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Crystal Structure of the *p*-Bromophenylhydrazone of Mannose

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The crystal structure of the *p*-bromophenylhydrazone of mannose has been determined by X-ray crystallographic methods and refined to an *R* index of 0.078. Three-dimensional film data were used. The compound is a true hydrazone, the mannose having an acyclic structure. The carbon atoms of the sugar form a nearly planar zigzag chain. Delocalization effects in the hydrazine part of the molecule are indicated.

Chemical evidence indicates that the phenylhydrazones of the sugars may occur in cyclic or acyclic forms.[1] The crystal structure of the *p*-bromophenylhydrazones of a number of sugars have been determined in this laboratory. Those of arabinose [2] and glucose [3] were found to be hydrazides with the sugar in the pyranose chair form, whereas that of ribose [4] is a true hydrazone, the sugar occurring in the open-chain form. In this paper the crystal structure of the mannose derivative is reported.

The formazan reaction of the phenylhydrazone of mannose would seem to indicate that it has an acyclic structure,[1] but recent infrared spectroscopic evidence suggests a cyclic structure for this compound in the solid state.[8] We have found no information on the structure of the *p*-bromophenylhydrazone of mannose in the literature.

Crystals of *p*-bromophenylhydrazone of mannose were grown from pyridine-water mixtures, and 1182 reflections recorded by taking Weissenberg photographs about the *b* axis. The structure was solved from the Patterson projection and stereochemical considerations, and refined by least squares methods to a final *R* value of 0.078. The positions of the atoms are listed in Table 1 and the corresponding bond lengths and angles in Table 2 and Fig. 1. Details of the structure analysis are given below. The estimated standard deviations are 0.02–0.03 Å in the bond lengths and 1–2° in the angles (Table 2).

It is evident from the atomic positions that the sugar has an acyclic structure and that the compound is a true hydrazone,

$$Br-C_6H_4-NH-N=CH(CHOH)_4CH_2OH.$$

Table 1. Final atomic coordinates (in fractions of cell edges) and temperature factors. Estimated standard deviations in parentheses.

Atom	*x*	*y*	*z*	*B*
Br	0.0000	0.0000	0.0000	[a]
O(2)	0.2902 (21)	0.5780 (21)	0.4534 (7)	2.00 (16)
O(3)	0.9903 (22)	0.9014 (21)	0.6601 (7)	2.15 (17)
O(4)	0.9706 (21)	0.3758 (21)	0.6452 (7)	2.12 (17)
O(5)	0.5782 (22)	0.8907 (22)	0.7971 (8)	2.16 (17)
O(6)	0.5765 (25)	0.3700 (24)	0.7829 (8)	2.81 (20)
N(2)	0.8405 (30)	0.1031 (29)	0.3594 (10)	2.63 (23)
N(1)	0.8458 (25)	0.9034 (26)	0.4020 (9)	2.06 (20)
C(7)	0.2634 (35)	0.0387 (36)	0.1142 (12)	2.82 (27)
C(8)	0.4795 (38)	0.2636 (38)	0.1484 (13)	3.23 (30)
C(9)	0.6581 (52)	0.2772 (52)	0.2334 (18)	3.54 (38)
C(10)	0.6449 (31)	0.0750 (31)	0.2780 (11)	2.20 (23)
C(11)	0.4263 (36)	0.8492 (36)	0.2375 (12)	2.88 (28)
C(12)	0.2406 (37)	0.8329 (37)	0.1569 (13)	3.08 (29)
C(1)	0.0800 (28)	0.9178 (30)	0.4517 (10)	1.85 (21)
C(2)	0.0985 (27)	0.7049 (28)	0.5006 (9)	1.67 (20)
C(3)	0.2026 (25)	0.8006 (28)	0.6112 (9)	1.46 (20)
C(4)	0.2370 (28)	0.5857 (29)	0.6631 (10)	1.79 (21)
C(5)	0.3175 (32)	0.6787 (34)	0.7777 (11)	1.67 (25)
C(6)	0.3606 (29)	0.4729 (30)	0.8291 (10)	1.98 (22)

[a] $\beta_{11} = 0.04515$ (75) $\beta_{22} = 0.03051$ (79)
$\beta_{33} = 0.00286$ (6) $\beta_{12} = 0.03486$ (103)
$\beta_{13} = -0.00496$ (31) $\beta_{23} = 0.00443$ (29)
in exp $-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{13}hl)$

Table 2. Bond lengths (Å units) and bond angles (°) with estimated standard deviations.

Bond lengths		Bond angles	
Br —C(7)	1.894 (17)	Br —C(7) —C(8)	119.8 (1.4)
C(7) —C(8)	1.372 (25)	Br —C(7) —C(12)	118.1 (1.3)
C(8) —C(9)	1.384 (29)	C(7) —C(8) —C(9)	116.0 (1.9)
C(9) —C(10)	1.380 (31)	C(8) —C(9) —C(10)	123.7 (2.2)
C(10)—C(11)	1.395 (21)	C(9) —C(10) —C(11)	117.3 (1.6)
C(11)—C(12)	1.352 (24)	C(10)—C(11) —C(12)	120.3 (1.7)
C(7) —C(12)	1.376 (27)	C(7) —C(12) —C(11)	120.5 (1.7)
C(10)—N(2)	1.373 (19)	C(12)—C(7) —C(8)	122.0 (1.7)
N(2) —N(1)	1.370 (20)	C(9) —C(10) —N(2)	119.7 (1.6)
N(1) —C(1)	1.254 (18)	C(11)—C(10) —N(2)	123.0 (1.6)
C(1) —C(2)	1.504 (22)	C(10)—N(2) —N(1)	121.4 (1.3)
C(2) —C(3)	1.513 (16)	N(2) —N(1) —C(1)	117.8 (1.3)
C(3) —C(4)	1.561 (21)	N(1) —C(1) —C(2)	120.2 (1.3)
C(4) —C(5)	1.545 (19)	C(1) —C(2) —C(3)	110.3 (1.2)
C(5) —C(6)	1.525 (24)	C(2) —C(3) —C(4)	111.5 (1.2)
C(2) —O(2)	1.422 (16)	C(3) —C(4) —C(5)	111.4 (1.2)
C(3) —O(3)	1.428 (16)	C(4) —C(5) —C(6)	112.1 (1.4)
C(4) —O(4)	1.438 (16)	C(1) —C(2) —O(2)	111.8 (1.0)
C(5) —O(5)	1.428 (19)	O(2) —C(2) —C(3)	109.7 (1.1)
C(6) —O(6)	1.433 (18)	C(2) —C(3) —O(3)	109.3 (1.0)
		O(3) —C(3) —C(4)	108.0 (1.0)
		C(3) —C(4) —O(4)	111.3 (1.0)
		O(4) —C(4) —C(5)	109.1 (1.1)
		C(4) —C(5) —O(5)	109.9 (1.1)
		O(5) —C(5) —C(6)	110.1 (1.2)
		C(5) —C(6) —O(6)	110.5 (1.1)

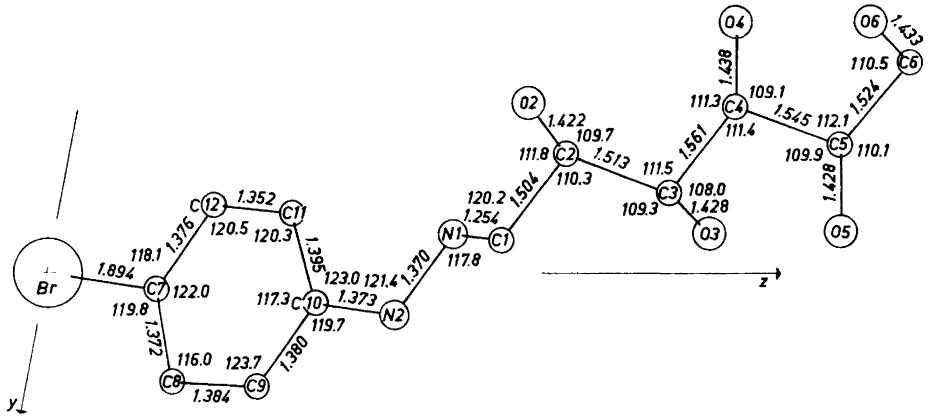

Fig. 1. The molecular structure of mannose-*p*-bromophenylhydrazone (seen along *a*). Bond lengths in Å units.

The carbon atoms of the mannose form a nearly planar zigzag chain, the largest deviation from the best least squares plane through these atoms being only 0.04 Å. The mean bond lengths and bond angles in this part of the molecule are 1.530 Å (C—C), 1.430 Å (C—O), 111.3° (C—C—C), and 109.9° (C—C—O). The corresponding values reported for galactitol are 1.520 Å, 1.432 Å, 111.6°, and 110.0°, respectively.[9] The conformation of mannose is the same as in the polymorphs of mannitol.[5] The terminal oxygen atom O(6) is not a linear extension of the zigzag chain.

Table 3. Short intermolecular distances (Å units) and their angles (°) with adjacent bonds.

Distances		Angles	
O_b(2)...N (2)	2.940 (18)	C (10)—N (2)...O_b (2)	124.4 (1.1)
O (2)...N_a(1)	2.934 (16)	N (1) —N (2)...O_b (2)	114.2 (0.9)
O (3)...O_b(4)	2.770 (17)	C_a (1) —N_a (1)...O (2)	117.4 (1.0)
O_a(3)...O (5)	2.745 (15)	N_a (2) —N_a (1)...O (2)	119.2 (0.9)
O_a(4)...O (6)	2.692 (15)	C_b (2) —O_b (2)...N (2)	98.3 (0.8)
O (5)...O_b(6)	2.769 (19)	C (2) —O (2)...N_a (1)	115.4 (0.8)
		N (2) ... O_b (2)...N_{ab} (1)	137.2 (0.5)
		C (3) —O (3)...O_b (4)	120.6 (0.8)
		C_a (3) —O_a (3)...O (5)	150.7 (0.9)
		C_b (4) —O_b (4)...O (3)	120.4 (0.8)
		C_a (4) —O_a (4)...O (6)	117.0 (0.8)
		C (5) —O (5)...O_a (3)	116.7 (0.9)
		C (5) —O (5)...O_b (6)	123.0 (1.0)
		C (6) —O (6)...O_a (4)	148.9 (1.0)
		C_b (6) —O_b (6)...O (5)	120.4 (0.9)
		O_a (3) ... O_{ab} (4)...O_b (6)	92.0 (0.5)
		O_{ab} (4) ... O_b (6)...O (5)	89.0 (0.5)
		O_b (6) ... O (5)...O_a (3)	91.9 (0.5)
		O (5) ... O_a (3)...O_{ab} (4)	87.9 (0.4)

A_a is an atom in $(x+1, y, z)$, A_b in $(x, y+1, z)$ and A_{ab} in $(x+1, y+1, z)$.

Table 4. Observed (F_o) and calculated (F_c) structure factors.

h	k	l	Fo	Fc
5	0	7	37	35
5	0	6	40	49
5	0	5	71	78
5	0	4	48	54
5	0	3	89	99
5	0	1	54	55
5	0	0	72	75
5	0	-1	118	129
5	0	-3	94	100
5	0	-4	43	38
5	0	-5	85	82
5	0	-6	65	63
5	0	-7	50	51
5	0	-8	38	31
5	0	-9	35	37
4	0	11	52	71
4	0	10	58	58
4	0	9	87	88
4	0	8	74	71
4	0	7	75	77
4	0	6	131	142
4	0	5	93	95
4	0	3	66	66
4	0	2	212	223
4	0	1	131	123
4	0	0	98	104
4	0	-1	65	69
4	0	-2	73	86
4	0	-3	221	237
4	0	-4	108	105
4	0	-6	78	78
4	0	-7	89	85
4	0	-8	90	83
4	0	-9	128	125
4	0	-10	27	32
4	0	-11	50	42
4	0	-12	71	68
4	0	-13	41	39
3	0	13	79	80
3	0	12	85	90
3	0	11	115	115
3	0	10	51	38
3	0	9	156	162
3	0	8	147	149
3	0	7	106	102
3	0	6	96	87
3	0	5	115	110
3	0	4	207	200
3	0	3	211	211
3	0	2	162	160
3	0	1	96	97
3	0	0	206	217
3	0	-1	211	224
3	0	-2	74	67
3	0	-3	88	86
3	0	-4	159	173
3	0	-5	176	182
3	0	-6	224	216
3	0	-7	111	102
3	0	-9	146	139
3	0	-10	64	72
3	0	-11	117	109
3	0	-12	54	60
3	0	-13	32	31
3	0	-14	47	48
3	0	-15	43	42
2	0	15	71	71
2	0	14	98	104
2	0	13	79	71
2	0	12	116	115
2	0	11	153	145
2	0	10	141	140
2	0	9	147	143
2	0	8	151	139
2	0	7	96	91
2	0	6	292	289
2	0	5	196	193
2	0	4	212	194
2	0	3	287	283
2	0	2	132	129
2	0	1	266	285
2	0	0	200	222
2	0	-1	208	216
2	0	-2	190	211
2	0	-3	199	203
2	0	-4	286	296
2	0	-5	186	194
2	0	-6	151	140
2	0	-7	107	111
2	0	-8	190	180
2	0	-9	167	167
2	0	-10	96	92
2	0	-11	75	58
2	0	-12	116	118
2	0	-13	66	61
2	0	-14	123	123
2	0	-15	69	65
2	0	-16	33	36
1	0	16	77	74
1	0	15	106	109
1	0	14	90	82
1	0	13	102	101
1	0	12	135	132
1	0	11	184	168
1	0	10	113	106
1	0	9	158	147
1	0	8	279	265
1	0	7	109	107
1	0	6	473	462
1	0	5	91	87
1	0	4	274	272
1	0	3	491	486
1	0	2	402	396
1	0	1	117	144
1	0	0	303	319
1	0	-1	86	88
1	0	-2	621	722
1	0	-3	532	594
1	0	-4	125	125
1	0	-5	254	254
1	0	-6	192	188
1	0	-7	226	233
1	0	-8	167	157
1	0	-9	195	189
1	0	-10	148	134
1	0	-11	169	166
1	0	-12	174	168
1	0	-13	61	54
1	0	-14	109	106
1	0	-15	56	60
1	0	-16	91	81
1	0	-17	58	73
0	0	17	57	62
0	0	16	36	33
0	0	15	71	90
0	0	14	120	124
0	0	13	119	112
0	0	12	118	111
0	0	11	154	142
0	0	10	105	106
0	0	9	272	263
0	0	8	300	275
0	0	7	131	111
0	0	6	423	426
0	0	5	457	451
0	0	4	228	226
0	0	3	252	231
0	0	2	77	66
0	0	1	90	64
5	1	4	20	26
5	1	3	35	24
5	1	2	74	87
5	1	1	34	21
5	1	0	77	73
5	1	-1	74	34
5	1	-2	40	5
5	1	-3	80	73
5	1	-4	35	58
5	1	-5	27	43
4	1	9	64	65
4	1	8	48	50
4	1	7	70	75
4	1	6	91	76
4	1	5	79	73
4	1	4	95	92
4	1	3	35	20
4	1	2	105	92
4	1	1	105	96
4	1	0	89	82
4	1	-1	99	103
4	1	-2	80	69
4	1	-3	59	49
4	1	-4	106	83
4	1	-5	54	35
4	1	-6	103	93
4	1	-7	53	36
4	1	-8	44	53
4	1	-9	49	43
4	1	-10	76	68
4	1	-11	34	29
3	1	12	84	83
3	1	11	68	62
3	1	10	83	78
3	1	9	116	118
3	1	8	130	121
3	1	7	106	80
3	1	6	115	98
3	1	5	81	51
3	1	4	237	226
3	1	3	181	169
3	1	2	109	115
3	1	1	160	142
3	1	0	95	86
3	1	-1	158	158
3	1	-2	125	122
3	1	-3	108	121
3	1	-4	130	129
3	1	-5	114	109
3	1	-6	105	96
3	1	-7	93	94
3	1	-8	104	94
3	1	-9	89	73
3	1	-10	103	93
3	1	-11	55	53
3	1	-12	61	53
3	1	-13	29	27
3	1	-14	74	78
3	1	-15	28	23
2	1	14	72	75
2	1	13	79	74
2	1	12	95	91
2	1	11	143	139
2	1	10	117	97
2	1	9	129	126
2	1	8	91	72
2	1	7	89	80
2	1	6	351	351
2	1	5	131	128
2	1	4	182	172
2	1	3	162	168
2	1	2	190	197
2	1	1	219	209
2	1	0	213	214
2	1	-1	88	96
2	1	-2	301	298
2	1	-3	214	203
2	1	-4	152	163
2	1	-5	161	171
2	1	-6	121	123
2	1	-7	201	198
2	1	-8	101	106
2	1	-9	144	135
2	1	-10	74	88
2	1	-11	113	115
2	1	-12	115	107
2	1	-13	97	88
2	1	-14	86	71
2	1	-15	89	76
2	1	-16	88	101
1	1	15	74	77
1	1	14	81	77
1	1	13	115	102
1	1	12	113	107
1	1	11	141	128
1	1	10	58	54
1	1	9	199	200
1	1	8	225	205
1	1	7	135	123
1	1	6	219	206
1	1	5	265	273
1	1	4	200	192
1	1	3	295	295
1	1	2	111	117
1	1	1	153	163
1	1	0	516	598
1	1	-1	180	192
1	1	-2	302	328
1	1	-3	124	144
1	1	-4	246	269
1	1	-5	223	233
1	1	-6	219	219
1	1	-7	186	189
1	1	-8	120	136
1	1	-9	191	191
1	1	-10	122	125
1	1	-11	94	93
1	1	-12	140	131
1	1	-13	190	194
1	1	-14	92	80
1	1	-15	45	46
1	1	-16	25	34
1	1	-17	54	50
0	1	16	56	61
0	1	15	83	86
0	1	14	93	99
0	1	13	99	83
0	1	12	113	101
0	1	11	109	104
0	1	10	175	160
0	1	9	153	144
0	1	8	241	214
0	1	7	247	249
0	1	6	100	111
0	1	5	315	319
0	1	4	126	123
0	1	3	366	400
0	1	2	276	293
0	1	1	389	426
0	1	-2	246	290
0	1	-3	286	326
0	1	-4	254	274
0	1	-5	177	192
0	1	-6	224	243
0	1	-7	223	233
0	1	-8	206	206
0	1	-9	165	154
0	1	-10	201	209
0	1	-11	168	171
0	1	-12	108	104
0	1	-13	104	94
0	1	-14	84	73
0	1	-15	127	129
0	1	-16	84	93
0	1	-17	60	74
-1	1	16	32	49
-1	1	15	94	90
-1	1	14	47	47
-1	1	13	102	94
-1	1	12	128	120
-1	1	11	157	150
-1	1	10	176	159
-1	1	9	166	154
-1	1	8	128	113
-1	1	7	281	290
-1	1	6	203	194
-1	1	5	149	148
-1	1	4	107	110
-1	1	3	352	375
-1	1	2	538	668
-1	1	1	384	448
-1	1	0	112	124
-1	1	-1	231	251
-1	1	-2	177	187
-1	1	-3	299	318
-1	1	-4	201	203
-1	1	-5	342	358
-1	1	-6	274	269
-1	1	-7	253	242
-1	1	-8	145	134
-1	1	-9	201	198
-1	1	-10	168	152
-1	1	-11	173	165
-1	1	-12	146	139
-1	1	-13	111	109
-1	1	-14	80	79
-1	1	-15	109	106
-1	1	-16	88	90
-1	1	-17	60	84
-2	1	16	25	33
-2	1	15	76	73
-2	1	14	72	64
-2	1	13	89	81
-2	1	12	113	102
-2	1	11	117	101
-2	1	10	99	89
-2	1	9	239	229
-2	1	8	95	81
-2	1	7	138	136
-2	1	6	81	69
-2	1	5	356	379
-2	1	4	371	430
-2	1	3	159	159
-2	1	2	81	76
-2	1	1	183	186
-2	1	0	246	260
-2	1	-1	204	230
-2	1	-2	219	232
-2	1	-3	290	293
-2	1	-4	310	312
-2	1	-5	150	138
-2	1	-6	164	162
-2	1	-7	214	210
-2	1	-8	175	162
-2	1	-9	234	220
-2	1	-10	105	97
-2	1	-11	131	117
-2	1	-12	122	118
-2	1	-13	160	168
-2	1	-14	72	70
-2	1	-15	107	114
-2	1	-16	38	48
-3	1	15	37	47
-3	1	14	68	64
-3	1	13	59	48
-3	1	12	92	85
-3	1	11	86	69
-3	1	10	59	55
-3	1	9	139	131
-3	1	8	111	104
-3	1	7	194	205
-3	1	6	143	132
-3	1	5	104	93
-3	1	4	87	74
-3	1	3	240	235
-3	1	2	115	132
-3	1	1	161	180
-3	1	0	100	104
-3	1	-1	254	253
-3	1	-2	186	181
-3	1	-3	126	127
-3	1	-4	200	194
-3	1	-5	124	121

Table 4. Continued.

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-3	1	-13	98	94
-3	1	-14	60	56
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-4	1	11	55	45
-4	1	10	73	69
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-4	1	8	90	81
-4	1	7	67	60
-4	1	6	111	106
-4	1	5	96	94
-4	1	4	104	88
-4	1	3	107	121
-4	1	2	103	104
-4	1	1	145	155
-4	1	0	77	62
-4	1	-1	155	160
-4	1	-2	103	97
-4	1	-3	111	107
-4	1	-4	107	88
-4	1	-5	110	96
-4	1	-6	105	102
-4	1	-7	119	109
-4	1	-8	124	113
-4	1	-9	81	68
-4	1	-10	103	97
-4	1	-11	59	61
-4	1	-12	54	91
-5	1	10	51	59
-5	1	9	52	63
-5	1	8	45	45
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-5	1	5	66	63
-5	1	4	53	102
-5	1	3	52	38
-5	1	2	74	59
-5	1	1	87	88
-5	1	0	97	84
-5	1	-1	53	43
-5	1	-2	71	54
-5	1	-3	81	74
-5	1	-4	88	77
-5	1	-5	68	63
-5	1	-6	67	63
-5	1	-7	69	70
-5	1	-8	56	66
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5	2	-1	51	67
5	2	-2	28	35
5	2	-4	18	36
4	2	7	40	42
4	2	6	56	56
4	2	5	34	35
4	2	4	88	85
4	2	2	81	82
4	2	1	56	50
4	2	0	42	43
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4	2	-2	50	40
4	2	-3	90	89
4	2	-4	64	65
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3	2	9	68	63
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3	2	7	96	98
3	2	6	124	125
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3	2	3	92	89
3	2	2	163	161
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3	2	0	113	110
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3	2	-3	107	101
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2	2	-3	100	94
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0	2	-2	294	307
0	2	-3	299	316
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0	2	-7	298	304
0	2	-8	37	36
0	2	-9	216	221
0	2	-10	104	95
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0	2	-12	186	180
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-5	2	-1	118	126
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4	3	2	21	44
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4	3	-2	48	58
4	3	-3	25	54
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4	3	-5	24	35
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3	3	8	23	45
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2	3	5	65	72
2	3	4	84	81
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2	3	2	120	132
2	3	1	99	101
2	3	0	114	116
2	3	-1	116	116
2	3	-2	47	51
2	3	-3	94	101
2	3	-4	51	53
2	3	-5	192	176
2	3	-6	183	174
2	3	-7	59	58
2	3	-8	53	55
2	3	-9	65	65
2	3	-10	53	47
2	3	-11	126	121
2	3	-12	48	50
2	3	-13	56	60
2	3	-14	58	60
2	3	-15	17	30
1	3	12	45	64
1	3	11	116	121
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1	3	8	63	76
1	3	7	115	104
1	3	6	158	143
1	3	5	139	133
1	3	4	101	108
1	3	3	126	137
1	3	2	152	154
1	3	1	91	89
1	3	0	184	176
1	3	-1	78	105
1	3	-2	166	160
1	3	-3	222	200
1	3	-4	201	196
1	3	-5	109	91
1	3	-6	193	192
1	3	-7	145	137
1	3	-8	109	104
1	3	-9	148	153
1	3	-10	47	52
1	3	-11	146	140
1	3	-12	87	79
1	3	-13	75	78
1	3	-14	75	81
1	3	-15	36	45
1	3	-16	37	47
0	3	13	37	41
0	3	12	25	16
0	3	11	59	65
0	3	10	88	91
0	3	9	192	167
0	3	8	174	171
0	3	7	78	73
0	3	6	114	114
0	3	5	185	178
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0	3	3	251	212
0	3	2	182	169
0	3	1	188	177

Table 4. Continued.

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0	3	-5	34	41
0	3	-6	162	165
0	3	-7	124	130
0	3	-8	151	152
0	3	-9	182	172
0	3	-10	173	162
0	3	-11	86	88
0	3	-12	155	145
0	3	-13	91	90
0	3	-14	76	80
0	3	-15	84	87
0	3	-16	51	61
-1	3	14	16	29
-1	3	13	58	67
-1	3	12	124	127
-1	3	11	101	95
-1	3	10	112	111
-1	3	9	72	59
-1	3	8	178	169
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-1	3	6	157	149
-1	3	5	205	185
-1	3	4	160	146
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-1	3	2	119	129
-1	3	1	233	217
-1	3	0	202	192
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-1	3	-2	316	286
-1	3	-3	37	24
-1	3	-4	212	196
-1	3	-5	257	230
-1	3	-6	196	187
-1	3	-7	213	196
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-2	3	-3	222	211
-2	3	-4	120	126
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-2	3	-6	167	157
-2	3	-7	306	262
-2	3	-8	252	220
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-2	3	-12	146	132
-2	3	-13	143	138
-2	3	-14	100	105
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1	4	4	128	126
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1	4	1	204	181
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1	4	-2	81	67
1	4	-3	64	77
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0	4	-5	80	88
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-1	4	4	148	139
-1	4	3	89	99
-1	4	2	120	122
-1	4	1	182	171
-1	4	0	180	168
-1	4	-1	146	159
-1	4	-3	61	76
-1	4	-4	190	179
-1	4	-5	178	167
-1	4	-6	104	113
-1	4	-7	193	179
-1	4	-8	69	85
-1	4	-9	153	142
-1	4	-10	194	170
-1	4	-11	78	80
-1	4	-12	66	76
-1	4	-13	98	108
-1	4	-14	47	62
-1	4	-15	94	105
-1	4	-16	59	80
-2	4	12	42	60
-2	4	11	38	50
-2	4	10	65	76
-2	4	9	30	27
-2	4	8	47	55
-2	4	7	148	143
-2	4	6	67	79
-2	4	5	174	166
-2	4	4	65	60
-2	4	3	132	128
-2	4	2	194	176
-2	4	1	290	257
-2	4	0	152	144
-2	4	-1	107	119
-2	4	-2	57	76
-2	4	-3	193	181
-2	4	-4	249	226
-2	4	-5	135	130
-2	4	-6	121	123
-2	4	-7	246	206
-2	4	-8	193	171
-2	4	-9	41	63
-2	4	-10	138	133
-2	4	-11	75	79
-2	4	-12	131	121
-2	4	-13	146	142
-2	4	-14	60	67
-2	4	-15	80	98
-3	4	10	48	59
-3	4	9	42	58
-3	4	8	110	107
-3	4	7	67	68
-3	4	6	33	12
-3	4	5	162	147
-3	4	4	173	164
-3	4	3	131	133
-3	4	2	88	94
-3	4	1	40	53
-3	4	0	107	88
-3	4	-1	331	298
-3	4	-2	186	158
-3	4	-3	90	106
-3	4	-4	115	114
-3	4	-5	235	206
-3	4	-6	236	200
-3	4	-7	178	156
-3	4	-8	65	67
-3	4	-9	108	99
-3	4	-10	185	166
-3	4	-11	91	95
-3	4	-12	97	102
-3	4	-13	90	96
-3	4	-14	44	69
-4	4	10	30	47
-4	4	9	26	33
-4	4	8	48	52
-4	4	7	68	67
-4	4	6	64	75
-4	4	5	76	80
-4	4	4	56	64
-4	4	3	47	27
-4	4	2	149	136
-4	4	1	141	126
-4	4	0	84	78
-4	4	-1	125	121
-4	4	-2	97	105
-4	4	-3	215	195
-4	4	-4	93	94
-4	4	-5	137	113
-4	4	-6	32	43
-4	4	-7	153	145
-4	4	-8	93	90
-4	4	-9	123	123
-4	4	-10	89	93
-4	4	-11	65	72
-4	4	-12	47	68
-5	4	7	37	49
-5	4	5	32	43
-5	4	4	43	51
-5	4	3	55	53
-5	4	2	59	69
-5	4	1	50	55
-5	4	0	62	75
-5	4	-1	99	97
-5	4	-2	43	43
-5	4	-3	49	58
-5	4	-4	65	76
-5	4	-5	55	60
-5	4	-6	70	81
-5	4	-7	80	95
-5	4	-8	49	62

The atoms N(1), N(2), C(1), and C(2) are coplanar (to within 0.002 Å), as is to be expected for a true hydrazone structure. This plane forms an angle of 21.3° with the benzene ring plane and of 124.0° with the plane of the sugar carbon atoms. The bond N(1)—C(1) is *trans* to the bisecting line of the angle O(2)C(2)C(3). Essentially the same relative orientation of the sugar and hydrazine part of the molecule with respect to the bond C(1)—C(2) was found also in the ribose derivative.[4] This conformational feature may well be preferred for all hydrazones as it implies *cis* relation between N(1) and the hydrogen atom at C(2). The N(1)—C(1) bond length of 1.25 Å is close to a normal double bond, whereas the bonds N(1)—N(2) (1.37 Å) and N(2)—C(10) (1.37 Å) are significantly shorter than normal single bonds. The angles at N(1) and N(2) are close to 120°, and it is possible that both these atoms are nearly sp^2 hybridized. At least some of the shortening may be explained on this basis, but additional delocalization effects probably also occur.

The azimuthal angle at the N—N bond is 157°, not far from the value of 165° found in the ribose derivative.

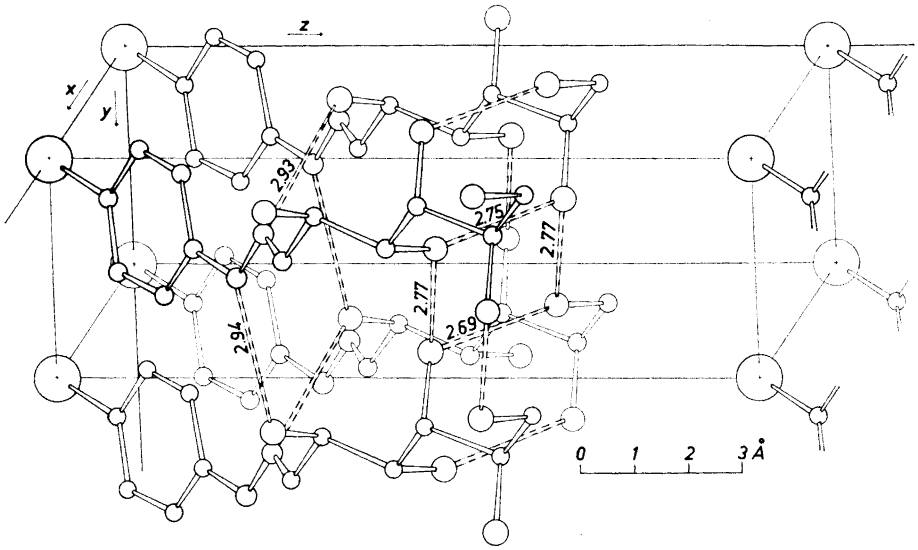

Fig. 2. Arrangement of the molecules in the crystal. Four neighbouring molecules are projected into the plane (1$\bar{1}$1). Broken lines indicate hydrogen bonds.

The arrangement of the molecules in the crystal is shown in Fig. 2. The hydrogen atoms were not located in the present analysis, but distances and directions strongly suggest that all oxygen and nitrogen atoms in the structure are involved in hydrogen bonds. There are six intermolecular O···O and O···N distances shorter than 3.0 Å, corresponding to six different hydrogen bonds, one for each hydrogen atom attached to oxygen or nitrogen atoms. The atom

O(2) is linked to nitrogen atoms in two different neighbouring molecules by bonds N(2)—H···O(2) (2.94 Å) and O(2)—H···N(1) (2.93 Å). The remaining four oxygen atoms are all connected to two different neighbouring molecules by O—H···O bond of lengths 2.69—2.77 Å. These bonds form a closed roughly planar square ring, the angle between the two hydrogen bonds being close to 90° at each oxygen atom (range 88°—92°).

As there is only one molecule per unit cell, all molecules have the same orientation. They are stacked in layers parallel to the *xy* plane, with their "axes" roughly perpendicular to this plane, which is also the predominant crystal face. There are no hydrogen bonds between these layers.

EXPERIMENTAL. STRUCTURE ANALYSIS

The compound was prepared by mixing aqueous solutions of D-mannose and *p*-bromophenylhydrazine hydrochloride at room temperature. It is almost insoluble in most of the usual solvents, except boiling pyridine. Crystals were grown by slow cooling of a saturated pyridine-water solution. Flat needles, elongated along *a*, and with (001) as the predominant face, were obtained.

X-Ray diagrams showed that the crystals were triclinic. The unit cell dimensions were derived from 15 well resolved low order lines recorded on a Guinier camera calibrated against KCl. The following values were found: $a=4.750$ (0.006) Å, $b=5.685$ (0.007) Å, $c=13.577$ (0.021) Å, $\alpha=100.43°$ (0.11), $\beta=92.13°$ (0.09), $\gamma=107.09°$ (0.12). The uncertainties indicated are estimated standard deviations. As the compound is optically active, the space group is $P1$. There is only one molecule in the unit cell. The density was found to be 1.70 g/cm³. The calculated value is 1.69 g/cm³.

A crystal of dimensions $0.26\times0.09\times0.04$ mm was used to record layers $h0l-h4l$ by Weissenberg integrating techniques, employing Cu$K\alpha$ radiation ($\lambda=1.542$ Å). The intensities were measured on a Hilger & Watts photometer. The weakest ones were estimated visually. In all 1182 non-equivalent reflections were recorded with measurable intensities. They were corrected for absorption effects. The non-observed reflections were not included in the analysis.

The structure was solved by the heavy atom procedure, deriving first the ($h0l$) projection. A program based on the "minimum residual method"[6] proved useful in locating the atoms. The structure was refined by block diagonal least squares calculations. The weighting scheme used was $w=10.0$ for $F\leq6.0$ and of the form $w=17.1\ F^{-0,30}$ for $F>6.0$. The scale factors for the different layers were adjusted by means of the calculated values of the structure factors. Anisotropic temperature factor was used only for the bromine atom, the vibrations of the light atoms being treated as isotropic. The temperature factors are given in Table 1. The hydrogen atoms could not be unequivocally located from difference maps. The positions of 13 of them were postulated on the basis of stereochemical considerations, but not refined. A temperature factor $B=2.5$ Å² was applied. The contribution from the remaining four hydrogen atoms [those attached to O(3), O(4), O(5), and O(6)] was neglected. The final value of the R index is 0.078. In Table 4 observed and calculated structure factors are compared.

The atomic form factors of Hanson *et al.*[7] were used. The programs applied were written, or revised, for CDC 3300 by T. Dahl, F. Gram, P. Groth, B. Klewe and Chr. Rømming.

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