THE ESSENTIAL OIL OF EUCALYPTUS MACULATA HOOKER.

PART I.

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SUMMARY.

Essential oils from E. maculata have been examined from both Queensland and N.S.W. trees. The latter appear to produce oils of uniform composition, containing as major constituents cineole, (+)-α-pinene, dipentene and (+)-limonene, cadinene, cadinol and a levo-rotatory sesquiterpene. The Queensland trees so far examined, whilst containing only (+)-α-pinene as the major constituent, show some variations among themselves with respect to the minor constituents. Similar oils have been observed from some of the progeny of the low-aldehyde form of E. citriodora (Penfold et al., 1953), and the specific status of the two species is discussed.

INTRODUCTION.

The essential oil of E. maculata was first described by Baker and Smith (1920,) who examined two oils, one from southern and one from northern New South Wales. These authors reported the presence of cineole, pinene and sesquiterpene (assumed by them to be aromadendrene) in these oils. They could find no evidence for the presence of citronellal. Since this date no further work on the essential oil of this species has been carried out, owing to the fact that the oil showed no promise of either commercial value or scientific interest.

However, following the discovery by Penfold et al. (1948, 1951) of variant oil forms within the species E. citriodora Hooker, it has been found necessary to define the essential oil status of E. maculata more accurately both in Queensland and New South Wales.

This arises from the fact that some of the progeny from the low-aldehyde form of E. citriodora have been shown by Penfold et al. (1953) to yield oils strikingly similar in composition to oils from E. maculata trees naturally occurring in Queensland. Secondly, although the geographical ranges of these two trees overlap northwards from about latitude 25°S. each species seems to occupy its own distinct area within this range, and they rarely intermingle to any great extent. Notwithstanding this, several individual trees within well-defined populations of E. citriodora, and remote from any occurrences of E. maculata, have given oils very similar in composition to E. maculata oils.

This evidence has led us to review the relationship between E. citriodora and what is known in Queensland as E. maculata. Morphologically, the two species, as they occur in Queensland, are remarkably alike, and it is virtually impossible to separate them on these grounds alone. Mueller (1879) maintained
there were no morphological differences between the two, and considered *E. citriodora* to be merely a variety of *E. maculata*. Maiden (1922, 1924) agreed, as he considered the two trees did "not differ in important morphological characters". Blakely (1934) mentions that the pedicels of *E. citriodora* are more slender than those of *E. maculata*, the buds less pointed, and the leaves, on the whole, shorter, but in our experience these characters are too variable to be of much value as specific differences. In addition, a critical examination of the wood anatomy of the two trees, carried out on our behalf by Byrnes (1953), has failed to show any differences between *E. citriodora* and Queensland *E. maculata*. Consequently, it is the opinion of the present authors that the name *E. maculata* has, up to the present time, been employed in Queensland solely to designate those trees whose leaves do not give an odour of citronella when crushed. In view of what is now known of the occurrence of physiological forms or chemical varieties within a single species (Penfold, 1949), the separation of trees into species on purely chemical grounds can no longer be justified.

It may also be of significance that the oils from the various collections of *E. maculata* so far examined from Queensland sources, although varying somewhat among themselves (e.g. guaiol present in some oils) are all fundamentally different in composition from oils from the tree known in New South Wales as *E. maculata*. The relationship between N.S.W. *E. maculata* and the Queensland *E. maculata-E. citriodora* complex is also at present being examined at this Institution.

### THE ESSENTIAL OILS.

The essential oils obtained by steam-distillation of the foliage showed marked variations in composition both between the Queensland and New South Wales samples, as well as within the Queensland samples.

The two N.S.W. oils were similar in composition, consisting principally of cineole, (+)-x-pinene, dipentene, (+)-limonene, cadinene, cadinol, a laevorotatory sesquiterpene yielding cadalone on dehydrogenation, and small amounts of an unidentified sweet-smelling substance.

The two Queensland oils, differing from each other and from other Queensland oils in the course of examination, differed markedly from the N.S.W. oils. Although the major constituent in each case was found to be (+)-x-pinene, it was associated, in the case of the Brisbane oil, with iso-valeric aldehyde, dipentene, terpinolene, an ester of terpinol (?), a laevorotatory and a dextrorotatory sesquiterpene, both yielding an azulene on dehydrogenation, and a sesquiterpene alcohol fraction giving a mixture of cadalone and an azulene on dehydrogenation. In the case of the Tiaro oil, the pinene was associated with guaiol, together with dipentene, a laevorotatory sesquiterpene and a sweet-smelling constituent which could not be identified. The occurrence of guaiol in this oil may be not without significance in the question of the *E. maculata-E. citriodora* relationship, as Harris and McKern (1950) have already demonstrated the frequent occurrence of this compound in oils of the low-aldehyde form of *E. citriodora*. Data for the crude oils are given in Table I.

### EXPERIMENTAL.

(In each case the essential oils were obtained by the steam-distillation of leaves and terminal branchlets. All melting points are uncorrected.)

**New South Wales Trees.**

The oils from Moorebank and Bateman’s Bay (see Table 1) were examined separately; however, as the oils were subsequently shown to be of similar composition, a typical examination only will be described.
Fractional distillation: 475 ml of oil after washing with alkali to remove acidic and phenolic constituents had $\rho_0 = 0.9206$; $n_20 = 1.4861$; $\alpha_20 = +2.40^\circ$. On fractional distillation at reduced pressure the fractions described in Table II were obtained.

**Table II.**

<table>
<thead>
<tr>
<th>Origin of Material</th>
<th>Date Received</th>
<th>Weight of Foliage</th>
<th>Oil Yield</th>
<th>$d_{15}^{15}$</th>
<th>$n_{20}^{20}$</th>
<th>$\alpha_{20}$</th>
<th>Solubility in Aqueous Alcohols</th>
<th>Acid Number, mg KOH/g</th>
<th>Ester Number, mg KOH/g</th>
<th>Ester Number After Acetylation</th>
<th>Cineole Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moorebank, N.S.W.</td>
<td>19/7/51</td>
<td>lb. 208</td>
<td>% 0.49</td>
<td>0.9201</td>
<td>1.4857</td>
<td>+6.70°</td>
<td>Insoluble in 10 vols.</td>
<td>1.1</td>
<td>6.1</td>
<td>46.8</td>
<td>27%*</td>
</tr>
<tr>
<td>Bateman's Bay, N.S.W.</td>
<td>13/9/51</td>
<td>255</td>
<td>% 0.78</td>
<td>0.9208</td>
<td>1.4835</td>
<td>+2.25°</td>
<td>Insoluble in 8.4 vols.</td>
<td>2.0</td>
<td>6.5</td>
<td>19.6</td>
<td>26%*</td>
</tr>
<tr>
<td>Brisbane, Queensland</td>
<td>6/6/52</td>
<td>200</td>
<td>1.0</td>
<td>0.8758</td>
<td>1.4727</td>
<td>+30.85°</td>
<td>Insoluble in 10 vols. (turbidity)</td>
<td>1.5</td>
<td>6.2</td>
<td>18.9 Absent</td>
<td></td>
</tr>
<tr>
<td>Tiaro, Queensland</td>
<td>14/3/51</td>
<td>107</td>
<td>1.1</td>
<td>0.8712</td>
<td>1.4702</td>
<td>+33.62°</td>
<td>Insoluble in 10 vols.</td>
<td>1.1</td>
<td>3.4</td>
<td>16.8 Absent</td>
<td></td>
</tr>
</tbody>
</table>

* The cineole contents given for the crude oils were determined by calculation from the cineole found by the o-cresol method in the fractions boiling up to 60° at 10 m.m.
Essential Oil of Eucalyptus Maculata Hooker.

Diminished pressure yielded 3.8 ml. of a greenish-brown oil having $d_{15}^5 = 0.9817$ and $n_D^{20} = 1.5680$. It gave a good yield of an orange picrate of m.p. $116^\circ$, undepressed by an authentic specimen of cadalene picrate. The fraction yielded also a nitrosochloride of m.p. $155^\circ$ (with decomposition) but a hydrochloride could not be prepared.

**Determination of Cadinene.** Refractionation of fractions 5 and 6 gave a fraction $b = 133-139^\circ$; $d_{15}^5 = 0.9250$; $n_D^{15} = 1.5097$; $\alpha_D = +43.27^\circ$. The fraction gave a good yield of a glistening white hydrochloride of m.p. $119^\circ$, undepressed by an authentic specimen of cadinene dihydrochloride. Dehydrogenation with sulphur gave a green oil $122^\circ$; $d_{15}^5 = 0.9826$; $n_D^{15} = 1.5747$. It gave an orange picrate of m.p. $115^\circ$, undepressed by an authentic specimen of cadalene picrate.

**Determination of Cadinol.** Refractionation of fraction 8 gave a fraction $b = 124^\circ$; $d_{15}^5 = 0.9783$; $n_D^{15} = 1.5083$; $\alpha_D = -24.4^\circ$. This highly viscous oil yielded a hydrochloride of m.p. $119^\circ$, undepressed by an authentic specimen of cadinene dihydrochloride. It also was dehydrogenated with sulphur to yield an oil which readily formed a picrate of m.p. $116^\circ$ undepressed by cadalene picrate.

**Alkali-soluble Constituents.** The various consignments of oil contained about 0.2% of acidic and phenolic substances which were not further investigated.

**Queensland Trees.**

(a) Tiaro District. Four hundred and twenty-seven grammes of the crude oil (Table I) were fractionally distilled at reduced pressure to give the fractions shown below in Table IV.

**Table IV.**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Range</th>
<th>Pressure</th>
<th>Volume</th>
<th>$d_{15}^5$</th>
<th>$n_D^{20}$</th>
<th>$\alpha_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40–60°</td>
<td>10</td>
<td>203.0</td>
<td>0.8970</td>
<td>1.4632</td>
<td>+9.2°</td>
</tr>
<tr>
<td>2</td>
<td>60–110°</td>
<td>9</td>
<td>30·5</td>
<td>0.9109</td>
<td>1.4846</td>
<td>-5.8°</td>
</tr>
<tr>
<td>3</td>
<td>110–112°</td>
<td>9</td>
<td>31·0</td>
<td>0.9149</td>
<td>1.5034</td>
<td>-9.85°</td>
</tr>
<tr>
<td>4</td>
<td>112–113°</td>
<td>9</td>
<td>39·0</td>
<td>0.9181</td>
<td>1.5061</td>
<td>-0.6°</td>
</tr>
<tr>
<td>5</td>
<td>113–125°</td>
<td>9</td>
<td>50·0</td>
<td>0.9239</td>
<td>1.5094</td>
<td>+21.0°</td>
</tr>
<tr>
<td>6</td>
<td>125–128°</td>
<td>9</td>
<td>30·0</td>
<td>0.9307</td>
<td>1.5006</td>
<td>+33.0°</td>
</tr>
<tr>
<td>7</td>
<td>128–132°</td>
<td>10</td>
<td>22·0</td>
<td>0.9519</td>
<td>1.5080</td>
<td>+9.0°</td>
</tr>
<tr>
<td>8</td>
<td>120–125°</td>
<td>5</td>
<td>57·0</td>
<td>0.9797</td>
<td>1.5075</td>
<td>-23.0°</td>
</tr>
</tbody>
</table>

**Determination of Cineole.** Fraction 1 had a cineole content (Cocking method) of 60.5%. The cineole was removed from 190 ml. by repeated extraction with 50% aqueous resorcinol solution. The aqueous solution of the cineole-resorcinol addition compound was steam-distilled with an excess of sodium hydroxide solution to give a colourless oil of camphoraceous odour having $d_{15}^5 = 0.9281$; $n_D^{20} = 1.4607$; $\alpha_D = \pm 0^\circ$. The identity of the cineole was confirmed by the preparation of the $o$-creosol addition compound of m.p. 56–56.5°, undepressed by an authentic specimen.

The cineole-free oil from fraction 1 was refractionated at reduced pressure to give the fractions described in Table III.

**Table III.**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Range</th>
<th>Pressure</th>
<th>Volume</th>
<th>$d_{15}^5$</th>
<th>$n_D^{20}$</th>
<th>$\alpha_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>42–52°</td>
<td>19</td>
<td>11·6</td>
<td>0.8569</td>
<td>1.4681</td>
<td>+30.3°</td>
</tr>
<tr>
<td>B</td>
<td>52–58°</td>
<td>19</td>
<td>9·2</td>
<td>0.8529</td>
<td>1.4706</td>
<td>+26.66°</td>
</tr>
<tr>
<td>C</td>
<td>58°</td>
<td>17</td>
<td>24·8</td>
<td>0.8450</td>
<td>1.4707</td>
<td>+19.35°</td>
</tr>
</tbody>
</table>

**Determination of (+)-\(\alpha\)-pinene.** Fraction A yielded a nitrosochloride of m.p. 109°, undepressed by an authentic specimen of \(\alpha\)-pinene nitrosochloride. Confirmation was obtained by permanganate oxidation of the fraction to an oily acid which gave a semicarbazone of m.p. 205°, undepressed by an authentic specimen of \textit{pinonic acid semicarbazone}.

Alkaline permanganate oxidation gave no indications for either \(\beta\)-pinene or sabinene.

**Determination of Dipentene.** Fraction C in glacial acetic acid readily yielded a bromide of m.p. 124–125°, undepressed by an authentic specimen of \textit{dipentene tetrabromide}.

**Determination of (+)-limonene.** Using amyl alcohol and ether a second bromide preparation from fraction C gave, on fractional crystallisation, a bromide of m.p. 104°, undepressed by an authentic specimen of \textit{limonene tetrabromide}.

The *Laevorotatory Sesquiterpene.** Refractionation of fractions 2, 3 and 4 at reduced pressure gave a fraction $b = 112–117°$; $d_{15}^5 = 0.9082$; $n_D^{20} = 1.5001$; $\alpha_D = -22.2°$. Dehydrogenation of 10 ml. with sulphur for $2\frac{1}{2}$ hours at 185–220°, followed by extraction with ether and distillation under
diminished pressure yielded 3.8 ml. of a greenish-brown oil having $d_{15}^{15} 0.9817$ and $n_{D}^{20} 1.5880$. It gave a good yield of an orange picate of m.p. 116°, undepressed by an authentic specimen of cadalene pinate. The fraction yielded also a nitrosochloride of m.p. 155° (with decomposition) but a hydrochloride could not be prepared.

**Determination of Cadinene.** Refractionation of fractions 5 and 6 gave a fraction $b_1 133–139°$; $d_{15}^{15} 0.9250$; $n_{D}^{20} 1.5097$; $\alpha_D^D +43.27°$. The fraction gave a good yield of a glistening white hydrochloride of m.p. 119°, undepressed by an authentic specimen of cadinene dihydrochloride. Dehydrogenation with sulphur gave a green oil $b_1 122°$; $d_{15}^{15} 0.9826$; $n_{D}^{20} 1.5747$. It gave an orange picate of m.p. 115°, undepressed by an authentic specimen of cadalene pinate.

**Determination of Cadinol.** Refractionating of fraction 8 gave a fraction $b_2 124°$; $d_{15}^{15} 0.9783$; $n_{D}^{20} 1.5083$; $\alpha_D^D -24.4°$. This highly viscous oil yielded a hydrochloride of m.p. 119°, undepressed by sulphur to yield an oil which readily formed a picate of m.p. 116° undepressed by cadalene pinate.

*Alkali-soluble Constituents.* The various consignments of oil contained about 0.2% of acidic and phenolic substances which were not further investigated.

**Queensland Trees.**

(a) **Tiaro District.** Four hundred and twenty-seven grammes of the crude oil (Table I) were fractionally distilled at reduced pressure to give the fractions shown below in Table IV.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Range.</th>
<th>Pressure.</th>
<th>Volume.</th>
<th>$d_{15}^{15}$</th>
<th>$n_{D}^{20}$</th>
<th>$\alpha_D^D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39–40°</td>
<td>11</td>
<td>373</td>
<td>0.8640</td>
<td>1.4662</td>
<td>+39.4°</td>
</tr>
<tr>
<td>2</td>
<td>40–55°</td>
<td>9</td>
<td>8</td>
<td>0.8527</td>
<td>1.4782</td>
<td>+19.6°</td>
</tr>
<tr>
<td>3</td>
<td>55–120°</td>
<td>9</td>
<td>5</td>
<td>0.9103</td>
<td>1.4840</td>
<td>+4.0°</td>
</tr>
<tr>
<td>4</td>
<td>120–144°</td>
<td>9</td>
<td>Remainder</td>
<td>solidified.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The first runnings had an odour of iso-valeric aldehyde. Its amount was too small to investigate, but the presence of this aldehyde was demonstrated in the Brisbane oil which will be described later. Refractionating of fraction 1 failed to alter significantly the physical data.

**Determination of (+)-\(\alpha\)-pinene.** 32 g. of a fraction having $d_{15}^{15} 0.8636$; $n_{D}^{20} 1.4668$; $\alpha_D^D +39.87°$ on oxidation with permanganate gave an excellent yield of a crystalline acid of m.p. 68.5°, undepressed by an authentic specimen of pinonic acid. The semicarbazon was prepared and melted at 204°, also undepressed on admixture with an authentic specimen of pinonic acid semicarbazone.

**Determination of Dipentene and Limonene.** Fraction 2 yielded a bromide of m.p. 120°, undepressed by admixture with dipentene tetrabromide of m.p. 124–125°. It thus appears that both dipentene and (+)-limonene are present. Fraction 3 failed to give an \(\alpha\)-naphthyl urethane and was not further investigated.

**Determination of Guaiol.** Fraction 4 solidified to a crystalline mass. The liquid portion was filtered off at the pump and the solid purified first by draining on a porous tile, then by recrystallisation from alcohol to m.p. 91.5°, undepressed by admixture with an authentic specimen of guaicol.

The Laevo-rotatory Sesquiterpene. The filtrate from fraction 4 had $d_{15}^{15} 0.9806$; $n_{D}^{20} 1.5044$; $\alpha_D^D -23.15°$ and was still heavily contaminated with guaicol. It was redistilled at 8 mm. to give
Attempts to prepare hydrochlorides and trinitrobenzoates failed with all fractions. Water was formed during the dehydrogenation of fractions 14 and 15. The ester number after acetylation indicated 51% of acetylisable constituents.

Fractions 14 and 15, as well as yielding the royal-blue azulene as the main dehydrogenation product, also gave a yellow fraction, which reacted with picric acid to give an orange-yellow product, m.p. 114.5° C, identical in physical characteristics with, and undepressed by, admixture with cadalene picrate.

**ACKNOWLEDGEMENTS.**

We should like to express our thanks to the District Forester at Bateman's Bay, N.S.W., for securing material from his area. The Queensland Sub-Department of Forestry has given great assistance in arranging collections of material from various localities in that State. Much help in the analytical determinations was given by Mr. E. O. Hellyer, A.S.T.C. (Chem.). Micro-analyses are by the Division of Industrial Chemistry of the C.S.I.R.O., Melbourne. Our thanks are due to the Director (Mr. A. E. Penfold, F.E.A.C.I.) and the Trustees of the Museum for permission to publish this work.

**References.**


1924. Ibid., 6, p. 433.


**TABLE V.**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Range.</th>
<th>Pressure.</th>
<th>Volume.</th>
<th>$d_{15}^{15}$</th>
<th>$n_{D}^{20}$</th>
<th>$\alpha_{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trap</td>
<td>10 °C.</td>
<td>mm.</td>
<td>ml.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>38</td>
<td>10</td>
<td>35.0</td>
<td>0.8640</td>
<td>1.4667</td>
<td>+37.7°</td>
</tr>
<tr>
<td>2</td>
<td>39</td>
<td>10</td>
<td>42.0</td>
<td>0.8634</td>
<td>1.4662</td>
<td>+41.5°</td>
</tr>
<tr>
<td>3</td>
<td>39-43</td>
<td>10</td>
<td>6.0</td>
<td>0.8664</td>
<td>1.4669</td>
<td>+37.0°</td>
</tr>
<tr>
<td>4</td>
<td>43-51</td>
<td>10</td>
<td>5.0</td>
<td>0.8690</td>
<td>1.4715</td>
<td>+14.9°</td>
</tr>
<tr>
<td>5</td>
<td>51-58</td>
<td>10</td>
<td>20.0</td>
<td>0.8616</td>
<td>1.4745</td>
<td>+4.8°</td>
</tr>
<tr>
<td>6</td>
<td>58-61</td>
<td>10</td>
<td>4.0</td>
<td>0.8608</td>
<td>1.4796</td>
<td>+2.5°</td>
</tr>
<tr>
<td>7</td>
<td>61-66</td>
<td>10</td>
<td>2.0</td>
<td>0.8251</td>
<td>1.4803</td>
<td>+10.1°</td>
</tr>
<tr>
<td>8</td>
<td>86-96</td>
<td>5</td>
<td>3.0</td>
<td>0.9475</td>
<td>1.4870</td>
<td>+10.1°</td>
</tr>
<tr>
<td>9</td>
<td>96-108</td>
<td>5</td>
<td>9.0</td>
<td>0.9281</td>
<td>1.4958</td>
<td>-7.3°</td>
</tr>
<tr>
<td>10</td>
<td>108-111</td>
<td>5</td>
<td>10.0</td>
<td>0.9221</td>
<td>1.5002</td>
<td>-3.4°</td>
</tr>
<tr>
<td>11</td>
<td>111-114</td>
<td>5</td>
<td>8.0</td>
<td>0.9241</td>
<td>1.5025</td>
<td>+8.0°</td>
</tr>
<tr>
<td>12</td>
<td>114-120</td>
<td>5</td>
<td>8.5</td>
<td>0.9279</td>
<td>1.5054</td>
<td>+12.4°</td>
</tr>
<tr>
<td>13</td>
<td>120-123</td>
<td>5</td>
<td>17.5</td>
<td>0.9358</td>
<td>1.5088</td>
<td>+12.7°</td>
</tr>
<tr>
<td>14</td>
<td>123-125</td>
<td>5</td>
<td>11.0</td>
<td>0.9618</td>
<td>1.5073</td>
<td>+5.0°</td>
</tr>
<tr>
<td>15</td>
<td>125-126</td>
<td>5</td>
<td>7.0</td>
<td>0.9757</td>
<td>1.5052</td>
<td>+5.0°</td>
</tr>
</tbody>
</table>

**Determination of (±)-α-pinene.** Fraction 1 gave on permanganate oxidation an acid of m.p. 68.5° C. The semicarbazone of the acid melted at 205° C. Alkaline permanganate oxidation of fraction 4 failed to yield any benzene-soluble acidic material.

**Determination of Dipentene.** Fraction 5 gave a good yield of a bromide of m.p. 124-125° C. undepressed by an authentic specimen of dipentene tetrabromide.

**Determination of Terpinolene.** Fraction 6 yielded a bromide which was fractionally crystallised into two main fractions. The first melted at 120° C and was undepressed by an authentic specimen of dipentene tetrabromide. The second fraction melted at 116° C, was depressed by dipentene tetrabromide, but undepressed by terpinolene tetrabromide.

**Terpenyl Ester?** Fraction 8 was saponified with 0.5 N alcoholic potassium hydroxide for 2 hours on a steam-bath. Steam distillation of the reaction mixture gave 3 ml. of a colourless oil of a pronounced terpineol odour and having $d_{15}^{15}$ 0.9395 and $n_{D}^{20}$ 1.4880. Attempts to prepare a crystalline derivative failed.

**Sesquiterpenes and Sesquiterpene Alcohols.** All of the fractions boiling above 96° C. at 5 mm. were separately dehydrogenated with sulphur. The dehydrogenation products in petroleum ether were chromatographed through an alumina column. On removal of the solvent from the various fractions, the main dehydrogenation product in each case was an intensely royal-blue azulene. The picrate in each case formed as very dark olive-green needles melting at 115-15° C.
Attempts to prepare hydrochlorides and trinitrobenzoates failed with all fractions. Water was formed during the dehydrogenation of fractions 14 and 15. The ester number after acetylation indicated 51% of acetylsable constituents.

Fractions 14 and 15, as well as yielding the royal-blue azulene as the main dehydrogenation product, also gave a yellow fraction, which reacted with picric acid to give an orange-yellow product, m.p. 114.5° C., identical in physical characteristics with, and undepressed by, admixture with cadalene picrate.

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