

Fig. 3. A stereoview of a portion of an infinite sheet of hydrogen-bonded molecules. The two mirrors of $Cmcm$ (\perp to the plane of the figure) intersect at the midpoint of the central molecule; screw axes relate the central to the other four molecules.

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Methyl α -D-Xylopyranoside*

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Abstract. $C_6H_{12}O_5$, $M_r = 164.16$, monoclinic, $P2_1$, $Z = 4$, $a = 11.197(1)$, $b = 6.722(1)$, $c = 11.123(1)$ Å, $\beta = 111.79(1)^\circ$, $[\lambda(Cu K\alpha_1) = 1.54051 \text{ Å}]$, $V = 777.37 \text{ Å}^3$, $d_m = 1.406$, $d_c = 1.402 \text{ g cm}^{-3}$. The structure was solved by *MULTAN* and refined to $R_f = 0.033$ for

1777 unique reflections measured with $Cu K\alpha$ radiation. The two independent molecules in the asymmetric unit have slightly distorted 4C_1 chair conformations; one distortion is in the direction of a twist and the other towards the boat conformation. The acetal C–O bond lengths and valence angles are in good agreement with those observed in other methyl α -xylopyranosides and predicted by *ab initio* quantum-mechanical calculations. All the hydroxyl groups are

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involved in the hydrogen bonding, which consists of infinite chains, thereby excluding the ring and glycosidic O atoms.

Introduction. The objective of this study was to compare the molecular dimensions and hydrogen-bond structure of methyl α -D-xylopyranoside (I) with those of the corresponding β compound (II) (Brown, Cox & Llewellyn, 1966; Takagi & Jeffrey, 1977). Suitable crystals of (I) (Sigma Chemical Company) were grown by slow evaporation of a 95% ethanol-water solution at room temperature.

A crystal of dimensions 0.29 \times 0.37 \times 0.45 mm was used for data collection with graphite-monochromated Cu $K\alpha$ radiation on a CAD-4 automatic diffractometer. The cell constants were obtained by least-squares refinement of the setting angles of 25 reflections with $114^\circ < 2\theta < 133^\circ$. 3872 intensities in the hkl , $hk\bar{l}$, $\bar{h}kl$ and $\bar{h}\bar{k}l$ octants were measured by θ - 2θ scans to $2\theta = 156^\circ$. The 2θ scan width was $3.15^\circ + 0.426^\circ \tan \theta$. Absorption corrections were made with the program *ABSOR* (Templeton & Templeton, 1973), using a linear absorption coefficient for Cu $K\alpha$ of 10.17 cm^{-1} . The minimum and maximum corrections to F_o^2 were 1.25 and 1.37 respectively. The symmetry-related measurements were averaged to give 1777 independent reflections, of which 16 had $F_o^2 \leq \sigma_{F_o^2}$. The R factor between symmetry-equivalent intensities was 0.020.

Table 1. Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms in methyl α -D-xylopyranoside

Molecule 1	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	8621 (2)	8513 (4)	2599 (2)
C(2)	7193 (2)	9037 (4)	2058 (2)
C(3)	6348 (2)	7218 (4)	1929 (2)
C(4)	6730 (2)	5578 (4)	1207 (2)
C(5)	8173 (2)	5233 (5)	1797 (2)
C(6)	10308 (2)	7806 (6)	4588 (3)
O(1)	8955 (1)	7939 (4)	3893 (1)
O(2)	6938 (2)	10491 (4)	2861 (2)
O(3)	5038 (2)	7704 (4)	1218 (2)
O(4)	6098 (2)	3758 (4)	1265 (2)
O(5)	8877 (2)	7004*	1842 (1)
Molecule 2			
C(1')	1622 (2)	13590 (4)	2730 (2)
C(2')	2616 (2)	13146 (4)	4069 (2)
C(3')	3640 (2)	11775 (5)	3955 (2)
C(4')	3025 (3)	9948 (5)	3190 (2)
C(5')	1973 (3)	10503 (6)	1919 (3)
C(6')	1377 (4)	15243 (6)	789 (3)
O(1')	2235 (2)	14616 (4)	2037 (1)
O(2')	3157 (2)	14953 (4)	4698 (2)
O(3')	4496 (2)	11266 (5)	5232 (2)
O(4')	3964 (3)	8826 (5)	2892 (2)
O(5')	1047 (2)	11805 (4)	2115 (2)

* Fixed parameter.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) using 250 reflections with $E \geq 1.37$ for phase generation. The 22 highest peaks on the E map corresponded to all of the non-hydrogen atoms. The H atoms, with the exception of H(O3'), were located from a difference Fourier synthesis. Refinement was by least squares using *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962), to minimize $\sum w|F_o - kF_c|^2$, with $w^{-1} = [\sigma_c^2(F_o^2) + (0.01F_o^2)^2]/4F_o^2$, where σ_c is from counting statistics. The non-hydrogen and H atom parameters [except H(O3')] were refined anisotropically and isotropically, respectively, together with a Zachariasen isotropic extinction parameter (Coppens & Hamilton, 1970), which refined to $2.5(2) \times 10^4$. The refined position for H(O4') was stereochemically unreasonable with a C—O—H angle of 86° ; an assumed position with O—H...O = 180° and O—H = 0.97 \AA was used. The final $R = \sum |F_o - kF_c|/\sum |F_o|$, and $R_w = (\sum w|F_o - kF_c|^2/\sum w|F_o|^2)^{1/2}$ for 1777 reflections were 0.033 and 0.040 respectively.

The atomic scattering factors used for O and C are those tabulated by Doyle & Turner (1968) and for H those given by Stewart, Davidson & Simpson (1965). The final positional parameters are given in Tables 1

Table 2. Fractional atomic coordinates ($\times 10^3$), isotropic thermal parameters (\AA^2) and bond distances (\AA) for the hydrogen atoms in methyl α -D-xylopyranoside

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (iso)	C, O—H
H(C1)	913 (2)	956 (4)	254 (2)	3.0 (5)	0.92 (3)
H(C2)	690 (3)	961 (6)	117 (3)	5.4 (7)	1.00 (3)
H(C3)	642 (2)	675 (5)	278 (2)	3.6 (6)	0.97 (3)
H(C4)	649 (2)	603 (4)	32 (2)	4.0 (6)	0.97 (2)
H(C51)	832 (3)	469 (5)	265 (3)	3.9 (6)	0.97 (3)
H(C52)	840 (3)	439 (6)	123 (3)	5.8 (7)	0.95 (3)
H(C61)	1059 (4)	901 (8)	451 (4)	8.0 (1.3)	0.88 (5)
H(C62)	1065 (3)	676 (7)	415 (3)	6.9 (1.2)	1.01 (4)
H(C63)	1051 (4)	750 (7)	552 (4)	8.0 (1.4)	1.00 (4)
H(O2)	663 (3)	1148 (6)	243 (5)	5.0 (8)	0.82 (4)
H(O3)	467 (3)	816 (5)	173 (3)	5.2 (8)	0.87 (3)
H(O4)	569 (4)	340 (7)	46 (4)	7.9 (1.4)	0.87 (4)
H(C1')	92 (2)	1437 (4)	278 (2)	3.3 (5)	0.96 (3)
H(C2')	218 (2)	1255 (5)	451 (2)	4.0 (6)	0.90 (3)
H(C3')	420 (3)	1252 (7)	350 (4)	6.7 (9)	1.07 (4)
H(C4')	268 (3)	914 (6)	373 (3)	4.6 (7)	0.99 (3)
H(C5'1)	241 (4)	1118 (8)	145 (3)	7.4 (1.1)	0.95 (4)
H(C5'2)	149 (4)	937 (9)	163 (4)	8.2 (1.1)	0.92 (5)
H(C6'1)	192 (4)	1618 (7)	52 (3)	7.1 (9)	1.00 (4)
H(C6'2)	60 (5)	1594 (9)	88 (4)	9.9 (1.3)	1.03 (5)
H(C6'3)	108 (3)	1416 (7)	22 (3)	6.6 (8)	0.94 (5)
H(O2')	309 (3)	1498 (7)	531 (3)	6.2 (9)	0.71 (3)
H(O3')*	533	1080	526	8.0	0.97
H(O4')	397 (4)	817 (8)	340 (4)	7.4 (1.2)	0.71 (4)
H(O4')*	451	793	355	7.4	0.97

* Calculated position, based on O—H = 0.97 \AA and O—H...O = 180° .

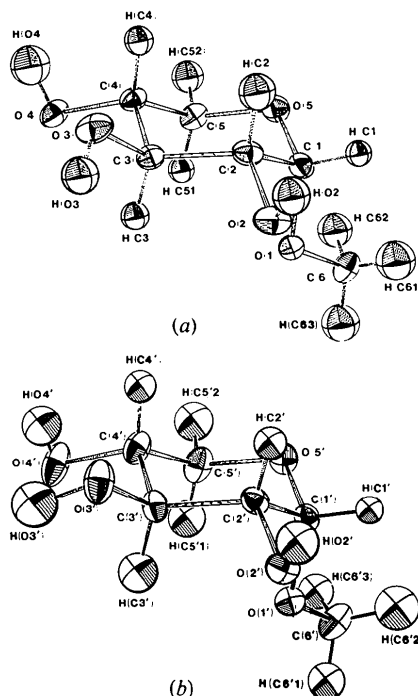


Fig. 1. Atomic notation and thermal ellipsoids at 20% probability (Johnson, 1976) for two independent molecules of methyl α -D-xylopyranoside. (a) Molecule 1, (b) molecule 2.

and 2.* The conformation and atomic numbering of molecules 1 and 2 of (I) are shown in Fig. 1. Selected molecular dimensions are reported in Table 3.

* Lists of structure factors and anisotropic thermal parameters, and Tables 4 and 6 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33641 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (\AA) and selected valence and torsion angles ($^\circ$) in methyl α -D-xylopyranoside

C(1)—C(2)	1.526 (3)	1.522 (3)
C(2)—C(3)	1.520 (3)	1.513 (3)
C(3)—C(4)	1.516 (3)	1.507 (4)
C(4)—C(5)	1.519 (3)	1.513 (4)
C(1)—O(5)	1.414 (3)	1.413 (3)
C(1)—O(1)	1.400 (2)	1.391 (3)
C(5)—O(5)	1.418 (3)	1.434 (4)
C(6)—O(1)	1.425 (3)	1.427 (3)
C(2)—O(2)	1.423 (3)	1.420 (3)
C(3)—O(3)	1.422 (2)	1.429 (3)
C(4)—O(4)	1.427 (3)	1.429 (3)
C(6)—O(1)—C(1)—O(5)	70.5 (2)	62.5 (2)
O(5)—C(1)—C(2)	110.2 (2)	110.1 (2)
O(5)—C(1)—O(1)	112.2 (2)	112.5 (2)
C(5)—O(5)—C(1)	113.0 (2)	111.5 (2)
C(1)—O(1)—C(6)	113.5 (2)	113.1 (2)
C(1)—C(2)—C(3)	112.1 (2)	109.8 (2)
C(2)—C(3)—C(4)	110.3 (2)	110.0 (2)
C(4)—C(5)—O(5)	112.0 (2)	111.4 (2)

Results of a rigid-body-motion analysis (Schomaker & Trueblood, 1968) are given in Table 4.* Thermal-motion corrections would lengthen the C—C bonds by 0.008 and 0.007 \AA and the C—O bonds by 0.010 and 0.009 \AA for molecules 1 and 2 respectively over the uncorrected values given in Table 3.

Discussion. The two symmetry-independent molecules of (I) have ${}^4C_1(D)$ chair conformations with small, but significant, differences between their ring torsion angles as shown in Table 5. The pyranose ring in molecule 2 is the more distorted, in the direction of the boat conformation, as shown by Cremer & Pople (1975) puckering parameters. In (I), the ring distortion is less, however, than that in (II) (Takagi & Jeffrey, 1977). It is a general observation that the puckering parameters, θ , are larger for β pyranoses and pyranosides than those for the corresponding α anomers (*cf.* Table 7 of Jeffrey, McMullan & Takagi, 1977). This is due to larger ring torsion angles at the O atoms in the β anomers.

Since pyranose rings in the chair conformation are not 'flexible', differences in ring conformations must be accompanied by differences in bond lengths and/or ring valence angles (*cf.* Dunitz & Waser, 1972). Only the bond length C(5)—O(5), and the angles C(5)—O(5)—C(1), and C(1)—C(2)—C(3) in the two symmetry-independent molecules have differences which are greater than $2.5\sqrt{(\sigma_1^2 + \sigma_2^2)}$. The bond-distance difference of $3.2\bar{\sigma}$ is barely significant, but the two angle differences of $5.3\bar{\sigma}$ and $8.2\bar{\sigma}$ are significant. One can

* See previous footnote.

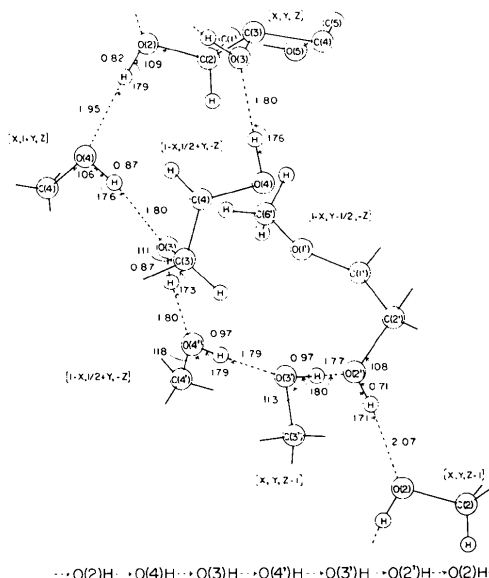
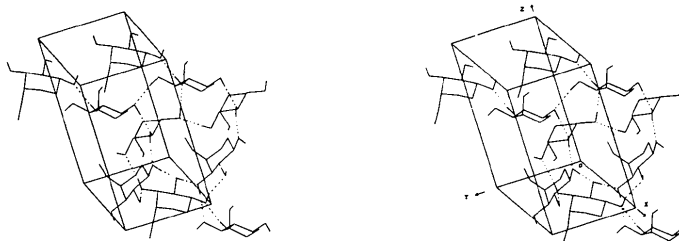
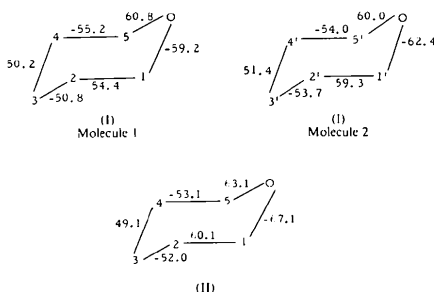


Fig. 2. Hydrogen bonding in the structure of methyl α -D-xylopyranoside.

Fig. 3. Stereoview of the unit-cell contents of methyl α -D-xylopyranoside.Table 5. Ring-puckering parameters (Cremer & Pople, 1975) and ring torsion angles ($^{\circ}$) for methyl α -D-xylopyranoside (I) and methyl β -D-xylopyranoside (II)

	(I) Molecule 1	(I) Molecule 2	(II)
q_2	0.028 Å	0.044 Å	0.088 Å
q_3	0.545	0.565	0.572
Q	0.546	0.567	0.579
φ_2	353.2 $^{\circ}$	50.2 $^{\circ}$	34.0 $^{\circ}$
θ	3.0	4.4	8.8



conclude, therefore, that the differences in dimensions, which must accompany those in the ring torsion angles, are located principally in the two ring valence angles at O(5) and C(2).

The glycosidic torsion angles are $+sc$ in both molecules, as predicted by the anomeric effect (Jeffrey, Pople & Radom, 1972, 1974). The bond lengths and bond angles in the acetal moiety C(5)–O(5)–C(1)–O(1)–CH₃ are in good agreement with those observed in other methyl α -D-pyranosides and predicted theoretically from *ab initio* quantum-mechanical calculations of dimethoxymethane (Jeffrey, Pople, Binkley & Vishveshwara, 1978).

The hydrogen bonding and molecular packing in the crystal structure of (I) are shown in Figs. 2 and 3. All hydroxyl groups are involved in the hydrogen-bond structure, which consists of infinite chains. The ring and glycosidic O atoms are excluded. The H \cdots O distances and O–H \cdots O angles obtained by normalizing the covalent O–H bond to a standard neutron diffraction value of 0.97 Å by moving the H position in the direction of the O–H bond are given in Table 6.* These

corrected H positions changed the range of the H \cdots O distances in the infinite chains from 1.79–2.07 Å to 1.70–1.82 Å, in good agreement with hydrogen-bond lengths observed in the neutron diffraction studies of other methyl pyranosides by Jeffrey, McMullan & Takagi (1977), and discussed by Jeffrey & Takagi (1978).

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