

Quantitative studies indicated the following as being present:

Per cent of volatile substance	31.50
Per cent of ash	3.07
Per cent solubility in water	52.00
Per cent solubility in alcohol	43.10
Per cent solubility in dilute alcohol	58.00
Per cent tannin	4.83
Per cent arbutin	10.67

The tannin was determined according to the method of Löwenthal as given in "Tentative Methods of Analysis" (1930) of the A. O. A. C. (8). The arbutin was determined by the method of Zechner (7). Many of these two assays were made but are not reported here.

#### SUMMARY.

1. Fluidextract of *Uva Ursi* has been studied with respect to stability according to changes in  $p_H$ .
2. The crystalline character and solubility of the precipitate in official fluid-extracts of *Uva Ursi* have been described.
3. An insoluble gum in *Uva Ursi* has been obtained and its physical properties studied.
4. Urson has been isolated and studied.
5. The effects of menstruums upon the character of the precipitate have been shown.

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## THE WOOD OIL OF DOUGLAS FIR.\*

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The volatile oil from the wood of *Pseudotsuga taxifolia* (Poir.) Britt., commonly known as Douglas fir has been examined by various investigators. The data obtained, however, in most cases is limited to the percentage yield of the oil and a few physical constants.

Frankforter (1) in 1906 extracted from 11.6 to 42.4 per cent of pitch from the wood in which was contained approximately 22 per cent of oil. From the data submitted it was apparent that the terpenes consisted entirely of alpha pinene.

In 1912 Benson (2) steam distilled the wood and obtained a colorless oil which he

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claimed was similar to French turpentine. He also obtained what he termed a "yellow oil," which contained approximately 48 per cent of terpineol.

In the following year Beath (3) collected an oleoresin by boring into the trunk of the tree, which on steam distillation yielded 15 per cent of volatile oil. A nitrosochloride was obtained which apparently indicated alpha pinene although the author failed to give its melting point.

The oil obtained by Schorger in 1917 (4) by distilling the oleoresin from the pockets in the wood contained alpha pinene, levo limonene and alpha terpineol. Benson and McCarthy (5) also investigated the oleoresin found in the pockets of the wood. The presence of levo alpha pinene and levo beta pinene was recorded based apparently upon the physical constants of the fractions since no derivatives were reported.

#### EXPERIMENTAL.

The oil used in this investigation was obtained by steam distilling selected pieces of pitchy wood collected during the autumn of 1935. From 40 pounds of fresh material there were obtained 675 cc. of oil which corresponded to a yield of 3.29 per cent.

The physical constants were determined in the usual manner  $d_{20} 0.8968$ ;  $n_D^{20} 1.4773$ ;  $[\alpha]_D^{23} -41.50^\circ$ ; saponification number 2.3; acid number 1.6; ester number, calculated 0.7; per cent ester (calculated as terpinyl acetate) 0.1; saponification number after acetylation 99.0; per cent of total alcohol (calculated as terpineol) 28.9; per cent of free alcohol (calculated as terpineol) 28.7.

*Free Acids.*—Extraction of 50.0 cc. of oil with a 5 per cent aqueous solution of sodium carbonate yielded 1.955 Gm. of a brown viscous liquid which was strongly acid to litmus and possessed a decidedly pungent odor. Steam distillation of the residue resulted in the formation of an aqueous distillate on the surface of which floated a small amount of oily material. Several unsuccessful attempts were made to positively identify constituents in both of the layers of distillate, although the odor of the oily residue suggested the possible presence of at least traces of higher fatty acids such as caproic, caprylic, capric or lauric.

*Phenols.*—Extraction with a 5 per cent aqueous solution of sodium hydroxide yielded 0.1911 Gm. of dark brown residue which corresponded to 0.04 per cent of original oil. The residue did not respond to any of the general tests for phenols.

*Fractionation.*—The remaining oil which totaled 472 cc. was next subjected to fractional distillation at 25-mm. pressure. As a result of this fractionation the oil was divided into two parts, that which boiled below 100° C. and a higher boiling fraction which distilled above 100° C. The low boiling portion which amounted to 251 cc. and represented 50 per cent of the total oil was subjected to several refinements.

Fraction No.	Boiling Point at 25 Mm.	Amount.	Sp. Gr. at 20° C.	$n_D^{20}$	$[\alpha]_D^{23}$	Color.
I	60-72° C.	140 cc.	0.8590	1.4732	-52.70°	Colorless
II	72-75	35	0.8613	1.4762	-57.58	Colorless
III	75-82	28	0.8597	1.4793	-61.64	Colorless
IV	82-100	42	0.8624	1.4836	-53.33	Colorless

*Levo Alpha Pinene.*—A portion of the first fraction was oxidized by means of an 8 per cent aqueous solution of potassium permanganate according to the method of Tiemann and Semmler (6). The semicarbazone of pinonic acid was prepared in the usual manner by treating the residue resulting from the oxidation, with semicarbazide hydrochloride. The purified semicarbazone melted at 204° C., and thereby identified the fraction as consisting of alpha pinene.

*Levo Camphene.*—The first fraction, in addition to alpha pinene, contained a relatively large quantity of camphene. A portion of the fraction was hydrated according to the method of Bertram and Walbaum (7), which was modified to the extent that the non-hydrated oil was removed from the mixture. Saponification of the hydrated oil resulted in the formation of iso-

borneol, which when purified melted at 201° C. The phenylurethane derivative of the alcohol melted at 135° C. The identification, therefore, of isoborneol served to indicate the presence of camphene.

*Levo Limonene.*—Both the third and fourth fractions yielded a tetrabromide when brominated according to Wallach's method (8). The purified limonene tetrabromide melted at 101° C.

*Saponification of the Higher Boiling Portion.*—The higher boiling oil was saponified by heating with alcoholic potassium hydroxide. The saponified oil was washed, dried and subjected to fractional distillation, whereupon the following fractions were obtained:

Fraction No.	Boiling Point at 16 Mm.	Amount.	Sp. Gr. 20° C.	$n_{D}^{20}$	$[\alpha]_{D}^{20}$	Color.
I	100–125° C.	161 cc.	0.9417	1.4889	–42.83°	Yellowish
II	125–150	1	0.8620	1.5068	–3.80	Yellow
III	150–200	8	0.8880	1.5204	–78.07	Amber
IV	200 and over	4	....	....	....	Tarry residue

*Levo Alpha Terpineol.*—The first fraction which distilled between 100° and 125° C., and represented approximately 92 per cent of the higher boiling portion of the wood oil was examined for terpineol according to the method of Wallach (9). The nitrosochloride which melted at 113° to 114° C. identified alpha terpineol as being the chief if not the sole constituent of the fraction.

*Fraction II.*—No attempts were made to identify the second fraction because of the small amount.

*Fraction III.*—The third fraction probably consisted of a sesquiterpene although no derivatives could be prepared.

*Fraction IV.*—This last portion possessed a burnt odor which indicated decomposition, hence no attempt was made to identify its components.

*Combined Acids: Acetic Acid.*—Acidification and steam distillation of the potassium hydroxide solution resulting from the saponification produced an aqueous distillate upon the surface of which there floated a small amount of insoluble material. Since no silver salt could be prepared from the insoluble distillate it was assumed that it did not consist of acids. The aqueous portion was made alkaline and evaporated to dryness. The residue obtained responded to the general qualitative tests for acetic acid.

#### SUMMARY.

The wood yielded 3.29 per cent of volatile oil which consisted of 50 per cent of terpenes and 32.2 per cent of an alcohol together with smaller amounts of probable sesquiterpenes. The oil contained about: 30 per cent levo alpha pinene; 6 per cent levo camphene; 14 per cent levo limonene; 32.2 per cent levo alpha terpineol, present almost entirely as the free alcohol; a small amount of higher boiling constituents probably sesquiterpenes. Acetic acid was present in the combined state.

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