5. Essential Oils from the Queensland Flora
   Part XIV.—Eucalyptus conglomerata
   BY
   F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

6. l-a- Phellandrene and its Monohydrochloride
   Part I.
   BY
   N. C. HANCOX, B.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

7. A New Derivative of Terpinen-4-ol
   BY
   N. C. HANCOX, B.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

8. Essential Oils from the Queensland Flora
   Part XV.—Backhousia Bancroftii and Daphandra rapandula
   BY
   F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

9. Essential Oils from the Queensland Flora
   Part XVI.—Eucalyptus micrccorys
   BY
   F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

REPRINTED
   from
THE PROCEEDINGS OF THE ROYAL SOCIETY OF QUEENSLAND
VOL. L, Nos. 2, 3, 6, 7, and 8, pp. 10-13, 14-20, 40, 41-42, 43-45
8th JUNE, 1939
I-α-PHELLANDRENE AND ITS MONOHYDROCHLORIDE.

PART I.

By

N. C. Hancox, B.Sc.,

and

T. G. H. Jones, D.Sc., A.A.C.I.

Department of Chemistry, University of Queensland.

[Reprinted from the Proceedings of the Royal Society of Queensland,
l-a-Phellandrene and its Monohydrochloride—Part I.

BY N. C. Hancox, B.Sc., and T. G. H. Jones, D.Sc., A.A.C.I.

Department of Chemistry, University of Queensland.

[Read before the Royal Society of Queensland, 28th November, 1938.]

The present paper contains a description of the following work:

(a) Isolation of pure l-a-phellandrene and determination of its physical constants;

(b) Observations on the loss of optical activity of a-phellandrene, and its stabilisation;

(c) Investigation of the products obtained by hydrolysis of phellandrene monohydrochloride.

(a) The a-phellandrene used was obtained from the essential oil of Eucalyptus dives by fractional distillation under diminished pressure. Besides phellandrene, the oil was known to contain pinene; piperitone, and a little cineol. Repeated fractionation removed the pinene and piperitone, while the cineol, whose boiling-point is too close to that of phellandrene to admit of separation in this way, was removed from the product in the final stages by extraction with resorcinol. As phellandrene is extremely susceptible to change on heating, the temperature during distillation was kept as low as possible by working at pressures between 1 and 5 mm. of mercury. The phellandrene fractions then distilled at temperatures below 45°C. Any rise in temperature above about 50° resulted in rapid destruction of the phellandrene, as indicated by impoverished yields and a falling-off in the rotation of the product. The final material obtained had a much higher specific rotation than any previously recorded in the literature, and so may be regarded as the purest samples of l-a-phellandrene hitherto obtained.

The first lot of oil distilled, consisting of about 1,400 c.c., yielded 122 c.c. of phellandrene with the following constants:

\[
\begin{align*}
\text{b-p} & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \text{(5 m.m.)} \quad 41^\circ C. \\
\frac{d_{15.5}}{2} & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 0.8455 \\
\frac{n_{20}}{D} & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1.4727 \\
[a]_D & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad -133
\end{align*}
\]

A fresher sample of oil used to obtain material for later work yielded a product of still greater purity. The purest sample obtained consisted of about 240 c.c. with the following constants:

\[
\begin{align*}
\text{b-p} & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \text{(4.5 m.m.)} \quad 39^\circ C. \\
\frac{d_{20}}{4} & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 0.8369 \\
\frac{n_{20}}{D} & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1.4728 \\
[a]_D & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad -168.5
\end{align*}
\]

The purest sample previously described in the literature (Smith, Hurst, and Read, 1923), obtained also from E. dives, had the constants:

\[
\begin{align*}
\frac{d_{20}}{4} & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \text{} \quad 0.8410 \\
\frac{n_{20}}{D} & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1.4732 \\
[a]_D & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad -112
\end{align*}
\]
The phellandrene used in the experiments on the hydrolysis of phellandrene hydrochloride had specific rotations of between -136 and -146, and material of this quality could be obtained in yields of about 12-14 per cent. of the original oil.

By repeated fractionation of the residual phellandrene fractions to remove phellandrene as far as possible, a product was obtained with a rotation of $-1^\circ$, and $n_0^{20} 1.4880$. This was identified as practically pure $p$-cymene.

(b) The Loss of Activity of 1-α-Phellandrene and its Stabilisation.
—The instability of phellandrene to heat has already been remarked on. It also undergoes rapid decomposition on standing in contact with air at atmospheric temperatures, with diminution of rotation, finally turning to a yellow, viscous, and extremely sticky material. Observations on the change in rotation with time were taken, with a view to finding the conditions necessary for successful preservation of samples of pure phellandrene. The use of solid hydroquinone as a preservative was suggested by the known efficacy of this substance as an antioxidant in other cases. The accompanying table contains readings, taken over a period of several months, of the rotations of two samples of phellandrene, to one of which hydroquinone was added, while the other served as a control. No special care was taken to exclude air, the test-tubes containing the samples being stoppered with ordinary corks. It will be seen that the hydroquinone has the effect of diminishing the rate of change and, finally, after a value of about $-80^\circ$ had been reached, of stopping it entirely. Hydroquinone was added to samples of phellandrene intended for use, but the most important precaution was found to be the use of tightly-fitting rubber stoppers to exclude air, for it can be seen from the table that hydroquinone alone will not entirely prevent the very rapid initial fall that the rotation of highly purified phellandrene suffers. A sample of phellandrene, of initial rotation $-102.2^\circ$, without preservative, but very carefully stoppered, showed a diminution in rotation of only 0.4° on keeping in the dark for three months. On removing the stopper and allowing to stand for a further two days, the rotation fell by 3.0°.

| Table showing the Effect of Hydroquinone on the Optical Activity of 1-α-Phellandrene. |
|-----------------------------------------|---------|---------|
| Days.        | Sample 1 (Control) | Sample 2 (1 gm. Hydroquinone). |
| 0            | 105.2           | 105.2          |
| 2            | 102.0           | 103.5          |
| 9            | 93.5            | 98.2           |
| 14           | 87.0            | 94.7           |
| 24           | 74.9            | 88.1           |
| 35           | 64.4            | 85.8           |
| 52           | 54.8            | 82.7           |
| 72           | 45.0            | 81.3           |
| 100          | 39.8            | 81.1           |
| 154          | 28.1            | 80.0           |
| 218          | 14.9            | 79.3           |
| 246          | 9.0             | 78.8           |
| 356          | 0               | 78.8           |

Curves on the attached graph are from the above figures.
(The above figures are actual rotations in degrees, not specific rotations.)
(c) \textit{Hydrolysis of Phellandrene Hydrochloride.}—Bacon (1909) has described a monohydrochloride of \(\alpha\)-phellandrene, prepared by passing dry hydrochloride acid gas to saturation into a solution of the phellandrene in light petroleum. On distilling off the solvent, he describes the monohydrochloride obtained as distilling at 80-83° (10 mm.), undergoing slight decomposition if heated above 84°C, and having the constants:

\begin{align*}
\text{d}^{20}_{4} & \quad \cdots \cdots \cdots \cdots \cdots \quad 0.960 \\
\eta_{D}^{20} & \quad \cdots \cdots \cdots \cdots \quad 1.4770
\end{align*}

\text{Cl} = 20.2 \text{ per cent.} \quad \text{(theoretical for C}_{10}\text{H}_{17} \text{Cl} = 20.6 \text{ per cent. erroneously given at 20.3 per cent. in the original paper).}

On treatment under reflux for six hours with alcoholic soda, he claims that the material is converted to dipentene, which he identified by means of its tetrabromide. Referring to Bacon’s work, Simonsen (1931) says: “These results are somewhat unexpected, since the formation of dipentene requires a curious rearrangement of the ethylenic linkages, and the formation of \(\alpha\)-terpinene might have been anticipated. Wallach has, in fact, shown that, with an alcoholic solution of H\(_2\)SO\(_4\), \(\alpha\) phellandrene does isomerise to \(\alpha\)-terpinene, and a possible explanation of Bacon’s results is that the \(\alpha\)-phellandrene used contained some dipentene.” The present work fails to confirm Bacon’s results, either as to the nature of \(\alpha\)-phellandrene monohydrochloride, or as to the formation of dipentene. On the contrary, it is shown that the hydrolytic product is a mixture of substances, among which the expected product, \(\alpha\)-terpinene, is actually present.

To prepare the hydrochloride, \(1\)-\(\alpha\)-phellandrene with (specific rotations of between 136 and 146 was used. It was treated with HCl, as in Bacon’s experiment, using a solution of the material in an approximately equal volume of petroleum ether. In order to determine the number of molecules of HCl added per molecule of phellandrene, an analysis was carried out on a small portion of the hydrochloride obtained as described above. The passage of HCl was continued until copious evolution of fumes indicated that saturation had been reached, and the material was then transferred to a known volume of standard alcoholic soda. The whole was boiled under reflux, and the excess NaOH titrated with standard acid. The result indicates only a small excess of HCl over that required for the monohydrochloride, so that the formation of dihydrochloride does not appear to occur to any appreciable extent.

Details:

2 c.c. of phellandrene taken—i.e., 1.688 gm.

Hydrochloride treated with 30 c.c. alcoholic NaOH, equivalent to 22.8 c.c. N.Acid.

After hydrolysis 9.5 c.c. of acid was required to titrate excess NaOH.

\(\therefore\) HCl used \(= 13.3 \text{ c.c.} ; \) 1 mol. of HCl requires 12.4 c.c.

An attempt was made to isolate the phellandrene hydrochloride in the pure state by removing the solvent at the water-pump. Contrary to Bacon’s observations, however, it was found that the material underwent considerable decomposition with loss of HCl during this process,
and that, on attempting to distil the material obtained, under a pressure even as low as 3 mm., complete loss of HCl occurred, although the temperature was much lower than the published boiling-point of 83° (10 mm.).

The material obtained after removal of the solvent at the water-pump had the following constants:—

\[d_{15.5}^{15.5} = 0.9000\]
\[n_{D20} = 1.4731\]
\[[\alpha]_D = -45°\]

A chlorine analysis gave the result Cl = 12.3 per cent., very much lower than the theoretical—viz., 20.6 per cent.

This material smelled strongly of HCl, and gave off fumes at the room temperature. It was then distilled at 3-4 mm.; distillation occurred at 40-44°, and the distillate gave no reaction at all when tested for the presence of chlorine. Its constants were:—

\[d_{15.5}^{15.5} = 0.8476\]
\[n_{D20} = 1.4770\]
\[[\alpha]_D = -44°\]

Combustion results:—C = 88.0 per cent., H = 11.9 per cent. (theoretical for C\textsubscript{10}H\textsubscript{16}:—C = 88.2 per cent., H = 11.8 per cent.)

Examination disclosed the presence of \(\alpha\)-phellandrene and \(\alpha\)-terpinene. \(\alpha\)-Phellandrene was identified by means of its nitrosite, which melted after recrystallisation at 112° C. A portion of the substance was next subjected to oxidation with alkaline permanganate in order to obtain the characteristic oxidation product of \(\alpha\)-terpinene. This substance, \(\alpha\beta\)-dihydroxy \(\alpha\)-methyl \(\alpha\)isopropyl adipic acid, after repeated crystallisation from ethyl acetate melted at 190° C., and showed no depression in a mixed melting-point test with a sample of the acid obtained from authentic \(\alpha\)-terpinene. The terminal decomposition of phellandrene hydrochloride is thus found to follow the course expected in theory.

In the first experiment on the hydrolysis of phellandrene hydrochloride with alcoholic soda, as performed by Bacon, the product was partially separated into two fractions. These had the constants:—

(i.) b.p. below 45° (4 m.m.)
\[d_{15.5}^{15.5} = -8645\]
\[n_{D20} = 1.4802\]
\[[\alpha]_D = -30°\]

(ii.) b.p. 50°–65°
\[d_{15.5}^{15.5} = -8793\]
\[n_{D20} = 1.4660\]
\[[\alpha]_D = -31°\]

Combustion results (i.) C = 87.8 per cent. H = 11.8 per cent.
(ii.) C = 80.1 per cent. H = 11.8 per cent.
These figures are consistent with the assumption that the fraction (ii.) is an oxygenated compound of formula \( C_{16}H_{18}O \) or \( C_{10}H_{16}O \), contaminated with fraction (i.) of the formula \( C_{10}H_{16} \). Fraction (i.) contained \( \alpha \)-phellandrene and \( \alpha \)-terpinene; no tetrabromide could be obtained, contrary to Bacon's observation. Fraction (ii.), which, in view of its physical constants, was thought to be of a ketonic nature, gave a product containing nitrogen after treatment with hydroxylamine, but only a very small amount of semicarbazide could be prepared.

In a second experiment, using 180 c.c. of phellandrene, the hydrochloride was submitted to hydrolysis without previous removal of the light petroleum solvent, in order to ensure that the alcoholic soda played the greatest possible part in bringing about the removal of HCl. The product was then treated with semicarbazide, which yielded only a small amount of non-volatile material. The portion recovered was separated into two fractions:

(i.) b.p. 40–45° (4 m.m.)

\[
\begin{align*}
&\text{d}_{15.5} \ldots \ldots \ldots \ldots \ldots 0.8519 \\
&\text{n}_{D}^20 \ldots \ldots \ldots \ldots \ldots 1.4751 \\
&[\alpha]D \ldots \ldots \ldots \ldots \ldots -20°
\end{align*}
\]

(ii.) b.p. 60–66° (4 m.m.); 207–210° (760 m.m.)

\[
\begin{align*}
&\text{d}_{15.5} \ldots \ldots \ldots \ldots \ldots 0.8828 \\
&\text{n}_{D}^20 \ldots \ldots \ldots \ldots \ldots 1.4450 \\
&[\alpha]D \ldots \ldots \ldots \ldots \ldots -36°
\end{align*}
\]

Fraction (i.) appeared to be similar to the hydrocarbon fractions obtained in previous experiments.

Fraction (ii.) was found to absorb bromine readily, indicating an unsaturated character. A combustion gave the following results:

\[
\begin{align*}
&\text{C} = 77.3 \text{ per cent., } \text{H} = 11.6 \text{ per cent. (theoretical for } C_{10}H_{18}O: \text{C} = 77.9 \text{ per cent., } \text{H} = 11.7 \text{ per cent.)}, \text{ which suggest an unsaturated secondary alcohol of the formula } C_{10}H_{18}O.
\end{align*}
\]

A portion (10 c.c.) was submitted to oxidation with chromic acid:

\[
\begin{align*}
&\text{4 c.c. of a material was recovered with the constants:—} \\
&\text{b.p. (760 m.m) } \ldots \ldots \ldots \ldots \ldots 200°
\end{align*}
\]

\[
\begin{align*}
&\text{d}_{15.5} \ldots \ldots \ldots \ldots \ldots 0.9148 \\
&\text{n}_{D}^20 \ldots \ldots \ldots \ldots \ldots 1.4783 \\
&[\alpha]D \ldots \ldots \ldots \ldots \ldots -29°
\end{align*}
\]

A combustion gave the results:

\[
\begin{align*}
&\text{C} = 78.9 \text{ per cent., } \text{H} = 10.7 \text{ per cent. (theoretical for } C_{10}H_{18}O: \text{C} = 79.0 \text{ per cent., } \text{H} = 10.5 \text{ per cent.)}.
\end{align*}
\]

On the assumption that fraction (ii.) above consists of secondary alcohol, this substance would be the corresponding ketone. Attempts to determine the constitution of the material in fraction (ii.) by isolation of the decomposition products firstly with permanganate in acetone solution and secondly with aqueous alkaline permanganate were, however, unsuccessful.

A third and much larger sample of phellandrene (400 c.c.) was used to obtain material for further investigation of the oxygenated products. This, treated as previously described, yielded a hydrolytic
product, which was separated into the hydrocarbon fraction and a higher boiling fraction, these being obtained in equal amounts (180 c.c. of each). The hydrocarbon fraction was similar to that obtained in the other experiments and had the constants:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{15.5}$</td>
<td>0.8476</td>
</tr>
<tr>
<td>$n_{D_{20}}$</td>
<td>1.4770</td>
</tr>
<tr>
<td>$[a]_D$</td>
<td>$-22^\circ$</td>
</tr>
</tbody>
</table>

A different method (Read and Storey, 1930) was used in this case to establish the presence of $\alpha$-phellandrene and $\alpha$-terpinene—viz., by separating the mixed nitrosites with ether, making use of the solubility of the $\alpha$-terpinene nitrosite and the insolubility of $\alpha$-phellandrene nitrosite in this solvent. After recrystallisation, the phellandrene nitrosite melted at $113^\circ$, and the terpinene nitrosite at $146^\circ$.

The higher fraction was found to be non-homogeneous, as further fractionation resolved it into two further fractions:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Volume</th>
<th>B.p. (5 m.m)</th>
<th>$d_{15.5}$</th>
<th>$n_{D_{20}}$</th>
<th>$[a]_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i.)</td>
<td>240 c.c.</td>
<td>65°–68°</td>
<td>0.8840</td>
<td>1.4580</td>
<td>$-24^\circ$</td>
</tr>
<tr>
<td>(ii.)</td>
<td>10 c.c.</td>
<td>72°–75°</td>
<td>0.8914</td>
<td>1.4634</td>
<td>$+34^\circ$</td>
</tr>
</tbody>
</table>

The most striking difference here is the change of sign of rotation of the second fraction.

With the object of removing any possible ketonic material, fraction (i.) was treated under reflux with semicarbazide. An unexpected result was here obtained, as, when the material was distilled to separate what should have been unchanged product, the latter was found to have been practically completely decomposed, and now distilled uniformly at $52^\circ$C. (7-8 mm.), and had the constants:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{15.5}$</td>
<td>0.8428</td>
</tr>
<tr>
<td>$n_{D_{20}}$</td>
<td>1.4730</td>
</tr>
<tr>
<td>$[a]_D$</td>
<td>$-76^\circ$</td>
</tr>
</tbody>
</table>

It consisted of $\alpha$-phellandrene and only a small amount of $\alpha$-terpinene. The semicarbazide obtained in this experiment was decomposed with 10 per cent. oxalic acid, and the liberated ketone recovered by steam distillation. It had the constants:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{15.5}$</td>
<td>0.8751</td>
</tr>
<tr>
<td>$n_{D_{20}}$</td>
<td>1.4741</td>
</tr>
<tr>
<td>$[a]_D$</td>
<td>$-35^\circ$</td>
</tr>
</tbody>
</table>

As it was considered that the acetic acid generated in the course of treatment with semicarbazide might be responsible for the behaviour described above, a small portion of fraction (ii.) was treated under identical conditions, but with 2 per cent. acetic acid and no semicarbazide. The material was, however, recovered quite unchanged. It was also recovered unchanged after treatment with semicarbazide alone; a faint nitrosite test was obtained, but its constants were not appreciably affected, and no material of lower boiling point could be obtained on distillation.
Theoretical Considerations.—α-Phellandrene has the constitution I. Assuming the addition of HCl proceeds in the normal manner to the conjugated double-bond system, phellandrene monohydrochloride has either of the constitutions II. or III. Loss of HCl from III. would then be expected to regenerate the original α-phellandrene, while II. would be expected to give α-terpinene, IV., and it is difficult to see how any other product, especially dipentene, could be formed.

I. These expectations have been confirmed by experiment. If, however, instead of causing the -Cl atom to unite with a neighbouring H-atom, the hydrolysis were to bring about the exchange of a -Cl atom for an -OH group, one would expect an alcohol. The following are possibilities:—Assuming normal addition of HCl to the conjugated system, we might obtain V. or VI., or in the event of abnormal addition, to one or other of the double bonds individually, VI., VIII., IX., or X. might result:—

Of these, VIII. is identical with VI. V. is the known alcohol piperitol, while the others have not been described. The physical constants of piperitol, however, are completely unlike those of the substances actually obtained. There is still the possibility of some more complex change, but the reconversion of the oxygenated material to phellandrene seems to preclude this.

Summary.—l-α-Phellandrene has been prepared in a higher state of purity than hitherto described, and its constants recorded. Addition of dry HCl in petroleum ether gives a monohydrochloride which is very unstable and readily decomposes to a mixture of α-phellandrene and α-terpinene. Decomposition with alcoholic soda yields, not dipentene, as previously stated, but (a) a mixture of the above two hydrocarbons and (b) a complex mixture of substances of higher boiling point with the probable formula C_{10}H_{18}O, which have not yet been identified and which probably have not been previously recorded. No trace of γ-terpinene was observed in any of the terpene fractions examined. Further work is in progress in connection with the alcohol recorded above, and the action of HCl gas on phellandrene in other solvents is also being investigated.

REFERENCES.

TEXT FIGURE 1.

GRAPH

Loss of Optical Activity of α-Phellandrene with and without Preservative

Sample 1 (with Hydroquinone)

Sample 2 (without Hydroquinone)

Time in days from commencement →