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1,3(*R*):4,6(*R*)-Di-*O*-benzylidene-D-mannitol

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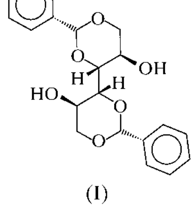
The title compound, $C_{20}H_{22}O_6$, has crystallographic twofold symmetry. The central six-C-atom chain has an extended conformation similar to that of D-mannitol, with two independent C—C—C—C torsion angles of 165.69 (14) and 177.60 (12)°. The 1,3-dioxane ring has a chair conformation. All chiral centers have the *R* configuration.

Comment

The use of carbohydrates as inexpensive starting materials and building blocks is of great interest (Bols, 1996). For example, D-mannitol, which has C_2 symmetry, offers unique synthetic approaches to chiral auxiliaries (Defoin *et al.*, 1991; Masaki *et al.*, 1992) and chiral drugs (Poitout *et al.*, 1994). Benzylidene acetal is a commonly used temporary protective group for D-mannitol because of its stability to most reaction conditions and high-yielding deprotection step (Greene & Wuts, 1991). The title compound, (I), is a benzylidene-protected mannitol. The elucidation of its structure was carried out to study the effect of the two six-membered 1,3-dioxane rings on the conformation of the central six-C-atom mannitol core.



(I)

Fig. 1 shows the atomic numbering scheme and conformation of (I). The molecule lies on a crystallographic twofold axis. The chiral centers C2, C3 and C7 all have the *R* configuration. The six-membered benzylidene acetal 1,3-dioxane ring adopts a chair conformation, with endocyclic torsion angles in the range 44.54 (14)–68.55 (13)°. All substituents are in equatorial positions. The torsion angles formed by the six central C atoms of (I) are comparable with those in DL-mannitol (Kanters *et al.*, 1977), D-mannitol (Berman *et al.*, 1968; Kim *et al.*, 1968) and hexaacetal-D-mannitol (Stein *et al.*, 1992), despite the presence of the 1,3-dioxane ring. While in all these cases the conformation is *anti-anti-anti*, deviations from 180° vary by up to about 20°. In (I), there are only two such independent torsion angles, as a result of the molecular symmetry. These are C1—C2—C3—C3^{i} [165.69 (14)°; symmetry code: (i) $1 - x, y, -z$] and C2—C3—C3^{i}—C2^{i} [177.60 (12)°]. None of the other mannitols retain their C_2 symmetry in the crystal, and thus have three independent torsion angles. In DL-mannitol (Kanters *et al.*, 1977) they are −175.9 (4), −176.5 (4) and 174.8 (4)°, in β-D-mannitol (Berman *et al.*, 1968) they are −175.3 (6), 175.8 (6) and −179.8 (6)°, in K-D-mannitol (Kim *et al.*, 1968) they are −174.8 (3), 175.8 (3) and −176.5 (3)°, and in hexaacetal-D-mannitol (Stein *et al.*, 1992) they are −175.3 (5), 159.8 (5) and −173.2 (5)°. The main difference in conformation between (I) and the cited acyclic mannitols is the torsion angle involving vicinal O atoms, O1—C1—C2—O2 [−169.52 (11)°]. Cyclization forces the O atoms to be antiperiplanar, while they are *gauche* [torsion angle magnitudes 58.0 (3)–65.6 (7)°] in the acyclic mannitols.

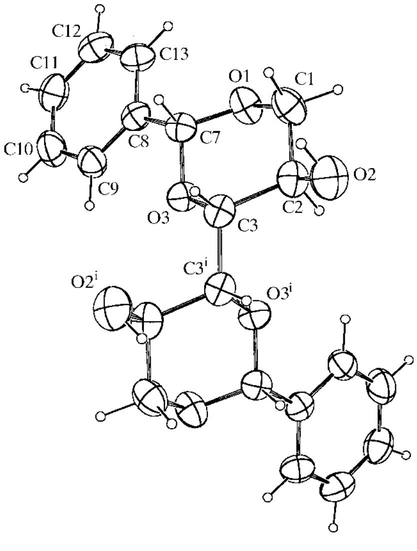


Figure 1
The molecular structure of (I) showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

The phenyl ring in (I) is planar, with a maximum deviation of 0.006 (2) Å for C11. Molecules form weakly hydrogen-bonded chains in the symmetry direction, *via* pairs of O2—H···O1^{ii} interactions [symmetry code: (ii) $x, y - 1, z$]. Both OH groups of each molecule donate to 1,3-dioxane O atoms of the same translation-related adjacent molecule. The O···O distance in this interaction is 3.183 (2) Å and the angle about the H atom is 158 (3)°.

Experimental

Compound (I) was prepared by acetalization of D-mannitol with benzaldehyde (Baggett & Stribblehill, 1977). A crystal suitable for data collection was obtained by slow evaporation of an ethanol solution at room temperature.

Crystal data

$C_{20}H_{22}O_6$
$M_r = 358.4$
Monoclinic, $C2$
$a = 17.472$ (4) Å
$b = 4.9237$ (10) Å
$c = 9.956$ (2) Å
$\beta = 94.08$ (3)°
$V = 854.4$ (3) Å^3
$Z = 2$

$D_x = 1.391$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.4$–44.7°
$\mu = 0.851$ mm^{-1}
$T = 293$ K
Lath, colorless
0.53 × 0.20 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.668$, $T_{\max} = 0.934$
4158 measured reflections
1703 independent reflections
1669 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\max} = 75°$
$h = -21 \rightarrow 21$
$k = -6 \rightarrow 5$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 2.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.093$
$S = 0.933$
1703 reflections
123 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 0.1745P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0112 (14)
Absolute structure: Flack (1983)
Flack parameter = −0.10 (17)

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.4179 (15)	O3—C7	1.4076 (14)
O1—C1	1.4328 (18)	O3—C3	1.4370 (15)
O2—C2	1.4273 (17)	C3—C3$^{\rm i}$	1.512 (2)
C7—O1—C1	108.34 (10)	C7—O3—C3	111.17 (9)
C7—O1—C1—C2	58.34 (15)	C1—C2—C3—C3$^{\rm i}$	165.69 (14)
O1—C1—C2—O2	−169.52 (11)	C2—C3—C3$^{\rm i}$—C2$^{\rm i}$	177.60 (12)
O1—C1—C2—C3	−47.14 (16)	C3—O3—C7—O1	68.30 (12)
C7—O3—C3—C2	−55.36 (13)	C1—O1—C7—O3	−68.55 (13)
C1—C2—C3—O3	44.54 (14)		

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

The absolute configuration of (I) was determined by refinement of the Flack (1983) parameter, based on 713 Friedel pairs, and is in accord with the known absolute configuration. The hydroxyl-H atom was refined isotropically. Other H atoms were placed in calculated positions with C—H bond distances of 0.93 (phenyl) and 0.97 Å (sp^3), and $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached C atom, and thereafter treated as riding.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1113). Services for accessing these data are described at the back of the journal.

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