Acta Cryst. (1996). C**52**, 117–118

Emmotin 2: (2*R*,3*S*)-2,6-Dihydroxy-3-(1-hydroxy-1-methylethyl)-8-methyl-1,2,3,4-tetrahydronaphthalene-5-carbaldehyde

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(*Received 14 June 1994; accepted 24 July 1995*)

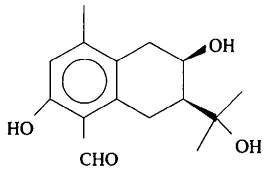
Abstract

The cyclohexene ring in the title compound, $C_{15}H_{20}O_4$, adopts a half-chair conformation. The C(11) and O(3) atoms are *cis* to each other. The molecules are linked through intermolecular hydrogen bonds.

Comment

In the course of a systematic investigation of the Brazilian Icacinaceae family, rearranged eudesmane sesquiterpenes with 1,4-substitution and a 7-isopropyl skeleton were found in all the analysed species (Kaplan, Ribeiro & Gottlieb, 1991). These types of compounds were named emmotins. The emmotins from Icacinaceae can be considered as chemotaxonomic markers and are certainly natural defences for the species that produce them.

Emmotin 2, (I), was isolated from the trunkwood ethanolic extract of the tropical amazonian plants *Poraqueiba guianensis Aubl* and *P. paraensis Ducke* (de Oliveira, de Oliveira, Maia, Goulart & Alves, 1982). In order to unambiguously determine the configuration of this compound, a crystal structure determination was undertaken.



(I)

The cyclohexene ring is in an essentially half-chair conformation, the Cremer & Pople (1975) ring-puckering parameters being: q_2 = 0.090 (3), q_3 = −0.072 (3), Q = 0.116 (3) Å; θ = 129 (2), φ = 29 (2)°. The molecules are linked *via* hydrogen bonding: O(1)···O(2)^{i} = 2.873 (4), O(2)^{i}···H(O1) = 1.814 (3), O(1)—H(O1) = 1.070 (3) Å, O(1)—H(O1)···O(2)^{i} = 170.0 (5)°; (i) $1-x, 0.5+y, 0.5-z$. There are also two intramolecular hydrogen bonds: O(1)···O(3) = 2.730 (4), O(1)···H(O3) = 1.845 (3), O(3)—H(O3) = 1.012 (3) Å, O(1)···H(O3)—O(3) = 144.1 (3)°; O(2)···O(4) = 2.547 (5), O(2)···H(O4) = 1.727 (3), O(4)—H(O4) = 1.019 (4) Å, O(2)···H(O4)—O(4) = 134.5 (2)°.

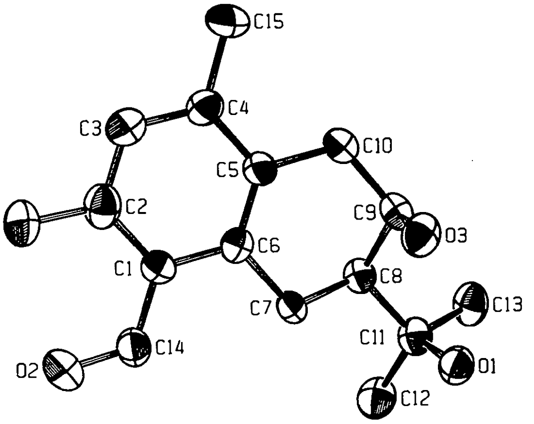


Fig. 1. Projection of $C_{15}H_{20}O_4$ showing the atom labelling. 50% displacement ellipsoids are shown for the non-H atoms.

Experimental

Crystal data

$C_{15}H_{20}O_4$
M_r = 264.32
Orthorhombic
$P2_12_12_1$
a = 9.851 (1) Å
b = 10.563 (2) Å
c = 12.933 (3) Å
V = 1345.6 (3) Å^3
Z = 4
D_x = 1.305 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9–15°
μ = 0.09 mm^{-1}
T = 292 K
Irregular
0.37 × 0.20 × 0.20 mm
Colourless
Crystal source: from cold pentane

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1468 measured reflections
1378 independent reflections
978 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.012
$\theta_{\rm max}$ = 25°
$h = -1 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 15$
2 standard reflections
frequency: 60 min
intensity decay: 0.7%

Refinement

Refinement on F
R = 0.0452
wR = 0.0493
S = 1.41
978 reflections
173 parameters
$w = 1/[\sigma^2(|F_o|) + 0.0005|F_o|^2]$

$(\Delta/\sigma)_{\rm max}$ = 0.002
$\Delta\rho_{\rm max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.20 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O(1)	0.2365 (3)	0.2387 (3)	0.4128 (3)	3.6 (1)
O(2)	0.4921 (3)	−0.2801 (3)	0.1671 (3)	4.5 (1)
O(3)	0.2149 (4)	0.0306 (3)	0.5369 (2)	3.9 (1)
O(4)	0.3908 (4)	−0.4690 (3)	0.2621 (3)	4.8 (1)
C(1)	0.3188 (4)	−0.2545 (4)	0.2904 (3)	2.7 (1)
C(2)	0.3124 (5)	−0.3851 (4)	0.3138 (4)	3.6 (2)
C(3)	0.2265 (6)	−0.4297 (4)	0.3887 (4)	3.6 (2)
C(4)	0.1460 (5)	−0.3487 (4)	0.4441 (4)	3.0 (1)
C(5)	0.1508 (5)	−0.2161 (4)	0.4238 (3)	2.9 (1)
C(6)	0.2333 (4)	−0.1711 (4)	0.3473 (3)	2.5 (1)
C(7)	0.2362 (5)	−0.0304 (4)	0.3201 (3)	2.9 (1)
C(8)	0.1170 (5)	0.0439 (4)	0.3644 (3)	2.9 (1)
C(9)	0.0943 (5)	0.0090 (4)	0.4773 (3)	3.0 (1)
C(10)	0.0610 (5)	−0.1289 (4)	0.4872 (4)	3.5 (2)
C(11)	0.1311 (5)	0.1898 (4)	0.3469 (3)	3.2 (1)
C(12)	0.1650 (6)	0.2198 (4)	0.2341 (4)	4.4 (2)
C(13)	0.0012 (5)	0.2576 (5)	0.3780 (4)	4.2 (2)
C(14)	0.4142 (5)	−0.2093 (4)	0.2159 (4)	3.3 (1)
C(15)	0.0533 (6)	−0.4013 (5)	0.5238 (4)	4.6 (2)

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

O(1)—C(11)	1.443 (6)	O(2)—C(14)	1.247 (6)
O(3)—C(9)	1.436 (6)	O(4)—C(2)	1.354 (6)
C(1)—C(2)	1.414 (6)	C(1)—C(6)	1.424 (6)
C(1)—C(14)	1.433 (6)	C(2)—C(3)	1.366 (7)
C(3)—C(4)	1.368 (7)	C(4)—C(5)	1.422 (6)
C(4)—C(15)	1.485 (7)	C(5)—C(6)	1.369 (6)
C(5)—C(10)	1.513 (7)	C(6)—C(7)	1.527 (6)
C(7)—C(8)	1.522 (6)	C(8)—C(9)	1.520 (6)
C(8)—C(11)	1.567 (6)	C(9)—C(10)	1.503 (6)
C(11)—C(12)	1.522 (7)	C(11)—C(13)	1.519 (7)
C(2)—C(1)—C(6)	117.8 (4)	C(6)—C(7)—C(8)	113.5 (3)
C(2)—C(1)—C(14)	120.3 (4)	C(7)—C(8)—C(9)	110.5 (4)
C(6)—C(1)—C(14)	121.9 (4)	C(7)—C(8)—C(11)	112.7 (4)
O(4)—C(2)—C(1)	120.3 (4)	C(9)—C(8)—C(11)	112.8 (4)
O(4)—C(2)—C(3)	118.4 (4)	O(3)—C(9)—C(8)	111.0 (3)
C(1)—C(2)—C(3)	121.2 (4)	O(3)—C(9)—C(10)	106.8 (4)
C(2)—C(3)—C(4)	120.6 (4)	C(8)—C(9)—C(10)	110.2 (4)
C(3)—C(4)—C(5)	120.2 (4)	C(5)—C(10)—C(9)	114.8 (4)
C(3)—C(4)—C(15)	118.8 (4)	O(1)—C(11)—C(8)	109.4 (4)
C(5)—C(4)—C(15)	120.9 (4)	O(1)—C(11)—C(12)	109.5 (4)
C(4)—C(5)—C(6)	119.6 (4)	O(1)—C(11)—C(13)	106.2 (4)
C(4)—C(5)—C(10)	118.8 (4)	C(8)—C(11)—C(12)	111.2 (4)
C(6)—C(5)—C(10)	121.6 (4)	C(8)—C(11)—C(13)	110.6 (4)
C(1)—C(6)—C(5)	120.6 (4)	C(12)—C(11)—C(13)	109.8 (4)
C(1)—C(6)—C(7)	118.2 (4)	O(2)—C(14)—C(1)	122.9 (4)
C(5)—C(6)—C(7)	121.2 (4)		

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. H atoms were found in a difference synthesis and included as fixed contributors with an overall isotropic temperature factor that refined to U_{iso} = 0.074 (4) Å². Programs used were: *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). The refinement was by block-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Fisica e Quimica de Sao Carlos.

This work received partial support from CNpq, FAPEAL, FAPESP and FINEP.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1016). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 118–122

Conformation of Acyclic Derivatives of 1,1,4,4-Tetraphenyl-1,3-butadiene

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(*Received 16 May 1995; accepted 14 August 1995*)

Abstract

The structures of three functionally different acyclic derivatives of 1,1,4,4-tetraphenyl-1,3-butadiene, dimethyl 2,3-bis(diphenylmethylene)-1,4-butanedioate, $C_{32}H_{26}O_4$, 2,3-bis(diphenylmethylene)-1,4-butanedioic acid diethanol solvate, $C_{30}H_{22}O_4.2C_2H_6O$, and 2,3-bis(bromomethyl)-1,1,4,4-tetraphenyl-1,3-butadiene, $C_{30}H_{24}Br_2$, have been determined characterizing the preferred conformational mode of this moiety in the solid state. The diphenylmethylene groups adopt a *syn* conformation with respect to the central bond of the butadiene segment, the C=C—C=C torsion angles about this bond varying within 48–49°. In the observed structures, two of the phenyl rings are almost parallel to one another and partly overlap. The different crystalline environments seem to have little effect on the overall molecular conformation.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996