PART IV

STUDIES ON A NEW HYDROCARBON ISOLATED FROM
THE ESSENTIAL OIL OF ALPINIA GALANGA WILDE.
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Alpinia galanga Willd. is a plant belonging to the family zingiberaceae. The essential oil from this plant has not received much attention since its first examination by Ultee in 1911.

The oil for the present studies was extracted from rhizomes procured from Bangalore, India. During the course of the investigation of this oil, a new hydrocarbon of the sesquiterpene group was isolated, with particularly low density and refractive index which called for attention. The percentage of the hydrocarbon in the whole oil was rather low and only just enough could be obtained to make a preliminary investigation. A very similar substance was isolated from the essential oil of Piper longum, a plant belonging to the family Piperaceae. It is present in a relatively larger amount in the latter.

A comparison of the following constants will make the resemblances clear.

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<table>
<thead>
<tr>
<th></th>
<th>Hydrocarbon from Alpinia galanga</th>
<th>Hydrocarbon from Piper longum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{4}^{25}$</td>
<td>0.7743</td>
<td>0.7668</td>
</tr>
<tr>
<td>$n_{D}^{25}$</td>
<td>1.4340</td>
<td>1.4378</td>
</tr>
<tr>
<td>Analysis data</td>
<td>C 84.63</td>
<td>85.11</td>
</tr>
<tr>
<td></td>
<td>H 14.88</td>
<td>14.58</td>
</tr>
</tbody>
</table>

Though the hydrocarbon from Piper longum did not decolourise aqueous potassium permanganate or bromine in carbon tetrachloride and gave a faint yellow colour with tetranitromethane, the present hydrocarbon can be said to decolourise bromine in carbon tetrachloride and decolourise aqueous permanganate on heating. The infra-red spectrum of the substance did not show any sign of unsaturation and hence it may probably be a tetra-substituted double bond. The molecular weight and combustion results, coupled with molecular refractivity studies tend to indicate that the hydrocarbon is a $C_{16}$ one and it may have a formula of $C_{16}H_{30}$.  

Dehydrogenation with selenium and oxidation with aqueous potassium permanganate were attempted. No picrate forming material could be obtained from the dehydrogenation products and the substance was almost recovered unchanged. This shows
that the substance may not have a ring skeleton of either cadalene, eudalene or even azulene type.

The dehydrogenated hydrocarbon was, therefore, oxidised by alkaline potassium permanganate. Though its presence could not be established unambiguously, the formation of a carbonyl compound is indicated by the infra-red spectrum (which shows a peak in the carbonyl region).

**EXPERIMENTAL**

The essential oil of Alpinia galanga $d^{23}$, 0.87175 and $n_D^{23}$, 1.4808 was fractionated in a modified claisen's flask fitted with a vigreux column. The fractions obtained thereby excepting the first were mixed together and refractionated. The second and third fractions from this operation were mixed together and subjected to chromatography over silica gel. (Details of fractionation and chromatography are given on pages 66, 67 and 69.

The first two fractions so obtained had the following refractive indices.

**TABLE I**

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>$n_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.4300</td>
</tr>
<tr>
<td>2</td>
<td>1.4339</td>
</tr>
</tbody>
</table>
They were therefore mixed together and fractionally distilled in a small claisen's flask, when two fractions A and B were collected, having the properties given in Table II.

**TABLE II**

Weight of the oil taken for fractionation = 0.89 gms.
Pressure = 15 - 16 mm.

<table>
<thead>
<tr>
<th>Fraction Number</th>
<th>Boiling range</th>
<th>Weight in grams</th>
<th>(d^28)</th>
<th>(d_4^{25})</th>
<th>(n_D^{26})</th>
<th>(n_D^{25})</th>
<th>([R_L]<em>D) calc. for (C</em>{15}H_{30})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>153-161</td>
<td>0.6459</td>
<td>0.7743</td>
<td>0.7745</td>
<td>1.4335</td>
<td>1.4339</td>
<td>70.6</td>
</tr>
<tr>
<td>B</td>
<td>Above 162</td>
<td>0.1665</td>
<td>0.7657</td>
<td>0.7659</td>
<td>1.4300</td>
<td>1.4304</td>
<td>71.00</td>
</tr>
<tr>
<td>Loss</td>
<td></td>
<td>0.0783</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The oil itself had a very low rotation. But the fractions A and B did not give any rotation in a micro-polarimeter tube in dilute chloroform solutions.

The second fraction (B) (Table II) was not proceeded with as the infra-red spectrum of the compound showed an extra peak therein indicating the possibility of its not being a single substance. (The infra-red spectra of the fractions A and B, were taken by a Perkin-Elmer infra-cord machine No.137-003 (Serial No.686), and
a smear of the compound was used. (Figs. 1 and 2). The spectra did not show any functional groups, unsaturation etc., as mentioned earlier.

Tests for unsaturation

The substance (Fraction A) was tested with bromine in carbon tetrachloride (2 - 3%) and ~1% aqueous permanganate. While it took four drops of bromine solution to develop a permanent yellow colour to one drop of the substance in carbon tetrachloride, only one drop of the reagent brought a colour with a blank, thus showing the presence of unsaturation. The substance in acetone had to be boiled with aqueous permanganate before the latter could be decolourised. Thus it is seen that there is decided unsaturation though not a pronounced one.

Molecular weight and molecular formula

The molecular weight was determined by the Beckmann freezing point method.²

\[
\begin{align*}
\text{Weight of sample} & = 0.2845 \text{ gms.} \\
\text{Weight of benzene} & = 21.975 \text{ gms.} \\
\text{Volume of benzene} & = 25 \text{ ml.} \\
\text{Density of benzene} & = 0.879. \\
\text{Freezing point of benzene} & = 5.035 \\
\text{Freezing point of solution} & = 4.745, 4.740, 4.740 \\
\text{Depression observed} & = 0.290, 0.295, 0.295 \\
\text{Molecular weight} & = \frac{1000 \times 5.035 \times 0.2845}{25 \times 0.879 \times \Delta T} \\
& = 227.1, \text{ or } 223.2
\end{align*}
\]

(where 5.085 is the depression constant for benzene and \( T = 0.290 \) or \( 0.295 \))

The combustion results were: (Found: C, 84.63%; H, 14.88%
C_{15}H_{30} requires: C, 85.7%; H, 14.3%)

**Selenium dehydrogenation**

0.2438 gm. of the substance was mixed with 0.6770 gm. of selenium in a 5 ml. distillation flask, the side arm of which was plugged. It was fitted with a long air condenser. The hydrogen selenide formed was absorbed in strong caustic soda. The heating was effected in a nitrate bath (10 parts of potassium nitrate and 7 parts of sodium nitrite) heated by an electric heater coupled with a dimmerstat for temperature control. The experiment was performed at a temperature of 280 - 300°C. for thirteen and one half hours, after which period the flask was raised from the bath to prevent its getting cracked by the cooling bath. After cooling the contents of the flask were extracted with light petroleum (b.p. 40 - 60°C), filtered and concentrated to a small volume.

It was then poured over a column of alumina (Brockmann chromatographic grade - activated under water pump vacuum and with an external bath-temperature of about 200°C, for 4 - 6 hours) 15.5 cm. long and 0.7 cm. diameter. The hydrocarbon was then eluted with three 25 ml. portions of petroleum ether. On evaporating the solvent, 0.2133 gm. of the substance was obtained, having $n_D^{24}$, 1.4322. Attempts to prepare a picrate with the hydrocarbon were unsuccessful.

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Oxidation with potassium permanganate

The substance was refluxed with aqueous potassium permanganate (approx. 10%) for two hours in permanganate treated acetone. The product was extracted with a 1:1 mixture of benzene and ether. On removal of the solvent, a small quantity of a substance which gave a peak in the carbonyl region of the infra-red spectrum was obtained. Attempts to prepare a 2:4 dinitrophenyl hydrazone of the carbonyl compound were unsuccessful, owing probably to the small quantity of the material.

CONCLUSION

Further experiments to establish the structure of the compound could not be undertaken for the present, due to paucity of material, but are certainly indicated. Thus further oxidative degradations and identification of the fragments involved, ozonolysis, peracid titrations, hydrogenation and probably nuclear magnetic resonance studies will help in the unambiguous assignment of a structure, which could then be proved by synthesis. At present it can only be said to be a sesquiterpene hydrocarbon of the molecular formula C_{15}H_{30}, containing a tetra substituted double bond (as other types would have shown up in the infra-red spectrum). The hydrocarbon may possibly be a straight chain compound, as it did not undergo dehydrogenation to give either a cadalenic, eudalenic, naphthalenic or azulenic hydrocarbon. Molecular refractivity too points to the same conclusion.