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Crystal Structure of Methyl α-D-Mannopyranoside

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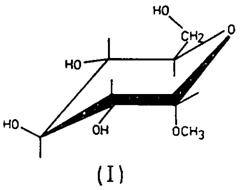
Methyl α-D-mannopyranoside crystallizes in the orthorhombic system: space group $P2_12_12_1$. Cell dimensions at room temperature are $a=9{\cdot}42_3$, $b=9{\cdot}30_8$ and $c=10{\cdot}04_5$ Å. The structure was solved by direct phasing methods with automatic diffractometer data and refined to a final reliability index of 0·044. Bond lengths and angles are similar to those encountered in other pyranose sugars and all oxygen atoms are involved in the hydrogen bonding network which comprises two terminating chains.

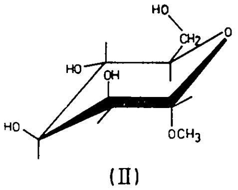
Introduction

The methyl α-glycosides of glucose, mannose and altrose constitute a valuable series of compounds in the study of hydrogen bonding patterns and conformational stability in pyranose sugars and their derivatives.

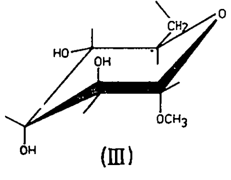
In changing from methyl α-glucoside (I) through methyl α-mannoside (II) to methyl α-altroside (III) the number of axial substituents in the *C*1 conformation is increased from one to three. At the same time the energy difference of the two alternative chair conformations for each compound decreases as steric interaction between the more bulky hydroxyl axial groups increases. With methyl α-altroside this results in the energies of the two conformations (III, IV) being almost identical (Eliel, Allinger, Angyal & Morrison, 1965) so that the conformation of the molecule in the crystal will be controlled by hydrogen bonding and packing requirements. Interest in this series of compounds is heightened further by the similar configuration of *C*1 methyl α-mannoside (II) and 1*C* methyl α-altroside (IV). All three materials crystallize in the orthorhombic space group $P2_12_12_1$ with a single molecule per asymmetric unit.



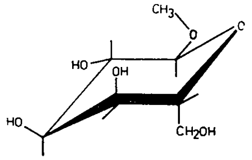
(I)



(II)



(III)



(IV)

The structure of methyl α-glucoside has been determined (Berman & Kim, 1968): this paper reports that of methyl α-mannoside.

Experimental

Methyl α-D-mannopyranoside, $C_7H_{14}O_6$, F.W. 194·19
Orthorhombic:

$a=9{\cdot}42_3$ Å
$b=9{\cdot}30_8$
$c=10{\cdot}04_5$
$D_m=1{\cdot}459$ g.cm^{-3} $D_x=1{\cdot}463$ g.cm^{-3}

Systematic absences: *h*00 for *h* odd; 0*k*0 for *k* odd; 00*l* for *l* odd

Space group: $P2_12_12_1$
μ 11·29 cm^{-1}
Cu $K\alpha_1$ 1·5405 Å .

These cell dimensions were measured with a Picker automatic four-circle diffractometer using high-order axial reflexions for which the Cu $K\alpha_1$ and α_2 peaks were resolved. A set was also obtained from film data with Si ($a=5{\cdot}4305$ Å) as internal standard. The agreement between the two sets was better than 0·25% but both were approximately 1% greater than those recorded by Cox & Goodwin (1932).

Three sets of intensity data were collected. Two were from different octants of the same crystal using the diffractometer operating in the θ–2θ scanning mode with a scan rate of 0·5° min^{-1} and stationary-crystal stationary-counter background counts of 40 sec at each end of the scan. The third set comprised film data collected at room temperature about two axes and cross-correlated *via* common reflexions. Intensities were estimated visually on a logarithmic scale against an appropriate standard series.

The common observed structure factors of the two diffractometer data sets had an agreement index, $R_f=2\sum||F_1|-|F_2||/\sum(|F_1|+|F_2|)$, of 0·015; the corresponding R_f between diffractometer and film data was 0·065. The diffractometer datum set used in the refinement was chosen arbitrarily.

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All crystals were approximate cubes with edges 0·15–0·20 mm, obtained by recrystallization from ethanol of material supplied by Nutritional Biochemical Corporation. Lorentz–polarization corrections were applied to all intensities but no allowance was made for absorption. The structure factors were placed on an approximate absolute scale using a Wilson plot and final scaling was achieved by equating the calculated to the observed values of the structure factors during the least-squares refinement.

The atomic scattering factors for carbon, oxygen, and hydrogen were those of Freeman (1959), Hoerni & Ibers (1954) and Stewart, Davidson & Simpson (1965) respectively.

Structure determination and refinement

The initial attempt to solve the structure was made using a vector map synthesized with film data. Several plausible orientations of the molecule for both chair conformations (*C*1 and 1*C*), were deduced from the 2·4 Å vector distribution about the origin but numerous attempts to locate the molecule within the cell using Harker sections were unsuccessful.

The positioning of the molecule was next approached by generating an '*R*' map for a particular molecular orientation and conformation. This *R* map was produced by calculating the conventional reliability index, *R*, for seventeen low-angle reflexions as the molecular model was stepped systematically through the asymmetric unit. A number of minima were found but comparison of the observed and calculated structure factors at each position showed poor agreement which could not be improved satisfactorily using Fourier and difference syntheses. The probable reasons for failure were: firstly, most of the seventeen inner reflexions suffered significantly from extinction and/or absorption; secondly, only part of the molecule could be specified, *i.e.* the labile primary hydroxyl group and the methyl group were omitted from the model. Of the two factors the second was undoubtedly the more important.

The structure was finally solved by direct phasing methods using programs* incorporating the tangent formula of Karle & Hauptman (1956). Initial phases were assigned to three origin-defining reflexions of high E value and three structure invarient phases, the latter using the E_1 formula. The repeated application of the tangent formula with decreasing E values yielded 123 phased reflexions with $E \geq 1{\cdot}53$. From the resultant E map eleven atoms of the molecule were clearly revealed with some indication of the remaining two. An electron density map phased on these eleven confirmed the location of all thirteen heavy atoms; a knowledge of the expected structure of methyl mannoside allowed the carbon and oxygen atoms to be differentiated from the beginning.

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters for methyl* α-D-*mannopyranoside*

The temperature factor expression is

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

Estimated standard deviations are given in parentheses and refer to the last significant figure. $\beta_{ij} \times 10_4$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·3591 (5)	0·0419 (5)	0·3896 (5)	51 (5)	49 (5)	47 (5)	−2 (5)	−2 (5)	−11 (5)
C(2)	0·4749 (5)	0·0738 (5)	0·2887 (5)	56 (6)	41 (5)	43 (5)	1 (5)	−5 (5)	3 (5)
C(3)	0·6205 (5)	0·0490 (5)	0·3489 (5)	49 (6)	39 (5)	37 (5)	2 (5)	1 (5)	−2 (5)
C(4)	0·6369 (5)	0·1324 (5)	0·4784 (5)	49 (6)	48 (5)	38 (5)	2 (5)	−4 (5)	9 (5)
C(5)	0·5158 (5)	0·0960 (5)	0·5726 (5)	50 (6)	60 (6)	36 (5)	4 (5)	3 (5)	7 (5)
C(6)	0·5153 (7)	0·1866 (6)	0·6983 (5)	93 (8)	95 (7)	41 (5)	7 (7)	−1 (6)	−27 (6)
C(7)	0·2571 (7)	−0·1561 (7)	0·5053 (6)	108 (8)	113 (9)	74 (7)	−40 (7)	36 (7)	2 (7)
O(1)	0·3644 (4)	−0·1069 (3)	0·4135 (3)	84 (5)	46 (4)	56 (4)	−17 (4)	25 (4)	−1 (4)
O(2)	0·4546 (4)	0·2217 (4)	0·2528 (4)	60 (5)	51 (4)	75 (5)	4 (4)	−3 (4)	28 (4)
O(3)	0·7284 (4)	0·0974 (4)	0·2585 (3)	55 (4)	72 (5)	42 (4)	−10 (4)	12 (4)	−8 (4)
O(4)	0·7672 (3)	0·0891 (3)	0·5429 (3)	44 (4)	66 (5)	50 (4)	−9 (4)	−1 (3)	7 (3)
O(5)	0·3807 (3)	0·1223 (3)	0·5081 (3)	49 (4)	60 (4)	46 (3)	5 (4)	−1 (3)	−16 (3)
O(6)	0·5133 (4)	0·3360 (4)	0·6715 (4)	58 (4)	87 (5)	104 (4)	3 (4)	−2 (4)	−44 (4)
HC(1)	0·258 (5)	0·068 (5)	0·357 (4)						
HC(2)	0·462 (5)	0·003 (5)	0·194 (4)						
HC(3)	0·633 (5)	−0·048 (5)	0·368 (4)						
HC(4)	0·633 (5)	0·248 (5)	0·456 (4)						
HC(5)	0·528 (4)	−0·019 (5)	0·589 (4)						
HC(6′)	0·425 (5)	0·156 (5)	0·763 (4)						
HC(6″)	0·622 (5)	0·167 (5)	0·748 (4)						
HC(7′)	0·177 (5)	−0·115 (5)	0·481 (5)						
HC(7″)	0·248 (5)	−0·261 (5)	0·489 (5)						
HC(7‴)	0·294 (5)	−0·131 (5)	0·600 (5)	Isotropic temperature factor = 2·2 Å					
HO(2)	0·507 (6)	0·249 (6)	0·215 (5)						
HO(3)	0·774 (6)	−0·048 (5)	0·694 (5)						
HO(4)	0·833 (6)	0·167 (7)	0·538 (5)						
HO(6)	0·428 (6)	0·365 (6)	0·006 (5)						

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* A modified set of the D.P. suite of programs written by Dr S. R. Hall.

The structure was refined by full-matrix least-squares (Busing, Martin & Levy, 1962) using $\sum w(F_o - F_c)$. The film data were refined with both unit and individual weights. The latter were set proportional to $1/F^2$ which was appropriate to the method used in estimating intensity. Both schemes yielded a final overall R of 0·095. With unit weights a satisfactory agreement, R, with $\sin\theta/\lambda$ was obtained in that each zone was equally reliable; with individual weights there was significantly poorer agreement at higher angles. The atomic positional parameters were altered by up to 10σ in changing the weighting scheme but the unit weight refined parameters were within 3σ of the final diffractometer refined values. A difference electron density synthesis with $\sin\theta/\lambda \leq 0·45$ ($R=0·095$, unit weights) showed peaks at acceptable hydrogen atom locations. However numerous other peaks of equal height were also present which vitiated the confident assignment of any of the peaks to hydrogen.

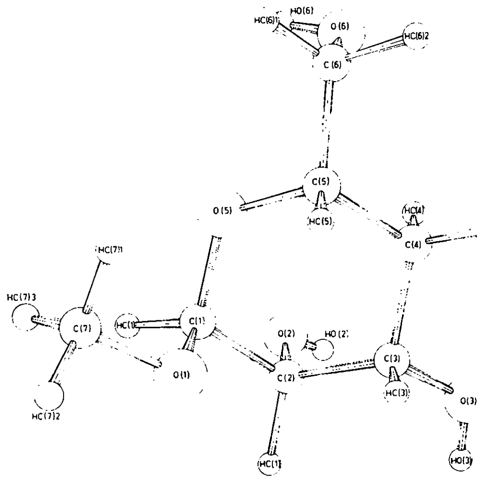

Fig. 1. Conformation of α-D-mannopyranoside and atom numbering.

Refinement was continued using diffractometer data with individual weights based on counting statistics. A difference electron synthesis ($R=0·074$; $\sin\theta/\lambda \leq 0·45$) revealed most of the hydrogen atoms. Those attached to carbon atoms, with the exception of the methyl group, were well defined and with continued refinement all hydrogen atoms were eventually located unambiguously. The final difference Fourier synthesis showed electron density fluctuations not exceeding 0·4 e.Å^{-3} ($R=0·044$). Several low-angle reflexions showed evidence of absorption or extinction but in this refinement no reflexions were rejected.

Final values of the atomic coordinates and thermal parameters, together with their estimated standard deviations are given in Table 1; Table 2 contains the list of observed and calculated structure factors.

Description of the structure

Methyl α-D-mannopyranoside in the crystal has the $C1$ chair conformation for which the ring substituents are arranged in the sequence $1a2a3e4e5e$. The molecule and the numbering of the atoms is shown in Fig. 1.

Bond lengths and angles derived from the coordinates of Table 1 are listed in Table 3. The carbon–carbon bonds are between 1·517 and 1·524 Å with a mean of 1·520 Å which is in good agreement with values reported for other carbohydrates. The carbon–oxygen bond distances, however, show a greater variation and range between 1·407 and 1·450 Å with a mean value of 1·432 Å; this mean is not significantly greater

Table 2. *Calculated and observed structure factors*

0	0	L
2	63	62
4	625	648
6	51	39
8	134	133
10	35	30
0	1	L
1	509	574
2	453	471
3	206	202
4	340	334
5	401	388
6	209	206
7	26	19
8	99	98
9	18	22
10	47	51
11	35	37
0	2	L
0	186	184
1	451	470
2	254	246
3	621	645
4	365	361
5	233	236
6	77	64
7	90	88
8	9	10
9	168	181
10	19	18
11	6	1
0	3	L
1	552	567
2	18	22
3	127	126
4	20	33
5	246	238
6	29	16
7	58	59
8	39	41
9	22	25
10	36	45
11	94	96
0	4	L
0	760	810
1	172	166
2	505	501
3	265	267
4	276	262
5	188	175
6	78	70
7	97	100
8	10	12
9	22	18
10	47	49
0	5	L
1	46	53
2	53	47
3	96	86
4	184	167
5	148	150
6	9	0
7	57	63
8	137	145
9	37	43
10	34	33
0	6	L
0	306	295
1	252	213
2	8	1
3	146	136
4	67	96
5	51	47
6	256	262
7	93	105
8	11	0
9	17	14
0	7	L
1	51	34
2	7	16
3	305	294
4	105	139
5	135	134
6	38	43
7	10	6
8	92	94
0	8	L
0	46	16
1	4	7
2	230	215
3	353	378
4	115	110
5	71	76
6	16	16
7	147	130
0	9	L
1	17	13
2	100	93
3	39	31
4	57	58
5	49	46
6	10	14
0	10	L
0	47	42
1	11	15
2	4	3
3	12	16
4	75	74
1	0	L
1	291	293
2	308	304
3	119	112
4	297	295
5	210	211
6	6	18
7	247	240
8	101	100
9	102	135
10	72	74
11	15	14
1	1	L
0	172	120
1	582	685
2	426	437
3	45	40
4	245	242
5	56	49
6	64	57
7	86	90
8	52	50
9	94	104
10	217	228
11	25	29
1	2	L
0	558	593
1	557	618
2	122	119
3	222	217
4	452	456
5	256	263
6	23	21
7	152	153
8	99	98
9	85	85
10	49	53
11	80	88
1	3	L
0	146	159
1	292	289
2	147	143
3	433	428
4	316	295
5	121	119
6	126	116
7	150	148
8	39	45
9	81	79
10	93	94
11	69	78
1	4	L
0	192	187
1	265	288
2	111	100
3	116	109
4	216	199
5	16	16
6	107	104
7	65	67
8	49	42
9	95	98
10	88	91
1	5	L
0	187	156
1	275	260
2	315	302
3	111	105
4	266	257
5	94	89
6	71	73
7	69	64
8	48	44
9	23	21
10	104	113
1	6	L
0	180	172
1	348	338
2	292	289
3	158	143
4	188	189
5	89	85
6	115	119
7	79	80
8	28	29
9	45	45
1	7	L
0	123	124
1	110	108
2	112	114
3	210	209
4	195	194
5	65	73
6	104	104
7	127	132
8	13	14
1	8	L
0	118	113
1	74	71
2	114	117
3	24	22
4	94	92
5	89	90
6	59	56
7	80	96
1	9	L
0	6	11
1	86	82
2	50	43
3	87	79
4	67	64
5	28	25
6	19	17
1	10	L
0	69	43
1	35	43
2	68	64
3	47	50
4	76	77
2	0	L
0	242	238
1	334	330
2	488	475
3	203	197
4	181	185
5	129	127
6	13	11
7	81	77
8	186	190
9	141	144
10	71	76
11	87	85
2	1	L
0	65	60
1	305	317
2	75	69
3	283	273
4	211	209
5	204	196
6	127	122
7	206	202
8	148	152
9	179	190
10	36	35
11	88	93
2	2	L
0	413	415
1	115	106
2	422	427
3	123	118
4	241	235
5	127	121
6	108	107
7	180	179
8	94	95
9	62	61
10	56	61
11	48	47
2	3	L
0	155	150
1	79	78
2	217	210
3	132	132
4	88	60
5	94	84
6	179	175
7	58	61
8	76	85
9	52	53
10	89	91
2	4	L
0	259	261
1	250	251
2	64	65
3	120	119
4	278	273
5	10	21
6	100	105
7	136	130
8	135	136
9	43	48
10	57	50
2	5	L
0	114	107
1	179	173
2	36	36
3	154	146
4	25	24
5	95	93
6	153	157
7	84	87
8	35	38
9	122	128
10	67	62
2	6	L
0	161	149
1	148	139
2	142	129
3	132	124
4	147	142
5	137	142
6	51	57
7	69	94
8	54	58
9	54	57
2	7	L
0	51	42
1	70	69
2	41	45
3	48	46
4	100	103
5	160	159
6	177	186
7	18	12
8	16	17
2	8	L
0	68	75
1	55	55
2	102	102
3	30	26
4	98	92
5	69	73
6	30	22
7	28	20
2	9	L
0	13	13
1	64	68
2	59	56
3	68	69
4	38	39
5	21	18
2	10	L
0	16	18
1	60	61
2	45	45
3	33	34
3	0	L
1	491	493
2	35	28
3	545	546
4	128	122
5	62	74
6	47	52
7	71	73
8	269	281
9	63	68
10	41	40
11	23	26
3	1	L
0	450	449
1	403	405
2	205	200
3	445	441
4	283	272
5	82	81
6	216	210
7	255	254
8	96	95
9	50	49
10	15	11
11	60	70
3	2	L
0	24	20
1	306	298
2	101	87
3	306	294
4	114	109
5	264	253
6	302	300
7	182	182
8	194	203
9	119	119
10	39	43
3	3	L
0	124	123
1	173	164
2	131	128
3	277	262
4	113	112
5	141	131
6	82	77
7	156	158
8	102	103
9	60	64
10	74	75
3	4	L
0	37	23
1	250	238
2	122	112
3	54	55
4	77	73
5	147	155
6	60	57
7	104	106
8	145	144
9	37	35
10	60	61
3	5	L
0	260	209
1	86	84
2	117	110
3	71	73
4	172	170
5	110	110
6	152	139
7	82	87
8	15	11
9	40	53
3	6	L
0	66	72
1	120	114
2	61	54
3	190	187
4	276	287
5	142	136
6	99	101
7	110	113
8	125	131
9	14	12
3	7	L
0	146	152
1	121	133
2	158	154
3	158	156
4	174	171
5	122	117
6	71	73
7	64	71
8	53	50
3	8	L
0	251	248
1	34	37
2	27	27
3	27	16
4	62	65
5	92	94
6	58	58
7	27	29
3	9	L
0	154	162
1	52	54
2	34	31
3	104	104
4	70	81
5	36	32
3	10	L
0	73	78
1	22	26
2	74	75
4	0	L
0	349	349
1	202	200
2	358	357
3	55	56
4	303	298
5	115	111
6	118	110
7	17	13
8	160	163
9	49	52
10	70	78
4	1	L
0	189	191
1	179	177
2	445	436
3	411	404
4	398	380
5	210	202
6	128	129
7	273	275
8	124	125
9	105	105
10	47	48
4	2	L
0	227	225
1	240	258
2	131	122
3	206	248
4	161	141
5	75	76
6	155	136
7	145	140
8	55	64
9	22	16
10	34	38
4	3	L
0	43	38
1	141	141
2	120	122
3	36	28
4	147	134
5	160	152
6	128	125
7	277	283
8	50	56
9	70	73
10	54	57
4	4	L
0	49	22
1	47	42
2	169	186
3	208	205
4	103	102
5	96	90
6	87	89
7	61	64
8	55	57
9	66	69
4	5	L
0	41	34
1	71	67
2	197	194
3	328	324
4	251	244
5	174	168
6	42	37
7	45	44
8	46	44
9	67	85
4	6	L
0	43	58
1	112	112
2	47	47
3	119	115
4	145	145
5	120	131
6	150	145
7	59	59
8	7	8
4	7	L
0	95	99
1	159	168
2	110	120
3	101	101
4	23	23
5	109	196
6	58	57
7	78	77
4	8	L
0	138	153
1	103	105
2	107	114
3	72	69
4	135	132
5	36	39
6	55	52
4	9	L
0	7	3
1	200	209
2	70	65
3	62	59
4	58	55
4	10	L
0	102	102
5	0	L
1	119	109
2	108	105
3	265	271
4	58	53
5	215	235
6	220	223
7	61	81
8	177	175
9	107	108
10	52	52
5	1	L
0	234	225
1	349	337
2	200	190
3	108	93
4	125	156
5	164	146
6	169	202
7	100	184
8	11	0
9	35	34
10	59	54
5	2	L
0	67	87
1	123	112
2	252	235
3	211	194
4	24	22
5	94	89
6	210	225
7	75	75
8	107	119
9	41	40
10	17	11
5	3	L
0	91	93
1	117	114
2	28	21
3	341	341
4	71	67
5	68	64
6	130	135
7	185	194
8	77	79
9	43	45
5	4	L
0	81	81
1	54	55
2	61	64
3	114	113
4	79	73
5	63	65
6	87	85
7	18	18
8	87	90
9	86	69
5	5	L
0	305	315
1	100	106
2	28	21
3	170	177
4	139	134
5	58	66
6	153	157
7	75	70
8	40	41
5	6	L
0	14	8
1	146	145
2	57	52
3	117	111
4	114	114
5	95	99
6	107	112
7	57	59
8	34	37
5	7	L
0	55	42
1	63	64
2	175	170
3	175	177
4	77	74
5	102	104
6	52	50
7	23	25
5	8	L
0	156	161
1	41	40
2	63	69
3	38	38
4	52	54
5	66	70
5	9	L
0	86	85
1	40	40
2	59	62
3	94	99
6	0	L
0	95	86
1	103	106
2	87	90
3	6	5
4	228	215
5	101	102
6	14	8
7	60	57
8	117	117
9	63	63
6	1	L
0	68	62
1	86	87
2	114	107
3	104	95
4	60	56
5	122	122
6	107	106
7	95	101
8	40	40
9	22	11
6	2	L
0	44	38
1	33	25
2	140	136
3	96	96
4	72	72
5	98	105
6	86	88
7	121	120
8	49	48
9	73	70
6	3	L
0	16	24
1	55	64
2	103	110
3	38	41
4	125	123
5	83	77
6	93	97
7	15	15
8	146	151
9	28	25
6	4	L
0	21	12
1	94	95
2	63	57
3	8	11
4	122	119
5	32	37
6	16	8
7	29	30
8	53	51
6	5	L
0	140	144
1	136	138
2	93	86
3	61	57
4	78	81
5	120	122
6	86	85
7	91	92
8	27	28
6	6	L
0	61	69
1	18	16
2	76	78
3	83	80
4	138	148
5	80	88
6	34	33
7	71	70
6	7	L
0	52	53
1	125	131
2	33	31
3	87	89
4	40	43
5	46	51
6	40	41
6	8	L
0	39	42
1	95	98
2	74	76
3	20	14
4	19	21
7	0	L
1	108	106
2	132	127
3	194	188
4	159	161
5	89	103
6	54	55
7	52	51
8	73	20
7	1	L
0	113	115
1	352	358
2	226	221
3	127	117
4	18	17
5	73	70
6	58	65
7	34	30
8	29	30
7	2	L
0	99	96
1	132	130
2	232	230
3	65	71
4	73	74
5	91	91
6	115	114
7	47	48
8	14	12
7	3	L
0	62	55
1	66	61
2	121	119
3	125	124
4	141	150
5	54	52
6	87	87
7	29	29
8	18	12
7	4	L
0	108	116
1	60	60
2	24	19
3	61	60
4	64	65
5	50	51
6	30	26
7	49	52
7	5	L
0	0	4
1	162	166
2	117	113
3	114	119
4	65	67
5	8	9
6	52	53
7	41	41
7	6	L
0	39	39
1	34	34
2	77	78
3	13	16
4	126	126
5	111	118
6	49	53
7	7	L
0	154	151
1	24	28
2	92	93
3	71	71
4	144	147
7	8	L
0	49	49
1	18	22
2	52	57
8	0	L
0	409	503
1	121	126
2	161	170
3	108	110
4	40	35
5	88	92
6	86	93
7	40	36
8	1	L
0	38	32
1	216	217
2	177	170
3	27	25
4	97	100
5	147	147
6	104	109
7	59	53
8	2	L
0	130	122
1	55	41
2	37	40
3	115	129
4	30	25
5	102	110
6	98	101
7	10	6
8	3	L
0	56	43
1	153	159
2	165	167
3	58	58
4	11	13
5	80	93
6	22	18
7	39	44
8	4	L
0	249	252
1	110	123
2	142	143
3	102	105
4	141	147
5	50	48
6	56	57
8	5	L
0	132	138
1	63	66
2	57	71
3	58	60
4	49	47
5	100	106
8	6	L
0	41	43
1	29	27
2	62	69
3	127	136
4	17	18
8	7	L
0	47	46
1	113	119
2	130	135
9	0	L
1	14	9
2	155	169
3	9	8
4	16	19
5	15	17
6	20	23
9	1	L
0	42	38
1	97	102
2	42	46
3	52	51
4	39	48
5	73	28
6	16	12
9	2	L
0	71	61
1	160	160
2	36	39
3	96	108
4	87	89
5	33	34
6	9	7
9	3	L
0	17	11
1	38	39
2	36	34
3	88	98
4	40	40
5	32	30
9	4	L
0	98	98
1	41	43
2	93	104
3	69	67
4	13	15
9	5	L
0	25	33
1	30	32
2	64	63
3	28	28
9	6	L
0	51	52
10	0	L
0	94	94
1	47	47
2	29	28
3	108	113
4	48	50
10	1	L
0	59	71
1	35	34
2	60	58
3	32	30
4	48	46
10	2	L
0	18	9
1	29	27
2	44	48
3	21	21
4	63	66
10	3	L
0	14	17
1	12	10
2	54	57
3	8	3
10	4	L
0	11	12
1	35	38

than that met with in other pyranose structures. It is interesting to observe that the C(1)O(1) bond is significantly shorter than the average and therefore the methyl group does not completely eliminate the anomeric shortening observed in the free sugar (Berman, Chu & Jeffrey, 1967). The variations of C(5)O(5), O(5)O(1) and C(1)O(1) from the mean (+0·018, −0·011, −0·025 Å), has the same pattern as that found in methyl α-glucoside (+0·010, −0·10, −0·013 Å), (Berman & Kim, 1968). These discrepancies, and the greater variation of the C–O bond lengths about the mean, as compared with the C–C bond lengths, may be significant and associated with the type of hydrogen bond involved although no correlation is apparent in methyl α-mannoside. A more careful analysis taking account of such factors as extinction, absorption and bonding elecrons will be needed to determine to what extent the variations are genuine. These remarks apply also to the CH and OH bond lengths, the mean values of which are 1·04 and 0·82 Å and therefore somewhat shorter than the usually accepted values of 1·09 and 0·96 Å respectively. A correction for riding motion of the light hydrogen atom on the heavier oxygen and carbon atoms (Busing & Levy, 1964) would probably improve the agreement.

Table 3. *Bond lengths and angles in methyl α-D-mannopyranoside*

Bond lengths

C(1)–C(2)	1·517 Å	C(2)–HC(1)	1·04 Å
C(2)–C(3)	1·518	C(2)–HC(2)	1·16
C(3)–C(4)	1·524	C(3)–HC(3)	0·93
C(4)–C(5)	1·521	C(4)–HC(4)	1·10
C(5)–C(6)	1·518	C(5)–HC(5)	1·09
C(1)–O(1)	1·407	C(6)–HC(6′)	1·04
C(2)–O(2)	1·436	C(6)–HC(6″)	1·13
C(3)–O(3)	1·435	C(7)–HC(7′)	0·88
C(4)–O(4)	1·445	C(7)–HC(7″)	1·00
C(5)–O(5)	1·450	C(7)–HC(7‴)	1·05
C(6)–O(6)	1·417	O(2)–HO(2)	0·67
C(1)–O(5)	1·421	O(3)–HO(3)	0·80
C(7)–O(1)	1·442	O(4)–HO(4)	0·96
		O(6)–HO(6)	0·85

Bond angles

O(1)C(1)O(5)	111·7°	C(3)C(4)C(5)	110·0°
C(2)C(1)O(1)	106·4	C(3)C(4)O(4)	109·1
C(2)C(1)O(5)	110·7	C(5)C(4)O(4)	107·2
C(1)C(2)C(3)	110·7	C(4)C(5)C(6)	113·3
C(1)C(2)O(2)	105·1	C(4)C(5)O(5)	110·1
C(3)C(2)O(2)	111·4	C(6)C(5)O(5)	106·0
C(2)C(3)C(4)	110·8	C(5)C(6)O(6)	112·8
C(2)C(3)O(3)	109·9	C(1)O(1)C(7)	113·4
C(4)C(3)O(3)	107·9	C(1)O(5)C(5)	114·3

Dihedral angles around the pyranose ring were between 53·5 and 59·3° and therefore in the range found for other pyranose rings (Kim & Jeffrey, 1967). Also consistent with other carbohydrate structures is the 114·3° angle at the ring oxygen atom, O(5), and the mean value of 110·0° for the carbon valence angles. In the latter there is no significant variation with type, *viz.* CCO, OCO, and CCC, from the tetrahedral angle of 109·5°. The bond angles involving hydrogen were also normal: an average of 110·0° with a range of 108 to 114°.

The plane of the molecular ring comprising C(1), C(2), C(3), C(4), C(5) and O(5) is defined by the equation:

$$0{\cdot}0661\,x - 0{\cdot}9736\,y + 0{\cdot}2185\,z = 0{\cdot}4774\,.$$

Four of the atoms are $0{\cdot}23_1$ Å from this plane; the remaining two, C(1) and C(2), both of which have substituents that are axial, are marginally closer to the ring plane at $\pm 0{\cdot}21_9$ Å – the calculated standard deviations are 0·005 Å.

The oxygen–oxygen contact distances ≤ 3·25 Å are listed in Table 4 together with O···HO distances and O···H–O angles. The hydrogen bonding system comprises two short terminated chains: O(2′)H → O(1), O(6″)H → O(3)H → O(4‴)H → O(5⁗). Two oxygen atoms [O(2) and O(6)] are donors only, two [O(3) and O(4)] are both donors and acceptors, and two [O(1) and O(5)] are acceptors only. One distance [O(3)··· O(4)] is characterized by being significantly shorter than the others and at the same time possesses an almost linear arrangement of atoms (174°). The longest oxygen–oxygen contact distance [O(4)···O(5)] on the other hand has the least linear atomic arrangement (151°). All four contacts suggested as hydrogen bonds have H···O distances which are approximately 0·5 Å less than the sum, 2·60 Å, of the van der Waals radii of hydrogen and oxygen (Pauling, 1960). As a group, the oxygen–oxygen contact distances in methyl α-mannoside tend to a longer average distance than in many other carbohydrates (Jeffrey & Rosenstein, 1964).

Although C(7) has a high thermal parameter its associated hydrogen atoms were clearly resolved and indicate that at room temperature the methyl group is not free to rotate. The contact distances of atoms around this group are consistent with van der Waals radii with no unusually close contacts which may help to stabilize the conformation (Mathieson & Poppleton, 1966). The location of the methyl group with respect to the ring is the same as that found in methyl α-glucoside.

The primary hydroxyl group, however, differs in its position. Thus in methyl α-mannoside the C(6)–O(6) bond is approximately perpendicular to the general

Table 4. *Hydrogen bond distances* (≤ 3·25 Å) *and angles in methyl α-D-mannopyranoside*

Distances				Angles	
O(1)···O(2)	2·872 Å	O(1)···HO(2)	2·22 Å	O(1)···HO(2)O(2)	163°
O(3)···O(6)	2·844	O(3)···HO(6)	2·05	O(3)···HO(6)O(6)	156
O(4)···O(3)	2·776	O(4)···HO(3)	1·98	O(4)···HO(3)O(3)	174
O(5)···O(4)	2·937	O(5)···HO(4)	2·07	O(5)···HO(4)O(4)	151

plane of the molecule and consequently O(6) is *trans* to HC(5) whilst in methyl α-glucoside O(6) is approximately in the plane of the ring and *trans* to C(4) (Berman & Kim, 1968).

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The Crystal and Molecular Structure of 5-Iodouridine

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The crystal structure of 5-iodouridine ($C_9H_{11}IN_2O_6$) has been determined from data collected on a Hilger and Watts linear diffractometer. The crystals are monoclinic, space group $P2_1$, with cell dimensions: $a=4{\cdot}683\pm0{\cdot}005$, $b=17{\cdot}14\pm0{\cdot}01$, $c=14{\cdot}58\pm0{\cdot}01$ Å and $\beta=90{\cdot}85\pm0{\cdot}1^\circ$. The structure was solved by the heavy-atom method and the positional and thermal parameters were refined by the method of least-squares. The final R value for 2143 observed reflexions is 0·061. There are two molecules in the asymmetric unit and the dihedral angle between the base and sugar planes in both is 69°. However, the glycosidic torsion angle, φ_{CN}, is $-13{\cdot}2^\circ$ in molecule I and $-58{\cdot}7^\circ$ in molecule II. In molecule I atom C(3′) of the sugar ring is displaced 0·54 Å *endo*, and in molecule II atom C(2′) is displaced 0·63 Å *endo*. The orientation of the C(5′)–O(5′) bond is *gauche* to both the C(4′)–O(1′) and C(4′)–C(3′) bonds in molecule I, but in molecule II it is *trans* to C(4′)–O(1′) and *gauche* to C(4′)–C(3′).

Introduction

The structure determination of 5-iodouridine (IUR) (Fig. 1) was undertaken as part of a series of structure determinations of nucleic acid components and their analogues. Single-crystal studies of nucleosides and nucleotides give important information about the bond lengths and angles, and about the conformations of the molecules, which can be used when molecular models of polynucleotide structures are constructed. It was mainly to obtain information about the conformation of the molecule that IUR was studied. Knowledge of the crystal and molecular structure of IUR was also desirable as a first step in the study of the effects of ionizing radiations on single crystals of IUR by electron-spin resonance. Such studies have already been made on 5-iodo-2′-deoxyuridine (Nice & Rorke, 1969). It is hoped that similar studies will eventually elucidate the effects of ionizing radiations on the nucleic acids themselves, and explain the change in sensitivity when certain analogues are incorporated into the structure in place of a normal component. A preliminary account of the conformations of the molecules has been given recently (Rahman & Wilson, 1970).

Experimental

Crystal of 5-iodouridine ($C_9H_{11}IN_2O_6$) were obtained by evaporation from aqueous solutions. The unit-cell dimensions were first obtained from Weissenberg photographs and were then refined on a Wooster four-circle diffractometer using Cu $K\alpha$ radiation. The crystals are monoclinic and elongated along the a axis. The unit-cell dimensions are: