

The Structure of Methyl 3,4-Dideoxy- α -DL-*threo*-hex-3-enopyranoside

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Abstract. $C_7H_{12}O_4$, $M_r = 160.17$, monoclinic, $P2_1/n$, $Z = 4$, $a = 8.634$ (2), $b = 7.884$ (2), $c = 11.730$ (3) Å, $\beta = 92.88$ (1)°, $V = 797.5$ Å³, $D_c = 1.35$ Mg m⁻³, Cu $K\alpha$ radiation. 1375 independent reflections were measured on a single-crystal diffractometer. The structure was solved by direct methods and refined by the full-matrix least-squares method to a final $R = 0.067$ ($R_w = 0.051$). The six-membered hetero ring has the half-chair 0H_1 conformation. The compound forms hydrogen-bonded chains lying parallel to the b axis. The chains are cross-bridged in pairs by strong hydrogen bonds.

Introduction. The title compound represents an important class of unsaturated sugars. The compound was obtained (Banaszek & Zamojski, 1972) by total synthesis from butyl 5,6-dihydro-2-methoxy-2H-pyran-6-carboxylate (Konowal, Jurczak & Zamojski, 1968) and was further used as the substrate in the syntheses of altrose and talose (Banaszek, 1972), idose and mannose (Banaszek, 1974), and curamicose (Banaszek, 1975).

1H NMR studies of the conformational equilibrium of the title compound as well as its 6-*O*-acetyl and 2,6-di-*O*-acetyl derivatives seem to indicate that the equilibrium, ${}^0H_1 = {}^1H_0$ [for nomenclature see Schwartz (1973)], is completely shifted towards the 0H_1 conformer (Achmatowicz, Banaszek, Chmielewski, Zamojski & Lobodzinski, 1974).

The present investigations (see Krajewski, Urbanczyk-Lipkowska & Gluzinski, 1978) were performed in order to confirm the above statement and to elucidate the structure of the compound in the crystalline state.

Colourless crystals of the title compound were obtained by crystallization from diethyl ether solution. The coarse lattice constants and systematically extinct reflections were found from Weissenberg photographs. The latter ($h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$) define the space group $P2_1/n$.

The single crystal chosen for data collection (dimensions $0.3 \times 0.2 \times 0.26$ mm) was sealed in a capillary tube to protect it from air humidity. Data were collected ($\omega/2\theta$ scan) using an automatic CAD-4 four-circle diffractometer (SLAF & BS Laboratory, Kraków, Poland) using graphite-monochromatized Cu

$K\alpha$ radiation. 1375 independent reflection measurements were collected up to $2\theta = 110^\circ$, 900 of which had $I > 2\sigma_I$. These were used in the refinement of the structure.

All necessary computations were done using a CDC-Cyber-73 computer. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The crystal structure was solved by direct methods using the *SHELX* 76 program (Sheldrick, 1976). The initially determined non-hydrogen atom coordinates gave the reliability factor $R = 0.172$. All further computations were performed by means of the XRAY 70 program system (Stewart, Kundell & Baldwin, 1970) and the *XANADU* program. Initially three cycles of refinement by the full-matrix least-squares method (isotropic individual temperature factors) reduced R to 0.150 and R_w to 0.139 (weights from counting statistics). A further three cycles of refinement with anisotropic thermal parameters resulted in $R = 0.130$ and $R_w = 0.099$ and a satisfactory molecular geometry. At this stage the coordinates of all H atoms except of the hydroxylic H atoms were calculated. The latter were found from the difference Fourier synthesis. The last refinement step involved all atomic coordinates including those of the hydroxyl H atoms. For the latter a damping factor of 0.1 was used. The final R values were $R = 0.067$ and $R_w = 0.051$. The average shift/error value was then 0.0019. The refined atomic parameters are listed in Table 1.*

Discussion. The interatomic distances and bond angles are listed in Tables 2 and 3. The bonding distances in the ring are: C(sp^2)–C(sp^2) = 1.322 (6), C(sp^2)–C(sp^3) = 1.50 (1) Å (average value). The average distance C(sp^3)–O is 1.421 (3) Å. Jeffrey & Rosenstein (1964) and Berman, Chu & Jeffrey (1967) reported the C–O bond lengths in sugar rings to be 1.40–1.45 Å; Gould, Gould, Rees & Wight (1976) found these values to average 1.45 (1) Å; López de Lerma, Martínez-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34059 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso} (\AA^2)
C(1)	-68 (6)	3413 (5)	1765 (3)	
C(2)	204 (5)	4550 (5)	2797 (4)	
C(3)	1124 (5)	3634 (6)	3734 (3)	
C(4)	1306 (5)	1970 (6)	3698 (3)	
C(5)	544 (5)	870 (5)	2798 (4)	
O(1)	-566 (3)	1779 (3)	2084 (2)	
C(6)	-316 (6)	-554 (5)	3342 (4)	
C(7)	1137 (6)	2524 (6)	97 (4)	
O(2)	1314 (4)	3365 (4)	1181 (2)	
O(3)	-1260 (3)	5053 (3)	3215 (3)	
O(4)	-1078 (4)	-1629 (3)	2529 (2)	
H(103)	-1421 (46)	6280 (55)	3042 (29)	0.089 (14)
H(104)	-2253 (48)	-1092 (58)	2033 (29)	0.096 (16)

Table 2. Bond distances (\AA) with *e.s.d.*'s in parentheses

C(1)–C(2)	1.515 (7)	C(5)–O(1)	1.43 (1)
C(1)–O(1)	1.414 (5)	C(5)–C(6)	1.505 (9)
C(1)–O(2)	1.41 (1)	C(6)–O(4)	1.41 (1)
C(2)–C(3)	1.51 (1)	O(2)–C(7)	1.434 (6)
C(2)–O(3)	1.43 (1)	O(3)–H(103)	1.00 (3)
C(3)–C(4)	1.322 (6)	O(4)–H(104)	1.22 (4)
C(4)–C(5)	1.49 (1)		

Table 3. Bond angles ($^\circ$) with *e.s.d.*'s in parentheses

O(1)–C(1)–C(2)	111.4 (3)	C(3)–C(4)–C(5)	123.4 (4)
O(1)–C(1)–O(2)	112.4 (3)	C(4)–C(5)–C(6)	110.0 (4)
C(2)–C(1)–O(2)	107.7 (4)	O(1)–C(5)–C(6)	106.9 (4)
C(1)–O(2)–C(7)	112.9 (3)	C(4)–C(5)–O(1)	112.4 (3)
C(1)–C(2)–C(3)	110.7 (3)	C(5)–C(6)–O(4)	112.6 (3)
C(1)–C(2)–O(3)	109.5 (4)	C(5)–O(1)–C(1)	114.0 (3)
O(3)–C(2)–C(3)	108.9 (4)	C(2)–O(3)–H(103)	108 (2)
C(2)–C(3)–C(4)	120.7 (4)	C(6)–O(4)–H(104)	117 (2)

Carrera & García-Blanco (1973) reported the lengths 1.393 (6) and 1.423 (6) \AA .

The bond angles at $C(sp^2)$ atoms in the investigated monosaccharide differ somewhat from each other: 120.7 (4) $^\circ$ at C(3) and 123.4 (4) $^\circ$ at C(4). According to López de Lerma *et al.* (1973) these values are: 122.4 (4) and 121.0 (4) $^\circ$, whereas Gould *et al.* (1976) reported 120 (1) $^\circ$ as the average value.

The bond angle at the ring O atom is found to be 114.0 (3) $^\circ$, a somewhat higher value than those reported by the authors cited above [112.0 (9) and 112.8 (3) $^\circ$]. The bond lengths $C(sp^3)$ –O in the methoxy group are 1.41 (1) and 1.434 (6) \AA and the bond angle at O(2) is 112.9 (3) $^\circ$. In both hydroxy groups the C–O bond lengths are approximately equal, averaging 1.41 (1) \AA .

The present investigations confirmed the 0H_1 conformation of the 3,4-unsaturated monosaccharide ring, formerly suggested by Achmatowicz *et al.* (1974).

Table 4. Least-squares planes

The equation of the plane is of the form $Px + Qy + Rz = S$, where *x*, *y* and *z* are in (\AA) in orthogonal space.

Plane	Atoms defining the plane or line	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>
1	C(2), C(3), C(4), C(5)	0.8420	0.0908	-0.5318	-1.4555
Line					
1	C(1), O(2)				
2	C(2), O(3)				
3	C(5), C(6)				
4	C(6), O(4)				
Distances of atoms from plane 1 (\AA)					
C(2)	0.008	C(1)	0.423		
C(3)	-0.018	C(6)	-1.101		
C(4)	0.019	O(2)	1.817		
C(5)	-0.009	O(3)	-1.301		
O(1)	-0.270	O(4)	-1.186		

Angles between the lines (*L*) and their projections on the planes (*P*) ($^\circ$) $P(1)$ – $L(1)$ = 98, $P(1)$ – $L(2)$ = 114, $P(1)$ – $L(3)$ = 133.

Table 5. Torsion angles ($^\circ$) defining the ring conformation

O(1)–C(1)–C(2)–C(3)	46.28
C(4)–C(5)–O(1)–C(1)	42.20
C(1)–C(2)–C(3)–C(4)	-14.19
C(3)–C(4)–C(5)–O(1)	-8.36

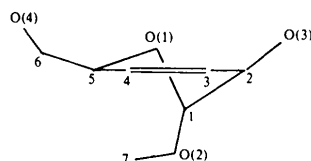


Fig. 1. View of the molecule showing atom numbering.

After completion of the refinement process, the least-squares plane of the ring fragment [defined by atoms C(2), C(3), C(4) and C(5)] was calculated (Table 4). The final deviations of O(1) and C(1) from that plane were -0.270 and 0.423 \AA , respectively. [According to the IUPAC numbering rule (Fig. 1), all the signs of the deviations should be reversed.] The asymmetry parameter (Duax & Norton, 1975) calculated from suitable torsion angles of the ring (Table 5) is $\Delta C_2^{3-4} = 5.03^\circ$.

In order to compare the above result with those of other unsaturated sugars the appropriate calculations were made from X-ray structural data reported for 2-(4-*O*-acetyl-2,3-dideoxy- β -L-glycero-pent-2-enopyranosyl)-5,6-dichlorobenzotriazole (*trans*-CLBA) (López de Lerma *et al.*, 1973). In the above-mentioned compound the deviations of O(1) and C(5) from the analogous least-squares plane (the ring conformation is 0H_3) are,

despite the much more bulky substituents, close to those of the compound presently investigated and have the values of -0.25 and 0.44 Å, respectively. Stokhuyzen & Chung Chieh (1976) have found more varied deviations of O(1) and C(5) from the least-squares plane for ethyl 6-*O*-benzoyl-4-iodo-2,3,4-trideoxy- α -D-hex-2-enopyranoside (0H_5 ring conformation): 0.16 and -0.60 Å, respectively.

As can be seen from the *ORTEP* diagram of the molecule (Fig. 2), the pseudo-equatorial hydroxymethyl and pseudo-axial hydroxy groups are situated above the ring plane contrary to the pseudo-axial methoxy group which lies below that plane. The deviations of O(3), O(4) and O(2) are -1.301 , -1.186 and $+1.817$ Å, respectively. The angle formed by the C(1)–O(2) bond [line 1, Table 4] with its projection on the ring plane is 98° .

The presence of two hydroxy groups in the molecule creates a possibility of inter- and intramolecular hydrogen bridges. The appropriate H atom coordinates were found from a difference Fourier synthesis. Two

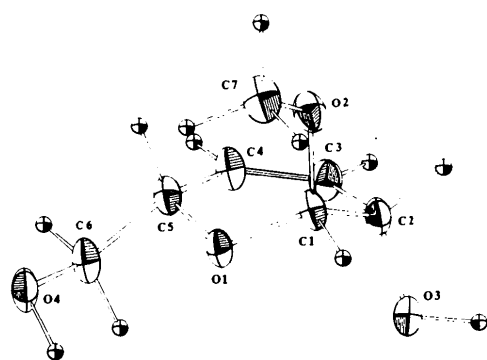


Fig. 2. *ORTEP* diagram of the molecule. Thermal motion ellipsoids are at the 40% probability level.

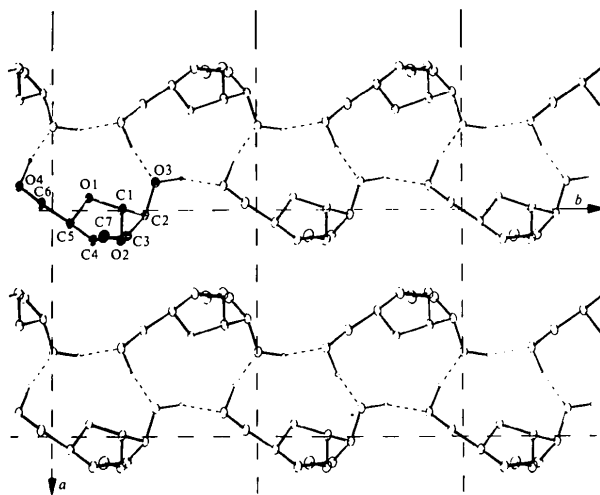


Fig. 3. *ORTEP* projection on the *ab* plane. Non-bonding hydrogen atoms are omitted.

Table 6. Distances and angles in the hydrogen bonds $D-H \cdots A$ (Å)

Donor <i>D</i>	Acceptor <i>A</i>	In molecule at	<i>D</i> – <i>A</i> (Å)	<i>H</i> – <i>A</i> (Å)	<i>D</i> – <i>H</i> ⋯ <i>A</i> (°)
O(3)	O(4)	$x, 1 + y, z$	2.744 (4)	1.78 (4)	160 (3)
O(4)	O(3)	$-0.5 + x, -0.5 + y, 0.5 + z$	2.76 (2)	1.58 (4)	159 (3)

Table 7. Intermolecular distances less than 3.5 Å

C(2)–O(4 ⁱ)	3.219 (5)	C(1)–O(1 ⁱⁱ)	3.47 (2)
O(3)–O(1 ⁱⁱ)	3.064 (7)	O(1)–O(4 ⁱⁱ)	3.211 (9)

Symmetry code: (i) $x, 1 + y, z$, (ii) $-0.5 + x, 0.5 + y, 0.5 + z$.

types of intermolecular hydrogen bonding occur in the unit cell (Table 6): O(3)⋯O(4ⁱ) and O(4)⋯O(3ⁱⁱ) (' and '' denote different symmetry operations). Although the interatomic contact distances between the donor (*D*) and acceptor (*A*) are equal within two standard deviations, the hydrogen-bridge types differ in the *H*⋯*A* distances and *D*–*H*⋯*A* angles (Table 6). The hydrogen bridges, O(3)⋯O(4ⁱ), form the straight molecular chains which are cross-bonded in pairs by the O(4)⋯O(3ⁱⁱ) bridges. These double chains repeat, parallel to each other, with no hydrogen bonding between them. No internal hydrogen bonds were found. The double-chain directions are parallel to the *b* axis of the crystal (Fig. 3). Only a few contact distances less than 3.5 Å were found (Table 7).

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Octaphenylcyclotetrasiloxane: The Monoclinic Form

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Abstract. $C_{48}H_{40}O_4Si_4$, $M_r = 792.34$, $a = 21.962$ (2), $b = 10.139$ (1), $c = 21.722$ (1) Å, $\beta = 115.99$ (1)°, $U = 4347.5$ Å³, $D_m = 1.20$, $D_c = 1.21$ Mg m⁻³, $Z = 4$, space group $P2_1/c$, $F(000) = 1664$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 1.502$ mm⁻¹. The structure was refined to $R = 0.0711$ for 4009 unique reflections. The Si_4O_4 ring is unusually flat.

Introduction. Previous work has shown that octaphenylcyclotetrasiloxane is polymorphic, occurring in monoclinic and triclinic forms and also as a benzene solvate (Hyde, Frevel, Nutting, Petrie & Purcell, 1947). As part of an investigation of the structure and conformation of cyclosiloxanes and related species, we have begun a crystallographic study of this system. Here we report the analysis of the monoclinic form.

The compound was prepared by the condensation of phenylsilanediol in alkaline medium and recrystallized from benzene–95% ethanol to obtain colourless needles. The cell parameters were initially determined from photographs and subsequently refined on a Nonius CAD-4 diffractometer from the setting angles for 25 reflections. The intensities of 7191 reflections ($3 < \theta < 60^\circ$) were recorded on the diffractometer with Ni-filtered Cu $K\alpha$ radiation, an ω – 2θ scan technique and a crystal $0.40 \times 0.15 \times 0.12$ mm. Two reference reflections, measured periodically, showed only minor fluctuations. The intensities were corrected for Lp factors but not for absorption. 4009 unique reflections with $F_o > 3\sigma(F_o)$ were considered observed and used in the analysis.

The structure was determined by direct methods and refined by a full-matrix least-squares procedure to a

final R of 0.0711. All non-hydrogen atoms were treated anisotropically. The H atoms were inserted in calculated positions (C–H = 1.08 Å) but individual U_{iso} values were refined. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$, which gave flat analysis of $w\Delta^2$ with $\sin \theta$ and $[F_o/F_{max}]^{1/2}$. The final non-hydrogen atomic coordinates are given in Table 1, selected interatomic distances and angles in Table 2, and least-squares plane data in Table 3.* Neutral-atom scattering factors were taken from Stewart, Davidson & Simpson (1965) for H and from Cromer & Mann (1968) for Si, O and C.

Discussion. The molecular structure is illustrated in Fig. 1, which also shows the atom numbering. The Si–O and Si–C lengths are in good agreement with values found in other cyclotetrasiloxanes (Steinfink, Post & Fankuchen, 1955; Shklover, Kalinin, Gusev, Bokii, Struchkov, Andrianov & Petrova, 1973; Carlström & Falkenberg, 1973; Söderholm & Carlström, 1977; Söderholm, 1978). In addition the angles around Si are close to expected tetrahedral values but with the C–Si–C angles consistently a few degrees larger. An unusual feature of the structure however is the size of the Si–O–Si angles, 152 ($\times 2$) and 167° ($\times 2$). These are correlated with a much

* Lists of structure factors, thermal parameters, H atom positional parameters and dimensions of the phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34092 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.