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THE CONSTITUENTS OF THE ESSENTIAL OIL
OF
AMERICAN PENNYROYAL

BY
MARMADUKE BARROWCLIFF, A.I.C.

(From the Transactions of the Chemical Society, 1907)



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LXXXI.—*The Constituents of the Essential Oil of American Pennyroyal. Occurrence of a Dextro-Menthone.*

By MARMADUKE BARROWCLIFF.

THE essential oil obtained by distillation from the labiate plant *Hedeoma pulegioides* (Linné) Persoon, commonly known as American Pennyroyal, was first investigated by Kremers (*Proc. Amer. Pharm. Assoc.*, 1887, 35, 546), who stated that it contained esters of formic, acetic, and isoheptic acids, together with two compounds having the empirical formula $C_{10}H_{18}O$, which were designated "hedeomol." These compounds, which were separated by the fractional distillation of the hydrolysed oil, were found to boil respectively at 168—171° and 206—209°. In a subsequent communication (*Pharm. Rundschau*, 1891, 9, 130), Kremers showed that both these compounds were ketones. From the fraction of the oil boiling at 168—171° he prepared a crystalline oxime melting at 41—43°, whilst the fraction boiling at 206—209° yielded an oxime melting at 52°, which he indicated might possibly be *l*-menthoxime. Somewhat later, Habegger (*Amer. J. Pharm.*, 1893, 65, 417) identified pulegone as a constituent of the oil.

The necessity having arisen for preparing a quantity of pulegone, for which the oil of hedeoma appeared to be a convenient source, it was deemed desirable to examine more completely the other constituents of this oil, and the results are embodied in the present communication.

EXPERIMENTAL.

The material employed for this investigation was obtained from Messrs. Fritzsche Brothers, New York, and possessed the characters of a genuine hedeoma oil. It had a density of 0.9297 at 15°/15°, an optical rotation at 22° of +25°44' in a 1-dm. tube, and was soluble in twice its volume of 70 per cent. alcohol. By a preliminary determination of the amount of free and combined acids, it was found that 20 grams of the oil required 0.064 gram NaOH to neutralise the free acids and 0.1025 gram NaOH to hydrolyse the esters present.

Treatment with Sodium Carbonate.—The entire amount of oil (2200 grams) was first shaken three times successively with a 10 per cent. solution of sodium carbonate. The combined alkaline liquids were extracted with ether to remove any suspended oil, then acidified with sulphuric acid, and distilled in steam. The distillate, which contained some oily drops, was extracted with ether, and the ethereal

solution well washed with water, the washings being added to the aqueous distillate. From the acids remaining in the latter a barium salt was prepared, which gave the reactions of formic and butyric acids. The oily acids which had been extracted by ether were neutralised with potassium hydroxide, and subsequently converted into silver salts by fractional precipitation with a solution of silver nitrate. These were washed, dried, and analysed:

Fraction	I.	0.1837	of silver salt gave	0.0707	Ag.	Ag = 38.4.
„	II.	0.1286	„ „	0.0514	Ag.	Ag = 39.9.
„	III.	0.2251	„ „	0.0918	Ag.	Ag = 40.7.
„	IV.	0.2205	„ „	0.0914	Ag.	Ag = 41.4.
„	V.	0.2329	„ „	0.0975	Ag.	Ag = 41.8.
„	VI.	0.1844	„ „	0.0786	Ag.	Ag = 42.6.
			$C_{10}H_{19}O_2Ag$ requires	Ag = 39.0	per cent.	
			$C_8H_{15}O_2Ag$ „	Ag = 43.0	„	

The oily acids therefore appear to be a mixture of octoic and decylic acids. No indication was obtained of the presence of isoheptoic acid, which Kremers (*Proc. Amer. Pharm. Assoc.*, 1887, 35, 546) considered to be a constituent of the oil.

Treatment with Potassium Hydroxide.—After the treatment with sodium carbonate the oil was extracted three times successively with a 5 per cent. solution of potassium hydroxide, then washed with water, and dried with anhydrous sodium sulphate. The combined alkaline liquids were extracted with ether to remove a small amount of suspended oil, then acidified with sulphuric acid, and again extracted with ether. This ethereal liquid was shaken with a solution of sodium carbonate, washed, dried, and the solvent removed, when a very small amount of a viscid oil was obtained which had a creosote-like odour and gave a brown coloration with ferric chloride. This substance was evidently a phenol, but an attempt to obtain a crystalline benzoyl derivative from it was unsuccessful.

Identification of Salicylic Acid.

The alkaline liquid obtained by shaking the above-mentioned ethereal liquid with a solution of sodium carbonate was acidified with sulphuric acid and extracted with ether. This ethereal liquid, after the removal of the solvent, yielded a small amount of a crystalline solid, which was brought on a porous plate to remove a little adhering oil, and then recrystallised from water, from which it separated in needles melting at 156°. It gave a violet coloration with ferric chloride:

0.1046	gave	0.2332	CO ₂	and	0.0411	H ₂ O.	C = 60.8; H = 4.4.
			$C_7H_6O_3$	requires	C = 60.9; H = 4.3	per cent.	

This substance was thus identified as salicylic acid. As the original oil had previously been extracted with sodium carbonate, this acid could not have existed in it in a free state, and was probably present in the form of methyl salicylate, which had become hydrolysed in the process of isolation.

Preliminary Examination of the Terpenes.—In order to test for the presence of an olefinic or other unstable terpene, the oil which had previously been extracted with sodium carbonate and caustic alkali, as above described, was distilled under 60 mm. pressure, and the portion which passed over below 120° (about 50 c.c.) separately collected. This was again distilled under the same pressure, when it was resolved into the following fractions: below 105°, 105—120°; above 120°. The fraction boiling below 105°/60 mm. had the odour of pinene and a density of 0.8508 at 15°/15°, which indicated the absence of any olefinic terpene. The fraction 105—120°/60 mm. was specially tested for phellandrene, but with a negative result. All the above fractions were subsequently added to the main portion of the oil after the latter had been hydrolysed.

Isolation of Pulegone.

The entire portion of the oil boiling above 120°/60 mm. was treated with a solution of sodium bisulphite according to the method employed by Baeyer for the separation of pulegone from the oil of *Mentha Pulegium* (Ber., 1895, 28, 652), and the mixture actively shaken for ten days. This effected the separation of a large quantity of a crystalline bisulphite compound, which was removed by filtration and washed with alcohol and ether. The uncombined oil contained in the filtrate and washings was extracted with ether, and the ethereal solution dried with anhydrous sodium sulphate. After the removal of the ether the residual oil was rectified under 60 mm. pressure, when a small quantity of resinous matter remained in the flask. The further treatment of this portion of the oil is subsequently described.

The solid bisulphite compound and the aqueous filtrate therefrom, which had been freed from uncombined oil, were then separately decomposed by warming with a solution of potassium hydroxide, and the liberated ketone extracted with ether and dried. That obtained from the solid bisulphite compound distilled at 135—140°/65 mm. as a colourless oil, which acquired a slight yellow colour on standing, and amounted to 390 grams:

0.1027 gave 0.2966 CO₂ and 0.0979 H₂O. C = 78.8; H = 10.6.

C₁₀H₁₆O requires C = 78.9; H = 10.5 per cent.

$d = 0.9377$ at 20°/20°; $n_D + 19.50'$ in a 1-dcm. tube, whence $[\alpha]_D + 21.15^\circ$.

A portion of this ketone was treated with semicarbazide hydro-

chloride and sodium acetate, when a semicarbazone was obtained which, after crystallisation from methyl alcohol, melted sharply at 171° , the melting point of pulegone semicarbazone.

The oil obtained by treating the aqueous bisulphite liquid with alkali likewise distilled at $135\text{--}140^{\circ}/65$ mm., and amounted to 140 grams. It had an optical rotation of $+18^{\circ}28'$ in a 1-dcm. tube, and yielded a semicarbazone melting at 171° . It therefore also consisted of pulegone, and the somewhat lower rotatory power may be due to its having become partially racemised. The total quantity of pulegone obtained by the above treatment with bisulphite thus corresponds to 24.1 per cent. of the original oil.

Hydrolysis of the Oil.

The oil from which the pulegone had been removed as completely as possible by the above-described treatment with bisulphite was hydrolysed by boiling it for two hours with a solution of 16 grams of potassium hydroxide in 400 c.c. of 90 per cent. alcohol, the mixture being frequently shaken. After removing the greater portion of the alcohol, a quantity of water was added, and the mixture extracted with ether, the ethereal solution being subsequently washed with water and dried with anhydrous sodium sulphate. After the removal of the ether the product was distilled under a pressure of 60 mm., when the greater portion passed over between 135° and 155° , a small quantity of resinous substance being left in the flask. The weight of the hydrolysed oil thus obtained was 1115 grams.

Fractional Distillation of the Oil.

The whole of the oil remaining from the foregoing treatment, to which was added the small portion that had been separated for the preliminary examination of the terpenes, was then subjected to repeated fractional distillation under the ordinary pressure, when the following fractions were finally collected: $155\text{--}165^{\circ}$, $165\text{--}170^{\circ}$, $170\text{--}180^{\circ}$, $180\text{--}190^{\circ}$, $190\text{--}200^{\circ}$, $200\text{--}207^{\circ}$, $207\text{--}212^{\circ}$, $212\text{--}217^{\circ}$, $217\text{--}224^{\circ}$, $224\text{--}240^{\circ}$, $240\text{--}250^{\circ}$, $250\text{--}260^{\circ}$, $260\text{--}270^{\circ}$, $270\text{--}280^{\circ}$, $280\text{--}290^{\circ}$, $290\text{--}300^{\circ}$, $300\text{--}310^{\circ}$.

Identification of Pinene.

Fraction $155\text{--}165^{\circ}$.—This was a colourless, mobile liquid and amounted to 7 grams:

0.1237 gave 0.3536 CO_2 and 0.1248 H_2O . $\text{C} = 78.0$; $\text{H} = 11.2$.

$d_{16.5^{\circ}}^{16.5^{\circ}} = 0.8867$; $\alpha_D - 3^{\circ}32'$ in a 1-dcm. tube.

The characters of this fraction indicated that it consisted of a

terpene, mixed with some of the oxygenated constituents of the oil. In order to remove the latter as completely as possible, it was washed several times with 70 per cent. alcohol, when a small amount of liquid remained which was sparingly soluble in this solvent. It then yielded a small quantity of a crystalline nitrosochloride, melting at $103-104^{\circ}$, from which the corresponding nitrolbenzylamine, melting at 122° , was prepared. The presence of a small amount of *l*-pinene in the oil was thus established.

Identification of 1-Methyl-3-cyclohexanone.

Fraction 165—170°.—This was a colourless, limpid liquid having an agreeable odour. It distilled for the most part at $166-168^{\circ}$ and amounted to 87 grams:

0.1337 gave 0.3780 CO_2 and 0.1324 H_2O . $\text{C} = 77.1$; $\text{H} = 11.0$.

$d_{16.5^{\circ}}^{16.5^{\circ}} = 0.9006$; $\alpha_D - 0^{\circ}10'$ in a 1-dcm. tube.

This fraction, although consisting chiefly of an oxygenated substance, evidently contained some pinene. Its solution in chloroform decolorised a considerable amount of bromine, hydrogen bromine being evolved.

On treatment with hydroxylamine an oxime was obtained which distilled at 130° under 33 mm. pressure, and then slowly solidified in fine needles melting at $41-43^{\circ}$. This melting point corresponds with that of an oxime obtained by Kremers (*Pharm. Rundschau*, 1891, 9, 130) from a fraction of hedeoma oil boiling at $168-171^{\circ}$, but which appears not to have been identified or further examined by him:

0.1073 gave 0.2585 CO_2 and 0.0985 H_2O . $\text{C} = 65.7$; $\text{H} = 10.2$.

$\text{C}_7\text{H}_{13}\text{ON}$ requires $\text{C} = 66.1$; $\text{H} = 10.2$ per cent.

A portion of the fraction was treated with semicarbazide hydrochloride and sodium acetate, when a semicarbazone was readily obtained. After crystallisation from alcohol it was obtained in glistening plates melting at $182-183^{\circ}$:

0.1164 gave 0.2420 CO_2 and 0.0919 H_2O . $\text{C} = 56.7$; $\text{H} = 8.8$.

$\text{C}_8\text{H}_{15}\text{ON}_3$ requires $\text{C} = 56.8$; $\text{H} = 8.9$ per cent.

Nine grams of the semicarbazone were decomposed with dilute sulphuric acid and the liberated ketone distilled in steam. The distillate was then extracted with ether, the ethereal solution dried, and the solvent removed, when a residue was obtained which distilled at $167-168^{\circ}$ as a colourless, mobile oil:

0.1098 gave 0.3018 CO_2 and 0.1068 H_2O . $\text{C} = 75.0$; $\text{H} = 10.8$.

$\text{C}_7\text{H}_{12}\text{O}$ requires $\text{C} = 75.0$; $\text{H} = 10.7$ per cent.

$d = 0.9154$ at $20^{\circ}/20^{\circ}$; $\alpha_D + 12^{\circ}0'$ in a 1-dcm. tube, whence $[\alpha]_D + 13.1^{\circ}$.

This ketone is thus seen to agree in its composition and characters with 1-methyl-3-cyclohexanone (compare Aschan, *Chemie der alicyclischen Verbindungen*, 1905, p. 651), and it appears to be the first instance in which its occurrence in nature has been observed. Further confirmation of its identity was afforded by condensing a portion with benzaldehyde in the presence of a dilute solution of sodium hydroxide, when a dibenzylidene compound was obtained, which crystallised from alcohol in yellow needles melting at 125—126°.

By the treatment of the above fraction (b. p. 165—170°) with an excess of hydroxylamine hydrochloride and distillation of the product under diminished pressure, a small fraction was obtained which distilled below the boiling point of the oxime (130°/33 mm.). This, on redistillation at the ordinary pressure, boiled at 170—176°, had the odour of limonene, and an optical rotation of -42° in a 1-dcm. tube. When treated with a slight excess of bromine, and the product crystallised from ethyl acetate, dipentene tetrabromide (m. p. 124°) was obtained. The mother liquors from the crystallisation of the latter compound yielded a small amount of limonene tetrabromide (m. p. 104°):

Fraction 170—180°.—This amounted to 7 grams:

0.1170 gave 0.3276 CO₂ and 0.1154 H₂O. C = 76.4; H = 10.9.

$d_{16.5^\circ/16.5^\circ} = 0.9048$; $\alpha_D + 2^\circ 4'$ in a 1-dcm. tube.

This fraction was tested for cineol, but with a negative result. It was distilled twice over sodium, when the greater portion of the oxygenated substances was removed, and was then found to contain small amounts of dipentene and limonene, which were identified by means of their tetrabromo-derivatives:

Fraction 180—190°.—The amount of this fraction was 7 grams:

0.0984 gave 0.2748 CO₂ and 0.0981 H₂O. C = 76.2; H = 11.1.

$d_{16.5^\circ/16.5^\circ} = 0.9051$; $\alpha_D + 3^\circ 12'$ in a 1-dcm. tube.

Fraction 190—200°.—This amounted to only 3 grams:

0.1075 gave 0.3039 CO₂ and 0.1082 H₂O. C = 77.1; H = 11.2.

$d_{16.5^\circ/16.5^\circ} = 0.9023$; $\alpha_D + 5^\circ 40'$ in a 1-dcm. tube.

Fraction 200—207°.—This was the same in amount as the preceding fraction:

0.1047 gave 0.2966 CO₂ and 0.1055 H₂O. C = 77.2; H = 11.2.

$d_{16.5^\circ/16.5^\circ} = 0.9031$; $\alpha_D + 7^\circ 12'$ in a 1-dcm. tube.

The three preceding fractions were too small in amount to admit of further examination. They evidently consisted of mixtures of the constituents of the fractions of lower and higher boiling point.

Fraction 207—212°.—The amount of this fraction was 65 grams:

0.1165 gave 0.3302 CO_2 and 0.1176 H_2O . $\text{C} = 77.3$; $\text{H} = 11.2$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C} = 77.9$; $\text{H} = 11.7$ per cent.

$d_{20^\circ/20^\circ} = 0.9048$; $\alpha_D + 16^\circ 22'$ in a 1-dcm. tube.

This fraction was examined after the composition of the following one had been determined, and was found to consist largely of the constituents of that fraction.

Fraction 212—217°.—This was by far the largest fraction obtained and amounted to 620 grams :

0.1349 gave 0.3849 CO_2 and 0.1358 H_2O . $\text{C} = 77.8$; $\text{H} = 11.2$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C} = 77.9$; $\text{H} = 11.7$ per cent.

$\text{C}_{10}\text{H}_{16}\text{O}$ „ $\text{C} = 78.9$; $\text{H} = 10.5$ „

$d_{20^\circ/20^\circ} = 0.9121$; $\alpha_D + 19^\circ 8'$ in a 1-dcm. tube.

This fraction combined completely with hydroxylamine, yielding an oily oxime which deposited no solid, even on long standing. As there appeared to be still some pulegone present, 100 grams of the fraction were treated with sodium bisulphite solution in the manner previously described, when 8.5 grams of a bisulphite compound were obtained. This, when decomposed with a solution of potassium hydroxide, yielded an oil which, both by its boiling point and by its semicarbazone, was identified as pulegone.

Isolation of l-Menthone and d-isoMenthone.

Ten grams of the fraction (b. p. 212—217°) from which the further quantity of pulegone had been removed, were treated with semicarbazide hydrochloride and sodium acetate. The semicarbazone thus obtained was dissolved in hot absolute alcohol, in which the greater portion appeared to be very sparingly soluble. On cooling, a quantity (8.5 grams) of a substance separated in long, handsome needles which melted at 184—186°, and this melting point was not altered by further crystallisation. This substance corresponded in melting point with *l*-menthone semicarbazone, and a mixture of it with the semicarbazone from pure *l*-menthone (Kahlbaum) showed no diminution in melting point. The ketone was regenerated from it by distilling rapidly in steam with dilute sulphuric acid. The distillate was then extracted with ether, the ethereal solution dried with anhydrous sodium sulphate, and the solvent removed, when a liquid was obtained which distilled completely at 207—208° :

0.1320 gave 0.3768 CO_2 and 0.1370 H_2O . $\text{C} = 77.8$; $\text{H} = 11.5$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C} = 77.9$; $\text{H} = 11.7$ per cent.

$d = 0.8957$ at $20^\circ/20^\circ$; $\alpha_D - 10^\circ 8'$ in a 1-dcm. tube, whence $[\alpha]_D - 11.3^\circ$.

This substance was evidently *l*-menthone, and the difference between

its optical rotation and that of pure *l*-menthone may be attributed to its having become partially racemised by the action of the sulphuric acid during its liberation from the semicarbazone.

The oxime was prepared, and, after recrystallisation from alcohol, melted at 58—59°.

The mother liquors from the above-mentioned semicarbazone were concentrated, and the solid obtained from them fractionally crystallised from alcohol. A further small quantity of *l*-menthone semicarbazone was thus separated, and also 3.5 grams of a substance melting at 136—139°, which crystallised in hard masses of imperfectly formed cubes. The ketone regenerated from this was found to distil at 211—216°:

0.0954 gave 0.2730 CO₂ and 0.0975 H₂O. C = 78.0; H = 11.3.

$d_{20}/20^{\circ} = 0.9148$; $\alpha_D + 24^{\circ}16'$ in a 1-dcm. tube.

From the analytical figures and physical characters it appeared probable that this substance was a mixture of a strongly dextrorotatory ketone, C₁₀H₁₈O, with some pulegone.

The above-mentioned mother liquors also yielded about 3 grams of an uncrystallisable oil from which the ketone was regenerated. This distilled at 210—214° and had $\alpha_D + 31^{\circ}36'$ in a 1-dcm. tube:

0.1157 gave 0.3302 CO₂ and 0.1182 H₂O. C = 77.8; H = 11.3.

C₁₀H₁₈O requires C = 77.9; H = 11.7 per cent.

It was evident that this substance also consisted largely of a ketone of the formula C₁₀H₁₈O.

It therefore seemed probable that if the pulegone still contained in the fraction of oil boiling at 212—217° could be removed, the semicarbazone of the dextrorotatory ketone might be isolated in a state of purity. With this object in view 100 grams of the respective fraction were warmed with a mixture of 33 grams of potassium dichromate and 11 grams of sulphuric acid in 250 c.c. of water, the mixture being frequently shaken. The unchanged ketone was then distilled in steam and extracted, when a liquid was obtained which distilled at 211—213°, and had $\alpha_D + 15^{\circ}36'$ in a 1-dcm. tube. Fifteen grams of this liquid were converted into semicarbazones, which were fractionally crystallised from alcohol, when 12.5 grams of *l*-menthone semicarbazone were obtained. The remainder consisted almost entirely of a compound which, after drying at 100°, melted at 125—126°, only a very small amount of the product being uncrystallisable.

The semicarbazone melting at 125—126° was decomposed with dilute sulphuric acid and the liberated ketone distilled as rapidly as possible in steam. It was then extracted, and found to boil constantly at 209—210°;

0.1187 gave 0.3392 CO_2 and 0.1247 H_2O . $\text{C} = 77.9$; $\text{H} = 11.7$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C} = 77.9$; $\text{H} = 11.7$ per cent.

$d = 0.8961$ at $20^\circ/20^\circ$; $\alpha_D + 43^\circ 36'$ in a 1-dcm. tube, whence $[\alpha]_D + 48.6^\circ$.

It seemed likely that this ketone was a stereoisomeride of *l*-menthone, as the physical constants of the two compounds, with the exception of the optical rotation, were practically the same. Its oxime is an oil.

Beckmann (*Annalen*, 1889, 250, 322) has shown that when *l*-menthone ($[\alpha]_D$ about -28°) is treated with 90 per cent. sulphuric acid, a product is obtained which possesses a rotatory power of about $[\alpha]_D + 28^\circ$. It appeared probable that this change was due to the racemisation of one of the two asymmetric carbon atoms contained in the ketone, and that, if this were the case, the resulting mixture might be separated into its components by the fractional crystallisation of the semicarbazones obtained from it. In order to ascertain whether this could be accomplished, the following experiment was conducted.

Fifteen grams of *l*-menthone (Kahlbaum) having a rotation of $[\alpha]_D - 28.0^\circ$ were inverted according to the method employed by Beckmann (*loc. cit.*), when a product was obtained which had a rotation of $[\alpha]_D + 22^\circ$. Twelve grams of this were converted into the semicarbazones, which were fractionally crystallised from alcohol. A quantity (9.6 grams) of a compound melting at $184\text{--}186^\circ$ was thus obtained, which was shown to be *l*-menthone semicarbazone, both by comparison with the latter and by the characters of the regenerated ketone. The mother liquors yielded a substance melting at $126\text{--}127^\circ$ * which crystallised in imperfectly-formed cubes. This was found to be identical with the above-described semicarbazone melting at $125\text{--}126^\circ$. The ketone regenerated from it was found to boil at $208\text{--}209^\circ$, had $d = 0.8988$ at $20^\circ/20^\circ$, and $\alpha_D + 42^\circ 20'$ in a 1-dcm. tube, whence $[\alpha]_D + 47.1^\circ$. This menthone thus possesses the highest dextrorotatory power that has as yet been observed.

Beckmann (*J. pr. Chem.*, 1897, 55, 18), by oxidising *isomenthol* with chromic acid, obtained menthones varying in optical rotation from $[\alpha]_D + 30^\circ$ to $[\alpha]_D + 35^\circ$, values considerably lower than that recorded above.

The amount of *l*-menthone semicarbazone obtained from the above-described "inverted menthone" ($[\alpha]_D + 22^\circ$) indicates that it must have contained at least 60 per cent. of *l*-menthone ($[\alpha]_D - 28^\circ$). The specific rotation of the dextrorotatory constituent of this mixture, calculated from these figures, would therefore be $[\alpha]_D + 97^\circ$. It is

* The mother liquors from this second semicarbazone yielded a very small quantity of a substance which crystallised in fine needles melting at $161\text{--}163^\circ$. The nature of this compound has not been determined.

thus probable that the above-described dextrorotatory menthone did not possess its full degree of optical activity, and that the difference between the calculated value ($[\alpha]_D + 97^\circ$) and the figures actually obtained ($[\alpha]_D + 47.1^\circ$ to $+ 48.6^\circ$) may be attributed to racemisation having taken place during the liberation of the ketone from its semicarbazone.

Since the menthone molecule contains two asymmetric carbon atoms, ordinary *l*-menthone must be represented by either the configuration — — or — +. On treatment with sulphuric acid, one of these asymmetric carbon atoms, without doubt the one situated in the α -position to the keto-group, undergoes racemisation, and it has been shown that the resulting mixture consists of *l*-menthone, together with a second menthone possessing a rotatory power of opposite sign but of greater value than that of the former ketone. It follows from this that ordinary *l*-menthone must be represented by the second configuration, namely, — +, and that on treatment with sulphuric acid the carbon atom possessing a levorotatory power undergoes racemisation. The *d*-menthone contained in hedeoma oil, and also in Beckmann's "dextro-menthone" (*Annalen*, 1889, 250, 322), must therefore be represented by the configuration + +. As this ketone is not the optical antipode of *l*-menthone, it would seem advisable to denote it by some distinctive name, such as *d*-isomenthone.* The two other possible menthones, possessing the configurations — — and + — respectively, both of which are apparently at present unknown, would then be designated respectively as *l*-isomenthone and *d*-menthone.

Fraction 217—224°.—The amount of this fraction was 43 grams:

0.1616 gave 0.4638 CO₂ and 0.1565 H₂O. C = 78.3; H = 10.8.

$d_{20^\circ/20^\circ} = 0.9257$; $\alpha_D + 23^\circ 0'$ in a 1-dcm. tube.

A portion of this fraction was treated with semicarbazide and the resulting semicarbazones fractionally crystallised, when it was found to consist of the constituents of the preceding fraction, but containing a larger proportion of pulegone than the latter.

Fraction 220—240°.—This amounted to 10 grams:

0.1083 gave 0.3125 CO₂ and 0.1052 H₂O. C = 78.7; H = 10.8.

$d_{20^\circ/20^\circ} = 0.9270$; $\alpha_D + 12^\circ 4'$ in a 1-dcm. tube.

This consisted of pulegone and the constituents of the fractions of higher boiling point.

* This nomenclature is in accordance with that adopted by Aschan (*Chemie der alicyclischen Verbindungen*, 1905, p. 657), who designated the "*d*-menthone" of Beckmann as *d*-isomenthone, but recognised that this is a mixture of *l*-menthone and a hitherto unknown dextrorotatory menthone which, when isolated, would properly receive the name *d*-isomenthon.

Fraction 240—250°.—The amount of this fraction was only 3 grams :

0.1008 gave 0.2935 CO₂ and 0.0978 H₂O. C = 79.8 ; H = 10.8.

$d_{20^{\circ}/20^{\circ}} = 0.9296$; $\alpha_D + 4^{\circ}56'$ in a 1-dcm. tube.

Fraction 250—260°.—This amounted to 3 grams :

0.1173 gave 0.3415 CO₂ and 0.1145 H₂O. C = 79.4 ; H = 10.8.

$d_{20^{\circ}/20^{\circ}} = 0.9302$; $\alpha_D - 0^{\circ}24'$ in a 1-dcm. tube.

Fraction 260—270°.—This amounted to 3 grams :

0.1100 gave 0.3163 CO₂ and 0.1067 H₂O. C = 78.4 ; H = 10.8.

$d_{20^{\circ}/20^{\circ}} = 0.9322$; $\alpha_D + 0^{\circ}12'$ in a 1-dcm. tube.

Fraction 270—280°.—This amounted to 3 grams :

0.1289 gave 0.3717 CO₂ and 0.1245 H₂O. C = 78.6 ; H = 10.7.

$d_{20^{\circ}/20^{\circ}} = 0.9385$; $\alpha_D + 1^{\circ}56'$ in a 1-dcm. tube.

Fraction 280—290°.—This amounted to 3 grams :

0.1090 gave 0.3121 CO₂ and 0.1055 H₂O. C = 78.1 ; H = 10.7.

$d_{20^{\circ}/20^{\circ}} = 0.9375$; $\alpha_D + 4^{\circ}56'$ in a 1-dcm. tube.

As the five preceding fractions were all so very small in amount, they were not further examined.

Fraction 290—300°.—The amount of this fraction was 8 grams :

0.1099 gave 0.3187 CO₂ and 0.1092 H₂O. C = 79.1 ; H = 11.0.

$d_{20^{\circ}/20^{\circ}} = 0.9307$; $\alpha_D + 9^{\circ}32'$ in a 1-dcm. tube.

The characters of this fraction indicated it to consist of a mixture of the constituents of the preceding and the following fractions.

Fraction 300—310°.—The amount of this fraction was 7 grams :

0.1150 gave 0.3375 CO₂ and 0.1151 H₂O. C = 80.0 ; H = 11.1.

C₁₅H₂₆O requires C = 81.1 ; H = 11.7 per cent.

$d_{20^{\circ}/20^{\circ}} = 0.9259$; $[\alpha]_D + 12^{\circ}48'$ in a 1-dcm. tube.

The analysis and boiling point of this fraction indicated that it might contain a sesquiterpene alcohol, and as it was impossible to obtain the latter in a state of purity, it was deemed of interest to prepare the corresponding sesquiterpene from it. The entire fraction was accordingly distilled several times over phosphoric oxide, and then twice over metallic sodium under 60 mm. pressure, when it finally passed over between 160° and 170°. Under the ordinary pressure it distilled between 270° and 280° :

0.0890 gave 0.2872 CO₂ and 0.0916 H₂O. C = 88.0 ; H = 11.4.

C₁₅H₂₄ requires C = 88.2 ; H = 11.8 per cent.

$d_{20^{\circ}/20^{\circ}} = 0.8981$; $\alpha_D + 1^{\circ}4'$ in a 1-dcm. tube ; $n_D^{20} = 1.5001$.

Molecular refraction, 66.80.

The value obtained for the molecular refraction indicates that this

substance belongs to the group of bicyclic sesquiterpenes with two ethylenic linkings. By the production of this sesquiterpene indirect evidence is afforded of the presence of a small amount of a sesquiterpene alcohol in hedeoma oil.

Acids Obtained by the Hydrolysis of the Oil.

The strongly alkaline aqueous liquid which was separated from the hydrolysed oil, and from which all adhering oil had been removed by extraction with ether, as previously described, was concentrated to a small bulk, then acidified with sulphuric acid, and distilled with steam. The distillate contained a small amount of an oily liquid, which was extracted with ether, the ethereal solution being subsequently washed with water and dried. The acids remaining in the aqueous distillate were converted into their barium salts and found to be formic and acetic acids. After removing the solvent from the ethereal solution of volatile acids, the latter were converted into the sodium salts, from which, by the addition of silver nitrate, the corresponding silver salts were precipitated in five fractions. These were washed, dried, and analysed:

Fraction	I.	0.2130 of silver salt gave 0.0827 Ag.	Ag = 38.82.
"	II.	0.1154 " " 0.0455 Ag.	Ag = 39.42.
"	III.	0.1214 " " 0.0493 Ag.	Ag = 40.60.
"	IV.	0.1048 " " 0.0435 Ag.	Ag = 41.50.
"	V.	0.1179 " " 0.0500 Ag.	Ag = 42.40.
		$C_{10}H_{19}O_2Ag$ requires Ag = 39.0 per cent.	
		$C_8H_{15}O_2Ag$ " Ag = 43.0 "	

These volatile acids would thus appear to consist of a mixture of octoic and decylic acids.

After the distillation of the volatile acids there remained in the distilling flask about 5 grams of an oily liquid which was not volatile in steam. This was extracted with ether, and the ethereal liquid subsequently shaken with a solution of sodium carbonate. The aqueous alkaline liquid was then acidified, when a viscous, brown oil was precipitated, which was extracted with ether, and, after the removal of the solvent, distilled under 20 mm. pressure. The main portion passed over at 180—240° as a viscid, pale brown oil, which, after standing for some weeks, deposited a fatty-looking solid substance. This was separated by filtration, brought on a porous plate to remove a little adhering oil, and then crystallised from ethyl acetate, from which it separated in needles melting at 83—85°:

0.1072 gave 0.2136 CO_2 and 0.0762 H_2O . C = 54.3; H = 7.9.

$C_8H_{14}O_4$ requires C = 55.4; H = 8.0 per cent.

From the ammonium salt of this acid the silver salt was prepared and analysed :

0.0896 of silver salt gave 0.0491 Ag. $\text{Ag} = 54.8$.

$\text{C}_8\text{H}_{12}\text{O}_4\text{Ag}_2$ requires $\text{Ag} = 55.6$ per cent.

These analytical figures render it probable that this crystalline substance is a dibasic acid of the formula $\text{C}_8\text{H}_{14}\text{O}_4$.

Summary.

From the results of this investigation the essential oil of *Hedeoma pulegioides* is seen to contain the following substances :

1. An undetermined phenol, in very small amount.
 2. *l*-Pinene
 3. *l*-Limonene
 4. Dipentene
 5. 1-Methyl-3-cyclohexanone, about 8 per cent.
 6. Pulegone, about 30 per cent.
 7. *l*-Menthone
 8. *d*-iso Menthone
 9. A sesquiterpene alcohol, about 2 per cent.
 10. An ester of salicylic acid, probably methyl salicylate.
 11. Esters of formic, acetic, octoic, and decylic acids, together with an ester of a dibasic acid of the probable formula $\text{C}_8\text{H}_{14}\text{O}_4$.
 12. Formic, butyric, octoic, and decylic acids in the free state.
- All the above-mentioned esters and acids are present only in small amount.

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