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A NEW DITERPENE FROM THE SPONGE APLYSILLA ROSEA

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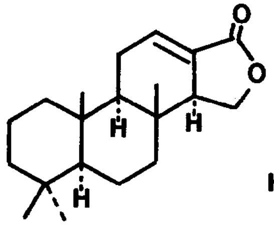
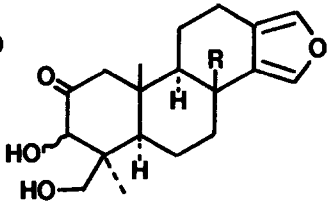
Sponges of the orders Dictyoceratida and Dendroceratida, the spiculeless horny sponges, have produced a plethora of terpenoid metabolites[1] including a new diterpenoid ring system of which isoagathalactone (1), from certain collections of the Dictyoceratid sponge Spongia officinalis, was the first example[2].

We have reported[3] the isolation of the four closely related diterpene alcohols (2)-(5) and their acetates, which incorporated the same diterpene carbocyclic ring system as (1), from various collections of several related species of the genus Spongia, collected on the Australian Great Barrier Reef. We now describe the isolation of a novel diterpene triacetate, aplysillin (6) from the Dendroceratid sponge Aplysilla rosea collected in New Zealand.

Aplysilla rosea is a small red-purple coloured sponge which occurs as isolated individuals in localised areas and is difficult to collect in reasonable quantity. Extraction of a small homogenised sample of A. rosea (50g wet weight) with methanol/diethyl ether (1:1) followed by partition of the total extract between diethyl ether and water gave an ether layer from which 34mg of the new diterpene (6)*, m.p. 169-171° $[\alpha]_D^{20}$ + 13° (c = 0.5, $CHCl_3$), was isolated by preparative layer chromatography on silica gel.

The CI (NH_3) mass spectrum of (6) showed a strong $M^+ + 18$ at 482 a.m.u. and the formula $C_{26}H_{40}O_7$ was established by analysis. Major fragment ions at 345 and 285 a.m.u. in the CI mass spectrum suggested the loss of two and three molecules of acetic acid respectively. The 70 e.v. EI mass spectrum of (6) showed no molecular ion, the first fragment ion appearing at 284 a.m.u. ($C_{20}H_{28}O$, $M^+ - 3$ AcOH).


(1)

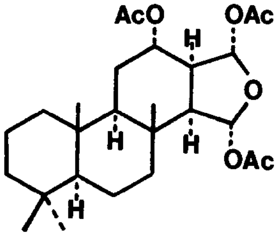


(2) R = CH_3, 3 β-OH

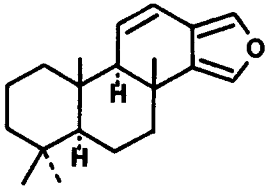
(3) R = CH_3, 3 α-OH

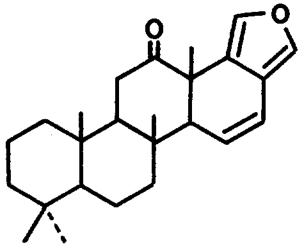
(4) R = CH_2OH, 3 β-OH

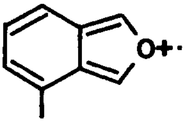
(5) R = CH_2OH, 3 α-OH



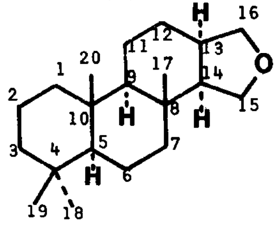
(6)


(7)


(9)



(8)



(10)

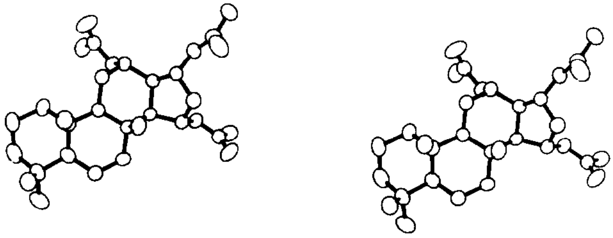


Figure 1

A 15 MHz ^{13}C n.m.r. spectrum of (6) [$CDCl_3$, repetition rate 10 secs, pulse width 90°] showed 24 of the 26 carbon resonances as follows: δ170.2(s), 170.0(s), 169.7(s), 99.7(d,2C), 67.8(d), 57.1, 56.7, 49.9, 45.5, 42.6, 41.9, 39.7, 36.9, 34.6, 33.3(2C), 23.4, 21.4(3C), 18.2, 16.9, 16.2. These data showed that aplysillin (6) contained three ester carbonyls (established as acetates from ^1H n.m.r. and m.s. data) and no olefinic double bonds in the molecule which must therefore be tetracyclic. The occurrence of a doublet resonance at δ67.8 suggested the presence of a secondary acetoxyl group whilst the appearance of a two carbon doublet at δ99.7 was consistent with AcO-CH-O- groups. Six of the seven oxygen atoms in (6) could be accounted for as acetoxyl groups therefore the two AcO-CH-O groups must contain the remaining oxygen atom as an ether link and the partial structure AcO-CH-O-CH-OAc could be written.

The ^1H n.m.r. spectrum of (6) in deuterochloroform indicated the presence of four quaternary methyl groups at δ0.80, 0.82, 0.84 and 0.92 and three acetate methyl groups at δ2.04, 2.05 and 2.08. Other features of the spectrum included a one proton multiplet centred at δ2.58, a one proton multiplet at δ5.08 (m, $W1/_2$ 7Hz, equatorial-C$\underline{H}$-OAc), an apparent one proton singlet at δ6.07 and a one proton 8Hz doublet centred at δ6.08 (Ac-O-C$\underline{H}$-O-C$\underline{H}$-OAc). Irradiation at δ2.58 collapsed the doublet at 6.08 to a singlet and sharpened the δ5.08 multiplet which supported the partial structure $-CH_2$-CH(OAc)-CH-CH(OAc)-O-CH(OAc)-. The tentative structure (6) without stereochemistry, which accounted for all spectral data, was used as a working hypothesis.

It was argued that thermolysis of (6) should produce the vinyl furan (7) and previous work in this laboratory[4] had established the spectral and mass spectral characteristics of similar vinyl furans. Pyrolysis of (6) at 230° for 5 minutes gave (7) in high yield. The mass spectrum of (7) showed a molecular ion at 284 a.m.u. ($C_{20}H_{28}O$) and a base peak at 132 a.m.u. (C_9H_8O) which could be rationalised as the ion (8). The ^1H n.m.r. spectrum of (7) showed two α-furan protons at δ7.04 and 6.82, two olefinic doublet of doublets at δ6.42 (J=9, 3Hz) and 5.64 (J=9, 2.5Hz) very similar to the pattern previously found for the vinyl furan (9)[4].

To resolve any doubts about the working hypothesis and to establish the relative stereochemistry at the chiral centres a single crystal X-ray analysis of (6) was carried out. The colourless orthorhombic crystals of (6), $\underline{M}$ = 464.4, have the space group $P2_12_12_1$ with $\underline{a}$ = 20.689 (7), $\underline{b}$ = 8.102 (3), $\underline{c}$ = 14.859 (5) Å, $\underline{U}$ = 2490.6 Å^3, $\underline{Z}$ = 4, $\underline{D}_c$ = 1239 kg m^{-3}, Mo-$\underline{K}_\alpha$ radiation, λ = 0.71069 Å, μ = 52 m^{-1}. The structure was determined by direct methods using four circle diffractometer data and 1932 planes with $F_o > 5\ F_o$ were refined by full matrix least squares to convergence[5] at $R = 0.063$. Hydrogen atoms were included at their calculated positions during refinement. A stereoprojection of the molecule is shown in Figure 1.

The X-ray analysis confirms the validity of the working hypothesis and gives the relative configurations of the chiral centres shown in (6).

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* We have suggested[3a] the name 'spongan' for the hypothetical diterpene ether (10). Thus (6) can be named 12α,15α,16α triacetoxyspongan.

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