(+)-Ovalifolienalone, a Novel Sesquiterpenoid Ketone of the *ent*-2,3-seco-Alloaromadendrane Group from *Plagiochila semidecurrens* (Liverwort): *X*-Ray Crystal and Molecular Structure

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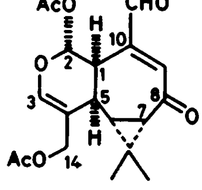
Summary The structure and absolute configuration of a novel sesquiterpenoid ketone, (+)-ovalifolienalone, isolated from *Plagiochila semidecurrens* has been determined as (3) on the basis of spectral evidence and *X*-ray analysis.

IN the previous communication,[1] we reported the isolation and structural determination of (+)-ovalifoliene (1) and (−)-hanegokedial (2), containing the novel carbon skeleton *ent*-2,3-seco-alloaromadendrane, from the liverwort *Plagiochila semidecurrens* [see previous communication for structures (1) and (2)]. We describe here the structure and absolute configuration of an additional sesquiterpenoid, (+)-ovalifolienalone (3), isolated from the same liverwort.

The ketone (3), $C_{19}H_{22}O_7$, m.p. 203 °C, $[\alpha]_D$ +165·5°, was isolated from the methanol extract, and its spectroscopic properties showed that it was a tricyclic sesquiterpenoid containing the novel carbon skeleton of (1) and (2).[1] Both the chemical shifts and the coupling constants of all signals in the ^1H n.m.r. spectrum were in agreement with the stereostructure (3): δ 3·58 (dd, *J* 10·0 and 4·0 Hz, 1-H), 6·35 (d, *J* 10·0 Hz, 2-H), 6·48 (s, 3-H), 2·65 (dd, *J* 6·0 and 4·0 Hz, 5-H), 1·37 (dd, *J* 8·0 and 6·0 Hz, 6-H), 2·37 (d, *J* 8·0 Hz, 7-H),† 6·62 (s, 9-H), 1·12 and 1·30 (each s, $12\text{-}H_3$



(3)

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† This signal was observed when the shift reagent, $Eu(fod)_3$, (7·6 mg) was added to the ketone (30·0 mg).

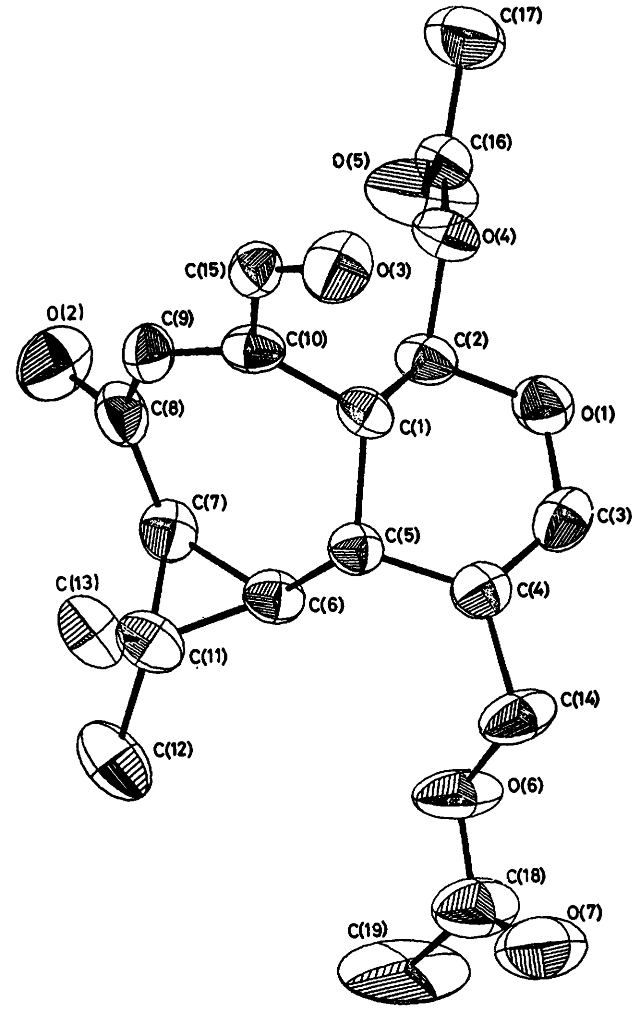

FIGURE. A computer generated perspective drawing of the ketone (**3**).

and/or 13-H_3), 4·45 and 4·70 (each 1H, d, J 12·0 Hz, 14-H_2), 9·57 (s, 15-H), and 1·98 and 2·07 (each s, 2 MeCO). This structure was also supported by the off-resonance ^{13}C n.m.r. spectrum which showed 6 singlets (δ 29·6, 116·0, 145·2, 160·6, 169·1, and 198·8 p.p.m.), 8 doublets (δ 32·3, 35·4, 37·9, 39·1, 92·2, 141·6, 146·5, and 193·5 p.p.m.), 1 triplet (δ 63·4 p.p.m.), and 4 quartets (δ 16·7, 20·7, 21·0, and 23·9 p.p.m.).

X-Ray analysis of the ketone was carried out to obtain a direct proof of the structure. The ketone afforded colourless monoclinic crystals from chloroform. *Crystal data:* a = 20·785(4), b = 7·131(2), c = 16·957(5) Å, β = 132·21(1)°, space group $C2$, D_c = 1·28, D_m = 1·28 g cm^{-3} (in $ZnCl_2$), Z = 4. The diffraction intensities were collected in ω scan mode using graphite monochromated Mo-K_α radiation on a Syntex R3 diffractometer. A total of 2307 reflections was measured, and 1864 (80·8%) were judged to be observed after correction for Lorentz, polarization, and background effects. The structure was solved by direct methods using MULTAN in Syntex XTL program. Full matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the hydrogen atoms converged to a final R factor of 0·060.‡ The stereostructure, excluding absolute configuration, of the ketone (**3**) is shown in the Figure. As expected from the spectral data, the 6- and 7-membered rings are joined in a *cis*-fashion. Although most bond lengths and bond angles are not significantly different from the expected values, some distortion is observed in the 7-membered ring owing to conjugation of the ketone with both the cyclopropane ring and the trisubstituted double bond.

Finally the absolute configuration of (+)-ovalifolienalone was shown to be as (**3**) by analysis of the c.d. spectrum of the ketone ($[\theta]_{378}$ +13900, $[\theta]_{269}$ +6470)[2] and was shown to have an *ent*-2,3-seco-alloaromadendrane skeleton.

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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.

[1] A. Matsuo, K. Atsumi, M. Nakayama, S. Hayashi, and K. Kuriyama, *J.C.S. Chem. Comm.*, preceding communication.
[2] G. Snatzke and F. Snatzke, 'Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism,' eds. F. Ciardelli and P. Salvadori, Heyden, London, 1973, p. 109.