

Calculated weights

$$w = 1/[\sigma^2(F) + 0.000673F^2]$$

$$(\Delta/\sigma)_{\max} = 0.2$$

The absolute structure was confirmed by refinement of $\eta = 0.91$ (9) (Rogers, 1981)

Data collection: Nicolet R3m/V software, Release 4.11. Cell refinement: Nicolet R3m/V software. Data reduction: Nicolet R3m/V software. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983); *PLATON* (Spek, 1982); *MISSYM* (Le Page, 1987).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Pb(1)	0.0	0.0	0.0	384
C(1)	0.0205 (4)	0.1467 (5)	0.1916 (8)	340
C(2)	-0.0539 (5)	0.2359 (5)	0.173 (1)	463
C(3)	-0.0421 (6)	0.3272 (5)	0.295 (1)	569
C(4)	0.0434 (7)	0.3356 (6)	0.431 (1)	564
C(5)	0.1136 (6)	0.2509 (7)	0.455 (1)	539
C(6)	0.1038 (6)	0.1586 (7)	0.335 (1)	456

Table 2. Geometric parameters (\AA , $^\circ$)

Pb(1)—C(1)	2.194 (6)	C(3)—C(4)	1.374 (10)
C(1)—C(2)	1.416 (8)	C(4)—C(5)	1.345 (11)
C(1)—C(6)	1.387 (9)	C(5)—C(6)	1.374 (11)
C(2)—C(3)	1.373 (9)		
C(1)—Pb(1)—C(1 ⁱ)	109.1 (2)	C(1)—C(2)—C(3)	120.1 (6)
C(1)—Pb(1)—C(1 ⁱⁱ)	110.3 (2)	C(2)—C(3)—C(4)	121.1 (6)
Pb(1)—C(1)—C(6)	123.6 (5)	C(3)—C(4)—C(5)	119.7 (7)
Pb(1)—C(1)—C(2)	120.0 (4)	C(4)—C(5)—C(6)	120.4 (7)
C(2)—C(1)—C(6)	116.4 (6)	C(1)—C(6)—C(5)	122.2 (7)

Symmetry code: (i) $-y, x, -z$; (ii) $-x, -y, z$.

The title compound was prepared by a procedure described by Pfeiffer & Truskier (1904) and modified by Horn (1966). Single crystals were obtained from chloroform. The crystal was mounted on the tip of a glass fibre with shellac. The lattice constants were determined from a symmetry-constrained least-squares fit. ω scans of low-order reflections along the three crystal axes showed acceptable mosaicity. Data were collected with $2\theta/\omega$ scans of speed $1.50\text{--}14.65^\circ \text{ min}^{-1}$ in θ and with θ scan width $(1.2 \text{ plus dispersion})^\circ$. Lorentz-polarization and absorption (via ψ scans) corrections were made. H atoms were placed in calculated positions and a common isotropic displacement parameter was refined. The weighting scheme used led to an analysis of variance which was featureless in terms of $\sin\theta$ and F . A search for higher symmetries was performed using *MISSYM* (Le Page, 1987).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71125 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1039]

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Structure of a Keto Derivative of 9,11-Dihydrogracilin A

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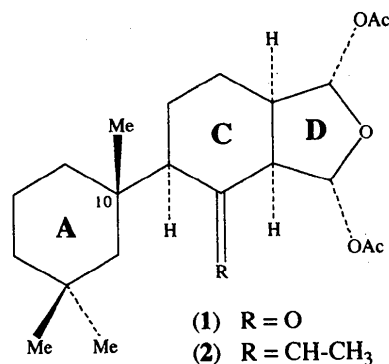
(Received 18 September 1992; accepted 26 January 1993)

Abstract

The X-ray analysis was carried out on the 8-keto derivative of 9,11-dihydrogracilin A, 1,3,3a,4,5,6,7,7a-octahydro-4-oxo-5-(1,3,3-trimethylcyclohexyl)-1,3-isobenzofurandiol diacetate, the major metabolite from the Antarctic sponge *Dendrilla membranosa*. The present study confirms the norditerpenoid skeleton of the spongian type proposed for the natural product by Molinski & Faulkner [*J. Org. Chem.* (1987), **52**, 296–298] on the basis of spectral data and chemical correlations, and also fixes the unknown relative stereochemistry at C10. This result gives further support to the hypothesis regarding the biogenetic origin of the gracilins. The six-membered rings are both in chair conformations and the furan ring is in an envelope form. The molecular packing is governed by normal van der Waals interactions.

Comment

Norditerpenes, as well as bisnorditerpenes, are substances rarely found in marine organisms (Faulkner, 1991). A series of interesting norditerpene metabolites, called gracilin A, E and F, have been isolated from Mediterranean sponge, *Spongionella gracilis* (Mayol, Piccialli & Sica, 1985, 1986), and their structural characterization carried out by means of NMR data and chemical correlations, except for the undetermined stereochemistry at C10. More recently, the 9,11-dihydro derivative of gracilin A was identified in the Antarctic sponge *Dendrilla membranosa* (Molinski & Faulkner, 1987) and it is probably involved, together with the closely related minor metabolite membranolide, in the chemical defence of the sponge. In order to confirm the structure of this class of gracilins and to establish the relative stereochemistry at C10, the X-ray analysis of the 8-keto derivative (1), obtained from ozonolysis of the 9,11-dihydrogracilin A (2), was carried out.



The molecule has a norditerpenoid tricyclic skeleton formed by a trimethylcyclohexane residue (ring A), axially linked at C10 to a bicyclic system, which consists of a cyclohexanone (ring C) *cis* fused to a diacetyltetrahydrofuran moiety (ring D).

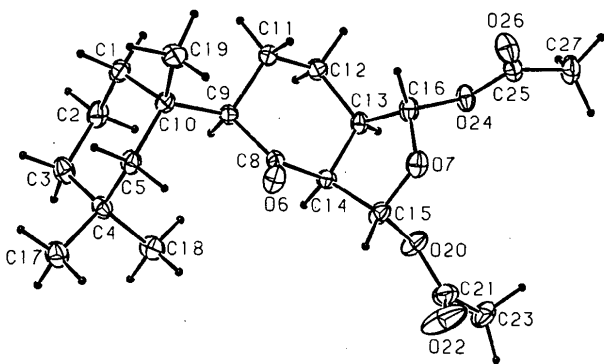


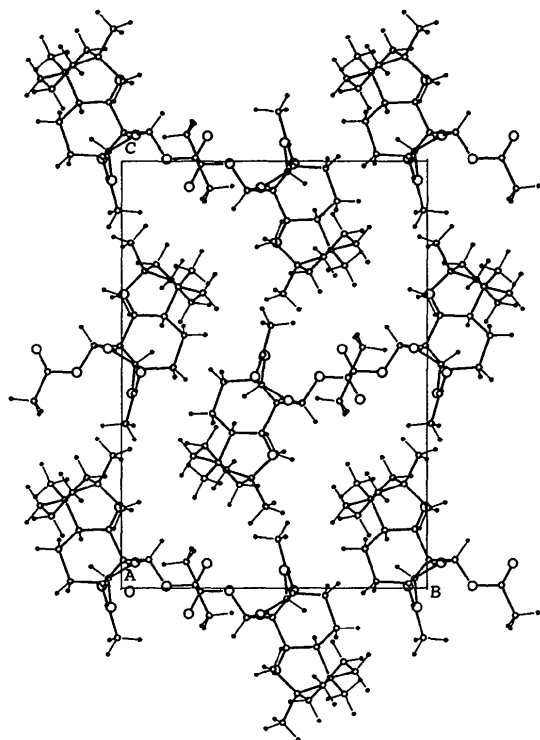
Fig. 1. Perspective view of (1) with the atomic numbering scheme for non-H atoms. Thermal ellipsoids are at the 30% probability level.

The results of the present analysis are in agreement with the structural elucidation of 9,11-dihydrogracilin A (Molinski & Faulkner, 1987) and gracilin A (Mayol, Piccialli & Sica, 1985) on the basis of spectral and chemical evidence. Moreover, the stereochemistry at the chiral center C10, which in both molecules could not be determined, is fixed as *S*^{*}, relative to the configuration of the *cis*-fused ring system. This stereochemistry is in agreement with that of the hypothetical 'spongian' skeleton precursor (Kazlauskas, Murphy, Wells, Noack, Oberhansli & Schonholzer, 1979) and gives further support to the hypothesis, proposed by Mayol, Piccialli & Sica (1986), for the biogenetic origin of the gracilins, which involves the cleavage of ring B of the spongian precursor.

The C—C bond lengths range from 1.501 (7) to 1.560 (6) Å and the average value of the endocyclic bond angles in the A and C rings is 111.7° with an r.m.s. deviation of 3.7° from the mean. As a consequence of the axial disposition of ring A and the *cis* fusion in the benzofuran system, few 1–5 intramolecular contacts are less than 3.3 Å. This atomic crowding is probably responsible for the few significant deviations of the geometrical parameters from normal values (Puliti, De Rosa, Mattia & Mazzarella, 1990; Puliti, Gavagnin, Cimino, Mattia & Mazzarella, 1992), in particular, the lengthening of the C9—C10 bond to 1.560 (6) Å and the opening of the C5—C10—C9 and C10—C9—C8 angles to 114.9 (4) and 117.3 (3)°, respectively.

Ring A is almost in the ideal chair conformation, with C2 and C5 displaced 0.654 (5) and 0.555 (4) Å in opposite directions from the best plane through the remaining endocyclic atoms. For this ring, ϱ and θ puckering parameters (Cremer & Pople, 1975) are 0.521 (8) Å and 6.91 (8)°, respectively. The *cis*-fused six-membered C ring is in a chair form, distorted towards a half boat, $\varrho = 0.595$ (7) Å and $\theta = 19.23$ (8)°, with C13 flattened with respect to C9 [0.511 (5) and 0.817 (5) Å out of the best plane through the C8, C11, C12 and C14 atoms], which helps to release the intramolecular contacts across the *cis* fusion. The furan ring has an envelope conformation with C14 0.581 (4) Å out to the best plane through the remaining atoms. Both β -axial acetoxy groups have the carbonyl O22 and O26 atoms eclipsed with the intracyclic atoms C15 and C16, respectively.

In the absence of hydrogen donors, no hydrogen bonds are formed and all the intermolecular contacts are greater than 3.4 Å. Molecules related by the screw axis parallel to a pack with one of the two acetoxy groups stacked on top of the corresponding acetoxy group from another molecule. The best plane through the O20, C21, O22 and C23 atoms is almost normal to the screw axis. In this group, O22

Fig. 2. Crystal packing in the *bc* plane.

refines with an anomalously large B_{11} component, corresponding to an r.m.s. displacement of 0.544 (4) Å. The difference Fourier map, calculated without the contribution of this atom, has a maximum density in this region, highly elongated along *a*, at the refined position of O22. The large value of B_{11} for O22, together with the less pronounced anisotropy of the other atoms of the group, is an indication of disorder which probably arises from imperfect stacking of the acetoxy moiety. The small tilting of the group with respect to the screw axis destroys a local symmetry centre and probably causes the stabilization of two or more slightly different orientations of the group, which are averaged out in the final structure.

Experimental

Crystal data

$C_{21}H_{32}O_6$
 $M_r = 380.49$
 Orthorhombic
 $P2_12_12_1$
 $a = 7.9122$ (8) Å
 $b = 13.788$ (2) Å
 $c = 19.150$ (4) Å
 $V = 2089.2$ (9) Å³
 $Z = 4$
 $D_x = 1.21$ Mg m⁻³

Cu $K\alpha$ radiation
 $\lambda = 1.54056$ Å
 Cell parameters from 24 reflections
 $\theta = 20\text{--}24^\circ$
 $\mu = 0.679$ mm⁻¹
 $T = 293$ K
 Prism
 $0.44 \times 0.07 \times 0.05$ mm
 Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: none
 2419 measured reflections
 2419 independent reflections

1555 observed reflections [$I \geq 2.5\sigma(I)$]
 $\theta_{\max} = 74^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 17$
 $l = 0 \rightarrow 23$
 3 standard reflections
 frequency: 240 min
 intensity variation: 3%

Refinement

Refinement on F
 Final $R = 0.050$
 $wR = 0.049$
 $S = 0.22$
 1555 reflections
 245 parameters
 H-atom parameters not refined
 $w = 1/[\sigma^2(F_o) + (0.03F_o)^2 + 3]$ (Killean & Lawrence, 1969)

$(\Delta/\sigma)_{\max} = 0.01$
 $\Delta\rho_{\max} = 0.28$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³
 Extinction correction: Stout & Jensen (1968)
 Extinction coefficient: $9.3(5) \times 10^{-7}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)
$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
C1	0.1587 (8)	0.2347 (4)	0.3084 (3)	4.4 (1)
C2	-0.0121 (7)	0.2721 (4)	0.3314 (3)	4.4 (1)
C3	-0.0865 (7)	0.3404 (4)	0.2767 (3)	4.7 (1)
C4	0.0292 (6)	0.4243 (4)	0.2569 (2)	3.5 (1)
C5	0.2082 (7)	0.3866 (4)	0.2413 (2)	3.5 (1)
O6	0.4996 (5)	0.4932 (3)	0.3113 (2)	4.42 (8)
O7	0.7300 (4)	0.5455 (3)	0.4394 (2)	4.17 (7)
C8	0.4365 (6)	0.4586 (3)	0.3623 (2)	2.88 (9)
C9	0.3441 (6)	0.3607 (3)	0.3645 (2)	2.86 (9)
C10	0.2909 (7)	0.3152 (3)	0.2932 (2)	3.3 (1)
C11	0.4639 (7)	0.2961 (3)	0.4085 (2)	3.7 (1)
C12	0.4723 (7)	0.3330 (3)	0.4837 (2)	3.6 (1)
C13	0.5286 (6)	0.4389 (3)	0.4884 (2)	3.14 (9)
C14	0.4475 (6)	0.5062 (3)	0.4337 (2)	3.05 (9)
C15	0.5690 (7)	0.5898 (4)	0.4328 (2)	3.8 (1)
C16	0.7139 (6)	0.4571 (4)	0.4764 (2)	3.6 (1)
C17	-0.0385 (8)	0.4716 (4)	0.1898 (3)	5.1 (1)
C18	0.0282 (7)	0.5040 (4)	0.3138 (3)	4.6 (1)
C19	0.4444 (7)	0.2701 (4)	0.2560 (3)	4.9 (1)
O20	0.5370 (6)	0.6469 (2)	0.4947 (2)	4.86 (8)
C21	0.5728 (8)	0.7410 (4)	0.4926 (3)	5.1 (1)
O22	0.621 (1)	0.7792 (3)	0.4417 (2)	11.1 (2)
C23	0.5559 (9)	0.7873 (4)	0.5624 (3)	5.7 (1)
O24	0.7952 (4)	0.4675 (3)	0.5433 (2)	3.91 (7)
C25	0.9674 (6)	0.4601 (4)	0.5443 (2)	3.8 (1)
O26	1.0466 (5)	0.4367 (3)	0.4948 (2)	5.28 (9)
C27	1.0349 (8)	0.4873 (4)	0.6141 (3)	5.1 (1)

Table 2. Geometric parameters (Å, °)

C1—C2	1.513 (8)	C10—C19	1.540 (7)
C1—C10	1.553 (7)	C11—C12	1.528 (7)
C2—C3	1.527 (8)	C12—C13	1.529 (7)
C3—C4	1.522 (8)	C13—C14	1.540 (6)
C4—C5	1.538 (7)	C13—C16	1.506 (7)
C4—C17	1.538 (7)	C14—C15	1.501 (7)
C4—C18	1.547 (7)	C15—O20	1.444 (6)
C5—C10	1.544 (7)	C16—O24	1.441 (5)
O6—C8	1.196 (5)	O20—C21	1.329 (7)
O7—C15	1.419 (7)	C21—O22	1.173 (8)

O7—C16	1.416 (6)	C21—C23	1.488 (8)	Cremer, D. & Pople, J. A. (1975). <i>J. Am. Chem. Soc.</i> 97 , 1354–1361.
C8—C9	1.536 (6)	O24—C25	1.367 (6)	Faulkner, D. J. (1991). <i>J. Nat. Prod. Rep.</i> 8 , 97–147, and references therein.
C8—C14	1.521 (6)	C25—O26	1.181 (6)	Ireland, C. & Faulkner, J. (1981). <i>Tetrahedron</i> , 37 , W233–W240.
C9—C10	1.560 (6)	C25—C27	1.488 (7)	Kazlauskas, R., Murphy, P. T., Wells, R. J., Noack, K., Oberhansli, W. E. & Schonholzer, P. (1979). <i>Aust. J. Chem.</i> 32 , 867–880.
C9—C11	1.550 (7)			Killean, R. C. G. & Lawrence, J. L. (1969). <i>Acta Cryst.</i> B25 , 1750–1752.
C2—C3—C4	114.0 (4)	C5—C10—C9	114.9 (4)	Mayol, L., Piccialli, V. & Sica, D. (1985). <i>Tetrahedron Lett.</i> 26 , 1357–1360.
C5—C4—C18	112.4 (4)	C5—C10—C19	107.1 (4)	Mayol, L., Piccialli, V. & Sica, D. (1986). <i>Tetrahedron</i> , 42 , 5369–5376.
C4—C5—C10	118.7 (4)	C12—C13—C14	114.5 (4)	Molinski, T. F. & Faulkner, D. J. (1987). <i>J. Org. Chem.</i> 52 , 296–298.
C15—O7—C16	109.5 (4)	C12—C13—C16	115.7 (4)	Puliti, R., De Rosa, S., Mattia, C. A. & Mazzarella, L. (1990). <i>Acta Cryst.</i> C46 , 1533–1536.
O6—C8—C9	124.9 (4)	C14—C13—C16	101.6 (4)	Puliti, R., Gavagnin, M., Cimino, G., Mattia, C. A. & Mazzarella, L. (1992). <i>Acta Cryst.</i> C48 , 2145–2147.
O6—C8—C14	122.6 (4)	C8—C14—C13	112.0 (4)	Stout, G. H. & Jensen, L. H. (1968). In <i>X-ray Structure Determination</i> . New York: Macmillan.
C8—C9—C10	117.3 (4)	C8—C14—C15	111.0 (4)	
C8—C9—C11	103.2 (4)	C13—C14—C15	101.8 (4)	
C10—C9—C11	114.2 (4)	O7—C15—C14	104.1 (4)	
C1—C10—C5	106.9 (4)	O7—C16—C13	108.0 (4)	
C1—C10—C9	107.8 (4)			
C4—C5—C10—C9	−71.0 (6)	C12—C13—C14—C15	−159.5 (4)	
C4—C5—C10—C10	165.5 (4)	C16—C13—C14—C8	84.6 (4)	
O6—C8—C9—C10	−15.4 (7)	C14—C13—C16—O24	135.9 (4)	
O6—C8—C14—C15	−9.5 (6)	C13—C14—C15—O20	−76.6 (4)	
C8—C9—C10—C5	−45.1 (6)	C15—O20—C21—O22	3.6 (9)	
C11—C9—C10—C1	74.9 (5)	C16—O24—C25—O26	−7.6 (7)	

The structure was solved using *SIR88* (Burla *et al.*, 1989) and all calculations were made using Enraf–Nonius *SDP* (B. A. Frenz & Associates Inc., 1985) software on a MicroVAX 3100 computer.

Compound (2), 9,11-dihydrogracilin A, was obtained, after purification by chromatography on silica gel, as a colourless oil from the diethyl ether soluble fraction of the acetone extract of sponge *Dendrilla membranosa*, which was collected in the Ross Sea, Antarctica, at depths of 50 m or more, during January 1990.

The derivative (1), used in the X-ray analysis, was obtained by ozonolysis of the natural compound, which has an olefinic bond at C8. The reaction was carried out using the procedure described by Ireland & Faulkner (1981). The major reaction product was purified over silica gel and recrystallized from *n*-hexane.

Characterization of (1): $[\alpha]_D^{20} = +20^\circ$ ($c = 8 \text{ g dm}^{-3}$, diethyl ether). $^1\text{H NMR}(\text{CDCl}_3)$: 0.83 (3H, *s*), 0.94 (3H, *s*), 1.05 (3H, *s*), 1.12 (2H, *m*), 1.28 (4H, *bd*), 1.45 (1H, *m*), 1.53 (1H, *d*), 1.63 (1H, *m*), 1.79 (1H, *m*), 1.96 (1H, *m*), 2.06 (3H, *s*), 2.09 (3H, *s*), 2.22 (1H, *dd*), 3.02 (1H, *d*), 3.07 (1H, *m*), 6.06 (1H, *d*), 6.72 (1H, *s*).

The $^1\text{H NMR}$ measurements were recorded on a Bruker WM 500 spectrometer.

We would like to thank Dr Mariella Morbidoni who was responsible for the collection of biological material in Antarctica, and the staff of the ICMIB–NMR Service. This work was partially supported by the National Research Program in Antarctica, CNR.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71046 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1024]

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Structure of the Benzo-15-crown-5– 3,5-Dinitrobenzoic Acid–Water (1/1/1) Complex

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Abstract

In the title complex, benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene-3,5-dinitrobenzoic acid–water (1/1/1), the structure of which was determined by X-ray diffraction methods at 100 K, the water molecule is involved as a donor in hydrogen bonding to three O atoms of the most flexible part of the crown and as an acceptor in a hydrogen bond with the carboxyl group of 3,5-dinitrobenzoic acid.

Comment

Nature discriminates markedly between the chemically similar pairs of cations Na^+ and K^+ , and Mg^{2+} and Ca^{2+}