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DITERPENE METABOLITES OF THE MARINE SPONGE CHELONAPLYSILLA VIOLACEA: APLYVIOLENE AND APLYVIOLACENE

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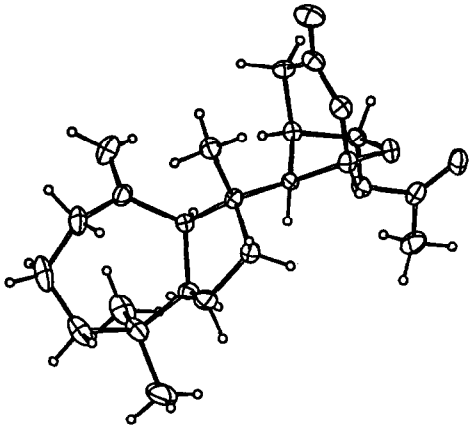
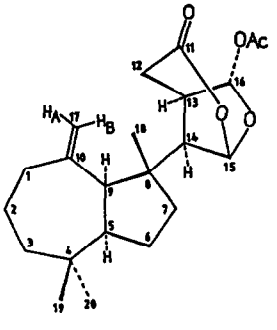
Abstract: The major diterpene constituents of the marine sponge Chelonaplysilla violacea have been shown to be aplyviolene (1) and aplyviolacene (2).

Chelonaplysilla violacea is a purple encrusting sponge found in shallow waters off the coast of temperate eastern Australia. In the course of a survey[1] of chemical constituents of local species within the family Aplysillidae (order, Dendroceratida) we have isolated from this sponge, by chromatography of the concentrated light petroleum extract, two new diterpenes, aplyviolene (1) (1.1%) and aplyviolacene (2) (0.4%).

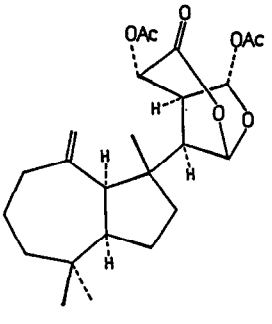
Detailed analysis of the ^{1}H and ^{13}C n.m.r. spectral data (2D COSY and ^{1}H-^{13}C correlation) for aplyviolene, $C_{22}H_{32}O_5$, m.p. 163°, $[\alpha]_D^{25}$ -29.5° (c, 1.0), ν_{max} 1750 cm^{-1}, indicated the structure (1) (relative stereochemistry). The structure was established unequivocally by single crystal X-ray methods. All data were collected on an Enraf-Nonius CAD4-F diffractometer with MoKα radiation. The structure was solved by direct methods[2] and refined by full-matrix least-squares methods to an R of 0.036 (on 1125 F with I>2.5σ(I), anisotropic non-H atoms, H-atoms at calculated sites with isotropic thermal parameters). An ORTEP projection is shown below.



ORTEP Projection of Aplyviolvene (1)



(1)



(2)

Sullivan and Faulkner[3] have claimed that an oil, $[\alpha]_D^{20}$ + 88°, isolated from a Dendrilla sp. and named dendrillolide A has the structure (1). Their (incomplete) spectroscopic data differ from ours and it is not clear to us what the correct structure for dendrillolide A is.

Aplyviolacene (2), $C_{24}H_{34}O_7$, gum, (HMRS, Found: $M^{+\cdot}-CH_3CO_2H$, 374.2074; $C_{22}H_{30}O_5$ requires 374.2093), $[\alpha]_D^{25}$ - 31.8° (c, 1.0), ν_{max} 1780, 1760 cm^{-1}, differed from aplyviolene by the presence of an additional acetoxy group. The group is located at C12 since the n.m.r. resonance for H12 (δ^{CDCl_3} 5.8) is a doublet ($J_{12,13}$ 5.0 Hz) which replaces the multiplets for H_AH_B12 showing the characteristically large geminal J value of 19.5 Hz in the spectrum of (1). The 12α configuration is based on the observation of n.O.e. enhancements to H7α and 18-Me (and not to H16) on irradiation of H12, on the absence of a long-range, W, coupling between H12 and H14 [for (1), $J_{12\alpha,14}$ = 0.8 Hz], and on a strong correlation between H12 and C16 (anti-planar). In the ^{13}C n.m.r. spectrum of (2) a methine resonance at δ 66.2 has replaced a methylene resonance at δ 33.1 in the spectrum of (1). The remainder of the ^1H and ^{13}C n.m.r. data for aplyviolacene compared closely with those of aplyviolene.

Aplyviolene and aplyviolacene can be considered to be biogenetically derived from a spongian precursor.[3]

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References

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