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THE CONSTITUENTS OF THE ESSENTIAL OIL

OF

ASARUM CANADENSE

BY

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AND

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VII.—*The Constituents of the Essential Oil of Asarum Canadense.*

By Frederick B. Power and Frederic H. Lees.

The aromatic essential oil distilled from the underground portion, rhizome, and rootlets of *Asarum canadense*, commonly known as Canada Snake-root, was first investigated by one of us a number of years ago (Power, *Inaug. Diss.*, Strassburg, 1880; *Proc. Amer. Pharm. Assoc.*, 1880, **28**, 464). In that investigation, the following substances were isolated. (1) A terpene, $C_{10}H_{16}$, b. p. 163—166°; (2) two fragrant alcohols, differing considerably in their boiling points and also in their odour, but both possessing the same empirical formula, $C_{10}H_{18}O$. The alcohol of lower boiling point, 196—199°, was termed *asarol*, and had an odour which recalled that of coriander, but was also somewhat camphoraceous, whilst the alcohol of higher boiling point, 222—226°, had a rose-like fragrance; (3) a fraction, possessing but little odour, b. p. 254—257°, representing the largest single constituent of the oil, which, upon oxidation with chromic acid, afforded an acid of the composition $C_9H_{10}O_4$. This acid was subsequently shown by Petersen (*Ber.*, 1888, **21**, 1062) to be veratric acid and was obtained by him by the oxidation of an analogous substance contained in the oil of *Asarum europaeum*, boiling at about 250°, which he proved to be eugenol methyl ether; (4) a fraction collected at 275—350°, which contains a deep blue oil of undetermined composition; (5) a large amount of acetic acid, combined with the above-mentioned alcohols in the form of acetic esters, together with a very small amount of a less soluble, oily acid, which appeared to consist of, or at least to contain, valeric acid.

In consideration of the advance in knowledge of the constituents of essential oils since the period of the first investigation, and the means which are now available for the more positive identification and classification of these constituents by the preparation of well-defined and mostly crystallisable derivatives, it has seemed desirable again to subject the oil in question to a careful chemical examination.

Experimental.

The oil employed for this research, about 2 kilos. in amount, was distilled by Messrs. Schimmel & Co. of Leipzig. Its density at 15°/15° was 0·952, and its rotation $a_D = -3°24'$ in a 100 mm. tube.

The oil was first shaken with a 5 per cent. solution of sodium carbonate in order to remove the free acids, which were examined in connection with the acids obtained by the subsequent hydrolysis of the

oil. It was then shaken three times successively with a 5 per cent.
solution of sodium hydroxide, and afterwards with water until the
washings were neutral. The combined alkaline liquids were shaken
twice with ether to remove any adhering oil, then acidified with
sulphuric acid, completely extracted with ether, and the ethereal
liquid dried with calcium chloride. After distilling off the ether, the
residual liquid was distilled in a vacuum. Under 10 mm. pressure, it
began to distil at 155°, rising rapidly to 250°, and the last portion
was observed to solidify in the condenser. When refractionated, there
were obtained :

I. A light coloured oil boiling at 172° under 35 mm. pressure.

II. A dark oil which boiled somewhat below 200° under 10 mm.
pressure and solidified on cooling.

The Phenol, $C_9H_{12}O_2$.

The first of the preceding fractions was distilled under the ordinary
(762 mm.) pressure and afforded :

(1) A light greenish liquid, becoming brown on standing, and
boiling below 245°.

(2) A light yellow liquid, boiling at 245—260°, which did not
solidify at $-16°$.

(3) A small residue, from which a little crystalline substance
separated on cooling.

Of these fractions, (1) and (2) were analysed.

(1) 0·1402 gave 0·3606 CO_2 and 0·1008 H_2O.   C = 70·1 ; H = 8·0.

(2) 0·1493 „   0·3922 CO_2 „ 0·1066 H_2O.   C = 71·6 ; H = 7·9.

These two fractions were then subjected to a final fractionation
under the ordinary pressure, with the following result :

(*a*) A few drops only distilled below 220°.

(*b*) From 220° the mercury rose rapidly to 245°.

(*c*) The chief portion distilled between 245° and 255°, and was
fairly constant at 248—252°.

(*d*) Only a few drops distilled above 255°.

Fraction (*c*) was then analysed.

0·1523 gave 0·3992 CO_2 and 0·1073 H_2O.   C = 71·5 ; H = 7·8.

$C_9H_{12}O_2$ requires C = 71·1 ; H = 7·9 per cent.

These results indicate that the phenol contained in asarum oil has
the empirical formula $C_9H_{12}O_2$. It is a nearly colourless, oily liquid,
having an odour recalling, but more agreeable than, that of creosote.
In the process of liberating the phenol from its alkaline solution a
somewhat clove-like odour was developed, and this at first led us to
suspect that the phenol contained some eugenol. This, however, is

rendered highly improbable, both on account of the constancy of the analytical results and the characteristic colour reaction which was afforded by all the fractions, but most strikingly by the principal fraction (c). Thus a very small quantity of the phenol, when dissolved in 90 per cent. alcohol, gives, with a trace of very dilute ferric chloride, a beautiful violet colour which only gradually fades, whilst eugenol, under the same conditions, gives a green. If, however, the phenol from asarum oil be dissolved in absolute alcohol, and a trace of a stronger solution of ferric chloride added, it affords a green colour, whilst eugenol, under these conditions, gives a deep blue. The amount of the phenol available did not permit of the formation of any derivatives, but as it is not identical with any of the known phenols of the formula indicated, it is evidently a new substance, and we shall endeavour to determine its constitution by some synthetical experiments.

Identification of Palmitic Acid.

It was noted that in the first distillation of the phenol, a solid substance separated in the condenser, and that in a subsequent fractionation the higher fraction, designated as II (p. 60), solidified on cooling. This was, therefore, brought upon a porous tile, and the substance subsequently dissolved in hot light petroleum, from which, on cooling it crystallised in colourless, pearly plates. Its melting point was 60—61°, and this remained unchanged on recrystallisation. On analysis, it was identified as palmitic acid :

0·0874 gave 0·2382 CO_2 and 0·0982 H_2O. C = 74·3 ; H = 12·5.
$C_{16}H_{32}O_2$ requires C = 75·0 ; H = 12·5 per cent.

Identification of Pinene.

Separation of the Terpene.—The oil, which had been shaken with a dilute solution of sodium hydroxide as previously described, was washed with small, successive portions of water until the washings were neutral, and dried with anhydrous sodium sulphate. It was then distilled under diminished pressure and the portion collected which boiled below 100° under 10 mm. pressure. After several fractionations of this portion and drying with potassium carbonate, the lowest fraction, which distilled below 85° under 10—15 mm. pressure, was collected. Its density was 0·8566 at 18°/16°, which proved the absence of any olefinic terpene. These liquids were then further fractionated under the ordinary pressure, when the greater portion finally distilled below 165°, (a), chiefly at 159—161°, and only exceedingly small fractions were collected between 165° and 170° (β) and from 170—180° (γ). These were analysed, with the following results :

(α) 0·1252 gave 0·4003 CO_2 and 0·1320 H_2O.   C = 87·2 ; H = 11·7.
(β) 0·1526   „   0·4873 CO_2 „   0·1606 H_2O.   C = 87·1 ; H = 11·7.
(γ) 0·1558   „   0·4920 CO_2 „   0·1628 H_2O.   C = 86·1 ; H = 11·6.
        $C_{10}H_{16}$ requires C = 88·2 ; H = 11·8 per cent.

Fraction below 165°.—This fraction, boiling chiefly between 159°
and 161°, which is seen to consist of a nearly pure hydrocarbon,
amounted to about 2 per cent. of the original oil. Its physical con-
stants were as follows : $d\ 16°/16° = 0·8563$. $a_D^{17°} = +1°36'$. It readily
formed a crystallisable nitrosochloride melting sharply at 103—104°.
From the latter, the nitrolpiperidide was prepared, which, after re-
crystallisation from methyl alcohol, melted sharply at 118—119°.
This fraction thus consisted of *pinene*, and its low rotation indicates it
to be a mixture of the *d*- and *l*-forms. Petersen (*Ber.*, 1888, **21**,
1059) has previously recognised the terpene existing in the oil of both
the European and American species of *Asarum* as pinene, in the former
as the *l*-variety, but identified it only by the formation of an oily
monobromide and by its conversion into dipentene.

As it was possible that the very small fraction of our oil collected
between 170° and 180° might contain dipentene or limonene, it was
treated with bromine, but only an uncrystallisable, oily product was
obtained. After being carefully dried, a bromine determination was
made of this, with the following result :

    0·2915 gave 0·3762 AgBr.   Br = 54·9.
        $C_{10}H_{16}Br_2$ requires Br = 54·1 per cent.

This result serves to prove the absence of either dipentene or
limonene, both of which form crystallisable tetrabromides, $C_{10}H_{16}Br_4$.
By a careful examination of all the fractions, no terpene other than
pinene could be detected in the oil.

Hydrolysis of the Oil.

For further examination, all the oil boiling above the terpene frac-
tion was now hydrolysed by boiling with alcoholic potassium hydr-
oxide for about 2 hours in a flask provided with a reflux condenser.
After distilling off the greater portion of the alcohol from a water-
bath, the liquid was brought into a separating funnel and sufficient
water added to effect the separation of the oil. The latter was then
drawn off, the aqueous alkaline liquid shaken with successive portions
of ether, and the ether extracts mixed with the separated oil. The
latter was then washed several times with water, and these washings
added to the aqueous alkaline liquid. The ethereal solution of the oil
was quickly dried with calcium chloride, filtered, the ether distilled
off, and the residue finally subjected to fractional distillation, first

under diminished pressure, and then in part under the ordinary pressure. The following fractions were eventually obtained : 195—203°, 203—208°, 208—216°, 216—222°, 222—235°, 235—245°, and 245—260°.

Identification of Linalool.

Fraction 195—203°.—This was a large fraction which, when redistilled under the ordinary pressure, passed over mainly at 199° and almost entirely at 198—202° under 768 mm. pressure. It is a colourless, fragrant liquid. It was analysed and its physical constants were determined with the following results :

0·1372 gave 0·3910 CO_2 and 0·1436 H_2O.　C = 77·7 ; H = 11·6.

$C_{10}H_{18}O$ requires C = 77·9 ; H = 11·7 per cent.

d 15·5°/15° = 0·8711. a_D = +10°48' in a 100 mm. tube ; $[a]_D$ = +12·4°.

When oxidised with chromic acid, it afforded citral, which was obtained as a pale yellow liquid of strong, lemon-like odour, distilling at 110—115° under a pressure of 10—12 mm. The latter, by condensation with pyruvic acid and β-naphthylamine, was converted into the crystalline α-citryl-β-naphthacinchoninic acid, melting at 195—198°.

The identity of this fraction with d-*linalool* is therefore definitely established. It corresponds to the substance $C_{10}H_{18}O$ (b. p. 196—199°), which in the first investigation of the oil was designated *asarol*.

Fraction 203—208°.—This fraction was too small for further examination, and evidently consisted simply of a mixture of the preceding and the following fractions.

Fraction 208—216°.—This was a small fraction, which distilled mostly between 208° and 212°. It was analysed, and its physical constants were determined, with the following results :

0·1368 gave 0·3866 CO_2 and 0·1424 H_2O.　C = 77·1 ; H = 11·6.

0·1472　,,　0·4154 CO_2　,,　0·1524 H_2O.　C = 77·0 ; H = 11·5.

$C_{10}H_{18}O$ requires C = 77·9 ; H = 11·7 per cent.

d 15·5°/15° = 0·911 ; a_D = −0°24' in a 100 mm. tube.

Identification of Borneol.

The liquid had a camphoraceous and also somewhat rose-like odour. When subjected to a temperature of −10° for an hour, no crystalline substance separated. As this fraction of the oil was relatively small, and as its constituents were evidently contained to some extent in the next higher fraction, the two fractions were mixed. A portion, however, of the higher fraction was reserved for special examination.

This mixture of the two fractions was now gently oxidised with Fittig's oxidation mixture (*Ber.*, 1885, **18**, 3207) in the following

proportions: 10 parts of oil, 80 parts of potassium dichromate, and 120 parts of sulphuric acid, the latter diluted with three times its volume of water. The oxidising mixture was added in small amounts at a time to the oil, which was kept cool by immersion of the containing flask in water. After all the chromic acid solution had been added, the mixture was heated on a water-bath for about 20—30 minutes. It was then distilled from a water-bath under diminished pressure and the camphor which separated in the condenser and distillate was collected by filtration, and dried on a porous tile. A little of the sublimed product was found to melt sharply at 175°. A determination of its specific rotation in 90 per cent. alcohol gave the following result:

$$a_D = -1°45'; \quad l = 0.5 \text{ dcm.}; \quad c = 8.684; \quad [a]_D = -40.3°.$$

For further identification of the camphor, the oxime was prepared, and found to melt at 115—116°. As camphor could not be detected in the fraction of the original oil, its formation by the above method of oxidation is conclusive proof of the presence of l-*borneol* in the oil.

The chromic acid liquor remaining from the distillation of the camphor was subsequently shaken out several times with ether, the ethereal solution washed with a little water, dried with calcium chloride, and the ether removed by distillation. The residual light yellow oil, which had a strong odour of acetic acid, was found to be not entirely soluble in cold sodium carbonate solution. It was consequently redissolved in ether and the ethereal solution shaken out several times with a dilute solution of sodium carbonate in order to remove the acids. The ethereal solution was then washed with a little water, dried with calcium chloride, and the ether removed by distillation. The residue was a light yellow oil possessing a coumarin-like odour, and on standing a short time became a crystalline paste. This was drained on a porous tile, when the substance was obtained quite white. After recrystallisation from dry ether it melted at 62°, and was insoluble in sodium carbonate solution. On analysis:

0.1148 gave 0.2731 CO_2 and 0.0902 H_2O.   C = 64.9; H = 8.7.
$C_{10}H_{16}O_3$ requires C = 65.2; H = 8.7 per cent.

This substance is undoubtedly identical with the *ketolactone*, $C_{10}H_{16}O_3$ (m. p. 62—63°), which was isolated as a product of the oxidation of terpineol by chromic acid by Wallach, and has been further studied by him, as also by Tiemann and others (*Annalen*, 1893, 275, 153; 277, 118; *Ber.*, 1895, 28, 1773, 1781).

The sodium carbonate solution from which the ethereal solution of the above ketolactone had been separated was acidified with hydrochloric acid, and shaken out several times with ether. The

ethereal solution was washed once with water, dried with calcium chloride, and the ether removed by distillation. The residue was a light yellow syrup, which, on standing, deposited a crystalline acid. The syrup was consequently diluted with ether, in which the crystals appeared to be sparingly soluble, and from which they were easily separated by filtration. After washing with dry ether, the substance was finally recrystallised from boiling ether. It melted at 173—174° and dissolved with effervescence in a cold solution of sodium carbonate.

0·1168 gave 0·2266 CO_2 and 0·0695 H_2O.   C = 52·9 ; H = 6·6.
$C_7H_{10}O_4$ requires C = 53·2 ; H = 6·3 per cent.

This acid is evidently identical with *terebic acid*, $C_7H_{10}O_4$ (m. p. 175°), which has been found as a direct oxidation product of terpineol, as also of the ketolactone, $C_{10}H_{16}O_3$ (Tiemann and Mahla, *Ber.*, 1896, 29, 2621). The syrup from which the terebic acid crystallised was not examined but probably contained terpenylic acid, which always accompanies terebic acid when terpineol or the ketolactone is oxidised with chromic acid mixture. It is thus shown that the fractions of the oil which served for the identification of borneol also contained a considerable amount of *terpineol*.

In the first investigation of asarum oil, a considerable fraction was collected at 222—226°, and as a portion of this was still available it was thought of interest to examine it again. It was therefore oxidised with a chromic acid mixture in the manner just described, and among the products of oxidation there were isolated and identified : camphor (m. p. 175°); the ketolactone, $C_{10}H_{16}O_3$ (m. p. 62°); and terebic acid (m. p. 173—174°). It therefore contained borneol and terpineol, and, apparently, a small amount of geraniol, as it had the characteristic rose-like odour.

Identification of Terpineol.

Fraction 216—222°.—This was a small fraction. It had a camphoraceous and also a somewhat rose-like odour. It was analysed and its physical constants were determined, with the following results :

0·1647 gave 0·4682 CO_2 and 0·1698 H_2O.   C = 77·5 ; H = 11·4.
0·1633 ,,   0·4610 CO_2 ,,   0·1680 H_2O.   C = 77·0 ; H = 11·4.
$C_{10}H_{18}O$ requires C = 77·9 ; H = 11·7 per cent.
$d\ 15\cdot5°/15° = 0\cdot9267$; $a_D = -8°26'$ in a 100 mm. tube.

The portion of this fraction which had not been used in connection with the preceding one, as described under the latter, was employed for the direct identification of terpineol. In view of the presence of small amounts of other alcohols, the following method was employed.

The liquid was shaken with a concentrated solution of hydriodic acid (sp. gr. 2·0), when a heavy, dark oil was formed. This was separated from the aqueous layer, and shaken with a dilute solution of sodium bisulphite to remove any free iodine. The oil was then washed with water and allowed to stand, when after a short time crystals began to form, and finally the whole became a crystalline paste. This was spread on a porous tile, when a small quantity of nearly white needles was obtained, which, after recrystallisation from light petroleum (b. p. 30—40°), melted at 80°. This melting point was identical with that of dipentene dihydriodide, $C_{10}H_{18}I_2$, which, for the purpose of comparison, we had also prepared from pure crystallised terpineol, and when the two hydriodides were intimately mixed, the melting point remained unchanged. The formation of this derivative, and of the products of oxidation described in the preceding section, proves conclusively the presence of *terpineol* in the oil. The optical rotation of the fraction from which it was obtained indicates it to be the *l*-form.

Identification of Geraniol.

Fraction 222—235°.—This fraction was collected within the above limits, in view of the possible presence of both citronellol and geraniol. It was relatively small in amount, and was analysed, and its physical constants were determined, with the following results :

0·1544 gave 0·4370 CO_2 and 0·1549 H_2O.   C = 77·2 ; H = 11·1.
0·1420 „   0·3999 CO_2 „   0·1433 H_2O.   C = 76·8 ; H = 11·2.
$C_{10}H_{18}O$ requires C = 77·9 ; H = 11·7 per cent.
d 15·5°/15° = 0·9340 ; a_D = − 9°8′ in a 100 mm. tube.

It possessed a camphoraceous and also a fragrant, rose-like odour. Although its high density and rotation indicated that it contained a considerable amount of terpineol, and its analysis also showed an admixture with some of the next higher fraction, the small amount of liquid precluded its further purification by simple distillation.

The odour of this fraction afforded such convincing evidence of the presence of geraniol that Erdmann's method, which depends on the formation of the crystalline geranioldiphenylurethane (m. p. 82°), was resorted to for the identification of the substance (*J. pr. Chem.*, 1897, [ii], **56**, 8). The oil was treated with diphenylcarbamic chloride in presence of pyridine, as described by Erdmann ; the syrupy residue left after distilling the product with steam was then purified by extraction with ether, and the ethereal solution evaporated after extraction with dilute hydrochloric acid. The residual light brown oil was mixed with a little alcohol, when it soon formed a crystalline paste, which was drained on a porous tile. The substance was finally recrystallised

from a little alcohol, from which it separated in fine, glistening needles melting sharply at 81—82°. On analysis:

0·1444 gave 0·4163 CO_2 and 0·1015 H_2O.   C = 78·6 ; H = 7·8.
$C_{23}H_{27}O_2N$ requires C = 79·1 ; H = 7·7 per cent.

The fraction by gentle oxidation with chromic acid afforded a little citral, but although the amount of the latter was too small for conversion into the naphthacinchoninic acid derivative, the evidence was already sufficiently conclusive of the presence of *geraniol* in this fraction of the oil. There was, on the other hand, no indication of the presence of citronellol.

It may be noted that in the first investigation of asarum oil by one of us, a fraction was obtained corresponding approximately in boiling point (222—226°) to that just described, and that this, on more energetic oxidation with chromic acid, afforded, besides acetic acid, a small amount of a crystallisable acid. As a specimen of the latter had been preserved, it has been re-examined and shown to be a mixture of terebic and terpenylic acids.

Fraction 235—245°.—This was very small in amount, and was evidently a mixture of the preceding and following fractions; a little of the crystallised geranioldiphenylurethane was obtained from it by the method previously described.

Identification of Eugenol Methyl Ether.

Fraction 245—260°.—This constitutes the largest fraction of the oil. On redistillation under the ordinary pressure it was easily resolved into a large fraction, which was collected between 250° and 256°, but distilled for the most part between 252° and 254°. It is a colourless, nearly odourless liquid, and was analysed, and its physical constants were determined, with the following results :

0·1648 gave 0·4522 CO_2 and 0·1238 H_2O.   C = 74·8 ; H = 8·3.
$C_{11}H_{14}O_2$ requires C = 74·2 ; H = 7·9 per cent.
d 15°/16° = 1·0239 ; a_D = − 2°44′ in a 100 mm. tube.

It has been shown by Petersen (*Ber.*, 1888, **21**, 1064) that the oil obtained from the allied European species of *Asarum* contains a substance of the same composition, boiling at about 250°, which on oxidation affords veratric acid, and was fully identified as eugenol methyl ether. In the first investigation of the oil of *Asarum canadense* by one of us, a fraction was collected at 254—257°, which on oxidation with chromic acid afforded a small amount of a crystalline acid, $C_9H_{10}O_4$, and this Petersen has likewise found to be identical with veratric acid. The same specimen of acid, after recrystallisation from water, we now find to soften at 172°, and to melt completely at 177—178°.

The confirmation of the identity of this fraction with eugenol methyl ether has now been effected by the preparation of the crystalline bromoeugenol methyl ether dibromide, $C_6H_2Br(OCH_3)\cdot C_3H_5Br_2$, which melts at 78—79° (Wasserman, *Compt. rend.*, 1879, **88**, 1206). This was accomplished as follows : To the liquid dissolved in dry chloroform, and cooled in a mixture of ice and salt, the requisite quantity of bromine, also dissolved in chloroform, was added, drop by drop, and any slight excess of bromine removed afterwards by shaking the solution with a little sulphurous acid. The chloroform solution was separated, dried, and filtered, and the chloroform removed by rapidly drawing dry air through the solution. The residue was a thick syrup, which, when dissolved in alcohol, deposited a quantity of glistening crystals. These, on recrystallisation from absolute alcohol, separated in glistening, felt-like needles, which melted at 78—79°.

The optical activity of the fraction is due to admixture with a small amount of a higher fraction, which it is difficult to separate completely by fractional distillation.

Search for iso*Eugenol Methyl Ether.*—As it has been assumed by Mittmann (*Arch. Pharm.*, 1889, **227**, 543) that the substance contained in asarum oil is not eugenol methyl ether but the isomeride, we have thought it desirable to ascertain the correctness of this opinion. For this purpose, a portion of the original oil which had been deprived of terpene was fractionated under diminished pressure before being subjected to hydrolysis. As eugenol methyl ether boils at 128—130° (10 mm.) and *iso*eugenol methyl ether at 142° (10 mm.), fractions were first collected at 130—140° and at 140—155° under a pressure of about 10 mm. Further fractionation was conducted under 60 mm. pressure, at which eugenol methyl ether was found to boil at 166°, and *iso*eugenol methyl ether at 179°. A large fraction was thus collected at 163—167° (60 mm.), and also a fraction at 175—185° (60 mm.). For the differentiation of these two substances recourse was had to bromination, as eugenol methyl ether in the cold yields the bromo-bromide, whereas *iso*eugenol methyl ether under the same conditions yields only a dibromide melting at 99—101° (*Ber.*, 1890, **23**, 1167). On applying this test to the two fractions, only the crystalline derivative melting at 78—79° was obtained, which proves that the original oil does not contain *iso*eugenol methyl ether.

Fraction boiling above 260°.

This fraction was distilled under reduced pressure, and after a large number of distillations under 60 mm. pressure the following fractions were obtained : Below 175°, 175—195°, 195—210°, 210—220°, and 220—230°.

The characters of these fractions are shown in the following table :

Boiling point (60 mm.).	Analysis.	Rotation in 100 mm. tube.	Solubility in 70 per cent. alcohol.	Colour.
Below 175°	—	—	Very freely soluble	Slight
175—195	$C = 76·0$; $H = 9·3$	$a_D = -10°12'$	Very freely soluble	Light yellow
195—210	$C = 78·4$; $H = 10·3$	$a_D = -41\ 40$	Very freely soluble	Bluish
210—220	$C = 81·1$; $H = 10·5$	$a_D = -100$	Less freely soluble	Bluish
220—230	—	—	Turbid	Greenish

The fraction collected below 175° consisted chiefly of eugenol methyl ether. The three subsequent fractions had an odour resembling that of cedar wood, and when a few drops were dissolved in glacial acetic acid and a drop of concentrated hydrochloric or sulphuric acid added, an intense reddish-violet colour was produced. The fraction 220—230° was very small in amount. The analysis of the principal fractions, and particularly their ready solubility in dilute alcohol, proved that they consisted of oxygenated compounds, and did not contain a sesqui-terpene.* As the fraction 210—220° was the largest, this was again carefully distilled, and the following fairly constant fraction obtained, which was more fully examined.

Fraction 212—217° (60 mm.).—This is a thick, viscid liquid, having a fine blue colour and an odour recalling that of cedar wood. It does not solidify when exposed for some time to a temperature of $-18°$. It is very freely soluble in 70 per cent. alcohol and affords the same colour reaction as the fraction from which it was obtained. It was analysed, and its physical constants were determined, with the following results :

0·1069 gave 0·3133 CO_2 and 0·1009 H_2O. $C = 79·9$; $H = 10·5$.
$d\ 15°/16° = 1·0063$; $a_D = -3°$; $l = 100$ mm; $c = 3·678$; $[a]_D = -81·5°$.

A molecular weight determination gave the following result : 0·4184 gram depressed the freezing point of 30·17 grams of phenol by 0·48°, whence mol. wt. = 214.

This result would agree very well with a sesquiterpene alcohol of the formula $C_{15}H_{26}O$ (mol. wt. = 222), but the analytical figures do not accord with those required for this substance ($C = 81·1$; $H = 11·7$ per cent.). It is probable, therefore, that the fraction analysed still consisted of more than one substance.

* The statement in "The Volatile Oils," by Gildemeister and Hoffmann (p. 123) that "Semmler, in 1889, obtained from asarum oil a hydrocarbon, $C_{15}H_{24}$, boiling at about 255°" is an error of translation. It properly refers to the oil of *Carlina acaulis* or Carline thistle (German, *Eberwurz*), which is described on p. 690 of the same work.

Treatment with Phosphoric Oxide.—In order to obtain further evidence respecting the character of these bluish fractions, an attempt was made to dehydrate them. The remainder of the fractions 195—210° and 210—220° (60 mm.), about 5 grams of each, was separately dissolved in dry benzene, phosphoric oxide added, and the liquids boiled for about an hour, when they acquired a deep purple-red colour. After distilling off the benzene, the residues were distilled under diminished pressure.

Fraction 195—210° (60 mm.) afforded a liquid which distilled between 175° and 210° under 60 mm. pressure. It had a bright green colour, a cedar-like odour, and was insoluble in 70 per cent. alcohol.

0·1068 gave 0·3198 CO_2 and 0·1000 H_2O. C = 81·7; H = 10·4 per cent.

$$d \ 15°/15° = 0·975 \ ; \ [a]_D = \ -37°.$$

Fraction 210—220° (60 mm.) afforded a liquid which distilled chiefly between 200° and 220° under 60 mm. pressure. It had an olive-green colour, a cedar-like odour, and was insoluble in 70 per cent. alcohol.

0·1073 gave 0·3300 CO_2 and 0·1006 H_2O. C = 83·9; H = 10·4 per cent·

$$d \ 15°/15° = 0·985 \ ; \ [a]_D = \ -35·5°.$$

Both these liquids, when dissolved in glacial acetic acid and treated with a drop of hydrochloric acid, afforded a purplish or red colour. Although the insolubility of these products in alcohol and the increase in the percentage of carbon by the above treatment was evidence of the formation of a hydrocarbon, the substances themselves were not sufficiently pure to admit of further identification. They were finally dissolved in dry ether, the solutions saturated with dry hydrogen chloride, and allowed to stand for several days, but from the very dark, oily residues no crystallisable hydrochloride could be obtained.

Although several essential oils are known to afford high boiling fractions of a deep blue colour, which have been designated as *cœrulein* by Gladstone, and as *azulene* by Piesse, no properly characterised compound has as yet been isolated from any one of them.

Acids obtained by the Hydrolysis of the Oil.

The strongly alkaline, aqueous liquid, separated from the hydrolysed oil and completely extracted with ether, as previously described, was evaporated to a small bulk, then acidified with sulphuric acid and distilled with steam. The first portion of the distillate was slightly turbid, but it soon became clear. The entire acid liquid was then made alkaline with sodium carbonate, and extracted several times with ether. After distilling off the ether there remained a small amount of a dark coloured, highly aromatic oil. This was insoluble

in a cold solution of sodium hydroxide, but dissolved readily on warming. The alkaline solution of the substance was shaken with ether to remove any impurity, and then acidified with sulphuric acid, which liberated the original oil. This was again taken up with ether, the ethereal solution washed with a little water, dried, evaporated, and the slightly coloured, oily residue finally placed in a vacuous desiccator over paraffin to remove the last traces of ether, and then analysed.

0·0463 gave 0·1292 CO_2 and 0·0403 H_2O. C = 76·1 ; H = 9·7.
$C_{14}H_{20}O_2$ requires C = 76·4 ; H = 9·1 per cent.

This substance, to which we assign the provisional formula $C_{14}H_{20}O_2$, is evidently a *lactone*. Although existing in extremely small amount, so that we have not been able to examine it further, its powerful odour indicates that it must have considerable influence on the odour of the original oil. To it is also possibly due the somewhat clove-like odour which was observed in the isolation of the phenol (p. 60).

After the lactone had been separated from the liquid which had been made alkaline with sodium carbonate, this liquid was concentrated, strongly acidified with sulphuric acid, and shaken four times successively with ether. The ethereal solution was washed twice with water, dried, and distilled. On fractionating the residue, nearly all distilled between 110° and 120°. A portion of this was converted into the barium salt, and from the latter the silver salt was prepared which gave the following figures on analysis :

0·085 gave on ignition 0·0550 Ag. Ag = 64·7.
$C_2H_3O_2Ag$ requires Ag = 64·7 per cent.

This served to confirm the presence of *acetic acid*, the previous investigation having shown that esters of this acid were present in considerable amount in the oil.

Acids of Higher Boiling Point.—The residue from the distillation of the acetic acid was very small in amount, and was therefore mixed with a larger portion of acids obtained by shaking the original oil with a solution of sodium carbonate. The whole of the acids of higher boiling point, after standing over potash in a vacuous desiccator, was first fractionated under 10 mm., and then under the ordinary pressure, when the following three fractions were obtained.

(1) Below 240° ; (2) 240—280° ; (3) 280—300°.

The last fraction became solid on standing, and from the residue in the flask crystals were separated which, after recrystallisation from hot light petroleum, melted at 57—58° ; these consisted apparently of palmitic acid, which had been extracted by means of caustic alkali from the original oil. The first two fractions were redistilled and the follow-

ing fractions collected : A, 140—200 ; B, 200—230° ; C, 230—270°. D was fraction (3) from the first distillation (b. p. 280—300°).

They were yellowish, oily liquids, nearly equal in amount, and were present altogether to the extent of about 2 grams in a kilo. of the original oil. They were first converted into ammonium salts, and then fractionally precipitated by silver nitrate. The various silver salts were spread on porous plates, and then dried at 80° for half-an-hour. On analysis, they gave the following results :

A_1. $Ag = 46 \cdot 1$ per cent. ; A_2. $Ag = 48 \cdot 4$ per cent
B_1. $Ag = 45 \cdot 1$,, B_2. $Ag = 47 \cdot 1$,,
C_1. $Ag = 36 \cdot 7$, C_2. $Ag = 39 \cdot 5$,,
D_1. $Ag = 34 \cdot 5$,, D_2. $Ag = 39 \cdot 2$,,
$C_6H_{11}O_2Ag$ requires $Ag = 48 \cdot 4$. $C_{12}H_{23}O_2Ag$ requires $Ag = 35 \cdot 1$ per cent.

It is thus seen that these acids of high boiling point constitute an exceedingly complicated mixture, the amounts of silver found corresponding to those required for salts of acids ranging from $C_6H_{12}O_2$ to $C_{12}H_{24}O_2$. A further separation and identification of them would require a very much larger quantity of material than was available for the purpose. It may also be noted that from the method by which the chief portion of these acids was obtained, it is evident that they exist in the oil in a free state, and not in the form of esters.

Summary.

From the results of this investigation, the oil of *Asarum canadense* is seen to contain the following substances :
1.   A phenol, $C_9H_{12}O_2$,
2.   Pinene, apparently a mixture of the *d*- and *l*-forms,
3.   *d*-Linalool,
4.   *l*-Borneol,
5.   *l*-Terpineol,
6.   Geraniol,
7.   Eugenol methyl ether,
8.   A blue oil, of undetermined composition, consisting of oxygenated substances of alcoholic nature,
9.   A lactone, $C_{14}H_{20}O_2$,
10.   Palmitic acid,
11.   Acetic acid, and
12.   A mixture of fatty acids intermediate between acetic and palmitic acids.

In order to ascertain approximately the amounts of the principal constituents, the following determinations were made with the original oil :

1. The eugenol methyl ether was determined by Zeisel's method. 0·1898 gram of oil gave 0·1846 gram AgI, whence eugenol methyl ether $= 36·9$ per cent.

2. The amount of esters, calculated as $C_{10}H_{17}·C_2H_3O_2$, is 27·5 per cent.

3. The total amount of alcohols, $C_{10}H_{18}O$, free and as esters, after acetylating the hydrolysed oil, was found to be 34·9 per cent., hence the amount of free alcohols is 13·3 per cent. In reality, the amount of free alcohols is somewhat larger than this, as it is known that linalool and terpineol cannot be quantitatively acetylated.

4. As about 2 per cent. of pinene was found in the oil, the constituents of high boiling point, blue oil, &c., would amount to somewhat less than 20 per cent.

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