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The Crystal Structure of α-Rhamnose Monohydrate

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The crystal structure of α-rhamnose monohydrate has been determined by the interpretation of the three-dimensional Patterson function and refined on two projections with data derived from Geiger-counter measurements. There are possibly significant deviations from the expected values of three bond lengths, which include both the axial C–OH bonds in the molecule. There are several significant deviations from the tetrahedral angle in the observed bond angles, which appear to indicate a repulsion between the hydroxyl groups, and the angle at the oxygen atom in the ring is 120°. The molecular packing is determined by a very complete scheme of hydrogen bonding in three dimensions. The hydrogen atoms appear with moderate definition on $(F_o - F_c)$ syntheses but their positions are not completely unambiguous, largely owing to the non-centrosymmetrical nature of the crystal, the poor resolution of the atoms in projection and the occurrence of anisotropic thermal vibrations of the atoms.

Experimental

α-Rhamnose (6-desoxy mannose) is easily crystallized as a monohydrate by evaporation of a solution in methyl alcohol (90%) and water (10%). The crystals are monoclinic and the cell dimensions, obtained by extrapolation from measurements of high-order reflexions on Weissenberg photographs, are:

$$a = 7{\cdot}910 \pm 0{\cdot}005, \quad b = 7{\cdot}914 \pm 0{\cdot}005, \quad c = 6{\cdot}674 \pm 0{\cdot}004 \text{ Å}; \quad \beta = 95^\circ\ 37' \pm 5' .$$

These values agree well with those given by Cox (1931) and Andress & Reinhardt (1931). The density was found, by flotation in a mixture of benzene and chloroform, to be $1{\cdot}457 \pm 0{\cdot}005$ g.cm.$^{-3}$. This gives the number of units of $C_6H_{12}O_5 . H_2O$ in the cell as $Z = 2{\cdot}005$. The only systematic absences observed in the reflexions were $(0k0)$ for k odd, and so the probable space group is $P2_1$.

Weissenberg photographs, using copper radiation, were taken about the three axes, for layer lines up to the fourth, and the intensities were estimated visually. The specimens used were approximately cylindrical with diameters of about 0·1–0·2 mm.; no absorption corrections were applied.

At a later stage the intensities of the $(h0l)$ and $(hk0)$ reflexions were measured, using a Geiger-counter technique. Cochran's (1950) procedure, in which the integrated intensity is obtained from the total number of counts recorded while the crystal is rotated through the reflecting position, was examined. The factor k_1, by which the dead time of the counting tube has to be multiplied to correct for the varying counting rates during this rotation, was taken, in practice, to be constant by Cochran, although he pointed out that it would be expected to be a function of θ. Tests of this indicated that in the experimental arrangement used here k_1 could not be taken to be independent of θ without a considerable loss of accuracy. The much more tedious method was therefore employed, in which, for each reflexion, measurements of the counting rate were taken from the stationary crystal at sufficiently close intervals of the crystal setting; these were adjusted individually for the dead-time correction and plotted against the angular setting. The area under the resulting curve, due consideration being taken of the background, gave the integrated intensity of the reflexion. The counting rates used were kept under 500 counts per sec. by inserting calibrated foils. Readings were taken on a standard reflexion before and after each measurement to correct for the diminution of the X-ray output of the set used, which was a Raymax fitted with rectifying and stabilizing equipment. The diminution in output is due to the contamination of the target by tungsten, which could cause the output to fall by 20% in a week. A series of measurements on one reflexion, taken at intervals during the course of the work, indicated that the standard deviation of the observed intensities was of the order of 2·5%.

Solution and refinement of the structure

The structure was solved by three-dimensional Patterson superposition (Beevers & Robertson, 1950; Shoemaker, Barieau, Donohue & Lu, 1953). The orientation of the pyranose ring was easily deduced from the Patterson function, and the six atoms of one ring were used as searchers. Trial-and-error methods and packing considerations led to the location (although not with certainty) of the remaining atoms of this molecule, and when these were used as additional searchers the positions of the other molecule and the water molecules were revealed quite clearly. The discrepancy factor R_{h0l} for this trial structure was 33%. Accounts of this work have been given (McGeachin, 1954, 1956).

The structure was refined by electron-density projections, least-squares methods and latterly by (F_o-F_c) projections. Some difficulty was encountered in the interpretation of these projections because of the poor resolution, particularly when the hydrogen atoms were considered. In this crystal only 10 of the 28 hydrogen atoms in the unit cell (those bonded to the carbon atoms of the ring) occur in predictable positions. Of the others, a number may lie close to the heavy atoms in projection, and the electron density to which they give rise in the (F_o-F_c) projections may be erroneously interpreted as a shift or a thermal vibration of a heavy atom. The difficulties of refinement are further increased in non-centrosymmetrical projections where the phases of the structure factors are certainly incorrect unless the hydrogen atoms are included in their calculations; thus the positions of the heavy atoms cannot be expected to be accurate until the hydrogen atoms are included, while the position of the hydrogen atoms are not revealed until the heavy atoms are placed with accuracy. The resolution of this dilemma demands great caution in the advanced stages of refinement.

The refinement of the $(h0l)$ reflexions was carried out, using individual isotropic temperature factors for the heavy atoms. Some evidence was obtained for the positions of the hydrogen atoms which enabled those which take part in hydrogen bonding to be placed with reasonable confidence. These fall into three sets: that in the bond O_3–O_5 (see Fig. 1 for the numbering of the atoms), which must belong to O_3 since O_5 is the oxygen atom of the ring; those in the bonds O_4–O_6, O_4–O_6', which form an infinite chain round one of the screw axes; and those in the chain O_1–O_6, O_6–O_2', O_2'–O_1. If the position of one hydrogen atom in either of the latter sets is fixed, the positions of the others in the same set are also fixed, but the two sets are independent of each other. A statistical distribution throughout the crystal is, of course, not impossible. The hydrogen atoms of the methyl group C_6 appeared with rather poor definition, but it was possible, by the use of a model, to assign tentative positions for them. The hydrogen atom contributions for these assumed positions were calculated and used in the refinement. The final b-axis difference maps are shown in Fig. 2 (Fig. 2(a) having all atoms removed, and Fig. 2(b) having only oxygen and carbon atoms removed).

Similar refinements on the $(hk0)$ reflexions were carried out; some evidence was gained for the positions of the hydrogen atoms which led to their being placed in the same positions as had been found in the $(h0l)$ refinement. A comparison of the x parameters obtained from the two projections showed close agree-

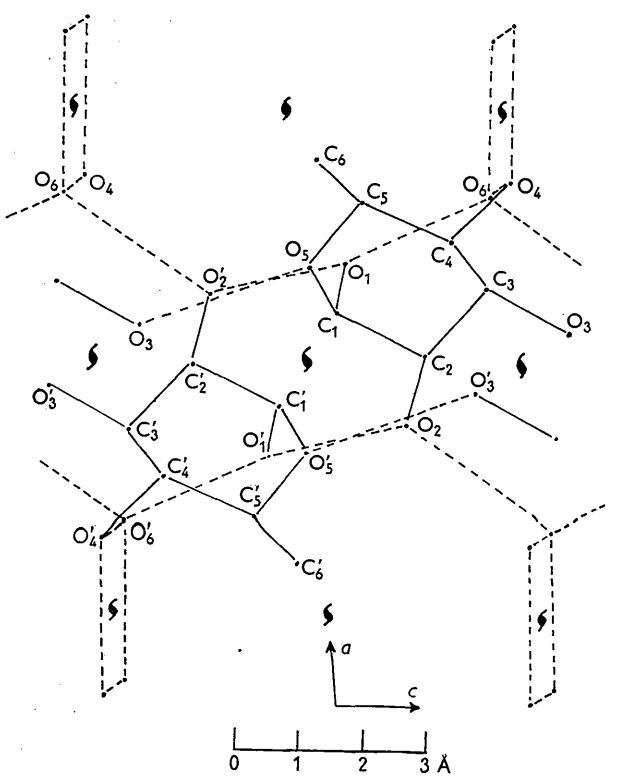

Fig. 1. Plan of the structure projected down the b axis. The hydrogen bonds are shown by broken lines.

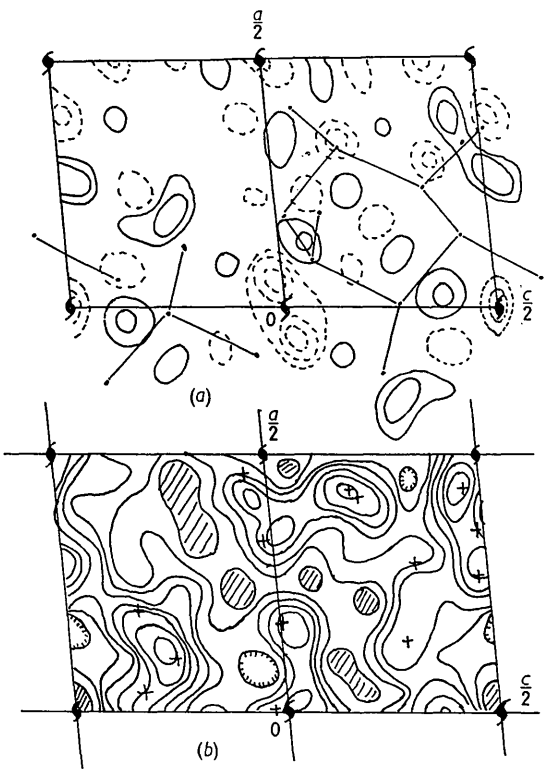

Fig. 2. (a) (F_o-F_c) projection down the b axis with all the atoms removed. Contours at 0·25 e.Å^{-2}; zero contour omitted. Negative contours are in broken lines. (b) (F_o-F_c) projection down the b axis with carbon and oxygen atoms removed. The assumed positions of the hydrogen atoms are indicated by crosses. Contours at 0·25 e.Å^{-2}; negative areas shaded.

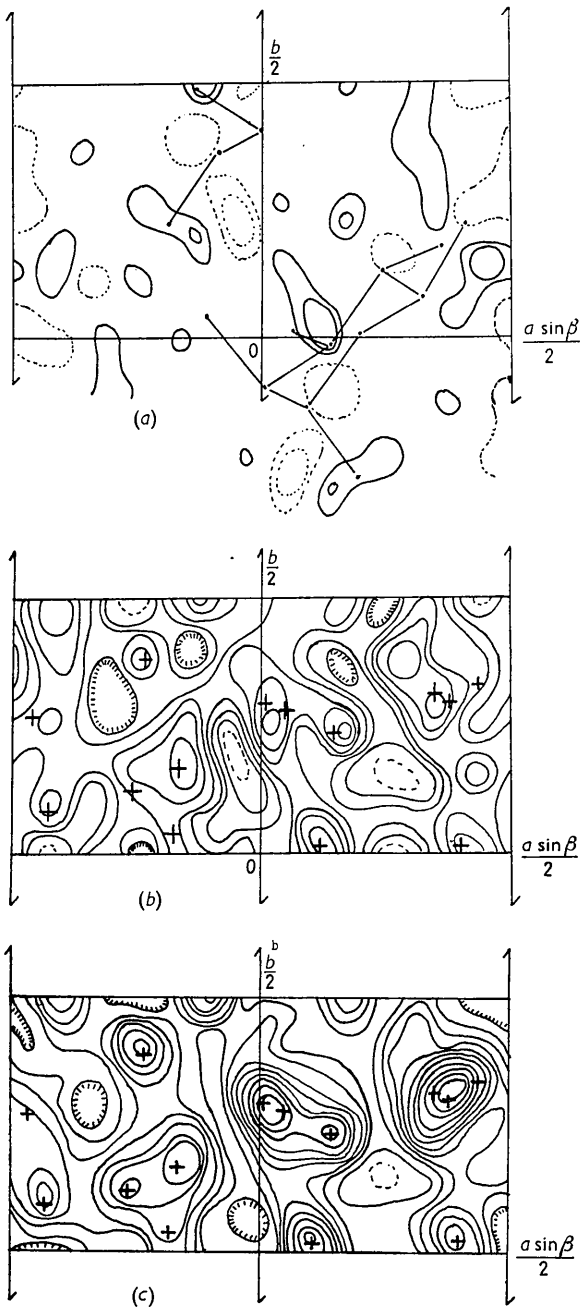

Fig. 3. (*a*) (F_o-F_c) projection down the *c* axis with all atoms removed. Contours at 0·2 e.Å^{-2}; zero contour omitted. (*b*) (F_o-F_c) projection down the *c* axis with carbon and oxygen atoms removed. The phases used are due to carbon and oxygen atoms only. The assumed positions of the hydrogen atoms are marked by crosses. Contours at 0·2 e.Å^{-2}. (*c*) As (*b*) but with phases calculated from the complete structure.

ment, with the exception of O_3 where there was a discrepancy of 0·007 of the cell edge. A mean corresponding to a shift of 0·002 from the value obtained in the centrosymmetrical refinement was taken for this parameter, since a non-centrosymmetrical projection is inherently less accurate and in this case the resolution is bad. The final (F_o-F_c) maps for this axis are shown in Fig. 3; in Fig. 3(*b*) the phases of the carbon and oxygen atoms only were used, while in Fig. 3(*c*) the phases of the complete structure, including hydrogen, were employed.

The values of the discrepancy factor R for these zones, using the limited number of reflexions which the geometry of the counter diffractometer made it possible to measure, were: $R_{h0l} = 7{\cdot}6\%$, $R_{hk0} = 6{\cdot}3\%$. F_{100} was excluded from both these summations and from the difference maps; but values of F_c where F_o was unobserved were included in the calculation of R. The I_o were corrected for secondary extinction by means of the equation $I' = I/(1-gI)$, with $g = 8{\cdot}1\times10^{-5}$.

The mean coordinates and temperature factors are shown in Table 1.

Table 1. *Final atomic coordinates and temperature factors*

	x/a	*y/b*	*z/c*	B_{h0l} (Å^2)	B_{hk0} (Å^2)
O_1	0·188	0·726	0·110	2·4	1·5
O_2	0·880	0·040	0·225	0·8	1·0
O_3	0·060	0·007	0·605	1·5	2·0
O_4	0·358	0·182	0·504	0·8	1·0
O_5	0·187	0·002	0·016	1·5	2·0
O_6	0·328	0·533	0·460	2·0	1·5
C_1	0·087	0·867	0·080	2·0	0·8
C_2	0·008	0·906	0·272	0·5	0·3
C_3	0·143	0·976	0·431	0·5	2·4
C_4	0·232	0·130	0·353	1·0	1·5
C_5	0·315	0·079	0·159	1·5	1·5
C_6	0·402	0·224	0·059	2·4	2·4

The variation in the temperature factors of the same atoms in the two projections was larger than had been expected, even taking into account the anisotropy clearly visible in the difference maps for which no corrections were applied. Because of the empirical methods used to scale the observed structure factors, the values of B listed have no absolute significance. The assumed coordinates of the hydrogen atoms are given in Table 2; no temperature factor was applied to their scattering factors.

Table 2. *Coordinates of the hydrogen atoms*

	60*x/a*	60*y/b*	60*z/c*		60*x/a*	60*y/b*	60*z/c*
H_1	0	48	59	H_8	33	15	2
H_2	58	47	20	H_9	6	1	44
H_3	14	53	29	H_{10}	21	16	29
H_4	8	14	18	H_{11}	26	35	28
H_5	24	1	12	H_{12}	10	40	0
H_6	26	20	11	H_{13}	16	37	20
H_7	20	18	59	H_{14}	11	32	40

(H_6, H_7 and H_8 are the hydrogens of the methyl group.)

The values of the standard deviations $\sigma(\varrho)$ of the electron density for the two projections, calculated by Cruickshank's (1949) formula

$$\sigma(\varrho) = \frac{1}{A}\{\Sigma(F_o - F_c)^2\}^{\frac{1}{2}},$$

are

$$\sigma(\varrho_{h0l}) = 0{\cdot}245 \text{ e.Å}^{-2}, \quad \sigma(\varrho_{hk0}) = 0{\cdot}36 \text{ e.Å}^{-2}.$$

Here $\sigma(\varrho_{hk0})$ has been multiplied by 2 because the projection is non-centrosymmetrical (Cruickshank, 1950). In these calculations when F_o is zero the highest value of F_o which could remain unobserved has been estimated and used to give $(F_o - F_c)$; this applies also to the computation of the difference syntheses. The corresponding standard deviations in the atomic parameters, given by

$$\sigma(x) = 2\pi\{h^2(F_o - F_c)^2\}^{\frac{1}{2}}/aAC,$$

where C is the central curvature of the atom in question, are given in Table 3. These values include the factor $(u/(u-n))^{\frac{1}{2}}$, where u is the number of independent F's and n the number of parameters to be refined (Cruickshank, 1949), which is here 36 (two coordinates and a temperature factor for each of the 12 heavy atoms); in addition, the value of $\sigma(y)$ includes the factor 2 because of the lack of a centre of symmetry. The curvatures C were estimated from electron-density projections with some difficulty because of the poor resolution; mean values over several atoms were used for each projection.

Table 3. *Standard deviations in atomic positions*

		b-axis projection	*a*-axis projection
O	$\sigma(x)$	0·0075 Å	—
	$\sigma(y)$	—	0·018 Å
	$\sigma(z)$	0·0064	—
C	$\sigma(x)$	0·011	—
	$\sigma(y)$	—	0·020
	$\sigma(z)$	0·010	—

The peak heights in the centrosymmetrical *b*-axis projection were about 14 e.Å^{-2} for the oxygen atoms and 9·0–10·4 e.Å^{-2} for the carbon atoms; in the non-centrosymmetrical *c*-axis projection the respective values were 12·5 e.Å^{-2} and 8·0–9·5 e.Å^{-2}. The variations in peak height showed no striking correlation with the temperature factors of the atoms, and the variations are ascribed to termination-of-the-series effects which are expected to be large because of the limited number of reflexions used.

The (0*kl*) reflexions were not measured with the Geiger counter, but these intensities had been estimated visually and used in the refinement of the structure before the more accurate data were obtained. The structure factors of this zone were calculated with the final parameters as a check, using a common temperature factor and excluding the contributions of the hydrogen atoms. The agreement was good with $R = 11{\cdot}8\%$. This value was almost the same as that which had been obtained under the same conditions in the refinement with visually estimated intensities for all three projections, in spite of the fact that there were considerable differences in the two sets of atomic coordinates. The most disquieting feature of this is that the former refinement seemed to be near an end as regards changes in the coordinates. It seems worth while stressing that in a non-centrosymmetrical structure such as this, where resolution is poor, good agreement can be obtained with a comparatively inaccurate structure. The inaccuracy of this projection when the structure was based on visually estimated intensities alone must be due to the neglect of the hydrogen atoms and the failure to use individual temperature factors. This emphasizes the dilemma outlined above that in a non-centrosymmetrical structure, particularly when resolution is bad, the contributions of the hydrogen atoms are necessary for accurate refinement, but that until an advanced stage is reached, their positions may remain unknown.

Observed and calculated values of F_{h0l} and F_{hk0} are shown in Table 4.

Discussion of the structure

The bond lengths are shown in Fig. 4(*b*). The standard deviation $\sigma(l)$ of a bond length depends here on its

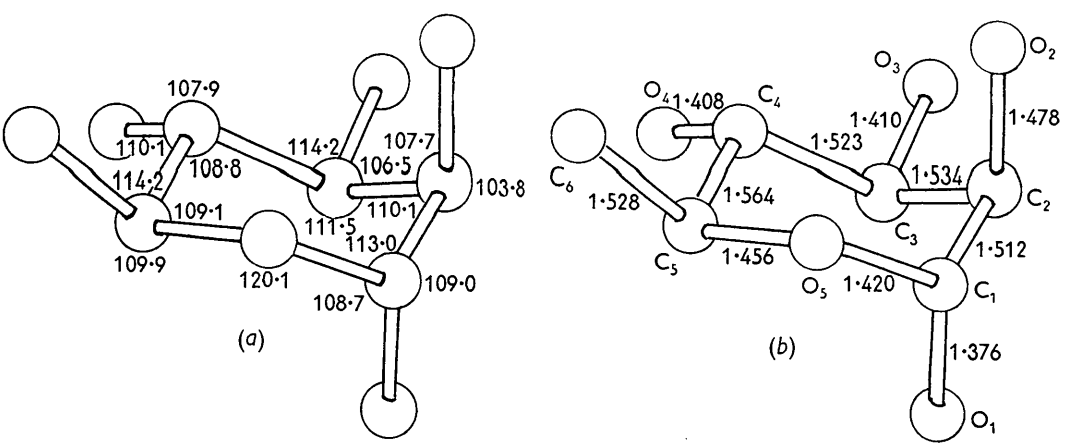

Fig. 4. Perspective drawing of the rhamnose molecule, showing bond angles and lengths.

Table 4. *Observed and calculated structure factors*

F_o from Geiger-counter measurements, F_c from parameters of Tables 1 and 2

b-axis projection

h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c
1	0	25·5	34·5	$\bar{8}$	1	6·6	−6·7	$\bar{2}$	3	18·9	18·1	$\bar{5}$	5	7·8	−7·6
2	0	18·6	−17·8	$\bar{8}$	2	6·6	−6·9	$\bar{1}$	3	50·3	48·5	$\bar{4}$	5	0	−0·1
3	0	4·2	−4·6	$\bar{7}$	2	3·2	−4·7	0	3	6·9	−7·1	$\bar{3}$	5	0	−3·0
4	0	23·2	−22·2	$\bar{6}$	2	14·2	15·1	1	3	13·5	−12·8	$\bar{2}$	5	0	0·2
5	0	4·9	4·6	$\bar{5}$	2	12·3	13·3	2	3	4·3	−3·8	$\bar{1}$	5	10·3	10·0
6	0	11·1	11·0	$\bar{4}$	2	9·6	−9·8	3	3	15·2	−15·2	0	5	0	0·0
7	0	5·1	−6·1	$\bar{3}$	2	18·1	17·8	4	3	22·6	24·0	1	5	8·2	8·4
8	0	2·5	−2·5	$\bar{2}$	2	10·5	−9·0	5	3	24·5	23·6	2	5	1·9	1·9
$\bar{8}$	1	6·7	−6·3	$\bar{1}$	2	9·7	−9·4	6	3	0	−1·0	3	5	15·9	−15·0
$\bar{7}$	1	9·3	9·6	0	2	32·9	34·3	7	3	3·6	3·5	4	5	2·0	−0·3
$\bar{6}$	1	2·2	1·5	1	2	30·2	−28·8	$\bar{7}$	4	2·9	−2·4	5	5	0	−2·3
$\bar{5}$	1	8·7	9·6	2	2	21·7	−21·2	$\bar{6}$	4	16·4	17·7	$\bar{5}$	6	5·5	6·4
$\bar{4}$	1	4·8	−4·2	3	2	8·7	−8·9	$\bar{5}$	4	10·5	11·7	$\bar{4}$	6	2·7	−4·4
$\bar{3}$	1	47·1	−46·9	4	2	17·4	−16·8	$\bar{4}$	4	13·7	−13·8	$\bar{3}$	6	0	−1·2
$\bar{2}$	1	18·6	−18·1	5	2	1·1	0·7	$\bar{3}$	4	12·9	12·9	$\bar{2}$	6	17·0	−17·1
$\bar{1}$	1	29·7	31·2	6	2	0	−2·4	$\bar{2}$	4	13·7	14·0	$\bar{1}$	6	18·3	−18·5
0	1	7·2	−5·5	7	2	16·3	−16·1	$\bar{1}$	4	1·6	−1·6	0	6	3·6	−2·7
1	1	20·4	−20·2	$\bar{8}$	2	8·4	−7·5	0	4	8·3	8·0	1	6	7·0	−6·8
2	1	15·0	13·6	$\bar{8}$	3	2·6	−3·1	1	4	9·3	−8·7	2	6	6·2	−5·0
3	1	14·7	−13·7	$\bar{7}$	3	4·2	−4·1	2	4	13·0	−10·2	3	6	7·9	9·0
4	1	11·2	11·2	$\bar{6}$	3	14·8	−16·5	3	4	1·0	−1·8	4	6	7·7	8·5
5	1	10·5	11·2	$\bar{5}$	3	0	−2·1	4	4	5·3	−4·6	$\bar{1}$	7	10·0	9·5
6	1	7·4	−7·3	$\bar{4}$	3	5·0	6·2	5	4	6·1	−4·9	0	7	0	−2·1
7	1	0	−1·4	$\bar{3}$	3	11·9	−12·6	6	4	3·2	2·4	1	7	2·9	−1·7

c-axis projection

h	k	F_o	A	B	F_c	h	k	F_o	$-A$	B	F_c
0	2	41·2	32·3	27·2	42·2	1	1	26·1	5·0	26·2	26·7
1	2	39·6	32·9	−23·1	40·2	2	1	44·9	−39·7	18·5	43·8
2	2	26·8	−2·1	−27·7	27·8	3	1	8·0	4·8	4·5	6·6
3	2	1·4	−0·7	2·6	2·9	4	1	6·4	5·5	−0·7	5·5
4	2	9·7	−3·1	−8·7	9·2	5	1	9·6	−1·8	9·2	9·4
5	2	15·3	−14·5	−1·1	14·6	6	1	13·6	4·6	12·5	13·3
6	2	5·0	4·8	3·0	5·7	7	1	5·4	−5·1	3·7	6·3
7	2	6·2	4·2	−5·2	6·7	8	1	0	−0·3	1·6	1·6
8	2	3·0	−2·2	−1·4	2·6	1	3	6·0	−4·3	−5·7	7·1
0	4	25·0	25·8	0·9	25·8	2	3	24·5	2·4	24·8	25·1
1	4	7·3	5·7	2·2	6·1	3	3	20·7	−20·7	−3·8	21·0
2	4	6·4	−4·9	−1·8	5·2	4	3	15·3	−7·8	−12·7	14·9
3	4	12·2	−11·6	1·4	11·8	5	3	7·8	4·8	6·3	7·9
4	4	13·2	−12·5	−2·1	12·7	6	3	4·8	3·9	3·8	5·4
5	4	16·5	3·2	−16·0	16·3	7	3	9·9	6·3	9·0	11·0
6	4	7·8	6·1	−2·6	6·6	1	5	13·6	−14·1	0·9	14·1
7	4	0	−0·2	1·4	1·4	2	5	2·8	−3·5	−0·3	3·5
0	6	22·7	7·7	21·1	22·4	3	5	9·7	3·3	8·8	9·4
1	6	3·8	2·7	3·1	4·1	4	5	6·0	4·1	−3·5	5·4
2	6	0	−1·8	1·4	2·3	5	5	8·1	8·6	−1·7	8·8
3	6	5·4	−2·8	4·2	5·0	6	5	4·8	0·4	5·2	5·2
4	6	13·9	−7·2	−10·2	12·5	1	7	8·6	−3·8	8·5	9·3
5	6	4·6	−2·6	−2·9	3·9	2	7	15·9	−2·9	15·9	16·2
0	8	6·1	5·8	3·4	6·7	3	7	2·2	1·2	0·9	1·5
1	8	9·3	8·0	3·7	8·8	4	7	4·3	−0·4	−3·9	3·9
2	8	4·1	−0·2	3·7	3·7						
3	8	10·3	−6·8	6·7	9·5						

direction, since $\sigma(x) \neq \sigma(y) \neq \sigma(z)$. The formula of Ahmed & Cruickshank (1953) was used to evaluate $\sigma(l)$. If the difference dl of a bond length from the accepted value (taken to be C–C = 1·542 and C–O = 1·430 Å) is such that dl/σ is greater than 1·645, the difference is regarded as of possible significance (Cruickshank, 1949). In this determination three bonds are found to have possibly significant differences, the values of dl/σ for these bonds being: C_1–O_1, 2·00; C_2–O_2, 1·78; C_1–C_2, 2·00.

The hydrogen bond lengths between adjacent molecules are shown in Table 5. The bond angles within the molecule are shown in Fig. 4(*a*). The minimum standard deviation $\sigma(\varphi)$ of bond angle, which would occur when all three atoms have the same y coordinate, was calculated by Ahmed & Cruickshank's

Table 5. *Hydrogen bond lengths*

$O_1 \cdots O_2'$	2·69 Å	$O_3 \cdots O_5$	2·83 Å
$O_1 \cdots O_6$	2·91	$O_4 \cdots O_5$	2·80
$O_2 \cdots O_6'$	2·79	$O_4 \cdots O_6'$	2·74

(1953) method to be 0·7°; if the y parameters are largely involved it can rise to $\sigma_{max.} = 1·7°$. Six angles show significant or possibly significant variations $d\varphi$ from the tetrahedral angle. These are (with $d\varphi/\sigma_{max.}$ in brackets):

C_5–O_5–C_1, 120·1° (6·2); C_1–C_2–O_2, 103·8° (3·4); C_4–C_3–O_3, 114·2° (2·8); C_4–C_5–C_6, 114·2° (2·8); O_5–C_1–C_2, 113·0° (2·1); and C_2–C_3–O_3, 106·5° (1·8).

Consideration of the y coordinates involved shows that all these angles are significantly different from 109·5°, even when $d\varphi/\sigma_{max.} < 2·327$. The positions of the hydrogen atoms are not known with sufficient accuracy to make the calculation of C–H and O–H distances of any value.

The molecule is thus based on a Sachse–Mohr 'chair-shaped' pyranose ring with the angle at the oxygen atom 120°; in sucrose sodium bromide (Cochran, 1946) and glucose (MacDonald & Beevers, 1952) this angle was considered to be not significantly different from 109·5°. The significant variations in the angles involving the extra-cyclic atoms appear to indicate a repulsion between them which results in a tendency to move towards the empty spaces round O_5. The two axial C–O bonds in the molecule show possible significant deviations from 1·43, C_1–O_1 being short as in glucose.

There is some evidence that the assumed positions of the hydrogen atoms are correct, but it is hardly conclusive, particularly for those of the methyl group where it is felt that different orientations or oscillations of the group might be possible, and for those in the hydrogen bonds O_4–O_6, O_4–O_6' where the other set of positions might be occupied or a statistical distribution might occur. It should be emphasized that the hydrogen atoms in this structure were included on the basis of reasonable but not conclusive evidence primarily to ensure the proper refinement of the coordinates of the carbon and oxygen atoms, from which in many cases they are poorly resolved. The fact that the majority of them appear satisfactorily on the centric b-axis (F_o-F_c) projection is reasonably good evidence, but the non-centric c-axis projection needs to be treated with more caution. According to Cochran (private communication), if the phases of the heavy atoms alone are used, the hydrogen atoms should appear in the correct positions but with half their correct heights, and with an added random background. Fig. 3(*b*) shows the (F_o-F_c) map with the phases of carbon and oxygen atoms only, and Fig. 3(*c*) shows the map with the phases of the complete structure with the hydrogen atom contributions included in the calculation of the phases. The improvement in the appearance of the map when the complete phases are used is, as expected, striking.

The crystal structure is determined by a three-dimensional array of hydrogen bonds in which all the available hydrogen atoms are utilized and in which all the oxygen atoms take part. The water molecule forms four hydrogen bonds, which are arranged in a roughly tetrahedral configuration. The bond $O_1 \cdots O_6$ is unusually long; but one of length 2·93 Å, again linking a hydroxyl group and a water molecule, has been reported (Pitt, 1948).

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References

Ahmed, F. R. & Cruickshank, D. W. J. (1953). *Acta Cryst.* **6**, 385.
Andress, K. & Reinhardt, L. (1931). *Z. Kristallogr.* **78**, 477.
Beevers, C. A. & Robertson, J. H. (1950). *Acta Cryst.* **3**, 164.
Cochran, W. (1946). Thesis, University of Edinburgh.
Cochran, W. (1950). *Acta Cryst.* **3**, 268.
Cox, E. G. (1931). *J. Chem. Soc.* p. 2313.
Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 154.
Cruickshank, D. W. J. (1950). *Acta Cryst.* **3**, 72.
MacDonald, T. R. R. & Beevers, C. A. (1952). *Acta Cryst.* **5**, 654.
McGeachin, H. McD. (1954). *Publ. Dept. Crist. Min. Barcelona*, **1**, 145.
McGeachin, H. McD. (1956). Thesis, University of Edinburgh.
Pitt, G. J. (1948). *Acta Cryst.* **1**, 168.
Shoemaker, D. P., Barieau, R. E., Donohue, J. & Lu, C.-S. (1953). *Acta Cryst.* **6**, 241.