Table 3. *Selected geometric parameters (Å, °) for (2)*

S1—O1	1.431 (1)	C4—C5	1.515 (3)
S1—O2	1.441 (1)	C5—C6	1.524 (3)
S1—N2	1.626 (2)	C7—C8	1.394 (3)
S1—C7	1.760 (2)	C7—C12	1.387 (3)
N1—N2	1.390 (2)	C8—C9	1.378 (3)
N1—C1	1.288 (2)	C9—C10	1.388 (3)
C1—C2	1.501 (3)	C10—C11	1.394 (3)
C1—C6	1.491 (3)	C10—C13	1.499 (3)
C2—C3	1.522 (3)	C11—C12	1.384 (3)
C3—C4	1.513 (4)		
O1—S1—O2	119.49 (8)	C3—C4—C5	110.7 (2)
O1—S1—N2	109.66 (8)	C4—C5—C6	111.8 (2)
O1—S1—C7	107.60 (9)	C1—C6—C5	111.8 (2)
O2—S1—N2	103.63 (8)	S1—C7—C8	118.9 (2)
O2—S1—C7	108.54 (8)	S1—C7—C12	120.3 (1)
N2—S1—C7	107.35 (8)	C8—C7—C12	120.7 (2)
N2—N1—C1	117.5 (2)	C7—C8—C9	118.8 (2)
S1—N2—N1	116.2 (1)	C8—C9—C10	121.7 (2)
N1—C1—C2	115.9 (2)	C9—C10—C11	118.6 (2)
N1—C1—C6	127.6 (2)	C9—C10—C13	120.9 (2)
C2—C1—C6	116.3 (2)	C11—C10—C13	120.6 (2)
C1—C2—C3	112.9 (2)	C10—C11—C12	120.8 (2)
C2—C3—C4	111.1 (2)	C7—C12—C11	119.4 (2)
S1—N2—N1—C1	172.8 (1)	N2—S1—C7—C8	−62.7 (2)
O1—S1—N2—N1	46.3 (2)	N2—S1—C7—C12	119.4 (1)
O1—S1—C7—C8	179.4 (1)	N2—N1—C1—C2	171.7 (2)
O1—S1—C7—C12	1.4 (2)	N2—N1—C1—C6	−2.3 (3)
O2—S1—N2—N1	174.9 (1)	C1—C2—C3—C4	50.4 (3)
O2—S1—C7—C8	48.7 (2)	C1—C6—C5—C4	−51.6 (3)
O2—S1—C7—C12	−129.2 (1)	C2—C1—C6—C5	46.0 (3)
N1—N2—S1—C7	−70.3 (2)	C2—C3—C4—C5	−57.0 (3)
N1—C1—C2—C3	139.3 (2)	C3—C2—C1—C6	−46.0 (3)
N1—C1—C6—C5	−140.0 (2)	C3—C4—C5—C6	58.1 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O2^{i}	0.81 (2)	2.17 (2)	2.969 (2)	169 (2)

Symmetry code: (i) $-x, 1-y, -z$.

In both (1) and (2), only the H-atom positions were refined; in (1), N—H = 0.86 (2) and C—H = 0.88 (3)–1.03 (3) Å, while in (2), N—H = 0.81 (2) and C—H = 0.87 (2)–1.02 (2) Å].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989) for (1); *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) for (2). Cell refinement: *CAD*-4 *Software* for (1); *MSC/AFC Diffractometer Control Software* for (2). For both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1033). Services for accessing these data are described at the back of the journal.

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Methoxyamericanolide B†

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Abstract

The title compound, $C_{16}H_{20}O_5$, was isolated from the gorgonian coral *P. americana* found in the Caribbean zone of the West Indies. The compound belongs to a well known family of sesquiterpenoid lactones. Its structure features a guaiane skeleton incorporating three types of oxygen functionalities. Thus, the five O atoms that are incorporated in the skeleton form two epoxy groups, a lactone moiety and an ether link. This study assigns the relative stereochemistry at the six chiral centers as 1*R*,2*R*,4*S*,5*S*,8*R*,10*S*.

Comment

Pseudopterogorgia americana is widespread in the Caribbean zone of the West Indies and contains a large number of pharmacologically active compounds (Rodríguez, 1995). As part of our continued investigation of the sea plume *P. americana* from Puerto Rico, we isolated and spectroscopically identified a new compound, methoxyamericanolide B, (I). In order to confirm the identity and to reveal the absolute stereochemistry of this compound, a single-crystal X-ray structure analysis was carried out.

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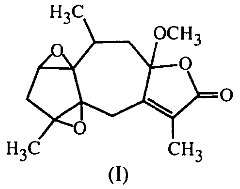
† Systematic name: 7-methoxy-4,9,13-trimethyl-6-oxa-1,13:10,11-diepoxytricyclo[8.3.0.0^{3,7}]tridec-3-en-5-one.



(I)

An *ORTEP*II (Johnson, 1976) representation of (I) is presented in Fig. 1. The molecular structure of this compound possesses a 15-carbon guaiane skeleton incorporating five O atoms. Thus, a seven-membered ring is fused with a five-membered carbon ring, containing two epoxy groups, and an α-methylbutenolide (or γ-lactone) ring. The five O atoms in the molecule form two epoxy groups [O(1)—C(1) 1.446 (4), O(1)—C(2) 1.427 (5), O(2)—C(4) 1.457 (4) and O(2)—C(5) 1.446 (4) Å], a lactone moiety [O(4)—C(8) 1.465 (4), O(4)—C(12) 1.367 (4) and O(3)—C(12) 1.194 (4) Å] and an ether link [O(5)—C(8) 1.392 (4) and O(5)—C(16) 1.411 (4) Å]. The shortest C—C distance [*i.e.* C(7)—C(11) 1.330 (4) Å] in the molecule is assigned as a double bond. In this data, the Flack parameter (Flack, 1983) is not well enough defined to distinguish between the absolute structure and its enantiomorph. The relative configuration at the six chiral centers is 1*R*,2*R*,4*S*,5*S*,8*R*,10*S*.

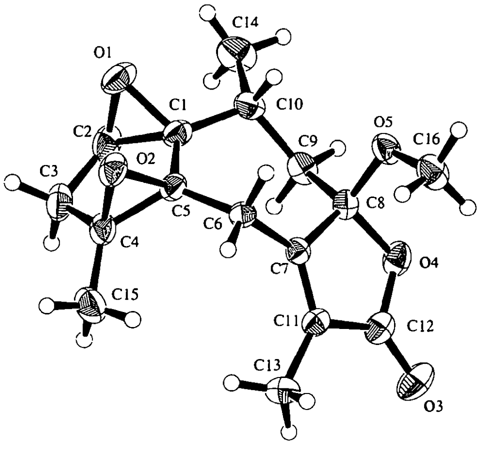


Fig. 1. An *ORTEP*II (Johnson, 1976) representation of the title compound showing 50% probability displacement ellipsoids.

Experimental

The detailed isolation and spectroscopic identification of the title compound has been described elsewhere (Rodríguez & Boulanger, 1996). Slow evaporation of a methanol solution of the compound at room temperature afforded colorless single crystals of X-ray quality.

Crystal data

$C_{16}H_{20}O_5$
$M_r = 292.33$

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å

Orthorhombic
$P2_12_12_1$
$a = 9.032\ (3)$ Å
$b = 9.897\ (2)$ Å
$c = 16.231\ (3)$ Å
$V = 1450.9\ (5)$ Å^3
$Z = 4$
$D_x = 1.338$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 10$–$12°$
$\mu = 0.099$ mm^{-1}
$T = 295\ (1)$ K
Prism
0.62 × 0.43 × 0.43 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1649 measured reflections
1501 independent reflections
1303 reflections with $I > 2.5\sigma(I)$

$R_{\rm int} = 0.013$
$\theta_{\rm max} = 24.97°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 19$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0504$
$wR = 0.0632$
$S = 1.783$
1303 reflections
190 parameters
H atoms not refined
Weighting scheme based on measured s.u.'s; $w = 1/[\sigma_c^2(F_o) + (p^2/4F_o^2)]$, with $p = 0.045$

$(\Delta/\sigma)_{\rm max} = 0.0004$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O(1)—C(1)	1.446 (4)	O(4)—C(8)	1.465 (4)
O(2)—C(4)	1.457 (4)	O(5)—C(8)	1.392 (4)
O(3)—C(12)	1.194 (4)	O(5)—C(16)	1.411 (4)
C(1)—O(1)—C(2)	61.3 (2)	C(8)—O(5)—C(16)	116.1 (3)
C(8)—O(4)—C(12)	109.0 (2)		

Refinement on F^2 did improve the s.u.'s of the molecular geometry.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1025). Services for accessing these data are described at the back of the journal.

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erythro-1-(Benzothiazol-2-yl)-1,2-dibromo-2-(2-chloro-5-nitrophenyl)ethane†

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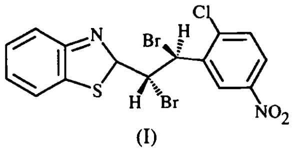
Abstract

The title compound, $C_{15}H_9Br_2ClN_2O_2S$, was synthesized by electrophilic addition of bromine to 2-(2-chloro-5-nitrostyryl)benzothiazole. The molecule consists of benzothiazole and 2-chloro-5-nitrophenyl rings linked by a 1,2-dibromoethane moiety. The dihedral angle between the benzothiazole and phenyl rings is 8.2 (9)°. The benzothiazole ring is planar with a mean deviation of 0.168 (7) Å. The Br1—C8 and Br2—C9 bond distances are 1.972 (5) and 2.007 (6) Å, respectively.

Comment

We have been interested in utilizing 2-styrylbenzazols and their oxo and thio derivatives as potential ligands in the synthesis of new platinum-based anticancer agents (Cox *et al.*, 1982; Gòmez *et al.*, 1988; Muir *et al.*, 1987, 1988, 1992*a*,*b*,*c*,*d*, 1993; Muir, Cox, Rivera *et al.*, 1992). As part of our continuing work on the benzothiazole series, we studied the electrophilic addition of bromine to 2-(2-chloro-5-nitrostyryl)benzothiazole. Such a reaction produced the corresponding dibromide in excellent yield. The proton–proton coupling constant (J = 11.1 Hz) in the NMR spectrum indicates that the compound is an *erythro* isomer. In order to confirm the identity of this compound, (I), a single-crystal X-ray structure analysis was carried out.



(I)

An *ORTEP*II (Johnson, 1976) representation of the title compound is presented in Fig. 1. The molecular structure of this compound features a benzothiazole and a 2-chloro-5-nitrophenyl ring linked by a 1,2-dibromoethane moiety that is in an *anti* conformation. The dihedral angle between the two aromatic rings is 8.2 (9)°. The C—N and S—C bond distances in the benzothiazole ring are similar to those found in other similar structures (Alegría *et al.*, 1993). In summary, the X-ray structure of the title compound confirms that the electrophilic addition of bromine to (E)-2-(2-chloro-5-nitrostyryl)benzothiazole proceeds by a stereoselective *anti* process to produce the racemic *erythro*-dibromide. Furthermore, the conformation observed in the solid state is also the most stable conformation in solution as evidenced by the proton–proton coupling constant.

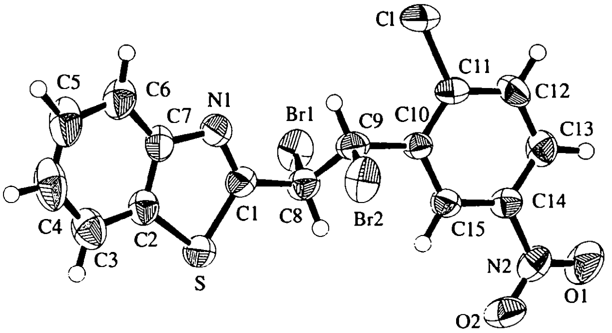


Fig. 1. An *ORTEP*II (Johnson, 1976) representation of the title compound showing 50% probability displacement ellipsoids.

Experimental

A solution of (E)-2-(2-chloro-5-nitrostyryl)benzothiazole (8.0 g, 25.0 mmol) in 200 ml of a benzene–dioxane (3:1) mixture was allowed to react with bromine (8.0 g, 50.0 mmol) to afford 9.5 g (79% yield) of the title compound as a pale yellow solid (m.p. 411–413 K). Single crystals suitable for X-ray diffraction studies were obtained from acetonitrile by slow evaporation of the solvent.

Crystal data

$C_{15}H_9Br_2ClN_2O_2S$
M_r = 476.57
Monoclinic
$P2_1/c$
a = 10.557 (4) Å
b = 14.518 (5) Å
c = 11.094 (3) Å
β = 104.51 (2)°
V = 1646.1 (9) Å^3
Z = 4
D_x = 1.923 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 12–13°
μ = 5.237 mm^{-1}
T = 295 (1) K
Prism
0.66 × 0.54 × 0.51 mm
Yellow

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† Alternative name: 2-[*erythro*-1,2-dibromo-2-(2-chloro-5-nitrophenyl)-ethyl]-1,3-benzothiazole.

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