(average 4·7 and 5·5 Å^2) than for the (C)–H atoms (average 0·8 and 1·5 Å^2). No such trend was found in the neutron diffraction analysis of ascorbic acid.

Residual electron density

During the refinements of this structure no attempt was made to pick out one particular oxygen atom as carrier of the negative charge of the anion. The form factor was always the one given in *International Tables for X-ray Crystallography* (1962) for the free oxygen atom.

One extra electron is thus present in the anion in addition to those included in the calculations, and to conclude the analysis, a difference Fourier synthesis was evaluated. After omission of the uncertain 400 and 004 reflexions, the residual electron density in the region of the ascorbate anion is shown in Fig. 4. These maxima are clearly the largest in the unit cell, and some of them fall in the space between the carbon and oxygen atoms. This result is quite similar to that for ascorbic acid, but whether the peaks adjacent to the O(2), O(3) and O(4) atoms outside the bond area have relevance to the extra electron is questionable because of the low significance of such peaks in the present case.

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References

Ascorbinsäure (1965). *Wissenschaftliche Veröffentlichungen der Deutschen Gesellschaft für Ernährung*. Band 14. Darmstadt: Dr Dietrich Steinkopf Verlag.
Euler, H. von & Eistert, B. (1957). *Chemie und Biochemie der Reduktone und Reduktonate*. Stuttgart.
Grison, E. (1951). *Acta Cryst.* **5**, 68.
Hamilton, W. C. (1955). *Acta Cryst.* **8**, 185.
Hvoslef, J. (1968*a*). *Acta Cryst.* B**24**, 23.
Hvoslef, J. (1968*b*). *Acta Cryst.* B**24**, 1431.
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
Kresheck, G. C. (1968). Private communication.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
Woolfson, M. M. (1961). *Direct Methods in Crystallography*. Oxford Univ. Press.
Zachariasen, W. H. (1952). *Acta Cryst.* **5**, 68.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1969). B**25**, 2223

The Crystal Structure of Ribitol

By H. S. Kim, G. A. Jeffrey and R. D. Rosenstein
Crystallography Laboratory, University of Pittsburgh, Pittsburgh, Pennsylvania 15213, *U.S.A.*

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The crystal structure of ribitol, $C_5H_{12}O_5$, has been determined by means of a sign correlation procedure. The space group is $P2_1/c$ with four molecules in a unit cell with $a=8·990$, $b=4·946$, $c=15·730$ Å, $\beta=97·07°$. The crystal is a racemate mixture of left and right-handed conformers, with non-planar carbon chains. These conformers appear to be favored over that with mirror symmetry because of the non-bonding interactions between the hydroxyl groups attached to alternate carbon atoms along the chain.

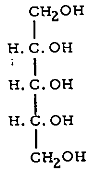
Introduction

Ribitol, $C_5H_{12}O_5$, is one of the four stereoisomeric pentitols. Like xylitol, it is a *meso* form; the other two pentitols are D- and L-arabinitol. Ribitol occurs in riboflavin (vitamin B_2) where it is combined with an isoalloxazine residue, and in certain plants. The structure of the ribitol residue has been studied in two crystal structure determinations; that of the *p*-bromophenylhydrazone of ribrose by Bjåmer, Furberg & Petersen (1964), and of riboflavin hydrobromide monohydrate by Tanaka, Ashida, Sasada & Kakudo (1967). In both these structures the conformation of the polyol residue was that with a non-planar zigzag carbon chain, although the planar conformation has been found consistently in the other polyol crystal structures which have been studied, *i.e. meso*-erythritol (Shimada, 1958; Bekoe & Powell, 1959), galactitol (Berman & Rosenstein, 1968), three forms of D-mannitol (Berman, Jeffrey & Rosenstein, 1968; Kim, Jeffrey & Rosenstein, 1968) and DL-arabinitol (Hunter & Rosenstein, 1968). Galactitol is also a *meso* form, in which the potential symmetry of the molecule is not used in the crystal symmetry. In that structure the observed conformation is very close to that of the symmetrical molecule, with small distortions which could be caused by the intermolecular forces characteristic of the crystal lattice.

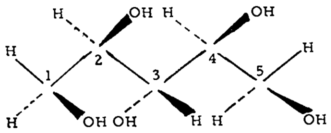
The primary interest in this investigation was, therefore, to determine whether the non-planar carbon chain conformation found in the isoalloxazine and *p*-bromophenylhydrazone derivatives persisted in the structure of the uncombined ribitol, and could be a structural property associated with the configuration of this particular carbohydrate molecule.

Molecular and crystal data

The Fischer projection of ribitol is shown in (I). The symmetrical conformation, shown in (II), has a mirror plane of symmetry, which includes the C(3).HOH atoms, normal to the plane of the zigzag carbon chain. In this conformation ribitol is optically inactive by intramolecular compensation. The conformation observed in the crystal structure is shown in Fig. 1. It differs from (II) by a rotation of 120° about C(3)–C(4), which brings C(5) into the position of the OH on C(4). The crystals are optically inactive by reason of being a mixture of diastereoisomers.



(I)



(II)

Ribitol, $C_5H_{12}O_5$, M.W. 152·15, m.p. 101 °C. Monoclinic.

Space group $P2_1/c$, from systematic absences ($0k0$) absent k odd, ($h0l$) absent l odd.

a = 8·990(1) Å
b = 4·946(2)
c = 15·730(5)
β = 97·07(2)°
V = 694·1(7).
Z = 4.
D_m = 1·454 g.cm^{-3}
D_x = 1·456 g.cm^{-3}.
$\mu_{\mathrm{Cu}\ K\alpha}$ = 11·48 cm^{-1}.

(The standard deviations given in parentheses refer to the last figure)

Experimental

Large transparent tabular crystals with well-developed {100} and {001} faces were obtained by slow evaporation from solution in ethanol. The crystal density was measured at 23 °C by flotation in a benzene and carbon tetrachloride mixture. The cell parameters were measured on a Picker 4-circle diffractometer from the principal zone reflections and refined by least-squares by means of an IBM 1130 program (Shiono, 1968).

The intensities were obtained from a prism of dimensions 0·14 × 0·25 × 0·50 mm with Cu $K\alpha$ radiation by a Picker diffractometer in the $\theta/2\theta$ scanning mode with the scan varying between 2° and 4° in low and high values of 2θ. Of the 1590 independent reflections within the Cu $K\alpha$ sphere, 1153 were recorded, of which 73 with intensities less than two standard deviations were given values of zero. No absorption corrections were applied. The intensities were reduced to structure amplitudes by the use of an IBM 1130 diffractometer data processing program (McGandy, 1968).

Determination and refinement of the structure

The structure was solved in three dimensions by a sign correlation procedure with the IBM 1620 program of Beurskens (1963). An interpretation of the first E map

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

Key to atomic numbering is given in Fig. 1. The estimated standard deviations in parentheses refer to the last decimal positions. The temperature expression used was

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·2613 (3)	0·5601 (6)	0·4722 (2)	0·0119 (4)	0·0422 (12)	0·0034 (1)	0·0005 (5)	0·0012 (1)	−0·0005 (3)
C(2)	0·3020 (2)	0·5814 (5)	0·5681 (1)	0·0072 (3)	0·0283 (10)	0·0036 (1)	−0·0003 (4)	0·0008 (1)	0·0009 (2)
C(3)	0·1708 (2)	0·5092 (4)	0·6176 (2)	0·0074 (3)	0·0202 (10)	0·0033 (1)	−0·0006 (3)	0·0002 (1)	−0·0008 (2)
C(4)	0·2008 (2)	0·5669 (4)	0·7135 (1)	0·0063 (3)	0·0250 (9)	0·0033 (1)	−0·0012 (4)	0·0005 (1)	−0·0005 (2)
C(5)	0·3302 (2)	0·4045 (5)	0·7589 (1)	0·0080 (3)	0·0368 (11)	0·0031 (1)	0·0021 (5)	−0·0003 (1)	−0·0012 (3)
O(1)	0·1625 (2)	0·7742 (4)	0·4415 (1)	0·0090 (2)	0·0496 (10)	0·0033 (1)	−0·0015 (3)	0·0002 (1)	0·0027 (2)
O(2)	0·3601 (2)	0·8426 (4)	0·5906 (1)	0·0072 (2)	0·0345 (9)	0·0042 (1)	−0·0039 (3)	−0·0005 (1)	0·0017 (2)
O(3)	0·1380 (2)	0·2311 (3)	0·6028 (1)	0·0085 (2)	0·0271 (9)	0·0039 (1)	−0·0021 (3)	0·0003 (1)	−0·0019 (2)
O(4)	0·0704 (2)	0·5044 (3)	0·7534 (1)	0·0084 (2)	0·0295 (9)	0·0039 (1)	0·0001 (3)	0·0019 (1)	−0·0001 (2)
O(5)	0·3621 (2)	0·5029 (4)	0·8440 (1)	0·0096 (3)	0·0603 (12)	0·0031 (1)	0·0074 (4)	−0·0005 (1)	−0·0023 (2)
H(C1)	0·348	0·570	0·437						
H′(C1)	0·210	0·400	0·455						
H(C2)	0·386	0·430	0·580						
H(C3)	0·070	0·610	0·590						
H(C4)	0·230	0·740	0·725						
H(C5)	0·306	0·190	0·748						
H′(C5)	0·420	0·420	0·733						
H(O1)	0·211	0·872	0·399						
H(O2)	0·279	0·956	0·588						
H(O3)	0·031	0·210	0·591						
H(O4)	−0·009	0·660	0·751						
H(O5)	0·461	0·411	0·869						

obtained from the signs of 183 normalized structure factors gave poor structure factor agreement, especially in reflections with l odd, and an R index of 0·62. A shift of the whole molecule by 0·25z then improved the agreement to $R=0{\cdot}39$ and gave a set of coordinates which refined smoothly to the final parameters.

The refinement was by least-squares, first with block-diagonal on the IBM 1130 (Shiono, 1968) to an $R=0{\cdot}12$ and then by full-matrix on the IBM 7090 (Shiono, 1966). The function minimized was

$$\sum_{i=1}^{n} \omega_i (K|F_o|-|F_c|)_i^2$$

where $\omega_i^{-1}=1+0{\cdot}1F_o+0{\cdot}001F_o^2$.

The isotropic refinement was terminated at $R=0{\cdot}07$ and the anisotropic refinement at $R=0{\cdot}055$. Of the twelve hydrogen atoms, those attached to the carbon atoms appeared on difference maps at the conclusion of the block-diagonal refinement; the remaining five appeared at the conclusion of the isotropic refinement. In the final calculation, the hydrogen atom coordinates were not varied and their thermal parameters were assumed to be the same as those of the atoms to which they were bonded.

The final parameters are given in Table 1 and the corresponding structure factors in Table 2. The conformation of the molecule, the atomic numbering and the thermal ellipsoids are shown in Fig. 1. The atomic scattering factors used were those of Cromer & Waber

Table 2. *Observed and calculated structure factors*

Columns are: Index, 10|F_{obs}|, 10F_{calc}.
* Indicates unobserved reflections.

K= 0 H= 0		
2	34	40-
4	60	68-
6	800	857-
8	123	133
10	143	143-
12	131	129
14	66	61-
16	17	14-
18	12	10
K= 0 H= 1		
0	202	214
2	443	464-
4	62	55
6	20	12
8	654	665
10	28	32
12	209	212-
14	43	35-
16	35	36
-2	258	279
-4	310	321
-6	566	591-
-8	446	446-
-10	1*	1-
-12	75	72
-14	99	109-
-16	95	93
-18	12	4
K= 0 H= 2		
0	772	814-
2	531	546-
4	530	549
6	374	386
8	52	55
10	207	215-
12	9	10
14	87	87-
16	77	67
-2	96	103-
-4	502	530-
-6	238	250-
-8	212	211
-10	182	185
-12	163	168
-14	16	18
-16	12	14-
-18	64	63-
K= 0 H= 3		
0	113	115
2	264	251-
4	152	145-
6	71	60
8	90	83
10	180	179-
12	84	85
14	17	22-
16	29	31-
-2	155	166-
-4	445	463
-6	77	80-
-8	8	9
-10	130	133-
-12	419	429
-14	38	37
-16	35	34-
-18	112	98-
K= 0 H= 4		
0	558	542-
2	10	11
4	5*	2-
6	123	119
8	87	88-
10	209	209
12	69	69-
14	80	76
-2	22	6
-4	785	783
-6	300	297
-8	30	30
-10	248	238-
-12	162	166-
-14	27	30-
-16	47	47
K= 0 H= 5		
0	25	17
2	113	118
4	54	49
6	38	38-
8	229	230-
10	144	138
12	93	106
14	62	63
-2	136	135-
-4	315	314-
-6	292	286
-8	115	123
-10	17	20-
-12	320	308-
-14	24	28
-16	54	52-
K= 0 H= 6		
0	283	293
2	145	141
4	184	187-
6	189	207-
8	35	46
10	56	54-
12	25	26-
-2	21	7
-4	253	232-
-6	15	16-
-8	158	151-
-10	91	90
-12	14	14
-14	38	31
-16	50	46
K= 0 H= 7		
0	105	101-
2	183	178
4	44	36-
6	14	15
8	71	74-
10	8	6-
12	102	102-
-2	281	286
-4	115	119-
-6	12	7-
-8	51	60-
-10	104	105
-12	43	43-
-14	7*	8-
K= 0 H= 8		
0	48	41-
2	78	78
4	72	82-
6	181	181
8	18	21-
10	25	26
-2	158	159
-4	197	197-
-6	7*	3
-8	21	28-
-10	99	91
-12	9	8
K= 0 H= 9		
0	79	80-
2	52	58-
4	15	19-
6	89	85
-2	83	84-
-4	73	78
-6	63	64-
-8	85	79-
-10	26	25
K= 0 H= 10		
0	84	81-
2	41	47-
-2	17	22-
-4	62	57
-6	65	55
K= 1 H= 0		
1	178	193
2	124	140-
3	285	306
4	246	246-
5	68	77
6	5*	2
7	152	143-
8	114	109-
9	106	92
10	10	4-
11	42	39-
12	42	35-
13	130	131-
14	67	61
15	77	84
16	50	46
17	0*	0
K= 1 H= 1		
0	338	349
1	484	495-
2	76	75-
3	40	38-
4	261	264-
5	41	39-
6	47	41-
7	255	244
8	110	109-
9	57	58-
10	0*	5-
11	151	146
12	29	32-
13	83	89
14	62	61
15	4*	3
16	25	27
17	23	19-
-1	755	806
-2	651	705
-3	481	512-
-4	334	350
-5	57	49-
-6	118	126-
-7	58	51-
-8	377	395-
-9	87	94
-10	97	102-
-11	137	139-
-12	12	11-
-13	43	50-
-14	96	94
-15	49	52-
-16	18	14-
-17	20	19-
-18	8	4
K= 1 H= 2		
0	121	125-
1	332	343-
2	177	160-
3	67	66-
4	462	466
5	295	293-
6	80	97
7	261	264
8	24	18
9	5*	2
10	215	208-
11	81	84-
12	38	40-
13	20	26
14	27	24
15	37	25
16	56	56
17	2*	1-
-1	185	189-
-2	172	174-
-3	78	72-
-4	252	268
-5	148	141
-6	121	116
-7	148	158-
-8	160	167-
-9	79	83-
-10	214	226-
-11	193	196
-12	97	94-
-13	53	52
-14	76	74
-15	62	67-
-16	81	79
-17	19	22
-18	21	20
K= 1 H= 3		
0	113	133-
1	333	320-
2	401	395
3	492	480
4	366	366
5	88	88-
6	9	10
7	70	71-
8	147	157-
9	301	306-
10	109	104-
11	88	92
12	13	15
13	116	117-
14	17	21
15	79	69
16	19	23-
-1	79	69
-2	446	441-
-3	204	209
-4	390	397-
-5	95	84
-6	16	18
-7	83	73-
-8	131	123
-9	114	116
-10	53	55
-11	43	45-
-12	54	54
-13	77	73
-14	3*	2-
-15	30	32
-16	49	46
-17	28	28
K= 1 H= 4		
0	77	75-
1	118	126
2	181	175
3	113	110
4	91	90-
5	98	98-
6	27	16
7	68	62
8	16	13
9	142	139-
10	78	78
11	181	176
12	12	11
13	4*	4-
14	60	57-
15	22	23-
-1	355	349
-2	15	13-
-3	271	263-
-4	185	190-
-5	265	257
-6	10	6
-7	71	67-
-8	55	49
-9	72	62
-10	90	93
-11	254	253-
-12	56	51
-13	143	138
-14	31	30
-15	99	96-
-16	7*	6
-17	23	18
K= 1 H= 5		
0	37	43-
1	16	11-
2	108	99-
3	0*	0
4	26	24-
5	55	46-
6	3*	1
7	91	83
8	81	78
9	212	222
10	75	71
11	37	40-
12	49	49
13	42	40-
14	33	31-
-1	98	111-
-2	134	129-
-3	198	184-
-4	69	64
-5	201	193
-6	89	85
-7	189	187-
-8	197	199
-9	59	59
-10	2*	2
-11	84	80-
-12	71	69-
-13	2*	2-
-14	75	76-
-15	36	34-
-16	30	29-
K= 1 H= 6		
0	162	152
1	188	181-
2	69	60-
3	99	93
4	154	155-
5	10	13
6	99	96-
7	34	35-
8	27	24
9	28	33-
10	106	110
11	17	16-
12	29	32
13	37	36-
-1	92	93
-2	14	13
-3	177	175-
-4	9	17-
-5	101	102-
-6	78	74-
-7	3*	12-
-8	62	62
-9	136	143
-10	64	63
-11	7*	13
-12	3*	1-
-13	10	11-
-14	82	77-
-15	69	65
K= 1 H= 7		
0	43	38
1	7*	3-
2	96	92-
3	67	65-
4	112	117-
5	122	131-
6	26	20-
7	69	76
8	24	22
9	70	70-
10	7*	1
11	19	16-
-1	223	221
-2	219	218
-3	14	9-
-4	64	63
-5	32	32
-6	45	36-
-7	5*	1-
-8	162	159-
-9	11	3-
-10	5*	8
-11	36	38
-12	7*	5
-13	43	43
-14	54	50
K= 1 H= 8		
0	7*	6
1	11	14-
2	10	8-
3	29	30-
4	73	70
5	59	63
6	8	8
7	36	31
8	16	18-
9	54	55
-1	137	141-
-2	56	55
-3	211	213
-4	48	47
-5	29	30
-6	19	16
-7	10	15
-8	53	57-
-9	57	59-
-10	60	56-
-11	13	9
-12	5*	0
-13	43	43-
K= 1 H= 9		
0	16	16-
1	31	36
2	45	45
3	13	11
4	39	36
5	136	136
6	43	41
-1	120	118-
-2	25	16-
-3	3*	3
-4	4*	5-
-5	89	92-
-6	33	33-
-7	32	39
-8	9	15-
-9	20	13-
-10	23	24-
K= 1 H= 10		
0	88	91-
1	85	84
2	10	12
-1	7	6
-2	54	50-
-3	44	42-
-4	12	13-
-5	24	25
-6	20	19
K= 2 H= 0		
0	339	352
1	9	4
2	393	404-
3	18	6
4	212	220
5	23	21-
6	144	135
7	91	87
8	202	205
9	69	66-
10	166	168-
11	1*	1
12	29	24
13	118	116-
14	17	12-
15	9	14-
16	5*	2
17	19	19-
K= 2 H= 1		
0	119	104-
1	269	268
2	175	161-
3	69	68
4	129	125
5	228	245
6	209	208-
7	144	154-
8	200	186
9	36	34
10	20	22
11	67	69-
12	81	76
13	44	43
14	95	101
15	4*	4
16	32	28
-1	153	159-
-2	267	267-
-3	88	81-
-4	301	310
-5	36	46
-6	50	19
-7	88	83
-8	72	67
-9	49	59
-10	9	14-
-11	91	91-
-12	76	73-
-13	19	20-
-14	166	171-
-15	4*	6
-16	38	39
-17	18	17
K= 2 H= 2		
0	81	74-
1	60	51
2	298	295-
3	166	148-
4	121	104
5	118	105-
6	151	149-
7	50	42-
8	120	113-
9	181	174
10	39	34-
11	94	96
12	142	146
13	61	60
14	1*	4-
15	38	29-
16	29	24
-1	107	102
-2	89	105
-3	82	78-
-4	44	28
-5	126	124-
-6	63	56-
-7	2*	7-
-8	162	156
-9	18	14
-10	77	83-
-11	91	90
-12	32	29-
-13	101	99-
-14	46	41-
-15	13	19-
-16	45	46
-17	50	51-
K= 2 H= 3		
0	310	295
1	357	344-
2	282	267
3	62	56-
4	39	41-
5	117	120-
6	121	115-
7	172	175
8	165	158-
9	2*	2
10	160	158-
11	28	28-
12	52	52
13	55	54-
14	26	22
15	10	7
-1	90	75
-2	108	107-
-3	26	16
-4	38	20
-5	65	67
-6	9	10
-7	38	32-
-8	22	24
-9	0*	0
-10	115	114-
-11	42	45
-12	122	120
-13	22	16
-14	32	31-
-15	11	10
-16	23	21
K= 2 H= 4		
0	130	116
1	147	140
2	359	347
3	92	84
4	24	24-
5	44	39
6	99	95-
7	107	111-
8	64	67-
9	137	139-
10	151	152
11	63	70-
12	67	67-
13	41	43
14	29	29-
-1	28	26-
-2	76	77
-3	65	69
-4	45	4
-5	52	57-
-6	202	205-
-7	84	85
-8	61	60-
-9	10	9-
-10	40	39
-11	6*	6
-12	9	8
-13	29	26
-14	12	6-
-15	18	17-
-16	6*	8
K= 2 H= 5		
0	19	21-
1	164	166
2	108	106-
3	78	73-
4	32	29-
5	44	39-
6	184	184
7	14	22-
8	66	64
9	27	25
10	121	115
11	67	68
12	70	65-
13	13	9-
-1	50	47
-2	33	33
-3	181	175
-4	217	211-
-5	45	43-
-6	33	25-
-7	44	42-
-8	21	15-
-9	75	83-
-10	40	37
-11	10	9-
-12	44	42-
-13	12	10-
-14	85	83
-15	15	12-
K= 2 H= 6		
0	100	93-
1	147	142-
2	34	30-
3	25	30
4	108	96-
5	104	104
6	102	89
7	91	90
8	97	104
9	16	13
10	37	42-
11	3*	2-
12	82	78-
-1	75	77-
-2	61	65-
-3	70	73-
-4	119	118-
-5	99	96
-6	102	102
-7	59	57-
-8	52	55-
-9	22	26
-10	125	124
-11	91	85-
-12	29	32
-13	20	18
-14	19	16
K= 2 H= 7		
0	178	177-
1	55	56
2	22	21-
3	57	59
4	85	80-
5	36	29
6	16	22
7	91	95-
8	22	23-
9	8*	12-
10	29	27
-1	20	21-
-2	241	236
-3	166	166-
-4	38	39
-5	35	41-
-6	79	76
-7	6*	8
-8	59	60-
-9	51	56
-10	86	81
-11	37	37
-12	37	40-
-13	22	21
K= 2 H= 8		
0	112	112-
1	15	13
2	15	12-
3	45	48-
4	24	29-
5	99	99-
6	123	122
7	8	12-
8	70	69-
-1	64	73
-2	125	115
-3	93	86
-4	32	27
-5	20	18-
-6	137	138
-7	17	15
-8	46	38-
-9	45	44-
-10	57	58-
-11	64	58
K= 2 H= 9		
0	23	20-
1	86	83-
2	127	123
3	19	19
4	32	33
-1	9	11-
-2	92	89-
-3	21	19
-4	2*	2-
-5	40	39
-6	13	14
-7	49	47
-8	48	45-
K= 3 H= 0		
1	213	221
2	286	283
3	36	42
4	139	132
5	167	173-
6	22	29
7	113	107-
8	183	190-
9	119	116
10	26	28-
11	28	24
12	71	62-
13	76	72-
14	23	19-
15	7*	5-

Table 2 (*cont.*)

K= 3 H= 1			-11	80	88	-7	66	70	-11	44	46-	3	77	69-	6	134	138	-6	51	50	-5	45	56-
0	194	187	-12	69	71-	-8	119	120-	-12	11	7-	4	37	34	7	21	19	-7	52	55	-6	20	17
1	198	177-	-13	31	30	-9	24	24-	K= 3 H= 7			5	30	26	8	7•	6-	-8	25	25	-7	40	38
2	187	177	-14	63	66-	-10	12	12-	0	43	37-	6	82	78-	9	57	55-	-9	9	5	-8	24	24-
3	138	136-	-15	54	57-	-11	141	144-	1	5•	3	7	91	92-	10	32	39-	-10	72	73-	-9	28	29
4	25	28-	K= 3 H= 3			-12	60	65	2	47	45	8	106	103	11	4•	6-	K= 4 H= 6			K= 5 H= 2		
5	88	81	0	56	55-	-13	68	67	3	46	44-	9	43	34	-1	27	30-	0	5•	3	0	35	34
6	18	20-	1	218	221-	-14	37	40	4	55	52	10	69	69-	-2	73	75-	1	13	11-	1	28	26-
7	215	217	2	142	133-	K= 3 H= 5			5	41	35	11	36	26-	-3	146	147-	2	122	119	2	30	23-
8	46	44-	3	107	105	0	39	33	6	31	30-	12	31	28-	-4	97	102	3	15	15-	3	34	27
9	20	20-	4	118	112-	1	93	88	7	67	72	-1	128	128	-5	53	56-	4	100	94-	4	51	46
10	119	114	5	67	60-	2	36	35-	8	30	33-	-2	26	27-	-6	127	133	5	3•	4-	5	71	66-
11	38	32-	6	36	32-	3	154	157	-1	34	34	-3	110	124	-7	9	7	6	14	10	6	30	29-
12	7•	9-	7	19	8-	4	63	62	-2	67	64-	-4	10	7-	-8	27	30-	-1	12	14	7	18	18
13	57	55-	8	68	67	5	150	144-	-3	10	9-	-5	31	29	-9	39	41	-2	11	13	-1	67	75
14	5•	6-	9	45	42-	6	49	51	-4	117	113-	-6	203	226-	-10	48	54-	-3	72	69-	-2	12	10-
15	3•	4	10	5•	4-	7	52	55-	-5	3•	2	-7	84	91-	-11	50	56	-4	91	94-	-3	8	8
-1	258	255	11	101	99	8	11	14-	-6	29	27	-8	14	15	-12	29	30	-5	0•	1-	-4	14	18-
-2	28	28-	12	6•	3-	9	4•	5	-7	30	27	-9	35	40-	K= 4 H= 4			-6	76	75	-5	82	93
-3	4•	5	13	35	29-	10	37	42-	-8	20	16-	-10	72	81	0	94	89-	-7	46	47-	-6	14	18-
-4	126	133-	14	9	3-	11	47	43	-9	4•	7-	-11	48	45-	1	44	43	-8	8	6-	-7	64	77-
-5	58	71-	-1	86	84	-1	9	13-	-10	99	97	-12	75	77	2	71	69	-9	88	81	-8	30	35-
-6	26	23-	-2	68	65	-2	51	47	-11	10	3	-13	24	22	3	4•	6-	K= 4 H= 7			K= 5 H= 3		
-7	69	67-	-3	84	82	-3	199	197-	K= 3 H= 8			K= 4 H= 2			4	70	72	0	19	19	0	80	75-
-8	21	23	-4	49	51-	-4	188	185	0	28	24	0	34	22	5	36	40-	1	20	24-	1	67	72-
-9	35	34-	-5	58	70	-5	85	88	1	40	33	1	83	77-	6	65	66-	2	53	49	2	32	25-
-10	116	122	-6	10	5	-6	40	42-	2	32	29-	2	210	211-	7	4•	8-	3	49	39-	3	64	64
-11	32	33-	-7	150	156-	-7	19	20-	3	32	31	3	0•	0	8	34	33-	-1	54	57	4	40	35
-12	55	57-	-8	16	17	-8	32	32-	4	8	9-	4	48	45	9	31	26-	-2	70	67	5	6•	3
-13	8	8	-9	66	67	-9	87	87	5	8	10	5	92	87	10	25	24	-3	18	17-	6	26	22
-14	11	10	-10	50	45	-10	148	150-	-1	19	23-	6	73	74	-1	14	17	-4	94	91-	-1	29	21
-15	14	12	-11	10	7	-11	62	62-	-2	29	29	7	31	30	-2	80	81-	-5	14	16	-2	20	25-
K= 3 H= 2			-12	68	70	-12	12	16-	-3	46	42	8	50	47	-3	57	55	-6	59	61-	-3	35	35-
0	88	80	-13	103	104	-13	32	30-	-4	7•	5-	9	48	48	-4	40	39	K= 5 H= 0			-4	34	35-
1	123	125-	-14	62	60-	-14	29	30	-5	58	54-	10	26	25-	-5	56	53-	1	70	68-	-5	66	76
2	263	256-	-15	9	12-	K= 3 H= 6			-6	73	69	11	35	32-	-6	65	70	2	51	55-	-6	33	34
3	173	158	K= 3 H= 4			0	45	38-	-7	52	52-	12	19	22-	-7	31	27	3	10	7-	-7	41	46-
4	43	26-	0	16	17	1	37	31-	-8	50	46	-1	23	28-	-8	20	15	4	84	79-	-8	14	14-
5	40	39-	1	118	123-	2	20	19	K= 4 H= 0			-2	99	96	-9	20	24-	5	2•	2-	K= 5 H= 4		
6	103	102-	2	72	72	3	43	37-	0	179	175	-3	13	12-	-10	4•	0	6	25	24	0	37	31-
7	141	149	3	39	38	4	112	114	1	35	32	-4	100	111	-11	35	32	7	48	53	1	14	12
8	230	229	4	121	125-	5	92	88-	2	40	30-	-5	72	75	-12	25	25-	8	11	4	2	91	82
9	125	123-	5	48	43	6	96	87	3	10	3	-6	164	177-	K= 4 H= 5			9	40	43	3	49	52
10	107	103	6	12	9-	7	23	21-	4	53	57-	-7	4•	6-	0	19	21	K= 5 H= 1			4	28	28
11	41	42-	7	71	71	8	16	20-	5	17	13-	-8	25	23-	1	47	39	0	37	39	5	18	12-
12	71	68	8	74	75-	9	48	47	6	35	20-	-9	83	84-	2	24	25	1	17	16	-1	27	24
13	11	13	9	80	79-	10	13	13	7	19	17-	-10	27	30-	3	30	32-	2	4•	5-	-2	36	37-
14	28	29-	10	75	72-	-1	174	172	8	70	71	-11	40	41-	4	34	34-	3	24	25-	-3	75	82-
-1	67	56-	11	49	47	-2	210	206-	9	105	102-	-12	98	104	5	20	18	4	43	45	-4	26	24-
-2	51	53-	12	24	24-	-3	8	10-	10	36	33-	-13	64	64-	6	26	28-	5	28	24	-5	18	16-
-3	162	159-	13	6•	2	-4	15	16-	11	16	12-	K= 4 H= 3			7	20	19	6	31	25	-6	23	21
-4	9	6	-1	19	13-	-5	51	53-	12	4•	8-	0	165	163-	8	55	52-	7	10	6	K= 5 H= 5		
-5	81	77	-2	266	268	-6	5•	6-	13	42	37-	1	78	66-	-1	68	66-	8	37	33-	0	55	55
-6	8	7-	-3	91	90-	-7	64	68-	K= 4 H= 1			2	61	63-	-2	28	29	-1	12	1	1	1•	2-
-7	95	105-	-4	70	64	-8	16	29	0	173	176	3	141	136	-3	54	54	-2	0•	1-	-1	50	46
-8	52	45	-5	230	233	-9	69	68	1	136	126	4	41	43	-4	25	27-	-3	8	6	-2	14	11
-9	30	33	-6	44	44-	-10	21	21-	2	24	13-	5	36	31-	-5	38	39	-4	71	81	-3	41	43-
-10	44	43																					

(1965) for carbon and oxygen and that of Stewart, Davidson & Simpson (1965) for hydrogen.

Discussion

The interatomic distances and angles in ribitol are given in Table 3. The C–C distances range from 1·510 to 1·534 Å and are not significantly different from the mean value of 1·524 Å. The C–O distances range from 1·419 to 1·429 Å and are not significantly different from the mean of 1·423 Å. These values agree with the mean values of 1·522 Å for C–C and 1·421 Å for C–O from some recent studies of the cyclic monosaccharides (Berman, Chu & Jeffrey, 1967). The C–C–C bond angles are systematically about 4° greater than the C–C–O angles, which are close to the tetrahedral value. These results are in excellent agreement with other studies of the polyols. The thermal parameters gave a reasonable fit for rigid-body motion analysis (Schomaker & Trueblood, 1968), if the hydrogen atoms were excluded. The bond length corrections for this motion (Busing & Levy, 1964) were +0·003 to +0·005 Å, *i.e.* about one standard deviation. These corrections are not considered significant.

The interesting feature of the structure is the nonplanar conformation of the five carbon chain. Atoms C(1) to C(4) lie in one plane within 0·05 Å, and C(5) is 1·12 Å out of the plane. The rotation about C(3)–C(4) from the planar carbon chain conformation is about 120° which brings O(4) into the plane of C(1), C(2), C(3), C(4) in place of C(5), as shown in the Newman projections for the C(2)–C(3) and C(3)–C(4) bonds, given in Fig. 2. The equations of the planes and the deviations from these planes are given in Table 4.

The observation of a non-planar carbon chain conformation for the ribitol configuration in three crystal structures suggests that this is a consequence of the intramolecular non-bonding interactions, rather than the result of intermolecular hydrogen-bonding or molecular packing forces. As would be expected and is observed, in all known polyol structures, the conformation about the C–C bonds is invariably staggered. Of the three possible staggered conformations illustrated in Fig. 3, (*ap*) will generally be most favored, where the oxygen atoms attached to adjacent carbon atoms lie in the sector of the Newman diagram between a carbon atom and a hydrogen atom rather than between a carbon atom and an oxygen atom. This gives rise to two third neighbour O...O, C...O or C...C distances of the order of 2·9 Å, rather than three, as shown in Fig. 3. However, the O...O interactions at these distances are not likely to be strongly repulsive.

In ribitol, the (*ap*) conformation about both C(2)–C(3) and C(3)–C(4) would form the planar carbon chain. This is observed about C(2)–C(3), but is overruled about C(3)–C(4), since it would lead to a stronger repulsive interaction of the type O($n-1$)...O($n+1$). The distance from O(1) to O(3) is 3·7 Å, *i.e.* on opposite sides of the molecule, but the (*ap*) conformation about C(3)–C(4) would bring O(2) to within 2·55 Å of O(4), with the C(2)–O(2) and C(4)–O(4) bonds parallel [or eclipsed if viewed down a C(2)...C(4) axis]. This repulsion is therefore relieved by a 120° rotation to the observed (*Msc*) orientation, shown in Figs. 2 and

3. The C(4)–H(4) bond is then parallel to C(2)–O(2) and C(4)–O(4) is on the other side of the molecule. The other alternative (*Psc*) would bring C(5) into the position occupied by O(4) with parallel C(2)–O(2) and C(4)–C(5) bonds and an equally unfavorable O(2)... C(5) approach. The observed ribitol conformation is, therefore, fully consistent with a model based on minimizing these third and fourth neighbour repulsive interactions, with the latter taking precedence over the former, because the non-bonding distance is shorter.

Table 3. *Intramolecular distances and angles in ribitol.*

The estimated standard deviations given in parentheses refer to the last decimal positions of respective values. The mean values are calculated from

$$\bar{l}=\sum_i\left(\frac{l_i}{\sigma_i^2}\right)\Big/\sum_i\left(\frac{1}{\sigma_i^2}\right),\quad \sigma_{\text{mean}}=\left(\frac{\sum_i(\bar{l}-l_i)^2}{N-1}\right)^{1/2}$$

i	j	D_{ij}	D_{ij}*
C(1)	C(2)	1·510 (4) Å	[1·515] Å
C(2)	C(3)	1·534 (3)	[1·537]
C(3)	C(4)	1·525 (3)	[1·530]
C(4)	C(5)	1·518 (3)	[1·521]
C(1)	O(1)	1·427 (3)	[1·430]
C(2)	O(2)	1·421 (3)	[1·426]
C(3)	O(3)	1·420 (3)	[1·424]
C(4)	O(4)	1·429 (3)	[1·433]
C(5)	O(5)	1·419 (3)	[1·424]
C(1)	H(C1)	1·012	
C(1)	H′(C1)	0·939	
C(2)	H(C2)	1·063	
C(3)	H(C3)	1·078	
C(4)	H(C4)	0·907	
C(5)	H(C5)	1·092	
C(5)	H′(C5)	0·952	
O(1)	H(O1)	0·969	
O(2)	H(O2)	0·917	
O(3)	H(O3)	0·962	
O(4)	H(O4)	1·045	
O(5)	H(O5)	1·032	

Non-bonded O···O distances

O(1)	O(2)	2·782
O(1)	O(3)	3·720
O(2)	O(3)	3·642
O(3)	O(4)	2·856
O(4)	O(5)	2·826

i	j	k	$<(ijk)$
C(1)	C(2)	C(3)	112·5 (2)°
C(2)	C(3)	C(4)	113·9 (2)
C(3)	C(4)	C(5)	113·5 (2)
O(1)	C(1)	C(2)	110·5 (2)
C(1)	C(2)	O(2)	110·4 (2)
O(2)	C(2)	C(3)	111·5 (2)
C(2)	C(3)	O(3)	107·4 (2)
O(3)	C(3)	C(4)	110·6 (2)
C(3)	C(4)	O(4)	109·8 (2)
O(4)	C(4)	C(5)	107·5 (2)
C(4)	C(5)	O(5)	108·5 (2)

Mean C–C	1·524 (10) Å
Mean C–O	1·423 (5)
Mean C–C–C	113·3 (7)°
Mean C–C–O	109·5 (15)

* Bond lengths corrected for libration.

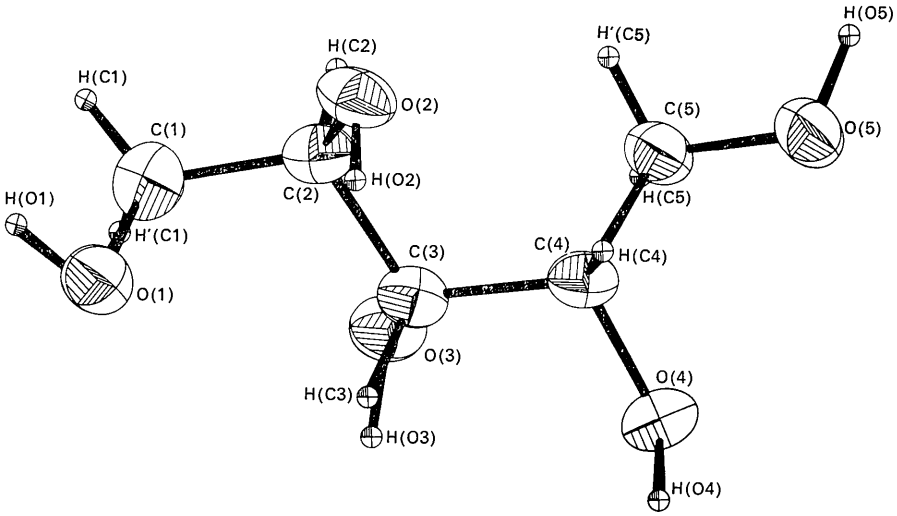


Fig. 1. Molecular conformation observed in the crystal structure of ribitol, showing atomic numbering used and the anisotropic thermal ellipsoids.

The same configuration is observed in the ribitol residue of the riboflavin monohydrate. In the ribose-*p*-bromophenylhydrazone, however, the conformation about C(3)–C(4) is (*Psc*), but this conformer is stabilized by the formation of an intramolecular hydrogen bond between O(2) and O(5).

Xylitol has parallel C(2)...O(2), C(4)...O(4) bonds in the planar carbon chain conformation in which the molecule is mirror-symmetrical. It is expected to have a non-planar carbon chain about C(3)–C(4) also, but in this case, the diastereoisomeric rotomers must be resolved on crystallization, since the crystal structure has symmetry $P2_12_12_1$. Of the ten hexitols, similar eclipsed C–O bonds on alternate carbon atoms occur in seven of the stereoisomers in the planar-chain conformation. These are D- and L-glucitol (sorbitol), D- and L-idtiol, D- and L-talitol (altritol) and *meso*-allitol, none of which have yet been studied by crystal structure determination. In DL-arabinitol, galactitol and D-mannitol, which have been studied, the configurations are all such that the observed planar carbon chain conformation gives rise to no short interactions of the type O($n-1$)...O($n+1$) or C($n+2$).

The extent to which the unsymmetrical rotomers of ribitol persist in solution depends upon the potential energy functions for rotation about the C–C bonds. In view of the arguments above, it seems likely that the symmetrical rotomer is a high energy form and that the unsymmetrical rotomers will predominate. As with the *meso*-tartrates (Kroon, Peerdeman & Bijvoet, 1965) and *meso*-tartaric acid (Bootsma & Schoone, 1967), lack of optical activity in solution, as well as in the solid, probably results more from compensation by conformational antipodes than from the mirror or centric symmetry in the molecules. This is in contrast to the crystal structures of the various forms of D-mannitol and of galactitol, where the conformation in the solid is very close to the symmetrical average of those of the rotomers expected to occur in solution. Some recent nuclear magnetic resonance spectroscopic data also support the view that in solution the planar carbon chain conformation is favored, except for those roto-

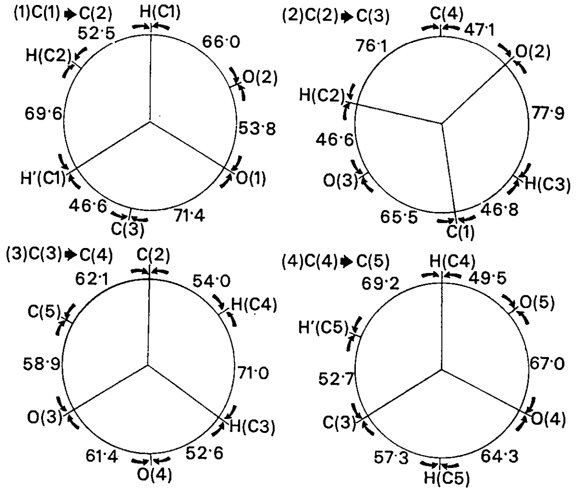


Fig. 2. Newman projections down the C–C bonds in ribitol, showing the conformation angles in degrees.

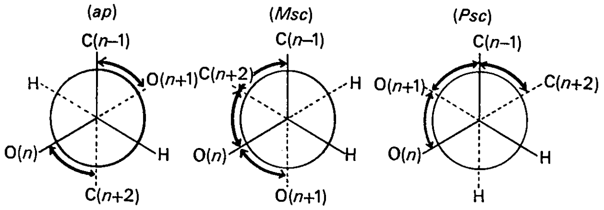


Fig.3. Newman projections for the three preferred conformations down a C(n)–C($n+1$) bond in a polyol. The (*ap*) conformers have the linear carbon chain.

Table 4. *Least-squares planes in ribitol*

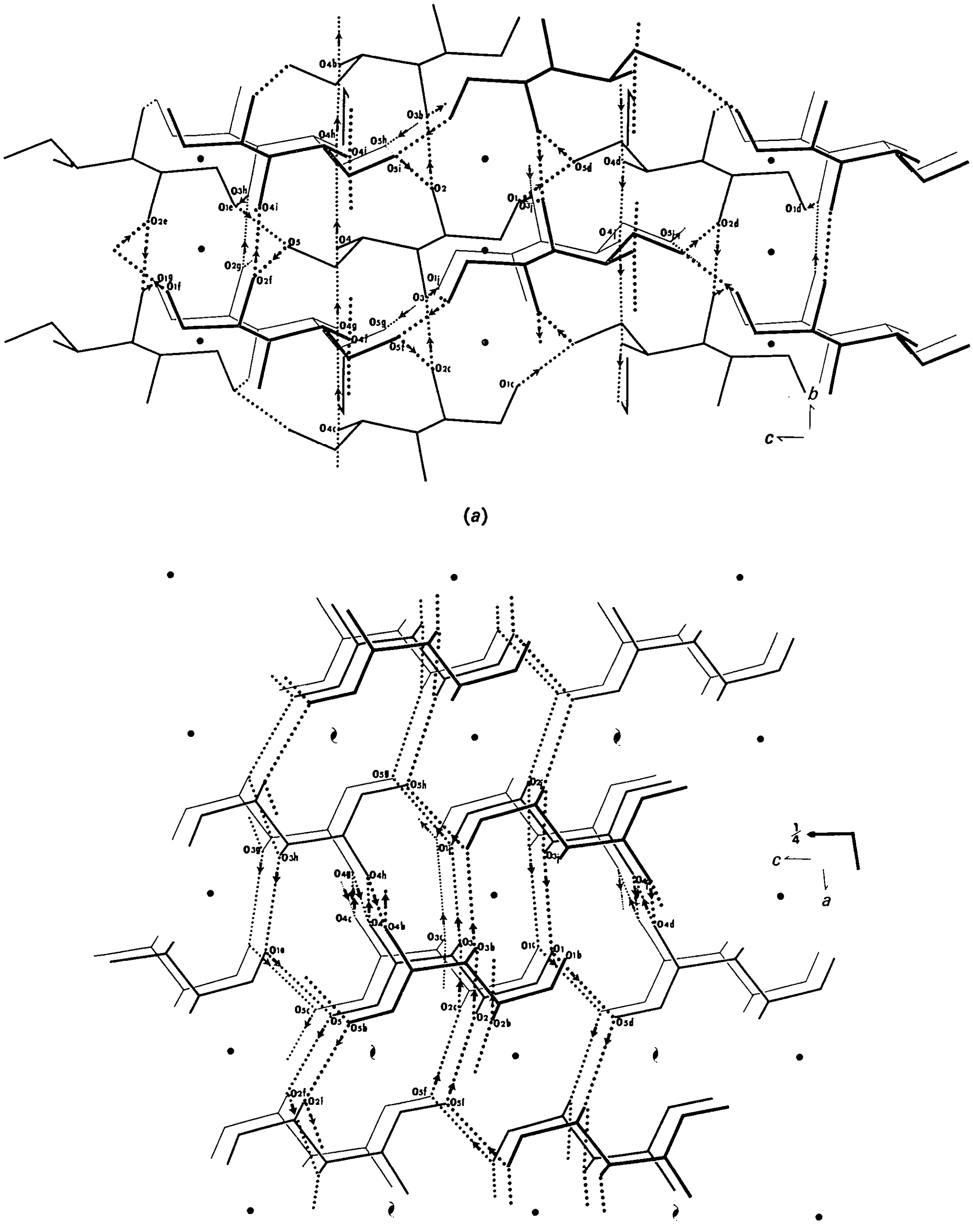
Equation for plane: $Ax+By+Cz=D$, where x,y,z are in Å.

Atoms in plane		Distance from best plane		Given constant
A	C(1)	C(1)	+0·050 Å	$A=-0·319$
	C(2)	C(2)	−0·049	$B=\ 0·943$
	C(3)	C(3)	−0·051	$C=-0·054$
	C(4)	C(4)	+0·050	$D=\ 1·412$
		O(4)	+0·098	
		C(5)	−1·117	
B	C(1)	C(1)	+0·055	$A=-0·278$
	C(2)	C(2)	−0·028	$B=\ 0·957$
	C(3)	C(3)	−0·084	$C=-0·055$
	C(4)	C(4)	+0·031	$D=\ 1·537$
	O(4)	O(4)	+0·026	
		C(5)	−1·099	
C	C(3)	C(3)	+0·050	$A=\ 0·682$
	C(4)	C(4)	−0·055	$B=\ 0·691$
	C(5)	C(5)	−0·048	$C=-0·323$
	O(5)	O(5)	+0·052	$D=-0·398$

mers where it gives rise to eclipsed oxygen atoms on alternate carbon atoms (El Khadem, Horton & Page, 1968). This non-bonding interaction is usually referred to as a 1–3 interaction by the organic chemists.

The hydrogen bonding

The hydrogen bonding is all intermolecular and is illustrated in Fig. 4. Each hydroxyl group forms



(*a*)

(*b*)

Fig. 4. The crystal structure of ribitol. Solid lines indicate primary C–C and C–O bonds. Dotted lines indicate hydrogen bonds with arrows pointing in the donor direction. (*a*) view down the *a* axis; (*b*) view down the *b* axis.

Table 5. *Intermolecular hydrogen-bond distances and angles in ribitol*

i	*j*		*k*	*l*	D_{jk}	$\angle_{ijk}$	$\angle_{jkl}$
C(1)	O(1)	→	O(5*d*)	C(5*d*)	2·732 Å	93·7°	126·7°
C(2)	O(2)	→	O(3*b*)	C(3*b*)	2·794	113·5	122·8
C(3)	O(3)	→	O(1*j*)	C(1*j*)	2·705	103·4	129·8
C(4)	O(4)	→	O(4*h*)	C(4*h*)	2·773	100·7	124·8
C(5)	O(5)	→	O(2*f*)	C(2*f*)	2·700	109·2	130·9

Symmetry code:

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

→: direction of O–H···O bond.

two hydrogen bonds, one as donor and one as acceptor. As is commonly observed, the spread of C–O–H angles at the donor oxygen atom of the hydrogen bond is less than those of H...O–C at the acceptor oxygen, being 100·7 to 129·8° *versus* 93·7 to 130·9° respectively. The O...O distances are given in Table 5. They vary over the range 2·701 to 2·795 Å which is narrower than usually found in carbohydrates. The hydrogen atoms deviate from the line of O...O centers by less than 0·28 Å, which is consistent with the small variation in hydrogen-bond distances.

The hydrogen bonds form infinite spirals and zigzag chains parallel to the *a* and *b* axes respectively, as shown in Fig. 4. The sequences are O(5*f*)→O(2*c*)→O(3)→O(1*j*)→O(5*g*)→*etc.* parallel to the *a* axis and O(4*c*)→O(4*g*)→O(4)→O(4*h*)→O(4*b*)→*etc.* parallel to the *b* axis. In common with the other polyol structures which have been studied, the molecules are arranged in a very regular and elegant pattern which utilizes their full potential for hydrogen-bond formation.

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References

Bekoe, A. & Powell, H. M. (1959). *Proc. Roy. Soc.* A**250**, 801.

Berman, H. M., Chu, S. C. & Jeffrey, G. A. (1967). *Science*, **157**, 1576.

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

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

Beurskens, P. T. (1963). *Sign Correlation by the Sayre Equation.* Technical Report, Crystallography Laboratory, Univ. of Pittsburgh.

Bjåmer, K., Furberg, S. & Petersen, C. S. (1964). *Acta Chem. Scand.* **18**, 587.

Bootsma, G. A. & Schoone, J. C. (1967). *Acta Cryst.* **22**, 522.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.

El Khadem, A. S., Horton, D. & Page, T. F. Jr (1968). *J. Org. Chem.* **33**, 734.

Hunter, F. D. & Rosenstein, R. D. (1968). *Acta Cryst.* B**24**, 1652.

Kim, H. S., Jeffrey, G. A. & Rosenstein, R. D. (1968). *Acta Cryst.* B**24**, 1449.

Kroon, J., Peerdeman, A. F. & Bijvoet, J. M. (1965). *Acta Cryst.* **19**, 293.

McGandy, E. L. (1968). Unpublished work.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63.

Shimada, A. (1958). *Acta Cryst.* **11**, 748.

Shiono, R. (1966). Modification of the Oak Ridge Least-Squares Program, ORNL-TM-305 (1962) of Busing, Martin & Levy.

Shiono, R. (1968). Unpublished work.

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

Tanaka, N., Ashida, T., Sasada, Y. & Kakudo, M. (1967). *Bull. Chem. Soc. Japan,* **40**, 1739.