Crystal Structure of Methyl α-D-Galactopyranoside Monohydrate

By B. M. Gatehouse and B. J. Poppleton*

Chemistry Department, Monash University, Clayton, Victoria 3168, Australia

Methyl α-D-galactopyranoside monohydrate crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a=6\cdot130$, $b=7\cdot486$, $c=21\cdot202$ Å. The structure was solved using the tangent formula and refined by full-matrix least-squares to a final reliability index of $0\cdot032$. Bond lengths and angles are normal with the primary hydroxyl group in the *gauche–trans* arrangement; the ring conformation is the expected chair form ($C1$). The ring oxygen atom participates in the hydrogen bonding scheme which also contains a bifurcated hydrogen bond. The environment of the water molecule comprises a planar array of oxygen atoms which approximate a square.
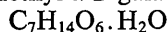
Introduction

In a systematic study of the Fischer method of preparation of the methyl D-galactopyranosides Frahn & Mills (1965) report that the α isomer crystallizes only as the monohydrate, with a melting point which is dependent on its previous treatment and the method of measurement. Thus a large sample of the pure material, obtained by crystallization from water, when sealed in a glass capillary melted over the range 107–113°C. On a Fischer–Johns hot plate the corresponding range was 96–99°C. Dehydration of a powdered sample at 83°C under 2 mm pressure in the presence of phosphoric oxide caused partial fusion without changing the melting point. No fusion occurred if the temperature of dehydration was reduced to 61°C but the anhydrous residue then had a higher and sharper melting point at 116–116·5°C. Exposure of the residue to air resulted in a weight gain corresponding to reformation of the monohydrate but the melting point remained unaltered at 116–116·5°C.

This paper reports the crystal structure determination of methyl α-D-galactopyranoside monohydrate which was undertaken to assist in understanding the above behaviour and to provide information on the nature of the interactions between water and carbohydrates.

Crystal data

Methyl α-D-galactopyranoside monohydrate,
$C_7H_{14}O_6 . H_2O$
M.W. 212·21
$a=6\cdot130$ (1) Å
$b=7\cdot486$ (1) Å
$c=21\cdot202$ (3) Å
$D_x=1\cdot448$ g.cm^{-3}, $Z=4$
$\mu=11\cdot48$ cm^{-1}
Systematic absences: $h00$ for h odd, $0k0$ for k odd and $00l$ for l odd.
Space group: $P2_12_12_1$

* Permanent address: Division of Forest Products, C.S.I.R.O., South Melbourne, Victoria 3205, Australia.

Cell dimensions were measured using a Picker diffractometer and agree within 0·6% with those reported by Cox, Goodwin & Wagstaff (1935) although the a and c axes have been interchanged in the present work.

The crystal had forms {001}, {201} and {011} with maximum dimensions in the directions [100], [010] and [001] of 0·309, 0·750 and 0·466 mm respectively.

Experimental

A suitable crystal was selected from a batch crystallized from a warm solution in water, and mounted for rotation about the b axis on a Picker four-circle diffractometer. A full set of data to sin $\theta=0\cdot9$ using Cu $K\alpha$ radiation was collected in the θ–2θ scanning mode with angle limits of 1° on each side of the reflexion (α_1, α_2) and with 20 sec background count times. The general reflexion 333 was measured throughout the data collection at fifty-reflexion intervals as a monitor of crystal stability. A decrease to 95% of the initial intensity occurred at a steady rate over the collection period and all intensities were corrected for this deterioration of the crystal by the data reduction program. The data were collected in a sequence which was not systematic with h, k, l, or sin θ but depended solely on the minimization of the shifts of setting angles between reflexions.

No correction was made for absorption.

Calculations were executed on the C.S.I.R.O. CDC 3200 and 3600 computers. The major programs used were modified versions of the full-matrix least-squares of Busing, Martin & Levy (1962), the Fourier of White (1965) and the direct phasing (D.P.) series of Hall (1968). The operations of the D.P. programs have been described by Oh & Maslen (1968).

Scattering curves for all atoms were those quoted in *International Tables for X-ray Crystallography* (1962).

Determination and refinement

The structure was solved by direct phasing methods employing the tangent formula of Karle & Hauptman (1956).

The observed structure factors were placed on an approximate absolute scale using a Wilson plot; the scale factor so obtained was within 1% of that finally obtained by equating the sum of the observed and calculated structure factors. The same plot gave a temperature factor of 2·82 Å². These constants were used to generate a list of normalized structure factors the statistics for which are compared with idealized centric and non-centric cases in Table 1.

Table 1. *E statistics*

	Observed	Non-centric	Centric
Mean $|E|$	0·855	0·886	0·798
Mean E^2	1·037	1·000	1·000
Mean $|E^2-1|$	0·895	0·736	0·968

After an initial false start a solution was finally achieved with the origin and enantiomorph defining phases given in Table 2 in which n refers to the position of the reflexion in a list sorted on $|E|$. The 3,3,12 reflexion ($n=2$) was then assigned arbitrary starting phases of 0·0, $\pi/2$, π and $3\pi/2$ in four phasing runs using the 126 reflexions for which $|E|>1·49$. The $\sum_1$ expression of Karle & Hauptman (1956) had given a phase of 0·0, with high probability, for the 060 ($n=12$) reflexion. However, it was not used as a starting phase but only to check the phasing process.

Table 2. *Origin and enantiomorph defining phases*

n	Reflexion	$|E|$	Phase	Type
8	209	2·66	$\pi/2$	Origin
21	120	2·30	$\pi/2$	Origin
26	072	2·21	$\pi/2$	Origin
23	305	2·28	$\pi/2$	Enantiomorph

One set of phases ($\varphi_{3,3,12}=\pi/2$) was significantly better than the other three; a check at intervals of $\pi/4$ for the starting phase confirmed this conclusion. The phas-
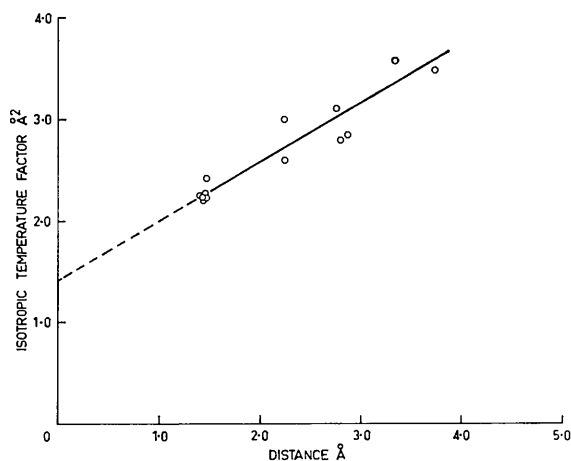

Fig. 1. Individual atom isotropic temperature factors vs. radial distance of the atom from the geometric centre of the pyranose ring.

ing was then extended to include the 208 reflexions for which $|E|>1·20$, equivalent to approximately fifteen reflexions per non-hydrogen atom in the asymmetric unit. These had a reliability index $R_E=\sum||E_{obs}|-k|E_{calc}||/\sum|E_{obs}|$ of 0·15 with all reflexions phased and with each $|E_{calc}|>1·0$. An E map calculated on the basis of these phases revealed clearly both sugar and water molecules. The reliability index of the initial set of structure factors calculated with the positional parameters from the E map, and the scale and isotropic temperature factors given above was 0·19.

A full-matrix least-squares refinement of positional parameters reduced the conventional reliability index R to 0·13 and a further cycle refining both positional and individual isotropic temperature factors yielded an R of 0·093. A difference Fourier synthesis then showed the hydrogen atoms although one, attached to the water molecule was subsequently found to be in error. A third cycle varying only heavy-atom positions and individual temperature factors reduced R to 0·076. At this point the atoms were grouped according to their temperature factor as shown in Table 3. When the individual temperature factors were plotted against distance of the corresponding atom from the geometric centre of the pyranose ring the pattern shown in Fig. 1 emerged. The molecule clearly appears to be vibrating as a rigid body with a residual translational component of approximately 1·4 Å²; this feature was used to assign temperature factors to the various hydrogen atoms in in the structure.

Table 3. *Atoms grouped according to isotropic temperature factors*

		Type	B_{iso}	Mean
I	C(1)	Ring atoms	2·21	
	C(2)		2·25	
	C(3)		2·28	2·27 Å²
	C(4)		2·42	
	C(5)		2·24	
	O(5)		2·26	
II	O(1)	Ring atom substituents	2·61	
	O(2)		3·12	
	O(3)		2·81	2·88 Å²
	O(4)		3·01	
	C(6)		2·87	
III	C(7)	Appendages	3·60	3·55 Å²
	O(6)		3·50	
IV	O(W)	Isolated	5·30	5·30 Å²

Several cycles of least-squares, with unit weights, varying the heavier atom positions and their anisotropic thermal parameters with relocation of one hydrogen atom as mentioned above gave the final agreement index of 0·032 at which level parameter shifts were equal to, or less than, the estimated standard deviations. The corresponding difference electron density map contained a number of features with peak heights of 0·15–0·17 e.Å⁻³ which could be attributed to the bonding electrons because of their character and position with

respect to the carbon and oxygen atom sites. Details other than these were less than 0·10 e.Å^{-3}.

The final list of structure factors, Table 4, indicates that the affects of absorption and secondary extinction are small; thus in the latter case the four reflexions 004, 013, 103 and 120, each of which required four attenuators, show no pronounced systematic difference between |F_{obs}| and |F_{calc}|, and a similar comment applies also to the eight reflexions for which three attenuators were necessary.

The final atom position and thermal parameters are listed in Table 5. Estimated standard deviations (e.s.d.) of the heavier atom coordinates are isotropic with values of 0·002 Å for the oxygen atoms and 0·003 Å for the carbon atoms. Therefore the approximate e.s.d.'s of the bond lengths and angles are 0·005 Å and 0·3° respectively.

The e.s.d. of the mean-square displacements of the heavier atoms are about 0·002 Å^2.

Description of the structure and discussion

In a crystal of the monohydrate, methyl α-D-galactopyranoside has the generally expected chair conformation (C1) depicted in Fig. 2. The primary hydroxyl oxygen atom, O(6), is *gauche* to the pyranose ring oxygen atom, O(5), and *trans* to O(4), and therefore in this respect the structure is similar to those of a number of other sugars (Sundaralingam, 1968). At the same time the carbon atom, C(7), of the methyl group is *gauche*

to O(5) and *trans* to C(2). Thus these two groups effectively shield the ring oxygen atom from an equatorial hydrogen bonding approach but not an axial approach, as discussed below.

Within the unit cell the geometric centre of the pyranose ring is positioned at $x/a = 0.3174$, $y/b = 0.6443$ and

Fig. 2. Molecular configuration and atom designation; drawn by ORTEP (Johnson, 1965).

Table 4. Observed and calculated structure factors

F_o and F_c are × 10.

* Unobserved reflexions signal/noise ≤1·5.

$z/c = 0.3473$ with the primary hydroxyl group within 1·86 Å of a screw axis at x, $\frac{1}{4}$, $\frac{1}{2}$. The latter, with the water molecule, forms a tightly hydrogen-bonded column parallel to the x axis. The methyl group is similar, being within 1·20 Å of a screw axis at x, $\frac{3}{4}$, $\frac{1}{2}$ and forms a second column parallel to the first in which only van der Waals forces are involved. The mean plane through the six atoms of the pyranose ring is given by (1) which shows it to be very nearly perpendicular to the long, z, axis of the cell. The deviations of the atoms from the plane are: C(1), -0.206; C(2), 0·203; C(3), -0.231; C(4), 0·246; C(5), -0.251 and O(5), 0·240 Å.

$$0.3447X - 0.1264Y - 0.9302Z + 6.760 = 0 \qquad (1)$$

The bond lengths and angles calculated using the coordinates of Table 5 are given in Table 6. The mean distances for the C–H and O–H bonds are 1·04 and 0·99 Å and show no unusual departures from expected values (Sutton, 1965). The mean distances for the C–C and C–O bonds are 1·518 and 1·428 Å respectively, which agree well with values observed in other structures (Berman, Chu & Jeffrey, 1967). The variations of the C–O bonds from the mean are, in general, greater than those displayed by the C–C bonds and for the sequence C(5)–C(5), O(5)–C(1) and C(1)–O(1) the differences are $+0.011$, -0.010 and -0.023 Å. Similar variations in the bond lengths have been observed in a number of the other methyl pyranosides (Berman, Chu

& Jeffrey, 1967; Berman & Kim, 1967; Gatehouse & Poppleton, 1970, 1971).

The shortening of the axial anomeric bond, C(1)–O(1), is less pronounced than with equatorial configurations. However, where there is rigid group thermal motion the apparent shortening of a bond as a result of librational motion will be a function of radial distance of the atoms involved from the librational centre of the molecule. An axially disposed atom, therefore, at C(1) for example, will be less affected by libration than an equatorial substituent to the same atom, provided the librational centre is not displaced greatly from the centre of mass by forces such as strong intermolecular hydrogen bonding. As the observed variations of these bonds from the mean are small it is possible that they are manifestations of thermal motion rather than anything of structural significance.

The methyl α-galactoside molecule has a short C(5)–C(6) bond (-0.011 Å) but as the change is only 2σ it is not considered significant. On the other hand a similar short C(5)–C(6) bond has been observed in methyl α-D-altropyranoside (Gatehouse & Poppleton, 1971).

Bond angles, Table 6, between the heavier atoms have a mean value of 110·8° from which those associated with C(5) show the maximum deviation. The final difference electron density map gave no anomalous residual density in the region and the distortion of this part of the molecule appears genuine subject to the

Table 5. *Atomic positional and thermal parameters*

Terms are $\times 10^4$. Temperature factor expression is

$$\exp\left[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\right].$$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4278	8079	3618	325	280	314	18	39	-16
C(2)	2264	8058	3196	316	360	235	43	29	10
C(3)	846	6448	3341	248	414	232	14	7	19
C(4)	2154	4734	3321	293	355	303	-1	46	-10
C(5)	4087	4916	3772	276	273	321	-2	9	22
C(6)	4447	8301	1219	379	354	448	-67	-17	-9
C(7)	4630	3696	332	478	534	441	-5	-177	61
O(1)	3589	8468	4235	324	393	255	52	-21	-61
O(2)	1083	9665	3290	572	383	330	208	-57	13
O(3)	915	1365	2111	250	553	284	-28	-26	3
O(4)	3011	4428	2702	381	474	332	18	24	-138
O(5)	4598	1425	1408	229	280	352	-8	45	8
O(6)	2754	8471	761	347	538	461	-114	-47	-32
O(W)	645	1296	4586	755	920	452	488	-119	-207
HC(1)	4806	4019	1544	279					
HC(2)	2653	7831	2732	279					
HC(3)	88	6751	3829	279					
HC(4)	1074	3619	3500	279					
HC(5)	3584	5000	4260	279					
HC(6')	3739	8042	1653	355					
HC(6'')	4569	2285	3928	355					
HC(7')	3454	4365	517	443					
HC(7'')	4729	9272	5037	443					
HC(7''')	4083	2500	192	443					
HO(2)	667	83	2917	355					
HO(3)	2333	1500	1833	355					
HO(4)	2035	3638	2522	355					
HO(6)	3500	8667	375	443					
HO(W')	833	6792	583	633					
HO(W'')	1000	50	4267	633					

$U_{11} = U_{22} = U_{33}$
$U_{12} = U_{13} = U_{23} = 0$

conditions mentioned above. The angles at the two ether oxygen atoms, O(1) and O(5), are 113·5 and 113·0° respectively, and therefore also greater than the mean but consistent with values found for other sugars (Jeffrey & Rosenstein, 1964). Angles involving hydrogen atoms range between 101 and 114° with a mean of 108°. The angle HO(W')–O(W)–HO(W'') is 103° which agrees well with the value of 104·5° in an isolated water molecule as well as with those observed in a variety of crystalline hydrates (Hamilton & Ibers, 1968).

Conformation angles in the pyranose ring range between 52·1 and 61·6° which by comparison with the idealized ring angle range of 55·8 to 61·7° (Kim & Jeffrey, 1967) suggests some distortion of the ring. The idealized ring is one in which the C–C bonds are 1·525 Å, and C–O bonds are 1·430 Å and the valence angles for the carbon and ring oxygen atoms are 109·5 and 113·3°; thus the bonds C(1)–C(2) and C(4)–C(5) must be coplanar. The ring distortion in the present structure is revealed in the bonds O(5)–C(1) and C(3)–C(4) being

coplanar to less than 0·001 Å. The remaining atoms C(2) and C(5) are out of the plane by 0·638 and 0·688 Å respectively. The plane equation is given by (2).

$$0·1856X + 0·1475Y - 0·9715Z + 6·074 = 0 . \qquad (2)$$

The hydrogen bonding scheme, Fig. 3, is unusual in the variety of bonding arrangements which are displayed and comprises two more or less independent systems linked via a bifurcated hydrogen bond. The appropriate oxygen–oxygen and oxygen–hydrogen approach distances with angles at the hydrogen positions are given in Table 7.

The first of the systems involves O(2), O(3), O(4) and O(5): O(5) acts as a single acceptor, O(4) as a single donor, O(3) as an acceptor of two bonds and donor of one, and O(2) as a donor but also it is an acceptor in one arm of the bifurcated bond. An interesting feature of this region of the crystal is the participation of the ring oxygen atom of the glycoside in a hydrogen bond; thus the O(3) atom donates to atom O(5) of an equiv-

Table 6. Bond lengths and angles

Bond lengths

C(1)–C(2)	1·525 Å		HC(1) —C(1)	0·96 Å
C(2)–C(3)	1·518		HC(2) —C(2)	1·03
C(3)–C(4)	1·514		HC(3) —C(3)	1·16
C(4)–C(5)	1·528		HC(4) —C(4)	1·13
C(5)–C(6)	1·507		HC(5) —C(5)	1·08
			HC(6′)—C(6)	1·03
O(1)–C(1)	1·405		HC(6″) –C(6)	1·02
O(1)–C(7)	1·437		HC(7′) –C(7)	0·96
O(2)–C(2)	1·419		HC(7″) –C(7)	0·98
O(3)–C(3)	1·446		HC(7‴)–C(7)	1·00
O(4)–C(4)	1·433			
O(5)–C(1)	1·418		HO(2)——O(2)	0·89
O(5)–C(5)	1·439		HO(3)——O(3)	1·06
O(6)–C(6)	1·427		HO(4)——O(4)	0·92
			HO(6)——O(6)	0·95
HO(W')–O(W)	1·04		HO(W'')–O(W)	1·06

Bond angles

Central atom	i	j	α_{ij}	Central atom	i	j	α_{ij}
C(1)	C(2)	O(1)	107·8°	C(2)	C(3)	C(1)	110·7°
	O(1)	O(5)	111·3		O(2)	C(1)	108·8
	O(1)	HC(1)	110·8		O(2)	C(3)	110·6
	O(5)	HC(1)	109·9		HC(2)	C(1)	112·1
	C(2)	HC(1)	105·7		HC(2)	C(3)	101·3
	C(2)	O(5)	111·2		HC(2)	O(2)	113·2
C(3)	C(4)	C(2)	111·3	C(4)	C(5)	C(3)	108·5
	O(3)	C(2)	109·1		O(4)	C(3)	110·8
	O(3)	C(4)	109·9		O(4)	C(5)	107·6
	HC(3)	C(2)	104·8		HC(4)	C(3)	107·8
	HC(3)	C(4)	113·8		HC(4)	C(5)	108·1
	HC(3)	O(3)	107·6		HC(4)	O(4)	113·8
C(5)	C(6)	C(4)	113·5	C(6)	O(6)	C(5)	111·8
	O(5)	C(4)	109·8		HC(6′)	C(5)	112·9
	O(5)	C(6)	107·4		HC(6′)	O(6)	108·4
	HC(5)	C(4)	112·5		HC(6′)	HC(6)	112·3
	HC(5)	C(6)	101·8		HC(6″)	C(5)	104·5
	HC(5)	O(5)	111·6		HC(6″)	O(6)	106·8
C(7)	O(1)	HC(7′)	111·8	O(1)	C(1)	C(7)	113·0
	O(1)	HC(7″)	105·0	O(2)	C(2)	HO(2)	108·6
	O(1)	HC(7‴)	109·8	O(3)	C(3)	HO(3)	103·9
	HC(7′)	HC(7″)	113·4	O(4)	C(4)	HO(4)	104·1
	HC(7″)	HC(7‴)	109·6	O(5)	C(1)	C(5)	113·8
	HC(7‴)	HC(7′)	107·0	O(6)	C(6)	HO(6)	104·5
				O(W)	HO(W')	HO(W'')	102·9

alent molecule translated one unit-cell in the x direction. The bonding approach is from an axial direction with respect to the plane of the molecule, and adjudged on the criteria of short OH$\cdots$O distance and linearity of the atomic arrangement is the strongest bond present.

The second system is confined to the water molecule and the primary hydroxyl groups. The sequence O(W)–HO(W')$\cdots$O(6)–HO(6)$\cdots$O'(W)–HO'(W')$\cdots$O'(6)–HO'(6)$\cdots$O(W) forms a firmly bound left-handed spiral system parallel to the x axis. The two oxygen–oxygen approach distances are significantly different but

Table 7. *Hydrogen bonding distances and angles*

* Oxygen–oxygen intermolecular distances less than 3·25 Å

O(Wa)$\cdots$O(6c)	2·684 Å		O(4)$\cdots$O(3e)	2·903 Å
O(3)$\cdots$O(5)	2·706		O(Wa)$\cdots$O(1e)	2·880
O(6b)$\cdots$O(Wd)	2·744		O(Wa)$\cdots$O(2e)	3·018
O(2)$\cdots$O(3a)	2·807			

Hydrogen contact distances and angles

	Distance	Angle
O(W)–HO(W') $\cdots$O(6)	1·76 Å	155°
O(3)—HO(3) $\cdots$O(5)	1·66	172
O(6)—HO(6) $\cdots$O(W)	1·75	166
O(2)—HO(2) $\cdots$O(3)	1·97	158
O(4)—HO(4) $\cdots$O(3)	2·03	159
O(W)–HO(W'')$\cdots$O(1)	2·07	131
O(W)–HO(W'')$\cdots$O(2)	2·12	142

* The letters refer to the symmetry elements to be applied to the coordinates listed in Table 5.

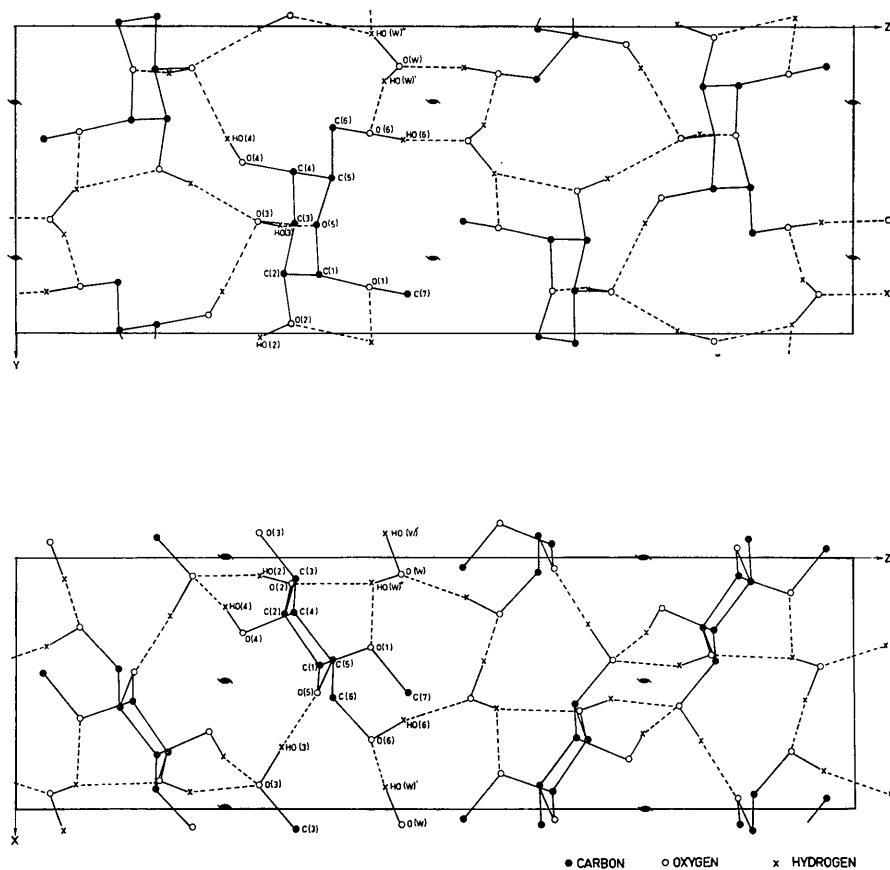|			
a	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
b	$\frac{1}{2}+x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
c	x	$1\frac{1}{2}-y$	$1-z$
d	$\frac{1}{2}-x$	$-1+y$	z
e	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$

Fig. 3. Hydrogen bonding scheme.

the strengths of the two bonds are probably very similar. Thus the longer distance of 2·74 Å involves the shorter OH · · · O distance with a more linear configuration.

The bifurcated bond involves HO(W''), and O(1) and O(2) of a single residue. The associated OH · · · O distances of 2·07 and 2·12 Å are less than 2·6 Å which corresponds to van der Waals contact (Pauling, 1960). The bonds have pronounced non-linearity; the shorter contact is associated with the greater bond angle suggesting that in this case also, the interactions, although weak, are of approximately equal strength. The oxygen atoms O(W), O(1), O(2), O'(6) and O''(6) lie very nearly in a plane given by equation (3).

$$0·6596X + 0·6969Y - 0·2816Z - 2·254 = 0 \qquad (3)$$

The distorted square-planar arrangement about the water group contrasts with the tetrahedral arrangement found in rhamnose monohydrate (McGeachin & Beevers, 1957), α-glucose monohydrate (Killean, Ferrier & Young, 1962) and β maltose monohydrate (Quigley, 1969). It is interesting to note, however, that the midpoint of the line joining O(1) and O(2), which are the two atoms associated with HO(W'') and the bifurcated bond, together with O'(6) and O''(6) form a threefold planar array about the water molecule in which HO'(6) and HO''(6) also participate. Such a threefold planar environment has been observed in a number of hydrated crystals although it is less common than the tetrahedral arrangement (Clark, 1963). The coordinates and perpendicular distances of selected atoms from the plane are given in Table 8.

Table 8. *Hydrogen bonded planar arrangement around the water molecule*

Plane equation $0·6596X + 0·6969Y - 0·2816Z - 2·2537 = P$.

	X	Y	Z	P
O(W)	6·525	0·970	9·723	−0·012
O(6)	4·442	2·598	8·988	−0·045
O'(1)	8·330	−1·147	8·978	−0·087
O'(2)	6·794	−0·250	6·976	0·088
O''(6)	7·507	1·145	12·215	0·056
HO(W1)	5·619	1·342	9·365	−0·250
HO(W2)	6·743	0·187	9·046	−0·223
HO(6)	3·985	2·745	9·806	−0·474
HO''(6)	7·050	0·998	11·396	−0·118

The reason for the unusual melting point behaviour of methyl α-D-galactopyranoside monohydrate remains unresolved. However it is worth noting again that the water molecule is tightly hydrogen bonded to the primary hydroxyl group only, in an unbroken channel parallel to [100], suggesting that it provides a pathway for movement of the water into and out of the structure. The packing changes, which must occur, do not appear to alter extensively the hydrogen bonding pattern, provided it is assumed that the melting point is a valid criterion. If this is the case, then there are several possibilities for packing of the primary hydroxyl groups of which the *trans–gauche* conformation, with O(6) *trans*

to O(5) and *gauche* to C(4) is favoured. This conformation has not been found with monosaccharides in which C(4) is equatorial to the ring, presumably because of interaction between O(4) and O(6). Where, as in galactose derivatives, O(4) is axial, such a conformation is more likely, with the *gauche–gauche* arrangement the least energetically favoured, for the same reason.

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