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THE VOLATILE OIL OF COLLINSONIA ANISATA.

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Collinsonia anisata Sims, *Micheliella Anisata* (Sims) Briq. is an herbaceous plant of the Labiatae or mint family growing in sandy pine or oak woods from South Carolina to Florida and Alabama.

The plant has a ligneous, knotted root-stock and grows generally from one to two feet high. Usually it blooms about the first of September, the flowering period extending over several weeks. The corollas are cream-colored. The anise-scented leaves have at times been used medicinally as a carminative and stomachic under the name of "citronella tea".

The odor of the plant suggests that it contains either anethol or its isomer, methyl chavicol, or both. These are respectively the *p*-propenyl and *p*-allyl derivatives of anisol.

It is known that anethol has been identified less frequently in plants than methyl chavicol. In some cases they seem to occur together, but always one or the other predominates. The present work was undertaken to determine which one is the characteristic constituent of this plant.

The oil used in this investigation was obtained by steam distillation in October 1909, from fresh material collected near Auburn, Alabama. The above-ground portions of the plants were used. Some of the plants were still in bloom but most had entered the fruiting stage. The yield of oil based on the weight of fresh green plant material was 0.138%. No doubt the yield would have been larger if the plants had been collected and distilled a few weeks earlier.

PHYSICAL CONSTANTS OF THE OIL.

Three samples of oil were obtained, the total volume being about 170 cubic centimeters. The optical activity of one of these was determined soon after distillation. The rotation in a 100-mm. tube was —2.34° at 21° C. The rotation of all three samples determined in 1914 was —0.4°, —2.3°, —1.65°, respectively, in a 100-mm. tube. Since the rotation of sample No. 2 was —2.34°, determined soon after the oil was distilled, it will be seen that practically no change in rotation had occurred by standing five years.

The index of refraction as determined in 1914 by means of an Abbé refractometer was 1.5225, 1.5185, 1.5195, respectively, at 19.2° C.

CHEMICAL EXAMINATION.

Test for Phenol.—When shaken with 5% sodium hydroxide solution in a

cassia flask the oil showed practically no diminution in volume, indicating the absence of phenols. However, when the total amount of the oil was treated in the usual way for the removal of phenol evidence of the presence of a small amount of salicylic acid was obtained.

Test for Aldehyde.—With Schiff's reagent the oil immediately gave a pink color, indicating the probable presence of aldehyde.

Test for Ketone.—Mulliken's test indicated the presence of ketone. By heating the oil with a 40% solution of sodium sulphite there was shown a diminution in volume corresponding to 6% of ketone. Owing to the small amount of oil available it was not possible to identify either aldehyde or ketone.

Tests for Free Acid and Ester.—The following values were obtained:

Sample.	Acid number.	Saponification number.	Ester number.
1	3.40	21.20	17.80
2	0.48	4.37	3.89
3	0.43	9.13	8.70

The high values obtained for sample No. 1 are no doubt due to the fact that this sample was kept several years in a partly filled bottle and had undergone resinification.

Estimation of Methoxyl.—The percentage of methoxyl was determined by Perkin's modification of the Zeisel method. The following values were obtained: 16.6, 17.4, 17.1% OCH_3 respectively for the three samples.

Identification of Methoxyl.—By boiling the oil with concentrated hydriodic acid (specific gravity 1.7) and passing the gas thus liberated into an alcoholic solution of dimethyl aniline there was obtained a white crystalline solid which, after purification, melted at 212–214° C. This is known to be the melting point of trimethyl phenyl ammonium iodide. Hence the alkoxy compound present in the oil contained the methoxyl group.

Saponification of the Oil.—Preparatory to saponification the three samples of oil were now mixed and shaken with 40% solution of sodium bisulfite, in order to remove aldehyde, washed, shaken with 5% solution of potassium hydroxide in order to remove acid and phenol and again washed. It was now heated on a boiling water-bath with 0.5N alcoholic potassium hydroxide solution under a reflux condenser for thirty minutes and the greater part of the alcohol distilled off on the water-bath.

Fractionation of the Oil.—The alkaline mixture remaining in the flask after distilling off most of the alcohol was washed with water until free from alkali, dried by means of anhydrous sodium sulphate and fractionated, first under diminished pressure, then three times under atmospheric pressure. Fractions were obtained as follows:

No. of fraction.	Volume.	Boiling point.	Optical activity.	Index of refraction.	Specific gravity.
1	6 cc.	150–200° C.			
2	8 cc.	200–208° C.			
3	40 cc.	208-211° C.	inactive	1.522	
4	70 cc.	211–215° C.	inactive	1.521	0.972
5	4 cc.	215–220° C.			
	Residue				

Identification of Methyl Chavicol.—The odor of most of these fractions suggested methyl chavicol or anethol and at the same time safrol. No. 4, the largest fraction, agrees fairly well with methyl chavicol in boiling point, specific gravity, and index of refraction as shown by the following comparison:

	Index of refraction.	Specific gravity.	Boiling point.
Fraction No. 4	1.521	$0.972\ \frac{26°}{26}$	211–215° uncor.
Methyl chavicol	1.5238 1.5244	0.9714 $0.9720\ 15°$	215–216° cor.

This sample also agreed with methyl chavicol in that it did not possess the intensely sweet taste characteristic of anethol.

In order to obtain further evidence of the presence of methyl chavicol, a portion of fraction No. 4 was oxidized by means of potassium permanganate according to the method of Bertram and Walbaum.[1] There was thus obtained an acid having the melting point 173° C. In another experiment in which a mixture from fractions Nos. 3 and 4 was used there was obtained an acid which melted at 183° C.

Depending upon conditions methyl chavicol may yield either homoanisic acid, m. p. 84° C. or anisic acid, m. p. 184.2° C., while anethol yields only the latter acid. The results of these oxidation experiments show that the methoxy compound contained in the oil is either methyl chavicol or anethol or both. The physical properties of the oil, however, agree more closely with those of methyl chavicol.

The results obtained in the quantitative estimation of the methoxy group show that the oil contains about 80% by weight of methyl chavicol.

Probable Presence of Safrol.—In one of these oxidation experiments the odor of piperonal was distinctly noticeable. Since the odor of some fractions of the oil suggested the presence of safrol, which may give piperonal as one of its oxidation products, it is quite probable that safrol is a constituent of the oil.

Presence of Terpene.—When the alcohol recovered by distillation from the saponification mixture was diluted with water an oil separated, which possessed terpene characteristics, but the amount of material obtained was not sufficient for further identification.

SUMMARY.

Collinsonia anisata Sims in late flowering stage yielded about 0.14% of a volatile oil about 80% of which is methyl chavicol. Other constituents are salicylic acid and unidentified terpene, aldehyde, ketone and ester. Safrol, also, is probably a constituent.

INAUGURAL DISSERTATION.

Further Investigations Relating to the Constituents of Rhubarb.—Presented as part of the requirement for the Doctor's degree at the University of Basel, by Hans Göldlin von Tiefenan. The candidate expresses thanks to members of the Faculty of Pharmacy—Prof. Dr. H. Zörnig and Dr. P. Casparis.

The report covers 62 pages and concludes with a summary and conclusions, and references to other investigations. A sketch of the candidate for the degree is included.

[1] Archiv der Pharmacie 235, 179–182 (1897).