THE LEAF OILS OF WASHINGTON CONIFERS: VI. ABIES NOBILIS.*

BY E. V. LYNN AND SUKEO NAKAYA.

Few trees of Washington forests can equal *Abies nobilis* in grandeur and nobility of form and appearance, so that the designation "noble fir" is an appropriate one. The lumbermen also call it red fir and frequently larch, although there is little reason for either name. It is most abundant on the western slopes of the Cascade range at elevations of 2500 to 5000 feet.

It is a tall, straight tree, ranging up to 220 feet in height and to a diameter of 6 feet. The bark is purplish in color and 1–2 inches thick, being divided by narrow ridges. In younger trees the crown extends well toward the ground and the bark is gray, thin and flat, with conspicuous resin-blisters. The leaves occur singly, without a distinct petiole, and are turned upward so they appear to grow from the top sides of the branches. The leaves of the upper crown are sharply pointed and less than an inch in length but the lower needles are notched at the tip and longer. The cones are very distinctive in that they stand upright and that the extruding, sharply pointed bracts completely cover the outer surface. They are 4–7 inches long and 2–3 inches in diameter.

No investigation has hitherto been made of the leaves, but the balsam was examined by Rabak¹ to a limited extent.

The samples of leaves used in this investigation were gathered on the west side of the Cascade Mountains about eighty miles from Seattle. They were immediately distilled with steam, giving 1025 cc. of oil from 780 pounds. By cohobation of the aqueous distillate, a further 55 cc. was obtained, making a total yield of about 0.3 per cent. It should be noted here that the aqueous distillate was acid and turned to a red color after standing, but this color disappeared upon boiling.

The freshly distilled oil was greenish yellow, turning slightly darker on standing, and possessed a strong, limonene-like odor. It did not deposit any solid when exposed to a freezing mixture for several hours. The specific gravity at 20° C. was 0.8552; the index of refraction at 20° C. was 1.4780 and at 25° C. 1.4744; the optical rotation at 25° C. in a 100-mm. tube was +3.89°; the acid number of 2.61 corresponded to 0.28 per cent acetic acid; the ester number of 1.12 corresponded to 0.39 per cent of bornyl acetate. By the usual methods, it was found that the oil contained about 4 per cent of substances soluble in sodium bisulphite and less than 1 per cent of phenols. One can conclude that about 95 per cent of the oil consists of hydrocarbons or alcohols. Furfural was found in quantity in the aqueous distillate.

The whole oil was fractionated and repeatedly refractionated at ordinary pressure, the higher portions at 45-50 mm.

The first and second fractions were found to contain $1-\alpha$ -pinene which was converted to the nitrosochloride and to the nitrolpiperidide, melting at 119° C. The third consisted chiefly of $1-\beta$ -pinene as shown by oxidation to nopinic acid,

^{*} Scientific Section, A. Ph. A., Toronto meeting, 1932.

¹ Pharm. Review, 23 (1905), 46.

Fraction.	Amount.	n _D 23.	d ₂₅ .	$[\alpha]_{D}25$.
155-160° C.	5.0%	1.4729	0.8501	
160-163	4.0	1.4725	0.8530	-17.75°
163-168	22.0	1.4749	0.8575	-20.67
168-173	37.0	1.4772	0.8556	-23.50
173-177	6.0	1.4810	0.8444	-32.50
177-179	3.5	1.4812		
179-203	4.0	1.4839	0.8595	
At 45-50 mm.				
94-145	5.0	1.4825	0.8880	-34.50
145-190	2.0	1.4982	0.8942	
190-208	2.0	1.5051	0.9389	
208-216	6.0	1.5125	0.9389	
Residue	3.5			

melting point 124–125° C. The second and third fractions undoubtedly contained some camphene, but this could not be proved. Hydration gave the typical odor of isoborneol, which could not be separated in the solid state, and oxidation of the hydrated mixture produced the characteristic odor of camphor, although neither oxime nor semicarbazone could be prepared.

The fourth and largest portion was mainly 1- β -phellandrene, as was also the fifth. The nitrite, which was easily produced from either by the usual methods, melted at 99–100° C. No limonene or dipentene could be detected in any of the terpene fractions, in spite of the characteristic odor.

The portions boiling at $145-208^{\circ}$ C. under 45-50 mm. pressure contained most of the ester. After saponification, the aqueous solution was neutralized and precipitated fractionally with silver nitrate. The first 0.5 Gm. contained 43.7 per cent of silver, corresponding to caprylic acid. The chief acid, however, was acetic, identified by odor and conversion to ethyl acetate.

The oil therefore contains approximately 78 per cent of terpenes, over half of which is 1- β -phellandrene and the balance the two pinenes and probably camphene. The other 22 per cent is mostly sesquiterpenes or derivatives, with small amounts of phenols, of esters of acetic and possibly caprylic acids, and of aldehydes and ketones.

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AMPHIACHYRIS DRACUNCULOIDES (DC.) NUTT.*

A STUDY OF THE FLOWERING BRANCHES.

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This plant has been called *Brachyris dracunculoides* DC., *Brachyris ramosissima* Hook, and *Amphipappus dracunculoides*, Torr. and Gray (1). Local names used

^{*} Scientific Section, A. Ph. A., Toronto meeting, 1932.

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² Part of a thesis submitted to the Graduate Faculty of the University of Oklahoma in partial fulfilment of the requirements for the degree of Master of Science in Pharmacy.