Elemi—The Oleo-resin of *Canarium Muelleri*.

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The similarity to pharmaceutical elemi of the oleo-resin of *Canarium muelleri* (N.O. Burseraceae), a lofty tree endemic in tropical Queensland and of exclusively Australian occurrence, is cited by F. M. Bailey (Comprehensive Catalogue of Queensland Plants).

The constituents of elemi resins of commerce have been investigated by Tschirch and collaborators (Arch. Phar. 1902, 240, 293-294; 1903, 241, 149-159); the composition of elemi oils by several investigators, notably that of *Canarium luzonicum* (Manila elemi) by Clover, and subsequently by Bacon (Phil. Journ. Sci. 2, 1907, A, i.; 4, 1909, A, 93).

According to Clover the dominant constituent in the essential oil of this species is either limonene or phellandrene, there being, as observed also by Bacon, a remarkable variation in the composition of individual oils of the species.

Tschirch and Cremer (*loc. cit.*) found as characteristic and sole alcoholic constituents of elemi resins examined by them crystalline isomeric α and β amyрин, C$_{30}$H$_{50}$O, and as minor constituents, together with resene, crystalline and amorphous acids of either the eleminic acid (C$_{37}$H$_{50}$O$_4$) or eleminic acid (C$_{39}$H$_{50}$O$_4$) group.

Vesterberg, however (Ber. 20, 1241-1246; 23, 3186-90; 24, 3836-43), to whom investigation of amyрин is principally due, found certain elemis to contain also non-crystalline alcohols.

Examination by the authors of three samples of oleo-resin derived from *Canarium muelleri* does not reveal any such variation in the constituents of the essential oil as recorded by Clover for Manila elemi oil.

The principal constituent of the oil was constantly 1-α-pinene; α-terpineol, dipentene, and 1-α-phellandrene also occurring. The high boiling constituent, oxygenated sesquiterpene, obtained by Clover was not present.

In contrast to the elemis described by Tschirch the resin of *Canarium muelleri* does not contain crystalline amyрин as a separable entity, but in amount constituting it the major constituent amorphous alcoholic material, possibly a mixture of closely related bodies, isomeric with amyрин and distinguished therefrom by lower optical rotation and wholly non-crystalline character of derivatives.
The identification of "amorphous amyrin" in the resin of *Canarium muelleri* is significant both in relation to Tschirch's suggested classification of true elemis as containing α and β amyrin or related alcohols, and to Vesterberg's indication of the presence of non-crystalline alcohols in certain Canarium resins.

The alcohol slowly combines with phthalic anhydride, being separable from resene by that means, and is oxidised by chromic acid to resinous aldehyde or ketone. Acetyl and benzoyl derivatives are amorphous, and sparingly soluble in alcohol.

Other constituents of the resin are isomeric crystalline and amorphous acids of molecular composition distinct from elemic and elemirbe acids, and amorphous resene material possessing molecular composition approximating that required for \( \text{C}_{15}\text{H}_{24}\text{O} \).

**Experimental.**—The oleo-resin of *Canarium muelleri* is a viscous mass, light amber in colour, possessing the odour of turpentine. On long exposure it becomes resinous, hard, and brittle; 1,909 grammes collected in 1922 distilled with steam yielded 550 grammes (28.8 per cent.) of essential oil; 1,916 grammes collected in 1924, distilled at 100 mm. and subsequently at 2 mm. pressure from an oil-bath heated at 200° C., yielded 636 grammes (33 per cent.) of essential oil. In the latter case, approximately 100 ccs. of water were collected with the oil, and in each case about 1,100 grammes of hard brittle resin remained in the still. The one other sample examined gave similar results.

The following constants were recorded:

<table>
<thead>
<tr>
<th>1922 sample (distilled in steam)</th>
<th>1924 sample (distilled in vacuo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{15.5} )</td>
<td>0.868</td>
</tr>
<tr>
<td>( N_{D20} )</td>
<td>1.463</td>
</tr>
<tr>
<td>([\alpha]_D)</td>
<td>-16.2</td>
</tr>
<tr>
<td>Acid and ester values, Nil</td>
<td>Acid value, 5</td>
</tr>
<tr>
<td>Acetyl value, 10.3</td>
<td>Acetyl value, 28</td>
</tr>
<tr>
<td>Resin.</td>
<td>Ester value, 1.5</td>
</tr>
<tr>
<td>Acid value, 9</td>
<td>Acid value, 2</td>
</tr>
<tr>
<td>Ester value, nil</td>
<td>Ester value, 13</td>
</tr>
<tr>
<td>Acetyl value, 78</td>
<td>Acetyl value, 71</td>
</tr>
</tbody>
</table>

The higher alcohol constant of the essential oil distilled from the oil-bath in vacuo (Clover, *loc. cit.*) is due to more efficient removal of the higher boiling constituent, and altered acid, ester, and acetyl values of the resin are no doubt attributable to the interaction of the resin alcohol and acid.

**Examination of the Essential Oil.**—The examination of the essential oil obtained from the oleo-resin by distillation in vacuo is alone described, the oil obtained by steam distillation differing materially only in alcohol content and somewhat lower optical rotation.
A slight odour of volatile fatty acid was perceptible, and extraction with dilute NaOH solution gave on isolation an acid which was identified as butyric or iso-butyric acid by means of its silver salt (Found Ag = 54.8 per cent.).

600 ccs. of oil were fractionated at 30 mm. pressure, and after several refractions yielded ultimately—

(a) 350 ccs. boiling at 155-156° C. (760 mm.)
(b) 32 ccs. boiling at 160-170° C. (760 mm.)
(c) 33 ccs. boiling at 170-180° C. (760 mm.)
(d) 65 ccs. boiling at 110-118° C. (24 mm.)

Fraction (a) twice distilled over sodium possessed the following constants:—B.P. 155-156° d_{15.5} 0.8636 N_{D_{20}} 1.4651 (a)_D — 21.7°. (Found C = 87.7, H = 11.9.) Identity with 1a-pinene was confirmed by the preparation of a nitrosyl chloride melting at 107°C and of pinonic acid.

Oxidation with permanganate in the prescribed manner and search for nopinic acid failed to reveal the presence of β pinene.

Fraction (b) consisted largely of pinene; phellandrene and dipentene were also detected as in fraction (c) described below.

Fraction (c) redistilled from sodium gave the following results on analysis:—d_{15.5} 0.8554 N_{D_{20}} 1.473 (a)_D — 33.6 (Found C = 87.8, H = 118)— and proved to be a mixture of terpenes.

Dipentene was identified by means of its tetra-bromide, prepared by addition of bromine to a solution of 5 ccs. of the fraction in ether amyl alcohol solution. An oily bromine separated which slowly solidified. On recrystallisation several times from alcohol it melted at 124° C., and failed to depress the melting point of an authentic specimen of dipentene tetra-bromide.

The presence of 1a-phellandrene was determined by the formation of phellandrene nitrosite melting at 115° after isolation and purification in the manner prescribed by Smith, Hurst, and Read (J.C.S. Trans. 1923, 123, 1657).

The presence of 1-limonene, β-pinene, and p-cymene could not be detected.

Fraction (d) possessed the characteristic odour of terpineol. By refractionation there was obtained a portion with the following constants:—

d_{15.5} 0.9421, N_{D_{20}} 1.4773, (a)_D — 33.7 B.P. 115°C (20 mms.) 218°C (760 mms.). (Found C = 77.7, H = 11.5).

Identity with α-terpineol was established by means of the nitrosyl chloride melting at 112° C. and by reaction with phenyl isocyanate, the resulting phenyl urethane after purification melting at 113° C.
The essential oil is composed of approximately 75-80 per cent. of lα-pinene, 12 per cent. of α-terpineol (as determined from the acetyl value) with small amounts of lα-phellandrene and dipentene.

Examination of the Resin.—The amber-coloured, brittle resin, which in contrast to the essential oil was dextro-rotatory, was readily soluble in chloroform, ether, turpentine, and petroleum ether, but incompletely soluble in alcohol.

Isolation of a Resin Acid C_{28}H_{45}O_{2}.—In order to isolate resin acids, the resin, in lots of 100 grs. for each experiment, was boiled under reflux with alcoholic sodium hydroxide solution in order to decompose resin esters, the alcoholic solution evaporated, and the residue extracted with petroleum ether. Sodium salts of resin acids obtained as a residue were collected, thoroughly washed with petroleum ether, and decomposed with dilute sulphuric acid, the liberated acid being taken up with ether. On evaporation of the solvent a resinous mass remained which, after solution in ether petroleum mixture, slowly crystallised as the solvent evaporated. After repeated crystallisation the acid was obtained as needles melting at 215°C. Found C = 80.7, H = 10.8 Acid No. 133 (α)D in chloroform + 43. Calculated from these results the formula of the acid which is monobasic is C_{28}H_{45}O_{2}. (Required C = 81.3, H = 10.9).

The mother liquors after removal of the crystalline acid could not be induced to crystallise further, and by isolation by means of a silver salt there was obtained therefrom a small amount of amorphous acid material. Found C = 80.8, H = 10.8 Acid No. 132, (α)D in chloroform + 48.0. Melting point 82-84°C.

The alkali salts of both acids were insoluble in water and amorphous, but soluble in alcohol. (Found Na = 5.4.) The amorphous silver salts tended to rapidly gelatinise. Found Ag = 20.5, 20.4 (C_{28}H_{44}O_{2}Na reqs. Na = 5.2; C_{28}H_{44}O_{2}Ag reqs. Ag = 20.8).

These figures indicate that the amorphous acid is isomeric with the crystalline, and that neither acid conforms to the formulae ascribed by Tschirch to elemic and eleminic acids, although it is to be noted that the melting point of the crystalline acid is identical with the melting point recorded for these.

Separation of Resin Alcohol, "Amorphous Amyrin."—The resin after removal of the acids possessed an acetyl value of 90, and gave in chloroform (α)D + 60.8. As all attempts to isolate crystalline alcohols in the manner prescribed for the separation of amyrrin, and from various mixtures of solvents, were unsuccessful, 100 grammes of material were heated in an oil-bath under reflux with 75 grammes of phthalic anhydride and 50 ccs. of dry benzene for eight hours. On treatment of the melt with excess aqueous sodium hydroxide an insoluble sodium salt separated, apparently readily hydrolysed. Addition of concentrated brine facilitated separation. In all, three treatments with phthalic
anhydride were necessary to completely remove all alcohol, as shown by absence of acetyl value in the residual resene. Purification of the acid phthalate was accomplished by repeated precipitation as sodium salt from ethereal solution. The silver salt was readily prepared. Found Ag = 16.0\% \text{(C}_3\text{H}_6\text{O})_2\text{Ag reqs. Ag = 15.9).}

The acid phthalate was hydrolysed by alcoholic sodium hydroxide, and the resin alcohol separated by solution in ether. Evaporation of the solvent left a brittle, resinous mass which could not be induced to crystallise. Fifty grammes of alcohol (melting indefinitely between 75° and 80° C.) were obtained in this manner from each 100 grammes of material treated, loss being difficult to avoid. Found C = 84.4, H = 11.6; (a)D in chloroform + 50.7. \text{(C}_9\text{H}_9\text{O})_2\text{O reqs. C = 84.3, H = 11.7; α-amyrin (α}_D = 99; β-amyrin (α}_D = 96).\

The acetyl derivative was likewise amorphous. (α}_D in chloroform + 33.6 ester value, 118. Found C = 81.2, H = 10.8. \text{(C}_9\text{H}_4\text{O})_2\text{O reqs. C = 82.0, H = 11.1; ester value 120; (a amyрин acetate (α}_D = 77; β amyрин acetate (α}_D = 78).}

In order to determine the homogeneity or otherwise of the alcoholic material, recourse was had to a method suggested by the recorded difference in solubilities of the esters of α and β amyрин (Vesterberg, Tschirch). Forty grammes of the finely powdered acetyl derivative were fractioned by successive treatments with boiling alcohol (300 c.c.s.), the solution being removed at room temperature, and five fractions were thereby obtained. The amounts, ester values, and specific rotations of the fractions are recorded in the subjoined table:—

<table>
<thead>
<tr>
<th>Fract.</th>
<th>Grms.</th>
<th>e.v.</th>
<th>(α)_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.3</td>
<td>119</td>
<td>+ 33.4</td>
</tr>
<tr>
<td>2</td>
<td>7.0</td>
<td>118</td>
<td>+ 33.5</td>
</tr>
<tr>
<td>3</td>
<td>6.9</td>
<td>119</td>
<td>+ 33.6</td>
</tr>
<tr>
<td>4</td>
<td>7.3</td>
<td>120</td>
<td>+ 33.6</td>
</tr>
<tr>
<td>Res.</td>
<td>9.0</td>
<td>118</td>
<td>+ 33.6</td>
</tr>
</tbody>
</table>

Similar results were afforded by parallel fractionation of the amorphous benzoyl derivative.

The figures may be interpreted as affirming at least preponderance of one alcoholic body, although the assumption of considerable admixture of isomers closely similar in properties is by no means negatived.

Oxidation of the Resin Alcohol.—Five grammes of alcohol were heated with 5 grammes chromic acid in acetic acid until reduction of the chronic acid was complete. On pouring the product into water a resinous mass separated, which in subsequent treatment showed no sign of crystallisation. Its aldehyde or ketonic property was demonstrated by reaction with hydroxylamine.
Attempts to remove a molecule of water from the alcohol by interaction with phosphorus pentachloride and with phosphorus pentoxide with production of hydrocarbon were not successful. Vigorous reaction occurred with charring, but nothing definite could be separated from the reaction product.

"Amorphous amyrin" yields with concentrated sulphuric and acetic acids the purple red colour reaction described as characteristic of crystalline amyrin.

The Resene.—The residual resinous material after separation of the alcohol was dark in colour, and powdered with difficulty. Aldehydic or ketonic properties could not be demonstrated in it, and both ester and acetyl values were nil. Found C = 81.5, H = 10.7 (C_{15}H_{24}O reqs. C = 81.8, H = 10.9). Evidently resene, the material constituted about 30 per cent. of the resin, and was not further examined.

Summary.—The oleo-resin of Canarium muelleri has been found to contain:

(1) 30 per cent. of essential oil consisting principally of 1-α-pinene with α-terpineol, dipentene, 1-α-phellandrene, and a trace of butyric acid.

(2) A residual resin consisting of:

(a) Acid material (7 per cent.), comprising crystalline and amorphous isomers (C_{28}H_{45}O_{2}) differing from elemic and eleminic acids of elemi resins previously described.

(b) Amorphous alcoholic material (60 per cent.), conforming to the formula C_{30}H_{50}O, possibly a mixture, isomeric with the crystalline amyrin occurring generally in elemis.

(c) Resene material (30 per cent.) of composition approximating to the molecular formula C_{15}H_{24}O.

We are indebted to Mr. E. H. F. Swain, Director of Forests, Brisbane, for supply of material utilised in the above investigation, and to Mr. C. T. White, Government Botanist, for verification of the authenticity of specimens.

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