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Structures of 2-(3,5-Dibromo-4-butoxy-1-hydroxy-4-methoxy-2,5-cyclohexadien-1-yl)ethanamide (I) and 2-(3,5-Dibromo-1-hydroxy-4,4-dimethoxy-2,5-cyclohexadien-1-yl)ethanamide (II). Two Marine Compounds

BY R. A. TOSCANO,* F. CRUZ,† L. QUIJANO, F. GÓMEZ-GARIBAY AND T. RIOS

Instituto de Química, Universidad Nacional Autónoma de México,‡ Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, *Mexico DF*

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Abstract. (I) $C_{13}H_{19}Br_2NO_4$, $M_r = 413.15$, monoclinic, $P2_1/c$, $a = 8.235$ (4), $b = 12.649$ (6), $c = 15.896$ (8) Å, $\beta = 93.60$ (4)°, $V = 1652$ (1) Å^3, $Z = 4$, $D_x = 1.66$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, $\mu = 48.68$ cm^{-1}, $F(000) = 824$, $T = 293$ K, $R = 0.059$ for 1501 unique observed reflections. (II) $C_{10}H_{13}Br_2NO_4$, $M_r = 371.03$, monoclinic, $P2_1/n$, $a = 9.057$ (2), $b = 12.720$ (3), $c = 11.678$ (4) Å, $\beta = 101.66$ (2)°, $V = 1318$ (1) Å^3, $Z = 4$, $D_x = 1.87$ g cm^{-3}, λ(Cu $K\bar{\alpha}$) = 1.54178 Å, $\mu = 79.38$ cm^{-1}, $F(000) = 728$, $T = 293$ K, $R = 0.045$ for 1639 unique observed reflections. For both molecules the cyclohexadiene rings are planar, the acetal groups show an *anti–anti* conformation and the conformation of the acetamide group is governed by an O—H···O intramolecular hydrogen bond. In compound (I) the butyl group is fully extended and *anti*-related to the acetamide. Molecules are held together in the crystal by N—H···O hydrogen bonds.

Experimental. The title compounds were isolated from the marine sponges *Aplysina* (*Verongia*) *thiona* (I) and *Aplysina* sp. (II). Suitable single crystals were obtained from acetone solutions by slow evaporation.

For compound (I), a cube-like yellow crystal, 0.38 × 0.38 × 0.4 mm, was used for data collection on a Nicolet *R3m* diffractometer with incident-beam graphite monochromator. 25 centered reflections with $4.12 \leq 2\theta \leq 17.13°$ were used for determining cell parameters. Data were collected using ω scans of width 1.2° and rate a function of count rate (4° min^{-1} minimum, 30° min^{-1} maximum), to maximum $(\sin\theta)/\lambda$ of 0.5946 Å^{-1}, and over range of hkl of $0 \leq h \leq 8$, $0 \leq k \leq 13$, $-16 \leq l \leq 16$. Two standards ($\bar{1}\bar{1}\bar{3}$ and $00\bar{2}$) monitored every 50 reflections showed random variation of ±3%, no decay correction was applied. 2463 reflections were measured, of which 2155 were unique ($R_{\rm int} = 0.035$) and 654 were unobserved [$F_o \leq 3\sigma(F_o)$]. Data were corrected for Lorentz and polarization effects but not for absorption. Space group was determined from absences: $h0l$ with l odd, $0k0$ with k odd and $00l$ with l odd.

Direct methods were applied to solve the phase problem. Block-matrix least-squares refinement was based on F magnitudes, with $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = [\sigma^2(F) + 0.001F_o^2]^{-1}$. Refinement included an isotropic extinction correction according to $F_c^* = F_c/[1 + 0.002\chi(F_c^2)/\sin2\theta]^{0.25}$, with $\chi = 0.0006$. H atoms on heteroatoms (N or O) were located by difference Fourier method, those on C atoms were fixed (C—H = 0.96 Å). 191 parameters were refined: atom coordinates and anisotropic temperature factors for all non-H atoms, coordinates of H atoms on O(1) and N(1), scale factor, and one extinction parameter. All H-atom thermal parameters were fixed at $U = 0.06$ Å^2. Refinement converged to give $R = 0.059$, $wR = 0.055$ for 1501 unique observed reflections ($R = 0.095$, $wR = 0.068$ for all data), $S = 1.211$, $(\Delta/\sigma)_{\rm max} = 0.035$, $\Delta\rho_{\rm min}$ and $\Delta\rho_{\rm max}$ in final difference map −0.58 and +0.58 e Å^{-3} respectively. Complex atomic scattering factors were taken from *International Tables for*

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* To whom correspondence should be addressed.

† Present address: Departamento de Biotecnología, Universidad Autónoma Metropolitana-Iztapalapa, Apdo. Postal 55-535, Iztapalapa 09340, Mexico DF.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for compound* (I)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
Br(1)	−4288 (1)	2879 (1)	2905 (1)	72 (1)
Br(2)	1960 (1)	977 (1)	2584 (1)	74 (1)
O(1)	396 (8)	3264 (5)	4973 (4)	46 (2)
O(2)	−1333 (7)	2073 (4)	1905 (3)	48 (2)
O(3)	−1828 (7)	979 (5)	2901 (4)	53 (2)
O(4)	3206 (8)	4272 (5)	5006 (4)	66 (3)
N(1)	3665 (10)	5454 (6)	4015 (5)	63 (3)
C(1)	341 (10)	3502 (7)	4089 (5)	36 (3)
C(2)	−1409 (10)	3498 (7)	3799 (5)	38 (3)
C(3)	−2039 (9)	2828 (7)	3224 (5)	39 (3)
C(4)	−1127 (10)	1984 (6)	2783 (5)	41 (3)
C(5)	647 (9)	2014 (6)	3093 (5)	39 (3)
C(6)	1306 (10)	2666 (7)	3656 (5)	40 (3)
C(7)	1077 (10)	4586 (6)	3943 (5)	39 (3)
C(8)	2740 (11)	4744 (6)	4367 (5)	41 (3)
C(9)	−803 (13)	3041 (7)	1560 (6)	66 (4)
C(10)	−1835 (12)	593 (8)	3747 (6)	62 (4)
C(11)	−3083 (12)	−281 (7)	3740 (7)	63 (4)
C(12)	−3139 (13)	−820 (8)	4568 (7)	79 (5)
C(13)	−4456 (14)	−1694 (9)	4542 (8)	92 (5)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for compound* (I)

Br(1)—C(3)	1.891 (7)	Br(2)—C(5)	1.911 (8)
O(1)—C(1)	1.44 (1)	O(2)—C(4)	1.40 (1)
O(2)—C(9)	1.42 (1)	O(3)—C(4)	1.41 (1)
O(3)—C(10)	1.43 (1)	O(4)—C(8)	1.22 (1)
N(1)—C(8)	1.32 (1)	C(1)—C(2)	1.49 (1)
C(1)—C(6)	1.51 (1)	C(1)—C(7)	1.52 (1)
C(2)—C(3)	1.33 (1)	C(3)—C(4)	1.50 (1)
C(4)—C(5)	1.51 (1)	C(5)—C(6)	1.31 (1)
C(7)—C(8)	1.50 (1)	C(10)—C(11)	1.51 (1)
C(11)—C(12)	1.49 (2)	C(12)—C(13)	1.55 (2)

C(4)—O(2)—C(9)	115.7 (6)	C(4)—O(3)—C10	117.2 (7)
O(1)—C(1)—C(2)	105.9 (7)	O(1)—C(1)—C(6)	108.2 (7)
C(2)—C(1)—C(6)	112.5 (7)	O(1)—C(1)—C(7)	110.5 (6)
C(2)—C(1)—C(7)	110.1 (7)	C(6)—C(1)—C(7)	109.5 (7)
C(1)—C(2)—C(3)	123.1 (7)	Br(1)—C(3)—C(2)	119.8 (6)
Br(1)—C(3)—C(4)	114.1 (6)	C(2)—C(3)—C(4)	126.1 (7)
O(2)—C(4)—O(3)	100.4 (6)	O(2)—C(4)—C(3)	112.0 (7)
O(3)—C(4)—C(3)	110.9 (7)	O(2)—C(4)—C(5)	112.2 (7)
O(3)—C(4)—C(5)	111.9 (6)	C(3)—C(4)—C(5)	109.3 (7)
Br(2)—C(5)—C(4)	113.9 (6)	Br(2)—C(5)—C(6)	120.0 (6)
C(4)—C(5)—C(6)	126.1 (8)	C(1)—C(6)—C(5)	122.9 (7)
C(1)—C(7)—C(8)	114.3 (7)	O(4)—C(8)—N(1)	121.6 (8)
O(4)—C(8)—C(7)	122.7 (8)	N(1)—C(8)—C(7)	115.7 (7)
O(3)—C(10)—C(11)	106.7 (8)	C(10)—C(11)—C(12)	112.9 (8)
C(11)—C(12—C(13)	111.4 (9)		

C(9)—O(2)—C(4)—O(3)	177.6 (7)	C(10)—O(3)—C(4)—O(2)	179.5 (7)
O(3)—C(10)—C(11)—C(12)	175.5 (8)	C(10)—C(11)—C(12)—C(13)	178.8 (9)

Table 3. *Fractional coordinates and equivalent isotropic temperature factors* ($Å^2$) *for compound* (II)

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}].$$

	x	y	z	B_{eq}
Br(1)	0.26061 (7)	0.33052 (4)	0.61710 (5)	4.37 (4)
Br(2)	0.25195 (6)	0.10075 (4)	1.03880 (4)	3.26 (4)
O(1)	−0.1913 (4)	0.1592 (2)	0.7135 (3)	3.0 (1)
O(2)	0.3957 (3)	0.1946 (2)	0.8394 (3)	3.2 (1)
O(3)	0.2512 (3)	0.3134 (2)	0.8895 (3)	2.8 (1)
O(4)	−0.3019 (4)	−0.0310 (2)	0.6975 (3)	3.5 (1)
N(1)	−0.1502 (5)	−0.1646 (3)	0.6825 (4)	3.4 (2)
C(1)	−0.0469 (5)	0.1117 (3)	0.7105 (4)	2.0 (2)
C(2)	0.0368 (5)	0.1891 (3)	0.6498 (4)	2.5 (2)
C(3)	0.1638 (5)	0.2335 (3)	0.7012 (4)	2.4 (2)
C(4)	0.2419 (5)	0.2187 (3)	0.8270 (4)	2.4 (2)
C(5)	0.1603 (5)	0.1349 (3)	0.8827 (4)	2.0 (2)
C(6)	0.0333 (5)	0.0902 (3)	0.8324 (4)	2.1 (2)
C(7)	−0.0706 (5)	0.0083 (3)	0.6377 (3)	1.9 (2)
C(8)	−0.1832 (5)	−0.0654 (3)	0.6756 (4)	2.2 (2)
C(9)	0.4282 (8)	0.0988 (4)	0.7851 (7)	5.1 (3)
C(10)	0.1092 (7)	0.3555 (5)	0.9017 (6)	4.4 (3)

Table 4. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for compound* (II)

Br(1)—C(3)	1.898 (4)	Br(2)—C(5)	1.895 (4)
O(1)—C(1)	1.447 (5)	O(2)—C(4)	1.405 (5)
O(2)—C(9)	1.432 (7)	O(3)—C(4)	1.401 (5)
O(3)—C(10)	1.427 (7)	O(4)—C(8)	1.234 (5)
N(1)—C(8)	1.296 (6)	C(1)—C(2)	1.505 (6)
C(1)—C(6)	1.487 (7)	C(1)—C(7)	1.557 (5)
C(2)—C(3)	1.312 (7)	C(3)—C(4)	1.509 (7)
C(4)—C(5)	1.516 (6)	C(5)—C(6)	1.311 (6)
C(7)—C(8)	1.515 (6)		

C(4)—O(2)—C(9)	115.4 (4)	C(4)—O(3)—C10	114.4 (4)
O(1)—C(1)—C(2)	106.4 (3)	O(1)—C(1)—C(6)	108.8 (4)
C(2)—C(1)—C(6)	112.1 (4)	O(1)—C(1)—C(7)	109.9 (3)
C(2)—C(1)—C(7)	108.9 (3)	C(6)—C(1)—C(7)	110.7 (3)
C(1)—C(2)—C(3)	123.0 (4)	Br(1)—C(3)—C(2)	119.8 (4)
Br(1)—C(3)—C(4)	114.2 (3)	C(2)—C(3)—C(4)	125.9 (4)
O(2)—C(4)—O(3)	100.4 (3)	O(2)—C(4)—C(3)	112.7 (4)
O(3)—C(4)—C(3)	111.6 (3)	O(2)—C(4)—C(5)	111.2 (3)
O(3)—C(4)—C(5)	111.4 (4)	C(3)—C(4)—C(5)	109.4 (4)
Br(2)—C(5)—C(4)	114.6 (3)	Br(2)—C(5)—C(6)	120.4 (3)
C(4)—C(5)—C(6)	124.9 (4)	C(1)—C(6)—C(5)	124.3 (4)
C(1)—C(7)—C(8)	112.9 (3)	O(4)—C(8)—N(1)	122.2 (4)
O(4)—C(8)—C(7)	120.5 (4)	N(1)—C(8)—C(7)	117.4 (4)

O(2)—C(4)—O(3)—C(10)	−175.2 (4)	O(3)—C(4)—O(2)—C(9)	179.4 (4)

X-ray Crystallography (1974, Vol. IV, pp. 72–98). All calculations and graphics preparation were performed with the *SHELXTL* (Sheldrick, 1983) program system on a Data General Nova 4S computer.

For compound (II), a cube-like light-yellow crystal, 0.2 × 0.2 × 0.2 mm, was used for data collection on a Nicolet *P*3*F* diffractometer with Ni-filtered radiation. 25 centered reflections with $10.90 \leq 2\theta \leq 30.73^\circ$ were used for determining cell parameters. Data were collected using θ–2θ scans of width $[2\theta(K\alpha_1) - 1.0]$ to $[2\theta(K\alpha_2) + 1.0]^\circ$ and rate a function of count rate (4° min^{-1} minimum, 30° min^{-1} maximum), to maximum $(\sin\theta)/\lambda$ of 0.5317 Å^{-1}, and over range of *hkl* of $0 \leq h \leq 9$, $0 \leq k \leq 13$, $-12 \leq l \leq 12$. Two standards $(11\bar{2}$ and $11\bar{1})$ monitored every 50 reflections showed random variation of ±3%; no decay correction was applied. 1892 reflections were measured, of which 1790 were unique ($R_{int} = 0.012$) and 151 were unobserved $[I \leq 3\sigma(I)]$. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was made after structure solution using *DIFABS* (Walker & Stuart, 1983), which resulted in relative correction factors ranging from 1.22 to 0.83. Space group was determined from systematic abscences: $h0l$ with $h + l$ odd, $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd.

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984). Full-matrix least-squares refinement was based on observed F magnitudes, with $\sum w(|F_o| - |F_c|)^2$ minimized. H atoms were located by ΔF synthesis, those on C atoms included as fixed contributions while those bonded to heteroatoms (N or O) had positional parameters refined, with isotropic B values assigned as $1.2B_{eq}$ of the bonded atoms. 164 parameters were refined: atom coordinates and anisotropic temperature factors for all non-H atoms, coordinates of H atoms on O(1) and N(1), scale factor, and secondary-extinction parameter ($\chi = 7.5 \times 10^6$). Refinement converged to give $R = 0.045$, $wR = 0.068$ for 1639 unique observed reflections ($R = 0.048$, $wR = 0.071$ for all data), $S = 1.52$, $(\Delta/\sigma)_{\max} = 0.04$, $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ in final ΔF map -0.79 and 1.11 (near Br atom) e Å^{-3}, respectively. Complex atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72–98). All calculations were performed with the *TEXSAN* (Molecular Structure Corporation, 1985) program package on a DEC VAX station II computer.

Atom numbering for Tables 1–4, listing atomic parameters and molecular geometry for molecules (I) and (II), follows that shown in Figs. 1 and 2.* Molecular packing is shown in Figs. 3 and 4.

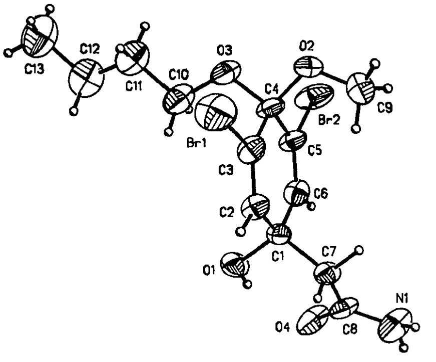

Fig. 1. Molecular structure and numbering scheme for compound (I); thermal ellipsoids at 50% probability level.

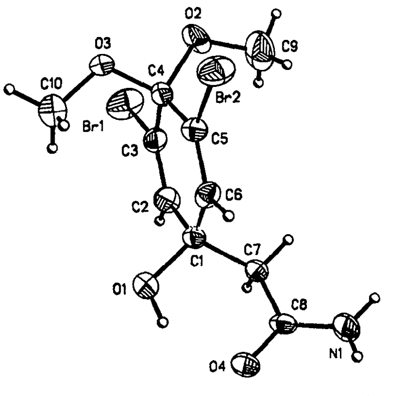

Fig. 2. Molecular structure and numbering scheme for compound (II); thermal ellipsoids at 50% probability level.

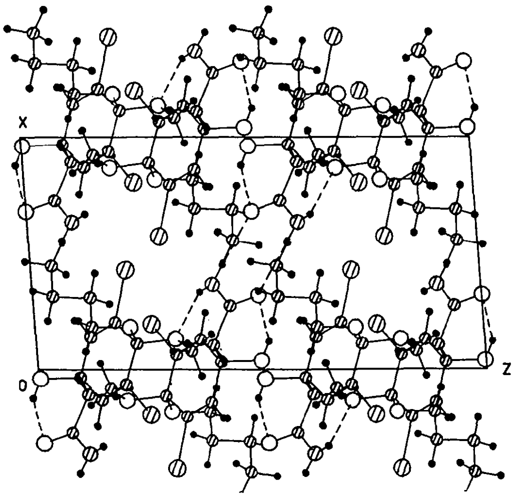

Fig. 3. The packing of compound (I) viewed along the *b* axis.

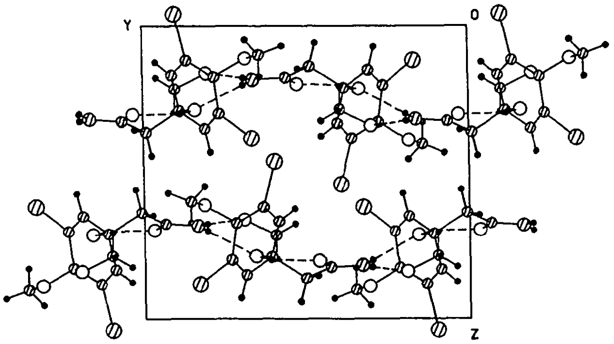

Fig. 4. The packing of compound (II) viewed along the *a* axis.

Related literature. A similar *anti–anti* conformation of acetals in sterically hindered 1,4-cyclohexadiene rings has been reported by Nørskov-Lauritsen, Larsen, Ettlinger & Jaroszewski (1982), *versus* the *gauche–gauche* conformation found in 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (Liebich, Yvon & Margaretha, 1976). Compound (II) is also found in *Verongia fistularis* (Sharma, Vig & Burkholder, 1970).

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, hydrogen-bond geometries and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55344 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.