

The difference between the balance points achieved by KNbO_3 and BaTiO_3 is apparent from Table 4. Both substances have the same differences between long and short K–O(2) or Ba–O(2) bonds (KA and KC of Fig. 4). For BaTiO_3 , however, the difference between long and short Ba–O(1) bonds is 0.12 Å, and between long and short O(1)–O(2) edges is 0.04 Å, while for KNbO_3 the relative magnitudes are roughly interchanged, being 0.04 Å and 0.10 Å respectively. This supports the earlier suggestion that the K–O(1) links are already in compression and resistant to further compression. By contrast, either Ba is intrinsically smaller than K or it is more capable of polarizing the O atom to give unequal bonds; again, both causes may cooperate in the observed effect.

We put forward this qualitative treatment in the hope that it may direct attention to aspects of the structures where more rigorous treatment might lead to very profitable results.

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The Crystal Structure of α -L-Sorbose

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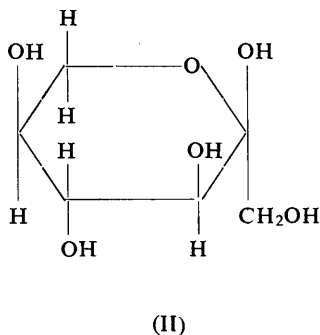
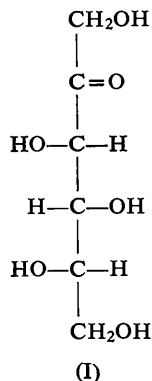
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The crystal structure of L-sorbose $\text{C}_6\text{H}_{12}\text{O}_6$ has been determined from the three-dimensional sharpened Patterson function by superposition and convolution methods on an IBM 1620 computer. Both photographic and automatic diffractometer data were measured. The former gave a final *R* index of 8.1% and the latter 5.1%. The space group is $P2_12_12_1$ with four molecules in a unit cell of dimensions $a = 6.535$ ($\sigma = 0.004$), $b = 18.069$ ($\sigma = 0.007$), $c = 6.305$ ($\sigma = 0.004$) Å. The molecules are the α -anomer of the pyranose form. They are associated in the crystal by extensive hydrogen-bonding, which includes all the hydroxyl groups and the ring oxygen atom. The primary alcohol group is disordered, and this leads to an apparent shortening of corresponding C–OH bonds. With the exception of these bonds, the C–C and C–O distances do not differ significantly from the mean values of 1.516 and 1.424 Å respectively.

Introduction

L-Sorbose ($\text{C}_6\text{H}_{12}\text{O}_6$, also called sorbinose) is found in the enzyme hydrolyzate of certain pectins. It is believed to exist in both the ketohexose (I) and the pyranose (II) forms.



As an important intermediate in the commercial synthesis of ascorbic acid, it is most conveniently obtained by the biochemical oxidation of sorbitol (Bertrand, 1898; Wells, Stubbs, Lockwood & Roe, 1937). Hudson (1925) suggested, on the basis of the calculation of the specific rotation, that the common form is the α -anomer of the pyranose (II) which is confirmed by this work. The conventional numbering of the carbon and oxygen atoms used in this paper is shown in Fig. 1.

Crystal data

Large transparent crystals were obtained by slow evaporation of an aqueous solution of the compound supplied by Pfanstiehl Laboratories, Inc. The cell parameters were measured at 22°C with $\text{Cu } K\alpha_1$ and $\text{Cu } K\alpha_2$ radiation using a Picker 4-angle automatic diffractometer. The crystal density was measured by flotation in a liquid mixture of carbon tetrachloride, chloroform and bromoform.

α -L-Sorbose, $C_6H_{12}O_6$, M.W. 180.16

Orthorhombic, space group $P2_12_12_1$ from the systematic absences for $h00$, $0k0$ and $00l$, when h , k or $l = 2n + 1$.

$a = 6.535$ ($\sigma = 0.004$) Å

$b = 18.069$ ($\sigma = 0.007$)

$c = 6.305$ ($\sigma = 0.004$)

$Z = 4$

$D_m(23^\circ C) = 1.607$ ($\sigma = 0.003$) $g \cdot cm^{-3}$

$D_x(22^\circ C) = 1.607$ $g \cdot cm^{-3}$

$\mu(Cu K\alpha) = 12.85$ cm^{-1} .

The corresponding cell parameters reported by Cox, Goodwin & Wagstaff (1935) were 6.51, 18.01 and 6.26 Å respectively.

Experimental

The photographic data were recorded on four layers of multiple-film equi-inclination Weissenberg photographs about both the a and c axes with $Cu K\alpha$ radiation. The crystals used were approximately cylindrical with mean diameters of 0.30 and 0.25 mm for the a and c axes respectively. Of the 1030 theoretically possible, 881 symmetry independent reflections (87%) were recorded and estimated visually by comparison with a standard scale. No absorption corrections were made. The intensities were correlated and reduced to the structure amplitudes with an IBM 7090 program (Shiono, 1966a) which uses the procedure by Hamilton, Rollett & Sparks (1965).

After the structure was solved, a Picker 4-angle automatic diffractometer became available and a sec-

ond set of data was collected using an approximately square prismatic crystal of $0.3 \times 0.3 \times 0.5$ mm. A $\theta/2\theta$ scanning mode over 2° was used to measure 804 independent reflections with 2θ values below 130° . Background measurements were made at both ends of the 2° scan range of each peak. The same number of equivalent reflections were measured in a different octant of the reciprocal lattice, and the conventional R index between the two sets of diffractometer data was 0.06. However, the reference reflections, which were repeated every hour, were significantly more constant for one set and these data were used in the refinement rather than the mean values. No absorption corrections were applied in reducing to structure amplitudes.

Determination of the structure

The orientation of the pyranose ring in the structure was found by inspection of the three-dimensional ($E^2 - 1$) Patterson synthesis. From consideration of this orientation, a sharp peak in the Patterson synthesis was chosen, which proved to be a C(6)–O(2) vector (see Fig. 1). With this as the initial vector, the Harker peaks for C(6) and O(2) and their related vector set were identified, and the coordinates of C(6) and O(2) were thereby obtained. The relationship between this vector set and the Harker peaks in two-dimensions is shown in Fig. 2. These two atomic positions and their symmetry ($P2_12_12_1$) related positions were used to calculate an M_8 multiple minimum function (Buerger, 1959). Since the resulting function contained too many peaks for the structure to be uniquely recognized, it was convoluted with the original sharpened Patterson function. The structure was recognized in the resulting function which showed all the atomic peaks except those for hydrogen atoms, and in addition, two spurious peaks. Instead of using Fourier methods, the convolution $\widehat{PM}(\mathbf{r})$ was computed. The result is

$$\widehat{PM}(\mathbf{r}) = \sum_{\mathbf{r}'} P(\mathbf{r}') \cdot (M(\mathbf{r} + \mathbf{r}')),$$

where $P(\mathbf{r})$ represents the value of the Patterson function at point \mathbf{r} , and $M(\mathbf{r})$ the value of the M_8 function at \mathbf{r} , $\widehat{PM}(\mathbf{r})$ being calculated at various points \mathbf{r} in the cell. Only positive values of the two functions were included in the summation. All the above calculations were performed with an IBM 1620 program prepared by Corfield (1965). The first structure factor calculation for six carbon and six oxygen atoms gave an R value of 0.33 for all observed reflections. These parameters were refined isotropically with one scale factor using the Busing–Martin–Levy (1962) full-matrix least-squares IBM 7090 program until $R = 0.18$. The three-dimensional Fourier and difference Fourier syntheses then revealed an additional peak of about 2.5 e at an alternate position for the oxygen atom of the primary alcohol group, O(1). In addition, the peak on the Fourier synthesis at the original position for O(1) was about 25% lower than for the other oxygen atoms.

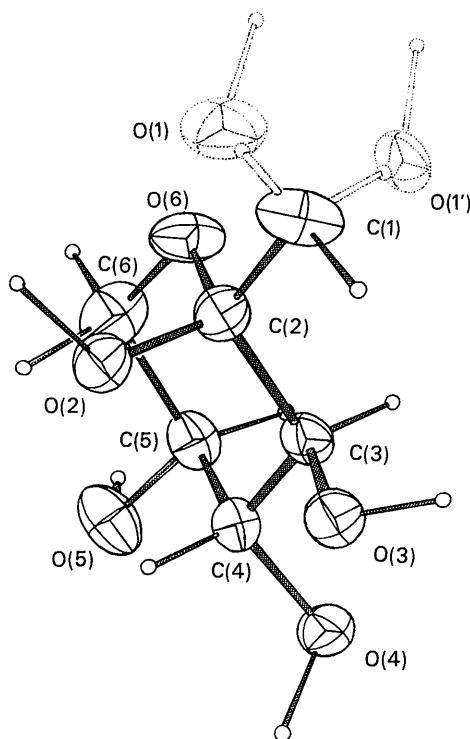


Fig. 1. Identification and numbering of the atoms in the molecule. Dotted ellipsoids represent the disordered atoms.

Interchanging the coordinates for O(1), and recalculating the Fourier syntheses did not eliminate the original peak, and therefore it was assumed that O(1) was disordered over these two stereochemically feasible positions. With fixed occupancy factor of 0.5 for O(1) and O(1'), the *R* value dropped from 0.18 to 0.13 in one cycle of the least-squares isotropic refinement. The significance test of Hamilton (1965) showed that the hypothesis that O(1) is ordered could be rejected at the significance level of 0.5%.

Refinement of the structure

The refinement of the positional parameters, the anisotropic thermal parameters, the occupancy factors for O(1) and O(1'), and one scale factor was carried out by Shiono's (1966*b*) version of the Busing, Martin & Levy (1962) full-matrix least-squares IBM 7090 program. All the unobserved reflections and four very strong low-order reflections were excluded from both the photographic and diffractometer data. Cruickshank's (1961) weighting scheme was used for both sets of data. The final *R* values of 0.081 and 0.051 were obtained for the photographic and diffractometer data respectively. Only those hydrogen atoms that are

bonded to the ring carbon atoms were located on the difference synthesis using the photographic data, but with the diffractometer data, all the hydrogen atoms, except those on the disordered O(1') and C(1), were clearly revealed at reasonable locations with respect to the carbon and oxygen atoms. Their positional parameters were not refined and they were assigned the

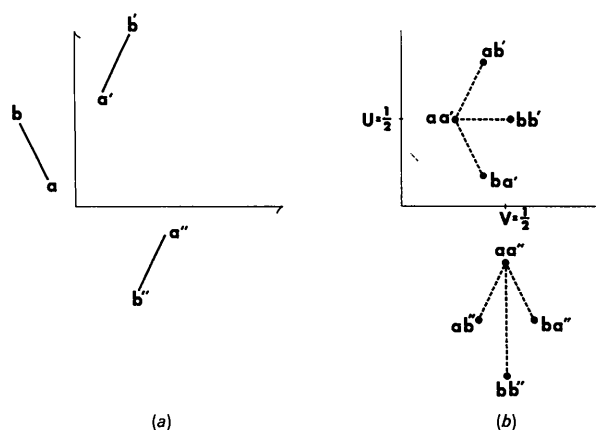


Fig. 2. (a) Two independent atoms in *pgg*. (b) Their corresponding Patterson vectors.

Table 1. Fractional atomic coordinates in α -L-sorbose

The estimated standard deviations are given in parentheses, and refer to the last decimal positions of respective values.

	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy		<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
C(1)	0.5335 (7)	0.1629 (3)	0.5202 (7)	1.0	H(C1-1)	0.628	0.194	0.408	1.0
C(2)	0.3938 (7)	0.1204 (2)	0.3722 (6)	1.0	*H(C1-2)	0.609	0.132	0.625	0.37
C(3)	0.3341 (5)	0.1662 (2)	0.1782 (6)	1.0	*H(C1-2')	0.473	0.208	0.589	0.63
C(4)	0.1761 (6)	0.1274 (2)	0.0430 (6)	1.0	H(C3)	0.268	0.213	0.234	1.0
C(5)	-0.0059 (6)	0.1049 (2)	0.1771 (6)	1.0	H(C4)	0.260	0.080	-0.023	1.0
C(6)	0.0633 (7)	0.0622 (2)	0.3707 (8)	1.0	H(C5)	-0.112	0.155	0.220	1.0
O(1)	0.6321 (11)	0.1218 (3)	0.6580 (9)	0.63 (2)	H(C6-1)	0.130	0.013	0.290	1.0
O(1')	0.4584 (15)	0.2188 (4)	0.6051 (13)	0.37 (1)	H(C6-2)	-0.045	0.040	0.470	1.0
O(2)	0.4899 (4)	0.0553 (1)	0.2973 (5)	1.0	H(O1)	0.620	0.140	0.825	1.0
O(3)	0.5111 (5)	0.1809 (1)	0.0518 (4)	1.0	H(O2)	0.510	0.010	0.420	1.0
O(4)	0.1132 (5)	0.1761 (1)	-0.1229 (4)	1.0	H(O3)	0.525	0.240	0.080	1.0
O(5)	-0.1367 (4)	0.0592 (1)	0.0521 (5)	1.0	H(O4)	0.110	0.152	-0.282	1.0
O(6)	0.2154 (4)	0.1022 (2)	0.4898 (4)	1.0	H(O5)	-0.295	0.064	0.118	1.0

* The coordinates of these two hydrogen atoms are calculated from the geometry.

Table 2. Anisotropic thermal parameters in α -L-sorbose

The temperature factor expression used was
 $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$

The estimated standard deviations in parentheses refer to the last decimal position of respective values.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0170 (11)	0.0047 (2)	0.0161 (10)	-0.0016 (4)	0.0010 (11)	-0.0019 (4)
C(2)	0.0158 (9)	0.0021 (1)	0.0161 (9)	-0.0009 (3)	0.0042 (9)	0.0003 (3)
C(3)	0.0143 (9)	0.0018 (1)	0.0136 (9)	0.0000 (2)	0.0051 (8)	-0.0008 (3)
C(4)	0.0163 (9)	0.0015 (1)	0.0149 (9)	0.0004 (2)	0.0004 (8)	-0.0003 (2)
C(5)	0.0142 (8)	0.0017 (1)	0.0178 (9)	0.0002 (3)	0.0010 (9)	-0.0009 (3)
C(6)	0.0166 (9)	0.0028 (1)	0.0220 (12)	-0.0014 (3)	-0.0027 (10)	0.0016 (3)
O(1)	0.0295 (17)	0.0045 (2)	0.0186 (14)	0.0022 (6)	-0.0078 (16)	-0.0004 (5)
O(1')	0.0227 (25)	0.0019 (2)	0.0189 (21)	-0.0003 (6)	0.0096 (22)	-0.0015 (6)
O(2)	0.0176 (6)	0.0021 (1)	0.0177 (7)	0.0006 (2)	-0.0022 (7)	0.0002 (2)
O(3)	0.0176 (7)	0.0023 (1)	0.0180 (7)	-0.0014 (2)	0.0077 (7)	-0.0004 (2)
O(4)	0.0248 (8)	0.0021 (1)	0.0138 (6)	0.0022 (2)	-0.0014 (7)	0.0003 (2)
O(5)	0.0150 (6)	0.0025 (1)	0.0257 (9)	-0.0001 (2)	-0.0032 (7)	-0.0030 (2)
O(6)	0.0165 (7)	0.0035 (1)	0.0121 (6)	-0.0020 (2)	0.0024 (6)	0.0000 (2)

served in the glucopyranose and fructofuranose rings in sucrose (Brown & Levy, 1963) (see Table 6).

The carbon valence angles inside the ring range from 109.5 to 112.1° with the mean value of 110.9° and those outside the ring range from 107.2 to 111.9° with the mean value of 109.6°. The valence angle of the ring oxygen atom is close to 115° as is commonly observed in pyranose rings (*cf.* Jeffrey & Rosenstein, 1964). The conformation angles fall well within the range observed in other sugars (see Table 6 of Kim & Jeffrey, 1967).

The molecules are associated in the crystal by a very extensive hydrogen bonding, as shown in Fig. 3, with the distances and angles given in Table 7. All the hy-

droxyl groups participate in the hydrogen bonding, both as donor and as acceptor, except the disordered atom O(1), O(1'), which is a donor only. The ring oxygen atom O(6) is also involved as a hydrogen-bond acceptor. The hydrogen bonding forms two unconnected systems. One is a continuous chain spiraling throughout the structure in the direction of the *c* axis, *i.e.* $\rightarrow\text{O}(2, c)\rightarrow\text{O}(5, b)\rightarrow\text{O}(2, h)\rightarrow\text{O}(5, e)\rightarrow\text{O}(2)\dots\dots$ (where \rightarrow indicates the donor direction, and the small letter refers to the symmetry operations given in Table 7). The other one consists of discontinuous fragments involving three hydrogen bonds, *i.e.* O(1, *c*) or O(1', *c*) \rightarrow O(3) \rightarrow O(4, *d*) \rightarrow O(6, *i*). These three hydrogen bonds lie approximately in one plane.

Table 4. *Principal axes of thermal ellipsoids*

The root mean square displacement U_i corresponds to the *i*th principal axis of the ellipsoid and $\theta_{ia}, \theta_{ib}, \theta_{ic}$ are angles between the *i*th axis and the crystallographic axes *a, b, c*.

	<i>i</i>	B_i^*	U_i^\dagger	θ_{ia}	θ_{ib}	θ_{ic}
C(1)	1	2.369 Å ²	0.1732 (0.1749) Å	89.9°	77.3°	12.7°
	2	2.740	0.1863 (0.2100)	167.7	102.0	87.2
	3	6.508	0.2871 (0.2811)	102.3	17.6	102.4
C(2)	1	1.774	0.1499 (0.1523)	48.9	66.8	130.0
	2	2.767	0.1872 (0.1869)	90.2	148.4	121.6
	3	3.413	0.2079 (0.2045)	138.9	69.7	123.9
C(3)	1	1.365	0.1315 (0.1408)	126.1	73.1	41.1
	2	2.328	0.1717 (0.1663)	112.3	157.5	86.6
	3	3.225	0.2021 (0.2070)	44.5	104.5	49.1
C(4)	1	1.824	0.1520 (0.1583)	101.3	18.8	75.2
	2	2.404	0.1745 (0.1700)	88.1	74.5	164.4
	3	2.814	0.1888 (0.2080)	11.4	79.7	85.2
C(5)	1	1.966	0.1578 (0.1584)	111.4	36.5	62.0
	2	2.488	0.1775 (0.1938)	156.7	113.2	92.2
	3	3.074	0.1973 (0.2058)	98.8	63.6	151.9
C(6)	1	2.476	0.1771 (0.1663)	26.4	64.1	85.4
	2	2.893	0.1914 (0.1971)	78.5	123.7	36.1
	3	4.689	0.2437 (0.2434)	113.4	44.9	54.3
O(1)	1	2.322	0.1715 (0.1452)	63.3	94.9	27.3
	2	4.743	0.2452 (0.2576)	50.5	131.9	112.7
	3	6.701	0.2924 (0.2830)	51.1	42.4	104.2
O(1')	1	1.539	0.1396 (0.1476)	118.6	62.0	42.1
	2	2.656	0.1834 (0.2069)	115.8	149.4	74.7
	3	5.195	0.2565 (0.2234)	40.3	101.4	52.0
O(2)	1	2.358	0.1728 (0.1767)	125.3	54.2	124.7
	2	2.838	0.1896 (0.1977)	96.5	138.4	130.9
	3	3.344	0.2058 (0.2185)	36.1	71.7	119.9
O(3)	1	1.581	0.1415 (0.1595)	45.4	76.6	132.3
	2	2.871	0.1907 (0.1928)	96.9	153.2	115.7
	3	4.495	0.2376 (0.2420)	134.6	67.3	126.8
O(4)	1	1.951	0.1572 (0.1637)	110.2	52.4	135.5
	2	2.415	0.1749 (0.1904)	73.5	131.0	134.4
	3	4.766	0.2457 (0.2371)	26.6	63.7	93.1
O(5)	1	2.001	0.1592 (0.1779)	55.4	52.2	56.7
	2	2.761	0.1870 (0.1855)	36.0	122.4	103.8
	3	5.170	0.2559 (0.2531)	81.5	54.6	143.2
O(6)	1	1.732	0.1481 (0.1655)	116.3	98.0	27.6
	2	2.607	0.1817 (0.1903)	143.6	112.0	117.4
	3	4.998	0.2516 (0.2581)	113.3	23.6	93.1

* $B_i = 8\pi^2 U_i^2$.

† The values in parentheses are U_i values calculated from the photographic data.

The disordered atom

The observation that the O(1) hydroxyl group is disordered is unusual in a hydrogen-bonded structure. Even more unexpected were the unequal occupancy factors. Therefore alternative interpretations were considered, although they were inherently less plausible than disorder.

The only possibility in accord with the observed density and occupancy factors would be a 40% impurity of a hitherto unknown oxidation product of sorbose, the aldehyde (III). Moreover, if the aldehyde oxygen were in position O(1'), both the abnormally short C–O distance and the non-appearance of the hydroxyl hydrogen atom would have a natural explanation. However, the infrared spectra of the original

crystalline sample and of the recrystallized material showed no indication of the characteristic absorption

associated with the aldehyde ($\text{C}=\text{O}$) group in carbohydrate compounds (Neely, 1957; Spedding, 1964). Hence, at the concentration assumed, this suggestion is untenable.

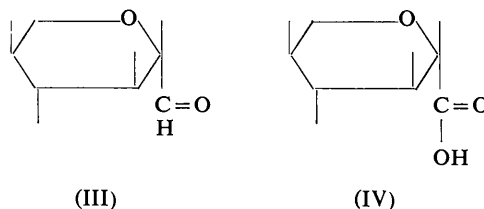


Table 5. Bond lengths and angles

The estimated standard deviations are given in parentheses, and refer to the last decimal positions of respective values.

<i>i</i>	<i>j</i>	<i>D</i> (<i>ij</i>)	<i>i</i>	<i>j</i>	<i>k</i>	Angle
		\AA				(<i>ijk</i>)
C(1)	C(2)	1.515 (6)	C(2)	C(1)	O(1)	114.7 (5)°
C(2)	C(3)	1.527 (5)	C(2)	C(1)	O(1')	116.0 (5)
C(3)	C(4)	1.511 (5)	O(1)	C(1)	O(1')	111.6 (6)
C(4)	C(5)	1.515 (5)	C(1)	C(2)	C(3)	111.9 (3)
C(5)	C(6)	1.513 (6)	C(1)	C(2)	O(2)	111.1 (3)
C(6)	O(6)	1.440 (5)	C(1)	C(2)	O(6)	106.9 (3)
O(6)	C(2)	1.420 (5)	C(3)	C(2)	O(2)	107.2 (3)
C(1)	O(1)	1.312 (10)*	C(3)	C(2)	O(6)	109.5 (3)
C(1)	O(1')	1.244 (8)*	O(2)	C(2)	O(6)	110.2 (3)
C(2)	O(2)	1.415 (5)	C(2)	C(3)	C(4)	112.1 (3)
C(3)	O(3)	1.429 (5)	C(2)	C(3)	O(3)	109.9 (3)
C(4)	O(4)	1.427 (5)	C(4)	C(3)	O(3)	108.9 (3)
C(5)	O(5)	1.426 (5)	C(3)	C(4)	C(5)	110.3 (3)
			C(3)	C(4)	O(4)	108.9 (3)
			C(5)	C(4)	O(4)	110.4 (3)
			C(4)	C(5)	C(6)	110.7 (3)
			C(4)	C(5)	O(5)	108.5 (3)
			C(6)	C(5)	O(5)	109.2 (3)
			C(5)	C(6)	O(6)	111.8 (3)
			C(6)	O(6)	C(2)	114.2 (3)

* Apparent distances due to disordered atom O(1).

Table 6. Bond lengths and angles in some pyranose carbohydrates

Bond lengths (\AA)	C–C		C–OH*		C–O (ring)	C(1)–OH	Δ †	Reference
	Range	Mean	Range	Mean				
Sucrose	1.520–1.534	1.525	1.413–1.423	1.418	1.408, 1.436			Brown & Levy (1963)
α -D-Glucose	1.511–1.535	1.524	1.414–1.426	1.418	1.427, 1.428	1.391	10 σ	Brown & Levy (1965)
β -D-Glucose	1.512–1.544	1.527	1.442–1.450	1.446	1.437, 1.455	1.404	4 σ	Ferrier (1963)
L-Sorbose	1.511–1.527	1.516	1.415–1.429	1.424	1.420, 1.440			This paper
D, L-Arabinose	1.518–1.535	1.528	1.415–1.428	1.423	1.438, 1.444	1.392	7 σ	Kim & Jeffrey (1967)
β -Arabinose	1.523–1.554	1.535	1.426–1.454	1.437	1.421, 1.440	1.382	4 σ	Hordvik (1961)

* Excluding short C(1)–OH, where observed.

† Δ is the difference between average C–OH and C(1)–OH distances and σ is the estimated standard deviation of the difference.

Valence and conformation angles (°)

	C (inside the ring)*		C (outside the ring)*		O (ring)	Reference
	Range	Mean	Range	Mean		
Sucrose						
(pyranose part)	108.2–111.2	110.3	106.1–112.5	109.8	116.1	Brown & Levy (1963)
α -D-Glucose	108.7–111.1	110.2	108.3–112.3	110.3	113.7	Brown & Levy (1965)
						(private communication)
β -D-Glucose	107.2–110.9	109.4	107.3–115.5	109.2	113.1	Ferrier (1963)
L-Sorbose	109.5–112.1	110.9	107.2–111.9	109.6	114.2	This paper
D, L-Arabinose	109.0–111.4	108.3	108.3–112.9	111.3	113.2	Kim & Jeffrey (1967)
β -Arabinose	107.1–111.9	109.5	107.3–113.1	109.9	112.7	Hordvik (1961)

* Angles involving hydrogen atoms are excluded.

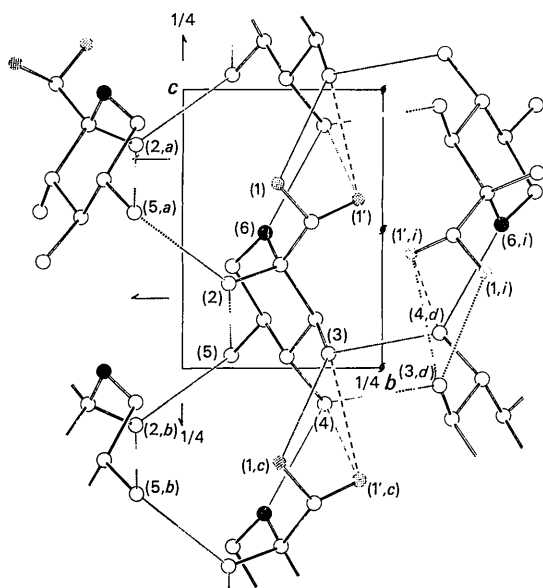


Fig. 3. The crystal structure viewed along the a axis. Dotted lines represent hydrogen bonds. Shaded circles represent ring oxygen atoms. Cross-hatched circles represent the disordered hydroxyl oxygen atoms. Numbers and alphabetic symbols are identification numbers and symmetry codes of oxygen atoms respectively.

In fact, the characteristic absorptions of the keto (>C=O) and carboxy (>C(=O)O^-) groups were also

absent. This in itself would exclude the hypothetical acid (IV) without even taking the density into consideration. In addition, the agreement could not be improved by least squares below $R=0.15$ without reducing the occupancy of both O(1) and O(1').

The density and occupancy also rule out the possibility of a disordered partial water of hydration,* but even more convincing is the behavior of the positional parameters during the course of the refinement. The partial oxygen atoms spontaneously appeared close to the carbon atom C(1) in (q_o-q_c) syntheses and neither oxygen atom showed any tendency during least-squares cycles to shift away to a distance more in conformity with a hydrogen bond or a van der Waals contact.

It appears therefore that the disorder is real and the environment of O(1) and O(1') is such as to be consistent with two alternate hydrogen-bonding schemes, one of which has energetically more favorable stereo-

* Suggested by a referee. It is conceivable that a hydrate could be prepared at low temperatures.

Table 7. Intermolecular distances and angles in α -L-sorbose

(i) Hydrogen-bonds except those involving the disordered atoms O(1) and O(1').

i	j	k	$D(jk)$	Angle ijk
C(2)	O(2)	O(5, a)*	2.890 Å	122.2°
C(3)	O(3)	O(4, d)	2.705	106.5
C(4)	O(4)	O(6, c)	2.863	105.7
C(5, e)	O(5, e)	O(2)	2.890	103.0

* See symmetry code (iv) below.

(ii) Non-bonded distance less than 3.3 Å between carbon and oxygen atoms excluding the disordered atoms.

i	j	$D(ij)$
O(3)	O(5, e)	3.183 Å

(iii) Distances and angles related to the disordered atom.

i	j	k	jk	Angle ijk	Remarks
C(1, c)	O(1, c)	O(3)	2.815 Å	103.4°	Hydrogen bond†
C(1, c)	O(1, c)	O(5, e)	3.121	166.0	Non-bonded contact
C(1, c)	O(1', c)	O(3)	2.919	100.2	‡
C(1, c)	O(1', c)	O(4, e)	2.937	109.9	‡

† H(O1) was found along the bond from the difference synthesis.

‡ H(O1') was not found, probably owing to the low occupancy of the atom.

(iv) Symmetry code

—	x	y	z
a	$0.5-x$	$-y$	$0.5+z$
b	$0.5-x$	$-y$	$-0.5+z$
c	x	y	$-1.0+z$
d	$0.5+x$	$0.5-y$	$-z$
e	$1.0+x$	y	z
f	$-0.5+x$	$0.5-y$	$-z$
g	$1.5-x$	$-y$	$0.5+z$
h	$1.5-x$	$-y$	$-0.5+z$
i	$1.5+x$	$0.5-y$	$-z$

chemistry than the other. The environment of the disorder atom sites is given in Table 7. O(1) has two oxygen atoms, O(3) and O(5), at the distances of 2.815 and 3.121 Å respectively. A hydrogen atom was located along the line of O(1)···O(3), so presumably this is the hydrogen bond and the other distance is a non-bonded O···O contact. O(1') has similar environment with O(3) and O(4) at the distances of 2.919 and 2.937 Å respectively. Owing to the lower occupancy factor of O(1'), the attached hydrogen atom was not located from the difference synthesis, but both O···O distances and their angles with C(1)–O(1') bond are consistent with the formation of one weak hydrogen bond or a bifurcated bond. We suggest with caution therefore, that the occupancy factors represent the probability of two alternate positions for the primary hydroxyl group, which correspond to the hydrogen-bonding situations of nearly but not exactly equal contribution to the lattice energy.

The bond distances involving the disordered atom, C(1)–O(1), C(1)–O(1'), appear abnormally short. This is likely to be caused by two effects which cannot be distinguished; (i) the statistical overlap of the electron density of the oxygen O(1), O(1') with the two hydrogen atoms attached to C(1) in the two disordered positions (Fig. 4, top), and (ii) a correlation of thermal displacements between C(1) and O(1), O(1'), (Fig. 4, bottom), which has similar effect to the antiparallel displacement of thermal motion, as described by Busing & Levy (1964). The larger than normal valence angles involving the disordered atoms and the eccentricity of the thermal ellipsoid of C(1) are also likely to be artifacts resulting from the superimposed electron density distributions.

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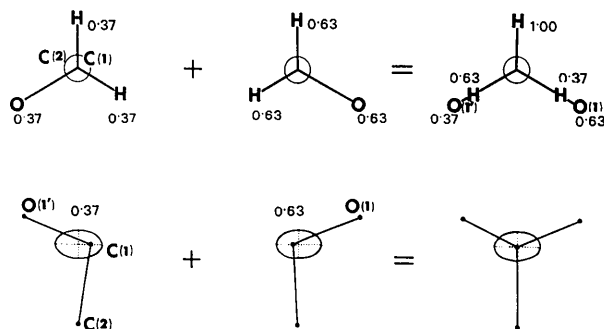


Fig. 4. (top) The statistical overlapping of the electron densities of oxygen and hydrogen atoms. (bottom) The correlation of thermal displacements between C(1) and O(1), O(1'). Fractional numbers are occupancies of atoms.

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