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SHORT COMMUNICATION

A NEW OCCURRENCE OF HEDYCARYOL, THE PRECURSOR OF ELEMOL, IN *PHEBALIUM OZOTHAMNOIDES* (RUTACEAE)

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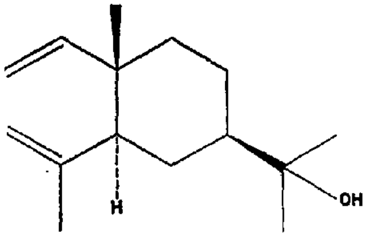
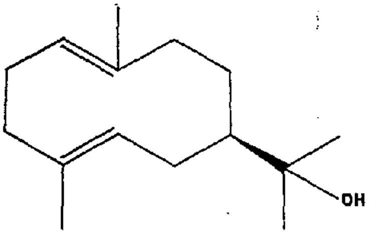
Abstract—The steam-volatile leaf oil of *Phebalium ozothamnoides* has been shown to contain elemol as the major component and α-pinene, myrcene, α- and β-eudesmol as minor components. Extraction of the leaf yielded hedycaryol, the heat-labile precursor of elemol.

Phebalium ozothamnoides F. Muell. (Rutaceae) is an erect shrub about 1 m high growing in mountainous regions from the N.E. Victorian Alps to the Blue Mountains of New South Wales. Steam distillation of the leaf of *P. ozothamnoides* from Mt. York, New South Wales, yielded 1·64% volatile oil. The main oil component (*ca.* 35%) was identified as elemol (I). Myrcene (*ca.* 15%), α-pinene (*ca.* 8%), α-eudesmol (*ca.* 11%) and β-eudesmol (*ca.* 14%) were also identified by i.r. spectroscopy, GLC retention times and co-chromatography with authentic specimens.

(I)



(II)



The isolation of precursors has established that some essential oil components are artefacts of the steam distillation.[1-3] These arise from the Cope rearrangement of cyclodecadiene systems. Sutherland[2] has shown that elemol (I) is formed from the thermal rearrangement of hedycaryol (II) when the leaves of *Hedycarya angustifolia* are steam-distilled for several hours.

The macerated leaves of *P. ozothamnoides* were extracted with light petroleum. The extract was shaken with aq. $AgNO_3$ to yield hedycaryol. The NMR spectrum showed a sharp singlet at δ 1·19 (6H, dimethyl) and three unresolved multiplets at δ 4·95 (2H, vinylic), δ 2·12 (8H, allylic methylenes) and δ 1·50 (10H, 2 allylic methyls, exchangeable hydroxyl, methylene and tertiary proton). GLC with block and column temperature at 95° on LSX-3-0295 showed substantially one peak with a relative retention of 2·07 with respect to elemol. Increasing the block temperature to 170° showed one peak with the same retention time as elemol. This occurrence of hedycaryol supports Sutherland's suggestion[2] that elemol may only be an artefact and not a natural product.

EXPERIMENTAL

All m.ps are uncorrected. Light petroleum had a b.p. of 40–60°. Analytical gas chromatography was carried out on a Perkin–Elmer 226 gas chromatograph. Retention time comparisons and co-injections were checked on two 150 ft × 0·01 in. Golay columns containing Castorwax and Apiezon L as stationary phases. I.r. spectra were determined as films unless stated otherwise. Nuclear magnetic resonance spectra were run in $CDCl_3$ with tetramethylsilane as internal reference.

Isolation of Volatile Material

The freshly collected leaf from several shrubs growing at Mt. York, New South Wales, was steam distilled with cohobation in an all-glass apparatus to yield 1·64% volatile oil (n_D^{20} 1·4925, α_D^{24} +16·50°, d_4^{20} 0·9164).

Identification of Constituents

Hydrocarbons. The low boiling fraction of the oil was refractionated under vacuum to yield α-pinene and myrcene (i.r., GLC retention times and co-chromatography with authentic samples).

Elemol. A portion of the oil (1·02 g) in hexane (20 ml) was extracted with 20% aq. $AgNO_3$ (2 × 20 ml). The $AgNO_3$ adduct, after treatment with excess conc. NH_4OH and extraction with ether, yielded elemol (0·21 g, m.p. 49–51°, b_5 108–110°, $[\alpha]_D^{25}$ −4·9° (*ca.* 33% $CHCl_3$), ν_{max} (nujol mull) 3360, 3078, 1644, 910 and 892 cm^{-1}).[4] The NMR showed singlets at δ 0·97 (3H, methyl), δ 1·17 (6H, gem-dimethyl) and δ 1·49 (1H, D_2O exchanged, hydroxyl), quartets at δ 1·70 (3H, allylic methyl, $J \sim 1$ c/s) and δ 5·83 (1H, vinyl, $J_{cis} = 10$ c/s, $J_{trans} = 18$ c/s) and a multiplet at δ 4·80 (4H, terminal methylenes). The phenylurethane was identical with that of elemol from Java citronella oil (m.p. and mixed m.p. 110–112°, i.r. spectra superimposable).[5]

Eudesmol. The hexane fraction (0·50 g) was adsorbed on a silica gel column (30 g). Elution with light petroleum removed the hydrocarbon fraction (0·09 g). The remaining components (0·31 g) were eluted with ether and re-chromatographed to yield a trace of an unidentified ester (light petroleum–ether, 12:1) and an alcohol (light petroleum–ether, 4:1). The alcohol crystallized on the addition of aqueous acetone to yield a mixture of α- and β-eudesmol (m.p. 69–73°, i.r., GLC retention times and co-chromatography with authentic samples).[6]

Isolation of Hedycaryol

The macerated leaves (138 g) were extracted with light petroleum (3 × 500 ml). The solution was concentrated by evaporation under vacuum at room temperature. The concentrate in hexane (150 ml) was shaken with 20% aq. $AgNO_3$ (3 × 40 ml). Excess concentrated ammonia was added and extraction with ether

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[1] R. V. H. JONES and M. D. SUTHERLAND, *Australian J. Chem.* 21, 2255 (1968).

[2] R. V. H. JONES and M. D. SUTHERLAND, *Chem. Commun.* 1229 (1968).

[3] K. MORIKAWA and Y. HIROSE, *Tetrahedron Letters* 1799 (1969).

[4] T. G. HALSALL, D. W. THEOBALD and K. B. WALSHAW, *J. Chem. Soc.* 1029 (1964).

[5] J. PLÍVA, M. HORÁK, V. HEROUT and F. ŠORM, *Die Terpene*, Vol. 1, *Sesquiterpene*, spectrum, s. 25, Akademie-Verlag, Berlin (1960).

[6] J. PLÍVA, M. HORÁK, V. HEROUT and F. ŠORM, *Die Terpene*, Vol. 1. *Sesquiterpene*, spectrum s. 87 and s. 88, Akademie-Verlag, Berlin (1960).

yielded hedycaryol (0·34 g, GLC pure at 95°, $[\alpha]_D^{25}$ +24·5° (*ca.* 5·7 in $CHCl_3$), ν_{max} 3420, 1660, 1130, 940–840 cm^{-1}; *p*-nitrobenzoate, m.p. 110–111°, i.r. superimposable with spectrum of authentic derivative). The NMR and i.r. spectra were identical with those of authentic hedycaryol.

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