Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.194$
$S = 1.022$
5307 reflections
395 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.242$ e Å^{-3}
$\Delta\rho_{\min} = -0.245$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0111 (16)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

C8—N1—C10—C11	−94.0 (4)	C2—C28—C29—C30	80.7 (6)
N1—C10—C11—C12	6.7 (5)	C28—C29—C30—C31	165.7 (10)
C17—C22—C23—N27	130.9 (4)	C28—C29—C30′—C31′	87.2 (14)
N1—C2—C28—C29	−175.9 (3)	C4—C5—C32—N37	115.0 (3)
C2—C28—C29—C30′	62.6 (10)		

Data collection: local program (Yoon *et al.*, 1994). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

This work was supported by the Korea Science and Engineering Foundation through the Centre for Molecular Catalysis at Seoul National University, Korea, and, in part, by the Ministry of Science and Technology, Korea.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1305). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1347–1349

(1*S*,2*S*,5*S*,6*S*)-5,6-Dihydroxy-6-methylcyclohex-3-en-1,2-diyl diacetate

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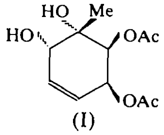
(*Received 17 December 1998; accepted 6 April 1999*)

Abstract

The title compound, $C_{11}H_{16}O_6$, has been synthesized and isolated as the major product of the osmylation of (5*S*,6*R*)-5,6-diacetoxy-1-methyl-1,3-cyclohexadiene. The molecule crystallizes in the monoclinic space group $P2_1$. The hexene ring exhibits a puckered distorted half-chair conformation, with all the chiral centres (C3, C4, C5 and C6) in the *S* configuration. One intramolecular and two intermolecular hydrogen bonds stabilize the molecule by the formation of infinite chains along **b**.

Comment

The use of *cis*-cyclohexadienediols has become relevant in organic synthesis because of their rich functionality and highly selective reactivity. The dihydroxylation of chiral *cis*-cyclohexadienediols is usually used in the synthesis of a wide variety of biologically active products. These dienes are produced by microbial oxidation of aromatic substrates with enzymes from a mutant strain of *Pseudomonas*, *P. putida* 39D. Osmylation of (5*S*,6*R*)-5,6-diacetoxy-1-methyl-1,3-cyclohexadiene was performed to synthesize the title compound, (I), as the major product of the reaction. The compound was isolated and spectroscopically characterized by Brovetto *et al.* (1999). It was determined that C5 and C6 kept the same configurations as in the parent compound. The assignments for C3 and C4 were made by comparing the relative configurations with respect to the known configurations of C5 and C6 (Hudlicky *et al.*, 1988).



(I)

The hexene ring in (I) exhibits a puckered distorted half-chair conformation, as shown in Fig. 1. The puckering parameters (Cremer & Pople, 1975) are Q_2 = 0.330 (4) and Q_3 = 0.320 (4) Å, and φ_2 = 217.7 (7)°. The molecule adopts a conformation with the hydroxy and acetoxy groups on C4 and C5 axial. In addition, the hydroxy and acetoxy groups on C3 and C6 are pseudo-equatorial and the methyl group on C4 is equatorial. The angles of the substituent bonds with the Cremer & Pople plane normal are 9.6 (2) and 6.5 (2)° for the axial substituents, 50.6 (2) and 57.5 (2)° for the pseudo-equatorial and 74.5 (2)° for the equatorial. There is an *anti* relationship of the diol functionality to the acetates.

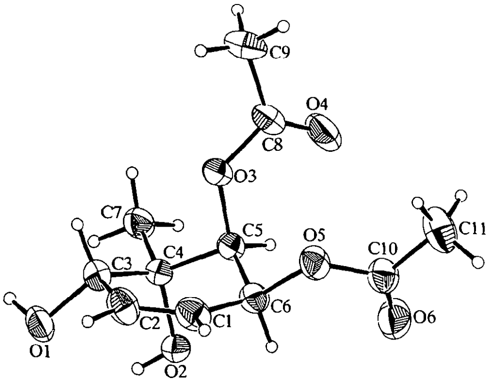


Fig. 1. *ZORTEP* (Zsolnai & Pritzkow, 1995) drawing of (I), showing the atom-labelling scheme and the conformation of the molecule. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as circles of an arbitrary radius.

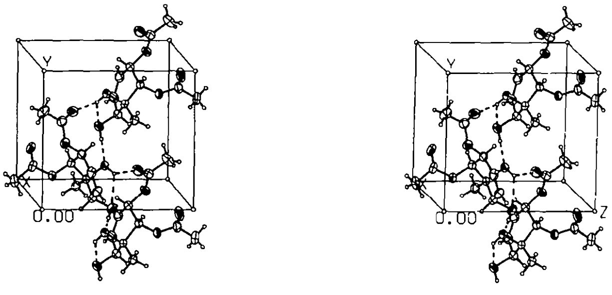


Fig. 2. Stereoview of the crystal packing and unit cell for (I). Hydrogen bonds are represented by dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

The packing of the molecules in the unit cell is given in Fig. 2. Infinite one-dimensional chains along the *b* axis are produced by intermolecular hydrogen bonds at O1—H1*A*···O2^{i} and O2—H2*A*···O6^{i} [see Table 2; symmetry code: (i) $1-x$, $y-\frac{1}{2}$, $1-z$]. One intramolecular hydrogen bond at O2—H2*A*···O1 was also found in the compound. The sum of the three angles about H2*A* is 358.9 (3)°, suggesting that this is a bifurcated or three-centred hydrogen bond (Jeffrey *et al.*, 1985).

Experimental

The title compound was synthesized as described previously by Brovetto *et al.* (1999). Crystals suitable for X-ray diffraction were obtained by vapour diffusion (ethyl acetate/hexane) at room temperature.

Crystal data

$C_{11}H_{16}O_6$
M_r = 244.24
Monoclinic
$P2_1$
a = 7.935 (7) Å
b = 8.656 (3) Å
c = 9.389 (3) Å
β = 97.87 (4)°
V = 638.9 (6) Å^3
Z = 2
D_x = 1.270 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 29.97–38.71°
μ = 0.104 mm^{-1}
T = 293 (2) K
Prismatic
0.37 × 0.22 × 0.18 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1993)
$T_{\min}$ = 0.963, $T_{\max}$ = 0.982
1592 measured reflections
1484 independent reflections

1178 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.045
$\theta_{\max}$ = 27.47°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = -12 \rightarrow 12$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.145
S = 1.041
1484 reflections
160 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.1062P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max}$ = 0.260 e Å^{-3}
$\Delta\rho_{\min}$ = −0.165 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.088 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—C2	1.324 (6)	C5—C6	1.526 (5)
C1—C6	1.484 (5)	O3—C8	1.352 (4)
C2—C3	1.501 (5)	C8—O4	1.184 (5)
C3—O1	1.431 (4)	C8—C9	1.493 (6)
C3—C4	1.540 (4)	C6—O5	1.456 (4)
C4—O2	1.435 (3)	O5—C10	1.358 (5)
C4—C7	1.514 (4)	C10—O6	1.194 (5)
C4—C5	1.528 (4)	C10—C11	1.482 (5)
C5—O3	1.449 (4)		

C2—C1—C6	122.0 (3)	C6—C5—C4	111.2 (2)
C1—C2—C3	124.6 (3)	C8—O3—C5	117.2 (3)
O1—C3—C2	107.4 (3)	O4—C8—O3	122.8 (4)
O1—C3—C4	109.3 (3)	O4—C8—C9	126.2 (4)
C2—C3—C4	112.7 (3)	O3—C8—C9	111.0 (4)
O2—C4—C7	110.2 (2)	O5—C6—C1	109.4 (3)
O2—C4—C5	103.2 (2)	O5—C6—C5	108.7 (2)
C7—C4—C5	110.6 (2)	C1—C6—C5	112.8 (3)
O2—C4—C3	109.2 (2)	C10—O5—C6	115.9 (3)
C7—C4—C3	112.6 (3)	O6—C10—O5	122.7 (3)
C5—C4—C3	110.7 (2)	O6—C10—C11	125.2 (4)
O3—C5—C6	108.8 (3)	O5—C10—C11	112.1 (3)
O3—C5—C4	106.7 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O2^{i}	0.82	2.02	2.793 (4)	157
O2—H2*A*···O1	0.82	2.33	2.707 (4)	110
O2—H2*A*···O6^{i}	0.82	2.24	2.873 (4)	135

Symmetry code: (i) $1 - x, y - \frac{1}{2}, 1 - z$.

The H atoms were placed at geometrically suitable positions and refined with fixed isotropic displacement parameters $U_{\rm iso} = 1.2U_{\rm eq}$ of the parent atom, except those belonging to O1, O2, C9 and C11, which were refined with $U_{\rm iso} = 1.5U_{\rm eq}$. The absolute stereochemistry could not be determined from refinement of the Flack parameter because intensities from Friedel mates were not measured. The reported stereochemistry of the structure is consistent with the stereochemistry of the starting material and with spectroscopic studies (Brovetto *et al.*, 1999).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995). Software used to prepare material for publication: *PLATON*98 (Spek, 1990).

This research was supported by CONICYT (Consejo Nacional de Investigacíon Científica y Tecnológica), Uruguay.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1084). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1349–1351

3,4,5,6-Tetrahydro-2*H*-naphtho[1,2-*b*]pyran-2-spiro-2′-1′,2′,3′,4′-tetrahydronaphthalene-1′-one

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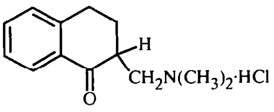
(*Received 22 January 1999; accepted 19 April 1999*)

Abstract

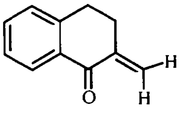
The title compound, $C_{22}H_{20}O_2$, was unexpectedly obtained in an attempt to synthesize 2-methylene-3,4-dihydronaphthalen-1(2*H*)-one, a candidate cytotoxic and anticancer agent, and is a dimer of the expected product.

Comment

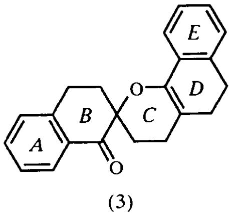
Recently, the cytotoxic evaluation of the Mannich base (1) revealed that its IC_{50} figure towards murine P388 leukaemia cells was 2.3 µ*M* (Dimmock *et al.*, 1998). Since Mannich bases are highly susceptible to deamination, liberating the corresponding α,β-unsaturated ketones (Carey & Sundberg, 1977), the preparation and bioevaluation of (2) was planned, with the aim of understanding whether (1) or its putative breakdown product (2) was principally responsible for cytotoxicity. After heating an aqueous solution of (1) with a slight molar excess of potassium carbonate, a product was obtained whose mass spectrum indicated a molecular ion of 316, *i.e.* twice the value of (2). A survey of the literature revealed that a dimer of (2) had been reported previously (Brugidou & Christol, 1966), for which structure (3) had been proposed (Mühlstädt & Gensrich, 1966; Brugidou *et al.*, 1967).



(1)



(2)



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Acta Crystallographica Section C
ISSN 0108-2701 © 1999