THE ESSENTIAL OIL CONTENT OF THE
CHAMAECYPARIS NOOTKATENSIS

BY

COLIN CAMERON LUCAS
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CHAMAECYPARIS NOOTKATENSIS

Chamaecyparis nootkatensis is one of the evergreen trees native to British Columbia. Indeed, it is not found native elsewhere since its occurrence is confined to the Pacific Slope from Alaska to Northern Oregon. Around Vancouver the tree is commonly called yellow cedar, or cypress, to distinguish it from the giant cedar (Thuja plicata), known locally as red cedar. Owing to the confusion arising from the diversity of common names for the same tree, the correct generic and specific names have been determined, and these will be used in preference to local names which vary in different parts of the world. The Chamaecyparis nootkatensis (Lamb) Spach. is variously known as yellow cedar, cypress, yellow cypress, Alaska cedar, Alaska cypress, Sitka cypress, and Nootka Sound cypress.

THE TREE AND ITS ECONOMIC IMPORTANCE

The tree grows on the west slopes of the Pacific Coast range and on the islands along the coast. In the vicinity of the Straits of Georgia it seldom grows below 2000 feet elevation, but in Alaska it is found from tide water to the timber line.

(1) Forests of British Columbia. H.H. Whitford & R.D. Craig
It occurs as a distinct "Yellow Cypress Type," in which it is the predominating tree, with some mountain hemlock (Tsuga Mertensiana) and other species in mixture. Numerous stands of this species occur throughout the coastal regions, but only a small percentage can be considered merchantable at the present time as they consist largely of small poles and have a very light volume per acre. The merchantable stands occur in patches usually less than 20 acres, and seldom more than 100 acres, in extent; here the trees range from 18 to 60 inches in diameter and 75 to 100 feet high.

The Chamaecyparis nootkatensis is often mistaken for the Western Red Cedar (Thuja plicata) on account of the resemblance of the foliage (scale-like leaves) and bark. It is a smaller tree, however, usually growing from 80 to 125 feet in height, with an average diameter of less than 30 inches. In the more northern regions, and where the tree is in an exposed situation, a low, scraggly form is found, whence the name -- from the Greek "Chamaï," on the ground, and "Kyparissos", a cypress. In the south of the province the trunk of the tree is usually pillar-like, being clear of branches for about the first 60 feet. All the branches droop more or less and the terminal branches hang down giving the crown as a whole a drooping appearance. The cones are six-sided, almost spherical in shape, less than one half inch in diameter, and when green are covered with a glaucous white
bloom. When ripe they are reddish brown in color. The wood is creamy to light sulphur-yellow in color, and is exceedingly fine grained, resembling in appearance and properties the Port Orford Cedar (Chamaecyparis Lawsoniana) of Oregon, U.S.A. It is the hardest wood of any of the so-called North America Cedars, and is comparatively heavy for its class (29 lbs. per cubic foot kiln dried). The wood is tight, stiff and strong, has a good figure, is easily worked and takes a good polish. It has a characteristic pungent odour caused by the oil in the wood. This oil prevents the use of ordinary stains, but lumber stained with an acid stain and then varnished is as beautiful a finished wood as can be found. Since the wood is practically unaffected by changes in moisture it is in great demand by local boat builders. Lately it has been tested out as a battery separator wood, and the Prest-O-Lite Company of Canada, after service tests, place it second only to Port Orford cedar for that purpose. It is very durable in contact with soil, is not attacked by the South African red ant, nor Japanese white ant, and is much less susceptible to attack by teredos than fir or spruce. The wood apparently contains in the oil some valuable preservative constituent. Yellow cedar wood is used to make chests and wardrobes in which to store furs, etc., as moths and other insects will not come near the wood of this cedar. "Cedar chests" made from the wood of Thuja plicata (the western red cedar) are practically valueless
in this regard. On account of its creamy colour and straight fine grain this wood is used a great deal in ornamental and fancy inlay work. It has recently found favour as a wood for panels and general interior finishing purposes.

Yellow cedar is not very well known on the market, the uncertainty of supply being a great drawback. Eighty to one hundred and fifty dollars per thousand board feet is the rate at the local mills for clear lumber. Local use indicates that it is entitled to be classed among the more valuable woods of Canada, rather than among the general construction woods.

PREVIOUS WORK

No work has been reported on the oil of the Chamaecyparis nootkatensis. In 1914 W.A. Schorger at the University of Wisconsin, in co-operation with the Forest Products Laboratory, Forest Service, United States Department of Agriculture, examined the oil from the wood of a tree of the same genus, Chamaecyparis Lawsoniana, (the Port Orford cedar), and found steam distillation of the wood to give a 10% yield of oil. (2) The properties of this oil were as follows: $d_{20}^\circ = 0.8905$, $n_{D}^1 = 1.4758$, acid value 0.30, ester value 32.8. On distillation 67.5% of the oil came over between 155° and 180°.

(2) Journ. Ind. Eng. Chem. 6(1914), 631
28.5% between 100° and 190° at 15 mm pressure, and 4% was lost by polymerization. The oil was shown to consist of α-pinene, dipentene, free borneol and its acetic, formic and caprinic esters, and in the high boiling fractions cadinene was found. The oil from the leaves was not investigated.

SOURCE OF THE OIL INVESTIGATED

During the fall of 1924, 85 lbs. of twigs were collected from trees growing on Grouse Mountain (at 3800') and Hollyburn Ridge (at 3400'). These were air-dried for about one week, and then steam-distilled without pressure. Fifty-six pounds of air-dried leaves gave 205 cc. of crude oil, or a yield of about 0.7%.

With this oil a preliminary investigation was made to determine the approximate composition of the leaf oil and then a larger amount of material was obtained as described below.

Some sawdust of the Chamaecyparis nootkatensis was also steam distilled, and a dark red blood-coloured oil was obtained.

A tree 5 feet in diameter and 800 - 1000 years old was felled on November 1. On November 26th. the log was sawn up, and 22 lbs. of coarse sawdust (from the butt log) were obtained. This was steam-distilled on December 1. The wood was not in salt water at any time. During the first hour of
24 cc. of oil came over, during the first 10 hours a total of 70.5 cc., and after 18 hours a total of 85.5 cc.
The oil collected during the first 10 hours had d₂₀° 0.9452. The last 15 cc. of oil were very dark-coloured and quite viscous. When they were added to the oil the density at 20° was 0.9544. The saponification value was 10.2. Some fine sawdust (58 lbs.) was obtained from wood which had been kilndried, in order to compare the yields. This sawdust gave 255 cc. of oil, with d₂₀° 0.9550, or a yield of 0.93%, compared to 0.81% in the case of the coarse sawdust. The wood oil is at present being examined.
<table>
<thead>
<tr>
<th>NO.</th>
<th>DATE OF COLLECTION</th>
<th>TIME TILL DIST'N</th>
<th>WT. IN KGM</th>
<th>% LOSS</th>
<th>VOL.</th>
<th>YIELD</th>
<th>D2O</th>
<th>S.V.</th>
<th>S.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>GREEN</td>
<td>DRY</td>
<td>(CRUDE)</td>
<td>DRY</td>
<td>GREEN</td>
<td>CRUDE</td>
<td>CRUDE</td>
</tr>
<tr>
<td>1</td>
<td>April 17</td>
<td>15 days</td>
<td>---- 16.5</td>
<td>------ 89 cc</td>
<td>0.48</td>
<td>------</td>
<td>0.8880</td>
<td>21.4</td>
<td>46.4</td>
</tr>
<tr>
<td>2</td>
<td>April 100</td>
<td></td>
<td>---- 15(?)</td>
<td>------ 305</td>
<td>1.7(?)</td>
<td>------</td>
<td>0.8628</td>
<td>13.0</td>
<td>22.8</td>
</tr>
<tr>
<td>3</td>
<td>Aug. 6</td>
<td>39</td>
<td>---- 8.85</td>
<td>------ 125</td>
<td>1.22</td>
<td>------</td>
<td>0.8633</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>&quot;</td>
<td>15</td>
<td>---- 9.05</td>
<td>------ 206</td>
<td>1.95</td>
<td>------</td>
<td>0.8595</td>
<td>10.35</td>
<td>19.8</td>
</tr>
<tr>
<td>5</td>
<td>Sept. 7</td>
<td>15</td>
<td>8.15 6.35</td>
<td>22% 119</td>
<td>1.61</td>
<td>1.25</td>
<td>0.8577</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>6QD</td>
<td>&quot;</td>
<td>12</td>
<td>9.1     6.8</td>
<td>25% 126</td>
<td>1.58</td>
<td>1.18</td>
<td>0.8553</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>6A</td>
<td>&quot;</td>
<td>12</td>
<td>5.2     5.0</td>
<td>4% 37</td>
<td>0.84</td>
<td>0.61</td>
<td>0.8664</td>
<td>17.85</td>
<td></td>
</tr>
<tr>
<td>6B</td>
<td>&quot;</td>
<td>12</td>
<td>4.5     4.3</td>
<td>4.5% 42</td>
<td>0.94</td>
<td>0.80</td>
<td>0.8589</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6C</td>
<td>&quot;</td>
<td>12</td>
<td>4.5     4.2</td>
<td>6.7% 42</td>
<td>0.86</td>
<td>0.80</td>
<td>0.8597</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6D</td>
<td>&quot;</td>
<td>12</td>
<td>4.5     3.65</td>
<td>19% 30</td>
<td>----</td>
<td>----</td>
<td>0.8710</td>
<td>27.65</td>
<td></td>
</tr>
<tr>
<td>6E</td>
<td>&quot;</td>
<td>12</td>
<td>5.4     4.1</td>
<td>24% 58</td>
<td>1.21</td>
<td>0.92</td>
<td>0.8603</td>
<td>20.1</td>
<td></td>
</tr>
<tr>
<td>6$D</td>
<td>&quot;</td>
<td>12</td>
<td>9.1     ----</td>
<td></td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7A</td>
<td>Oct. 10</td>
<td>24</td>
<td>5.9     3.3</td>
<td>44% 43</td>
<td>1.12</td>
<td>0.63</td>
<td>0.8623</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>24</td>
<td>7.05    4.65</td>
<td>34% 8.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>24</td>
<td>2.4     1.35</td>
<td>43% 9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10A</td>
<td>Nov. 9</td>
<td>19</td>
<td>6.35    3.65</td>
<td>42.5% 74</td>
<td>1.75</td>
<td>1.00</td>
<td>0.8612</td>
<td>13.35</td>
<td></td>
</tr>
<tr>
<td>10B</td>
<td>&quot;</td>
<td>9</td>
<td>6.35    4.77</td>
<td>25% 72</td>
<td>1.32</td>
<td>0.99</td>
<td>0.8621</td>
<td>13.55</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Dec. 3</td>
<td>28</td>
<td>6.8     3.4</td>
<td>50% 25</td>
<td>0.64</td>
<td>0.32</td>
<td>0.8764</td>
<td>26.95</td>
<td></td>
</tr>
</tbody>
</table>
THE INVESTIGATION OF THE LEAF OIL

COLLECTION

Leaves were collected from mountains to the north of Vancouver at irregular intervals for over a year, in order to investigate any seasonal changes in the nature of the oil. It was found that different methods of drying the leaves caused greater changes in the oil than did changing seasons. During the summer and autumn months the crude oil was always of a pale brown colour and had a density at 20° of about 0.860. During the winter and spring months the yields were poorer, the oil was very dark coloured and the density was greater. (See Table 1.)

The leaves were collected at altitudes of 1800' to 3800' on Grouse Mountain and Hollyburn Ridge, north of Vancouver. Small branches were removed from the trees and these were stripped by hand, only the green leaves being retained. These leaves were tightly packed in sacks, and generally about forty-eight hours elapsed before they were spread out to dry.

DRYING

At first the leaves were dried by hanging up in loose sacks for several weeks. They were weighed when dry and then distilled. Later it was decided to investigate the effect of drying on the nature and yield of oil obtained, since a batch of leaves collected in April and not distilled until August
gave an astonishing yield of oil. (Oil No.2, Table 1). This very high yield may have been caused by one or several of the following:

1. Improper, or insufficient distillation of previous batches of leaves.
2. Greater dessication of the leaves.
3. Production of oil in the twigs on standing, giving increased oil content with increasing time between collection and distillation.

An investigation of distilling conditions (see page 11) showed that the leaves previously distilled had had all the oil extracted, so the problem of the effect of drying was next looked into. One hundred pounds of leaves were collected (#6) and divided up into two twenty-pound portions, and the remainder into ten-pound portions. One twenty pound lot was dried on a screen in the sun. In ten days it lost five pounds in weight; the leaves were dry and brittle, and as they seemed to be at constant weight they were distilled. The other twenty pound portion was tied up loosely in a sack. It took 80 days to lose 5 lbs., but owing to an accident, the oil was lost during distillation so the yield could not be determined. The rate of drying of the ten pound portions, and yields of oil are as follows:
Since all these leaves were collected at the same place, at the same time, and treated alike, the yield on the green weight should be alike in each case if there is no oil production on standing, yet we find a regular increase in the yield. Hence, the longer the leaves stand after collection, the greater the yield of oil on distillation. That this is not due to drying alone is shown by considering 6E and 6Qd, both of which lost 25% in weight on drying yet gave different yields. From this we see that slow drying causes an increased yield of oil, but quick, drastic drying gives much higher yields for the same amount of drying.

Some leaves had been dried on a rack several feet above a furnace. It was feared that the warm, dry air might have caused some volatilization of oil before distillation, but this was shown not to be the case. A 28 lb. portion of leaves (#10) was divided into two equal portions. One was dried for 14 days above the furnace, yielding 74cc. of oil. The other was dried for 21 days on a screen just off the

---

TABLE 2.

<table>
<thead>
<tr>
<th>OIL</th>
<th>TIME DRYING</th>
<th>LOSS IN WT.</th>
<th>YIELD</th>
<th>DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6A</td>
<td>12 days</td>
<td>3.85%</td>
<td>0.61%</td>
<td>0.64%</td>
</tr>
<tr>
<td>6E</td>
<td>21</td>
<td>4.45</td>
<td>0.80</td>
<td>0.86</td>
</tr>
<tr>
<td>6C</td>
<td>32</td>
<td>6.66</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>6D</td>
<td>45</td>
<td>18.9</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>6E</td>
<td>81</td>
<td>25.0</td>
<td>0.92</td>
<td>1.21</td>
</tr>
<tr>
<td>6QD</td>
<td>20</td>
<td>25.3</td>
<td>1.18</td>
<td>1.58</td>
</tr>
</tbody>
</table>
floor, yielding 72cc. Quick drying does not appear to volatilize the oil.

**DISTILLATION**

Ten to fifteen pound portions of leaves were placed on the perforated platform of an autoclave connected to a long water-cooled condenser, and steam was passed through them for about ten hours. The steam was condensed and the oily layer was removed from the surface of the water in the receiver.

The oil comes over fairly rapidly for the first three or four hours, but after that the rate usually falls off. With ten pounds of leaves in the still, four hours distillation gave 51.5cc, 3-1/4 hours longer gave 7cc more and 3 hours longer gave 9cc, but this last portion was very dirty and probably only about 5cc. was actually oil. The rate (no. of cc. per hour) for these three periods is, therefore, 12.9, 2.2, 1.7, showing a rapid decline. Another 10 pound portion gave the following figures:

<table>
<thead>
<tr>
<th>Duration</th>
<th>Volume</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1/4 hrs.</td>
<td>36 cc.</td>
<td>8.4</td>
</tr>
<tr>
<td>2-1/2 hrs. longer</td>
<td>12 cc.</td>
<td>4.8</td>
</tr>
<tr>
<td>8-1/4 hrs.</td>
<td>10 cc.</td>
<td>1.2</td>
</tr>
</tbody>
</table>

And yet another:

<table>
<thead>
<tr>
<th>Duration</th>
<th>Volume</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>First 2 hrs.</td>
<td>35 cc.</td>
<td>17.5</td>
</tr>
<tr>
<td>2-3/4&quot; longer</td>
<td>30.5 cc.</td>
<td>11.1</td>
</tr>
<tr>
<td>8 &quot; &quot;</td>
<td>38 cc.</td>
<td>4.75</td>
</tr>
<tr>
<td>3-1/2&quot; &quot;</td>
<td>2 cc.(dirty)</td>
<td>0.57</td>
</tr>
</tbody>
</table>
These examples suffice to show that with the apparatus used, over 80% of the oil comes over inside of 8 hrs. with continuous distillation. To ensure complete distillation, each batch was treated for at least twelve hours, and usually longer.

TREATMENT OF THE OIL

After steam-distillation had driven the oil out of the leaves, the liquid in the receiver was transferred to a separating funnel and the water was run off from the oil. The volume of the crude oil was noted and each batch was kept in dark glass bottles with ground glass stoppers.

Before beginning to work on the oils they were filtered through filter paper to remove particles of dirt and then they were dried for a week over anhydrous sodium sulphate. They were then filtered again, and the physical and chemical constants determined for each oil. The oils were then distilled at reduced pressure and the values were re-determined in order to see what effect distillation had on the oil. (See table 3).
TABLE 3.

<table>
<thead>
<tr>
<th>OIL NO.</th>
<th>DENSITY AT 20°</th>
<th>SAPONIFICATION VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CRUDE</td>
<td>DISTILLED</td>
</tr>
<tr>
<td>1</td>
<td>0.8880</td>
<td>0.8728</td>
</tr>
<tr>
<td>2</td>
<td>0.8628</td>
<td>0.8611</td>
</tr>
<tr>
<td>4</td>
<td>0.8595</td>
<td>0.8576</td>
</tr>
</tbody>
</table>

These figures show that there is practically no change in the oil during distillation.

PHYSICAL CONSTANTS

The density of the oils was determined by means of a specific gravity bottle of 10cc. capacity; all determinations were made at 20°. The density of the crude oil, filtered and dried, was usually from 0.855 to 0.863 but leaves collected in 1924 (Nov.) gave an oil with the rather higher value of 0.8705. In January leaves were collected and an oil with d20° 0.8770 was obtained. In April the leaves gave an oil with d20° 0.8880. The leaves seem to give a heavier oil in the winter and spring months than in the summer. Another factor influencing the density of the oil is the degree of dessication of the leaves. The longer the leaves are dried, the lighter the oil. Distillation under reduced pressure (15 mm) did not cause any appreciable change in the density of the oils as shown by Table 3. Even in the case of oil #4 which was distilled at 80 mm. pressure, there was no change in the constants of the oil.

The oil was dextro-rotary.
The refractive index, determined by means of a Pulfrich refractometer was found to vary from 1.4718 to 1.4841, although most samples fell between 1.472 and 1.474. These determinations were made at 20°, with sodium light.

The information obtained from the boiling point range of an oil is often of great value in suggesting what compounds are likely to be present. As the presence of certain compounds necessitates special treatment of the oil before fractionation, a small amount was distilled at atmospheric pressure in order to obtain an idea as to the boiling point range of the oil.

**TABLE 4.**

<table>
<thead>
<tr>
<th>FRACTION</th>
<th>TEMP.</th>
<th>VOL.</th>
<th>DENSITY</th>
<th>% OVER (BY WT.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>160-165°</td>
<td>8cc.</td>
<td>.852</td>
<td>7.9</td>
</tr>
<tr>
<td>2.</td>
<td>165-167°</td>
<td>22cc</td>
<td>.8567</td>
<td>29.8</td>
</tr>
<tr>
<td>3.</td>
<td>167-169°</td>
<td>28</td>
<td>.8563</td>
<td>57.5</td>
</tr>
<tr>
<td>4.</td>
<td>169-171°</td>
<td>12.5</td>
<td>.8563</td>
<td>69.9</td>
</tr>
<tr>
<td>5.</td>
<td>171-173°</td>
<td>11</td>
<td>.8572</td>
<td>80.8</td>
</tr>
<tr>
<td>6.</td>
<td>173-178°</td>
<td>7.5</td>
<td>.859</td>
<td>88.3</td>
</tr>
<tr>
<td>7.</td>
<td>178-190°</td>
<td>5.0</td>
<td>.866</td>
<td>93.2</td>
</tr>
<tr>
<td>8.</td>
<td>190-300°</td>
<td>6.0</td>
<td>.910</td>
<td>99.6</td>
</tr>
</tbody>
</table>

**SOLUBILITY**

The solubility of the oil in alcohol was determined. All volatile oils are soluble in ether, chloroform, benzene and absolute alcohol, but only a few oils are entirely soluble in dilute alcohol. The richer an oil is in oxygen, the more water it dissolves, from which it follows that the
solubility of the oil in dilute alcohol may be taken as a measure of its oxygen content. The oils rich in terpenes are insoluble in 70% alcohol, whereas oils rich in alcohols, phenols, and the like are readily soluble. Two cc. of oil were put into a test tube and 90% ethyl alcohol was added 1 cc. at a time. The oil was insoluble in 5 cc. of alcohol, but quite soluble in 6 cc., giving a clear solution. Hence the oil of Chamaecyparis nootkatensis is soluble in 3 parts of 90% ethyl alcohol, (percentage by weight). As regards 80% ethyl alcohol, oil distilled in Nov. 1924 was soluble in 14 parts, but did not give an entirely clear solution, a slight opalescence persisted. Oil #1 was soluble in 15 parts, oil #2 in 13 parts, and oil #6E in 11 volumes of 80% alcohol. In every case a very slight opalescence remained even with considerably larger amounts of alcohol. From 40 to 50 volumes of 70% alcohol were required for solution of the oil, and again a slight opalescence was noticed. The very low solubility indicates a high terpene content.

**SAPONIFICATION**

In order to determine the amount of ester in an oil or fat, the standard procedure is to treat about 2 gms. of the material (accurately weighed) with 25 cc. of N alcoholic KOH. The mixture is heated to boiling on a water bath, with a reflux condenser, for one hour. The mixture is cooled,
diluted with an equal volume of cold water, phenolphthalein is added, and the excess caustic potash is titrated at once against standard \( \frac{1}{2} \) hydrochloric acid. Preliminary experiments having shown the saponification value to be quite low, only 10cc. of the alkali were used, as this was considered to be a plentiful excess. Following this procedure, values of from 10 to 30 were obtained, with the value after acetylation ranging from 20-50. This indicated a small ester and alcohol content for the oil.

Since the terpenes are known to be quite susceptible to change, it was decided to see what effect alcoholic potash would have on a pure terpene compound. Ten cc. (8.613 gms) of carefully re-distilled \( \alpha \)-pinene (155°- 157°, over sodium) were heated on a water bath for one hour with 10cc. of alcoholic potash. The mixture darkened. When the reaction mixture was cooled and diluted by pouring into 100 cc. of cold water, a white emulsion formed. Phenolphthalein was added and the excess of caustic potash was titrated against standard acid. This gave an ester value of 6.22. The experiment was repeated, using 6 cc. of \( \alpha \)-pinene and 10 cc. of alcoholic potash. The saponification value was now found to be 16.0. It appeared as if the greater the excess of caustic potash, the higher the S.V. obtained. This was confirmed by treating 3.44 gms. of \( \alpha \)-pinene with 10 cc.
alcoholic potash for one hour. The saponification value rose to 20.8. This seems to be the maximum value, for 1.72 gms. of α-pinene treated for one hour, with 10 cc. alcoholic potash gave the same value, 20.8.

The fact that a pure hydrocarbon such as α-pinene should give such large values in these simple determinations made it seem desirable to investigate this matter further, so known mixtures of hydrocarbon and ester were made up and saponified. The ester chosen was terpinyl acetate, since it is common in tree oils, and is one of the most difficult to saponify quantitatively. (Terpineol and acetic anhydride were refluxed in the presence of anhydrous sodium acetate for 45 minutes. The mixture was cooled and shaken repeatedly with water until the aqueous layer gave only a very weak acid reaction. After drying for three days over anhydrous sodium sulphate, the filtered oil was fractionated at reduced pressure:

134° - 135° (at 36 mm) collected as Terpinyl acetate).

(1) 1.596 gms. terpinyl acetate + 8.613 gms. α-pinene, contains 15.8% ester. Using 3.115 gm. sample with 20 cc. alcoholic potash for 1 hour. S.V. = 45.7, which corresponds to 16.1% ester.

(2) 0.848 gms. terpinyl acetate + 3.445 gms. α-pinene, with 20 cc. KOH for 1 hour. S.V. = 55. Actual ester content 19.8%; found 19.25%.
(3) 1.163 gms. Terp. Acet. + 1.723 gms. \( \alpha \)-pinene, with 20 cc. KOH, 1 hour. S.V. = 91.9. Actual ester content 40.3\%; found 32.2\%.

(4) 1.200 gms. terpinyl acetate, with 20 cc. alc. KOH, 2 hours. S.V. = 211. Ester content 100\% (？); found 73.9\%.

**ACETYLATION**

To determine the alcohol content of essential oils, 10 cc. of oil mixed with 10 cc. of acetic anhydride and 2 gms. of dry sodium acetate, are refluxed for one hour. After shaking with water to decompose the excess acetic anhydride, the oil is dried over anhydrous sodium sulphate, and the saponification value is determined. Values from 20 to 50 were found.

In order to ascertain the effect of this treatment upon a terpene, some \( \alpha \)-pinene was acetylated by the standard procedure, and the oil resulting was saponified as before:

(1) 1.640 gms. oil heated for 1 hour with 10 cc. alcoholic KOH. S.V. = 40.6.

(2) 1.057 gms. oil heated for 2 hours with 20 cc. alcoholic KOH. S.V. = 46.3.

It is seen here that a larger excess of alkali and longer heating does not raise the value very much.

(3) 10 gms. \( \alpha \)-pinene + 5 gms. menthol heated with excess acetic anhydride, and the oil was then saponified:

1.057 gms. oil, 20 cc. alc. KOH, for 2 hours gave
S.V. = 159.2.

This corresponds to 43% alcohol (C_{10}H_{18}O). It may be noted that if the S.V. of the \alpha-pinene alone is subtracted, we get a very close agreement, 159.2 - 46.3 = 112.9, which corresponds to 31% of alcohol in the original oil. (Actually 33%).

Although the terpenes are acted upon both during acetylation and saponification, in the presence of alcohols and esters the latter are acted upon most readily, and the values obtained while not giving absolute amounts of these compounds, give the comparative amounts fairly accurately. Saponification values below 20, however, are probably due to action of the alkali on the terpenes in the oil. Hence it would appear as if there are no esters in the leaf oil of the yellow cedar, or if any ester is present it is in very small amount. The same may be said of alcoholic constituents, from the very low saponification values after acetylation.

**PHENOLS**

To determine the amount of phenolic constituents, 10 gms. of oil were shaken with 100 cc. of a 5% solution of caustic potash. After standing for 16 hours the aqueous layer was separated and 100 cc. of 1 normal sulphuric acid were added. Phenolic compounds such as P.OH form water soluble potassium salts, P.OK, decomposed by mineral acid to give
back the phenol. This acid mixture was extracted repeatedly with ether, and upon evaporation of the ether 0.5 gms. of oil were left as residue. Hence 5% of the oil is capable of reacting with caustic potash. About 5% also reacts with acetic anhydride upon acetylation. Probably the same compound is acted upon in both cases.

**ALDEHYDES**

Aldehydes were tested for by shaking 10 cc. of oil with 200 cc. of a saturated solution of sodium acid sulphite. Most aldehydes give crystalline addition products, but in some cases these are soluble in excess of reagent. After some days a very small amount of flaky material appeared at the interface between the two liquids. Even after two months there was only a very slight diminution of volume. Ammoniacal silver nitrate gave a weak positive test fairly quickly. Hence a small amount of aldehyde appears to be present.
FRACTIONATION.

Those oils whose physical and chemical constants were similar were united before fractionation was commenced. Three main portions, known as A, B, and C were obtained.

A #4, 5, 6D, 6B, and 6C
B #2, 3, 6A, 7A, 10A and 1CB
C #1, 6D, 6T, 6SD, 7B and 1l

"A" consisted of 353 cc. (303 gms.) of oil, d20° 0.856, and nD20° 1.47491. This was fractionally distilled at reduced pressure, using a Hempel column. The oil started to come over at 55 degrees at 10 mm. pressure.

<table>
<thead>
<tr>
<th>FRACTION</th>
<th>TEMP.</th>
<th>PRESS.</th>
<th>VOL.</th>
<th>D20°</th>
<th>ND20°</th>
<th>% OVER (BY WT.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>52-56°</td>
<td>8 mm</td>
<td>110cc</td>
<td>0.8528</td>
<td>1.47047</td>
<td>30.9</td>
</tr>
<tr>
<td>A.2</td>
<td>53-57°</td>
<td>6 mm</td>
<td>129</td>
<td>0.8506</td>
<td>1.47199</td>
<td>67.1</td>
</tr>
<tr>
<td>A.3</td>
<td>57-62°</td>
<td>6 mm</td>
<td>30</td>
<td>0.8555</td>
<td>1.47906</td>
<td>75.6</td>
</tr>
<tr>
<td>A.4</td>
<td>58-72°</td>
<td>5 mm</td>
<td>40</td>
<td>0.8560</td>
<td>1.47932</td>
<td>86.9</td>
</tr>
<tr>
<td>A.5</td>
<td>60-200°</td>
<td>2.5</td>
<td>34</td>
<td>0.8550</td>
<td>-------</td>
<td>97.7</td>
</tr>
</tbody>
</table>

The distillation loss was 2.3% and was mainly due to polymerization. Fractions A.1 to A.4 were again fractionated at reduced pressure and the lower boiling fractions were distilled at atmospheric pressure.

<table>
<thead>
<tr>
<th>FRACTION</th>
<th>TEMP.</th>
<th>VOL.</th>
<th>DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.22</td>
<td>Below 161°</td>
<td>8 cc.</td>
<td>--------</td>
</tr>
<tr>
<td>A.23</td>
<td>161°-163°</td>
<td>18 cc.</td>
<td>0.8546</td>
</tr>
<tr>
<td>A.24</td>
<td>163°-165°</td>
<td>21 cc.</td>
<td>0.8532</td>
</tr>
<tr>
<td>A.25</td>
<td>165°-167°</td>
<td>40 cc.</td>
<td>0.8526</td>
</tr>
<tr>
<td>A.26</td>
<td>167°-169°</td>
<td>38 cc.</td>
<td>0.8520</td>
</tr>
</tbody>
</table>
As practically no separation was yet apparent these fractions were again repeatedly fractionated at reduced pressure, using a Hempel column to give a better separation. After several distillations at atmospheric pressure an \( \alpha \)-pinene fraction was separated: Boiling point 155° - 158° d\textsubscript{20°} 0.8553, n\textsubscript{D20°} 1.46696. The boiling point and refractive index indicate \( \alpha \)-pinene, but the density is a little low. If contaminated with camphene (b.p. 159°) or \( \beta \)-pinene (b.p. 164°) the density should be too high. The presence of sabinene (b.p. 162°, d\textsubscript{20°} 0.840) would explain this low density, and is the only terpene which could cause such an effect. The refractive index of sabinene is very similar to that of \( \alpha \)-pinene, so its presence could not be detected in that way.

The very low density values and small amounts distilling at 159° - 160° preclude the presence of camphene.

The \( \beta \)-pinene fraction, 160° - 166°, was next obtained, but the density was again much too low. This was the largest fraction of the oil, but owing to the breaking of a flask and the oil catching on fire, only about 25 cc. out of 100 cc. were left to work on.

At 170° there was a sudden rise in the amount of oil distilling over per degree of temperature. This temperature when corrected is 173° - 174°. The oil had a density of 0.8502 at 20°.
At this point oil "B" was fractionated to see how the fractions would correspond. There were 375cc. (320 gms.) of this oil, which had d22° .8624, nD20° 1.47441. This was distilled at reduced pressure with a Hempel column just as was oil "A".

<table>
<thead>
<tr>
<th>FRACTION</th>
<th>TEMP.</th>
<th>PRESS.</th>
<th>VOL.</th>
<th>DENSITY</th>
<th>% OVER (BY WT.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.1</td>
<td>66-67°</td>
<td>21 mm</td>
<td>59cc</td>
<td>.8552</td>
<td>15.8</td>
</tr>
<tr>
<td>B.2</td>
<td>65-67°</td>
<td>19 mm</td>
<td>59cc</td>
<td>.8546</td>
<td>31.5</td>
</tr>
<tr>
<td>B.3</td>
<td>67-68.5°</td>
<td>19 mm</td>
<td>65cc</td>
<td>.8540</td>
<td>48.3</td>
</tr>
<tr>
<td>B.4</td>
<td>66-68.5°</td>
<td>16 mm</td>
<td>60cc</td>
<td>.8536</td>
<td>64.3</td>
</tr>
<tr>
<td>B.5</td>
<td>68-70°</td>
<td>14 mm</td>
<td>60cc</td>
<td>.8540</td>
<td>80.3</td>
</tr>
<tr>
<td>B.6</td>
<td>68-75°</td>
<td>12 mm</td>
<td>24cc</td>
<td>.8543</td>
<td>87.2</td>
</tr>
<tr>
<td>B.7</td>
<td>70-180°</td>
<td>6 mm</td>
<td>30cc</td>
<td>.9283</td>
<td>95.9</td>
</tr>
</tbody>
</table>

There was a loss of 13 gms., or 4.1%. After six fractionations at reduced pressure, the fractions boiling up to 60 degrees at 15 mm. were distilled at atmospheric pressure.

154° - 159° 45 cc.
159° - 160° 15 cc
160° - 161° 14.5 cc
161° - 162° 11
162° - 165° 19

After many fractionations the separation finally obtained was

1. 155° - 159° 45 cc
2. 159° - 160° 11
3. 160° - 161° 12.5
4. 161° - 164° 29.5
5. 164° - 166° 28
6. 166° - 168° 12
7. 168° - 178° 80

This would indicate that about 20% of the oil boiled below 159° (α-pinene?), about 40% between 159° - 168° (β-pinene?), about 30% between 168° - 178° (limonene, phellandrene,
sylvestrene, terpinene or p-cymene?), and 10% of high-boiling material. Fraction 7 was distilled several times and eventually fractions 8,9,10 were separated.

8. 168°- 170° 29 cc.
9. 170°- 173° 24 cc. d20° 0.8550
10. 173°- 176° 18 cc. d20° 0.8573

The high boiling fraction was distilled at atmospheric pressure as the saponification value of this portion was rather low, about 20, indicating the absence of esters.

190°- 205° 4.5 cc.
205°- 225° 8.0 cc.
225°- 240° 4.5 cc.
240°- 270° 7.0 cc.

This would indicate the presence of at least two distinct compounds, one boiling below 220° probably, and the other above 240°. As there seemed to be no decomposition during distillation, the distillations were conducted at atmospheric pressures.

It is customary, however, to saponify the fractions boiling above 180°, before distillation. A saponification value determination on one fraction from oil "A" gave 43.5. About 60 cc. of 0.51 N. alcoholic potash were heated with 40 gms. of oil (boiling above 180°) on a water bath for one hour, and then the mixture was steam-distilled. Only 17 cc. of oil were recovered! If an ester such as

\[ \text{CH}_3 \text{C}^\infty \text{C}_\text{10} \text{H}_{17} \]

were present, a water soluble potassium salt \( \text{CH}_3\text{COOK} \)
and a volatile alcohol $\text{C}_{10}\text{H}_{17}\text{OH}$ should result. If the oil had been all ester, at least 30 gms. of oil should have been recovered, and the smaller the ester content the more oil should have been obtained on steam distillation, since only esters (theoretically) would be attacked by alcoholic potash.

The oil recovered was dried over calcium chloride for three days. After filtering the oil a white precipitate appeared spontaneously. The oil was packed in ice and salt to freeze out any solid alcohol, phenol or ketone, if present. The precipitate was filtered out and saved, and the density of the remaining oil was determined. During this determination a white precipitate again appeared in the oil. Freezing did not improve the precipitation, but heating did! The precipitate was insoluble in alcohol, ether chloroform and petroleum ether! It proved to be water soluble, gave a brick-red colour to a Bunsen burner flame, and a dense white precipitate with ammonium oxalate, hence was a calcium compound; and since calcium chloride was used to dry the oil, it was almost certainly calcium chloride.

The oil gave a weak test for aldehyde with ammoniacal silver nitrate, and reacted very slightly (if at all) with potassium acid sulphite. It had a density of 0.898. On distillation, 3 cc. were collected below 178° and all came over below 215°. The latter fraction was distilled once more, and 180° to 210° collected and examined. It had $d_{20}°$ 0.8925.
From all the properties listed above it appeared to be a ketone, and fenchone (b.p. 192°, d20° .946) or thujone (b.p. 201°, d20° .916) seemed the most likely possibilities. The boiling point range and density both indicated thujone rather than fenchone, so an attempt was made to prepare the crystalline thujone tribromide. Wallach (Liebig's Annalen 275 (1893), 179; and 286 (1895),109) directs that 5 cc. of bromine be added all at once to 5 gm. of thujone in 30 cc. of petroleum ether contained in a large beaker. An extremely vigorous reaction occurred, and copious fumes of hydrobromic acid were evolved. By heating on a water bath to about 40 degrees the excess bromine was expelled and the petroleum ether volatilized. No crystals were obtained; but only an oily mass resulted.

Oil "C" was similarly distilled at reduced pressure, and after several fractionations the corresponding fractions of "A" and "C" were united and called "D". As the constants of the "B" oil seemed somewhat different, it was kept separate.
Finally, from "D", a fraction with b.p. 156° - 158°, d20° 0.8570 was obtained, and from "E" a fraction 155° - 159°, d20° 0.8605 and nD20 1.46750. These values indicate α-pinene.

\[
\begin{align*}
\text{CH}_3 & \\
\text{H}_2\text{C} & \quad \text{C} \\
\text{H}_3 & \quad \text{CH}_3
\end{align*}
\]

Five cubic centimeters of the "E" fraction were dissolved in one volume of ether and one half volume of glacial acetic acid. The mixture was put in a test-tube and packed in an ice and salt freezing mixture. Nitrosyl chloride gas (generated as described below) was passed into the solution until a crystalline nitrosochloride precipitated.

"A suction flask containing a thin paste of sodium chloride in concentrated hydrochloric acid is provided with a two-holed cork carrying two dropping funnels. One funnel contains concentrated sulphuric acid, the other a saturated solution of sodium nitrite. Two parts of sulphuric acid are run in to every three parts of nitrite solution, excess of hydrochloric acid being avoided in the gas mixture at all times. The gases are cooled and dried by passing over calcium chloride in large U-tubes packed in ice and salt, and led into the well-cooled pinene solution." (3) H.Rupe Chem. Abst. 15, (1921), 1892
At first a beautiful pale green colour appeared which rapidly turned a light blue, and this became a robin-egg blue as the white needle-like crystals precipitated. Toward the end of the reaction the solution turned a brownish colour due to an excess of nitrogen oxides. The fine, needle-like crystals were filtered out, washed twice with the ether-acetic acid mixture and dissolved in 10 cc. of chloroform. The compound was reprecipitated by adding 20 cc. of pure methyl alcohol and packing in ice and salt. A white fleecy precipitate came down which was filtered at the pump and sucked dry. Upon drying in the air, overnight, very delicate leaf-like crystals were obtained, which melted at 108° with decomposition. After dissolving in 3 cc. of chloroform and precipitating with 10 cc. of methyl alcohol several times the melting point was again determined: 108°, 109°, 108.5°. Recrystallized from benzene, m.p. 108°, 111°, 108°.

The experiment was repeated with the "D" oil and crystals were again obtained melting, with decomposition, at 108°.

Van Romburgh gives 108° as the melting point of the pure nitrosochloride; Tilden records 109° - 111°, and by several recrystallizations from chloroform he obtained values as high as 115°.

(4) Chemisches Zentralblatt, 1901, 1, 1006.
The generally accepted value for the melting point of pure pinene nitrosochloride (precipitated from chloroform solution by methyl alcohol) is that given by Wallach, 103°, but it is apparently for an impure sample.

An attempt was made to prepare pinene hydrochloride following the procedure given by H.L. Fischer. Pure dry hydrogen chloride gas was passed into a well-cooled -pinene fraction for three days. The solution became reddish-brown in colour and a strong camphoraceous odour was noticed, but no crystals could be separated. The experiment was repeated following the directions of Frankfurter and Frary. The terpene, dissolved in an equal volume of chloroform, cooled below 0°, was saturated with pure dry hydrogen chloride gas. The chloroform solution turned red in colour. An equal volume of water was added, the excess acid neutralized with sodium bicarbonate (upon which the chloroform solution was decolorized), and the mixture was steam-distilled at once. The chloroform layer of the condensate was separated from the water, and evaporation of the solvent left an oily liquid which crystallized on cooling to -30°. Recrystallized from alcohol the melting point was 129° - 130°, the melting point of pinene hydrochloride.

(6) Liebig's Ann. 245 (1888), 252; 253 (1889) 251
(7) Laboratory Manual of Organic Chemistry
(8) Journ. Am. Chem. Soc. 28 (1906), 1461
Hence this fraction of the oil is \( \alpha \)-pinene.

**CAMPHENE TEST.**

The fraction 159° - 160° had much too low a density for a camphene fraction. A camphene fraction from the oil of the Cuban pine (Pinus heterophylla) had \( d_{15} \) 0.8666; from the oil of the Longleaf pine (Pinus palustris) \( d_{15} \) 0.8886; and from the white fir (Abies concolor) a fraction 160° - 164° (giving a good test for camphene) had \( d_{15} \) 0.8695. This fraction from different oils of the Chamaecyparis nootkatensis varied in density from 0.8580 to 0.8540 at 20° (about .862 to .858 at 15°). Since camphene is a solid at ordinary temperatures (m.p. 49° to 50°), an attempt was made to freeze it out. A portion of the 158° - 160° fraction was kept packed in solid carbon dioxide and ether for several days, but in spite of inoculation with a camphene crystal, no crystallization occurred. The isochoroneol test for camphene is claimed by Gildemeister and Hoffmann to be the best, so it was carried out as follows: 10 cc. of oil (b.p. 159° - 160°, \( d_{20} \) 0.8577) were heated with 25 cc. glacial acetic acid and 1 cc. of 50% sulphuric acid to 60° on a water bath.


(10) *Ibidem* 6, (1914), 726.

(11) *Ibidem* 6, (1914), 809.

The solution reddened and turned dark brown, and a light-coloured oil floated on the darker portion. When camphene is present the solution usually becomes homogeneous, but the two layers persisted, even after eight hours. After dilution with water and neutralization of the acid, the oil was separated and saponified. No isoborneol could be obtained, although an isoborneol-like odour was noticed. The $\beta$-pinene in the oil would be converted by the above treatment into terpinene and isofenchyl acetate, and the latter upon saponification would give isofenchyl alcohol, which doubtless resembles isoborneol in odour. Camphene certainly appears to be absent from the oil.

$\beta$-PINENE.

A fraction, 163° - 166° with $d_{20}^\circ .8623$ was obtained from one oil; from the other a fraction 162° - 164°, $d_{20}^\circ .8578$. Repeated distillation would not raise these values. They are quite low for $\beta$-pinene; A.W. Schorger gives $d_{15}^\circ .8715$ for a fraction 164° - 166° from the white fir (Abies concolor); from the Cuban pine (Pinus heterophylla), $d_{15}^\circ .8704$; and from the Longleaf pine (P. palustris), $d_{15}^\circ .8724$.

(15) Ibidem 6, (1914), 724.
(16) Ibidem 6, (1914), 726.
Schimmel & Co., give d15°.8650 for a fraction 164° - 166°
(17) from oil of hyssop, and Wallach gives d22°.8660 for a
13-pinene boiling at 162° - 163°.

For the identification of this fraction 50 gms. of oil
(b.p. 162° - 166°, d20°.857) were oxidized according to
(19) Wallach's directions for the preparation of sodium	nopinate. The oil was shaken with 116 gms. of potassium
permanganate dissolved in 1500 cc. of water to which 25 gms.
of sodium hydroxide had been added. In the presence of
alkali, the oxidation mixture becomes decidedly warm, so that
the oxidation is usually completed in about twenty minutes.
The mixture was vigorously shaken in a two-litre flask, at
intervals, for an hour and then steam-distilled to remove
the excess hydrocarbon. The oil recovered measured 23 cc.
and had a density of 0.857.

The distillation residue was filtered to remove the
manganese dioxide and then evaporated to 250 cc. while
injecting a current of washed carbon dioxide gas. By cooling
with ice and salt and letting stand for several days, 5.8 gms.
of white crystals were obtained. Since the free nopinic acid
changes very readily, splitting off water in the presence of
mineral acids, some precautions have to be observed in pre-
paring it.

(18) Liebig's Annalen, 363 (1908), 1.
(19) ibidem, 356, (1907), 228
Assuming the powder to be pure sodium nopinate, \( \text{C}_{10}\text{H}_{15}\text{O}_3\text{Na} \) of molecular weight 206, the amount of acid required to decompose it according to the equation

\[ \text{C}_{10}\text{H}_{15}\text{O}_3\text{Na} + \text{H}_2\text{SO}_4 = \text{C}_{10}\text{H}_{15}\text{O}_4\text{H} + \text{Na HSO}_4 \]

was calculated, and an amount slightly less than required was added, to avoid an excess of free acid. Dissolved 2.0 gms. in hot water, cooled and added 170 cc. of .1124 N. sulphuric acid.

The solution was then repeatedly extracted with ether. A semi-crystalline mass was obtained on evaporation of the ether, but a melting point could not be obtained. Thinking that the crystals of sodium nopinate might be contaminated with oily material which interfered with the crystallization of the nopinic acid, the remaining crystals of sodium nopinate were well washed with ether to remove any oily impurities. The crystals were dried. They weighed 3.30 gms.

These crystals were dissolved in 120 cc. of hot water, and then chilled in ice water. Treated with 45 cc. of 0.614 N. sulphuric acid. Kept in ice for several hours, during which the mixture was extracted ten times with ether. Evaporation of the ether gave a very small amount of oily residue. This was dissolved in benzene. Evaporation of the solvent gave only an oily residue, no crystals of nopinic acid could be obtained.
The formulae for β-pinene and its oxidation products are

\[
\begin{align*}
\text{β-pinene} & : \quad CH_2 \quad C \quad CH_2 \\
& \quad H \quad H \\
& \quad H \quad C \quad C \quad CH_3 \quad H \\
& \quad H \quad C \quad C \quad CH_2 \\
\text{β-pinene glycol} & : \quad CH_2(OH) \quad C \quad CH_2 \\
& \quad H \quad H \\
& \quad H \quad C \quad C \quad CH_3 \quad H \\
& \quad H \quad C \quad C \quad CH_2
\end{align*}
\]

nopinic acid

nopinone

An isomeric, and closely related terpene hydrocarbon, is sabinene

\[
\begin{align*}
& : \quad CH_2 \\
& \quad H \quad C \quad C \quad CH_2 \\
& \quad H \quad H \\
& \quad H \quad C \quad C \quad CH_3 \quad H \\
& \quad H \quad C \quad C \quad CH_2
\end{align*}
\]

b.p. 162° - 166°, d₂₀°.840. The boiling point range is the same as for β-pinene, but the density is much lower. It is identified most simply by following Wallach's procedure for conversion to sodium sabinate. A large vessel is charged with 30 gm. crystallized potassium permanganate, 200 cc. of water, 200 gms. of ice and 6.5 gms. of caustic soda; 12.5 gms. of oil are added and the mixture is shaken for one hour. This procedure was followed, the mixture was steam-distilled to remove unchanged oil (6.5 cc. were recovered), and the

(20) Liebig's Annalen 359 (1908), 266
distillation residue was filtered to remove the manganese dioxide. The pale yellow liquid obtained was evaporated to 50 cc. and packed in ice and salt. A white precipitate was obtained, but when the sodium salt was treated as above described (under \( \beta \)-pinene) in order to liberate the free acid, only an oily material resulted. It is very possible that both \( \beta \)-pinene and sabinene are present, (as evidenced by the low density shown in the case of fractions 160° - 166° from oils "B" and "D"), and if this were so, the sabinic acid (m.p. 57°) and nopinic acid (m.p. 126°) resulting from treatment of the sodium salts with sulphuric acid would interfere with the crystallization of each other, and very likely an oily mixture would result.

**PHELLANDRENE TEST**

The fraction 170° - 180° might contain phellandrene, a terpene which is very unstable at its boiling point. Its boiling point at 10 mm. pressure is between 50° and 60°, so a fraction 54° - 57° at 10 mm. was tested for phellandrene since the densities were in fair agreement, and since this terpene is found widely distributed, occurring in pine-needle oils, spruce and juniper oils, eucalyptus, peppermint, water-fennel and many other oils. Phellandrene varies in density from 0.844 to 0.856, and the density of this fraction was 0.852.
Phellandrene is defined, by Wallach, as "a hydrocarbon, C\textsubscript{10}H\textsubscript{16}, which when brought into contact with N\textsubscript{2}O\textsubscript{3}, in an indifferent, non-aqueous solvent (e.g. petroleum ether) at a temperature below 0° — hence under conditions that exclude inversion as much as possible — yields at once a well characterized nitrite." This nitrite is the only solid derivative of phellandrene, hence is used for its identification. A solution of 5 gms. of sodium nitrite in 8 cc. of water is placed beneath a layer of a solution of 5 cc. of oil in 10 cc. of petroleum ether. The mixture in a test-tube is packed in ice to keep it quite cool and 5 cc. of glacial acetic acid is added. The mixture is shaken. The nitrous acid liberated should produce a voluminous crystalline magma if phellandrene were present, but only a brown, slimy mixture resulted. A fraction with slightly higher boiling point (68° - 70° at 14 mm. pressure) was tested by the same method with the same negative results. Phellandrene is absent from the oil of the yellow cedar.

**TERPINENE TEST**

Terpinene, b.p. 174° - 179°, d\textsubscript{20} .846, also gives an addition product with nitrous acid. The identification is made by adding 1.5 cc. of glacial acetic acid and 4.5 cc. of water to 3 cc. of the fraction in a narrow test-tube.

(21) Ann. 336 (1904), 10
To the well-cooled mixture a saturated solution of sodium nitrite is added, small portions at a time, until 1.5 gms. of salt have been added. No crystals could be obtained, and as this fraction would not give a dihydrochloride of m.p. 51° - 52°, it was decided that no terpinene was present in the oil.

**LIMONENE**

Sylvestrene b.p. 175° - 177°, d20° .848 gives a dihydrochloride, m.p. 72°. In order to prove the presence or absence of this terpene an attempt was made to prepare the chlorhydrate.

Five cc. of the fraction 170° - 173° (uncorr), dissolved in 5 cc. of anhydrous ether, were placed in a test-tube and packed in ice and salt. Dry hydrogen chloride gas was led in for one hour. After having stood for three hours on ice, the ether was distilled off and a brown liquor of disagreeable odour remained. On freezing in ice and salt this solidified, and 1.7 gms. of crude product were obtained. After being pressed out between filter paper until dry, and then recrystallized from hot alcohol these crystals melted at 49.5°. After a second recrystallization beautiful white crystals were obtained, with the melting point still at 49.5°. Hence there is no sylvestrene, but limonene (or dipentene) is present in the oil, since 49° - 50° is the
melting point of dipentene dihydrochloride. From the small yield of chlorhydrate and high specific gravity of this fraction (d$_{20}^\circ$ 0.8512, compared to limonene with d$_{20}^\circ$ 0.844 to 0.848) it is apparent that only a small amount of the fraction is limonene.

**CYMENE**

The only common compound occurring in essential oils, with a boiling point between 170° and 180° and a density of about 0.860, is p-cymene, b.p. 174° - 176°, d$_{20}^\circ$ 0.8586. Limonene is readily attacked by dilute permanganate solution (22) and p-cymene is not, so an attempt was made to remove the limonene by oxidation with a 1% cold, neutral solution of potassium permanganate. After treating 20 cc. of oil with 600 cc. of permanganate solution for 12 hours, steam-distillation recovered 14 cc. of oil, and a second treatment only left 9 cc. of oil. The density was no higher, indeed, it had fallen to 0.8487. If the limonene had broken down first the density should have risen, but this was not the case. The refractive index was n$_{D20}^\circ$ 1.47383, much too low for p-cymene, being very close to the value for limonene.

The action of dilute permanganate solutions on pure p-cymene was then investigated. Even a solution as weak

as one-tenth of one per cent acts slowly on p-cymene, but it was decided to use this as it was considered strong enough to oxidize limonene at a fairly rapid rate while leaving p-cymene almost untouched. By this treatment a fraction was recovered with $d_{20^\circ} = 0.855$, quite close to the value for p-cymene. Three cc. of this were refluxed with 10 gms. of chromic acid ($Cr_2O_3$) dissolved in 8 cc. of concentrated sulphuric acid and 60 cc. of water. After ten hours, small white crystals appeared adhering to the walls of the flask, and six hours later the solution was cooled, diluted with 15 cc. of cold water and filtered. The precipitate was washed with cold water, then a boiling solution of sodium carbonate was poured on the filter. The precipitate dissolved. Upon acidifying the filtrate with hydrochloric acid a heavy flocculent precipitate appeared. This was filtered out and dried. The melting point could not be determined as the material sublimed at about $300^\circ$. This seemed to indicate terephthalic acid. An attempt was made to identify this with certainty by converting to dimethyl terephthalate (m.p. $140^\circ$ - $141^\circ$). The white powder was heated in a small dry test-tube with phosphorus pentachloride. The resulting compound was dissolved in methyl alcohol. On adding cold water a white precipitate appeared, but there was not enough of it to get a melting point as the experiment was started with only about 0.03 gms. of acid.
Since limonene and other terpenes may be oxidized by concentrated sulphuric acid to p-cymene, the foregoing test was not considered proof of the presence of p-cymene in the oil. The limonene known to be present may have been oxidized to p-cymene and this converted to terephthalic acid. Potassium permanganate oxidizes limonene to the saturated tetratomic alcohol, limonetrite, and other oxidation products of similar nature. Cymene is converted into p-hydroxyisopropyl-benzoic acid, (m.p. 155°), by concentrated hot permanganate solution. Three 2cc. portions of oil were added, at intervals, to 12 gms. of potassium permanganate dissolved in 330 cc. of water. The mixture was refluxed on a boiling water bath for several days. The manganese dioxide was filtered out and the solution evaporated to dryness. Since the potassium salt of p-hydroxyisopropyl-benzoic acid is soluble in alcohol, the crystals were boiled with 95% alcohol, the solution was filtered, and the alcoholic filtrate evaporated. A few crystals were obtained, which were soluble in cold water, but upon acidifying the solution with dilute sulphuric acid, although a milkiness appeared, no crystals could be separated upon which to take a melting point. After repeating this test several times, without obtaining definitely positive results, a more energetic oxidation was resorted to.

(23) Wagner, Ber. 23 (1890), 2315
According to Widman & Bladin, p-cymene (I) is slowly oxidized to a mixture of p-hydroxyisopropyl-benzoic acid (II) and terephthalic acid (III) by hot permanganate solution in the presence of free alkali. One part of the p-cymene fraction is mixed with ten parts of a sodium hydroxide solution (of s.g. 1.25) and concentrated permanganate solution is added from time to time. The reaction is conducted on a boiling water-bath since it goes very slowly. After about 25 hours, when the oil is all used up, the mixture is decolorized with alcohol and the manganese dioxide is filtered out. The filtrate is well-cooled and made weakly acid with dilute hydrochloric acid. A precipitate appears which is filtered out and may be readily identified as terephthalic acid. The filtrate is extracted with ether, evaporation of which leaves an oil. This soon solidifies to a white crystal mass. When the hydroxyisopropyl-benzoic acid is recrystallized from hot water, long triclinic crystals, m.p. 156°, are obtained. These are readily soluble in alcohol, ether and hot water. This procedure was carefully followed, with the following results.

(24) Ber. 19 (1886), 583
SUMMARY.

The Chamaecyparis nootkatensis, commonly known as yellow cedar, is a tree native to British Columbia. The wood is heavier and stronger than that of any of the other so-called North America cedars. Its light colour and straight fine grain make it a very desirable wood for ornamental work, and since it is practically unaffected by changes in moisture it is in great demand by local boat-builders. New uses are constantly being found for the wood.

Since the wood is not attacked by most wood-boring insects, and on account of its great durability in contact with soil and water, some valuable preservative would appear to be present in the oil of the tree.

Both the leaves and the wood of the yellow cedar have been steam-distilled and two quite different oils obtained.

The sawdust gives a 0.9% yield of blood-red coloured oil, d$20^\circ$ 0.955. This oil has not yet been fully investigated.

The leaves when air-dried lose about 30% of their weight, and steam distillation then gives yields from 0.7% up to 2.0% of an oil, usually light-brown in colour, with a decided smell of the yellow-cedar foliage. When re-distilled at 15 mm pressure this oil has average values as follows:

d$20^\circ$ 0.862  ,n$_D20^\circ$ 1.4718 to 1.4744, S.V.=12  A.V.= 0

The oil is soluble in 3 parts of 90% ethyl alcohol, 14 parts of 80% and 50 parts of 70% alcohol, the solutions are not
entirely clear in the latter case.

The boiling point range is from 155° to 280°. Although different samples of oil varied considerably, the average distribution of the fractions was

- 155° - 160°: 20%
- 160° - 170°: 40%
- 170° - 180°: 30%
- 180° - 220°: 6%
- 220° - 280°: 4%

The oil has been shown to contain α-pinene, β-pinene (probably mixed with sabinene), limonene, p-cymene,
The writer wishes to take this opportunity of expressing his thanks to Dr. R.H. Clark for the many timely suggestions and criticisms which were offered; to Mr. George Miller for obtaining the sawdust; and to his father, Mr. G.H. Lucas, for collecting the leaves.
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