Table 3. *Hydrogen-bonding geometry* (Å, °) *for* (I)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
173 K				
N—H(11)···Cl^{i}	0.91 (2)	2.32 (2)	3.178 (1)	158 (2)
N—H(12)···Cl^{ii}	0.84 (2)	2.27 (2)	3.099 (2)	172 (2)
N—H(13)···Cl^{iii}	0.96 (2)	2.20 (2)	3.148 (2)	168 (2)
293 K				
N—H(11)···Cl^{i}	1.02 (4)	2.20 (4)	3.180 (3)	161 (3)
N—H(12)···Cl^{ii}	0.83 (4)	2.27 (4)	3.102 (3)	173 (3)
N—H(13)···Cl^{iii}	1.10 (4)	2.06 (4)	3.143 (3)	169 (3)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x, y, 1 + z$.

Table 4. *Predicted bond angles* (°) *within the phenyl ring of a* 2,6-*dimethylphenylammonium cation*

	(*a*)	(*b*)
C(2)—C(1)—C(6)	123.8	123.7 (2)
C(1)—C(2)—C(3)	117.3	117.3 (2)
C(2)—C(3)—C(4)	120.6	120.7 (2)
C(3)—C(4)—C(5)	120.7	120.4 (3)
C(4)—C(5)—C(6)	120.6	120.7 (2)
C(5)—C(6)—C(1)	117.3	117.3 (2)

References: (*a*) Domenicano & Murray-Rust (1979); (*b*) Norrestam & Schepper (1981).

Although the crystals were anisotropically shaped, an absorption correction was not applied because ψ scans of three reflections produced flat absorption curves and the value of the linear absorption coefficient is small.

MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1991) was used for data collection and cell determination, and *TEXSAN* software (Molecular Structure Corporation, 1989) was used for data reduction, structure refinement and the preparation of publication material. The structures were solved using *SHELXS*86 Patterson methods (Sheldrick, 1990) and molecular graphics were produced using *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1275). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 2,2^1-Anhydro-4,6-*O*-benzylidene-3-deoxy-3-*C*-[(*R*)-2-hydroxyethyl]-α-D-*allo*-pyranoside at 173 K

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(*Received* 7 *June* 1995; *accepted* 3 *July* 1995)

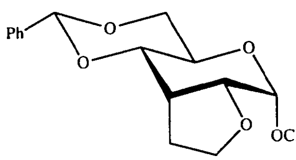
Abstract

The 1,3-dioxane ring in the title compound, $C_{16}H_{20}O_5$, has an almost undistorted $^{\alpha4}C_{\alpha1}$ conformation, while the pyranose ring has a more distorted $^4C_1$ conformation. The five-membered C(2,2^1) anhydro ring has an envelope conformation, with C(3) lying out of the plane formed by the other four atoms.

Comment

Many naturally occurring compounds which possess biological activity have furopyran structures. Notable among these are azadirachtin (Broughton, Ley, Slawin, Williams & Morgan, 1986; Ley, Santafianos, Blaney & Simmonds, 1987) and miharamycin A and B (Seto *et al.*, 1983); azadirachtin is an insect anti-feedant (Rembold, 1984; Koul, 1984*a*,*b*) and miharamycin A and B are active against the rice blast disease caused by *Pyricularia oryzae* (Seto *et al.*, 1983). As a result of increasing interest in using simple sugars as chiral synthons, we are pursuing the search for convenient and efficient approaches to the synthesis of furopyran and related fused-ring systems from readily available sugars and their derivatives. In this paper, we describe the synthesis and crystal structure of the title compound, (I).

Acta Crystallographica Section C
ISSN 0108-2701 ©1995



(I)

Fig. 1 depicts the correct absolute configuration of the molecule, which was assigned to agree with the known chirality of methyl α-D-glucopyranoside, from which (I) was synthesized. The bond lengths and angles, except C(1)—C(2)—C(3) [115.0 (2)°], are normal and generally agree with those of other sugars. The large C(1)—C(2)—C(3) angle is due to the strain introduced by the *cis*-fused five-membered $C(2,2^1)$ anhydro ring. The pyranose and the 1,3-dioxane rings adopt a double-chair conformation with the phenyl group attached to the 1,3-dioxane ring at C(7) being in an equatorial orientation, so that C(7) has an *R* configuration. The plane of this phenyl ring is inclined at about 48° to the plane of the 1,3-dioxane ring [H(7)—C(7)—C(11)—C(16) = 42 (2)°]. In this orientation, the C(11)—C(12) bond is only 18.4 (3)° from eclipsing the C(7)—O(4) bond.

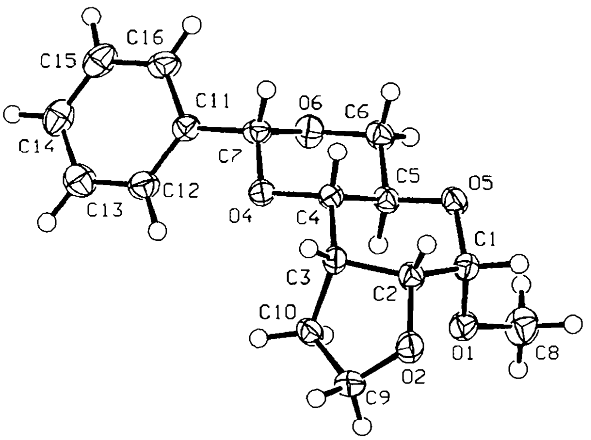


Fig. 1. View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

The torsion angles around the pyranose ring show that the ring conformation is quite distorted. This distortion, which results from the flattening of the C(2) apex due to the *cis*-fused five-membered $C(2,2^1)$ anhydro ring, is also evident from the puckering parameters (Cremer & Pople, 1975) (Table 3). The distortion is in the direction of the ${}^0H_5$ conformation, as indicated by the φ_2 value. The 1,3-dioxane ring adopts a form closer to the ideal ${}^{\alpha 4}C_{\alpha 1}$ conformation [$\theta = 3.5\,(3)°$, ideal $\theta = 0°$]. The fused five-membered anhydro ring has an almost perfect envelope conformation (Table 3) with C(3) lying 0.57 Å above the least-squares plane through C(2), O(2), C(9) and C(10). The maximum deviation of these four atoms from the mean plane is 0.012 Å ($\chi^2 = 27.7$).

The torsion angles about the glycosidic bond, C(1)—O(1), deviate only very slightly from those of the most stable +synclinal and antiperiplanar conformations. This corresponds to the *A*1 conformer and is generally found for most crystalline α-D-pyranosides (de Hoog, Buys, Altona & Havinga, 1969; Brown *et al.*, 1972; Taga, Senma & Osaki, 1972; Jeffrey & Nanni, 1985; Lee & Linden, 1994).

Experimental

A solution of the carbanion (Wadsworth & Emmons, 1961) prepared from ethyl diethylphosphonoacetate (0.7 g) and NaH (20% in oil, 0.36 g) in dry ether (20 ml) was added in portions at 273 K to a solution of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose (0.8 g) (Carey & Hodgson, 1970) in a mixture of ether (10 ml) and tetrahydrofuran (20 ml). The mixture was stirred for 12 h at 273 K, poured into saturated aqueous ammonium chloride, and extracted with ethyl acetate. The extract was dried with Na_2SO_4, concentrated to a syrup, dissolved in ether (50 ml) and stirred with $LiAlH_4$ (0.2 g) for 12 h at 278 K. Excess $LiAlH_4$ was destroyed by dropwise addition of ethyl acetate and the solution was filtered and concentrated. The syrupy residue (0.52 g) in toluene (0.55 g) was treated with triphenylphosphine (0.55 g) and diisopropyl azodicarboxylate (0.5 g) and refluxed for 2 h. Flash column chromatography (1:2 ether–hexane) of the syrup obtained on concentration of the mixture, gave (I) (0.12 g). Further purification using preparative TLC (1:1 ether–hexane) gave pure (I), m.p. 413–415 K (ether); $[\alpha]_D$ +124.3° (*c* 1.0, $CHCl_3$); analysis calculated for $C_{16}H_{20}O_5$ C 65.74, H 6.90%; found C 66.02, H 6.77%. Crystals suitable for X-ray analysis were obtained by recrystallization from dry ether.

Crystal data

$C_{16}H_{20}O_5$
$M_r = 292.33$
Orthorhombic
$P2_12_12_1$
$a = 11.529\,(4)$ Å
$b = 17.725\,(5)$ Å
$c = 7.172\,(5)$ Å
$V = 1466\,(1)$ Å^3
$Z = 4$
$D_x = 1.325$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12.0$–$13.0°$
$\mu = 0.0978$ mm^{-1}
$T = 173\,(1)$ K
Prism
0.50 × 0.25 × 0.20 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2954 measured reflections
2833 independent reflections
2136 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.034$

$\theta_{\max} = 30°$
$h = 0 \rightarrow 16$
$k = -1 \rightarrow 24$
$l = -1 \rightarrow 10$
3 standard reflections monitored every 150 reflections
intensity decay: insignificant

Refinement

Refinement on F
$R = 0.0453$
$wR = 0.0399$
$S = 1.598$
2136 reflections
271 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$
$(\Delta/\sigma)_{\max} = 0.0002$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: $g = 6(1) \times 10^{-7}$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O(1)	0.3606 (2)	0.1180 (1)	0.5912 (3)	0.0344 (6)
O(2)	0.3362 (2)	−0.0046 (1)	0.8169 (3)	0.0372 (6)
O(4)	0.7248 (1)	0.08115 (9)	0.8273 (2)	0.0272 (5)
O(5)	0.5220 (1)	0.0669 (1)	0.4357 (2)	0.0297 (5)
O(6)	0.7941 (2)	0.1542 (1)	0.5770 (3)	0.0343 (6)
C(1)	0.4139 (2)	0.0513 (2)	0.5284 (4)	0.0279 (7)
C(2)	0.4337 (2)	−0.0021 (2)	0.6941 (4)	0.0290 (7)
C(3)	0.5375 (2)	0.0183 (1)	0.8203 (4)	0.0253 (7)
C(4)	0.6395 (2)	0.0463 (1)	0.7065 (4)	0.0239 (7)
C(5)	0.6028 (2)	0.1021 (1)	0.5591 (4)	0.0264 (7)
C(6)	0.7092 (2)	0.1252 (2)	0.4491 (4)	0.0317 (8)
C(7)	0.8236 (2)	0.1019 (1)	0.7207 (4)	0.0277 (7)
C(8)	0.3203 (3)	0.1634 (2)	0.4392 (6)	0.047 (1)
C(9)	0.3596 (3)	0.0410 (2)	0.9793 (5)	0.0376 (9)
C(10)	0.4829 (2)	0.0730 (2)	0.9596 (4)	0.0315 (8)
C(11)	0.9119 (2)	0.1403 (2)	0.8439 (4)	0.0275 (7)
C(12)	0.8822 (2)	0.1706 (2)	1.0165 (4)	0.0342 (8)
C(13)	0.9646 (3)	0.2077 (2)	1.1240 (5)	0.043 (1)
C(14)	1.0783 (3)	0.2151 (2)	1.0571 (5)	0.042 (1)
C(15)	1.1078 (2)	0.1851 (2)	0.8879 (5)	0.042 (1)
C(16)	1.0254 (2)	0.1475 (2)	0.7800 (5)	0.0365 (9)

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

O(1)—C(1)	1.406 (3)	O(6)—C(7)	1.427 (3)
O(1)—C(8)	1.433 (4)	C(1)—C(2)	1.537 (4)
O(2)—C(2)	1.428 (3)	C(2)—C(3)	1.544 (3)
O(2)—C(9)	1.443 (4)	C(3)—C(4)	1.515 (3)
O(4)—C(4)	1.449 (3)	C(3)—C(10)	1.527 (4)
O(4)—C(7)	1.421 (3)	C(4)—C(5)	1.508 (3)
O(5)—C(1)	1.440 (3)	C(5)—C(6)	1.516 (3)
O(5)—C(5)	1.428 (3)	C(7)—C(11)	1.511 (4)
O(6)—C(6)	1.436 (3)	C(9)—C(10)	1.537 (4)
C(1)—O(1)—C(8)	111.7 (2)	C(2)—C(3)—C(10)	102.3 (2)
C(2)—O(2)—C(9)	109.5 (2)	C(4)—C(3)—C(10)	117.7 (2)
C(4)—O(4)—C(7)	109.4 (2)	O(4)—C(4)—C(3)	110.1 (2)
C(1)—O(5)—C(5)	111.2 (2)	O(4)—C(4)—C(5)	109.2 (2)
C(6)—O(6)—C(7)	113.0 (2)	C(3)—C(4)—C(5)	112.0 (2)
O(1)—C(1)—O(5)	111.4 (2)	O(5)—C(5)—C(4)	109.3 (2)
O(1)—C(1)—C(2)	109.6 (2)	O(5)—C(5)—C(6)	108.8 (2)
O(5)—C(1)—C(2)	110.3 (2)	C(4)—C(5)—C(6)	108.3 (2)
O(2)—C(2)—C(1)	112.2 (2)	O(6)—C(6)—C(5)	108.4 (2)
O(2)—C(2)—C(3)	104.8 (2)	O(4)—C(7)—O(6)	111.5 (2)
C(1)—C(2)—C(3)	115.0 (2)	O(2)—C(9)—C(10)	107.7 (2)
C(2)—C(3)—C(4)	111.3 (2)	C(3)—C(10)—C(9)	102.0 (2)
O(4)—C(4)—C(5)—C(6)	59.4 (3)		
O(4)—C(7)—O(6)—C(6)	−59.2 (3)		
O(4)—C(7)—C(11)—C(12)	−18.4 (3)		
O(5)—C(1)—O(1)—C(8)	68.7 (3)		
O(5)—C(1)—C(2)—C(3)	45.7 (3)		
O(5)—C(5)—C(4)—C(3)	−59.9 (3)		
O(6)—C(6)—C(5)—C(4)	−56.1 (3)		
O(6)—C(7)—O(4)—C(4)	60.0 (3)		
O(6)—C(7)—C(11)—C(12)	102.8 (3)		
C(1)—O(5)—C(5)—C(4)	68.2 (2)		
C(1)—C(2)—C(3)—C(4)	−38.9 (3)		
C(2)—O(2)—C(9)—C(10)	−1.7 (3)		
C(2)—C(1)—O(1)—C(8)	−168.9 (2)		
C(2)—C(1)—O(5)—C(5)	−60.3 (3)		
C(2)—C(3)—C(4)—C(5)	45.1 (3)		
C(5)—C(4)—O(4)—C(7)	−61.0 (2)		
C(5)—C(6)—O(6)—C(7)	56.5 (3)		

Table 3. *Ring-puckering parameters* (*Cremer & Pople*, 1975)

	Pyranose ring	1,3-Dioxane ring	Anhydro ring
Q (Å)	0.544 (3)	0.581 (3)	0.362 (3)
q_2 (Å)	0.150 (3)	0.039 (3)	0.362 (3)
q_3 (Å)	0.523 (3)	0.580 (3)	–
φ_2 (°)	328 (1)	68 (4)	250.9 (5)
θ (°)	16.0 (3)	3.5 (3)	–

MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1991) was used for data collection and cell determination, and *TEXSAN* software (Molecular Structure Corporation, 1989) was used for data reduction, structure refinement and the preparation of publication material. The structure was solved using *SHELXS*86 direct methods (Sheldrick, 1990) and molecular graphics were produced using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1289). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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