

—17.02 to —22.17°; acid number, 0.65–1.10; ester number, 11.13–24.25; ester number after acetylation, 27.50–51.78; ester as bornyl acetate, 3.91–8.49% (mean 6.1%); free alcohol as borneol, 4.56–8.46% (mean 6.5%). The initial boiling point of the oil was 157.3°, 2.5% distilling below 160°, 73.5% between 160 and 170°, and 7.5% between 170 and 180°.

Furfural.—The first fraction was shaken out with water and the aqueous extract tested by the aniline-hydrochloric acid method. A deep rose-red color characteristic of furfural was obtained.

α-Pinene.—By repeated fractionation, 151 grams of oil (25.2%) were obtained between 156–160°. From a fraction, b. p. 156–157°, $d_{15} = 0.8682$, $\alpha_{D22} = -11.94^\circ$, pinene nitrosochloride, m. p. 103°, was easily prepared; its nitropiperidine melted at 118°.

Only 28.8 grams (4.8%) of oil boiled, finally, between 160 and 162°. Camphene could not be detected by either the method of Bertram and Walbaum¹ or the method of Balbiano and Paolini.² Brandel and Sweet³ state that they detected camphene by the latter method.

β-Pinene.—The β -pinene fraction, b. p. 160–170°, amounted to 288 grams (48%). This distilled mainly between 164–167°. A fraction, b. p. 164–166°, $d_{15} = 0.8720$, $\alpha_{D22} = -17.19^\circ$, was oxidized with alkaline $K_2Mn_2O_8$ and a large yield of sodium nopinate obtained. The free nopinic acid melted at 126°.

Dipentene.—Two fractions were collected as follows: (1) Weight 17.2 grams (2.9%), b. p. 170–172°, $d_{15} = 0.8628$, $\alpha_{D25} = -28.12^\circ$. (2) Weight 15.6 grams (2.6%), b. p. 172.6–178.2°, $d_{15} = 0.8616$, $\alpha_{D25} = -26.24^\circ$. Fraction 1 readily yielded a dihydrochloride, melting sharply at 50° after several crystallizations from alcohol. Ten cc. of fraction 2 were dissolved in glacial acetic acid and treated with bromine. After standing in the ice box 20 days, about 0.2 gram of tetrabromide was obtained. After two crystallizations from ethyl acetate it melted at 117–119°, and after a third crystallization, at 121–2°. From the melting points of the tetrabromide and rotation of the fractions, it is very probable that both limonene and dipentene are present.

Borneol.—The oil recovered from the saponified ester fraction boiled between 208 and 231°. The fraction, b. p. 208–213°, $\alpha_{D26} = -19.42^\circ$ would not yield solid borneol by cooling to —15°, nor was camphor isolated by direct oxidation with chromic acid mixture. The borneol fractions were finally heated with an equal weight of phthalic anhydride for eight hours. The acid phthalic ester was converted into the sodium salt and extracted repeatedly with ether. The aqueous solution of the sodium phthalic ester was now saponified and the oil obtained oxidized with chromic

¹ *J. prakt. Chem.*, **49**, 1 (1894).

² *Ber.*, **36**, 3575 (1903).

³ *Loc. cit.*

acid mixture. By steam distillation camphor was recovered, melting at 174° after crystallization from petroleum ether and sublimation.

Acetic Acid.—The acids obtained from the saponification of the ester were neutralized with caustic soda and treated with AgNO_3 . Five fractional precipitates were collected, containing 62.98–63.17% Ag without further purification. It is very probable that only acetic acid is present, since silver propionate requires 59.91% Ag, silver acetate 64.64% Ag, and silver formate 70.59% Ag. For further confirmation the silver salts were recrystallized from water and analyzed as follows: 0.1970 gram silver salt gave 0.1266 gram Ag = 64.26% Ag.

"Green Oil."—After removal of the esters, 14.5 grams of oil distilled between $125\text{--}151^{\circ}$ at 20 mm. and 6.5 grams between $151\text{--}205^{\circ}$ at 20 mm., $d_{20} 0.9370$. The first fraction was colored pale greenish yellow and the second deep green. No solid derivatives could be obtained from either fraction. The following color reactions were obtained for the "green oil." A drop dissolved in acetic anhydride and treated with a drop of H_2SO_4 produced a deep blue color, changing to green; when glacial acetic acid was used in place of acetic anhydride the solution turned crimson, and on standing two hours became purple; a glacial acetic acid solution of the oil treated with bromine vapors became first purple, then ammoniacal copper blue.

Summary.

The constituents of the leaf oil of Douglas fir with their approximate percentages are as follows:

Constituent.	Percentage.
1- α -Pinene.....	25
1- β -Pinene.....	48
<i>i</i> or <i>l</i> -Limonene.....	6
Furfural.....	..
Ester as bornyl acetate.....	6.1
Free alcohol as borneol.....	6.5
"Green oil".....	3.0
Losses by polymerization.....	5.0

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STUDIES ON ENZYME ACTION. VIII. A CONTINUATION OF THE STUDY OF THE ACTION OF AMINO ACIDS AND CASTOR BEAN LIPASE ON ESTERS.

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I. Introduction.

For a long time many enzymes have been considered to be protein in character, and this supposition holds well in the case of the castor bean