

Neutron Diffraction Refinement of the Crystal Structures of Methyl α -D-Galactopyranoside Monohydrate and Methyl β -D-Galactopyranoside*

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Abstract

The crystal structures of methyl α -D-galactopyranoside monohydrate ($C_7H_{14}O_6 \cdot H_2O$) and methyl β -D-galactopyranoside ($C_7H_{14}O_6$) have been refined using neutron diffraction data. The hydrogen-bond structure is essentially the same as described from previous X-ray studies, but more accurately determined. In the methyl α -D-galactopyranoside monohydrate structure, all hydroxyl groups, the glycosidic O, and the ring O are involved in the hydrogen bonding, which consists of an infinite and a finite chain with a symmetrical bifurcated interaction. The $H \cdots O$ bifurcated bond lengths are 2.128 and 2.210 Å, at an angle of 76.8°. In the methyl β -D-galactopyranoside structure, all hydroxyl groups, the glycosidic O, and the ring O are also involved in hydrogen bonding, which consists of an infinite chain and an asymmetrical bifurcated interaction with $H \cdots O$ distances of 2.240 and 2.746 Å, at an angle of 53.1°.

Introduction

This work forms part of a series of neutron diffraction investigations of pyranose and methyl pyranoside crystal structures which is directed towards a better understanding of the cohesive forces between carbohydrate molecules in the crystalline state (*cf.* Jeffrey & Takagi, 1978).

Experimental and refinement methods

Methyl α -D-galactopyranoside monohydrate (I) and methyl β -D-galactopyranoside (II) were obtained from Sigma Chemical Co. Transparent crystals of both

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Table 1. Crystal data and neutron diffraction experimental and refinement parameters for the crystal structures of methyl α -D-galactopyranoside monohydrate (I), and methyl β -D-galactopyranoside (II)

X-ray values from Gatehouse & Poppleton (1971) for (I) and from Takagi & Jeffrey (1978) for (II) are given in square brackets.

	(I) $C_7H_{14}O_6 \cdot H_2O$	(II) $C_7H_{14}O_6$
Crystal data		
<i>a</i>	6.122 (1) [6.130 (1)] Å	7.779 (2) [7.774 (1)] Å
<i>b</i>	7.486 (2) [7.496 (1)] Å	8.535 (2) [8.530 (1)] Å
<i>c</i>	21.198 (6) [21.202 (3)] Å	13.131 (5) [13.126 (1)] Å
<i>V</i>	971.49 [972.94] Å ³	871.82 [870.41] Å ³
<i>M_r</i>	212.21	194.19
<i>D_x</i>	1.451 [1.449] Mg m ⁻³	1.479 [1.482] Mg m ⁻³
Space group	$P2_12_12_1$	$P2_12_12_1$
<i>Z</i>	4	4
Experimental and refinement data		
Crystal weight	0.0196 g	0.0132 g
Crystal volume	13.57 mm ³	8.87 mm ³
Crystal faces	(210) (102) (112) (013) (013) (158) (001) (014) (134) (101)	(110) (110) (110) (110) (101) (101) (011) (001)
Number of reflections		
Total measured	4388 ($2\theta_{max} = 105^\circ$) <i>hkl</i> and <i>hkl</i> octants	1938 ($2\theta_{max} = 105^\circ$) <i>hkl</i> octant
Averaged	2093 [213 with $F_o^2 \leq \sigma(F_o^2)$]	1854 [224 with $F_o^2 \leq \sigma(F_o^2)$]
Data collection mode and scan width	θ - 2θ step scan with fixed width of 2.6° for $2\theta < 60^\circ$; variable width calculated by $1.90^\circ + 1.52^\circ \tan \theta$ for $2\theta = 60^\circ$ - 105°	θ - 2θ step scan with fixed width of 2.8° for $2\theta < 60^\circ$; variable width calculated by $2.30^\circ + 1.104^\circ \tan \theta$ for $2\theta = 60^\circ$ - 105°
Wavelength (neutron)	1.0415 Å [Be(002) reflection plane]	
Absorption correction	ABSOR (Templeton & Templeton, 1973)	
μ (neutron)	0.2630 mm ⁻¹	0.2574 mm ⁻¹
Maximum correction to F_o^2	1.879	1.718
Minimum correction to F_o^2	1.570	1.396
Average correction to F_o^2	1.675	1.506
Final refinement cycles		
Number of reflections in refinement, <i>m</i>	2093	1854
Number of variables, <i>n</i>	266*	245
<i>R</i> (F^2) for all reflections	0.055	0.058
<i>R_w</i> (F^2) for all reflections	0.074	0.072
Goodness of fit, <i>S</i>	1.027	1.019
$\sigma^2(F_o^2)$	$\sigma^2(F_o^2) + (0.04F_o^2)^2$	$\sigma^2(F_o^2) + (0.022F_o^2)^2$
	(where σ_c is from counting statistics)	
Extinction parameter, <i>g</i>	$2.8 (2) \times 10^4$	$0.28 (3) \times 10^4$

* No refinement on temperature factors of H(OH2) owing to a limitation of variables to be refined (maximum 270) in least squares.

compounds suitable for single-crystal neutron diffraction were grown by slow evaporation of a solution of the compound in a 95% ethanol–water mixture at room temperature. The crystal and experimental data and the structure refinement parameters are given in Table 1.

The cell constants and the three-dimensional neutron diffraction data ($\sin \theta_{\max}/\lambda = 0.762 \text{ \AA}^{-1}$) for (I) and (II) were collected at room temperature on the Brookhaven High Flux Beam Reactor single-crystal diffractometer as described by Takagi & Jeffrey (1977).

The atomic coordinates for the X-ray determinations [Gatehouse & Poppleton (1971) for (I) and Takagi & Jeffrey (1978) for (II)] were used as the initial values for refinement by full-matrix least squares, minimizing $\sum w|F_o^2 - k^2 F_c^2|^2$ (Busing, Martin & Levy, 1962). A difference Fourier map revealed the positions of all H atoms. The refinement parameters and neutron scattering lengths used are defined in Takagi & Jeffrey (1977). Eight reflections for (I) were severely affected by the extinction ($0.32 \leq E < 0.50$), but not in (II). The final positional parameters for all atoms are listed in Table 2. The atomic notation and thermal ellipsoids are shown in Figs. 1 and 2, and the molecular dimensions are given in Figs. 3 and 4. The calculation of distances and angles with their estimated standard

deviations was made using a variance–covariance matrix (Busing, Martin & Levy, 1964). The more accurate X-ray values of the cell dimensions were used. The contents of the unit cells are shown in Figs. 5 and 6. Results of a rigid-body thermal-motion analysis (Schomaker & Trueblood, 1968) are given in Table 3.*

* Lists of structure factors and anisotropic thermal parameters for both compounds, and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34135 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

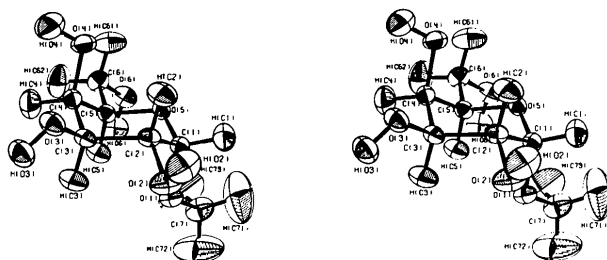


Fig. 1. Methyl α -D-galactopyranoside monohydrate, without a water molecule. The thermal ellipsoids are at 50% probability (Johnson, 1976).

Table 2. Fractional atomic coordinates ($\times 10^4$) for methyl α -D-galactopyranoside monohydrate (I), and methyl β -D-galactopyranoside (II)

	(I)			(II)		
	x	y	z	x	y	z
C(1)	4283 (2)	8076 (2)	3620 (1)	1641 (2)	5372 (2)	9163 (1)
C(2)	2263 (2)	8058 (2)	3196 (1)	192 (2)	6575 (2)	9231 (1)
C(3)	831 (2)	6442 (2)	3340 (1)	154 (2)	7552 (2)	8260 (1)
C(4)	2175 (2)	4725 (2)	3318 (1)	1919 (2)	8219 (2)	8003 (1)
C(5)	4091 (2)	4908 (2)	3772 (1)	3241 (2)	6893 (2)	7999 (1)
C(6)	5568 (3)	3289 (2)	3783 (1)	5041 (2)	7490 (2)	7786 (1)
C(7)	5360 (3)	8701 (3)	4667 (1)	2727 (4)	3183 (3)	10025 (2)
O(1)	3607 (3)	8460 (2)	4234 (1)	1777 (3)	4596 (2)	10089 (1)
O(2)	1077 (3)	9667 (2)	3286 (1)	-1430 (2)	5813 (3)	9324 (1)
O(3)	-906 (2)	6375 (3)	2890 (1)	-1109 (3)	8743 (3)	8306 (2)
O(4)	3004 (3)	4415 (3)	2703 (1)	2357 (2)	9407 (2)	8722 (1)
O(5)	5404 (2)	6423 (2)	3591 (1)	3237 (2)	6139 (2)	8971 (1)
O(6)	7254 (3)	3463 (3)	4235 (1)	6222 (2)	6227 (3)	7716 (2)
O(W)	663 (5)	1294 (4)	4590 (1)			
H(C1)	5463 (6)	9069 (4)	3454 (2)	1373 (5)	4534 (4)	8542 (2)
H(C2)	2864 (6)	7949 (5)	2707 (1)	432 (4)	7331 (5)	9889 (2)
H(C3)	138 (5)	6592 (5)	3814 (1)	-211 (5)	6763 (5)	7628 (3)
H(C4)	1154 (6)	3595 (5)	3476 (2)	1853 (4)	8745 (4)	7236 (2)
H(C5)	3462 (5)	5142 (5)	4251 (1)	2880 (4)	6023 (4)	7413 (3)
H(C61)	6337 (8)	3111 (6)	3323 (2)	5018 (5)	8124 (6)	7065 (3)
H(C62)	4543 (8)	2118 (5)	3878 (3)	5447 (5)	8321 (5)	8380 (3)
H(C71)	6598 (12)	9516 (13)	4478 (3)	2689 (14)	2604 (9)	10709 (5)
H(C72)	4717 (11)	9290 (12)	5076 (3)	4009 (11)	3398 (11)	9813 (9)
H(C73)	6020 (13)	7434 (10)	4797 (3)	2243 (16)	2439 (9)	9479 (8)
H(O2)	915 (7)	10270 (5)	2891 (2)	-1791 (5)	5785 (4)	10031 (3)
H(O3)	-2274 (4)	6259 (5)	3117 (1)	-1326 (8)	9078 (6)	8958 (4)
H(O4)	2043 (7)	3615 (7)	2486 (2)	2951 (4)	10227 (4)	8329 (3)
H(O6)	6625 (7)	3582 (6)	4656 (2)	6947 (5)	6197 (5)	8313 (3)
H(OW 1)	-505 (7)	1964 (6)	4420 (2)			
H(OW 2)	1168 (8)	477 (7)	4288 (2)			

minations. The neutron diffraction data provide additional accuracy for the H atom positions, the geometrical details of which are shown in Figs. 7 and 8.

In the methyl α -D-galactopyranoside monohydrate structure (I) the hydrogen bonding consists of infinite chains linking O(6)H and O W[H(O W 1)] and finite chains which originate at O W[H(O W 2)] and terminate at O(1) and O(5), with a single-link branch from O(4)H to O(3). O(3) therefore donates one and accepts two hydrogen bonds, having a short hydroxyl to ring oxygen type bond. Similar hydrogen-bond geometry involving a double-acceptor hydroxyl is observed in β -L-lyxopyranose (Nordenson, Takagi & Jeffrey, 1978), where the H...O distance is 1.718 Å. The donor-acceptor H...O bond length, O(2)H...O(3), and the

donor-only H...O bond length, O(4)H...O(3), are longer than the 'average' values of 1.815 and 1.940 Å respectively (Jeffrey & Takagi, 1978). There is also a symmetrical bifurcated interaction from O W[H(O W 2)] to the glycosidic oxygen O(1) and the hydroxyl oxygen O(2). This is similar to the bifurcated interactions observed in the methyl α -D-altropyranoside structure (Poppleton, Jeffrey & Williams, 1975), where the H...O distances are 2.085, 2.140 Å and 2.138, 2.185 Å. The shortest hydrogen bond, 1.706 Å, is to the three-planar-coordinated water molecule [the sum of the H-O(W)-H angles is 360°].

In the methyl β -D-galactopyranoside structure (II) the hydrogen bonding consists of an infinite chain of strong bonds, ...O(2)H...O(4)H...O(6)H...O(2)H..., and an asymmetrical bifurcated interaction between O(3)H and the glycosidic oxygen O(1) and the ring oxygen O(5) (as defined by Jeffrey & Takagi, 1978). The three normal donor-acceptor H...O bond lengths are in the range observed for this type of interaction (1.735–1.869 Å) (Jeffrey & Takagi, 1978). The bifurcated interaction from O(3)H is weak and similar to that observed in methyl α -D-glucopyranoside (Jeffrey, McMullan & Takagi, 1977), where there are two H...O distances of 2.328 and 2.633 Å.

Table 4. Thermal-motion corrections (Å) in methyl α -D-galactopyranoside monohydrate (I), and methyl β -D-galactopyranoside (II)

	Rigid-body thermal motion*		Riding motion† (lower bound)		Riding motion†	
	(I)	(II)	(I)	(II)	(I)	(II)
C—C	0.004	0.004				
C—O	0.004	0.004				
C—H (ring)	0.004	0.003	0.004	0.003	0.023	0.020
C—H (methylene)			0.007	0.006	0.035	0.030
C—H (methyl)			0.028	0.046	0.092	0.120
O—H			0.002	0.003	0.018	0.021

* With the model consisting of the six atoms of the pyranose ring and O(1), O(2), O(3), O(4) and C(6).

† See Busing & Levy (1964) for definition.

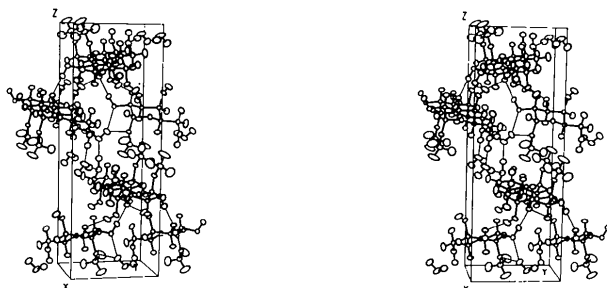


Fig. 5. Unit-cell contents in methyl α -D-galactopyranoside monohydrate. The thermal ellipsoids are at 20% probability (Johnson, 1976).

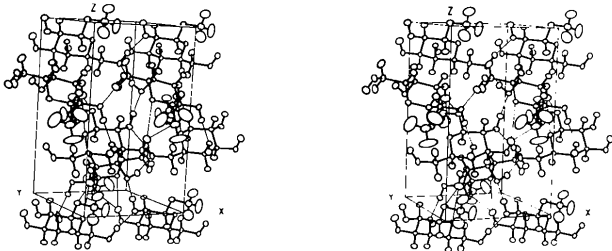


Fig. 6. Unit-cell contents in methyl β -D-galactopyranoside. The thermal ellipsoids are at 20% probability (Johnson, 1976).

The molecular dimensions

Both molecules have slightly distorted 4C_1 ring conformations. The departure from the ideal chair conformation is greater for the β anomer, as is generally observed in comparisons of α and β methyl pyranosides. The Cremer & Pople (1975) puckering

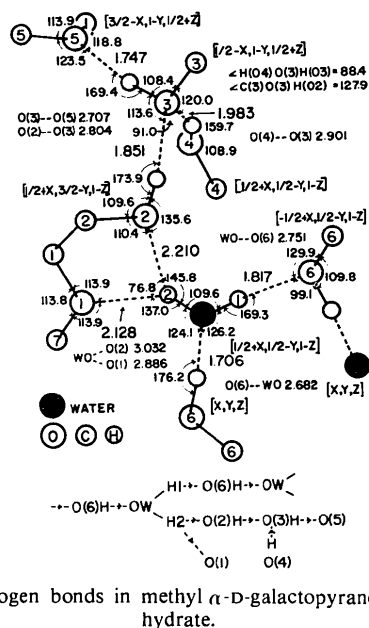
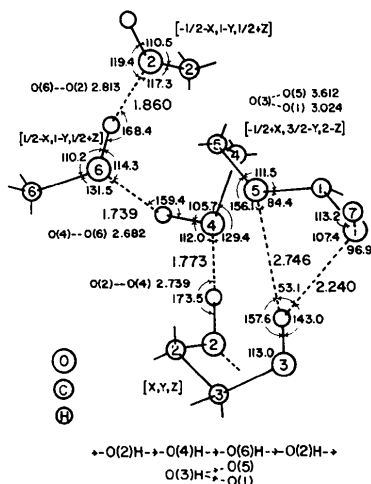


Fig. 7. Hydrogen bonds in methyl α -D-galactopyranoside monohydrate.

Table 5. Acetal geometry in methyl aldopyranosides

	Bond distances (Å)				Valence angles (°)		
	C(5)—O(5)	O(5)—C(1)	C(1)—O(1)	O(1)—CH ₃	α	β	γ
Methyl α -aldopyranosides							
(I)	1.443	1.417	1.396	1.425	113.9	111.4	113.8
Mean of eight X-ray studies	1.4354	1.4163	1.4044	1.4305	113.4	112.3	113.1
Mean of three neutron studies	1.4353	1.4157	1.4007	1.4170	113.9	112.5	113.9
<i>ab initio</i> theory	1.444	1.423	(1.423)	(1.444)	115.9	113.9	115.9
Methyl β -aldopyranosides							
(II)	1.429	1.425	1.389	1.416	111.5	109.3	113.2
Mean of eight X-ray studies	1.4329	1.4281	1.3829	1.4270	111.4	107.9	113.4
One neutron study	1.421	1.427	1.381	1.426	111.1	107.4	113.0
<i>ab initio</i> theory	1.434	1.425	1.400	1.443	115.8	110.9	116.1

Fig. 8. Hydrogen bonds in methyl β -D-galactopyranoside.

parameters for the α and β anomers are, respectively, Q , 0.570, 0.582 Å; θ , 4.87, 5.89°; φ_2 , 83.61, 13.36°. The distortions are therefore different, that of α being in the direction of a boat, 3_0B , and that of β towards a twist boat, 5S_1 (cf. Jeffrey & Yates, 1979).

The acetal moieties of the two molecules show the characteristic bond-length and valence-angle variations observed in other methyl pyranosides and predicted by *ab initio* theory (Jeffrey, Pople, Binkley & Vishveshwara, 1978), as shown in Table 5. It confirms the difference in the two C(1)—O bonds in the α case, which was unpredictable from the theoretical treatment due to the limitations of the model compound used, *i.e.* CH₃—O—CH₂—O—CH₃, to simulate the acetal moiety.

The remainder of the molecular dimensions show no differences from generally accepted dimensions for pyranose sugars. The ring C—C bond lengths range from 1.523 to 1.530 Å, with a mean of 1.5261 Å. The C(5)—C(6) bond lengths are observed to be 0.010 Å shorter; this is likely to be a thermal-motion effect, as shown from the results of the rigid-body-motion analysis shown in Table 4.

The C—O bond lengths, excluding those involved in the acetal system, range from 1.414 to 1.431 Å with a mean value of 1.4209 Å. The C—H bond lengths range from 1.050 to 1.104 Å with a mean of 1.1002 Å, excluding the methyl C—H bonds which are 0.050 Å shorter due to the foreshortening effect of the thermal motion.

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