

T H E S I S

on

An Investigation of the Oil from the Wood of
Port Orford Cedar (*Chamaecyparis Lawsoniana*)
with Special Reference to the Fraction Boil-
ing Between 200° C. and 230° C.

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Port Orford Cedar (*Chamaecyparis Lawsonia*) from which the oil is obtained, is found in southwestern Oregon and northwestern California, known as the Coos Bay region. There are no pure stands of this timber, yet it is estimated that at the present rate of cutting, this stand will last fifty or sixty years. The Port Orford Cedar is the only tree on the Pacific Coast that carries a large per cent of oil in the wood. This oil can be obtained with very little expense as a by-product from sawmill waste. If some commercial use can be developed for this oil, it will mean another large industry for the State of Oregon.

Some of the sawmills located at Marshfield, Oregon cut Port Orford Cedar exclusively. The sawdust from one of these mills is conveyed to three large vats where it is steam distilled. The oil, being volatile in steam, distills over with it. On condensing, the oil separates out and floats on top of the water. After filtration, the oil is clear and slightly yellow in color, the yield being about 1.6 per cent. By using three vats the process is made continuous; while one vat is being filled, another is being steam distilled, and the third is being emptied.

The first analysis of the oil was published by Schorger (1914).¹ This oil was distilled from select

resinous pieces of wood, therefore the yield of oil, which was 10 per cent, was much larger than that obtained at the plant from the sawdust. Schorger's analysis showed the oil to contain the following:

D-alpha-pinene.....	60-61 per cent
Dipentene.....	6-7 per cent
Free l-borneol.....	11 per cent
Ester as bornylacetate.....	11.5 per cent
Cadinene.....	6-7 per cent
Losses.....	5 per cent

The second analysis of the Port Orford Cedar wood oil was published by F. H. Thurber and L. J. Roll, (1927).² The results differ in some of the percentages from the analysis by Schorger, the difference being due to the type of wood from which the oil was obtained. Using practically the same procedure that Schorger used, Thurber and Roll published the following results:

D-alpha-pinene.....	45.7 per cent
D-limonene.....	3.2 per cent
D-borneol.....	26.0 per cent
D-cadinene.....	21.0 per cent
L-cadinol.....	3.9 per cent

The d-borneol reported in the original oil is not all free borneol as about half of it is borneol acetate which can be easily converted into free borneol accord-

ing to Schorger.

The writer took a fresh sample of the oil obtained from the sawdust and following the methods published by Thurber and Roll went through the analysis. The same percentages, as to boiling points, were obtained as reported by them. The pinene fraction was identified by the pinene hydrochloride. Limonene fraction treated with HCl gas also yielded a crystalline product identified as dipentene dihydrochloride. The attempt to identify free borneol in the amounts reported was a failure. The cadinene was treated with HCl gas and the dihydrochloride was obtained.

The only fraction of the oil that has a ready market is borneol, so our efforts were turned to obtaining free borneol. Repeated failures by the writer to obtain more than a fraction of one per cent of free borneol led to the belief that this fraction of the oil was not all borneol.

The Port Orford Cedar wood oil is very reactive to HCl gas. A solid crystalline product can be obtained from every fraction of the oil except that boiling between 200° C. and 230° C. There is no mention in the literature of this fraction being treated with HCl gas, so the writer investigated this reaction. The

oil darkened and the specific gravity increased from 0.9289 to 1.0323 and water split off.

EXPERIMENTAL WORK

The original cedar oil was distilled under atmospheric pressure up to a temperature of 180°C . to remove the lower fractions. The remainder was distilled under 13 mm pressure, as high temperature seems to decompose the oil. The fraction boiling at 104° - 107°C ., 13 mm pressure, was collected which corresponds roughly to 205° - 215°C . at atmospheric pressure and amounts to about 10% of the original oil.

Of this oil, 250 cc were placed in a small flask and packed in ice, and dry HCl gas bubbled through it. After about six hours the oil was saturated with the gas. The oil was transferred to a separatory funnel and 6 cc of water removed. The oil was then warmed over a water bath until the odor of HCl gas had disappeared. The specific gravity was 1.0323 while that of the oil before treating with HCl was 0.9289. The oil was dark red in color and more viscous and an attempt to freeze out some crystals gave no results. Distillation of a small part of the oil at atmospheric pressure gave no results as there was no definite boiling point so the remaining oil was distilled under 13 mm pressure.

A small amount of water came over at first, then the temperature rose rapidly to 95°C ., at which

temperature a white solid appeared in the distillate and at 98° C. the solid stopped appearing. The temperature dropped to about 70° C. and did not rise until more heat was applied, then it rose rapidly to 105° C. and a clear oil came over which was the same as the original oil before treating with HCl gas.

The fraction with the white solid was cooled to -10° C. and then filtered by suction to remove the solid. It was sucked as dry as possible and re-crystallized from hot alcohol. The crystals were thin, flat, flaky and white with the melting point of 197.8° C. and had a camphor-like odor.

Observed melting point.....	191.5° C.
Stem correction 180(191-30).000154....	+ 4.5° C.
Calibration correction.....	<u>+ 1.8° C.</u>
	197.8° C.

The molecular weight was determined by the freezing point method using benzene as a solvent. The first determination gave 154 as the molecular weight and the second trial gave 160. The last run was made three hours after the first and the same materials used. The difference may be due to the fact that some benzene evaporated and that would tend to increase the molecular weight.

$$m = 1000 K_f \frac{g}{G \cdot dT}$$

$$\text{1st Trial} = 1000 \times 5.12 \frac{.2043}{25 \times .899 \times .302} = 154.1$$

$$\text{2nd Trial} = 1000 \times 5.12 \frac{.2043}{25 \times .899 \times .290} = 160.5$$

One gram of the crystals were oxidized, using nitric acid. The resulting compound was camphor which melted at 170° C. because it was not pure.

The melting point, molecular weight, the odor of the crystals, and the fact that it can be oxidized to camphor, proves it to be borneol.

The following table shows the temperature range and the corresponding volume range of the oil treated with HCl gas:

Up to 40° C. at 13 mm.....	8 cc
40° to 90° C. " " ".....	1 cc
90° to 95° C. " " ".....	11 cc
95° to 98° C. " " ".....	6 cc
98° to 101° C. contained crystals...	40 cc
101° to 105° C. at 13 mm.....	61 cc
105° to 110° C. " " ".....	88 cc
110° to 120° C. " " ".....	0 cc
120° to 125° C. " " ".....	12 cc
Residue.....	<u>23 cc</u>
Total.....	250 cc

The results of this research show that the Port Orford Cedar wood oil contains free borneol, but in very small amounts, about one tenth of one per cent. The borneol was also obtained without combining it with some other compound and subsequently freeing it. Just what the action of the HCl gas had on the oil has not been determined, but it did change the oil in such a way that the borneol separated out on distillation, which we have never succeeded in doing before.

The HCl gas split off 8 cc of water and it came from some other source than the borneol because HCl gas will not react with borneol under the conditions of the experiment. The chloride must be contained in the fraction that boiled above 110°C . at 13 mm since the oil used did not boil over 108°C . The possibility of it being in the fraction that came over with the crystals is small since the specific gravity of this fraction was very little more than the original oil.

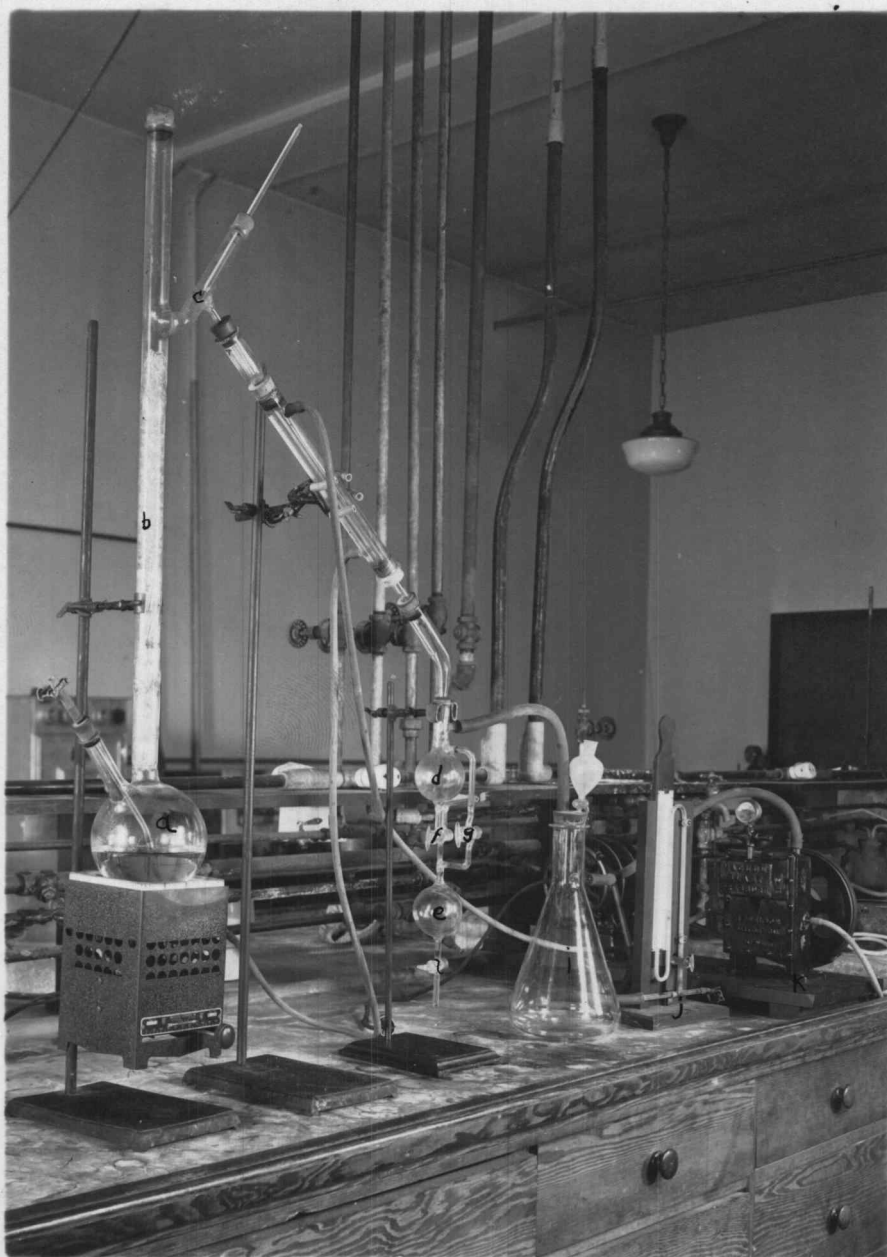
Further research is necessary to determine what alcohol is reacted upon by the HCl gas and the other constituents present if any. It has been proven that the analysis of this fraction published in the literature is incorrect.

Description of Apparatus Used for Fractional
Distillation Under Reduced Pressure:

The distilling flask used was designed and made by Dr. Floyd E. Rowland for the purpose of fractionating oils.

Flask (a) is a one liter flask with a small side neck that can be used for a thermometer or for a capillary tube to prevent bumping. The column (b) is 28 mm in diameter and 50 cm from the top of flask to the side neck (c), then 15 cm to the top of column. A thermometer can be placed in this top part or a small test tube condensor can be used that will extend down to the top of the side opening. If a condensor is used, it gives a much sharper fractionation. The column is packed with short pieces of glass tubing. A thermometer is placed in the side neck (c) to obtain the temperature of the vapors distilling over. The distillate is collected in (d) which is cut off from (e) by two stopcocks (f) and (g). When the desired fraction is obtained or a cut is wanted, keep stopcocks (f) and (l) closed and open (g). This lets the small volume of air contained in (e) into the system but it is not enough to change the vacuum. Then (f), which is a two-way stopcock can be turned so that the liquid

will run down into (e), close (g) and turn (f) to the position that will let the air in to make (e) atmospheric pressure, then the oil can be drained thru (l). The large flask (i) is for the purpose of furnishing a large vacuum space to take care of any small fluctuation in pressure, (j) is a mercury manometer and (k) is a vacuum pump.



BIBLIOGRAPHY

- (1) Journal of Industrial and Engineering Chemistry, Vol. 6, p. 631 (1914).
- (2) Journal of Industrial and Engineering Chemistry, Vol. 19, p. 739 (1927).