[CONTRIBUTION FROM THE RESEARCH LABORATORY OF FRITZSCHE BROTHERS, INC.]

INVESTIGATION OF THE CHEMICAL CONSTITUENTS OF BRAZILIAN SASSAFRAS OIL

MICHAEL J. HICKEY

Received February 16, 1948

This oil is commonly called *Ocotea Cymbarum* [H. B. K.] and *Ocotea pretiosa* Benth. and Hook f (Fam. Lauracae). The earlier literature (1) also describes an oil from the wood of *Cryptocaria pretiosa* Mart., but this designation is falling into disuse as a generic name in favor of *Ocotea pretiosa* (the essential oil described, however, was rich in alcohol calculated as linalool and hence it is not similar to the present-day oil of commerce).

E. Guenther (2), in an effort to clarify the botany of this oil observed the steam distillation of the wood in Brazil, and claims that according to reliable private information the product is derived from *Ocotea pretiosa* Benth. and Hook f (Fam. Lauracae).

A. A. Dodge (3) agrees with this taxonomy in a recent paper discussing the odor and flavor similarity between this variety and the sassafras officially recognized in the U.S.P. XIII.

The purpose of the present investigation is to show the qualitative and to some extent the quantitative relationship between the U.S.P. XIII product [*sassafras albidum* (Nutall) Nees (Fam. Lauracae)] and the imported oil which has not been chemically investigated. A tabulation follows showing the composition relationship between the two products. The official product was also investigated in the laboratories of Fritzsche Brothers, Inc. (4). It is worth while to note the fact that the identified optically active compounds in the Brazilian oil are levorotatory, while those in the *Sassafras albidum* (Nutall) Nees (Fam. Lauracae) are dextrorotatory.

The product used in the investigation was imported from Brazil in December 1944. It represented oil derived from the trunk and large branches of the tree, and had been recently distilled. The preliminary chemical and physical properties follow: d_{15} 1.076; n_D^{20} 1.5350; α_D^{20} $-1.42°$; solubility 20°, 2.0 volumes of 90% alcohol, opalescent in 10.0 volumes; congealing point $+9.0°$; acid number 0.3; ester number 5.0; ester number after acetylation 9.0; aldehyde calculated as furfural, less than 0.1%. All of these properties are normal for commercial oil.

In order that handling would be facilitated, a primary fractionation of 45.4 kg. in a commercial still with a six-foot column was resorted to; all vapors were condensed at a temperature below $+10.0°$. The oil was fractionated and analyzed as shown in Table II.

EXPERIMENTAL

Fraction I

The forerun (Fraction I) was then subdivided by fractionation at 759 mm. through an electrically heated 36-inch column of the Young type. This column had 22 discs and bulbs. The main subfractions are described below.

Identification of valeraldehyde (Ia). This consisted of 0.05% of Fraction I and distilled at 101–103°. A portion of an aqueous suspension was subjected to an alkaline 0.5% solution of sodium nitroprusside and gave a violet-red color which disappeared.

The fraction had a harsh odor. A 2,4-dinitrophenylhydrazone was prepared; it melted at 97–98° and showed no depression when mixed with a similar derivative prepared from a known sample of *n*-valeraldehyde.

TABLE I

COMPARISON OF CONSTITUENTS OF THE OILS OF BRAZILIAN AND AMERICAN SASSAFRAS

	OCOTEA PRETIOSA, %	SASSAFRAS ALBIDUM, %
Safrol	92.9	80
α-Pinene	(1) 0.7	less than 10
Phellandrene		less than 10
d-Camphor		6.8
Eugenol	0.6	0.5
n-Valeraldehyde	0.001	
Furfural	0.17	
Cineol	0.21	
Benzaldehyde	0.03	
Sesquiterpenes, high-boiling constituents and residue	*circa* 5.1	3

TABLE II

PHYSICAL AND CHEMICAL PROPERTIES OF THE MAIN FRACTIONS

	FRACTION I	FRACTION II	FRACTION III
Percent (by weight) of original oil	2.1	92.2	4.4
Boiling range, °C	up to 91[a] 4 mm.	91.0–91.5 4 mm.	above 91.5 4 mm.
d_{15}	0.941	1.103	1.051
α_D^{20}	−17°13′	−0°27′	−4°2′
n_D^{20}	1.4860	1.5379	1.5283
Aldehyde as furfural[b]	10.0%	0.0%	0.0%
Acid number	0.7	0.0	30.1
Ester number	3.0	0.0	0.1
Ester number after acetylation[c]	3.1	0.0	30.6
Congealing point		+10.8°	

[a] Distillation began at atmospheric pressure and was gradually reduced to 4mm.

[b] National Formulary, Second Supplement, p. 97.

[c] E. Gildemeister & Fr. Hoffmann, "Die Ätherische Öle," 3rd ed. 1928, p. 724.

An unidentified compound (Ib). On continued distillation at 759 mm., a liquid that distilled at 129–132° was collected (0.8% of Fraction I). The fraction did not yield a derivative. This liquid darkened on standing.

Identification of l-α-pinene (Ic). This fraction, representing 33.0% of Fraction I, was distilled over metallic sodium at 155–160.0° at 760 mm. The following physical properties were determined: d_{15}, 0.860; n_D^{20}, 1.4673; α_D^{20}, −40° 53′.

When *l*-pinonic acid was prepared (5) the semicarbazone melted at 203.5–204.5° and showed no depression in melting point when mixed in equal quantity by weight with pinonic acid prepared from the pinene fraction of commercial turpentine.

Identification of furfural (Id). The fraction that distilled from 160–165° at 759 mm. (8.1% of Fraction I) had a strong wood-like odor and darkened to a light brown on standing. The color was removed by washing with water; the aqueous solution was then extracted with ether. It gave an intense red color with an aniline acetate-acetic acid solution. A *p*-nitrophenylhydrazone derivative was prepared; it melted at 153–154°. No depression was noted on a mixed melting point with the *p*-nitrophenylhydrazone prepared from commercial furfural.

Identification of cineol (Ie). Progressive distillation led to a fraction that distilled at 170–180° at 760 mm. This fraction showed partial reaction with alcoholic hydroxylamine hydrochloride.

The fraction amounting to about 11.5% of Fraction I was treated with a 20% sodium bisulfite. The oil layer was separated from the aqueous solution, dried with sodium sulfate and redistilled over sodium. It yielded an *o*-cresol addition compound that melted at 55.5–56.5°, after being washed with five 200-ml. portions of water at 5°. A mixed melting point with cineol *o*-cresol addition compound showed no depression. This cineol addition compound was prepared from an Oil Eucalyptus USP XIII grade and mixed with an equal (by weight) portion of the compound prepared from the unknown.

Identification of benzaldehyde (If). The sodium bisulfite solution from above was washed with ether and the reacting compound regenerated with 3% aqueous KOH solution; the oil layer was taken up in ether. After evaporation of the ether, 1.5% of Fraction I remained. The 2,4-dinitrophenylhydrazone of this residue melted at 237° and was not depressed on mixing with the 2,4-dinitrophenylhydrazone of a synthetic commercial benzaldehyde.

An unidentified compound (Ig). This fraction (12.2% of Fraction I) had a camphoraceous odor. It distilled at 215–225° at 758 mm. On alkaline permanganate oxidation, it gave a minute amount of acid which melted at 163.5–164.5° on recrystallization from chloroform. Unsuccessful efforts to produce a camphor derivative were made (6, 7). The neutralization equivalent of the acid was 146.[1]

The next part of this fraction distilled at 231.0° at 756 mm. and amounted to 35.0% of Fraction I. It was added to Fraction II because of its similarity in physical and chemical properties.

Fraction II

With this addition, Fraction II amounted to 92.9% of the total oil. The physical and chemical properties correspond to those of safrol (see Table II). A picrate was prepared which melted at 104–105.2° and when this derivative was mixed with one prepared from the safrol of *Sassafrass albidum*, no depression of melting point was noted.

Fraction III

(IIIa). The forerun of this fraction (20.1% of the fraction) was identified as safrol.

Identification of eugenol (IIIb). The fraction distilling at 118–120° at 6 mm. (13.6% of Fraction III) had a spicy clove-like odor. This oil was washed with 6.5% NaOH aqueous solution; the non-reacting globules of oil were extracted with benzene. A 5% solution of sulfuric acid was used to regenerate the reacting chemical from the washed aqueous solution. Recovery was made with ether and after the evaporation of this extractant, an oil that distilled from 251–253.0° at 759 mm. was recovered. Two derivatives were made. The eugenolglycolic acid (4-allyl-2-methoxyphenoxyacetic acid) was recrystallized from dilute alcohol and melted at 96.5–97.5°. A benzoate was prepared which melted at 68.5–69.5°. Neither showed depression on a mixed melting point with the corresponding derivative prepared from the eugenol fraction of Madagascar clove oil.

An unidentified hydrocarbon (IIIc). The remaining fraction was further subdivided, 60.2% of the total distilled from 110–114° at 1 mm. Two carbon-hydrogen determinations[2]

---

[1] A greater quantity of these compounds will be isolated and further work on identification and structure will be undertaken.

[2] Carbon-hydrogen analyses by Miss L. Baker, Columbia Univ. N. Y. C., N. Y.

indicated that the ratio of carbon to hydrogen was 15:24 which is the ratio of these elements in the sesquiterpene series. A derivative was not obtained.[1]

(IIId). A dark blue residue with a "tarry" odor remained in the flask, representing 14.1% of Fraction III. It was tested for azulene (8) but none was detected; however, the compound gave a light green color in phosphoric acid-glacial acetic acid solution (equal parts by weight).[1]

SUMMARY

This investigation led to the conclusion that *Ocotea pretiosa* Benth & Hook f (Fam. Lauracae) contains the following constituents: *n*-valeraldehyde, *l*-α-pinene, furfural, cineol, benzaldehyde, safrol, and eugenol.

An unknown compound with a camphoraceous odor was found as was a hydrocarbon (probably a sesquiterpene).[1]

New York 11, N. Y.

REFERENCES

(1) Ber. von Roure-Bertrand Fils, 3, Oct. 1910.
(2) Guenther, *Drug & Cosmetic Ind.*, **55**, 538 (1944).
(3) Dodge, *Am. J. Pharm.*, **118**, 4, (1946).
(4) Power & Kleber, *Pharm. Rev.*, **14**, 101, (1896).
(5) Gildemeister and Hoffman, "Die ätherische Öle" 3rd ed. Schimmel & Co. 352 (1928).
(6) Mulliken, "Method" I 150 (1904).
(7) Tiemann, *Ber.*, **28**, 2191 (1895).
(8) Sherndal, *J. Am. Chem. Soc.*, **37**, 167 (1915).