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Botanical Medicine Monographs and Sundry

EUONYMUS ATROPURPUREUS.

Contribution from the Chemical Laboratory of the Philadelphia College of Pharmacy. No. 53. By FRANK V. CASSADAY, PH.G.

As there has been no complete analysis made of the root bark of Wahoo, the following investigation was undertaken with a view of determining all the important constituents, and adding, at the same time, to what is already known about the active principles.

The analysis of Clothier (AM. JOUR. PHARMACY, Nov., 1861), showed the presence of sugar, starch, etc., and, by agitating the tincture with chloroform, "yellow crystals," which were very bitter, soluble in chloroform and boiling alcohol, and of a neutral reaction, were obtained. These results were in part confirmed by Wenzell (Am. JOUR. PHARMACY, Sept., 1862), and be added *euonic acid* to the list of constituents, although he did not find the *euonymin* of Clothier to be crystalline. Miller (AM. JOUR. PHARMACY, Sept., 1878) added a volatile oil to the list, and with a larger quantity of the euonymin determined it to be uncrystalline.

By my method of procedure the drug was exhausted by cold maceration with petroleum ether, which yielded 0.06 per cent. of volatile oil and 1.24 per cent. of a wax-like body melting at 42°C., sparingly soluble in absolute alcohol, less so in 95 per cent. alcohol, but freely soluble in ether and chloroform.

The drug then yielded to stronger ether a dark-brown substance representing 1.5 per cent. This residue was partly soluble in water, the solution having an acid reaction. This aqueous solution was warmed with barium carbonate until the evolution of CO_2 ceased, filtered and the filtrate slowly evaporated over sulphuric acid, but no crystals formed. Oil redissolving, treating with dilute sulphuric acid until all the barium precipitated, and agitating with ether, crystals were obtained from the ethereal solution. These crystals were found to be strongly acid with a sour astringent taste. They gave no peculiar reactions with a number of reagents tried, but from their general characters were undoubtedly the euonic acid of Wenzell.

Tests on the ethereal extract for glucosides, alkaloids, gallic and tannic acids gave negative results. The resin, after separation of euonic acid was found to be sparingly soluble in 95 per cent. and absolute alcohol, soluble in aqueous solution of sodium hydrate, from which it was precipitated on the addition of an acid.

Absolute alcohol extracted from the original drug 2.16 per cent., 1.58 per cent. was

soluble in water, to which it imparted an acid reaction due to euonic acid. Negative results were gotten for tannic acid, alkaloids and glucosides. Ether was the only one of a number of solvents agitated with the above aqueous solution that extracted anything, and it on evaporation yielded a dark-brown, amorphous mass, having a very bitter and somewhat benumbing taste. This, no doubt, represented the euonymin of previous investigators. The insoluble part of the alcoholic extract consisted of an acid resin apparently identical with that found in the ether extract of the drug.

It will be seen from the results so far that in order to obtain the two active principles of Wahoo, it should first be exhausted with ether to extract euonic acid, and then with alcohol to obtain euonymin. The method used by Carpenter and Wenzell of making a tincture with diluted alcohol and agitating with chloroform was also tried on a much larger quantity of the drug, but in this way mixtures of the two principles were obtained, which would account for Carpenter stating that the active constituent was crystalline with a bitter taste, as he, no doubt, had the crystals of euonic acid mixed with the very bitter euonymin. The remaining results which are much the same as those previously noted by Miller are given in the following summary:

Volatile oil and wax	1.30 per cent.
Euonic acid and resin	1.49 per cent.
Euonymin and resin	2.16 per cent.
Mucilage	1.50 per cent.
Dextrin,	5.53 per cent.
Saccharose	1.88 per cent.
Albumenoids and pectin	8.34 per cent.
Calcium oxalate	1.20 per cent.
Coloring, etc., extracted by chlorine water	6.66 per cent.
Ash	11.65 per cent.
Moisture	9.25 per cent.
Cellulose, lignin and loss	49.05 per cent.
Total	100.00 per cent.

SO-CALLED AMBER GUAIAC.

By C. CARROLL MEYER, PH. G.

Read at the Pharmaceutical Meeting, May 21st.

A short time ago I received some guaiac from a prominent wholesale drug house, which was so entirely different in appearance from that usually found in the market (being perfectly clear and free from pieces of wood and bark), I concluded to see if it was pure guaiac. The name given it by the trade is amber guaiac. Its slight resemblance to black pitch (pix nigra), caused me to think pitch was a possible adulterant, also its transparency might be due to resin (Resina, U. S. P.). A given quantity of amber guaiac and black pitch were treated separately in solution of potassa, amber guaiac being completely soluble, black pitch but slightly. Then on burning the two there is an entirely different odor, showing pitch not to be an

adulterant. The amber guaiac was treated with hot oil of turpentine, and remained undissolved, showing it was not mixed with resin.

Four fluidounces of tincture were made up with amber guaiac and ordinary guaiac; 275 grains of guaiac of the shops was used to make 4 oz. of tincture (that being about the strength of U. S. P.). It was left standing for over two weeks, being agitated frequently, filtered through tared filter paper, and found to leave $102^{5/8}$ grs. undissolved, a little over sixty per cent. of the guaiac used being soluble.

The same quantity of amber guaiac was treated in same manner, and found to be almost completely soluble, leaving about 14 grs. or five per cent. undissolved. Amber guaiac is also completely soluble in aromatic siript of ammonia, and the tincture gives the characteristic blue color with fumes of nitric acid.

The U. S. Dispensatory, page 730 states, amber is said to be an adulteration. Professor Maisch states in his "Materia Medica," that amber is almost insoluble in alcohol, and as amber guaiac is almost completely soluble, that proves amber is not an adulterant. Now the point I wish to make is this: If we can get guaiac that is so soluble should we not use less in making the officinal tincture ?

Philadelphia 5, 21, 1889.

INSECT FLOWERS.¹

By PROF. JOS. SCHRENK.

The author has investigated the structural characteristics of the commercial insect flowers, and has pointed out certain differences which may be useful in determining the purity of commercial insect powder, and also its origin. The most important results may be summarized as follows:

The stem of the Dalmatian plant (*Chrysanthemumcinerariaefolium*) consists in the ridges of collenchyma tissue, which is also found in the depressions in the Persian plant (*Chrys. roseum*); but in a good insect powder fragments, composed of collenchyma cells, should be met with only sparingly.

Fragments of the involucral scales, composed of sclerenchyma cells, are much more numerous in the Persian than in the Dalmatian powder.

The outer surface and edges of the scales of the Dalmatian flowers contain numerous hairs consisting of a long cell with attenuated ends placed horizontally upon a one- to three-celled stalk. The Persian flowers are almost entirely glabrous, a white hoariness being found only at and near the base of the scales, and very few hairs near the apex; the hairs are of the same structure as the preceding, only the terminal cell being much longer.

These hairs are entirely absent from the involucre and stem of the so-called

¹ Abstract of a paper published in *American Druggist*, March, 1889.

Hungarian or Russian daisy; but the scales contain hairs consisting of from four to ten cells and terminating with a much elongated thin-walled, or with an inflated cell. Another form of glandular trichome consists of ten or twelve cells forming a globular head supported on a short stalk.

Besides the usual fluids for clearing up or bleaching the tissues, Schulze's reagent (chloroiodide of zinc) will prove very useful in examining the powder. It will bring out very clearly the hairs and collenchyma cells, which are stained blue, while the sclerenchyma, cells and the pollen grains will assume a yellow color. At the same time, of course, starch, a very common adulteration of insect powder, will become plainly distinguishable if present.

The author also directs attention to the presence in the powder of conspicuous fragments consisting of papillae covering the upper epidermis of the marginal corolla. The petals of other related species are similarly constructed. The pollen grains of the species mentioned are likewise similar in structure. Moeller (*Mikroskopie*, etc., 1886) stated that the petals contain no stomata ; but the author found stomata quite numerous on the marginal corolla of *Chrys. cinerariaefolium*, especially on the lower side.

NOTES ON ESSENTIAL OILS FROM MESSRS. SCHIMMEL AND CO.'S REPORT - Part 1.²

Angelica Oil—The results obtained from the parcel of angelica root imported from Japan, to which reference was made in the previous report (1888), differ essentially from those experienced with the German drug. The Japanese roots have the same tufted form as the German, but are lighter and nearly white and are provided with stronger rootlets. They are referred to one of two species, Angelica refracta, Fr. Schmidt (Jap. "Senkiyu"), or A. anomala, Lall. (Jap, "Biyakushi"), both of which, according to Rein, are cultivated in the open fields of Japan. This Japan angelica root proved to be comparatively very poor in essential oil, the yield being only one-tenth per cent., the oil also being essentially different from commercial angelica oil. Whilst the German distillate has a specific gravity of 0.853 at 20°C., that of the Japanese is 0.912 at the same temperature. At 10° it gives a separation of crystals, and at 0° it solidifies to a paste. The crystalline mass obtained by cooling and draining had the properties of a fatty acid melting at 62°-63° C. The oil boils between 170° and 310° C., the last portion that passes over having a beautiful blue-green color. The residue solidifies upon cooling and consists principally of the non-volatile fatty acid. The odor of the oil is unusually intense and persistent, more acrid than that of the German angelica oil, but possessing the characteristic suggestion of musk. The cost of this oil deprives it of any industrial importance.

Anise Oil.—The statement made on "high authority" in the paper read at a recent evening meeting of the Pharmaceutical Society by Mr. J. C. Umney, to the effect that for every pound of aniseed oil from *Pimpinella Anisum* a thousand pounds of staranise oil are met with, and the subsequent statement of Mr. John Moss that he would

² From the April *Bericht* of Messrs. Schimmel and Co. of Leipzig; reprinted from *Phar. Jour. and Trans.*, April 6 and 20.

put the proportion as one to ten thousand, are sharply criticized as underestimating the importance of the aniseed oil industry. Messrs. Schimmel say that in their factory alone under ordinary circumstances 7000 kilos of aniseed are worked up daily, yielding 200 kilos of aniseed oil. They place the annual production of oil from seeds of Pimpinella Anisum at 42,000 kilos, or equal to about 1400 canisters of star-anise oil, and they raise the question whether the annual production of star-anise oil amounts to 1400 canisters, to say nothing of one thousand or ten thousand times that quantity. Messrs. Schimmel make this correction in the hope that in future such questions may be discussed "with more care and upon a better basis, bearing in mind that the centre of gravity of the manufacture of essential oils lies in Germany, and not in England."

Bay Oil (*Myrcia acris*).—Under this heading the following two recipes for the preparation of "bay rum" are given:

I.

Bav Oil	2 drachms.
Pimento Oil	1 drachm.
Cloves Oil	10 drops.
Alcohol (95 per cent.)	$1/_2$ gallon.
Water	1/2. gallon.

Mix and allow to stand for several days, then filter.

II.

Bay Oil	1 ounce.
Alcohol (95 per cent.)	¹ /2 gallon.

Mix and allow to stand for a fortnight. Then add one gallon of good Jamaica rum. The bay rum made according to this recipe is said to correspond with the imported article.

Betel Oil.—A statement made in a previous report to the effect that the essential oil of betel leaves contained eugenol was considered to be opposed to a report by Professor Eykman upon the composition of a sample of betel oil examined by him; a fresh investigation has therefore been made with the following result. The sample of betel oil examined was a slightly brown colored liquid, sp. gr. 1.024 at 15°C. It consisted up to about two-thirds or three-fourths of a phenol, the boiling-point of which in partial vacuum, under a pressure of 12 mm., lay at 131-132°C.; under ordinary atmospheric pressure it underwent decomposition on boiling. The specific gravity of the phenol was 1.067 at 15°C. Examination Of the oxidation products, acetyl compound and methyl ether showed that this compound was not eugenol, but an isomer, the composition of the new compound and of eugenol being represented as follows:

New Compound.	Eugenol.
$[1]C_3H_5$	$[^{1}]C_{3}H_{5}$
$C_6H_3[3]OH$	C ₆ H ₃ ^[3] OČH
[4]OCH ₃ .	[4]OH.

The second constituent of betel oil boiled practically between 250° and 275°C., had a very agreeable tea-like odor, and consisted for the greater part of a sesquiterpene

 $(C_{15}H_{24})$, cubebene, which is characterized by its dihydrochlorate melting at 117-118°C. This composition differs considerably from that given by Professor Eykman, but how far the difference may depend upon the oil examined by Professor Eykman having been distilled from fresh leaves, whilst that examined by Messrs. Schimmel was distilled from dried leaves has not been determined.

Bergamot Oil—Some question having been raised recently as to the natural color of bergamot oil, Messrs. Schimmel publish some information on the subject obtained from two of the largest producers in Reggio. One of them says: "This essence occurs for the most part of a brown-yellow color. A certain quantity approximates more to green, but this is an essence prepared only from unripe fruit. In commerce it seldom occurs pure, since it is ordinarily mixed with the essence prepared later from ripe fruit. Carefully examined in a glass tube it cannot properly be called 'green,' but there is always a yellow color perceptible. The emerald green essences which have been exported from Messina are such as have been allowed to stand for a long time in badly tinned vessels, and the color is due to oxide of copper." The second correspondent says: "After the working of the bergamot fruit the essence obtained is honey colored, and it is usually put forward and sought for of this color. The green color is acquired when the oil is allowed to stand a certain time-about seven or eight months-in the vessels; it attacks the tinning and becomes green through contact with the copper. This is the correct explanation of the two colors; any other is false."

Cajeput Oil.—Referring to a large consignment from Macassar, Messrs. Schimmel state that according to their experience cajeput oil directly imported is always genuine and trustworthy, but that in intervening commerce, and, as they hear, especially in America, it gets adulterated with camphor oil. On practical grounds an adulteration with eucalyptus oil is not to be feared, as that oil is more costly.

Calamus Oil—Reporting on the Japanese calamus root referred to in the previous Bericht it is stated that these roots do not differ externally from European calamus roots, and are no doubt derived from the same species. They contain 5 per cent. of a highly aromatic essential oil which is considerably heavier than the German calamus oil, having a specific gravity of 0.991 at 16° C. It boils between 210° and 290°C.; if the distillate be collected in two fractions, the lower portion has the characteristic calamus odor, while the higher boiling portion gives off the peculiar sesquiterpene odor. Japanese calamus oil also differs from the European in solubility, 1 part dissolving in 500 parts of 50 per cent. spirit, the German oil requiring 1000 parts of spirit.

Camphor Oil.—Under this name the light-boiling portion of the crude camphor oil appears to find enormously increasing industrial application as a substitute for turpentine oil. More detailed information is now given concerning its characters and composition. It is stated that after the preliminary runnings, smelling disagreeably of aldehydes and acids, the oil begins to boil at about 158°C. The first fraction, boiling between 158° and 162°C., consists of right-handed pinene, identified by the formation of the hydrochlorate, $C_{10}H_{16}HCl$, as well as of nitrosoterpene, melting at 130°, obtained by treatment of pinene nitrosochloride with alcoholic potash. In the portion boiling between 169° and 171° phellandrene was detected, but in very small quantity; it was identified by its nitrite, melting at 102°. Dipentene was found in camphor oil by

Wallach, and the tetrabromide and nitrosylchloride compound maybe easily obtained from the fraction boiling at 180°. The occurrence of terpineol in camphor oil has not been determined with certainty. Whilst the formation of a compound having the composition $C_{10}H_{16}$ 2Hl, as well as of terpin hydrate, dipentene and terpinene, rendered its presence highly probable, it was, on the other hand, rendered doubtful by repeated failures to obtain the dipentene dihydrochlorate and, tetrabromide. There is also in camphor oil a considerable quantity of a hydrocarbon, boiling about 260° to 270°, from which was obtained the hydrochloric acid compound, melting at 117°, characteristic of the sesquiterpene cubebene. In the highest boiling fractions of camphor oil occurs an intensely blue colored oil, which is probably identical with the constituent, boiling at about the same temperature, occurring in chamomile, millefolium, wormwood and other oils. The constituents of camphor oil found up to the present are

Boiling point.	Constituent.	Formula.
158°–162°	Pinene	$C_{10}H_{16}$
1 7 0°	Phellandrene	$\dots C_{10}H_{16}$
176°	Cineol	C ₁₀ H ₁₀ O.
180°	Dipentene	$C_{10}H_{16}$
204°	Camphor	$C_{10}H_{10}O.$
215°–218°	Terpineol	$C_{10}^{10}H_{17}^{10}OH.$
23 2°	Safrol	$C_{10}H_{10}O_{0}$
248°	Eugenol	$C_{10}H_{10}O_{0}$
274°	Sesquiterpene	$C_{15}H_{24}$.

CanangaOil.—The opinion is expressed that the finer sorts of Java cananga oil can be used for all purposes for which the ordinary qualities of ylang-ylang oil suffice, since both oils are derived from the same plant and the extraordinary differences in quality are due to the more or less perfect methods of preparation.

Chamomile Oil—In order to prevent as much as possible the original blue color of this oil from changing to green it is recommended that it should be protected carefully from the influence of light and heat.