

Fig. 1. ORTEP (Johnson, 1965) plot of 5-isopropyl-4-methyl-1,3-diphenyl-3a,4,5,9b-tetrahydropyrazolo[3,4-c]isoquinoline.

mean plane of the benzo ring (Table 2) in a pseudoaxial *trans* configuration corresponding to (1a) [torsion angle C(4)—N(4)—C(5)—C(51) 157.8°]. The pyrazolonic ring lies on the same side of the six-membered ring as the R¹ group.

It is interesting to note the coplanarity of the C(5)—H(5) and C(3a)—H(3a) bonds, this mean plane being orthogonal to that of the benzo ring. The 'W' geometry of H(5)—C(5)—N(4)—C(3a)—H(3a) is also evident, the N atom being slightly displaced from the mean plane formed by the two C—H bonds.

The C(3a)—H(3a) bond is pseudoaxial (62.6°) whereas the C(5)—H(5) and C(9b)—H(9b) bonds are effectively equatorial (they form angles of 24.4 and 20.5° respectively with the benzo ring).

The regiospecificity of the cycloaddition is clearly confirmed. The bond lengths in the pyrazolonic ring are quite normal (C=N 1.280 Å) (Mercier, Vebrel, Schmidt & Sheldrick, 1984). The C—C bond common to the five- and six-membered rings is comparable to analogous bonds observed in fused pentagonal rings (Mercier, Ramah, Laude, Faure & Loiseleur, 1984). The C=N double bond is conjugated with the α -phenyl group (dihedral angle 12.7°).

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Structure Determination of Aplyviolene from *Chelonaplysilla violacea*

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Abstract. 6-Acetoxy-8-(decahydro-1,4,4-trimethyl-8-methylene-1-azulenyl)-2,7-dioxabicyclo[3.2.1]octan-3-one, C₂₂H₃₂O₅, *M_r* = 376.50, orthorhombic, *P*2₁2₁2₁, *a* = 8.103 (2), *b* = 11.632 (2), *c* = 21.774 (3) Å, *V* = 2052.22 Å³, *T* = 293 ± 1 K, *D_m* = 1.214 (5), *D_x* = 1.218 g cm⁻³, *Z* = 4, *Mo K α* , λ = 0.71073 Å, Zr filter, μ = 0.091 cm⁻¹, *F*(000) = 816, *R* = 0.042 for 1260 [*I* > 2.5 σ (*I*)] reflections. The X-ray analysis indicates that the previously proposed structure of dendrillolide

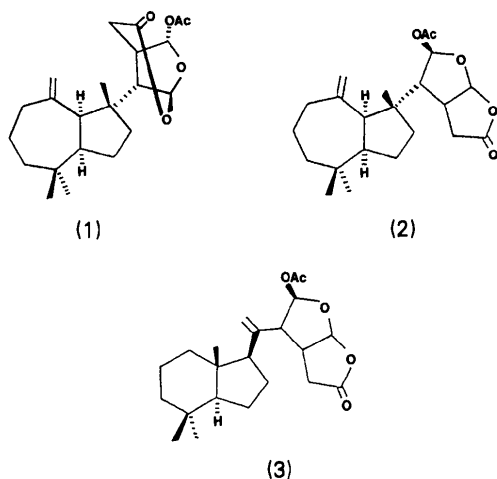
A is incorrect. There is a long C—C bond [1.577 (6) Å] within the five-membered ring of the azulenyl moiety, apparently caused by steric crowding around the 1-methyl substituent. The ring oxygens are involved in short [1.412 (6)] and long [1.447 (6) Å] C—O bonds at the bridgehead of the bicyclooctanone fragment. Other bond lengths are normal.

Introduction. Recently, Sullivan & Faulkner (1984) reported the isolation and structural determination of some metabolites from an unidentified species of *Dendrilla* sponge from Palau. They included dendrillolide A (1) and dendrillolide B (2), with a novel

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rearranged skeleton, and norrisolide (3) (Hochlowski, Faulkner, Matsumoto & Clardy, 1983).



During an investigation of the metabolites of the Dendroceratid sponge *Chelonaplysilla violacea* collected from Leigh, New Zealand, we have isolated a series of related diterpenoid compounds, including a dendrillolide, and norrisolide. Our spectral data of the major compound, aplyviolene* was consistent with the assigned structure of dendrillolide A but did not match the published data. In particular, the IR spectrum of our compound showed a band at 1760 cm^{-1} consistent with a bridging δ -lactone while the literature value of 1785 cm^{-1} suggests a γ -lactone. Also, the specific rotation of our compound was $[\alpha]_D -26.1^\circ$ (lit. $+83.5^\circ$) and the NMR spectral data were substantially different. Thus we concluded that the published structure of dendrillolide A was incorrect but that the structure (1) corresponded to our compound aplyviolene. We record here confirmation of the structure of the major compound aplyviolene (1) by a single-crystal X-ray determination.

Experimental. Crystals were prepared by slow evaporation of a 5% methylene chloride/hexane solution to yield colourless needles. Density measured by flotation in aqueous KCl/KI. Fragment $0.6 \times 0.4 \times 0.2\text{ mm}$ mounted on Nonius CAD-4 diffractometer; Zr-filtered Mo $K\alpha$ radiation; unit-cell dimensions from 25 reflections, $10.9 < \theta < 15.0^\circ$; systematic absences $h00, h = 2n + 1, 0k0, k = 2n + 1, 00l, l = 2n + 1$ defined space group as $P2_12_12_1$; 1914 unique reflections, $0.05 < 2\theta < 52^\circ$ ($\sin\theta/\lambda_{\text{max}}$ 1.109 \AA^{-1}); 1260 with $I > 2.5\sigma(I)$, $0 \leq h \leq 9, 0 \leq k \leq 14, 0 \leq l \leq 26$; three intensity standards checked every 100 reflections showed no non-statistical variation during X-ray exposure; absorption corrections not required because

* Taylor *et al.* (private communication) have recently isolated aplyviolene from the same sponge.

of low μ . Data processed using the Enraf-Nonius (1981) *Structure Determination Package* on a PDP-11 computer. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and refined using *SHELX76* (Sheldrick, 1976) on the University of Auckland IBM 4341 computer. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms were placed in geometrically derived positions (C-H 1.0 \AA) with fixed $U = 0.05\text{ \AA}^2$. Non-hydrogen atoms were assigned anisotropic thermal parameters. Reflection weights in the final cycle of refinement were $w = 1.1053/[\sigma^2(F) + gF^2]$ with g being 1.721×10^{-3} . Final R and wR were 0.042 and 0.048 respectively, $\Delta_{\text{max}}/\sigma = 0.11$ for positions; max. $\Delta\rho$ excursion in final difference map 0.17 e \AA^{-3} . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Diagrams were produced using *ORTEP* (Johnson, 1965).

Discussion. Atomic positions and equivalent isotropic thermal parameters are given in Table 1.* The molecular geometry and atomic numbering are shown in Fig. 1, which does not necessarily depict the true chirality of the molecule. The unit-cell packing is given in Fig. 2.

The X-ray analysis establishes the structure to be that of (1). Interatomic distances and angles are listed in Table 2, together with their estimated standard deviations.

The carbon-carbon single bond between C(8) and C(9) of $1.577(6)\text{ \AA}$ is considered long. The lengthening of this bond may have a steric explanation, since C(17) and C(10) make a close approach of 2.81 \AA . Steric crowding in this region may also be an explanation for the opening of the angles C(9)-C(8)-C(17) and C(14)-C(8)-C(17). The small angle C(13)-C(14)-C(15) at $95.6(4)^\circ$ is noted.

The carbon-oxygen single bonds C(11)-O(21) and C(24)-O(23) are normal for oxygens adjacent to a carbonyl group. There are four other carbon-oxygen single bonds; two of these, C(16)-O(23) and C(16)-O(22), are considered normal while C(15)-O(21) and C(15)-O(22) are long and short respectively, suggesting the possibility of a contribution from a canonical form having a double bond between C(15) and O(22).

The carbon-carbon double bond C(10)-C(20) and the two carbonyl bonds C(11)-O(27) and C(24)-O(26) have normal values, as do the remaining carbon-carbon single bonds. There are no significant intermolecular interactions.

* Lists of anisotropic thermal parameters, hydrogen-atom positions, and observed and calculated structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43222 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positions and equivalent isotropic thermal parameters for the title compound

	x	y	z	B _{eq} ^a (Å ²)
C(1)	-0.3017 (8)	0.3078 (5)	-0.7190 (2)	6.0
C(2)	-0.3364 (10)	0.4267 (5)	-0.6917 (3)	7.2
C(3)	-0.2295 (10)	0.4625 (4)	-0.6381 (3)	6.7
C(4)	-0.2219 (8)	0.3865 (4)	-0.5813 (2)	5.0
C(5)	-0.1443 (6)	0.2669 (4)	-0.5925 (2)	3.9
C(6)	0.0229 (6)	0.2665 (4)	-0.6240 (2)	4.5
C(7)	0.0588 (5)	0.1406 (4)	-0.6340 (2)	3.9
C(8)	-0.1092 (5)	0.0796 (3)	-0.6430 (1)	3.0
C(9)	-0.2422 (5)	0.1728 (3)	-0.6252 (1)	3.1
C(10)	-0.3539 (7)	0.2103 (5)	-0.6776 (2)	4.5
C(11)	-0.1503 (8)	-0.2135 (4)	-0.6738 (2)	4.4
C(12)	-0.3041 (5)	-0.1697 (4)	-0.6430 (2)	3.9
C(13)	-0.2717 (5)	-0.0965 (3)	-0.5859 (1)	3.0
C(14)	-0.1217 (6)	-0.0188 (3)	-0.5952 (1)	3.0
C(15)	0.0033 (6)	-0.1148 (4)	-0.5962 (2)	3.6
C(16)	-0.2106 (5)	-0.1715 (4)	-0.5346 (1)	3.5
C(17)	-0.1218 (7)	0.0414 (4)	-0.7107 (1)	3.9
C(18)	-0.3970 (8)	0.3704 (5)	-0.5545 (2)	6.3
C(19)	-0.1174 (11)	0.4490 (5)	-0.5331 (2)	8.2
C(20)	-0.4983 (7)	0.1597 (6)	-0.6851 (3)	7.1
O(21)	-0.0008 (4)	-0.1808 (2)	-0.6525 (1)	4.2
O(22)	-0.0394 (4)	-0.1890 (3)	-0.5475 (1)	4.1
O(23)	-0.2276 (4)	-0.1103 (2)	-0.4779 (1)	3.7
C(24)	-0.1934 (5)	-0.1720 (5)	-0.4262 (2)	4.0
C(25)	-0.2269 (7)	-0.1024 (5)	-0.3702 (2)	5.4
O(26)	-0.1465 (4)	-0.2690 (3)	-0.4269 (1)	5.0
O(27)	-0.1538 (6)	-0.2737 (3)	-0.7188 (1)	6.9

* Temperature factors of anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

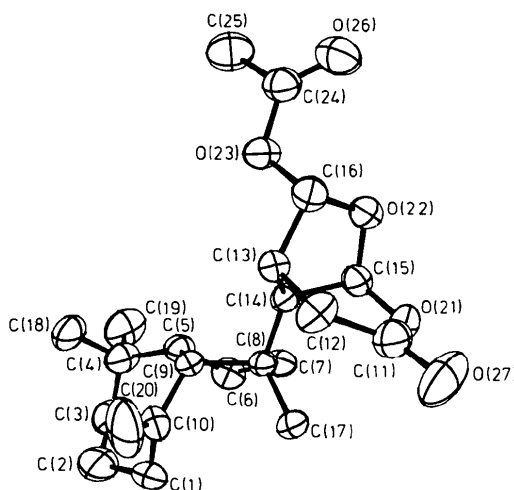


Fig. 1. The molecular geometry and atomic numbering for (1). Atoms are represented as 50% probability boundaries.

Table 2. Bond lengths (Å) and angles (°)

C(2)–C(1)	1.532 (9)	C(20)–C(10)	1.320 (9)
C(10)–C(1)	1.509 (8)	C(12)–C(11)	1.504 (8)
C(3)–C(2)	1.511 (9)	O(21)–C(11)	1.351 (7)
C(4)–C(3)	1.523 (8)	O(27)–C(11)	1.204 (6)
C(5)–C(4)	1.546 (7)	C(13)–C(12)	1.530 (6)
C(18)–C(4)	1.545 (9)	C(14)–C(13)	1.529 (7)
C(19)–C(4)	1.530 (9)	C(16)–C(13)	1.501 (6)
C(6)–C(5)	1.519 (7)	C(15)–C(14)	1.508 (7)
C(9)–C(5)	1.529 (6)	O(21)–C(15)	1.447 (6)
C(7)–C(6)	1.509 (8)	O(22)–C(15)	1.412 (6)
C(8)–C(7)	1.548 (6)	O(22)–C(16)	1.430 (6)
C(9)–C(8)	1.577 (6)	O(23)–C(16)	1.433 (5)
C(14)–C(8)	1.550 (6)	C(24)–O(23)	1.364 (6)
C(17)–C(8)	1.542 (6)	C(25)–C(24)	1.488 (7)
C(10)–C(9)	1.519 (7)	O(26)–C(24)	1.190 (6)
C(10)–C(1)–C(2)	113.2 (5)	C(20)–C(10)–C(1)	120.7 (6)
C(3)–C(2)–C(1)	116.3 (6)	C(20)–C(10)–C(9)	119.5 (6)
C(4)–C(3)–C(2)	119.4 (5)	O(21)–C(11)–C(12)	119.6 (4)
C(5)–C(4)–C(3)	114.2 (4)	O(27)–C(11)–C(12)	112.7 (6)
C(18)–C(4)–C(3)	109.9 (5)	O(27)–C(11)–O(21)	117.6 (6)
C(18)–C(4)–C(5)	108.9 (4)	C(13)–C(12)–C(11)	114.1 (4)
C(19)–C(4)–C(3)	107.7 (5)	C(14)–C(13)–C(12)	110.9 (4)
C(19)–C(4)–C(5)	108.1 (5)	C(16)–C(13)–C(12)	109.7 (4)
C(19)–C(4)–C(18)	107.9 (5)	C(16)–C(13)–C(14)	100.4 (4)
C(6)–C(5)–C(4)	115.9 (4)	C(13)–C(14)–C(8)	125.3 (4)
C(9)–C(5)–C(4)	120.5 (4)	C(15)–C(14)–C(8)	119.5 (4)
C(9)–C(5)–C(6)	104.4 (4)	C(15)–C(14)–C(13)	95.6 (3)
C(7)–C(6)–C(5)	103.9 (4)	O(21)–C(15)–C(14)	113.0 (4)
C(8)–C(7)–C(6)	107.1 (4)	O(22)–C(15)–C(14)	106.1 (4)
C(9)–C(8)–C(7)	104.7 (4)	O(22)–C(15)–O(21)	107.8 (4)
C(14)–C(8)–C(7)	108.1 (4)	O(22)–C(16)–C(13)	104.9 (4)
C(14)–C(8)–C(9)	107.3 (3)	O(23)–C(16)–C(13)	108.7 (4)
C(17)–C(8)–C(7)	108.2 (4)	O(23)–C(16)–O(22)	109.4 (4)
C(17)–C(8)–C(9)	112.8 (4)	C(15)–O(21)–C(11)	117.4 (4)
C(17)–C(8)–C(14)	115.1 (4)	C(16)–O(22)–C(15)	107.4 (4)
C(8)–C(9)–C(5)	104.6 (3)	C(24)–O(23)–C(16)	115.5 (4)
C(10)–C(9)–C(5)	117.0 (4)	C(25)–C(24)–O(23)	110.6 (5)
C(10)–C(9)–C(8)	114.9 (4)	O(26)–C(24)–O(23)	123.6 (5)
C(9)–C(10)–C(1)	119.8 (5)	O(26)–C(24)–C(25)	125.7 (5)

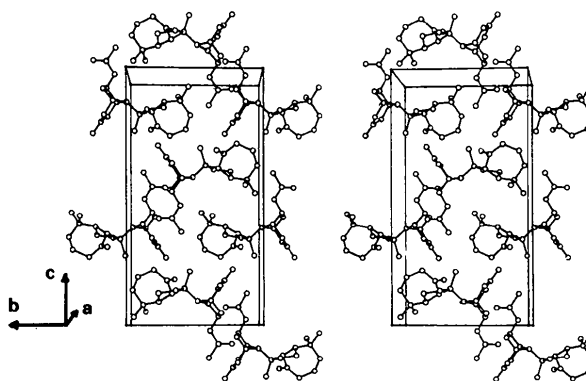


Fig. 2. A packing diagram of the unit cell of (1).

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