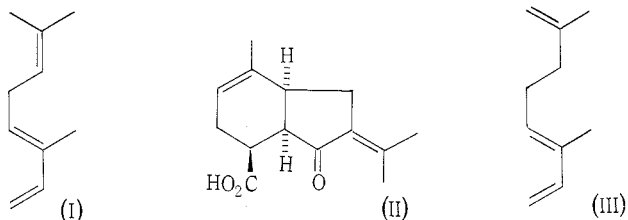


THE STEAM-VOLATILE CONSTITUENTS OF *MELALEUCA VIRIDIFLORA* SOL. EX GAERTN.*

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Melaleuca viridiflora Sol. ex Gaertn. belongs to the group of broad-leaved tea-trees of northern Australia. It occurs from Maryborough in Queensland into New Guinea and across northern Australia into the 15-in. rainfall region.¹ It is quite distinct from *Melaleuca quinquenervia* (Cav.) S. T. Blake, formerly designated as *Melaleuca viridiflora* Gaertn.² The steam-volatile oils of this latter species, which exists in two morphologically indistinguishable forms, are characterized by the presence of either nerolidol and linalool or 1,8-cineole and viridiflorol.³



The steam-volatile oils of *Melaleuca viridiflora* obtained from foliage collected in two different localities on the Cape York Peninsula in northern Queensland were shown to consist of methyl cinnamate (c. 75%) and *trans*- β -ocimene (I) (c. 20%), with only small amounts of other components. Amongst these, only eugenol (c. 1%) and linalool (c. 0.5%) were identified with certainty. The identification of *trans*- β -ocimene was based on spectral and other physical data (see Table 1). This identification was confirmed by the preparation of 7-carboxy-2-isopropylidene-4-methyl-2,3,3a,6,7,7a-hexahydroindanone (II) from its maleic anhydride adduct according to the method of Joseph and Rao.⁴ The indanone derivative (II) was obtained in a high yield (c. 70%). It also has a high melting point (m.p. 213–214°) and thus appears suitable for the purpose of identifying *trans*- β -ocimene, a hydrocarbon otherwise difficult to characterize. However, the possibility that *trans*- α -ocimene (III) would yield the same indanone derivative (II) at the high temperature used cannot be ruled out completely.

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¹ Blake, S. T., personal communication.

² Blake, S. T., *Proc. R. Soc. Qd.*, 1957, **69**, 77.

³ Jones, T. G. H., and Haenke, W. L., *Proc. R. Soc. Qd.*, 1936, **48**, 41; 1937, **49**, 95.

⁴ Joseph, K. T., and Krishna Rao, G. S., *Tetrahedron*, 1967, **23**, 519, 3215.

Reinvestigation of the steam-volatile oil of *Homoranthus flavescens* A. Cunn. showed that the ocimene previously reported⁵ is, in fact, *trans*- β -ocimene.

Experimental

All melting points are uncorrected. Silica gel used in column chromatography had a particle size 0.2–0.5 mm. Gas chromatography was conducted in a Bodenseewerk Perkin–Elmer Vapor Fractometer 116, using $\frac{1}{4}$ in. by 12 ft aluminium columns packed with 30–60 mesh Silanized Embacel coated with 15% Carbowax 20M. Ultraviolet spectra were determined in alcoholic solution. Infrared spectra were determined in Nujol mulls in the case of solid substances and in liquid film in the case of liquids.

TABLE 1
PHYSICAL CHARACTERISTICS OF OCIMENE
 λ in $m\mu$; ν in cm^{-1}

Compound	n_D^{20}	λ_{max}	ϵ_{max}	ν_{max} (double-bond bands)
Ocimene from				
<i>M. viridiflora</i>	1.4884	232.5	27800	1791, 1673, 1642, 1610, 989, 892, 830
<i>cis</i> - α -Ocimene ^a	1.4789	234.5	21600	1810, —, 1651, 1598, 988, 903, 825
<i>trans</i> - α -Ocimene ^a	1.4802	231	27300	1785, —, 1645, 1605, —, 880–895, 825
<i>cis</i> - β -Ocimene ^a	1.4877	237.5	21000	1806, 1671, 1641, 1593, 985, 897–905, 825
<i>trans</i> - β -Ocimene ^a	1.4893	232	27600	1788, 1670, 1640, 1608, 986, 890–902, 831

^a Ohloff, G., Seibel, J., and Kovats, E., *Liebigs Ann.*, 1964, **675**, 84.

(a) Isolation of Volatile Material

Dry foliage was steam-distilled in a tin-lined apparatus to yield straw-coloured oils lighter than water. These oils partly solidified on standing. Cooling of the milky aqueous distillates resulted in the separation of considerable amounts of crystalline solids. These were filtered off and united with the oily fractions. The crude oils obtained from foliage collected at Laura and Coen had the following characteristics: oil yield, 1.55–1.96%; ester No., 262–271; acid No., 1. Higher oil yields, up to 3.32%, were obtained by cohobation of small samples of foliage in an all-glass apparatus.

(b) Identification of Constituents

The crude oil (100 g) was kept in the refrigerator for several days. The solid mass was filtered with suction. A 10-ml aliquot of the filtrate (20 ml) was chromatographed on a silica gel column (150 g) using n-hexane (200 ml, fraction (1)), n-hexane–chloroform, 1:1 by volume (500 ml, fraction (2)), n-hexane–chloroform, 3:7 by volume (500 ml, fraction (3)), and diethyl ether (2 \times 500 ml, fraction (4)) as eluents.

(i) *Methyl cinnamate*.—The solid obtained from the initial filtration (70 g) as well as fraction (2) (6 g) were recrystallized from aqueous methanol. The white crystalline solid, m.p. 35–36°, was identified as methyl cinnamate by a mixed melting point determination and a comparison of the infrared spectrum with that of an authentic specimen.

(ii) *trans*- β -Ocimene.—Fraction (1) was submitted to gas chromatography and a homogeneous fraction corresponding to a peak with the same retention time as ocimene (from *Homoranthus flavescens*) was condensed. The physical constants and spectral data are summarized in Table 1.

⁵ Penfold, A. R., *J. Proc. R. Soc. N.S.W.*, 1922, **56**, 193.

A portion of fraction (1) (1 g, about 1/20 of total fraction) was refluxed with maleic anhydride (1 g) in dry benzene (2 ml) for 4 hr. The solvent was distilled off and the crude product was heated under nitrogen for 1 hr at 210–215° (oil-bath). Recrystallization of the heat-treated material (1.12 g, 68% yield) from ethyl acetate yielded a white crystalline powder, m.p. 213–214°. Its identity with (II) was established by a mixed melting point determination and comparison of its infrared spectrum with that of an authentic specimen.

(iii) *Eugenol*.—Fraction (3) (1.6 g) was rechromatographed on a small silica gel column using n-hexane–diethyl ether, 19:1 by volume, as eluent (in 25-ml aliquots). The initial four fractions yielded an additional small amount of methyl cinnamate. The fifth fraction was submitted to gas chromatography and a homogeneous peak with the same retention time as eugenol was condensed. Its infrared spectrum was identical with that of an authentic specimen.

(iv) *Linalool*.—Fraction (4) was submitted to gas chromatography and a homogeneous fraction corresponding to a peak with the same retention time as linalool was condensed. It was identified by a comparison of its infrared with that of an authentic specimen and by the preparation of its α -naphthylurethane, m.p. and mixed m.p. 53°.

(c) *Preparation of (II) from the Steam-Volatile Oil of Homoranthus flavescens*

A mixture of maleic anhydride (2.5 g), anhydrous benzene (10 ml), and oil of *H. flavescens* (7.5 ml) was treated as described previously. The indanone derivative (II) was obtained as a white powder, m.p. 211–212.5°. A mixed melting point determination and infrared spectrum were used to establish its identity.

Acknowledgments

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