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Botanical Medicine Monographs and Sundry

ESSENTIAL OIL PAPERS.

By ALBERT M. TODD.

OILS OF ERIGERON AND FIREWEED.

The oil of erigeron (oleum erigerontis canadensis) and the oil of true fireweed, (oleum erechthitis hieracifoliæ), are distilled from plants of the most distinct types possible, and seem to be almost as distinct in therapeutic action; both are highly valuable in medicine when pure, but their usefulness has been nearly destroyed and their value little understood since they have been almost universally confounded with each other, both in science and commerce, and even when not so confounded are rarely met with in a state of purity.

A growing interest being manifested in the subject, I had already made some observations with the oils referred to, which interest was further enhanced by an urgent request from Messrs. J. U. & C. G. Lloyd, that I should make more complete investigations, the results of which might be embodied in their valuable work now in progress on the "Drugs and Medicines of North America." I also had the pleasure of sending them a full collection of our essential oil plants in the living state, with which to embellish their work; and through their courtesy the plate of fireweed prepared for that purpose, is here shown.

As no tests existed for the identification of the oils, and possessing, fortunately, samples distilled by myself directly from the plants, so that I was able to be positive as to their purity, which is a condition of vital importance; the investigations recorded were made.

The credit of the first researches is due to Prof. J. M. Maisch, which happened through a curious circumstance—that the fields of peppermint had been reported to be contaminated with a weed called "fireweed." This error was the fault of the farmers, who, from a lack of botanical knowledge, gave the wrong name for the plant. Prof. Maisch rightly believing that the contaminating weed was the erigeron canadense, corresponded with various peppermint growers, sending them botanical specimens, that them should be no mistake; which correspondence and specimens I had the pleasure of seeing. The correction of the error was then for the first time made public by Prof. Maisch in an article in the AMERICAN JOURNAL OF PHARMACY for 1870, page 120, as well as in the report on the progress of pharmacy in the proceedings of the Am. Pharm. Assoc. for that year. The principal object sought in the present article is to establish tests for the identification of the oils rather than to treat of the botany of the plants ; but a crude description regarding their general characteristies may be of interest.¹

The true fireweed—*Erechthitis hieracifolia*—is seldom found in open fields or by the roadside, growing exclusively in, or adjacent to, clearings where timber has recently been burned. The plant strangely seems to spring spontaneously from the ashes of old log piles soon after their formation, and continues to sprout up for several seasons there-after. Its height varies from two to six feet, having a single stalk with a diameter of from three-fourths to one and one-half inches, and a bright green leaf from one to two inches in width and from three to eight inches in length. Its flowers appear only near the top, and when mature, are covered with fine white down, much resembling that of the common thistle, which is carried by the wind to a great distance. The effect of the maturing of the plant and its coming into flower is so marked that the yield of essential oil is decreased thereby within a single week fully 50 per cent. ; and indeed, if the plant is not cut promptly at maturity, the yield of essential oil is only about one-third of what it would have been two weeks preceeding. The fireweed plant has a most thrifty, robust and glossy appearance, and is never seen in the peppermint plantations, excepting in the rarest instances, and then is usually found growing singly.

The *Erigeron (Conyza) canadense* is entirely distinct in its nature, growing almost entirely in open stubble fields and "summer fallows," and along the roadside, its stalks scarcely ever exceeding a half or threefourths inch in diameter, and the leaves scarcely a half inch in width, and two or three in length. Its flowers are very minute, and are distributed more uniformly over the surface of the plant. Erigeron is much richer in essential oil than fireweed, the former sometimes yielding over 20 lbs.of essential oil to a charge of 2000 lbs. of plants. The yield of fireweed seems to average about 50 per cent. of that of erigeron, the plants being distilled under like favorable conditions.

Now as to the characteristics of their essential oils: Unfortunately, most of the physical tests, and the reagents usually employed in such analyses do not give as widely varying results between these, as between most other oils; but when submitted to spectral analysis, I find fortunately, a test which is quite decisive, and this accordingly has the greater prominence; but others more easily operated and equally as certain, if due precautions are taken, are also given.

First, eight samples of natural oil of erigeron were operated upon, (the natural oil being taken, as it is this quality which has hitherto been mostly known in commerce.)

¹*A more scientific description of the plants in question may be found in Gray's *Hand Book of Botany*, as follows:

Erechthites hieracifolia, Raf. (Fireweed.) Often hairy; stem grooved (1° to 5° high) ; leaves lanceolate or oblong, acute, cut-toothed , sessile; the upper with an auricled clasping base. (*Senecio hieracifolius*, L.)—Moist woods. Common especially northward, and in recent clearings, where the ground has been burned over; whence the popular name. July-Sept.

Erigeron canadense, L. (Horse-weed. Butter-weed.) Bristly-hairy: stem grooved (1° to 5° high); leaves linear, mostly entire; those from the root cut-lobed; heads very numerous and small, cylindrical, panicled. Waste places; a common weed, now widely diffused over the world. July-Oct. Ligules much shorter than their tube, white. (Nat. in Eur. etc).

For the purpose of showing the relationship between specific gravity and polarization, these two tests are given in conjunction with each other. The polariscope used is a "Mitscherlich," with a perception tube 200 mm. in length, made by De Sage of Heidelberg, being the instrument referred to in the first article of this series, (in the April No. of the AMERICAN JOURNAL OF PHARMACY); the temperatures for sp. gr. and boiling points were taken by a thermometer specially created at Yale Observatory. ²

NATURAL OIL OF ERIGERON

No.	sp. gr. at 15° C. 59° F	Polarizing Angle.	
1. 2. 3.	.870 (resinous.) .864 .856	60° 51 23	
4. 5. 6. 7.	.865 .864 .861 .864	-58 -51 -30 -47.5	
8.	.865	—57	
Totals	6.909	377.5	

Dividing totals by 8 gives average polarization of -47.19, and sp. gr. .8636.

Having five samples of the oil of fireweed of my own distillation, they were submitted to like tests at the same temperature, with the following results :

No.	Sp. Gr.	Polarizing Angle	
1.	.858	—4	
2.	.854	—3.5	
3.	.847	+35.5	
4.	.905 (resinous),	+33	
5.	.907	+44	
Totals	4.366	+110.	

Dividing by 5 gives average polarization of +22 and Sp. Gr. .8732.

² The importance of having thermometers in chemical analyses, which have been standardized and corrected by the astronomer of Yale Observatory or some other equally reliable authority cannot be over-estimated The writer has found that many finely constructed and expensive thermometers which he had formerly placed much confidence in after having been used for some time in chemical work, had their readings changed fully 10° C. (18° F) rendering them unfit for use. Thermometers corrected and standardized can be obtained at prices ranging from \$5 to \$10.

It will be noticed that the fireweed polarizes with wider variations than does the erigeron, yet fortunately in no case within the limitations of the former; the two most nearly approaching each other being No. 1 fireweed and No. 3 erigeron, which still show a difference of 19° while the average difference, as will be noticed, is 69.19°. It will also be seen that sample No. 3 of erigeron gives not only the lowest polarizing angle, but is also the lowest in sp. gr., and this seems to hold good in nearly all the essential oils the spectral analysis of which I have undertaken. This I found to be caused by the resin which had formed in the oil by oxidation. This resin is opaque and cannot of course of itself produce an optical test, but when added to the oil increases its optical activity. This discovery was verified by the fact that all rectified samples, except in the cases hereafter referred to, were found to have less rotatory power than the original oil operated upon. This phenomenon was noticed when pipmenthol and menthol, both of which were found showing no distinct polarization, are added to oil of peppermint, the rotatory power being increased the same as with the addition of the opaque resin.

By the tests given above it will be noticed that the average of the sp. gr. of the fireweed samples is .0096 greater than the average of the erigeron; but this is accounted for by the fact that Nos. 4 and 5 of the fireweed were extremely resinous; whereas quite the reverse result is obtained when samples of the oils are compared under like conditions of oxidation. This should be borne in mind as having an important bearing on the test. It was found that when samples of the oil in like conditions either of freshness or oxidation, were examined, that the sp. gr. of the fireweed was about .012 less than that of erigeron; and upon submitting the oils to fractional distillation and taking a like number of fractions of both, the sp. gr. of the fireweed was about .011 less than the erigeron.

To find the varying characteristics of the products obtained by fractional distillation, careful distillations were made by diffusion or steam, the distillate being divided in each case in 20 fractions by weight, the process being continued as slowly as practicable, that the fractions should be present as distinct characteristics as possible.

In the distillation of erigeron, 100 pounds of natural oil was used, the polarizing test of which was, —50.5°. After 18 full fractions of 5 pounds each had been recovered, it was found from the slowness with which distillation progressed, and the high color and sp. gr. of the distillate , that but little more could be obtained; but the process being continued for a long time with increased power, 3 pounds more were obtained for the 1 the fraction [93 pounds in all.] The remaining 7 pounds which was not recovered, was drawn from the still mixed with the water which had condensed therein, and separated, when cooled, into a solid resin of a dark reddish brown color.

In the rectification of the fireweed, divided in like manner, 18 full fractions only were obtained, the portion representing the last two fractions forming also a solid resin; but that of the fireweed was, of a light straw color. Upon submitting the different fractions to the sp. gr. and polarizing test, the following results were obtained:

ERIGERON.

FIREWEED.

No. of	Sp. Gr.		No. of Sp. (No. of Sp. Gr.	
fraction.	at 15°C.	Polarization.	fraction.	at 15°c.	Polarization.
1.	.8598	+10	1.	.825	—4
2.	.860	+13	2.	.82575	-4
3.	.862	+15	3.	.8263	—4
4.	.862	+15	4.	.8268	+1
5.	.86225	+15	5.	.827	+5
6.	.86225	+15	6.	.8273	+4
7.	.86225	+15	7.	.8275	+4
8.	.86225	+15	8.	.8255	—2
9.	.86225	+14.5	9.	.8267	0
10.	.8622	+14	10.	.8269	+1
11.	.86275	+12.5	11.	.6277 (?)	+1
12.	.8628	+12	12.	.8282	+1
13.	.8629	+11	13.	.8292	+4
14.	.8635	+8	14.	.831	+5
15.	.865	0	15.	.840	+2
16.	.8672	—3	16.	.8568	—9
17.	.8684	—35	17.	.888	—53
18.	.9169	-43.5	18.	.919	—85
19. 3 lbs	.9388		19.	Resin	
20. 7 lbs	Resin		20.	Resin	

It will be noticed that the same phenomenon occurs in the fractional distillation of fireweed, as that which the writer discovered in oil of peppermint, recorded in the Proceedings of the American Pharmaceutical Association for 1885, vol. 33, page 579, and farther mentioned in vol. 34, page 129), viz: That after several fractions have been recovered in which the sp. gr. constantly increases, there is a point found near the middle of the distillate (which in this case occurs in the 8th fraction) where the direction is changed to a decreasing one. In the case of fireweed however, there was but one fraction which showed the decreasing tendency, although fraction 9 as well was lighter than fraction 7. When peppermint is divided in the same manner, there is a greater number of fractions showing this phenomenon. It is also a remarkable fact that the polarizing test is similarly affected at this stage, as the polarization is also changed from + 4 to -2.

None of the fractions of erigeron show this change from *rising* to *falling* gravity; but it will be noticed that there is a *tendency in that direction* as the fractions from 5 to 9 inclusive *remain stationary* rather than rising, while in both there is a rapid increase in the last fractions.

Taking now the eighteen fractions of each oil united in equal parts by weight, the following results were obtained:

ERIGERON

FIREWEED.

Temperature F.	Sp. Gr.	Temperature F.	Sp. Gr.
40°	.878	40°	.867
60°	.86975	60°	.85925
80°	.8603	80°	.8501

It will thus be seen that the rectified fireweed is about .011 lighter than erigeron. In this test, however, the last 3 pounds obtained from the erigeron was not used, being rank in odor. Had this been used to fairly represent the fresh oil in a state of purity, it would have raised the sp. gr. about .001, so that it is safe to say that the density of fireweed under the same conditions of freshness as erigeron, is about .011 to .012 lighter.

It will be noticed that the first 15 fractions of fireweed average about .035 lighter than the same fractions of erigeron. Fractions 16 and 17 when united are about equal. The 18th fraction of fireweed is somewhat heavier than the corresponding one of erigeron, and nearly though not quite so heavy as the equivalent last portions obtained from the erigeron when proportionately united.

A distinct test, and easy in the hands of the pharmacist, is here obtained; that when erigeron is fractionally distilled in the presence of water and divided in fractions either of 20 or 2, the first portion recovered will not vary from .860. When fireweed is treated in like manner the first portion (no matter how many the fractions) will not be far from .826. And this wide difference is certainly sufficient to identify the one from the other.

As a phenomenal feature in the polarization of the fractions of erigeron, it will be noticed that while the oil originally operated upon was strongly lævogyre (polarizing - 50.5°) the first 14 fractions are actively dextrogyre, and the 15th neutral; with the 16th a lævogyre rotation is shown of 3°, which tendency is rapidly augmented in the 17th fraction by an increase of 32°, finally reaching in the 18th a point -43.5. These 18 fractions when united polarize at -28°.5. The first 3 fractions from oil of fireweed are lævogyre; the rotation changes in the 4th to dextrogyre, which is continued until the 8th fraction is reached, when the left-handed rotation again occurs. The 9th is neutral; with the 10th the dextrogyre rotation is shown, which is continued until the 16th, when the direction is suddenly changed again to the left by a reversion from +2 to -9. The rotatory activity in the 17th fraction is *rapidlyaugmented* the same as in the erigeron, but in a still more marked degree, rising from -9° to -53°. In the 18th fraction a remarkable polarization of -85° takes place, being the highest yet noticed in an essential oil.

Boiling Points.—In making this test, 20 cc. of each oil were placed in a test tube, immersed in an oil bath of ordinary temperature and slowly heated.³ When the bath <u>had attained a temperature</u> of 340° the boiling began slightly in the fireweed at 331°; ³ This precaution of immersing the oil under analysis in a bath at a temperature below its boiling point is important, as more exact and uniform result can be obtained in the earlier stages.

the bulb of the thermometer being immersed in the liquid, as there was not sufficient vapor to give a good indication. Within the space of a minute the temperature of the oil rose to 360°, boiling violently. The temperature of the vapor was found to be 358°. By applying more heat and raising the bath to a temperature of 410°, the oil attained a temperature of 370° with the vapor at 365°. On continuing the boiling for some time, it was found quite difficult to increase the temperature more than 3°. It was not found that the oil had evaporated to the extent of 5 per cent., so that the boiling point of the vapor of fireweed during the progress of the distillation of the first 5 per cent is mostly between 358° and 365°. The oil used in the above test was the natural oil of fireweed used for the rectification mentioned.

In oil of erigeron at 340° slight ebullition was shown, the thermometer immersed in the oil. At 347° boiling progressed vigorously with the vapor at 342°. Continuing the boiling four minutes, the temperature of the vapor had risen to 347°, at which it was practically constant.

From this it will be observed that the boiling point of the fireweed-oil under the same circumstances is about 18° to 20° higher than that of the oil of erigeron.

Chemical Reactions.-This branch of investigation was unfortunately quite unfruitful, both oils fulminating vigorously with iodine, yet with less violence than spirit of turpentine. Upon adding to 50 drops of each oil from one to three drops of nitric acid alternately, (sp. gr., 1.2), there were no special colors produced, the only effect being that in eight hours the erigeron had changed to a dark straw color, the fireweed being of a medium brown. (in the case of peppermint a beautiful spectral effect is produced.)

Treating the oils in the same way with pure sulphuric acid, the fireweed changed within thirty minutes to a very dull brown, the erigeron to a bright red color.

Upon moistening chloral hydrate with the oils, there was very quickly produced in the erigeron a delicate green tint, which remained permanent for some time. With the fireweed a similar but less delicate tint was produced, disappearing however, within a few minutes. (Peppermint produced with chloral hydrate a beautiful rose.)

Further, as to physical characteristics, both oils are quite alike in oxidation, since resin is formed rapidly within both upon exposure to air. There is fortunately a distinguishing characteristic in the resin of the two oils, that of erigeron being a deep brown red, imparting its color to the oil. The oxidation of fireweed has but a slight effect on its color ; indeed, as has been stated, its resinoid when separated is of itself light in color. Both the oils, when oxidizing, deposit a layer of resin upon the sides and bottom of the bottle, differing in this respect greatly from peppermint, which holds the resin suspended in the oil.

One other interesting phenomenon was observed which I will mention in closing. This happened in the last pound obtained in the rectification of 100 lbs. erigeron. The bottle containing the same was set aside during the mouth of November last for future investigation, remaining in a cool room, but exposed to the action of the light during the winter. In the meantime a delicate formation had spread through the oil somewhat resembling the aquatic form of life known as the sea-urchin. An effort was

made to separate this from the oil, and had due precautions been taken by maintaining the same temperature throughout the process, the separation might have been accomplished; but the structure being extremely delicate, was dissolved and lost. The same bottle is still retained with the hopes that the formation may again appear, when an effort will again be made to separate it.

From the experiments made in the foregoing, the following comparisons between the two oils may be made, and the following *conclusions* drawn:

1. **Polarization**. Pure oil of erigeron in the natural state should not polarize nearer the zero point than -26, nor farther than -60; rectified oil freed from resin may polarize some nearer the zero point than the limit given, and the first fractions should be dextrogyre. Pure fireweed if lævogyre should not polarize farther than -4, and if dextrogyre farther than +4.

2. **Specific gravity**. Pure natural oil of fireweed unless resinous (which may be noted by leaving a stain upon paper when evaporated) should not possess a sp. gr. above .855, nor below .845; and erigeron under like circumstances not above .865, nor below .855. The difference in sp. gr. being about .010.

3. **Boiling point**. The temperature of the *vapor* being taken, fireweed should not vaporize to any marked extent below 355°; nor should this temperature be increased more than 10° F., until five per cent. of the oil has been evaporated. Erigeron should not boil vigorously below 342° F., nor above 347° F., until five per cent. has been volatilized.

4. **Resinoid**. When distilled with water or steam, the resinous product of erigeron is a deep reddish-brown; that of fireweed a light straw color. The effect of rectification by steam with both is to produce a brilliant and colorless oil. Both oils possess characteristic odors. As these cannot be well described, I may find occasion to comply with the requests made that samples of both shall be furnished the different pharmaceutical colleges and associations of the country, where those interested may have an opportunity of comparing for themselves both oils in a state of purity.

The investigations recorded are, by no means, considered complete or sufficient, and it is hoped that farther research will develop some tests which may be both efficient and easy of application. The need is evident from that fact that the writer has not been able to find in the hands of a pharmacist, except in the rarest instances, a sample of the oil of true fireweed, which showed by its odor even a trace of the oil.



Erechtites hieraciifolia

NOTES ON A FEW DRUGS.

By G. M. BERINGER, PH. G.

Read at the Pharmaceutical Meeting, May 17.

Having occasion to examine some **Oil of Erigeron** recently, the spec. gravity was carefully ascertained, at the temperature of 60° F., with the 1000 grain bottle; it proved to be 0.8454. The gravity given by the U. S. Pharmacopeia a is 0.850; Professor Procter's experiments in 1854, place it at 0.845. The figures correspond very closely and within a limit that may be accounted for by the age of the oil.

Oil of Peppermint, Three samples of American oil recently examined, showed varying densities ; Hotchkiss' oil sp. gr. .9074, rich in menthol; one of A. M. Todd, sp. gr. .9074, not quite so rich in menthol; and a sample of another Western distiller sp. gr., .9112, contained but a small quantity of menthol, being undoubtedly a skimmed oil. These figures correspond closely with the statement of Mr. Todd in his article on the subject of "Oil of Peppermint," read at the last meeting of the American Pharmaceutical Association. Mr. Todd states that pure oil of peppermint is never below 0.908 sp. gr., nor when fresh and soluble above 0.917, so that the difference formerly allowable, that is from 0.840 to 0.950, is made ten times as small.

Oil of Bay. The sp. gr. of this oil is stated in the U. S. Pharmacopeia, as about 1.040. A sample obtained from an American distiller, who guaranteed the purity, showed a sp. gr. of 0.9750 ; another sample from a St. Thomas distiller, showed 0.9945; both of these oils were of fine odor and appearance, and would indicate that the Pharmacopeia had stated the sp. gr. a trifle high.

Popp's stomach powders. At the suggestion of a customer for whom I had purchased the article, I made an examination of the same and found each paper contained about thirty grains of very coarsely powdered sulphide of iron; two dozen of these powders being put up in a box for which \$1.25 was asked. This was to me a novel use of sulphide of iron.

Ground Flaxseed. The U. S. Pharmacopoeia requires that ground flaxseed shall yield not less than 25 per cent. of fixed oil when extracted with disulphide of carbon. A sample recently ground to order, yielded thirty per cent. when thus treated, and another lot offered in the market, gave thirty-one. This would show that the requirement is not as full as it should be.

Job's tears. Coix lachryma, Lin.; nat. order *Graminaceae*. These fruits are being again called for occasionally by fond mothers for the purpose of making into necklaces under the impression that children wearing such ornaments will cut their teeth more easily. The peculiarity of this grass is the formation of the pistillate spikelet being one to two flowered, inclosed within a bract which becomes a round bony shining involucre.

SYRUP OF TOLU.

EDITOR: AMERICAN JOURNAL of PHARMACY:—I have read with interest the article by F. Stevenson on Syrup of Tolu, in the May issue of the JOURNAL, and would like to add my little experience in the manufacture of this syrup. I think the pharmaeopeial process can be improved upon. The process which I have used for some time—and for which I am indebted to Prof. Remington—is this: For making twenty-five ounces of syrup, take one ounce of Balsam of Tolu, one pound of granulated sugar, and water which has been previously filtered through animal charcoal, enough to make twenty-five ounces (these are essentially the quantities directed by the U. S. P.); rub the Tolu to a fine powder, aided by some of the sugar, and mix this with the remainder of the granulated sugar; now prepare a percolator by placing a piece of cotton in the neck, pack the powder in it, pour in the filtered water and receive twenty-five ounces of percolate. As seen, this is simply a process of cold percolation, but if carried out as described, will furnish a beautiful, clear and highly flavored syrup, which is so desirable. This formula, I m sure,not fail to give satisfaction. Yours,

W. H. HOSTELLEY. Philadelphia, May 7th, 1887.

ABSTRACTS FROM THE FRENCH JOURNALS

Translated for the AMERICAN JOURNAL of PHARMACY

DANGER IN SANTONIN, even when given in moderate doses, was reported some weeks since in the *LyonMédical* to have been observed so frequently that the matter has been inquired into by the *Rép. de Pharm.*, with the following results. The effects of white santonin were more toxic than that which had become yellow through exposure, to sunlight, though the latter did not show any diminution in its therapeutic properties. Lawre thinks that the dose for a child of less than two years should not exceed 0.05 gm. In all Cases it should be associated with a purgative—calomel, for example—to facilitate its elimination. "Santonin is innocuous or toxic," he says, "in proportion to the rapidity with which it may be eliminated, and this varies in individuals." Lewin and Caspari recommend that it be "administered in oily solutions. In this form it is absorbed by the intestines slowly enough to permit a direct and prolonged contact with the worms."

ESCHSCHOLTZIA. — In the *Bull. Gén de Thérap.* (April 30), Stanislas Martin advises chemists to make a careful investigation of the *Eschscholtzia Californica* in order to separate the unknown active principles to which it owes its calmative action. The character of the sedative effect following the use of eschscholtzia, is said to be superior to that of other papaveraceous plants, such as *Sanguinaria canadensis, Papaver album*, etc., and, so far as clinical experiments have extended, it seems likely to be preferred to codeine. Martin and Prudhomme will soon enter upon its investigation. American chemists have an opportunity to forestall them.⁴

Editor AMERICAN JOURNAL PHARMACY.

⁴ In 1844 Walz discovered in the root of this plant sanguinarine, and two other alkaloids. The herb contains the two last alkaloids, and in autumn also sanguinarine.