ment of the Ag atom from the centre of symmetry depending on the orientation of the neighbouring CN groups.

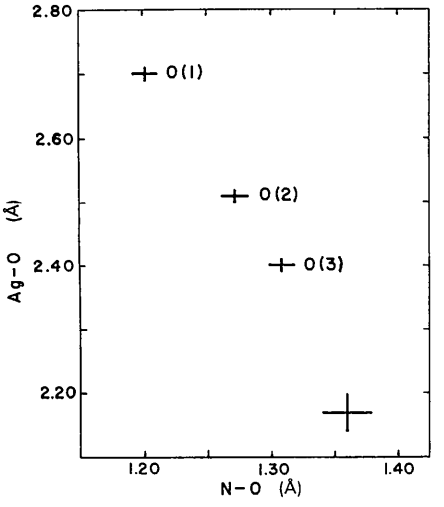

Fig. 3. N–O bond lengths *versus* Ag–O distances. The points are labelled with the numbers from Table 2. The unlabelled point corresponds to an N–O single bond and a Ag–O single bond, from CH_3ONO and $Ag_2C_2O_4$ respectively.

This work was performed in part during the tenure of a fellowship for which D.B. would like to thank the National Science Foundation. The preliminary calculations were carried out on the IBM 1620 computer of this laboratory, using programs prepared by M. Dobler, H. C. Mez, P. Strickler, and H. P. Weber. The least-squares calculations were carried out on the CDC 1604 computer at the Numerical Analysis Center of the University of Minnesota, using programs prepared at Princeton University under the direction of Professor R. Jacobson. This part of the work was performed by Mr E. O. Schlemper and Mrs Judith Konnert, and supported by a grant from the National Science Foundation. We thank them all for their help.

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The Crystal Structure of α-Methyl D-Galactoside 6-Bromohydrin

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The crystal structure of α-methyl D-galactoside 6-bromohydrin has been determined by the heavy-atom method, at 125 °K. The bromine atom coordinates were derived from Harker sections. Three-dimensional structure factors and least-squares refinement of 1203 reflexions with anisotropic temperature factors gave a final residual $R=0{\cdot}108$. All bonds, including the C(1)–O(1) bond, were found to be of normal length. The positions of the hydrogen atoms were found from the final 3-D Fourier synthesis. The hydrogen bonding system, which gives good agreement with the infrared spectroscopic data, consists of spiral linkages about the screw axes parallel to the *b* axis.

Experimental

α-Methyl D-galactoside 6-bromohydrin was prepared by Valentin (1952); unit-cell and density measurements were made by Cox, Goodwin & Wagstaff (1935). The unit-cell dimensions were re-measured at 125 °K by the extrapolation to $\theta=90°$ of high order reflexions on zero layer Weissenberg photographs, calibrated with aluminum wire powder lines. The *a* and *c* axes of Cox *et al.* were interchanged for convenience. The unit cell is orthorhombic with systematic absences of *h*00 for *h* odd and 0*k*0 for *k* odd. The space group is $P2_12_12$ and the cell dimensions are:

$a=11{\cdot}142\pm0{\cdot}005$ Å	*cf.* Cox, *et al.*	11·23 Å
$b=7{\cdot}815\pm0{\cdot}003$	at room temperature	7·81
$c=10{\cdot}612\pm0{\cdot}010$		10·58

The value of the density observed, 1·86 g.cm^{-3}, gave a cell weight of 1035 and hence $Z=4{\cdot}03$ ($C_7H_{13}BrO_5=257$).

The material was recrystallized from water, on a greased microscope slide, and a crystal with dimensions

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0·25 mm × 0·25 mm × 0·21 mm was selected. Full three-dimensional data were collected with the use of Cu $K\alpha$ radiation and the Weissenberg equi-inclination technique. The crystal was cooled to 125 °K by a stream of dry, cold nitrogen gas from apparatus similar to that described previously (Robertson, 1960). 1203 independent *hkl* reflexions were measured by the multiple film technique and correlated by hand calculation. 62 reflexions (marked with an asterisk in Table 6) were too weak to be measured. These were included in the least-squares refinement as $\frac{1}{2}F_{\min}$ but without separate weighting.

Solution of the structure

The position of the bromine atom was found from the Patterson–Harker sections at $x=\frac{1}{2}$, $y=\frac{1}{2}$ and $z=0$. Examination of the three mutually perpendicular Patterson projections showed that the x coordinate was general (at 5/60th a) but y was approximately $\frac{1}{4}$ and $z=0$ (or $\frac{1}{2}$). From the Harker sections it was possible to establish that the bromine atom coordinates were not quite so unfavourable as was first feared. The coordinates were specified as $x=5/60$, $y=14/60$ and $z=1/120$. A three-dimensional Fourier synthesis was computed on the Leeds University Ferranti Pegasus computer by the program written by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), with the phase angles specified by the bromine atoms. The resultant synthesis contained some spurious symmetry due to the near-special position of the bromine atom. Five definite light atom peaks were selected, two cycles of structure-factor least-squares (SFLS) refinement were carried out with the program written by Cruickshank *et al.* (1961) and the modified phase angles were used to

Table 1. *Atomic coordinates and estimated standard deviations* (Å)

	x	σ	y	σ	z	σ
Br	0·8976	0·0014	1·7809	0·0015	−0·1230	0·0016
O(1)	2·855	0·007	0·535	0·008	7·511	0·009
O(2)	9·663	0·008	0·083	0·008	5·211	0·007
O(3)	5·692	0·008	1·726	0·008	4·363	0·009
O(4)	3·568	0·007	0·062	0·008	3·404	0·008
O(5)	7·409	0·007	1·627	0·009	7·671	0·009
C(1)	7·879	0·011	0·624	0·011	6·781	0·011
C(2)	9·079	0·010	1·132	0·014	6·020	0·013
C(3)	10·184	0·010	1·627	0·012	6·983	0·014
C(4)	4·033	0·010	1·223	0·012	2·722	0·013
C(5)	2·851	0·010	1·828	0·012	1·984	0·011
C(6)	2·197	0·013	0·865	0·011	1·046	0·016
C(7)	3·940	0·012	1·200	0·015	8·178	0·015

Table 2. *Anisotropic temperature factors and estimated standard deviations*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0·0308	0·0242	0·0363	0·0036	0·0074	−0·0169
O(1)	0·0202	0·0147	0·0315	−0·0179	−0·0017	−0·0134
O(2)	0·0238	0·0098	0·0328	0·0016	−0·0134	0·0142
O(3)	0·0202	0·0135	0·0388	0·0099	−0·0156	−0·0128
O(4)	0·0121	0·0106	0·0392	0·0139	0·0035	−0·0053
O(5)	0·0137	0·0180	0·0350	0·0111	0·0021	−0·0020
C(1)	0·0235	0·0135	0·0268	−0·0227	0·0021	0·0035
C(2)	0·0133	0·0312	0·0290	−0·0089	0·0049	0·0087
C(3)	0·0112	0·0177	0·0454	−0·0061	0·0007	0·0137
C(4)	0·0134	0·0175	0·0426	−0·0049	0·0165	−0·0035
C(5)	0·0196	0·0217	0·0169	−0·0119	0·0102	−0·0085
C(6)	0·0299	0·0090	0·0532	−0·0049	0·0117	−0·0279
C(7)	0·0159	0·0401	0·0471	−0·0372	−0·0109	−0·0100
	σ_{11}	σ_{22}	σ_{33}	σ_{12}	σ_{13}	σ_{23}
Br	0·0007	0·0007	0·0007	0·0010	0·0011	0·0010
O(1)	0·0037	0·0035	0·0042	0·0066	0·0074	0·0069
O(2)	0·0040	0·0032	0·0042	0·0060	0·0085	0·0071
O(3)	0·0034	0·0033	0·0042	0·0068	0·0086	0·0073
O(4)	0·0031	0·0031	0·0043	0·0058	0·0084	0·0066
O(5)	0·0032	0·0034	0·0040	0·0060	0·0088	0·0068
C(1)	0·0052	0·0045	0·0054	0·0085	0·0096	0·0091
C(2)	0·0040	0·0062	0·0054	0·0101	0·0117	0·0086
C(3)	0·0040	0·0048	0·0067	0·0086	0·0112	0·0090
C(4)	0·0043	0·0050	0·0067	0·0091	0·0109	0·0094
C(5)	0·0047	0·0052	0·0040	0·0093	0·0085	0·0073
C(6)	0·0059	0·0044	0·0080	0·0102	0·0108	0·0123
C(7)	0·0043	0·0073	0·0071	0·0121	0·0149	0·0110

compute a second three-dimensional Fourier synthesis. In this all the atoms of the structure, with the exception of the carbon atom of the methyl group, could be distinguished. Seven cycles of SFLS were carried out with isotropic temperature factors for all the atoms except the methyl group carbon atom. This atom was then found by computing a difference Fourier synthesis for the sections where it was thought the methyl group should occur.

This atom was then introduced and four cycles of SFLS refinement were carried out with anisotropic temperature factors. Form factors published by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal were used for carbon and oxygen atoms and by Thomas & Umeda (1957) for bromine. The weighting scheme used was $w=1/(2F_{\min}+F+2F^2/F_{\max})$. The final cycle gave a residual, $R=0{\cdot}108$ and the observed and calculated structure factors are tabulated in Table 6.

A final three-dimensional Fourier synthesis was carried out and examined for variations of electron density. Some small positive regions were noted, of peak heights 0·7–1·2 e.Å^{-3}. Some of these were in positions in which would be plausible for hydrogen atoms to occur. As confirmation, the standard deviation of the electron density was calculated by the formulae given by Cruickshank (1949) and by Cruickshank & Rollett (1953):

$$\sigma(\varrho) = \frac{1}{V}\{\Sigma(\Delta F)^2\}^{\frac{1}{2}}$$

using a program written by one of us (B.S.) and found to be

$$\sigma(\varrho)=0{\cdot}37 \text{ e.Å}^{-3},$$

i.e. a peak height of 0·8 e.Å^{-3} would probably be significant. Thirteen possible hydrogen atoms were found and their positions were accurate enough to define the hydrogen bonding system. The coordinates of the atoms of one molecule are given in Table 1, together with the estimated standard deviations. The anisotropic temperature factors and their estimated standard deviations are given in Table 2, and the positions of the hydrogen atoms in Table 3.

Attempts were made to refine the data further by including the hydrogen atoms isotropically ($R=0{\cdot}105$) and by correcting the data (40 reflexions) for the presence of secondary extinction ($R=0{\cdot}096$). These measures had little effect on the atomic coordinates and the reduction of the e.s.d.'s was comparable to the reduction of the residual R. The stereochemical arrangement is shown in Fig. 1.

Table 3. *Atomic coordinates of hydrogen atoms (unrefined)* (Å)

	x	*y*	*z*
H(1)	4·04	0·80	6·19
H(2)	8·73	1·91	5·40
H(3)	10·46	0·78	7·57
H(4)	4·74	1·17	2·03
H(5)	8·73	1·43	9·37
H(6)	1·76	1·40	1·68
H(7)	1·80	0·00	8·91
H(8)	4·36	1·04	9·29
H(9)	4·55	1·04	7·16
H(10)	8·91	1·82	1·77
H(11)	6·59	1·04	4·51
H(12)	4·77	0·00	3·86
H(13)	9·42	0·13	6·37

The bond lengths, bond angles and related e.s.d.'s were calculated by a program written by Dr Mary R. Truter and the results are shown in Figs. 2 and 3 and Tables 4 and 5.

Structure of the molecule

The molecule has the expected chair form with the configuration 1*a*2*e*3*e*4*a*, as found for β-arabinose by Fur-

Table 4. *Bond lengths and estimated standard deviations*

Bond	*l*(Å)	e.s.d. (Å)
Br–C(6)	1·974	0·014
C(1)–C(2)	1·509	0·016
C(2)–C(3)	1·551	0·017
C(3)–C(4)	1·502	0·017
C(4)–C(5)	1·524	0·015
C(5)–C(6)	1·492	0·018
O(1)–C(1)	1·430	0·014
O(1)–C(7)	1·436	0·016
O(2)–C(2)	1·448	0·015
O(3)–C(3)	1·414	0·014
O(4)–C(4)	1·425	0·014
O(5)–C(5)	1·461	0·013
O(5)–C(1)	1·421	0·014

Table 5. *Bond angles and estimated standard deviations*

	Angle (°)	e.s.d.
Br–C(6)–C(5)	111°02′	0°47′
O(5)–C(1)–C(2)	109 56	58
O(5)–C(1)–O(1)	110 16	56
O(1)–C(1)–C(2)	107 39	54
C(1)–C(2)–C(3)	111 18	1 2
C(1)–C(2)–O(2)	111 02	1 1
O(2)–C(2)–C(3)	107 09	54
C(2)–C(3)–C(4)	109 05	53
C(2)–C(3)–O(3)	110 19	1 4
O(3)–C(3)–C(4)	109 49	58
C(3)–C(4)–C(5)	108 28	1
C(3)–C(4)–O(4)	113 55	1 3
O(4)–C(4)–C(5)	107 26	50
C(4)–C(5)–C(6)	112 46	1 1
C(4)–C(5)–O(5)	110 03	54
C(6)–C(5)–O(5)	108 13	55
C(5)–O(5)–C(1)	113 40	49
C(1)–O(1)–C(7)	113 20	51

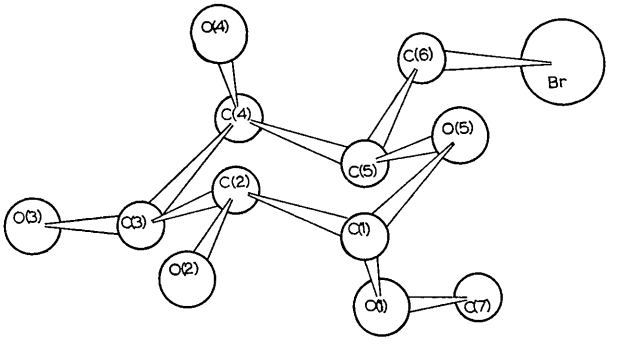

Fig. 1. Stereochemical arrangement.

Table 6. *Observed and calculated structure factors*

In each group headed by the values of h and k, the columns give l, $10|F_o|$, $10F_c$, $10A_c$, $10B_c$.

Table 6 (*cont.*)

4	5				
0		333	330	-330	0
1		531	520	-477	209
2		435	431	-420	-99
3		374	358	-357	27
4		349	314	-307	65
5		288	254	-251	38
6		333	334	-323	86
7		256	237	-230	54
8		259	252	-195	160
9		169	141	-141	3
10		219	211	-201	63
11		104	100	-89	45
4	6				
0		292	231	-231	0
1		365	330	287	-162
2		317	274	243	126
3		198	170	169	20
4		43	36	9	35
5		201	197	170	100
6		190	182	84	162
7		191	172	115	128
8		170	132	48	123
9		174	185	128	133
10		88	91	-16	90
4	7				
0		183	104	104	0
1		217	204	190	-73
2		238	215	214	8
3		231	217	191	-101
4		218	209	207	33
5		225	247	226	-98
6		183	177	164	-66
7		172	181	166	-71
8		143	134	105	-83
4	8				
0		180	159	-159	0
1		93	67	16	65
2		192	186	-105	-154
3		115	99	-77	-61
4		165	164	-127	-104
5		131	89	28	-85
6		111	115	-90	-73
7		84	100	-42	-91
4	9				
0		209	231	-231	0
1		150	148	2	148
2		48	54	-40	-35
3		134	150	-148	28
4		71	77	-48	59
5		27	75	-52	54
5	0				
1		169	156	0	156
2		310	304	0	304
3		46	31	0	-31
4		509	515	0	515
5		77	100	0	100
6		294	261	0	261
7		166	109	0	109
8		117	134	0	134
9		303	337	0	337
10		51	71	0	71
11		172	178	0	178
12		200	224	0	224
5	1				
0		365	378	-378	0
1		280	251	189	165
2		238	172	5	-172
3		348	285	-285	11
4		276	272	-79	260
5		291	274	36	272
6		340	300	-266	-138
7		70	33	30	-13
8		249	266	-50	261
9		108	106	11	105
*10		51	67	-22	63
11		63	81	5	80
12		59	77	-8	77
5	2				
0		204	156	-156	0
1		201	175	-64	-163
2		237	185	-174	-63
3		224	184	-163	85
4		435	433	-128	-413
5		115	131	35	-126
6		173	165	-131	-99
7		352	386	-199	-331
8		108	112	46	-103
9		106	235	29	-233
10		98	205	-105	-176
5	3				
0		36	50	50	0
1		340	323	304	109
2		242	188	188	-8
3		314	277	251	-118
4		156	125	116	-46
5		367	320	294	-128
6		151	144	95	-109
7		163	134	128	39
8		153	138	108	-86
9		145	150	28	-148
10		78	87	38	-78
11		85	71	60	-39
12		13	32	14	-29
5	4				
0		80	84	84	0
1		294	273	255	-98
2		314	264	242	104
3		163	154	153	-8
4		153	108	91	58
5		300	267	193	185
6		263	213	154	146
7		234	202	123	160
8		231	194	68	182
9		223	172	79	153
10		160	145	45	138
11		139	131	102	82
5	5				
0		537	632	-632	7
1		198	194	-174	58
2		297	269	-264	-5
3		319	294	-283	-26
4		276	260	-217	143
5		166	112	-94	61
6		202	170	-172	-11
7		186	171	-167	33
8		129	98	-63	75
9		142	126	-125	19
10		156	151	-132	75
5	6				
0		391	329	-329	0
1		306	270	-237	-129
2		76	85	-74	50
3		221	174	-138	-108
4		347	361	-330	-147
5		105	84	-80	-28
6		135	133	-125	-46
7		221	216	-159	-146
5	7				
0		481	447	447	0
1		209	199	189	62
2		258	218	218	-2
3		307	304	295	-76
4		146	142	141	6
5		265	297	297	-2
6		55	79	68	-39
7		195	185	195	13
5	8				
0		262	275	275	0
1		266	247	229	-93
2		197	150	-11	150
3		185	200	194	46
4		259	234	234	-8
5		133	133	120	57
6		88	92	87	30
5	9				
0		269	327	-327	0
1		37	86	-79	-36
2		161	187	-185	-32
3		204	242	-234	65
4		108	109	-109	-5
6	0				
0		430	390	-390	0
1		932	1007	-1007	0
2		619	692	-692	0
3		710	673	-673	0
4		556	525	-525	0
5		581	562	-562	0
6		666	694	-694	0
7		310	277	-277	0
8		276	252	-252	0
9		239	232	-232	0
10		190	224	-224	0
11		216	243	-243	0
12		50	64	-64	0
6	1				
0		300	295	-295	0
1		320	250	-76	238
2		168	138	3	-138
3		173	123	-118	-34
4		297	279	-69	271
5		138	89	-68	-58
6		127	93	0	93
7		128	104	6	104
8		189	156	-150	45
*9		53	68	-65	-20
*10		48	68	-52	45
11		126	74	-38	64
12		86	56	-56	-6
6	2				
0		646	636	636	0
1		739	749	747	-55
2		703	698	696	-50
3		583	571	569	-58
4		430	431	431	-14
5		482	481	462	-133
6		700	731	720	127
7		196	154	144	56
8		263	242	235	-57
9		307	336	332	50
10		91	183	183	-4
6	3				
0		142	54	-54	0
1		201	176	11	175
2		139	122	71	-99
3		286	232	76	-219
4		110	91	90	-7
5		130	98	93	-32
6		219	175	22	-174
7		192	172	171	-17
8		82	77	-15	-75
9		146	135	32	-131
10		104	102	64	-79
11		33	46	-6	-46
6	4				
0		428	448	-448	0
1		583	612	-609	56
2		498	477	-462	-122
3		339	298	-294	48
4		399	377	-376	-10
5		474	480	-480	-5
6		327	300	-298	35
7		245	209	-207	-32
8		262	228	-227	16
9		261	255	-249	52
10		110	103	-103	-7
11		177	194	-191	-33
6	5				
*0		51	26	-26	0
1		102	90	89	17
2		257	224	-186	-125
3		267	236	-43	232
4		94	105	59	87
5		107	68	-67	13
6		211	197	-85	178
7		201	168	-23	166
8		57	54	-15	52
9		134	113	-21	111
10		190	203	-36	199
6	6				
0		537	523	523	0
1		296	241	241	13
2		170	135	129	38
3		313	299	296	44
4		341	351	351	9
5		188	157	155	-22
6		236	257	256	-18
7		196	189	189	-9
6	7				
*0		55	57	57	0
1		79	52	43	-29
2		81	52	11	51
3		209	190	61	-180
4		82	82	-75	-35
5		105	121	5	-121
6		101	126	-24	-124
7		87	87	19	-84
6	8				
*0		46	28	-28	0
1		235	210	-206	-37
2		161	153	-141	60
3		94	56	-37	42
4		141	154	-154	5
5		185	202	-201	13
6		63	63	-62	11
6	9				
*0		27	8	-8	0
1		13	24	-7	23
*2		15	21	14	-16
7	0				
1		54	31	0	31
2		194	133	0	133
3		71	57	0	-57
4		125	117	0	117
5		194	148	0	148
6		125	146	0	146
7		268	293	0	293
8		115	95	0	95
9		169	178	0	178
10		142	169	0	169
11		132	140	0	140
7	1				
0		56	74	-74	0
1		294	256	-244	-75
*2		56	58	57	-4
3		146	118	-106	-51
4		283	237	-55	-230
5		322	259	-133	-222
6		197	139	-124	62
7		177	141	-119	-75
8		185	168	8	-168
9		173	157	-98	-123
10		107	95	-1	-95
11		146	99	-16	-98
7	2				
0		279	246	246	0
1		180	166	-74	-149
2		113	84	-29	-78
3		111	111	109	23
4		313	275	123	-248
5		101	77	52	-57
6		152	165	-25	-163
7		242	227	144	-175
8		165	119	-43	-111
9		96	168	-37	-164
10		83	103	6	-102
7	3				
0		677	656	656	0
1		255	191	39	-187
2		231	184	143	114
3		209	178	178	-3
4		356	332	318	95
5		201	175	89	150
6		188	119	76	91
7		129	102	92	44
8		285	210	176	114
9		197	189	66	177
10		114	103	69	76
11		74	57	25	51
7	4				
0		159	141	-141	0
1		147	119	-86	82
2		149	161	-141	78
3		55	43	-1	43
4		239	203	-82	185
5		128	121	-104	62
6		63	63	3	63
7		164	148	-69	131
8		58	52	-24	46
9		161	160	-3	160
*10		22	29	-15	24
7	5				
0		401	361	-361	0
1		260	203	-198	-43
2		171	136	-138	3
3		430	424	-413	93
4		282	266	-154	-217
5		306	303	-254	-75
6		170	127	-127	3
7		240	226	-219	-57
8		167	154	-125	-90
9		173	154	-115	-103
7	6				
1		201	158	158	0
2		211	178	167	60
3		129	97	34	-91
4		97	91	77	48
5		133	119	105	-56
*6		105	77	36	-69
7		85	83	4	-23
7	7				
0		279	289	289	0
1		187	169	169	-12
2		350	361	355	45
3		207	232	227	51
4		223	219	212	57
5		167	155	154	39
6		217	223	221	31
7		144	170	168	-20
7	8				
0		145	180	-180	0
1		77	62	-61	13
*2		29	41	-20	-36
3		111	107	-107	6
4		111	103	-103	-4
5		42	59	-58	14
8	0				
0		306	260	-260	0
1		478	413	-413	0
2		388	369	-369	0
3		583	538	-538	0
4		136	76	-76	0
5		243	207	-207	0
6		243	262	-262	0
7		238	227	-227	0
8		137	152	-152	0
9		279	310	-310	0
10		67	41	-41	0
11		136	140	-140	0
8	1				
0		340	345	345	0
1		552	543	530	-117
2		499	465	465	-10
3		355	320	299	116
4		452	446	399	-200
5		388	356	345	87
6		241	253	240	81
7		193	152	150	-24
8		227	231	231	10
9		204	231	207	101
10		76	93	88	-29
8	2				
0		329	263	263	0
1		338	272	268	41
2		455	403	403	-17
3		303	252	236	-88
4		468	439	431	79
5		118	90	89	-12
6		314	283	243	-144
7		221	209	202	-54
8		241	269	269	-8
9		87	113	92	-66
10		70	140	119	-74
8	3				
0		206	119	-119	0
1		531	502	-451	-220
2		464	440	-399	184
3		297	242	-242	1
4		389	370	-363	-73
5		294	266	-263	-41
6		271	232	-232	16
7		257	244	-235	-65
8		190	180	-145	-107
9		152	137	-134	28
10		154	139	-115	-77
8	4				
0		137	147	-147	0
1		288	307	-304	-46
2		123	127	8	127
3		432	429	-421	79
4		262	271	-270	-21
5		191	161	-111	116
6		217	207	-186	90
7		212	199	-178	88
8		194	163	-139	86
9		153	146	-146	8
10		103	118	-39	111
8	5				
0		157	140	140	0
1		303	264	246	94
2		368	337	332	57
3		269	243	238	48
4		173	144	142	-22
5		211	218	175	131
6		245	249	249	-11
7		116	103	103	-3
8		142	142	116	82
9		102	107	104	23
8	6				
0		123	89	89	0
1		200	170	156	69
2		255	246	220	-110
3		158	159	44	-153
4		190	179	178	23
5		117	116	86	-78
6		149	169	80	-149
7		27	48	-2	-48
8	7				
0		155	130	-130	0
1		188	183	-165	-79
2		158	150	-149	16
3		167	162	-154	-49
4		110	105	-95	-43
5		105	99	-78	62
6		108	146	-88	-117
8	8				
0		51	53	0	-53
1		65	56	0	-56
*2		34	50	0	50
3		103	82	0	82
*4		123	102	0	-102
5		35	36	0	-36
6		53	66	0	66
7		130	118	0	-118
8		28	1	0	1
*1		22	23	0	-23
9	1				
0		55	29	29	0
1		73	67	-14	66
2		277	236	-145	-235
3		53	47	3	47
4		134	95	39	-87
5		204	194	-121	-166
6		163	170	37	-166
7		171	194	-35	-191
8		207	206	-30	-204
9		182	165	0	-165
9	2				
0		114	88	-88	0
1		371	351	235	265
2		338	322	289	-145
3		81	41	34	-23
4		108	83	23	85
5		101	68	48	82
6		97	116	101	-33
7		81	64	49	42
8		88	91	67	62
9		74	30	28	-12
10		51	93	93	-2
9	3				
0		129	84	84	0
1		215	166	-49	159
2		225	180	139	115
3		53	43	12	41
4		153	127	-26	125
5		149	135	56	123
6		116	127	83	96
7		170	163	33	160
8		134	127	-26	124
9		110	105	69	79
9	4				
0		164	153	-153	0
1		190	195	-193	-27
2		204	196	-196	3
3		242	271	-262	-68
4		154	151	-144	46
5		174	147	-133	-63
6		129	136	-131	-38
7		175	179	-177	25
8		122	112	-84	-73
*9		15	27	-24	11
9	5				
0		131	79	79	0
1		115	94	-91	23
2		247	209	-155	-141
3		125	101	28	-97
4		60	66	25	61
5		196	173	-159	-88
6		129	127	1	-127
7		131	128	-39	-122
9	6				
0		235	229	229	0
1		177	160	160	13
2		279	263	261	-27
3		177	166	161	40
4		246	262	262	8
5		221	229	229	7
6		73	87	83	-26
7		63	153	146	42
9	7				
0		125	118	118	0
1		20	21	-12	-17
2		68	66	62	24
3		73	63	62	-10
10	0				
0		432	400	400	0
1		543	499	493	75
2		314	240	240	25
3		365	330	324	-64
4		477	480	476	64
5		247	227	225	23
6		234	270	257	-82
7		251	272	271	-14
8		221	243	243	3
9		135	129	108	-72
10	2				
0		147	127	-127	0
1		51	31	-29	11
2		290	259	-256	-41
3		130	142	-138	35
4		113	106	-81	-59
5		56	67	-54	-38
6		77	74	-67	-31
7		81	104	-97	-37
8		74	61	-42	-70
10	3				
0		372	311	-311	0
1		379	349	-348	17
2		333	301	-298	-41
3		330	308	-308	22
4		330	300	-294	56
5		271	246	-245	-13
6		223	245	-244	14
7		264	242	-222	97
8		150	145	-140	35
9		72	127	-125	70
10	4				
0		74	91	91	0
1		78	80	76	-23

Table 6 (*cont.*)

2		153	152	127	32	11	1					11	5					5		228	253	-231	-28	5		70	81	30	76
3		157	195	134	63	*0		55	38	38	0	*0		39	6	6	0	6		167	214	-207	54	13	2				
4		113	117	113	28	1		163	114	101	53	1		210	201	197	38	7		89	113	-111	19	*0		61	48	48	0
5		122	106	87	61	2		71	59	-34	-49	2		104	91	88	21							1		69	61	-13	59
6		44	72	25	68	3		97	55	23	-50	3		139	129	129	4	12	3					*2		55	46	-37	-27
7		75	81	78	22	4		74	74	21	-71	4		118	108	64	-87	0		63	60	-60	0	3		65	72	-40	60
8		58	101	49	89	5		123	111	104	-38	5		138	150	149	9	1		154	144	-90	112	4		61	85	41	75
						6		103	109	-103	-36							2		36	24	-8	-23	*5		30	15	14	-4
10	5					*7		35	68	64	-23	11	6					3		85	75	-65	-37						
0		237	237	207	0	*8		29	33	27	18	0		149	165	165	0	4		142	162	-157	136	13	3				
1		235	213	218	-4							1		214	132	131	-22	5		33	46	27	32	*0		27	22	22	0
2		283	282	260	-109	11	2					2		146	154	148	42	6		58	61	-57	22	1		154	142	-111	89
3		173	160	159	-18	0		157	142	142	0	3		75	88	88	5							2		125	135	-131	-33
4		229	250	240	-72	1		95	53	-1	-53							12	4					3		122	142	-103	-97
5		170	148	144	-33	2		88	51	20	46	12	0					0		287	352	352	0	4		59	60	-49	35
6		150	168	168	-10	3		207	202	95	178	0		406	462	462	0	1		221	242	233	63						
7		149	203	191	-70	4		89	64	64	5	1		313	263	263	0	2		132	115	96	-63	13	4				
						5		170	138	101	94	2		169	136	136	0	3		240	264	264	-6	0		122	152	-152	0
10	6					6		155	186	67	173	3		345	387	387	0	4		136	138	138	0	1		99	115	115	-1
0		135	123	-123	0	*7		53	59	36	46	4		226	259	259	0	5		156	199	197	24	2		61	104	104	0
1		115	80	-58	-67							5		231	223	223	0												
2		110	87	-87	12	11	3					6		162	222	222	0	12	5					14	0				
3		79	64	-56	-35	0		328	326	-326	0	7		235	294	294	0	*0		26	22	22	0	0		138	141	141	0
4		74	91	-66	-63	1		214	183	-6	-183							1		113	101	89	-47	1		119	146	146	0
5		112	144	-59	-132	2		119	92	-50	77	12	1					2		63	48	-44	19	2		132	185	185	0
						3		98	76	-74	15	*0		50	35	-35	0	3		27	41	40	8	3		98	105	105	0
10	7					4		142	140	-140	-10	1		73	53	40	-34												
1		158	144	-144	3	5		25	40	-3	39	2		148	142	138	-33	13	0					14	1				
2		113	110	-97	53	6		107	111	-106	32	3		102	89	86	23	*1		27	21	0	21	0		160	165	-165	0
						*7		20	49	4	49	4		51	53	42	-33	2		54	58	0	-58	1		115	115	-112	-26
11	8											5		106	100	35	-94	3		123	141	0	-141	2		136	161	-161	15
1		159	147	0	-147	11	4					6		123	120	105	58	4		35	39	0	-39	3		74	129	-129	2
2		184	154	0	154	*0		43	40	-40	0	*7		51	87	86	-10	*5		19	16	0	16						
3		189	176	0	-176	1		159	186	-163	-90													14	2				
4		103	90	0	-90	2		179	190	-186	35	12	2					13	1					0		142	174	-174	0
5		79	88	0	-88	3		75	67	17	-65	0		441	448	-448	0	*0		43	27	-27	0	1		80	118	-118	-12
6		89	113	0	-113	4		189	188	-89	-166	1		228	211	-210	-26	*1		33	39	31	-24						
7		206	213	0	-213	5		194	189	-188	-14	2		292	281	-281	22	*2		35	34	34	3						
8		76	68	0	-68	6		59	58	-31	-50	3		231	225	-213	-72	3		120	119	83	85						
						7		71	113	-48	-103	4		237	242	-240	29	4		60	67	-12	66						

berg & Hordvik (1957). All the bond lengths are normal with an average carbon–carbon length of 1·516 Å and an average carbon–oxygen length of 1·434 Å. The average estimated standard deviations are 0·015 Å and 0·013 Å respectively. The largest deviation from the mean, for the C–C bonds is the C(2)–C(3) distance of 1·551 Å, a difference of 0·035 Å, about 2·3 standard deviations and, for the C–O bonds, the O(5)–C(5) distance of 1·461 Å, a difference of 0·027 Å, *i.e.* about 2·1 standard deviations.

Previous structure determinations of monosaccharides have been carried out on α-glucose (McDonald & Beevers, 1952), α-rhamnose (McGeachin & Beevers, 1957), β-arabinose (Furberg & Hordvik, 1957) and β-glucose (Ferrier, 1963). In all these cases the C(1)–O(1) bond length has been found to be much shorter than other, similar bonds in the same molecule, *e.g.*

	Average C–O (Å)	C(1)–O(1) (Å)	e.s.d. (Å)
α-D-Glucose	1·40	1·32	–
α-Rhamnose	1·435	1·376	–
β-Arabinose	1·434	1·382	0·009
β-D-Glucose	1·444	1·404	0·010
cf. α-Methyl galactoside 6-bromohydrin	1·434	1·430	0·014

The amount of shortening in each of the four cases is equivalent to about 10% double bond character (Pauling, 1960) and may be related to the differences of reactivity noted for this hydroxyl group. In the case of α-methyl D-galactoside 6-bromohydrin, in which the O(1) carries a methyl group and not a hydrogen atom, the bond length C(1)–O(1) is not shorter than the average but is almost exactly equal to the average. This would suggest that the short bond in the α position is an effect which is eliminated completely when the hydrogen atom is substituted.

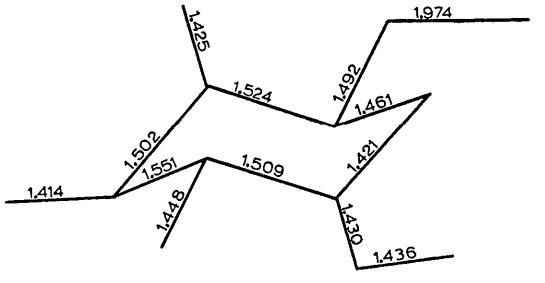

Fig. 2. Bond lengths (Å).

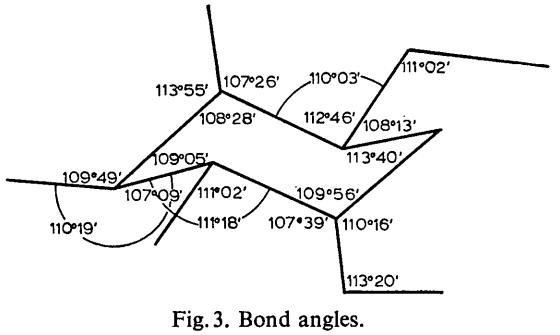

Fig. 3. Bond angles.

Crystal structure and hydrogen bonding

The crystals have cleavage planes perpendicular to the *z* axis but are resistant to cleavage in any other direction. Examination of the crystal structure shows that the bromine atoms are arranged in the form of layers with the galactose molecules filling the space between the layers. No hydrogen bonds can pass through the layer of bromine atoms which thus becomes the cleavage plane, but the molecules are bound together by the hydrogen bonding system in the other directions. Details of the crystal structure are shown in Figs. 4 and 5.

Before the structure was solved the infrared spectrum was examined in order to gain some information about

the hydrogen bonds to be expected. The spectrum is shown in Fig. 6. This shows no peak at a wavelength of 2·8μ which would correspond to a free hydroxyl group. The peaks which do occur were thought to represent a double-weight peak at 3·03μ and a single-weight peak at 2·92μ. These may be related to the length of the O–H · · · O distance to be expected following Nakamoto, Margoshes & Rundle (1955). The values calculated by this process were:

2 O–H---O distances of 2·78 Å
1 O–H---O distances of 2·85

The values obtained in the final structure were:

	l	σ
O(4)–H---O(2)	2·733 Å	0·010 Å
O(3)–H---O(4)	2·778	0·011
O(2)–H---O(3)	2·824	0·011

and this agreement is quite good.

The hydrogen bonds form spiral arrangements around the screw axes of the unit cell at $x=\frac{1}{4}$ or $\frac{3}{4}$ and $z=\frac{1}{2}$, and extend through the crystal parallel to the b axis. Examination of the hydrogen atom positions showed that the directions of the bonds are as shown in the diagrams, *i.e.* the spiral around the $\frac{1}{4}$, y, $\frac{1}{2}$ screw axis is directed in a positive direction with respect to the b axis while the spiral around the $\frac{3}{4}$, y, $\frac{1}{2}$ screw axis has the opposite sense. The absolute sense of the direction of these spirals follows from the choice of the correct absolute configuration for the D-galactose molecule.

The dimensions of the unit cell in the x and y directions appear to be mainly dependent upon the size and packing of the bromine atoms. This produces some gaps or holes in the structure parallel to the b axis at $\frac{1}{2}$, y, $\frac{2}{5}$ and 0, y, $\frac{3}{5}$. These channels are quite empty as they are not quite wide enough to contain water molecules and the material is thus anhydrous.

We wish to thank those named in the text for the use of their programs, the Director and staff of the University of Leeds Computing Laboratory for the calculations carried out on the Ferranti Pegasus computer and Sir Gordon Cox, K.B.E., F.R.S., for his initiation and encouragement of this work.

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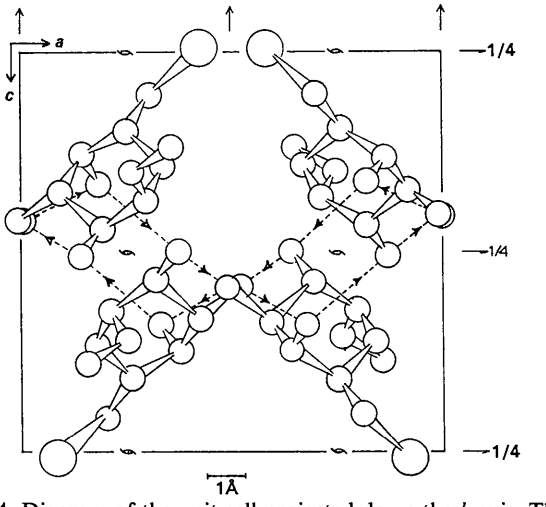

Fig. 4. Diagram of the unit cell projected down the b axis. The channels through the structure at $\frac{1}{2}$, y, $\frac{2}{5}$ and 0, y, $\frac{3}{5}$ are prominent. Hydrogen bonds are shown as dashed lines.

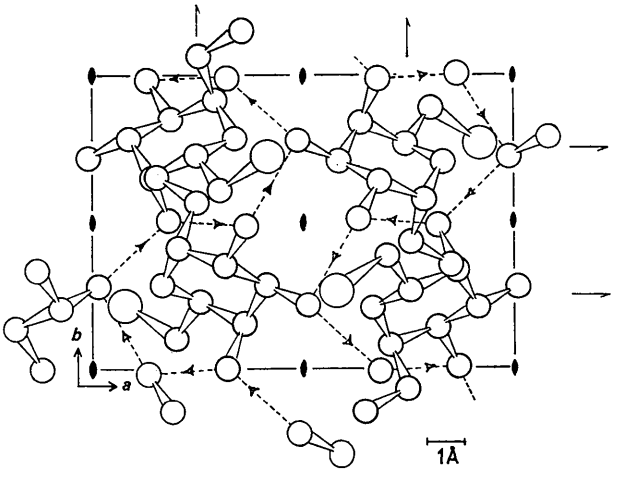

Fig. 5. Diagram of the unit cell projected down the c axis.

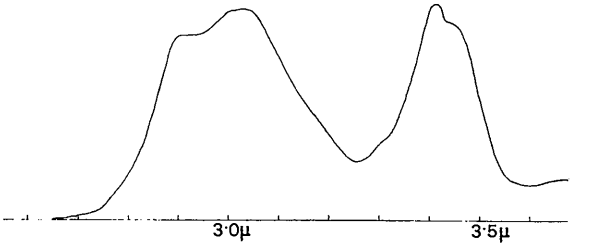

Fig. 6. Infrared spectrum.