Occurrence of Some Unusual Compounds in the Leaf Oils of *Eriostemon obovalis* and *Phebalium glandulosum* subsp. *glandulosum*

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Abstract

The steam-volatile leaf oils of *Eriostemon obovalis* A. Cunn. and *Phebalium glandulosum* subsp. *glandulosum* Hook. (Rutaceae) contain substantial amounts of methyl p-methoxycinnamate and (+)-2,6-dimethyloct-7-en-4-one respectively.

In the course of our survey of the Australian essential-oil-bearing flora, we investigated the volatile oils of *Eriostemon obovalis* A. Cunn. and *Phebalium glandulosum* subsp. *glandulosum* Hook. foliage. Both species belong to the family Rutaceae, tribe Boroniae, subtribe Eriostemoninae.

*Eriostemon obovalis* is a small white flowering shrub growing to a height of about 1 m on exposed sandstone cliffs tops in the Blue Mountains of New South Wales.\(^1\) Steam distillation of dried leaf material collected at Walls Lookout in the Blue Mountains National Park yielded a volatile oil which deposited on standing white plates shown by spectral evidence and synthesis to be methyl p-methoxycinnamate (1). To our knowledge this is the first occurrence of (1) in an essential oil, although it has been isolated as a fungal metabolite\(^2\) and as an artefact from the methanol extraction of a plant rich in *p*-methoxycinnamic acid (2).\(^3\)

\[\text{(1)} \quad \text{Me} \quad \text{Me} \]
\[\text{(2)} \quad \text{H} \quad \text{Me} \]
\[\text{(3)} \quad \text{H} \quad \text{H} \]

\[\text{p-Coumaric acid (3) has been reported to function as a plant growth inhibitor}^{4} \text{ and a coumarin precursor.}^{5,6} \text{ The co-occurrence of comparatively large quantities of (1)}\]

with the phloroglucinol-type coumarins bergapten, xanthoxyletin and limettin in *Eriostemon obovalis* suggests that the function of (1) is related to coumarin biosynthesis.

*Phebalium glandulosum* subsp. *glandulosum* is a medium-sized yellow flowering shrub widely distributed from southern Queensland, through central New South Wales to Victoria and the south-eastern corner of South Australia. Steam distillation of foliage collected in the Goonoo State Forest north of Dubbo in N.S.W. yielded a volatile oil of characteristic fruity odour. Gas-chromatographic examination revealed the presence of one major component (97·4 %) and of about seven minor components. The physical constants of the major component as well as its i.r. and p.m.r. spectral characteristics suggested that it was (+)-2,6-dimethyloct-7-en-4-one (4). This was verified by comparison with authentic (4) in freshly distilled *Tagetes minuta* L. oil.

It is noteworthy that a sample of *T. minuta* from Port Stephens, N.S.W., yielded an oil much richer in (4) (c. 50 %) than previously recorded.

**Experimental**

Melting points were determined with a Kofler block and are uncorrected. Gas-liquid chromatography was conducted on a Perkin–Elmer 900 gas chromatograph using 15 m by 0·5 mm i.d. FFAP coated S.C.O.T. columns with helium as carrier gas. Infrared spectra were measured as Nujol mulls and liquid films for solids and liquids respectively using a Unicam SP 1200G spectrophotometer. P.m.r. spectra were recorded in CDC1₃ solution on a Varian A60 spectrometer with Me₄Si as internal reference. Chemical shifts are in p.p.m. Mass spectra were determined on a GEC AEI MS902 instrument operated at 70 eV. Botanical voucher specimen numbers are those of the Museum of Applied Arts and Sciences Herbarium.

**Isolation of Methyl p-Methoxycinnamate (1)**

Dried *Eriostemon obovalis* foliage (114 g, voucher No. 72-096) was steam distilled with cohabation in an all-glass apparatus to yield a yellow oil (1·5 ml), nD 1.4895, from which white crystals precipitated. Recrystallization from methanol yielded methyl p-methoxycinnamate (50 mg), m.p. and mixed m.p. 90-90·5 ° (lit.* 90 °); ν max 1715 (α,β-unsaturated ester), 1642 (olefinic), 1602, 1520, 841 and 825 cm⁻¹ (aromatic). P.m.r.: δ 3·78 (3H, s, OCH₃), 3·83 (3H, s, OCH₂), 6·32 (1H, d, J 16 Hz, H₆), 7·70 (1H, d, J 16 Hz, H₅), 6·90 (2H, d, J 9 Hz, H₃-H₄), 7·50 (2H, d, J 9 Hz, H₅-H₆); mass spectrum m/e (%): 192 (M⁺, 98), 162 (11), 161 (100), 134 (9), 133 (18), 132 (5), 118 (6), 90 (5), 89 (6), 77 (5), 63 (5).

**Essential Oil of Phebalium glandulosum subsp. glandulosum**

Fresh foliage and terminal branchlets of *P. glandulosum* subsp. *glandulosum* (400 g, voucher No. 73-098) were cohabated for 6 h in an all-glass apparatus to yield a pale yellow oil (12·5 ml), nD 1.4318, [α]D +11.2 ° (c, 10.0 in hexane) (lit.* [α]D +1.5 °); ν max 1708 (C=O), 3075, 1640, 992 and 913 (CH=CH₂) cm⁻¹. P.m.r.: δ 5·75 (octet, C7-H), 4·95 (m, C8-H, J₂,₃-trans 17 Hz), 4·92 (m,

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C\textsubscript{8}H\textsubscript{10}, J\textsubscript{7,8} 6 Hz), 2·69 (m, C\textsubscript{6}H, J\textsubscript{6,7} 6 Hz), 2·2−2·5 (m, C\textsubscript{3}H\textsubscript{2} and C\textsubscript{5}H\textsubscript{2}), 0·91 (d, C\textsubscript{2}Me\textsubscript{2}, J\textsubscript{6−5} 5 Hz), 1·01 (d, C\textsubscript{6}Me, J\textsubscript{6−5} 5 Hz).

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