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THE LEAF OILS OF WASHINGTON CONIFERS: III. PINUS MONTICOLA.

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This tree is commonly called western white pine. It is frequently 100 feet in height, with a straight trunk 4-5 feet in diameter and comparatively slender and spreading branches, which in young trees clothe the stem to the ground, forming a narrow, open pyramid. The symmetry is often broken in later years by the greater development of one or two of the upper branches. The young bark is thin, smooth and light green; on full grown trunks it is thick and has deep, longitudinal and cross fissures. The surface is covered with purplish scales, under which lies the cinnamon-red inner bark. The leaves, borne in clusters of five, are thick, rigid, blue-green and glaucous, 3 to 10 centimeters in length, and serrate, with small, minute teeth. In autumn the young cones are about two centimeters long but, when mature late the next summer, they are 12 to 25 centimeters long, shedding the seeds in early fall. The latter are about 8 millimeters long and colored a pale, red-brown, mottled with black.

Western white pines are scattered in considerable numbers throughout forests of the coast ranges and are not rare in the Cascades, where they occur at elevations of 5000 to 6000 feet. It reaches its noblest dimensions in northern Idaho, where it is found 2000 to 2500 feet above sea-level in river bottoms of streams flowing into Lake Pend Oreille. It is not, however, very abundant in Washington. The material for this work was gathered, partly in the spring and partly in the fall, from trees growing in a sphagnum-covered bog, well saturated with water, within a few miles of Seattle. The stand was quite abundant and consisted almost entirely of young trees, although a few older ones were found along the boundary of the swamp.

The leaves were separated as far as possible from the twigs and immediately distilled with steam. After roughly separating the oil, the aqueous distillate was once cohobated and the cohobated liquid was extracted with ether, which was then added to the oil. After carefully drying the ethereal solution, the solvent was largely removed by distillation, the last portions by means of a vacuum. The amount of oil thus obtained from 750 pounds was 180 cc., equivalent to 0.053 per cent.

The fresh oil had a pleasing, balsamic odor and was colorless, but became lemon-yellow on standing. The general constants were: d_{25}^{20} 0.8695; n_D^{20} 1.4724; $[\alpha]_D^{25}$ -17.31° ; acid number 4.24; saponification value 26.78. Calculating the ester as bornyl acetate, the amount was 7.88 per cent, the quantity of alcohol from this 6.19 per cent.

The oil was first shaken with a 5 per cent solution of sodium carbonate to re-

move the free acids and then with a 5 per cent solution of sodium hydroxide to separate the phenols. The aqueous liquids were then extracted with ether to remove adhering oil, and the ethereal solution was added to the residual oil. The latter mixture was washed with water until the washings were neutral, and the washings were added to the sodium hydroxide liquid. This was then made acid and completely extracted with ether. After drying with calcium chloride, the solvent was evaporated, leaving a small, dark brown liquid with an odor like creosote and methyl salicylate. It was too small in amount for further investigation.

After drying and removing the ether, the remainder of the oil was fractionated under reduced pressure. That portion which boiled below 100° C. at 10 mm. was purified by repeatedly distilling up to the same temperature, the residues in each case being added to the main body of oil. It was then fractionated under ordinary pressure and submitted to several refractionations. The following portions were eventually collected: 157–163° 34.5; 163–169° 31.8; 169–173° 9.0; 173–177° 3.6 per cent of the total oil.

Alpha Pinene.—The first fraction distilled almost entirely between 157° and 159° C.

0.1992 gave 0.4168 CO₂ and 0.1332 H₂O. Found: C, 88.0; H, 11.5. Calculated for C₁₀H₁₈: C, 88.2; H, 11.8.

When 5 cc. of the fraction was treated with nitrosyl chloride, the entire liquid became a solid mass of crystals. These were rapidly filtered and washed with alcohol. After recrystallization from chloroform or methyl alcohol, the product had a melting point of 105° C., confirming the presence of alpha pinene.

Camphene.—Since the limits of boiling point of the first fraction might also include camphene, a portion boiling between 161° and 163° C. was hydrated with a sulphuric-acetic mixture. Distillation of the resulting yellow oil gave a strong camphoraceous odor at 200–220°, but the distillate gave no indication of crystallizing. An analysis indicated that about 25 per cent had been hydrated and, although no camphor could be obtained upon oxidation, the formation of isoborneol was strongly evident and camphene is probably present in the original oil.

Beta Pinene.—The second fraction, which was almost as large, distilled mainly between 164° and 166° C.

0.1310 gave 0.4223 CO₂ and 0.1458 H₂O. Found: C, 87.9; H, 12.3. Calculated for C₁₀H₁₈: C, 88.2; H, 11.8.

The presence of beta pinene was demonstrated by oxidation with alkaline potassium permanganate. After distillation with steam to remove excess of oil, and filtration from the manganese sludge, the aqueous liquid was evaporated to a small volume in a stream of carbon dioxide. The precipitated sodium salt was acidified and extracted with ether, giving a yellow syrup which gradually crystallized. After purifying, the crystals were found to melt at 126° C. and gave no depression of melting point when mixed with nopinic acid.

Beta Phellandrene.—The third fraction was comparatively small.

0.1377 gave 0.4419 CO₂ and 0.1441 H₂O. Found: C, 87.5; H, 11.6. Calculated: C, 88.2; H, 11.8.

The fraction, dissolved in twice its own volume of petroleum ether, was treated

with nitrous anhydride. The magma which formed was removed by rapid filtration and washed with methyl alcohol. This gave a melting point of 103° C., not depressed by admixture with β -phellandrene nitrite, showing the presence of β -phellandrene in the fraction.

The small fourth fraction gave no crystalline product with bromine, although it might have been expected to contain limonene or dipentene.

Saponification.—Since the terpenes constitute almost 80 per cent, the remainder of the oil was very small in amount. It was hydrolyzed with alcoholic potash, the saponified oil being finally removed with ether and washed until free from alkali. The ether solution was dried and the solvent was removed by distillation. The residual oil was then fractionated, giving a few drops below 208° C., a large share between 208° and 220° and the balance above 260°.

Borneol.—The fraction 208–220° constituted about 6 per cent of the original. It had a strong camphoraceous odor. Oxidation with chromic acid solution produced solid camphor, which collected as a sublimate on the neck of the flask and was found to melt at 175° C. The presence of borneol was further confirmed by the preparation of camphor semicarbazone melting at 236° C.

The acid liquor remaining from oxidation of the borneol was extracted with ether and the ethereal solution was washed and dried. Evaporation of the solvent left a brown, syrupy residue which was not completely soluble in sodium carbonate solution. It was dissolved again in ether and extracted with ether to remove the free acids. The oily residue had a pleasant, aromatic odor and soon deposited feathery crystals. After purification these were found to melt at 110° C. The substance is evidently a lactone, but the amount was too small for analysis.

The oil boiling above 260° C. represented about 6 per cent of the total. It was light blue in color, practically odorless, and insoluble in 70 per cent alcohol.

0.1309 gave 0.4129 CO₂ and 0.1440 H₂O. Found: C, 86.0; H, 12.2. Calculated for C₁₈H₃₄: C, 88.2; H, 11.8.

The analysis indicated a large proportion of sesquiterpenes but saturation with dry hydrogen chloride gave no solid product. The blue color indicated some azulene.

The Acids.—The alkaline solution from saponification was evaporated to a small volume, acidified and extracted with ether. The liquid remaining after evaporation of the ether was yellow and had a pronounced odor of butyric acid. The small amount prevented any exact identifications, but butyric acid was strongly suspected because of the odor of the percentage of silver in a prepared salt, 58.5 per cent, and the boiling point. In addition there was also a high boiling acid which gave a silver salt having 65.2 per cent of silver, and which was probably dibasic.

SUMMARY.

Pinus monticola furnishes, by steam distillation of the leaves, 0.053 per cent of oil. The terpenes constitute about 80 per cent, chiefly α -pinene, β -pinene, β -phellandrene and probably camphene. Borneol is the main oxygenated compound, presumably present as butyrate. Azulene is contained in the higher fractions, and an unidentified lactone was found as an oxidation product. There is apparently about 6 per cent of sesquiterpenes.