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AN EXAMINATION OF BURDOCK FRUIT.

A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE
PHILADELPHIA COLLEGE OF PHARMACY.

By HENRY TRIMBLE AND F. D. MACFARLAND.

Read at the Pharmaceutical Meeting, February 17, 1885.

The following analysis of the fruit of *Lappa officinalis*, while incomplete, gives, we believe, the important constituents of this drug. The moisture determined in the usual way was found to be 7.30 per cent., and the ash 5.34 per cent.

Ten grams reduced to No. 60 powder were thoroughly exhausted with petroleum spirit. This solution, on evaporation and heating to 110°C., was found to consist of a bland light yellow fixed oil, representing 15.4 per cent. of the fruit.

The following are some of the important characteristic reactions. With fuming nitric acid a brown color and aromatic odor, but not becoming solid. With strong sulphuric acid a brown color, becoming thick and syrupy. Exposed to the air in thin layers the oil solidifies. Alcohol and absolute alcohol do not dissolve it, but hot absolute alcohol, ether, chloroform and benzol are good solvents. The specific gravity is .930, determined with a larger amount of the oil prepared from 75 grams of the drug. That portion of the original ten grams remaining after treatment with petroleum spirit was exhausted with ether which dissolved 1.15 per cent. of a resin soluble in alcohol. Absolute alcohol extracted from the remainder of the drug 12.6 per cent. 8.3 per cent. being insoluble in water, appeared to be resin soluble in dilute alcohol; the remaining 4.3 per cent. were soluble in water and were examined for alkaloids. A small quantity of crystals separated on evaporating the chloroform solution of this aqueous portion, first made alkaline with potassium hydrate. The amount, however, was so small that the 75 grams of the drug remaining after extracting the oil with petroleum spirit were exhausted with dilute alcohol, the alcohol evaporated, and the residue, after rendering alkaline, was shaken repeatedly with chloroform until that solvent contained all the bitter principle. On evaporating the chloroform a residue was obtained which all efforts, so far, have failed to get in a crystalline condition. It is intensely bitter, of a faintly alkaline reaction, gives precipitates with phosphomolybdic acid, Mayer's test, tannic acid, and gives off ammonia on beating with potassium hydrate. It is therefore quite certain that this bitter principle is an alkaloid, and we suggest for it the name of *Lappine*.

The other constituents were not determined, but they with the bitter principle will be further investigated.

We were induced to make this analysis from an account of the medicinal value of the so-called burdock seed in Dr. Squibb's "Ephemeris," vol. i, page 115.

PHILADELPHIA, Feb. 17, 1885.

THE ESSENTIAL OIL INDUSTRY IN GRASSE.¹

By F. A. FLUCKIGER.

The world-wide fame of Grasse depends upon the essential oils of plants which there grow wild or are cultivated. Among the former may be named: —(1) *Lavandula Spica*, Chaix (*L. latifolia*, Villars), the "aspic" of the French, which occurs plentifully in the country all around Grasse, and even quite close to the city. (2) *Lavandula vera*, DC. (*L. officinalis*, Chaix, *L. angustifolia*, Moench), which not only grows together with *L. latifolia*, but more frequently on high ground in the mountain region; generally *L. vera* is a much more widely spread plant throughout the Mediterranean region, and is also easily cultivated throughout Europe. Both these plants have stout woody stems, which are very enduring; those of thyme are still more vigorous. (3) *Thymus vulgaris*, L., a real ornament of the Mediterranean region, where it is found plentifully both in the Grasse district—not making its way so high up the mountains, but growing in the light thickets—and on unsheltered coast. (4) *Rosmarinus officinalis*, L., the erect but always bent stems of which, reaching a height of two metres, and often several centimetres thick, probably overtop most other labiates, or, at any rate, are not equalled in any other European species of this family. At Mentone and Nice it is difficult to say whether *Thymus vulgaris* or *Rosmarinus* grows most abundantly. At Grasse the latter manifestly loses ground, notwithstanding that it is by far more conspicuous than the lower lying thyme. Here and there *Cuscuta* selects the rosemary stalks for its home.

The oil of these four labiates constitute an important export industry of Grasse. The plants being vigorous, persistent bushes, they require no cultivation, as the tops, bearing leaves and flowers, taken for distillation, are always replaced, even though the collector does his work in a most unskilful manner. The large distilleries in Grasse conclude arrangements with the communities in the districts round about, by which they become entitled to the produce of large tracts of land. The work itself is done for the Grasse firms by the rural population, who set up their simple copper stills on the spot and only carry the distillate to the city. Many of these traveling stills (*alambics voyageants*) are indeed the property of the large houses in Grasse. Probably the work has long been carried on in this way. The Parisian druggist, Pierre Pomet who was well informed in such objects, said in 1694 in his "Histoire Générale des Drogues," concerning *Lavandula Spica*, "elle est si commune dans le Languedoc et en Provence . . . qu'elle ne coûte qu'à prendre," and he drew from this country the essential oils in question. That the oils are obtained in the manner indicated very cheaply is very probable, but it is a question whether a systematic cultivation and an economical manufacture would not induce greater progress. According to estimates for which the

¹ Abstract from a paper in the Archiv der Pharmacie, xxii., 473.

author is indebted to the kindness of M. Roure, proprietor of one of the largest manufactories, the following quantities of each oil are delivered in Grasse every year: from *Lavandula vera*, 80,000 to 100,000 kilograms; from *Thymus vulgaris*, 40,000; from *Lavandula Spica*, 20,000 to 25,000; from rosemary an equal quantity. The quantity sent out from Grasse probably covers the requirements of the whole world; at least the author only knows of rosemary that it is cultivated also in Dalmatia, which country sends about 20,000 kilos. of the essential oil into the market.

Oil of thyme furnished the first materials, in 1847 and 1853, for the investigation of thymol, but this substance is no longer prepared from it. The amount of thymol in the oil appears to vary considerably, and more exact information on this point is desirable.

Of the oils which, unlike those already mentioned, are regularly distilled in the laboratories of the Grasse manufactories, those of species of Citrus must be named, and especially oil of neroli. The flowers of the bigarade tree (*Citrus vulgaris*, Risso) are not submitted to distillation for the oil, of which they yield at most one part from one thousand parts, but for the production of the thousands of hectolitres of "eau de fleurs d'oranger," "aqua florum aurantii," and "aqua naphae," upon which Grasse prides itself; the oil of neroli is a byproduct, though of course very costly. According to the author's informants, about 2,000 kilograms of this beautiful oil is prepared in Grasse yearly, but nominally much more is exported. When a proper price is paid a pure oil of neroli may be obtained; but the perfumers and druggists require it at reduced prices. In order, therefore, to accommodate them the producers add some "essence de petit grain," which, however, is no longer distilled from "petit grain," i. e. the small unripe fruit of the bigarade tree, but from its leaves. No other species or form, however, of the genus Citrus is endowed with so fine an aroma in the leaves, as the bitter-fruited orange tree, the "bigaradier." The blossoms of the ordinary sweet-fruited orange, which are not used for distillation, yield only an oil of inferior value. In competition with the products of the bigaradier, the sweet orange which is cultivated in Grasse is disappearing. Neither the bergamot nor the lemon occur there.

At the time of the author's visit the enormous metal tanks and cemented cisterns for holding rose water in the factory of M. Roure were ready for the reception of the products of the coming season, which, like that of the neroli flowers, is at its height in the month of May, when thousands of kilograms of rose leaves are passed daily into the stills. The rose oil collected in small quantity during the distillation of the rose water is probably equally as fine as the oil of roses from the Balkans or from India; but notwithstanding it grows in nearly the same geographical latitude, the rose in Provence produces far more of the worthless solid constituent, dissolved in the liquid portion, which alone is odorous. The question arises whether a change in the strain of the roses so largely cultivated in Grasse might not lead to an improvement in respect to the oil. However, the rose water has for a century found a good sale, so that Grasse is not under the necessity to seek for further progress. The oil at present obtained in the manufacture amounts to about one kilogram from each 12 000 kilograms of fresh rose leaves; to completely satisfy the requirements of customers, oil is obtained from the Balkans. The author thinks that the manufacture in Grasse affords a favorable opportunity to determine the chemical properties, hitherto completely unknown, of the oil to which the rose owes its perfume.

In perfumery “beurre d’iris” justly enjoys great popularity. It is distinguished above many other perfumes by an agreeable softness and great permanence. With the help of the most perfect methods of distillation, iris root yields scarcely one part per thousand of the so-called “orris-root camphor.” The above named house in Grasse prepares four to ten kilograms yearly. Probably an equal quantity is distilled in London and in Leipzig. A specimen of orris butter presented by M. Roure to the author enabled him to make a comparison of it with preparations from the two other sources.² In the case of orris butter also we have to do with an oil, entirely uninvestigated as to its composition, occurring in minute quantity together with the odorless principal constituent, in this case myristic acid. In Grasse “beurre d’iris” is valued at 1,500 to 1,800 francs the kilo. It is noteworthy that the local manufacturers draw their supplies of raw material from Florence and Verona, whilst there cannot be the remotest doubt that *Iris germanica* and other species of *Iris* flourish equally as well on the mountains and hills of Basse-Provence as in the fields of Tuscany or at Verona. In this case, however, also there is no necessity to give up the old custom, which is indeed carried so far that in no case is the *Iris germanica*, abundant in the district, made use of.

Besides the wholesale distillation of orange flowers and roses, some other aromatic plants are occasionally worked up when required, though not to any very great extent. But another source of considerable revenue is the manufacture of “pommades” and “extracts.” In this extensive branch of industry the essential oil is utilized from flowers containing it only in very small quantity. Among these are (1) the bigarade orange flowers, and (2) roses. In the following the essential oil is present in so minute a quantity that it is scarcely practicable to obtain it by distillation.

(3). *Cassie*.—This is the name given by the French to the elegant yellow flower-heads of the *Acacia Farnesiana*, Willd., a small tree which first reached the Farnese gardens at Rome from the West Indies and Central America. The fine odor of the flower’s brought about its introduction into Provence, which it appears did not take place, at least for industrial purposes, until 1825.³ At present “cassie,” is cultivated very carefully and on a large scale throughout the entire district between Canne and Grasse. The plantations are usually the property of the manufacturers or other landed proprietors and are worked by lessees, the terms being the simple and primitive arrangement of sharing the proceeds with the proprietors. This system extends in this country to other perfumery plants, as well as to the olive.

(4). *Jasmin*.—The fields near Grasse are generally planted with *Jasminum officinale*, L., which was probably first brought to Italy from Asia Minor or India in the sixteenth century; but it is found advantageous to graft upon it the *Jasminum grandiflorum*, L., bearing larger flowers, having a more powerful odor; this also is an Indian species, which probably came to Europe before the time of Rheede, in whose ‘Hortus

² See Flückiger’s “Pharmacognosie,” p. 314

³ “Apportées en France vers l’année, 1825” (Guib. Hist. Dr. iii, 1869), 396. Ricord-Madiana, as well as Bonastre, attempted in 1830 and 1831 the chemical investigation of the flowers of the West Indian *Acacia Farnesiana*, though without any result worth mentioning (*Journ. Pharm*, xvi, 571; xvii, 419). In the East Indies a gum exuding from the stem of the plant is collected. The root bark is said to have a very strong garlic-like odor; it therefore probably contains an allyl compound. (Flückiger, *Pharm. Chemie*, 1879, p. 65.)

Malabaricus' (v., tab. 52) it is figured. But the *Jasminum grandiflorum*, here known as "Jasmin d'Espagne," even in the beautiful Paradise of Provence, requires some shelter in winter, and this is effected by simply covering the small bushes with earth. Since only the flowers are required, the plants are allowed to grow scarcely half a metre high, and they are planted close to one another in regular rows. In the spring the young shoots are cut back. The flowering takes place in August. Professor Flückiger suggests that an enterprising cultivator might make experiments at Grasse with the *Jasminum Sambac*, Vahl, which in India is far more highly prized and appears to possess a perfume far more powerful than that of any other species of jasmine, as was pointed out two hundred years ago by Rumphius. A figure of *Jasminum Sambac* is given in the *Botanical Magazine*, vol. xliii. (1816) No. 1785.

(5). The *jonquille* (*Narcissus Jonquilla*, L.), probably of oriental origin, bears two to five extremely odorous yellow flowers, with a short funnel-shaped perianth and a corona four times as long. The name of the species (Italian, *giunchiglia*) is derived from the nearly cylindrical, leaves, grooved on their upper side, recalling those of species of *Juncus*. When the author was in Grasse, in April, the flowering of the jonquil was already over.

(6). *Réséda* (*Reseda odorata*), cultivated throughout Central Europe as a favorite garden and pot plant; it is alleged to have been derived from Egypt.

(7). *Tubéreuse* (*Polianthes tuberosa*, L.) an Amaryllidaceous plant, belonging to the Agave division, and a native of Mexico. Its beautiful white flowers give its name to the genus (*polios*, white or grey); the single species has a short tuberculous thickened rhizome. The Polianthes was introduced in Europe during last century as an ornamental plant. On account of its noble head of odorous flowers, which probably are nowhere else cultivated in such quantity as at Grasse. Already, between 1571 and 1577 it had attracted the attention of the Spanish physician Francisco Hernandez, who undertook the scientific exploration of Mexico at the cost of King Philip. In his "Nova Plantarum, Animalium et Mineralium Mexicanorum Historia," (Rome 1651, p. 27), the indefatigable physician gives a modest but unmistakable figure, with a corresponding description of the beautiful plant, under the name "Omizochitl, seu Flos osseus." He also mentions its use in making odorous wreaths. Upon this point the scanty notice which Clusius gives in 1601 of the "hyacinthus indicus tuberosa radice" in the 'Rariorum Plantarum Historia' is silent. Clusius' figure is not so faithful as the one previously mentioned. Since the time of Clusius the name tuberosa has clung to the plant.

(8). *Violette*.—The *Viola odorata* is not grown in the open field, like the other perfumery plants, but in the olive groves, which here extend over hill and valley in special beauty. The Riviera can show far larger and wider spreading olive trees, but those in the neighborhood of Grasse are remarkable for their fresher and greener foliage. Besides this, the ground shaded by the trees is there richly overgrown with grass, so that the color of the landscape recalls the loveliness of the hills near Florence. With such surroundings, the violet plantations spread out here and there, both in the immediate neighborhood of Grasse and on higher slopes, present a charming appearance. Occasionally the *Sarothamnus* is associated with it also. At the time of the author's visit he saw at the factory a large sack of the last violets of

the season, which had been delivered fresh by the collectors only an hour before. The flower was the ordinary *Viola odorata*, neither darker nor brighter in color, nor possessing a stronger perfume. But he was told that “les dernières de la saison” had a decidedly weaker odor, and he heard also that the collectors were dissuaded from bringing any more.

A great part of the industry and trade of Grasse is dependent upon the foregoing eight plants and it does not suffer from fluctuations due to change of fashion like many other industries. Year after year the manufacturers supply to their customers the same favorite “pommades” and “extracts,” and it is noteworthy that no perfumer from the large centres of fashion should direct his attention to other preparations of the kind. The explanation may be that the introduction of novelties into this domain requires an acquaintance with the vegetable kingdom which is scarcely possessed by the purchasers of the pommades and extracts of Grasse.

The “pommades” are prepared by two methods, “infusion” and “enfleurage.” In the former the transfer of the odorous principles to fat is brought about by intimate contact and warming. The predilection of the human family for unguents may not be easy to explain, but probably it goes back to the highest antiquity. Pliny ascribes their discovery to the Persians, and Pliny, Dioscorides, and other old writers refer in great detail to these preparations. In the present day pharmacy seeks not so much to convey to fat the agreeable odor of flowers as the healing properties of particular plants.

Dioscorides gives quite a detailed introduction to the purification of the fat for the purpose, and the preparation of this basis of pommades in the best condition is still the first endeavor of the manufacturers in Grasse. The best pig’s lard or beef suet is selected, a considerable portion being contributed by the populous towns of the Riviera, as well as Lombardy. The melting of the fat, its mechanical purification and washing, are conducted with exemplary care and cleanliness. The digestion of fat with benzoin has long been carried on in Grasse on the largest scale, furnishing an incontestable opportunity of demonstrating its effectiveness; and the fact that the stability of fat is essentially increased by the process admits of no doubt. Lard and beef tallow, either separate or mixed in the proportion of 2:1, are kept until required for use in tinned iron vats, in fine dry ventilated cellars. The “infusion” is effected in large jacketed boilers, in which the fat is warmed by steam heat, and the flowers are added. In the month of May over 10,000 kilograms of rose or bigarade flowers pass daily, for many days in succession, into the boilers of the factory of Roure-Bertrand fils alone, and this is only a part of the daily consumption in the factories in Grasse. The diligent stirring of the flowers in the fatbath is carried on by female workers, the expression by means of hydraulic presses is done by men. After the clearing of the fat by deposition and straining, the finished pommade is at once weighed off in tin boxes or passes into the large subterranean storerooms, in which it will remain very good until at least the next season.

Notwithstanding the exemplary pains which are spent upon this “infusion à chaud,” the fat still remains fat, gradually but inevitably undergoing change and becoming rancid. The question suggests itself whether the fat might not be replaced by the unalterable paraffin which has so successfully competed with fat in pharmacy. It

might be thought that such a preparation as the unguentum. paraffini of the German Pharmacopoeia would be particularly suited to acquire the most delicate perfume and preserve it faithfully. But Professor Flückiger was assured by M. Roure that this is by no means the case. Why this should be, appears inexplicable, but the inapplicability of paraffin is so decided that even the addition of it to fat in the preparation. of pommades by the foregoing method is said to have proved injurious. Professor Flückiger considers this point worthy of further investigation, and remarks that results obtained by himself, some experiments upon a small scale, were hardly confirmatory of the statements.

In the incorporation of the most delicate perfumes with fat the above. method of that of "infusion à chaud" is replaced by "enfleurage." For this purpose, light, square wooden frames, about 18 inches each way, in which a plate of glass can be placed, are used. All the frames and glass plates are of the same size; when piled up one upon another, therefore, they form small, tolerably well-closed compartments. Upon each glass is spread a weighed quantity of fat in a thin layer, and this is strewn thickly with flowers. Sometimes, however, the one side of the glass plate is covered with flowers only, and the layer of fat is confined to the other glass wall of each compartment, so that contact of the flowers with the fat is avoided. When a perfumed oil is desired, use may be made of cloths saturated with oil for the enfleurage. The fat is kept shut up in these glass compartments for a longer or shorter time according to the nature of the flowers and the qualities of the article required and the flowers have to be repeatedly removed, even as often as. every day. Many kinds of pommades require some weeks of enfleurage.

A portion of the pommades obtained by these methods is eventually used in the preparation of the odorous "extraits." This is the name by which the extracts obtained by treatment of these preparations (and other odorous substances) with strong alcohol are known in French perfumery. For this purpose the pommades are placed in copper drums, where by means of powerful stirrers a most intimate mixing of the alcohol with the fat is continued for hours. The alcohol takes up scarcely any of the fat, but the greater part of the odorous substances. By this method the odorous constituents, whether essential oils or other compounds is not known, which cannot be satisfactorily obtained by distillation, are transferred in a pure and unaltered form to the alcohol. The fat takes up little else from the respective flowers, and probably retains a small quantity of matter unconnected with the perfume which it gives up very pure to the alcohol. After this has been removed, the fat is placed in a still and the alcohol recovered for further use; the fat, on the contrary, is not again employed in any part of the manufacture. It would appear that decomposition commences during the long kneading with alcohol in contact with air, although the drums in which the "extraits" are made are kept closed. But, there can be no doubt the fat could be rendered serviceable again; at present it passes from the perfume manufacturer to the soap boiler.

Similar "extraits" may be prepared from plants, when no coloring matter interferes, by simple digestion with alcohol.—*Pharm. Jour. and Trans.* Dec. 13, 1884, p. 468.

GLEANINGS IN MATERIA MEDICA.

BY THE EDITOR.

Buxussempervirens, Lin.—G. A. Barbaglia has separated from the leaves and twigs of the box a fourth alkaloid, which he names *parabuxinidine*. It crystallizes in thin colorless prisms, is insoluble in water, soluble in ether, freely soluble in alcohol, colors turmeric paper deep red, and gives with an alcoholic solution of oxalic acid a heavy white precipitate consisting of minute colorless rhombic plates.—*Ber. d. Chem. Ges.*, 1884, 2655.

Chaulmoogra Seed.—Dr. Jos. Moeller has examined the seeds of three species of Bixaceae, with the following results:

1. *Gynocardia odorata*, R. Brown. The seeds are about 3 Cm. long and 1-5 Cm. in their greatest breadth, elongated ovate, somewhat flattened and irregularly angular; the hilum is at the pointed end. The surface is dull yellowish gray, and somewhat scurfy to the touch from an adhering thin layer of pulp. The seeds weigh about 3 Gm., of which the integument is 0.8 Gm. The latter consists of an outer and inner layer of stone cells placed parallel to the surface, and between these two layers of two or three rows of stone cells, the long axes of which are nearly at right angles with the former cells. The inner surface of the sclerenchymatous tissue is covered with a delicate and partially broken layer of elongated parenchyma cells. The endosperm consists of tolerably thick-walled cells filled with solid colorless fat and large yellow spherical or irregularly rounded bodies, insoluble in alcohol and benzol; starch and tannin are absent; calcium oxalate crystals were not observed.

2. *Hydnocarpus anthelmintica*, Pierre. (See "Amer. Jour. Phar.," 1884, p. 526.) The seeds are about 18.14 Mm. broad, little longer, resemble a small bulb in shape, weigh barely 2 Gm. (the albumen 0.6 Gm.), are brownish black, rough, hard, and have a large rayed hilum. The integument is 1.5 Mm., thick, and has a lighter colored inner layer, 0.15 Mm. thick, and consisting of tangentially arranged, and relatively little thickened, stone cells; the cells of the middle layer are placed at right angles to the surface; those of the exterior layer are tangentially arranged, and those of the adhering pulp are rather small and frequently interspersed with groups of stone cells. The cells of the endosperm. are smaller than in *Gynocardia*, and do not contain the yellow bodies seen in the latter, but besides oil contain numerous colorless roundish albuminoid granules.

3. *Hydnocarpus inebrians*, Vahl. Some of the seeds resemble the preceding, but are flatter, whilst others are pointedly elliptical in shape. They attain a length of 3 Cm., a breadth of 15 Mm. and a thickness of 10 or 12 Mm. The hilum. is prominent and warty, the surface longitudinally wrinkled. The weight of the smaller seeds is about 1 Gm. (the integument one-third), of the larger seeds, about 2 Gm. The integument is 0.2 Mm. thick, and consists of three layers of stone cells, arranged as in the two preceding seeds, but the middle layer has only one, or at most two, rows of cells. The adhering pulp resembles that of *H. anthelmintica*. The endosperm. is covered with a

layer of thin-walled brownish red cells, but is itself colorless, and teems with fat and protein glob Liles. —*Phar. Jour. and Trans.*, October 25, 1884, p.321.