Modhephene: a Sesquiterpenoid Carbocyclic [3.3.3]Propellane. *X*-Ray Crystal Structure of the Corresponding Diol

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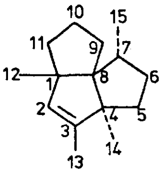
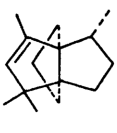
Summary Modhephene (**2**), a new sesquiterpene representing the first naturally occurring carbocyclic [3.3.3]propellane, has been isolated from the toxic plant *Isocoma Wrightii;* its structure was confirmed by *X*-ray analysis of the corresponding diol (**3**).

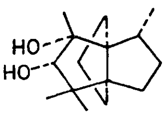
RAYLESS GOLDENROD (*Isocoma Wrightii*) has been a rich source of novel compounds such as benzofurans,[1] steroids,[2] and the unusual sesquiterpene isocomene (**1**).[3] We now report the isolation of another unexpected compound, namely, the first natural sesquiterpenoid carbocyclic [3.3.3]-propellane, which we have given the trivial name modhephene (**2**).



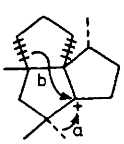
(1)



(2)



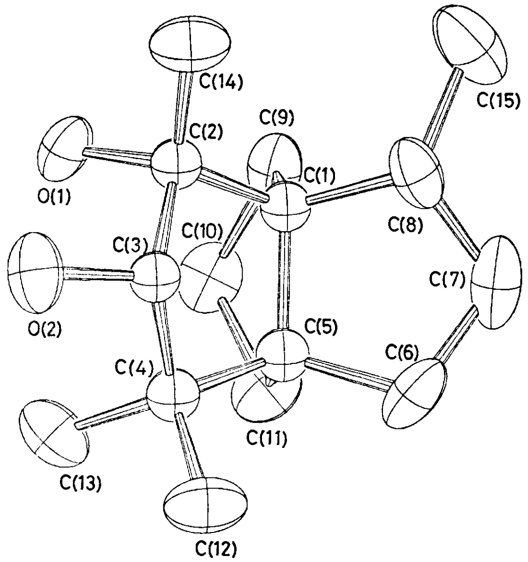
(3)



(4)

Steam distillation of the saponified methanolic extract of the dried leaves and stems provided a yellow oil which was fractionally distilled. The fraction of b.p. 65—75 °C at 0·05 mmHg was chromatographed on silica gel impregnated with silver nitrate (20%) to give, in the pentane–methylene chloride (95 : 5) eluent, first isocomene (**1**) and then modhephene (**2**) [ratio of (**1**) to (**2**) 2 : 1] as a colourless oil, b.p. 65—70 °C at 0·25 mmHg (bath), *m/e* 204 (M^+, 19%), 189(100%), 161(29), 149(36), 147(30), 133(26), and 119(32); ν_{max} (CCl_4) 3010, 1650, 1380, and 840 cm^{-1}; ^1H n.m.r.: δ 0·99 (3 H, d, *J* 5·5 Hz), 0·97 (6 H, s), 1·58 (3 H, d, *J* 1·5 Hz), and 4·80 (1 H, m); ^{13}C n.m.r.: δ 45·7, 65·9, 71·9 (s, quaternary C's), 134·8 (d, olefinic C with single H), and 140·2 (s, olefinic C with no H) p.p.m.

On treatment with osmium tetroxide in pyridine, (**2**) gave a 4 : 1 mixture of *cis* diols, from which the major diol (**3**) was separated by chromatography on alumina (activity III), m.p. 145—145·5 °C; *m/e* 238 (M^+, 8%), 220 ($M^+ - H_2O$, 40%), 192(73), 164(90), 136(100), 124(77), 110(72), and 96(76); ν_{max} (KBr) 3500, 3375, and 1070 cm^{-1}; δ 0·98 (3 H, d, *J* 6 Hz), 1·00 (6 H, s), 1·25 (3 H, s), and 3·38 (1 H, br d, *J* 6 Hz). The structure of the diol (**3**) was established by a single crystal *X*-ray analysis (Figure). It crystallized from ether–pentane (vapour diffusion) in the orthorhombic space group $P2_12_12_1$ with $a = 8{\cdot}456(3)$, $b = 9{\cdot}877(4)$, $c = 16{\cdot}467(6)$, $Z = 4$. The intensity data were measured with a Syntex $P2_1$ four-circle diffractometer, equipped with a graphite monochromator, using the θ–2θ scan technique. The structure was solved using direct methods. An *E*-map generated by MULTAN contained peaks corresponding to all non-hydrogen atoms in the molecule. Two cycles of least squares refinement gave $R = 0{\cdot}16$. Hydrogens were then located from a



combination of difference Fourier peaks and calculated positions. The final refinement gave $R = 0{\cdot}055$ and $R' = 0{\cdot}058$ for 1168 reflections with $I > 3\ \sigma(I)$† (see Figure). The temperature factors of the oxygens and C(7)—C(15) were varied anisotropically while those of the remaining atoms were isotropic and the hydrogen temperature factors were fixed at 5·0. The hydrogen co-ordinates were not varied.

Since caryophyllene is the major sesquiterpenoid component obtained from the essential oil of *I. Wrightii*, it is tempting to suggest it as a precursor to isocomene (**1**) and modhephene (**2**) and indeed it is possible to write such a biogenesis. However, it does seem very likely that isocomene (**1**) and modhephene (**2**) arise from the common precursor (**4**) *via* methyl migration (path a) to give isocomene (**1**) or migration of bond C(1)–C(11) to give modhephene (**2**) (path b). The relative configurations of these two sesquiterpenes are consistent with this postulation.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table may be obtained as a Supplementary publication (SUP 22300; 7 pp.) from the British Library. For details of obtaining this material, see Notice to Authors No. 7, Index Issues of *J.C.S. Perkin I* or *II*.

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[2] L. H. Zalkow, N. I. Burke, and G. Keen, *Tetrahedron Letters*, 1964, 217; L. H. Zalkow, G. A. Cabat, G. L. Chetty, M. Ghosal, and G. Keen, *ibid.*, 1968, 5727.

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