

Hedycaryol, the Precursor of Elemol

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THE isolation¹ of a precursor (I) of geijerene (II) from *Geijera parviflora* Lind. supports the view² that elemane-type sesquiterpenes may arise by Cope rearrangements of terpenoid cyclodecadienes. We report that the sesquiterpene alcohol, elemol, is indeed such an artefact in one essential oil, and suggest that this may be generally true of elemol and the elemenes.

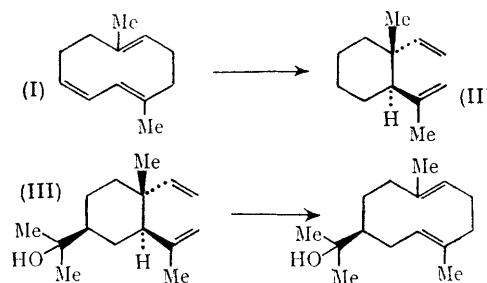
The essential oil of *Hedycarya angustifolia* A. Cunn. is described³ as a rich source of elemol (III), but when the leaves are extracted at room temperature, they yield, principally, a new sesquiterpene alcohol, hedycaryol, and only a trace of elemol.

Hedycaryol, $C_{15}H_{26}O$, $[\alpha]_D^{25} + 30.8^\circ$ ($CHCl_3$), [*p*-nitrobenzoate, m.p. 110–112°, $[\alpha]_D^{25} + 21.4^\circ$ ($CHCl_3$)], ν_{max} 3420 vs and 1660 cm^{-1} , $\lambda_{max} < 210 m\mu$, shows a relative retention of 1.80 with respect to elemol on gas chromatography at 105° on SF96. It is converted to elemol, m.p. 51–52°, $[\alpha]_D^{25} - 4.5^\circ$ ($CHCl_3$), upon being heated at 100° (half life ~3 hr.) gas chromatogram at 170° is indistinguishable from that obtained from elemol. The ¹H n.m.r. spectrum of the *p*-nitrobenzoate shows signals for four aromatic protons, a very broad multiplet (2H) at τ 5.05, an unresolved signal (8H; τ 7.4–8.25) for allylic methylene protons and allylic methyl proton signals at τ 8.53 and 8.40, the last being obscured by a sharp peak (6H) from two CH_3 -C-O groups. The latter two signals appear at τ 8.40 (3H; relatively broad) and 8.75 (6H) with hedycaryol itself. Levulinic acid has been identified as an ozonolysis product of the *p*-nitrobenzoate.

Refluxing hedycaryol with 1% toluene-*p*-sulphonic acid in ether (2 hr.) yields 90% of a

mixture of α -, β -, and γ -eudesmols and three minor unidentified products.

From the evidence presented and by analogy with the structure of (I),⁴ it is suggested that hedycaryol possesses structure (IV) and that it is the precursor of the elemol found in *H. angustifolia* oil.³



Java citronella oil, another source of elemol, extracted with 20% silver nitrate solution, yields a mixture of elemol (~7%), and hedycaryol (0.8%) and various other substances including a hydrocarbon which undergoes thermal isomerization to β -elemene. Countercurrent partition of the extract between ethyl acetate and 20% silver nitrate solution yields substantially pure hedycaryol [*p*-nitrobenzoate, m.p. 110–112°, $[\alpha]_D^{25} + 21.3^\circ$ ($CHCl_3$)].

Whether elemol is ever a natural product rather

than an artefact remains to be determined. conversion in the living plant may be significant.¹
Extrapolation suggests that the rate of thermal

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¹ R. V. H. Jones and M. D. Sutherland, *Austral. J. Chem.*, in the press.

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³ L. Ruzicka, *Experientia*, 1953, **9**, 357; D. H. R. Barton and P. de Mayo, *Quart. Rev.*, 1957, **11**, 189; J. B. Hendrickson, *Tetrahedron*, 1959, **7**, 82; A. S. Rao, A. Paul, Sadgopal, and S. C. Bhattacharyya, *Tetrahedron*, 1961, **13**, 319; A. J. Birch, T. Grimshaw, A. R. Penfold, N. Sheppard and R. N. Speake, *J. Chem. Soc.*, 1961, 2286; J. Gough, V. Powell and M. D. Sutherland, *Tetrahedron Letters*, 1961, 763.

⁴ R. O. Hellyer, *Austral. J. Chem.*, 1962, **15**, 157.

⁵ Professor G. Sim, University of Sussex, personal communication.