

THE LEAF OILS OF WASHINGTON CONIFERS: IV. TSUGA
HETEROPHYLLA.

BY ARNOLD J. LEHMAN AND E. V. LYNN.

Tsuga heterophylla is a tree, frequently 200 feet high, with a trunk 6-10 feet in diameter and short, slender branches. The bark is thin and dark, orange-brown changing to a cinnamon-red on older trees, and separated into narrow, flat plates by shallow fissures. The leaves are rounded at the apex, conspicuously grooved, dark green and lustrous on the upper surface, and marked below with broad white bands of rows of stomates. The leaves are from 6 to 18 millimeters long and 1.5 to 2 millimeters wide. The cones are small, being 18 to 25 millimeters long. The seeds are also small with a total length of about 3 millimeters.

The tree is known under various names. The ones in common use are hemlock, western hemlock, hemlock spruce, western hemlock spruce, western hemlock fir, Prince Albert fir, gray fir and Alaska pine. The last two are favorite names among lumbermen of the Pacific northwest.

Western hemlock is found along the Pacific coast from Alaska to northern California and as far inland as northern Idaho and northwestern Montana. It constitutes approximately 13 per cent of our forests and attains magnificent proportions in regions abundantly supplied with moisture. Exceptional trees have measured 8 feet in diameter and 250 feet in height. It is a constant companion of the western white pine, the two being found growing together in many localities.

The material for this work was obtained from trees growing in the same sphagnum bog from which the western white pine was taken. The younger trees were again selected. One sample of oil was prepared from 162 pounds of air-dried leaves, giving 90 Gm. of oil, corresponding to a yield of 0.12 per cent. It was somewhat viscid and deep red-brown in color with a yellow-brown fluorescence. Another sample was distilled from the fresh leaves and twigs, after separating the latter to some extent. After one cohobation, the amount of oil obtained from 290 pounds of material was 120 cc., corresponding to 0.09 per cent. This oil was light yellow and had an unpleasant odor. Constants of the two oils were:

	Leaves.	Leaves and twigs.
d_{25}°	0.9499	0.8741
n_D^{20}	1.4935	1.4804
$[\alpha]_{25}^{\circ}$	-17.33
Acid number	45.74	3.11
Saponification value	78.51	16.51
Ester as bornyl acetate	11.49%	4.69%
Alcohol as ester	9.01%	3.68%

The leaf oil was extracted with a 5 per cent solution of sodium carbonate to remove the free acids. After removing adhering oil by washing with ether, the aqueous liquid was acidified with sulphuric acid and completely extracted with ether. Upon evaporation of the solvent, there was left a solid mass which crystallized readily from petroleum ether in colorless, shiny plates. Analysis and the melting point of 121° C. identified this as benzoic acid.

0.1086 gave 0.2757 CO₂ and 0.0575 H₂O; 0.1050 gave 0.2664 CO₂ and 0.0500 H₂O. Found: C, 69.1 and 69.1; H, 5.8 and 5.4. Calculated: C, 68.8; H, 4.9.

The leaf and twig oil was rotated in a similar manner but only an oil residue was obtained, which was too small for further investigation.

The two oils were then mixed and extracted with 5 per cent sodium hydroxide. The aqueous liquid was shaken with ether to remove adhering oil and then acidified and completely extracted with ether. Removal of the ether from the extract resulted in a light green liquid which distilled between 250° and 260° C. The amount was too small to permit formation of derivatives, but analysis indicated $C_{17}H_{30}O_2$.

0.1213 gave 0.3405 CO_2 and 0.1257 H_2O . Found: C, 76.5; H, 11.4. Required, C, 76.6; H, 11.2.

The residual oil was fractionated at a pressure of 10 mm., that portion boiling below 100° C. being collected and purified by repeated distillation up to this temperature. It was then carefully refractionated under ordinary pressure, giving the following results: 140–150°, 2.8; 150–159°, 10.4; 159–164°, 9.5; 164–169°, 14.2; 169–173°, 16.1; 173–177, 8.5 per cent of the total oil.

The first fraction was light blue in color and possessed a very pleasant odor. Analysis showed that it contained oxygenated compounds, probably unsaturated, but no identifications could be made. The blue color gradually disappeared during further refractionation.

Alpha Pinene.—The second fraction, distilling mainly at 157° C., readily gave a nitrosochloride which mixed without depression of melting point with pure pinene nitrosochloride. The presence of α -pinene was still further confirmed by oxidation to pinonic acid, which was converted to the semi-carbazone, melting at 203° C.

Camphene.—The third fraction was treated with acetic and sulphuric acids as described by Bertram and Walbaum (1). The oily product was washed, dried and fractionally distilled. A small amount of solid isoborneol was obtained, melting point 206° C., which together with the odor is satisfactory identification for camphene in the original oil.

Beta Pinene.—The fourth fraction, which distilled chiefly at 164–167° C., was oxidized with potassium permanganate according to Wallach (2). The difficultly soluble sodium salt was acidified and extracted with ether, producing needles with a melting point of 120° C. These gave no melting point depression of pure nopinic acid, therefore identifying beta pinene in the fraction.

Beta Phellandrene.—The fifth and largest fraction was nitrosated in the usual way. A solution was made in twice its volume of petroleum ether, which was then superimposed upon a saturated solution of sodium nitrite, and the whole was maintained at -5° C. Glacial acetic acid was added slowly with continued shaking and, after it was all added, the crystalline magma was rapidly filtered. The product melted at 94° C., when rapidly heated at 103° C. From its amount, one may conclude that the whole fraction is almost entirely β -phellandrene, with possibly some of the alpha variety.

The last fraction, which was very small, should contain limonene or dipentene, but no hydrochloride or bromide could be obtained, at least not in the crystalline form.

Saponification.—The remainder of the oil was saponified with alcoholic potash for two hours. The greater part of the alcohol was then distilled off and water

was added to separate the oil, which was collected in ether, washed and dried. After removal of the solvent, it was subjected to repeated refractionation under reduced pressure and finally at ordinary pressure, collecting as follows: 177–185°, 2.8; 185–200°, 3.0; 200–216°, 3.7; 216–225°, 3.7; 225–260°, 6.6 per cent of the total oil. Analysis gave the following results:

Fraction	177–185	185–200	200–216	216–225	225–260
Sample, grams	0.1367	0.1501	0.1357	0.1352	0.1411
CO ₂ , grams	0.4232	0.4588	0.3916	0.3904	0.4313
H ₂ O, grams	0.1449	0.1586	0.1389	0.1418	0.1636
Per cent carbon	85.2	83.3	78.7	78.7	83.5
Per cent hydrogen	11.8	11.7	11.4	11.6	12.0

Attempts to prepare derivatives from any of these fractions were unsuccessful. The third and fourth were each oxidized with chromic acid to test for borneol and, although they gave a strong odor of camphor, no oxime or semicarbazone could be obtained in the crystalline state.

That portion of the oil boiling above 260° C. was fractionated repeatedly at 60-mm. pressure, the following fractions being obtained:

175–195°, 6.6; 195–215°, 3.7; 215–235°, 4.7; 235–260°, 1.8 per cent of total oil.

Cadinene.—The first two fractions were light green in color and insoluble in 70 per cent alcohol. Each was analyzed, the figures showing a composition C₁₅H₂₄. They were dissolved in dry ether and saturated with dry hydrogen chloride. After standing for some time, copious crystallization took place, especially from the second fraction which reacted almost completely. The crystals were identified as cadinene dihydrochloride, melting point 117–118° C.

Picene.—The third fraction was small, greenish yellow and also insoluble in dilute alcohol. It was treated with hydrogen chloride in the same way as above and set aside. After a few weeks plate-like crystals began to form and in another week practically all of it had crystallized. The crystals were purified from ethyl acetate and finally melted at 133° C. They proved to be identical with the hydrochloride of a sesquiterpene later found in spruce oil and named by us, picene.

The last fraction was not further investigated. It was dark brown, viscid and very small in amount.

The Acids.—The strongly alkaline liquid, which had been separated by saponifying the oil, was made acid with sulphuric acid and extracted with ether. After washing and drying the ether solution, the ether was removed, leaving a liquid which rapidly crystallized. This was found to consist entirely of benzoic acid, which had been previously identified in the free state.

SUMMARY.

The leaves of *Tsuga heterophylla*, mixed with some twigs, produced 0.09 to 0.12 per cent of an oil whose properties are described. The terpenes, constituting about 65 per cent, consisted of α -pinene, β -pinene, camphene and β -phellandrene. Benzoic acid was present, free and as ester, probably with borneol. Cadinene was identified, as well as a second sesquiterpene not previously described, which has been found later in *Picea sitchensis* and named picene.

REFERENCES.

- (1) Bertram and Walbaum, *J. prakt. Chem.* (2), 49 (1894), 1.
- (2) Wallach, *Ann.*, 356 (1907), 228.

THE DEPARTMENT OF MONOBROMATED CAMPHOR IN REFERENCE
TO COMPRESSED MEDICINAL TABLETS.*

BY GEORGE E. ÉWE.

Monobromated Camphor is "permanent in the air. . . . Melts at 76° C. and sublimates at a slightly higher temperature "according to the U. S. P. VIII." The U. S. P. IX also stated that Monobromated Camphor is "permanent in the air," but in addition, directed that it be preserved in well-closed containers, protected from light. In general, the literature does not emphasize the fact that this substance is definitely volatile; but in compressed medicinal tablet manufacturing practice it evidences a certain degree of volatility which warrants its consideration as a volatile substance.

Striking evidence of the volatile nature of this substance will be afforded by exposing a grain of the powdered substance to the air of the laboratory in a beaker covered with muslin, under which circumstances the monobromated camphor will have completely disappeared after several months. Two grains of the powdered substance when exposed to the air of the laboratory in a 100-cc. beaker covered with a single sheet of filter paper tied on with string required 7 months for complete volatilization. When 2 grains of powdered monobromated camphor were scattered on a 90-mm. filter paper with turned up edges and the paper so charged allowed to remain in a desiccator over sulphuric acid, a period of 2 months and 3 weeks was required for complete volatilization of the substance. About 2 Gm. of powdered monobromated camphor spread on a watch glass lost 0.7% in weight after 48 hours in a calcium chloride desiccator, 0.3% in the following 48 hours and exactly the same in 2 subsequent periods of 48 hours each. In an oven at 40-45° C. a 2-Gm. sample of the powdered substance lost 2.4% of its weight in 12 hours. At 50-55° C. a 2-Gm. sample lost 5.7% in weight in 7 hours.

A large number of various complex tablet granulations have been observed which suffered losses ranging from 1.3% to as much as 43% of their monobromated camphor content when subjected to drying operations on a manufacturing scale at practical degrees of elevated temperature, thereby necessitating adjustment of their content of this substance before compression into tablets. The windows of a room in which a tablet granulation containing this substance was being dried have been observed actually "frosted" with monobromated camphor when only a moderately excessive heat had been inadvertently applied.

Tablets containing monobromated camphor have been observed which became encrusted with glistening crystals of this substance after some time; although not to such a degree as to render the tablets unsightly. Apparently, the crystals were occasioned by volatilization of a portion of the monobromated camphor which subsequently re-deposited upon the outer surface of the tablets. Two such lots of tablets were assayed before and after brushing with a stiff camel's hair pencil with

* Scientific Section, A. P. H. A., Baltimore meeting, 1930.