

The difference between the balance points achieved by  $\text{KNbO}_3$  and  $\text{BaTiO}_3$  is apparent from Table 4. Both substances have the same differences between long and short  $\text{K}-\text{O}(2)$  or  $\text{Ba}-\text{O}(2)$  bonds ( $K_A$  and  $K_C$  of Fig. 4). For  $\text{BaTiO}_3$ , however, the difference between long and short  $\text{Ba}-\text{O}(1)$  bonds is  $0.12 \text{ \AA}$ , and between long and short  $\text{O}(1)-\text{O}(2)$  edges is  $0.04 \text{ \AA}$ , while for  $\text{KNbO}_3$  the relative magnitudes are roughly interchanged, being  $0.04 \text{ \AA}$  and  $0.10 \text{ \AA}$  respectively. This supports the earlier suggestion that the  $\text{K}-\text{O}(1)$  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.

We wish to express our indebtedness to Dr R. Ueda for his collaboration in the first part of the work. One of us (L.K.) is grateful for a National Science Foundation Science Faculty Fellowship.

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## The Crystal Structure of $\alpha$ -L-Sorbose

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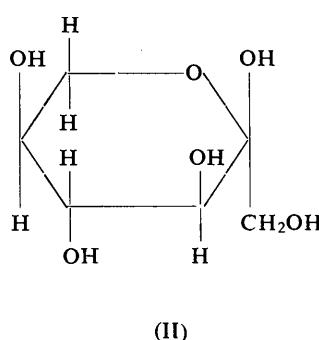
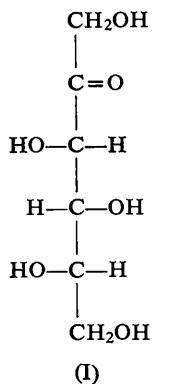
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(Received 25 July 1966)

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  $P2_{1}2_{1}2_{1}$  with four molecules in a unit cell of dimensions  $a=6.535$  ( $\sigma=0.004$ ),  $b=18.069$  ( $\sigma=0.007$ ),  $c=6.305$  ( $\sigma=0.004$ )  $\text{\AA}$ . The molecules are the  $\alpha$ -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  $1.424 \text{ \AA}$  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  $\alpha$ -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 Pfanziehl Laboratories, Inc. The cell parameters were measured at  $22^\circ\text{C}$  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.

$\alpha$ -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  $l=2n+1$ .

$$a = 6\cdot535 (\sigma=0\cdot004) \text{ \AA}$$

$$b = 18\cdot069 (\sigma=0\cdot007)$$

$$c = 6\cdot305 (\sigma=0\cdot004)$$

$$Z=4$$

$$D_m(23^\circ\text{C}) = 1\cdot607 (\sigma=0\cdot003) \text{ g.cm}^{-3}$$

$$D_x(22^\circ\text{C}) = 1\cdot607 \text{ g.cm}^{-3}$$

$$\mu(\text{Cu } K\alpha) = 12\cdot85 \text{ cm}^{-1}$$

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-

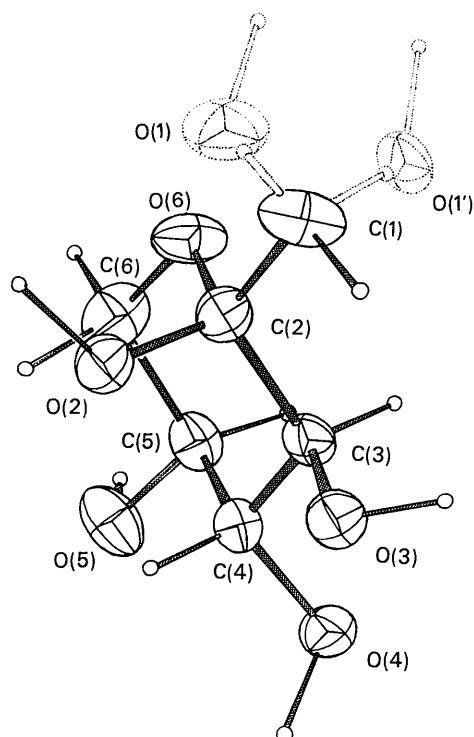


Fig. 1. Identification and numbering of the atoms in the molecule. Dotted ellipsoids represent the disordered atoms.

ond set of data was collected using an approximately square prismatic crystal of  $0\cdot3 \times 0\cdot3 \times 0\cdot5$  mm. A  $\theta/2\theta$  scanning mode over  $2^\circ$  was used to measure 804 independent reflections with  $2\theta$  values below  $130^\circ$ . Background measurements were made at both ends of the  $2^\circ$  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  $R=0\cdot18$ . 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.

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 (1966b) 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

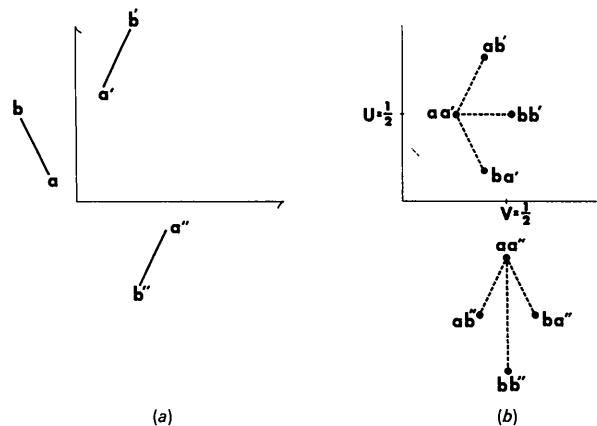


Fig. 2. (a) Two independent atoms in *pgg*. (b) Their corresponding Patterson vectors.

Table 1. Fractional atomic coordinates in  $\alpha$ -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  $\alpha$ -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.

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
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)

Table 3. Observed and calculated structure factors

Columns are: Index,  $|F_{\text{obs}}|$ ,  $|F_{\text{cal}}|$ ,  $A_{\text{cal}}$ ,  $B_{\text{cal}}$ .

(\* for unobserved reflections; † for reflections excluded in the least-squares refinement)

L= 0 H= 0	7 92 93 0 93-	1 198 188 182- 45	0 149 132 0 132-	1 28 23 5- 22
2 68 74 74 0	8 18 15 15 0	2 309 316 214 232	1 276 280 279 28	2 29 24 23 9-
4 647+1088 1088- 0	9 32 26 0 26	3 163 147 126 77-	2 374 364 224- 287-	3 86 85 38- 76-
6 48 54 54 0	10 29 23 23 0	4 94 79 30- 73	3 359 380 379- 37-	4 63 64 9 64
8 394 408 408- 0	11 45 35 0 35	5 138 134 74 112	4 344 343 342- 23-	5 27 27 27 4
10 101 99 99- 0	12 18 25 25- 0	6 226 234 10- 234-	5 158 137 19- 135-	6 38 32 3- 32-
12 39 33 33- 0	13 32 34 0 34-	7 199 202 48 196	6 213 221 84- 204	7 45 47 43 18
14 182 196 196- 0	14 70 65 65 0	8 47 56 36- 42-	7 188 188 150 112-	8 38 33 2- ?
16 181 198 198- 0	15 55 57 0 57	9 152 152 125- 87-	8 149 148 23 147	9 25 21 19- .
18 244 251 251- 0	16 3* 1 1- 0	10 200 207 116- 171-	9 191 189 95- 163-	10 35 38 21- 32
20 62 62 62- 0	L= 6 H= 0	11 103 102 51- 89-	10 115 103 46 92	11 82 88 29- 83
L= 1 H= 0	0 151 151 0 151	12 117 124 75 98-	11 140 126 29 122	L= 7 H= 2
1 133 139 0 139	1 122 119 0 119	13 143 156 153 30	12 42 41 3- 41-	0 16 6 0 6-
2 446+ 607 607- 0	2 27 25 25 0	14 155 158 77 138	13 197 204 47- 199	1 12* 8 8 0
3 213 207 0 207-	3 178 187 0 187-	15 44 44 44 5-	14 110 115 101 56-	2 22 15 14 5-
4 445+ 551 551- 0	4 149 148 148- 0	16 71 67 66- 8-	15 77 76 56- 51-	3 55 61 18 58
5 155 146 0 146-	5 29 24 0 24	17 51 62 52- 33-	16 60 62 57 24	4 10* 8 0 8
6 173 181 181- 0	6 18 20 20- 0	18 47 47 19- 43	17 72 74 71 19-	5 5* 35 13 33
7 390 431 0 431	7 63 62 0 62	19 16 15- 5	18 40 41 5- 41-	L= 0 H= 3
8 58 42 42- 0	8 48 42 42 0	L= 4 H= 1	19 43 43 8 42-	1 77 68 0 68-
9 122 113 0 113-	9 68 74 0 74	0 61 68 68 0	20 80 79 17- 77-	2 357 336 0 336-
10 71 73 73 0	10 36 33 33 0	1 137 149 144 36	L= 2 H= 2	3 19 14 0 14
11 140 155 0 155-	11 47 47 0 47	2 62 60 13 58-	0 181 149 149- 0	4 27 9 0 9
12 95 82 82 0	12 34 30 30 0	3 37 31 12 28	1 197 189 131- 137-	5 182 166 0 166
13 64 60 0 60	13 3* 21 0 21-	4 60 59 22 55	2 376 377 369- 76	6 326 327 0 327-
14 108 114 114- 0	L= 7 H= 0	5 145 150 12 150-	3 184 181 21 180-	7 21 23 0 23-
15 119 123 0 123-	1 72 69 0 69-	6 139 141 16 140-	4 189 181 162 81-	8 95 97 0 97-
16 101 101 101 0	2 115 114 114- 0	7 65 60 59 11	5 267 259 245 82	9 75 72 0 72-
17 78 83 0 83	3 76 74 0 74	10 181 184 136- 124-	6 499 534 396 357	10 129 132 0 132
18 15* 1 1- 0	4 37 34 34 0	9 160 163 81- 142	12 60 58 56 56	11 31 34 0 34-
19 39 39 0 39	5 38 36 0 36	10 178 192 43- 187	8 163 149 108- 103	12 56 56 0 56
20 80 81 81- 0	6 29 25 25- 0	11 19 14 4 4	13 9 183 172 29-	170 13 8* 7 0
21 67 63 0 63-	7 55 54 0 54	12 91 90 90 0	10 272 274 34- 272-	14 127 126 0 126
L= 2 H= 0	L= 0 H= 1	13 59 60 54 26-	11 133 123 39- 117	15 33 31 0 31
0 376+ 449 449 0	1 363 383 0 383	14 28 25 16- 20-	12 118 121 115 37-	16 35 34 0 34
1 10* 9 9 0	2 206 210 0 210	15 36 41 40- 9-	13 84 87 80- 33-	17 60 58 0 58
2 118 119 0 119-	3 482 531 0 531	16 51 57 32- 47	14 72 72 6- 72	18 75 77 0 77-
3 267 265 0 265-	4 476 531 0 531	17 57 58 34- 46-	15 80 78 4 78-	19 18 19 0 19-
4 213 198 198- 0	5 79 87 0 87-	18 3* 41 41 6-	16 61 60 14- 58-	L= 1 H= 3
5 13 11 0 11-	6 145 122 0 122-	19 54 26- 29-	17 53 52 22 47-	0 13 10 0 10-
6 16 16 16 0	7 131 134 0 134	20 15* 4 0 4	4 18 35 33 31-	1 139 121 112- 45
7 73 66 0 66	8 145 138 0 138-	21 24 23 7 20	5 219 206 203 37-	2 219 206 37- 203-
8 54 43 43- 0	9 149 135 0 135	22 3* 64 57- 28	3 213 203 86 184-	4 180 177 149 94-
9 154 140 0 140	10 41 32 0 32	23 3 85 91 77 48	4 16 61 60 14- 58-	L= 1 H= 3
10 99 100 100 0	11 140 138 0 138	24 4 46 44 33 29-	17 53 52 22 47-	0 13 10 0 10-
11 31 30 0 30-	12 31 27 0 27	25 5 91 99 84- 52	1 123 132 78 106	6 158 145 116 67
12 38 38 38 0	13 60 60 0 60-	26 6 36 32 16- 27	2 61 51 51 1-	7 113 107 21 105
13 7* 11 0 11	14 22 19 0 19	27 7 59 64 57- 29	3 86 91 3 91	8 63 53 53 53
14 36 31 31- 0	15 89 89 0 89	28 8 63 67 62- 25	4 122 120 120 7-	9 133 127 112 60-
15 56 56 0 56-	16 34 26 0 26	29 9 61 60 60- 0	5 148 146 10 146	10 131 127 49 118
16 53 54 54 0	17 49 49 0 49	30 10 58 61 19- 58-	6 34 37 8- 36	11 49 43 33 28-
17 41 40 0 40-	18 22 18 0 18-	31 11 50 51 26- 44-	7 84 86 8- 85	12 167 164 128- 102
18 31 36 36- 0	19 23 21 0 21-	32 12 57 60 60 5	8 81 87 17- 85	13 99 109 79 75
19 29 27 0 27	20 6* 3 0 3	33 13 27 27 9 25-	9 125 120 77- 91-	14 113 115 59- 58-
20 53 56 56- 0	21 45 44 0 44-	34 14 30 26 15 21	10 72 75 65 37-	15 134 131 128- 27
L= 3 H= 0	L= 1 H= 1	15 34 30 28 11-	11 55 45 45 21 39-	16 89 88 22 85-
1 61 59 0 59-	0 98 112 0 112-	16 72 72 0 72	17 84 85 82- 20-	18 49 46 41 22
2 157 140 140- 0	1 363 393 357 162-	17 0 70 71 71- 0	19 98 103 103 9-	L= 2 H= 3
3 172 153 0 153	2 125 136 84 107	18 1 64 63 66- 61	20 1 123 132 78 106	6 158 145 116 67
4 176 166 166- 0	3 256 259 185- 181	19 2 47 46 44 12-	21 1 219 206 203 37-	2 219 206 37- 203-
5 313 306 0 306	4 451 514 508 80-	20 3 77 81 78- 23-	22 1 405 403 43 400-	3 229 230 165- 160
6 77 74 74 0	5 210 206 145- 147	21 4 66 66 63 20	23 1 240 239 230 37-	4 229 230 165- 160
7 22 17 0 17	6 281 284 101 266-	22 5 118 121 118- 23-	24 1 259 258 258 37-	5 239 238 178 228
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9 88 94 0 94	8 325 332 217- 251	24 7 27 24 21- 11-	26 1 297 296 296 37-	7 257 256 196 256
10 30 27 27- 0	9 116 122 53 109-	25 8 74 76 34- 68-	27 1 316 315 315 37-	8 266 265 205 265
11 22 0 0 0	10 136 134 12- 133	26 9 27 29 18 22-	28 1 335 334 334 37-	9 275 274 214 274
12 8* 7 7- 0	11 162 159 151- 49-	27 10 32 28 7 27	29 1 354 353 353 37-	10 284 283 223 283
13 313 332 0 332-	12 69 69 22- 65-	28 11 53 52 41 31	30 1 373 372 372 37-	11 293 292 232 292
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16 19 17 17- 0	15 19 17 15 7	31 14 54 53 43 4-	33 1 430 429 429 37-	14 320 319 260 319
17 154 152 0 152	16 58 67 23- 63-	32 15 44 43 42 30	34 1 449 448 448 37-	15 339 338 278 338
18 77 76 76- 0	17 42 46 46 5	33 16 44 43 42 29	35 1 468 467 467 37-	16 358 357 297 357
19 32 40 0 40	18 54 54 49- 22-	34 17 45 44 43 28	36 1 487 486 486 37-	17 377 376 315 376
L= 4 H= 0	19 52 53 44- 30-	35 18 46 45 44 27	37 1 506 505 505 37-	18 396 395 334 395
0 56 55 55- 0	20 53 51 39 34	36 19 47 46 45 26	38 1 525 524 524 37-	19 415 414 353 414
1 158 151 0 151	21 5* 34 33- 6-	37 20 48 47 46 25	39 1 544 543 543 37-	20 544 543 482 543
2 84 95 95 0	L= 2 H= 1	38 21 49 48- 6-	40 1 563 562 562 37-	21 563 562 501 562
3 57 53 0 53	0 349 366 366 0	39 22 50 49 48- 6-	41 1 582 581 581 37-	22 581 580 519 580
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6 75 71 71- 0	3 325 343 318- 130	42 25 53 52 51 50-	44 1 639 638 638 37-	25 638 637 576 637
7 123 129 0 129-	4 455 490 111- 478	43 26 54 53 52 51-	45 1 658 657 657 37-	26 657 656 595 656
8 7* 11 11 0	5 347 341 179- 290	44 27 55 54 53 52-	46 1 677 676 676 37-	27 676 675 614 675
9 186 186 0 186-	6 94 98 75- 63	45 28 56 55 54 53-	47 1 696 695 695 37-	28 695 694 633 694
10 8* 3 3 0	7 298 293 282 77	46 29 57 56 55 54-	48 1 715 714 714 37-	29 714 713 652 713
11 122 125 0 125-	8 83 85 85- 0	47 30 58 57 56 55-	49 1 734 733 733 37-	30 733 732 671 732
12 34 33 33 0	9 303 303 127- 275	48 31 59 58 57 56-	50 1 753 752 752 37-	31 752 751 690 751
13 22 19 0 19-	10 63 63 7- 62	49 32 60 59 58 57-	51 1 772 771 771 37-	32 771 770 709 770
14 25 21 21 0	11 110 114 111- 26	50 33 61 60 59 58-	52 1 791 790 790 37-	33 790 789 728 789
15 123 120 0 120	12 158 166 33- 163-	51 34 62 61 60 59-	53 1 810 809 809 37-	34 808 807 746 807
16 44 46 46- 0	13 136 141 113- 83-	52 35 63 62 61 60-	54 1 829 828 828 37-	35 828 827 765 827
17 77 79 0 79	14 130 132 44- 124-	53 36 64 63 62 61-	55 1 848 847 847- 47-	36 847 846 785 846
18 5* 39 39- 0	15 31 31 30 7-	54 37 65 64 63 62-	56 1 867 866 866 47-	37 866 865 804 865
L= 5 H= 0	16 76 81 80 6	55 38 66 65 64 63-	57 1 885 884 884 47-	38 884 883 822 883
1 45 46 0 46-	17 25 24 11 21-	56 39 67 66 65 64-	58 1 904 903 903 47-	39 904 903 842 903
2 125 124 124- 0	18 27 31 29 11 17-	57 40 68 67 66 65-	59 1 921 920 920 47-	40 920 919 858 919
3 71 69 0 69-	19 54 50 38 32-	58 41 69 68 67 66-	60 1 938 937 937 47-	41 937 936 875 936
4 52 51 51 0	20 36 34 1- 34	59 42 70 69 68 67-	61 1 956 955 955 47-	42 955 954 893 954
5 31 26 0 26-	L= 3 H= 1	60 43 71 70 69 68-	62 1 974 973 973 47-	43 973 972 912 972
6 54 45 45- 0	0 72 70 0 70	L= 1 H= 2	63 1 993 992 992 47-	44 992 991 930 991
			64 1 1012 1011 1011 47-	45 1011 1010 949 1010
			65 1 1030 1029 1029 47-	46 1029 1028 987 1028
			66 1 1049 1048 1048 47-	47 1048 1047 925 1047
			67 1 1068 1067 1067 47-	48 1067 1066 964 1066
			68 1 1086 1085 1085 47-	49 1085 1084 905 1084
			69 1 1108 1107 1107 47-	50 1084 1083 946 1083
			70 1 1127 1126 1126 47-	51 1083 1082 885 1082
			71 1 1146 1145 1	

Table 3 (cont.)

2	195	202	12-	201-	7	99	93	48	79-	4	51	51	51	5-	0	69	67	0	67	0	21	6	6-	0		
3	189	191	158	106	8	36	27	15	21-	5	23	28	25-	12-	1	73	78	78-	0	67	1	134	139	91-	105	
4	75	72	3-	72-	9	71	72	68	23-	6	44	48	19-	44-	2	100	96	95-	6	2	40	44	44-	0		
5	63	60	21-	56	10	87	83	54	63-	7	33	32	31	6-	3	96	91	73-	54-	3	143	150	104-	107-		
6	107	103	48	91	11	113	112	9-	111-	8	22*	16	4	15-	4	53	60	16	58-	4	40	40	1-	39		
7	110	111	104	37	12	55	56	47-	29	9	14*	14	6-	13-	5	69	76	60	46-	5	24	24	4	24-		
8	38	41	41-	2-	13	55	54	46-	28	10	1	0	1-	6	72	72	72-	5-	6	75	81	50	63-			
9	24	21	11-	18	14	69	69	25	64-	11	46	42	23-	35	7	125	130	121	47-	7	26	25	3	24		
10	40	37	36-	7-	15	24	17	2	17-	L=	6	H=	4		8	75	77	62-	46	8	70	67	7	67-		
11	61	59	54-	23-	16	62	63	48	41-	0	26	31	31	0	9	26	28	11-	25	9	17*	15	8	13-		
12	30	25	25	1	17	35	34	7-	33	1	72	72	7-	72-	10	81	81	79	15-	10	65	69	4	69		
13	18	16	13-	8	18	5*	46	0	46	2	49	47	27	39-	11	68	63	15-	61	11	27	27	15	22		
14	39	38	3	38	L=	2	H=	4		3	35	33	33	0	12	59*	54	41	34-	12	5	20	20-	5-		
15	91	89	89-	9	0	42	48	48	0	4	24	18	16-	7-	13	26	21	21	4	L=	3	H=	6			
16	5*	31	17	25	1	62	61	60	5-	5	40*	33	23	23	14	3	3	2-	1	0	17	12	0	12-		
	L=	5	H=	3		2	173	171	171-	7-	6	5	60	36-	47-	L=	4	H=	5	1	84	85	85-	2-		
0	214	223	0	223-	3	211	213	63	203-	L=	0	H=	5		0	31	25	25-	0	2	7	11	6-	9		
1	151	158	155	34	4	95	96	84-	45	1	75	85	0	85	1	63	66	65	14-	3	31*	24	22	8-		
2	80	84	83-	11	5	96	95	47-	82	2	17	12	0	12-	2	43	37	36-	10	4	55	59	56	16		
3	114	112	63-	93	6	164	164	163	18	3	188	188	0	188	3	73	76	76	1	5	29	28	4	28		
4	83	78	29-	72	7	128	120	112-	42	4	110	115	0	115	4	45	48	44-	17-	6	12	4	4-	0		
5	58	61	34-	51	8	58	62	40	47-	5	105	112	0	112-	5	49	49	49	2-	7	47	49	45	19		
6	44	48	46	16-	9	68	68	18	65	6	322	331	0	331-	6	36	28	27	3	8	33	29	10-	27-		
7	49	47	14-	44-	10	87	92	85	34	7	202	201	0	201-	7	27	24	20	13-	9	22	20	20	0		
8	78	77	50	59	11	136	137	76	114	8	203*	199	0	199-	8	71	69	68	6-	10	20	22	10	20-		
9	69	75	75-	10	12	103	104	93	46-	9	8	13	0	13	9	54	50	49-	11	54	61	70	63-	30		
10	38	39	36-	14-	13	63	58	0	58-	10	236	243	0	243	10	45	45	39	22-	0	68*	58	58	0		
11	39	38	32	20	14	66	67	63-	25-	11	81	82	0	82-	11	54	54	0	54	2	56	52	4	51-		
12	19	11	10-	5	15	58	57	11-	55-	12	96	95	0	95	L=	5	H=	5	1	6	14	13	9-	9		
13	56	60	22-	56-	16	59	57	44-	35	13	19*	15	0	15	0	45	41	0	41-	4	25*	19	18-	6		
	L=	6	H=	3	17	27	23	0	23	14	6	9	0	9-	1	42	40	37	15-	7	5	23	4-	22-		
0	52	55	55-	0	0	52	55	0	55-	15	72	66	0	66	2	23	21	4	20-	5	40*	41	39	9		
1	56	58	45	36-	0	52	55	0	55-	16	30	30	0	30	3	32*	26	15-	21-	6	18*	18	15	10		
2	49	49	6	49	1	34	31	5-	30-	L=	1	H=	5		4	32	36	35	9-	7	L=	0	H=	7		
3	46	49	30-	39	2	105	98	29	94	0	21	15	0	15-	5	14*	12	10	7	1	6	8	0	8		
4	47	46	42	20-	3	186	190	64-	179-	1	98	98	85-	47	6	34*	32	30-	11-	1	2	56	60	0	60-	
5	86	90	80-	42	4	193	195	192	37	2	101	105	81	67-	7	10	2	0	2	2	48	46	46-	2-		
6	16	9	5-	7-	5	53	56	50-	23	3	118	120	114	38-	8	3	36	9	35	3	32	32	31	4-		
7	43	42	42	3-	6	141	147	8	146-	4	105	99	55-	87-	7	1	72	176	176	0	4	20	18	0	18	
8	16	12	1	12	7	244	249	106	226	5	117	119	14-	118-	0	156	176	176	0	5	21	17	0	17-		
9	43	43	2-	43-	8	41	30	27-	12-	6	46	40	40-	5	1	72	65	65-	0	6	24*	19	0	19-		
10	3*	20	20-	4	10	95	102	79	63	8	122	125	55-	112-	3	137	131	131-	0	8	29	28	0	28-		
	L=	0	H=	4	10	107	100	3	100-	8	10	104	103	22	101	5	16	2	2	0	L=	1	H=	7		
0	42	45	45	0	0	11	107	100	3	100-	9	36	38	20	33	4	63	53	53-	0	9	5	0	0	0	
1	6*	13	13-	0	0	12	91	100	100-	8-	10	104	103	22	101	5	16	2	2	0	27	31	0	31-		
2	14*	6	6	0	0	13	29	25	24-	8	11	97	99	92-	35	6	49	47	47	0	1	90	94	93	15-	
3	87	80	80	0	0	14	65	66	66-	1	12	48	49	49	0	7	27*	24	24	0	2	48	46	46-	2-	
4	49*	62	62	0	0	15	18	11	11-	0	13	59	59	40	43	8	45	47	47-	0	3	32	32	31	4-	
5	13	13	0	0	16	5*	1	0	1	14	47	44	0	44-	9	7	1	1-	0	2	30	33	29	15-		
6	100	97	97-	0	L=	4	H=	4		15	49*	45	40	20-	10	24*	20	20-	0	4	24	25	3-	25-		
7	279	276	276-	0	0	184	183	183	0	16	5	27	16-	22-	11	36	35	35	0	5	83	88	87-	5		
8	77	70	70-	0	0	2	27	32	26-	18	L=	2	H=	5		12	14	3-	0	6	58*	60	56	21-		
9	58	57	57	0	0	3	113	112	74	84-	0	29	29	29	0	13	21	18	18	0	7	74	77	48-	59-	
10	104	98	98	0	0	4	100	103	98-	30-	1	35	29	1	29	L=	1	H=	6	8	66	70	23-	66		
11	217	228	228	0	0	5	109	105	20	103	2	28	24	8	22	0	39	40	0	40-	9	3*	5	4	2	
12	45	45	45	0	0	6	51	54	52	15-	3	61	69	55-	42	1	104	117	60-	100	0	56	54	54-	0	
13	60	64	64-	0	0	7	19	22	8	20	4	103	102	35-	96	2	90	100	97-	21	0	1	14	12	5-	10-
14	36	40	40-	0	0	8	26	31	26-	17	5	49	51	38-	33-	3	98	99	65	75	1	14	12	5-	10-	
15	17	22	22-	0	0	9	91	95	22-	92-	6	40	41	25	33-	4	80	80	1	80	2	30	33	29	15-	
16	68	70	70-	0	0	10	39	32	18	27	7	69	74	3-	74-	5	25	25	5	25-	3	77	82	78-	26	
17	28	25	25-	0	0	11	27	27	20-	19	8	33	36	33-	14-	6	28	24	16-	18-	4	52*	57	39	41	
18	13*	0	0	0	0	12	19	21	9	18-	9	18	9	8	2-	7	27	17	0	17-	5	80*	81	74-	34-	
	L=	1	H=	4	13	16	13	11	6	10	63	64	31-	56	8	44	43	29-	32-	7	5	15	14	4-	4-	
0	114	104	0	104	14	77	75	75-	4-	11	40	36	13	33	9	23	17	4	17-	7	26	25	3	24-		
1	63	62	15-	60-	L=	5	H=	4		12	68	68	52	44-	10	70</td										

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.* →O(2, *c*)→O(5, *b*)→O(2, *h*)→O(5, *e*)→O(2)..... (where → 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*)→O(3)→O(4, *d*)→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>	$B_i^*$	$U_i \dagger$	$\theta_{ia}$	$\theta_{ib}$	$\theta_{ic}$
C(1)	1	2.369 Å <sup>2</sup>	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.

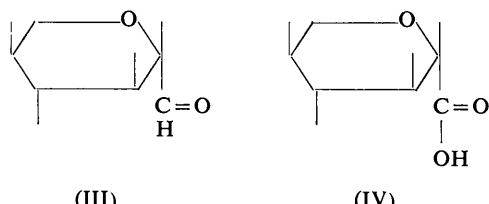


Table 5. Bond lengths and angles

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

$i$	$j$	$D(ij)$	$i$	$j$	$k$	Angle ( $ijk$ )
C(1)	C(2)	1.515 (6) Å	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 (Å)

	C–C	C–OH*		C–O (ring)	C(1)–OH	$\Delta \dagger$	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)	
$\alpha$ -D-Glucose	1.511–1.535	1.524	1.414–1.426	1.418	1.427, 1.428	1.391	10 $\sigma$	Brown & Levy (1965)
$\beta$ -D-Glucose	1.512–1.544	1.527	1.442–1.450	1.446	1.437, 1.455	1.404	4 $\sigma$	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 $\sigma$	Kim & Jeffrey (1967)
$\beta$ -Arabinose	1.523–1.554	1.535	1.426–1.454	1.437	1.421, 1.440	1.382	4 $\sigma$	Hordvik (1961)

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

†  $\Delta$  is the difference between average C–OH and C(1)–OH distances and  $\sigma$  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)
$\alpha$ -D-Glucose	108.7–111.1	110.2	108.3–112.3	110.3	113.7	Brown & Levy (1965) (private communication)
$\beta$ -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)
$\beta$ -Arabinose	107.1–111.9	109.5	107.3–113.1	109.9	112.7	Hordvik (1961)

\* Angles involving hydrogen atoms are excluded.

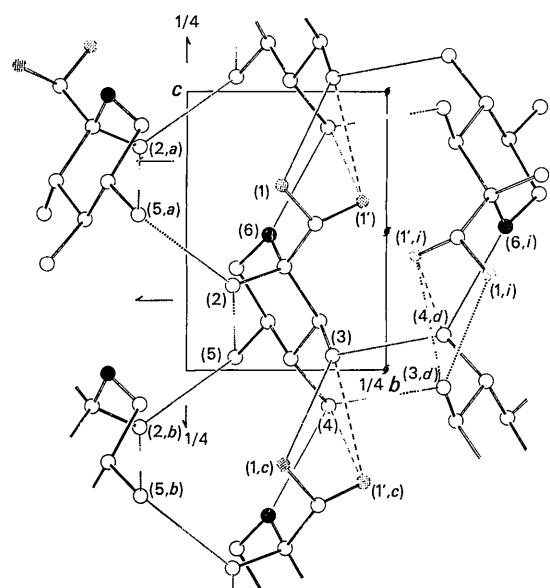


Fig. 3. The crystal structure viewed along the  $a$  axis. Dotted lines represent hydrogen bonds. Shaded circles represent ring oxygen atoms. Cross-hatched circles represent the disordered hydroxyl oxygen atoms. Numbers and alphabetic symbols are identification numbers and symmetry codes of oxygen atoms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

Table 7. Intermolecular distances and angles in  $\alpha$ -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

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

In fact, the characteristic absorptions of the keto ( $>\text{C}=\text{O}$ ) and carboxy ( $\text{C}(=\text{O})\text{O}^-$ ) 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 ( $\rho_o - \rho_c$ ) 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.

chemistry than the other. The environment of the disordered 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.

This research has been supported by the U.S. Public Health Service, National Institutes of Health, through grant no. GM-11293.

We are very grateful to Professor G. A. Jeffrey for his encouragement and valuable suggestions throughout this work. We would also like to thank Dr P. W. R. Corfield for his help in using his computer programs.

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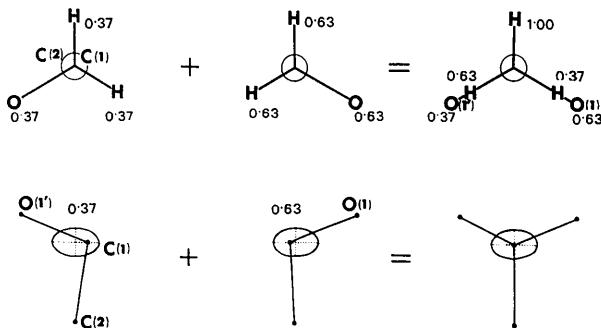


Fig. 4. (top) The statistical overlapping of the electron densities of oxygen and hydrogen atoms. (bottom) The correlation of thermal displacements between C(1) and O(1), O(1'). Fractional numbers are occupancies of atoms.

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