Alliacolide, a New Bicyclic Sesquiterpene Epoxy-lactone with a Novel Carbon Skeleton from Cultures of the Fungus *Marasmius alliaceus* (Jacques ex Fr.)Fr; *X*-Ray Structure

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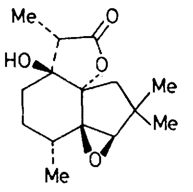
Summary From a culture of the fungus *Marasmius alliaceus* (Jacques ex Fr.) Fr. alliacolide, a new sesquiterpene hydroxy-epoxy-lactone, $C_{15}H_{22}O_4$, has been isolated; its structure, which has been established by *X*-ray diffraction analysis, has a new sesquiterpene carbon skeleton.

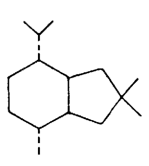
In the course of screening fungal cultures for polyacetylenes, we have isolated from culture fluids of the Basidiomycete *M. alliaceus* alliacolide, a new sesquiterpene lactone (**1**) with the novel carbon skeleton (**2**).† The structure and *relative* configuration of the chiral centres of the lactone (**1**) (or its enantiomer) were established by single-crystal *X*-ray diffraction.

The crystals were large rhombs. The cell parameters were determined from oscillation and Weissenberg photographs and refined on a Hilger-Watt four-circle diffractometer. *Crystal data*: $C_{15}H_{22}O_4$, $M = 266{\cdot}3$, monoclinic, $a = 13{\cdot}421(3)$, $b = 6{\cdot}529(2)$, $c = 8{\cdot}462(3)$ Å, $\beta = 105{\cdot}6(1)°$, $U = 714{\cdot}3$ Å^3, $D_c = 1{\cdot}24$, $D_m = 1{\cdot}23$ g cm^3, $Z = 2$, $F_{000} = 288$, space group $P2_1$, Mo-K_α radiation (graphite monochromator), $\lambda = 0{\cdot}71069$ Å.

Data were collected for $\theta \leqslant 27{\cdot}5°$, and 1605 observed reflections $[I > 3\sigma(I)]$ were found. The structure was solved routinely using MULTAN.[1] Refinement was complicated by the discovery that in the solid state the 6-membered carbocyclic ring exists in two conformations in the approximate ratio 70:30. The current *R*-value, with three carbon atoms each occupying two sites partially, non-hydrogen atoms refined anisotropically, and hydrogen included in calculated positions, is 4·95%.‡



(1)



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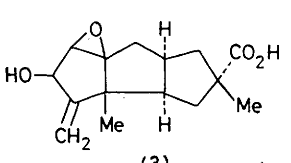

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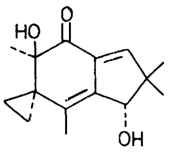

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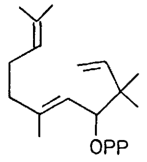

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† The name alliacane is proposed for this carbon skeleton based on the name alliacolide for the lactone.

‡ 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.

Alliacolide (**1**) constitutes 75% of the dry ether-extract from the *M. alliaceus* culture fluid. It was isolated from the extract by a combination of sublimation (the compound sublimes readily), silica gel chromatography, and crystallisation (ethyl acetate–light petroleum), m.p. 192—194 °C (corr.) (sealed capillary), $[\alpha]^{20}$ $-35°$ (589 nm), $-62°$ (431 nm), and $-80°$ (365 nm) (c 0·1 in chloroform). A molecular ion was obtained at m/e 266·1518 and the compound analysed correctly for $C_{15}H_{22}O_4$. In the u.v. spectrum only end absorption was observed whilst the i.r. spectrum showed bands at 3590, 3450, and 1785 cm^{-1}. Both the ^1H n.m.r. [τ (CCl_4) 8·78—8·88 (12H, m, 4Me), 7·8—8·1 (7H, m, $3CH_2$ and C*H*Me), 7·3 (1H, q, *J* 7 Hz, CO.C*H*Me), 7·12 (1H, s, exchanges with D_2O, OH), and 6·75 (1H, s, O–C–H)] and the ^{13}C n.m.r. spectra [(p.p.m. from Me_4Si) quaternary C, 176·12, 92·5, 77·2, 68·6, and 38·6; tertiary C, 68·3, 45·0, and 31·4; secondary C, 40·8 and 28·3; and primary C, 24·3, 24·0, 17·4, and 7·6] are in agreement with structure (**1**), but the spectral data were not sufficiently characteristic to permit an unequivocal structure deduction.

The hydroxy function could not be acetylated (Ac_2O–pyridine) but it was removed with $POCl_3$–pyridine and an $\alpha\beta$-unsaturated lactone was formed [λ_{max} (EtOH) 237 nm (ϵ 8600)].

The carbon skeleton (**2**) of alliacolide is different from that of other sesquiterpenes. Its biogenesis has still to be established but it is significant that it includes the geminally substituted dimethylcyclopentane ring found in other sesquiterpenes isolated from the Basidiomycetes, *e.g.* hirsutic acid C (**3**) and illudin M (**4**). Evidence has been obtained[2] which indicates that these could arise from farnesyl pyrophosphate *via* a humulene intermediate. It is of interest however that the skeleton of alliacolide is very similar to that of the sesquiterpene analogue (**5**) of the pyrophosphate of artemesia alcohol. The question therefore arises whether precursors such as (**5**) should be considered in addition to farnesyl pyrophosphate in the biosynthesis of fungal sesquiterpenes.

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[1] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[2] *Cf.* J. R. Hanson, T. Marten, and R. Nyfeler, *J.C.S. Perkin I*, 1976, 876; T. C. Feline, G. Mellows, R. B. Jones, and L. Philips, *J.C.S. Chem. Comm.*, 1974, 63.