drug. An odor suggesting nitrogen bases was noticed while distilling, therefore the fraction boiling between 95 degrees and 99 degrees was collected in hydrochloric acid. The crystalline hydrochloride was obtained by evaporation. This was dissolved in alcohol and precipitated by acid platinic chloride solution. A bright yellow precipitate was obtained. This was found to contain 41.9 p. c. of platinum. By computation, the platinum content of the platinic chloride double salt of methylamine hydrochloride, $(CH_3NH_3)_2PtCl_6$, was found to be 41.3 p. c. The basic substance is therefore, undoubtedly, methylamine.

The sodium salt of the acid, remaining in the still, was crystallized and the acid was determined as before through the silver and zinc salts. Like the acid in the volatile oil, it was found to be valeric acid. Here, again, in evaporating the salt solutions to crystallization a strong celery-like odor was noticed.

SUMMARY.

The root of *Leptotæmia dissecta* contains about 0.6 p. c. of a volatile oil of high boiling point and high specific gravity. The oil is devoid of aldehydes and phenols, but contains 20–30 p. c. of the valeric acid ester of an as yet unidentified alcohol, and about as much free alcohol. From the fraction of saponified oil boiling between 200 degrees and 230 degrees a white crystalline substance separated while redistilling under diminished pressure.

The alcoholic extract of the drug separated, after the evaporation of the solvent, into an aqueous and an oily layer, both acid in reaction. The oily layer contains much acid and ester. In the aqueous distillate from this oily portion valeric acid, methyl alcohol and methylamine have been identified.

Further work is in progress, especially upon the oily and the aqueous extracts, of which a considerable quantity remains. This will be reported upon later.

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THE VOLATILE OIL OF MENTHA CANADENSIS L.*

BY ROLAND E. KREMERS.[1]

The statement which is frequently made that the Japanese menthol-producing peppermint is a variety of the species *Mentha arvensis*, makes it very desirable to investigate the native American mints of the *arvensis* and *canadensis* species. It is to be expected that such studies will not only help to clear up the relationships existing between the various plants, but that they ought also to throw light on the general mechanism of oil production.

Through the kind coöperation of Mr. O. A. Beath of the Wyoming Experiment Station, Laramie, a large quantity of *Mentha candensis* herb was received for investigation. The material was collected in Plumbago Canyon, Albany County, Wyo., August 20–23, 1922, at an altitude of 7000 feet. The plants were mostly in bloom

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* Contribution from the Wisconsin Pharmaceutical Experiment Station. Studies in the Genus *Mentha V.*

[1] National Research Council Fellow in Chemistry.

at the time; of the original 1000 lbs. gathered, 144.5 lbs. of air-dry drug were received at Madison. The loss due to water content is accordingly about 85.5 p. c. in this instance. The distillation was immediately carried out under the supervision of Prof. W. O. Richtmann; the primary distillation was performed by G. Bents, the cohobation by G. C. Jenison. The yield of primary oil amounted to 1175 Gm., an additional 245 Gm. was obtained by cohobating the aqueous distillate, giving a total of 1420 Gm. This represents 2.16% based on the air dry herb; the cohobated oil amounted to a 20.85% increase over the primary oil.

Physical and Chemical Constants.—The following data were obtained by the determination of certain physical and chemical constants.

		Original oil.	Cohobated oil.
Density 25	=	0.931	0.937
n_{D25}	=	1.4835	1.4852
α_{D25}; 10 cm. tube	=	+18.75°	+20.60
Pulegone neutral sulfite assay	=	90.0 p. c.	95.0 p. c.
Acid No.	=		5.6
Ester No.	=	11.2	11.2
Per cent. ester	=	4.0 p. c.	4.0 p. c.
Ester no. after acetyl	=	33.6	
Per cent. total alcohol	=	9.6	
Per cent. free alcohol	=	6.5	

Fractionation.—A liter of oil was fractionally distilled in a vacuum three times through a 15-inch Vigreaux column. The final series of fractions and their constants were as follows:

Frac.	B. P. 22–24 mm.	Vol.	d_{22}	N_{22}	α_{22}
1.	−90° C.	39 cc.	0.8488	1.4678	−45.1°
2.	90–00°	9 cc.	0.8582	1.4690	−26.1°
3.	100–10°	22 cc.	0.9052	1.4742	+16.1
4.	110–14°	41 cc.	0.9260	1.4795	+26.2°
5.	114–16°	808 cc.	0.9332	1.4845	+22.9°
6.	116–20°	35 cc.	0.9296	1.4862	+19.4°
7.	120°+	36 cc.			
	Water and loss	10 cc.			
		1000 cc.			

Examination of Fractions.—Fractions 1 and 2 were mixed and examined together because of the similarity of their physical properties. A trace of acid was present as indicated by most blue litmus. This was removed by sodium bicarbonate solution. The disagreeable component of the odor of this fraction was also removed by this treatment. Schiff's reagent failed to show the presence of any aldehyde.

Following this, the oil was twice distilled over metallic sodium. The resultant material gave the folowing data:

B. p. 25 = 70–76° C., with oil bath at 95–110° C.
Vol. = 30 cc.; d = 0.839; n = 1.4672; α = −52.25°

These values agree in general with those of the monocyclic terpenes. The material yielded neither terpinene nitrosite nor phellandrene nitrite. Ten cc. of oil were treated according to Wallach's method [*Ann.*, 227, 281 (1885)] for the preparation of terpene tetrabromides. The resultant crystals were recrystallized from ethyl acetate. M. p. 100–01° C.

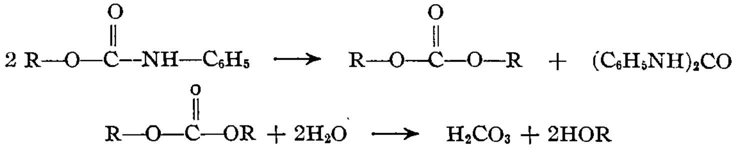
The nitrosochloride prepared in the usual way from 5 cc. of this fraction melted at 102° C.

The sodium-alcoholate residues obtained by purifying the terpene fraction were suspended in ether and treated with 5 Gm. of phthalic anhydride. A reaction took place after some time. However, it was not possible to isolate any definite compound.

Fractions 3 and 4, b. p. 100–114° were mixed and examined together. Being transition fractions, they were first subjected to the neutral sulfite assay treatment for pulegone. When the reaction became sluggish the oil was separated and fractionated.

Frac. 1, b. p. 25 –110°, vol. = 7.5 cc.
Frac. 2, 110– 18°, vol. = 15.0 cc.

In order to isolate any alcohols which might be present, these fractions were mixed with some phenyl-isocyanate (Kahlbaum). Fraction 1 deposited crystals after an hour's time. After standing two weeks, a slight odor of the reagent was still noticeable. However, the crystals were filtered out and the oil was subjected to steam distillation. The crystals were found to be diphenyl urea, m. p. over 230° C. The very viscous residue left from the distillation was dissolved in boiling 50 p. c. alcohol. An oil separated on cooling, but crystallized on standing. The mother liquor deposited during evaporation both an oil and crystals. The latter also proved to be diphenyl urea, m. p. 235° C. As diphenyl urea is not so very readily soluble even in strong alcohol, it seems certain that an unstable phenylurethane was formed and decomposed into the urea according to the well-known reaction.



$$2\,R{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}C_6H_5 \longrightarrow R{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}R + (C_6H_5NH)_2CO$$

$$R{-}O{-}\overset{\overset{O}{\|}}{C}{-}OR + 2H_2O \longrightarrow H_2CO_3 + 2HOR$$

An odor reminding of geraniol accompanied the process.

Frac. 114–16°.—The oil boiling between 114–16° C. at 22 mm. pressure had physical properties in close agreement with those recorded for pulegone. The values previously given are repeated for ease of comparison with those found by Wallach.

$d = 0.936$; $n = 1.4846$; b. p. 221–22°

Observed, b. p. = 114–16°; $d_{22} = 0.9332$; $n_{22} = 1.4845$; $\alpha = +22.85°$

To confirm this evidence a portion was involved in reaction with semicarbazide. After the usual procedure, a crystalline semi-carbazone was obtained which was resolved into two fractions by repeated recrystallization The higher fraction (*a*) melted at 168–71° C. when obtained from 95 p. c. alcohol. The lower melting fraction (*b*) was also more soluble. It melted somewhat indefinitely, but a portion was finally obtained from 50 p. c. alcohol which fused rather sharply between 137–38° C.

A repetition of the above experiment with 56 grams of ketone fraction gave similar results. The final melting points in this series were a little higher, namely 172–73° C. and 138–40° C. respectively. The difference in crystal form was very noticeable. The higher melting compound was obtained in short rhomboid crystals, the lower melting in slender prismatic crystals.

As a further study of the behavior of fraction 114–16° C., a small quantity of oil was submitted to hydrolysis according to the method used by Wallach for the decomposition of pulegone. [*Ann.*, 289, 338 (1896).] (1) It was thought that any more stable compound present might be detected after the removal by this means of most of the pulegone.

Seventy cc. of oil were mixed with an equal volume of 85 p. c. formic acid and refluxed for 16 hours. The mixture was neutralized with KOH, the precipitated oil washed with water and then dried over sodium sulphate. About 45 cc. of oil were recovered. After two fractionations through a short Vigreux column, the following series resulted:

Frac.	B. p.	Vol.
1.	−165° C.	..
2.	165– 75°	24 cc.
3.	175– 95°	6 cc.
4.	195–215°	5 cc.
5.	215°+	..

Fraction 2 possessed the following physical properties:

$d_{21} = 0.909;\ n = 1.4460;\ \alpha = +12.5°.$

Wallach* observed for pure d-methyl-l cyclohexanone-3

$d_{21} = 0.915;\ n = 1.4456;\ [\alpha] = +13.38°;$ b. p. = 169° C.

The semicarbozone prepared from this fraction melted at 180° C. after recrystallization from 50 p. c. alcohol; Wallach has recorded its m. p. at 180° C.

Accordingly *d*-methyl-*l* cyclohexanone-3 has resulted by the hydrolysis of fraction 114–16°. The second product of hydrolysis, acetone, was easily detected in fraction —165° C. by the preparation of its characteristic *p*-nitrophenylhydrazone, m. p. 148° C. Hence the two hydrolysis products derivable from *d*-pulegone have been obtained.

The high boiling fraction, 195–215° C. was converted into a semicarbazone m. p. 170–72° C. after recrystallization from hot 95 p. c. alcohol. This appears to be unchanged pulegone.

Fraction 116–20° was subjected to the neutral sulphite assay for pulegone. The entire fraction dissolved, hence it was composed essentially of the same material as the preceeding.

Summary.—*d*-Pulegone is the chief constituent of *Mentha canadensis* oil from Wyoming. It is accompanied by another ketone, as yet not positively identified yielding a semicarbazone melting at 138–40° C.

The lower boiling fractions contain chiefly *l*-limonene.

Evidence was obtained of the presence of an alcohol but it is not *l*-menthol.

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* "Terpene end Campher." Ed. 2, p. 420.