Burawoy, A., Liversedge, F., Vellins, C. E., Bartindale, G. W. R. & Farrow, G. (1954). *J. Chem. Soc.* 4481.
Chaudhuri, B., Kakati, K. K. & Bhattacharyya, G. C. (1963). *Indian J. Pure Appl. Phys.* **1**, 272.
Cochran, W. (1951). *Acta Cryst.* **4**, 408.
Crowder, M. M., Morley, K. A. & Taylor, C. A. (1959). *Acta Cryst.* **12**, 108.
Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Hanson, A. W., Lipson, H. & Taylor, C. A. (1953). *Proc. Roy. Soc.* A, **218**, 371.
International Tables for X-ray Crystallography (1952). Birmingham: Kynoch Press.
McWeeny, R. (1951). *Acta Cryst.* **4**, 513.
Pinnock, P. R. & Lipson, H. (1954). *Acta Cryst.* **7**, 594.
Pinnock, P. R., Taylor, C. A. & Lipson, H. (1956). *Acta Cryst.* **9**, 173.
Taylor, C. A. & Lipson, H. (1964). *Optical Transforms*, p. 128. London: Bell.
Woolfson, M. M. (1957). *Acta Cryst.* **10**, 116.

Acta Cryst. (1968). B**24**, 1652

The Crystal Structure of D,L-Arabinitol

By F. D. Hunter* and R. D. Rosenstein
Crystallography Laboratory, University of Pittsburgh, Pittsburgh, Pa. 15213, *U.S.A*

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The crystal structure of D,L-arabinitol, $C_5H_7(OH)_5$, was derived from the three-dimensional E^2-1 Patterson function by means of minimum functions. The structure was refined anisotropically by least squares to an R value of 0·037 for 557 reflections. The lattice parameters are $a=9{\cdot}213(1)$, $b=4{\cdot}855(2)$ and $c=15{\cdot}490(2)$ Å ($Z=4$). The D and L molecules are related by glide planes in the space group $Pna2_1$. The molecule has a planar zigzag carbon chain with oxygen atoms above and below the plane. All oxygen atoms are involved in a three-dimensional hydrogen-bonding scheme consisting of chains coiled around the screw axes.

Introduction

Arabinitol (lyxitol) is an acyclic polyalcohol formerly known as arabitol. Since D-arabinitol is 40–60% as sweet as sucrose, and experiments have shown that little or none is assimilated in the body, this substance has been suggested as a sugar substitute in foods (Crick, 1958).

The D form occurs in lichens (Lindberg, Misiorny & Wachtmeister, 1953) as the free carbohydrate and also as the galactoside, umbilicin. Neither L- nor D,L-arabinitol is found naturally. The L form is prepared by the catalytic reduction (Prince & Reichstein, 1937) of β-L-arabinose, which is obtained from mesquite gum (Anderson & Sands, 1929), and crystallization of a solution of an equimolar mixture of the enantiomorphs yields D,L-arabinitol.

As can be seen from the Fischer formulas below (with the terminal hydroxyls turned to the right by convention), arabinitol lies in a configurational sequence of increasing chain length between erythritol (*meso*-erythritol) and mannitol and also between threitol and galactitol. The terminal hydroxyls in these polyols are found in two different staggered conformations. The hydroxyl either continues the carbon chain to give an 'extended' conformation or it turns away from the chain in what might be called a 'flexed' conformation. Erythritol and mannitol are flexed at both ends. Threitol has not been studied, but the hydroxyls at both ends of galactitol are extended, as is the ter-

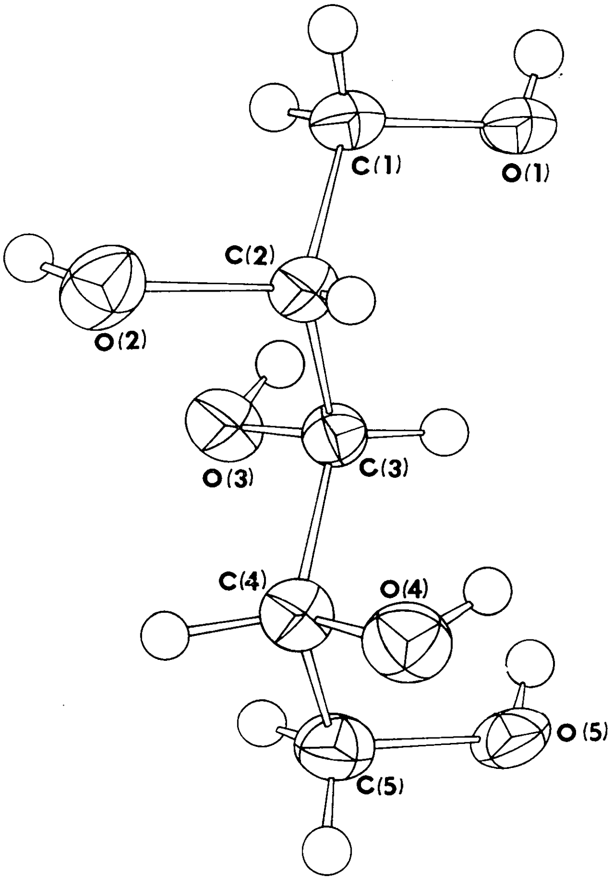

Fig. 1. D-Arabinitol molecule, showing atomic identification and thermal ellipsoids.

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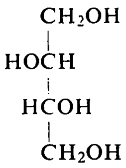
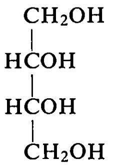
* Present address: W. R. Grace and Company, Research Division, Washington Research Center, Clarksville, Md. 21029, U.S.A.

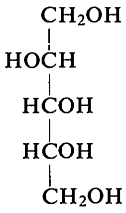
minal hydroxyl in the arabonate ion (Fig. 4). It seemed possible that arabinitol might be an example of a polyol in which the terminal hydroxyls differ in conformation.



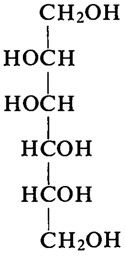
D-Threitol



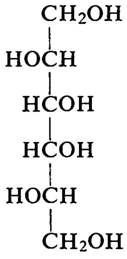
Erythritol



D-Arabinitol



D-Mannitol



Galactitol

Crystal data

Large transparent crystals were obtained by slow evaporation of a 1:1 water–ethanol solution of the compound supplied by Nutritional Biochemicals Corporation. The cell parameters were derived from general *hkl* reflections measured with Cu $K\alpha_1$ radiation using a Picker 4-angle automatic diffractometer. The crystal density was measured by flotation in a mixture of carbon tetrachloride and acetone.

D,L-arabinitol, $C_5H_7(OH)_5$, $M=152{\cdot}15$.

Orthorhombic, probable space group $Pna2_1$, from systematic absences $h0l$ for $h=2n+1$, $0kl$ for $k+l=2n+1$*.

$a=9{\cdot}213(1)$ Å, $b=4{\cdot}855(2)$ Å, $c=15{\cdot}490(2)$ Å.

$Z=4$, $D_m=1{\cdot}458$ g.cm^{-3}, $D_x=1{\cdot}462$ g.cm^{-3}.

$\mu_{\text{Cu } K\alpha}=11{\cdot}55$ cm^{-1}. $V=692{\cdot}8$ Å^3.

Experimental

The data were collected on a Picker 4-angle automatic diffractometer using a $\theta/2\theta$ scanning mode and a scan of 2°. The crystal used was pyramidal, $0{\cdot}40\times0{\cdot}20$ mm at the base and 0·54 mm in height. Of the 977 independent reflections in the limiting sphere for Cu $K\alpha$ radiation, 600 in each octant with 2θ values below 130° were accessible to the diffractometer.

The mean values of the intensities recorded in two octants were used in the structure determination. The average value recorded for systematic absences indicated that 43 reflections with $I\le1{\cdot}5\sigma(I)$ should be considered unobserved.

Determination of the structure

A variation of the method used to solve the structure of β-D-glucurono-γ-lactone (Kim, Jeffrey, Rosenstein & Corfield ,1967) was employed. The orientation of the molecule was found by inspection of the three-dimensional E^2-1 Patterson function and confirmed by minimum functions. The location of the 2_1 screw axis relative to two atoms of the molecule was found from a vector shift assumed to be from O(1) to O(3), see Fig. 1. Subsequently, nine out of the ten independent carbon and oxygen atoms were located in an M_4 multiple minimum function (Buerger, 1959) with $P2_1$ symmetry. In $Pna2_1$, locating the screw axis correctly relative to any atomic position is sufficient to determine the location of the other symmetry elements. A difference synthesis based on the structure factors of nine atoms supplied coordinates for the tenth atom and improved parameters for the other nine. This trial model gave an R value of 0·19 for all reflections.

Refinement of the structure

The refinement of the positional and thermal parameters was carried out by full-matrix least squares on the 557 observed reflections weighted as follows:

$$w=\frac{1}{(7{\cdot}88+1{\cdot}0F_o+0{\cdot}0095F_o^2)}\ \text{(Cruickshank, 1961).}$$

Two cycles of isotropic least-squares refinement reduced the R value to 0·097, at which stage a difference synthesis clearly revealed the seven hydrogen atoms attached to carbon atoms. After another cycle of isotropic least squares, in which the contribution to the structure factors of these seven hydrogen atoms were included without varying their positions, the remaining five hydrogens were located from a second difference map. After one cycle of anisotropic least squares, varying only the carbon and oxygen parameters, the hydrogen atoms were assigned the anisotropic thermal parameters of the atoms to which they were bonded. Three more cycles were run, varying all positional parameters and thermal parameters for oxygen and carbon only. This reduced the disagreement index to 0·037 and produced no shift greater than a standard deviation, at which stage the refinement was terminated.

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* The non-centrosymmetric alternative, $Pna2_1$, rather than the centrosymmetric space group *Pnam*, which has the same systematic absences, was chosen on the basis of the statistical distribution of the normalized structure factors as well as considerations of molecular symmetry. In *Pnam*, with $Z=4$, each arabinitol molecule would occupy a special position with *m* symmetry, contrary to its known optical activity.

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

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

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0·5189 (4)	0·4109 (8)	−0·0023 (4)	0·0114 (4)	0·0612 (19)	0·0020 (1)	0·0092 (8)	0·0008 (2)	0·0026 (4)
O(2)	0·7710 (3)	−0·1100 (5)	0·0749 (4)	0·0082 (4)	0·0238 (11)	0·0032 (1)	0·0014 (5)	0·0012 (2)	0·0005 (3)
O(3)	0·7823 (3)	0·4116 (5)	0·1625 (4)	0·0078 (3)	0·0284 (11)	0·0035 (1)	−0·0035 (2)	−0·0009 (2)	0·0012 (4)
O(4)	0·5304 (3)	−0·1091 (5)	0·2419 (4)	0·0091 (4)	0·0254 (11)	0·0030 (1)	−0·0014 (5)	−0·0001 (2)	0·0021 (3)
O(5)	0·5196 (3)	0·4106 (6)	0·3320 (4)	0·0108 (4)	0·0320 (13)	0·0022 (1)	0·0043 (6)	0·0012 (2)	0·0001 (4)
C(1)	0·6422 (5)	0·2379 (11)	−0·0041 (3)	0·0091 (6)	0·0405 (23)	0·0020 (1)	0·0036 (8)	0·0005 (3)	0·0009 (5)
C(2)	0·6479 (4)	0·0715 (8)	0·0789 (3)	0·0068 (5)	0·0270 (18)	0·0022 (1)	0·0022 (6)	0·0003 (2)	−0·0006 (5)
C(3)	0·6525 (3)	0·2494 (7)	0·1600 (0)	0·0060 (3)	0·0241 (11)	0·0024 (1)	0·0006 (6)	−0·0002 (2)	−0·0004 (6)
C(4)	0·6350 (4)	0·0773 (8)	0·2425 (3)	0·0075 (5)	0·0301 (20)	0·0024 (2)	0·0018 (6)	−0·0000 (2)	0·0005 (5)
C(5)	0·6510 (5)	0·2520 (3)	0·3240 (4)	0·0103 (7)	0·0365 (22)	0·0022 (1)	0·0026 (7)	−0·0005 (2)	−0·0002 (5)
H(C1)	0·636 (6)	0·130 (10)	−0·059 (3)						
H′(C1)*	0·732 (6)	0·332 (10)	−0·012 (3)						
H(C2)	0·575 (5)	−0·048 (9)	0·083 (3)						
H(C3)	0·566 (5)	0·375 (8)	0·163 (4)						
H(C4)	0·751 (5)	−0·033 (10)	0·247 (3)						
H(C5)	0·636 (5)	0·116 (10)	0·373 (3)						
H′(C5)*	0·745 (5)	0·398 (10)	0·324 (4)						
H(O1)	0·499 (6)	0·461 (11)	−0·050 (4)						
H(O2)	0·857 (5)	−0·034 (10)	0·062 (3)						
H(O3)	0·766 (5)	0·589 (10)	0·131 (3)						
H(O4)	0·470 (5)	−0·010 (11)	0·221 (3)						
H(O5)	0·525 (5)	0·565 (10)	0·300 (3)						

* [H′ atoms extend backwards from C(1) and C(5) respectively in Fig. 1.]

Table 2. *Observed and calculated structure factors*

Columns are: l index, $10|F_{\rm obs}|$, $10|F_{\rm cal}|$, $10A_{\rm cal}$, $10\,B_{\rm cal}$.
(* for unobserved reflections).

H= 0 K= 0				
2	543	544	223-	496
4	445	448	284	347
6	354	353	352	14-
8	285	283	47	279-
10	178	167	151-	71-
12	679	706	642	293-
14	134	131	40	124
16	96	100	92	39
18	86	88	88	7-
H= 2 K= 0				
0	40	38	38-	0
1	643	701	635-	297
2	628	677	113-	668-
3	385	415	186	371
4	452	493	492	35
5	67	66	17	64
6	160	155	155	9
7	48	54	49	22
8	337	352	285	207-
9	194	203	23-	202
10	277	290	71	281
11	188	187	187	12
12	46	46	20	42
13	201	204	121-	164
14	115	112	44-	103-
15	64	61	41	44
16	53	56	53	17-
17	17	18	3-	18
H= 4 K= 0				
0	309	312	312	0
1	184	181	150-	100
2	59	47	45-	13
3	47	43	32-	29-
4	95	90	68	58
5	23	24	9	23
6	77	79	77	19
7	16	15	14-	6-
8	61	58	4	58-
9	33	34	34-	1-
10	30	33	27-	18
11	64	66	60	29
12	65	63	62	11-
13	16	15	14-	3
14	37	37	8	36-
15	23	21	19-	9
16	10*	10	9	5
H= 6 K= 0				
0	339	339	339	0
1	197	205	89	184-
2	128	131	75-	108-
3	235	235	170	161
4	143	143	138	38
5	88	92	80-	47
6	144	139	134	38-
7	60	54	54	1-
8	123	122	93	80-
9	162	170	90-	144
10	85	87	3-	87
11	92	93	76-	54-
12	176	175	161	69-
13	92	96	5	96-
14	35	32	24-	21
H= 8 K= 0				
0	174	183	183	0
1	369	370	321-	182
2	57	53	53	3-
3	37	36	5	36
4	82	76	40	65
5	18	19	17	9
6	46	40	40	2
7	21	21	21-	2
8	55	55	10-	54-
9	44	43	8-	43
10	26	28	19	20-
11	195	200	198	26
H= 10 K= 0				
0	131	135	135-	0
1	25	26	3	26-
2	48	48	22	43-
3	121	117	62	99
4	43	38	24-	29-
5	38	39	10-	37
6	35	35	30	18-
H= 0 K= 1				
1	538	540	455-	290
3	337	348	54	343
5	664	676	636	229
7	472	484	336-	349
9	147	147	32	144
11	166	164	155	54
13	160	158	101-	121
15	72	73	27	68
17	104	102	102	12-
H= 1 K= 1				
0	27	24	24	0
1	219	229	108	202-
2	480	492	367	328-
3	231	229	133	186-
4	216	216	96-	193
5	551	559	514	220
6	523	545	533	114-
7	443	449	278-	352
8	87	90	87-	21-
9	87	87	85-	20-
10	161	155	145	54
11	69	72	70-	20-
12	51	50	31	39
13	68	71	3-	71-
14	122	120	52	109-
15	33	34	10	33-
16	49	49	1-	49
17	95	92	92	0
H= 2 K= 1				
0	662	641	641-	0
1	209	210	198	69
2	120	89	88-	10-
3	375	389	259-	291
4	137	118	5-	118-
5	102	101	2-	101-
6	233	228	222-	52
7	91	93	38-	85-
8	68	62	21	59
9	154	149	127	78
10	37	32	27-	17
11	61	63	23-	59
12	195	185	169-	76
13	64	62	54	31-
14	31	29	24-	16-
15	105	107	19-	105
16	42	41	30-	28-
17	9*	6	2-	6-
H= 3 K= 1				
0	455	477	477	0
1	128	131	131	2
2	119	105	88	59-
3	280	275	134-	241
4	75	70	31-	63
5	98	94	60-	72-
6	283	294	286	69-
7	83	79	31-	72-
8	52	44	3-	44-
9	119	117	90	75
10	33	25	25	2-
11	38	41	28-	30
12	154	155	153	24-
13	47	45	42	16-
14	30	28	28	0
15	82	84	22-	81
16	32	32	11	29
17	8*	8	6-	5-
H= 4 K= 1				
0	249	244	244	0
1	255	253	206	147-
2	79	74	54-	50
3	28	23	11	21
4	113	112	80	78
5	157	146	136	53
6	110	110	110-	7
7	106	108	78-	74
8	62	63	12	62-
9	24	23	7-	22
10	19	17	16-	2
11	90	90	90-	8
12	93	97	73	63-
13	107	107	28	103-
14	48	46	10-	45
15	9*	6	4-	5
16	29	30	29	6
H= 5 K= 1				
0	100	99	99	0
1	141	147	126-	75
2	229	235	197	128-
3	73	69	11-	68
4	201	204	16	204
5	142	139	130	47
6	57	57	55	15-
7	87	85	70-	48
8	127	131	41-	125-
9	52	52	7	52
10	96	98	97	11
11	64	63	53	38
12	42	43	43	0
13	60	59	44-	38
14	68	69	44	53-
15	22	23	13-	19
H= 6 K= 1				
0	168	165	165	0
1	200	193	146-	127
2	123	114	103-	50
3	141	135	57-	122
4	108	108	48	96-
5	58	59	55	20-
6	51	52	50	15-
7	62	62	59-	18
8	65	63	46	44
9	72	71	47	54
10	50	48	48-	1-
11	98	98	97	14
12	86	82	66	49-
13	99	98	38-	91
14	50	51	23-	45
H= 7 K= 1				
0	14*	16	16-	0
1	47	45	27	36
2	48	50	10-	49-
3	143	147	87-	118
4	94	92	39-	83-
5	72	67	66	11-
6	225	231	225	51-
7	77	77	76-	10
8	81	82	4-	82
9	62	63	52	36
10	36	36	9	35
11	25	28	1-	28
12	22	20	13-	15
13	22	25	24	1
H= 8 K= 1				
0	156	152	152-	0
1	42	31	21-	23
2	28	14	11	10-
3	75	72	23	69
4	39	39	33	21
5	50	54	41	35
6	178	175	172-	35
7	42	38	12-	37
8	36	35	9	34-
9	61	57	13	56
10	11*	8	8	1
11	27	26	18	19
H= 9 K= 1				
0	65	59	59	0
1	70	66	56	36-
2	29	25	24	5-
3	66	62	10-	62
4	85	86	38	78
5	92	94	92	22
6	77	80	79-	14
7	83	85	67-	53
8	69	72	1	72-
9	43	49	16	47
H= 10 K= 1				
0	12*	14	14-	0
1	46	50	44	25-
2	62	66	64-	17
3	8*	4	1	4-
4	49	47	0	47-
5	20	25	25-	3-
H= 0 K= 2				
0	208	212	212	0
2	136	133	70-	114
4	107	107	51	94
6	288	279	264-	90
8	97	93	6	93-
10	68	64	57-	28-
12	47	42	35	23
14	30	25	4	24
16	20	20	9	18
H= 1 K= 2				
0	277	273	273-	0
1	215	205	205-	4-
2	225	215	25-	214-
3	325	322	198	254
4	133	125	122	28-
5	123	121	42	113
6	118	107	107-	11-
7	55	53	14-	51
8	128	129	119	51-
9	235	233	69-	222
10	100	100	38	92
11	86	82	75	32-
12	94	81	72-	38
13	61	60	59-	11
14	37	33	26-	20-
15	74	74	50	54
16	26	26	24	10-
H= 2 K= 2				
0	136	143	143	0
1	114	110	84	72-
2	173	164	21	163-
3	16	21	0	21-
4	110	110	91	61
5	234	235	222-	78-
6	145	143	139	30-
7	232	225	162	156-
8	74	63	40	48-
9	22	19	19-	0
10	83	84	33	78
11	33	37	36-	8
12	48	46	46	7-
13	46	47	12	45-
14	27	28	2-	28-
15	24	24	20-	14-
16	29	29	21	20
H= 3 K= 2				
0	172	161	161	0
1	487	495	431-	243
2	237	224	100	201
3	153	156	67	141
4	137	139	131-	45
5	63	67	56-	37
6	48	41	40-	8
7	90	92	63	68-
8	141	143	139-	34
9	118	116	27-	113
10	141	142	7-	142-
11	204	211	210	21
12	54	54	39	37-
13	164	170	102-	136
14	61	61	43	43
15	33	37	14	34
16	20	22	10-	20
H= 4 K= 2				
0	291	296	296	0
1	162	151	129-	79
2	52	37	28-	24-
3	62	62	15-	60
4	33	28	9	26-
5	138	137	134	30
6	267	274	267	59-
7	142	143	107-	95
8	38	33	3	33
9	22	23	3	23
10	28	24	6	23
11	60	61	60	13
12	114	116	110	37-
13	60	60	40-	46
14	9*	5	3-	5-
15	24	25	5	25
H= 5 K= 2				
0	445	439	439-	0
1	54	53	14-	51-
2	146	119	52	107-
3	246	245	124	211
4	121	111	76-	80-
5	62	58	3-	58
6	111	110	91	62-
7	34	33	27	20
8	103	103	19-	101
9	163	164	32-	161
10	83	84	71	45
11	27	26	0	26-
12	182	185	171-	71
13	20	20	16-	12-
14	45	48	12-	46-
H= 6 K= 2				
0	63	56	56-	0
1	26	23	21-	8
2	37	34	8	33-
3	129	127	33	122
4	62	66	54	37
5	76	78	64	44
6	127	131	127-	32
7	86	87	47-	74
8	64	67	29	60-
9	82	79	9-	78
10	18	14	2	14
11	17	17	16	7
12	34	34	27-	21
13	18	18	15-	11
H= 7 K= 2				
0	59	58	58-	0
1	71	76	59-	49
2	86	85	50	69
3	38	31	29-	9
4	68	62	58-	22
5	79	79	78	13
6	61	62	62-	7
7	81	82	72-	39
8	77	78	75-	23
9	22	19	19	1
10	66	67	11	66-
11	41	41	39	12
12	31	32	32-	1-
H= 8 K= 2				
0	9*	2	2	0
1	23	23	18-	14
2	18	21	18-	11
3	8*	4	3-	2
4	16	18	9-	15
5	64	68	66-	16-
6	41	44	43-	10
7	74	74	52	52-
8	17	20	19-	6-
9	8*	7	5-	5
10	13	14	14-	2-
H= 9 K= 2				
0	33	37	37-	0
1	31	34	17	29-
2	38	39	12	37
3	69	69	40	56
4	40	43	38-	20-
5	17	18	16-	7
6	24	26	20-	16-
7	21	25	24	5
H= 10 K= 2				
0	33	36	36	0
1	8*	14	5-	13-
H= 0 K= 3				
1	26	29	12-	27-
3	35	34	0	34
5	153	157	149	52
7	72	70	68-	16
9	36	33	13-	31
11	36	34	13	31
13	44	42	33-	27-
15	25	27	23-	13
H= 1 K= 3				
0	27	26	26	0
1	43	37	3-	36
2	39	38	37-	9-
3	40	40	32-	25
4	62	63	51	36-
5	35	33	32-	9-
6	36	32	30-	12
7	36	38	9	37-
8	37	37	36	9
9	23	24	23	6-
10	32	33	24-	23
11	9*	17	10	14
12	16*	6	2-	6-
13	18	16	9	13
14	19	20	8-	18
15	15	15	0	15
H= 2 K= 3				
0	51	49	49	0
1	83	87	47	73
2	61	59	59-	4-
3	339	332	168-	286
4	121	116	16-	115-
5	107	108	87	64-
6	247	249	239	70-
7	103	102	100-	19-
8	116	111	8	111
9	162	166	116	119
10	25	24	3-	24
11	35	34	8	33
12	40	37	24	28-
13	23	24	22	9
14	22	23	23-	4
H= 3 K= 3				
0	17	21	21	0
1	31	33	14-	30-
2	44	45	37-	27
3	86	91	89	15
4	34	30	23	19
5	60	63	23	59
6	86	85	83-	19
7	49	49	13	47
8	25	23	3	23-
9	55	60	43-	42
10	18	17	15-	9
11	18	20	11-	17-
12	19	11	9	7-
13	9*	9	8-	1-
14	35	32	7-	31
H= 4 K= 3				
0	55	51	51-	0
1	25	26	26-	2-
2	39	38	15-	35
3	100	102	17	100
4	111	114	88	72
5	331	337	318	112
6	313	316	311-	56
7	307	306	225-	207
8	96	95	31	90-
9	77	77	11	76
10	25	22	12-	19-
11	22	19	13	15
12	33	33	33-	1-
13	32	33	33-	2
H= 5 K= 3				
0	19	22	22-	0
1	60	67	58-	35
2	44	45	42-	14
3	9*	10	10-	3-
4	37	32	1	32-
5	65	64	61-	18-
6	27	24	24-	4
7	51	50	17	47-
8	26	24	10	21
9	10*	8	5	5
10	29	27	24-	11
11	28	29	28	8-
12	16	13	13-	3
H= 6 K= 3				
0	19	20	20-	0
1	37	40	1	40
2	136	133	113-	69
3	96	98	53-	82
4	91	88	20	85-
5	116	113	98-	56-
6	125	123	122-	19
7	119	118	65	99-
8	52	52	25	46
9	51	55	37	40
10	78	75	73-	18-
11	21	25	19	16
H= 7 K= 3				
0	11*	2	2-	0
1	20	19	14-	13-
2	15*	17	14	10
3	43	40	39	2-
4	8*	4	2-	4
5	27	27	21-	17
6	22	21	20-	5
7	23	21	21	0
8	10*	10	10-	0
9	31	31	22-	22
H= 8 K= 3				
0	8*	7	7-	0
1	17	16	3-	16-
2	7*	4	3-	2
3	20	20	8	18
4	8*	11	10	5
5	12*	10	3	9-
6	14	15	9-	12-
7	9*	10	1-	10-
H= 9 K= 3				
0	23	25	25-	0
1	23	23	18-	14
2	8*	11	10-	5-
H= 0 K= 4				
0	161	162	162-	0
2	79	71	39	59-

Table 2 (*cont.*)

4	66	64	31-	55-	5	106	104	104	9	3	18	18	7-	17	5	38	36	6-	36-	H= 2 K= 5				
6	147	150	141	52-	6	69	70	69-	10	4	44	43	6-	43-	6	40	39	38	10-	0	134	130	130-	0
8	76	75	11-	74	7	116	116	87-	77	5	41	40	39-	10-	7	17	23	5-	23-	1	37	40	25	31-
10	63	64	60	23	8	83	84	78-	32	6	86	87	86-	8	H= 7 K= 4					2	34	30	17	25-
12	52	58	51-	29	9	31	33	32	5-	7	38	36	31	19-	0	9•	8	8-	0	3	32	35	25	24
H= 1 K= 4					10	88	86	7	86-	8	28	28	12	25	1	8•	10	7-	7	4	23	21	11-	18-
0	44	38	38-	0	11	40	37	33	17	9	14	9	8	3-	2	28	32	1-	32	5	12•	14	10-	10
1	30	26	22-	14-	12	32	34	33-	10	10	19	17	15	8	3	8•	2	2	1-	6	29	34	34-	5
2	37	31	7-	30-	H= 3 K= 4					H= 5 K= 4					4	18	16	11-	11-	7	14	16	15	6-
3	103	103	38	95	0	35	32	32	0	0	155	155	155-	0	H= 0 K= 5					H= 3 K= 5				
4	56	54	40	37	1	158	157	144-	63	1	28	28	3	28-	1	150	146	126-	73	0	58	59	59-	0
5	59	58	50	31	2	83	82	18-	80	2	57	55	35	43-	3	18	13	6-	12	1	29	34	28-	18-
6	93	93	93-	10	3	31	33	4	33	3	66	63	24	58	5	21	20	19	5	2	8•	9	4	8
7	49	47	30-	36	4	46	46	42-	17-	4	42	42	11-	41-	7	27	32	31-	2-	3	75	78	54	57-
8	54	54	26	47-	5	41	40	33-	23-	5	15•	14	13-	4-	H= 1 K= 5					4	27	35	30	17-
9	75	73	20-	71	6	36	33	32-	9	6	44	40	35	19-	0	17•	9	9	0	5	29	32	11	30
10	26	26	4	26	7	45	47	16	44-	7	8•	13	8	10-	1	38	34	17-	29	6	58	62	62-	9
11	8•	10	10	1-	8	48	49	43-	23	8	39	39	0	39	2	71	75	58-	48	H= 4 K= 5				
12	13	13	12-	5-	9	31	31	7-	31	9	46	47	12-	45	2	76	75	58-	48	0	30	30	30	0
H= 2 K= 4					10	50	50	19-	46-	H= 6 K= 4					3	46	46	30-	35	1	39	40	33	22-
0	46	42	42-	0	11	89	89	89	5	0	31	33	33	0	4	55	53	38	37-	2	17	18	5-	18
1	71	70	42-	56	H= 4 K= 4					1	42	40	35	20	5	115	114	101-	53-	3	8•	12	3-	11-
2	136	137	82	110	0	227	229	229-	0	2	55	53	22	48	6	102	102	101-	17	4	8•	10	10-	3
3	44	45	45-	3	1	121	125	114	52-	3	80	79	68-	42-	7	80	101	56	84-	5	8•	9	9-	1
4	88	92	90-	20	2	50	40	7	40-	4	47	47	47-	1	8	37	37	33	16					

Table 3. *Principal axes of thermal ellipsoids*

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

	i	U_i	θ_{ia}	θ_{ib}	θ_{ic}
O(1)	1	0·1488 Å	95·6°	98·6°	10·3°
	2	0·1921	149·9	60·0	90·6
	3	0·2952	60·6	31·4	79·7
O(2)	1	0·1634	55·4	140·1	107·4
	2	0·1715	58·8	52·1	126·6
	3	0·2176	50·1	79·4	41·8
O(3)	1	0·1604	42·2	48·3	84·2
	2	0·1855	115·5	54·4	133·6
	3	0·2230	121·1	62·1	44·1
O(4)	1	0·1562	99·1	145·6	57·1
	2	0·1952	149·7	98·7	118·8
	3	0·2085	118·6	57·0	46·5
O(5)	1	0·1518	115·3	75·9	29·4
	2	0·1841	110·7	32·7	114·1
	3	0·2349	33·6	61·2	74·2
C(1)	1	0·1535	102·4	93·6	13·0
	2	0·1857	146·4	57·8	98·6
	3	0·2324	59·4	32·4	80·3
C(2)	1	0·1513	125·6	60·9	49·4
	2	0·1710	124·2	70·3	139·0
	3	0·1903	54·1	36·3	94·4
C(3)	1	0·1569	23·5	100·1	68·9
	2	0·1656	83·9	139·5	129·8
	3	0·1762	112·6	128·7	47·2
C(4)	1	0·1686	61·9	117·6	41·3
	2	0·1753	44·5	107·6	129·2
	3	0·1972	58·7	33·5	79·1
C(5)	1	0·1622	77·1	91·9	13·0
	2	0·1959	129·4	71·0	80·2
	3	0·2248	42·2	49·0	98·4

The final positional and thermal parameters are listed in Table 1 and the corresponding structure factors are given in Table 2. The principal axes of the thermal ellipsoids are given in Table 3 and illustrated in Fig. 1. The scattering factors for C and O were taken from *International Tables* (1962) and the Stewart, Davidson & Simpson (1965) values were used for H.

The programs used were as follows:

For the IBM 1620: lattice parameter refinement by Schwarzenbach (1967), diffractometer settings by Chu & Craven (1965), data reduction by Chu (1967), structure factor normalization by Beurskens (1963), minimum functions by Corfield (1965), structure factor, Fourier synthesis and distances and angles by Shiono (1963), dihedral angles by Chu (1965), and standard deviations and thermal corrections by Craven (1965).

For the IBM 7090: least-squares refinement by Busing, Martin & Levy (1964), modified by Shiono (1966*a*), Fourier synthesis by Zalkin, modified by Shiono (1966*b*), and thermal ellipsoid plotter by Johnson (1965).

Description

Arabinitol has a zigzag carbon skeleton linked to a series of hydroxyls, all of which are above or below the plane of the carbon atoms. The D-enantiomer in this D,L-structure is depicted in Fig. 1, as can be seen by comparison with the Fischer projection in the *Introduction*.* The carbon chain lies almost parallel to the (100) crystallographic plane, as shown by the equation of the plane given in Table 4, and is quite flat, the mean deviation being 0·016 Å. The atom in the chain farthest from the plane is C(3), with a distance of 0·036 Å. The conformation angles are given in Fig. 2.

The bond lengths and valence angles are given in Tables 4 and 5. The C–C distances are equivalent within experimental error, with a mean value of 1·523 Å. The C–O distances have a mean value of 1·434 Å, with the C(1)–O(1) distance being significantly shorter than the mean value by 3·5σ. The shortness of this bond length can probably be attributed to thermal motion, since correcting for this effect, assuming a 'riding' mode (Busing & Levy, 1964), increased the value to 1·423 Å, which differs from the mean of all the corrected C–O distances by less than 2σ.

The hydrogen-bond distances in D,L-arabinitol vary from 2·692 to 2·768 Å, O(3)–O(4*a*) being the shortest (Table 6). Each molecule in the structure is

---

* Each carbon atom in the Fischer projection is assumed to have its vertical bonds pointed away from the viewer and hence its horizontal bonds out of the page. Since the hydroxyl attached to the highest-numbered 'asymmetric' carbon atom, C(4), points to the right (as well as out), this is the D-form. The Fischer projection of D-arabitol differs from the view in Fig. 1 at C(3), which has its vertical bonds pointing out of the page.

surrounded by six other molecules. The enantiomers are related by an *a*-glide to form D,L pairs which are connected by two hydrogen bonds, O(2*a*)–O(1) and O(4)–O(3*a*′), according to the symmetry code given in Table 6. The D molecule is joined to two other D-enantiomers at a distance of a unit-cell translation along the short axis by hydrogen bonds from O(3)–O(2′) and O(5)–O(4′) in the positive *y* direction and from O(3′) to O(2) and O(5′)–O(4) in the negative *y* direction. This molecule is also joined to two others related to it by a twofold screw axis along the long axis by hydrogen bonds from O(1) to O(5*c*′) in the negative *z* direction and O(1*c*) to O(5) in the positive *z* direction. Finally, this D-enantiomer is hydrogen-bonded to a second L-enantiomer by bonds from O(2) to O(1*b*) and O(4*b*) to O(3) in the positive *x* direction. Symmetrically, the same type of hydrogen bonding is formed by the L-enantiomer.

Because of this sequence of bonding, each oxygen has two hydrogen bonds, one donor and one acceptor,

Table 4. *Bond lengths and least squares plane in* D,L-*arabinitol*

The equation used was $AX+BY+CZ=D$, where X, Y, Z are in Å and $A=0{\cdot}9996$, $B=0{\cdot}0200$, $C=-0{\cdot}0167$ and $D=5{\cdot}956$. The estimated standard deviations given in parentheses refer to the last decimal position.

i	j	D_{ij}
C(1)	C(2)	1·520 (7) Å
C(2)	C(3)	1·525 (5)
C(3)	C(4)	1·527 (5)
C(4)	C(5)	1·520 (8)
C(1)	O(1)	1·413 (6)
C(2)	O(2)	1·437 (5)
C(3)	O(3)	1·432 (4)
C(4)	O(4)	1·447 (5)
C(5)	O(5)	1·440 (6)
C(1)	H(C1)	1·00 (5)
C(1)	H′(C1)	0·95 (5)
C(2)	H(C2)	0·89 (5)
C(3)	H(C3)	1·00 (4) Å
C(4)	H(C4)	1·05 (5)
C(5)	H(C5)	1·01 (5)
C(5)	H′(C5)	1·12 (5)
O(1)	H(O1)	0·80 (6)
O(2)	H(O2)	0·90 (4)
O(3)	H(O3)	1·00 (5)
O(4)	H(O4)	0·81 (5)
O(5)	H(O5)	0·90 (5)

Atoms in plane	Deviation in Å from plane
C(1)	−0·017
C(2)	−0·002
C(3)	0·036
C(4)	0·003
C(5)	−0·020

Table 5. *Bond angles in* D,L-*arabinitol*

The estimated standard deviations given in parentheses refer to the last decimal position.

i	j	k	$\angle(ijk)$
C(1)	C(2)	C(3)	113·3 (3)°
C(2)	C(3)	C(4)	112·3 (3)
C(3)	C(4)	C(5)	112·9 (4)
O(1)	C(1)	C(2)	109·1 (4)
O(2)	C(2)	C(1)	108·4 (4)
O(2)	C(2)	C(3)	111·2 (3)
O(3)	C(3)	C(2)	110·9 (3)
O(3)	C(3)	C(4)	106·0 (3)
O(4)	C(4)	C(3)	109·5 (3)
O(4)	C(4)	C(5)	110·2 (4)
O(5)	C(5)	C(4)	112·4 (4)
C(2)	C(1)	H(Cl)	116 (3)
O(1)	C(1)	H(Cl)	106 (3)
H′(Cl)	C(1)	H(Cl)	102 (4)
C(2)	C(1)	H′(Cl)	109 (3)
O(1)	C(1)	H′(Cl)	115 (3)
O(2)	C(2)	H(C2)	101 (3)
C(1)	C(2)	H(C2)	112 (3)
C(3)	C(2)	H(C2)	109 (3)
C(2)	C(3)	H(C3)	111 (3)
C(4)	C(3)	H(C3)	108 (3)
O(3)	C(3)	H(C3)	109 (3)
C(3)	C(4)	H(C4)	110 (3)°
C(5)	C(4)	H(C4)	104 (3)
O(4)	C(4)	H(C4)	110 (3)
C(4)	C(5)	H(C5)	100 (3)
O(5)	C(5)	H(C5)	105 (3)
H′(C5)	C(5)	H(C5)	121 (4)
C(4)	C(5)	H′(C5)	108 (3)
O(5)	C(5)	H′(C5)	110 (3)
C(1)	O(1)	H(O1)	110 (4)
C(2)	O(2)	H(O2)	117 (3)
C(3)	O(3)	H(O3)	110 (3)
C(4)	O(4)	H(O4)	100 (4)
C(5)	O(5)	H(O5)	110 (3)

and there are infinite hydrogen-bonding chains having the donor sequence O(1*c*′)–O(5)–O(4′)–O(3*a*′)–O(2*a*′)–O(1) extending in the negative *z* direction. The chain develops around a twofold screw axis to form a helical-type scheme with each molecule participating in four of these schemes; see Fig. 3. Each of these chains involves both terminal hydroxyls from one of the four molecules per unit cell. None of the other chains involves more than one hydroxyl from that molecule. There are four helices per unit cell, and by symmetry, two are left-handed and two right-handed.

Discussion

As shown in Fig. 4, the corresponding segments of D-arabinitol and D-mannitol (Berman, Jeffrey & Rosenstein, 1968; Kim, Jeffrey & Rosenstein, 1968) have the same conformation as the *meso*-erythritol molecule. (Bekoe & Powell, 1959; Shimada, 1959). In general, the conformation angles in these compounds show differences of less than 5° which can be attributed to hydrogen bonding and packing. It may be fortuitous that for the bond labelled '*a*' in the three molecules, the hydroxyls form dihedral angles of 59·0° with each other. The other angles involved in this projection are 59·4° and 63·6° in arabitol and 62·8° and 62·4° in the *B*-form of mannitol.

The apparent shortness of the terminal C–C bonds in D,L-arabinitol, which could be brought significantly closer to the average value by applying corrections for thermal motion, is also found in the structure of *meso*-erythritol, D-mannitol and galactitol, and could be corrected in the same way. The range of the C–C–C valence angles, from 112·3 to 113·3°, agrees with the trend noted before (Berman, Jeffrey & Rosenstein, 1968; Berman & Rosenstein, 1968) that the valence angles in the carbon chain in acyclic polyols are generally greater than the ideal tetrahedral angles.

It is noteworthy that the conformation of arabinitol is not the same as that of the arabonate ion. The conformation angles of this ion in calcium arabonate pentahydrate (Furberg & Helland, 1962) are given in Fig. 5. Since the arabonate ion has a carboxyl group at one end and a hydroxyl in the extended conformation at the other end, only the two inner C–C bonds in these two compounds can be similar. Even here,

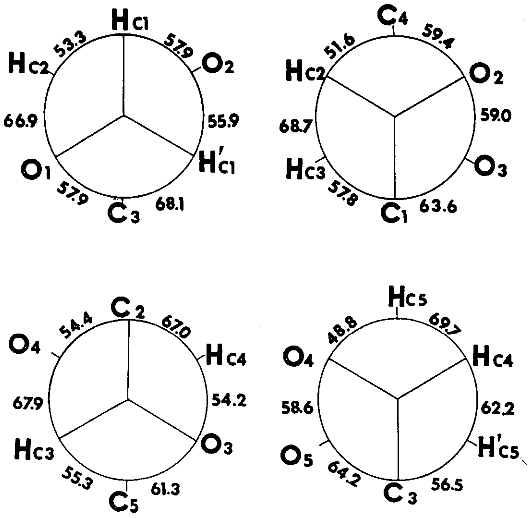

Fig. 2. Conformation angles (in degrees) for the D-arabinitol molecule in D,L-arabinitol. The Newman projections are of the C(1)–C(2), C(2)–C(3), C(3)–C(4) and C(4)–C(5) bonds from left to right and top to bottom, respectively.

Table 6. *Hydrogen bond distances and angles*

Symmetry code

–	*x*	*y*	*z*
a	$\frac{1}{2}+x$	$\frac{1}{2}-y$	*z*
b	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}+z$
c	$\bar{x}$	$\bar{y}$	$\frac{1}{2}+z$

(A prime denotes a unit cell translation)

The estimated standard deviations are given in parentheses.

i	*j*	*k*	*D*(*ij*)	*D*(*jk*)	∠(*ijk*)
C(1)	O(1)	O(5*c*′)		2·732 (8) Å	105·9 (3)°
C(2)	O(2)	O(1*a*)		2·753 (6)	117·3 (3)
C(3)	O(3)	O(2′)		2·692 (5)	115·4 (2)
C(4)	O(4)	O(3*a*′)		2·768 (5)	115·5 (3)
C(5)	O(5)	O(4′)		2·720 (5)	112·5 (3)
O(5*c*′)	O(1)	O(2*a*′)	2·732 (8) Å	2·753 (6)	100·9 (2)
O(1*a*)	O(2)	O(3′)	2·753 (6)	2·692 (5)	119·3 (2)
O(2′)	O(3)	O(4*a*)	2·692 (5)	2·768 (5)	87·5 (2)
O(3*a*′)	O(4)	O(5′)	2·768 (5)	2·720 (5)	119·6 (2)
O(4′)	O(5)	O(1*c*′)	2·720 (5)	2·732 (8)	102·4 (2)
O(1)	H(O1)	O(5*c*′)			172 (6)
O(2)	H(O2)	O(1*a*)			161 (4)
O(3)	H(O3)	O(2′)			170 (4)
O(4)	H(O4)	O(3*a*′)			157 (5)
O(5)	H(O5)	O(4′)			176 (5)

however, the values listed in Figs. 2 and 5 show that there are large dissimilarities. Moreover, the C(5)–O(5) bond in the anion is displaced 15·5° out of the plane of the carbon chain, in contrast to the planarity of the extended zigzag in galactitol.

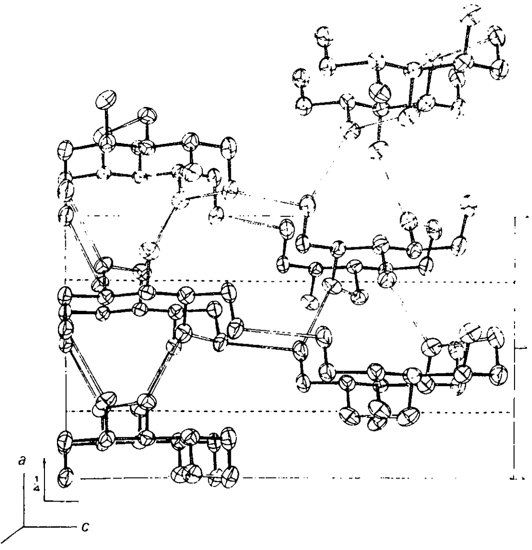

Fig. 3. Perspective view of the structure along the *b* axis showing the hydrogen bonding (solid white lines represent hydrogen bonding).

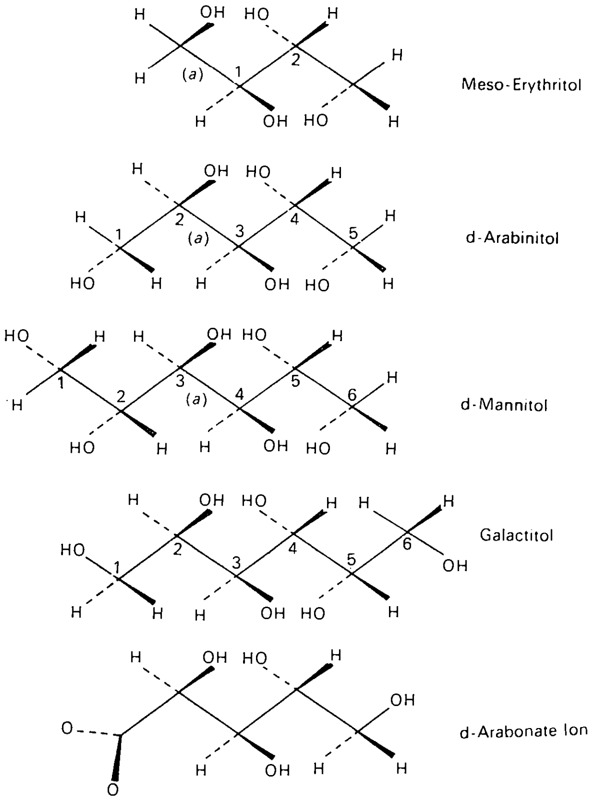

Fig. 4. Acyclic carbohydrate conformations.

Although the torsional barrier to rotation around the C–C bond is presumably small and comparable to the energy of the hydrogen bond, the persistence of the planar zigzag carbon chain throughout this series of structures suggests that this rotomer is energetically favored even outside a crystal environment. This has recently been demonstrated by El Khadem, Horton & Page (1968) with nuclear magnetic resonance spectroscopy in methyl sulfoxide-d_6 solutions of a series of osotriazoles of the sugars. While the errors arising from the approximations involved in quantum mechanical energy calculations are probably too serious to justify acceptance of the numerical values obtained, an estimate of the dipole moment may be obtained from calculations using self-consistent molecular orbitals with complete neglect of differential overlap (Pople, Santry & Segal, 1965 and Pople & Segal, 1965). Using this CNDO procedure, Stewart (1967) has found a value of 6·5 debye units for the arabinitol molecule, with the parameters reported in this paper. The general direction of the dipole moment is from the center of gravity of the molecule towards H′(Cl), inclined 5·8° to the plane of the zigzag and 78·2° from the C(2)–C(3) bond. The direction cosines for μ are 0·07556, 0·68691 and $-0·72281$, corresponding to angles of 85·7°, 46·6° and 43·7° to **a**, **b** and **c**. This direction evidently cannot be rationalized as resulting exclusively from cancellation between pairs of anti-parallel C–O bond moments, but must include the CH and OH contributions as well. The high value of the molecular moment may provide some clue to the conformation of the terminal hydroxyls in the acyclic polyols, since the only example of the extended conformation found so far is galactitol, where the moment is zero by $\bar{1}$ symmetry.

Since in contrast to D,L-arabinose (Kim & Jeffrey, 1967) which is centrosymmetric, D,L-arabinitol has a polar space group, the dipole stacking results in an estimated net dipole moment of $4 \times 0·7228 \times 6·5 = 18·8$ debye units per unit cell, in the negative *z* direction. Another example of a racemate with the same polar space group is aminomaleic acid (Kanters, Kroon, Beurskens & Vliegenthort, 1966).

Chu & Jeffrey (1967) observed that the helical hydrogen bonding scheme in methyl β-maltopyranoside was polar, as is the finite hydrogen bonding scheme in β-D-glucurono-γ-lactone (Kim, Jeffrey, Rosenstein & Corfield, 1967). Hydrogen bonding schemes winding around screw axes have been found in crystal structures of erythritol and mannitol, and also occur in D-galactono-γ-lactone (Jeffrey, Rosenstein & Vlasse, 1967). In these compounds, however, each helix involves only one oxygen from each molecule. D,L-arabinitol has a single helical hydrogen bonding scheme only, in contrast for example, to the *B* and *K* forms of mannitol and *meso*-erythritol, where there are closed-circuit quadrilaterals as well as helices. As Bekoe & Powell (1959) have pointed out, no necessary resemblance need be expected between molecular arrangements in crystals of either the *meso* or active forms and that of the racemate. Hence, the difference in hydrogen-bonding schemes might be attributed to the fact that D,L-arabinitol is racemic, with the enantiomers glide-related, whereas D- or L-arabinitol alone might have a hydrogen-bonding scheme more similar to its configurational relatives.

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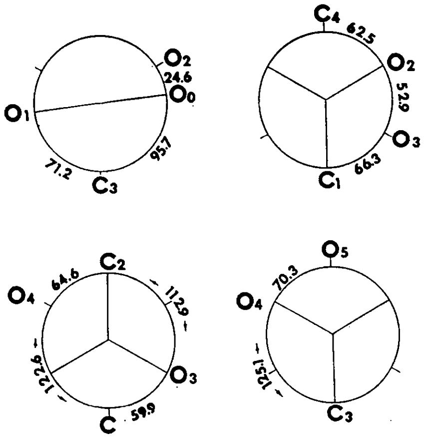

Fig. 5. Conformation angles (in degrees) for the arabonate ion in calcium arabonate. The Newman projections are in the same order as that for D-arabinitol.

References

Anderson, E. & Sands, L. (1929). *Org. Syntheses* **8**, 18.

Bekoe, A. & Powell, H. M. (1959). *Proc. Roy. Soc.* A**250**, 301.

Berman, H., Jeffrey, G. A. & Rosenstein, R. D. (1968). *Acta Cryst.* B**24**, 442.

Berman, H. & Rosenstein, R. D. (1968). *Acta Cryst.* B**24**, 435.

Beurskens, P. T. (1963). Technical Report, Crystallography Lab. University of Pittsburgh.

Buerger, M. J. (1959). *Vector Space*. New York: Wiley.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **18**, 142.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *FORTRAN Crystallographic Least Squares Program.* ORNL-TM-305, Oak Ridge National Laboratory.

Chu, S. C. (1965). *Dihedral Angles*. Unpublished work.

Chu, S. C. (1967). *Data Reduction*. Unpublished work.

Chu, S. C. & Craven, B. M. (1965). IBM 1620 Picker Diffractometer Data Processing Program, Crystallography Lab. University of Pittsburgh.

Chu, S. C. & Jeffrey, G. A. (1967). *Acta Cryst.* **23**, 1038.

Corfield, P. W. R. (1965). *IBM 1620 Programs for the Solution of the Patterson Function by Superposition Methods.* Technical Report, Crystallography Lab. University of Pittsburgh.

Craven, B. M. (1965). FORTRAN Program for Thermal Motion Corrections for Interatomic Distances. Crystallography Lab. University of Pittsburgh.

Crick, R. G. D. (1958). Brit. 884, 961. Distillers Co. Ltd. Appl. Feb. 4.

Cruickshank, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis,* Edit. Pepinsky *et al.* New York: Pergamon.

El Khadem, H. S., Horton, D. & Page, T. Jr. Private communication.

Furberg, S. & Helland, S. (1962). *Acta Chem. Scand.* **16**, 2373.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Jeffrey, G. A., Rosenstein, R. D. & Vlasse, M. (1967). *Acta Cryst.* **22**, 725.

Johnson, C. K. (1965). *A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations.* ORNL-3794, Oak Ridge National Laboratory.

Kanters, J. A., Kroon, J., Buerskens, P. T. & Vliegenthart, J. A. (1966). *Acta Cryst.* **21**, 990.

Kim, S. H. & Jeffrey, G. A. (1967). *Acta Cryst.* **22**, 537.

Kim, S.H., Jeffrey, G.A. & Rosenstein, R.D. (1968). In the press.

Kim, S. H., Jeffrey, G. A., Rosenstein, R. D. & Corfield, P. W. R. (1967). *Acta Cryst.* **22**, 733.

Lindberg, B., Misiorny, A. & Wachtmeister, C. A. (1953). *Acta Chem. Scand.* **7**, 591.

Pople, J. A. & Segal, G. A. (1965). *J. Chem. Phys.* **43**, 5136.

Pople, J. A., Santry, D. P. & Segal, G. A. (1965). *J. Chem. Phys.* **43**, 5129.

Prince, R. & Reichstein, T. (1937). *Helv. Chim. Acta* **20**, 101.

Schwarzenbach, D. (1967). *Lattice Parameter Refinement.* Unpublished work.

Shimada, A. (1959). *Bull. Chem. Soc. Japan,* **32**, 325.

Shiono, R. (1963). Technical Reports Nos. 43 and 45, Crystallography Laboratory, Univ. of Pittsburgh.

Shiono, R. (1966*a*). Oak Ridge Least Squares Program Modified for the Crystallography Laboratory of the University of Pittsburgh.

Shiono, R. (1966*b*). Adaption of the Zalkin Fourier Program for the 7090 Computer. Unpublished work.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Stewart, R. F. (1967). Private communication.