SUMMARY.

A diabetic having a sugar tolerance of 172 Gm. of glucose was fed 112 Gm. of inulin during four days' time in addition to a basal diet yielding 169 Gm. of available glucose. There was no increase in either blood sugar or urine sugar from which we conclude that the inulin was not utilized but was probably destroyed in the intestines. Inulin prepared from artichokes is of no value as a source of carbohydrate to a diabetic.

REFERENCES.

(1) L. E. Westcott and E. C. Wise, *Arch. Internal Med.*, 44 (1929), 362–367.
(2) A. T. Shohl, *J. Am. Chem. Soc.*, 45 (1923), 2754–2756.
(3) H. B. Lewis, *J. A. M. A.*, 58 (1912), 1176.
(4) H. B. Lewis and E. M. Frankel, *J. Biol. Chem.*, 17 (1914), 365.
(5) H. F. Root and M. L. Baker, *Arch. Internal Med.*, 36 (1925), 135.

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THE LEAF OILS OF WASHINGTON CONIFERS: V. PICEA SITCHENSIS.

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Picea sitchensis, or tideland spruce, is the greatest of all spruce trees, being rarely surpassed in massiveness of trunk and height of stem, and there are few more beautiful and impressive sights. Indeed, a view never to be forgotten by those who have visited the forests of Washington is that of a mighty spruce, with its spire-like crown raised high above the broad base of the graceful sweep of its long branches, whose lustrous foliage, now silvery white, now changing to varied shades of green, justifies the title of "the loveliest cone-bearing tree in America."

It is usually about 100 feet high, with a trunk tapering from 3–4 feet at just above its much enlarged base. Occasionally it is found growing 200 feet tall, with a trunk 15–16 feet in diameter but, at the extreme northern limits of its range, it is reduced to a low shrub. The upper branches are short and ascending to form an open, spear-like head, while the lower ones on older trees sweep out in long, graceful curves. The bark is scaly and cinnamon-red to red-brown. The leaves stand out from all sides of the branches, often at right angles, and frequently bring their white upper surfaces to view by a twist at the base. They are 3–12 mm. long and a lustrous green on the lower surface. The cones are 6–10 cm. long and, when full grown, tinged dark red on a yellow-green back-ground. The seeds are full and rounded, pale reddish brown and 8–10 mm. long, usually with four to five cotyledons.

The tideland spruce inhabits moist, sandy soil which is often swampy, or less frequently at the far north wet, rocky slopes. It grows at altitudes along the coast up to 2500 feet, gradually becoming smaller away from the ocean.

The material for the present investigation was obtained from trees growing in a wet, semi-swampy region, possessing a sandy, alluvial soil. The trees were cut down and the leaves and twigs collected. The oil for examination was secured by immediate steam distillation, 170 cc. being produced from 933 pounds. Cohobation of the distillate gave an additional 80 cc., or a total of 250 cc., equivalent to 0.059 per cent.

The oil when freshly distilled was light yellow, becoming slightly darker on standing, and possessed a disagreeable odor. Its general constants were: $d_{27°}$ 0.8806; $[\alpha]_D^{25°}$ —5.05; $n_D^{20°}$ 1.4684; acid number 2.04; saponification value 35.81, corresponding to 11.81 per cent of bornyl acetate and 9.28 per cent of isolated alcohol.

After removing the free acids with sodium carbonate solution, the oil was shaken with a 5 per cent solution of sodium hydroxide. This separated a small amount of a light yellow liquid with a powerful and penetrating odor similar to caraway. This boiled chiefly at 210–220° C. at 11-mm. pressure and did not solidify when cooled. The amount was too small to permit any further examination.

After washing and drying the residual oil, it was distilled under reduced pressure (5 mm.) up to 95° C. and purified by repeatedly distilling up to this temperature. Finally it was submitted to refractionation several times at ordinary pressures and the following portions collected: 154–160°, 1.5; 160–169°, 17.0; 169–174°, 12.0; 174–180°, 10.0; 180–190°, 10.0; 190–200°, 6.3 per cent of the total oil.

No pinene nitrosochloride could be obtained from the first fraction, from which one can conclude that α-pinene is absent.

Beta Pinene.—The second fraction, which distilled chiefly at 164–166° C., was oxidized in the usual way with alkaline potassium permanganate. There was obtained from the acidified sodium salt by ether extraction a yellow oil which did not crystallize on long standing. It was, therefore, oxidized in acid solution by potassium permanganate, distilled with steam and the distillate was extracted with ether. The oily product was treated with semicarbazide hydrochloride as usual and the resulting crystalline substance was found too small in amount to permit positive identification. The oil was identified as nopinone by ultimate analysis, showing the presence of β-pinene.

0.0584 gave 0.1711 CO_2 and 0.0536 H_2O. Found: C, 77.7; H, 10.1. Calculated for $C_9H_{14}O$: C, 78.2; H, 10.1.

Beta Phellandrene.—The third fraction boiling chiefly at 169–174° C., was quite large. Treatment of 5 cc. in petroleum ether with nitrous anhydride at a low temperature produced white microscopic needles which melted at 101° C., showing the presence of β-phellandrene whose nitrite melts at 103° C.

The fourth fraction also contained some phellandrene, but no crystalline derivatives could be obtained with bromine or hydrogen chloride, showing the absence of dipentene or linonene.

The fifth fraction, boiling at 180–190° C., was a colorless, mobile oil with an odor resembling camphor and menthol. Analysis indicated that it contained mostly a compound of the composition $C_{10}H_{16}O$. When distilled under atmospheric pressure, it was found to boil almost constantly at 184° C. Treated with semicarbazide, it gradually formed clusters of long, glistening needles, and finally almost the entire oily layer became a solid mass. This was filtered, well washed with alcohol and pressed out on a porous tile. After drying at 100° C. for ten minutes, it melted at 231–232° C. Recrystallized from ether, in which it was sparingly soluble, this melting point was unchanged. The semicarbazone of camphor, which is one of the few with such a high melting point, was found to depress the melting temperature to a gradual one of 230–233° C. Hydroxylamine produced with the fraction an uncrystallizable oil and, as no evidence of the presence of camphor could be obtained, it was concluded that the fraction contained a new ketone. Amount of material precluded further investigation.

Camphor.—The last fraction had a very pronounced camphoraceous odor. Upon treatment with hydroxylamine in the usual way, there was obtained a product which gradually solidified and which, after recrystallization from alcohol, melted at 117–118° C. This confirmed the presence of camphor, but a semicarbazone prepared from the fraction was found to melt gradually at 230–234° C., showing admixture with the ketone in the previous fraction.

Saponification.—The oil from which the terpenes had been removed was hydrolyzed by alcoholic potash in the usual way. After adding water to the dealcolized liquor, the saponified oil was extracted with ether and submitted to fractional distillation under atmospheric pressure. The results were:

200–208°, 1.0; 208–216°, 7.5; 216–222°, 6.3; 222–230°, 8.7; 230–240°, 5.5; 240–260°, 1.5 per cent of the total oil.

The first fraction was found to contain camphor and probably was mostly of this substance, although the amount was too small to get more than a semicarbazone.

Borneol.—The second fraction, which distilled chiefly at 208–212° C., solidified when cooled to a low temperature. Recrystallized from petroleum ether, the product melted at 203–204° C. The identity as borneol was further confirmed by oxidation to camphor melting at 175° C.

Terpineol.—The analysis and other properties of the third fraction indicated the presence of terpineol, but hydriodic acid gave a light yellow oil which did not crystallize after some time. Another portion was submitted to oxidation with chromic acid and, after end of the reaction, distilled with steam. The appearance of solid camphor in the condenser showed that the fraction contained some borneol. The aqueous residue was completely extracted with ether, which was separated, washed with sodium carbonate solution, and finally dried and evaporated. This process gave a yellow oil which soon crystallized to white granules which melted at 119° C. In all other properties this agreed with the indifferent body obtained by Wallach (1) as an oxidation product of terpineol, melting point 121–122° C.

The sodium carbonate solution from the above oxidation was acidified and extracted with ether, producing some of the indifferent body already mentioned and a small quantity of fine needles. These were identified as terebic acid which is also an oxidation product of terpineol. Attempts to prepare a phenyl urethane from the original fraction were unsuccessful, but it may be concluded that terpineol is probably present in small amounts.

The other three fractions were yellow and with odors reminding of camphor. Analyses indicated a large percentage of hydrocarbon, but no identifications could be made in any of the fractions.

Picene.—That portion of the oil boiling above 260° C. was fractionated at a pressure of 60 mm. Almost the entire residue passed over at 210–220° C. and represented about 5 per cent of the original oil. The liquid was greenish yellow and pleasantly aromatic and, when cooled in a freezing mixture for two hours, deposited a few needle-like crystals, which could not be readily separated because they dissolved again on raising the temperature slightly. A portion of the fraction was dissolved in anhydrous ether and saturated with dry hydrogen chloride. At the end of three days the solvent was allowed to evaporate spontaneously, leaving a large amount of solid which crystallized from ethyl acetate in colorless, rectangular plates melting at 133° C. Analysis of a partly purified product showed probably a trihydrochloride:

0.1065 gave 0.1370 AgCl. Found: 31.8. Calculated for $C_{15}H_{24}.3HCl$: 33.9 per cent of chlorine.

The molecular refraction, however (66.6) was somewhat too low for a monocyclic compound.

Since the boiling point and analysis of this fraction indicated the chief material as a sesquiterpene and no such compound with a hydrochloride of this melting point has before been described, we propose to designate the substance as "picene." The same substance was already found, together with cadinene, in the oil from *Tsuga heterophylla* (2). Picene has an odor like that of citronella oil and a cineol-like taste. Its specific gravity is 0.8997 at 25° C., the index of refraction at 20° C. is 1.4990, and the specific rotation in 1.4 per cent alcoholic solution is —80.33° at 25° C. It gives color reactions with acetic and sulphuric acids, similar to those of cadinene.

The Acids.—The alkaline liquid from saponification was acidified and distilled with steam. No acid was found in the distillate except a very small quantity of an oil which had the rancid odor of butyric acid. The residual liquid was made alkaline with sodium carbonate and extracted with ether, producing a crystalline paste. After purification, this became a white crystalline mass which melted sharply at 112° C., evidently a lactone.

After separation of the lactone, the sodium carbonate solution was made acid and again extracted with ether. After washing and drying the ethereal solution, the solvent was evaporated, leaving a liquid with an unpleasant odor. Distillation gave but one fraction at 220–260° C.

0.0383 gave 0.0955 CO_2 and 0.0396 H_2O. Found: C, 68.1; H, 11.4. Calculated for $C_9H_{18}O_2$: C, 68.3; H, 11.3.

This corresponds with nonylic acid, but the amount was too small to permit closer identification. From the results, it would be presumed that several other acids are present in small quantities.

SUMMARY.

The leaves and twigs of *Picea sitchensis* furnish a volatile oil to the extent of 0.059 per cent. The terpenes, which constitute more than 40 per cent, are chiefly β-pinene and β-phellandrene. Camphor and a new ketone (semicarbazone melting point 231–232° C.) are present, as also borneol and smaller amounts of terpineol. From the highest fractions was separated the hydrochloride of a new sesquiterpene, picene, whose constants are described. A lactone melting at 112° C. was isolated as saponification product. The acids appear to be chiefly nonylic acid and smaller amounts of butyric and others.

REFERENCES.

(1) Wallach, *Ann.*, 275 (1895), 151.
(2) Lehman and Lynn, JOUR. A. PH. A., 19 (1930), 843.