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The Crystal Structures of the α′ and β Forms of D-Mannitol*

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The crystal structures of β-D-mannitol and α′-D-mannitol have been solved in three and two dimensions respectively by superposition procedures on the Patterson synthesis. The space group of the β form is $P2_12_12_1$, with four molecules in the unit cell of dimensions $a=8{\cdot}672$, $b=16{\cdot}875$ and $c=5{\cdot}560$ Å; the space group of the α′ form is $C222_1$, with four molecules in special positions in a unit cell with dimensions $a=8{\cdot}94$, $b=4{\cdot}92$ and $c=18{\cdot}24$ Å. The molecules have the same conformation in both structures, with 2 symmetry and a planar carbon chain. The dimorphism is due to different systems of intermolecular hydrogen bonding.

Introduction

D-Mannitol, $C_6H_{14}O_6$, is an acyclic sugar alcohol found in seaweed, grass, fruits, and fungi. Its name derives from occurrence as a crystalline edible exudate of the flowering ash, *Fraxinus ornus*, of southern Europe, with its sweet taste, thereby resembling the manna of the Bible (*Exodus* 16: 14–36). A species of *Aspergillus* is capable of producing up to fifty per cent yields of mannitol from D-glucose (Lohmar, 1957). Since mannitol is converted to glycogen in diabetics without appreciably raising their blood sugar content, it has been suggested as a possible sweetening agent in the diabetic diet (Carr & Kranz, 1945).

Mannitol is unusual amongst carbohydrates in that it exists in several polymorphic crystalline forms (Table 1). The conditions of crystallization are not well-defined (Groth, 1910), and in some cases mixtures of the different forms are obtained. The α form was obtained by slow crystallization from 96% ethanol and the α′ form by evaporation of a solution prepared with 100% ethanol. We have not observed the α form reported by Rye & Sørum (1952). The similarity in unit-cell dimensions to α′ (with *b* and *c* interchanged) leads us to suspect that their set of systematic absences is incomplete. The structure of the α′ form has been solved in two dimensions and is briefly reported in this paper. The β form crystallizes easily from an aqueous ethanol solution and its three-dimensional structure determination is described in detail. The γ form was prepared by rapidly cooling a 1:1 water–ethanol solution. The κ form was found upon evaporation of a solution of mannitol and boric acid in methanol. The γ form, reported from powder data by Rye & Sørum (1952), could conceivably be the same as the κ form. Becker & Rose (1923), who obtained rotation pictures for D-mannitol, do not report the conditions of crystallization and their results have not been reproduced. The Fischer conventional formula for the molecule is shown

Table 1. *Crystal data of the polymorphic forms of mannitol,* $C_6H_{14}O_6$

M.W. 182·17, m.p. 166·1, $\mu CuK\alpha=11{\cdot}76$ cm^{-1}.

			Lattice parameters					
	Space group	*Z*	*a* (Å)	*b* (Å)	*c* (Å)	D_x (g.cm^{-3})	D_m (g.cm^{-3})	Reference
α	*Pmna*	4	8·94	18·41	4·92	1·494		Rye & Sørum, (1952)
α′	$C222_1$	4	8·94	4·92	18·24	1·494	1·487	Mak (1963)
β	$P2_12_12_1$*	4	8·65	16·90	5·56	1·488	1·497	Marwick (1931)
			8·66	16·58	5·50	1·522		McCrea (1931)
			8·672	16·875	5·560	1·487	1·485	This work
			(σ=0·008)	(σ=0·001)	(σ=0·005)			
κ	$P2_12_12_1$	4	8·91	18·69	4·93	1·474	1·487	Kim (1966)
γ	$P2_12_12$	4	9·33	17·36	4·99	1·496		Rye & Sørum (1952)
	Orthorhombic	2	10·36	8·10	4·55	1·555	1·521	Becker & Rose (1923)

* from absences; $h00$, $h=2n+1$,
$0k0$, $k=2n+1$,
$00l$, $l=2n+1$.

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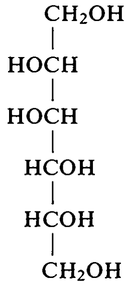
* *Note added in proof:–* In this paper we have followed the general practice of using lower case Greek letters for different solid phases. These should not be confused with the α, β nomenclature in carbohydrate chemistry which refers to the configuration of a cyclic sugar. Because of this possible ambiguity, we are proposing to use upper case Greek letters in subsequent references to polymorphism in the carbohydrates.

below. The atomic numbering is given in Fig. 1. The free molecule can have a twofold symmetry axis perpendicular to C(3)–C(4).



$$\begin{array}{c} CH_2OH \\ | \\ HOCH \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ CH_2OH \end{array}$$

Experimental

The three-dimensional data for the β form were collected on a Picker four-angle automatic diffractometer with Cu $K\alpha$ radiation. The crystal was a small transparent blade, $0{\cdot}1 \times 0{\cdot}05 \times 0{\cdot}25$ mm³, mounted about the c axis. Of the 850 reflections recorded, 600 were observed above background. The data were reduced to structure factors with no absorption corrections, using a series of programs by Craven & Chu (1967).

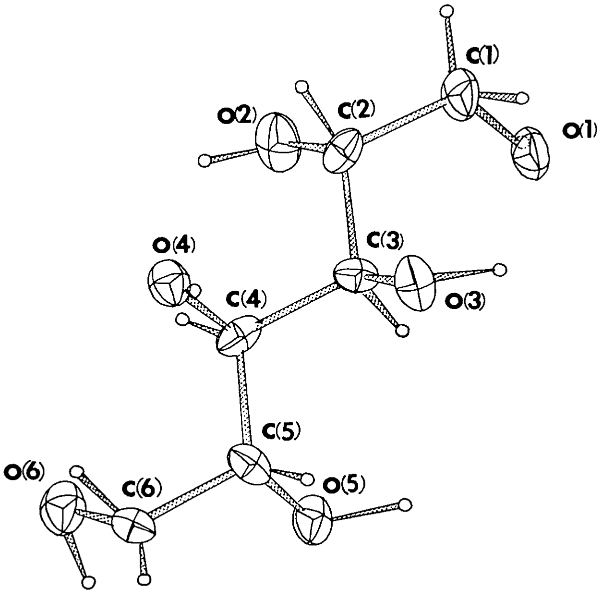


Fig. 1. Identification and numbering of the atoms in β-D-mannitol. Ellipsoids represent anisotropic thermal parameters.

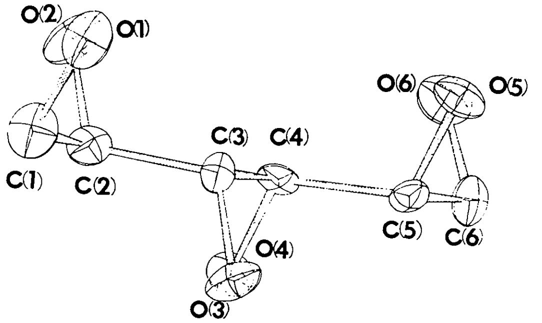


Fig. 2. c-Axis projection of β-D-mannitol showing the overlap of oxygen atoms.

The crystals of the α' form were small and bladelike and gave very elongated spots. No suitable crystals could be grown or cut for three-dimensional data. The $h0l$ reflections were recorded by multiple-film Weissenberg photographs with a 250 hr exposure. The intensities were estimated visually by comparison with a calibrated scale.

Determination of the structures

The structure of the β form was solved from the three-dimensional E^2-1 Patterson function. A peak at $(0,0,\frac{1}{2})$, with height five times that of any other, was interpreted as a coincidence of the intramolecular vectors O(1)–O(2), O(3)–O(4) and O(5)–O(6) (Fig. 2), when space-packing considerations ruled out the possibility that it could be a Harker peak. This gave a provisional fit to the Patterson map for a single molecule which was checked by multiple minimum functions calculated on the IBM 1620 (Corfield, 1965). The position of this molecule relative to the symmetry elements was found by first searching the Harker sections for the vector O(2)–O(5), then calculating a 2-atom symmetry minimum function (SMF) (Corfield & Rosenstein, 1966), with the vector O(2)–O(3) as the rigid body of known orientation. Of the four possible positions indicated for O(2) in the 2-atom SMF, only one was found to be consistent with the remainder of the molecule, as could be seen by preliminary inspection of the Patterson function. A multiple minimum function assuming only the positions of O(2) and O(3), together with the space group symmetry, showed all the non-hydrogen atoms in the structure, with a few spurious peaks. The complete set of structure factors calculated with atomic positional parameters taken from the M_8 function (Buerger, 1959) gave a conventional R value of 27%.

The structure of the α' form of D-mannitol has been solved in two dimensions. There are four molecules occupying eight equivalent positions in $C222_1$, and each molecule must therefore lie on a special position. The plane group is pmg where $a'=a/2$ and $c'=c$. Inspection of the Patterson map and a consideration of hydrogen bonding revealed that the more sensible of the two possible twofold special positions was that with the molecule lying with its twofold axis coinciding with the twofold symmetry axis along **a**. Coordinates were determined by application of superposition methods on the b-axis projection data. The two-dimensional Fourier synthesis of the first trial structure which gave a value of $R=0{\cdot}25$ is shown in Fig. 3. The results of the determination are presented as a projected electron density map to illustrate the general configuration of the molecule for comparison with that of β-D-mannitol.

Refinement

The structure of the β-form was refined with use of the modified version (Shiono, 1966) of the Busing, Martin & Levy (1962) full-matrix least-squares program for the IBM 7090 computer, with the Cruickshank (1961) weighting scheme. Difference Fourier syntheses using reflections with sin $\theta < 0{\cdot}7$ revealed the fourteen hydrogen atoms. The unobserved and eight strong low-order reflections were excluded from the refinement. The last cycle of least squares varied all parameters except those of the hydrogen atoms and gave an R value of 0·066. The final positional and thermal parameters are listed in Table 2. The structure factors of the observed reflections are listed in Table 3. The two-dimensional parameters of the α′ form were also refined with the least-squares procedure, varying positional and isotropic temperature parameters, to an R of 0·18. These positional and thermal parameters are shown in Table 4. Should suitable crystals become available, these results could form the basis of a more complete structure determination and refinement.

Description of the structure

The β form of D-mannitol has a planar zigzag chain of carbon atoms with deviations from the plane ranging from 0·04 to 0·07 Å (*cf.* Table 5.) The deviations of the heavier atoms from the ideal molecular twofold symmetry are remarkably small despite the asymmetric positions of the hydroxyl hydrogen atoms and the hydrogen bonding.

In the α′ form, the molecules have exactly twofold axial symmetry as a crystallographic requirement. Thus in both, the general molecular geometry is the same, except for the positions of the hydrogen atoms which are affected by the different intermolecular environment.

As in the structures of galactitol (Berman & Rosenstein, 1968), arabitol (Hunter & Rosenstein, 1967), gluconate ion (Littleton, 1953) and arabonate ion (Fur-

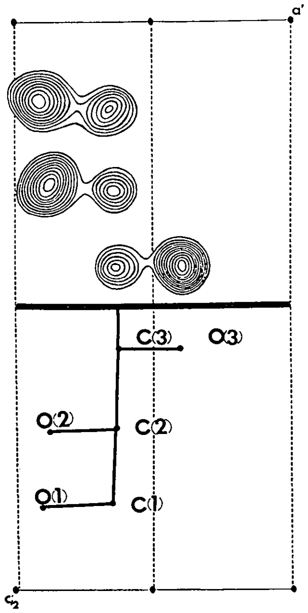


Fig. 3. Electron density projection $\varrho_0(xz)$ of α′-D-mannitol.

Table 2. *Fractional atomic coordinates and anisotropic thermal parameters in β-D-mannitol*

Key to atomic numbering is given in Fig. 1.

The temperature factor expression used was $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$ and the estimated standard deviations given in parentheses refer to the last decimal positions of respective values.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−0·0001(10)	−0·4934(4)	0·4257(13)	0·0104(12)	0·0021(2)	0·0167(25)	−0·0012(5)	0·0038(18)	−0·0004(7)
C(2)	0·0253(8)	−0·4561(4)	0·1832(13)	0·0060(10)	0·0019(2)	0·0147(23)	−0·0006(4)	0·0002(15)	−0·0023(7)
C(3)	0·0707(8)	−0·3692(4)	0·2051(14)	0·0060(9)	0·0014(2)	0·0180(22)	−0·0002(4)	−0·0016(15)	0·0004(6)
C(4)	0·0844(7)	−0·3284(4)	−0·0363(13)	0·0041(8)	0·0018(2)	0·0177(24)	0·0003(4)	−0·0032(14)	−0·0023(7)
C(5)	0·1186(8)	−0·2392(4)	−0·0160(14)	0·0042(8)	0·0019(2)	0·0173(22)	−0·0005(4)	−0·0017(14)	0·0011(7)
C(6)	0·1314(9)	−0·1987(4)	−0·2558(13)	0·0097(11)	0·0016(2)	0·0145(24)	−0·0002(4)	0·0009(14)	0·0010(6)
O(1)	−0·1121(6)	−0·4525(3)	0·5663(9)	0·0106(9)	0·0028(2)	0·0148(17)	−0·0015(4)	0·0014(12)	0·0007(6)
O(2)	−0·1163(6)	−0·4629(3)	0·0495(9)	0·0087(9)	0·0032(2)	0·0168(18)	−0·0023(4)	0·0005(12)	0·0007(6)
O(3)	0·2158(6)	−0·3634(3)	0·3271(9)	0·0059(7)	0·0029(2)	0·0146(18)	−0·0012(3)	−0·0025(11)	0·0011(6)
O(4)	0·2051(6)	−0·3653(3)	−0·1770(10)	0·0070(7)	0·0021(2)	0·0163(17)	0·0001(3)	0·0020(11)	0·0004(5)
O(5)	−0·0057(6)	−0·2006(3)	0·1112(9)	0·0071(7)	0·0022(2)	0·0169(17)	0·0009(3)	−0·0020(11)	0·0002(4)
O(6)	−0·0038(7)	−0·2107(3)	−0·4004(9)	0·0097(8)	0·0031(2)	0·0136(17)	0·0013(4)	0·0013(12)	−0·0007(5)
H(C1)	−0·025	−0·550	0·400						
H(C1′)	0·100	−0·490	0·550						
H(C2)	0·100	−0·500	0·100						
H(C3)	0·000	−0·330	0·300						
H(C4)	−0·013	−0·340	−0·150						
H(C5)	0·225	−0·228	0·100						
H(C6)	0·200	−0·230	−0·370						
H(C6′)	0·155	−0·140	−0·200						
H(O1)	−0·220	−0·460	0·550						
H(O2)	−0·100	−0·450	−0·100						
H(O3)	−0·180	−0·372	0·500						
H(O4)	0·325	−0·360	−0·125						
H(O5)	0·025	−0·210	0·300						
H(O6)	−0·075	−0·160	−0·350						

Table 3. *Observed and calculated structure factors*

Columns are index, $|F_{\text{obs}}|$, $|F_{\text{calc}}|$, A_{calc}, B_{calc}.
(+ indicates reflections excluded from refinement).

K= 0 H= 0				
2	178	186	186	0
4	87	81	81-	0
K= 1 H= 0				
1	289+	386	0	386-
2	97	89	0	89
3	75	69	0	69-
4	120	121	0	121-
5	102	111	0	111-
6	89	93	0	93-
K= 2 H= 0				
0	215	207	207-	0
1	272+	308	308-	0
2	190	207	207	0
3	218	223	223	0
4	42	31	31	0
K= 3 H= 0				
1	97	98	0	98
2	556+	798	0	798-
3	202	212	0	212
5	46	43	0	43-
6	40	38	0	38-
K= 4 H= 0				
0	263	240	240	0
1	54	52	52	0
2	503+	611	611	0
3	90	77	77-	0
5	57	55	55	0
6	138	152	152-	0
K= 5 H= 0				
2	303	313	0	313
3	50	40	0	40-
4	145	167	0	167
5	71	73	0	73-
K= 6 H= 0				
0	508	511	511	0
1	69	68	68-	0
2	78	72	72-	0
6	37	24	24-	0
K= 7 H= 0				
1	93	73	0	73-
2	67	81	0	81
3	49	33	0	33
4	88	83	0	83-
6	82	79	0	79
K= 8 H= 0				
1	47	42	42-	0
2	139	148	148-	0
K= 9 H= 0				
1	93	82	0	82-
2	278	294	0	294
4	83	81	0	81
5	113	130	0	130-
K= 10 H= 0				
0	210	204	204-	0
1	163	166	166-	0
2	55	42	42-	0
3	93	96	96-	0
4	62	70	70-	0
5	75	70	70-	0
K= 11 H= 0				
1	62	55	0	55
2	86	85	0	85
3	89	86	0	86
4	177	178	0	178
K= 12 H= 0				
0	471	488	488-	0
2	174	172	172	0
4	94	77	77	0
5	60	58	58-	0
K= 13 H= 0				
1	101	100	0	100-
2	96	96	0	96
3	137	136	0	136-
K= 14 H= 0				
0	94	83	83	0
1	62	48	48	0
2	147	140	140-	0
3	149	152	152-	0
4	106	106	106-	0
K= 15 H= 0				
1	90	94	0	94
2	196	190	0	190
3	43	38	0	38-
K= 16 H= 0				
0	75	98	98	0
1	46	38	38-	0
2	69	63	63-	0
K= 17 H= 0				
2	61	64	0	64-
3	42	32	0	32
K= 18 H= 0				
0	91	91	91-	0
2	111	114	114	0
K= 0 H= 1				
1	235	236	0	236
2	507	514	514	0
3	39	38	0	38-
5	79	89	0	89-
6	91	88	88	0
K= 1 H= 1				
0	101	102	0	102-
1	121	112	9	112-
2	511	525	397	343
3	104	100	98	22
4	82	84	60	58
5	131	154	138-	68-
6	143	128	69-	108-
K= 2 H= 1				
0	407	414	0	414
1	333	336	75-	327
3	107	91	27	87
4	149	144	103	100
5	100	97	15-	96
6	82	73	23	69
K= 3 H= 1				
0	617+	714	0	714
1	285	289	238	163
2	76	68	33-	59
3	66	59	59	3-
4	48	61	4	61-
5	46	42	25-	34
6	135	142	122	72
K= 4 H= 1				
0	744+	944	0	944
2	243	256	240-	89
3	115	102	30	98
4	241	250	217	124-
6	90	96	15	95-
K= 5 H= 1				
0	391	412	0	412
1	47	43	38	21
2	376	370	336	155-
3	62	62	51-	34
4	94	93	82	45
6	43	48	46	15
K= 6 H= 1				
0	290	272	0	272-
1	89	89	19	87
2	248	237	110	210
3	116	120	25	118
4	87	100	57-	82
5	45	36	33	16
K= 7 H= 1				
0	586	648	0	648-
1	41	40	2-	40-
2	270	274	238	135
3	46	36	11-	34
6	55	54	18	51-
K= 8 H= 1				
0	735+	819	0	819
1	122	108	44-	98
2	164	167	87	143
3	52	33	27-	19
4	163	163	161-	26-
5	109	116	12-	115
K= 9 H= 1				
0	89	109	0	109-
1	148	141	113	84
2	102	99	99-	6-
3	88	97	66	72-
K= 10 H= 1				
0	71	69	0	69
1	114	106	96	46-
2	209	213	178-	117-
3	183	189	97	162
4	39	25	17-	19
K= 11 H= 1				
0	67	66	0	66
1	62	79	56	55-
2	323	329	187	270-
3	129	147	146-	19
4	79	66	50	44-
K= 12 H= 1				
1	66	57	7-	57-
2	167	161	108-	119
5	36	29	9-	28
K= 13 H= 1				
0	94	92	0	92-
1	55	57	54	16-
2	188	194	194-	12-
4	77	75	74-	11-
K= 14 H= 1				
1	67	56	55	11-
4	112	109	106-	24-
K= 15 H= 1				
0	154	147	0	147-
1	76	79	79	7-
2	46	36	36-	0
4	49	38	27	27
K= 16 H= 1				
0	137	148	0	148-
1	45	32	3	32
2	44	30	22	20-
K= 17 H= 1				
2	61	63	61-	12
3	41	30	30	1
K= 18 H= 1				
0	47	49	0	49
2	51	47	38-	27-
K= 19 H= 1				
0	65	66	0	66
1	37	24	10	22
K= 0 H= 2				
0	681+	754	754	0
1	345	328	0	328
2	298	296	296	0
4	89	106	106-	0
5	62	69	0	69
6	152	140	140-	0
K= 1 H= 2				
0	626	681	681	0
1	235	229	201	108-
2	162	165	137-	93-
3	67	60	51-	32
4	296	296	147	257
6	83	78	52	58-
K= 2 H= 2				
0	35	33	33-	0
1	266	265	111-	240-
2	241	220	85-	203
3	218	203	72	190-
4	124	124	84	92
5	75	61	3	61-
6	80	60	37	47
K= 3 H= 2				
0	352	381	381-	0
1	166	166	140-	89-
2	375	356	355-	26-
3	143	151	127	81
6	93	84	63	56
K= 4 H= 2				
0	677	723	723	0
1	158	153	152-	19
2	121	118	29-	115
3	79	81	1-	81
K= 5 H= 2				
0	586	608	608-	0
1	115	98	64	74
2	468	479	78-	473
3	111	119	110-	46
4	55	60	8	60
5	45	37	1	37-
6	50	47	39	26-
K= 6 H= 2				
0	148	153	153	0
1	89	71	0	71-
2	169	176	141	105
3	62	59	31-	50-
4	181	180	13	180
6	93	97	60-	76
K= 7 H= 2				
0	315	331	331-	0
1	124	120	63-	102-
2	370	390	211-	328-
3	52	55	25-	49
4	96	101	3-	101
5	64	55	52-	17-
K= 8 H= 2				
0	380	382	382-	0
1	85	77	76-	11-
2	180	178	84	157
3	86	74	62	40-
4	162	174	113	133
5	71	72	14	71
K= 9 H= 2				
1	53	25	15	20
2	165	166	101-	132
4	84	74	33-	66
5	73	80	37	71-
K= 10 H= 2				
0	267	279	279	0
1	153	172	124-	119-
4	114	128	127-	9-
5	59	51	28-	43-
K= 11 H= 2				
1	74	70	61-	35
2	284	298	179-	239
4	117	103	5-	103-
K= 12 H= 2				
0	70	62	62-	0
1	75	88	49	73
3	111	110	9	109
4	72	70	62	32
K= 13 H= 2				
1	56	67	66-	9-
2	186	192	191	8
3	82	83	60	56-
K= 14 H= 2				
0	45	30	30-	0
1	52	44	11	43-
2	83	82	72	40-
3	76	71	66-	27-
4	48	53	33-	41-
K= 15 H= 2				
1	109	109	84	70
2	45	32	17	27
4	110	108	22-	105
K= 16 H= 2				
1	66	62	17	60
2	58	34	21	27-
3	39	27	26-	4-
K= 17 H= 2				
0	150	153	153	0
2	40	30	25-	17-
3	35	36	36	6
K= 18 H= 2				
0	70	69	69	0
1	40	43	9-	42
K= 19 H= 2				
1	40	33	3	33
K= 0 H= 3				
1	418	408	0	408
2	40	39	39-	0
4	403	402	402	0
5	45	46	0	46
K= 1 H= 3				
0	386	338	0	338
1	81	72	71	6-
2	430	432	418	109
3	80	89	78	43-
4	50	42	27-	32-
5	86	82	53-	62-
6	55	44	38-	23-
K= 2 H= 3				
0	445	432	0	432-
1	182	161	155-	43
2	112	106	31	102-
3	135	129	56	116
4	152	150	62	137
5	62	60	57-	20-
6	37	27	24	11-
K= 3 H= 3				
0	89	96	0	96
1	234	228	135	183
2	346	342	131-	316
3	94	97	97	6-
4	246	254	250-	43
5	66	50	40-	30
6	81	72	31	65-
K= 4 H= 3				
0	177	175	0	175
1	89	98	79	58
2	317	293	287	57-
3	89	78	55	55
4	207	215	76-	202-
K= 5 H= 3				
0	52	32	0	32-
1	91	104	103	8
2	150	137	134-	29-
3	64	62	4-	62
4	70	74	9-	73
K= 6 H= 3				
0	129	119	0	119-
1	94	92	37	84
2	303	316	67-	309-
3	42	37	25	26
4	134	136	64	120
5	68	62	56	26
K= 7 H= 3				
1	137	133	124	46-
2	99	90	7-	89-
4	109	131	68-	112-
5	59	57	26-	51-
K= 8 H= 3				
0	53	39	0	39
1	93	102	73-	71-
2	199	207	206-	20-
3	55	39	11-	37
4	112	116	42	108-
K= 9 H= 3				
1	115	126	32	122
2	52	54	52-	13-
3	88	96	55-	79-
4	189	200	192-	55
K= 10 H= 3				
0	125	121	0	121-
1	112	121	116	33
3	125	137	136	16
4	147	153	147-	43
5	43	33	11-	32
K= 11 H= 3				
0	240	235	0	235-
1	126	140	139	22-
2	184	187	109	152-
5	40	16	16-	4-
K= 12 H= 3				
0	65	68	0	68
1	84	91	6-	91-
2	86	81	54	61-
3	102	110	32-	105
4	122	125	125-	3
K= 13 H= 3				
0	79	68	0	68-
1	62	76	31-	70-
4	68	53	51	14-
K= 14 H= 3				
0	144	145	0	145
1	63	60	60	6-
2	128	147	103-	104
3	36	32	31-	4
4	59	64	24-	59-
K= 15 H= 3				
1	86	66	59	29-
2	80	71	21	68-
K= 16 H= 3				
0	105	88	0	88-
2	47	55	52-	19
K= 17 H= 3				
0	57	58	0	58-
2	38	34	32	9
K= 18 H= 3				
0	67	68	0	68
1	37	40	11	38-
K= 0 H= 4				
0	144	129	129	0
1	178	183	0	183
2	273	260	260-	0
4	313	311	311-	0
5	77	55	0	55
K= 1 H= 4				
0	155	130	130-	0
1	221	202	123	161
2	374	360	109	343
3	132	115	56-	100
4	193	195	94	170
5	50	48	19-	45
K= 2 H= 4				
0	257	224	224-	0
1	56	53	6	52-
2	274	269	154-	220-
3	89	107	61-	88-
4	283	283	178	221
K= 3 H= 4				
0	62	69	69-	0
1	143	125	3-	125-
2	149	138	40-	132-
3	82	74	62	40-
4	197	208	10	208
K= 4 H= 4				
0	148	124	124-	0
1	196	192	184-	53-
2	59	60	13-	58
3	48	59	59	7-
4	79	103	102-	15-
K= 5 H= 4				
0	80	77	77	0
1	112	96	78-	56
2	289	281	156-	234
3	120	126	10	126
4	169	184	55-	176
5	43	41	37-	18-
K= 6 H= 4				
0	164	158	158	0
1	47	46	14	43
2	174	159	70	143
4	90	78	26-	74-
K= 7 H= 4				
0	73	63	63	0
1	73	77	54	55-
3	101	102	71-	74
4	153	148	1	148-
K= 8 H= 4				
0	119	100	100	0
1	103	98	90-	39-
2	54	49	38-	31-
4	139	134	42	127
K= 9 H= 4				
0	129	124	124-	0
1	134	130	17	129
2	121	123	22-	121
K= 10 H= 4				
0	224	232	232	0
1	63	78	30-	72-
2	297	317	286	136-
3	52	28	12	26
4	109	107	64-	86
K= 11 H= 4				
0	50	62	62-	0
1	97	105	105-	1-
2	93	116	66-	95-
4	41	49	17-	46-
K= 12 H= 4				
0	62	79	79-	0
1	57	72	69	18
2	90	101	25	98
4	71	79	69	38-
K= 13 H= 4				
0	94	98	98	0
1	109	113	53-	100
2	52	37	18	33-
3	54	45	2	45
4	65	58	13-	57-
K= 14 H= 4				
1	67	59	45-	38-
K= 15 H= 4				
0	74	79	79-	0
1	69	62	47	41
2	114	110	10	110
3	51	43	6	42-
K= 16 H= 4				
1	80	72	72	1
2	82	72	27	67-
K= 0 H= 5				
1	147	135	0	135
2	45	42	42-	0
3	103	104	0	104
5	57	51	0	51
K= 1 H= 5				
0	325	322	0	322-
1	200	206	119	169
2	62	72	65	31
3	108	97	58	78-
K= 2 H= 5				
0	45	32	0	32-
1	65	68	62-	28
2	286	278	111-	254-
3	44	45	4-	45
5	56	46	39-	25-

Table 3 (*cont.*)

	K= 3 H= 5			
0	145	142	0	142
1	72	68	16-	66
2	323	326	310-	99-
3	73	64	61	21-
4	102	88	83-	31
	K= 4 H= 5			
0	51	39	0	39
1	117	103	11	102
3	62	52	46	23-
4	103	101	8-	100-
	K= 5 H= 5			
1	124	111	108	27-
2	124	118	114	32-
4	249	251	247-	46-
	K= 6 H= 5			
0	449	440	0	440-
1	71	79	57-	55
2	139	133	36	128-
3	63	59	14	57
4	137	156	28	153
	K= 7 H= 5			
1	168	162	160	21
2	61	73	45	58
4	119	118	118-	2
	K= 8 H= 5			
0	66	64	0	64
1	139	144	45-	137-
2	157	155	38	150-
4	132	146	1-	146-
	K= 9 H= 5			
0	44	32	0	32
1	78	75	24-	71
2	268	279	274-	54
3	76	69	65-	24
	K= 10 H= 5			
0	70	69	0	69
	K= 11 H= 5			
0	164	163	0	163
1	146	157	147	55
2	58	54	48	26-
	K= 12 H= 5			
0	125	116	0	116-
1	39	16	11-	12
3	48	56	5	56
	K= 13 H= 5			
0	72	74	0	74
1	75	78	23-	75-
2	60	64	25	59-
	K= 14 H= 5			
0	51	50	0	50
1	50	39	15-	36-
2	88	95	46	84
3	50	51	51-	4
	K= 15 H= 5			
0	43	39	0	39-
1	57	40	27	30-
2	84	91	8-	91
	K= 16 H= 5			
1	44	37	34	14
	K= 0 H= 6			
0	80	79	79	0
3	63	77	0	77-
4	152	145	145-	0
	K= 1 H= 6			
0	86	92	92	0
1	88	86	44	74
2	146	144	91-	111
3	72	72	5-	71
4	103	111	75-	82
5	42	27	12-	24
	K= 2 H= 6			
0	107	110	110-	0
1	138	131	62	115
4	136	144	83	117-
5	67	65	42-	50
	K= 3 H= 6			
0	419	420	420	0
1	84	70	45	54-
2	51	49	21	44-
4	96	106	38	99
5	41	39	39	3-
	K= 4 H= 6			
0	170	174	174	0
1	63	55	47-	29-
2	129	124	44-	116-
3	39	38	6	37-
5	67	61	52	32-
	K= 5 H= 6			
0	59	57	57-	0
2	190	195	100	167
4	92	87	3-	87
	K= 6 H= 6			
1	135	152	138-	64
2	215	231	20-	231-
3	63	59	19	56
4	58	49	38-	31
	K= 7 H= 6			
0	108	117	117	0
1	62	55	54	8
2	164	170	161	55-
3	76	72	13-	71
4	61	49	27	41-
	K= 8 H= 6			
0	92	97	97-	0
2	77	94	93	10-
4	66	79	25	75-
	K= 9 H= 6			
0	244	257	257	0
1	64	44	33-	28
2	175	175	132-	115
	K= 10 H= 6			
0	169	182	182	0
2	72	70	67	22
3	49	61	29-	53
4	55	63	38-	50-
	K= 11 H= 6			
1	52	52	51-	9-
	K= 12 H= 6			
1	66	62	9-	62-
	K= 13 H= 6			
0	149	150	150-	0
1	88	71	7-	71
3	47	47	31-	34
	K= 14 H= 6			
0	110	106	106	0
1	41	45	44-	8-
2	94	93	92	15
	K= 15 H= 6			
0	44	44	44-	0
1	61	53	35-	40
	K= 0 H= 7			
2	95	86	86-	0
3	100	112	0	112
4	77	84	84-	0
	K= 1 H= 7			
0	198	202	0	202-
1	57	55	54	10
2	193	202	199	35-
	K= 2 H= 7			
0	316	324	0	324-
1	87	75	1-	75
2	144	146	107-	99
	K= 3 H= 7			
0	75	84	0	84-
2	84	79	0	79-
4	40	42	40-	14-
	K= 4 H= 7			
0	317	328	0	328
1	80	69	23-	65
	K= 5 H= 7			
0	62	73	0	73-
1	81	83	62	56
	K= 6 H= 7			
0	67	70	0	70
2	91	93	2	93-
3	95	93	4-	93
	K= 7 H= 7			
0	91	86	0	86
1	81	85	58	62
2	63	73	65	33
3	43	30	15-	26-
	K= 8 H= 7			
0	52	49	0	49
3	53	44	42	12-
	K= 10 H= 7			
0	126	107	0	107-
1	89	89	89-	2-
2	111	118	75	91
3	62	55	14-	53
	K= 11 H= 7			
0	183	174	0	174
1	78	73	73	3
2	82	75	44	60
	K= 12 H= 7			
1	46	47	3	47
	K= 13 H= 7			
0	53	59	0	59
1	43	37	30	22
	K= 14 H= 7			
0	87	94	0	94
	K= 0 H= 8			
0	235	231	231	0
1	53	55	0	55-
2	135	145	145	0
3	70	68	0	68-
	K= 1 H= 8			
0	155	156	156-	0
3	53	50	4-	50-
	K= 2 H= 8			
1	64	60	10-	59
2	136	139	33	135-
	K= 3 H= 8			
1	47	54	17	52
2	98	94	70	63-
3	47	44	44-	8
	K= 4 H= 8			
0	269	280	280	0
	K= 5 H= 8			
0	184	203	203	0
1	83	89	49	74-
2	104	110	46-	100
	K= 6 H= 8			
0	51	48	48-	0
1	57	56	52-	22-
	K= 7 H= 8			
0	111	101	101	0
2	53	60	44-	41-
	K= 8 H= 8			
0	131	124	124-	0
2	110	118	94	71-
	K= 9 H= 8			
1	41	37	30-	22-
2	120	122	66	102
	K= 10 H= 8			
0	76	71	71	0
2	104	95	71-	62-
	K= 12 H= 8			
0	58	55	55-	0
	K= 0 H= 9			
2	51	46	46-	0
	K= 1 H= 9			
0	76	68	0	68
	K= 2 H= 9			
0	50	43	0	43
1	59	53	47	25
	K= 3 H= 9			
0	156	156	0	156-
2	72	66	49-	45
	K= 4 H= 9			
0	147	153	0	153
1	42	47	45-	13
2	64	74	36	65
	K= 5 H= 9			
2	114	110	108	21
	K= 6 H= 9			
0	55	61	0	61-
2	72	64	49-	41
	K= 7 H= 9			
0	87	80	0	80
	K= 8 H= 9			
0	170	167	0	167
	K= 0 H= 10			
0	218	214	214	0
	K= 3 H= 10			
0	44	37	37-	0

Table 4. *Fractional atomic coordinates and isotropic temperature factors of α′-D-mannitol*

Plane group is *pmg* and $a'=a/2$.

	x	*z*	*B*
C(1)	0·347	0·074	2·9
C(2)	0·337	0·146	4·8
C(3)	0·343	0·213	3·0
O(1)	0·094	0·067	4·3
O(2)	0·111	0·148	2·7
O(3)	0·571	0·212	3·6

Table 5. *Least-squares plane and twofold axis in β-D-mannitol*

Equation for plane, $Ax+By+Cz=D$, where x, y, z are in Å, and $A=0·9755$, $B=-0·2198$, $C=0·0006$ and $D=1·896$.

Atoms included in plane	Distance from best plane
C(1)	−0·065 Å
C(2)	+0·010
C(3)	+0·073
C(4)	+0·036
C(5)	−0·005
C(6)	−0·048

Parametric equation of the best twofold axis (Å):

$$x=+0·443 \quad +0·973t$$
$$y=-5·82 \quad -0·232t$$
$$z=+0·455 \quad -0·0082t$$

Atom pairs		Distance of mid-point of atom pairs from molecular twofold axis
C(1)	C(6)	0·023 Å
C(2)	C(5)	0·012
C(3)	C(4)	0·018

Table 5 (*cont.*)

Atom pairs		Distance of mid-point of atom pairs from molecular twofold axis
O(1)	O(6)	0·005
O(2)	O(5)	0·020
O(3)	O(4)	0·023

The angle between the best plane and the best axis is 88·5°.

berg & Helland, 1962), the C–C bonds have the staggered conformation of lowest energy leading to a planar zigzag chain of carbon atoms. There are three staggered positions for each of the terminal oxygen atoms corresponding to nine conformations of similar energy for an asymmetrical polyol. It might be expected, therefore, that acylic sugars would exhibit conformational polymorphism, in contrast to the ring sugars where there are no comparable opportunities for bond rotation. The mannitol molecule has six staggered conformations of which the three shown in Fig. 4 have the lowest energy, since they minimize the repulsion between oxygen atoms on the same side of the carbon chain. The conformational notation used is that of Klyne & Prelog (1960) and Cahn, Ingold & Prelog (1966).

Although mannitol is one of the few carbohydrates for which polymorphism is reported, we find that the conformation is the same, *i.e. Msc*, *ap*, *Psc*, *ap*, *Msc*, in both the α′ and β forms, as well as the κ form (Kim, (1966) [Fig. 4(*c*)]. In none of these forms do the molecules have the terminal oxygen atoms as a linear extension of the zigzag chain, as in galactitol (Berman & Rosenstein, 1967), although it would appear that this synclinal (*Psc*) conformation of the C(1)–C(2) bond should be energetically equally favorable [Fig. 4(*a*)]. The antiperiplanar conformations (*ap*) which would place O(1) in the H(Cl′) position are relatively less favored because of the repulsion between O(1) and O(3) (Fig. 5). The polymorphism thus corresponds to different hydrogen-bonded arrangements of nearly identical molecules, and it remains to be determined whether there are any examples of the conformational type of polymorphism in the acyclic sugars.

The bond lengths and angles of the *β* form are given in Table 7. The average lengths are 1·516 Å for C–C and 1·437 Å for C–O, without thermal corrections, with none varying more than 3σ from the mean. As in galactitol (Berman & Rosenstein, 1967) there is apparent opening in the C–C–C angles beyond 109°28′. The conformation angles are shown in Fig. 6. The C–C bonds have a staggered conformation with dihedral angles ranging from 55·6 to 64·9°. As judged from the two-dimensional study, there is no evidence of any significant differences in the α' molecules.

All the hydroxyl oxygen atoms in *β*-mannitol form one donor and one acceptor hydrogen bond (*cf.* Table 6). These link the molecules in sheets and provide the bonding between these sheets as shown in Fig. 7. The sheets are roughly parallel to the *bc* plane and are connected by series of parallel hydrogen bonds in the **c** direction, *i.e.* O(2)→O(1*c*), O(3)→O(4*b*), O(5)→ O(6*b*). These sheets are related by the screw axis along **a** to layers above and below by closed circuits of hydrogen bonds such as O(3)→O(4*b*)→O(5*i*)→O(6*f*)→ O(3)→. The hydrogen bonds O(2*d*)→O(1*e*)→O(2)→ O(1*c*)→ *etc.*, which form a helical chain, connect those molecules related by the screw axis along **c**. The possibility of the sense of the hydrogen bonding circuits being reversed is unlikely, since the C–O(H)···O angles would be less favorable in the reverse direction and inconsistent with the hydrogen positions found in the difference Fourier synthesis. This hydrogen bonding scheme is similar to that of *i*-erythritol (Shimada, 1959; Bekoe & Powell, 1959), which also has closed circuits and infinite spirals. It may be significant that in both galactitol and mannitol, there are two independent sets of hydrogen bonds. There are no nonbonded intermolecular contacts less than 3·3 Å.

Table 6. *Intermolecular distances and angles in β-*D*-mannitol*

i	*j*	*k*	D_{jk}	∠(*ijk*)
C(2)	O(2)	O(1)c	2·692 Å	119·9°
C(1)	O(1)	O(2)d	2·755	108·3
C(3)	O(3)	O(4)b	2·759	116·3
C(4)	O(4)	O(5)f	2·768	114·3
C(5)	O(5)	O(6)b	2·721	117·1
C(6)	O(6)	O(3)g	2·765	124·9

Symmetry code

a	x	y	z
b	x	y	$1+z$
c	x	y	$-1+z$
d	$-\frac{1}{2}-x$	$-1-y$	$\frac{1}{2}+z$
e	$-\frac{1}{2}-x$	$-1-y$	$-\frac{1}{2}+z$
f	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	$-z$
g	$-\frac{1}{2}+x$	$-\frac{1}{2}-y$	$-z$
h	$-\frac{1}{2}-x$	$-\frac{1}{2}-y$	$-1-z$
i	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	$+1-z$

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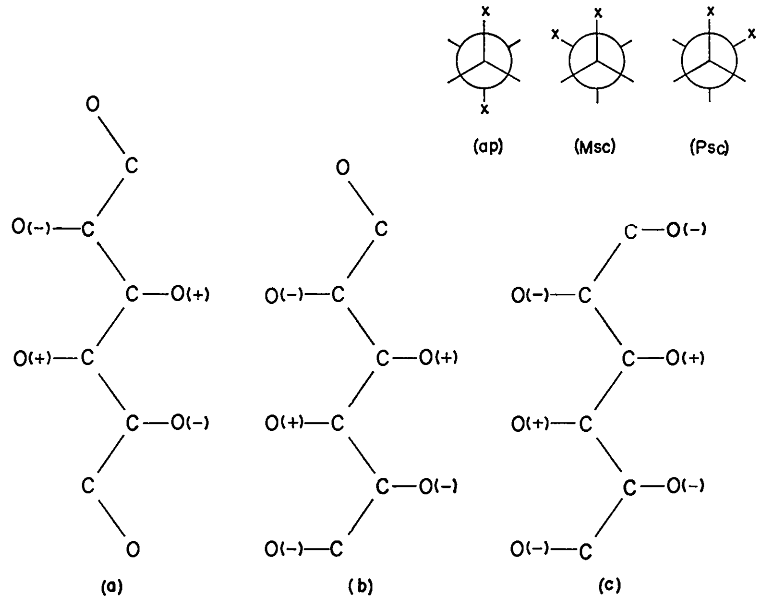

Fig. 4. The three likely conformations of mannitol. (*a*) *Psc*, *ap*, *Psc*, *ap*, *Psc*; (*b*) *Psc*, *ap*, *Psc*, *ap*, *Msc*; (*c*) *Msc*, *ap*, *Psc*, *ap*, *Msc*. *ap* antiperiplanar; *Msc* minus synclinal; *Psc* plus synclinal. (+) O is above plane of chain; (−) O is below plane of chain.

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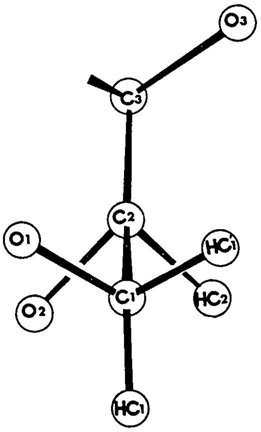

Fig. 5. Conformation of the C(1)–C(2) bond in β-D-mannitol.

Table 7. *Bond lengths and angles in β-D-mannitol*

The estimated standard deviations given in parentheses refer to the last decimal positions at respective values.

i	*j*	D_{ij}	D_{ij}*	*i*	*j*	*k*	∠(*ijk*)
C(1)	C(2)	1·505(10) Å	[1·514] Å	C(1)	C(2)	C(3)	111·6(6)°
C(5)	C(6)	1·503(10)	[1·508]	C(4)	C(5)	C(6)	113·2(6)
C(2)	C(3)	1·522(10)	[1·522]	C(2)	C(3)	C(4)	112·8(6)
C(4)	C(5)	1·537(10)	[1·538]	C(3)	C(4)	C(5)	113·3(6)
C(3)	C(4)	1·513(10)	[1·517]	O(1)	C(1)	C(2)	112·9(6)
C(1)	O(1)	1·425(9)	[1·442]	C(5)	C(6)	O(6)	111·8(6)
C(6)	O(6)	1·436(9)	[1·425]	O(5)	C(5)	C(6)	106·5(6)
C(2)	O(2)	1·440(9)	[1·448]	C(1)	C(2)	O(2)	107·7(6)
C(5)	O(5)	1·444(9)	[1·449]	O(2)	C(2)	C(3)	109·8(6)
C(3)	O(3)	1·433(9)	[1·440]	C(4)	C(5)	O(5)	109·5(6)
C(4)	O(4)	1·448(9)	[1·452]	C(2)	C(3)	O(3)	109·3(6)
				O(4)	C(4)	C(5)	108·7(6)
				O(3)	C(3)	C(4)	108·7(6)
				C(3)	C(4)	O(4)	109·9(6)

* Corrected bond lengths, assuming 'riding' motion (Busing & Levy, 1964).

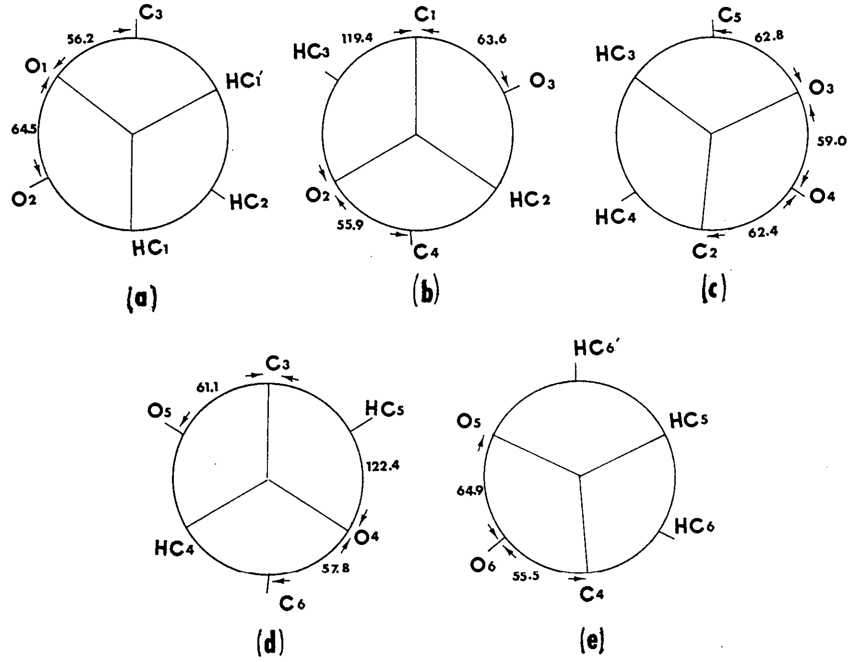

Fig. 6. Newman projection of the carbon–carbon bonds in β-D-mannitol. (*a*) C(1)→C(2), (*b*) C(2)→C(3), (*c*) C(3)→C(4), (*d*) C(4)→C(5), (*e*) C(5)→C(6).

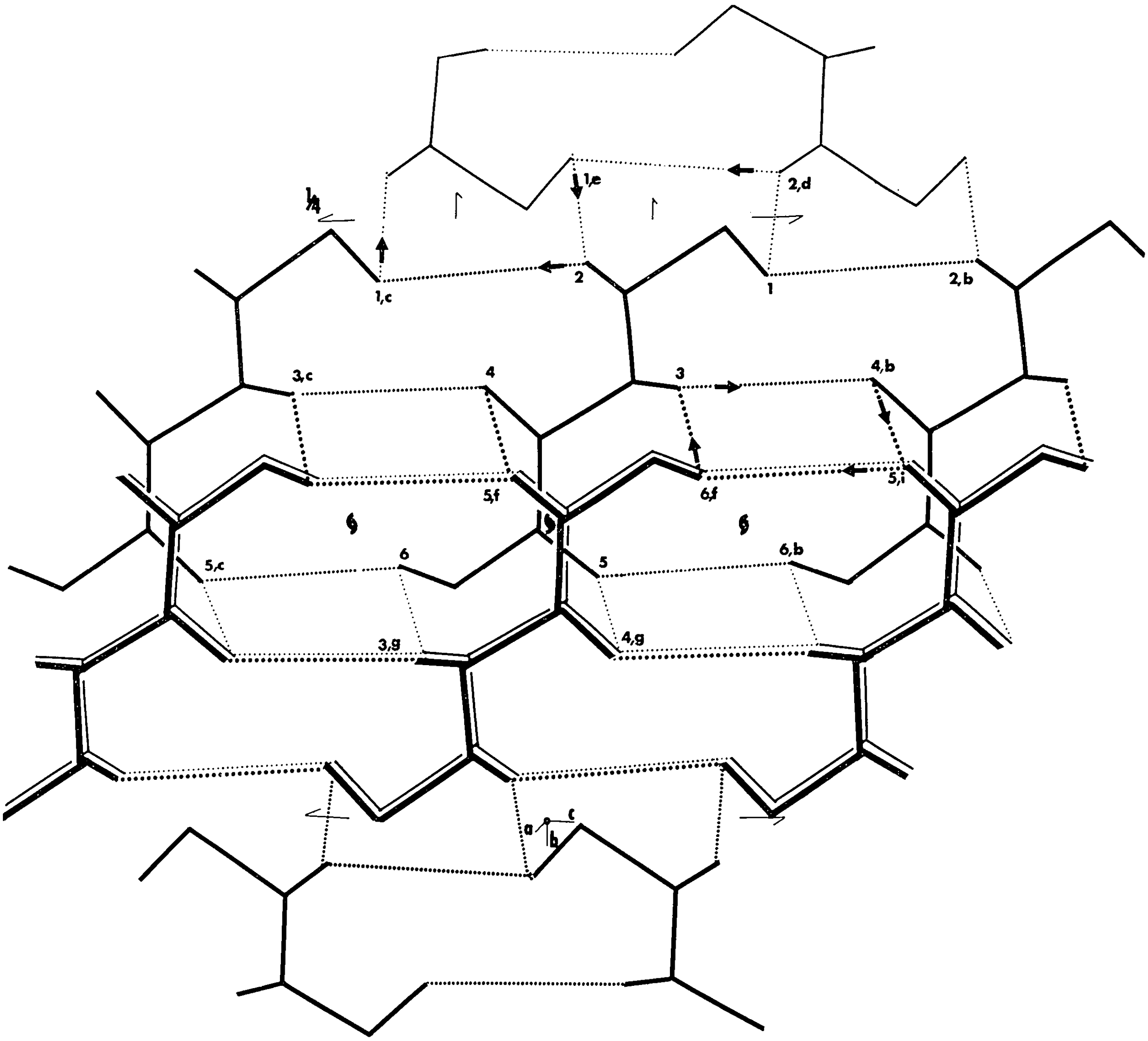

Fig. 7. The crystal structure of β-D-mannitol viewed down the *a* axis. Only the oxygen atoms are numbered and the alphabetic symbols refer to the symmetry code given in Table 6.

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