A Neutron Diffraction Study of the Hydrogen Bonding in the Crystal Structures of Methyl α-D-Mannopyranoside and Methyl α-D-Glucopyranoside*

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Single-crystal neutron diffraction refinements of the crystal structures of methyl α-D-mannopyranoside and methyl α-D-glucopyranoside provided accurate O—H, H···O distances and O—H···O angles. When the data are combined with those from the neutron diffraction refinement of methyl α-D-altropyranoside, five different O—H···O interactions can be recognized and identified, with five distinct ranges of H···O distances (separated by approximately 0·1 Å). These distances lie between 1·736 and 2·633 Å, and correspond to interactions varying from strong hydrogen bonds to van der Waals interactions. The conformation of the mannopyranose ring is unusual in that it corresponds to a perfect chair, as defined by its puckering parameters. The C—O bond lengths involving the ring and glycosidic oxygens show the usual variation associated with the C(5)—O(5)—C(1)—O(1)—CH$_3$ sequence. The mean values for the two structures are 1·432, 1·415, 1·401 and 1·422 Å.

Introduction

The structure associated with the interaction between the hydroxyls and O atoms in a carbohydrate crystal depends not only upon the hydrogen-bond formation, but also upon the other factors which determine the molecular packing, such as van der Waals and polar interactions. Correlations based on hydrogen-bond geometry alone may therefore be obscured if the carbohydrate molecules differ greatly in shape and size. The primary objective of this study was to examine in detail the hydrogen bonding of two closely related carbohydrate molecules and to attempt to correlate these results with those of a third methyl pyranoside (methyl α-D-altropyranoside) which has also been studied by means of neutron diffraction (Poppleton, Jeffrey & Williams, 1975).

Although methyl α-D-mannopyranoside (I) and methyl α-D-glucopyranoside (II) differ only in the configuration of the hydroxyl on C(2), there are significant conformational differences between the molecules in their crystal structures, as determined by the X-ray

(I) (II) (III)

analyses of Gatehouse & Poppleton (1970) and Berman & Kim (1968).

In (I) the pyranose ring is unusually regular, being almost a perfect chair, whereas in (II) there are small but significant deviations from regularity of the magnitude commonly observed in pyranose compounds in the crystalline state. The molecules also differ in the conformation of the primary alcohol groups, each providing an example of the two most common orientations. The hydrogen bonding in the crystal structures is also different. In (I) the molecules are linked by hydrogen bonds of moderate strength, as inferred from O···O distances of 2·79 to 2·93 Å; whereas in (II) the molecular arrangement is dominated by the formation of infinite spirals of strong hydrogen bonds with O···O distances of 2·71 Å.

Methyl α-D-altropyranoside (III) has a more distorted pyranose chair conformation; this is because of steric interactions between the axial substituents at the C(1) and C(3) positions. The hydrogen bonding is unusual for a carbohydrate in that it contains two examples of interactions of the bifurcated type, involving H···O distances between 2·085 and 2·185 Å. In these three structures, a variety of hydrogen-bond interactions can be observed, and the fact that the molecules are not too dissimilar in general shape encouraged us to believe that it might be possible to correlate their geometry. Such information would then serve as a basis for the more difficult problem of understanding the relationship between the molecular environment in the crystal and the conformational changes which may occur when a carbohydrate molecule goes from solution to the crystal.
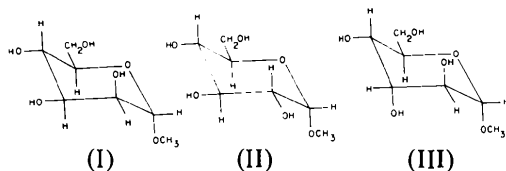
Crystal data

Transparent crystals of methyl α-D-mannopyranoside (I) and methyl α-D-glucopyranoside (II) ($C_7H_{14}O_6$, M_r = 194·19) with well-developed faces, were obtained by extremely slow evaporation of a solution of the compound in a 95% ethanol–water mixture at room temperature. The crystal data are in Table 1.

The cell constants for (I) and (II) were determined by the least-squares refinement of the setting angles of 18 and 28 reflections respectively; these were centered automatically on the neutron diffractometer with the NEXDAS program of McMullan (1976). The values obtained gave satisfactory agreement with the previously reported X-ray values, which are given in parentheses in Table 1. The wavelengths of the monochromated neutron beams were determined by least squares from the setting angles for 24 reflections of a standard KBr crystal ($a^* = 0·15154$ Å^{-1}).

Table 1. *Crystal data*

Previously reported X-ray values are in parentheses.

(I)	(II)
$a = 9·429 (3)$ Å $[9·423]$	$a = 11·311 (3)$ Å $[11·304]$
$b = 9·315 (3)$ $[9·308]$	$b = 14·781 (4)$ $[14·785]$
$c = 10·055 (3)$ $[10·045]$	$c = 5·281 (2)$ $[5·282]$
$V = 883·14$ Å^3	$V = 882·92$ Å^3
$D_m = 1·462$ g cm^{-3}	$D_m = 1·461$ g cm^{-3}
$D_n = 1·460$	$D_n = 1·460$

Orthorhombic, space group $P2_12_12_1$, $Z = 4$.

The measured density (D_m) was obtained from the weight of the crystal and the dimensions measured for the absorption corrections.

Experimental and structure refinement

Three-dimensional neutron intensity data were collected at room temperature on a Brookhaven High Flux Beam Reactor single-crystal diffractometer operating under the control of the program NEXDAS. A summary of the experimental conditions used in the data collections and the final values of the refinement parameters for the two structures are given in Table 2. The background corrections for crystal I were made as described by Lehmann & Larsen (1974). For crystal II the background was evaluated from counts summed at the scan extremes, with 20% of the total number of points sampled. The linear absorption coefficient for neutrons (2·538 cm^{-1}) was calculated from the mass absorption coefficient of 23·9 cm^2 g^{-1} for H, which corresponds to a value of 43 barns for the incoherent scattering cross-section (Koetzle, 1975). The atomic coordinates from the X-ray* determinations were used as the starting coordinates for refinement by full-matrix

* There are typographical errors in the reported X-ray coordinates; the z coordinate of H[O(6)] should read 0·666 (Gatehouse & Poppleton, 1970) and the x coordinate of H[C(7)] should read 0·700 (Berman & Kim, 1968).

Table 2. *Experimental data*

	(I)	(II)
Crystal weight	0·0074 g	0·0121 g
Crystal volume	5·06 mm^3	8·28 mm^3
Number of faces	12	10
Crystal habit	{111}{011}{010}	{010}{110}{101}
Number of reflections		
Total measured	2662 ($2\theta_{max} = 90°$), hkl and part of $hk\bar{l}$ octants	1825 ($2\theta_{max} = 100°$), hkl and part of $hk\bar{l}$ octants
Averaged	1304 (26 with $F_0^2 < 0$)	1123 (50 with $F_0^2 < 0$)
Data collection mode and scan width	θ–2θ step scan with fixed width of 2° for $2\theta < 55°$, variable width calculated by $-0·7° + 7·0° \tan\theta$ for $2\theta = 55$–90°	θ–2θ step scan with fixed width of 2·4° for $2\theta < 55°$ fixed width of 3·0° for $50 < 2\theta < 75°$ fixed width of 3·6° for $75 < 2\theta < 100°$
Absorption correction (neutron)	ABSOR (Templeton & Templeton, 1973) 2·538 cm^{-1}	2·538 cm^{-1}
Max. corr. to F_0^2	1·528	1·585
Min. corr. to F_0^2	1·381	1·442
Final refinement cycles		
Number of reflections in refinement, m	1304	1123
Number of variables, n	245	245
$R = \Sigma|F_0^2 - k^2 F_c^2|/\Sigma|F_0^2|$ (all reflections)	0·030	0·046
$R_w = (\Sigma w|F_0^2 - k^2 F_c^2|^2/\Sigma w|F_0^2|^2)^{1/2}$ (all reflections)	0·027	0·045
$S = [\Sigma w|F_0^2 - k^2 F_c^2|^2/(m - n)]^{1/2}$	1·69	1·07
Average shift/error	0·002	0·028
Maximum shift/error	0·021	0·679
Extinction parameter	0·34 (2) × 10^4	1·5 (1) × 10^4
$\lambda_{neut.}$	1·0188 Å	1·2072 Å

Table 3. *Fractional coordinates* ($\times 10^4$) *and thermal parameters for methyl* α-D-*mannopyranoside* (I)

The thermal parameters, $U_{ij}(\times 10^4 \text{ Å}^2)$, as given here are defined by:
$$\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	3595 (1)	418 (1)	3905 (1)	198 (5)	251 (4)	256 (4)	−6 (4)	9 (4)	−19 (4)
C(2)	4746 (1)	750 (1)	2886 (1)	213 (5)	216 (4)	209 (4)	−11 (4)	−8 (4)	2 (4)
C(3)	6214 (1)	497 (1)	3488 (1)	214 (5)	178 (4)	203 (4)	8 (4)	2 (4)	−15 (3)
C(4)	6376 (1)	1322 (1)	4783 (1)	224 (5)	182 (4)	205 (4)	−1 (4)	−7 (4)	−13 (3)
C(5)	5146 (1)	972 (1)	5719 (1)	246 (5)	244 (4)	199 (4)	15 (4)	11 (4)	−18 (3)
C(6)	5150 (1)	1866 (1)	6981 (1)	383 (7)	454 (6)	236 (5)	36 (6)	15 (6)	−107 (4)
C(7)	2563 (2)	−1547 (1)	5040 (1)	512 (9)	449 (7)	368 (7)	−218 (7	131 (6)	−1 (6)
O(1)	3625 (1)	−1064 (1)	4140 (1)	368 (6)	241 (5)	317 (5)	−81 (5)	96 (6)	−27 (5)
O(2)	4558 (1)	2204 (1)	2518 (1)	296 (7)	267 (6)	391 (7)	18 (6)	−33 (6)	97 (5)
O(3)	7279 (1)	965 (1)	2586 (1)	250 (6)	348 (6)	252 (5)	−36 (5)	51 (5)	−35 (5)
O(4)	7665 (1)	905 (1)	5425 (1)	231 (6)	325 (6)	270 (5)	−39 (6)	−50 (5)	38 (5)
O(5)	3809 (1)	1227 (1)	5078 (1)	221 (6)	274 (6)	277 (5)	28 (5)	27 (5)	−54 (4)
O(6)	5123 (2)	3357 (1)	6723 (1)	328 (8)	410 (7)	528 (7)	14 (7)	−1 (7)	−237 (6)
H[C(1)]	2543 (2)	753 (2)	3541 (2)	278 (11)	561 (12)	474 (11)	33 (10)	−54 (10)	−35 (10)
H[C(2)]	4604 (2)	35 (2)	2019 (2)	438 (12)	422 (10)	291 (8)	−37 (9)	−25 (10)	−60 (8)
H[C(3)]	6341 (2)	−656 (2)	3700 (2)	415 (11)	241 (9)	440 (10)	48 (9)	−24 (10)	4 (7)
H[C(4)]	6397 (2)	2482 (2)	4576 (2)	485 (12)	237 (8)	381 (9)	1 (9)	−15 (10)	−5 (8)
H[C(5)]	5215 (2)	−171 (2)	6008 (2)	438 (12)	345 (9)	409 (9)	16 (10)	40 (10)	69 (8)
H[C(61)]	4234 (3)	1556 (3)	7581 (2)	839 (20)	817 (18)	423 (13)	−111 (17)	261 (14)	−126 (13)
H[C(62)]	6114 (3)	1626 (3)	7543 (2)	770 (19)	871 (19)	444 (12)	252 (17)	−234 (14)	−197 (13)
H[C(71)]	1561 (4)	−1126 (5)	4795 (3)	499 (19)	1800 (43)	905 (21)	−241 (26)	159 (19)	376 (26)
H[C(72)]	2535 (5)	−2674 (3)	4985 (4)	1881 (42)	543 (19)	1460 (29)	−510 (23)	991 (29)	−107 (20)
H[C(73)]	2792 (3)	−1233 (4)	6028 (3)	926 (21)	1188 (24)	436 (13)	−325 (21)	167 (14)	−12 (16)
H[O(2)]	5363 (3)	2533 (2)	2025 (2)	474 (14)	404 (11)	477 (12)	−49 (11)	33 (12)	97 (10)
H[O(3)]	7298 (2)	308 (2)	1830 (2)	389 (12)	504 (12)	333 (10)	23 (11)	65 (10)	−73 (10)
H[O(4)]	8294 (2)	1713 (3)	5458 (2)	374 (13)	486 (13)	707 (15)	−141 (12)	−127 (12)	22 (12)
H[O(6)]	4161 (3)	3674 (3)	6774 (2)	419 (13)	559 (14)	725 (15)	89 (13)	−74 (13)	−201 (13)

Table 4. *Fractional coordinates* ($\times 10^4$) *and thermal parameters for methyl* α-D-*glucopyranoside* (II)

The thermal parameters, $U_{ij}(\times 10^4 \text{ Å}^2)$, as given here are defined by:
$$\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	5512 (2)	3749 (1)	4435 (4)	318 (9)	282 (8)	319 (10)	38 (7)	68 (10)	−17 (8)
C(2)	4316 (2)	4113 (1)	3553 (4)	375 (10)	281 (8)	269 (9)	42 (7)	9 (9)	−47 (9)
C(3)	3399 (2)	3967 (1)	5619 (4)	324 (9)	270 (9)	286 (10)	68 (7)	−5 (9)	−39 (8)
C(4)	3368 (1)	2963 (1)	6332 (4)	290 (9)	291 (8)	412 (11)	15 (7)	6 (10)	7 (10)
C(5)	4607 (1)	2633 (1)	7030 (4)	282 (9)	242 (8)	357 (11)	16 (6)	18 (9)	−3 (8)
C(6)	4638 (2)	1620 (1)	7472 (5)	293 (10)	250 (9)	553 (14)	7 (8)	−20 (12)	45 (11)
C(7)	7021 (2)	4076 (2)	7399 (6)	405 (13)	426 (12)	615 (16)	−8 (10)	−105 (13)	15 (14)
O(1)	5870 (2)	4285 (1)	6485 (5)	347 (10)	279 (10)	434 (13)	20 (8)	−19 (11)	−48 (11)
O(2)	4397 (2)	5022 (1)	2760 (5)	497 (12)	309 (11)	336 (13)	54 (10)	−34 (12)	18 (11)
O(3)	2276 (2)	4249 (2)	4713 (5)	385 (12)	439 (13)	384 (13)	134 (10)	−36 (12)	−66 (12)
O(4)	2637 (2)	2804 (2)	8459 (6)	362 (13)	500 (13)	667 (18)	62 (11)	195 (15)	169 (14)
O(5)	5430 (2)	2820 (1)	5048 (4)	334 (10)	252 (9)	375 (12)	43 (8)	62 (11)	−41 (10)
O(6)	5684 (2)	1350 (1)	8755 (5)	371 (13)	323 (10)	438 (14)	48 (10)	1 (13)	88 (11)
H[C(1)]	6177 (4)	3786 (3)	2897 (8)	549 (23)	556 (22)	487 (26)	24 (17)	216 (23)	4 (21)
H[C(2)]	4044 (3)	3726 (3)	1885 (7)	591 (23)	488 (20)	354 (22)	40 (17)	−26 (20)	−103 (20)
H[C(3)]	3635 (3)	4362 (2)	7300 (8)	497 (21)	451 (21)	383 (22)	67 (16)	−28 (20)	−104 (19)
H[C(4)]	3047 (4)	2593 (3)	4678 (11)	523 (23)	430 (19)	724 (31)	−32 (17)	−160 (24)	−63 (22)
H[C(5)]	4882 (3)	2975 (2)	8772 (8)	471 (20)	457 (21)	373 (21)	12 (16)	19 (18)	−61 (20)
H[C(61)]	4560 (4)	1270 (3)	5695 (11)	671 (28)	446 (22)	791 (36)	20 (20)	−212 (29)	−115 (27)
H[C(62)]	3893 (4)	1440 (3)	8660 (12)	478 (23)	535 (24)	1168 (44)	0 (18)	199 (29)	251 (31)
H[C(71)]	7057 (4)	3412 (4)	8221 (12)	752 (30)	708 (30)	1015 (44)	123 (23)	−229 (32)	258 (34)
H[C(72)]	7244 (5)	4566 (4)	8758 (17)	872 (38)	972 (40)	1492 (68)	64 (33)	−623 (48)	−411 (49)
H[C(73)]	7648 (5)	4086 (5)	5902 (16)	463 (28)	1410 (55)	1212 (54)	73 (32)	86 (38)	270 (53)
H[O(2)]	4470 (4)	5428 (3)	4231 (9)	580 (22)	392 (19)	486 (25)	−43 (18)	−45 (24)	−11 (20)
H[O(3)]	1813 (3)	4552 (3)	6003 (9)	467 (22)	449 (19)	521 (26)	139 (16)	45 (23)	−7 (21)
H[O(4)]	1869 (4)	2986 (3)	8156 (13)	452 (25)	760 (30)	1259 (52)	137 (21)	277 (33)	417 (37)
H[O(6)]	6298 (3)	1241 (3)	7521 (10)	371 (21)	535 (22)	610 (27)	2 (16)	34 (23)	89 (23)

least squares, minimizing $\Sigma\, w|F_o^2 - k^2|F_c|^2|^2$ with $w^{-1} = \sigma_c^2(F_o^2) + (aF_o^2)^2$, where σ_c is obtained from the counting statistics and the constant a (0·005 and 0·02 for crystals I and II respectively) was determined empirically to remove the dependency of $w(F_o^2 - F_c^2)$ on F_o^2. The 244 variable parameters, which included atomic coordinates, anisotropic thermal parameters for all atoms and a scale factor k, were refined together with Zachariasen's isotropic extinction parameter, g (Coppens & Hamilton, 1970). The extinction correction, applied to F_c^2, was given by

$$E = \left[1 + \frac{2\bar{T}|F_c^2|g}{V' \sin 2\theta}\right]^{-1/2},$$

where $\bar{T}$ is the effective mean path length approximated from the calculated absorption, A, by $(-\ln A)/\mu$ and $V' = V^2/\lambda^3$. The final positional and thermal
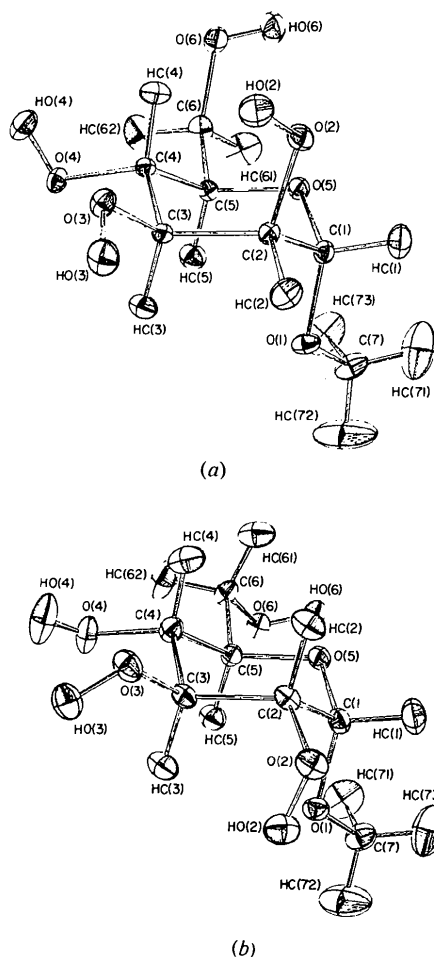

(a)

(b)

Fig. 1. *ORTEP* II plot at 20% probability (Johnson, 1976) for the neutron diffraction analysis of (a) methyl α-D-mannopyranoside and (b) methyl α-D-glucopyranoside.

parameters for all atoms are listed in Tables 3 and 4.* The neutron scattering lengths used were $b_C = 0·6648 \times 10^{-12}$, $b_H = -0·3740 \times 10^{-12}$, and $b_O = 0·5803 \times 10^{-12}$ cm (Shull, 1972). The rigid-body-motion analyses were calculated by the procedure of Schomaker & Trueblood (1968) and the results are reported in Table 5. The atomic notation and thermal ellipsoids are shown in the *ORTEP* plots [Fig. 1(a) and (b)]. The contents of the unit cells are shown in Fig. 2(a) and (b).

The molecular dimensions

The dimensions of the molecules from the neutron data are given in Figs. 3 and 4. The C—C bond lengths have similar variations to those observed in the X-ray studies, except that the span of values is less, 1·515 to 1·530 *versus* 1·506 to 1·531 Å. Differences of up to 0·01 Å in bond lengths appear to be characteristic of the C—C bonds in pyranose rings. Similar differences were observed in the neutron diffraction analysis of sucrose (Brown & Levy, 1973).

The C—O distances are all systematically shorter than the X-ray values by differences of up to 0·010 Å. This has been observed in other comparisons of neutron and X-ray results, such as sucrose (Brown & Levy, 1973) and methyl α-D-altropyranoside (Poppleton, Jeffrey & Williams, 1975).

The short anomeric bond C(1)—O(1) is observed, as is the bond-length variation in the sequence C(5)—O(5)—C(1)—O(1)—C(7). The mean values from the two structures of 1·432, 1·415, 1·401 and 1·422 Å agree well with the data summarized by Jeffrey, Pople & Radom (1974) in their quantum-mechanical treatment of the electronic basis for these differences. The glycosidic torsion angles of 60·5 and 62·6° are very close to the ideal preferred conformational angle of 60°. The conformation of the primary alcohol group is closer to the ideal staggered orientation in (I) with the O—C—C—O torsion angle of −65·2°, than in (II) where this angle is 73·9°.

The C—H bond lengths form a particularly self-consistent set of values in (I) with those attached to the ring having a mean value of 1·103, the methylene C—H bonds 1·093, and the methyl C—H bonds 1·054 Å. The corresponding bonds in (II) have mean values of 1·097, 1·080 and 1·062 Å. These differences between molecules and between C—H bonds in the same molecule could be the result of differences in thermal motion. As shown in Table 6, corrections between those for the minimum and the normal riding motion (Busing & Levy, 1964) would remove these differences.

Table 5. *Least-squares fit to rigid-body motion for methyl* α-D-*mannopyranoside* (I) *and methyl* α-D-*glucopyranoside* (II)

Model *A* comprises the six atoms of the pyranose ring. In model *B*, the atoms O(1), O(2), O(3), O(4) and C(6) are also included.

	(I)		(II)	
$\langle$R.m.s.$\lvert U_{ij} - U_{ij\,\text{RBM}}\rvert\rangle$	0.0004 Å²	0.0018 Å²	0.0007 Å²	0.0020 Å²
Max.$\lvert U_{ij} - U_{ij\,\text{RBM}}\rvert$	0.0011	0.0073	0.0015	0.0054
$\langle\sigma(U_{ij})\rangle$	0.0006	0.0022	0.0010	0.0024

Rigid-body **T** and ω elements and r.m.s. values for the principal axes of the **T** and ω tensors referred to the axes *a*, *b* and *c* of model *B* for structures I and II

	(I)				(II)		
T	208 (8)	17 (8)	10 (7) (Å × 10⁴)	**T**	294 (9)	38 (8)	20 (9)(Å × 10⁴)
		136 (11)	−6 (8)			254 (9)	−43 (10)
			211 (8)				280 (13)
ω	13·1 (1·0)	2·7 (0·7)	0·4 (0·7) (deg²)	ω	9·0 (1·0)	−7·4 (8)	4·6 (7) (deg²)
		5·2 (0·9)	0·4 (0·9)			14·0 (1·4)	−2·6 (1·0)
			12·2 (1·2)				5·8 (9)

		Directions relative to axes					Directions relative to axes		
Tensor	R.m.s. value	*a*	*b*	*c*	Tensor	R.m.s. value	*a*	*b*	*c*
T	0·15 Å	136·2°	95·5°	133·3°	**T**	0·18 Å	134·5°	129·0°	71·1°
	0·14	130·8	76·4	136·0		0·18	124·6	76·8	142·3
	0·11	76·7	165·3	96·1		0·14	64·9	138·0	121·3
ω	3·8°	156·6°	107·0°	105·5°	ω	4·6°	125·9°	41·5°	108·0°
	3·5	74·7	87·1	164·4		2·5	67·8	53·9	44·4
	2·1	72·8	162·7	88·3		1·4	44·2	72·4	128·9

(a)

(b)
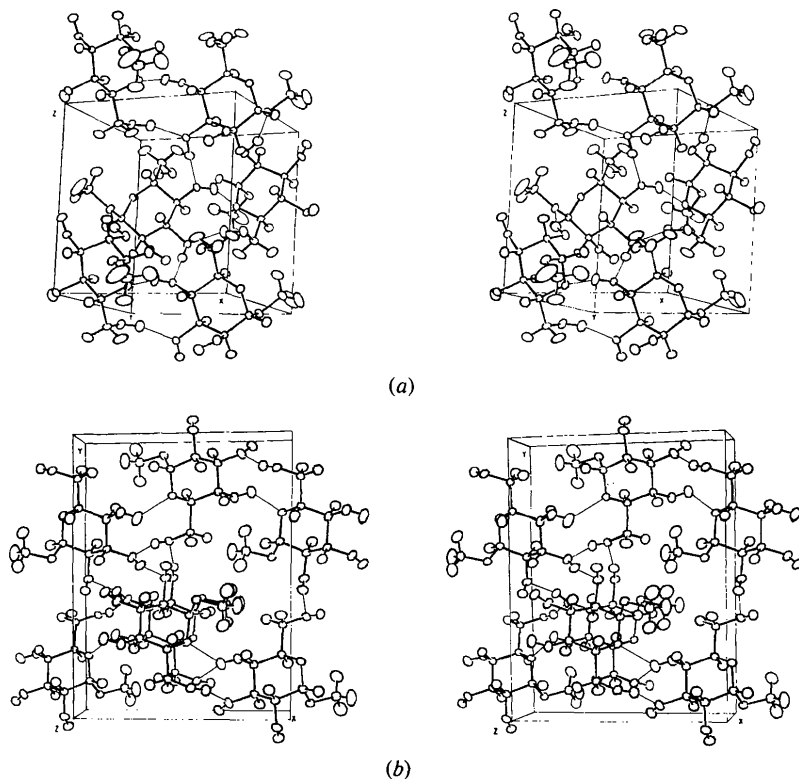
Fig. 2. Stereo views of unit-cell contents, with hydrogen bonding indicated in thinner lines, for (a) methyl α-D-mannopyranoside and (b) methyl α-D-glucopyranoside.

Table 6. *Thermal-motion corrections* (Å) *in methyl* α-D-*mannopyranoside* (I) *and methyl* α-D-*glucopyranoside* (II)

	Rigid-body thermal motion*		Minimum riding motion		Riding motion	
	(I)	(II)	(I)	(II)	(I)	(II)
C—C	0·004 (0·005)	0·004 (0·004)				
C—O	0·005 (0·005)	0·004 (0·005)				
C—H(on ring)	0·004 (0·005)	0·004 (0·005)	0·004	0·003	0·021	0·022
C—H(methylene)			0·009	0·009	0·042	0·041
C—H(methyl)†	0·065	0·047	0·024	0·015	0·083	0·065
O—H			0·003	0·001	0·022	0·012
O(4)—H				0·007		0·047

* Model *B*. The values in parentheses also included the H atoms attached to the pyranose ring.
† Rigid-body motion for O—CH₃ group only.

Fig. 3. Molecular dimensions of methyl α-D-mannopyranoside. The standard deviations in Å are C—C, 0·001; C—O, 0·002; O—H, 0·003; C—H, 0·002, except for C(6)—H, 0·003 and C(7)—H, 0·004. The standard deviations of the angles are 0·1°, except for those involving hydrogens on C(6) and C(7) where they are 0·2°.

H-C(I)C(2)-H	-69°	H-C(2)O(2)-H	-74°
H-C(2)C(3)-H	-54	H-C(3)O(3)-H	50
H-C(3)C(4)-H	172	H-C(4)O(4)-H	-5
H-C(4)C(5)-H	-174	H₁C(6)O(6)-H	-25
H-C(5)C(6)-H₁	-60	H₂C(6)O(6)-H	-144
H-C(5)C(6)-H₂	58		

Fig. 3 (*cont.*)

The molecular conformations

The pyranose rings in simple monosaccharides have approximate mirror symmetry normal to the mean plane of the ring and passing through the ring O and C(3). The rings are invariably more puckered at the O atoms and least puckered at C(3), as shown by the mean torsion angles across this plane given in Table 7 for some gluco- and mannopyranose compounds. The same general trend was noted, for a wide range of carbohydrates containing pyranose rings, by Arnott & Scott (1972).

Fig. 4. Molecular dimensions of methyl α-D-glucopyranoside. The standard deviations in Å are C—C, 0·002; C—O, 0·003; O—H, 0·007; C—H, 0·005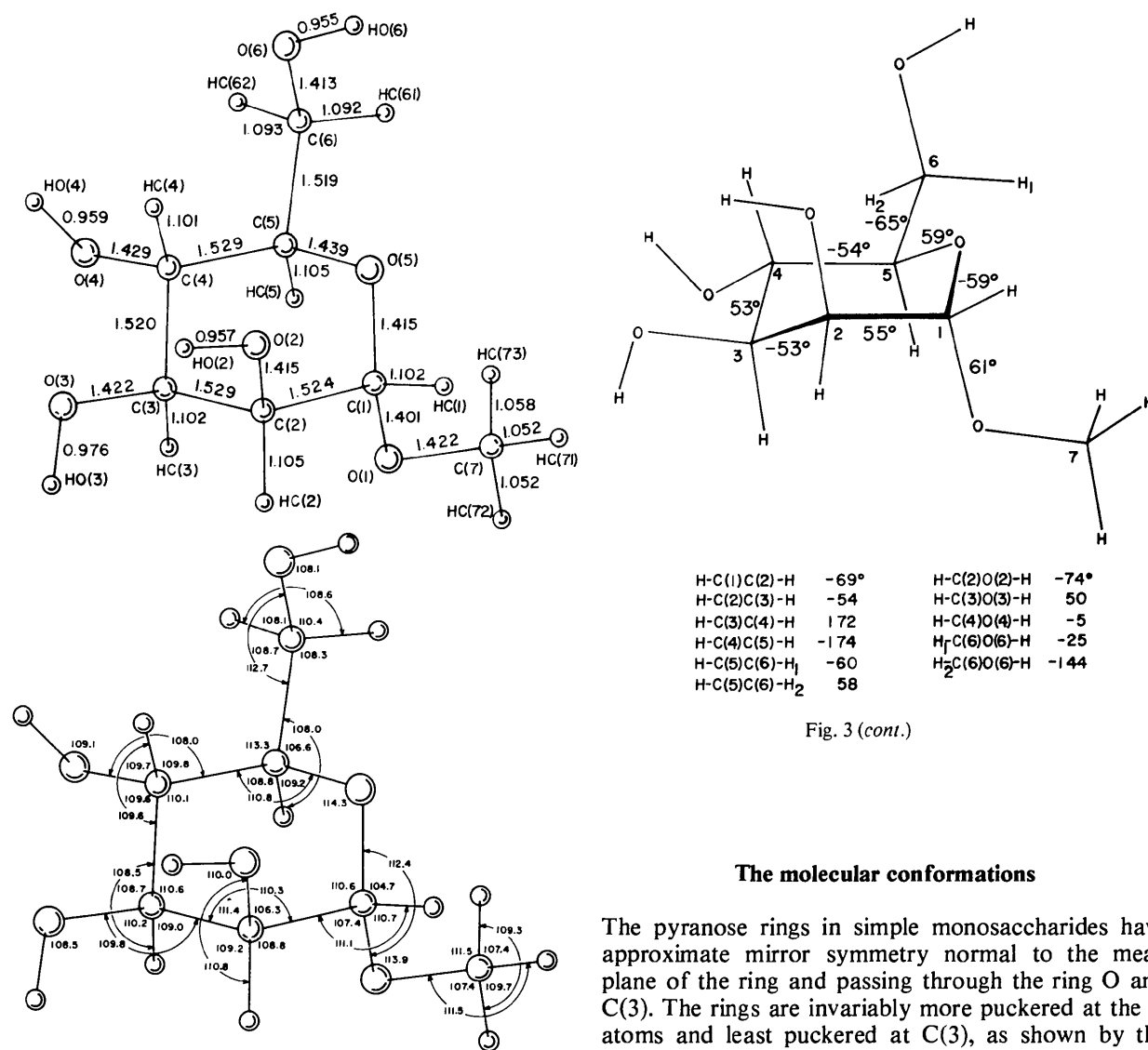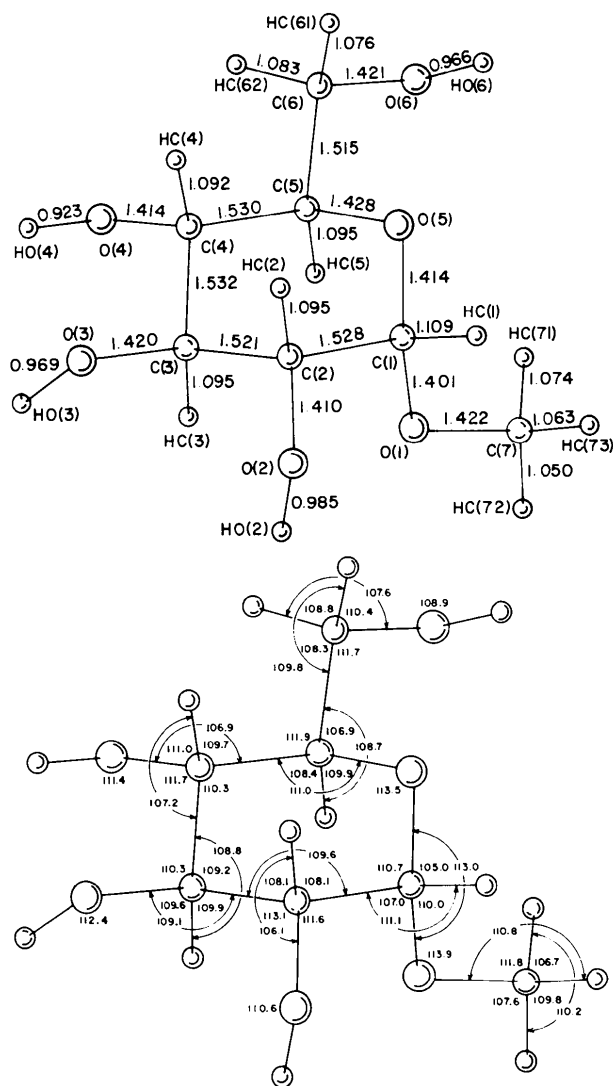, except for C(6)—H, 0·006 and C(7)—H, 0·009. The standard deviations of the angles are 0·2° for non-hydrogen atoms, 0·3 and 0·4° for those involving hydrogens.

Deviations from this mirror symmetry arise for two reasons. One is the asymmetric distribution of the substituents around the ring which gives rise to asymmetric intra- and intermolecular interactions. The other is that the C(5)—O(5) bond length is generally about 0·02 Å longer (as a result of the anomeric effect) than that of C(1)—O(5) (Jeffrey, Pople & Radom, 1974). Consequently, differences of the order of 5° are most frequently observed between the torsion angles related by the pseudo mirror plane. The molecule of methyl α-D-mannoside is unusual in that the corresponding torsion angles agree within less than 1°. The ring conformation is that of a perfect chair, as defined by

H-C(1)C(2)-H	57°	H-C(2)O(2)-H	168°
H-C(2)C(3)-H	-179	H-C(3)O(3)-H	-21
H-C(3)C(4)-H	175	H-C(4)O(4)-H	-60
H-C(4)C(5)-H	-176	H₁C(6)O(6)-H	35
H-C(5)C(6)-H₁	-168	H₂C(6)O(6)-H	154
H-C(5)C(6)-H₂	74		
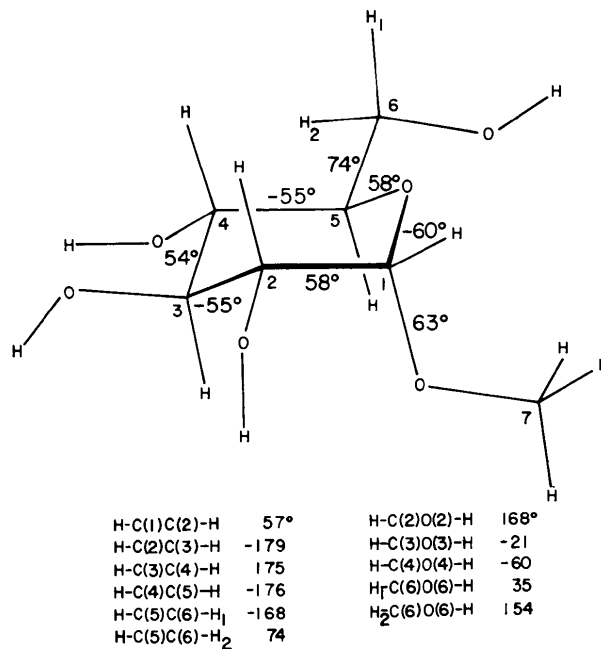
Fig. 4 (cont.)

Table 7. *Mean values of ring torsion angles (°) in some gluco- and mannopyranose molecules*

Δ, $\langle\Delta\rangle$ are maximum and mean differences between mirror-related torsion angles. $\theta(°)$ is the puckering parameter defined by Cremer & Pople (1975), which measures the distortion from the chair conformation, $\theta = 0°$.
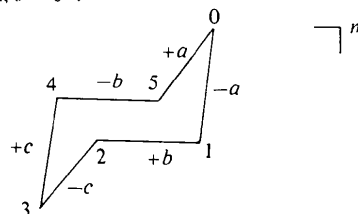
D-Mannopyranose molecules

	$\langle a\rangle$	$\langle b\rangle$	$\langle c\rangle$	Δ	$\langle\Delta\rangle$	θ	Ref.
α-Mannose	61	56	53	6	4	5	(1)
2-Fluoro-β-mannose	63	59	56	17	11	11	(2)
N-Acetyl-β-mannosamine	66	58	53	9	6	7	(3)
Methyl α-mannoside	59	55	53	1	0	0	

D-Glucopyranose molecules

	$\langle a\rangle$	$\langle b\rangle$	$\langle c\rangle$	Δ	$\langle\Delta\rangle$	θ	Ref.
α-Glucose	62	56	52	4	2	4	(4)
β-Glucose	65	57	52	6	3	7	(5)
N-Acetyl-α-glucosamine	62	56	56	4	3	3	(6)
Methyl α-glucoside	59	57	55	3	2	2	
Methyl 6-acetyl-β-glucoside	67	57	50	11	7	11	(7)
Methyl-4-fluoro-α-glucose	58	58	58	8	5	6	(8)
Methyl β-glucoside	67	58	53	8	6	7	(9)

(1) Planinsek & Rosenstein (1967). (2) Choong, Craig, Stephenson & Stevens (1975). (3) Neuman & Longchambon (1975). (4) Brown & Levy (1965). (5) Chu & Jeffrey (1968). (6) Mo & Jensen (1975). (7) Lindberg (1976). (8) Choong, Stephenson & Stevens (1975). (9) Jeffrey & Takagi (1977).

Cremer & Pople (1975), with $\theta = 0.0°$, $\varphi = 0.0°$, $q_2 = 0.0$ Å and $Q = q_3 = 0.556$ Å. In the methyl α-D-glucoside molecule, the torsion-angle differences are greater (between 1.5 and 3.7°) and the corresponding

puckering parameters are $\theta = 2.26°$, $\varphi = 116.8°$, $q_2 = 0.022$ Å, $q_3 = 0.569$ Å, $Q = 0.569$ Å. As shown in Table 7, the mean difference between the 'mirror-related' torsion angles gives a measure of the distortion

Fig. 5. Hydrogen-bond geometry in the crystal structure of methyl α-D-mannopyranoside.

Fig. 6. Hydrogen-bond geometry in the crystal structure of methyl α-D-glucopyranoside.

of the pyranose rings which is comparable to that provided by the θ values of the puckering parameters. As pointed out by Dunitz & Waser (1972), the chair form of the six-membered ring is a rigid conformation, and therefore differences in the ring torsion angles between different molecules will be accompanied by energetically comparable differences in the bond lengths and valence angles. This may account, at least in part, for differences of the order of 0·01 Å and 1° in the C—C ring bond lengths and angles, as observed between C(3)—C(4) and C(2)—C(3)—C(4) in these two molecules, for example.

The hydrogen bonding

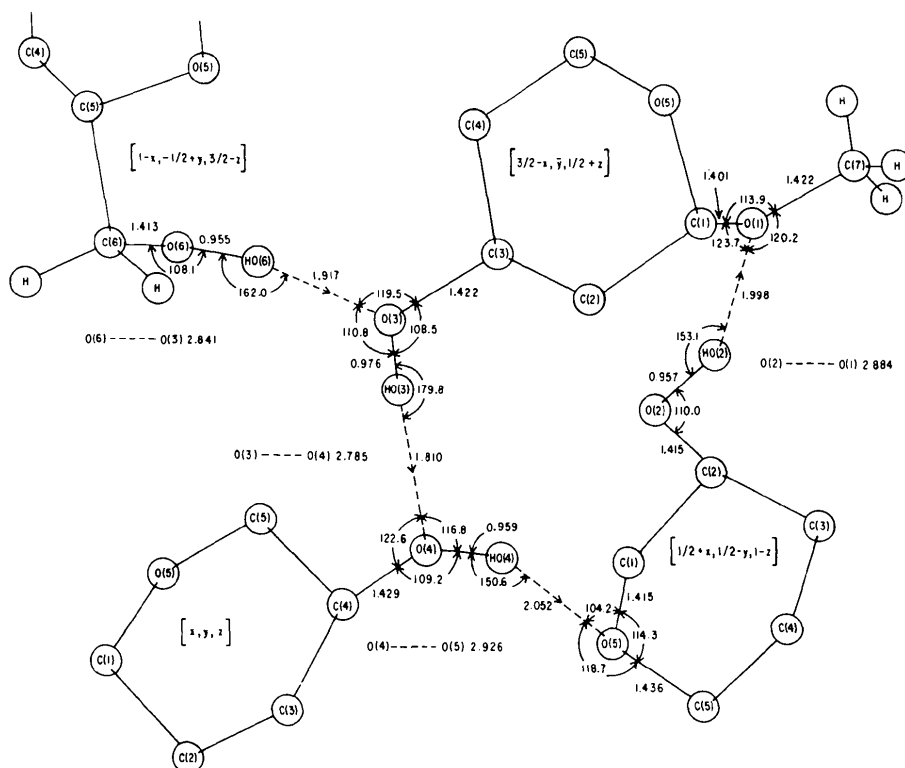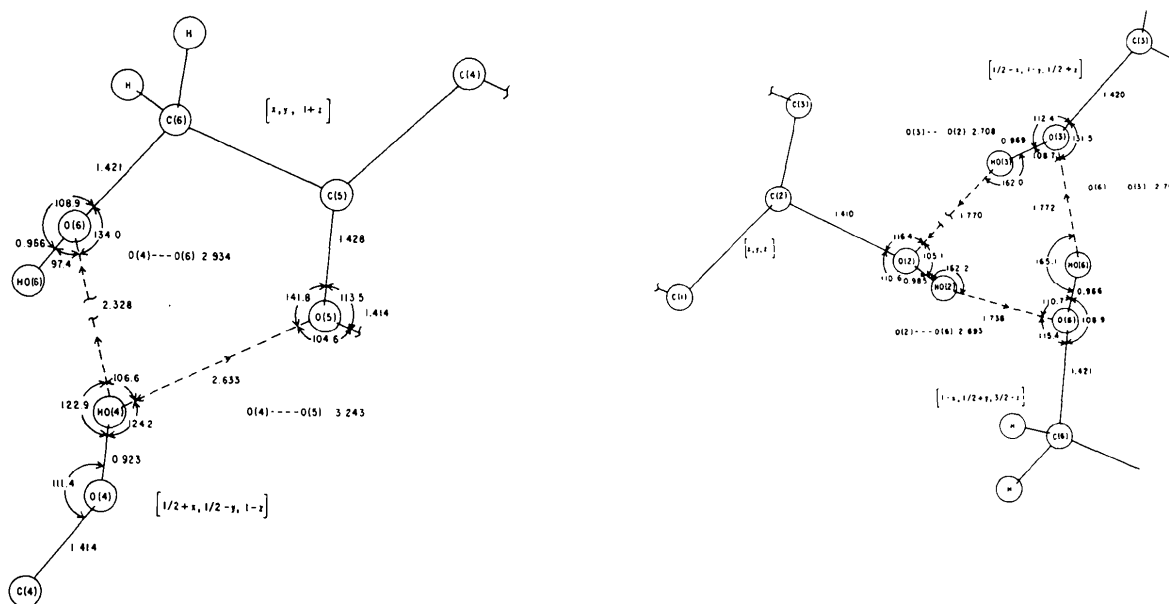The hydrogen-bonding schemes are unchanged from those deduced from the X-ray determinations. The neutron diffraction data provided additional accuracy for the H positions, the geometrical details of which are shown in Figs. 5 and 6.

In the mannopyranoside structure there is only one strong hydrogen bond O(3)—H · · · O(4) which is almost linear with an H · · · O distance of 1·810 Å. It is the central bond of a three-link chain originating at H[O(6)] and terminating at ring oxygen O(5). Both these links are relatively weak with H · · · O distances of 1·917 and 2·052 Å and large deviations from linearity. The remaining hydrogen bond from O(2)—H · · · O(1) is also weak (1·998 Å) and provides an unusual example of a hydrogen bond to a glycosidic oxygen.

In the glucopyranoside structure, the spirals of strong hydrogen bonds, which extend in the c direction

[as illustrated in Fig. 2 of Berman & Kim (1968)] involve three of the hydroxyl groups in approximate threefold screw symmetry. The remaining hydroxyl H[O(4)] has its H atom in a position appropriate for a bifurcated interaction with the primary alcohol group and ring O of an adjacent molecule, but the H · · · O distances are so long (2·328 and 2·633 Å) that the bonding interaction must be very small or negligible. These distances are similar to those found in sucrose (Brown & Levy, 1973) where there is also a hydroxyl with nearest-neighbor H · · · O distances close to the sum of the van der Waals radii of 2·40 Å, i.e. 2·309, 2·534 and 2·539 Å.

In methyl α-D-altropyranoside there are two normal hydrogen bonds and two bifurcated hydrogen bonds, one of which involves an intramolecular interaction. These are illustrated in Fig. 2 of Poppleton, Jeffrey & Williams (1975).

Despite the configurational and conformational differences between these molecules and the absence of any uniformity in their hydrogen-bonding schemes, there is a clear correlation between the H · · · O distances and the type of hydroxyl-to-hydroxyl and hydroxyl-to-oxygen interaction. This is shown in Table 8, where the hydrogen bonds are arranged in order of decreasing strength, as measured by the bond distances which are distributed in five well-defined groups. The relationship of these results to those obtained from the neutron diffraction studies of α-glucose (Brown & Levy, 1965), sucrose (Brown & Levy, 1973), and α-maltose monohydrate (Jeffrey & Gress, 1977) are discussed elsewhere (Jeffrey, Gress & Takagi, 1977).

The covalent O—H bond lengths are relatively

Table 8. *Hydrogen-bond geometry for different types of hydroxyl–oxygen interactions in three methyl pyranosides (the standard deviations are given in parentheses)*

Type of interaction	O—H (Å)	H · · · O (Å)	O · · · O (Å)	O—H · · · O (°)	
Hydroxyl–hydroxyl	0·971 (6)	1·736 (6)	2·703 (4)	172·8 (4)	(a)
(donor/acceptor)	0·976 (3)	1·810 (2)	2·785 (2)	179·8 (2)	(b)
· · · O—H · · · O(H)—	0·985 (6)	1·738 (5)	2·693 (4)	162·2 (4)	(c)
	0·969 (6)	1·770 (5)	2·708 (3)	162·0 (4)	(c)
	0·966 (7)	1·772 (6)	2·716 (4)	165·1 (4)	(c)
Hydroxyl–hydroxyl	0·961 (6)	1·922 (6)	2·879 (4)	173·0 (4)	(a)
(donor only)	0·955 (3)	1·917 (3)	2·841 (2)	162·0 (2)	(b)
O—H · · · O(H)—					
Hydroxyl–oxygen	0·957 (3)	1·998 (3)	2·884 (2)	153·1 (2)	(b)
O—H · · · O⟨	0·959 (3)	2·052 (3)	2·926 (2)	150·6 (2)	(b)
Bifurcated bonds	0·964 (7)	2·085 (6)	2·801 (5)	129·7 (4)	(a)
..O		2·140 (7)	2·943 (4)	139·7 (4)	
O—H:⟨	0·962 (7)	2·138 (6)	2·712 (4)	116·9 (4)	(a)
·O(H)		2·185 (7)	2·943 (4)	134·7 (4)	
Non-bonding	0·923 (7)	2·328 (7)	2·934 (5)	122·9 (5)	(c)
(or very weak bifurcated)		2·633 (7)	3·243 (4)	124·2 (5)	
O—H O(H)					
O⟨					

(a) Methyl α-D-altropyranoside. (b) Methyl α-D-mannopyranoside. (c) Methyl α-D-glucopyranoside.

insensitive to the differences in hydrogen-bond lengths. A minor trend for the shorter distances to correspond to the weaker hydrogen bonds could be due to differences in thermal motion. The application of a riding-motion correction (Busing & Levy, 1964) increased the short O—H distance for the non-bonded interaction to 0·970 Å, which was only 0·01 Å shorter than the mean of the other corrected distances. This may be an over-correction, as appeared to be the case with the C—H bonds. Careful thermal-motion analysis based on low-temperature data appears to be necessary before any conclusive evidence can be obtained relating the covalent O—H bond length to the hydrogen-bond length, or even to the presence or absence of a hydrogen bond in these structures.

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