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The Isoprene Units of the Sesquiterpenoid, Alliacolide

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Summary The enrichment and labelling patterns of alliacolide derived biosynthetically from [1-^{13}C]- and [1,2-$^{13}C_2$]-acetate have been used to define the isoprene units in the alliacane skeleton.

Alliacolide (**1**) is one of a group of metabolites of the fungus *Marasmius alliaceus*,[1,2] some of which have been shown[3] to possess tumour inhibitory properties. The unique alliacane carbon skeleton of these fungal sesquiterpenoids may be derived from three isoprene units in a number of ways [*e.g.* (**2**)—(**4**)]. These include two starting points for incorporating a C_{15} farnesyl pyrophosphate chain, one reminiscent of the illudane fungal sesquiterpenoids[4] and the other of the cadalenes (*cf.* the fungal metabolite, avocettin).[5,6]

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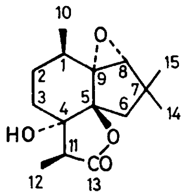
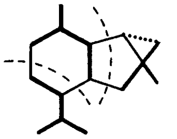


(1)



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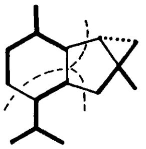

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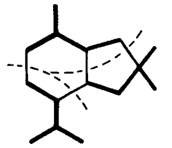

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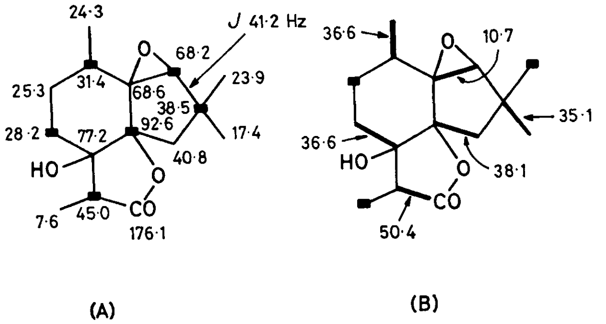

FIGURE. (A) ^{13}C N.m.r. signals and enrichment (■) pattern from [1-^{13}C]acetate. (B) Coupling (J/Hz) and enrichment (■) pattern from [1,2-$^{13}C_2$]acetate.

The enrichment and coupling patterns that are generated in alliacolide as a result of feeding [1-^{13}C]- and [1,2-$^{13}C_2$]-acetate to *Marasmius alliaceus* have served to distinguish between some of these possible isoprenoid arrangements. The ^{13}C n.m.r. resonances of alliacolide were assigned [see (Figure A)]. The optimum time of feeding the substrates (14 days from inoculation) and harvest of the metabolites (a further 21 days incubation) were determined in preliminary studies. The labelling and coupling patterns of the alliacolide derived from the [1-^{13}C]- and [1,2-$^{13}C_2$]-acetates are shown in the Figure.

A number of conclusions may be drawn from these results. The coupling of C-11 to C-13, C-4 to C-3, C-10 to C-1, C-9 to C-8, C-14 to C-7, and C-6 to C-5, the enrichment of C-11, C-2, and C-15 from the [1,2-$^{13}C_2$]acetate feed together with the fact that C-1 of acetate enriches those positions derived *via* C-3 and C-5 of mevalonate, demonstrate that the alliacane skeleton may be dissected into the isoprene units as shown in (**4**). In accordance with this, C-7 and C-8 show an 'induced' coupling (J 41·2 Hz) arising from the multiple enrichment by the [1-^{13}C]acetate. It is interesting to note that as a result of the [1,2-$^{13}C_2$]acetate feed, the carbonyl group of the lactone ring (C-13) was coupled to C-11, *i.e.* the carbonyl group must originate from the methyl group of mevalonic acid. In an isoprenoid chain, the methyl group of mevalonic acid becomes a pendant group rather than part of the chain. Consequently the lactone ring may not have its origin in the cleavage of the isoprene chain. This result may suggest that the isopropyl residue (C-11 to C-13) rather than the *gem*-dimethyl (C-14–C-15) forms the starting point for the isoprenoid chain. However efforts to clarify this using [1,2-$^{13}C_2$]farnesyl pyrophosphate have so far proved unsuccessful since the coupling patterns present in the ^{13}C n.m.r. spectrum of the resultant alliacolide suggested that prior degradation to acetate and resynthesis was more efficient than intact biosynthetic incorporation of the farnesyl pyrophosphate.

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