The absorbability of tincture of digitalis from the alimentary tract may be influenced by more than one factor; and there is no justification for the assumption that absorption of this preparation from the frog's lymph sac always parallels that from the mammalian intestine. Certainly, however, it seems proper to conclude that the change in tincture of digitalis which occurs with age and which lessens the absorbability of this preparation from the lymph sac of the frog affects the absorbability from the intestine of the cat and of the dog to practically the same extent; and, consequently, the frog assay method more truly indicates the potency of such preparations which are intended for oral administration.

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STUDIES IN THE GENUS MENTHA. VI. THE VOLATILE OIL OF A STRAIN OF JAPANESE PEPPERMINT GROWN BY THE WISCONSIN PHARMACEUTICAL EXPERIMENT STATION, AT MADISON.[1]

BY G. C. JENISON[2] AND R. E. KREMERS.[3]

The Japanese oil of peppermint holds a unique place in the world's commerce because of the comparative ease with which crystalline 1-menthol is obtained from it. Accordingly, attempts have been made from time to time to introduce strains of Japanese plants into other countries. These attempts have been by no means uniformly successful, and taken in conjunction with what is reported concerning the culture of mints in Japan itself, have only obscured the situation both botanically and economically, instead of clarifying it. The propagation of the strain under present consideration belongs in the category of those failures that have resulted in oils "deficient in menthol." Usually the matter has been dropped at this point. The further investigation of this "deficiency in menthol," especially as to what took the place of menthol, has led in this instance to some very interesting results. The theoretical consideration of these results is left to a later paper. For the moment only the actual examination of the oil will be discussed.

Material.—The strain of Japanese peppermint which yielded the oil for these investigations has been grown for some years by the Wisconsin Pharmaceutical Experiment Station in its gardens in the vicinity of Madison, Wisconsin.[4] The

[1] Contribution from the Wisconsin Pharmaceutical Experiment Station, Madison. Based in part on a section of the Master's Thesis submitted by G. C. Jenison to the University of Wisconsin, June, 1923.

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[4] The Station gardens are under the immediate supervision of Prof. W. O. Richtmann. The authors gratefully acknowledge their indebtedness to him for the large amount of material made available by his efforts.

original plants were obtained in 1913 from the Arlington Experimental Gardens of the Bureau of Plant Industry as progeny of plants imported from Japan. The plants constituting this importation were supposed to be *Mentha arvensis* var. *piperescens*.

The propagation at the Madison gardens has been by root-cuttings according to the usual procedure of mint culture. The distillation of the oil, including the cohobation, was done in the usual way. Although it had been known almost from the start that the oil produced by this particular strain was poor in menthol, there was no record of an examination to ascertain its components. This was all the more desirable after the preliminary study of the cohobated oil[1] had shown a noteworthy variation from the cohobated oil of American peppermint, although both had been produced from neighboring plants.

This report includes the three crops of 1920 to 1922 inclusive.

PHYSICAL CONSTANTS AND ASSAY.

Year	1920: original	1921: original	1921: cohobated	1922: original	1922: cohobated
Density	0.923 at 25°C.	0.925 at 24°C.	0.932 at 24°C.	0.924 at 22°C.	0.924 at 20°C.
Index of refraction	1.4845 at 25°C.	1.4846 at 24°C.	1.4838 at 24°C.	1.484 at 22°C.	1.483 at 20°C.
Optical rotation	———	+15.14° at 22°C.	+19.1° at 22°C.	+15.4° at 21°C.	+19.8° at 21°C.
Pulegone	86 p. c.	88 p. c.	88 p. c.	86 p. c.	84 p. c.
Ester				6.6 p. c.	
Alcohol				12.1 p. c.	
Total alcohol				17.3 p. c.	
Regenerated pulegone					
B. p.	103–05°C. at 12 mm.		110–12° at 21 mm.	115–20° at 27 mm.	110–12° at 19 mm.
d.	0.933 at 26°C.		0.934 at 25°C.	0.9229 at 25°C.	0.9312 at 22°C.
n.	1.4850		1.4842	1.4833	1.4862
				+22.15°	+21.4°
Semicarbazone			m. p. 168–69°C.	m. p. 171.5°C.	m. p. 168°C.

Preliminary Treatment and Fractionation.—The oils produced in these years show a remarkable uniformity as evidenced by the preceding table. The chemical examination reflects the same fact by the similarity of the procedure developed for each oil. Hence the following details, taken from the examination of the 1922 oil, describe accurately the work of the other years. Because more material was at hand, this oil was also studied more exhaustively.

A liter of unrectified 1922 oil was thoroughly extracted successively with sodium bicarbonate solution and with sodium bisulfite solution. The traces of acids and aldehydes thus removed were not identified. The oil was then rectified by steam distillation, dried over anhydrous sodium sulfate, and fractionated repeatedly. The data for the final series of fractions are given in the table on the following page.

Thus it is evident that the oil is largely composed of a few fractions whose physical constants suggest the presence of pulegone. This substance was further purified through reactions with sodium bisulphite. This was accomplished in two

[1] JOUR. A. PH. A., October, 1921, p. 834.

ways. First by the Baeyer technique of shaking together an hydroalcoholic mixture of the components until the reaction was complete. The second consisted in the adaptation to larger quantities of the neutral sulphite assay for pulegone. The results were identical.

B. p.	Vol.	d_{24}.	n_{24}.	$[\alpha]_{21}$.
155–60°C. at 750 mm.	56 cc.		1.4609	
160–70°	18		1.4662	
170–86°	6		1.4748	
105–10° at 27 mm.	26	0.919	1.4805	+ 9.89°
110–15°	14		1.4805	
115–20°	590	0.9229	1.4833	+22.15°
120–25°	40	0.9372	1.4839	+22.50°
125–30°	37	0.9383	1.4843	+22.45°
130–35°	24		1.4850	+18.52°
135°+	76			
	887			

Pulegone regenerated from addition product prepared according to Baeyer:

B. p.$_{12\text{ mm.}}$ = 103–05° C.; d_{26} = 0.933; $n_{26\,D}$ = 1.485; $[\alpha]_{25}$ = +22.15°.

Pulegone regenerated from addition product prepared with neutral sulphite:

B. p.$_{19\text{ mm.}}$ = 110–12° C.; d_{24} = 0.931; $n_{24\,D}$ = 1.481; $[\alpha]_{24}$ = +21.9°.

Semicarbazone: M. p. = 171.5° C. Hydroxylamine addition compd.:

M. p. = 156–57° C.

Further proof that the ketone behaves as pulegone was obtained by oxidation and hydrolysis. A 50-Gm. sample of pulegone fraction was oxidized according to Semmler[1] with potassium permanganate. A good yield of crude oxidation product was obtained, which yielded a small quantity of perfectly pure β-methyl adipic acid: M. p. 85° C. recrystallized from hot benzol.

A 70-cc. sample was hydrolyzed by boiling with an equal volume of formic acid.[2] The reaction mixture was freed of acid with sodium carbonate and the oil twice fractionated. The constants of the principal fraction were:

B. p. 165–75° C.; d_{22} = 0.919; n_D = 1.447; α_D = +12.65°.
Wallach records:[3] B. p. 169° C.; d = 0.915; n_D = 1.4456.

In addition to pulegone, the only other compound definitely identified in the oil was limonene. By following the technique of Graybeal and Kremers fraction b. p. 170–86° yielded a nitroso chloride which in turn gave a nitrolbenzylamine base, m. p. 92–93° C. The presence of pinene in the lowest fraction was not conclusively established.

Both menthol and menthone were specially sought for. If they were present at all, their quantity is too small for detection in a liter of oil. The assay of the

[1] F. W. Semmler, *Ber.*, 25, 3515 (1892).
[2] O. Wallach, *Ann.*, 289, 338 (1896).
[3] *Ibid.*

unrectified oil indicated an appreciable saponification value after acetylization. It was also found that fraction 8, b. $p_{.27}$ = 125–30°, had a high saponification value. Fractions 7, 8, and 9 were thereupon united, freed of pulegone by the neutral sulphite method, rectified, saponified, and again rectified. The resultant oil was found to distil over a wide range, 160–240° C. Each significant fraction was treated with phenylisocyanate. However, only diphenyl urea resulted. With different materials attempts were made to freeze out menthol, with negative results.

SUMMARY.

The strain of a so-called Japanese peppermint which is being cultivated at the Wisconsin Pharmaceutical Experiment Station has been shown to yield a volatile oil containing largely *d*-pulegone. *L*-limonene is the only other constituent of the oil definitely identified. Careful search for both menthone and menthol has so far failed to reveal the presence of either compound.

The study of the non-pulegone fractions of this oil is being continued with much larger quantities of oil.

MEDICINAL PLANTS OF THE AZTECS WHICH ARE STILL IN COMMON USE IN MEXICO.*

BY CHARLES BRAUBACH.

When the Spanish conquerors first arrived in Mexico in the year 1521, they were surprised to find there a number of the most beautifiul botanical gardens, as for example in Texcoco; that of Chapultepec and the royal gardens of Montezuma. The gardens of Chapultepec are now the magnificent park of the same name in the city of Mexico, and known to all visitors, with its giant conifer trees, called *Ahuehuetes*, an Aztec word, and surrounding the castle of Chapultepec, the residence of the presidents of Mexico. Many of these big trees are said to be about one thousands years old and are arranged in lanes, through which footwalks are leading.

According to the old Spanish historians, these botanical gardens of the Aztecs were in existence long before the discovery of the American continent; the oldest is stated to be that of the king of Texcoco, whose name was Netzahualcoyotl. This king had a large array of live plants and kept in his palace a collection of such desiccated plants from other regions as would not grow in the soil of his gardens, thus he became the founder of a museum of natural history. According to "Prescott's History of the Conquest of Mexico," Book VI, Chapter II, the gardens of Texcoco were arranged in such a manner and with such taste that one could safely say there was nothing equal in Europe at that time. In these botanical gardens a classification and arrangement of the plants could be observed: trees, medicinal plants, plants bearing flowers with fragrant odor and plants yielding dyes, with subdivisions of those resembling each other. One of the old Spanish monks by the name of Moxó expressed his opinion that the European botanists followed the

* Scientific Section A. PH. A., Buffalo meeting, 1924.