with about 5 cc. syrup phosphoric acid and ten to fifteen grams of active decolorizing carbon are added and the solution is stirred for a few minutes, usually by passing a current of air through it. The filtrate from the carbon should be perfectly clear and of a greenish color. . It is concentrated to about 750 cc. and 6 to 10 g. decolorizing carbon are added and filtered off, after which twice its volume of 95% ethyl alcohol is added to precipitate the remaining calcium sulfate. After filtration the solution is boiled under reduced pressure to a very thick sirup of 90–95% solids. To this sirup sufficient 95% ethyl alcohol is added to cause the sirup to be nearly saturated with alcohol after the homogeneous mixture is cooled to room temperature. The mixing of the alcohol with the very thick sirup may be accomplished by heating on the steam bath or by careful heating of the flask over a flame. The sirup must not contain so much alcohol that a separation into two liquid phases will occur when the mixture is cooled to room temperature. This saturation requires approximately 50–75 cc. ethyl alcohol. As crystallization proceeds at room temperature or lower more alcohol may be added to prevent the mass becoming too solid, but care should be taken that sirup is not precipitated. Crystallization is usually complete in from two to three hours, but the solution is ordinarily allowed to stand overnight at 0°. The crystals are filtered off in a Büchner funnel, washed with 75 and then with 95% ethyl alcohol, followed by absolute alcohol, and dried in a vacuum oven. The sugar is almost colorless, nearly pure, and the yield is 80–120 g., or 8–12%, depending upon the quality of the hulls used. Glacial acetic acid may be used for washing the crystals, and it may also be used instead of alcohol in the original crystallization. By either method the xylose crystallizes very readily. Xylose may be recrystallized so readily that it is not necessary to give accurate directions.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, U. S. DEPT. OF AGRICULTURE.]

THE OLEORESIN OF DOUGLAS FIR.

BY A. W. SCHORGER.

Received March 19, 1917.

The Douglas fir (*Pseudotsuga taxifolia* Britt.) apparently is the chief source of "Oregon balsam," which made its first appearance in commerce over forty years ago. The oleoresin is obtained mainly from natural cavities in the wood of the tree in which it has gradually collected.

Blasdale[1] appears to have first mentioned the volatile oil. He only states that the oil obtained from the "hardened natural exudation collected in Mendocino Co." (California) consisted of terpenes. In 1904,

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[1] THIS JOURNAL, 23, 163 (1901).

Rabak[1] reported on several samples of the oleoresin calling attention to the difficulty encountered in determining their authenticity. In the volatile oil pinene was identified as the principal constituent by means of the nitrosochloride and its derivatives. No additional constituents were reported. Two years later Frankforter[2] described some of the physical properties of Douglas fir "pitch" obtained by various methods. This was accompanied by a paper by Frankforter and Frary[3] in which was described the properties and derivatives of "firpene," a supposedly new terpene from Douglas fir. No mention was made of the work of previous investigators. The terpene was described as differing both physically and chemically from pure pinene. Firpene differed especially from pinene in that it did not form a nitrosochloride. It will be shown in this paper that the chief terpene present is highly active *l*-α-pinene which did not yield a nitrosochloride. Frankforter and Frary had evidently overlooked the fact previously pointed out by Tilden[4] and Kremers[5] that the yield of nitrosochloride decreases with the magnitude of the optical rotation of the hydrocarbon, frequently no nitrosochloride whatever being obtained.

Firpene as a distinct terpene is mentioned in recent chemical literature.[6] It is accordingly of interest to present the results of an examination of some authentic materials. Owing to hydration the oleoresin obtained from the heartwood of conifers invariably differs from that obtained from the sapwood in which it has been recently secreted from the living cells. Since the nature of the pitch from which "firpene" was obtained was somewhat indefinite oleoresins from both sources were examined.

EXPERIMENTAL PART.

Oleoresin from the Heartwood.

The oleoresins[7] were obtained at Carson, Washington. They were clear, amber-colored fluids, differing essentially from most coniferous oleoresins in that the resin acids show no tendency to separate in the crystalline form. Samples A and B were obtained from sound and decadent trees, respectively. The differences found were slight as will be noted in the following comparison:

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[1] *Pharm. Rev.*, **22**, 293 (1904).

[2] THIS JOURNAL, 28, 1467 (1906).

[3] *Ibid.*, 28, 1461 (1906).

[4] *J. Chem. Soc.*, **15**, 554 (1877); **85**, 759 (1904).

[5] *Pharm. Rundsch.*, **13**, 135 (1895).

[6] Abderhalden, "Biochemisches Handlexikon," VII, 328 (1912).

[7] The oleoresin was collected personally by Forest Ranger Kloe. A wind shake in a tree produces a pocket which in time fills with oleoresin. The collector, using a $^3/_4$ inch crank auger, bores a hole into the tree about 2 feet from the ground. If a pocket is struck the oleoresin soon flows out and is led into a vessel by means of a tin spout. Frequently from one to three gallons are obtained from a single boring.

Sample.	Sp. gr. at 20°.	Optical rotation. $[\alpha]_D^{24°}$.	Acid No.	Sap. No.	Volatile oil. %.	Colophony. %.	Water and losses. %.
A........	0.993	....	115.6	121.7	30.40	68.82	0.78
B........	0.989	+2.84°	114.2	120.5	28.64	69.77	1.59

Volatile Oil.

The properties of the oils after rectification with steam in presence of caustic soda were the following:

Sample.	Sp. gr. 20/15°.	$n_{D20°}$.	$[\alpha]_D^{20°}$.
A..................	0.8615	1.4688	—47.38°
B..................	0.8627	1.4690	—46.36°

Using a twelve-inch Hempel column up to a temperature of 190°, the oil distilled as follows: 155.5 to 157°, 38.46%; 157 to 158°, 22.45%; 158 to 160°, 16.03%; 160 to 165°, 7.14%; 165 to 190°, 6.56%; and 190 to 230°, 6.85%.

***l*-α-Pinene.**—Additional fractionation gave 304.4 g. (60.8%) distilling within one degree. A comparison between the firpene of Frankforter and Frary and the *l*-α-pinene obtained is given below.

	Firpene.		*l*-α-Pinene.
Boiling point..................	153–153.5°		156–157°
Sp. gr. at 20°..................	0.8598	$d_{15°}^{20°}$	0.8590
Index of refraction at 20°.......	1.47299	$n_D^{20°}$	1.4670
Optical activity $[\alpha]_D$...........	—47.2°	$[\alpha]_D^{22°}$	—47.52°

With the exception of the boiling point the similarity in physical properties between the two hydrocarbons is readily apparent. The optical rotations of the oils examined by Rabak[1] varied from $[\alpha]_D$ —34° 37′ to —39° 55′. A considerable portion (4.4%) of the oil is given as boiling below 154°, while 37.55% distilled between 154 and 156°. A plausible explanation is that the boiling points given by these investigators were not corrected. Aside from corrections for inaccuracy of the thermometer and emergent stem, the average correction for barometric pressure in this locality is about 1.5° and on occasions amounts to 2.5°.

On account of the high optical rotation of the hydrocarbon it was not expected that a nitrosochloride would be obtained. Experiment showed this to be the case. One hundred grams of the hydrocarbon were then oxidized with three liters of an 8% solution of potassium permanganate. The pinonic acid after liberation with dilute sulfuric acid was extracted with chloroform. After removing the solvent the acid distilled between 190 and 195° at 20 mm. pressure. On standing overnight about half of the pinonic acid had crystallized. The crystals were preferably freed from the liquid acid by spreading on a porous plate and letting stand for

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[1] *Pharm. Rev.*, 22, 297 (1904).

a day. After crystallization from petroleum ether, in which it is sparingly soluble, the pinonic acid melted at 68°. A solution of the acid in chloroform having a concentration of 0.03642 g. per cc. had the specific rotation $[\alpha]_D^{20°}$ —89.18°. The semicarbazone after repeated crystallization from alcohol melted at 207°, using a double bath and a Haak thermometer standardized by the Bureau of Standards. The semicarbazone began to draw away from the side of the capillary tube at about 200°. If the temperature was slowly raised to 205° and held at this temperature the crystals would melt after several seconds. The liquid pinonic acid obtained with a force filter gave a semicarbazone melting at the same temperature as that from the crystalline acid. According to the older results of Tiemann[1] the semicarbazone melts at 206–207°; Wallach[2] gives 205°; and Gildermeister and Hoffmann,[3] 204°. In the portions of the oil distilling between 159 and 168° neither camphene nor β-pinene were detected.

l-**Limonene.**—Between 168 and 178° there were collected 5% of oil having a pronounced limonene odor. The oil had the sp. gr. 0.8484 at 23° and the optical rotation $\alpha_D^{23°}$ —47.0°. A portion of the oil after dilution with ether that had been standing in contact with calcium chloride several months was saturated with hydrochloric acid gas, dried with concentrated sulfuric acid. After standing in a sealed vessel in the icebox overnight and the solvent then evaporated, a solid mass of the dihydrochloride was obtained immediately on cooling with ice; m. p. 49–50°.

l-α-**Terpineol.**—The highest boiling fraction gave no methoxy reaction and no addition product with sodium bisulfite. After acetylation in the ordinary manner the saponification number 132.3 was obtained pointing to a high alcohol content. The greater portion of the oil distilled between 115 and 120° and had the characteristic odor of terpineol. A 44% solution in alcohol had the rotation $\alpha_D^{19°}$ —10.25°. The nitrosochloride which was easily obtained melted very sharply at 116° after several crystallizations from ethyl acetate and further crystallization did not change the melting point. The melting point of the active modification of α-terpineol nitrosochloride is given as 107–108°. The nitrolpiperidine compound, crystallizing spontaneously from ether in rectangular prisms, melted normally at 152°.

Oleoresin from Living Wood.

The small sample of oleoresin available for examination was obtained by systematic scarification of the tree in the course of tapping experiments conducted by the Forest Service in California. Except for contamination with needles and other foreign matter the oleoresin had the same appearance as the samples from Washington. A yield of 22.7% of oil was

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[1] *Ber.*, **29**, 534 (1896); **33**, 2665 (1900).

[2] *Ann.*, **368**, 4 (1909).

[3] "Wallach-Festschrift," 414 (1909).

obtained having the following constants: sp. gr. at 19°, 0.8594; optical rotation $[\alpha]_D^{19^\circ}$ —22.36°. Using a three-bulb Ladenburg flask, the oil distilled as follows: 158 to 160°, 17.0%; 160 to 162°, 46.1%; 162 to 165°, 20.0%; 165 to 175°, 11.5%.

α-Pinene.—After repeated fractionation over sodium the greater portion of the oil distilled between 156 and 158°; its specific gravity at 15° was 0.8629 and optical rotation $[\alpha]_D^{23^\circ}$ —18.96°. The oil gave a good yield of nitrosochloride, m. p. 103°. However, the nitrolpiperidine compound melted at 132.5°. A second preparation from the original oil gave the same result. There was insufficient material available for oxidation to pinonic acid but further proof of the presence of pinene was obtained by formation of the nitrolbenzylamine melting at 122° and of bornyl chloride melting at 128°.

Camphene was not detected.

β-Pinene.—Twenty grams of oil distilling between 161 and 165° having the rotation $[\alpha]_D^{22^\circ}$ —26.2°, gave the characteristic crystals of sodium nopinate on oxidation with alkaline potassium permanganate. The free nopinic acid melted at 125°.

The small amount of oil distilling between 168 and 175° had a pronounced odor of limonene.

Summary.

The oleoresin from the heartwood of Douglas fir contains a volatile oil consisting chiefly of highly rotatory *l*-α-pinene with small amounts of *l*-limonene and *l*-terpineol.

The oil from the oleoresin obtained from the sapwood contained *l*-α-pinene, *l*-β-pinene and probably *l*-limonene.

The "firpene" previously described as a new terpene is evidently highly active *l*-α-pinene.

Madison, Wisconsin.

[Contribution from the Richardson Chemical Laboratory of Tulane University.]

THE USE OF POTASSIUM PERSULFATE IN THE DETERMINATION OF TOTAL NITROGEN IN URINE.

By Leonard C. Scott and Rollin G. Myers.

Received March 21, 1917.

The determination of the total nitrogen in urine by methods simpler than the ordinary Kjeldahl, has been the subject of attempts by numerous investigators. Speed and simplicity have been the main points to consider, as well as a relatively high degree of accuracy; and two, at least, of these advantages seem to have been fairly well attained in the microchemical methods of Folin and Farmer,[1] and Folin and Denis.[2] The

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[1] O. Folin and C. J. Farmer, *J. Biol. Chem.*, **11**, 493–501 (1912).

[2] O. Folin and W. Denis, *Ibid.*, **26**, 473–489 (1916).