tent of 45.74 per cent computed as $C_{10}H_{19}OH$. Hence, free alcohol is present to the extent of 17.46 per cent. Treatment with phenyl isocyanate yielded diphenyl urea, m. p. 230°, but no urethane.

It is apparent that a much larger amount of oil will be necessary to reveal its chemical composition.

STUDIES IN THE GENUS MENTHA, XI.

THE OIL OF MENTHA CANADENSIS, L.

BY H. A. BRAUN.*

The first oil to be distilled was reported by Schimmel & Company[1] in 1893 from material collected at Passiac, N. J. In 1898, Florence M. Gage[2] distilled an oil from material collected in the neighborhood of Madison. A larger quantity of of oil, distilled from material collected by O. A. Beath in Wyoming, was examined by R. E. Kremers[3] in 1923. During the summer of 1925 the opportunity presented itself to obtain material from the northern part of Wisconsin. About 450 pounds of fresh flowering material were collected between August 3rd and August 24th at Crandon, Wisconsin, along the banks of Swamp Creek, the outlet of Stone Lake, and in the marshes which border this stream. This yielded 170 pounds of dried herb which, in turn, yielded 936 grams of oil or 1.16 per cent.

Schimmel & Company[1] report a yield of 1.23 per cent from the dried herb. Miss Gage[2] reports 1.25 per cent from the dried herb. R. E. Kremers[3] reports a yield of 1.80 per cent of primary oil and 0.36 per cent of cohobated oil, making a total of 2.16 per cent.

The oil was of a greenish yellow color and possessed a penetrating minty odor. The physical and chemical constants are herewith tabulated with those of previous investigators for the sake of ready comparison.

	H. A. B.	R. E. K.	F. M. G.
$d_{25°}$	0.8974	0.931	−0.927 to 0.935
$\alpha_{D^{25}}$ 10 cm. tube	+32° 24′	+18.75°	+16° 11′ to 20° 32′
Phenol assay	none	none	traces of thymol or carvacrol
Ester value	22.78	11.2	
Per cent ester ($C_{10}H_{19}OCOCH_3$)	8.06 per cent	4.0 per cent	
Ester value after acetylation	32.00 per cent	33.6	
Per cent total alc.	15.69 per cent	9.6 per cent	
Per cent free alc.	7.90 per cent	6.5 per cent	
Pulegone assay (neutral sulphite)	20.00 per cent	90 per cent	
Pulegone assay (acid sulphite)	18.00 per cent		

Though the oil agrees better with the other Wisconsin oil than with the Wyoming oil, it differs appreciably even from the former. Five hundred and thirty-six grams of oil, when shaken with a 5 per cent solution of potassium hydroxide yielded no more than a few drops of oil on acidification. Flueckiger's test for thymol and carvacrol gave a negative result.

* Fritzsche Brothers Fellow.

[1] *Bericht S. & Co.*, p. 45 (Oct. 1893).

[2] *Pharm. Rev.*, 16, p. 422.

[3] JOUR. A. PH. A., Vol. XIV, p. 32.

Dried over anhydrous sodium sulphate, the oil, after having been shaken with aqueous potassa, revealed the following physical constants which are herewith contrasted with the corresponding constants observed before this treatment, *viz.*,

	Before.	After.
$d_{25°}$	0.8974	0.8905
m_D	1.4609 (at 25°)	1.4595 (at 22°)
α_D	+32° 24′ (at 25°)	+31° 15′ (at 22°)

The change, though apparent, is not great. Moreover, it is not in the direction in which one would expect to find it. Removal of presumably inactive phenol might be expected to increase the angle of rotation, whereas it has been reduced. However, the slight lowering of the density is in harmony with what we might expect.

One hundred cc. of the oil thus treated were then fractionated and the constants of the fractions determined. The results are herewith tabulated.

Fraction.	B. p.	Volume, cc.	$d_{25°}$.	$\alpha_{D^{25°}}$.
I	−100°	7.0	0.8756	.....
II	100–140°	33.5	0.8912	+15.9°
III	140–175°	31.4	0.8994	+25.5°
IV	175–190°	18.3	0.9051	+21.2°
V	190°+	5.4	....	.....
		95.6		

Fractionation revealed no pulegone, although the assay seemed to indicate the presence of about 20 per cent of this ketone.

The first fraction, when tested with Schiff's reagent, gave a negative test for aldehydes.

Upon acetylation, Fraction 100° to 140° revealed 25.27 per cent of alcohol computed as $C_{10}H_{19}OH$. Upon saponification it showed the presence of 17.37 per cent of esters computed as $C_{10}H_{19}OCOCH_3$, revealing, by difference, the presence of 6.79 per cent of free alcohol.

The balance of the oil, when fractionated, yielded rather different results as shown in the table:

Fraction.	B. p.	Volume, cc.	$d_{25°}$.	$\alpha_{D^{25}}$.
1	−100°	13.5	0.8710	− 3.25°
2	100–140°	22.0	0.8852	+ 6.35°
3	140–175°	36.0	0.8887	+ 7.50°
4	175–200°	243.0	0.8952	+21.22°
5	200–212°	231.0	0.9050	+31.95°
6	212°+	...	....	.....
		Total 545.0		

With semicarbazide hydrochloride, Fraction 1 yielded no crystalline product, Fraction 2 a small amount.

The third fraction (140–175°) when treated with semicarbazide hydrochloride gave a heavy precipitate, which, upon recrystallization, yielded two fractions; one sparingly soluble in 50 per cent alcohol which melted at 180°; the other more readily soluble, one which, after repeated crystallization from 50 per cent alcohol, melted at 137°.

According to Wallach, "Terpene und Campher," the semicarbazone of inactive Δ^4 mentheneone-3 melts at 142°, that of the active modification at 170–171°; the semicarbazone of methyl-1-cyclohexanone-3 at 180°.

No semicarbazone was obtained from Fraction 175–200°.