

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

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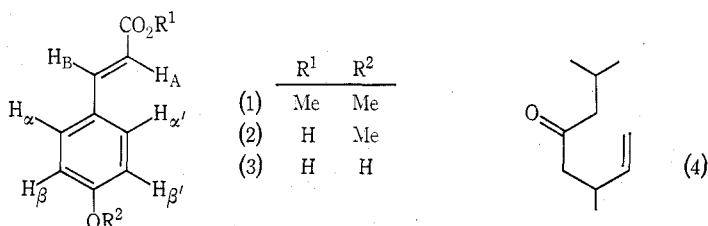
Museum of Applied Arts and Sciences,
Harris Street, Ultimo, N.S.W. 2007.

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 clifftops 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 metabolite² and as an artefact from the methanol extraction of a plant rich in *p*-methoxycinnamic acid (2).³



p-Coumaric acid (3) has been reported to function as a plant growth inhibitor⁴ and a coumarin precursor.^{5,6} The co-occurrence of comparatively large quantities of (1)

¹ Wilson, P. G., *Nuytsia* (Bulletin of the Western Australian Herbarium), 1970, 1, 3.

² Shimazono, H., *Arch. Biochem. Biophys.*, 1959, 83, 206.

³ Pillai, P. M., and Wariyar, N. S., *J. Inst. Chem., Calcutta*, 1962, 34, 197.

⁴ Fleming, N. J., and Howden, M. E. H., *Rev. Pure Appl. Chem.*, 1972, 22, 67.

⁵ Floss, H. G., and Paikert, H., *Phytochemistry*, 1969, 8, 589.

⁶ Brown, S. A., *Phytochemistry*, 1970, 9, 2471.

with the phloroglucinol-type coumarins bergapten, xanthoxyletin and limettin in *Eriostemon obovalis*⁷ 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.¹ 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.⁸

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 CDCl₃ 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 cohobation in an all-glass apparatus⁹ to yield a yellow oil (1.5 ml), n_D^{20} 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.¹⁰ 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, OCH₃), 6.32 (1H, d, *J* 16 Hz, H_A), 7.70 (1H, d, *J* 16 Hz, H_B), 6.90 (2H, d, *J* 9 Hz, H_B, H_{B'}), 7.50 (2H, d, *J* 9 Hz, H_A, H_{A'}); 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 cohobated for 6 h in an all-glass apparatus⁹ to yield a pale yellow oil (12.5 ml), n_D^{20} 1.4318, α_D^{21} +11.2°, d_4^{20} 0.8340.

(+)-2,6-Dimethyloct-7-en-4-one (4)

The semicarbazone of (4) prepared from the crude essential oil in the usual manner, m.p. 95–95.5° (lit.⁸ 92.5°) (Found: C, 62.5; H, 9.9; N, 20.1. C₁₁H₂₁N₃O requires C, 62.5; H, 10.0; N, 19.9%) was decomposed with warm 20% oxalic acid solution according to the method of Jones and Smith.⁸ The crude ketone was purified by steam distillation to yield pure (4) as a colourless liquid, n_D^{20} 1.4318, $[\alpha]_D^{20}$ +12.5° (c, 10.0 in hexane) (lit.⁸ n_D^{20} 1.4295, $[\alpha]_D^{20}$ +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, *J*_{7,8-trans} 17 Hz), 4.92 (m,

⁷ Southwell, I. A., *Phytochemistry*, 1973, **12**, 235.

⁸ Jones, T. G. H., and Smith, F. B., *J. Chem. Soc.*, 1925, **127**, 2350.

⁹ Hughes, A., *Chem. Ind.* (London), 1970, **48**, 1536.

¹⁰ Johnson, M. D., and Trachtenberg, E. N., *J. Chem. Soc. B*, 1968, 1018.

C8-H, $J_{7,8-cis}$ 10 Hz), 2.69 (m, C6-H, $J_{6,7}$ 6 Hz), 2.2-2.5 (m, C3-H₂ and C5-H₂), 0.91 (d, C2-Me₂, J 6.5 Hz), 1.01 (d, C6-Me, J 6.5 Hz).

Acknowledgments

The authors thank Mr V. Pickles, University of N.S.W., for p.m.r. spectra, Mr J. Keegan, N.S.W. Institute of Technology, for mass spectra, Mr J. Armstrong, Royal Botanic Gardens, for botanical identifications, the Director, National Parks and Wildlife Service, for permission to collect in the Blue Mountains National Park and Mrs B. R. Toyer for technical assistance.

Manuscript received 27 May 1974