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BY

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ESSENTIAL OILS FROM THE QUEENSLAND FLORA—PART XXI.

The Essential Oil of *Evodia Elleryana*.

By T. G. H. JONES, D.Sc., F.A.C.I., and S. E. WRIGHT, M.Sc., Dip. Pharm.

Evodia Elleryana is a tree growing abundantly in the Mackay area of Queensland, whilst scattered groups occur along the coastal fringe of Southern Queensland, including the Moreton Bay shore of Stradbroke Island. A small amount of oil obtained from the lastnamed locality was examined in this Department by Dr. F. N. Lahey and Mr. D. T. Robertson and the presence of a solid ketone established. Later, larger quantities of leaves became available from both Mackay and Stradbroke Island, and this paper deals with the chemical constituents of the volatile oils obtained from them.

The tree grows up to 20 feet high in places and the foliage is by no means dense. In both cases the yield of oil was poor. The Mackay leaves (air dried) gave 0.2 per cent. and the Stradbroke Island leaves (fresh) gave 0.23 per cent. An interesting local variation was discovered in the constituents of these oils. The Stradbroke Island sample consists of sesquiterpenes, a liquid sesquiterpene ketone, a crystalline methoxylated ketone M.P. 57° C., a small amount of a mixture of phenols and a small amount of a crystalline methoxylated neutral solid M.P. 81° C. The Mackay oil contains the same liquid sesquiterpene ketone and small amounts of sesquiterpenes, phenols and a neutral methoxylated solid, M.P. 107° C.

The solid ketone M.P. 57° C., which does not appear to have been isolated previously, has been named Evodione. Analysis indicate its molecular formula to be $C_{16}H_{20}O_5$ and the presence of three methoxyl groups and one carbonyl group was detected. This solid gives a red colour with concentrated sulphuric acid and may be recrystallised from alcohol or petrol. It may be characterised by a number of derivatives—a crystalline orange red 2 : 4 dinitrophenylhydrazone M.P. 153°C., an oxime M.P. 119° C., a semicarbazone, M.P. 184°–185° C., and a pale yellow benzylidene derivative M.P. 133° C. The liquid sesquiterpene ketone isolated from both oils by its semicarbazone (M.P. 177–179° C.) and subsequent regeneration also appears to be new and has been named Elleryone. Analysis indicate a molecular formula $C_{15}H_{22}O$. It gives a purple colour with bromine and glacial acetic acid, characteristic of many azulene-yielding sesquiterpenes.

Little information is available about the minor constituents of the oils because of the poor yields obtained. Analyses indicate a molecular formula $C_{16}H_{20}O_5$ for the neutral solid M.P. 81° C., isolated from the Stradbroke oil. This solid contains three methoxyl groups, gives a red colour with concentrated sulphuric acid but no carbonyl derivatives could be isolated. The crystalline solid, M.P. 107° C., isolated from the Mackay oil, appears to have the formula $C_{16}H_{20}O_4$, contains two methoxyl groups, gives a red colour with concentrated sulphuric acid, but no derivatives could be obtained.

EXPERIMENTAL.

All melting points uncorrected.

A. *From Stradbroke Island.*

68 kg. of leaves, collected in May were steam distilled for 2 days. The volatile oil was viscous and heavy and required collecting in light petroleum. After removing the petrol under reduced pressure, 150 ml. of oil were obtained having the following constants:—

| | |
|-------------------------------|--------------|
| $n_{D}^{15.5}$ | 1.523 |
| $D_{15.5}^{15.5}$ | 1.0189 |
| $[\alpha]_D$ | too dark |
| Ester value | 13.5 |
| Ester value of acetylated oil | .. 38.1 |

The oil was diluted with ether and shaken with sodium carbonate solution and sodium hydroxide. No acids were present, and 3 ml. of a dark yellow liquid phenol were extracted. The phenolic fraction gave a deep green colour with ferric chloride, and on distillation, a white solid phenol crystallised, which on recrystallisation from petrol, melted at 76° (20 mgm. obtained). It was not found possible to purify the liquid phenol any further. After removal of the ether, the oil (120 ml.) was distilled at 2 mm. pressure

| | | | |
|---------------------|--------|--------------------|----------------|
| <i>Fraction (1)</i> | | B.P. 76–85° C. | Vol. 14 ml. |
| $D_{15.5}^{15.5}$ | 0.9178 | | |
| n_D^{21} | 1.5020 | | |
| $[\alpha]_D$ | –21 | | |
| <i>Fraction (2)</i> | | B.P. 85–90° C. | Vol. 10 ml. |
| $D_{15.5}^{15.5}$ | 0.9383 | | |
| n_D^{21} | 1.5080 | | |
| $[\alpha]_D$ | –26 | | |
| <i>Fraction (3)</i> | | B.P. 90–100° C. | Vol. 40 ml. |
| $D_{15.5}^{15.5}$ | 0.9784 | | |
| n_D^{21} | 1.5140 | | |
| $[\alpha]_D$ | –106 | | |

The remainder of the oil was then diluted with light petrol and refrigerated. A crystalline mass of evodione formed overnight. The crystals were filtered and recrystallised from petrol, to give M.P. 57° C. Yield 17 gms. The petrol was removed from the oil and distillation continued.

| <i>Fraction</i> (4) | B.P. | Vol. |
|---------------------|-------------|-------|
| | 110–115° C. | 8 ml. |
| $D_{15.5}^{15.5}$ | 1.00 | |
| n_D^{21} | 1.5190 | |
| $[\alpha]_D$ | –15 | |

The residue was again diluted with petrol and after refrigeration a second crop of evodione (3 gms.) was obtained. The distillation was continued to give a fraction, the constants of which were not determined, but when diluted with petrol and refrigerated, deposited crystals which were recrystallised from petrol to give M.P. 82° C. Yield 0.6 gms.

Evodione.—This solid crystallised in large prisms from petrol. It gave a red colour with concentrated sulphuric acid and was optically inactive.

| | | | |
|----------------------------|-----------|---------|-----------|
| Found C | 65.5 | 65.7 | 65.6 |
| H | 6.9 | 6.8 | 6.9 |
| $C_{16}H_{20}O_5$ requires | C = 65.75 | H = 6.9 | per cent. |

Molecular weight by depression of freezing point of benzene 285. 298.

$C_{16}H_{20}O_5$ requires 292.

Methoxyl determinations 31.8 31.1 32.5 per cent.

$C_{16}H_{20}O_5$ (3CH₃O—) requires 31.85 per cent.

Derivatives of Evodione:—*Oxime*.—Prepared by the method of Cousins and Lions¹ 0.3 gms. was refluxed for eight hours with 3 gms of hydroxylamine hydrochloride dissolved in 20ml. of alcohol together with excess barium carbonate. The barium carbonate was then filtered off, the filtrate diluted with water, and extracted with ether. The ether was removed leaving a dark oil which crystallised slowly. After several recrystallisations from petrol, a white oxime, M.P. 114° C., was obtained. Yield 0.1 gm.

| | | | |
|-----------------------------|----------|----------|--------------------|
| Found C = | 62.5 | 62.8 | |
| H | 6.45 | 7.1 | |
| N = | 4.8 | | |
| $C_{16}H_{21}O_5N$ requires | C = 62.5 | H = 6.84 | N = 4.56 per cent. |

Benzylidene derivative.—0.5 gm. of evodione, 0.5 benzaldehyde, and 10 ml. of 4 per cent. NaOH solution were dissolved in 15 ml. of alcohol, shaken for 4 hours and then stood overnight. Pale yellow needles separated which were recrystallised from alcohol. M.P. 133° C. Yield 0.4 gm.

| | | | |
|----------------------------|----------|----------|-----------|
| Found C = | 72.9 | 72.6 | 72.5 |
| H = | 6.22 | 6.6 | 6.4 |
| $C_{23}H_{24}O_5$ requires | C = 72.6 | H = 6.36 | per cent. |

2 : 4 *dinitrophenylhydrazone*.—Brady's method—orange red needles recrystallised from alcohol, M.P. 153° C.

| | | | |
|-------------------------------|----------|---------|-----------|
| Found C = | 56.4 | H = 5.3 | N = 12.0 |
| $C_{22}H_{24}O_8N_4$ requires | C = 55.9 | H = 5.1 | N = 11.9 |
| | | | per cent. |

Semicarbazone.—Using semicarbazide hydrochloride and sodium acetate, obtained colourless needles, recrystallised from aqueous alcohol M.P. 184–185° C. Found N = 12.2

$C_{17}H_{23}O_5N_3$ requires N = 12.04 per cent.

Second Solid.—Crystallised in rhomboids from petrol, M.P. 82° C., gave a red colour with concentrated sulphuric acid.

| | | | |
|----------------------------|-----------|---------|-----------|
| Found C = | 65.4 | 65.8 | 66.3 |
| H = | 6.9 | 7.06 | 6.9 |
| $C_{16}H_{20}O_5$ requires | C = 65.75 | H = 6.9 | per cent. |

Molecular weight by depression of freezing point of benzene = 285.

$C_{16}H_{20}O_5$ requires 292

Methoxyl determination 32.6 per cent.

$C_{16}H_{20}O_5$ ($3CH_3O-$) requires 31.85 per cent.

Liquid constituents.—The constants of fractions (1) and (2) indicated sesquiterpenes and after several refractionations and final distillation over sodium the following constants were recorded :—

Fraction (1)

| | | |
|-------------------|--------|-------|
| $n_D^{15.5}$ | 1.5003 | 3 ml. |
| $D_{15.5}^{15.5}$ | .9101 | |
| $[\alpha]_D$ | —24 | |

Fraction (2)

| | | |
|-------------------|--------|-------|
| $n_D^{15.5}$ | 1.5030 | 5 ml. |
| $D_{15.5}^{15.5}$ | .9129 | |
| $[\alpha]_D$ | —10.5 | |

The high density and high rotation of fraction (3) indicated a sesquiterpene alcohol or ketone or both. This fraction (36 gms.) was diluted with alcohol and mixed with an aqueous solution of 20 gms. of semicarbazide hydrochloride and 26 gms. of sodium acetate. The solution was warmed on a water bath until turbid and set aside for several days. Crystals separated which were filtered and recrystallised from absolute alcohol to constant melting point 177–179° C. Yield 11.0 gms. The filtrate was shaken with petrol, and on standing a second crop of semicarbazone formed (2.2 gms.). After filtering and removing the petrol the residue was steam distilled to yield only a small amount of oil. The residue in the distillation flask was then refluxed with aqueous oxalic acid and again steam distilled. An oil was recovered (3.5 ml.) which was again treated with semicarbazide hydrochloride and sodium acetate to yield 3 gms. of semicarbazone identical with above.

Semicarbazone

$$[\alpha]_D = -143 \quad (C = 2.1 \text{ in alcohol})$$

$$\text{Found } C = 69.2 \quad 70.3$$

$$H = 9.1 \quad 8.9$$

$$N = 15.6 \quad 15.5$$

$$C_{16}H_{25}N_3 \text{ requires } C = 69.8 \quad H = 9.0 \quad N = 15.3 \text{ per cent.}$$

Regeneration of Elleryone from the semicarbazone.—5 gms. of the semicarbazone were refluxed with 4 gms. of oxalic acid dissolved in 60 ml. of water for 1 hour and then steam distilled. 2.2 G. of a pale yellow ketone were recovered. The ketone was distilled under reduced pressure and the following constants recorded

$$B. Pt. \quad (mm. 0.5) \quad 70-72^\circ C.$$

$$n_{D}^{15.5} \quad 1.5163$$

$$D_{15.5}^{15.5} \quad 0.9750$$

$$[\alpha]_D^{20} \quad -118$$

$$[R_L]_D \quad 67.63$$

$$\text{Found } C = 82.3$$

$$H = 9.96$$

$$C_{15}H_{22}O \text{ requires } C = 82.5 \quad H = 10.16 \text{ per cent.}$$

B. From Mackay.

70 kg. of air dried leaves (received in June) were steam distilled for 2 days and the oil collected in light petroleum. Yield of oil 130 ml., having the following constants.

$$n_{D}^{15.5} \quad 1.5147$$

$$D_{15.5}^{15.5} \quad 0.980$$

$$[\alpha]_D \quad \text{too dark}$$

Ester value 21.3.

Ester value of acetylated oil 51.3.

The oil was diluted with ether and extracted with sodium carbonate solution to give a small amount of a solid recrystallised with difficulty from petrol, M.P. 59–60° C. (15 mgs. of product obtained.)

The diluted oil was then extracted with sodium hydroxide solution to give a small amount of a solid white phenol recrystallised from petrol, M.P. 80° C.—(recovered 0.1 gm.). This phenol gave a purple colour with ferric chloride.

The ether was removed from the oil and the residue 120 ml. distilled at 2 mm. pressure to give the following fractions :—

Fraction (1)

| | | B.P. | Vol. |
|-------------------|--------|-----------|--------|
| | | 72–76° C. | 12 ml. |
| n_D^{22} | 1.5027 | | |
| $D_{15.5}^{15.5}$ | .9515 | | |
| $[\alpha]_D$ | –21 | | |

Fraction (2)

| | | B.P. | Vol. |
|-------------------|--------|-------------|--------|
| | | 110–112° C. | 20 ml. |
| n_D^{22} | 1.5092 | | |
| $D_{15.5}^{15.5}$ | .9724 | | |
| $[\alpha]_D$ | –82 | | |

Fraction (3)

| | | B.P. | Vol. |
|-------------------|--------|-------------|--------|
| | | 112–115° C. | 15 ml. |
| n_D^{22} | 1.5107 | | |
| $D_{15.5}^{15.5}$ | .9802 | | |
| $[\alpha]_D$ | –70 | | |

Fraction (4)

| | | B.P. | Vol. |
|-------------------|--------|-------------|--------|
| | | 116–118° C. | 20 ml. |
| n_D^{22} | 1.5120 | | |
| $D_{15.5}^{15.5}$ | .9852 | | |
| $[\alpha]_D$ | –70 | | |

The residue in the flask was then diluted with petrol and refrigerated. A colourless crystalline solid separated, which when filtered and recrystallised from petrol (sparingly soluble) melted at 107° C. Only 0.6 gm. of solid was obtained.

Found C = 69.7 69.3 .

H = 7.02 7.28

$C_{16}H_{20}O_4$ requires C = 69.5 H = 7.24 per cent.
Methoxyl determination 23.1 22.0 per cent.

$C_{16}H_{20}O_4$ (2CH₃O) requires 22.8 per cent.

All the above fractions gave a positive test for ketone with semicarbazide hydrochloride. Accordingly each fraction was treated with semicarbazide hydrochloride and sodium acetate, as outlined above for the Stradbroke Island oil. Each fraction gave a semicarbazone M.P. 177–179° C. which by mixed melting point was shown to be identical with the semicarbazone isolated from the Stradbroke Island oil. Total yield of semicarbazone from this oil = 20 gms.

$$[\alpha]_{\text{D}} = -144 \text{ (C = 2.0 in alcohol)}$$

Regeneration of Elleryone from the semicarbazone.—5 gms. of semicarbazone were treated with oxalic acid as above and the ketone Elleryone isolated. Yield 2.3 G. Its constants were determined after distillation and found to be

| | |
|----------------------------|-----------|
| B. Pt. $\frac{1}{2}$ mm. | 70–72° C. |
| $n_{\text{D}}^{15.5}$ | 1.5168 |
| $D_{15.5}^{15.5}$ | 0.9749 |
| $[\alpha]_{\text{D}}^{20}$ | –116 |

The fractions also contained small amounts of sesquiterpene and possibly sesquiterpene alcohol. These remained in the residues after extracting the ketone but little success was met with in fractionation because of the complex mixture and small amounts recovered.

REFERENCES.

- (¹) Cousins and Lions. Proc. Roy. Soc. N.S.W. Vol. LXX., 413.

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