ring, while the NO_2 group in molecule *A* is more out of the phenyl plane. The dihedral angles are 15.1 (4) and 44.9 (3)° in molecules *B* and *A*, respectively. In addition, the conformations of the two molecules are slightly different; the dihedral angle between the benzothiazole fragment and the phenyl ring is 6.1 (4)° in *A* and 19.5 (4)° in *B*. The molecules are packed in the unit cell in a pseudo-layered fashion, with the water molecules situated in the layer gap (Fig. 2). No hydrogen bonding is found between the organic molecules and the solvent. The structure is consistent with the spectroscopic data. All bond distances and angles are in the normal ranges.

Experimental

When 2,4-dichloro-5-nitrobenzaldehyde (1.50 g, 6.82 mmol) and 2-methylbenzothiazole (0.909 g, 6.02 mmol) were refluxed in acetic anhydride (35 ml), a yellow solid was obtained (Cox *et al.*, 1982; Muir, Cox, Rivera, Cadiz & Medina, 1992). The crude product (1.59 g, 77% yield) was recrystallized from acetone to give yellow single crystals (m.p. 441–443 K).

Crystal data

$2C_{15}H_8Cl_2N_2O_2S.H_2O$
$M_r = 720.43$
Monoclinic
$P2_1/c$
$a = 13.081\ (2)$ Å
$b = 13.473\ (2)$ Å
$c = 17.148\ (3)$ Å
$\beta = 93.73\ (1)°$
$V = 3015.8\ (7)$ Å^3
$Z = 4$
$D_x = 1.587$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 15 reflections
$\theta = 10–11°$
$\mu = 0.579$ mm^{-1}
$T = 295.2$ K
Parallelepiped
0.31 × 0.27 × 0.26 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6665 measured reflections
6494 independent reflections
3476 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.0454$
$\theta_{\text{max}} = 26.29°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = -21 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity decay: 3.11%

Refinement

Refinement on *F*
$R = 0.0706$
$wR = 0.0936$
$S = 2.161$
3476 reflections
407 parameters
H atoms not refined
$w = 1/\sigma^2(F_o) = 1/[\sigma^2(F_o) + 0.0009/4F_o^2]$
$(\Delta/\sigma)_{\text{max}} = 0.0004$

$\Delta\rho_{\text{max}} = 0.65$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.70$ e Å^{-3}
Extinction correction: Zachariasen type 2, Gaussian isotropic
Extinction coefficient: $2.676\ (2) \times 10^{-7}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

The crystal deteriorated during data collection, possibly due to loss of water. H atoms were placed in calculated positions.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4-*PC*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

This work was supported by the National Science Foundation (OSR-9452893) and the National Institute of Health (MBRS 2S06-GM08224).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Euniciniatin

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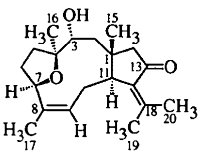
Abstract

Euniciniatin [4(*S*),7(*R*)-epoxy-3(*R*)-hydroxy-1(*R*),11(*S*)-dolabella-8(*Z*),12(18)-dien-13-one; (1*R*,3*R*,4*S*,7*R*,11*S*)-3-hydroxy-12-isopropylidene-15-oxa-1,4,8-trimethyltri-

cyclo[9.3.0.$1^{4,7}$]pentadec-8(*Z*)-en-13-one], $C_{20}H_{30}O_3$, was synthesized from a known dolabellane constituent of *E. laciniata*, namely, dolabellatrienone. The structure of this compound has a *trans*-bicyclo[9.3.0]tetradecane nucleus containing an additional 4,7-oxa bridge. The three O atoms in the molecule all belong to different functional groups, *i.e.* one is part of an ether bridge [O(3)—C(4) 1.452 (5) and O(3)—C(7) 1.429 (5) Å], one an alcohol [O(2)—C(3) 1.429 (6) Å] and one a ketone [O(1)—C(13) 1.233 (5) Å].

Comment

Gorgonian octocorals (sea whips and sea fans) of the genus *Eunicea* (family Plexauridae) have been recognized as an abundant source of structurally unique secondary metabolites possessing a formidable array of biological activities (Rodríguez, 1995). While cembranoid diterpenes are by far the most common natural constituents among the species of *Eunicea* found in the Caribbean Sea, an increasing number of a distinct class of non-cembranoid bicyclic diterpenoids have been reported since 1976 (Look & Fenical, 1982; Cáceres, Rivera & Rodríguez, 1990; Shin & Fenical, 1991; Rodríguez, Acosta & Dhasmana, 1993; Rodríguez, González & González, 1995; Govindan, Govindan & Kingston, 1995). As part of an ongoing synthetic study on the dolabellane constituents of *E. laciniata*, we synthesized a new tricyclic dolabellane, euniciniatin, (I), in two steps from a known compound, dolabellatrienone, found in the same organism.



(I)

In order to confirm the identity and to study the stereochemistry of this compound, a single-crystal X-ray structure analysis was carried out. The molecular structure of this compound has a tricyclic ring system derived from a dolabellane diterpenoid, *i.e.* a *trans*-bicyclo[9.3.0] carbon skeleton incorporating a 4,7-oxa bridge. There are three different oxygen-containing functional groups found in the structure, namely, an ether bridge, an alcohol and a ketone. The most conspicuous features are the 4,7-oxa bridge and the 8(*Z*)-cycloundecene moiety, which is very unusual in this class of compounds.

The absolute configuration of euniciniatin was assigned based on the starting material dolabellatrienone, whose absolute configuration has been unambiguously established (Corey & Kania, 1996). All the bond distances and angles are within normal ranges. The structure is consistent with the high-resolution electron-impact mass spectrometry (HREIMS) and ^{13}C NMR data.

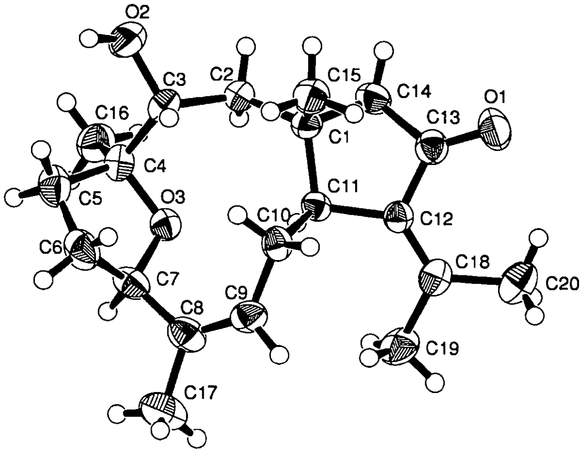


Fig. 1. An *ORTEP*II (Johnson, 1976) representation of euniciniatin showing 50% probability displacement ellipsoids.

Experimental

The detailed synthesis of euniciniatin will be described elsewhere. Slow diffusion of hexane into an EtOAc solution of the compound at room temperature yielded clear needle-shaped single crystals of X-ray quality.

Crystal data

$C_{20}H_{30}O_3$
$M_r = 318.46$
Orthorhombic
$P2_12_12_1$
$a = 10.154 (1)$ Å
$b = 10.923 (1)$ Å
$c = 16.698 (2)$ Å
$V = 1852.0 (3)$ Å^3
$Z = 4$
$D_x = 1.142$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 30$–$32°$
$\mu = 0.075$ mm^{-1}
$T = 295.2$ K
Needle
0.18 × 0.10 × 0.06 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2320 measured reflections
2320 independent reflections
1421 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 26.97°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.0585$
$wR = 0.0672$
$S = 1.584$
1421 reflections
209 parameters
H atoms not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.0056$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: Zachariasen (1968) type 2, Gaussian isotropic
Extinction coefficient: 3.60273
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Bond lengths (Å)*

O(1)—C(13)	1.233 (5)	C(6)—C(7)	1.530 (7)
O(2)—C(3)	1.429 (6)	C(7)—C(8)	1.519 (7)
O(3)—C(4)	1.452 (5)	C(8)—C(9)	1.328 (7)
O(3)—C(7)	1.429 (5)	C(8)—C(17)	1.506 (8)
C(1)—C(2)	1.530 (6)	C(9)—C(10)	1.511 (7)
C(1)—C(11)	1.579 (6)	C(10)—C(11)	1.566 (7)
C(1)—C(14)	1.532 (7)	C(11)—C(12)	1.530 (6)
C(1)—C(15)	1.531 (7)	C(12)—C(13)	1.471 (6)
C(2)—C(3)	1.537 (7)	C(12)—C(18)	1.351 (6)
C(3)—C(4)	1.542 (7)	C(13)—C(14)	1.511 (7)
C(4)—C(5)	1.543 (7)	C(18)—C(19)	1.495 (7)
C(4)—C(16)	1.512 (7)	C(18)—C(20)	1.520 (7)
C(5)—C(6)	1.507 (7)		

Data collection: *CAD-4-PC Software* (Enraf-Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

This work was supported by the National Science Foundation (USR-9452893, R11-8610677 and R11-8802961) and the National Institute of Health (MBRS S06RR08102-17).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(±)-2-[Hydroxy(4-methoxyphenyl)methyl]-2*H*-1,4-benzothiazin-3(4*H*)-one Hydrate

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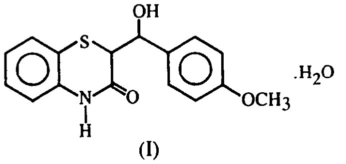
Abstract

The title compound, $C_{16}H_{15}NO_3S.H_2O$, is a derivative of benzothiazine. The molecular packing is stabilized by a three-dimensional hydrogen-bonding network. The benzothiazine ring is distorted, showing a half-chair conformation. The benzene ring is planar, but the methoxy group deviates significantly from planarity. A pair of intermolecular hydrogen bonds forms a centrosymmetric dimer in the crystal. There are intermolecular hydrogen bonds with a water molecule. The hydroxy(4-methoxyphenyl)methyl group and carbonyl O(20) atom are pseudo-equatorial with respect to the benzothiazine ring.

Comment

The title compound, (I), is a derivative of benzothiazine. This class of compounds possess potent Ca^{2+} antagonist activity, which is an important pharmacological activity (Ota, Ito & Kawashima, 1992), but the pharmacological action of (I) is unknown. In order to study the structure and geometrical conformation of the benzothiazine ring and its substituents, the X-ray analysis of (I) has been carried out.



(I)

The molecular structure of (I) is shown in Fig. 1. The interatomic distances and angles in the 1,4-benzothiazine ring are in agreement with the given atom type, hybridization and requirement of six-membered-ring geometry. The S—C bond lengths are not equal

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