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Botanical Medicine Monographs and Sundry

NOTE ON ADULTERATED SPANISH SAFFRON.

By G. M. BERINGER, PH.G.

Read at the Pharmaceutical Meeting November 19.

Two lots of adulterated saffron have recently come under my notice. The first was of a handsome color, excellent in odor, and brought a very high price. It yielded on incineration 40 per cent. of ash, On close inspection it was found to be an admixture of vegetable fibre of unknown origin with a small quantity of genuine saffron.

The fibre was in pieces from 1/2 inch to 1 1/2 inches long, and upon microscopic examination proved to be the stem of a monocotyledon, most likely a species of grass. This was loaded with a calcium sulphate artificially colored, and attached thereto with some saccharine substance, most likely glucose. A small quantity thrown on water soon deposited a heavy precipitate of the sulphate, tinting the water a pinkish yellow.

A portion was taken from the centre of the can, and of this 5 gms. was carefully weighed and then carefully picked over, separating the true saffron and the adulterant. The following statement exhibits the proportion of each :

.915 gms. genuine saffron.
3.745 gms. adulterant.
.240 gms. refuse so broken as to be impossible to separate.
.1 gm. loss in handling.

5.000 gms.

From these figures it would appear that the saffron contained only about 20 per cent. of genuine saffron.

The adulterant yielded 52.7 per cent. of ash, containing considerable calcium. sulphide.

The coloring matter of the adulterant was found to yield an orange-yellow solution to alcohol, and when thus extracted and the solvent evaporated was obtained as an orange-red powder, which dyed silk a bright yellow and showed with reagents the following reactions: With concentrated sulphuric acid a violet-red, on diluting the color gradually fades. With concentrated hydrochloric acid a violet-red, on diluting destroyed. With sodium hydrate the color gradually fades. With ammonium hydrate the aqueous solution produces a bright yellow color. Stannous chloride and

hydrochloric acid destroyed the color. Its aqueous solution is bleached by calcium hypochlorite and precipitated as a pale yellow precipitate by lead acetate. These reactions point to the presence of some artificial non-vegetable coloring.

The true saffron in the mixture yielded 5.7 per cent. of ash, about the normal amount, and deposited no pulverulent substance on soaking in water.

A somewhat similar adulteration of saffron was reported by W. Brandes, *Pharm. Ztg.*, 1879, p. 506 (see AMER. JOUR OF PHAR., 1879, p. 558), who reported 50 per cent. of stems obtained from a plant belonging to the Gramineae or Caricineae, probably from Cavex capillaris, the stems being loaded with calcium carbonate previously colored with cochineal.

The second lot of saffron was genuine Spanish saffron, excellent in color and odor, contaminated with but a small quantity of the yellow styles and a few stamens, but loaded with sodium sulphate. It yielded 17 per cent. of fusible ash. The adulteration of saffron with soluble salts, such as the borate, carbonate and sulphate of sodium and ammonium salts, has been previously reported in France by M. Adrian (Jour. de Pharmacie et de Chimie, 1889, p. 98), and in England by E. M. Holmes (*Phar. Journ. aud Trans.*, February, 1889, p. 666).

NATIVE WYOMING SOAP.

Contribution from the Chemical Laboratory of the
Philadelphia College of Pharmacy.—No. 63.

BY HERMANN WESTPHAL, PH. G.

This mineral, which is known locally under the name of “Native Wyoming Soap,” occurs in the Blue Ridge, 30 to 40 miles west and southwest of Sundance, Wyoming Territory, at an elevation of about 5,000 feet.

It is found in two distinct forms. 1.—*The wet variety*, which occurs in sink holes, or in the neighborhood of springs, and covers, probably, an area of several hundred acres. It forms a thick very tenacious pasty mass, about the consistency of butter. Its color is light yellowish gray. Taste slightly saline, clay-like. Odor argillaceous. Moistened between the fingers with a little water it feels like soap or some greasy substance: hence its name. This soapy feel is probably due to the extreme fineness of the silicates which it contains. In hot weather, the edges of the sink holes become hard and brittle, and on some places show an efflorescence of fine crystals of magnesium sulphate.

These holes, which seem to be almost bottomless, at times become very annoying to the ranchers, as cattle frequently get into them, and unless discovered in time and pulled out are sure to perish, as it is impossible for them to free themselves.

2.—*The dry variety* occurs underground in veins like coal. It is hard and dry, and looks very much like chalk; the color is somewhat darker, varying from yellowish-white to dirty greenish-yellow. On addition of a little water, however, it is converted into the soft variety as found on the surface of the earth. It appears probable that the wet

variety is formed by springs running over beds of the dry soap, washing it up and in time accumulating it in large quantities.

It is used by cowboys and ranchers who live in the vicinity as a substitute for soap, and for removing grease by absorption. They also use it for making "hard water."

Five grams of the soap, exposed to the atmosphere for several weeks, at a temperature of about 24°C. lost 41.20 per cent. of moisture. It had become a very hard and brittle mass varying from dirty white, grayish-green to orange-yellow. Taste and odor were unaltered; it adhered to the tongue, and when cut with a knife exhibited a very smooth and shining surface. On ignition the wet soap lost 53.30 per cent. while the air-dry lost 12.10 per cent. corresponding to 41.20 per cent. on exposure. The air-dry soap reduced to an impalpable powder gave the following composition on analysis:

SiO_2	61·08 per cent.
Fe_2O_3	3·71 "
Al_2O_3	17·12 "
MnO	traces
CaO	2·96 "
MgO	1·82 "
Na_2O	0·20 "
SO_3	0.88 "
H_2O	12·10 "
Total	99·87 "

THE RESIN OF MYOPORUM PLATYCARPUM.

By J. H. MAIDEN, F.L.S., Curator of the Technological Museum, Sydney.

A veritable natural sealing-wax is yielded by a small tree which is found in the interior of Australia; it occurs in the more arid portions .of all the colonies except Queensland. The tree is *Myoporum platycarpum*, R. Br., and it possesses a variety of local names, such as "Sandalwood," "Dogwood," and "Sugar tree;" the latter because a manna exudes from it which is greedily sought after by the blacks, and is likewise much appreciated by colonists. It yields a resin, which is used by the aboriginals as a substitute for pitch and wax; for example, they use it either alone, or mixed with fat, to cement the stone heads of their tomahawks to the fibre which joins them to the stick forming the handle. As has been already hinted, it forms a natural sealing-wax, and is sometimes used by people in the interior for this purpose. It would probably serve as a constituent of black sealing-wax; alone it is too soft for keeping in this climate.

It sometimes occurs in great quantities on the stem, is hard and brittle, breaks with a glassy fracture which is at first of a purple or indigo color, but becomes brown on keeping. Often it may be picked up from under the trees in rounded or globular pieces.

Two samples have come into the writer's hands, and a few notes concerning them will doubtless be interesting. The first, from the Lachlan River, New South Wales, is in small rounded lumps usually weathered on the outside, and having a pleasant empyreumatic odor; these are of a dark reddish-brown color, fly with the slightest touch of the pestle, and are easily powdered. The resin has a bright fracture, which appears almost black, but shows reddish-brown at the edges. It softens even with the warmth of the hand, and if kept in a bottle, the heat of an average summer day is sufficient to fuse pieces presenting fresh fractures.

It presents some external resemblance to guaiacum resin (especially when that substance comes to market in small lumps), but it is not so green in color as the latter. It has no taste. Cold water has no effect on it, but if the water be heated the resin melts and floats, forming a liquid much resembling tar, but of a purplish-brown color. The water remains clear, colorless and almost odorless.

Light petroleum dissolves 46.8 per cent. of a reddish-brown resin, destitute of odor. Alcohol dissolves from the residue 28.1 per cent. of a deep reddish-brown resin, which is almost black by reflected light.

The residue was boiled in water and 1.7 per cent. of saline matter was extracted, while 23.4 per cent. of accidental impurity was left behind. This is of a chocolate color, and under a lens was seen to consist of a little ligneous matter, with a large percentage of inorganic impurity. It was quite free from gum.

Summary.

α-Resin soluble in light petroleum	46·8
β- " " alcohol	28·1
Saline matters	1·7
Accidental impurity	23·4
	100·0

BOTANY BAY OR EUCALYPTUS KINO.

By J. H. MAIDEN, F. L. S., F. C. S., ETC.,
Curator of the Technological Museum of New South Wales, Sydney.

The first part of the author's interesting paper, published in *Phar. Jour. and Trans.*, September 21, states that in Australia, kinos are largely used in rural medicine, on account of their astringent properties, aqueous solutions being almost invariably made. Some of' them are used by the settlers for ink, or for staining leather black, the process, simply consisting in boiling the kino in an iron saucepan. The commerce with Europe and America in eucalyptus kino has never been important. A good kino of uniform composition, offered by Mr. Bosisto, is collected from *E. rostrata*.

Wounding the bark stimulates the flow of kino in some cases, but such a practice does not appear to be systematicallv resorted to. Usually it is collected from the

outside, which accounts for its occasional admixture with particles of bark, but sometimes it is contained between the concentric layers of the wood (chiefly in the case of *E. corymbosa*). In the latter case it has communication with the outside of the tree, though frequently the passage is blocked with indurated kino, which has to be removed to enable the store inside to be drawn off.

The eucalypts are popularly known in Australia as "gum trees," but certain species from the structure of their bark are called "iron barks" and "stringybarks." The "gums" are locally distinguished as red, white, blue and by other adjectives. The adjective is in one district employed to describe the leaves, in another the bark, and so on. Thus a "white gum" may be intended to denote a tree with white leaves, white bark, etc. The variations in some trees in different localities, due to climate, soil and similar causes, are sufficient to render terms like "white gum," etc., which may in some way describe a species in one district, totally inapplicable in another.

Classification of Eucalyptus Kinos.—Eucalyptus kinos can be very simply classified according to their behavior with alcohol or water. In all cases the writer made the tinctures of the strength of tinct. kino, B. P. The kinos experimented upon by the writer fall into three groups, which he has called, the Ruby group, the Gummy group, and the Turpid group respectively.

a. Ruby Group:—

E. amygdalina, Labill.	*E. piperita*, Sm.
E. eugenioides, Sieb.	*E. Sieberiana*, F. v. M. (syn. *E. virgata*,[Sieb.])
E. haemastoma, Sm.	*E. stellulata*, Sieb. .
E. macrorrhyncha, F. v. M.	*E melliodora*, A. Cunn.
E. pilularis, Sm.	*E. obliqua*, L'Her.

In the preparation of a tincture all the above kinos tend to dissolve entirely, forming clear ruby solutions of approximately the same tint. They also form clear ruby solutions to cold water, hardly differing in appearance from the tinctures. The aqueous solution of the alcoholic extract is similar in appearance. Members of this group are not very friable, breaking down into clean angular fragments, and never forming an impalpable powder. If acetate of lead or of copper be added to a moderately strong solution of these kinos, so strongly gelatinous a precipitate will be formed that the test-tube may be inverted without any liquid spilling. This distinguishes them, in one respect, from the Turbid Group.

At present I know of no constant characteristics to aid in further sub-dividing this group. The stringy barks (*E. obliqua*, *macrorrhyncha*, etc.) may often be distinguished (as a group) by means of fibrous bark either attaching to individual fragments of kino, or loose with a parcel of it, but it must be borne in mind that many other species (e. g., *piperita*) have more or less stringy bark.

b. Gummy Group:

E. leucoxylon, F. v. M.	*E. resinifera*, Sm.	*E. saligna*, Sm.
E. paniculata, Sm.	*E. robusta*, Sm.	*E. siderophloia*, Benth.

In spirit, these kinos scarcely dissolve, leaving abundant granular residue of gum. Supernatant liquid perfectly clear. These kinos tend to be perfectly soluble in cold water, and age seems to have but little effect on them in this respect. They are like the Ruby kinos in not forming impalpable powders, being even tougher than the members of that group. They form gelatinous precipitates with some metallic acetates, like the Ruby group.

c. Turbid Group:

E. goniocalyx, F. v. M.
E. hemiphloia, F. v. M.
E. rostrata, Schl.
E. punctata, DC.
E. odorata, Behr.
E. Gunnii, Hook.
E. Stuartiana, F. v. M.
E. viminalis, Labill.
E. terminalis, F. v. M.
Angophora lanceolata, Cav.
A. intermedia, DC.

The above yield orange-brown solutions.
E. corymbosa, Sm., yields solutions up to the brightest ruby.
E. microcorys, F. v. M., and *E. maculata*, Hook., yield solutions of various shades, from lemon-yellow to orange-brown.

All the members of this group yield turbid solutions to spirit, which require long standing or filtering to become clear. They behave in a similar manner to water, but become clear on boiling, indicating catechin. The aqueous solutions of the alcoholic extract are likewise turbid. They are all more or less friable, forming impalpable powders usually by pressure of the fingers. Addition of acetate of lead or copper produces only a very slight gelatinous precipitate, thus dividing them from the other two groups.

Sub-division of the Group.—E. corymbosa kino is usually so brilliant in color, and yields such rich-colored tinctures that it cannot well be mistaken for any other kino.

E. microcorys and *E. maculata* are often externally much alike, but they may be distinguished (1) by the facility with which the former dissolves in water, (2) by the yellow color which the latter yields to ether,

E. maculata, E. punctata and *A. lanceolata* possess odors. The essential oils which cause them may be removed by ether.

Definition of the terms “Botany Bay Kino” or “Australian Kino.” Not the product of *E. resinifera*. I propose to investigate the claim of certain species to be yielders of the kino which for over one hundred years has passed under one or other of the above names. The first published allusion to this kino will be found at p. 233, *Journal of a Voyage to New South Wales*, by John White, Esq., Surgeon-General to the Settlement, London, 1790. A plant is figured (flower-buds and bark), described by Dr. (afterwards Sir) James Smith, who wrote the botanical portion of White's book, as a new species, *Eucalyptus resinifera*, and the kino is thus alluded to:—“On making incisions in the trunk of this tree, large quantities of red resinous juice are obtained, sometimes even

more than 60 gallons from a single tree. When this juice is dried, it becomes a very powerfully astringent gum-resin, of a red color, much resembling that known in the shops by the name of kino, and for all medical purposes fully as efficacious. Mr. White administered it to a great number of patients in the dysentery which prevailed much soon after the landing of the convicts, and in no single instance found it to fail. This gum resin dissolves almost entirely in spirit of wine, to which it gives a blood-red tincture. Water dissolves about one-sixth part only, and the watery solution is of a bright red. Both these solutions are powerfully astringent." What particular tree is indicated in the above passage will probably never be known. The sample of bark figured is smooth and scribbly, like that of *E. haeemastoma* perhaps, and certainly as unlike that of the two trees named by Sir James Smith and Allan Cunningham, *E. resinifera*[1] (*vide infra*), as it is possible for it to be. Only two trees in the Sydney district yield kino in anything like the abundance it was alleged to have been yielded by the *E. resinifera* of Smith. They are *E. corymbosa* and *Angophora intermedia*, but although I am well acquainted with these trees, and have made the matter of exudations of our native trees my special observation for over three years, the highest reliable estimate of the quantity yielded by either of them would not be more than one-third of the quantity mentioned by White. The red color would, however, exclude the *Angophora*, while *E. corymbosa* yields a "blood-red tincture" to spirit of wine, and dissolves almost entirely in that liquid, but such a kino would be readily and almost entirely soluble in cold water. Smith's description also contains the statement: "The wood is extremely brittle, and from the large quantity of resinous gum it contains is of little use but for firewood." Not too much stress should be laid upon an expression of opinion of the value of a timber made only a few months after the settlement of this continent, but the description of the wood being full of gum-resins almost certainly applies to *E. corymbosa*, or to an *Angophora*. But the flower-buds figured are of a eucalypt (and that excludes *Angophora*), while they are as unlike those of *E. corymbosa* as possible. The bark figured is smooth, the flower-buds have something the shape of those of *E. punctata* (included by Bentham under Smith's resinifera), while the strongly-compressed peduncle, all taken in conjunction with the smooth bark (*E. resinifera* bark is never smooth, except occasionally on the branches), may show that Smith's figures refer to *E. punctata*. But the kino of *E. punctata* is liver colored or reddish brown, and that description does not tally with that of White. All this tends to prove the truth of my original assertion, that the origin of the figures in White's book will probably never be known. As likely as not the bark and the flower-buds (no other parts being figured) were from different species.

It will be seen later on that the name *resinifera* was a singularly unfortunate one to apply to any species of eucalyptus, firstly, because they are nearly free from resin, and secondly, because scores of species yield this exudation (called "gum resin" by Smith) very freely. All kinos yielded by eucalypts, if they have been exuded sufficiently long, will be found at a certain stage, to be only soluble in water to the extent of one-sixth, but a eucalyptus kino almost entirely soluble in spirit, and at the same time only one-sixth in water, is an impossibility.

White's description (for although penned by Smith, the substance of it must have been supplied by White) has partly been copied by many subsequent authors. A few extracts will suffice.

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[1] *E. punctata* (included in *E. resinifera*) has a smoothish bark, but is not scribbly.

"*E. resinifera*, the brown gum tree of New Holland, furnishes Botany Bay kino. A single tree will yield 60 gallons." Balfour, "Manual of Botany." *E. robusta* is the only eucalypt ever known as, "brown gum," but that species neither exudes kino freely, nor is the, product readily soluble in spirit.

"*Botany Bay Kino.*—The substance called by this name is the produce of *Eucalyptus resinifera* (Myrtaceae), and other species of eucalyptus, natives of Australia and Tasmania. It appears to be a kind of extract, and has properties similar to the official kino." (Pereira, "Materia Medica"). The surmise as to its being an extract has already been dealt with.

"*E. resinifera*, the Ironbark tree, a native of Australia and Van Diemen's Land, and several other species, yield an astringent substance called eucalptus, or Botany Bay kino. The kino resembles in its properties the official catechu and kino, and may be used for a similar purpose." (Bentley, "Manual of Botany"). The Ironbark tree above alluded to is the *E. resinifera* of A. Cunn. (*E. siderophloia*, Benth.), but neither it nor the *E. resinifera* of Smith extends to Tasmania.

As has already been mentioned, there are two eucalypts called *E. resinifera*. They are:

1. *E. resinifera*, Smith (White's "Voyages," p. 233; "B. Fl.," iii, 245 ; figured in Decade I. of Mueller's "Eucalyptographia"). It is commonly called "Red or Forest Mahogany," and is the tree to which the species-name attaches by priority.

2. *E. resinifera*, A. Cunn. (Syn., *E. siderophloia*, Benth.); "B. FL," iii, 220. Figured in Dec. IV. of Mueller's "Eucalyptographia."

"Ironbark" or "Red Ironbark."—At the latter place Baron Mueller states, "The Rev. Dr. Woolls observes that the Botany Bay kino is more extensively obtained from *E. siderophloia* than from *E. resinifera* (Smith, of course), which, as the specific name implies, is generally regarded as the main or even sole source of that drug."And Dr. Woolls, in his "Plants of New South Wales," (1885), states, "The Botany Bay kino was procured principally from this species, and hence Allan Cunningham and other botanists were accustomed to call it *E. resinifera*."

But what are the characteristics of kino? The official kino (*PterocarpusMarsupium*) is, according to the British Pharmacopoeia of 1885, "almost entirely soluble in rectified spirit." This is an important property, and on it the tinct. kino B. P. is based. Works on materia medica, while pointing out certain unimportant points of dis-similarity between the official and eucalyptus kino, never state that the latter does not dissolve in rectified spirit, while some make the specific statement that it is soluble in that liquid. But my experiments have shown that no kino is more insoluble in spirit than that of *E. siderophloia*. I obtained four samples from widely different localities in New South Wales and Queensland, and collected at different times. They all agree in their very partial solubility in alcohol, by reason of the very high percentage of gum they contain. The *E. resinifera* of Smith is also comparatively little soluble in spirit, for a similar reason. For this reason alone, I do not hesitate to say that "Botany Bay kino" is neither the produce of *E. resinifera*, Smith, nor *E. resinifera*

A. Cunn. Both these kinos would be quite useless for the preparation of a tincture, and would never be thought of a second time by any person who had made the experiment on either; it is therefore quite certain that these species have not caused pharmacists to use eucalyptus kino more or less for a century, but rather, it has doubtless been the admixture of such kinos as these with such eucalyptus kinos as are freely soluble in spirit, which has helped to bring eucalyptus kino into disrepute.

I now give a list of species which satisfy the requirements of the B. P., and it is hoped that systematic endeavors will be made to place kinos, which do, or should come into that list on the market Eucalyptus kino was official in the Edinburgh Dispensatory of 1811, but the different substances supplied under the same name doubtless led to its omission.

1. All members of the Ruby group.

2. The following members of the Turbid group:

E. goniocalyx, E. hemiphloia, E. rostrata, E. punctata, E. odorata, E. Gunnii, E. Stuartiana, E. viminalis, E. terminalis, E. corymbosa.

The remaining members of the turbid group in my list must be for the present omitted, on account of their color; perhaps *E. punctata* would have to be rejected only on that account.

All members of the gummy group must be rejected.

—*Important Note*.—The above list only contains those species which I have proved by experiment to be suitable. I can therefore guarantee them, and will only add others to the list as opportunities occur for testing them by other chemists or myself.

I suppose it is too much to expect that the specific name of *resinifera* shall be abandoned for any eucalypt. I know it is against botanical rules; but if the specific name *virgata* could be suppressed on account of the stature of a eucalypt, I think, on the ground of expediency, Baron Mueller may well suppress Smith's *E. resinifera*,[2] for this name has impeded attempts to obtain a knowledge of our kinos for a century. I have already specifically referred to two objections to the use of *E. resinifera* for Smith's species, and would now emphasize that it is a poor yielder of a poor kino. Out of nearly one hundred and fifty species of eucalyptus, most of them (perhaps all) yield it more or less, and of those which yield it most abundantly it is difficult to say which produces it the most freely, and to which the term “resinifera” would by right belong. Probably to *E. corymbosa*. But the name should be suppressed.

Gelatinization of Tincture of Kino.—The gelatinization of tincture of kino, by which it forms a substance like red-currant jelly, and more or less devoid of astringency, remains an unsettled question, although it has often been alluded to in journals devoted to pharmacy[3] during the last half century. Pereira following Thomson, and most other writers on materia medica following Pereira, state that where

[2] Another eucalyptus is usually called by a false name, the essential oils being generally labelled *E. Globulus*.

[3] Cf. *Pharm. Journ.*, i, 399; [3], x, 232.

gelatinization takes place, “Botany Bay Kino” has been used, by which is meant, as I have already shown, any of the kinos belonging to perhaps 40 or 50 species.

I have had over seventy eucalyptus and angophora kinos in spirit (to make tinctures of B. P. strength), for periods varying from a few days to twelve months, and have drawn the following conclusions:(1) Tinctures do not gelatinize if made from new kinos. By the word “new” I mean under one or two years old. (2) No kinos gelatinize other than the clear ruby ones. Five very old ruby kinos on which I experimented gelatinized in a month or two, (3) All kinos entirely soluble in spirit are ruby ones.

Whatever the cause of gelatinization may be, or rather, whatever the substance may be which, when formed, causes gelatinization, my experiments show that no chemist need have gelatinized tincture of kino if he chooses to avoid it. Old ruby kinos should be rejected for the purpose of tincture making. In the case of a member of the Ruby group, if the kino is not completely and readily soluble in cold water, forming a clear ruby solution, with no gelatinous ruby-colored residue of phlobaphene, it should be rejected. My tinctures were made in March, 1888, and perhaps sufficient time has not elapsed to justify one in being dogmatic on the matter, but I will engage to report these samples in another year or two.

The writer has little doubt that this gelatinous looking mass consists wholly or mainly of softened phlobaphenes. By direct experiment he has shown that insoluble phlobaphenes break down after a longer or shorter period of digestion in alcohol, and form the substance already likened to red-currant jelly. The subject will bear further inquiry, but certainly he cannot detect gum, or the somewhat unsatisfactory pectin in the gelatinized mass.—*Phar. Jour. and Trans.*, October 26, 1889.