[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ONTARIO RESEARCH FOUNDATION]

The Essential Oil of Tsuga Canadensis (L.) Carr

BY A. C. SHAW[1]

Foliage from *Tsuga canadensis* was distilled with steam to give a 0.249% yield of essential oil. Eleven constituents, totalling 90.6% of the original oil, were separated by fractional distillation, and tricyclene, *d*-α-pinene, *l*-camphene, *l*-β-pinene, myrcene, *d*-α-phellandrene, *l*-limonene, *l*-thujone and *l*-bornyl acetate were identified. Also isolated were an unidentified tertiary alcohol, and a new sesquiterpene related to *l*-cadinene, to which the name *d*-canadene is assigned.

In 1893, Bertram and Walbaum[2] reported the presence of *l*-α-pinene, *l*-bornyl acetate, and an unidentified sesquiterpene in oil of hemlock. In the very similar oil of black spruce (*Picea mariana* (Mill.) B.S.P.) the first natural occurrence of a tricyclic terpene hydrocarbon, tricyclene, was recently demonstrated, and the presence of a new dextrorotatory sesquiterpene related to *l*-cadinene indicated.[3] A reinvestigation of the composition of oil of *Tsuga canadensis*, or eastern hemlock, therefore seemed desirable.

The essential oil, prepared from material of known botanical origin was separated by fractional distillation into 59 fractions boiling below 105° (10 mm.) and comprising 90.3% of the oil. The properties of these fractions are shown in Fig. 1. The higher boiling material proved to be an exceedingly complex mixture which on fractional distillation gave the fractions illustrated in Fig. 2.

Fractions 1 and 2 were mainly tricyclene. It is now suggested that this compound may have widespread occurrence among coniferous oils, but has not been recognized because it is not easily separated from α-pinene by distillation.

Fractions 4 to 12 consisted mainly of *d*-α-pinene, and fraction 28 of *l*-β-pinene, since on permanganate oxidation they yielded *dl*- and *d*-pinonic acid and *l*-nopinic acid, respectively.

l-Camphene was identified in the solid fractions 22 to 26 by hydration to isoborneol.

Both fraction 30 and fraction 32 underwent the diene reaction with maleic anhydride, to give the adducts of myrcene and *d*-α-phellandrene, respectively. An α-phellandrene adduct was also formed when fraction 32 was heated with β-naphthol.

Fraction 35 contained limonene since *dl*- and *l*-limonene tetrabromides were separated from the products of bromination.

A tertiary alcohol was isolated from fraction 39, by means of the borate ester. It reacted with *p*-nitrobenzoyl chloride to give mainly *p*-nitrobenzoic acid, and a trace of *dl*-bornyl *p*-nitrobenzoate. The borneol probably derived from bornyl acetate. A *p*-nitrobenzoate m.p. 55.5–57° which has not been previously described, was prepared from the sodium alcoholate of the compound.

From fraction 38 a mixture of four semicarbazones was obtained, three of which were decomposed by oxalic acid to give, in each case, a ketone with a low refractive index, $n^{20}\text{D}$ 1.450. This ketone was oxidized by permanganate to α-thujaketonic acid, and was therefore either *l*-thujone or *d*-isothujone.

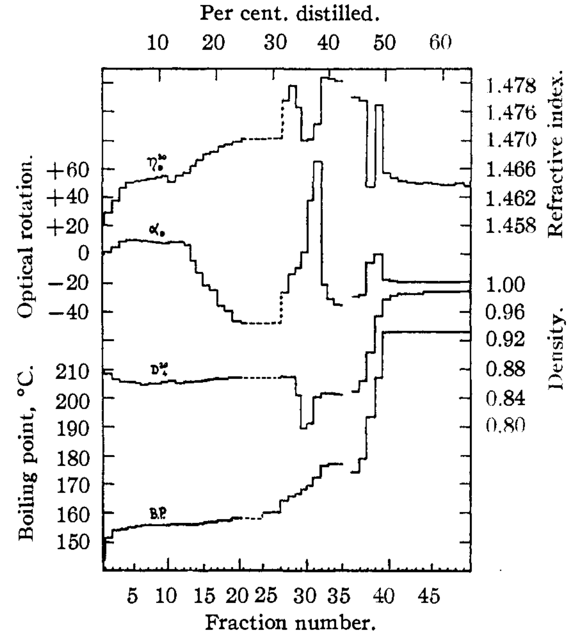

Fig. 1.—Properties of oil of *Tsuga canadensis* fractions boiling below 110° at 10 mm.

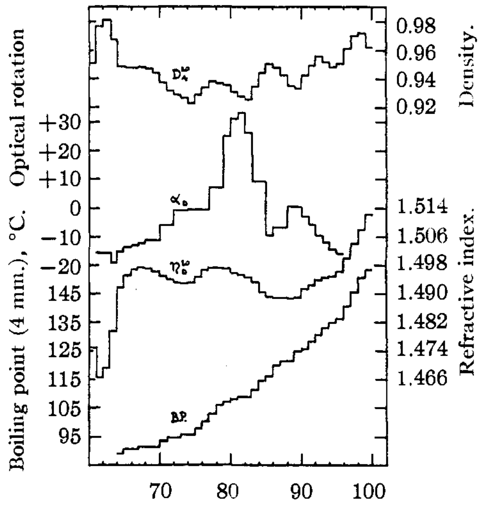

Fig. 2.—Properties of oil of *Tsuga canadensis* fractions boiling above 110° at 10 mm.

Fractions 40 to 50 consisted of an ester with properties in good agreement with those of bornyl acetate.[4] Following saponification a solid alcohol,

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[1] Presented before the Symposium on Wood Chemistry, 118th Meeting of the American Chemical Society.

[2] Bertram and Walbaum, *Arch. Pharm.*, **231**, 294 (1893).

[3] Shaw, *Can. J. Research*, **B28**, 268 (1950).

[4] Pickard and Kenyon, *J. Chem. Soc.*, **107**, 51 (1915).

and acetic acid (as the anilide) was isolated. With *p*-nitrobenzoyl chloride the alcohol gave an ester, m.p. 152–154°, which is not described in the literature. This ester must have been *dl*-bornyl *p*-nitrobenzoate since racemic borneol was obtained from it by saponification. A small amount of *l*-bornyl *p*-nitrobenzoate was isolated from the mother liquors.

Fractions 61 to 100 contained at least eight compounds each comprising 0.2 to 0.3% of the oil. On dehydrogenation only the dextrorotatory compound of fractions 80 to 83 yielded cadalene. It was isolated as the picrate in 60% of theoretical yield. From this same material *l*-cadinene dihydrochloride was obtained in 24.5% yield. However, the observed dextrorotation is not consistent with the presence of a large percentage of *l*-cadinene. (Fraction 82 had α_{D} + 33.73, n^{20}_{D} 1.4954, d^{20}_{4} 0.928). Dextrorotatory fractions which yielded derivatives of *l*-cadinene have been obtained previously from oils of *Picea mariana*,[3] *Dacrydium kirkii*,[5] *Myroxylon pereirae*[6] and others.

The existence of a previously unrecognized isomer of cadinene is therefore postulated. Since the sesquiterpene must have the same steric configuration as *l*-cadinene about the asymmetric carbon atoms in the 4, 9 and 10 positions it must be a structural isomer, rather than a diastereomer of *l*-cadinene. The name canadene is suggested.

Fractions 97 to 100 were green in color. Since this green coloration was extracted with 85% phosphoric acid, the presence is indicated of an azulene compound in amounts too minute to permit isolation or identification.

The approximate composition of the oil as estimated from the distillation data was tricyclene 2.2%, *d*-α-pinene 17.6%, *l*-camphene 11.5%, *l*-β-pinene 2.9%, myrcene 2.4%, *d*-α-phellandrene 1.8%, *l*-limonene 5.9%, *l*-thujone 1.3%, tertiary alcohol 1.3%, *l*-bornyl acetate 43.4%, *d*-canadene 0.2%.

Experimental

Preparation of the Oil.—Foliage and terminal branches of *Tsuga canadensis* (L) Carr., collected in April, 1948, were distilled with steam at 90 lb. pressure for 6 hours. The oil, obtained in a yield of 0.0249% had the following properties: d^{20}_{20} 0.9162, n^{20}_{D} 1.4684, α^{30}_{D} −12.9°, saponification number 130.8, saponification number after acetylation 154.1, aldehyde content as citral 0.5%, ketone content as carvone 2.5%, acid value 0.76.

Fractional Distillation of the Oil.—By simple distillation at reduced pressure, the oil was separated into a hydrocarbon fraction, b.p. (10 mm.) < 70°, a fraction containing oxygen compounds b.p. at 10 mm. 70–105°, and a high boiling fraction b.p. at 0.4 < 140°, comprising 48.5%, 46.0% and 3.9% of the original oil, respectively. The hydrocarbons were distilled through a 6-ft., 25-mm. i.d. Podbielniak column at reflux ratio 20/1 and an operating pressure drop of 15 mm. Fractions 1 to 26 were distilled at 50 mm. pressure, fractions 27 to 50 at 20 mm. pressure. After collection of fraction 35, volatile material was removed from the pot residue, combined with the oxygen compounds, and the resulting mixture fractionated as before. Fractions 51 to 59, amounting to 25.2% of the original oil, were obtained from the pot residue by simple distillation at 10 mm. pressure, and had n^{20}_{D} 1.4650 to 1.4667, α_{D} −19.95° to −20.60°. They consisted mainly of *l*-bornyl acetate. Non-volatile residues and loss amounted to 2.2% and 3.6% of the original oil respectively. The high boiling fraction was distilled at 4 mm. pressure, 3 mm. operating pressure drop, and reflux ratio 15/1, through a 1-ft. length of 25 mm. Podbielniak packing.

Tricyclene.—Fraction 2 (n^{20}_{D} 1.4599, d^{20}_{4} 0.875, α_{D} + 1.16, b.p. 151.8°) was added to 100 ml. of 10% aqueous permanganate, and the mixture heated to 65° with frequent shaking, until evolution of carbon dioxide ceased. After cooling solid tricyclene was removed, washed, twice crystallized from methanol, and twice sublimed from sodium. The purified product melted at 65° alone or in admixture with an authentic sample.

α-**Pinene.**—Thirty-four grams of fraction 6 (n^{20}_{D} 1.4640, d^{20}_{4} 0.861, α_{D} +10.11, b.p. 155.3°) were oxidized with neutral permanganate, according to Délépine.[7] 21.5 g. of crude acids were obtained, which after 4 crystallizations from benzene–hexane mixtures gave 9.6 g. of *dl*-pinonic acid m.p. 103.5–105°, undepressed by an authentic specimen.

The more soluble material from the mother liquors was sublimed at 100° in high vacuum, and the sublimate crystallized from benzene–hexane to give 0.2 g. of slightly impure *d*-pinonic acid m.p. 66–70°, $[\alpha]^{25}_{\mathrm{D}}$ +87.7° (c = 1.97 in chloroform).

l-**Camphene.**—Fraction 26 had specific rotation $[\alpha]^{20}_{\mathrm{D}}$ −74.7° (c = 10.16 in benzene), b.p. 160.1°. The melting point depression indicates a purity of 96.6%: No attempt was made to purify this material further. On hydration followed by saponification, according to Bertram and Walbaum[8] it gave an almost quantitative yield of isoborneol, which after crystallization from hexane melted at 210.5–212° undepressed by an authentic sample.

l-β-**Pinene.**—Ten grams of fraction 28 (n^{20}_{D} 1.4776, d^{20}_{4} 0.871, α_{D} −14.07, b.p. 165.8°) was oxidized under essentially the same conditions as were used for α-pinene; 3.1 g. of acid oil was obtained, which on treatment with 7 ml. of 10% sodium hydroxide, deposited a white powder, purified by crystallization from water. After three crystallizations the pure sodium salt (0.2 g.) was acidified and the free acid crystallized from benzene–hexane. Nopinic acid, m.p. 127° undepressed by an authentic sample, was obtained.

Myrcene.—Fraction 30 had properties n^{20}_{D} 1.4700, d^{20}_{4} 0.799, α_{D} +1.53, b.p. 168.0°. Its maleic anhydride adduct was prepared and purified according to Diels and Alder.[9] From 2.0 g. of oil 2.2 g. of *cis*-4-isohexenyl-Δ^4-tetrahydrophthalic anhydride m.p. 34–35° undepressed by an authentic sample, was obtained. The dicarboxylic acid, obtained by saponification of the adduct, melted at 120–122°.

d-α-**Phellandrene.**—Five grams of fraction 32 (n^{20}_{D} 1.4723, d^{20}_{4} 0.843, α_{D} +54.63, b.p. 172.8) was condensed with maleic anhydride by the method of Goodway and West,[10] to give 2.45 g. of adduct. After crystallization from methanol, ethanol, hexane, and ethyl ether it melted at 124–125°, $[\alpha]^{25}_{\mathrm{D}}$ +12.0° (c 4.184 in chloroform). The melting point was not depressed by mixing with an authentic sample prepared from Canada balsam turpentine oil.

When heated with two parts of β-naphthol for 15 hours at 130°, Fraction 32 underwent condensation to give an adduct m.p. 138–139°, in 26% yield. The sodium phenolate of this compound reacted immediately with *p*-nitrobenzoyl chloride to give an ester m.p. 166–168°; in quantitative yield. Salfeld[11] reported 139–140° and 164–165° for the α-phellandrene adducts.

dl- **and** *l*-**Limonene.**—Fraction 35 had n^{20}_{D} 1.4784, d^{20}_{4} 0.847, α_{D} −35.33, b.p. 177.3°. A solution of 5 g. of this material in one part amyl alcohol and two parts anhydrous ether was treated with bromine at 0°. A solid bromide separated in a yield of 4.38 g. on evaporation of the ether. After crystallization, twice from ethyl acetate and twice from ethanol, 0.6 g. of *dl*-limonene tetrabromide was obtained. The combined mother liquors, evaporated to 75 ml., were cooled to 0° and a crop of impure racemate removed. The mother liquors were then stored at Dry Ice temperature for three days. *l*-Limonene tetrabromide m.p. 103–104°, $[\alpha]^{25}_{\mathrm{D}}$ −69.7° (c = 1.46 in chloroform) separated in a yield of 0.8 g.

Tertiary Alcohol.—A mixture of 14 g. of Fraction 39, and 10 g. of tri-*n*-butyl borate was heated at 100° at 30 mm. pressure for 5 hours, during which time 2.50 g. of *n*-butyl

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(5) **Briggs and Taylor**, *J. Org. Chem.*, **12**, 551 (1947).

(6) **Naves**, *Helv. Chim. Acta*, **31**, 408 (1948).

(7) **Délépine**, *Bull. soc. chim. France*, [5] **3**, 1369 (1936).

(8) **Bertram and Walbaum**, *J. prakt. Chem.*, [2] **49**, 1 (1894).

(9) **Diels and Alder**, *Ann.*, **470**, 81 (1929).

(10) **Goodway and West**, *J. Soc. Chem. Ind.*, **56**, 472T (1937).

(11) **Salfeld**, *Ber.*, **73**, 382 (1940).

alcohol (n^{20}_D 1.3999, d^{20}_4 0.814) distilled over. Unchanged terpenes and butyl borate were removed at 100° and 1 mm. pressure, leaving 8.0 g. of non-volatile residue. This material was steam-distilled from 1 g. of sodium hydroxide and the resulting oil layer redistilled at 10 mm. to give 4.35 g. of optically inactive alcohol, b.p. 10 mm. 189–192°, n^{20}_D 1.4806, d^{20}_4 0.942.

The alcoholate, prepared by refluxing 0.5 g. of the compound in 4 ml. of benzene with excess sodium for half an hour, was decanted into a solution of 0.6 g. of *p*-nitrobenzoyl chloride in benzene. The ester obtained by evaporating the benzene melted at 55.5–57° after crystallization from methanol.

***l*-Thujone.**—A solution of 10 g. each of fraction 38, semicarbazide hydrochloride, and sodium acetate in 70 ml. of 70% ethanol was allowed to stand for three days at room temperature. Solvent and 2.9 g. of unchanged terpenes were removed in a current of steam, leaving 12.0 g. of mixed semicarbazones. The alcohol insoluble portion was crystallized from water to give 0.5 g. of white microcrystalline powder m.p. 251–253° which was not decomposed by the action of oxalic acid of 2 *N* sulfuric acid at 100°.

From the fraction slightly soluble in ethanol was obtained 0.5 g. of a pure compound m.p. 193°, $[\alpha]^{27}_D$ +57.1 (c = 4.763 in methanol), which was probably *l*-thujone semicarbazone.

The fraction soluble in cold ethanol was crystallized from aqueous ethanol to give a partial separation of two compounds. One formed anisotropic needles m.p. 176° which may have been *d*-isothujone semicarbazone. The other was an isotropic powder m.p. about 128°.

When the latter three compounds were steam distilled from an equal weight of oxalic acid, ketones were obtained with refractive indices n^{20}_D 1.4496, 1.4502 and 1.4509, respectively. The latter two ketones were combined and oxidized according to Tiemann and Semmler.[12] From 0.5 g. of oil, 0.36 g. of α-thujaketonic acid, m.p. 74.5–75.5°, was obtained.

***l*-Bornyl Acetate.**—Twenty grams of fraction 48 (n^{20}_D 1.4637, d^{20}_4 0.985, α_D −18.68) was boiled under reflux for 15 minutes with 60 ml. of 20% alcoholic potassium hydroxide, and poured into 250 ml. of water. The precipitate was crystallized from hexane to give crude borneol in a yield of 59%. The aqueous liquors were treated with excess carbon dioxide and evaporated to dryness. 9.2 g. of organic salts were leached from the residue with boiling alcohol. A mixture of 4 g. of the salt, 10 ml. of aniline, and 3 ml. of 35% hydrochloric acid was heated at 150–160° for one hour, then at 200° until excess aniline ceased to distill. A benzene extract of the residue on cooling deposited 1.86 g. of acetanilide m.p. 114–115°.

The crude borneol, after sublimation melted at 206–208° $[\alpha]_D$ −16.9° (c = 10.145 in toluene). The *p*-nitrobenzoyl ester of this substance was crystallized repeatedly from ethanol until melting point and rotation remained unchanged by further crystallization. It melted at 152–154°, $[\alpha]_D$ −0.8 (c = 10.05 in chloroform).

The ester was refluxed for one hour with excess 0.5 *N* alcoholic potassium hydroxide, and poured into water. After sublimation the recovered borneol melted at 201–206°, $[\alpha]_D$ −0.2° (c = 8.18 in toluene).

***d*-Canadene.**—A mixture of 1.0 g. of fraction 83 (n_D 1.4949, d^{20}_4 0.926, α_D +26.79) and 0.10 g. of palladium-charcoal was heated under carbon dioxide for 6.5 hours, during which time the temperature was slowly raised from 200 to 243°. The reaction mixture was diluted with hexane, filtered and the filtrate extracted with 5% aqueous sodium hydroxide. The extracted filtrate was added to 10 ml. of 10% absolute ethanolic picric acid and refluxed for 15 minutes. On cooling 540 mg. of cadalene picrate separated, m.p. 116.5–117.5°, identified by comparison with an authentic sample. A solution of 270 mg. of fraction 83 in an equal volume of dry ether was treated with dry hydrogen chloride at −20°; 90 mg. of *l*-cadinene dihydrochloride m.p. 120–120.5°, $[\alpha]^{27}_D$ −39.3° (c = 6.37 in chloroform) was obtained.

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[12] Tiemann and Semmler, *Ber.*, **30**, 431 (1897).

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Analysis of Fat Acid Oxidation Products by Countercurrent Distribution Methods. II. Methyl Oleate[2]

BY J. FUGGER,[3] K. T. ZILCH, J. A. CANNON AND H. J. DUTTON

Samples of methyl oleate, oxidized at 37° to levels of 0.482 and 0.854 mole oxygen per mole ester have been fractionated between 80% ethanol and hexane with the use of countercurrent distribution methods. Three major components are apparent from the weight distribution curve: (1) unoxidized methyl oleate accounting for 62.6 and 41.96%, respectively, of the total weights; (2) a component consisting primarily of methyl oleate hydroperoxide (maximum purity 78%); and (3) a component consisting of peroxides, acidic scission products, and other oxidized substances. While the monohydroperoxide component is greater at the higher oxidation level, the increase in the third component relative to the second is greater still. The peroxide value in the third component remains approximately equal to that of the second, yet its hydrogen absorption value is greatly reduced indicating reaction of oxygen at the double bond. The evidence supports the view that monohydroperoxides are the first stable product in the reaction with gaseous oxygen and that the ethylenic bond is not attacked until a subsequent oxidation. No evidence of dimer formation was observed.

Except for recent studies, chemical characterization of oxidation products of methyl oleate have been performed either on unfractionated oxidation mixtures[4,5,6] or on single compounds isolated from the mixture.[7,8,9] By either approach, the concept of the over-all composition of the original reaction mixture has been obscured and has been responsible in part for two widely divergent schools of inter-

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946. Article not copyrighted.

[2] A portion of this paper is based upon a thesis to be submitted by J. Fugger in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at the University of Pittsburgh. This work was carried out under an agreement between the University and the U. S. Department of Agriculture. Presented at 118th National Meeting of the American Chemical Society, September 3-8, 1950, in Chicago, Illinois.

[3] Fellow under the Research Internship program of the U. S. Department of Agriculture.

[4] D. Atherton and T. P. Hilditch, *J. Chem. Soc.*, 105 (1944).

[5] F. D. Gunstone and T. P. Hilditch, *ibid.*, 836 (1945).

[6] F. D. Gunstone and T. P. Hilditch, *ibid.*, 1022 (1946).

[7] E. H. Farmer and D. A. Sutton, *ibid.*, 119 (1943).

[8] C. E. Swift, F. G. Dollear and R. T. O'Connor, *Oil and Soap*, **23**, 355 (1946).

[9] J. Ross, A. I. Gebhart and J. F. Gerecht, THIS JOURNAL, **71**, 282 (1949).