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The Crystal Structure of Galactitol

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The crystal structure of galactitol, $C_6H_{14}O_6$, has been determined directly by the sign correlation procedure. Both photographic and automatic diffractometer data were used and gave positional parameters which agreed within 3σ. The space group is $P2_1/c$ with four molecules in the unit cell of dimensions $a=8{\cdot}446$, $b=11{\cdot}503$, $c=9{\cdot}042$ Å, and $\beta=113{\cdot}0°$. The molecule, which has approximate $\bar{1}$ symmetry, forms a planar zigzag chain including the carbon and two terminal oxygen atoms. All the hydroxyl oxygens act as both donors and acceptors in the hydrogen bonding scheme. None of the C–O or C–C bonds differ significantly in length from the mean values of 1·432 and 1·520 Å, respectively.

Introduction

Galactitol (dulcitol), $C_6H_{14}O_6$, an acyclic sugar alcohol of biological importance has widespread distribution among plant life. It is found, for example, in seaweed and is the sole constituent of Madagascar Manna (Lohmar, 1957). It occurs in the cataractous lenses of galactosemic animals as a metabolic product of galactose, causing a hypertonic condition whereby water is drawn into the lens fibres, which become opaque and may eventually rupture (Kinoshita, Merola & Dikmak, 1962). The Fischer conventional formula is shown below.

CH_2OH
HCOH
HOCH
HOCH
HCOH
CH_2OH

The atomic numbering of the molecule is shown in Fig. 1. Since this is a *meso* form, the free molecule can have $\bar{1}$ symmetry about the midpoint of the C(3)–C(4) bond.

Experimental

Large transparent prismatic crystals were obtained by evaporation of a saturated water–ethanol solution. Both film and Picker four-angle automatic diffractometer data were collected with Cu $K\alpha$ radiation. No absorption corrections were applied. Equi-inclination Weissenberg film data taken around two axes with crystals (0·2 mm)³ gave 1200 structure amplitudes when correlated and reduced with use of an IBM 7090 program by Hamilton, Rollett & Sparks (1965) as modified by Shiono (1966*a*). The diffractometer data were taken with a regular prismatic crystal which had been cut to dimensions of a cube with edge 0·3 mm. The $\theta/2\theta$ scanning mode was used to measure 1151 reflections in fifty hours with a 2° scan across each peak and 10 sec background measurements at each end. The criterion used for unobserved reflections was based on the measurement of the systematically absent reflections and from the counting statistics. If the $\sigma(I)/I \geq 0{\cdot}33$, the reflection was considered to be unobserved and not included in the refinement. These data were reduced and converted to structure amplitudes with a series of IBM 1620 programs written by Craven & Chu (1967).

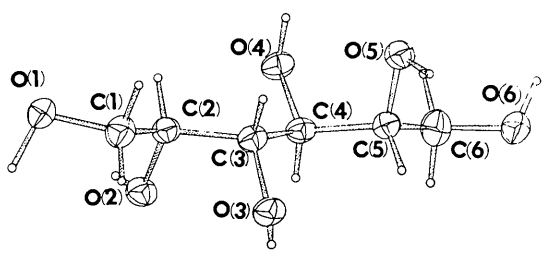

Fig. 1. Atomic numbering and identification of atoms in galactitol. Ellipsoids represent anisotropic thermal parameters.

Crystal data

Galactitol, $C_6H_{14}O_6$, M.W. 182·17, m.p. 188°.
Monoclinic, space group $P2_1/c$ from systematic absences, $0k0$ absent for k odd, $h0l$ absent for l odd.

$a = 8{\cdot}446 \pm 0{\cdot}008$ Å
$b = 11{\cdot}503 \pm 0{\cdot}01$
$c = 9{\cdot}042 \pm 0{\cdot}009$
$\beta = 113{\cdot}0 \pm 0{\cdot}1°$
$Z = 4$
$D_m = 1{\cdot}496$ g.cm^{-3}
$D_x = 1{\cdot}496$ g.cm^{-3}
$\mu_{\text{Cu } K\alpha} = 11{\cdot}83$ cm^{-1}, $\lambda = 1{\cdot}5418$ Å

Molecular symmetry, 1 (approximately $\bar{1}$)
The cell dimensions given by Marwick (1931) are $a=8{\cdot}61$, $b=11{\cdot}60$, $c=9{\cdot}05$ Å and $\beta=113°45'$.

Determination of the structure

The structure was solved directly in three dimensions by applying the sign correlation procedure of Beurskens (1963) to the film data. Of the 1158 reflections to which the procedure was applied, the signs of 314 were determined, of which 15, all with the lowest probability, were later observed to be incorrect. The structure, clearly revealed on the resulting three-dimensional *E*-synthesis, gave an initial *R* value of about 0·3.

Refinement of the structure

The refinement was carried out first with the film data, using the Busing, Martin & Levy (1962) full-matrix least-squares IBM 7090 program as modified by Shiono

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters in galactitol*

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 are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−0·0841 (3)	0·5068 (2)	0·2239 (3)	0·0096 (4)	0·0053 (2)	0·0091 (4)	0·0011 (2)	0·0033 (3)	0·0008 (2)
C(2)	0·0180 (3)	0·4087 (2)	0·1922 (3)	0·0087 (4)	0·0040 (2)	0·0060 (3)	−0·0006 (2)	0·0025 (3)	0·0004 (2)
C(3)	0·2089 (3)	0·4178 (2)	0·2981 (3)	0·0094 (2)	0·0036 (4)	0·0061 (3)	−0·0002 (2)	0·0025 (3)	0·0001 (2)
C(4)	0·3181 (3)	0·3259 (2)	0·2594 (3)	0·0099 (4)	0·0035 (2)	0·0055 (3)	−0·0006 (2)	0·0028 (3)	−0·0001 (2)
C(5)	0·5100 (3)	0·3508 (2)	0·3490 (3)	0·0084 (4)	0·0044 (2)	0·0067 (3)	−0·0003 (2)	0·0025 (3)	0·0007 (2)
C(6)	0·6207 (3)	0·2538 (2)	0·3305 (3)	0·0098 (4)	0·0062 (2)	0·0123 (4)	0·0014 (2)	0·0040 (3)	0·0008 (2)
O(1)	−0·2583 (2)	0·5045 (2)	0·1072 (2)	0·0090 (3)	0·0075 (2)	0·0098 (3)	0·0018 (2)	0·0030 (3)	0·0031 (2)
O(2)	−0·0451 (2)	0·2990 (1)	0·2197 (2)	0·0103 (3)	0·0039 (1)	0·0082 (3)	−0·0016 (1)	0·0033 (2)	−0·0001 (1)
O(3)	0·2367 (2)	0·4092 (1)	0·4652 (2)	0·0114 (3)	0·0048 (1)	0·0053 (3)	−0·0010 (1)	0·0025 (2)	−0·0009 (1)
O(4)	0·2752 (2)	0·3152 (1)	0·0915 (2)	0·0117 (3)	0·0046 (1)	0·0051 (2)	−0·0003 (1)	0·0027 (2)	−0·0006 (3)
O(5)	0·5494 (2)	0·4579 (1)	0·2889 (2)	0·0094 (3)	0·0047 (1)	0·0076 (3)	0·0014 (1)	−0·0025 (2)	0·0003 (1)
O(6)	0·7982 (2)	0·2787 (2)	0·4252 (2)	0·0091 (3)	0·0104 (2)	0·0102 (3)	0·0027 (2)	0·0039 (3)	0·0036 (2)
H(C1)	−0·037	0·585	0·200						
H(C1′)	−0·087	0·500	0·325						
H(C2)	0·007	0·412	0·075						
H(C3)	0·237	0·500	0·285						
H(C4)	0·300	0·250	0·300						
H(C5)	0·538	0·362	0·467						
H(C6)	0·600	0·250	0·200						
H(C6′)	0·600	0·175	0·387						
H(O1)	−0·330	0·475	0·175						
H(O2)	−0·100	0·250	0·125						
H(O3)	0·237	0·325	0·475						
H(O4)	0·300	0·390	0·050						
H(O5)	0·613	0·500	0·390						
H(O6)	0·850	0·287	0·350						

Table 2. *Principal axes of thermal ellipsoids*

The root mean square displacement U_i corresponds to the ith principal axis of the ellipsoid and θ_{ia}, θ_{ib}, θ_{ic} are angles between the ith axis and the crystallographic axes, a, b, c.

	i	U_i	θ_{ia}	θ_{ib}	θ_{ic}		i	U_i	θ_{ia}	θ_{ib}	θ_{ic}
C(1)	1	0·1615Å	130·91°	59·15°	104·78°	O(1)	1	0·1496Å	121·70°	63·75°	117·62°
	2	0·1827	47·07	85·29	159·37		2	0·1800	148·29	105·68	41·64
	3	0·1971	70·87	31·28	75·94		3	0·2441	89·84	31·21	61·57
C(2)	1	0·1422	99·38	110·75	24·32	O(2)	1	0·1454	55·77	34·61	98·37
	2	0·1558	133·24	129·11	93·87		2	0·1695	86·81	86·59	159·91
	3	0·1774	135·22	46·35	66·02		3	0·1931	34·41	124·40	108·11
C(3)	1	0·1460	91·08	101·23	24·48	O(3)	1	0·1309	90·50	73·16	27·81
	2	0·1545	101·81	163·81	95·80		2	0·1773	121·90	144·47	64·61
	3	0·1743	11·56	101·50	113·69		3	0·1974	31·90	120·24	100·61
C(4)	1	0·1378	98·22	91·24	14·81	O(4)	1	0·1300	95·37	77·30	21·49
	2	0·1507	106·93	162·66	86·80		2	0·1770	96·65	166·19	76·27
	3	0·1790	18·93	107·29	104·45		3	0·1940	8·56	95·33	106·21
C(5)	1	0·1481	92·72	114·34	31·11	O(5)	1	0·1529	43·87	48·69	94·98
	2	0·1594	149·80	116·07	83·52		2	0·1614	89·61	72·62	151·78
	3	0·1816	120·04	37·05	59·71		3	0·1988	133·87	46·42	62·30
C(6)	1	0·1643	31·23	114·07	92·25	O(6)	1	0·1561	39·97	108·35	77·51
	2	0·2052	121·21	130·73	44·65		2	0·1768	50·56	76·08	157·48
	3	0·2155	89·04	50·31	45·42		3	0·2785	84·46	23·34	71·57

Table 3. *Observed and calculated structure factors*

Columns are l index, F_{obs}, F_{calc}.

K= 0 H= -1			3	18	19	1	53	58	7	58	98	K= 9 H= -4			7	5*	2-	4	5*	2	3	87	83
2	38	58-	4	14	13	2	19	16-	K= 10 H= -3			2	35	35-	K= 9 H= -5			5	18	18-	4	46	47-
4	408	429	K= 13 H= -1			3	5*	6-	1	33	42-	3	33	31-	1	22	24	6	61	60-	5	82	82-
6	294	264-	1	5*	9-	4	34	33	2	102	104-	4	47	46	2	129	121-	K= 10 H= -6			6	5*	7-
8	81	94-	K= 0 H= -2			5	168	171-	3	22	20	5	57	55	3	59	54	1	47	51-	7	109	108
K= 1 H= -1			2	1157	1208-	K= 12 H= -2			4	91	92	6	27	26-	4	16	20-	2	29	35-	8	25	23
1	149	157-	4	544	535	1	15	9-	5	14	14-	7	79	78-	5	18	16-	3	54	54	K= 3 H= -8		
2	306	329-	6	147	136	2	32	14	6	49	47-	K= 10 H= -4			6	24	24-	4	18	16	1	63	68-
3	465	452	8	23	38	3	29	29-	K= 11 H= -3			1	37	32	7	68	70-	K= 0 H= -7			2	109	111-
4	476	532	10	67	69-	4	62	64-	1	19	20	2	56	60	K= 10 H= -5			2	132	135	3	230	231
5	408	442-	K= 1 H= -2			K= 0 H= -3			2	23	24-	3	92	76-	1	12	7	4	29	27	4	183	183
6	191	180-	1	41	33	2	69	57-	3	37	35	4	16	13-	2	60	68-	6	27	20-	5	68	70-
7	6*	12-	2	120	114-	4	93	72-	4	15	8	5	15	10	3	5*	16	8	46	52	6	6*	10-
8	60	67	3	233	230-	6	6*	2-	5	65	64	6	13	8-	4	19	29	K= 1 H= -7			7	49	54-
9	87	88-	4	5*	22-	8	217	210	K= 12 H= -3			K= 11 H= -4			5	15	12	1	121	123-	8	62	60
K= 2 H= -1			5	280	266-	10	81	84	1	90	94	1	20	22	K= 11 H= -5			2	256	255-	K= 4 H= -8		
1	13	3	6	52	52-	K= 1 H= -3			2	33	33	2	27	27	1	11	9	3	17	14	1	5*	2-
2	548 †	734-	7	16	6-	1	98	96	3	35	38-	3	48	48	2	39	39	4	67	68-	2	62	60-
3	45	40	8	6*	12-	2	205	210-	K= 0 H= -4			4	18	14-	3	38	37-	5	93	92	3	6*	12
4	366	376-	9	68	84	3	57	38-	2	67	58-	5	84	82	K= 0 H= -6			6	46	53	4	69	72-
5	344	336	10	51	45-	4	165	140-	4	89	88	K= 0 H= -5			2	138	139-	7	70	68	5	13	10
6	136	125	K= 2 H= -2			5	94	85	6	273	263-	2	15	13-	4	119	124	8	18	17	6	65	59-
7	43	55	1	178	165	6	99	99-	8	94	96	4	5*	19-	6	68	63-	9	67	67	7	5*	7
8	69	69	2	33	37-	7	241	231	10	5*	1-	6	52	58	8	75	74	K= 2 H= -7			K= 5 H= -8		
9	62	69-	3	366	376-	8	69	64	K= 1 H= -4			8	236	253-	K= 1 H= -6			1	87	90-	1	91	91-
K= 3 H= -1			4	27	23	9	5*	0	1	26	24-	10	5*	17-	1	102	106-	2	152	146	2	35	36-
1	479	486	5	215	203-	10	5*	7-	2	24	28	K= 1 H= -5			2	89	91	3	29	27-	3	110	109-
2	22	26	6	258	250-	K= 2 H= -3			3	115	97	1	298	302	3	33	31-	4	151	161-	4	57	55
3	74	60	8	16	10	1	42	44-	4	21	15-	2	368	392	4	44	40	5	36	34-	5	59	61
4	89	81	9	6*	9	2	885	842	5	239	236	3	89	86-	5	135	134-	6	99	102	6	51	55-
5	88	96	10	19	18-	3	179	173-	6	139	134-	4	67	65	6		98	7	89	88-	7	28	27-
6	6*	21	K= 3 H= -2			4	54	47-	7	33	34	5	27	27-	7	98	96-	8	132	131-	K= 6 H= -8		
7	84	86-	1	162	150-	5	180	173-	8	95	96	6	78	83	8	38	39-	9	5*	4	1	77	72-
8	58	63-	2	147	137-	6	79	75	9	32	27-	7	238	244-	9	114	115	K= 3 H= -7			2	18	18
9	40	41-	3	82	75-	7	111	111-	10	25	26	8	107	112-	K= 2 H= -6			1	26	23	3	15	12-
K= 4 H= -1			4	61	63	8	185	188-	K= 2 H= -4			9	37	35	1	183	177	2	32	29-	4	44	43-
1	262	262	5	13	10	9	15	5-	1	280	280	10	39	39-	2	25	23-	3	189	192-	5	42	39
2	63	53	6	189	176-	10	5*	2	2	34	29	K= 2 H= -5			3	151	144-	4	73	70	6	57	58-
3	302	283	7	36	44-	K= 3 H= -3			3	103	83	1	23	24	4	6*	4	5	6*	4	K= 7 H= -8		
4	56	43	8	113	116-	1	123	116	4	5*	5-	2	104	90-	5	25	27-	6	130	133-	2	12	1
5	262	251-	9	100	97	2	342	370-	5	128	123	3	103	101	6	27	25-	7	5*	3-	3	29	33
6	68	63	K= 4 H= -2			3	352	360-	6	164	171	4	264	260-	7	88	85-	8	58	59-	4	22	21-
7	35	32-	1	152	157	4	168	154	7	88	79	5	127	121	8	90	90-	9	19	20	5	5*	7
8	140	149	2	185	159-	5	63	64-	8	6*	16	6	192	194	9	60	63	K= 4 H= -7			K= 0 H= -9		
9	28	27-	3	169	168	6	113	104-	9	6*	7	7	152	155	K= 3 H= -6			1	6*	6	2	22	21-
K= 5 H= -1			4	541	580	7	134	128	10	5*	7-	8	28	28	1	214	213-	2	39	40	4	56	53-
1	319	315	5	72	71	8	6*	11-	K= 3 H= -4			9	102	104-	2	242	236-	3	21	17-	6	45	43
2	26	29	7	178	178-	9	42	40-	1	5*	7	10	13	13	3	62	62	4	24	19	K= 1 H= -9		
3	187	170	8	19	21	10	4*	3	2	69	61-	K= 3 H= -5			4	39	38	5	128	131-	1	67	65
4	141	135	9	101	102-	K= 4 H= -3			3	187	171	1	50	53	5	148	148-	6	19	10	2	121	115
5	56	46-	K= 5 H= -2			1	520	568-	4	87	77	2	98	96-	6	129	131-	7	125	126	3	13	6
6	17	6	1	569	644	2	33	30	5	185	185	3	68	63	7	75	81	8	75	80-	4	23	25
7	188	190	2	488	497-	3	356	363	6	133	127	4	67	74	8	105	107-	K= 5 H= -7			5	14	12-
8	54	59	3	167	162-	4	116	109-	7	253	246-	5	103	108	9	114	111	1	14	11	6	40	40
9	78	77-	4	15	13-	5	301	286-	8	105	101	6	63	65	K= 4 H= -6			2	29	29	7	127	132-
K= 6 H= -1			5	91	87	6	62	61-	9	67	67	7	6*	6-	1	7*	13-	3	108	104-	K= 2 H= -9		
1	226	224-	6	70	77	7	330	323	10	61	67	8	6*	1-	2	269	263	4	89	97-	1	29	25
2	53	55-	7	26	27-	8	31	21	K= 4 H= -4			9	40	38-	3	57	55	5	168	175	2	73	74-
3	56	54	8	61	58-	9	71	72-	1	75	79-	K= 4 H= -5			4	150	151	6	30	30	3	32	33
4	169	157	9	23	15-	K= 5 H= -3			2	154	140-	1	266	255	5	5*	13	7	5*	3-	4	5*	4-
5	80	80	K= 6 H= -2			1	98	91	3	92	99-	2	72	69-	6	6*	13-	8	5*	16-	5	15	16
6	81	74	1	62	46	2	181	171	4	28	28-	3	123	111	7	58	60-	K= 6 H= -7			6	133	138
7	30	31	2	58	52	3	337	323-	5	71	70-	4	44	47-	8	14	10	1	48	48	K= 3 H= -9		
8	78	76	3	369	355-	4	63	58-	6	345	336-	5	177	166-	9	114	115-	2	104	109	2	5*	6-
K= 7 H= -1			4	85	87	5	146	145	7	218	213	6	78	83	K= 5 H= -6			3	29	27-	3	77	75
1	65	64	5	147	137	6	241	248-	8	174	169	7	81	73	1	360	356	4	83	81-	4	16	12-
2	53	48-	6	134	135	7	57	50-	9	5*	13	8	68	65	2	185	187-	5	15	5-	5	5*	1-
3	37	36	7	19	15-	8	152	148	K= 5 H= -4			9	78	74-	3	57	56-	6	114	119-	6	91	94
4	80	80-	8	17	18	9	73	75-	1	193	201-	K= 5 H= -5			4	148	159	7	5*	3-	K= 4 H= -9		
5	66	69	9	69	68	K= 6 H= -3			2	60	54-	1	329	329	5	114	122	K= 7 H= -7			2	39	42-
6	178	181-	K= 7 H= -2			1	194	182	3	220	214-	2	136	138	6	74	80-	1	34	34-	3	35	29
7	56	54-	1	334	323	2	44	40-	4	155	145	3	144	147-	7	75	79-	2	102	103	4	34	34-
8	106	109	2	300	282	3	14	13-	5	60	62	4	73	75-	8	6*	0	3	6*	9-	5	20	17-
K= 8 H= -1			3	252	234-	4	168	170	6	43	42	5	17	10	9	5*	2-	4	32	30-	K= 0 H= 0		
1	396	382-	4	13	3	5	120	121-	7	7*	0	6	63	67	K= 6 H= -6			5	47	46-	2	792	766-
2	104	96-	5	47	49	6	401	389-	8	143	142-	7	34	38-	1	25	21-	6	48	48	4	139	117
3	122	124	6	106	101	7	54	55-	9	29	33-	8	71	73	2	28	33-	7	32	32-	6	212	202-
4	74	76-	7	18	21-	8	50	50	K= 6 H= -4			9	27	32	3	102	92-	K= 8 H= -7			8	91	91-
5	128	127-	8	38	40-	9	56	58	1	116	114	K= 6 H= -5			4	78	80	1	84	82	K= 1 H= 0		
6	14	13	K= 8 H= -2			K= 7 H= -3			2	43	46-	1	21	13-	5	144	143	2	58	58	1	60	59
7	28	30-	1	80	79	1	24	24-	3	120	108-	2	165	160	6	101	107	3	38	45	2	287	308
K= 9 H= -1			2	76	58	2	42	43	4	81	88-	3	6*	20	7	94	90-	4	37	37	3	139	137
1	166	162	3	154	141	3	89	75-	5	224	219	4	25	19	8	30	31	5	53	58	4	14	7
2	69	70-	4	22	24	4	80	73	6	158	160-	5	32	27	K= 7 H= -6			6	19	20	5	291	273
3	66	61	5	32	34-	5	71	66	7	196	194-	6	80	72	1	58	55	K= 9 H= -7			6	61	60
4	24	28-	6	5*	5-	6	145	143	8	89	88	7	42	41	2	49	48	2	73	70	7	19	15
5	29	32	7	73	71	7	154	153-	9	33	29-	8	136	130	3	126	134-	3	29	30-	8	144	145
6	58	60	8	55	50-	8	6*	7-	K= 7 H= -4			9	13	10-	4	5*	10-	K= 0 H= -8			9	64	62-
7	82	84-	K= 9 H= -2			K= 8 H= -3			1	61	61-	K= 7 H= -5			5	18	27	2	140	137	K= 2 H= 0		
K= 10 H= -1			1	52	49-	1	27	31-	2	72	73-	1	53	46-	6	111	112	4	186	186-	0	41	39-
1	112	110-	2	24	18	2	153	156	4	112	109-	2	134	123	7	48	50	6	177	184	1	1114	1135
2	288	278-	3	28	20	3	132	133	5	107	100	3	143	133	8	5*	10-	8	5*	2	2	147	150-
3	57	62	4	135	138-	4	41	45	6	89	87-	4	105	98-	K= 8 H= -6			K= 1 H= -8			3	17	10
4	115	109	5	56	58-	5	104	95	7	27	27-	5	6*	9	1	53	54	1	73	73-	4	118	122
5	66	63-	6	174	175	6	6*	9-	8	64	70	6	83	84-	2	172	168	2	78	80	5	247	231
K= 11 H= -1			7	73	78	7	6*	10	K= 8 H= -4			7	5*	2-	3	6*	18-	3	114	116	6	89	80
1	90	88-	K= 10 H= -2			8	66	71-	1	29	33-	8	5*	5	4	87	75-	4	167	168-	7	84	85
2	58	61	1	67	65	K= 9 H= -3			2	16	11	K= 8 H= -5			5	5*	15-	5	26	26	8	6*	4
3	30	27-	2	93	86-	1	79	77-	3	83	78-	1	257	260-	6	90	84	6	56	59-	9	30	28-
4	51	50-	3	18	15-	2	109	106	4	110	110-	2	59	61-	7	5*	7-	7	76	77	K= 3 H= 0		
5	97	101-	4	64	58	3	112	108-	5	16	24	3	22	30	K= 9 H= -6			8	60	64	1	178	179-
K= 12 H= -1			5	62	65	4	30	39	6	45	49	4	50	55-	1	18	21	K= 2 H= -8			2	61	59
1	41	45	6	20	23-	5	6*	5	7	58	61-	5	102	107-	2	5*	8-	1	75	71-	3	43	30-
2	85	81-	K= 11 H= -2			6	6*	5	8	59	58	6	6*	2	3	26	23-	2	75	79	4	65	64-

* indicates unobserved reflections.
† excluded from refinement.

Table 3 (*cont.*)

5 89 89	K= 0 H= 1	3 103 108	K= 5 H= 2	6 23 22-	1 5* 5	2 32 33-	0 166 165-								
6 177 161	0 49 46	4 136 138	C 268 264-	7 56 55-	2 113 115-	3 108 103	1 43 38-								
7 118 120-	2 158 159-	5 60 59	1 5* 12	K= 3 H= 3	3 79 77	4 184 182	2 6* 20								
8 31 33-	4 23 23	6 112 120-	2 34 14-	C 165 160	4 118 118	5 5* 5	3 5* 2-								
9 31 33	6 58 60	7 35 34-	3 42 39	1 247 249	5 113 117	6 18 16-	4 5* 4-								
K= 4 H= 0	8 23 21-	K= 9 H= 1	4 157 153-	2 63 55	6 77 77	K= 2 H= 5	K= 5 H= 6								
0 355 416	K= 1 H= 1	0 225 233	5 165 158-	3 185 176	K= 2 H= 4	0 87 80-	0 48 51-								
1 195 192-	0 169 184-	1 125 125-	6 41 40	4 255 258	0 174 165	1 6* 5-	1 6* 2-								
2 255 236-	1 210 239-	2 33 33-	7 21 21	5 55 61-	1 300 304	2 48 48	2 24 27-								
3 156 149-	2 275 336-	3 55 60-	K= 6 H= 2	6 84 83-	2 70 61-	3 117 122-	3 28 27-								
4 135 120-	3 274 298	4 5* 5	C 5* 7	7 58 59-	3 103 98	4 164 163	4 29 28-								
5 50 53-	4 207 203	5 59 59-	1 79 72	K= 4 H= 3	4 62 64-	5 5* 2	K= 6 H= 6								
6 154 153-	5 99 102-	6 37 35	2 24 22	C 47 32	5 14 14	K= 3 H= 5	0 37 37-								
7 220 226	6 30 24-	K= 10 H= 1	3 123 123-	1 102 97	6 31 31	0 99 96-	1 6* 13-								
8 20 15	7 219 217	C 295 287	4 144 149	2 74 62-	K= 3 H= 4	1 102 95-	2 80 83								
9 33 35-	8 45 44-	1 6* 2	5 24 27-	3 100 99	0 54 50	2 150 142-	3 59 60								
K= 5 H= 0	9 32 31-	2 121 120-	6 86 85	4 44 30-	1 162 158-	3 213 211-	K= 7 H= 6								
1 319 301-	K= 2 H= 1	3 5* 4	7 49 47	5 33 29-	2 281 280	4 75 72-	0 34 31								
2 245 233	0 61 54	4 19 16	K= 7 H= 2	6 183 184	3 100 98-	5 74 72	1 94 97								
3 29 33	1 26 27-	5 85 84	C 131 124	7 86 80-	4 67 66-	K= 4 H= 5	2 58 58								
4 5* 6-	2 570 625	K= 11 H= 1	1 212 215	K= 5 H= 3	5 6* 15	0 21 23	3 12 9-								
5 20 18	3 127 128-	0 18 19	2 146 142	0 92 91	6 6* 14	1 117 111	K= 8 H= 6								
6 119 120	4 187 161	1 121 120	3 6* 8-	1 192 189-	K= 4 H= 4	2 143 139	0 50 52-								
7 71 69	5 176 171-	2 5* 3-	4 34 33	2 111 107-	0 171 158-	3 156 155-	1 5* 4								
8 94 93-	6 45 50	3 6* 15	5 24 29	3 181 181	1 64 63	4 108 107-	2 56 60-								
K= 6 H= 0	7 28 35	4 62 65	6 76 77	4 45 43	2 207 208	5 95 93	K= 9 H= 6								
0 75 75	8 52 52-	K= 12 H= 1	7 51 50-	5 92 88	3 105 112-	K= 5 H= 5	0 6* 18-								
1 326 323	K= 3 H= 1	0 20 23	K= 8 H= 2	6 24 19-	4 70 77-	0 23 12-	1 21 25-								
2 97 100-	0 591 678-	1 46 46	C 6* 17	7 81 80	5 113 120	1 106 109-	K= 0 H= 7								
3 81 79-	1 371 413-	2 33 32	1 43 43	K= 6 H= 3	6 25 21-	2 96 95	0 104 110-								
4 101 93-	2 206 195-	3 28 30-	2 34 26	C 59 66	K= 5 H= 4	3 40 35	2 61 54-								
5 158 160	3 211 210-	K= 13 H= 1	3 108 112	1 91 89-	0 40 35-	4 21 20-	K= 1 H= 7								
6 186 202-	4 63 54-	0 123 124-	4 26 24-	2 89 85	1 205 202-	5 124 122-	0 71 67								
7 75 67-	5 45 51-	K= C H= 2	5 27 25	3 45 42-	2 26 18	K= 6 H= 5	1 79 69-								
8 151 160	6 64 65-	0 352 371-	6 14 15-	4 6* 5	3 92 87	0 388 385-	2 76 72-								
K= 7 H= C	7 210 217	2 417 486-	K= 9 H= 2	5 39 32	4 83 83	1 64 68	3 22 18								
1 157 161-	8 91 91	3	C 130 130-	6 22 20	5 110 110	2 114 117	K= 2 H= 7								
2 108 104-	K= 4 H= 1	4 63 57-	1 120 122-	K= 7 H= 3	6 27 23	3 22 21	0 51 55								
3 90 85-	C 36 37	6 320 313	2 168 170	C 126 123	K= 6 H= 4	4 45 43-	1 42 36								
4 173 167-	1 474 542-	8 55 61-	3 58 58	1 155 158	0 22 23	K= 7 H= 5	2 104 106-								
5 40 41	2 18 2	K= 1 H= 2	4 150 155-	2 134 132-	1 40 38-	0 162 153	3 5* 5								
6 17 12	3 69 72	0 137 141	5 82 77-	3 30 29	2 53 51	1 110 116-	K= 3 H= 7								
7 76 74	4 23 17-	1 25 27	K= 10 H= 2	4 21 23-	3 29 36	2 122 120-	0 35 30								
8 14 13-	5 5* 5-	2 14 24-	C 129 131-	5 77 75	4 255 261-	3 79 78-	1 120 118								
K= 8 H= 0	6 168 179-	3 111 110-	1 124 127	6 65 64-	5 6* 17-	4 129 131	2 20 22								
0 97 96-	7 95 92	4 92 90	2 120 119-	K= 8 H= 3	K= 7 H= 4	K= 8 H= 5	3 48 48								
1 103 96-	8 5* 6	5 295 292-	3 5* 3	C 50 55-	0 136 133-	0 16 11-	K= 4 H= 7								
2 76 73	K= 5 H= 1	6 356 355-	4 79 78	1 129 130-	1 39 40-	1 64 67-	0 21 22-								
3 74 70-	0 240 247	7 127 122	5 23 20	2 72 70-	2 54 56	2 97 93	1 75 79								
4 137 137-	1 211 212-	8 70 61	K= 11 H= 2	3 19 13	3 151 153-	3 34 32-	2 14 10								
5 82 84-	2 47 53-	K= 2 H= 2	0 57 54	4 73 69-	4 168 174-	K= 9 H= 5	K= 5 H= 7								
6 95 91	3 48 45-	0 95 95	1 94 95-	5 69 71	5 39 42	0 48 52	0 30 28								
7 79 79-	4 57 58	1 4* 2	2 34 36-	K= 9 H= 3	K= 8 H= 4	1 60 56	1 41 43-								
K= 9 H= 0	5 184 183-	2 70 53-	3 120 118	0 111 113-	0 88 89-	2 21 23	2 29 27-								
1 6* 14	6 161 167-	3 192 192-	4 5* 2-	1 32 38	1 53 58-	K= 10 H= 5	K= 6 H= 7								
2 182 180	7 38 37-	4 66 69	K= 12 H= 2	2 24 21	2 98 98	0 22 25	0 50 48								
3 152 156	8 55 53	5 249 247-	C 132 135-	3 48 53	3 56 55	1 19 24	1 5* 9								
4 145 139-	K= 6 H= 1	6 6* 1	1 26 27-	4 75 81-	4 5* 6	K= C H= 6	2 38 38								
5 107 109-	0 148 129-	7 53 45	2 55 56	5 5* 9-	K= 9 H= 4	0 158 148-	K= 7 H= 7								
6 31 31-	1 211 202	8 102 103-	K= 0 H= 3	K= 10 H= 3	0 92 104-	2 43 52-	0 77 84								
K= 10 H= 0	2 5* 5-	K= 3 H= 2	0 98 91	0 110 114	1 126 128-	4 67 63-	1 87 93								
C 194 189	3 57 55	0 317 356-	2 359 369-	1 80 82-	2 143 151	K= 1 H= 6	K= 8 H= 7								
1 117 120-	4 6* 12-	1 300 319	4 187 165	2 52 50-	3 156 161	0 204 198	0 55 55-								
2 35 24	5 81 85-	2 33 43	6 108 107-	3 5* 1	4 81 86-	1 142 147	K= 0 H= 8								
3 35 32	6 113 108-	3 41 30-	K= 1 H= 3	4 88 94-	K= 10 H= 4	2 28 36	0 13 13								
4 67 70	7 44 41-	4 120 116-	0 544 605	K= 11 H= 3	0 115 120	3 98 108-	2 72 70								
5 60 58-	8 30 29-	5 161 162	1 579 620-	0 6* 11-	1 98 103-	4 5* 5-	K= 1 H= 8								
6 87 86-	K= 7 H= 1	6 19 19	2 376 418-	1 57 60-	2 5* 10-	K= 2 H= 6	0 29 26-								
K= 11 H= 0	0 90 96-	7 126 124-	3 374 393	2 5* 2-	3 19 20-	0 176 177-	1 19 20								
1 85 89-	1 141 150-	8 34 35-	4 25 23	3 5* 9-	K= 11 H= 4	1 6* 1	K= 2 H= 8								
2 76 77-	2 33 35	K= 4 H= 2	5 257 262-	K= 12 H= 3	0 5* 13	2 83 81	0 39 33								
3 141 139	3 86 81-	0 112 93-	6 63 62-	0 44 44	1 83 91-	3 17 20-	1 15 13								
4 81 81	4 154 157	1 53 48	7 5* 2-	1 63 66	K= 0 H= 5	4 49 46-	K= 3 H= 8								
5 36 43	5 67 66	2 76 57-	K= 2 H= 3	K= 0 H= 4	0 77 68	K= 3 H= 6	0 6* 14								
K= 12 H= 0	6 50 51	3 111 102	0 193 195-	0 637 681	2 104 108	0 382 383-	1 5* 5-								
0 155 153	7 60 58-	4 126 127	1 114 119	2 248 236	4 53 59	1 153 158	K= 4 H= 8								
1 26 26	K= 8 H= 1	5 25 21-	2 96 95-	4 139 135-	6 77 78	2 32 32	0 33 28-								
2 34 19-	C 36 39-	6 57 51	3 78 74-	6 31 31	K= 1 H= 5	3 5* 5	1 37 36								
3 5* 10-	1 239 232-	7 63 68-	4 254 245-	K= 1 H= 4	0 18 22-	4 41 41-	K= 5 H= 8								
K= 13 H= 0	2 95 90	8 22 22-	5 222 222	0 258 248-	1 94 86-	K= 4 H= 6	0 18 17								
1 52 52						K=									

(1966*b*), and the Cruickshank (1961) weighting scheme. The quantity minimized was $\sum_{i=1}^{s} w_i(|F_{obs}| - k|F_{calc}|)_i^2$ and the atomic scattering factors were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). All the hydrogen atoms were located in difference syntheses. The refinement terminated at an R value of 0·095 (where $R = \Sigma \, ||F_{obs}| - |F_{calc}|| / \Sigma \, |F_{obs}|$) with an average e.s.d. of the atomic positions of 0·006 Å. The structure was later refined with the diffractometer data in the same manner. After two cycles of anisotropic refinement, all the hydrogen atoms were again located on a difference synthesis and found in approximately the same positions as from the film data. The hydrogen atoms were assigned the same thermal parameters as the atoms to which they were bonded, but were not refined. The final R value was 0·052 and the average e.s.d. of the atomic positions was 0·002 Å. The positional parameters from both sets of data agree within 3σ. The parameters in Tables 1 and 2 and the structure factors given in Table 3 are those derived from the diffractometer measurements.

Discussion

The molecules are in general positions and the potential symmetry centers of the *meso* conformation are not utilized in the crystal structure. The midpoints of the *meso* (centrosymmetrically) related pairs of carbon

and oxygen atoms differ from the midpoint of the molecule by distances varying from 0·03 Å for the C(2)–C(5) pair to 0·20 Å for O(3)–O(4) (Table 4). Neither the whole molecule nor its carbon chain is centrosymmetrical. The crystal structure is therefore a racemate of two isomers related by symmetrical distortion of the same conformation. This structure is analogous to those of tartronic acid (van Eijck, Kanters & Kroon, 1965) and the *meso*-tartrate ion (Kroon, Peerdeman & Bijvoet, 1965), in that the molecule is distorted from its idealized symmetry, thus giving rise to enantiomorphs. The symmetrical forms of those molecules appear to have some unfavorable intramolecular contacts, whereas the centrosymmetrical form of galactitol has no particularly short non-bonded distances. Since the deviations from centrosymmetry are of the same order of magnitude as the r.m.s. atomic thermal displacement, it is reasonable to presume that the distortion of the molecule is caused by its environment in the crystal and that the *meso* molecules will be formed on dissolution.

Table 4. *Least-squares planes and center of symmetry in galactitol*

Equation for plane, $Ax+By+Cz=D$, where x, y, z are in Å, and
$A=-0{\cdot}414$, $B=-0{\cdot}560$, $C=0{\cdot}822$, $D=-1{\cdot}353$ for (*a*),
$A=-0{\cdot}384$, $B=-0{\cdot}491$, $C=0{\cdot}870$, $D=-0{\cdot}847$ for (*b*).

	Atoms included in plane	Distance	Atoms excluded from plane	Distance
(*a*)	C(1)	+0·049 Å		
	C(2)	+0·088		
	C(3)	+0·149		
	C(4)	+0·071		
	C(5)	−0·095		
	C(6)	+0·005		
	O(1)	−0·195		
	O(2)	−0·072		
(*b*)	C(1)	+0·016	O(1)	−0·323 Å
	C(2)	−0·009	C(3)	+0·152
	C(4)	+0·013		
	C(5)	−0·046		
	C(6)	−0·001		
	O(6)	+0·027		

Deviations from centrosymmetry

Atom pair		Distance of mid-point of atom pair from average center
C(1)	C(6)	0·069 Å
C(2)	C(5)	0·032
C(3)	C(4)	0·092
O(1)	O(6)	0·188
O(2)	O(5)	0·141
O(3)	O(4)	0·201

The carbon chain and terminal oxygen atoms form an approximately planar chain (*i.e.* conformation *Msc*, *Msc*, *ap*, *Psc*, *Psc*) (for nomenclature, see Klyne & Prelog, 1960) as inferred by Horton (1965) from nuclear magnetic resonance observations on other acyclic sugars. In detail, however, there are deviations such that O(1) and C(3) are significantly out of the plane of the other six atoms (Table 4). The distortion is enough that the O(3)–O(4) contact which is ideally 3·5 Å reduces to 2·8 Å. These deviations from the ideal

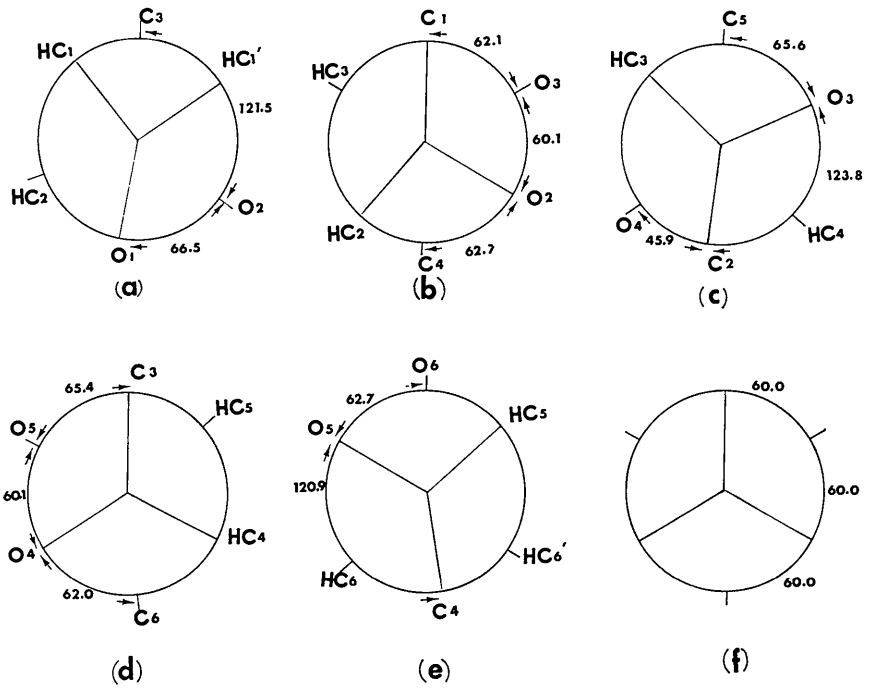

Fig. 2. Newman projections of the five carbon-carbon bonds in galactitol. (*a*) C(1)→C(2). (*b*) C(2)→C(3). (*c*) C(3)→C(4) (*d*) C(4)→C(5). (*e*) C(5)→C(6). (*f*) Idealized projection assuming 60° conformation angles.

meso form and from planarity are also apparent from the conformational angles shown in Fig. 2, a number of which are significantly different from 60°. The conformation of the C(1)–C(2) bond (*Msc*) is shown in Fig. 3. The C(5)–C(6) bond is centrosymmetrically related (*i.e. Psc*) and shows the same conformation as C(5)–C(6) in galactonolactone (Jeffrey, Rosenstein & Vlasse, 1967). In both these structures, the C(5)–C(6) conformation is *Psc* although the *ap* conformation seems just as likely.

The mean C–C and C–O bond lengths are 1·520 and 1·432 Å, respectively. The C–C lengths vary over a range of $\pm 4\sigma$, with the terminal C–C bonds having the largest deviations and shortest lengths (Table 5). The same effect is found in galactonolactone (Jeffrey, Rosenstein & Vlasse, 1967) and mannitol (Berman, Jeffrey & Rosenstein, 1968). The bond lengths became noticeably more uniform upon application of thermal corrections which assume a 'riding' motion (Busing & Levy, 1964).

The C–C–C angles are consistently greater than tetrahedral with a mean value of 111·6°. The C–C–O angles have a mean value of 110·0°. The widening of the C–C–C bond angles has been observed in paraffin and other long chain carbon structures and has been attributed to repulsion between substituent groups (*cf.* Pedley, 1961).

The hydrogen bonding is illustrated in Figs. 4 and 5. All the hydroxyl oxygen atoms are involved as donors and acceptors forming a very regular and elegant pattern. The sequence O(6*b*)→O(2)→O(6*e*) *etc.* which runs parallel to the *ac* plane at approximately $b=\frac{1}{4}$ forms hydrogen bonding sheets by connecting to the same sequence translated 1 unit cell in **a** (Fig. 5). An irregular chain O(5*i*)→O(3)→O(4*d*)→O(1*l*)→O(5*m*) weaves among three screw-related sheets and continues infinitely up in the **c** direction. Another centrosymmetrically related chain travels in the opposite direction in **c** and connects three screw-related sheets. The hydrogen bond O–O distances range from 2·63 to 2·79 Å,

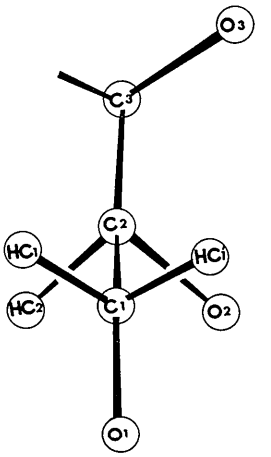

Fig. 3. Conformation of the C(1)–C(2) bond.

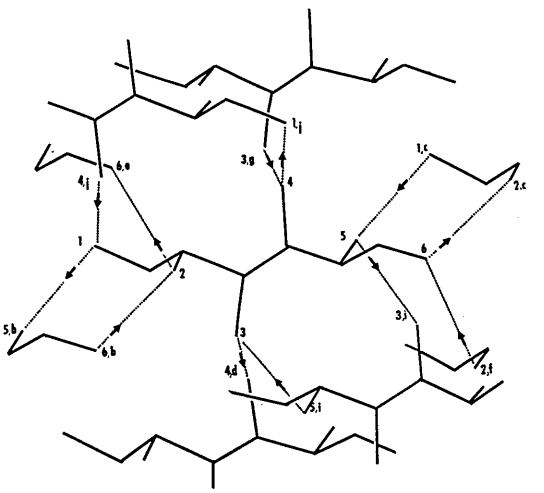

Fig. 4. Hydrogen bonding in one molecule. Dotted lines represent hydrogen bonds. Arrows indicate the direction of the bond.

Table 5. *Bond lengths and angles in galactitol*

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)	1·513 (4) Å	[1·520] Å	C(1)	C(2)	C(3)	111·8 (2)°
C(5)	C(6)	1·507 (4)	[1·518]	C(4)	C(5)	C(6)	112·1 (2)
C(2)	C(3)	1·523 (3)	[1·523]	C(2)	C(3)	C(4)	113·1 (2)
C(4)	C(5)	1·528 (3)	[1·531]	C(3)	C(4)	C(5)	110·9 (2)
C(3)	C(4)	1·531 (3)	[1·531]	O(1)	C(1)	C(2)	110·1 (2)
C(1)	O(1)	1·437 (3)	[1·442]	C(5)	C(6)	O(6)	109·6 (2)
C(6)	O(6)	1·435 (3)	[1·440]	C(1)	C(2)	O(2)	110·3 (2)
C(2)	O(2)	1·428 (3)	[1·432]	O(5)	C(5)	C(6)	110·3 (2)
C(5)	O(5)	1·436 (3)	[1·438]	O(2)	C(2)	C(3)	109·1 (2)
C(3)	O(3)	1·438 (3)	[1·442]	C(4)	C(5)	O(5)	108·4 (2)
C(4)	O(4)	1·421 (3)	[1·425]	C(2)	C(3)	O(3)	110·7 (2)
				O(4)	C(4)	C(5)	110·9 (2)
				O(3)	C(3)	C(4)	109·1 (2)
				C(3)	C(4)	O(4)	112·3 (2)

* Bond lengths corrected, assuming 'riding' motion (Busing & Levy, 1964).

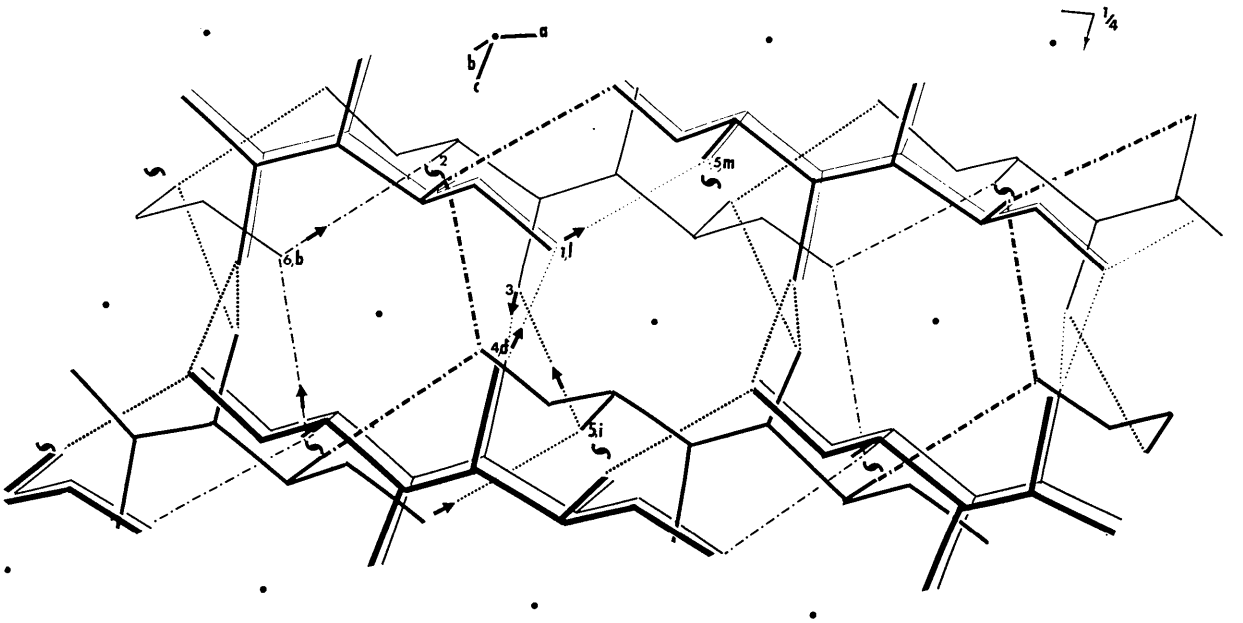

Fig. 5. Perspective drawing of the crystal structure of galactitol viewed down the *b* axis. The oxygen atoms are numbered according to the symmetry code given in Table 6. The arrows represent the sense of the bonding scheme. Dashed lines refer to the hydrogen bonding sheets. Dotted lines refer to the infinite hydrogen bonding chain.

the O(2)–O(6) and O(6)–O(2) being the shortest (2·63 and 2·68 Å respectively) (Table 6).

Table 6. *Hydrogen-bonding distances and angles in galactitol*

i	*j*	*k*	D_{jk}	$\angle(ijk)$
C(1)	O(1)	O(5*b*)	2·777 Å	103·7°
C(2)	O(2)	O(6*e*)	2·624	101·5
C(3)	O(3)	O(4*d*)	2·789	116·0
C(4)	O(4)	O(1*j*)	2·711	124·5
C(5)	O(5)	O(3*i*)	2·721	110·5
C(6)	O(6)	O(2*c*)	2·679	106·7

There are no non-bonded intermolecular contacts less than 3·3 Å.

Symmetry code

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

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