio)furan **[63012-97-5]**

Identified by Tressl and Silwar (1981) in roasted robusta coffee (only detectable in arabica) with a concentration of 0.025 ppm after ten days of storage (MS data).

It has been claimed in a meat aromatization patent (IFF Inc., 1979). At a concentration of 0.15 ppm, it has a brothy, fermented, green, nutty flavor (Chemisis, 1987). An odor threshold of 0.050 ppb in water is given by Tressl and Silwar (1981), with a meaty aroma up to 1 ppb, becoming thiamine-like at higher concentrations. Gasser and Grosch (1988) found that the thioether has a threshold (25–30 ppb) 2500 times higher than that of the corresponding thiol **I.120**.

(I.124) Furan, 2,5-dimethyl-3-(methylthio)-, *2,5-dimethyl-3-(methylsulfanyl)furan, 2,5-dimethyl-3-furyl(methyl)sulfane, 2,5-dimethyl-3-furyl methyl sulfide,* 2,5-dimethyl-3-(methylthio)furan **[63359-63-7]**

Identified by Tressl and Silwar (1981) (MS data).

(I.125) Furan, 2-methyl-3-(methyldithio)-, *2-methyl-3-(methyldisulfanyl)furan, methyl (2-methyl-3-furyl)disulfane, methyl 2-methyl-3-furyl disulfide,* 2-methyl-3-(methyldithio)furan **[65505-17-1]** ***FEMA 3573***

Identified by Tressl and Silwar (1981) (MS data), with concentration of 10 ppb in a robusta stored for 10 days after roasting, only detectable in arabica.

The preparation was achieved by reaction of the mercaptan with methanesulfenyl chloride.

The authors gave an odor threshold of 0.01 ppb in water and the same aroma description as for the methylthio compound **I.123**. At a concentration of 1 ppm, it has a vitamins-thiamine, meaty, roasted, alliaceous flavor (Chemisis, 1998).

(I.126) Furan, 2,5-dimethyl-3-(methyldithio)-, *2,5-dimethyl-3-(methyldisulfanyl)furan, 2,5-dimethyl-3-furyl(methyl)disulfane, 2,5-dimethyl-3-furyl methyl disulfide,* 2,5-dimethyl-3-(methyldithio)furan **[61197-06-6]**

Identified by Tressl and Silwar (1981) (MS data, preparation see **I.125**).

The odor threshold given by the authors is 0.01 ppb in water, with a cooked-meat aroma from 0.05–0.5 ppb becoming thiamine-like at higher concentrations. At a concentration of 0.3 ppm it has a roasted, meaty, rubbery, burnt flavor (Chemisis, 1996).

(I.127) Furan, 3,3′-dithiobis[2-methyl-, *3,3′-disulfanebis(2-methylfuran), bis(2-methyl-3-furyl)disulfane, bis(2-methyl-3-furyl) disulfide* **[28588-75-2]** ***FEMA 3259***

Identified by Blank *et al.* (1992a) in a roasted arabica by comparison with a reference substance (MS/electron impact and chemical ionization, retention index on several columns).

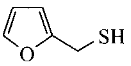
This disulfide had been previously identified by Golovnya *et al.* (1983) as a Maillard-reaction product involving treatment of baker's yeast autolyzate (see IFF. Inc., 1979).

The flavor is described as burnt, alliaceous, slightly egg (Chemisis, 1982). The odor threshold is 0.7–2.8 $\mu g/m^3$ air (Gasser and Grosch, 1990). The odor threshold of 0.02 ppt in water (Buttery *et al.*, 1984) classes it among the most powerful known compounds together with another characteristic component of coffee, the 2-isobutyl-3-methoxypyrazine (**O.77**) (a green bell pepper constituent detected at a concentration of 2 ppt by Buttery *et al.*, 1969c) and with the typical constituent of grapefruit, *p*-menth-1-ene-8-thiol, detected at 0.1 ppt by Demole *et al.* (1982).

(I.128) 2-Furanmethanethiol, *furan-2-methanethiol,* (2-furyl)methanethiol, 2-furfurylthiol, furfurylmercaptan **[98-02-2]** ***FEMA 2493***

The identification of this first member was certainly the most original discovery made by Reichstein and Staudinger (1926b). Whereas Bernheimer (1880a) had believed that the aromatic principle of coffee was a phenol, Erdmann (1902a) that it was a nitrogenous compound, and Bertrand and Weisweiller (1913), that it was pyridine, Reichstein and Staudinger (1926b) reported that the substance on which the aroma of coffee essentially depended was furfurylmercaptan. Obviously, numerous very typical constituents have since been identified but this discovery was certainly one of the milestones of flavor chemistry. With a high perspicacity, Reichstein and Staudinger thought even that unstable thioketals and hydroxysulfides formed by the reaction of aldehydes and ketones with the mercaptans were also formed during roasting and were important constituents of the coffee aromatic principle, but their presence was not confirmed because of their high chemical instability. The concentrations measured by Tressl and Silwar (1981) were 1.1 ppm in arabica and 2.0 ppm in robusta. Similar values were given by Silwar *et al.*

(1986) and Tressl (1989). Grosch *et al.* (1993) found small differences between a Columbian arabica (1.7 ppm) and an Indonesian robusta (1.95) by means of stable isotope dilution assays (IDA), but after storage at room temperature for 40 days the concentration decreased to 0.32 ppm in the arabica, even when vacuum packed. Semmelroch *et al.* (1995), using the same method, gave 1.08 ppm for an arabica and 1.73 for a robusta. The concentration increased with roasting temperature (5 min), from 0.05 ppm at 200 °C to 0.35 at 230 °C and even 0.70 at 260 °C in a robusta (Silwar and Lüllmann, 1993b).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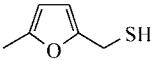
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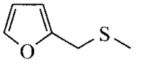
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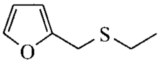
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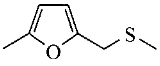
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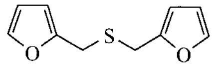
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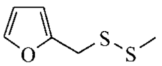
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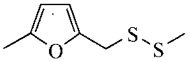
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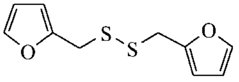
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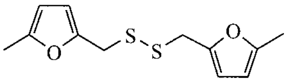
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It may be formed during roasting by reaction between hydrogen sulfide and 2-furaldehyde or furfuryl alcohol. It has been found as the main product (see **I.120** and also the thiophenone **J.25**) formed in the Maillard reaction mixture cysteine/ribose (Whitfield *et al.*, 1988). By studying and roasting different fractions of raw coffee, it was recently shown that 2-furanmethanethiol is formed by reaction of cysteine with arabinose, the only pentose occurring in raw coffee in considerable amounts (Grosch *et al.*, 2000).

The synthesis of furan-2-methanethiol was described by Reichstein and Staudinger (1928). Furfural (**I.63**) is converted into furfuryl disulfide (difurfuryl disulfide, **I.136**) by treatment with the sulfide or hydrosulfide of an alkaline-earth metal or of ammonia. The disulfide in an alcoholic solution can be reduced, for example, by addition of zinc dust and a small quantity of acetic acid. A method has been described by Kofod (1955).

The product is described as having an extremely powerful and diffusive penetrating odor; only in proper dilution does it become agreeable, coffee-like, caramellic-burnt, sweet (Arctander, 1967). The flavor threshold is estimated at 0.04 ppb in water by Golovnya and Rothe (1980). The odor threshold is only 5 ppt in water for Tressl and Silwar (1981) who perceived this thiol like freshly roasted coffee at a dilution of 0.01–0.5 ppb, then like stale coffee with sulfury note at 1–10 ppb; it could therefore be considered either as an impact component or as an off-flavor component. The odor threshold is 4.5–20 μg/m^3 air (probably a printing error in the table gives 0.0045–0.002 ng/L) for Gasser and Grosch (1990). Grosch (2000) considered 2-furanmethanethiol as the outstanding odorant of coffee, thus confirming the opinion of Reichstein and Staudinger.

(I.129) 2-Furanmethanethiol, 5-methyl-, *(5-methyl-2-furyl)methanethiol,* 5-methylfurfurylmercaptan **[59303-05-8]**

Identified by Tressl and Silwar (1981) who noticed (simultaneous steam distillation–extraction) that the concentration was weak in a freshly roasted arabica but increased markedly during storage: 0.19 ppm after 10 days for an arabica and 0.11 for a robusta and increased further after longer storage. Similar values were given by Silwar *et al.* (1986) and Tressl (1989), always slightly higher in arabicas than in robustas contrary to the more abundant **I.128**. The concentration also increased with roasting temperature (5 min), from < 0.01 ppm at 200 °C to 0.05 at 230 °C and 0.15 at the over-roasting temperature of 260 °C (Silwar and Lüllmann, 1993b).

It was synthesized by Reichstein and Staudinger (1928).

(5-Methyl-2-furyl)methanethiol has a burnt, onion, metallic flavor (Chemisis, 1961). It is a little less potent odorant than furanmethanethiol, detectable at a level of 0.050 ppb in water, developing a meaty flavor between 0.5 and 1 ppb and exhibiting a sulfury-mercaptan note at higher concentrations (Tressl and Silwar, 1981).

(I.130) Furan, 2-[(methylthio)methyl]-, *2-[(methylsulfanyl)methyl]furan, furfuryl(methyl)sulfane, furfuryl methyl sulfide* **[1438-91-1]** ***FEMA 3160***

Identified by Gianturco *et al.* (1964b), Stoll *et al.* (1967), Stoffelsma *et al.* (1968), Vitzthum and Werkhoff (1976b), and Cros *et al.* (1980). Shimoda and Shibamoto (1990a) found 0.09 % (GC) of the volatiles of a brew. Andrade-Aispuro and Crouzet (1983) found it (MS identification) when they analyzed the condensates from roasting fumes. For Tressl and Silwar (1981), the concentration of 1.1 ppm in arabica and 2.2 in robusta did not show appreciable variations after storage. Slightly lower values, but also lower in the arabicas, were given by Silwar *et al.* (1986), with 0.35 ppm in arabicas and 0.60–0.80 in robustas (after simultaneous distillation–extraction and GC with flame-ionization and flame photometric detectors) and by Tressl (1989) (0.25–0.50 and 0.5–1 ppm). Silwar and Lüllmann (1993b) noted a constant increase with roasting temperature (after 5 min): < 0.01 ppm at 200 °C, 0.2 at 230 °C and 1.5 with over-roasting at 260 °C in a robusta.

This product is easily obtained by methylation of the commercially available furan-2-methanethiol (**I.128**).

It has a coffee-like odor (Sakaguchi and Shibamoto, 1978b), and a strong, mustard, garlic, burnt flavor (Chemisis, 1961).

(I.131) Furan, 2-[(ethylthio)methyl]-, *2-[(ethylsulfanyl)methyl]furan, ethyl(furfuryl)sulfane, ethyl furfuryl sulfide* **[2024-70-6]**

Identified by Tressl and Silwar (1981) with a concentration of 10 ppb in a robusta, only detectable in arabica (MS data).

It was prepared by reaction of furan-2-methanethiol with ethyl iodide.

(I.132) Furan, 2-methyl-5-[(methylthio)methyl]-, *2-methyl-5-[(methylsulfanyl)methyl]furan, methyl(5-methylfurfuryl)sulfane, methyl 5-methylfurfuryl sulfide* **[13679-60-2]**

Identified by Stoll *et al.* (1967). For Tressl and Silwar (1981) the concentration was 0.09 ppm in a roasted arabica and 0.06 in a robusta, with little change during storage. Slightly lower values were found by Silwar *et al.* (1986) (see under **I.130**) with 0.05 and 0.02 ppm in arabicas and robustas respectively. Tressl (1989) also gave higher values for arabicas than for robustas. Silwar and Lüllmann (1993b) found only < 1 ppb after 5 min at 220–230 °C and < 10 ppb at 260 °C.

Stoll *et al.* prepared the thioether by reaction of (5-methyl-2-furyl)methanethiol (**I.129**) with dimethyl sulfate (MS and IR data).

According to Winter *et al.* (1976e), at a concentration of 0.1 ppm in a syrup base, it has a mustard, onion-like note; a geranium note being perceived when tasted, at 0.05 ppm, in a neutral soluble coffee base.

(I.133) Furan, 2,2′-[thiobis(methylene)]bis-, *difurfurylsulfane, difurfuryl sulfide* **[13678-67-6]** ***FEMA 3238***

Identified and by Stoll *et al.* (1967). Tressl and Silwar (1981) found concentrations of 0.06 ppm in a roasted arabica and 0.13 in a robusta. Lower values for arabicas (only 0.02–0.03 ppm) than for robustas (0.10–0.12 ppm) were also given by Silwar *et al.* (1986) (see **I.130**). For Silwar and Lüllmann (1993b) after 5 min of roasting the concentration increased from <10 ppb at 200 °C to 20 ppb at 230 °C and 100 ppb at 260 °C in a robusta.

Stoll *et al.* (1967) prepared it by reaction of furfuryl mercaptan with furfuryl bromide, giving a crystalline product. Tressl and Silwar obtained it by reaction of furfural with cysteine under roasting conditions.

It is described as having a toasted odor (Shibamoto, 1977). At a concentration of 0.5 ppm it has a mushroom, onion, garlic, meaty, caramel and sulfury flavor (Chemisis, 2000).

(I.134) Furan, 2-[(methyldithio)methyl]-, *2-[(methyldisulfanyl)methyl]furan, furfuryl(methyl)disulfane, furfuryl methyl disulfide*, (furfuryldithio)methane **[57500-00-2]** ***FEMA 3362***

Identified by Tressl and Silwar (1981) with a concentration of 0.12 ppm in arabica and 0.65 in robusta, that does not vary appreciably with storage (similar and significantly lower values for arabicas than for robustas were given in Silwar *et al.*, 1986 and Tressl, 1989). In a robusta, Silwar and Lüllmann (1993b) found only <1 ppb after 5 min at 230 °C (10 ppb at 260 °C).

The synthesis has been described by Dubs and Stüssi (1976a).

It had already been found in boiled pork liver flavor (Mussinan and Walradt, 1974) and in white bread of which it constitutes, according to Mulders *et al.* (1976) the characteristic component, with a threshold concentration in aqueous solution of only 0.04 ppb. Indeed, its odor has been described has having a fresh white bread crust (Mulders *et al.*, 1976; Ohloff and Flament, 1978, 1979), but with an alliaceous, burnt flavor (Chemisis, 1968).

(I.135) Furan, 2-methyl-5-[(methyldithio)methyl]-, *2-methyl-5-[(methyldisulfanyl)methyl]furan, methyl(5-methylfurfuryl)disulfane, methyl 5-methylfurfuryl disulfide* **[78818-78-7]**

Identified by Tressl and Silwar (1981), with concentrations of 0.03 ppm in a roasted arabica and 0.02 in a robusta (MS data, preparation see **I.125**).

It has an alliaceous, horseradish flavor (Chemisis, 1968).

Furan, 2-[(methyltrithio)methyl]-, *2-[(methyltrisulfanyl)methyl]furan, furfuryl(methyl)trisulfane, furfuryl methyl trisulfide* **[66169-00-4]**

Tentatively identified by Tressl and Silwar (1981) (MS data).

(I.136) furan, 2,2′-[dithiobis(methylene)]bis-, *difurfuryldisulfane, difurfuryl disulfide* **[4437-20-1]** ***FEMA 3146***

Identified by Tressl and Silwar (1981) (MS data). It was not detected by Silwar *et al.* (1986) in arabicas, but was detected at 1 ppb in robustas (see in **I.130**). The difuryl disulfide mentioned by Silwar and

Lüllmann (1993b) was probably the difurfuryl disulfide. The low concentration increased from <1 ppb to <10 ppb by roasting 5 min at 220 or 230 °C and increased slightly until 260 °C.

It was prepared by oxidation of the mercaptan **I.128** with iodine. A synthesis had been described by Reichstein and Staudinger (1928).

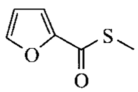
The odor is powerful, repulsively sulfuraceous, only in extreme dilution becoming attractive, caramellic-burnt, roasted (Arctander, 1967). At a concentration of 0.2 ppm the flavor is roasted, meaty, coffee, chicory (Chemisis, 1965). According to Winter *et al.* (1976e), at a concentration of 3 ppm in a neutral, soluble coffee base it has a burnt, metallic taste.

(I.137) Furan, 2,2′-[dithiobis(methylene)]bis[5-methyl-, *bis(5-methylfurfuryl)disulfane, bis(5-methylfurfuryl) disulfide* **[78818-79-8]**

Identified by Tressl and Silwar (1981) (MS data).

The preparation is similar to that of **I.136**, starting with **I.129**.

It has an alliaceous, sulfury, gassy flavor (Chemisis, 1968).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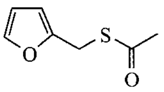
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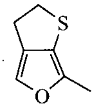
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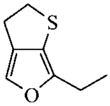
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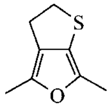
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(I.138) 2-Furancarbothioic acid, *S*-methyl ester, S-*methyl 2-furancarbothioate,* S-*methyl 2-thiofuroate,* furoyl methyl sulfide **[13679-61-3]** ***FEMA 3311***

Identified by Stoll *et al.* (1967).

It was prepared by the classic reaction of furoyl chloride with methanethiol (MS and IR data).

According to Winter *et al.* (1976e), it has a cabbage taste at 2–5 ppm in a syrup base and a sulfury, mercaptan-like note at 0.7 ppm in a neutral soluble-coffee base. It is also described as having a mercaptan, cabbage-like odor by Baltes (1979a) and Sakaguchi and Shibamoto (1978b).

(I.139) Ethanethioic acid, *S*-(2-furanylmethyl) ester, S-*furfuryl thioacetate,* S-*furfuryl ethanethioate,* furfurylthiol acetate **[13678-68-7]** ***FEMA 3162***

Identified by Stoll *et al.* (1967).

The preparation was similar to that of **I.138**: reaction of acetyl chloride or acetic anhydride with furfurylthiol.

At 0.2–0.4 ppm in a syrup base, it has typical coffee-like flavor, a sulfury note being perceived when tasted in a neutral, soluble coffee base (Winter *et al.*, 1976e). It is also described as having a coffee-like odor (Baltes, 1979a), a roasted, coffee, burnt flavor (Chemisis, 1994).

(I.140) Thieno[2,3-c]furan, 2,3-dihydro-6-methyl-, *2,3-dihydro-6-methylthieno[2,3-*c*]furan, 8-methyl-7-oxa-2-thiabicyclo[3.3.0]octa-1(8),5-diene, kahweofuran* **[26693-24-3]**

In 1967, Stoll *et al.* isolated a particular component with a very characteristic grilled note which was detected both by sniffing at the outlet of a gas chromatograph and by a combination of GC with TLC (Flament *et al.*, 1967b, 1968b). On silica plates sprayed with slightly acidic anisaldehyde (4-methoxybenzaldehyde), it was easily detected by the formation of a red spot, strongly fluorescent under UV light.

Mass spectrometry allowed confirmation of the presence of a sulfur atom and the molecular formula C_7H_8OS was proposed. Accordingly, the synthesis of a series of bicyclic thiophenes whose mass spectra were similar to that of the unknown natural product was undertaken. To evaluate its structure definitively, enough substance had to be isolated in order to record the IR and NMR spectra. According to Tressl and Silwar (1981), the concentration was 1.15 ppm in arabica and 0.85 ppm in robusta. Silwar *et al.* (1986) (see in **I.130**) found more difference between arabicas (1.75–2.0) and robustas (0.45–0.6 ppm) and Tressl (1989) reports ranges of 1.5–2.5 ppm for arabicas and 1–1.8 for robustas. Silwar and Lüllmann (1993b) noted an increase with roasting temperature in a robusta, from 200 °C only to 230 °C over 5 min (0.15–0.80 ppm).

The structure of the natural product, under the name of kahweofuran, was established in 1971 by Büchi *et al.* and the synthesis performed (the nomenclature given was 2-methyl-3-oxa-8-thiabicyclo[3.3.0]octa-1,4-diene; the numbering that we adopt is more consistent with IUPAC rules for replacement nomenclature in bicyclic compounds). Tetrahydro-3-thiophenone (**J.24**) was acetylated, then submitted to a Grignard reaction with dimethoxymethane (methylal) and treated with acid. Another synthesis was proposed by Gorzynski and Rewicki (1986). Starting with dihalofurans, a corresponding furyllithium was treated with ethylene oxide, the adduct transformed into a 3-lithium-4-(2-haloethyl)-furan which in turn reacts with sulfur at −80 °C with spontaneous cyclization, followed by methylation. More recently, Brenna *et al.* (1998) published a rather complicated synthesis, but starting with an acyclic precursor, the condensation product of α-methylcinnamaldehyde with dimethyl succinate.

When pure, the product has a very powerful sulfurous odor, but at high dilution it develops a pleasant, grilled, smoky and very characteristic note (Ohloff and Flament, 1979). At a concentration of 1 ppm, it has a rubbery, burnt, sulfury, seafood flavor (Chemisis, 1995). The odor threshold in water is 5 ppb (Tressl and Silwar, 1981), perceived as cooked meat with slight coffee note from 10–100 ppb. Tressl (1989) reported a threshold of 0.5 ppb with a roast sulfur note at 10–50 ppb.

(I.141) Thieno[2,3-*c*]furan, 6-ethyl-2,3-dihydro-, *2,3-dihydro-6-ethylthieno[2,3-*c*]furan, 8-ethyl-7-oxa-2-thiabicyclo[3.3.0]octa-1(8),5-diene,* ethylkahweofuran (confusing name, ethyl meaning replacement of H by ethyl and not methyl by ethyl)

Identified by Tressl (1989) who reported concentration ranges of 0.4–0.5 ppm in robusta and 0.3–0.4 ppm in arabica coffees.

It has a sulfury, meaty aroma and a threshold of 5 ppb.

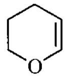
(I.142) Thieno[2,3-*c*]furan, 2,3-dihydro-4,6-dimethyl-, *2,3-dihydro-4,6-dimethylthieno[2,3-*c*]furan, 6,8-dimethyl-7-oxa-2-thiabicyclo[3.3.0]octa-1(8),5-diene,* methylkahweofuran, homokahweofuran (this name should really be avoided, as it brings confusion with the ethyl derivative **I.141**) **[78798-06-8]**

Identified only tentatively by Tressl and Silwar (1981), but confirmed later. Silwar *et al.* (1986) (see **I.130**) found 0.30–0.40 and 0.08–0.15 ppm respectively in two arabicas and two robustas, although Tressl (1989) reported lower values for arabicas than for robustas (respectively 0.5–0.8 and 0.6–1 ppm). Silwar and Lüllmann (1993b) noted an increasing concentration with roasting temperature (after 5 min), from <0.001 to 0.10 and 0.20 ppm at 200, 230 and 260 °C respectively.

A method of synthesis has been published by Gorzynski and Rewicki (1986).

Methylkahweofuran is perceived with sulfury mushroom-like aroma, with a threshold of 0.5 ppb (Tressl, 1989).

Pyrans, pyranols and pyranones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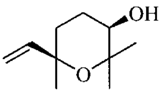
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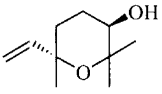
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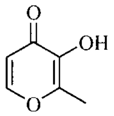
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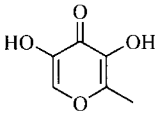
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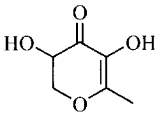
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(I.143) 2*H*-Pyran, 3,4-dihydro-, *3,4-dihydro-2*H*-pyran,* dihydropyran **[110-87-2]**

Identified by Wang *et al.* (1983) as a trace compound in a coffee headspace, and by Liardon and Ott (1984) in an analytical study applying multivariate statistics for the classification of coffee headspace profiles.

(I.144) **2*H*-Pyran-3-ol, 6-ethenyltetrahydro-2,2,6-trimethyl-, *cis*-,** *tetrahydro-2,2,6-trimethyl-*c*-6-vinyl-2*H*-pyran-*r*-3-ol, cis*-linalool 3,7-oxide, linalool oxide D **[14009–71–3]**; **3*R*,*cis*- [24048-52-0]**; **3*S*,*cis*- [22628-11-1]**; no stereochemistry **[14049-11-7]**

(I.145) **2*H*-Pyran-3-ol, 6-ethenyltetrahydro-2,2,6-trimethyl-, *trans*-,** *tetrahydro-2,2,6-trimethyl-*t*-6-vinyl-2*H*-pyran-*r*-3-ol,* trans-linalool 3,7-oxide, linalool oxide C **[39028-58-5]**; **3*R*,*trans*- [41720-62-1]**; **3*S*,*trans*- [10448-31-4]**

Both identified by Cantergiani *et al.* (2001) (like the two furanic isomers **I.56** and **I.57**) in a green Mexican arabica, representing respectively 0.25 and 0.47 % (GC polar) of the volatiles after vacuum hydrodistillation and extraction.

The formation and structures of the following maltol compounds **I.146** to **I.148** were particularly studied by Hodge (1953, 1967) and by Hodge *et al.* (1972). These pyranones are typical products generated from sugars as described extensively in a recent review by Tressl and Rewicki (1999) who described the improvements of the postulated pathways, based on the isolation and chromatographic and spectroscopic characterization of many amino-acid specific compounds found in Maillard model systems. Their work was based on labeling experiments using ^{13}C-labeled hexoses, pentoses, and disaccharides, and the article summarized with numerous schemes the chemistry of heat generated flavors from their precursors.

(I.146) 4*H*-Pyran-4-one, 3-hydroxy-2-methyl-, *3-hydroxy-2-methyl-4*H*-pyran-4-one,* maltol, Veltol® **[118-71-8]** ***FEMA 2656***

Identified by Reichstein and Staudinger (1926b). It has also been found by Stoll *et al.* (1967), and Vitzthum and Werkhoff (1976b). It was extracted from coffee under rapid brewing conditions ('fast extractor'; Lee *et al.*, 1992). Tressl *et al.* (1978a) found concentrations of 39 ppm in an arabica, 45 in a robusta (20 in arabusta). Maltol was formed after 5 min at 170 °C (60 ppm) and the concentration increased at 230 °C (230 ppm) to reach 415 ppm at the over-roasting temperature of 260 °C for a robusta coffee (Silwar and Lüllmann, 1993b).

The formation of maltol from maltose by action of piperidine phosphate has been described by Hodge *et al.* (1963). A scheme of its formation from Amadori intermediates has been given by Vernin (1981). Ledl (1990) proposed a formation pathway from disaccharides, maltol being the main degradation product, isomaltol (**I.94**) being simultaneously formed but only in small amounts.

Maltol was studied (with hydroxymethylfurfural, **I.72**) for antioxidative activity. The two compounds inhibited the formation of C_5 and C_6 acids from the corresponding aldehydes, showing an activity for this system comparable with 2,6-di-*tert*-butyl-4-methylphenol and α-tocopherol (Singhara *et al.*, 1998).

The odor is warm-fruity, caramellic-sweet with emphasis on the caramellic note in the dry state, while solutions of maltol show a pronounced fruity, jam-like odor of pineapple, strawberry-type. Depending of the solvent, sometimes more balsamic, pine-like with fruity undertones (Arctander, 1967). The measured flavor threshold in water is 20.0 ppm (Brulé *et al.*, 1971) or 7.1 ppm (Keith and Powers, 1968).

(I.147) 4*H*-Pyran-4-one, 3,5-dihydroxy-2-methyl-, *3,5-dihydroxy-2-methyl-4*H*-pyran-4-one*, 5-hydroxymaltol **[1073-96-7]**

Identified by Tressl *et al.* (1978a) among diphenols and other caramel constituents after silylation of roasted coffee. They gave concentrations of 15 ppm in arabica, 6 in robusta (13 in arabusta). Contrary to maltol (**I.146**), hydroxymaltol is degraded with over-roasting temperatures: the concentration after 5 min being ca 15 ppm at 170 °C, ca 20 at 230 °C and <10 ppm at 260 °C in a robusta (Silwar and Lüllmann, 1993b).

This pyranone probably results from the oxidation of the corresponding 2,3-dihydro compound **I.148**.

5-Hydroxymaltol is described as having a caramel-like odor (Nunomura *et al.*, 1980), a slightly astringent, weak flavor (Chemisis, 1998).

(I.148) 4*H*-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-, *2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one*, 5-hydroxy-5,6-dihydromaltol (DDMP) **[28564-83-2]**

Identified by Tressl *et al.* (1978a) among the caramel constituents of coffee extracts, with concentrations of 13, 10 and 12 ppm, respectively in arabica, robusta and arabusta. It has the same behavior as **I.147** during roasting, with a maximum of ca 10 ppm after 5 min at 230 °C (Silwar and Lüllmann, 1993b).

As explained by Ledl (1990), this pyranone, which has been detected in many heated or stored foods and results from the ring closure of a hexose, was previously isolated by Severin and Seilmeier (1968) and identified by Mills *et al.* (1970). It is a Maillard reaction product of glucose and glycine and has a mutagenic activity (Ref. 33 in Hiramoto *et al.*, 1998).

Other compounds containing a furan ring are present in sections 5.K (pyrroles) and 5.O (pyrazines)

5.J THIOPHENES

In a review of the role of thiophenes in food flavor (1975b), Maga mentioned that the structure of thiophene was not resolved until 1882, although thiophene and its derivatives had been known to organic chemists since the mid-1800s. The real interest in this chemistry arose when the drug industry found that thiophene derivatives were useful intermediates in the production of antihistaminic drugs. During the Sixties, it was shown that these sulfur-containing heterocycles contributed to the sensory properties of

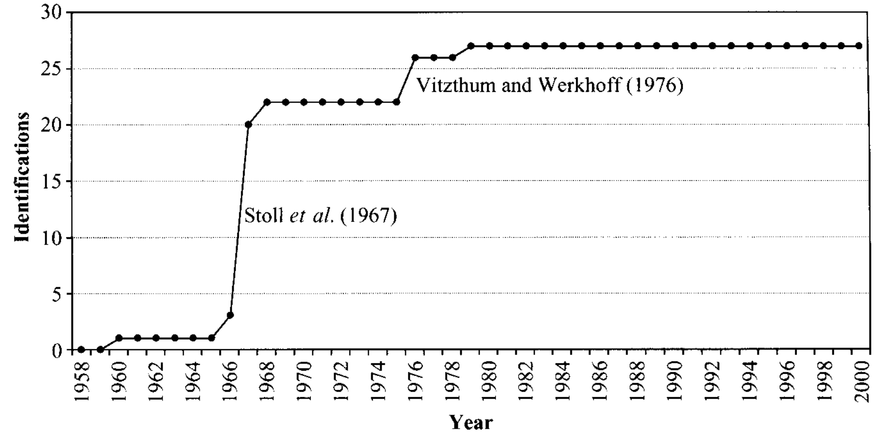


Fig. 5.10 Progressive identification of thiophene derivatives in roasted coffee volatiles

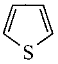
foods and consequently flavor chemists became interested. Vitzthum and Werkhoff (1976b) found 14 thiophenes in a roasted coffee fraction, among which were three new constituents. A total of 27 simple volatile thiophenes was identified in roasted coffee flavor, but these are also present in more complex structures such as those of kahweofurans (**I.140** to **I.142**). Looking at the figures for the concentrations of sulfur compounds, the differences between robustas and arabicas are less clear for the thiophene derivatives than for the furfuryl (Section 5.I) and the other sulfur compounds (Section 5.Q) in which robustas are generally richer (Silwar *et al.*, 1986, Tressl, 1989).

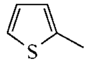
Thiophenes exist mainly in foods that have undergone some degree of heat treatment, implicating thermally induced reactions as a prerequisite for their occurrence in these foods. One exception would appear to be onion, in which other formation mechanisms are postulated. Their presence in various heated meat products and in roasted coffee is particularly significant. Thiophenes have been found in numerous model (browning system) reactions involving mainly cysteine and cystine or hydrolyzed vegetable proteins. Alkylthiophenes can be formed from cysteine alone without addition of a sugar by oxidative degradation (Sheldon and Shibamoto, 1987, quoted by Umano *et al.*, 1995), but acylthiophenes need the presence of sugar. Thiophenes can result, for instance, from the pyrolysis of cysteine alone (Kato *et al.*, 1973b) or with pyruvaldehyde (Kato *et al.*, 1973a), from a cysteine/cystine/ribose system (Mulders, 1973c) or simply from the action of hydrogen sulfide on D-glucose (Sakaguchi and Shibamoto, 1978b) or furfural (Shibamoto, 1977). With ribose and cysteine, Whitfield *et al.* (1988) identified alkylthiophenes, only two of them being present in roasted coffee, but of the eight acylthiophenes, seven are present in coffee. They also found (like Mulders, 1973c), two thienothiophenes, **J.9**, and the [3,4-*b*]isomer, but in another publication by the same group (Mottram and Whitfield, 1995), the two thienothiophenes were identified as **J.9** and **J.10**, the [2,3-*b*]-isomer **J.10** apparently being more abundant than the [3,2-*b*]-isomer, **J.9.** Silwar (1992) studied the cysteine/rhamnose system with results rather similar to those of Whitfield *et al.* (1988), at least for the comparison with coffee products. Umano *et al.* (1995) identified the volatiles formed by heating cysteine alone or with glucose: the only oxygenated thiophene, thiophenemethanol (**J.11**), needed the presence of glucose, the other thiophenes formed were alkylthiophenes, of which only a third has been found in coffee. It has to be noted that the sulfur amino acids have not been identified in appreciable proportions as free in green coffee: methionine has been found in small quantities in some arabicas by Arnold and Ludwig (1996), and the more complex thioether, cystathionine, by Tressl *et al.* (1983) in a decaffeinated coffee. Only 5–10% of the peptide amino acids are free in green coffee (Tressl, 1989), but proteins containing the amino acids gave the same pyrolysates as the free acids (Merritt *et al.*, 1970).

Formation pathways have been discussed by Mulders (1973c), who proposed detailed schemes for 3-methyl- (**J.13**) and 5-methylthiophene-2-carbaldehyde (**J.14**), the precursors being mercaptoacetaldehyde and 2-butenal; the former product has been identified upon boiling cysteine with α-diketone (Kobayasi and Fujimaki, 1965a). Mottram (1991) proposed a mechanism of formation for long-chain alkylthiophenes from α–γ-unsaturated dienals.

Various methods of synthesis of thiophenes have been described and applied by Winter *et al.* (1975a) and reviewed by Maga (1975b).

The sensory properties of numerous thiophenes in a syrup base or in two soluble neutral coffee bases have been described in a series of patents by Winter *et al.* (1972a, 1975a, 1976a,b, 1979) and by Firmenich *et al.* (1969d,g). Maga (1975b) concluded that the flavoring contribution of various thiophenes may indeed be quite potent but not necessarily desirable and characteristic, suggesting that limited application exists for synthetic thiophenes in food flavor formulations. He suggested that the presence of undesirable cooked and burnt flavors associated with certain processed foods may also partly be due to the presence of undetectable thiophene derivatives.


(J.1)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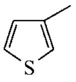
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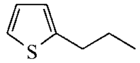
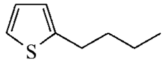
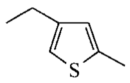
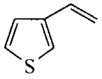

(J.4)


(J.5)


(J.6)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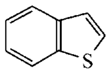
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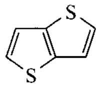
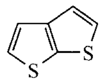

(J.9)


(J.10)

(J.1) Thiophene, *thiophene* [110-02-1]

Identified by Zlatkis and Sivetz (1960), Merritt *et al.* (1966), Gianturco *et al.* (1966), and Stoffelsma *et al.* (1968). It was in the headspace of a brewed Columbian arabica analyzed by Shimoda and Shibamoto (1990) and represented 0.28% of the volatiles (GC).

It was found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

It is described as having a benzene-like odor and being responsible for a sickly, pungent off-odor when present at a concentration of 2.5 ppb in canned beef (Maga, 1975b).

(J.2) Thiophene, 2-methyl-, *2-methylthiophene* [554-14-3]

Mentioned without the substitution site by Heins *et al.* (1966) and Merritt *et al.* (1970), but confirmed by Vitzthum and Werkhoff (1976b) (neutral fraction of a steam distillate). It was also found by Cros *et al.* (1980) in the headspace of a roasted Columbian arabica and by Shimoda and Shibamoto (1990a) in the headspace of a brewed Columbian arabica (0.09% of the volatiles by GC).

'Methylthiophene' is formed in the pyrolysis of cystine (Merritt *et al.*, 1970). It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

Among the numerous methods of synthesis of alkylthiophenes, Maga (1975b) suggested the treatment of levulinic acid (**E.41**) with phosphorous sulfides or the direct alkylation of thiophene via its iodo derivatives. According to a mechanism proposed by Mottram (1991), this thiophene could result from the reaction of hydrogen sulfide with 2,4-pentadienal.

2-Methylthiophene is described as responsible for a green, sweet off-odor when present at a concentration of 1.0 ppb in canned beef (Maga, 1975b). For Arnold *et al.* (1969) it has a heated onion, sulfury odor; for Winter *et al.* (1975a) a roasted, bitter, green note at 7.5 ppm in a sugar syrup, giving a nitrobenzene-like taste to a neutral soluble coffee at 11 ppm. The flavor is sulfury, cabbage, ash (Chemisis, 1998). Galetto and Hoffman (1976) measured a threshold of 3 ppm in water.

Thiophene, 2-ethyl-[872-55-9] ('ethylthiophene')

Formed in the pyrolysis of cystine (Merritt *et al.*, 1970). It is probably present, but not confirmed, in coffee volatile constituents.

(J.3) Thiophene, 3-methyl-, *3-methylthiophene* **[616-44-4]**

Identified by Gutmann *et al.* (1979), and by Liardon and Ott (1984). Shimoda and Shibamoto (1990a) found it in the headspace of a brewed Columbian arabica (0.04% of the volatiles by GC) with the two previous compounds, but it was the only thiophenic compound identified by Ho *et al.* (1993) in the headspace of a roasted Columbian coffee (0.30 ppm).

For Winter *et al.* (1975a) it impart a fatty and winey note when tasted in a sugar syrup at 8.5 ppm. The flavor note is ash, weak (Chemisis, 1998). A threshold of 5 ppm in water is measured by Galetto and Hoffman (1976).

(J.4) Thiophene, 2-propyl-, *2-propylthiophene* **[1551-27-5]**

Identified by Vitzthum and Werkhoff (1976b).

It can be formed during roasting by reaction of 2,4-heptadienal with hydrogen sulfide, according to a mechanism proposed by Mottram (1991).

The synthesis was described by Campaigne and Diedrich (1948). Maga (1975b) has reviewed other methods of synthesis.

2-Propylthiophene has a non-characteristic, chemical note when tasted at 10 ppm in sugar syrup (Winter *et al.*, 1975a).

(J.5) Thiophene, 2-butyl-, *2-butylthiophene* **[1455-20-5]**

Identified by Vitzthum and Werkhoff (1976b).

It can be formed during roasting by reaction of 2,4-octadienal with hydrogen sulfide, according to a mechanism proposed by Mottram (1991).

At a concentration of 2 ppm it has a fruity, slightly milky and floral note (Chemisis, 1981, 1993).

(J.6) Thiophene, 4-ethyl-2-methyl-, *4-ethyl-2-methylthiophene* **[13678-54-1]**

Identified and synthesized by Stoll *et al.* (1967) who gave the physico-chemical and spectroscopic characteristics of the product.

According to Winter *et al.* (1975a), it gives a burnt, horn-like note to a sugar syrup at a concentration of 1 ppm and a solvent, latex paint-like taste to a neutral soluble coffee base at 5 ppm.

(J.7) Thiophene, 3-ethenyl-, *3-vinylthiophene, 3-ethenylthiophene* **[13679-64-6]**

Identified by Stoll *et al.* (1967).

A synthesis from 3-bromothiophene is described by Troyanowsky (1955).

It has a burnt, cereal, roasted note (Chemisis, 1963).

(J.8) Benzo[*b*]thiophene, *benzo[*b*] thiophene,* thionaphthene **[95-15-8]**; benzothiophene **[11095-43-5]**

Identified by Stoll *et al.* (1967).

For Winter *et al.* (1975a) it imparts a rubbery, earthy note to a neutral soluble coffee base, when tasted at a concentration of 0.06 ppm. At 0.1 ppm it has cereal, burnt, coffee, rubbery tonalities (Chemisis, 1997).

(J.9) Thieno[3,2-*b*]thiophene, *thieno[3,2-*b*] thiophene,* thiopheno[3,2-*b*]thiophene, 1,4-thiophthene, 1,4-dithiapentalene **[251-41-2]**, or

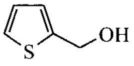
(J.10) Thieno[2,3-*b*]thiophene, *thieno[2,3-*b*] thiophene,* thiopheno[2,3-*b*]thiophene, 1,5-thiophene **[250-84-0]**

Identified by Stoll *et al.* (1967), the proposed alternative structure, **J.10**, being less probable.

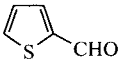
Isomeric thienothiophenes, **J.9** and, tentatively, the [3,4-*b*]-isomer, have been identified in the reaction products of ribose with cysteine and cystine (Mulders, 1973c). With cysteine and ribose, Mottram and Whitfield (1995) identified **J.9** and **J.10**.

The synthesis of **J.9** was described by Challenger and Holmes (1953), starting with cyclization of (3-thienylthio)acetic acid to 6-oxothieno[3,2-*b*]thiophene which was reduced. This compound is solid, the isomer is a liquid (the two compounds are obtained in the reaction between acetylene and boiling sulfur).

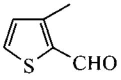
According to Winter *et al.* (1975a), **J.9** has a styrene-like taste at 0.5 ppm in a sugar syrup and a sulfury, nutty, buckwheat-like taste when incorporated at 0.1 ppm to a neutral soluble coffee base.



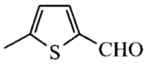
(J.11)



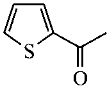
(J.12)



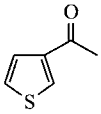
(J.13)



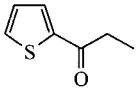
(J.14)



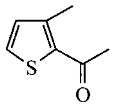
(J.15)



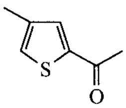
(J.16)



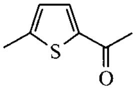
(J.17)



(J.18)



(J.19)



(J.20)

(J.11) 2-Thiophenemethanol, *thiophene-2-methanol, thenyl alcohol,* 2-thenyl alcohol, 2-thiophenecarbinol, 2-hydroxymethylthiophene **[636-72-6]**

Identified by Heins *et al.* (1966), and Stoffelsma *et al.* (1968). Silwar *et al.* (1986) after simultaneous distillation–extraction and using GC with simultaneous flame-ionization and flame-photometric detectors found 0.85–1.10 ppm in arabicas and 0.45–0.50 in robustas. Tressl (1989) gave a similar range of 0.6–1 ppm. Silwar and Lüllmann (1993b) observed an increasing concentration with increasing temperature, after 5 min roasting: from 0.01 ppm at 200 °C to 0.20 at 230 °C and 0.35 at the over-roasting temperature of 260 °C.

It can be obtained by hydrolysis of the corresponding chloride (Emerson and Patrick, 1949).

Even at a concentration of 10 ppm it has no flavoring characteristic.

(J.12) 2-Thiophenecarboxaldehyde, *thiophene-2-carbaldehyde,* 2-thienylaldehyde, 2-formylthiophene **[98-03-3]**

Identified by Stoll *et al.* (1967), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b). Silwar *et al.* (1986) (see **J.11**) found contents of 0.50–0.60 ppm in robustas and arabicas, slightly lower for robustas, and Tressl (1989) reported (see the remark in furanic sulfur compounds, Section 5.I) slightly lower values for arabicas (1–1.5 ppm) than robustas (1.2–1.8). As for the corresponding alcohol, **J.11**, Silwar and Lüllmann (1993b) observed a constant increase in the concentration with increasing roasting temperature: from <0.01 ppm at 200 °C to 0.30, 0.40 and 0.55 ppm at 220, 230 and 260 °C respectively.

Previously prepared by Reichstein (1930a) by formylation of thiophene.

For Winter *et al.* (1975a), it gave benzaldehyde-like note when added at 10 ppm to a sugar syrup.

(J.13) 2-Thiophenecarboxaldehyde, 3-methyl-, *3-methylthiophene-2-carbaldehyde,* 2-formyl-3-methylthiophene **[5834-16-2]**

Identified by Vitzthum and Werkhoff (1976b). Tressl (1989) gave a content of 0.05–0.1 ppm.

A possible route of formation has been proposed by Mulders (1973a), precursors being mercaptoacetaldehyde and crotonaldehyde. The former has been identified by Kobayasi and Fujimaki (1965a) on boiling cysteine with α-diketone, the second resulting from the aldol condensation of acetaldehyde.

The synthesis has been performed by Winter *et al.* (1975a) who characterized it as having a saffron taste (at 10 ppm in a sugar syrup) and as imparting a camphor note (at 1.4 ppm) to a neutral soluble coffee beverage. An iodoform tonality is also mentioned (Chemisis, 1964).

(J.14) 2-Thiophenecarboxaldehyde, 5-methyl-, *5-methylthiophene-2-carbaldehyde,* 2-formyl-5-methylthiophene **[13679-70-4]** ***FEMA 3209***

Identified by Stoll *et al.* (1967), and Vitzthum and Werkhoff (1976b). Silwar *et al.* (1986) (see **J.11**) found contents of 0.25–0.35 ppm in robustas and arabicas, the slightly lower figures corresponding to robustas (as for **J.12**). Tressl (1989) gave a range of 0.1–0.2 ppm. For Silwar and Lüllmann (1993b) the increase with roasting temperature is constant: <0.01, 0.05, 0.10, 0.20 ppm at 200, 220, 230, 260 °C respectively, as it is for **J.12**, but with lower values.

A possible route of formation has been proposed by Mulders (1973a), with the same precursors as for the 3-methyl isomer, **J.13**.

The usage level recommended by *FEMA* is 0.5 ppm. This aldehyde imparts a cherry-like taste to a sugar syrup at 10 ppm and a bitter almond note to a neutral soluble coffee base at 2.7 ppm (Winter *et al.*, 1975a). The odor threshold in air measured by Gasser and Grosch (1990) is 1.75–7.4 $\mu g/m^3$.

(J.15) Ethanone, 1-(2-thienyl)-, *1-(2-thienyl)ethanone, methyl 2-thienyl ketone,* 2-acetylthiophene **[88-15-3]**

Identified by Gianturco *et al.* (1966), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b). Silwar *et al.* (1986) (see **J.11**) found contents of 0.90–1.25 ppm in arabicas and 0.65–1.50 in robustas of two origins. Tressl (1993b) reported 0.4–0.6 ppm in arabicas and 0.6–1 in robustas. According to the figures given by Silwar and Lüllmann (1993b), the concentration increases with increasing temperature: <0.01, 0.30, 0.45, 1.30 ppm after 5 min at 200, 220, 230, 260 °C respectively, in a robusta. The increase seems to be more significant after 230 °C than it is for the corresponding aldehyde, **J.12**.

The synthesis was described by Farrar and Levine (1950).

It is reported by Maga (1975b) as having a mustard-like odor. Winter *et al.* (1975a) characterized it as having an onion-like taste (at 10 ppm in a sugar syrup) and a malty, roasted note (at 5 ppm in a neutral soluble coffee base).

(J.16) Ethanone, 1-(3-thienyl)-, *1-(3-thienyl)ethanone, methyl 3-thienyl ketone,* 3-acetylthiophene **[1468-83-3]**

Identified in roasted coffee flavor by Stoffelsma and Pypker (1968), Stoffelsma *et al.*(1968), and Vitzthum and Werkhoff (1976b). Tressl (1993b) gave contents of 0.15–0.3 ppm in arabicas and 0.3–0.5 in robustas.

It is considered as a pleasing component of white bread (Mulders *et al.*, 1973). At a concentration of 5 ppm it has a bitter, metallic, dirty note (Chemisis, 1993).

(J.17) 1-Propanone, 1-(2-thienyl)-, *1-(2-thienyl)propan-1-one, ethyl 2-thienyl ketone,* 2-propanoylthiophene, 2-propionylthiophene **[13679-75-9]**

Identified by Stoll *et al.* (1967), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b).

For Winter *et al.* (1975a) it gives a creamy, caramel-like note to a sugar syrup (20 ppm).

(J.18) Ethanone, 1-(3-methyl-2-thienyl)-, *1-(3-methyl-2-thienyl)ethanone,* 2-acetyl-3-methylthiophene **[13679-72-6]**

Identified by Stoll *et al.* (1967), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b).

The synthesis is described by Farrar and Levine (1950), this ketone being the main product of acylation of 3-methylthiophene.

It is reported by Maga (1975b) as having a methyl benzoate odor. It has a sweet, honey-like taste in a sugar syrup (2.5 ppm) and a nutty, starchy note in a neutral soluble coffee base (1 ppm) (Winter *et al.*, 1975a).

(J.19) Ethanone, 1-(4-methyl-2-thienyl)-, *1-(4-methyl-2-thienyl)ethanone,* 2-acetyl-4-methylthiophene **[13679-73-7]**

Identified by Stoll *et al.* (1967), Vitzthum and Werkhoff (1976b).

Farrar and Levine (1950) obtained this ketone as a secondary product of acylation of 3-methylthiophene, the acylation taking place mainly at the 2-position, giving **J.18**.

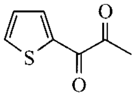
It was reported by Maga (1975b) as having an undecylic alcohol odor.

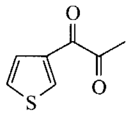
(J.20) Ethanone, 1-(5-methyl-2-thienyl)-, *1-(5-methyl-2-thienyl)ethanone,* 2-acetyl-5-methylthiophene **[13679-74-8]**

Identified by Stoll *et al.* (1967), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b). Silwar *et al.* (1986) (see **J.11**) found contents of 0.80–0.90 ppm in arabicas and 0.45–0.70 in two robustas. Tressl (1989) reported a smaller range (0.3–0.5 ppm). According to Silwar and Lüllmann (1993b), the concentration increased with increasing roasting temperature: <0.01, 0.10, 0.20, 0.50 ppm at 200, 220, 230 and 260 °C respectively (compare with **J.15**, and parallel with **J.14** and **J.12**).

The synthesis is described by Farrar and Levine (1950).

The product was reported by Maga (1975b) as having a phenylpropyl alcohol odor. For Winter *et al.* (1975a), it imparts a sweet, flowery note remembering heliotropine to a sugar syrup when incorporated at a concentration of 10 ppm.


(J.21)


(J.22)

(J.21) 1,2-Propanedione, 1-(2-thienyl)-, *1-(2-thienyl)propane-1,2-dione* **[13678-69-8]**

Identified by Stoll *et al.* (1967), and Vitzthum and Werkhoff (1976b).

The synthesis was described by Winter *et al.* (1975a) who submitted 2-propionylthiophene (**J.17**) to the action of nitrosyl chloride, the reaction product being hydrolyzed in formic acid solution.

The yellow crystals of the dione are characterized by a praline-like taste when added, at 10 ppm, to a sugar syrup. At a concentration of 20 ppm, the product imparts a woody, coffee-grounds note to a neutral instant coffee base.

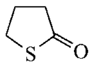
(J.22) 1,2-Propanedione, 1-(3-thienyl)-, *1-(3-thienyl)propane-1,2-dione* **[13678-78-9]**

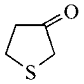
Identified by Stoll *et al.* (1967).

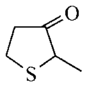
The authors synthesized it by oxidation of 3-propionylthiophene. They mentioned the physico-chemical, spectroscopic and organoleptic characteristics of the product which is a yellow liquid with a buttery and fruity odor.

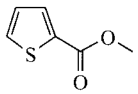
1,2-Propanedione, 1-(4/5-methyl-2-thienyl)-,

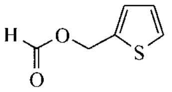
Isolated from coffee by Gautschi *et al.* (1968).

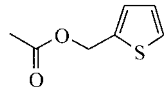

(J.23)


(J.24)


(J.25)


(J.26)


(J.27)


(J.28)

(J.23) 2(3*H*)-Thiophenone, dihydro-, *tetrahydrothiophen-2-one, thiolan-2-one,* 2-oxothiolane, 4-thiobutyrolactone, 4-butanethioic acid lactone **[1003-10-7]**

Identified by Stoffelsma and Pypker (1968), and Stoffelsma *et al.* (1968).

It has a burnt, chemical flavor (Chemisis, 1968).

(J.24) 3(2*H*)-Thiophenone, dihydro-, *tetrahydrothiophen-3-one, thiolan-3-one,* thiophan-3-one **[1003-04-9]** ***FEMA 3266***

Identified by Stoll *et al.* (1967). Tressl (1989) gave a concentration in the range of 0.1–0.2 ppm.

It is formed in the reaction of cysteine (not of cystine) with Furaneol® (**I.100**), together with other thiophenones (Shu *et al.*, 1986), in the cysteine/rhamnose system (Silwar, 1992).

The synthesis has been described by Woodward and Eastman (1946).

The usage level recommended by *FEMA* is 1.0 ppm. According to Winter *et al.* (1975a), it gives an onion and garlic note to a sugar syrup at a concentration of 1–10 ppm. It is also described as having alliaceous, coffee and chive tonalities (Chemisis, 1962).

(J.25) 3(2*H*)-Thiophenone, dihydro-2-methyl-, *tetrahydro-2-methylthiophen-3-one, 2-methylthiolan-3-one,* 2-methylthiophan-3-one **[13679-85-1]** ***FEMA 3512***

Identified by Stoll *et al.* (1967), Vitzthum and Werkhoff (1976b), and Cros *et al.* (1980). Silwar *et al.* (1986) (see **J.11**) found contents of 0.30–0.65 ppm in arabicas and 0.65–0.75 in robustas. Tressl (1989) gave a higher range of 1.5–2 ppm. Silwar and Lüllmann (1993b) found an increase with increasing roasting temperature: <0.01, 0.25, 0.30 and 0.65 ppm after 5 min at 200, 220, 230 and 260 °C respectively. At a constant temperature of 230 °C, Shibamoto *et al.* (1982) observed a maximum in the concentration after 27 min, decreasing by half after 30 min (simultaneous distillation/extraction).

It has been found in the reaction of cysteine (not cystine) with pyruvaldehyde (Kato *et al.*, 1973a), in a heated cysteine/glucose model system (Sheldon *et al.*, 1986), in a cysteine/xylose model (Tressl, 1989), in a cysteine/ribose system, being one of the most important thiophene derivatives, the most important compounds being the two furan derivatives, 2-furanmethanethiol (**I.128**) and 2-methyl-3-furanthiol (**I.120**) (Whitfield *et al.*, 1988).

The synthesis has been described by Karrer and Schmid (1944).

According to Winter *et al.* (1975a), it gives a green and burnt coffee note to a sugar syrup, at a concentration of 2.5–5.0 ppm.

3(2*H*)-Thiophenone, *2,3-dihydrothiophen-3-one*, thiophen-3-one **[19090-02-9]**

Present in the list of roasted coffee volatiles with their physical properties published by Clarke (1992), but we could not find this ketone in the references quoted.

(J.26) 2-Thiophenecarboxylic acid, methyl ester, *methyl 2-thiophenecarboxylate,* methyl 2-thiophenate, 2-(methoxycarbonyl)thiophene **[5380-42-7]**

Identified by Stoll *et al.* (1967).

The synthesis has been described by Weinstein (1955).

Winter *et al.* (1975a) characterized it as imparting an anthranilate-like (grape) taste with a burnt note to a sugar syrup (10 ppm).

(J.27) 2-Thiophenemethanol, formate, *thenyl formate, 2-thienylmethyl formate* **[13679-76-0]**

Identified by Stoll *et al.* (1967).

These authors prepared the ester by acylation, with the mixed anhydride of formic and acetic acids, of thiophene-2-methanol (**J.11**), itself prepared by reduction of thiophene-2-carbaldehyde (**J.12**).

According to Winter *et al.* (1975a), it is characterized by a mustard-like note when tasted in a sugar syrup, at a concentration of 10 ppm. It imparts a sweet, solvent-like note to a neutral soluble coffee base, when added at a concentration of 3.4 ppm.

(J.28) 2-Thiophenemethanol, acetate, *thenyl acetate* **[13679-77-1]**

Identified by Stoll *et al.* (1967). Tressl (1989) gave a content in the range 0.05–0.1 ppm.

Emerson and Patrick (1949) obtained it by treatment of thenyl chloride (2-thienylmethyl chloride) with sodium acetate and triethylamine.

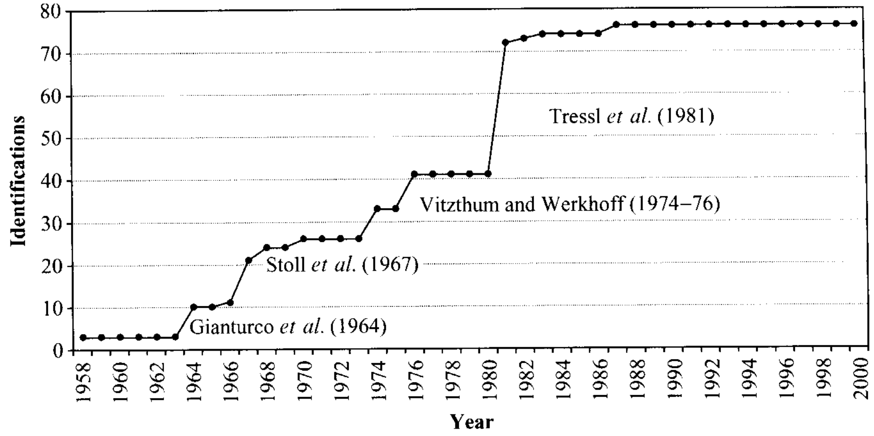


Fig. 5.11 Progressive identification of pyrrole derivatives in roasted coffee volatiles

It is described as having a fruity, estery taste and a light jasmine odor (Chemisis, 1962). It is characterized by a solvent, acetate-like taste (Winter *et al.*, 1975a).

5.K PYRROLES

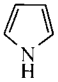
In 1981, Maga (1981b) published a review on 'Pyrroles in foods' and declared that at that time only 20 pyrroles had been identified as occurring in food systems. The author considered that they represented a minor class of potentially significant flavor-associated compounds. This present chapter includes nearly 70 compounds present in coffee flavor, some of them contributing significantly to the aroma. They were first identified in the mid-1960s in coffee. The groups having most contributed to the discovery of this class of compounds are Gianturco *et al.* (1964b), Stoll *et al.* (1967), Vitzthum and Werkhoff (1974b, 1976b) and Tressl *et al.* (1981a).

Pyrroles are primarily formed thermally, with other formation pathways existing. It appears that they are not present in fresh, raw foods (although 1-methylpyrrole, **K.2**, indole, **K.37**, and 2-acetylpyrrole, **K.50**, have been identified in green coffee). They are formed by reaction of aldoses (xylose) with alkylamines (Kato, 1966, 1967; Kato and Hiromichi, 1968), in reactions involving reducing sugars and amino acids, for instance by condensation of glucose and alanine (Shigematsu *et al.*, 1972), glucose and proline (see the reviews by Hodge *et al.*, 1972 and Helak *et al.*, 1989a,b) or hydroxyproline (Kobayasi and Fujimaki, 1965b; Tressl *et al.*, 1981b,c, 1985b, 1993a). Other model reactions involve glucose and methylamine (Olsson *et al.*, 1977), L-rhamnose and ammonia (Shibamoto and Bernhard, 1978), D-glucose and ammonia (Shibamoto *et al.*, 1979), eight of the nine pyrroles identified in this latter publication being present in roasted coffee. More recently, in their extensive study of the reaction of serine and threonine with sucrose under the conditions of coffee roasting, Baltes and Bochmann (1987b) found that most of the same 35 identified alkylpyrroles were formed in the absence of sucrose, or else when the hydroxyamino acids were in excess in the reaction mixture (although with lower yields). Sugar is needed for the formation of pyrroles containing acyl groups or furan residues. Shigematsu *et al.* (1975) have shown that pyrroles result from the thermal degradation of Amadori intermediates such as deoxy-1-L-prolino-1-D-fructose. Reactions of α-amino acids with furfural and 2-acetylfuran yield *N*-alkyl-2-acylpyrroles and it has been demonstrated that pyrroles are formed in general by the thermal reaction of furan derivatives with α-amino acids (Rizzi, 1974). 'There are apparent discrepancies in the literature as to the number and types of pyrroles that have been isolated and identified in various model systems' as declared by Maga (1981b), although the explanation 'that a high degree of sugar fragmentation is required to form pyrroles', is wrong; in fact, the authors quoted (Shibamoto *et al.*, 1979) say that 'it is possible that the formation of pyrroles... does not require a high degree of fragmentation', unlike pyrazines for example.

Tressl *et al.* (1981c) observed that arabicas contained lower amounts of alkylpyrroles but higher amounts of *N*-furfurylpyrroles than did robustas, and that the amounts of some *N*-substituted pyrroles increased with the storage of roasted coffee. Silwar and Lüllmann (1993b), in their investigation of aroma formation during roasting of a robusta, noted that *N*-alkylpyrroles form at 200–210 °C with increased formation at 250 °C, the *N*-furfuryl compounds forming at 190–200 °C with the increase at 250 °C.

Shigematsu *et al.* (1972) stated that alkylpyrroles have an intense petroleum-like odor but give a sweet, slightly burnt-like aroma on extreme dilution, acylpyrroles having a sweet, smoky, slightly medicine-like odor. The organoleptic properties of various pyrroles have been described by Winter *et al.* (1972b, 1975b, 1976f,g,i).

Pyrrole, alkylpyrroles (mono, bicyclic)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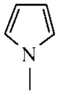
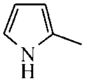

(K·2)
(K·2)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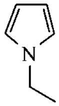
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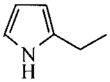
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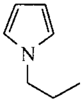
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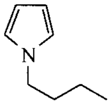
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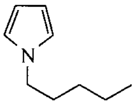
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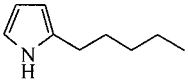
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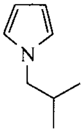
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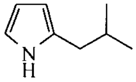
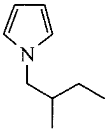

(K·11)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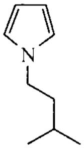

(K·13)

(K.1) 1*H*-Pyrrole, *pyrrole, 1*H*-pyrrole, azole* [109-97-7] *FEMA 3386*

Identified by Bernheimer (1880a), Gianturco *et al.* (1964b), Vitzthum and Werkhoff (1976b) in the neutral fraction of a steam distillate, and Baltes and Bochmann (1987a). The concentration in roasted coffee was estimated at 2.7 ppm by Stofberg and Stoffelsma (1981). Procida *et al.* (1997) observed a neat increase in the headspace of a Guatemala arabica when the roasting time at 218 °C was increased from 23 to 28 min.

It is formed in the pyrolysis of proline (Merritt *et al.*, 1970), of threonine (Kato *et al.*, 1970), during heating of hydroxyproline and glucose from 120 to 200 °C (Kobayasi and Fujimaki, 1965b), in a cysteine/cystine ribose browning system (Mulders, 1973c), in a L-rhamnose with ammonia (Shibamoto and Bernhard, 1978) or a D-glucose–ammonia model system (Shibamoto *et al.*, 1979), when heating serine and threonine alone (Baltes and Bochmann, 1987b).

It is characterized by a warm, slightly pungent, hay-like herbaceous odor of moderate to poor tenacity (Arctander, 1967).

(K.2) *(K.2)* 1*H*-Pyrrole, 1-methyl-, *1-methyl-1*H*-pyrrole, N*-methylpyrrole **[96-54-8]**

Identified by Reichstein and Staudinger (1926c), Merritt *et al.* (1963), Gianturco *et al.* (1964b), Viani *et al.* (1965), Vitzthum and Werkhoff (1976b) (see **K.1**), Cros *et al.* (1980), and Wang *et al.* (1983) in headspace of roasted coffee. It was also identified in green and roasted coffee (robusta and arabicas) volatiles by Merritt *et al.* (1970). Tressl *et al.* (1981a) found 2.08 ppm in a roasted robusta, after steam distillation, extraction, column chromatography, GC/MS ('semi-quantification'), a value of 3 ppm is given in (1981c) (a figure in the latter publication showed 0.6 ppm after roasting and 2.2 ppm after aging 39 days). A neat increase in the formation of 1-methylpyrrole was noted by Procida *et al.* (1997) when the roasting time at 218 °C for an arabica increased from 23 to 28 min. It is the only purely alkylpyrrole (the others being essentially acylpyrroles) identified in a brew by Ramos *et al.* (1998), and only with supercritical-CO_2 extraction.

It was formed in the pyrolysis of proline and 4-hydroxyproline (Merritt *et al.*, 1970) and is one of the pyrolysis products of trigonelline (Viani and Horman, 1974). Baltes and Bochmann (1987b) found 1-methylpyrrole in all their serine/threonine/sucrose reactions as well as in coffee.

It has a powerful and penetrating smokey-tarry odor, in extreme dilution sweet, woody-herbaceous, slightly animal (Arctander, 1967). It has a green, beany, metallic flavor (Chemisis, 1997).

(K.3) 1*H*-Pyrrole, 2-methyl-, *2-methylpyrrole, α*-methylpyrrole **[636-41-9]**

Identified by Merritt *et al.* (1970), Wang *et al.* (1983), and Baltes and Bochmann (1987b).

It has been detected among the pyrolysis products of threonine (Kato *et al.*, 1970), in the reaction of L-rhamnose with ammonia (Shibamoto and Bernhard, 1978) or D-glucose with ammonia (Shibamoto *et al.*, 1979).

The flavor is metallic, fruity (Chemisis, 1965).

(K.4) 1*H*-Pyrrole, 1-ethyl-, *1-ethylpyrrole* **[617-92-5]**

Identified by Merritt *et al.* (1970), Vitzthum and Werkhoff (1976b) (see **K.1**), Cros *et al.* (1980) and Wang *et al.* (1983) in headspace of roasted coffee, and by Tressl *et al.*(1981a) who found 1.91 ppm in a roasted robusta (see **K.2**). Procida *et al.* (1997) observed a smaller proportion of 1-ethyl than of 1-methylpyrrole in a roasted Guatemala arabica, but the increase with roasting time was similar.

1-Ethylpyrrole was isolated from a mixture of DL-α-alanine and D-glucose after heating for 1 h at 250 °C. (Shigematsu *et al.*, 1972). Like 1-methylpyrrole (**K.2**), this homolog was found by Baltes and Bochmann (1987b) in all their serine/threonine/sucrose reactions as well as in coffee.

It imparts a burnt flavor to a sugar syrup, at a concentration of 2 ppm (Winter *et al.*, 1976f).

(K.5) 1*H*-Pyrrole, 2-ethyl-, *2-ethylpyrrole* **[1551-06-0]**

Identified by Vitzthum and Werkhoff (1976b), and Baltes and Bochmann (1987b).

It was prepared by alkylation of pyrrolylmagnesium bromide (Vitzthum and Werkhoff, 1976b).

Shibamoto and Bernhard (1978) observed its formation from the reaction of L-rhamnose with ammonia.

Two **ethylpyrroles** without specification of the substitution site, but probably 1-and 2-ethylpyrroles, had been found previously by Heins *et al.* (1966).

(K.6) 1*H*-Pyrrole, 1-propyl-, *1-propylpyrrole* [5145-64-2]

Identified by Tressl *et al.* (1981a) (MS data) who gave a concentration of 85 ppb (see **K.2**).

It was found by Baltes and Bochmann (1987b) in coffee and when heating threonine (not serine) with sucrose, or the mixture of the two amino acids with or without sucrose.

It is described as having alliaceous, dirty, oily flavor (Chemisis, 1975).

(K.7) 1*H*-Pyrrole, 1-butyl-, *1-butylpyrrole, N-n*-butylpyrrole [589-33-3]

Identified by Merritt and Robertson (1966).

It was prepared by Reichstein (1927) with 'saccharic acid' (glucaric acid) and butylamine.

The flavor is green, woody, earthy, dirty (Chemisis, 1968).

(K.8) 1*H*-Pyrrole, 1-pentyl-, *1-pentylpyrrole, N-n*-amylpyrrole [699-22-9]

Identified by Bondarovich *et al.* (1967), Vitzthum and Werkhoff (1976b), and Baltes and Bochmann (1987a).

The latter authors did not find this compound in any of their reactions with serine/threonine/sucrose.

1-Pentylpyrrole is characterized by a green, fatty, somewhat rancid, flavor when added, at 1 ppm, to a sugar syrup (Winter *et al.*, 1976f). It is also described as having a tree moss, mushroom and garlic odor (Chemisis, 1962)

(K.9) 1*H*-Pyrrole, 2-pentyl-, *2-pentylpyrrole,* 2-amylpyrrole [1551-12-8]

Identified by Vitzthum and Werkhoff (1974b).

(K.10) 1*H*-Pyrrole, 1-(2-methylpropyl)-, *1-isobutylpyrrole, 1-(2-methylpropyl)pyrrole* [20884-13-3]

Identified by Tressl *et al.* (1981a) (MS data) who give a concentration of 340 ppb (see **K.2**). In the headspace of a brewed coffee, Shimoda and Shibamoto (1990a) found 'isobutylpyrrole', very probably the 1-isomer, representing 0.09% (GC) of the volatiles.

It has woody, chemical flavor (Chemisis, 1968).

(K.11) 1*H*-Pyrrole, 2-(2-methylpropyl)-, *2-isobutylpyrrole* [38954-30-2]

Identified by Vitzthum and Werkhoff (1974b).

(K.12) 1*H*-Pyrrole, 1-(2-methylbutyl)-, *1-(2-methylbutyl)pyrrole, 1-(*sec-*butyl)pyrrole, N*-(2-methylbutyl)pyrrole [13678-55-2]

Identified by Stoll *et al.* (1967). Tressl *et al.* (1981a) gave a concentration of 540 ppb.

This pyrrole was prepared (Stoll *et al.*, 1967) by reaction of 2-methylbutylamine on mucic (galactaric) acid according to a procedure described by Reichstein (1927).

It has a green, unpleasant flavor (Chemisis, 1963) and is characterized by a green, metallic taste when added at 1 ppm to a sugar syrup (Winter *et al.*, 1976f).

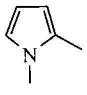
(K.13) 1*H*-Pyrrole, 1-(3-methylbutyl)-, *1-isopentylpyrrole, 1-(3-methylbutyl)pyrrole, N*-isoamylpyrrole [13679-79-3]

Identified by Stoll *et al.* (1967), Vitzthum and Werkhoff (1976b), and Tressl *et al.* (1981a) who found a concentration of 420 ppb (see **K.2**). As for 1-pentylpyrrole (**K.8**), Baltes and Bochmann

(1987b) found 1-isopentylpyrrole in coffee but not in any of the reactions with serine/threonine/sucrose.

Stoll *et al.* (1967) prepared it by reaction of 3-methylbutylamine on mucic (galactaric) acid, according to Reichstein (1927).

It is described with fatty, green, rancid flavor (Chemisis, 1963) and imparts an aldehyde-like flavor to a neutral soluble coffee at 0.2 ppm (Winter *et al.*, 1976f).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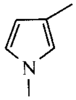
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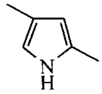
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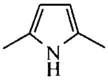
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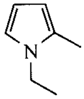
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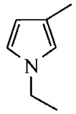
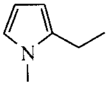

(K·19)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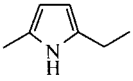
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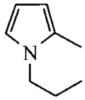
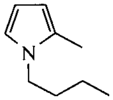

(K·22)


(K·23)

(K.14) 1*H*-Pyrrole, 1,2-dimethyl-, *1,2-dimethylpyrrole* [600-29-3]

Identified by Merritt *et al.* (1970). Tressl *et al.* (1981a) gave a concentration of 340 ppb in a roasted robusta (see **K.2**).

Baltes and Bochmann (1987b) found it in coffee and in reactions with threonine/sucrose or serine and threonine with or without sucrose.

The flavor is described as chemical, weak (Chemisis, 1964).

(K.15) 1*H*-Pyrrole, 1,3-dimethyl-, *1,3-dimethylpyrrole* [10524-65-9]

Identified by Tressl *et al.* (1981a) (MS data) who found a concentration of 940 ppb (see **K.2**) and by Baltes and Bochmann (1987b).

(K.16) 1*H*-Pyrrole, 2,4-dimethyl-, *2,4-dimethylpyrrole* [625-82-1]

Identified by Vitzthum and Werkhoff (1974b).

It was found by Baltes and Bochmann (1987b) when heating serine and threonine, sucrose being deficient or absent, but they did not characterize it in coffee.

(K.17) 1*H*-Pyrrole, 2,5-dimethyl-, *2,5-dimethylpyrrole* [625-84-3]

Identified by Wang *et al.* (1983) (the authors stated that is had been previously identified, but the reference quoted gave other dimethyl isomers). In a Guatemala arabica, Procida *et al.* (1997) noted an increase with increasing roasting time, 23–28 min at 218 °C.

It was isolated among the pyrolysis products of trigonelline by Viani and Horman (1974).

(K.18) 1*H*-Pyrrole, 1-ethyl-2-methyl-, *1-ethyl-2-methylpyrrole* [19983-83-6]

Identified by Tressl *et al.* (1981a) (240 ppb, see **K.2**).

Similarly to **K.6** and **K.14**, it was found by Baltes and Bochmann (1987b) in coffee and upon heating threonine with sucrose and serine/threonine with or without sucrose.

(K.19) 1*H*-Pyrrole, 1-ethyl-3-methyl-, *1-ethyl-3-methylpyrrole* **[13028-51-8]**

Identified by Tressl *et al.* (1981a) (260 ppb, see **K.2**), and by Baltes and Bochmann (1987b).

(K.20) 1*H*-Pyrrole, 2-ethyl-1-methyl-, *2-ethyl-1-methylpyrrole* **[24037-61-4]**

Identified by Tressl *et al.* (1981a) (20 ppb, see **K.2**).

The flavor is described as balsamic, chemical, petroleum (Chemisis, 1985).

(K.21) 1*H*-Pyrrole, 2-ethyl-5-methyl-, *2-ethyl-5-methylpyrrole* **[765-94-6]**

Mentioned by Tressl *et al.* (1981a), but not as a new identification.

Obtained by Baltes and Bochmann (1987b) after heating serine and threonine without sucrose or with an excess of amino acids compared to sucrose.

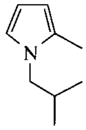
(K.22) 1*H*-Pyrrole, 2-methyl-1-propyl-, *2-methyl-1-propylpyrrole* **[24517-26-8]**

Identified by Tressl *et al.* (1981a) (90 ppb, see **K.2**).

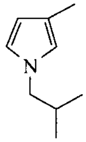
It was found by Baltes and Bochmann (1987b) in reactions of threonine with sucrose, serine/threonine in excess or without sucrose.

(K.23) 1*H*-Pyrrole, 2-methyl-1-(2-methylbutyl)-, *2-methyl-1-(2-methylbutyl)pyrrole, 1-(*sec*-butyl)-2-methylpyrrole* **[78368-65-7]**

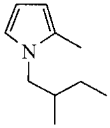
(180 ppb)



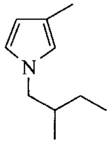
(K·24)



(K·25)



(K·26)



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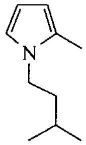
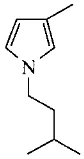


(K·28)



(K·29)

(K.24) 1*H*-Pyrrole, 2-methyl-1-(2-methylpropyl)-, *1-isobutyl-2-methylpyrrole, 2-methyl-1-(2-methylpropyl)pyrrole* **[78368-63-5]**

(80 ppb)

(K.25) 1*H*-Pyrrole, 3-methyl-1-(2-methylpropyl)-, *1-isobutyl-3-methylpyrrole, 3-methyl-1-(2-methylpropyl)pyrrole* **[78368-64-6]**

(25 ppb)

(K.26) 1*H*-Pyrrole, 2-methyl-1-(2-methylbutyl)-, *2-methyl-1-(2-methylbutyl)pyrrole, 1-(*sec*-butyl)-2-methylpyrrole* **[78368-65-7]**

(180 ppb)

(K.27) 1*H*-Pyrrole, 3-methyl-1-(2-methylbutyl)-, *3-methyl-1-(2-methylbutyl)pyrrole, 1-(*sec*-butyl)-3-methylpyrrole* **[78368-66-8]**

(20 ppb)

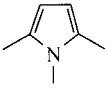
(K.28) 1*H*-Pyrrole, 2-methyl-1-(3-methylbutyl)-, *1-isopentyl-2-methylpyrrole, 2-methyl-1-(3-methylbutyl)pyrrole* **[78368-67-9]**

(215 ppb)

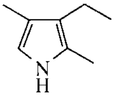
(K.29) 1*H*-Pyrrole, 3-methyl-1-(3-methylbutyl)-, *1-isopentyl-3-methylpyrrole, 3-methyl-1-(3-methylbutyl)pyrrole,* 1-isoamyl-3-methylpyrrole **[78368-68-0]**

(100 ppb)

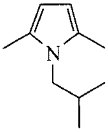
All were identified by Tressl *et al.* (1981a) in a robusta (see **K.2**), with the concentrations given.



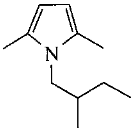
(K·30)



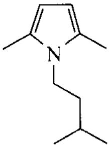
(K·31)



(K·32)



(K·33)



(K·34)

(K.30) 1*H*-Pyrrole, 1,2,5-trimethyl-, *1,2,5-trimethylpyrrole* **[930-87-0]**

Found by Tressl *et al.* (1981a) but not mentioned as a new identification.

(K.31) 1*H*-Pyrrole, 3-ethyl-2,4-dimethyl-, *3-ethyl-2,4-dimethylpyrrole* **[517-22-6]**

Identified by Vitzthum and Werkhoff (1974b).

(K.32) 1*H*-Pyrrole, 2,5-dimethyl-1-(2-methylpropyl)-, *1-isobutyl-2,5-dimethylpyrrole, 2,5-dimethyl-1-(2-methylpropyl)pyrrole* **[21407-84-1]**

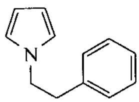
(30 ppb)

(K.33) 1*H*-Pyrrole, 2,5-dimethyl-1-(2-methylbutyl)-, *2,5-dimethyl-1-(2-methylbutyl)pyrrole, 1-(*sec-*butyl)-2,5-dimethylpyrrole* **[78368-69-1]**

(10 ppb)

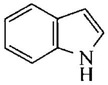
(K.34) 1*H*-Pyrrole, 2,5-dimethyl-1-(3-methylbutyl)-, *2,5-dimethyl-1-(3-methylbutyl)pyrrole, 1-isopentyl-2,5-dimethylpyrrole* **[78368-70-4]**

(10 ppb)

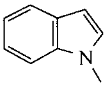


(K·35)

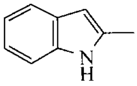
(K·36)



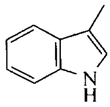
(K·37)
(K·37)



(K·38)



(K·39)



(K·40)

(K.35) 1*H*-Pyrrole, 1-(2-phenylethyl)-, *1-phenethylpyrrole, 1-(2-phenylethyl)pyrrole* **[50691-29-7]**

(10 ppb)

All were identified (see **K.2**) by Tressl *et al.* (1981a) with the concentrations given. For **K.32**, Silwar *et al.* (1987) found 50–150 ppb in arabica.

K.35 has a mushroom odor (Chemisis, 1973).

(K.36) Pyrrolidine, *pyrrolidine*, tetrahydropyrrole, azacyclopentane [123-75-1] *FEMA 3523*

Identified by Singer and Lijinsky (1976) who gave a concentration of 6 ppm. Neurath *et al.* (1977) gave concentrations of 7 to 11 ppm for two freeze-dried coffees and one coffee extract, after steam distillation and analysis of the trifluoroacetamides in the neutral fraction. The authors of the two publications were particularly looking for secondary amines in foodstuffs because of the potential carcinogenicity of the nitroso derivatives. Cros *et al.* (1980) identified pyrrolidine in the headspace of a roasted arabica.

Pyrrolidine has a penetrating amine-type odor, reminiscent of ammonia and piperidine, nauseating and diffusive, of very poor tenacity (Arctander, 1967). Ohloff and Flament (1979) mentioned that this amine accounted for the presence of fishy and fermented notes in numerous foodstuffs, for instance in caviar flavor. Flavor description is ripe, fruity, amines, chemical, bacon (Chemisis, 1999).

(K.37) *(K.37)* 1*H*-Indole, ***indole***, *1*H-*indole,* benzopyrrole [120-72-9] *FEMA 2593*

Identified by Vitzthum and Werkhoff (1974b). Silwar *et al.* (1987) gave a concentration of 0.30–0.80 ppm in an arabica. Silwar and Lüllmann (1993b) found (after 5 min at each temperature) 0.5 ppm at 170 °C and 2 at 260 °C in a robusta, with a twofold increase by over-roasting (from 230 to 260 °C). Lee *et al.* (1992) qualified indole as a 'slow extractor' (only 30–40 % extraction after rapid brewing conditions). Indole was identified in green coffee volatiles by Vitzthum *et al.* (1976), in green 'Rio' Puerto Rico and healthy reference by Spadone *et al.* (1990), in a green Mexican arabica by Cantergiani *et al.* (2001) (0.10 % of the volatiles, GC).

Viani and Horman (1976) found indole on roasting serotonin (hydroxytryptamine, 2-aminoethyl-1*H*-indol-5-ol), present as an amide in the waxes surrounding the coffee bean and which behaves like the related tryptophan. A pathway showing its formation in the thermal degradation of phenylalanine at 300 °C has been published by Kato *et al.* (1971).

Indole has an extremely diffusive and powerful odor, almost tarry-repulsive and choking when concentrated. In concentrations lower than 0.1 % or in compositions, it shows powerful floral notes and pleasant radiation (Arctander, 1967). For Kato *et al.* (1971), the odor is intense fecal.

(K.38) 1*H*-Indole, 1-methyl-, *1-methylindole* [603-76-9]

Identified by Tressl *et al.* (1981a) (not mentioned as first identification).

(K.39) 1*H*-Indole, 2-methyl-, *2-methylindole* [95-20-5]

Identified by Vitzthum and Werkhoff (1974b).

The odor is powerful and diffusive, yet very tenacious animal-indolic, fresher and not as repulsive as skatole. In fact, the animal notes of this isomer are rather attractive, not at all fecal (Arctander, 1967).

(K.40) 1*H*-Indole, 3-methyl-, *3-methylindole*, scatole, skatole [83-34-1] *FEMA 3019*

Identified by Silwar (1982). Silwar *et al.* (1987) found 0.10–0.15 ppm in an arabica. As for indole (**K.37**), Silwar and Lüllmann (1993b) noted an increase with increasing temperature, 0.02 ppm at 170 °C, to 0.15 at 230 and 0.3 at 260 °C.

It is formed in the pyrolysis of tryptophan (Kato *et al.*, 1971), in the roasting of serotonin (Viani and Horman, 1976) (see **K.37**).

The odor is very powerful and diffusive, also extremely tenacious, in high concentration repulsively unpleasant, only in very low concentration pleasant, sweet, warm, animal, with a note of over-ripe fruit (Arctander, 1967).

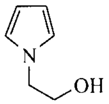
1*H*-Indole, 2,3-dihydro-, *indoline* **[496–15–1]**

Tentatively identified in roasted coffee and coffee extract by Elsmore and Nursten (1990).

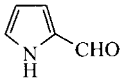
1*H*-Indole, 2,3-dihydro-1-methyl, *1-methylindoline* **[824–21–5]**

Tentatively identified in green coffee by Vitzthum *et al.* (1976).

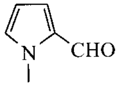
Pyrroles with alcohol or aldehyde function



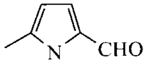
(K.41)



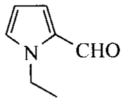
(K.42)



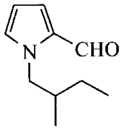
(K.43)



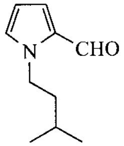
(K.44)



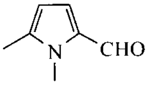
(K.45)



(K.46)



(K.47)



(K.48)

(K.41) 1*H*-Pyrrole-1-ethanol, *2-(pyrrol-1-yl)-1-ethanol* **[6719-02-4]**

Identified by Baltes and Bochmann (1987e), who proposed serine as precursor, the same product being formed by reaction between serine and sucrose under the conditions of coffee roasting.

(K.42) 1*H*-Pyrrole-2-carboxaldehyde, *pyrrole-2-carbaldehyde,* pyrrolealdehyde, 2-formylpyrrole **[1003-29-8]**

Identified by Gianturco *et al.* (1964b), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b). Silwar *et al.* (1987) found 1.3–1.5 ppm in roasted arabica. Lee *et al.* (1992) qualified it as 'fast extractor' (70–80% after rapid brewing conditions, compare with **K.37**)

It has been found in a glyoxal/glycine model system by Velisek *et al.* (1976), in the reaction of L-rhamnose with ammonia by Shibamoto and Bernhard (1978), of glutamine with ribose by Ho and Chen (1999). Baltes and Bochmann (1987b) did not find the aldehyde when heating serine and threonine without sucrose.

Pyrrole-2-carbaldehyde has a corny, pungent odor (Shibamoto, 1977).

(K.43) 1*H*-Pyrrole-2-carboxaldehyde,1-methyl-, *1-methylpyrrole-2-carbaldehyde, N*-methyl pyrrolealdehyde, 2-formyl-1-methylpyrrole **[1192-58-1]**

Identified by Gianturco *et al.* (1964b), Stoffelsma *et al.* (1968), and Vitzthum and Werkhoff (1976b). Tressl *et al.* (1981a) found 8.5 ppm in a robusta, Silwar *et al.* (1987) 1.15–1.30 ppm in an arabica. It is present in the headspace of a brew analyzed by Shimoda and Shibamoto (1990a) (0.07%, GC), in the headspace of a ground roasted Columbian coffee (as the only pyrrole identified, 1.14 ppm) by Ho *et al.* (1993), in the headspace of a freshly ground Guatemala arabica by Procida *et al.* (1997), the concentration slightly increasing with roasting time. It is a 'fast extractor' for Lee *et al.* (1992) like the lower homolog **K.42**, and was also identified in a brew after liquid–liquid extraction by Ramos *et al.* (1998).

1-Methylpyrrole is one of the four pyrroles isolated in the pyrolysis of trigonelline by Viani and Horman (1974). It was also formed by heating D-xylose with methylamine (Kato, 1966), from a cysteine/cystine ribose browning system (Mulders, 1973c). Kato and Fujimaki (1968) observed the formation of *N*-substituted pyrrole-2-carbaldehydes when D-xylose reacted thermally with various amines or amino acids (glycine, alanine, β-alanine, leucine). The intermediate 3,4-dideoxypentosulos-3-ene would either give 2-furaldehyde (mainly with α-amino acids) or substituted pyrrole-2-carbaldehydes and melanoidins (with β-alanine or other amines).

The product has been synthesized by Reichstein (1930a) by formylation of 1-methylpyrrole.

The flavor is weak, chemical (Chemisis, 1963). It has a cracker-popcorn like aroma character according to Buttery (1999) who gave a threshold in water of 37 ppb, ca 4500 times lower than that of 2-acetylpyrrole (**K.50**).

(K.44) 1*H*-Pyrrole-2-carboxaldehyde, 5-methyl-, *5-methylpyrrole-2-carbaldehyde*, 5-methyl pyrrolealdehyde, 2-formyl-5-methylpyrrole [1192-79-6]

Identified by Gianturco *et al.* (1964b), and Stoffelsma *et al.* (1968). Silwar *et al.* (1987) found 0.6–0.7 ppm in an arabica. Like **K.42** and **K.43**, it is a 'fast extractor' for Lee *et al.* (1992). It was also identified in a brew after solid-phase microextraction by Ramos *et al.* (1998) (compare with **K.43**).

It was isolated among the pyrolysis products of trigonelline by Viani and Horman (1974). Shibamoto *et al.* (1979) identified it in a D-glucose/ammonia model system and Shaw and Berry (1977) in a fructose/alanine degradation study. The latter authors proposed a formation mechanism through a hexosulos-3-ene resulting from the sugar, followed by a Strecker degradation and a cyclization reaction. Baltes and Bochmann (1987b) identified this aldehyde in coffee and when heating serine and/or threonine with (not without) sucrose.

This aldehyde was described by Shibamoto (1977) as having a pungent odor. It contributes to the off-flavors formed in dehydrated instant orange juice during storage at ambient temperature.

(K.45) 1*H*-Pyrrole-2-carboxaldehyde, 1-ethyl-, *1-ethylpyrrole-2-carbaldehyde*, *N*-ethyl-2-pyrrolecarbaldehyde, 1-ethylpyrrole-2-aldehyde, 1-ethyl-2-formylpyrrole [2167-14-8]

Identified by Stoll *et al.* (1967) (MS data), Stoffelsma *et al.* (1968), Vitzthum and Werkhoff (1976b), and Silwar *et al.* (1987) who found 0.5–0.6 ppm in an arabica.

It was prepared by a Vilsmeier formylation of 1-ethylpyrrole (Stoll *et al.*, 1967).

The flavor description is burnt, roasted (Winter *et al.*, 1976f).

(K.46) 1*H*-Pyrrole-2-carboxaldehyde, 1-(2-methylbutyl)-, *1-(2-methylbutyl)pyrrole-2-carbaldehyde*, *1-(sec-butyl)pyrrole-2-carbaldehyde*, 1-α-methylbutylpyrrole-2-aldehyde [13678-71-2]

Identified by Stoll *et al.* (1967) and prepared by formylation of the corresponding alkylpyrrole (IR and MS data).

This colorless liquid has a green odor and is characterized by a slightly minty flavor when tasted at a concentration of 10 ppm in a sugar syrup (Winter *et al.*, 1976f).

(K.47) 1*H*-Pyrrole-2-carboxaldehyde, 1-(3-methylbutyl)-, *1-(3-methylbutyl)pyrrole-2-carbaldehyde, 1-isopentylpyrrole-2-carbaldehyde*, *N*-isoamyl-2-pyrrolecarbaldehyde, 1-isoamyl-2-formylpyrrole **[13678-79-0]**

Identified by Stoll *et al.* (1967) (IR, MS data).

This liquid, which has a 'green' odor, was previously synthesized by Reichstein (1930a) by formylation of *N*-isopentylpyrrole (**K.13**).

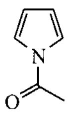
The flavor is a fatty, heavy, oily, flowery at 10 ppm in a sugar syrup (Winter *et al.*, 1976f), the odor is reminiscent of coffee and is somewhat rosy and cuminic.

(K.48) 1*H*-Pyrrole-2-carboxaldehyde, 1,5 dimethyl-, *1,5-dimethylpyrrole-2-carbaldehyde*, 2-formyl-1,5-dimethylpyrrole **[1193-59-5]**

Identified by Gianturco *et al.* (1964b).

It has a weak, almond, pistachio flavor (Chemisis, 1964).

Pyrroles with ketone function(s)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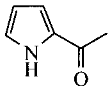
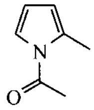

(K-50)
(K-50)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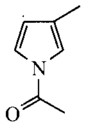
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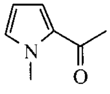
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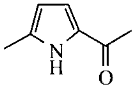
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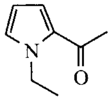
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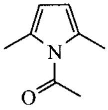
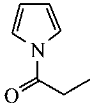

(K-56)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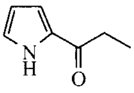
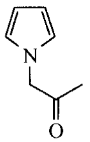

(K-58)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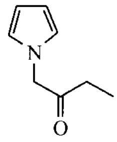

(K-60)

(K.49) 1*H*-Pyrrole, 1-acetyl-, *1-acetylpyrrole, 1-(pyrrol-1-yl)ethanone*, *N*-acetylpyrrole **[609-41-6]**

Identified by Vitzthum and Werkhoff (1976b) (MS data) being, together with the compounds **K.51** and **K.57**, one of the first *N*-acylpyrroles identified in coffee flavor.

The authors confirmed the structure by heating equimolecular amounts of pyrrole and *N*-acetylimidazole. It was identified by Kobayasi and Fujimaki (1965b) when hydroxyproline and glucose were heated at temperatures ranging from 120 to 200 °C.

1-Acetylpyrrole is characterized by an astringent, bitter, roasted flavor (Winter *et al.*, 1976f).

(K.50) ***(K.50)*** **Ethanone, 1-(1*H*-pyrrol-2-yl)-**, *1-(pyrrol-2-yl)ethanone, methyl pyrrol-2-yl ketone*, 2-acetylpyrrole **[1072-83-9]** ***FEMA 3202***

Identified by Gianturco *et al.* (1964b), Viani *et al.* (1965), Vitzthum and Werkhoff (1976b), and Silwar *et al.* (1987) who found 1.5–1.8 ppm in an arabica, and by Ramos *et al.* (1998) after liquid–liquid extraction of a brew with pentane. It was identified in green coffee volatiles by Vitzthum *et al.* (1976).

It has been identified when heating glucose or lactose with glycine, lysine, valine, or casein (Langner and Tobias, 1967), when heating DL-α-alanine and D-glucose for 1 h at 250 °C (Shigematsu *et al.*, 1972), from a lysine/lactose browning system (Ferretti and Flanagan, 1973), from a cysteine/cystine ribose browning system (Mulders, 1973c), from fructose/alanine or γ-aminobutyric degradation reactions (Shaw and Berry, 1977). The latter authors proposed a scheme of formation through a Strecker reaction of alanine with a 3-deoxyosulose derivative of fructose. Other models involve L-rhamnose/ammonia (Shibamoto and Bernhard, 1978), or D-glucose/ammonia (Shibamoto *et al.*, 1979). Baltes and Bochmann (1987b) identified 2-acetylpyrrole when heating serine and/or threonine with sucrose (as well as in coffee).

Watanabe and Sato (1972) observed that this product adds a slightly caramel-like character to the flavor of cooked beef, but Peterson *et al.* (1975), on the contrary, considered that it confered to canned beef stew an unpleasant antiseptic-like aroma, reminiscent of plastic. Buttery (1999) compared several 2-acyl nitrogen-containing heterocycles with a cracker, popcorn-like aroma character: 2-acetylpyrrole is the less potent with a threshold of 170 ppm in water (the 3,4-dihydro-2*H*-pyrrolyl derivative has a threshold of 0.1 ppb and the pyridyl derivative, **N.22**, of 19 ppb).

(K.51) 1*H*-Pyrrole, 1-acetyl-2-methyl-, *1-acetyl-2-methylpyrrole, N*-acetyl-2-methylpyrrole **[38207-11-3]**

Identified by Vitzthum and Werkhoff (1976b), who synthesized it for the first time by treating 2-methylpyrrole (**K.3**) with *N*-acetylimidazole and confirmed the structure by NMR spectroscopy. An MS fragmentation pathway is proposed.

(K.52) 1*H*-Pyrrole, 1-acetyl-3-methyl-, *1-acetyl-3-methylpyrrole, N*-acetyl-3-methylpyrrole **[823-75-6]**

Identified after liquid–liquid extraction of a brew with methylene chloride by Ramos *et al.* (1998) (compare with **K.50** and **K.53**).

(K.53) Ethanone, 1-(1-methyl-1*H*-pyrrol-2-yl)-, *1-(1-methylpyrrol-2-yl)ethanone, methyl 1-methylpyrrol-2-yl ketone*, 2-acetyl-1-methylpyrrole **[932-16-1]** ***FEMA 3184***

Identified by Gianturco *et al.* (1964b), Stoffelsma *et al.* (1968), Tressl *et al.* (1981a) (2.6 ppm in a robusta, see **K.2**), Silwar *et al.* (1987) (1.80–2.10 ppm in arabica), and Ramos *et al.* (1998) after liquid–liquid extraction of a brew with pentane.

Ferretti and Flanagan (1971a) found it in a lactose/casein browning system, Shibamoto *et al.* (1979) in a D-glucose/ammonia model system, Baltes and Bochmann (1987b) in serine/threonine/sucrose systems (and in coffee).

The flavor is described as nutty, floral, fruity, even smoky, musty (Chemisis, 1999).

(K.54) Ethanone, 1-(5-methyl-1*H*-pyrrol-2-yl)-, *1-(5-methylpyrrol-2-yl)ethanone, methyl 5-methylpyrrol-2-yl ketone*, 2-acetyl-5-methylpyrrole **[6982-72-5]**

Identified by Vitzthum and Werkhoff (1976b), and Silwar *et al.* (1987) who found 0.2–0.3 ppm in arabica.

It was identified by Baltes and Bochmann (1987b) in coffee and after heating serine and threonine with an equimolar amount of sucrose.

Vitzthum and Werkhoff prepared it by acetylation of 2-methylpyrrole.

The flavor is bitter, earthy, roasted (Winter *et al.*, 1976f).

Ethanone, 1-(3/4-methyl-1*H*-pyrrol-2-yl)-, 2-acetyl-3/4-methylpyrrole

Found by Baltes and Bochmann in coffee (1987e) and, like **K.50**, in the reactions of serine and/or threonine with an equimolar amount of sucrose (1987b).

(K.55) Ethanone, 1-(1-ethyl-1*H*-pyrrol-2-yl)-, *1-(1-ethylpyrrol-2-yl)ethanone, 1-ethylpyrrol-2-yl methyl ketone*, 2-acetyl-1-ethylpyrrole **[39741-41-8]** ***FEMA 3147***

Identified by Stoffelsma and Pypker (1968), and Stoffelsma *et al.* (1968).

Kato *et al.* (1972) have shown that it is formed in a Maillard reaction of L-rhamnose with ethylamine, the most abundant product being Furaneol ® (**I.100**). The proposed formation pathway involves a 1,2-enaminol of L-rhamnose.

The flavor is described as earthy, woody, dusty (Chemisis, 1999).

(K.56) 1 *H*-Pyrrole, 1-acetyl-2,5-dimethyl-, *1-acetyl-2,5-dimethylpyrrole* **[5044-31-5]**

Identified by Baltes and Bochmann (1987e) (MS data).

(K.57) 1*H*-Pyrrole, 1-(1-oxopropyl)-, *1-propanoylpyrrole, 1-propionylpyrrole, 1-(pyrrol-1-yl)propan-1-one, N*-propionylpyrrole **[59303-16-1]**

Identified by Vitzthum and Werkhoff (1976b).

These authors synthesized it for the first time by treatment of pyrrole with *N*-propanoylimidazole.

It is characterized by an astringent, peanut, roasted flavor (Winter *et al.*, 1976f).

(K.58) 1-Propanone, 1-(1*H*-pyrrol-2-yl)-, *1-(pyrrol-2-yl)propan-1-one*, 2-propanoylpyrrole, 2-propionylpyrrole **[1073-26-3]** ***FEMA 3614***

Identified by Gianturco *et al.* (1964b).

It was found by Baltes and Bochmann (1987b) in coffee and in model reactions involving serine and/or threonine with sucrose.

It is described with weak, fruity, caramel flavor (Chemisis, 1966).

(K.59) 2-Propanone, 1-(1*H*-pyrrol-1-yl)-, *1-(pyrrol-1-yl)propan-2-one*, 1-(1*H*-pyrrol-1-yl)acetone, 1-acetonylpyrrole **[4805-24-7]**

Identified by Tressl *et al.* (1981a) who found 1.3 ppm in a robusta (see **K.2**), and Silwar *et al.* (1987) who found 0.40–0.55 ppm in arabica.

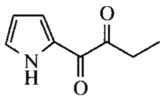
According to Kobayasi and Fujimaki (1965b), who identified it among the reaction products of hydroxyproline and glucose, it can be formed by reaction of 4-hydroxyproline with pyruvaldehyde derived from aldol cleavage of 3-deoxyglucosone, itself formed by dehydration of glucose. Baltes and Bochmann (1987b) found it when heating serine and/or threonine with sucrose (as well as in coffee).

Tressl (1979c) described this compound as bready and green and giving an odor threshold of 10 ppb in water.

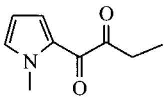
(K.60) 2-Butanone, 1-(1*H*-pyrrol-1-yl)-, *1-(pyrrol-1-yl)butan-2-one*, 1-(2-butanoyl)pyrrole (this last name is really incorrect, the suffix -oyl being used only for RCO-, directly derived from the corresponding acid) **[98612-19-2]**

Identified by Tressl *et al.* (1981a) (0.3 ppm in a robusta, see **K.2**), and Silwar *et al.* (1987) (0.15–0.20 ppm in arabica).

It is identified by Baltes and Bochmann (1987b) in coffee and after heating serine and/or threonine with an equimolar amount of sucrose (like **K.54**).



(K.61)



(K.62)

(K.61) 1,2-Butanedione, 1-(1*H*-pyrrol-2-yl)-, *1-(pyrrol-2-yl)butane-1,2-dione*, 2-(1,2-dioxobutyl)pyrrole **[13678-77-8]**

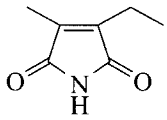
Identified by Stoll *et al.* (1967) who prepared it by acid hydrolysis of the oximinoketone obtained from 1-(pyrrol-2-yl)butan-1-one (2-butanoylpyrrole); MS and IR data are given.

The flavor is burnt sugar, fruity, cheesy (Chemisis, 1967). At a concentration of 10 ppm, it imparts a buttery, meaty flavor to a neutral soluble coffee base (Winter *et al.*, 1976f).

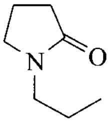
(K.62) 1,2-Butanedione, 1-(1-methyl-1*H*-pyrrol-2-yl)-, *1-(1-methylpyrrol-2-yl)butane-1,2-dione*

Identified by Gautschi *et al.* (1968) in a coffee aroma.

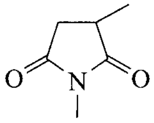
Pyrrolones, pyrolediones



(K.63)



(K.64)



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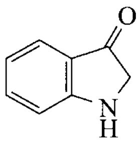


(K.66)

(K.63) ***1H*-Pyrrole-2,5-dione, 3-ethyl-4-methyl-**, *3-ethyl-2,5-dihydro-4-methylpyrrole-2,5-dione*, 2-ethyl-3-methylmaleimide **[20189-42-8]**

Identified by Cantergiani *et al.* (2001) in a green Mexican arabica after vacuum hydrodistillation and extraction (0.08 %, GC on a polar column).

(K.64) 2-Pyrrolidinone, 1-propyl-, *1-propyl-2-pyrrolidone, 1-propylpyrrolidin-2-one* **[3470-99-3]**

Identified in a brew by Lee *et al.* (1992), considered as a 'slow extractor' (see **K.37**).

(K.65) 2,5-Pyrrolidinedione, 1,3-dimethyl-, *1,3-dimethylpyrrolidine-2,5-dione*, *N*-2-dimethylsuccinimide, *N*-α-dimethylsuccinimide **[15542-96-8]**

Identified by Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968).

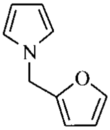
Proline (pyrrolidine-2-carboxylic acid) and related compounds are considered as amino acids (see Section 2.1.1.3).

(K.66) 3*H*-Indol-3-one, 1,2-dihydro-, *1,2-dihydro-3*H*-indol-3-one*, '3-oxoindole' (this name is incorrect, it could correspond to 3*H*-indol-3-one, C_8H_5NO, but in the review of Vitzthum (1976) 3-oxoindole is given with C_8H_7NO) **[67285-12-5]**

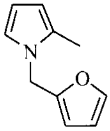
Identified by Vitzthum and Werkhoff (1974b).

Furfurylpyrroles

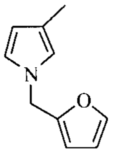
Shigematsu *et al.* (1972) considered that furfurylpyrroles could originate from the condensation of alkylfurans and alkylpyrroles.



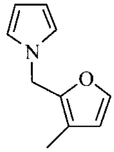
(K.67)



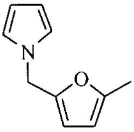
(K.68)



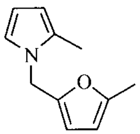
(K.69)



(K.70)



(K.71)



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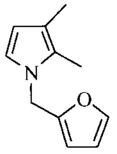
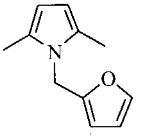
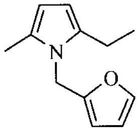


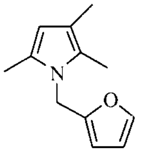
(K.73)



(K.74)



(K.75)



(K.76)

(K.67) 1*H*-Pyrrole, 1-(2-furanylmethyl)-, *1-furfurylpyrrole, 1-(2-furylmethyl)pyrrole,* *N*-furfurylpyrrole, *N*-(2′-furfuryl)pyrrole, 1-(2-furfuryl)pyrrole (furfuryl being used by IUPAC only for 2-furylmethyl, the figure can bring complication and confusion) **[1438-94-4]** ***FEMA 3284***

Identified by Reichstein and Staudinger (1926b), and Vitzthum and Werkhoff (1976b). According to Gianturco *et al.* (1964a), the concentration in a commercial blend of roasted coffee was 1.0 ppm, 2.0 ppm for Stofberg and Stoffelsma (1981), 2.2 ppm in a robusta (see **K.2**) for Tressl *et al.* (1981a), the concentration being constant during aging (1981c). Lee *et al.* (1992) qualified it as 'fast extractor' (see **K.42–44**). Among the extracted products from a brew, Ramos *et al.* (1998) listed this pyrrole under two names, *Chemical Abstracts* and IUPAC, identified in two different types of extracts and only very slightly different retention times (in this publication, the nomenclature differs several times for similar structures)!

Mulders (1973c) identified 1-furfurylpyrrole in a cysteine/cystine ribose browning system, Shibamoto *et al.* (1979) in a D-glucose/ammonia model system, Ho and Chen (1999) in a Maillard reaction of threonine with ribose as a main volatile product, Baltes and Bochmann (1987b) when heating serine and/or threonine with sucrose (and in coffee). According to Tressl *et al.* (1981c), this compound was also formed from 4-hydroxyproline and 2-furaldehyde.

It was synthesized by Reichstein (1930a) by dry distillation of saccharic (glucaric) acid in presence of furfurylamine, a synthesis considered as equivocal by Gianturco *et al.* (1964a) who nevertheless confirmed the structure by elemental analysis, retention time, MS and IR spectra.

The odor is green, hay-like (Walradt *et al.*, 1970), (Baltes, 1980), pleasant green, mushroom-like (Tressl *et al.*, 1981a).

(K.68) 1*H*-Pyrrole, 1-[(2-furanyl)methyl]-2-methyl-, *1-furfuryl-2-methylpyrrole* **[1438-95-5]**

Identified for the first time by Vitzthum and Werkhoff (1976b) who published the NMR spectrum and proposed a fragmentation pathway for the MS spectrum. Tressl *et al.* (1981a) found 270 ppb in a robusta (see **K.2**) and noted (1981c) a neat increase in the concentration with aging of roasted coffee, from ca 0.1 ppm after seven days to ca 0.7 ppm after 39 days.

Vitzthum and Werkhoff synthesized this new compound from 2-methylfuran (silvan I.2), by action of bromine and methanol, then hydrogenation leading to tetrahydro-2,5-dimethoxy-2-methylfuran which then reacts with furfurylamine.

(K.69) 1*H*-Pyrrole, 1-[(2-furanyl)methyl]-3-methyl-, *1-furfuryl-3-methylpyrrole* **[78368-71-5]**

(K.70) 1*H*-Pyrrole, 1-[(3-methyl-2-furanyl)methyl]-, *1-(3-methylfurfury)pyrrole* **[78368-72-6]**

These were identified by Tressl *et al.* (1981a), with 50 and 10 ppb respectively in a robusta (see **K.2**).

(K.71) 1*H*-Pyrrole, 1-[(5-methyl-2-furanyl)methyl]-, *1-(5-methylfurfuryl)pyrrole*, *N*-(2′-furfuryl-5′-methyl)pyrrole **[13678-52-9]**

Identified by Stoll *et al.* (1967), Stoffelsma *et al.* (1968), Vitzthum and Werkhoff (1976b), and Tressl *et al.* (1981a) who found 550 ppb in a robusta (see **K.2**), or (1981c) ca 150 ppb, with a slight increase to ca 200 ppb with coffee aging.

The latter authors also found it in reaction of 4-hydroxyproline with glucose and suggested the formation in coffee from 4-hydroxyproline and 5-methyl-2-furaldehyde. Shigematsu *et al.* (1972) identified it in the roasting of alanine with D-glucose, Shibamoto *et al.* (1979) in a D-glucose/ammonia model system, Baltes and Bochmann (1987b) in serine and/or threonine/sucrose systems (and in coffee).

Stoll *et al.* (1967) synthesized this pyrrole by reaction of 2,5-diethoxytetrahydrofuran with 5-methylfurfurylamine (MS, IR data).

The taste is fruity when the compound is incorporated at 20 ppm in a sugar syrup, and earthy, mushroom like in a neutral soluble coffee beverage (Winter *et al.*, 1976f). The odor threshold given by Tressl *et al.* (1981a) was 10 ppb in water, with a pleasant green, mushroom-like odor, like 1-furfurylpyrrole (**K.67**).

(K.72) 1*H*-Pyrrole, 2-methyl-1-[(5-methyl-2-furanyl)methyl]-, *2-methyl-1-(5-methylfurfuryl)pyrrole* **[78368-73-7]**

(10 ppb)

(K.73) 1*H*-Pyrrole, 1-[(2-furanyl)methyl]-2,3-dimethyl-, *1-furfuryl-2,3-dimethylpyrrole* **[78368-74-8]**

(50 ppb)

(K.74) 1*H*-Pyrrole, 1-[(2-furanyl)methyl]-2,5-dimethyl-, *1-furfuryl-2,5-dimethylpyrrole* **[5049-47-8]**

(10 ppb)

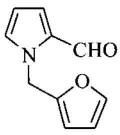
(K.75) 1*H*-Pyrrole, 2-ethyl-1-[(2-furanyl)methyl]-5-methyl-, *2-ethyl-1-furfuryl-5-methylpyrrole* **[78368-75-9]**

(10 ppb)

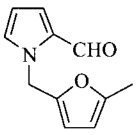
(K.76) 1*H*-Pyrrole, 1-[(2-furanyl)methyl]-2,3,5-trimethyl-, *1-furfuryl-2,3,5-trimethylpyrrole* **[78368-76-0]**

(10 ppb)

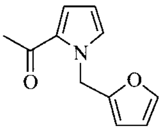
These were identified by Tressl *et al.* (1981a) in a robusta (see **K.2**) with the concentrations given.



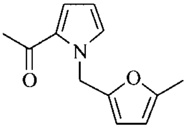
(K·77)



(K·78)



(K·79)



(K·80)

(K.77) 1*H*-Pyrrole-2-carboxaldehyde, 1-(2-furanylmethyl)-, *1-furfurylpyrrole-2-carbaldehyde*, 1-furfuryl-2-formylpyrrole **[13788-32-4]**

Identified by Stoll *et al.* (1967), and Tressl *et al.* (1981a) who found 3.4 ppm in a robusta (see **K.2**), Silwar *et al.* (1987) 2.5–3 ppm in an arabica.

Shibamoto *et al.* (1979) identified it in a D-glucose–ammonia model system and Baltes and Bochmann (1987b) after heating serine and/or threonine with an equimolar amount of sucrose (as well as in coffee).

Stoll *et al.* (1967) prepared this compound by a Vilsmeier formylation of 1-furfurylpyrrole (**K.67**) (Reichstein, 1930a).

The odor is green, minty (Stoll *et al.*, 1967) and the flavor burnt, acid (Winter *et al.*, 1976f).

(K.78) 1*H*-Pyrrole-2-carboxaldehyde, 1-[(5-methyl-2-furanyl)methyl]-, *1-(5-methylfurfuryl)pyrrole-2-carbaldehyde*, 1-(5-methylfurfuryl)-2-formylpyrrole **[78368-77-1]**

Identified by Tressl *et al.* (1981a) (0.3 ppm in a robusta, see **K.2**), and Silwar *et al.* (1987) (0.10–0.15 ppm in an arabica).

(K.79) Ethanone, 1-[1-(2-furanylmethyl)-1*H*-pyrrol-2-yl]-, *1-(1-furfurylpyrrol-2-yl)ethanone*, 2-acetyl-1-furfurylpyrrole **[13678-73-4]**

Identified and synthesized by Stoll *et al.* (1967), by Tressl *et al.* (1981a) who found 0.6 ppm in a robusta (see **K.2**), and by Silwar *et al.* (1987) who found 2.3–2.5 ppm in an arabica.

Baltes and Bochmann (1987b) identified it in coffee and in their model reactions involving serine and/or threonine with equimolar amounts of sucrose.

Stoll *et al.* (1967) prepared it by acetylation of 1-furfurylpyrrole (**K.67**) (IR, MS data).

The flavor is fruity, roselike when the compound is incorporated at 20 ppm to a sugar syrup (Winter *et al.*, 1976f).

(K.80) Ethanone, 1-{1-[(5-methyl-2-furanyl)methyl]-1*H*-pyrrol-2-yl}-, *1-[1-(5-methylfurfuryl)pyrrol-2-yl]ethanone*, *N*-(5-methylfurfuryl)-2-acetylpyrrole **[145209-09-2]**

Identified by Tressl *et al.* (1981a) with a concentration of 50 ppb in a robusta (see **K.2**. Silwar *et al.* (1987) found 0.10–0.15 ppm in an arabica. (In the two publications, the 5-is forgotten in the name in the table, but from the text it is obvious that it is the 5-methyl isomer).

Other compounds containing a pyrrole ring are present in Section 5.O (pyrazines).

5.L OXAZOLES

An exhaustive review on the chemistry of oxazoles has been published by Wiley (1945). The author described the methods of preparation, the physical and chemical properties and the structures of this class of compounds which can be considered as genetically related to natural products, as they can be prepared from α-amino acids and proteins. Karrer and Gränacher (1924) and Karrer *et al.* (1925) speculated that oxazole units may actually form a part of the protein molecule by the possible dehydration of a segment of a polypeptide chain. They also observed that oxazoles resembled the furans which could be prepared from the pentosans. Both are aromatic compounds and show typical aromatic properties. Oxazoles bear also some resemblance to the pyridines with a comparable ring nitrogen.

The first synthesis of an oxazole had already been achieved in 1840 by Zinin by the reaction of benzil with alcoholic ammonia, but the corresponding structure, 2,4,5-triphenyloxazole, was only elucidated 40 years later by Japp (1882, 1883). The name 'oxazole' for the ring was proposed by Hantzsch (1888). The direct formation of an oxazole by a trimolecular reaction (benzaldehyde certainly being formed and/or present in Zinin's reaction mixture), indicated that most of the oxazoles identified in coffee result mainly, during roasting, from the combination of three building blocks: (i) a dicarbonyl or an hydroxyketone at the origin of the oxygen ring atom and of the carbons in positions 4 and 5, (ii) a residual amine function from an amino acid (or free ammonia) at the origin of the ring-nitrogen atom, and (iii) an aldehyde, generally resulting from a Strecker degradation, that will close the ring and introduce the carbon atom in the 2-position. Other reviews on the chemistry of oxazoles are due to Turchi and Dewar (1975) and Turchi (1981).

The first member of this class identified in a coffee flavor, and even in food, was 5-acetyl-2-methyloxazole (**L.23**) found by Stoffelsma and Pypker (1968) and Stoffelsma *et al.* (1968) but without mention of a reference compound. An intensive study on the presence of oxazoles in coffee aroma was conducted somewhat later by Vitzthum and Werkhoff (1974a,b). A coffee extract was obtained by steam distillation, enriched by adsorption/desorption and extracted with dilute hydrochloric acid. The compounds in this basic fraction were identified by classical GC/MS combination, among them 20 oxazoles in concentrations of the order of 1–10 ppb. The reference standards were prepared or purchased and their NMR spectra were measured.

Oxazoles, but no oxazoline, have been found in coffee. Both structures occur in various other foods (essentially in heated, boiled or roasted products such as cocoa, meat, soy sauce or barley) and in model systems as mentioned in the reviews of Maga (1978c, 1981a). Besides the analytical work conducted on coffee, Vitzthum *et al.* (1975) identified four alkyloxazoles in cocoa flavor. Trimethyloxazole and oxazolines have also been identified in meat products: cooked pork liver (Mussinan and Walradt, 1974), canned beef stew (Peterson *et al.*, 1975), boiled beef (Chang *et al.*, 1977) and other heated products: roasted barley (Harding *et al.*, 1978), baked potatoes (Coleman *et al.*, 1981), roasted peanuts (Lee *et al.*, 1981). Twenty-four alkyloxazoles have subsequently been identified in the volatile compounds from French-fried potatoes (Carlin *et al.*, 1986), seven being also present in coffee.

As many oxazolines (but only one oxazole, trimethyloxazole, **L.11**) were identified in beef systems, always heated at lower temperatures than those used for coffee roasting, it seems reasonable to consider them as intermediates in oxazole formation. Hirai *et al.* (1973) and Peterson *et al.* (1975) actually observed that the peak area for 2,4,5-trimethyl-3-oxazoline is large to very large in boiled beef extracts. The work of Jassmann and Schulz (1963) had previously shown that this 2,4,5-trimethyl-3-oxazoline results from thermal interaction of ammonia, acetaldehyde and acetoin, all compounds that have been reported to be present in cooked beef, as well as in coffee volatiles.

According to Carlin *et al.* (1986), the exact mechanism of oxazole formation is not known, despite the previous schemes proposed by Vitzthum and Werkhoff (1974a,b) and by Ohloff and Flament (1978). Formation pathways were proposed by Baltes and Bochmann (1987d) and Mottram (1991). For Vitzthum and Werkhoff (1974b), one pathway could be the decarboxylation of serine or threonine into ethanolamine or methylethanolamine; condensation with an aldehydic compound into an oxazolidine, then oxidation into an oxazole unsubstituted or methylated on position 5 and bearing an alkyl or an acyl radical on position 2. Another pathway could be the condensation of amino acids with α-dicarbonyl compounds, followed by a Strecker degradation, formation of an α-amino ketone which, after acylation

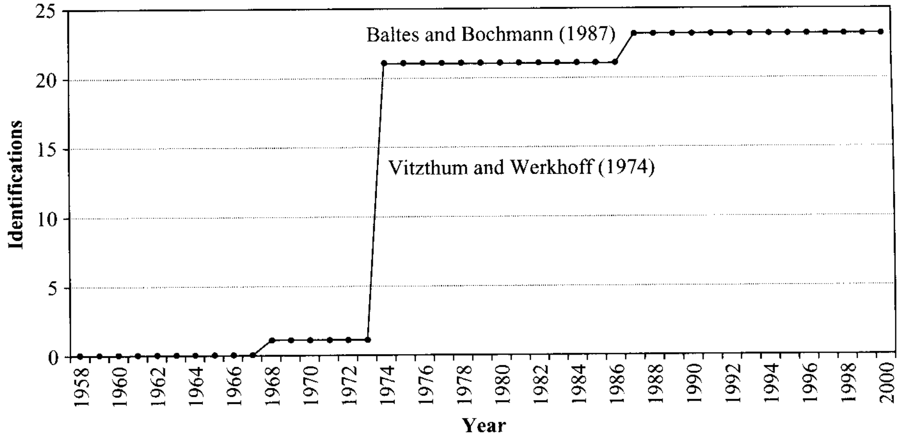


Fig. 5.12 Progressive identification of oxazoles in roasted coffee volatiles

and thermal condensation, can form an oxazole. The alkyl substituents in the 4-and 5-positions originate from the α-diketone, the substituent in the 2-position from the alkyl radical of the acylating agent. This sequence can explain the formation of mono-, di and tri-substituted compounds. Incidentally the α-amino ketones can also form pyrazines by autocondensation. More than 10 years later, Baltes and Bochmann (1987d) identified 20 oxazoles from model reactions with serine and/or threonine and sucrose under the conditions of coffee roasting, but they were unfortunately unable to determine the exact position of the alkyl substituents of five other oxazoles isolated from a roasted coffee. They partially inferred the formation routes summarized above, involving serine and threonine as precursors of oxazoles, because they only isolated traces of oxazoles in the volatiles of their model reaction and higher concentrations in roast coffee volatiles.

Various preparation methods have been described. Wiley (1945, 1947) converted α-amino acids to acetamido ketones by reaction with acetic anhydride in pyridine and obtained 2,5-dimethyl-4-substituted oxazoles after dehydration of the enol form of the intermediate. Theilig (1953) applied the reaction of α-bromoketones with the appropriate amides.

Concerning the organoleptic properties of oxazoles, we will mention that, as early as 1945, Wiley described the odors of oxazoles, which vary with the type of substituents on the ring. According to Ho *et al.* (1983b), alkyloxazoles are mainly associated with a green sweet, earthy, and vegetable-like odor perception. The mass spectra and the sensory properties of some 4,5-dialkyloxazoles have also been published by Ho and Tuorto (1981). These heterocycles have green, vegetable-like aroma. According to Jin *et al.* (1984), Shibamoto (1977) and Mussinan *et al.* (1976), several oxazoles have characteristic strong nutty, sweet, green, herbal, and vegetable-like notes. Flavor thresholds have also been measured by Mussinan *et al.* (1976).

Oxazole, 2-ethyl-, *2-ethyloxazole* **[54300-19-5]**

Oxazole, 4-ethyl-, *4-ethyloxazole* **[54300-20-8]**

Oxazole, 5-ethyl-, *5-ethyloxazole* **[32999-02-3]**

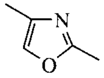
Tentatively identified by Vitzthum and Werkhoff (1974b), and Vitzthum (1976) because they occur as a small peak within the tailing of a large aroma constituent. The identification was deduced from mass spectral evidence, but without confirmation with a reference compound.

The synthesis of the 5-substituted isomer starting with *N,N*-dimethylpropionamide was described by Schröder *et al.* (1975).

The 4-substituted isomer, at a concentration of 10 ppm, has a burnt, cereal and gassy flavor (Chemisis, 1987).

Vitzthum and Werkhoff (1974b), and Vitzthum (1976) found also 2 or 4-butyloxazole.

Alkyloxazoles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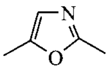
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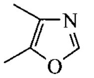
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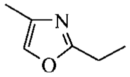
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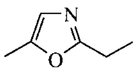
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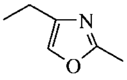
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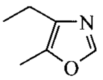
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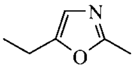
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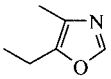
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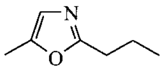

(L·10)

(L.1) Oxazole, 2,4-dimethyl-, *2,4-dimethyloxazole, 2,4-dimethyl-1,3-oxazole* **[7208-05-1]**

Identified by Vitzthum and Werkhoff (1974a,b) (MS and NMR data), in the basic fraction after steam distillation/extraction, and by Baltes and Bochmann (1987d).

The latter authors identified it in model systems serine or threonine/sucrose. It is formed also when furfural is treated with hydrogen sulfide and ammonia (Shibamoto, 1977). The product was isolated by Takken *et al.* (1976) when pyruvaldehyde and acetaldehyde reacted in closed vial glass systems at 90 °C with hydrogen sulfide and ammonia.

Vitzthum and Werkhoff (1974a) confirmed the structure of the product using the synthesis according to Theilig (1953) by reaction of acetol acetate with ammonia. The compound was previously synthesized by Lewy (1888) by the reaction of 1-chloro-2-propanone (chloroacetone) with acetamide. The same procedure was used by Zinsstag and Prijs (1949).

Wiley (1945) reported for this oxazole the odor of pyridine and a similarity with that of 2,4-dimethylthiazole (**M.9**). According to Shibamoto (1977), this compound has a nutty and sweet flavor. After the analysis of volatile basic compounds derived from roasted barley, Harding *et al.* (1978) reported that the inclusion of 2,4-dimethyloxazole to ale resulted in a soapy after taste, presumably at levels above the recognition threshold. At a concentration of 5 ppm it has a green, fruity and blackcurrant flavor (Chemisis, 1987).

(L.2) Oxazole, 2,5-dimethyl-, *2,5-dimethyloxazole, 2,5-dimethyl-1,3-oxazole* **[23012-11-5]**

Identified in a roasted coffee fraction by Vitzthum and Werkhoff (1974a,b), (see **L.1**) and by Baltes and Bochmann (1987d).

It can be formed by a decarboxylative acylation of glycine followed by dehydration of the dienolic form of the intermediate compound. The product was isolated by Takken *et al.* (1976) when pyruvaldehyde and acetaldehyde reacted in closed vial glass systems at 90 °C with hydrogen sulfide and ammonia. It is also present in roasting mixtures of serine and/or threonine and sucrose (Baltes and Bochmann, 1987d).

Preparation methods and toxicity have been described by Wiley (1945, 1947).

(L.3) Oxazole, 4,5-dimethyl-, *4,5-dimethyloxazole* [20662-83-3]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**), and by Wang *et al.* (1983) in a headspace analysis.

The formation from the reaction of L-cysteine with 2,3-butanedione has been observed by Ho and Hartman (1982). A possible formation pathway during the heat treatment should be a trimolecular reaction between biacetyl (2,3-butanedione), formaldehyde and ammonia. Baltes and Bochmann (1987d) identified this compound in roasting mixtures of serine and/or threonine and sucrose (as well as in coffee).

The product can be prepared according to the general procedure of Theilig (1953) by reaction of 3-bromo-2-butanone with formamide.

This oxazole is characterized by a fatty and burnt flavor (Chemisis, 1976).

(L.4) Oxazole, 2-ethyl-4-methyl-, *2-ethyl-4-methyloxazole* [24667-03-6]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**) and by Baltes and Bochmann (1987d).

Its presence in a roasting mixture of threonine (not serine) and sucrose was observed by the latter. The formation could also be explained by condensing pyruvaldehyde and propionaldehyde with ammonia.

At a concentration of 5 ppm it has a green, earthy, burnt, ethereal flavor (Chemisis, 1987).

(L.5) Oxazole, 2-ethyl-5-methyl-, *2-ethyl-5-methyloxazole* [42463-54-7]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**).

It can be prepared by a modification of Theilig's method (1953), by reaction of 1-bromo-2-propanone (bromoacetone) and propionamide.

(L.6) Oxazole, 4-ethyl-2-methyl-, *4-ethyl-2-methyloxazole* [53833-20-8]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**).

Its formation during roasting could result from a trimolecular reaction between ethylglyoxal, ammonia and acetaldehyde resulting from the Strecker degradation of alanine. The mechanism of chain elongation reactions of glyoxal has been elucidated by Yaylayan and Keyhani (1998).

At a concentration of 5 ppm it has a burnt, green, solvent flavor (Chemisis, 1987).

(L.7) Oxazole, 4-ethyl-5-methyl-, *4-ethyl-5-methyloxazole* [53833-28-6]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**) and by Baltes and Bochmann (1987d).

Its presence in roasting mixtures of serine and/or threonine with an equimolar amount of sucrose was observed by Baltes and Bochmann (1987d). This oxazole results, probably, from an interaction between 2,3-pentanedione, formaldehyde and ammonia present in the roasting coffee medium.

It can be synthesized by the general procedure of Theilig (1953) by reaction of 3-bromo-2-pentanone with formamide.

The flavor is pyridinic, caramel and burnt milk at a concentration of 0.5 ppm (Chemisis, 1987).

(L.8) Oxazole, 5-ethyl-2-methyl-, *5-ethyl-2-methyloxazole* [53833-29-7]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**) and by Baltes and Bochmann (1987d).

In their model systems, the latter authors found it only when heating equimolar amounts of serine and sucrose. This oxazole probably resulted from an interaction between ethylglyoxal, ammonia and acetaldehyde resulting from the Strecker degradation of alanine present in the coffee-roasting medium. The mechanism of chain elongation reactions of glyoxal has been elucidated by Yaylayan and Keyhani (1998).

A synthesis has been described by Karrer and Gränacher (1924).

The flavor is described as burnt, sweet, gassy, at a concentration of 10 ppm (Chemisis, 1986).

(L.9) Oxazole, 5-ethyl-4-methyl-, *5-ethyl-4-methyloxazole* [29584-92-7]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**).

Its origin in roasted coffee can be explained by an interaction between 2,3-pentanedione, formaldehyde and ammonia.

It can be synthesized by the general procedure of Theilig (1953) by reaction of 2-bromo-3-pentanone with formaldehyde.

At a concentration of 2 ppm, it has a floral, burnt, chemical flavor (Chemisis, 1987).

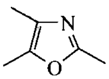
(L.10) Oxazole, 5-methyl-2-propyl-, *5-methyl-2-propyloxazole* [53833-31-1]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**).

Its presence in roasted coffee can be explained by an interaction between methylglyoxal, butyraldehyde and ammonia. A bimolecular reaction between 2-hydroxypropylamine, resulting from the decarboxylation of threonine, and a molecule of butyraldehyde is also to take into account.

This oxazole can be prepared by a modified method of Theilig (1953) by reaction of 1-bromoacetone with butyramide.

2-isopropyl-4/5-methyloxazole, *4-butyl-2/5-methyloxazole* have been found in coffee and not in their model systems by Baltes and Bochmann (1987d).



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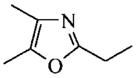

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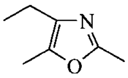

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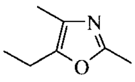

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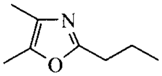

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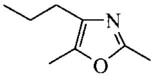

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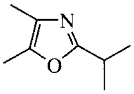

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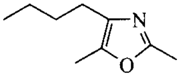


(L·18)

(L.11) Oxazole, trimethyl-, *2,4,5-trimethyloxazole, trimethyloxazole* [20662-84-4]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**) and by Baltes and Bochmann (1987d).

The latter authors also found it when serine and/or threonine reacted with sucrose. It was previously identified in other model reactions by treating furfural with hydrogen sulfide and ammonia (Shibamoto, 1977) or by heating rhamnose with ammonia (Shibamoto and Bernhart, 1978). Ho and Hartman (1982) proposed a plausible mechanism for the formation 2,4,5-trimethyloxazole from the reaction of DL-alanine or L-cysteine and 2,3-butanedione. Ho *et al.* (1982) also studied the formation of oxazoles and oxazolines in the Strecker degradation of DL-methionine and L-cysteine with 2,3-butanedione. In their proposed mechanisms, the authors suggested the formation of intermediate 3-oxazolines.

Trimethyloxazole can be prepared by the method of Wiley (1947) with an overall yield of 15.6% from alanine and acetic anhydride. It can also be prepared by the general procedure of Theilig (1953) by reaction of 3-bromo-2-butanone with acetamide. It has been synthesized in one step from 2-butanone and acetonitrile using copper(II) trifluoromethanesulfonate under acid catalysis (Nagayoshi and Sato, 1983).

Wiley (1947) characterized the odor as 'pyridinic'. According to Mussinan *et al.* (1976), the flavor is woody, musty, green with a threshold in water of 5.0 ppb. Bentz and Mezzino (1972) (quoted by Maga, 1981a) claimed that mixtures of trimethyloxazole and biacetyl can impart earthy, potato-like or mushroom-like flavor to foods. They reported that, alone, it has a sour and bitter taste and smells like sweet pyridine but, when mixed with diacetyl in molar ratios varying from 1 to 4, an earthy flavor note was predominant. Coleman *et al.* (1981), who reported it for the first time in baked potatoes, stated that it contributed importantly to the earthy and nutty notes of the total flavor. The flavor has been defined as burnt, nutty, hazelnut (Chemisis, 1970).

(L.12) Oxazole, 2-ethyl-4,5-dimethyl-, *2-ethyl-4,5-dimethyloxazole* [53833-30-0] *FEMA 3672*

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**) and by Baltes and Bochmann (1987d).

The last authors found it only when heating threonine (and not serine) with an equimolar amount of sucrose. The product was also tentatively identified by Shibamoto *et al.* (1979) from a reaction mixture of D-glucose and ammonia. Another possible pathway is the reaction between 2,3-butanedione and propionaldehyde in the presence of ammonia.

It can be prepared by the general procedure of Theilig (1953) by reaction of 3-bromo-2-butanone with propionamide.

The flavor is described as fatty, earthy, burnt (Chemisis, 1976).

(L.13) Oxazole, 4-ethyl-2,5-dimethyl-, *4-ethyl-2,5-dimethyloxazole* [30408-61-8]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**), confirmed by Baltes and Bochmann (1987d) who did not find it in their model reactions.

It could be formed during coffee roasting by reaction of 2,3-pentanedione with acetaldehyde in the presence of ammonia.

It can be prepared by the reaction of 2-pentanone with acetonitrile according to the method of Nagayoshi and Sato (1983).

At a concentration of 5 ppm it has a green, ethereal, hazelnut flavor (Chemisis, 1986).

(L.14) Oxazole, 5-ethyl-2,4-dimethyl-, *5-ethyl-2,4-dimethyloxazole* [33318-74-0]

Identified by Vitzthum and Werkhoff (1974a,b) (see **L.1**) and Baltes and Bochmann (1987d).

In model systems, the latter authors found it only when heating equimolar amounts of serine (and not threonine) with sucrose. Its formation during coffee roasting can be explained by reaction of 2,3-pentanedione with acetaldehyde in the presence of ammonia.

The synthesis has been described by Karrer *et al.* (1925). This product has also been prepared in one step from 2-pentanone and acetonitrile using copper(II) trifluoromethanesulfonate under acid catalysis (Nagayoshi and Sato, 1983).

The flavor is described as green, burnt at a concentration of 5 ppm (Chemisis, 1986).

(L.15) Oxazole, 4,5-dimethyl-2-propyl-, *4,5-dimethyl-2-propyloxazole* [53833-32-2]

Identified in coffee by Vitzthum and Werkhoff (1974a,b) (see **L.1**).

This oxazole is probably formed during roasting by the interaction of 2,3-butanedione with butyraldehyde in the presence of ammonia.

It can be prepared according to the general procedure of Theilig (1953), by reaction of 3-bromo-2-butanone with butyramide.

It has a fatty and metallic flavor (Chemisis, 1976).

(L.16) Oxazole, 2,5-dimethyl-4-propyl-, *2,5-dimethyl-4-propyloxazole* [30674-60-3]

Identified by Baltes and Bochmann (1987c) (not in their model reactions).

Its formation during roasting is probably due to the reaction of ammonia on 2,3-hexanedione and acetaldehyde, the Strecker degradation product of alanine.

The synthesis can be achieved by condensation of 3-acetylamino-2-hexanone in polyphosphoric acid following the procedure described by Wiegand and Rathburn (1970).

(L.17) Oxazole, 4,5-dimethyl-2-(1-methylethyl)-, *2-isopropyl-4,5-dimethyloxazole* [19519-45-0]

Identified by Baltes and Bochmann (1987d) (who did not find it in their model reactions).

Its origin can be explained by oxidation of the 2,5-dihydro 2-isopropyl-4,5-dimethyloxazole isolated from the Strecker degradation of DL-valine with 2,3-butanedione, as observed by Rizzi (1969).

It can be synthesized by condensation of 3-bromo-2-butanone with isobutyramide following the procedure described by van Bergen and Kellogg (1972).

At a concentration of 0.5 ppm it has a green, earthy, peanut flavor (Chemisis, 1986).

(L.18) Oxazole, 4-butyl-2,5-dimethyl-, *4-butyl-2,5-dimethyloxazole* [30408-62-9]

Identified in coffee by Vitzthum and Werkhoff (1974b) (see **L.1**).

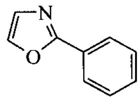
The origin is probably explained by the reaction of ammonia on heptanedione and acetaldehyde, the Strecker degradation product of alanine.

The synthesis can be achieved by condensation of 3-acetylamino-2-heptanone in polyphosphoric acid following the procedure described by Wiegand and Rathburn (1970).

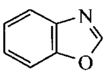
Ho *et al.* (1983a) gave the MS data and described its odor as fresh, acidic, green and pickle like. At a concentration of 5 ppm, it has a floral, woody, galbanum flavor (Chemisis, 1986).

Other trisubstituted oxazoles have been found in coffee (not in their model systems) by Baltes and Bochmann (1987d), but with unprecise substitution sites: 2-isopropyl ethylmethyloxazole, 4-propylethylmethyloxazole, 5-butylethylmethyloxazole. The MS identification was difficult, only a few fragments being formed in the mass spectrometer.

Phenyloxazole; benzoxazoles



(L.19)



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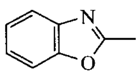

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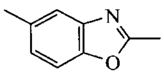


(L.22)

(L.19) Oxazole, 2-phenyl-, *2-phenyloxazole* [20662-88-8]

Identified by Vitzthum and Werkhoff (1974b) (see **L.1**).

Its presence can be explained by the interaction, during roasting, of glyoxal with benzaldehyde in the presence of ammonia. It can also result from condensation between the amino alcohol resulting from the decarboxylation of serine and benzaldehyde.

The synthesis can be carried out by deamination of 4-(2-oxazolyl)aniline [2-(*p*-aminophenyl)oxazole] with $NaNO_2$ and aqueous HCl according to the procedure of Rosenbaum and Cass (1942).

'The' phenylisoxazole (rather 'a' phenylisoxazole) has been found by Andrade-Aispuro and Crouzet (1983) in the volatiles emitted during roasting.

(L.20) Benzoxazole, *benzoxazole, 1,3-benzoxazole* [273-53-0]

Identified in the compounds emitted during coffee roasting by Andrade-Aispuro and Crouzet (1983), and in brews by Lee *et al.* (1992) when studying the effect of brewing time on extraction.

(L.21) Benzoxazole, 2-methyl-, *2-methylbenzoxazole* [95-21-6]

Identified by Vitzthum and Werkhoff (1974b) (see **L.1**).

The synthesis can be realized according to the procedure of Ladenburg (1876) by treatment of 2-aminophenol with acetic acid anhydride.

The compound has a very sweet odor of rather gassy-pungent character when undiluted, becoming floral-sweet, heavy, when diluted (Arctander, 1967). It is also characterized as having a tobacco, very powerful, heavy, tenacious odor (Chemisis, 1988), and a burnt, fatty, floral, phenolic flavor (Chemisis, 1973).

Benzoxazole, 4-methyl-, *4-methylbenzoxazole* **[107165-67-3],**

Benzoxazole, 2,4-dimethyl-, *2,4-dimethylbenzoxazole*

Benzoxazole, 2,6-dimethyl-, *2,6-dimethylbenzoxazole* **[53012-61-6]**

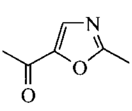
These were tentatively identified by Vitzthum and Werkhoff (1974b).

(L.22) Benzoxazole, 2,5-dimethyl-, *2,5-dimethylbenzoxazole* [5676-58-4]

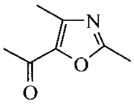
Identified by Vitzthum and Werkhoff (1974b) (see **L.1**).

It can be synthesized by the reaction of 2-amino-4-methylphenol with acetic acid anhydride and sodium acetate according to the method described by Nölting and Kohn (1884).

Acetyloxazoles



(L-23)



(L-24)

(L.23) Ethanone, 1-(2-methyl-5-oxazolyl)-, *1-(2-methyloxazol-5-yl)ethanone*, 5-acetyl-2-methyloxazole [78503-09-0]

Identified by Stoffelsma and Pypker (1968), Stoffelsma *et al.* (1968).

The possible origin of this compound can be explained by the following pathway. An aldol addition of glycine on pyruvaldehyde accompanied by decarboxylation produces the amino alcohol which, after condensation with acetaldehyde, cyclization and oxidation forms the oxazole.

(L.24) Ethanone, 1-(2,4-dimethyl-5-oxazolyl)-, *1-(2,4-dimethyloxazol-5-yl)ethanone*, 5-acetyl-2,4-dimethyloxazole **[23012-25-1]**

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b) (see **L.1**).

The possible origin of this compound could be the same pathway as described for the preceding homolog, the original step being an aldol addition of alanine on pyruvaldehyde.

The product can be synthesized according to the procedure of Jaworski and Mizerski (1981) by condensation of 3-chloro-2,4-pentanedione with acetamide.

For Coleman *et al.* (1981), it contributes importantly to the earthy and nutty notes of the total flavor of baked potatoes, where they reported it for the first time.

5.M THIAZOLES

The organoleptic importance of alkylthiazoles was already recognized in 1966 (Arnold *et al.*) when they were isolated for the first time in food aromas. They play an important role, for instance, in the flavors of roasted cocoa beans, in roasted peanut flavor (Ho *et al.*, 1983b) and in cooked beef flavor (Chang *et al.*, 1977). They were found for the first time in coffee by Stoll *et al.* (1967) who identified 2-acetyl-4-methylthiazole (**M.26**) and 2-propionyl-4-methylthiazole (**M-27**).

A remarkable study on nitrogen heterocycles in coffee aroma was realized by Vitzthum and Werkhoff (1974a,b) who identified 23 new thiazoles (Figure 5.13). These were isolated from the basic fraction of the extract obtained after adsorption of a steam distillate on Porapak Q, followed by an ether extraction. The identification was performed by using a combination of glass-capillary gas chromatography/mass spectrometry. The measured concentrations were of the order of 1–10 ppb and ca 0.1 ppb for thiazole itself.

Numerous publications have been dedicated to the genesis of alkylthiazoles. A model reaction based on a mixture of cysteine/xylose/tributyrin was studied by Ledl and Severin (1973), who proposed the decarboxylation of cysteine into cysteamine (2-aminoethanethiol), followed by a condensation with sugar degradation products and a subsequent oxidation. Mulders (1973c) also proposed a model based on a system of cysteine/cystine/carbohydrates, with the formation of thiazolidines subsequently oxidized into thiazoles. The same pathway has been proposed by Flament (Firmenich, 1973), thiazolidines easily being formed by the reaction of cysteamine with aldehydes. Kato *et al.* (1973a) also found thiazoles in the volatile compounds produced by the reaction of L-cystine with carbonyl compounds. Similarly,

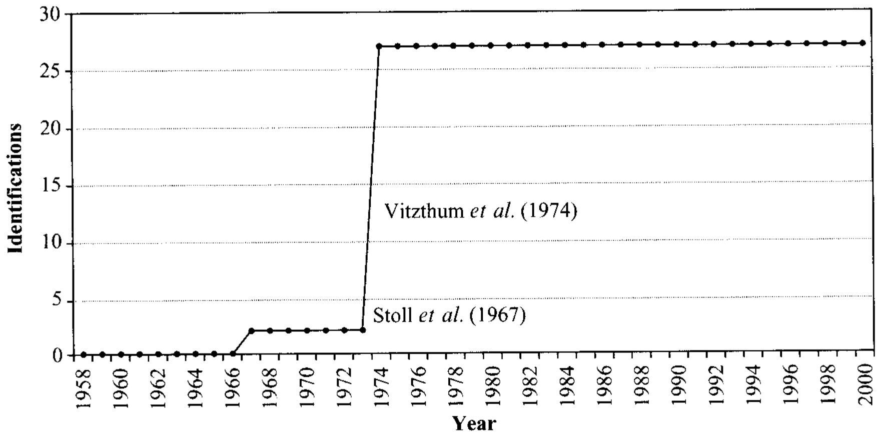


Fig. 5.13 Progresive identification of thiazoles in roasted coffee volatiles

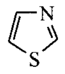
Sakaguchi and Shibamoto (1978a) identified a number of thiazolines and thiazolidines in the reactions of cysteamine with D-glucose, glyoxal and, to a lesser extent acetaldehyde. This reaction was used by Hayashi *et al.* (1986) and Shibamoto (1988) for the determination of formaldehyde in coffee (see C.1) as the thiazolidines have never been identified in food samples.

Pathways for formation of thiazole derivatives and 2-acetylthiazole have been proposed by Vernin and Parkanyi (1982) and by Mulders (1973c) respectively. Mottram (1991) extensively reviewed the numerous interactions of possible precursors of thiazoles.

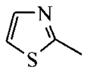
Reference standards were synthesized by procedures described in the literature or by some modifications thereof. The method mostly applicable to the synthesis of alkylthiazoles involves the reaction of α-halocarbonyls with thioamides. Dubs and Stüssi (1976b) described a simple new synthesis of 2,4-disubstituted and 2,4,5-trisubstituted 1,3-thiazoles.

Pittet and Hruza (1974) synthesized (giving MS data) a series of thiazoles with a view to making organoleptic comparisons of thiazoles with structurally related pyrazines and pyridines of analogous substitution. All these heterocyclic compounds have a planar ring and contain a tertiary nitrogen in an heteroaromatic ring. The lower 2-alkylthiazoles are described with green, vegetable-like flavors, like monoalkylpyridines. With increased substitution, alkylthiazoles tend to have nutty, meaty, roasted notes corresponding more to the di-and trialkylpyrazines. The authors discuss the variations in odor quality in terms of structure and charge distribution which certainly plays a role in determining the position of a compound at a nasal receptor. Thiazoles isolated from roasted peanut volatile flavor (Lee *et al.*, 1981) have a pleasant nutty aroma. The organoleptic properties of some thiazole alcohols and thiazole carbonyl compounds have been described by Winter *et al.* (1976r). Ho and Jin (1984) have also described the aroma qualities of 23 synthetic alkylthiazoles.

Alkylthiazoles; Benzothiazole



(M·1)



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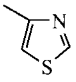

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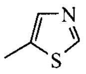

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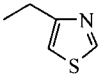
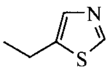


(M·5)



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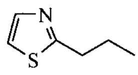

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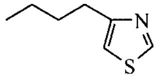


(M.8)

(M.1) Thiazole, *thiazole, 1,3-thiazole* [288-47-1] *FEMA 3615*

Identified in coffee aroma by Vitzthum and Werkhoff (1974a,b), the concentration being of the order of 0.1 ppb. Tressl (1989) found 0.1–0.2 ppm in roasted coffees (see remark in Section 5.I, sulfur compounds).

It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

The odor is pyridine-like (reported by Pittet and Hruza, 1974). At a concentration of 10 ppm the flavor is meaty, musty and green (Chemisis, 1999).

(M.2) Thiazole, 2-methyl-, *2-methylthiazole* [3581-87-1]

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

It has been prepared by Kurkjy and Brown (1952) by reaction of thioacetamide with chloroacetaldehyde. The flavor is green, vegetable (Pittet and Hruza, 1974).

(M.3) Thiazole, 4-methyl-, *4-methylthiazole* [693-95-8] *FEMA 3716*

Identified by Vitzthum and Werkhoff (1974a,b). Silwar *et al.* (1986) after steam distillation/extraction, used flame ionization and flame photometric detectors simultaneously for the sulfur compounds. They found contents of 0.4–0.45 ppm in arabicas and 0.65–0.70 in robustas. Tressl (1989) reported 0.5–1 and 0.8–1.5 ppm.

It was prepared *in situ* by reaction of formamide, phosphorus pentasulfide and bromoacetone (Kurkjy and Brown, 1952).

At a concentration of 10 ppm the flavor is described as tomato, fruity, nutty, green and meaty (Chemisis, 2000).

(M.4) Thiazole, 5-methyl-, *5-methylthiazole* [3581-89-3]

Identified by Vitzthum and Werkhoff (1974a,b).

The preparation is similar to that of M.3 using formamide, phosphorus pentasulfide and 2-bromopropanal (Kurkjy and Brown, 1952). By this method, the yields were lower with α-bromoaldehydes (ca 30 %) than with α-bromoketones (ca 70 %).

At a concentration of 6 ppm the flavor has a pyridinic, slightly mustard and spoilt dairy product note (Chemisis, 1993).

Thiazole, 2-ethyl-, *2-ethylthiazole* [15679-09-1]

Only tentatively identified in roasted coffee by Vitzthum and Werkhoff (1974a,b). It has been found in a heated cysteine/glucose model system (Sheldon *et al.* 1986). It can be prepared according to the procedure described by Kurkjy and Brown (1952). It has a burnt, meaty, mustard, horseradish flavor (Chemisis, 1975).

(M.5) Thiazole, 4-ethyl-, *4-ethylthiazole* [17626-72-1]

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974a,b).

It has been found in a heated cysteine/glucose model system (Sheldon *et al.* 1986).

The flavor has a burnt, pyridinic note (Chemisis, 1975).

(M.6) Thiazole, 5-ethyl-, *5-ethylthiazole* [17626-73-2]

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974a,b).

The flavor is described as green, burnt, alliaceous, horseradish (Chemisis, 1975).

(M.7) Thiazole, 2-propyl-, *2-propylthiazole* [17626-75-4]

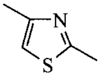
Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

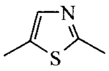
The flavor in water is described as green, herbal, nutty by Pittet and Hruza (1974). At a concentration of 3 ppm, it is characterized by a horseradish, asparagus, burnt flavor; at 1 ppm it becomes more floral and flowery (Chemisis, 1995).

(M.8) Thiazole, 4-butyl-, *4-butylthiazole* [53833-33-3]

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

At a concentration of 1.5 ppm the flavor is a green, herbal, minty, vegetal (Chemisis, 1986).


(M·9)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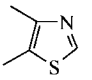
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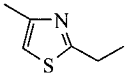
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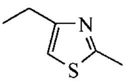
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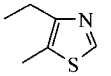
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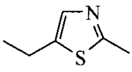
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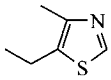
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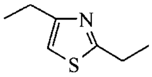
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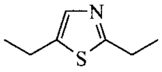
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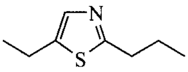

(M·19)

(M.9) Thiazole, 2,4-dimethyl-, *2,4-dimethylthiazole* **[541-58-2]**

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

It was also isolated by Takken *et al.* (1976) in a model reaction from pyruvaldehyde, acetaldehyde, H_2S and NH_3.

It can be prepared by reaction of thioacetamide and chloroacetone (Schwarz, 1945) or, using the improvement of Kurkjy and Brown (1952), by reaction of acetamide, phosphorus pentasulfide and bromoacetone (see **M.4**).

At a concentration of 1.5 ppm the flavor is described as acetone, fruity, tropical fruit and peach (Chemisis, 1993).

(M.10) Thiazole, 2,5-dimethyl-, *2,5-dimethylthiazole* **[4175-66-0]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974a,b) and by Takken *et al.* (1976) in a model reaction involving pyruvaldehyde, acetaldehyde, H_2S and NH_3. It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

It was prepared by Kurkjy and Brown (1952), with acetamide, phosphorus pentasulfide and 2-bromopropanal (see **M.4**).

At a concentration of 3 ppm the flavor note is vegetable, gassy, candle-wax (Chemisis, 1986).

(M.11) Thiazole, 4,5-dimethyl-, *4,5-dimethylthiazole* **[3581-91-7]** *FEMA 3274*

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

It was prepared by Kurkjy and Brown (1952), with formamide, phosphorus pentasulfide and 3-bromo-2-butanone (see **M.4**), by Pittet and Hruza (1974) from ammonium dithiocarbamate and 3-bromo-2-butanone, according a previously described procedure.

The latter authors described the flavor in water as roasted, nutty, green. At a concentration of 4 ppm it has a cereal, toasted, musty, mushroom, shellfish, etc., flavor (Chemisis, 2000). Buttery *et al.* (1976b), who synthesized other 4,5-dialkylthiazoles with potent bell pepper-like aromas, determined an odor threshold of 0.47 ppm in water.

(M.12) Thiazole, 2-ethyl-4-methyl-, *2-ethyl-4-methylthiazole* **[15679-12-6]** *FEMA 3680*

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974a,b).

It can be prepared according to the procedure described by Kurkjy and Brown (1952).

At a concentration of 2 ppm, the flavor has a chemical-solvent, sulfury, nutty, pyrazine note (Chemisis, 1998).

(M.13) Thiazole, 4-ethyl-2-methyl-, *4-ethyl-2-methylthiazole* **[32272-48-3]**

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

It has no particular flavor interest with an ethereal and solvent tonality (Chemisis, 1975).

(M.14) Thiazole, 4-ethyl-5-methyl-, *4-ethyl-5-methylthiazole* **[52414-91-2]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974a,b).

It can be prepared according to the procedure described by Kurkjy and Brown (1952).

At a concentration of 0.2 ppm, it has a burnt, pyridinic flavor (Chemisis, 1980).

(M.15) Thiazole, 5-ethyl-2-methyl-, *5-ethyl-2-methylthiazole* **[19961-52-5]**

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

The flavor is burnt, alliaceous, metallic, acrylate (Chemisis, 1975).

(M.16) Thiazole, 5-ethyl-4-methyl-, *5-ethyl-4-methylthiazole* **[31883-01-9]**

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

It can be prepared according to the procedure described by Kurkjy and Brown (1952).

Pittet and Hruza (1974) described the odor as nutty, green, earthy.

(M.17) Thiazole, 2,4-diethyl-, *2,4-diethylthiazole* **[32272-49-4]**

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

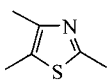
In a concentration of 1 ppm, it has an ethereal burnt flavor (Chemisis, 1980).

(M.18) Thiazole, 2,5-diethyl-, *2,5-diethylthiazole* **[15729-76-7]**

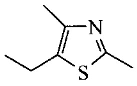
(M.19) Thiazole, 5-ethyl-2-propyl-, *5-ethyl-2-propylthiazole* **[54300-07-1]**

These were identified by Vitzthum and Werkhoff (1974a,b).

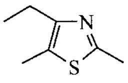
With a concentration of 1 ppm, **M.19** has a green, walnut, anise, vegetable flavor (Chemisis, 1981).



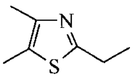
(M·20)



(M·21)



(M·22)



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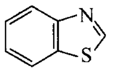


(M·24)

(M.20) Thiazole, trimethyl-, *trimethylthiazole, 2,4,5-trimethylthiazole* **[13623-11-5]** ***FEMA 3325***

Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

Kurkjy and Brown (1952) prepared trimethythiazole by reaction of acetamide, phosphorus pentasulfide and 3-bromo-2-butanone (see **M.4**).

The flavor in water is cocoa, nutty (Pittet and Hruza, 1974), also described as cocoa, roasted-toasted, slightly liquorice at a concentration of 1 ppm (Chemisis, 1993). A threshold of 1.8–7.2 μg/m^3 air was found by Gasser and Grosch (1990).

(M.21) Thiazole, 5-ethyl-2,4-dimethyl-, *5-ethyl-2,4-dimethylthiazole* **[38205-61-7]**

Identified by Vitzthum and Werkhoff (1974a,b).

It can be prepared by using a modification of the method described by Takahashi and Hayami (1961). The flavor in water is described as nutty, roasted, meaty (Pittet and Hruza, 1974).

(M.22) Thiazole, 4-ethyl-2,5-dimethyl-, *4-ethyl-2,5-dimethylthiazole* **[32272-57-4]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974a,b).

At a concentration of 0.2 ppm, it has burnt, earthy, coffee and potato flavor (Chemisis, 1980).

(M.23) Thiazole, 2-ethyl-4,5-dimethyl-, *2-ethyl-4,5-dimethylthiazole* **[873-64-3]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974a,b).

It can be prepared according to the procedure described by Kurkjy and Brown (1952).

The flavor has a burnt, hazelnut, cocoa and peanut character at a concentration of 1 ppm, (Chemisis, 1980).

Thiazole, 4,5-dimethyl-2-(1-methylethyl)-, *2-isopropyl-4,5-dimethylthiazole* **[53498-30-9]**

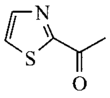
Present in the list of volatiles of roasted coffee published by Clarke (1992), but we could not find it in the quoted references.

(M.24) Benzothiazole, *benzothiazole, 1,3-benzothiazole* **[95-16-9]** ***FEMA 3256***

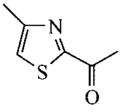
Identified in roasted coffee by Vitzthum and Werkhoff (1974a,b).

It was discovered for the first time in a sterilized milk concentrate (Arnold *et al.*, 1966). It has a burnt, phenolic, gassy flavor (Chemisis, 1965). As benzothiazole seems to be met in numerous flavor extracts and as its formation had never been rationalized, Ferretti and Flanagan (1973) were of the opinion that it could be a contaminant from rubber tubing (even with very short connections) and confirmed it with a blank experiment. The authors stated also that benzothiazole could contribute to stale flavor. Maga (1975c) described it as having a quinoline-like, rubbery odor.

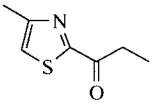
Acylthiazoles



(M.25)



(M.26)



(M.27)

(M.25) Ethanone, 1-(2-thiazolyl)-, *1-(thiazol-2-yl)ethanone*, 2-acetylthiazole **[24295-03-2]** ***FEMA 3328***

Identified by Vitzthum and Werkhoff (quoted in Vitzthum, 1976 as unpublished result). Tressl (1989) gave a content of 0.2–0.3 ppm.

(M.26) Ethanone, 1-(4-methyl-2-thiazolyl)-, *1-(4-methylthiazol-2-yl)ethanone, 1-(4-methyl-1,3-thiazol-2-yl)ethanone*, 2-acetyl-4-methylthiazole **[7533-07-5]**

Identified in a roasted coffee extract by Stoll *et al.* (1967).

It was found by Takken *et al.* (1976) in a model reaction between pyruvaldehyde, acetaldehyde, H_2S and NH_3, and by Sheldon *et al.* (1986) in a heated cysteine/glucose model system.

The organoleptic properties have been described by Winter *et al.* (1976r): at a concentration of 20 ppm in a syrup base it has a fruity, rose-like taste; it is also characterized as having an anthranilic burnt flavor.

(M.27) 1-Propanone, 1-(4-methyl-2-thiazolyl)-, *1-(4-methylthiazol-2-yl)propan-1-one,* 4-methyl-2-propanoylthiazole **[13679-83-9]**

Identified in roasted coffee flavor by Stoll *et al.* (1967).

This thiazole is prepared by reaction of 4-methylthiazole with ethylmagnesium bromide and acylation of the obtained Grignard intermediate with propionyl chloride (Winter *et al.*, 1976r).

The organoleptic properties have been described by these authors: at a concentration of 5 ppm in a syrup base it has a green taste; it is also described as having fruity, burnt, chemical notes (Chemisis, 1964).

5.N PYRIDINES

The first mention of the presence of pyridine in roasted coffee was made by Monari and Scoccianti (1895), but 18 years later Bertrand and Weisweiller (1913) continued to ignore this discovery. Hughes and Smith (1946) published an interesting study on the non-volatile nicotinic acid, but it was only after the advent of gas chromatography that the number of identifications increased, as was the case for many other classes of compounds. The main contributions were due to Vitzthum and Werkhoff (1974b) and Baltes and Bochmann (1987d,e).

A pathway leading to the formation of pyridines by aldolization of aldehydes, reaction with ammonia and intramolecular cyclization has been proposed by Vernin (1981). Mottram (1991) explained the formation of 2-alkylpyridines by reaction of ammonia on dienals.

Pyridines have been identified among the pyrolysis products of model reactions involving amino acids and sugars, for instance by Ledl and Severin (1973), Mussinan and Katz (1973), and Baltes and Bochmann (1987d). The latter authors identified 15 pyridines present in coffee flavor, 13 of them also being present in reactions of serine and/or threonine, with or without sucrose, under coffee-roasting conditions. Pyridines can also be formed by thermal degradation of Amadori intermediates (van den

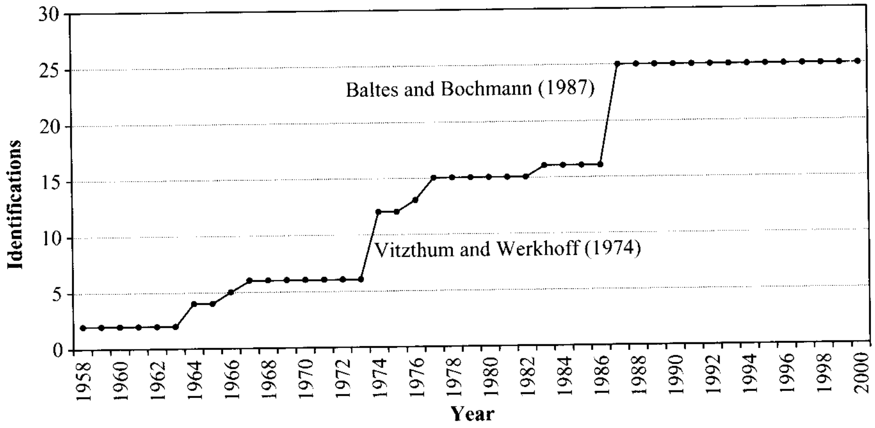


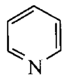
Fig. 5.14 Progressive identification of pyridines in roasted coffee volatiles

Ouweland *et al.*, 1978) or directly by the pyrolysis of amino acids (Fujimaki *et al.*, 1969). Another important, if not the main, precursor of pyridines in roasted coffee is trigonelline (see Section 2.1.1.2), a product isolated by Gorter (1910), identical to the product isolated from the seeds of *Trigonella foenum-graecum*. Viani and Horman (1974, 1976) identified 12 pyridinic compounds after pyrolysis of trigonelline, six of which have now been identified in roasted coffee (4-methylpyridine is noted as identified in coffee, but it is not present in the lists of quoted publications, and to our knowledge its identification has not yet been reported in the literature). The presence of four other alkyl derivatives and of two *N*-methylnicotinamides have not yet been confirmed in the flavor. The authors have also isolated two piperidylpyridines, 3-phenylpyridine and two of its methyl derivatives, as well as four unsubstituted and dimethyl-substituted dipyridyl compounds.

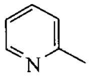
Most of the pyridinic constituents of coffee flavor are commercially available. 2-Acetylpyridine (**N.22**) and 3-acetylpyridine (**N.23**) can be synthesized according to Kollof and Hunter (1941).

As mentioned in the previous Section 5.M, Pittet and Hruza (1974) made a comparative study of flavors of some thiazoles, pyridines and pyrazines, and gave mainly green flavor for the simple alkylated pyridines. The syntheses and the organoleptic properties of numerous pyridines have been described by Winter *et al.* (1975d, 1977a,c,d). In a review, Maga (1981c) mentioned that pyridines generally have bitter, astringent, roasted and burnt notes.

Alkyl-, alkenylpyridines; quinolines



(N.1)
(N.1)



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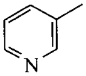
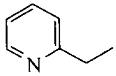
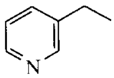


(N.3)



(N.4)
(N.4)



(N.5)
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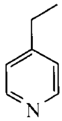
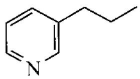
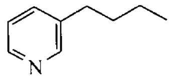


(N.6)



(N.7)



(N.8)

(N.1) *(N.1)* **Pyridine,** *pyridine* **[110–86–1]** *FEMA 2966*

Identified by Monari and Scoccianti (1895). This discovery was ignored by Erdmann (1902a) who isolated a compound having a strong pyridine odor which they considered as unstable and very typical. Pyridine was again identified by Bertrand and Weisweiler (1913) who considered their result to be original, ignoring the results published 18 years before, and gave a concentration of 200 to 500 ppm for pyridine in roasted coffee. Later Johnston and Frey (1938) confirmed the presence of this compound by determining the melting point of the picrate. Hughes and Smith (1946) have shown that pyridine is produced during roasting by decomposition of trigonelline, and that a high content is a characteristic feature of highly roasted coffee, the highest value obtained being 204 ppm. They also observed that the compound may be readily detected by smell in freshly ground coffee and that there was no appreciable loss during staling of coffee. It is generally presumed that the loss of pyridine by volatilization is prevented by combination with the natural acids of coffee. Moncrieff (1950a) commented on the previous work of Bertrand and Weisweiller (1913) who affirmed that after removal of pyridine by acidification, the true aroma of coffee was not recovered. This observation was made well before the identification of other very characteristic nitrogen-containing compounds (pyrazines, oxazoles, thiazoles, etc.) which are also discarded by the treatment, and the authors ingenuously claimed that if pyridine was added to the diluted extract, the true coffee aroma was immediately evident. Moreover, Moncrieff (1950a) rightly remarks that pyridine is well known to have an offensive odor, and that its presence as much more than a trace would ruin any coffee. He adds that it is, however, often found that the borderline is very narrow between the delicious and the disgusting. The concentration in roasted coffee was only estimated at 49 ppm by Stofberg and Stoffelsma (1981). For Shibamoto *et al.* (1982), the proportion increased drastically with roasting time, representing 1.88–15.67% (GC) of the volatiles by roasting 25–30 min at 230 °C of a Columbian arabica (simultaneous distillation–extraction). Pyridine was qualified as 'slow extractor' by Lee *et al.* (1992) studying brewed coffee as a function of brewing time. It was identified in green coffee by Vitzthum *et al.* (1976) and by Guyot *et al.* (1982) (1983) in 'stinking' and healthy green coffee.

For Viani and Horman (1974), pyridine represents 25% of the pyrolysis products of a trigonelline monohydrate sample. Pyridine has been found in model reactions between glucose and amino acids (Kato *et al.*, 1973b), when heating serine and/or threonine with or without sucrose under coffee-roasting conditions (Baltes and Bochmann, 1987d who found it also in coffee). Mottram (1991) explained the possible formation of pyridine by reaction of ammonia on 2,4-pentadienal.

Pyridine is characterized by a pungent, penetrating and diffusive odor, generally described as nauseating, but in extreme dilution it becomes warm, burnt and smokey (Arctander, 1967).

(N.2) *(N.2)* **Pyridine, 2-methyl-,** *2-methylpyridine*, α-picoline, picoline **[109-06-8]**

Identified in roasted coffee by Radtke (1964), Goldman *et al.* (1967), Shibamoto *et al.* (1982), and by Baltes and Bochmann (1987d), and in green coffee volatiles by Vitzthum *et al.* (1976).

Davidson and Wiggins (1956) isolated it from ammoniated molasses a few years before its discovery in coffee. It was identified in the pyrolysis products of amino acids by Kato *et al.* (1973a,b), in the pyrolysis products of trigonelline by Viani and Horman (1974), and in model reactions involving serine and/or threonine with or without sucrose under coffee-roasting conditions by Baltes and Bochmann (1987d). Mottram (1991) explained the possible formation of 2-methylpyridine by reaction of ammonia with 2,4-hexadienal.

2-Methylpyridine has an astringent, hazelnut, basic taste in a neutral soluble coffee beverage, at a concentration of 6 ppm (Winter *et al.*, 1977c). It is also described as having a roasted popcorn aroma (Vernin, 1979).

(N.3) **Pyridine, 3-methyl-,** *3-methylpyridine*, β-picoline **[108-99-6]**

Identified by Radtke (1964), Radtke *et al.* (1966a) tentatively (?), by Gianturco *et al.* (1966), Goldman *et al.* (1967), and Stoffelsma *et al.* (1968). It was found by Shibamoto *et al.* (1982) in a roasted Columbian arabica, but only after prolonged roasting time (30 min, 230 °C).

3-Methylpyridine was isolated among the pyrolysis products of trigonelline by Viani and Horman (1974). It was found in model reactions between glucose and amino acids (Kato *et al.*, 1973b), when heating serine and/or threonine with or without sucrose under coffee-roasting conditions (Baltes and Bochmann, 1987d, who identified it also in coffee).

It has a green flavor (Pittet and Hruza, 1974), a green, earthy, hazelnut-like flavor when tasted in a neutral soluble coffee beverage, at a concentration of 2.5 ppm (Winter *et al.*, 1977c).

As mentioned at the beginning of this section, Viani and Horman (1974) quoted 4-methylpyridine as identified in coffee, but to our knowledge the identification has not been reported in the literature.

(N.4) *(N.4)* **Pyridine, 2-ethyl-,** *2-ethylpyridine* **[100-71-0]**

Identified for the first time in green coffee by Vitzthum *et al.* (1976), in the volatiles (basic fraction, see **N.20**) formed during roasting by Andrade-Aispuro and Crouzet (1983).

Baltes and Bochmann (1987d) identified this compound in the roasting of serine and/or threonine with or without sucrose (as well as in coffee). Mottram (1991) explained the possible formation of 2-ethylpyridine by reaction of ammonia on 2,4-heptadienal.

According to Pittet and Hruza (1974), 2-ethylpyridine has a green flavor.

(N.5) *(N.5)* **Pyridine, 3-ethyl-,** *3-ethylpyridine,* β-lutidine **[536-78-7]** ***FEMA 3394***

Identified in roasted coffee by Goldman *et al.* (1967) and in green coffee by Vitzthum *et al.* (1976). As for **N.3**, Shibamoto *et al.* (1982) found it only after a prolonged roasting time (30 min, 230 °C).

It is one of the pyrolysis products of trigonelline (Viani and Horman, 1974). Baltes and Bochmann (1987d) identified it in model reactions, heating serine and/or threonine with or without sucrose (and in coffee).

At a concentration of 2.5 ppm in a syrup base, 3-ethylpyridine has been described as having a caramel, roasted and hazelnut-like taste. It imparts to a neutral soluble coffee beverage, at 0.1 ppm, a buttery, green, cereal, caramel note (Winter *et al.*, 1977c). It is also characterized by a tobacco flavor (Fors, 1983), caramel, burnt flavor (Chemisis, 1989).

(N.6) **Pyridine, 4-ethyl-,** *4-ethylpyridine,* 4-homopicoline **[536-75-4]**

Identified in coffee by Baltes and Bochmann (1987e).

It was isolated among the pyrolysis products of trigonelline by Viani and Horman (1974). Baltes and Bochmann (1987d) identified it when heating serine and threonine without or with a limited amount of sucrose (as well in coffee).

4-Ethylpyridine has a very powerful, sweet-green character, is nauseating in the pure state, but after dilution becomes slightly minty with a sweet-herbaceous odor, presenting mildly tarry-pungent undertones. There is a certain similarity to the odor of mushrooms and dry-rotted wood (Arctander, 1967).

(N.7) **Pyridine, 3-propyl-,** *3-propylpyridine,* 1-(3-pyridyl)propane **[4673-31-8]**

Identified by Baltes and Bochmann (1987d).

These authors also observed its formation by heating threonine (not serine) with sucrose under coffee-roasting conditions.

3-Propylpyridine has a sweet, musty, beany flavor (Polak's Frutal Works *et al.*, 1968). It is also described with woody, burnt, chemical, dirty flavor (Chemisis, 1991).

(N.8) **Pyridine, 3-butyl-,** *3-butylpyridine,* 1-(3-pyridyl)butane **[539-32-2]**

Identified by Baltes and Bochmann (1987e).

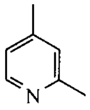
The flavor is described as floral, green, rooty, earthy (Chemisis, 2000).

(N.9) **Pyridine, 2,4-dimethyl-,** *2,4-dimethylpyridine,* 2,4-lutidine **[108-47-4]**

Identified by Baltes and Bochmann (1987e).

The same authors (1987d) observed its formation from the reaction of threonine (not serine) with sucrose under the conditions of coffee roasting, and also when heating a mixture of serine and threonine.

In a syrup base at a concentration of 10 ppm, it has a green taste and in a neutral soluble coffee beverage at the same concentration, it has a basic, bitter and astringent taste (Winter *et al.*, 1977c).



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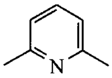

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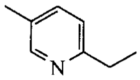

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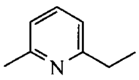
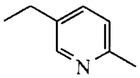


(N·12)



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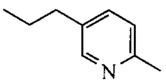

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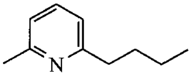

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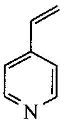

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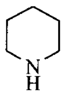

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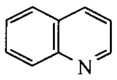
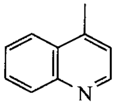


(N·18)



(N·19)

(N.10) *(N.10)* **Pyridine, 2,6-dimethyl-,** *2,6-dimethylpyridine,* 2,6-lutidine **[108-48-5]** ***FEMA 3540***

Identified in green beans by Vitzthum *et al.* (1976) and in roasted coffee by Baltes and Bochmann (1987d).

The latter authors also observed its formation from reactions of serine and/or threonine with or without sucrose under coffee-roasting conditions.

In a syrup base at a concentration of 10 ppm, it has a green taste and in a neutral soluble coffee beverage at 2 ppm, it gives a green, astringent and earthy taste (Winter *et al.*, 1977c).

(N.11) Pyridine, 2-ethyl-5-methyl-, *2-ethyl-5-methylpyridine* **[18113-81-0]**

Identified by Baltes and Bochmann (1987e).

It has been identified in the pyrolysis products of amino acids by Kato *et al.* (1973a). Baltes and Bochmann (1987d) observed its formation when heating threonine alone with sucrose or mixtures of serine and threonine, with or without sucrose.

It has a popcorn aroma (Vernin, 1979).

(N.12) Pyridine, 2-ethyl-6-methyl-, *2-ethyl-6-methylpyridine,* 6-ethyl-2-picoline **[1122-69-6]**

Identified by Baltes and Bochmann (1987e).

The same authors (1987d) found it after heating threonine alone with sucrose or mixtures of serine and threonine, without or with a limited amount of, sucrose.

(N.13) Pyridine, 5-ethyl-2-methyl-, *5-ethyl-2-methylpyridine,* 3-ethyl-6-methylpyridine, 5-ethyl-2-picoline **[104-90-5]** ***FEMA 3546***

Identified in roasted coffee flavor by Baltes and Bochmann (1987e).

It has also been found in a model reactions between glucose and amino acids (Kato *et al.*, 1973b) and only when heating serine and threonine without sucrose (Baltes and Bochmann, 1987d).

This compound, in a neutral soluble coffee base at a concentration of 0.5 ppm, has a winey, buttery, acid, cereal-like and caramel flavor (Winter *et al.*, 1977c).

(N.14) Pyridine, 2-methyl-5-propyl-, *2-methyl-5-propylpyridine* **[874-75-9]**

Identified by Baltes and Bochmann (1987e).

Baltes and Bochmann (1987d) found it only when heating serine and threonine without sucrose under coffee-roasting conditions, as **N.13**.

(N.15) Pyridine, 2-butyl-6-methyl-, *2-butyl-6-methylpyridine* **[5335-76-2]**

Identified by Baltes and Bochmann (1987e) in roasted coffee.

(N.16) *(N.16)* **Pyridine, 4-ethenyl-,** *4-vinylpyridine* **[100-43-6]**

Identified by Vitzthum *et al.* (1976) in green coffee volatiles and by Andrade-Aispuro and Crouzet (1983) when recovering the volatile compounds formed during roasting. It was tentatively identified in roasted coffee by Elmore and Nursten (1990).

(N.17) Piperidine, *piperidine,* hexahydropyridine, azacyclohexane **[110-89-4]** ***FEMA 2908***

Identified by Singer and Lijinsky (1976) at a concentration of 1 ppm. According to Neurath *et al.* (1977), the concentration in two coffees and one extract was 1–2 ppm, obtained after steam distillation, formation of trifluoroacetamides on the neutral fraction, separation from tertiary amines and GC.

Piperidine is described as having a heavy-sweet, nauseating, floral-animal odor (Arctander, 1967).

(N.18) **Quinoline,** *quinoline*, 2,3-benzopyridine **[91-22-5]**

Identified only in green coffee beans by Vitzthum *et al.* (1976).

The odor is heavy, penetrating and nauseating, yet sweet and of good tenacity, not as pungent-diffusive as pyridine, and not nearly as anisic as isoquinoline (Arctander, 1967).

(N.19) Quinoline, 4-methyl-, *4-methylquinoline*, lepidine **[491-35-0]**

Identified in roasted coffee by Vitzthum and Werkhoff (1974b).

It was found among other quinolines and quinoxalines by Baltes and Knoch (1993) after roasting tryptophan with D-glucose or D-xylose.

4-Methylquinoline has a powerful, rather repulsive, odor of animal-musty character in high concentration, but in extreme dilution the odor becomes pleasant, burnt-oily, herbaceous and floral-sweet of excellent tenacity (Arctander, 1967). The flavor is burnt, slightly phenolic (Chemisis, 1971).

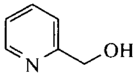
A 'methylquinoline' is listed by Spadone *et al.* (1990) in compounds of green coffee.

Pyridines, quinolines with oxygenated function

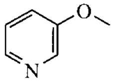
(N.20) 2-Pyridinemethanol, *pyridine-2-methanol,* 2-pyridyl carbinol, α-picolyl alcohol **[586-98-1]**

Identified by Andrade-Aispuro and Crouzet (1983) using original laboratory and pilot units allowing recovery of the volatiles produced during coffee roasting, with a system based on an absorption column equipped with Raschig rings and a countercurrent flow of water. The condensate was fractionated by chemical extraction into basic, acid, neutral and phenolic fractions. The constituents were separated and identified by the classical GC/MS technique. The basic fraction, which emits a rich and strong roasted and characteristic odor, consisted mainly of pyrazinic, pyridinic and pyrrolic compounds. Sixteen constituents were identified, among them 2-pyridinemethanol.

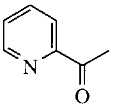
At a concentration of 40 ppm, in a sugar syrup, the compound has a roasted, moldy flavor (Winter *et al.*, 1977c).



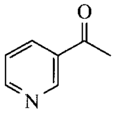
(N.20)



(N.21)



(N.22)
(N.22)



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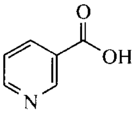

(N.24)
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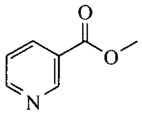
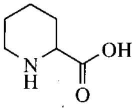
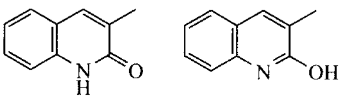


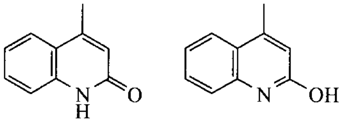
(N.25)



pipecolic acid



(N.26)



(N.27)

(N.21) Pyridine, 3-methoxy-, *3-methoxypyridine* **[7295-76-3]**

Identified, only with the mass spectrum, by Andrade-Aispuro and Crouzet (1983) in the volatiles emitted during roasting (see **N.20**).

(N.22) *(N.22)* **Ethanone, 1-(2-pyridinyl)-,** *1-(2-pyridyl)ethanone, 1-(pyridin-2-yl)ethanone,* 2-acetylpyridine **[1122-62-9]** ***FEMA 3251***

Identified by Vitzthum and Werkhoff (1974b) in roasted coffee and by Vitzthum *et al.* (1976) in green coffee volatiles. Its concentration in roasted coffee is estimated at 4.0 ppm by Stofberg and Stoffelsma (1981).

It has been identified in the degradation rearrangement products of glucose/glycine and fructose/glycine (van den Ouweland *et al.*, 1978). Baltes and Bochmann (1987d) observed that it was formed when heating, under the conditions of coffee roasting, serine and/or threonine only when sucrose is present.

The synthesis was described by Kolloff and Hunter (1941) by the action of methylmagnesium iodide on 2-cyanopyridine or from condensation of the 2-carboxylate with ethyl acetate, the resulting product being hydrolyzed with aqueous hydrochloric acid.

It is characterized by a popcorn (Ohloff and Flament 1978), bready (Tressl, 1979c), tobacco, and cracker-like odor. At a concentration of 1.2 ppm in a sugar syrup, it has a roasted, coffee-like flavor; at 0.8 ppm in a soluble coffee beverage, it has also a roasted, hazelnut note (Winter *et al.*, 1977c). It also contributes to the typical notes of roasted barley (Harding *et al.*, 1978). According to Teranishi *et al.* (1975) (quoted by Fors, 1983), the odor threshold in water is 19 ppb.

(N.23) *(N.23)* **Ethanone, 1-(3-pyridinyl)-,** *1-(3-pyridyl)ethanone, 1-(pyridin-3-yl)ethanone,* 3-acetylpyridine **[350-03-8]** ***FEMA 3424***

Identified by Vitzthum and Werkhoff (1974b) in roasted coffee and by Vitzthum *et al.* (1976) in green coffee volatiles.

The synthesis is similar to that of the 2-isomer (Kolloff and Hunter, 1941).

This product has a powerful, almost choking cigar-tobacco-type odor, which becomes pleasant only at extreme dilution, then also being more typically tobacco-like (Arctander, 1967). According to Winter *et al.* (1977c), at a concentration of 50 ppm in a sugar syrup it has a burnt, roasted flavor, and at 30 ppm in a neutral soluble coffee beverage, it gives an additional phenolic and basic taste.

(N.24) *(N.24)* **3-Pyridinecarboxylic acid,** *pyridine-3-carboxylic acid,* nicotinic acid, niacin **[59-67-6]**

The nicotinic acid content of coffee was studied by Teply *et al.* (1945) and by Hughes and Smith (1946) who described an efficient method for analyzing nicotinic acid and trigonelline in raw and roasted beans. They measured the contents in different varieties of coffee and their respective production and loss during roasting: nicotinic acid is produced during the roasting by decomposition of trigonelline although the amount represents only a small proportion (1–3%) of the trigonelline lost. A dark-roast coffee contains more acid than a lighter roast coffee. Green coffee of various origins (robustas and arabicas) contained 16–44 ppm and the roasted coffees 150–200 ppm of nicotinic acid, which is almost completely extracted in the preparation of the beverage. As the formation of nicotinic acid is directly related to the disappearance of trigonelline, the ratio of their content has been proposed as a method for assessing the degree of roast from analytical data (Kwasny and Werkhoff, 1978), the log of this ratio being linearly related to the dry weight roasting loss. There is no correlation between the perceived quality of coffee and the nicotinic acid content (Macrae, 1985). Bähre and Maier (1999), using a new analysis method for acids (see Section 5.E), could not detect nicotinic acid in green arabicas from Kenya and Columbia (steam treated or untreated), but found 160–190 ppm in the roasted Kenya arabica.

Viani and Horman (1974, 1976) (who also quoted Teply *et al.*, 1945) identified nicotinic acid in the non-volatile fraction of the thermal fragmentation of trigonelline (see Section 2.1.1.2).

(N.25) 3-Pyridinecarboxylic acid, methyl ester, *methyl pyridine-3-carboxylate,* 3-methoxycarbonylpyridine, methyl nicotinate **[93-60-7]** ***FEMA 3709***

Identified by Gianturco *et al.* (1966), and Stoffelsma *et al.* (1968).

It was isolated among the pyrolysis products of trigonelline by Viani and Horman (1974).

It is described as having a warm, but nauseating, sweet-herbaceous odor with mildly tobacco-like notes and moderate tenacity, but in extreme dilution it displays a sweet-herbaceous, quite pleasant odor (Arctander, 1967). According to Winter *et al.* (1977c), it imparts an astringent and bitter taste to a neutral soluble coffee beverage at a concentration of 40 ppm.

Pipecolic acid (piperidine-2-carboxylic acid) is considered as amino acid (see Section 2.1.1.3).

(N.26) 2(1*H*)-Quinolinone, 3-methyl-, *3-methyl-2-quinolone, 3-methyl-1*H*-quinolin-2-one,* 3-methylcarbostyril **[2721-59-7]**; tautomeric form: **2-quinolinol, 3-methyl-,** *3-methylquinolin-2-ol*

Identified in roasted coffee by Vitzthum *et al.* (1974b).

(N.27) 2(1*H*)-quinolinone, 4-methyl-, *4-methyl-2-quinolone, 4-methyl-1(*H*)-quinolin-2-one* [607-66-9]; tautomeric form: **2-quinolinol, 4-methyl-,** *4-methylquinolin-2-ol,* 2-hydroxy-4-methylquinoline **[84909-43-3]**

Identified (noted as the hydroxy tautomer) only by mass spectroscopy by Andrade-Aispuro and Crouzet (1983) in the volatile compounds emitted during roasting (see **N.20**).

The 2-methylcinnoline (?) in the list of identified compounds by Ho *et al.* (1993) might be 2-methylquinoline.

5.O PYRAZINES

Two unrelated works, one devoted to synthesis, the other to analysis, both published in 1879, characterize the doubly ambiguous discovery of this class of heterocyclic compounds. Gutknecht (1879) succeeded in preparing a pyrazine for the first time, namely tetramethylpyrazine, whereas Schrötter (1879) isolated, from a beet fusel oil, two basic constituents of formulae $C_8H_{12}N_2$ and $C_{10}H_{16}N_2$ to which he could not attribute any definite structure but which can reasonably be considered as being tetramethylpyrazine and a diethyldimethylpyrazine. In 1888, Morin isolated, from another fusel oil, a basic compound of formula $C_7H_{10}N_2$ having a 'characteristic nauseous odor', which was subsequently identified by Brandes and Stoehr (1896) as trimethylpyrazine. In 1897, Bamberger and Einhorn identified 2,5-dimethylpyrazine (**O.6**) in a fusel oil. At the outset of the Twentieth century, essentially thanks to the research groups of Brandes and Stoehr (Kiel), Gabriel and Pinkus (Berlin), and Meyer and Treadwell (Zürich), 15 alkylpyrazines had already been synthesized and some had been identified in products of natural origin, but essentially in alcoholic fermentation media. Today more than 180 pyrazines, cyclopentapyrazines, quinoxalines and pyrrolopyrazines have been identified in foods, more than 90 being reported as components of the volatile fraction of coffee.

A significant step in coffee flavor chemistry was taken in the 1920s when Reichstein and Staudinger (1926a, b, c) reported pyrazines for the first time, pyrazine (**O.1**), methylpyrazine (**O.2**), 2,5-dimethylpyrazine (**O.6**) and 2,6-dimethylpyrazine (**O.7**). Then, in the course of nearly 40 years, the analytical studies were relatively rare and unfruitful. Nevertheless, in 1956, Davidson and Wiggins reported that a pilot-plant run behaved abnormally when they were studying the high-temperature ammoniation of molasses. A vigorously exothermic reaction took place that resulted in the formation of a solid mass of cooked material. This event lent them to examine the pyrolysis products of ammoniated invert sugars. They were able to identify α-picoline (2-methylpyridine, **N.2**), 2,6-dimethylpyrazine (**O.7**) and a methylimidazole. This observation constituted a first step on the possible formation pathway of these heterocyclic compounds.

As for the volatile food aroma constituents, the 'modern period' of discovery of new pyrazinic compounds started with the advent of gas chromatography which induced an avalanche of identifications. One of the first was the finding of 2,6-dimethylpyrazine (**O.7**) and tetramethylpyrazine (**O.31**) in a cocoa flavor (Dietrich *et al.*, 1964). Indeed, other members of this family were more frequently found in coffee during the sixties, mainly by Reymond *et al.* (1966b), Gianturco *et al.* (1966), Goldman *et al.* (1967), Bondarovich *et al.* (1967), Stoffelsma *et al.* (1968) and Friedel *et al.* (1971). Bondarovich *et al.* (1967) noted that the information collected at that time was sufficient to attempt a determination of the relative organoleptic significance of the various identified compounds, and estimated that the pyrazines may contribute in an important way to the flavor, not only of coffee, but of a variety of roasted or otherwise cooked foods. In order to facilitate the identification of the members of this family, they published the IR and MS data and the retention times of 22 alkyl and alkenylpyrazines. It was then

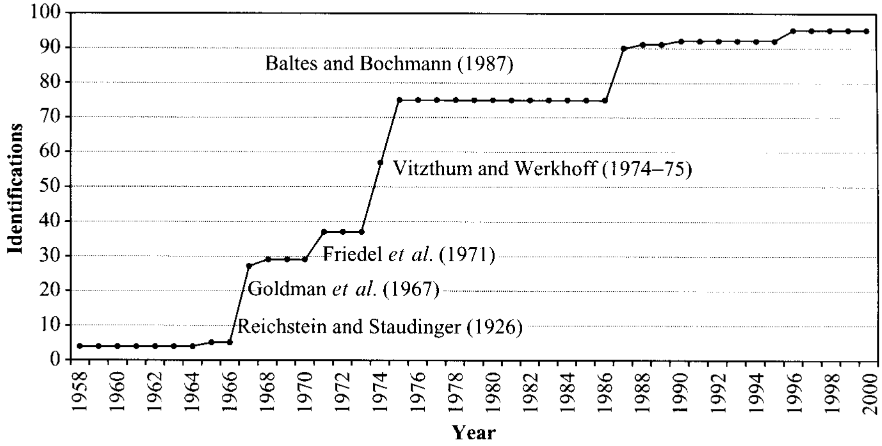


Fig. 5.15 Progressive identification of pyrazines in roasted coffee volatiles

proved that pyrazines derive, during the roasting, from a Maillard reaction between amino acids and sugars; they are formed in remarkable amounts and constitute about 14% of the overall volatile content. This pathway was specially studied, among numerous other investigations, by Dawes and Edwards (1966), Mason *et al.* (1966), Hodge (1967), van Praag *et al.* (1968), Koehler *et al.* (1969), Wang *et al.* (1969), Rizzi (1969), Koehler and Odell (1970), Kato *et al.* (1970), Hodge *et al.* (1972) and Maga and Sizer (1973a). Other mechanisms were also suggested by Bondarovich *et al.* (1967), Flament *et al.* (1967a) and Goldman *et al.* (1967). Reference compounds being needed to confirm the structures of isolated natural constituents, the synthetic chemistry of pyrazines experienced an active and prosperous period. The chemistry of pyrazines had been reviewed exhaustively in 1947 by Krems and Spoerri. The preparation methods published, for instance, by Klein and Spoerri (1951), Behun and Levine (1959, 1961) and Kamal *et al.* (1962) were extensively applied. Maga and Sizer (1973a,b), and Maga (1982a,b, 1992) published a series of reviews on the occurrence of pyrazines in food flavors.

The content in free amino acids being higher in green robustas than in arabicas (see 2.1.1.3), the contents in pyrazines after roasting was also higher (Silwar and Lüllmann, 1993a).

Dihydropyrazines

The probable organoleptic importance of dihydropyrazines which temporarily exist in freshly roasted coffee but are too unstable to be extracted, separated and isolated during analytical studies, has been frequently invoked. Bondarovich *et al.* (1967) observed that some of these intermediates in the synthesis of pyrazines possessed definite 'roasted peanuts' or 'popcorn' character.

2,3-Dihydropyrazines are formed by condensation of α-diketones with ammonia or α-diamines, as shown by Flament and Stoll (1967). They are sufficiently stable to be isolated and purified by distillation. One of the main pathways of formation is the autocondensation of α-aminoketones or aminohydroxy compounds generated by Strecker degradation. The intermediate 2,5-dihydropyrazines formed can condense with various carbonyl compounds resulting from the degradation of sugars, thus explaining the formation of numerous trisubstituted compounds with different alkyl radical lengths as studied by Flament *et al.* (1979). The synthesis and properties of 2,5-dihydro-3,6-dimethylpyrazine was studied by Wilen (1970), and a method for the synthesis of 1,2-dihydropyrazines by Williams *et al.* (1972). The reactivity of 2,3-and 2,5-dihydropyrazines, with their mechanisms of reaction, has been discussed by Flament (1981).

According to Sheldon *et al.* (1986), two molecules of the 2,3-dihydropyrazines can form a mixture of the corresponding pyrazine and 1,2,3,4-tetrahydropyrazine by disproportionation. It was also observed by Masuda *et al.* (1980) that dehydrogenation of 2,3-dimethyl-5,6-dihydropyrazine generated the disproportionation compounds 2,3-dimethyl-1,2,5,6-tetrahydropyrazine and 5-ethyl-2,3-dimethylpyrazine in addition to the desired 2,3-dimethylpyrazine in a sodium ethoxide/ethanol solution. It was then deduced that the carbanion of 2,3-dimethyl-5,6-dihydropyrazine was formed with the base and then reacted with acetaldehyde, present in ethanol in small quantities, to yield the 5-substituted pyrazine. On the basis of this result the authors prepared in high yield a series of nine, 5-substituted, 2,3-dimethylpyrazines by reaction of 2,3-dimethyl-5,6-dihydropyrazines with six aldehydes and three ketones under the same basic conditions.

Alkylpyrazines

A review of the presence of alkylpyrazines in a wide variety of foodstuffs has been published by Maier (1970b).

Two patents (Flament, 1973, 1975a) describe the synthesis of the 64 alkylpyrazines (among which 36 original compounds) having a molecular weight less than or equal to 150. Syntheses and organoleptic properties of 58 alkylpyrazines and quinoxalines were described by Winter *et al.* (1975g, 1981). Synthesis of 2,3-dialkylpyrazines by condensation of α-diketones with α-diamines, followed by catalytic dehydrogenation with copper chromite, has been described by Flament and Stoll (1967), or by oxidation at 140–190 °C in an alkaline ethyleneglycolic solution by Nakatani and Yanatori (1973). However, during the sixties, the complete GC-separation of the substituted isomers was not as easy as it became later with high resolution capillary columns. Therefore Goldman *et al.* (1967) reverted to catalytic hydrogenation to separate isomeric mixtures, piperazines being separated more easily than the corresponding pyrazines. This procedure may be difficult to follow when dealing with minute amounts of material, as mentioned by Bondarovich *et al.* (1967).

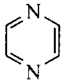
An exhaustive list of pyrazines identified in model system studies has been published (Maga, 1992). A mechanistic study of alkylpyrazine formation in model systems, with detailed reaction schemes, has been published by Rizzi (1972), pyrazines arising via complex interactions between α-amino acids and carbohydrates or small oxycarbon fragments derived therefrom such as, in this study, glyoxal, pyruvaldehyde and several α-diketones which were allowed to react with glycine, alanine and β-phenylalanine. Shibamoto and Bernhard (1977) investigated formation pathways of alkylpyrazines with sugar–ammonia model systems. They really identified pyrazine and 11 methyl and methylethylpyrazines (others being suggested), pentoses giving slightly higher yields than hexoses but with similar distribution patterns. Baltes and Bochmann (1986a, 1987c, 1987e) reported the reactions, under conditions of coffee roasting, of serine and threonine with sucrose, which are present in green coffee. In the reaction mixture they identified about 350 heterocyclic compounds (see Section 5.I). As expected, the formation of pyrazinic structures was favored, more than 120 compounds being identified, ca 65 of them being alkyl, alkenyl, and acylpyrazines (the others being bicyclic compounds). The presence of the carbohydrate explains, of course, the formation of furanyl- and furfurylpyrazines but the authors mentioned that when serine and threonine were heated, with or without low amounts of sucrose, the pyrazine concentrations related to all volatiles, amounted to 32–38 %, instead of 22 % in the reaction of threonine with an excess of sucrose and only 5 % in the reaction of serine with an excess of sucrose. The formation of alkylpyrazines is favored without sucrose, contrary to alkenylpyrazines, acylpyrazines not being formed. Interesting results were given by a study of the pairs, present as free amino acids in green coffee, asparagine (Asn)/aspartic acid (Asp) and glutamine (Gln)/glutamic acid (Glu) reacting with glucose. The amides on the side-chain gave more pyrazines than the acids (Koehler *et al.*, 1969). This was confirmed by Bohnenstengel and Baltes (1992) with the first pair treated under roasting conditions (220 °C) with glucose; the release of ammonia by deamidation explains the more important formation of nitrogen heterocycles; moreover the formation of vinylpyrazines could be explained by the dehydration of hydroxyethylpyrazines formed at lower temperature (100 °C) with asparagine. Ho *et al.* (1993) arrived to the same conclusion about the importance of deamidation on the formation of pyrazines using a glutamine labeled on the amide nitrogen. They also observed, comparing the dipeptides Ala-Asp and Ala-Asn, that the first gives more of the higher substituted pyrazines, the easy release of ammonia from the second leading to the formation of the simple pyrazines. This is in agreement with the results of Koehler *et al.* (1969). Ho and Chen (1999) have more recently quantified the pyrazines generated from Maillard reaction of serine, threonine and glutamine with monosaccharides and reviewed the different formation pathways of thermal processing to give pyrazine.

Rizzi (1988) examined the formation of alkylpyrazines from acyloins and ammonium salts under mild conditions, and suggested that some pyrazines could be formed by non-enzymic reactions between products of cell metabolism and ammonia.

The role of alkylpyrazines has been reviewed by Odell (1974), who measured the odor detection thresholds of ten pyrazines in water and mineral oil at 25 °C (underlining that these thresholds are probably different at the temperature at which coffee is served) and concluded that methylpyrazine and dimethylpyrazines are definitely involved in coffee and roasted peanut flavors (Mason *et al.*, 1966). Hashim and Chaveron (1996) studied the formation of methylpyrazines during roasting by varying time and temperature, a maximum being obtained after 10 min at 205 °C for an arabica and at 185 °C for a robusta, apart from tetramethylpyrazine which remains nearly constant (steam distillation/extraction–microdistillation). They suggest the possibility of monitoring the roasting process by evaluation of the ratios methyl/2,5-dimethyl and methyl/2,6-dimethylpyrazines. The concentration of methylpyrazines is ca 1.5 times higher in arabica than in robusta. Silwar and Lüllmann (1993b), studying the roasting of a robusta, from 170 to 260 °C, 5 min at each temperature (simultaneous steam distillation/extraction), obtained somewhat different results; they note differences in the behavior of pyrazines: some, like methylpyrazine, increased continuously, some reached a maximum and then decreased, some remained constant after the increase; the temperatures at which the formation starts also varied.

Grosch (1993, 1994) and Grosch *et al.* (1996) have commented on structure–odor activity relationships of pyrazines. They have shown by aroma-extract dilution analysis (AEDA) that only six alkyl-or alkenylpyrazines, all present in roasted coffee flavor and smelling earthy and roasty, might play a role in the aromas of food: trimethylpyrazine (**O.21**), 3-ethyl-2,5-dimethylpyrazine (**O.23**), 2-ethyl-3,5-dimethylpyrazine (**O.24**), 2-ethenyl-3,5-dimethylpyrazine (**O.46**), 2,3-diethyl-5-methylpyrazine (**O.27**) and 2-ethenyl-3-ethyl-5-methylpyrazine (**O.47**). A more recent publication on the same subject (Wagner *et al.*, 1999) mentioned odor descriptions and odor thresholds of 83 pyrazines, among them four of the six compounds quoted above (**O.24, 27, 46** and **47**) which have the lowest thresholds of the purely alkylpyrazines. The geometrical structure of a theoretical receptor was obtained by superimposing the minimized structures of pyrazines with low thresholds (Chem-X force-field minimization). Sterically forbidden regions in the resulting model were found by superimposing pyrazines with high thresholds. Structure–odor relationships had previously been developed by Rognon and Chastrette (1994) for methoxypyrazines having a bell-pepper aroma. The geometry of a hypothetical receptor was defined mainly on the basis of odor-threshold data published by Mihara and Masuda (1988) and by Mihara *et al.* (1991). This interaction model accounted for both the quality and intensity of the odor of the molecules studied. Other connections between molecular properties and physiological properties have been studied by Calabretta (1978), Fors (1983), Fors and Olofsson (1985), and Yoshii and Hirono (1996). Recently, Guyot *et al.* (1998) studied the inhibitory activity of 5-caffeoylquinic acid, the main component of the chlorogenic acids (see Section 2.1.4) on the formation of alkylpyrazines in Maillard reactions with model systems: valine or leucine and saccharose. Applying their results to green robustas, they concluded that the aroma quality increased when the chlorogenic-acids content decreased and when the sucrose content increased.

Alkylpyrazines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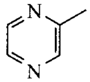
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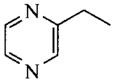
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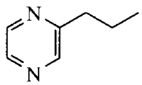
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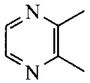
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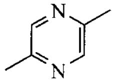
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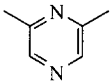
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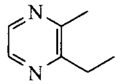
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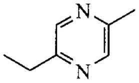
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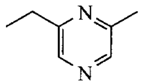
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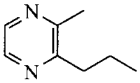

(O·11)

(O.1) ***(O.1)*** **Pyrazine,** *pyrazine, 1,4-diazine,* diazabenzene **[290-37-9]**

Identified in roasted coffee flavor as early as 1926 by Reichstein and Staudinger (1926a,b,c), and also by Goldman *et al.* (1967) (MS data). In the headspace of ground roasted coffee, it was found by Cros *et al.* (1980) with five alkylpyrazines, by Wang *et al.* (1983) only with methylpyrazine, by Ho *et al.* (1993) with 10 alkylpyrazines and in a concentration of 2.82 ppm. In the headspace of a brew, Shimoda and Shibamoto (1990a) identified it (0.10% of the volatiles, GC) with eight alkylpyrazines and 2-acetylpyrazine. From a brew, it was extracted only by liquid–liquid extraction with methylene chloride by Ramos *et al.* (1998), 11 alkylpyrazines and one acetylpyrazine being extracted by various methods. Koehler *et al.* (1971) gave a concentration of 5 ppm (extraction), Silwar *et al.* (1987) of 3.5–6.0 ppm (simultaneous distillation–extraction). It was found in a green Mexican arabica by Cantergiani *et al.* (2001), after vacuum hydrodistillation–extraction (0.17% of the volatiles by GC on a polar column).

It is present in the pyrolysis products of serine (Merritt *et al.*, 1970) and has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986), in a model with serine and threonine with and without sucrose (Baltes and Bochmann, 1987c). (Note: all the alkylpyrazines from **O.1** to **O.15** have been identified in this last publication in coffee as well as in the heating products of serine and threonine with or without sucrose, therefore we will mention it again after **O.15**).

It has a pungent, sweet odor, becoming by dilution floral with remote resemblance to heliotrope (Arctander, 1967). The odor threshold in water is 500 ppm according to Calabretta (1975), with strong sweet, slightly ammoniacal odor, or 175 ppm according to Vernin (1979).

(O.2) ***(O.2)*** **Pyrazine, methyl-,** *methylpyrazine,* 2-methylpyrazine **[109-08-0]** *FEMA 3309*

Identified in coffee flavor by Reichstein and Staudinger (1926a,b,c), and Goldman *et al.* (1967). In the headspace of ground coffee, it was found by Cros *et al.* (1980), and by Ho *et al.* (1993) (6.56 ppm). It is present in extracts of a brew: liquid–liquid extraction with pentane and methylene chloride, solid-phase microextraction, not in supercritical-CO_2 extraction (Ramos *et al.*, 1998). The concentration in roasted coffee has been estimated at 65 ppm by Koehler *et al.* (1971) (methylene chloride extraction of ground roasted coffee), 25 ppm by Stofberg and Stoffelsma (1981), 26.2 ppm by Tressl *et al.* (1982) in a roasted blend (range 30–60 ppm, Tressl, 1989), and 60–80 ppm by Silwar *et al.* (1987) in arabica (simultaneous distillation–extraction). For Hashim and Chaveron (1996), methylpyrazine is the main pyrazine that they studied, the concentration reaching a maximum of ca 25 ppm in an arabica after 10 min at 205 °C and about 13 ppm in a robusta after 10 min at 185 °C. For Silwar and Lüllmann (1993b), the concentration of methylpyrazine increased continuously in a robusta, from 170 to 260 °C, after 5 min at each temperature. Methylpyrazine has also been identified in green coffee volatiles by Vitzthum *et al.* (1976) and by Procida *et al.* (1997) in six green arabicas and six green robustas, reaching 7.7 % of the volatiles in the Angola robusta examined. Methylpyrazine was identified in a green Mexican arabica by Cantergiani *et al.* (2001) (0.31 % of the volatiles, see **O.1**).

It is formed in various model systems, for instance, in the reaction of asparagine with sugars, such as glucose, fructose, sucrose and arabinose (Odell, 1974). It can also be formed by condensation (involving the Strecker degradation of an amino acid) of pyruvaldehyde with glyoxal (Wang *et al.*, 1969).

This common compound has been found in numerous food flavors (TNO, 1997). The flavor is characterized as nutty, roasted (Pittet and Hruza, 1974), chocolatey in dilution (Calabretta, 1978), nutty, roasted, sweet (Masuda and Mihara, 1986), nutty, green (Masuda and Mihara, 1988), nutty, bitter almond, weak (Chemisis, 1998). The odor thresholds measured in water are 105 ppm at 25 °C (27 in oil) (Koehler *et al.*, 1971, 30 ppm (Masuda and Mihara, 1988), 100 ppm (Calabretta, 1975), 60 ppm (Guadagni *et al.*, 1972). In air the threshold is high, > 2000 $\mu g/m^3$ (Grosch *et al.*, 1996).

(O.3) *(O.3)* **Pyrazine, ethyl-,** *ethylpyrazine,* 2-ethylpyrazine **[13925-00-3]** ***FEMA 3281***

Identified and characterized (MS, IR data) in roasted coffee flavor by Goldman *et al.* (1967) and in green coffee bean volatiles by Vitzthum *et al.* (1976). The concentration measured by Silwar *et al.* (1987) was 13.5–16.5 ppm in roasted arabica. In the headspace of a brew, it represented 0.13 % (GC) for Shimoda and Shibamoto (1990a). Ramos *et al.* (1998) extracted it from a brew as for **O.2**.

Behun and Levine (1961) described its synthesis by alkylation of methylpyrazine (**O.2**) with methyl iodide in liquid ammonia, in the presence of sodium amide.

Ethylpyrazine is described as nutty, roasted (Pittet and Hruza, 1974), nutty, green, sweet (Masuda and Mihara, 1988), buttery, rum (Sizer *et al.*, 1975), with a burnt, praline-like flavor at 40 ppm in a sugar syrup (Winter *et al.*, 1975g). Measured threshold values in water are 21 ppm at 25 °C (17 in oil) (Koehler *et al.*, 1971), 6 ppm (Guadagni *et al.*, 1972), 4 ppm (Masuda and Mihara, 1988) and > 2000 $\mu g/m^3$ air at the sniffing-port of a GC system (Grosch *et al.*, 1996).

(O.4) **Pyrazine, propyl-,** *propylpyrazine,* 2-propylpyrazine **[18138-03-9]**

Identified in roasted coffee flavor by Goldman *et al.* (1967).

The synthesis was carried out according to the procedure of Behun and Levine (1961), as used for the preparation of ethylpyrazine.

The flavor is described as green vegetable (Pittet and Hruza, 1974), green and burnt at 10 ppm in a sugar syrup (Winter *et al.*, 1975 g).

(O.5) *(O.5)* **Pyrazine, 2,3-dimethyl-,** *2,3-dimethylpyrazine* **[5910-89-4]** ***FEMA 3271***

It was identified in the very volatile components of coffee flavor (steam distillate swept with nitrogen and condensed) by Viani *et al.* (1965) (MS and IR data). Its concentration in roasted coffee is estimated at 2.48 ppm by Ho *et al.* (1993) in a headspace analysis, 4.0 ppm by Stofberg and Stoffelsma (1981) and 4.5–5.3 ppm by Silwar *et al.* (1987) (simultaneous distillation–extraction). As for methylpyrazine (**O.2**), the formation increased continuously with increased roasting temperature, from 170 to 260 °C (Silwar and

Lüllmann, 1993b). Ramos *et al.* (1998) identified this dimethylpyrazine after liquid–liquid extraction of a brew (compare with **O.2**), Procida *et al.* (1997) in the headspace of three (of six) green arabicas and four (out of six) robustas, representing ca 0.1% of the volatiles (but 0.5% in the Angola robusta) and Cantergiani *et al.* (2001) in a green Mexican arabica (0.12% of the volatiles, see **O.1**).

The first synthesis was described in 1907 by Gabriel and Sonn and improved later by Ishiguro and Matsumura (1958). It is easily prepared by catalytic dehydrogenation of the condensation product of ethylenediamine with 2,3-butanedione, a procedure described by Flament and Stoll (1967).

This product is present in numerous food flavors. Its flavor has been described as green, nutty and roasted (Pittet and Hruza, 1974), pungent and in dilution chocolate type (Calabretta, 1978). At a concentration of 20 ppm, it imparts a slight caramel flavor to a sugar syrup (Winter *et al.*, 1975 g). The odor threshold in water is 2.5 ppm for Guadagni *et al.* (1972), 0.4 ppm for Calabretta (1975), 880 $\mu g/m^3$ air at the sniffing-port of a GC system for Grosch *et al.* (1996) (590–1170 μ/gm^3 air, Wagner *et al.*, 1999).

(O.6) *(O.6)* Pyrazine, 2,5-dimethyl-, *2,5-dimethylpyrazine* [123-32-0] *FEMA 3272*

Identified in roasted coffee flavor by Reichstein and Staudinger (1926a,b,c), and by Goldman *et al.* (1967) (MS data). It was present in headspace of roasted coffee for Cros *et al.* (1980) and Ho *et al.* (1993) who found 9.30 ppm. For Shimoda and Shibamoto (1990a), it represented 0.11% (GC) of the volatiles of a brew. Among the 13 pyrazines extracted from a brew by Ramos *et al.* (1998), only two, **O.6** and **O.10**, were extracted with supercritical CO_2 as well as other methods (see **O.2**). The concentration in roasted coffee was estimated at 25–35 ppm by Silwar *et al.* (1987) and 17 ppm by Stofberg and Stoffelsma (1981). Silwar and Lüllmann (1993b) observed that the formation of this pyrazine during roasting reached a maximum 240 °C then decreased, unlike **O.2** and **O.5**. Hashim and Chaveron (1996) also found a maximum in the concentration but only at 185 °C during 10 min for a robusta (ca 8 ppm). 2,5-Dimethylpyrazine was also identified in green coffee volatiles by Vitzthum *et al.* (1976), by Spadone *et al.* (1990) in 'Rio' and Santos reference, and by Cantergiani *et al.* (2001) (0.33% of the volatiles, see **O.1**).

Dawes and Edwards (1966) isolated it from the volatiles obtained by heating a mixture of D-fructose and glycine or L-β-phenylalanine. Wang *et al.* (1969) presented a model reaction in which the product of condensation of pyruvaldehyde with any amino acid degraded by a Strecker reaction can form an aminoketone which by subsequent steps of self-condensation and oxidation formed 2,5-dimethylpyrazine (Wang *et al.*, 1969; Manley *et al.*, 1974). It was found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

O.6 is present in numerous food flavors. According to the review by Fors (1983), the odor has been described as roasted, nutty, grassy, 'cornnuts' and its flavor as reminiscent of potato chips, chocolate, grilled chicken, roasted peanuts. The odor threshold in water at 25 °C is 35 ppm for Koehler *et al.* (1971) and only 1.8 ppm for Guadagni *et al.* (1972). A mean odor threshold of 1820 $\mu g/m^3$ air was measured at the sniffing-port of a GC system by Grosch *et al.* (1996) (1210–2430 $\mu g/m^3$ air, Wagner *et al.*, 1999). The flavor threshold of pure 2,5-dimethylpyrazine was found to be 2 ppm in oil and 1 ppm in water by multiple comparison and dilution tests (Deck and Chang, 1965).

(O.7) *(O.7)* Pyrazine, 2,6-dimethyl-, *2,6-dimethylpyrazine* [108-50-9] *FEMA 3273*

Identified by Reichstein and Staudinger (1926a,b,c) in a coffee flavor using classical techniques; the compound was only found again in a food more than 20 years later (1948–1955), in a chocolate extract also using exclusively classical analytical methods of derivatization (picrate technique) (Dietrich *et al.*, 1964). Since then, with the advent of gas chromatography, the compound has been identified in numerous other food flavors. Cros *et al.* (1980) found it in headspace of ground coffee, and Shimoda and Shibamoto (1990a) in headspace of a brew (0.14%, GC). The concentration in roasted coffee was estimated at 19 ppm by Stofberg and Stoffelsma (1981) and at 30–35 ppm by Silwar *et al.* (1987). For Silwar and Lüllmann (1993b), 2,6-dimethylpyrazine behaved like the 2,5-dimethyl isomer (**O.6**), formation reaching a peak at 240 °C. The same similarity is observed by Hashim and Chaveron (1996), but the maximum was at 185 °C with 10 min roasting for a robusta (ca 6.5 ppm). This dimethylpyrazine has been identified in green coffee volatiles by Vitzthum *et al.* (1976), by Procida *et al.* (1997) in six green arabicas and six robustas (like **O.2** and **O.5**, more abundant in the Angola robusta, 2.5%), and by Cantergiani *et al.* (2001) with a green Mexican arabica (0.47%, see **O.1**).

The odor is sweet, fried, resembling that of fried potatoes, but not as typical as that of the 2,5-isomer (Arctander, 1967) and nutty (Wagner *et al.*, 1999). The flavor has been described as 'chocolate' (Vernin, 1979), nutty, earthy, cocoa, roasted (Chemisis, 1999). The odor threshold in water at 25 °C is 54 ppm (8 in oil) for Koehler *et al.* (1971) but Guadagni *et al.* (1972) perceive it at 1.5 ppm. In air, Grosch *et al.* (1996) measured a mean odor threshold of 1720 μ/gm^3 air (1140–2300 μ/gm^3, Wagner *et al.*, 1999).

(O.8) Pyrazine, 2-ethyl-3-methyl-, *2-ethyl-3-methylpyrazine* [15707-23-0] *FEMA 3155*

Identified in roasted coffee by Goldman *et al.* (1967), in the headspace of ground roasted coffee by Cros *et al.* (1980) and Ho *et al.* (1993) (1.14 ppm). The concentration was estimated at 0.15–0.20 ppm by Silwar *et al.* (1987).

It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

A synthesis has been achieved by catalytic dehydrogenation of the condensation product of ethylenediamine with 2,3-pentanedione (Flament and Stoll, 1967). A slight modification of the oxidation procedure was later proposed by Nakatani and Yanatori (1973).

The product is described as nutty and roasted by Pittet and Hruza (1974). At a concentration of 3 ppm in a sugar syrup, it gives a nutty and hardnut taste and, at 4 ppm in a neutral soluble coffee base, it enhances the woody and ground-coffee note (Winter *et al.*, 1975g). It is also been described as having a raw potato flavor (Parliament, 1980). The odor threshold value of 0.13 ppm in water is given by Buttery *et al.* (1972) and of 23–46 $\mu\mathrm{g/m}^3$ air measured at the sniffing-port of a GC system by Wagner *et al.* (1999).

(O.9) *(O.9)* Pyrazine, 2-ethyl-5-methyl-, *2-ethyl-5-methylpyrazine* [13360-64-0] *FEMA 3154*

Identified in roasted coffee by Goldman *et al.* (1967), in the headspace of a brew by Shimoda and Shibamoto (1990a) (0.05%, GC), and in the headspace of ground coffee by Ho *et al.* (1993) (0.95 ppm). The concentration was estimated by Silwar *et al.* (1987) as 7.5–8.6 ppm. Ramos *et al.* (1998) extracted it from a brew (like **O.2**). It was found in green coffee bean volatiles by Vitzthum *et al.* (1976), and by Cantergiani *et al.* (2001) (0.34%, see **O.1**).

It is probably formed during the roasting by condensation (involving the Strecker degradation of an amino acid) of pyruvaldehyde with ethylglyoxal (Wang *et al.*, 1969).

It was prepared by Winter *et al.* (1975g) by alkylation of 2,5-dimethylpyrazine following the procedure of Behun and Levine (1961).

It imparts a coffee-like taste to a sugar syrup (20 ppm). Guadagni *et al.*(1972) found an odor threshold of 0.1 ppm in water.

(O.10) *(O.10)* Pyrazine, 2-ethyl-6-methyl-, *2-ethyl-6-methylpyrazine* [13925-03-6]

Identified in roasted coffee by Goldman *et al.* (1967), in the headspace of roasted coffee by Cros *et al.* (1980), Ho *et al.* (1993) (7.53 ppm), in the headspace of a brew (0.09%, GC) by Shimoda and Shibamoto (1990a), and extracted from a brew with various methods (see **O.2** and **O.6**) by Ramos *et al.* (1998). It is present at a concentration of 8.5–10.5 ppm in roasted coffee for Silwar *et al.* (1987). It was identified in green coffee volatiles by Vitzthum *et al.* (1976), by Procida *et al.* (1997) in six robustas and six arabicas, and by Cantergiani *et al.* (2001) (0.19 %, see **O.1**).

It has been found in a heated cysteine/glucose model system (Sheldon *et al.*, 1986).

Kamal and Levine (1962) prepared this pyrazine by methylation of 2,6-dimethylpyrazine (**O.7**), by the method described by Behun and Levine (1961).

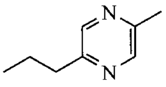
It imparts a roasted hazelnut-like taste at 20 ppm in a sugar syrup (Winter *et al.*, 1975 g).

(O.11) Pyrazine, 2-methyl-3-propyl-, *2-methyl-3-propylpyrazine* [15986-80-8]

Identified in coffee by Baltes and Bochmann (1987c).

The synthesis is realized by catalytic dehydrogenation of the condensation product of ethylenediamine with 2,3-hexanedione (Flament and Stoll, 1967), with a slight modification for the dehydrogenation step by Nakatani and Yanatori (1973).

At a concentration of 5 ppm in a sugar syrup, it imparts an earthy flavor and, at 2 ppm in a neutral soluble coffee base, it adds a green, nitrobenzene-like note (Winter *et al.*, 1975g).



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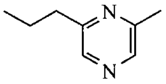

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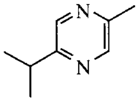
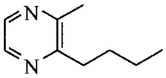
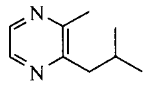


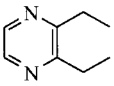
(O.14)
(O.14)



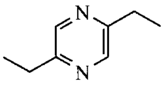
(O.15)



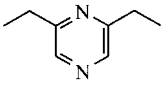
(O.16)



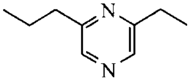
(O.17)



(O.18)
(O.18)



(O.19)
(O.19)



(O.20)

(O.12) Pyrazine, 2-methyl-5-propyl-, *2-methyl-5-propylpyrazine* [29461-03-8]

Identified in roasted coffee flavor by Friedel *et al.* (1971) (IR, MS data).

It has also been identified in wheaten bread and in cocoa. The flavor is characterized as roasted, cereal, greasy (Chemisis, 1970).

(O.13) Pyrazine, 2-methyl-6-propyl-, *2-methyl-6-propylpyrazine* [29444-46-0]

Identified in roasted coffee flavor by Goldman *et al.* (1967).

It was prepared by Kamal and Levine (1962) by alkylation of 2,6-dimethylpyrazine (**O.7**) after metalation by means of sodium amide in liquid ammonia.

According to Winter *et al.* (1975g), at a concentration of 10 ppm in a sugar syrup base, it has a burnt, hazelnut-like taste and, at the same concentration, it enhances the green and nutty note of a neutral soluble coffee beverage. It has also been described as having a burnt, butterscotch odor and an odor threshold < 0.1 ppm in water (Sizer *et al.*, 1975).

(O.14) *(O.14)* Pyrazine, 2-methyl-5-(1-methylethyl)-, *2-isopropyl-5-methylpyrazine, 2-methyl-5-(1-methylethyl) pyrazine* [13925-05-8] ***FEMA 3554***

Identified in roasted coffee flavor by Goldman *et al.* (1967) and by Andrade-Aispuro and Crouzet (1983) in the volatile compounds recovered during roasting. It was also found in a green Mexican arabica by Cantergiani *et al.* (2001) (0.18 % of the volatiles, see **O.1**).

This compound was prepared by Winter *et al.* (1975g), obtained as a by-product of alkylation of 2,5-dimethylpyrazine (**O.6**) using to the procedure of Behun and Levine (1961), then separated by GC.

The flavor is green, fatty, pyridinic (Chemisis, 1971).

(O.15) Pyrazine, 2-butyl-3-methyl-, *2-butyl-3-methylpyrazine* [15987-00-5]

Identified in roasted coffee by Baltes and Bochmann (1987c) (but not in their model system of heating serine and threonine with or without sucrose, see Note under **O.1**).

The synthesis was carried out by catalytic dehydrogenation of the condensation product of ethylenediamine with 2,3-heptanedione (Flament and Stoll, 1967), with a slight modification by Nakatani and Yanatori (1973).

At a concentration of 2.5 ppm, it imparts an anise-like, liquorice flavor to a sugar syrup (Winter *et al.*, 1975g).

Another **butylmethylpyrazine** was found in coffee by Baltes and Bochmann (1987b) but not in model systems (see above).

(O.16) Pyrazine, 2-methyl-3-(2-methylpropyl)-, *2-isobutyl-3-methylpyrazine, 2-methyl-3-(2-methylpropyl)pyrazine* [13925-06-9] *FEMA 3133*

Identified in roasted coffee flavor by Goldman *et al.* (1967).

It was prepared by catalytic dehydrogenation of the condensation product of ethylenediamine with 5-methyl-2,3-hexanedione (Flament and Stoll, 1967) and with a slight modification by Nakatani and Yanatori (1973).

It imparts a green, vegetable-like note at 5 ppm in a sugar syrup and gives an earthy, potato-like taste at 1.7 ppm in a neutral soluble coffee base (Winter *et al.*, 1975g). In her review on the sensory properties of Maillard-reaction products, Fors (1983) indicated a flavor of roasted hazelnuts and a green (bell-pepper like) odor with dry and sweet notes, and quoted odor thresholds in water varying from 35 to 400 ppb in water. The value given by Guadagni *et al.* (1972) is 35 ppb.

Contrary to the butylpyrazines, the three isobutylmethylpyrazines have been found by Baltes and Bochmann (1987c) when heating serine and threonine without sucrose, but not in coffee.

(O.17) *(O.17)* Pyrazine, 2,3-diethyl-, *2,3-diethylpyrazine* [15707-24-1]

Identified in roasted coffee by Baltes and Bochmann (1987c) and in green coffee by Cantergiani *et al.* (2001) (0.24% of the volatiles, see **O.1**).

Wagner *et al.* (1999) described this compound as earthy, with an odor threshold of 4.4–8.8 $\mu g/m^3$ air.

(O.18) *(O.18)* Pyrazine, 2,5-diethyl-, *2,5-diethylpyrazine* [13238-84-1]

Identified in roasted coffee by Goldman *et al.* (1967), by Friedel *et al.* (1971). The concentration was estimated to 0.05–0.10 ppm by Silwar *et al.* (1987) and 0.12% of the volatiles of a green coffee (see O.1) by Cantergiani *et al.* (2001).

Baltes and Bochmann (1987b) identified 2,5-diethylpyrazine when heating serine with sucrose, or serine and threonine (double molar) with or without sucrose.

It was prepared by Winter *et al.* (1975g) by a double methylation of 2,5-dimethylpyrazine (**O.6**), or from 2-ethyl-5-methylpyrazine (**O.9**) according to the procedure of Behun and Levine (1961).

2,5-Diethylpyrazine gives an hazelnut-like taste to a sugar syrup at a concentration of 10 ppm (Winter *et al.*, 1975g). Guadagni *et al.* (1972) gave an odor threshold of 20 ppb in water and 270 ppb in oil.

(O.19) *(O.19)* **Pyrazine, 2,6-diethyl-,** *2,6-diethylpyrazine* **[13067-27-1]**

Identified in roasted coffee flavor by Goldman *et al.* (1967), by Silwar *et al.* (1987) who found a concentration of 0.1–0.15 ppm and in a brew only after solid-phase microextraction (see **O.2**) by Ramos *et al.* (1998). It represented 0.51 % in the volatiles (see **O.1**) of a green arabica for Cantergiani *et al.* (2001).

Baltes and Bochmann (1987c) identified 2,6-diethylpyrazine in coffee and in their model reactions (see **O.1**).

Winter *et al.* (1975g) prepared this pyrazine by alkylation of 2-ethyl-6-methylpyrazine (**O.10**) using the method described by Behun and Levine (1961).

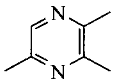
The flavor is hazelnut-like, at a concentration of 5 ppm in a sugar syrup (Winter *et al.*, 1975g). Guadagni *et al.* (1972) found an odor threshold of 6 ppb in water.

(O.20) Pyrazine, 2-ethyl-6-propyl-, *2-ethyl-6-propylpyrazine* **[32736-92-8]**

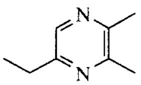
Identified in roasted coffee flavor by Friedel *et al.* (1971) (IR, MS data).

It was prepared by alkylation of metalated 2,6-dimethylpyrazine (**O.7**) (Kamal and Levine, 1962).

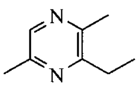
The flavor is fruity, rosy (Chemisis, 1970).



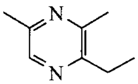
(O·21)
(O·21)



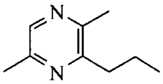
(O·22)



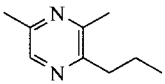
(O·23)
(O·23)



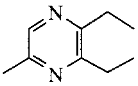
(O·24)
(O·24)



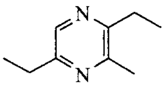
(O·25)



(O·26)



(O·27)



(O·28)
(O·28)

(O.21) *(O.21)* **Pyrazine, trimethyl-,** *trimethylpyrazine*, 2,3,5-trimethylpyrazine, 2,3,6-trimethylpyrazine **[14667-55-1]** ***FEMA 3244***

Identified in roasted coffee flavor by Goldman *et al.* (1967), in the headspace of a brew (0.04 %, GC) by Shimoda and Shibamoto (1990a), and in a brew (liquid–liquid extraction, solid-phase microextraction) by Ramos *et al.* (1998). The concentration was estimated as 4.0 ppm by Stofberg and Stoffelsma (1981), 8–10 ppm by Silwar *et al.* (1987) and was about 5 ppm for Hashim and Chaveron (1996). Trimethylpyrazine was found in green coffee volatiles by Vitzthum *et al.* (1976), and by Cantergiani *et al.* (2001) (0.54 %, see **O.1**). Procida *et al.* (1997) identified trimethylpyrazine in roasted coffee but not in the green coffees examined.

Trimethylpyrazine is probably formed by condensation (involving the Strecker degradation of an amino acid) of pyruvaldehyde with biacetyl (Wang *et al.*, 1969). Baltes and Bochmann (1987c) identified it in coffee and in their model reactions (see **O.1**).

The product was described as nutty and roasted by Pittet and Hruza (1974) and is very similar to 2,3-dimethylpyrazine (**O.5**) but slightly heavier for Calabretta (1978). At 30 ppm in a sugar syrup it has an interesting coffee-like taste (Winter *et al.*, 1975g). Wagner *et al.* (1999) characterized it as having a roasty odor. The threshold in water is 9 ppm (at 25 °C) according to Koehler *et al.* (1971), 0.4 ppm for Calabretta (1975) and 1.8 ppm according to Vernin (1979). The odor threshold of 33–66 $\mu g/m^3$ air (ca

35 times lower than that of 2,5-dimethyl (**O.6**) and 2,6-dimethylpyrazine (**O.7**)) was measured by Wagner *et al.* (1999). These authors also noticed that trimethylpyrazine had the lowest threshold amongst mono-, di-, tri-and tetramethylpyrazines and they are rather in agreement with Fors and Olofsson (1985), except for **O.6** which in the last quoted work had a threshold equal to that of trimethylpyrazine.

(O.22) pyrazine, 5-ethyl-2,3-dimethyl-, *5-ethyl-2,3-dimethylpyrazine*, 2-ethyl-5,6-dimethylpyrazine **[15707-34-3]**

Identified by Friedel *et al.* (1971) (IR, MS data).

The synthesis was realized by Flament (1975a) by addition of the ethyl group to 2,3-dimethylpyrazine (**O.5**) using the procedure described by Klein and Spoerri (1951).

The product was described as having a roasty and earthy odor (Wagner *et al.*, 1999); its flavor was described as chocolate and sweet at 6 ppm in water (Polak Frutal Works and Douwe Egberts, 1968), ethereal, burnt, cocoa (Chemisis, 1986). The odor threshold is 1 ppb in water (quoted in Fors, 1983) and a mean odor threshold of 200 $\mu g/m^3$ air has been measured by Grosch *et al.* (1996) (135–270 $\mu g/m^3$ air, Wagner *et al.*, 1999).

(O.23) ***(O.23)*** **Pyrazine, 3-ethyl-2,5-dimethyl-**, *3-ethyl-2,5-dimethylpyrazine,* 2-ethyl-3,6-dimethylpyrazine **[13360-65-1]** ***FEMA 3149***

Identified in roasted coffee flavor by Goldman *et al.* (1967), in the headspace of a brew (0.03 %, GC) by Shimoda and Shibamoto (1990a), in the headspace of roasted coffee (0.37 ppm) by Ho *et al.* (1993) and in green coffee volatiles by Vitzthum *et al.* (1976). The concentration in roasted coffee was 0.70–0.85 ppm according to Silwar *et al.* (1987).

This product is probably formed by condensation (involving the Strecker degradation of an amino acid) of pyruvaldehyde with 2,3-pentanedione (Wang *et al.*, 1969). It is formed in the Maillard reaction of the dipeptide Ala-Asp (alanine-aspartic acid) with glucose.

It can be prepared by the addition of an ethyl group to 2,5-dimethylpyrazine (**O.6**) by the alkyllithium method described by Klein and Spoerri (1951).

It imparts a hazelnut taste at 20 ppm in a sugar syrup (Winter *et al.*, 1975g) and is also described as earthy, baked and potato-like (Coleman and Ho, 1980), and roasty, earthy (Wagner *et al.*, 1999). A rather different note of lard is quoted by Vernin (1979). Tressl (1989) considered it as contributing to coffee aroma with an important flavor unit value. An odor threshold of 43 ppm in water at 25 °C has been measured by Koehler *et al.* (1971). Belitz and Grosch (1999) reported 40 $\mu g/L$ (40 ppb). Buttery and Ling (1997) corrected their previous value of 'order of' 1 ppb (Buttery *et al.*, 1973) to 8.6 ppb (confidence limits 5.6–13.6). Grosch *et al.* (1996) gave a value of 2.5 $\mu g/m^3$ air (2.4–4.8 $\mu g/m^3$ air, Wagner *et al.*, 1999).

(O.24) ***(O.24)*** **Pyrazine, 2-ethyl-3,5-dimethyl-**, *2-ethyl-3,5-dimethylpyrazine*, 2,6-dimethyl-3-ethylpyrazine **[13925-07-0]** ***FEMA 3150***

Identified in roasted coffee flavor by Goldman *et al.* (1967) who confirmed the structure by synthesis (MS data), and by Friedel *et al.* (1971). It has also been found in green coffee bean volatiles by Vitzthum *et al.* (1976). The concentration in roasted coffee was estimated at 2.0–2.2 ppm by Silwar *et al.* (1987). Using stable isotope dilution assays, Grosch *et al.* (1993) found ca 0.5 ppm in arabica and ca 0.8 in a robusta, Semmelroch *et al.* (1995), Grosch (1998b) ca 0.3 in arabica and 0.9 in robusta, concentration always significantly higher in robusta than in arabica (see also **O.27**).

Baltes and Bochmann (1987c) identify this compound in coffee and in their model reactions (see **O.1**).

It can be prepared by addition of an ethyl group to 2,6-dimethylpyrazine (**O.7**) with the alkyl-lithium method described by Klein and Spoerri (1951).

2-Ethyl-3,5-dimethylpyrazine, like the 3-ethyl-2,5-dimethyl isomer (**O.23**), is considered as contributing to coffee aroma with an important flavor unit value (Tressl, 1989). At a concentration of 5 ppm in a sugar syrup, it has a burnt almond taste, but at 2.0–4.0 ppm it enhances the woody note of a neutral soluble coffee beverage (Winter *et al.*, 1975g). It has been described as nutty and roasted by Pittet and Hruza (1974) and roasty, earthy by Wagner *et al.* (1999). The odor threshold in water at 25 °C was 15 ppm according to Koehler *et al.* (1971). The value given by Grosch (1998b), and Belitz and Grosch (1999) was 0.16 ppb (0.16 μg/L). The value of 0.04 ppb (95 %, confidence limits 0.02–0.05 ppb) in water was found by Buttery and Ling (1997) correcting their previous value of 0.4 ppb. Czerny and Grosch (1996) found an odor threshold of 0.011 $\mu g/m^3$ air (0.007–0.014). Wagner *et al.* (1999) noted that this product had the lowest odor threshold of the three ethyldimethylpyrazines, approximately 250 times lower than that of **O.23** and one of the four lowest thresholds of the alkylpyrazines (see **O.27**, **46** and **47**). They particularly insisted on the necessity for careful purification before measuring the sensory properties, specially with these low values. They recommend, therefore, that the presence of impurities must always be checked for by nasal appraisal of the GC effluent, the classical analysis by high-resolution GC not being suitable for the detection of traces of highly potent odorants. Buttery and Ling (1997) confirmed these remarks: the former value given for 3-ethyl-2,5-dimethylpyrazine (**O.23**) was too low, the sample being contaminated by 5 % of the more potent 2-ethyl-3,5-dimethyl isomer (**O.24**).

(O.25) pyrazine, 2,5-dimethyl-3-propyl-, *2,5-dimethyl-3-propylpyrazine* [18433-97-1]

Identified in roasted coffee by Baltes and Bochmann (1987c).

The authors also found this pyrazine when heating serine and threonine with or without sucrose.

The product was prepared by Winter *et al.* (1975g) by addition a propyl group to 2,5-dimethylpyrazine according to the method described by Klein *et al.* (1951) with propyllithium.

At a concentration of 40 ppm in a sugar syrup, the compound has a mild hazelnut taste (Winter *et al.*, 1975g), also described as green, soy, sweet, caramel (Chemisis, 1987). A mean odor threshold > 2000 $\mu g/m^3$ air was measured by GC-olfactometry by Grosch *et al.* (1996).

(O.26) Pyrazine, 3,5-dimethyl-2-propyl-, *3,5-dimethyl-2-propylpyrazine*, 2,6-dimethyl-3-propylpyrazine [32350-16-6]

Identified in roasted coffee flavor by Baltes and Bochmann (1987c) who also found it upon heating serine and threonine with or without sucrose.

The flavor is described as chocolate, praline (Chemisis, 1970). A mean odor threshold of 23 $\mu g/m^3$ air has been measured at the sniffing-port of a GC system by Grosch *et al.* (1996). Wagner *et al.* (1999) underlined the fact that the presence of a propyl group instead of an ethyl group increased the odor threshold by a factor of 230. The difference is even higher on introduction of an isopropyl or a butyl substituent.

(O.27) Pyrazine, 2,3-diethyl-5-methyl-, *2,3-diethyl-5-methylpyrazine*, 5,6-diethyl-2-methylpyrazine [18138-04-0] *FEMA 3336*

Identified by Bondarovich *et al.* (1967). The concentrations measured (stable isotope dilution assays) by Grosch *et al.* (1993) were 0.112 ppm in an arabica and 0.233 in a robusta, by Semmelroch *et al.* (1995), Grosch (1998b) 0.061–0.095 ppm in roasted arabicas and 0.31 in a robusta.

Baltes and Bochmann (1987c) identified this diethylmethylpyrazine and the two isomers **O.28** and **O.29** heating serine and threonine with or without sucrose, as well as in coffee.

This product can be prepared by catalytic dehydrogenation of the condensation product of 1,2-diaminopropane with 3,4-hexanedione following the method described by Flament and Stoll (1967).

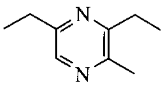
The product, mentioned in a patent by Winter *et al.* (1975g) has an hazelnut-like taste when incorporated in a sugar syrup at a concentration of 5 ppm. According to Pittet and Hruza (1974), it has an earthy odor and a nutty, roasted flavor. An odor threshold of 0.009–0.018 μg/m^3 air has been measured by GC olfactometry by Czerny *et al.* (1996). Wagner *et al.* (1999) commented that, with its planar structure, the compound has a very low odor threshold, 0.09 ppb in water (Grosch, 1998b) because it matches the geometry of the receptor for the earthy/roasty odor (like **O.24**, **46** and **47**) and has therefore been detected preferentially by aroma-extract dilution analysis (AEDA) as a potent odorant of heated foods (pyrazines **O.21** and **O.24** can be detected even with lower thresholds because of higher concentrations).

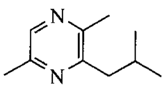
(O.28) *(O.28)* Pyrazine, 2,5-diethyl-3-methyl-, *2,5-diethyl-3-methylpyrazine* [32736-91-7]

Identified in roasted coffee aroma by Friedel *et al.* (1971) (IR, MS data), Baltes and Bochmann (1987c), and in green coffee volatiles by Vitzthum *et al.* (1976).

It can be prepared (Winter *et al.*, 1975g) by introduction of a methyl group to 2,5-diethylpyrazine with methyllithium, according to the method described by Klein and Spoerri (1951).

This pyrazine gives a hazelnut, slightly burnt taste to a sugar syrup at a concentration of 30 ppm (Winter *et al.*, 1975g). The odor threshold of 1.8 ppm in water quoted by Vernin (1979) has to be taken with precaution, as there is a printing error in the name (*diméthyl-2,5 méthyl-3-pyrazine*).


(O·29)
(O·29)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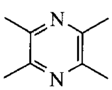
(O·31)
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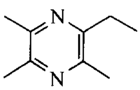
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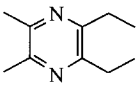
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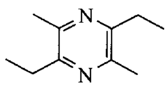
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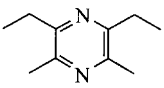
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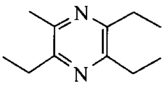

(O·36)

(O.29) *(O.29)* Pyrazine, 3,5-diethyl-2-methyl-, *3,5-diethyl-2-methylpyrazine*, 2,6-diethyl-3-methylpyrazine [18138-05-1]

Identified in roasted coffee flavor by Bondarovich *et al.* (1967) and in green coffee volatiles by Vitzthum *et al.* (1976). Ramos *et al.* (1998) found it in a brew after solid-phase microextraction (see **O.1**).

The product was prepared by treatment of 2,6-diethylpyrazine (**O.19**) with methyllithium according to the method described by Klein *et al.* (1951).

For Winter *et al.* (1975g) this pyrazine imparts a coffee-like taste to a sugar syrup at a concentration of 10 ppm, and enhances the green and nutty notes at the same concentration in a neutral soluble coffee beverage.

(O.30) Pyrazine, 2,5-dimethyl-3-(2-methylpropyl)-, *3-isobutyl-2,5-dimethylpyrazine, 2,5-dimethyl-3-(2-methylpropyl)pyrazine* [32736-94-0]

Identified in roasted coffee by Friedel *et al.* (1971) (IR, MS data).

The flavor is earthy, burnt (Chemisis, 1978). An odor threshold > 2000μg/m^3 air has been measured by GC-olfactometry (Wagner *et al.*, 1999).

(O.31) *(O.31)* **Pyrazine, tetramethyl-,** *tetramethylpyrazine* **[1124-11-4]** *FEMA 3237*

Identified in roasted coffee flavor by Stoffelsma *et al.* (1968), and Friedel *et al.* (1971). The concentration was estimated at 0.35–0.60 ppm by Silwar *et al.* (1987). It has also been identified in green coffee volatiles by Vitzthum *et al.* (1976), and by Cantergiani *et al.* (2001) (0.54%, see **O.1**).

The formation of tetramethylpyrazine in the Strecker degradation of DL-valine with 2,3-butanedione has been studied by Rizzi (1969) with a scheme explaining the formation of **O.31** by the self-condensation of the intermediate 3-amino-2-butanone. The amino acid is simultaneously decarboxylated and deaminated to yield a structurally related aldehyde containing one fewer carbon atoms (Schönberg and Moubacher, 1952). Tetramethylpyrazine is the only pyrazinic product in the reaction of 2,3-butanedione with alanine at 150–160 °C (Rizzi, 1972). For Flament *et al.* (1976a) it could also be formed very simply by direct condensation of 2,3-butanedione with ammonia. A similar route of formation was postulated by Kosuge and Kamiya (1962), Kosuge *et al.* (1962), Kosuge *et al.* (1971) and Demain *et al.* (1967) from broths of a strain of *Bacillus subtilis*, tetramethylpyrazine deriving from 2 moles of acetoin and 2 moles of ammonia.

Tetramethylpyrazine has also been identified in numerous food flavors (TNO, 1997). The compound is apparently responsible for the characteristic odor of fermented soybean or 'natto'. According the review by Fors (1983) it has a fermented soybean odor and a lard flavor; mentioned odor thresholds varying from 10 to 1000 ppb in water (38 ppm in oil). For Calabretta (1978) it is similar to trimethylpyrazine (**O.21**) (pungent, chocolate-type in dilution) but without the intensity, and has an odor threshold of 1 ppm in water. The odor threshold is 10 ppm in water at 25 °C as measured by Koehler *et al.* (1971) and $> 2000\,\mu g/m^3$ air measured by Grosch *et al.* (1996).

(O.32) Pyrazine, ethyltrimethyl-, *ethyltrimethylpyrazine,* 2-ethyl-3,5,6-trimethylpyrazine **[17398-16-2]**

Identified in roasted coffee flavor by Stoffelsma and Pypker (1968), and Friedel *et al.* (1971).

Various methods of synthesis have been described by Marion (1967, 1971): ethylation of trimethylpyrazine (**O.21**), methylation of tetramethylpyrazine (**O.31**) or of an ethyldimethylpyrazine. The product can also be obtained by condensation of 2,3-diaminobutane with 2,3-pentanedione or from 2,3-diaminopentane with 2,3-butanedione, followed by oxidation of the corresponding dihydropyrazine.

The resulting pyrazine has a chocolate flavor.

(O.33) Pyrazine, 2,3-diethyl-5,6-dimethyl-, *2,3-diethyl-5,6-dimethylpyrazine* **[106060-96-2]**

(O.34) Pyrazine, 2,5-diethyl-3,6-dimethyl-, *2,5-diethyl-3,6-dimethylpyrazine* **[18903-30-5]**

(O.35) Pyrazine, 2,6-diethyl-3,5-dimethyl-, *2,6-diethyl-3,5-dimethylpyrazine* **[18940-74-4]**

Identified in roasted coffee by Baltes and Bochmann (1987e).

The same authors (1987c) also identified the three isomers when heating serine and threonine with or without sucrose. **O.34** and/or **O.35** are the pyrazinic compounds formed in the reaction of 2,3-pentanedione with alanine at 150–160 °C (Rizzi, 1972).

O.34 has been prepared by Winter *et al.* (1975g) by alkylation of 3-ethyl-2,5-dimethylpyrazine **O.23** with ethyllithium according to the method described by Klein and Spoerri (1951).

O.34 has a coffee, green and earthy flavor (Chemisis, 1960), and **O.35** a burnt, chocolate, molasses flavor (Chemisis, 1971).

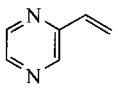
(O.36) Pyrazine, triethylmethyl-, *triethylmethylpyrazine* **[106073-56-7]**

Identified in roasted coffee by Baltes and Bochmann (1987e).

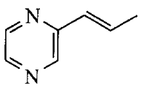
It is also formed when heating serine and threonine without sucrose or heating an excess of the amino acids with sucrose (Baltes and Bochmann, 1987c).

An **ethylmethylpropylpyrazine [107054-27-3]** with unspecified substitution position has been isolated by Baltes and Bochmann (1987c) and by Silwar *et al.* (1987).

Alkenylpyrazines



(O·37)



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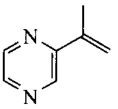

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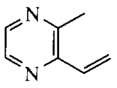

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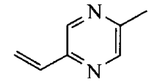
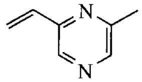


(O·41)
(O·41)



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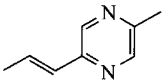

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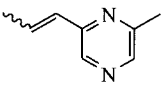

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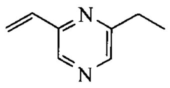

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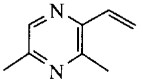
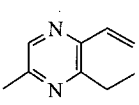


(O·46)



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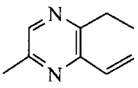


(O·48)

The formation and synthesis of alkenylpyrazines have been studied by Kleipool and Tas (1974), and Tas and Kleipool (1974). The synthesis of vinylpyrazine and its homologues has been described by Kamal *et al.* (1962).

(O.37) Pyrazine, ethenyl-, *vinylpyrazine, ethenylpyrazine* **[4177-16-6]**

Identified in roasted coffee flavor by Goldman *et al.* (1967). According to Silwar *et al.* (1987) the concentration is 1.2–1.3 ppm. Silwar and Lüllmann (1993b) observed that, during roasting, the vinylpyrazines were not formed before 190 °C, and the content of vinylpyrazine itself increased continuously until 260 °C (compare with methyl and dimethylpyrazines).

The synthesis has been carried out by Kamal *et al.* (1962) through an Hofmann exhaustive methylation of the Mannich product obtained by reaction of methylpyrazine with formaldehyde and dimethylamine hydrochloride. Goldman (1963) prepared vinylpyrazine by pyrolysis of pyrazine–ethanol.

The product imparts a green and burnt note to a sugar syrup at a concentration of 40 ppm (Winter *et al.*, 1975g). An odor threshold > 2000 μg/m^3 air has been measured at the sniffing-port of a GC system by Wagner *et al.* (1999).

(O.38) Pyrazine, 1-propenyl, (*E*)-, *(*E*)-prop-1-enylpyrazine,* 2-(*trans*-1-propenyl)pyrazine; no stereochemistry **[34413-32-6]**

It was identified in roasted coffee by Bondarovich *et al.* (1967).

Propenylpyrazine (without mention of stereochemistry) was found by Baltes and Bochmann (1987c) after heating serine and threonine with or without sucrose.

Tas and Kleipool (1974) proposed the synthesis from acetonylpyrazine by reduction with sodium borohydride followed by dehydration of the obtained 1-pyrazinyl-2-propanol. The formed allylpyrazine [(2-propenyl)pyrazine], (*E*)- and (*Z*)-(1-propenyl)pyrazines were separated by GC.

(1-Propenyl)pyrazine (no stereochemistry) has a burnt, animal flavor (Chemisis, 1973).

(O.39) Pyrazine, 1-methylethenyl-, *isopropenylpyrazine, (1-methylethenyl)pyrazine* [38713-41-6]

Identified by Lee *et al.* (1992) in extracts of brews with short brewing time, therefore qualified as a 'fast extractor', also by Ho *et al.* (1993) in headspace of roasted coffee (1.26 ppm).

(O.40) Pyrazine, 2-ethenyl-3-methyl-, *2-methyl-3-vinylpyrazine* [25058-19-9]

Identified in roasted coffee by Baltes and Bochmann (1987c).

The latter authors found it when heating serine and threonine with or without sucrose (but not when threonine alone was heated with sucrose).

The product can be prepared from 2,3-dimethylpyrazine (**O.5**) by the method of Kamal *et al.* (1962) by way of a Hofmann exhaustive methylation reaction on the Mannich product obtained from the reaction of the corresponding methylpyrazine with formaldehyde and dimethylamine hydrochloride.

In a sugar syrup at a concentration of 3 ppm, it has a fresh, hazelnut, earthy note, and in a neutral soluble coffee base at 0.7 ppm, it gives an earthy, green character (Winter *et al.*, 1975g). An odor threshold of 58–116 μg/m^3 air was measured with GC-olfactometry by Wagner *et al.* (1999).

(O.41) *(O.41)* Pyrazine, 2-ethenyl-5-methyl-, *2-methyl-5-vinylpyrazine, 2-ethenyl-5-methylpyrazine* [13925-08-1] *FEMA 3211*

Identified in roasted coffee flavor by Goldman *et al.* (1967). The concentration in roasted beans was estimated at 0.25–0.35 ppm by Silwar *et al.* (1987). Silwar and Lüllmann (1993b) observed that the formation started at 190 °C (5 min), the concentration increased until 240 °C and remained at the same level until 260 °C. Cantergiani *et al.* (2001) identified it in a green Mexican arabica (0.15% of the volatiles, see in **O.1**).

It is formed when heating serine and threonine with or without sucrose (Baltes and Bochmann, 1987c who found it also in coffee).

It has been prepared by Winter *et al.* (1975g) from 2,5-dimethylpyrazine (**O.6**) by the method of Kamal *et al.* (1962).

It imparts a coffee-like taste to a sugar syrup (10 ppm).

(O.42) Pyrazine, 2-ethenyl-6-methyl-, *2-methyl-6-vinylpyrazine,* 2-vinyl-6-methylpyrazine [13925-09-2]

Identified in roasted coffee flavor by Goldman *et al.* (1967). The concentration in roasted coffee was estimated at 0.50–0.65 ppm by Silwar *et al.* (1987) and followed the same curve as the 5-methyl isomer (**O.41**) during roasting (Silwar and Lüllmann, 1993b).

Baltes and Bochmann (1987c) found it (as well as in coffee) in their model systems only when serine and threonine were heated with sucrose.

It has been prepared from 2,6-dimethylpyrazine (**O.7**) using the procedure of Kamal *et al.* (1962) by Winter *et al.* (1975g).

It imparts a fresh hazelnut taste to a sugar syrup, at a concentration of 40 ppm.

(O.43) Pyrazine, 2-methyl-5-(1-propenyl)-, (*E*)-, *(E)-2-methyl-5-(prop-1-enyl)pyrazine,* 2-methyl-5-(*trans*-1-propenyl)pyrazine **[18217-82-8]**; no stereochemistry **[108653-51-6]**

(O.44) Pyrazine, 2-methyl-6-(1-propenyl), (*E*)-, *(E)-2-methyl-6-(prop-1-enyl)pyrazine,* 2-methyl-6-(*trans*-1-propenyl)pyrazine **[18217-81-7]**; no stereochemistry **[104638-11-1]**

These were identified in roasted coffee by Bondarovich *et al.* (1967) as (*E*)-isomers. Ho *et al.* (1993) found **O.43** (without mention of stereochemistry) in the headspace of roasted coffee.

Baltes and Bochmann (1987c) identified the two compounds (without mention of the stereochemistry) in coffee and in their model systems (see above).

(O.45) Pyrazine, 2-ethenyl-6-ethyl-, *2-ethyl-6-vinylpyrazine, 2-ethenyl-6-ethylpyrazine* **[32736-90-6]**

Identified by Friedel *et al.* (1971) (IR, MS data).

(O.46) Pyrazine, 2-ethenyl-3,5-dimethyl-, *3,5-dimethyl-2-vinylpyrazine* **[157615-33-3]**

Identified by Grosch *et al.* (1996), with a concentration of about 0.053 ppm in a roasted Columbia arabica, 0.037 in a Kenya arabica.

It was synthesized by Czerny *et al.* (1996) by reaction of 2,6-dimethylpyrazine (**O.7**) with vinylmagnesium bromide.

The odor threshold (earthy/musty note) given in this work was 0.008–0.016 μg/m^3 air. It is one of the compounds detected preferentially, by aroma extraction dilution analysis, as a potent odorant of heated foods (see in **O.27**).

(O.47) Pyrazine, 2-ethenyl-3-ethyl-5-methylpyrazine, *3-ethyl-5-methyl-2-vinylpyrazine* **[181589-32-2]**

Identified by Grosch *et al.* (1996), with a concentration of 0.014 ppm in a roasted arabica.

Synthesis by Czerny *et al.* (1996), see **O.46**.

The odor threshold given is 0.009–0.018 μg/m^3 air with an earthy/musty smell. It is considered to be a potent odorant of heated foods (see **O.24**, **27** and **46**).

(O.48) Pyrazine, 3-ethenyl-2-ethyl-5-methyl-, *2-ethyl-5-methyl-3-vinylpyrazine* **[181589-33-3]**

Identified by Czerny *et al.* (1996).

These authors synthesized it together with the above isomer from 2,3-diethyl-5-methylpyrazine (**O.27**) which was treated by *N*-bromosuccinimide. The two bromo derivatives were separated by TLC, then treated with dicyclohexylamine to give the vinyl compounds. The two alkenylpyrazines could not be separated in the coffee volatiles of arabica and robusta. The mixture was therefore treated with hydrogen bromide, the bromides analyzed by high resolution GC and their EI-MS compared with data of the bromides from **O.27**.

It is noteworthy that this isomer is not a potent odorant, with a threshold of 73–146 μg/m^3 air (ca 10^4 higher than that of **O.46** and **O.47**, but it has also the earthy/musty note.

An **ethenylethylmethylpyrazine** was found by Baltes and Bochmann (1987c) in coffee and after heating serine and threonine with sucrose.

Dihydrocyclopentapyrazines

The flavoring interest of 6,7-dihydro-5*H*-cyclopentapyrazines was revealed for the first time in patents by Polak's-Douwe Egberts (1968, 1969), and by Mookherjee *et al.* (International Flavors and Fragrances, 1972). The syntheses described in the first patent were achieved by reaction of ethylene-or propylenediamine with 2-chlorocyclopentanone, followed by dehydrogenation of the intermediate hexahydro compounds with copper chromite at 400 °C.

As observed by Johnson *et al.* (1971), these bicyclic compounds had sometimes been confused with isopropenylpyrazines which have the same molecular weights. At the beginning of the Seventies a few alkyl homologs had been identified in various roasted and heated foods. A series of dihydrocyclopentapyrazines was prepared by condensing hydroxycyclopentenones with alkylenediamines (according to Mookherjee *et al.*, 1972) or aliphatic α-diketones with diaminocyclopentane (Flament *et al.*, 1973).

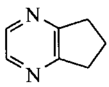
Flament *et al.* (1976a) confirmed that the flavor precursors of these bicyclic pyrazines were indeed amino acids and carbohydrates. Upon roasting, aminoacids liberated ammonia and, by caramelization, sugars generated the parts of the skeleton, alkylated hydroxycyclopentenones (tautomeric forms of cyclopentanediones), α-ketoaldehydes or aliphatic α-diketones.

In agreement with the proposed pathway, Flament *et al.* (1976a) obtained 2,3,5-trimethyl-6,7-dihydro-5*H*-cyclopentapyrazine (**O.60**) from the condensation of 2,3-butanedione with 2-hydroxy-3-methylcyclopent-2-en-1-one (**D.68**) in an ammoniacal solution at 100 °C. The reaction mixture also contained the predicted tetramethylpyrazine (**O.31**), resulting simply from the condensation of two molecules of butanedione with ammonia, and the intermediate key-product for the formation of cyclopentapyrazines, the 5-imino-2-methylcyclopent-1-en-1-ol. The formation of more oxidized products such as 2,3,5-trimethyl-5*H*-cyclopentapyrazine and 2,3-dimethyl-5-methylene-6,7-dihydro-5*H*-cyclopentapyrazine, compounds potentially present in roasted flavors, was also observed. In fact, 7-methyl-5*H*-cyclopentapyrazine and 6,7-dihydro-5-methylene-5*H*-cyclopentapyrazine (and homologs) had been patented as flavoring agents (Flament, Firmenich, 1975c). Alkyl-5*H*-cyclopentapyrazines being characterized by particularly powerful and typical roasted notes, a series of alkyl homologs has been synthesized by Flament *et al.* (1976b) using pyrolysis of the esters of the corresponding dihydroderivatives obtained by acylation of their *N*-oxides. Physical, spectroscopic and organoleptic properties were given. Other methylcyclopentapyrazines have been identified in bread, beer, malt and shoyu (soy sauce). Less volatile tricyclic compounds, bicyclopentapyrazines, are potentially present in roasted food flavors but have not yet been identified: tetrahydrodimethylbicyclopentapyrazines were found by Rizzi (1972) when treating 2-hydroxy-3-methylcyclopent-2-en-1-one (**D.68**) with alanine at 150–160 °C.

Manley *et al.* (1974) suggested that cyclopentapyrazines may result from the condensation of 2-hydroxy-3-methylcyclopent-2-en-1-one (**D.68**) with glyoxal or pyruvaldehyde and amino acids, and a mechanism of formation has also been suggested from a study on popcorn flavor by Walradt *et al.* (1970). Vitzthum and Werkhoff (1975) reported 17 new alkylated five-and six-membered bicyclic pyrazines in roasted coffee; the mass spectra of these new constituents and particularly the fragmentation pathways of 2-methyl-(**O.50**) and of 6,7-dihydro-5-methyl-5*H*-cyclopentapyrazine (**O.51**) are discussed in detail.

A more original pathway for formation of dihydrocyclopentapyrazines has been proposed by Flament (1981). The reaction of 2,3-dihydropyrazines with aldehydes and ketones allowed the preparation of numerous and original trisubstituted pyrazines. When α, β-unsaturated carbonyl compounds were used, the formation of bicyclic pyrazines was observed. Transitory 2,3-dihydropyrazines which certainly result from the trimolecular condensation of an α-dicarbonyl fragment with a diol in the presence of ammonia can condense with α, β-unsaturated compounds, giving 6,7-dihydro-5*H*-cyclopentapyrazine (**O.49**) and various alkylated homologs.

Baltes and Bochmann (1987e) found higher amounts of these bicyclic compounds when they used sucrose with threonine rather than serine, the higher reactivity possibly being due to the additional methyl group of threonine.



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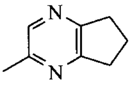

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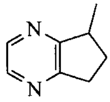

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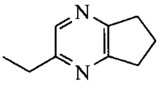

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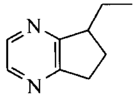

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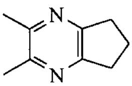

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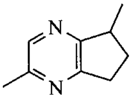

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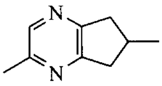

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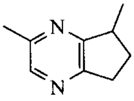

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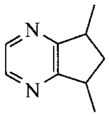

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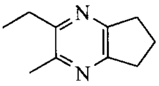

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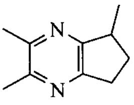

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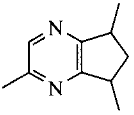


(O.61)

(O.49) 5*H*-Cyclopentapyrazine, 6,7-dihydro-, *6,7-dihydro-5*H*-cyclopentapyrazine*, 6,7-dihydro-5*H*-cyclopenta[*b*]pyrazine **[23747-47-9]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1975) (MS data). Shibamoto *et al.* (1982) observed an increasing concentration (0.22 to 0.39% of the volatiles, by GC after simultaneous distillation extraction) with roasting time (25 to 30 min at 230 °C). Silwar *et al.* (1987) found a concentration of 0.25–0.30 ppm.

Baltes and Bochmann (1987c) found it in their model reactions involving serine, threonine and sucrose (but not in coffee).

The synthesis was realized by condensation of ethylenediamine with 1,2-cyclopentanedione, followed by catalytic dehydrogenation (Flament *et al.*, 1973).

This product has a green and phenolic odor and taste at 4 ppm in water (Polak's-Douwe Egberts, 1968).The flavor is also described as burnt, animal, nutty, chocolate (Chemisis, 1972).

(O.50) 5*H*-Cyclopentapyrazine, 6,7-dihydro-2-methyl-, *6,7-dihydro-2-methyl-5*H*-cyclopentapyrazine* **[23747-46-8]**

Identified by Vitzthum and Werkhoff (1975) (MS data) and the concentration is estimated to 0.55–0.65 ppm by Silwar *et al.* (1987).

Baltes and Bochmann (1987c) found it in their model systems with and without sucrose as well as in coffee.

The product is described as having a chocolate note (odor, flavor) at 0.2 ppm in water (Polak's-Douwe Egberts, 1968) and an earthy, baked and potato-like odor (Coleman and Ho, 1980).

(O.51) 5*H*-Cyclopentapyrazine, 6,7-dihydro-5-methyl-, *6,7-dihydro-5-methyl-5*H*-cyclopentapyrazine* **[23747-48-0]** ***FEMA 3306***

Identified in roasted coffee volatiles by Vitzthum and Werkhoff (1975) (MS data). The concentration is estimated at 0.45–0.55 ppm by Silwar *et al.* (1987).

It was found by Baltes and Bochmann (1987c) in coffee as well as following reactions of serine and threonine with (and without) sucrose. Its formation has been explained by Flament *et al.* (1976a).

The structure was confirmed by condensation (although in low yields) of ethylenediamine with 2-hydroxy-3-methylcyclopent-2-en-1-one (**D.68**), followed by catalytic dehydrogenation (Flament *et al.*, 1973; Nakatani and Yanatori, 1973).

This compound is described as having a peanut note, odor and flavor, at 6 ppm in water (Polak's-Douwe Egberts, 1968) and an earthy, baked and potato-like odor (Coleman and Ho, 1980).

(O.52) 5*H*-Cyclopentapyrazine, 2-ethyl-6,7-dihydro-, *2-ethyl-6,7-dihydro-5*H*-cyclopentapyrazine* **[38917-60-1]**

Identified by Vitzthum and Werkhoff (1975).

(O.53) 5*H*-Cyclopentapyrazine, 5-ethyl-6,7-dihydro-, *5-ethyl-6,7-dihydro-5*H*-cyclopentapyrazine* **[52517-53-0]**

Identified in coffee flavor by Vitzthum and Werkhoff (1975).

Baltes and Bochmann (1987c) found it in coffee and when heating serine and threonine with or without sucrose (but not threonine alone with sucrose).

(O.54) 5*H*-Cyclopentapyrazine, 6,7-dihydro-2,3-dimethyl-, *6,7-dihydro-2,3-dimethyl-5*H*-cyclopentapyrazine* **[38917-63-4]**

Identified by Vitzthum and Werkhoff (1975).

It has a weak, burnt flavor (Chemisis, 1972).

(O.55) 5*H*-Cyclopentapyrazine, 6,7-dihydro-2,5-dimethyl-, *6,7-dihydro-2,5-dimethyl-5*H*-cyclopentapyrazine* **[38917-61-2]**

Identified by Vitzthum and Werkhoff (1975) and measured at a concentration of 0.75–0.80 ppm (Silwar *et al.*, 1987).

Baltes and Bochmann (1987c) identified it in coffee and when heating serine and threonine with or without sucrose.

The flavor is burnt, cocoa (Chemisis, 1974).

(O.56) 5*H*-Cyclopentapyrazine, 6,7-dihydro-2,6-dimethyl-, *6,7-dihydro-2,6-dimethyl-5*H*-cyclopentapyrazine* **[61928-63-0]**

Identified in coffee flavor by Baltes and Bochmann (1987e).

These authors (1987c) also found it in their model reactions involving serine, threonine with (not without) sucrose.

(O.57) 5*H*-Cyclopentapyrazine, 6,7-dihydro-2,7-dimethyl-, *6,7-dihydro-2,7-dimethyl-5*H*-cyclopentapyrazine* **[38917-62-3]**

Identified by Vitzthum and Werkhoff (1975) and present at a concentration of 0.10–0.15 ppm for Silwar *et al.* (1987).

Baltes and Bochmann (1987c) identified it in coffee and when heating serine and threonine with or without sucrose.

It is described as having an earthy, baked, potato-like odor (Coleman and Ho, 1980).

(O.58) 5*H*-Cyclopentapyrazine, 6,7-dihydro-5,7-dimethyl-, *6,7-dihydro-5,7-dimethyl-5*H-*cyclopentapyrazine* **[41330-21-6]**

Identified by Vitzthum and Werkhoff (1975).

Baltes and Bochmann (1987c) identified it to be like **O.55** and **O.57**.

The flavor is earthy, mouldy (Chemisis, 1972).

(O.59) 5*H*-Cyclopentapyrazine, 2-ethyl-6,7-dihydro-3-methyl-, *2-ethyl-6,7-dihydro-3-methyl-5*H-*cyclopentapyrazine* **[41330-35-2]**

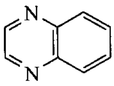
(O.60) 5*H*-Cyclopentapyrazine, 6,7-dihydro-2,3,5-trimethyl-, *6,7-dihydro-2,3,5-trimethyl-5*H-*cyclopentapyrazine* **[41330-39-6]**

(O.61) 5*H*-Cyclopentapyrazine, 6,7-dihydro-2,5,7-trimethyl-, *6,7-dihydro-2,5,7-trimethyl-5*H-*cyclopentapyrazine*

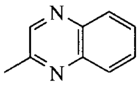
These were identified by Vitzthum and Werkhoff (1975) (MS data).

The flavors are described as weak, earthy for **O.59**, burnt, caramel for **O.60**, burnt, chocolate, sweet, coumarinic for **O.61** (Chemisis, 1972).

Quinoxalines



(O·62)
(O·62)



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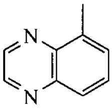

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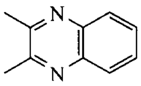

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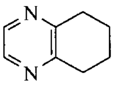
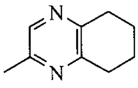
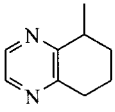


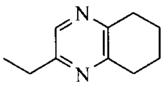
(O·66)



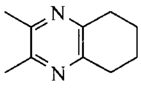
(O·67)



(O·68)



(O·69)



(O·70)

As mentioned above, Vitzthum and Werkhoff (1975) reported for the first time 17 alkylated five-and six-membered bicyclic pyrazines in roasted coffee The tetrahydroquinoxalines reference standards were synthesized according to the IFF British Patient 1 310 771. The mass spectra of these new constituents are discussed and fragmentation pathways for 2-ethyl-5,6,7,8-tetrahydroquinoxaline **O.69** and 2,3-dimethyl-5,6,7,8-tetrahydroquinoxaline **O.70** are commented upon in detail.

(O.62) *(O.62)* **Quinoxaline,** *quinoxaline*, benzopyrazine, 1,4-benzodiazine, quinazine, 1,4-naphthyridine **[91-19-0]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974b) and in green coffee volatiles by Spadone *et al.* (1990).

(O.63) Quinoxaline, 2-methyl-, *2-methylquinoxaline* **[7251-61-8]**

Identified in roasted coffee by Vitzthum and Werkhoff (1974b).

Baltes and Bochmann (1987c) identified it in coffee and when heating serine and threonine with or without sucrose.

2-Methylquinoxaline is synthesized according to the procedure described by Jones and McLaughlin (1950).

It imparts a phenolic, burnt and earthy taste to a sugar syrup at a concentration of 40 ppm (Winter *et al.*, 1975g).

(O.64) Quinoxaline, 5-methyl-, *5-methylquinoxaline* [13708-12-8] *FEMA 3203*

Identified in roasted coffee flavor by Goldman *et al.* (1967).

The first direct syntheses of quinoxalines were carried out by Hinsberg (1887) using the condensation of *o*-phenylenediamine with glyoxal or its higher homologs.

5-Methylquinoxaline gives a burnt, roasted and hazelnut-like taste to a syrup sugar at a concentration of 10 ppm, and a toasted flavor to a neutral soluble coffee base at 2.7 ppm (Winter *et al.*, 1975g).

(O.65) Quinoxaline, 2,3-dimethyl-, *2,3-dimethylquinoxaline* [2379-55-7]

Identified in roasted coffee by Vitzthum and Werkhoff (1974b).

It was identified by Baltes and Bochmann (1987c) in coffee and when heating threonine or serine and threonine with (not without) sucrose.

The synthesis can be carried out using the procedure of Gabriel and Sonn (1907).

2,3-Dimethylquinoxaline gives an astringent, fatty and earthy character to a neutral soluble coffee base at a concentration of 25 ppm (Winter *et al.*, 1975g).

2,5-Dimethylquinoxaline [26941–20–8] has been tentatively identified by Vitzthum and Werkhoff (1974b).

(O.66) Quinoxaline, 5,6,7,8-tetrahydro-, *5,6,7,8-tetrahydroquinoxaline* [34413-35-9] *FEMA 3321*

Identified in coffee by Vitzthum and Werkhoff (1975).

It was found by Baltes and Bochmann (1987c) in their model reactions with serine and threonine with sucrose (as well as in coffee).

It was prepared by Nakatani and Yanatori (1973) similarly to **O.51**, using cyclohexanedione.

The flavor is described as caramel, grilled (Chemisis, 1995).

(O.67) Quinoxaline, 5,6,7,8-tetrahydro-2-methyl-, *5,6,7,8-tetrahydro-2-methylquinoxaline* [38917-65-6]

Identified by Vitzthum and Werkhoff (1975).

Baltes and Bochmann (1987c) identified it when heating threonine, or serine and threonine, with or without sucrose (as well as in coffee).

(O.68) Quinoxaline, 5,6,7,8-tetrahydro-5-methyl-, *5,6,7,8-tetrahydro-5-methylquinoxaline* [52517-54-1]

Identified in coffee (and for the first time in a foodstuff) by Vitzthum and Werkhoff (1975).

It was prepared by Nakatani and Yanatori (1973) using ethylenediamine and 3-methylcyclohexane-1,2-dione (see **O.51**).

The flavor is weak, meaty, burnt (Chemisis, 1975).

(O.69) Quinoxaline, 2-ethyl-5,6,7,8-tetrahydro-, *2-ethyl-5,6,7,8-tetrahydroquinoxaline* [55968-42-8]

Identified in coffee (and for the first time in a foodstuff) by Vitzthum and Werkhoff (1975).

It was synthesized by condensation of ethylglyoxal in ethanol with 1,2-diaminocyclohexane at −20 °C followed by aromatization with oxygen to the corresponding bicyclic pyrazine according to Nakatani and Yanatori (1973). A similar method was reported by Pittet *et al.* (1974).

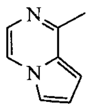
(O.70) Quinoxaline, 5,6,7,8-tetrahydro-2,3-dimethyl-, *5,6,7,8-tetrahydro-2,3-dimethylquinoxaline* **[35149-10-1]**

Identified in coffee (first report in a foodstuff) by Vitzthum and Werkhoff (1975).

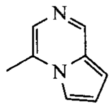
It was found in coffee by Baltes and Bochmann (1987c); in their model reactions they identified this quinoxaline when threonine was heated with sucrose (or by heating an equimolecular mixture of serine threonine and sucrose).

It has a cedar wood, tobacco, buttery odor (Pittet *et al.*, IFF Pat., 1969).

Pyrrolo[1,2-*a*]pyrazines



(O.71)



(O.72)

(O.71) Pyrrolo[1,2-*a*]pyrazine, 1-methyl-, *1-methylpyrrolo[1,2-*a*]pyrazine* **[64608-59-9]**

(O.72) Pyrrolo[1,2-*a*]pyrazine, 4-methyl-, *4-methylpyrrolo[1,2-*a*]pyrazine* **[64608-60-2]**

These were identified by Baltes and Bochmann (1987e).

The same authors (1987c) identified them when heating serine or threonine, with or without sucrose.

The flavor of **O.72** is slightly burnt, animal (Chemisis, 1976).

An **ethyl-** or **dimethylpyrrolo[1,2-*a*]pyrazine** has also been found by Baltes and Bochmann (1987c) in coffee as well as in model reactions involving serine, threonine and sucrose.

Methoxypyrazines

The organoleptic significance of alkoxy (and alkylthio) pyrazines has been suggested in the patent literature prior to the appearance of any reports of their occurrence in nature or in cooked foodstuffs (Firmenich & Co, Patents, 1965, 1967). Later, Buttery *et al.* (1969c) reported the isolation, identification and synthesis of the first original and characteristic highly potent aroma component of bell pepper, 2-isobutyl-3-methoxypyrazine (**O.77**) (green bell pepper must not be confused with 'poivre vert' as it was translated in Vernin, 1979). The same year, Bramwell *et al.* (1969) characterized 2-*sec*-butyl-3-methoxypyrazine (**O.76**) from galbanum oil where they suspected the presence of other pyrazines. Shortly after, Murray *et al.* (1970) mentioned the presence in green peas (*Pisum sativum*) of three extremely odorous pyrazines, likely to be of major significance in the flavor of peas, 2-isopropyl-3-methoxypyrazine (**O.75**), 2-*sec*-butyl-3-methoxypyrazine (**O.76**) and 2-isobutyl-3-methoxypyrazine (**O.77**). These and other homologues of methoxypyrazines with typical notes have been identified in galbanum oil and their synthesis described (Burrell *et al.*, 1970).

Unlike the majority of the ca 90 pyrazines identified in roasted coffee, the methoxyalkylpyrazines are not formed by Maillard reaction but must be of biogenetic origin. They have been identified in

13 of the 27 vegetable tissues examined by Murray and Whitfield (1975) who gave a survey of the occurrence and relative amounts of isopropyl (**O.75**), *sec*-butyl (**O.76**) and isobutylpyrazine (**O.77**) in a broad selection of raw vegetables. Vitzthum *et al.* (1976) also identified the lower homologues, 2-methyl- (**O.73**) and 2-ethyl-3-methoxypyrazines (**O.74**) in green coffee. Murray *et al.* (1970) suggested their formation in plant tissue by condensation of amides of α-amino acids with α-dicarbonyl derivatives. This pathway was criticized by Nursten and Sheen (1974), as neither glyoxal nor the α-amino amides had been isolated from plant tissues. Nevertheless these precursors could be present only at extremely low concentrations and consequently not easily detectable; moreover the fact that glyoxylic acid or glyoxylates could be involved in ring formation is attractive (Murray and Whitfield, 1975).

The synthesis, the MS and IR data of some 2-alkyl-3-methoxypyrazines with 'strong bell pepper-like odors' have been described by Seifert *et al.* (1970). According to Murray and Whitfield (1975), previously described syntheses of alkoxypyrazines gave low yields and the final product had to be separated by preparative GC. Several workers suffered unpleasant side-effects, notably persistent rhinitis, from long contact with significant amounts of the 3-alkyl-2-methoxypyrazines. The method they proposed involved the amidation of an amino acid, condensation of the amide with glyoxal under the conditions described by Jones (1949). The obtained 1,2-dihydropyrazin-2-one was treated with phosphorus oxichloride according to Karmas and Spoerri (1952) and the resulting chloropyrazine methoxylated with sodium methoxide in methanol. The overall yield from the free amino acid amide was in the region of 50%.

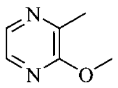
The olfactory properties of a number of alkoxyalkylpyrazines have been studied by Seifert *et al.* (1970). Shortening of the alkyl chain to the methyl compound results in the weakening of odor strength and in fact the odor of methoxypyrazine is not very characteristic, with a relatively high odor threshold of 700 ppb. Takken *et al.* (1975) also reported the odor thresholds in water. The odor thresholds of 46 pyrazines, not present in coffee (alkyl, alkoxy, phenoxy and alkylthio), were measured by Shibamoto (1986) who also observed the highest thresholds for the alkyl and the lowest for the alkoxy derivatives and concluded that the functional groups are more probably related to the threshold values than the molecular shape of the molecules. Chastrette *et al.* (1992), and Rognon and Chastrette (1994) developed structure–odor relationships for pyrazines causing the bell-pepper aroma and found that the substituents must meet precise geometrical requirements. Moreover Wagner *et al* (1999) claimed that both steric and electrostatic interactions with a receptor were the basis for odor recognition.

For Vitzthum *et al.* (1976), methoxypyrazines were the main source for the green coffee odor. Becker *et al.* (1988), when tracking the compounds responsible for the undesirable flavor of 'peasy' coffee beans (other defects being present in 'stinker' and 'Rio' beans) that gave to the brews a flavor of fresh green peas, found that the isobutyl derivative (**O.77**) was much less important than the 'peasy' isopropyl derivative (**O.75**).

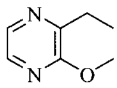
(O.73) **Pyrazine, 2-methoxy-3-methyl-,** *2-methoxy-3-methylpyrazine,* 2-methyl-3-methoxypyrazine **[2847-30-5]** *FEMA 3183*

Identified in green coffee volatiles by Vitzthum *et al.* (1976), and by Cantergiani *et al.* (2001) (0.08% GC, see **O.1**).

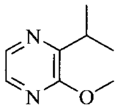
The flavor is described as popcorn, hazelnut, slightly earthy (Chemisis, 1981). The odor threshold in water is 4 ppb for Seifert *et al.* (1970), 2000 times that of the isopropylpyrazine (**O.75**) (but about 170 times lower than that of methoxypyrazine). Similar figures were given by Calabretta (1975), 3 ppb, with a vegetable note in concentration and popcorn/potato in dilution, and by Masuda and Mihara (1988), 7 ppb.



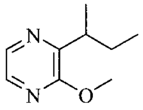
(O·73)



(O·74)



(O·75)
(O·75)



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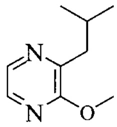
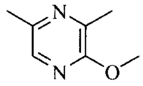


(O·77)
(O·77)



(O·78)
(O·78)

(O.74) **Pyrazine, 2-ethyl-3-methoxy-**, *2-ethyl-3-methoxypyrazine,* 2-methoxy-3-ethylpyrazine **[25680-58-4]**

Identified in green coffee volatiles by Vitzthum *et al.* (1976).

The odor threshold is 0.425 ppb in water for Seifert *et al.* (1970) (compare with **O.73**).

(O.75) ***(O.75)*** **Pyrazine, 2-methoxy-3-(1-methylethyl)-**, *2-isopropyl-3-methoxypyrazine, 2-methoxy-3-(1-methylethyl)pyrazine,* 3-isopropyl-2-methoxypyrazine **[25773-40-4]** ***FEMA 3358***

Identified in green coffee by Vitzthum *et al.* (1976), Cantergiani *et al.* (2001) and also found in roasted coffee (Becker *et al.*, 1988). Czerny and Grosch (2000) found 2.3 ppb in a green and 2.4 ppb in a medium-roasted arabica, the quantification being realized by the use of deuterated internal standards (see Section 3.2).

The precursors could be valine and glyoxal according to Murray and Whitfield (1975).

The synthesis of the compound is achieved by condensation of the amide hydrochloride of valine with glyoxal (Jones, 1949), followed by treatment with diazomethane (Seifert *et al.*, 1970) or successive chlorination with phosphorus oxychloride and methoxylation (Murray and Whitfield, 1975).

This methoxypyrazine possesses a strong vegetable-like odor (potatoes for Belitz and Grosch, 1999) and has been identified particularly in green peas (Murray *et al.*, 1970) at an estimated concentration of 10 μg/ton (10 ppt). Whereas there is no question that the isobutyl isomer (**O.77**) is strongly characteristic of bell peppers (Murray *et al.*, 1970), Murray and Whitfield (1975) observed that in dilute solution (between 0.1 and 10 ppb), 2-isopropyl-3-methoxypyrazine is likened to the odor of freshly shelled green peas, pea shells and the pea-shelling process, sometimes also with raw potatoes. Flavor descriptions are earthy, nutty, green, potato (Chemisis, 1989). Excessive amounts of 2-isopropyl-3-methoxypyrazine have been described as the reason for a 'peasy' off-flavor (or potato taste) in certain batches of roasted East African coffee (Becker *et al.*, 1988; Vitzthum, 1999). The odor threshold in water is estimated at 1 ppt (Murray *et al.*, 1970) or 2 ppt (Seifert *et al.*, 1970), values mentioned by Belitz and Grosch (1999). The odor threshold of 1–2 ng/m^3 air has been measured at the sniffing-port of a GC system (Wagner *et al.*, 1999). The value measured by Czerny and Grosch (2000) was 0.1 μg/kg cellulose.

(O.76) **Pyrazine, 2-methoxy-3-(1-methylpropyl)-**, *2-methoxy-3-(1-methylpropyl)pyrazine, 2-*sec-*butyl-3-methoxypyrazine,* 3-*sec*-butyl-2-methoxypyrazine **[24168-70-5]; (±)- [123625-20-7]; (*R*)- [124151-14-0]; (*S*)- [124151-13-9]**

Identified by Cantergiani *et al.* (2001) in a green Mexican arabica with (400 ppt) or without (300 ppt) the mouldy/earthy defect (0.06 % of the volatiles, see **O.1**).

The precursors could be isoleucine and glyoxal for Murray and Whitfield (1975) who performed the synthesis from these two compounds (see **O.75**).

The odor threshold in water is ca 1 ppt (Murrary *et al.*, 1970). The odor threshold (peasy note or earthy for Belitz and Grosch, 1999) is 2–4 ng/m^3 air as measured by Wagner *et al.* (1999), similar to those of the isopropyl (**O.75**) and isobutyl (O.77) compounds.

(O.77) ***(O.77)*** **Pyrazine, 2-methoxy-3-(2-methylpropyl)-,** *2-isobutyl-3-methoxypyrazine, 2-methoxy-3-(2-methylpropyl)pyrazine,* 3-isobutyl-2-methoxypyrazine **[24683-00-9]** ***FEMA 3132***

Identified in roasted coffee by Friedel *et al.* (1971) (IR, MS data), in green coffee volatiles by Vitzthum *et al.* (1976), by Spadone *et al.* (1990) in green 'Rio' Puerto Rico and in a healthy variety, and by Cantergiani *et al.* (2001) in a green Mexican arabica with (17 ppb) or without (8 ppb) the earthy/mouldy defect (0.73 % of the volatiles, see **O.1**). In medium-roasted arabicas, Grosch *et al.* (1996) found concentrations of 50–83 ppb. Czerny and Grosch (2000) found 97 ppb in a green arabica as well as in the medium-roasted sample (see **O.75**).

According to the mechanism proposed by Murray *et al.* (1970), the precursors could be leucine and glyoxal (Murray and Whitfield, 1975).

The synthesis, similar to that of the lower homolog (**O.75**) starting from leucine and glyoxal, was described in the latter publication and by Seifert *et al.* (1970).

2-Isobutyl-3-methoxypyrazine contributes to the final aroma impression after coffee roasting. It is the main member of the methoxypyrazine series and the principal contributor to the green bell-pepper note. Bramwell *et al.* (1969) found a typical odor of galbanum oil in which it has been tentatively identified. Belitz and Grosch (1999) noted a red pepper (hot paprika) aroma quality. Cantergiani *et al.* (2001), in their study of the mouldy/earthy off-flavor of a Mexican green arabica, found that the three methoxypyrazines (**O.75–77**) gave only a minor contribution to the defect, the main culprits being 2-methylisoborneol (**B.44**), 2,4,6-trichloroanisole (**H.82**) and geosmin (**B.46**). The flavor is described as green, bell-pepper, peas, slightly earthy (Chemisis, 1995). The odor threshold in water is 2 ppt for Seifert *et al.* (1970) and 16 ppt for Takken *et al.* (1975), but 10 ppb for Calabretta (1975). (For comparison, the odor threshold of isobutylpyrazine is 0.4 ppm, measured by Seifert *et al.*, 1970). The peasy odor and the odor threshold 0.2 μg/kg cellulose measured by Czerny and Grosch (2000) and 2–4 μg/m^3 air measured by Wagner *et al.* (1999) confirmed that 3-alkyl-2-methoxypyrazines are a special class of odorants.

(O.78) ***(O.78)*** **Pyrazine, 2-methoxy-3,5-dimethyl-,** *2-methoxy-3,5-dimethylpyrazine* **[92508-08-2]**

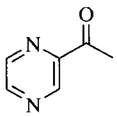
Identified in green and roasted arabica coffee by Czerny and Grosch (2000) in an extract analyzed by multidimensional high resolution GCMS. The concentration is 0.5 ppb in green and 1.1 ppb in the medium-roasted sample (see **O.75**).

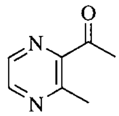
The synthesis is described. 2,6-Dimethylpyrazine (**O.7**) was first treated with chlorine and then by sodium methoxide in methanol. The 3-methoxy-2,5-dimethyl isomer was also prepared for comparison.

2-Methoxy-3,5-dimethylpyrazine is another potent odorant of green and roasted coffee. The odor description is earthy and the odor threshold 0.006 μg/kg cellulose, lower than those of the isopropyl and isobutyl analogs **O.75** and **O.77**.

Acetylpyrazines

The acetylpyrazines constitute a class of particularly valuable natural products. They have a surprisingly intense and characteristic roasted note reminiscent of popcorn (Roberts, 1968). The identification of this family in roasted coffee flavor was essentially made by Vitzthum and Werkhoff (1974b). The formation of acetylpyrazines, identified at nearly the same time in roasted sesame seed (Manley *et al.*, 1974), may result from the condensation of a known browning-reaction product (3,4-dihydroxy-3-buten-2-one or *C*-methyl reductone) with glyoxal in the presence of an amino acid. The same type of reaction, involving glyoxal, methylglyoxal (pyruvaldehyde) or biacetyl and 3,4-dihydroxy-3-penten-2-one could explain the formation of the methyl and dimethyl homologs. A comparative study of the flavor properties of alkyl, alkoxy and acetylthiazoles, pyrazines and pyridines (Pittet and Hruza, 1974) has shown that the characteristic nutty, corny and bready odors of these heterocyclic compounds is related to the presence of the functional groups in the position adjacent to the nitrogen atom. The same odor quality is particularly exhibited by the 2-acetyl derivatives of 4,5-dihydrothiazole (Tonsbeek *et al.*, 1971) and 2-acetyl-1,4,5,6-tetrahydropyridine (Hunter *et al.*, 1969) where the acetyl group and the nitrogen atom are in the same plane as is the case with 2-acetylthiazole and 2-acetylpyridine.


(O.79)
(O.79)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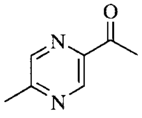
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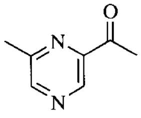
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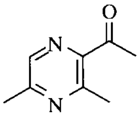
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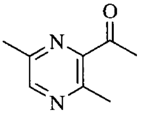
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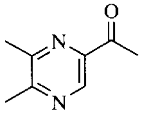

(O.85)

(O.79) ***(O.79)*** **Ethanone, 1-pyrazinyl-,** *1-pyrazinylethan-1-one, acetylpyrazine* **[22047-25-2]** ***FEMA 3126***

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974b) and in stinking green coffee by Guyot *et al.* (1982, 1983), who characterized it as having an acrid note. According to Stofberg and Stoffelsma (1981), the concentration in coffee is 1.3 ppm. For Shimoda and Shibamoto (1990a) it represented 0.03% (GC) in the headspace of a brew.

Baltes and Bochmann (1987c) identified pyrazinylethanone when heating serine and threonine with (but not without) sucrose (as well as in coffee).

The product had already been synthesized by Kushner *et al.* (1952), and Smith (V.K.) and Kushner (1954) and Shindo (1960), in relation with a study on the antituberculous activity of pyrazinamide, an aza-analog of nicotinamide (Coté *et al.*, 1953). A preparation procedure was also described by Wolt (1975a). The synthesis is usually performed by dehydration of the commercially available pyrazinamide into 2-cyanopyrazine followed by a Grignard reaction (Ohloff *et al.*, 1985).

1-Pyrazinylethanone was identified for the first time in an investigation of the components of sesame oil (Takei *et al.*, 1969). It was described as having a popcorn and nutty flavor (Roberts, Reynolds Tobacco Co, 1968), or (after sublimation) animal, burnt and (after recrystallization) sweet, caramel, popcorn (Chemisis, 1984). An odor threshold value of 62 ppb (62 μg/L) in water is mentioned by Belitz and Grosch (1999).

(O.80) Ethanone, 1-(3-methylpyrazinyl)-, *1-(3-methylpyrazin-2-yl)ethanone,* 2-acetyl-3-methylpyrazine **[23787-80-6]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974b). Ramos *et al.* (1998) found it in a brew after liquid–liquid extraction with pentane (see **O.2**).

Its formation during roasting can be explained by an interaction between cysteine and ribose (Mulders, 1973).

The synthesis has been described in a patent of Polak's Frutal Works and Douwe Egberts (1968) by application of a scheme used for the preparation of acetylpyridines (Kolloff and Hunter, 1941). The corresponding monocarboxylate is condensed with ethyl acetate in the presence of anhydrous sodium ethoxide, and the condensation product then hydrolyzed with aqueous hydrochloride. Another procedure has been applied by Mookherjee and Klaiber (1972) who treated 2-ethyl-3-methylpyrazine (**O.8**) successively with *N*-bromosuccinimide and the sodium salt of 2-nitropropane or pyridine 1-oxide (66% overall yield). Another method has been published by Wolt (IFF, 1975a).

The product is described as having a cereal, roasted bean odor and flavor at 4 ppm in water (Polak's Frutal Works and Douwe Egberts, 1968). Other flavor descriptions are caramel, praline, bready, roasted (Chemisis, 1995).

(O.81) Ethanone, 1-(5-methylpyrazinyl)-, *1-(5-methylpyrazin-2-yl)ethanone,* 2-acetyl-5-methylpyrazine **[22047-27-4]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974b). A concentration of 0.25–0.30 ppm in roasted coffee was measured by Silwar *et al.* (1987).

Baltes and Bochmann (1987c) identified it when heating serine and threonine with (but not without) sucrose (as well as in coffee).

It has been prepared from 2-cyano-5-methylpyrazine (obtained by dehydration of the corresponding amide) by reaction with methylmagnesium iodide and decomposition with ice and hydrochloric acid (Schwaiger and Ward, 1972). A synthesis has also been described by Wolt (1975a).

According to Roberts (1968) it has a popcorn-like flavor.

(O.82) Ethanone, 1-(6-methylpyrazinyl)-, *1-(6-methylpyrazin-2-yl)ethanone,* 2-acetyl-6-methylpyrazine **[22047-26-3]**

Identified in roasted coffee flavor by Vitzthum and Werkhoff (1974b). A concentration of 0.50–0.55 ppm was measured by Silwar *et al.* (1987).

It was found by Baltes and Bochmann (1987c) like **O.79** and **O.81**.

The compound can be prepared by direct oxidation with sodium dichromate of 2-ethyl-6-methylpyrazine (**O.10**) as described by Wolt (1975b).

It is characterized by a popcorn flavor (Roberts, Reynolds Tobacco Co, 1968).

(O.83) Ethanone, 1-(3,5-dimethylpyrazinyl)-, *1-(3,5-dimethylpyrazin-2-yl)ethanone,* 2-acetyl-3,5-dimethylpyrazine **[54300-08-2]** *FEMA 3327*

(O.84) Ethanone, 1-(3,6-dimethylpyrazinyl)-, *1-(3,6-dimethylpyrazin-2-yl)ethanone,* 2-acetyl-3,6-dimethylpyrazine, 3-acetyl-2,5-dimethylpyrazine **[54300-09-3]**

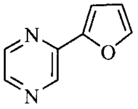
(O.85) Ethanone, 1-(5,6-dimethylpyrazinyl)-, *1-(5,6-dimethylpyrazin-2-yl)ethanone,* 2-acetyl-5,6-dimethylpyrazine, 5-acetyl-2,3-dimethylpyrazine **[54300-10-6]**

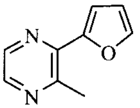
These were identified in coffee by Vitzthum and Werkhoff (1974b).

They can be prepared by direct oxidation using sodium dichromate of the corresponding ethyldimethylpyrazines, as described by Wolt (1975a,b).

The flavors are described as earthy, nutty, hazelnut, coffee for **O.83**, and earthy, green for **O.84** and **O.85** (Chemisis, 1976).

(2-Furyl)- and (2-furylmethyl)pyrazines


(O.86)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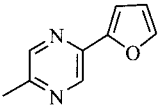
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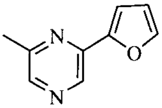
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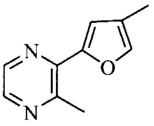
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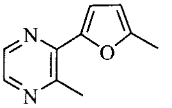
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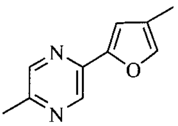
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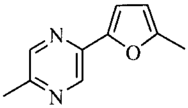
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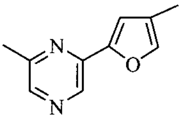
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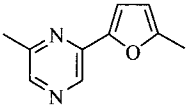
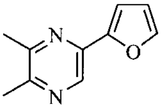

(O.95)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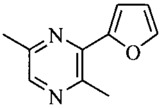
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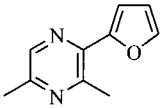
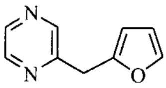

(O.98)


(O.99)

In 1971, for the first time, a (2-furyl)pyrazine was identified in coffee (Friedel *et al.*, 1971), then in 1974 numerous other homologs (Vitzthum and Werkhoff, 1974b) and two more in 1982 (Silwar) were found. (2-Furyl)pyrazines may arise from the condensation of a known Maillard browning product, 1-(2-furyl)-1,2-propanedione (Gianturco *et al.*, 1964b; Ferretti and Flanagan, 1971b), with glyoxal and an amino acid (Manley *et al.*, 1974). In model reactions involving serine, threonine and sucrose, the furyl and furfurylpyrazines were not found in the absence of sucrose, as expected (Baltes and Bochmann, 1987c). Chun and Ho (1997) examined the volatile nitrogen-containing compounds formed by Maillard reaction, but under deep-fat frying conditions. The model systems were glutamine, glutamic acid, asparagine and aspartic acid with glucose. Glutamine easily released free ammonia in the working conditions and gave the highest yields of pyrazines, **O.86**, **O.88** and **O.89** being the most important. In fact, of the four amino acids, only glutamine was not mentioned as free in green coffee.

(O.86) Pyrazine, 2-furanyl-, *(2-furyl)pyrazine* [32736-95-1]

Identified for the first time by Friedel *et al.* (1971) (IR, MS data). Silwar *et al.* (1987) found a concentration of 0.6–0.7 ppm.

Baltes and Bochmann (1987c) identified this pyrazine in coffee and when heating serine and threonine with (but not without) sucrose.

This first member of the series was found afterwards in numerous food flavors (TNO, 1997). It has a weak, burnt flavor (Chemisis, 1975).

(O.87) Pyrazine, 2-(2-furanyl)-3-methyl-, *2-(2-furyl)-3-methylpyratine* **[32737-01-2]**

Identified by Vitzthum and Werkhoff (unpublished results quoted by Vitzthum, 1975).

Nakatani and Yanatori (1973) synthesized this furylpyrazine in the same way as the cyclopentapyrazines and the quinoxalines, using 1-(2-furyl)-1,2-propanedione (I.8) and ethylenediamine.

(O.88) Pyrazine, 2-(2-furanyl)-5-methyl-, *2-(2-furyl)-5-methylpyrazine* **[27610-38-4]**

(O.89) Pyrazine, 2-(2-furanyl)-6-methyl-, *2-(2-furyl)-6-methylpyrazine* **[32737-03-4]**

These were identified in roasted coffee by Vitzthum and Werkhoff (unpublished results quoted by Vitzthum, 1975), and by Silwar (1982). Silwar *et al.* (1987) found concentrations of 0.35–0.40 ppm in roasted coffee for the two compounds. (It had also been identified in cocoa by Vitzthum *et al.*, 1975).

They were found by Baltes and Bochmann (1987c) like (2-furyl)pyrazine (**O.86**).

(O.90) Pyrazine, 2-methyl-3-(4-methyl-2-furanyl)-, *2-methyl-3-(4-methyl-2-furyl)pyrazine* **[54300-16-2]**

(O.91) Pyrazine, 2-methyl-3-(5-methyl-2-furanyl)-, *2-methyl-3-(5-methyl-2-furyl)pyrazine* **[54300-13-9]**

(O.92) Pyrazine, 2-methyl-5-(4-methyl-2-furanyl)-, *2-methyl-5-(4-methyl-2-furyl)pyrazine* **[54300-17-3]**

(O.93) Pyrazine, 2-methyl-5-(5-methyl-2-furanyl)-, *2-methyl-5-(5-methyl-2-furyl)pyrazine* **[54300-14-0]**

(O.94) Pyrazine, 2-methyl-6-(4-methyl-2-furanyl)-, *2-methyl-6-(4-methyl-2-furyl)pyrazine* **[54300-18-4]**

(O.95) Pyrazine, 2-methyl-6-(5-methyl-2-furanyl)-, *2-methyl-6-(5-methyl-2-furyl)pyrazine* **[54300-15-1]**

(O.96) Pyrazine, 5-(2-furanyl)-2,3-dimethyl-, *5-(2-furyl)-2,3-dimethylpyrazine* **[36238-34-3]**

(O.97) Pyrazine, 3-(2-furanyl)-2,5-dimethyl-, *3-(2-furyl)-2,5-dimethylpyrazine* **[54300-12-8]**

(O.98) Pyrazine, 2-(2-furanyl)-3,5-dimethyl-, *2-(2-furyl)-3,5-dimethylpyrazine* **[54300-11-7]**

All were identified in coffee by Vitzthum and Werkhoff (1974b).

O.97 has a weak, burnt flavor (Chemisis, 1975).

(O.99) Pyrazine, (2-furanylmethyl)-, *furfurylpyrazine* **[110674-44-7]**

Identified in ground roasted coffee and in a commercial coffee extract by Elmore and Nursten (1990).

One **pyrazine, 2-methyl[(5-methyl-2-furanyl)methyl]-,** or *2-(5-methyl-2-furfuryl)methylpyrazine* **[110587–10–5]** was been identified by Baltes and Bochmann (1987c) in coffee and the three in reactions of serine and threonine with (not without) sucrose.

5.P AMINES AND MISCELLANEOUS NITROGEN COMPOUNDS

Amines being characteristic constituents of fishery products and cheeses, they have too often been considered in coffee as undesirable spoilage products, as pointed out in the extensive review by Maga

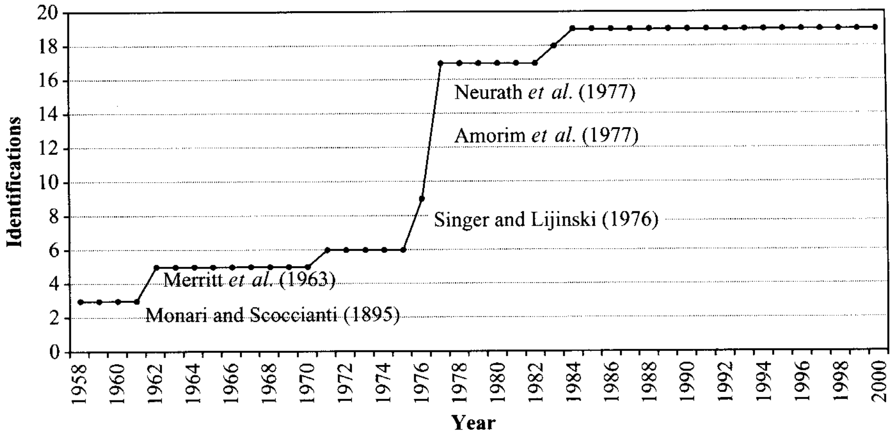


Fig. 5.16 Progressive identification of the other N-containing components in roasted coffee volatiles

(1978b). Nevertheless, they certainly play a positive role in the flavors of some foodstuffs such as wines, fruit, vegetables and cereals. Few lower amines have been identified in coffee volatiles, methylamine having been identified as early as 1880 by Bernheimer (1880a), ammonia and trimethylamine by Jaeckle in 1898, others more recently by Singer and Lijinsky in 1976 and Neurath *et al.* in 1977. Fujimaki *et al.* (1969) identified ammonia and various alkyl- and alkenylamines in the pyrolysis products of sulfur-containing amino acids. According to these authors, little ammonia was detected because the major part reacts with carbon dioxide to form ammonium carbonate. In fact, during coffee roasting, numerous degradation products of sugars containing aldehydic or ketonic functions react immediately with ammonia and amines, forming aldimines and ketimines and leading to the formation of nitrogen-containing heterocyclic compounds. Baltes (1979a) explained the formation of amines, especially in bread-aroma volatiles, by the condensation of a furfural with an amino acid, followed by hydrolytic cleavage of the resulting Schiff base. As amines, particularly morpholine, can react with nitrites to form undesirable carcinogenic nitrosamines, their occurrence has been carefully investigated in various foodstuffs, particularly in fish, meat, beer, milk, coffee, tea and wine (Singer and Lijinsky, 1976). Fortunately, Gray and Dugan (1975) postulated that in model food systems, the appreciable amount of ascorbic acid present in coffee beans may contribute to the inhibition of nitrosamine formation, and Amorim *et al.* (1977) mentioned that no nitrite could be detected in green coffee beans.

Aromatic amines (aniline and its homologues) and methyl anthranilate were identified in green coffee beans for the first time by Vitzthum in 1977.

Three polyamines, putrescine (butane-1,4-diamine, **P.11**), spermidine [1-(3-aminopropyl)butane-1,4-diamine, **P.12**] and spermine [*N*,*N*′-bis(3-aminopropyl)butane-1,4-diamine, **P.13**], have been isolated from green coffee by Amorim *et al.* (1977). Only putrescine could be detected in light roasted coffee, **P.12** and **P.13** being degraded in the roasting process. The presence of these compounds, with threshold levels between 10^{-4} and 10^{-5} M/L in water (Wang *et al.*, 1975), could explain the putrid odor of certain green beans although Amorim *et al.* (1977) did not find noticeable differences between the concentrations in mild and 'Rio' arabica coffees. They could possibly contribute indirectly to the coffee flavor generally, putrescine being, for instance, converted into pyrrolidine by roasting (Lijinsky and Epstein, 1970).

Nitriles were also identified for the first time by Merritt *et al.* (1963).

Ammonia; Aliphatic amines and polyamines

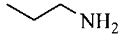
NH_3

(P.1)

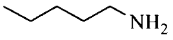
$CH_3{-}NH_2$

(P.2)

(P.3)



(P.4)
(P.4)



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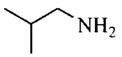

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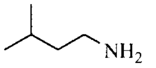

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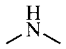

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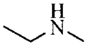

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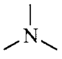

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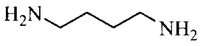

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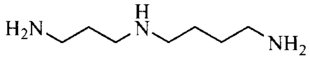

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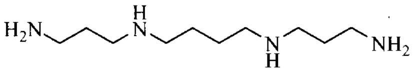


(P.13)

(P.1) Ammonia [7664-41-7]

Identified by Jaeckle (1898). Neurath *et al.* (1977) found concentrations of 560 and 760 ppm in two coffees and 820 in an extract (see **P.2**).

Ammonia results from the thermal degradation of amino acids and is at the origin of the formation of numerous nitrogen-containing constituents of coffee flavor.

(P.2) Methanamine, *methanamine, methylamine, methylazane,* aminomethane [74-89-5]

Identified by Bernheimer (1880a). Neurath *et al.* (1977) found concentrations of 16 and 80 ppm in two coffees and 27 in an extract (steam distillation, formation of trifluoroacetamides on the neutral fraction, separation of tertiary amines and GC).

Methylamine was identified by Mulders (1973c) in a cysteine/cystine–ribose model system by thin layer chromatography through the 2,4-dinitrofluorobenzene derivative.

(P.3) Ethanamine, *ethanamine, ethylamine, ethylazane,* aminoethane [75-04-7]

Identified by Neurath *et al.* (1977) who measured concentrations of 1.5 to 2.0 ppm in two coffees and an extract (see **P.2**).

It could simply result from the degradation of the 2-mercaptoethylamine found among the pyrolysis products of L-cystine, as shown by Fujimaki *et al.* (1969).

(P.4) *(P.4)* 1-Propanamine, *propanamine, propylamine, propylazane,* 1-aminopropane [107-10-8]

Identified by Neurath *et al.* (1977) who estimated the concentration in two coffees and one extract as 0.2–0.5 ppm (see **P.2**). The fragment $m/z = 60(MH^+)$, corresponding to propylamine and trimethylamine, was used by Dyszel (1985), applying combined thermogravimetric analysis/atmospheric pressure chemical ionization, for the identification of the origin of green coffees.

It was identified by Mulders (1973c) in a cysteine/cystine–ribose model system by TLC through the 2,4-dinitrofluorobenzene derivative. It was also formed in the pyrolysis of methionine possibly through 3-(methylthio)propylamine (Fujimaki *et al.*, 1969).

Propanamine has a weak, amine flavor (Chemisis, 1979).

(P.5) 1-Pentanamine, *pentanamine, pentylamine, pentylazane,* amylamine **[110-58-7]**

Identified by Neurath *et al.* (1977) who found 10 and 15 ppm in two coffees and 2 in an extract (see P.2).

The flavor is weak, fishy (Chemisis, 1979).

(P.6) 1-Propanamine, 2-methyl-, *isobutanamine, 2-methylpropan-1-amine, isobutylamine, isobutylazane,* valamine **[78-81-9]**

Identified by Neurath *et al.* (1977) who found 1 ppm in two coffees and an extract (see **P.2**).

The flavor is described as cocoa, weak (Chemisis, 1979).

(P.7) 1-Butanamine, 3-methyl-, *3-methylbutan-1-amine, isopentylamine, isopentylazane,* isoamylamine leucamine **[107-85-7]** ***FEMA 3219***

Identified by Neurath *et al.* (1977) who measured a concentration of 1 ppm in two coffees and one extract (see **P.2**).

It is formed in nature by decarboxylation of leucine and is one of many common degradation products of proteins.

Isopentylamine has an unpleasant ammonia type odor with a decay-like decomposition odor (Arctander, 1967). The flavor is described as weak, cocoa (Chemisis, 1979).

(P.8) Methanamine, *N*-methyl-, *dimethylamine, dimethylazane,* *N*-methylmethanamine **[124-40-3]**

Identified by Singer and Lijinsky (1976) who mentioned a concentration of 2 ppm. Neurath *et al.* (1977) found 3.0–6.0 ppm in two coffees and an extract.

(P.9) Ethanamine, *N*-methyl-, N-*methylethanamine, N-methylethylamine, ethyl(methyl)azane,* methylaminoethane **[624-78-2]**

Identified by Singer and Lijinsky (1976) at a concentration < 0.5 ppm. Neurath *et al.* (1977) found 0.5 to 2.0 ppm in two coffees and an extract.

(P.10) ***(P.10)*** **Methanamine, *N,N*-dimethyl-,** *trimethylamine, trimethylazane* **[75-50-3]** ***FEMA 3241***

Suspected by Monari and Scoccianti (1895) and identified by Jaeckle (1898). Dyszel (1985) used the ion $m/z = 60(\mathrm{MH}^+)$ corresponding to trimethylamine and propanamine, in an attempt to characterize green coffees of various origins (see **P.4**).

(P.11) ***(P.11)*** **1,4-Butanediamine,** *butane-1,4-diamine, tetramethylenediamine, tetramethylenediazane,* butylenediamine, 4-aminobutylamine, 1,4-diaminobutane, putrescine **[110-60-1]**

Identified in green and roasted beans by Amorim *et al.* (1977) by fluorometry and densitometry of the dansyl (5-dimethylamino-1-naphthalenesulfonyl) derivative by TLC. Unlike to the other polyamines, putrescine could be detected in the light-roasted coffee (1–3 ppm), but the polyamine content does not seem to have a connection with the 'Rio' flavor ('stinking' notes), concentrations being similar in Brazilian arabica with mild or 'Rio' flavor (38–54 ppm, dry material basis).

The average odor threshold in water given by Wang *et al.* (1975) is 18–27 ppm with an odor described as putrid at a concentration of 17 ppm in water.

(P.12) **1,4-Butanediamine, *N*-(3-aminopropyl)-,** *N-(3-aminopropyl)butane-1,4-diamine,* 4-aza-1,8-octanediamine, 4-aza-1,8-diaminooctane, triazadecane, spermidine **[124-20-9]**

Identified only in green coffee beans by Amorim *et al.* (1977) by fluorometry and densitometry of the dansyl (see **P.11**) derivative by TLC. This polyamine is destroyed even with light roasting, but the degradation products might contribute to the coffee flavor generally. The content is 15–20 ppm (dry material basis) in mild-flavored or 'Rio' Brazilian arabica.

A pathway of formation from L-methionine, through L-ornithine and diaminobutane has been proposed by Tabor and Tabor (1964).

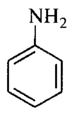
Wang *et al.* (1975) find an average odor threshold of 115–145 ppm in water, with an odor description as putrid at 115 ppm in water.

(P.13) **1,4-Butanediamine, *N,N'*-bis(3-aminopropyl)-,** *N,N'-bis(3-aminopropyl)butane-1,4-diamine,* 4,9-diaza-1,12-dodecanediamine, spermine **[71-44-3]**

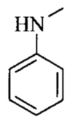
Identified only in green coffee beans by Amorim *et al.* (1977) by fluorometry and densitometry of the dansyl derivative by TLC (see **P.11**). The content is 7–10 ppm (dry material basis) in mild-flavored or 'Rio' Brazilian arabica.

The average odor threshold in water is not very different of that of putrescine (**P.11**), 17–34 ppm and the odor description is putrid at 18 ppm in water (Wang *et al.*, 1975).

Amines with aromatic ring



(P.14)
(P.14)



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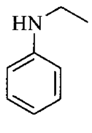

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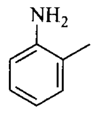

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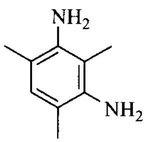

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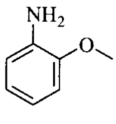

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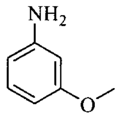

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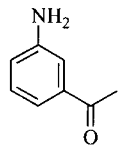

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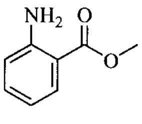

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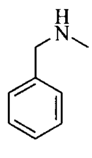


(P.23)

(P.14) *(P.14)* **Benzenamine,** *aniline, phenylamine, benzenamine, phenylazane,* aminobenzene **[62-53-3]**

Identified in green coffee by Vitzthum *et al.* (1976). In their study on the influence of brewing time on the composition of brewed coffee, Lee *et al.* (1992) qualified aniline of 'fast extractor' (70–80% extracted after 5 min).

When absolutely pure, in suitable dilution, aniline has a warm, sweet and actually pleasant odor (Arctander, 1967).

(P.15) **Benzenamine, *N*-methyl-,** N-*methylaniline methyl(phenyl)amine* **[100-61-8]**

(P.16) **Benzenamine, *N*-ethyl-,** N-*ethylaniline, ethyl(phenyl)amine, ethyl(phenyl)azane,* *N*-ethylbenzenamine **[103-69-5]**

(P.17) **Benzenamine, 2-methyl-,** *2-methylaniline, (2-methylphenyl)azane,* o-*toluidine,* 2-methylbenzenamine, *o*-tolylamine, 2-aminotoluene **[95-53-4]**

These were identified in green coffee by Vitzthum *et al.* (1976).

(P.18) 1,3-benzenediamine, 2,4,6-trimethyl-, *2,4,6-trimethylbenzene-1,3-diamine, 2,4,6-trimethyl-1,3-phenylenediamine,* mesitylenediamine **[3102-70-3]**

Identified by Bicchi *et al.* (1997) in a 1:1 roasted blend of robusta and arabica, using headspace-solid phase microextraction/GC.

(P.19) Benzenamine, 2-methoxy-, *2-methoxyaniline, (2-methoxyphenyl)amine,* 2-aminoanisole **[90-04-0]**

Identified in brews by Lee *et al.* (1992) and qualified of 'slow extractor' (only 30–40% extracted after 5 min brewing time) contrary to aniline (**P.14**).

(P.20) **Benzenamine, 3-methoxy-,** *3-methoxyaniline, (3-methoxyphenyl)amine, o*-anisidine **[536-90-3]**

(P.21) **Ethanone, 1-(3-aminophenyl)-,** *1-(3-aminophenyl)ethanone,* 3-aminoacetophenone, 3-acetylaniline **[99-03-6]**

(P.22) **Benzoic acid, 2-amino-, methyl ester,** *methyl anthranilate, methyl 2-aminobenzoate,* anthranilic acid methyl ester **[134-20-3]** ***FEMA 2682***

These were identified in green coffee by Vitzthum *et al.* (1976).

The amino ester **P.22** occurs in numerous essential oils, such as neroli, ylang-ylang, bergamot or jasmine. It has a musty-fruity and somewhat dry-floral odor reminiscent of Concord grapes, orange blossom and a good tenacity. The odor appears much sweeter in high dilution (Arctander, 1967). The flavor has a grape note (Chemisis, 1988).

(P.23) Benzenemethanamine, *N*-methyl-, N-*methylbenzylamine, benzyl(methyl)amine, benzyl(methyl)azane* **[103-67-3]**

Identified in coffee beverage by Singer and Lijinsky (1976), who found a concentration of 1 ppm (dry material). Of three samples examined (two coffees and one extract), Neurath *et al.* (1977) identified this amine only in one coffee (0.2 ppm, see **P.2**).

Miscellaneous

(P.24) Acetonitrile, *acetonitrile, ethanenitrile,* cyanomethane **[75-05-8]**

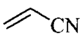
Identified by Liardon and Ott (1984).

(P.25) 2-Propenenitrile, *acrylonitrile, prop-2-enenitrile, vinyl cyanide* **[107-13-1]**

Identified by Merritt *et al.* (1963) representing 0.6% of their 'coffee aroma' (see Section 5.B).

H_3C-CN

(P.24)



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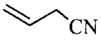

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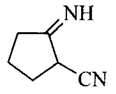

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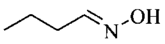

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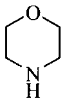

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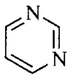

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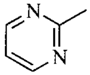

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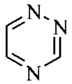


(P.32)

(P.26) 3-Butenenitrile, *but-3-enenitrile, allyl cyanide,* 3-butenonitrile, allylnitrile, 3-cyano-1-propene **[109-75-1]**

Identified by Merritt *et al.* (1963), representing 1.1% of the 'coffee aroma'. It was also identified, but tentatively, by Heins *et al.* (1966).

(P.27) Cyclopentanecarbonitrile, 2-imino-, *2-iminocyclopentane-1-carbonitrile* **[2321-76-8]**

Identified in brews by Lee *et al.* (1992). In the brewing, the extraction exhibited a maximum followed by losses after brewing time of more than 11 min.

(P.28) Butanal, oxime, *butanal oxime, butyraldehyde oxime,* butyraldoxime **[110-69-0]; (*E*)- [5775-75-7]; (*Z*)- [5780-41-6]**

Identified by Friedel *et al.* (1971). It is the unique oxime which has been identified in coffee flavor.

Oximes are not frequent in flavors and essential oils; nevertheless they have been identified in flower headspaces. For instance, Kaiser (1993) identified 2-methylbutyraldoxime, isovaleraldoxime and phenylacetaldoxime in the volatiles of the orchid *Diaphananthe pellucida* (Lindl.) Schltr.

(P.29) Morpholine, *morpholine, tetrahydro-1,4-oxazine* **[110-91-8]**

Identified by Singer and Lijinsky (1976) who mentioned a concentration of 1 ppm.

(P.30) Pyrimidine, *pyrimidine, 1,3-diazine,* 1,3-diazabenzene **[289-95-2]**

Identified by Lee *et al.* (1992), when they evaluated the composition of brews as a function of brewing-time. The compound was qualified as a 'slow extractor' (low concentration under rapid brewing conditions, see **P.14**, **P.19** and **P.27**).

(P.31) Pyrimidine, 2-methyl-, *2-methylpyrimidine* **[5053-43-0]**

Identified by Lee *et al.* (1992) in brews and qualified as a 'fast extractor' (see **P.30**).

(P.32) 1,2,4-Triazine, *1,2,4-triazine, as*-triazine **[290-38-0]**

Identified by Wang *et al.* (1983). The discovery of this heterocyclic compound was the result of a performant analysis of trace constituents, a technique combining headspace sampling, heart cutting, collection, sensory evaluation and two-dimensional GC. There are no comments on the reference compound or on its organoleptic properties.

5.Q MISCELLANEOUS SULFUR COMPOUNDS

Sulfur-containing volatile compounds contribute to the pleasant as well as the unpleasant overall flavors in many foods. Of durian, very rich in sulfur compounds, it is said 'it smells like hell, it tastes like heaven'. They are essential for the impact character of roasted coffee and play an important role in the development of its flavor. They may be formed by the natural metabolic pathways of the plant or, as is mostly the case, be produced during the roasting process or during storage of the foodstuff. Numerous reviews dealing with the occurrence, formation, properties, and importance of sulfur compounds have been published, including by Schwimmer and Friedman (1972), Schutte (1974), Maga (1976) and Shankaranarayana *et al.* (1974, 1982).

The identification in coffee of the first members of this class is attributed to Reichstein and Staudinger (1926b). Rhoades (1960), Merritt *et al.* (1963) and Stoll *et al.* (1967) extended the discoveries during the Sixties, followed by Tressl and Silwar (1981) and Silwar (1982) in the Eighties. Nurok *et al.* (1978) used GC with sulfur-specific detectors for comparing the headspace profiles of roasted coffee, coffee oils and brewed coffee using arabicas and robustas. They found significant differences between the species, a few components being up to 20 times more concentrated in robusta than in arabica. This could be used to detect 1 % of robusta in an arabica. The method is described and the retention times given but there is no indication of the compounds. The specific detectors allowed identification of more sulfur compounds (Silwar *et al.*, 1986; Guyot and Vincent, 1990). The latter authors thus found that some of the volatile sulfur derivatives were eight-to ten fold more concentrated in 'stinking' arabica coffees than in healthy (**Q.2**, **3**, **11** and **14**). They attributed this fact to the important concentration of free sulfur amino acids in 'stinking' coffee, specially methionine (about double the concentration in healthy coffee). The most volatile compounds were found to be more abundant in the arabicas than in the robustas, a result which seems to contradict Nurok *et al.* (1978), probably due to different analytical conditions. Holscher *et al.* (1990, 1992) added three powerful and characteristic compounds to the list. After simultaneous distillation–extraction, their volatiles were pre-separated and finally investigated by GC-olfactometry. 3-Methyl-2-butene-1-thiol (**Q.10**), 3-mercapto-3-methylbutanol (**Q.19**) and 3-mercapto-3-methylbutyl formate (**Q.20**) were located and afterwards identified by classical methods. As the identified components were very likely to be related to each other by their common precursor, prenyl alcohol (3-methyl-2-buten-l-ol, **B.27**), the formation pathway was investigated by means of model reactions. The overall results indicated that the formation of volatiles derived from prenyl alcohol seems to be an important

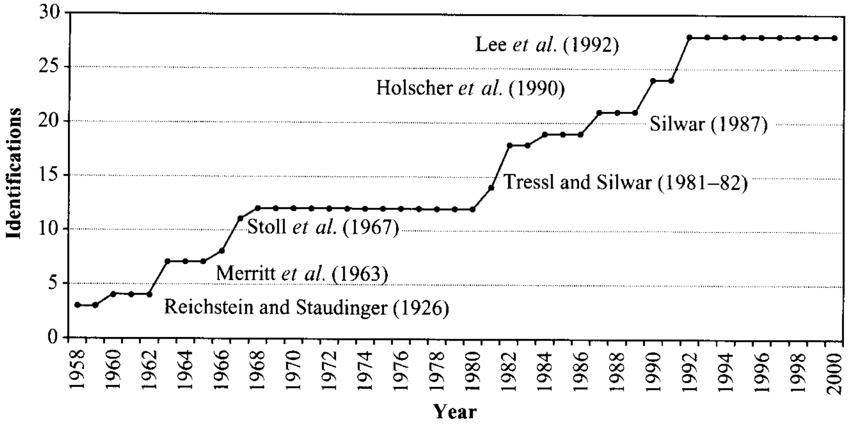


Fig. 5.17 Progressive identification of the remaining S-containing components in roasted coffee volatiles

pathway to roasted-coffee flavor in addition to the well-known Strecker degradation and the Maillard reaction.

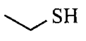
Hydrogen sulfide; Thiols

SH_2

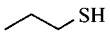
(Q·1)
(Q·1)

H_3C-SH

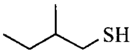
(Q·2)
(Q·2)



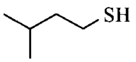
(Q·3)



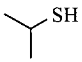
(Q·4)



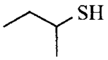
(Q·5)



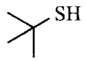
(Q·6)



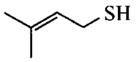
(Q·7)



(Q·8)



(Q·9)



(Q·10)

(Q.1) *(Q.1)* **Hydrogen sulfide [7783-06-4]** *FEMA 3779*

This gas was mentioned for the first time in roasted coffee by Reichstein and Staudinger (1926b). Hughes and Smith (1949) tried to quantify hydrogen sulfide during roasting and staling of coffee by absorbing the gas flow in an alkaline zinc acetate solution and measuring photometrically the blue color produced by reaction with *p*-aminodimethylaniline in the presence of ferric chloride. They quantified the compound in the freshly roasted samples, and again at intervals up to 15 days after roasting and observed that only small amounts of H_2S were found, and that these amounts decreased rapidly within a few days following roasting. They concluded that hydrogen sulfide did not form an essential part of coffee aroma, the concentration being too low. Hydrogen sulfide has also been found in green coffee by Rhoades (1960) who gave concentrations of 0.1–1.0 ppm for green and 0.7–4.3 for roasted coffees, by Stoffelsma *et al.* (1968) in coffee aroma, and by Gibson (1974a) in volatiles (static headspace) of green arabicas.

It is produced in the pyrolysis of sulfur-containing amino acids such as cysteine and cystine, or by interaction of these with various sugars.

The odor is very unpleasant, shockingly repulsive, often described as reminiscent of rotten eggs or decaying seaweed, etc., both materials literally oozing hydrogen sulfide in the states described (Arctander, 1967). Threshold concentrations quoted by Shankaranarayana *et al.* (1982) were 5 ppb in water and 4.7 ppb in air.

(Q.2) *(Q.2)* **Methanethiol,** *methanethiol,* methyl mercaptan, methyl thioalcohol **[74-93-1]** *FEMA 2716*

Identified in roasted coffee by Reichstein and Staudinger (1926b), Radtke *et al.* (1966b), Stoll *et al.* (1967), Stoffelsma *et al.* (1968) and in green coffee by Rhoades (1960) who gave concentrations of 0.1–0.3 ppm for the green and 1.5–4.3 for the roasted coffees. In green coffee, it was been found by Rodriguez *et al.* (1969), and by Gibson (1974a). Using a method involving a preconcentration of the volatile compounds and specific detectors, Guyot and Vincent (1990) found decreasing concentrations from 'stinking' arabicas to arabicas and to robustas. On the contrary, for Holscher and Steinhart (1992a) the concentration in headspace of freshly roasted coffees was more than twice as high in robustas than in arabicas, and it increased first slowly to medium roast then strongly to dark roast. By comparison, the concentration of dimethyl sulfide (**Q.11**) remained nearly constant or decreased slightly. After 8 days of storage, the absolute peak area of methanethiol in a headspace chromatogram decreased to a level of about 30% and after 3 weeks to 10–20% relative to the starting value.

Methanethiol results among others from the pyrolysis of methionine (Merritt *et al.*, 1970). Like short-chain aliphatic thiols, it is also produced in model reactions involving cysteine and sugars, and also by heat treatment of methional (**Q.22**).

The odor of rotten cabbage is very diffusive and objectionable (Arctander, 1967) . On the other hand, despite these characteristics and certainly thanks to its originality, this mercaptan gives one of the most intense noted to roasted coffee. The threshold concentration in water varies between 0.02 ppb (Guadagni *et al.*, 1963a), and 2.1 ppb (quoted by Persson and von Sydow, 1973).

(Q.3) Ethanethiol, *ethanethiol,* ethyl mercaptan, ethyl thioalcohol, thioethanol **[75-08-1]**

Identified by Self *et al.* (1963) in an instant powder together with dimethyl sulfide. It was tentatively identified by Stoffelsma *et al.* (1968).

This compound is very powerful. Thresholds in water vary from 0.19 ppb to 4.3 ppm (quoted by Shankaranarayana *et al.*, 1982), 1 ppb (quoted by Persson and von Sydow, 1973).

(Q.4) 1-Propanethiol, *propane-1-thiol, n*-propyl mercaptan **[107-03-9]** ***FEMA 3521***

Tentatively identified by Stoffelsma and Pypker (1968), and Stoffelsma *et al.* (1968). It was found in traces by Guyot and Vincent (1990) who used pre-concentration on Tenax GC of the separated sulfur compounds, followed by desorption, to obtain a good chromatographic analysis (see **Q.2**).

This compound has a very powerful, penetrating and diffusive cabbage-like odor which is obviously unpleasant unless extremely diluted (Arctander, 1967). The odor threshold concentration in air is 6 ppb (quoted by Shankaranarayana *et al.*, 1982).

(Q.5) 1-Butanethiol, 2-methyl-, *2-methylbutane-1-thiol* **[1878-18-8]** ***FEMA 3303***

(Q.6) 1-Butanethiol, 3-methyl-, *3-methylbutane-1-thiol,* isopentyl mercaptan **[541-31-1]** ***FEMA 3858***

(Q.7) 2-Propanethiol, *propane-2-thiol,* isopropylmercaptan, 1-methylethanethiol **[75-33-2]** ***FEMA 3897***

(Q.8) 2-Pentanethiol, *pentane-2-thiol, sec*-butyl mercaptan **[2084-19-7]** ***FEMA 3792***

(Q.9) 2-Propanethiol, 2-methyl-, *2-methylpropane-2-thiol,* 1,1-dimethylethanethiol, *tert*-butyl mercaptan **[75-66-1]**

These were identified by Guyot and Vincent (1990) in traces from their analysis of volatile sulfur compounds (see **Q.2** and **Q.4**).

(Q.10) 2-Butene-1-thiol, 3-methyl-, *3-methylbut-2-ene-1-thiol,* prenylthiol, prenyl mercaptan **[5287-45-6]** ***FEMA 3896***

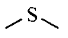
Identified in roasted coffee volatiles by Holscher *et al.* (1990). A concentration of 8.2 ppb in freshly roasted ground coffee was measured by Grosch (1996) using the isotope dilution technique and the deuterated compound as internal standard.

The product was previously identified in beer by Andrews (1987) and in human sweat by Polak *et al.* (1988), and characterized as sunstruck or lightstruck off-flavor. The cause has been attributed to the degradation of bitter isohumulones from hops under the influence of ultraviolet light (Bondeel *et al.*, 1987). By photofragmentation *trans*-isohumulone liberates a prenyl radical which can trap a thiol radical, producing an undesired flavor for beer. Holscher *et al.* (1992) have also shown that 3-methyl-2-buten-1-thiol and 3-mercapto-3-methylbutanol are principally formed under pyrolytic conditions in roast model reactions of prenyl alcohol and sulfur-containing amino acids.

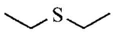
The synthesis was carried out by Holscher *et al.* (1992), by treatment of the corresponding alcohol, **B.27**, with thiourea.

The pure substance smells pungent or leek-like, whereas a penetrating animal-like, foxy or even skunky odor predominates at low concentrations (ca 0.1 ppm) (Soeltoft, 1988). At a concentration of 0.04 ppm, the flavor is perceived as skunky, meaty, coffee, fatty, tarry, etc. (Chemisis, 2000). The odor and taste thresholds in air and water measured by Grosch (1996) were 0.2–0.4 g/m^3 and 0.2–0.3 ppt (0.0002–0.0003 μg/L) respectively. The low detection threshold in water explains the important olfactory contribution of this compound even at the measured low concentration.

Alkyl sulfides and polysulfides


(Q·11)
(Q·11)


(Q·12)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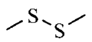
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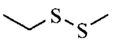
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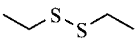
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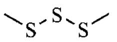
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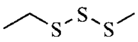

(Q·18)

(Q.11) ***(Q.11)*** **methane, thiobis-,** *dimethylsulfane, dimethyl sulfide, (methylsulfanyl)methane, 2-thiapropane*, dimethyl thioether **[75-18-3]** ***FEMA 2746***

Identified but not proved by Reichstein and Staudinger (1926b), confirmed by Rhoades (1958) (dynamic headspace and GC) who also found it in green coffee (Rhoades, 1960) and gave concentrations of 0.1–3.5 ppm in green coffees and 0.5–3.5 in roasted coffees. Merritt *et al.* (1970) identified it in headspace condensates of green and roasted coffees. In green coffee, it was identified by Rodriguez *et al.* (1969), and by Procida *et al.* (1997) in six arabicas and six robustas, but not in a roasted sample. Gibson (1974a) found widely different contents in the same hybrid species grown in different locations in East Africa. When there was a high concentration in dimethyl sulfide, there was also an increase in the acidity, and the corresponding coffees showed a desirable blue pigmentation (see comment in Section 2.2). Dimethyl sulfide was present in the headspace of brewed coffee analyzed by Shimoda and Shibamoto (1990a) representing 4% (GC) of the volatiles. Using a flame photometric sulfur-specific detector, Guyot and Vincent (1990) found 0.1–0.2 ppm in a healthy roasted arabica, but 0.8–1.0 ppm in one having a 'stinking' quality (see **Q.2** and **Q.4**). Contrary to what was observed for methanethiol (**Q.2**), the concentration in the headspace decreased from light to medium roast in arabicas and remained constant for the robustas but with a lower value. The concentration decreased also on storage, reaching ca 40% of the value of freshly roasted coffee after 3 weeks (Holscher and Steinhart, 1992a).

Dimethyl sulfide is formed by oxidation of methanethiol (**Q.2**), a degradation product of methional (**Q.22**).

The odor is extremely diffusive, repulsive, reminiscent of wild radish, sharp, green, cabbage-like. Only in very high dilution it becomes bearable and almost acceptable, pleasant, vegetable-like (Arctander, 1967). For Radtke *et al.* (1966b) it was not specific for roasted coffee and lacked the typical character of coffee aroma (see also **Q.32**). Odor thresholds in water quoted by Shankaranarayana *et al.* (1982) vary between 0.3 and 60.0 ppb, and 1 ppb is quoted by Persson and von Sydow (1973), 0.33 ppb measured by Guadagni *et al.* (1963a).

(Q.12) Ethane, (methylthio)-, *ethyl(methyl)sulfane, ethyl methyl sulfide, (methylsulfanyl)ethane*, 2-thiabutane **[624-89-5]** ***FEMA 3860***

Identified by Sullivan *et al.* (1959), Stoll *et al.* (1967), and Stoffelsma *et al.* (1968). Merritt *et al.* (1963, 1970) identified it in roasted but not in green coffee. Guyot and Vincent (1990) found traces when specifically analyzing volatile sulfur compounds (see **Q.4**).

At a concentration of 1 ppm it is characterized by cooked-vegetable, green, alliaceous, mushroom, shellfish flavor with a tropical and fruity undertone (Chemisis, 1999).

Methyl propyl sulfide (2-thiapentane) was mentioned by Merritt *et al.* (1970) as a pyrolysis product of methionine but its presence in coffee volatiles needs confirmation.

(Q.13) Ethane, 1,1′-thiobis-, *diethylsulfane, diethyl sulfide*, 3-thiapentane, diethyl thioether, ethylthioethane **[352-93-2]** ***FEMA 3825***

Identified as traces in an analysis of volatile sulfur compounds by Guyot and Vincent (1990) (see **Q.4**).

(Q.14) Disulfide, dimethyl, *dimethyldisulfane, dimethyl disulfide*, 2,3-dithiabutane **[624-92-0]** ***FEMA 3536***

Identified in roasted coffee by Sullivan *et al.* (1959), Heins *et al.* (1966), and Stoffelsma *et al.* (1968). Merritt *et al.* (1970) characterized it in roasted but not in green coffee. It is present in the headspace of roasted coffee (Cros *et al.*, 1980; Wang *et al.*, 1983), in the headspace of a brew (Shimoda and Shibamoto, 1990a) where it represents 0.67% (GC). Silwar *et al.* (1986) found concentrations of 0.01 ppm in arabicas and 0.10–0.12 in robustas after simultaneous distillation/extraction, capillary GC using simultaneously flame ionization or flame photometric (for sulfur-selective analysis) detectors (FID/FPD). With a similar detection method in the GC analysis of the headspace compounds, Guyot and Vincent (1990) found 0.04–0.05 ppm in a roasted healthy arabica and 0.3–0.4 in the ‘stinking’ quality (see **Q.4**). Procida *et al.* (1997) identified dimethyl disulfide in a roasted arabica but in none of the green coffees examined, contrary to their result for dimethyl sulfide (**Q.11**).

It has an intensive onion-like character (Arctander, 1967). Odor threshold concentrations in water from 3 ppb to 7.6 ppb were mentioned by Shankaranarayana *et al.* (1982) and 12 ppb was found by Buttery *et al.* (1976b).

(Q.15) Disulfide, ethyl methyl, *ethyl(methyl)disulfane, ethyl methyl disulfide, (methyldisulfanyl)ethane* **[20333-39-5]**

Identified by Merritt *et al.* (1963), and Heins *et al.* (1966).

It is characterized by an onion flavor (Chemisis, 1960).

(Q.16) Disulfide, diethyl, *diethyldisulfane, diethyl disulfide*, 3,4-dithiahexane **[110-81-6]**

Identified only tentatively by Heins *et al.* (1966). It was confirmed by the analysis of the sulfur compounds of Silwar *et al.* (1986) (see **Q.14**). The concentration was 0.01 ppm in two arabicas and 0.50–0.60 in two robustas.

(Q.17) Trisulfide, dimethyl, *dimethyltrisulfane, dimethyl trisulfide*, 2,3,4-trithiapentane **[3658-80-8]** ***FEMA 3275***

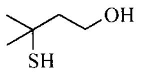
Identified by Cros *et al.* (1980) in a dynamic headspace of roasted coffee when studying the influence of storage, and by Tressl *et al.* (1981). Silwar *et al.* (1986) found 1 ppb in two arabicas and 0.1 ppm in two arabicas (see **Q.14**).

It has a very powerful and diffusive, penetrating odor of fresh onion, greener and more ethereal than the odor of the methyl propyl trisulfide (Arctander, 1967). The flavor is perceived as cabbage, burnt, cooked (Chemisis, 1968). The odor threshold in water is 0.01 ppb (Buttery *et al.*, 1976b).

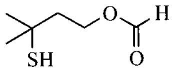
(Q.18) Trisulfide, ethyl methyl, *ethyl(methyl)trisulfane, ethyl methyl trisulfide,* (methyltrithio)ethane, 2,3,4-trithiahexane **[31499-71-5]** ***FEMA 3861***

Identified by Tressl *et al.* (1981).

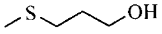
Thiols and sulfides with another function, thioester



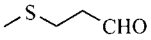
(Q·19)



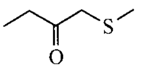
(Q·20)



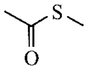
(Q·21)



(Q·22)
(Q·22)



(Q·23)



(Q·24)

(Q.19) 1-Butanol, 3-mercapto-3-methyl-, *3-methyl-3-sulfanylbutan-1-ol, 3-mercapto-3-methylbutan-1-ol* **[34300-94-2]** ***FEMA 3854***

Identified by Holscher *et al.* (1990).

It results very likely from the addition of hydrogen sulfide to prenyl alcohol (**B.27**) according to Markovnikov's rule (Holscher *et al.*, 1992).

Sensory properties were presented in the same publication. The aroma strength of this mercaptan is very far from that of prenyl mercaptan (**Q.10**) which is also formed under roasting conditions. The pure substance has a sweet, soup-like odor, which is perceived as cooked meat and spicy when diluted in water to ca 0.1 ppm. Odor and taste thresholds, 2–6 and 8–10 ppb respectively, are relatively high compared to those of **Q.10** and **Q.20**. The use of this alcohol and of its formate (see below) for artificial aromatizing of various foods has been patented (DE Patent 23.16465, 1973). At a concentration of 0.1 ppm it is characterized by a meaty, sulfury, skunky, cabbage flavor (Chemisis, 1999).

(Q.20) 1-Butanol, 3-mercapto-3-methyl-, 1-formate, *3-methyl-3-sulfanylbutyl formate, 3-mercapto-3-methylbutyl formate* **[50746-10-6]** ***FEMA 3855***

Identified by Holscher *et al.* (1990). Semmelroch *et al.* (1995) found similar concentrations in arabica (0.13 ppm) and robusta (0.115 ppm) coffees, using stable isotope dilution assays.

It can be assumed that this compound is formed during roasting from the biogenic precursor prenyl diphosphate, hydrogen sulfide and formic acid (Holscher *et al.*, 1992).

According to the latter authors, the pure substance has a sweaty, fruity odor, becoming black currant-like and catty in aqueous solution (ca 0.1 ppm). The odor and taste thresholds, 2–5 and 5–8 ppt respectively, are nearly ten times higher than those of prenyl mercaptan (**Q.10**). This mercaptan has also been characterized by Grosch (1996), as having a cat urine, roasted character with detection thresholds in air and in water of ca $3 \times 10^{-4}\,\mu g/m^3$ and 3.5 ppt (0.0035 μg/L, similar to the value given above) respectively. According to Pearce *et al.*, (1967) such mercapto compounds possess a characteristic penetrating sweaty odor described as 'catty', being similar to that of cats excrements. They belong to the most potent odorants known so far. For Polak *et al.* (1988), their essential element is the tertiary mercaptopentyl substructure; the other functional groups eventually present in the molecule appearing to contribute only moderately to the aroma quality. At a concentration of 0.1 ppm it has tropical fruit, green, sulfury, hop flavor, and the odor is reminiscent of black currant leaves, clary sage and orange flowers (Chemisis, 1995). Only when in great dilution in a coffee beverage does this compound justify the term 'roast coffee likeness' (Vitzthum, 1999).

(Q.21) 1-Propanol, 3-(methylthio)-, *3-(methylsulfanyl)propan-1-ol, 3-(methylthio)propan-1-ol,* 3-methylmercapto-1-propanol, 3-hydroxypropyl methyl sulfide, methionol **[505-10-2]** ***FEMA 3415***

Identified in roasted coffee flavor by Silwar *et al.* (1987).

It has a powerful and sweet soup or meat-like odor and flavor, and displays a rather repulsive odor with perceptible notes of sulfuraceous character. Only upon extreme dilution there is a marked improvement to the agreeable and pleasant, food-like note (Arctander, 1967). At a concentration of 3 ppm it is characterized by fatty, cheesy, milky and cooked notes (Chemisis, 1995).

(Q.22) *(Q.22)* **Propanal, 3-(methylthio)-,** *3-(methylsulfanyl)propanal, 3-(methylthio)propanal,* 3-(methylmercapto)propionaldehyde, 4-thiapentanal, methional **[3268-49-3]** ***FEMA 2747***

Identified in green and roasted coffee volatiles by Silwar *et al.* (1987). The concentration found by Semmelroch *et al.* (1995), using stable isotope dilution assays, was higher in a Columbian arabica (240 ppb) than in an Indonesia robusta (95 ppb). Using multidimensional high resolution GC/MS with a labeled internal standard, Czerny and Grosch (2000) found 22 ppb in a green arabica with a large increase after roasting (213 ppb)

Methional results from a Strecker degradation of methionine. It is at the origin of formation of methanethiol (**Q.2**), dimethyl disulfide (**Q.14**) and acrolein (**C.16**).

The odor is powerful, diffusive onion and meat-like, in dilution more pleasant, less onion-like, reminiscent of bouillon (Arctander, 1967). At a concentration of 2 ppm it has a typical meaty and sulfury flavor (Chemisis, 1993). An odor threshold of 0.2 ppb in water is given by Semmelroch *et al.* (1995) and of 9 μg/kg cellulose by Czerny and Grosch (2000), being classified among the potent odorants of green and medium-roasted arabica coffee.

(Q.23) 2-Butanone, 1-(methylthio)-, *1-(methylsulfanyl)butan-2-one, 1-(methylthio)butan-2-one* **[13678-58-5]** ***FEMA 3207***

Identified in roasted coffee by Stoll *et al.* (1967).

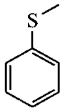
The flavor is described as mustard and the odor as mushroom, garlic (Chemisis, 1963).

(Q.24) Ethanethioic acid, *S*-methyl ester, S-*methyl thioacetate,* S-*methyl ethanethioate* **[1534-08-3]** ***FEMA 3876***

Identified by Liardon *et al.* (1984).

At a concentration of 1 ppm it is characterized by a cheesy, gruyere, cheddar, buttermilk flavor (Chemisis, 1999).

Aromatic sulfides



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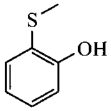


(Q·26)

(Q.25) Benzene, (methylthio)-, *(methylsulfanyl)benzene, (methylthio)benzene, methyl phenyl sulfide,* thioanisole **[100-68-5]** ***FEMA 3873***

Identified in roasted coffee flavor by Stoll *et al.* (1967).

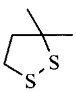
At a concentration of 0.1 ppm it has a phenolic, quinoline, dirty flavor (Chemisis, 1997).

(Q.26) Phenol, 2-(methylthio)-, *2-(methylsulfanyl)phenol, 2-(methylthio)phenol,* 2-(methylmercapto)phenol, *o*-hydroxythioanisole **[1073-29-6]** ***FEMA 3210***

Identified by Stoll *et al.* (1967).

The flavor is described as burnt, phenolic, straw, groundsy (Chemisis, 1964).

Miscellaneous



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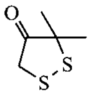

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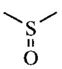

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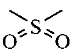


(Q·30)

SO_2

(Q·31) *(Q·31)*

CS_2

(Q·32) *(Q·32)*

(Q.27) 1,2-Dithiolane, 3,3-dimethyl-, *3,3-dimethyl-1,2-dithiolane* **[58384-57-9]**

Identified by Tressl *et al.* (1981) after distillation–extraction, separation by chromatography, preparative GC, then capillary GC with either flame ionization or flame photometric (for sulfur-selective analysis) detector. Silwar *et al.* (1986) after simultaneous distillation–extraction used the two detectors simultaneously for quantifying the sulfur compounds (see **Q.14**). They found less than 0.01 ppm of this dithiolane in arabicas as well as in robustas.

The dithiolane was prepared by Schröbel and Gräfje (1958) by oxidative cyclization of 3-methyl-1,3-butanedithiol in the presence of *tert*-butyl hydroperoxide, the thiol itself being obtained by reaction of the corresponding dibromo compound with thiourea.

(Q.28) 1,2-Dithiolan-4-one, 3,3-dimethyl-, *3,3-dimethyl-1,2-dithiolan-4-one* **[62738-29-8]**

Identified by Tressl and Silwar (1981) (MS data) with the method described under **Q.27**. Also with the method described above, Silwar *et al.* (1986) found 0.15–0.20 ppm in roasted arabicas and robustas.

The dithiolanone was prepared by Luhmann *et al.* (1977) by treatment of 1,3-dibromo-3-methyl-2-butanone with sodium sulfide (together with another cyclization product, the thietanone).

(Q.29) Methane, sulfinylbis-, *(methylsulfinyl)methane, dimethyl sulfoxide* **[67-68-5]** ***FEMA 3875***

Identified by Silwar (1982) .

At a concentration of 30 ppm it has a milky, creamy, meaty, roasted corn flavor (Chemisis, 1999) .

(Q.30) Methane, sulfonylbis-, *(methylsulfonyl)methane, dimethyl sulfone* **[67-71-0]**

Identified by Silwar (1982).

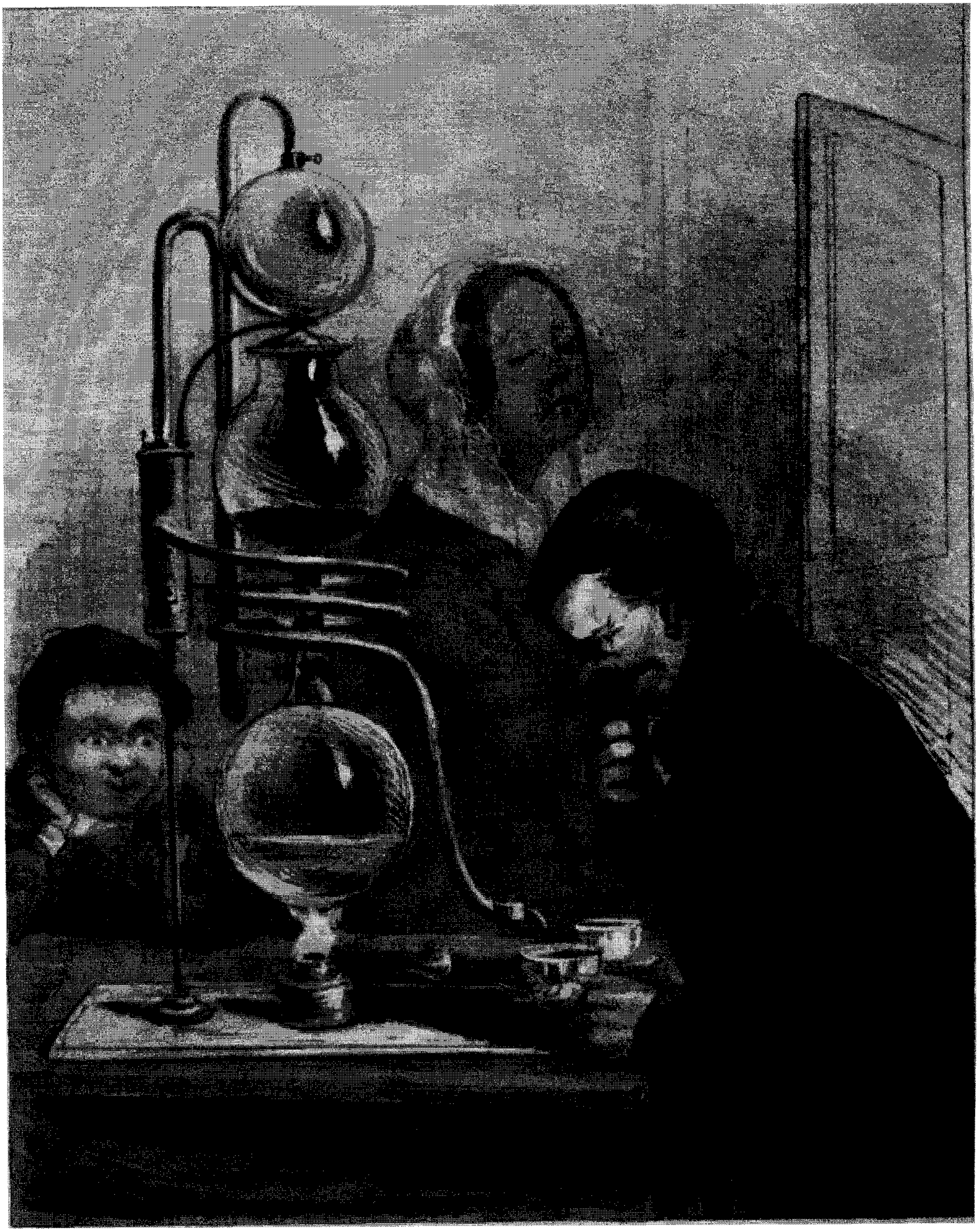
(Q.31) ***(Q.31)*** **Sulfur dioxide,** *sulfane dioxide,* sulfurous anhydride, sulfur oxide **[7446-09-5]** ***FEMA 3089***

Identified in green and roasted coffee by Merritt *et al.* (1970).

(Q.32) ***(Q.32)*** **Carbon disulfide,** *carbon disulfide,* dithiocarbonic anhydride **[75-15-0]**

Identified in roasted coffee by Sullivan *et al.* (1959), Zlatkis and Sivetz (1960), Stoll *et al.* (1967), in green and roasted coffee by Merritt *et al.* (1970). For Radtke *et al.* (1966b), it is not specific for roasted coffee and lacks the typical character of coffee aroma (see **Q.11**).

Other S-containing compounds are present in Sections 5.I (furans) and, of course, 5.J and 5.M (thiophenes and thiazoles).



A ‘patented’ percolator (J.P. Moynet, paris, in about 1850)

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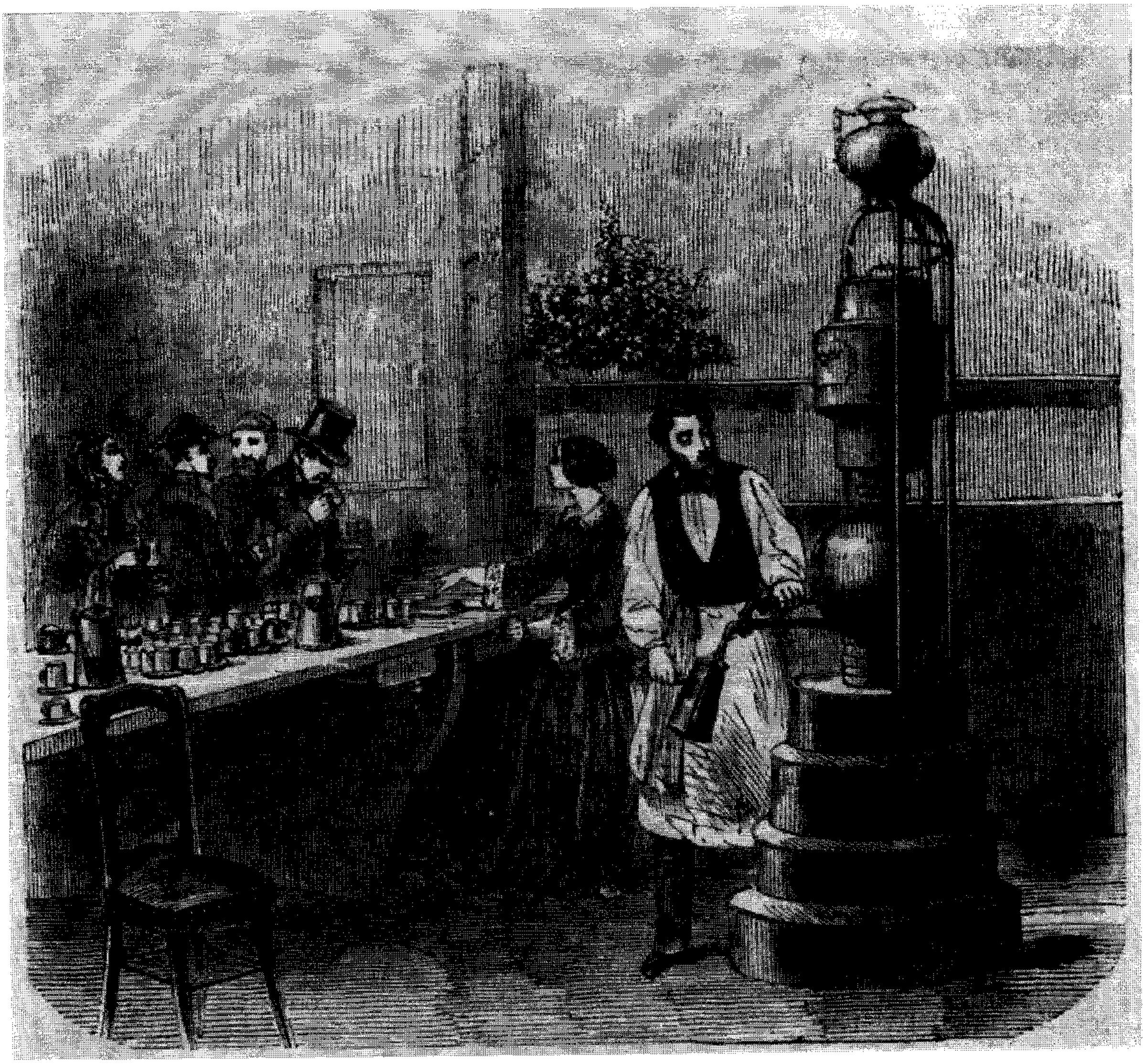

The Loysel's percolator at the Industrial Exhibition of Paris (1855)

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The page numbers in **bold** correspond to the chemical structure of the reference compounds.