plication of the factor $\exp\{-2\pi i\mathbf{p}\,.\,\mathbf{d}_m\}$ which, from (12*A*), is necessary to preserve the symmetry in the phases.

The effect of changing S *to a space-group symmetry related position*

The argument of the exponential term in (10) involving **h** and S is

$$\varphi=\alpha_h-2\pi\mathbf{h}\,.\,\mathrm{S}\,.$$

Let us now use, instead of S, the space-group symmetry related position S′, where

$$\mathrm{S}=[\mathbf{C}']\mathrm{S}'+\mathbf{d}'$$

and [**C**′] and **d**′ are the space group operators. This space group operation has the effect in reciprocal space of producing symmetry related structure factors $\mathbf{F}_h$ and $\mathbf{F}_{h'}$ such that $\mathbf{h}'=\mathbf{h}[\mathbf{C}']$ and $\alpha_{h'}=\alpha_h-2\pi\mathbf{h}\,.\,\mathbf{d}'$ [see equations (11*A*) and (12*A*)]. If we sum the right hand side of (10) over **h**′ instead of **h**, φ' will be given by

$$\varphi'=\alpha_{h'}-2\pi\mathbf{h}'\,.\,\mathrm{S}'$$

i.e. $$\varphi'=\alpha_h-2\pi\mathbf{h}\,.\,\mathbf{d}'-2\pi\mathbf{h}\,.\,[\mathbf{C}'][\mathbf{C}']^{-1}(\mathrm{S}-\mathbf{d}')\,.$$

Therefore $\varphi'=\alpha_h-2\pi\mathbf{h}\,.\,\mathrm{S}=\varphi\,.$

Since φ is unchanged, it is clearly immaterial which of the equivalent positions of S is used in setting up the equations.

A corollary is that if S is changed to a molecular equivalent position, but one without any crystallographic equivalence, we form a different set of equations.

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The Crystal and Molecular Structure of Methyl 1-Thio-β-D-xylopyranoside

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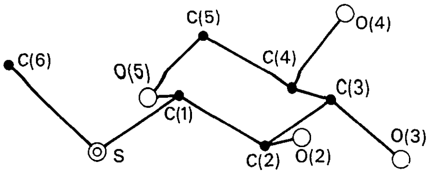
Methyl 1-thio-β-D-xylopyranoside crystallizes in the triclinic system: space group *P*1. Cell dimensions at −150°C are $a=4\cdot320$, $b=7\cdot611$, $c=13\cdot285$ Å, $\alpha=92\cdot3$, $\beta=92\cdot4$, $\gamma=112\cdot1°$. There are two molecules in the asymmetric unit. Both molecules are present in the *C*1 chair conformation with normal bond lengths and angles, although there appears to be some shortening of the anomeric carbon–sulphur bond and the ring angle C(2)C(3)C(4) is significantly larger than tetrahedral.



The ring oxygen atom, O(5), does not participate in the hydrogen bonding system which is confined to the hydroxyl groups on C(2), C(3), and C(4). Data were recorded at a low temperature (−150°C) and atom coordinates refined to $R=0\cdot105$.

Introduction

Xylan, the main chain of the acidic non-cellulosic polysaccharides found in higher plant tissues, is a polymer of (1→4) linked β-D-xylose residues. Although normally found with attached side chains whose number, point of attachment to the main chain and constituent monosaccharide residues vary with the source and method of isolation (see Timell, 1964) it has been obtained as single crystals in which the molecules are virtually free of side chains (Yundt, 1952; Bishop, 1953). Little is known, however, of its fine structure.

The structurally similar polysaccharide cellulose differs from xylan in that the monomeric unit is β-D-glucose. Furthermore, it is generally believed to be unbranched and at least partly crystalline (Mann, 1962), but in spite of extensive study no fully satisfactory description of its fine structure has been advanced (Jones, 1960).

As the initial step toward a detailed investigation of these materials the crystal and molecular structure determination of methyl 1-thio-β-D-xylopyranoside was undertaken. This particular derivative of β-D-xylose was chosen because the substituent is small in comparison with the pyranose ring. Moreover, it contains a moderately heavy atom, sulphur, which was expected to allow a direct determination of the structure.

The crystal structure of methyl β-D-xylopyranoside, the oxygen homologue of the present material, has been reported by Brown (1960). The two xylosides are not isomorphous.

Experimental

Methyl 1-thio-β-D-xylopyranoside was prepared by a method developed originally for glucopyranosides by Lemieux & Shyluk (1953). Xylose tetra-acetate and methanethiol were allowed to react in anhydrous benzene, in the presence of stannic chloride as catalyst, to yield methyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside, from which the required material was obtained by alkaline hydrolysis. m.p. 160° (uncorr.).

Analysis: Found: C 39·8%, H 6·6%, S 17·2%; calculated for $C_6H_{12}O_4S$: C 39·9$_8$%, H 6·7$_1$%, S 17·7$_9$%.

Sublimation produced crystals which, depending on the growth conditions, were either chunky and twinned, or thin laths. Specimens, suitable for the present work, which were well developed along the *a* axis, were obtained by crystallization from ethanol. Initially 1 mm × 0·2 mm × 0·1 mm, they were mounted for rotation about the *a* axis and excess material was removed by careful dissolution in water to leave a crystal of sides approximately 0·2 mm × 0·2 mm × 0·1 mm with which diffraction data were collected. All three forms of the material, namely chunky, lath and ethanol-recrystallized, gave identical infrared absorption spectra.

Cell dimensions were measured from zero layer photographs against silicon powder diffraction lines as an internal standard (Si, $a = 5{\cdot}4305_4$ Å). Methyl 1-thio-β-D-xylopyranoside, $C_6H_{12}O_4S$, crystallizes from ethanol in the triclinic system with cell dimensions at −150°C of:

$$a = 4{\cdot}320 \pm 0{\cdot}004 \text{ Å} \qquad \alpha = 92{\cdot}3 \pm 0{\cdot}3°$$
$$b = 7{\cdot}611 \pm 0{\cdot}008 \qquad \beta = 92{\cdot}4 \pm 0{\cdot}3$$
$$c = 13{\cdot}285 \pm 0{\cdot}013 \qquad \gamma = 112{\cdot}1 \pm 0{\cdot}3$$
$$V = 403{\cdot}5 \text{ Å}^3 \quad Z = 2 \qquad D_{\text{calc}} = 1{\cdot}482 \text{ g.cm}^{-3}$$

At 21°C the cell parameters are:

$$a = 4{\cdot}422 \pm 0{\cdot}004 \text{ Å} \qquad \alpha = 92{\cdot}4 \pm 0{\cdot}3°$$
$$b = 7{\cdot}704 \pm 0{\cdot}008 \qquad \beta = 92{\cdot}0 \pm 0{\cdot}3$$
$$c = 13{\cdot}312 \pm 0{\cdot}013 \qquad \gamma = 113{\cdot}2 \pm 0{\cdot}3$$
$$V = 415{\cdot}9 \text{ Å}^3 \qquad D_{\text{calc}} = 1{\cdot}438 \text{ g.cm}^{-3}$$

The observed density of 1·446 g.cm^{-3} was measured by flotation in a carbon tetrachloride–benzene mixture. Statistical tests of average (Wilson, 1949), variance (Wilson, 1951) and zero moment (Howells, Phillips & Rogers, 1950) confirmed the unit cell as non-centrosymmetric. The space group, therefore, is $P1$.

Weissenberg photographs were taken on a multiple film pack about [100] at low temperature (−150°C) with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5405$ Å). Intensities were estimated visually and Lorentz and polarization corrections were applied. Scale factors to reduce observed intensities to absolute values were obtained with a Wilson plot initially and later by direct scaling of ΣF_o against ΣF_c for individual layers.

The atomic scattering factors for sulphur, carbon and oxygen used throughout were those of Dawson (1960), Freeman (1959) and Hoerni & Ibers (1954) respectively.

The crystallographic programs used were those devised by Drs P. J. Wheatley and J. J. Daly for the Elliott 803 computer. Their least-squares program for structure factors incorporates the weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) and uses the block-diagonal approximation. The Lp corrections were obtained on a CDC 3600 machine with a program written by Dr J. A. Wunderlich.

Structure determination

The presence of the moderately heavy sulphur atom and two molecules unrelated by symmetry in the asymmetric unit suggested that the structure determination could proceed directly. It was expected also that most, if not all, atoms would be well resolved in projection down the short *a* axis.

A Patterson projection, $P(vw)$, exhibited, in the half cell, four main peaks of equal height from which the one due to the sulphur–sulphur vector was not resolved even in the corresponding three-dimensional vector maps. However, three were associated with interatomic vectors of approximately 2·5 Å and with their symmetry-related peaks formed a hexagonal array centred on the origin. From the method of synthesis together with a consideration of Reeves instability factors (Reeves, 1951) it was assumed that the molecule was in the $C1$ chair conformation for which all substituents are disposed equatorially. This assumption was supported by the similar conformation of the β-anomers of other mono- and di-saccharides for which structures have been determined (Brown, 1960; Ferrier, 1963; Hordvik 1961; Jacobson, Wunderlich & Lipscomb, 1961). On this basis the three peaks were assumed to correspond to overlap of vectors between atoms β to each other. In the space group $P1$ the choice of origin is arbitrary and for convenience was assumed coincident with one of the sulphur atoms, S. Hence the remaining peak gave the location of the other sulphur atom, S′.

Inspection of a Fourier synthesis for the [100] projection, phased on the two sulphur atoms, allowed the ring carbon and substituent oxygen atoms to be located approximately. The methyl carbon atoms, C(6) and C(6′), on the other hand, were very poorly defined but were given reasonable coordinates on the basis of expected bond lengths and angles. The reliability index R $[R=(\Sigma||KF_o|-|F_c||/\Sigma|KF_o|)]$ calculated with these coordinates was fairly high at 0·35. Fourier and difference syntheses were used to refine the coordinates in a straightforward way until $R(0kl)$ approached 0·23. The scale and isotropic temperature factors for these calculations had been obtained previously from a Wilson plot.

Several cycles of least squares with individual isotropic thermal parameters then improved $R(0kl)$ to 0·17. The reliability index, at this stage, showed no sign of further improvement and from the behaviour of the thermal parameters it was clear that the methyl carbon atoms had to be relocated. New coordinates were found from a projected electron density distribution, and with their inclusion further cycles rapidly reduced $R(0kl)$ to 0·11.

From the three-dimensional vector maps, the orientations of the two molecules together with the third coordinate of the second sulphur atom S′ were obtained. On the assumption of a $C1$ chair conformation for both molecules, reasonable values could be assigned for the b coordinates of all ring atoms, and those attached directly to them. The short projected S–C(6) bond lengths suggested two alternatives for the x coordinate of each of the methyl carbon atoms. The coordinates used initially were chosen arbitrarily.

In subsequent least-squares cycles, in which individual anisotropic temperature factors were used, one methyl carbon atom migrated more than 1 Å in the [100] direction. Also, from the behaviour of the temperature factor of the second methyl group C′(6) (Fig. 1), a similar shift in its x coordinate was indicated, and made. With these changes the discrepancy between all reflexions was reduced to 0·105 after an overall total of approximately twenty cycles. At this stage, shifts in atomic parameters were less than half their estimated standard deviations.

Attempts to locate the hydrogen atoms were only partially successful. Approximate positions for those attached directly to the ring, however, were calculated on the assumption of tetrahedral bond angles and C–H bond lengths of 1·09 Å. When these atoms were included $R(0kl)$ decreased slightly to 0·102. A difference Fourier synthesis in which reflexions with $2\sin\theta/\lambda \geq$

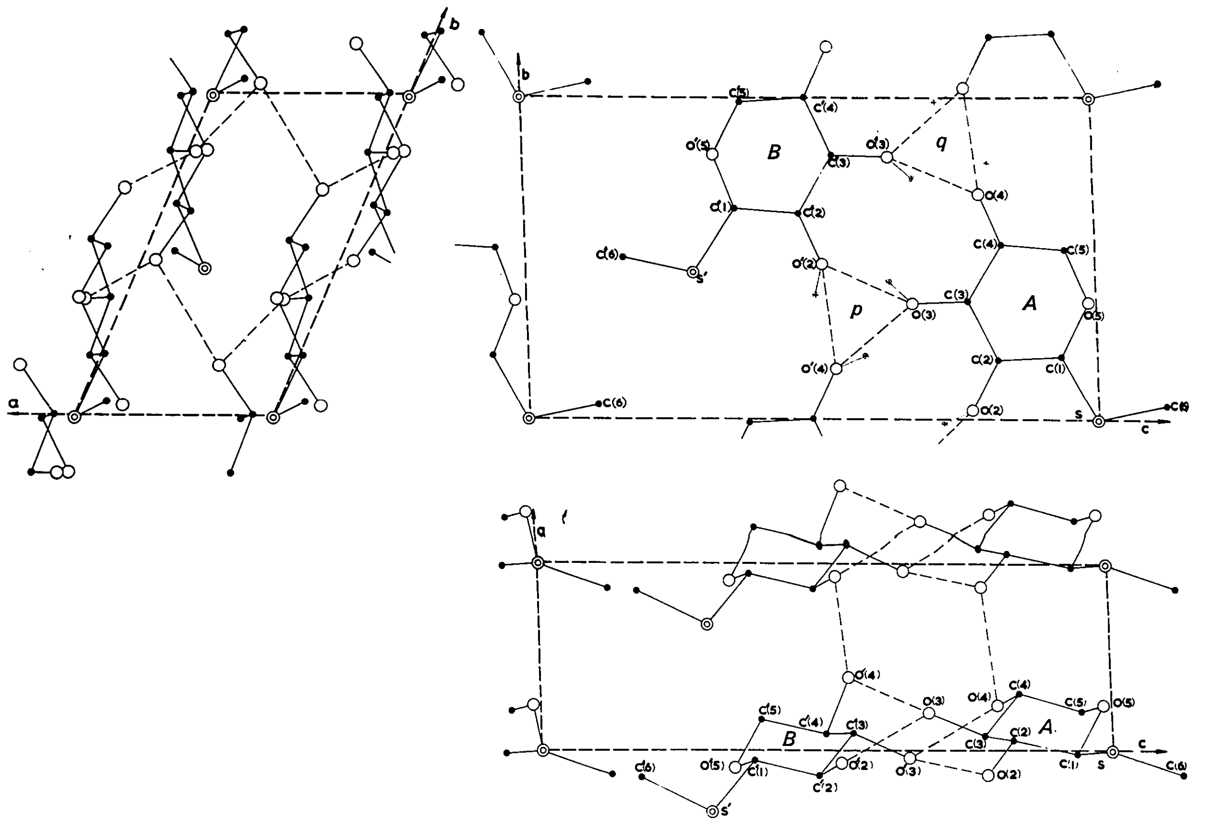


Fig. 1. Unit cell of methyl 1-thio-β-D-xylopyranoside.

1·05 were omitted gave an indefinite indication of the hydroxyl protons and their inclusion reduced $R(0kl)$, but again only slightly, to 0·100.

Final values of the atomic coordinates and thermal parameters, together with their estimated standard deviations are shown in Table 1 and 2, and a comparison of the observed and calculated structure factors is made in Table 3.

Discussion

The two independent molecules in the asymmetric unit are confirmed as being in the $C1$ chair conformation (Fig. 1). The bond lengths and angles for both molecules are listed, with their standard deviations, in Table 4; mean values are shown in Fig. 2.

The average lengths of the CC, CO and CS bonds are 1·53, 1·43 and 1·81 Å respectively, which agree with accepted values based on covalent radii (Pauling, 1960) as well as with those found in other pyranoid sugars and their derivatives (Jeffrey & Rosenstein, 1964). The bond which shows the greatest deviation, namely C(3)C(4), is within twice its standard deviation of the mean value and therefore the difference is not considered significant.

Recently Brown & Levy (1965) have refined the structure of α-D-glucose using neutron diffraction data

Table 1. *Final atomic coordinates and standard deviations*

	x (Å)	σ_x	y (Å)	σ_y	z (Å)	σ_z
S	4·291	0·004	7·563	0·003	13·249	0·003
C(1)	4·235	0·012	1·502	0·010	12·438	0·010
C(2)	0·230	0·013	1·421	0·010	10·958	0·010
C(3)	0·338	0·012	2·818	0·010	10·304	0·009
C(4)	1·288	0·012	4·160	0·011	11·123	0·010
C(5)	0·876	0·012	4·048	0·010	12·583	0·009
C(6)	3·749	0·017	0·342	0·013	1·605	0·013
O(5)	1·012	0·009	2·790	0·007	13·097	0·007
O(2)	3·364	0·008	0·228	0·007	10·325	0·007
O(3)	0·868	0·008	2·770	0·008	9·015	0·007
O(4)	1·032	0·009	5·365	0·008	10·608	0·007
S′	2·850	0·003	3·464	0·003	3·897	0·003
C′(1)	4·094	0·013	5·002	0·011	4·907	0·011
C′(2)	3·720	0·012	4·856	0·011	6·401	0·010
C′(3)	0·391	0·012	6·246	0·010	7·228	0·010
C′(4)	0·452	0·013	0·021	0·010	6·605	0·010
C′(5)	0·675	0·013	7·540	0·011	5·098	0·011
C′(6)	3·686	0·014	3·901	0·012	2·291	0·012
O′(5)	3·912	0·009	6·273	0·008	4·452	0·007
O′(2)	4·016	0·008	3·692	0·007	6·917	0·007
O′(3)	4·157	0·009	6·238	0·008	8·517	0·007
O′(4)	1·667	0·008	1·200	0·008	7·183	0·008

Table 2. *Anisotropic thermal parameters and standard deviations*

$$U_{ij} = B_{ij}/8\pi^2$$

	U_{11}	σ_{11}	U_{22}	σ_{22}	U_{33}	σ_{33}	$2U_{12}$	σ_{12}	$2U_{23}$	σ_{23}	$2U_{13}$	σ_{13}
S	0·027	0·002	0·024	0·001	0·023	0·001	0·021	0·002	0·015	0·002	−0·005	0·002
S′	0·020	0·002	0·026	0·001	0·020	0·001	0·006	0·002	0·001	0·002	0·001	0·002
C(1)	0·003	0·006	0·026	0·005	0·027	0·005	0·014	0·007	−0·004	0·007	−0·007	0·007
C′(1)	0·017	0·007	0·028	0·005	0·028	0·005	0·021	0·009	0·017	0·008	−0·002	0·008
C(2)	0·028	0·007	0·012	0·004	0·018	0·004	0·007	0·007	0·005	0·006	0·011	0·008
C′(2)	0·011	0·007	0·031	0·005	0·019	0·004	0·026	0·008	0·006	0·007	−0·013	0·007
C(3)	0·015	0·006	0·018	0·004	0·015	0·004	0·001	0·007	0·001	0·006	−0·001	0·007
C′(3)	0·017	0·007	0·024	0·005	0·020	0·005	0·017	0·008	0·005	0·007	−0·009	0·008
C(4)	0·013	0·007	0·023	0·004	0·025	0·005	0·014	0·007	0·021	0·007	−0·002	0·007
C′(4)	0·025	0·007	0·014	0·004	0·019	0·004	0·007	0·007	0·011	0·006	−0·006	0·007
C(5)	0·018	0·006	0·021	0·004	0·014	0·004	0·009	0·007	−0·001	0·006	−0·004	0·007
C′(5)	0·016	0·007	0·026	0·005	0·025	0·005	0·002	0·008	0·021	0·007	0·008	0·008
C(6)	0·050	0·009	0·028	0·005	0·030	0·006	0·024	0·010	0·019	0·009	0·010	0·010
C′(6)	0·016	0·007	0·032	0·005	0·031	0·006	0·006	0·009	−0·004	0·008	0·008	0·009
O(2)	0·014	0·005	0·022	0·003	0·020	0·003	0·008	0·005	0·004	0·005	0·002	0·005
O′(2)	0·007	0·004	0·018	0·003	0·025	0·003	0·012	0·005	0·014	0·005	−0·006	0·005
O(3)	0·013	0·005	0·028	0·003	0·018	0·003	0·016	0·006	0·016	0·005	0·010	0·005
O′(3)	0·021	0·005	0·031	0·004	0·017	0·003	0·023	0·006	0·003	0·005	−0·007	0·006
O(4)	0·025	0·005	0·023	0·003	0·021	0·003	0·020	0·006	0·009	0·005	−0·018	0·006
O′(4)	0·009	0·004	0·022	0·003	0·027	0·004	0·003	0·005	0·004	0·005	0·001	0·005
O(5)	0·029	0·005	0·017	0·003	0·017	0·003	0·010	0·006	0·003	0·005	−0·014	0·005
O′(5)	0·026	0·005	0·024	0·003	0·019	0·003	0·012	0·006	0·006	0·005	−0·014	0·005

Table 3. *Observed and calculated structure factors*

Unobserved reflexions which were included as $\frac{1}{2}F_{\min}$ are indicated by an asterisk.

	$\lvert F_o\rvert$	$\lvert F_c\rvert$
00ℓ		
1	141	154
2	179	241
3	62	104
4	276	338
5	223	242
6	442	409
7	201	187
8	138	148
9	91	99
10	122	110
11	79	76
12	33	22
13	97	99
14	70	70
15	8	7*
16	67	53
17	72	80
01ℓ		
-17	26	25
-16	68	52
-15	89	78
-14	54	53
-13	63	61
-12	148	121
-11	77	79
-10	42	36
-9	130	140
-8	232	212
-7	164	173
-6	155	119
-5	150	160
-4	129	147
-3	176	161
-2	261	278
-1	243	265
0	51	50
1	154	181
2	178	205
3	178	174
4	155	160
5	214	237
6	12	24*
7	117	122
8	139	144
9	219	197
10	94	97
11	86	70
12	41	33
13	153	142
14	98	80
15	80	77
16	78	73
02ℓ		
-16	47	43
-15	47	37
-14	101	96
-13	127	118
-12	60	64
-11	50	46
-10	188	192
-9	51	55
-8	69	101
-7	108	128
-6	129	127
-5	117	122
-4	230	237
-3	314	353
-2	132	125
-1	175	162
0	264	310
1	280	269
2	200	190
3	261	322
4	200	176
5	18	15
6	123	144
7	147	182
8	173	160
9	219	210
10	146	134
11	73	73
12	31	24
13	85	81
14	44	45
15	50	43
16	11	10
03ℓ		
-16	35	36
-15	50	50
-14	100	89
-13	29	20
-12	84	78
-11	56	48
-10	267	270
-9	116	112
-8	290	321
-7	27	35
-6	64	82
-5	179	198
-4	299	318
-3	290	275
-2	156	136
-1	161	175
0	173	170
1	226	215
2	191	158
3	338	348
4	46	42*
5	219	221
6	110	115
7	17	16*
8	87	102
9	254	248
10	247	197
11	52	47
12	100	94
13	79	64
14	54	46
15	65	72
04ℓ		
-15	40	40
-14	96	76
-13	85	86
-12	49	53
-11	66	61
-10	180	172
-9	136	131
-8	19	3*
-7	85	86
-6	92	88
-5	70	68
-4	123	137
-3	48	36
-2	161	157
-1	41	50
0	128	122
1	188	159
2	64	75
3	67	72
4	135	154
5	47	50
6	29	37
7	45	47
8	128	122
9	64	62
10	95	88
11	63	61
12	77	56
13	61	52
14	91	102
05ℓ		
-14	120	121
-13	72	64
-12	71	70
-11	96	83
-10	49	56
-9	71	68
-8	170	139
-7	114	106
-6	19	17*
-5	126	117
-4	145	133
-3	111	117
-2	83	82
-1	169	173
0	156	164
1	160	173
2	125	141
3	96	110
4	49	45
5	95	123
6	110	131
7	68	69
8	29	26
9	78	87
10	33	31
11	34	23
12	110	94
13	52	50
06ℓ		
-13	71	65
-12	78	82
-11	47	30
-10	29	30
-9	111	111
-8	56	58
-7	98	81
-6	116	89
-5	194	164
-4	41	40
-3	113	116
-2	89	94
-1	197	216
0	266	233
1	146	145
2	95	103
3	69	81
4	98	103
5	85	78
6	119	130
7	112	100
8	69	69
9	25	23
10	39	29
11	108	90
12	37	26
07ℓ		
-11	77	75
-10	66	72
-9	23	21
-8	76	81
-7	72	62
-6	32	35
-5	114	99
-4	90	94
-3	53	43
-2	20	16*
-1	63	55
0	33	23
1	21	17*
2	62	64
3	59	59
4	109	88
5	62	53
6	70	60
7	46	47
8	21	20
9	43	46
10	50	59
08ℓ		
-9	44	60
-8	46	59
-7	31	29
-6	86	86
-5	37	42
-4	68	66
-3	105	102
-2	97	96
-1	17	12*
0	35	31
1	41	40
2	74	75
3	23	24
4	119	117
5	57	57
6	12	13*
7	21	25
09ℓ		
-3	47	59
-2	73	39
-1	56	66
0	29	39
1	24	31
19ℓ		
-5	34	51
-4	20	26
-3	30	34
-2	52	55
-1	53	58
0	14	7*
1	14	15*
2	104	112
3	27	23
4	116	104
5	54	56
6	67	64
18ℓ		
-8	28	31
-7	41	41
-6	31	41
-5	43	47
-4	58	75
-3	114	107
-2	68	72
-1	63	57
0	78	69
1	49	40
2	52	46
3	67	63
4	123	106
5	17	11*
6	48	47
7	56	90
8	33	39
9	20	14
10	45	58
17ℓ		
-11	69	72
-10	29	28
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6	288	279
7	76	83
8	39	33
9	76	94
10	162	158
11	68	70
12	110	122
13	112	127
14	37	56
31ℓ		
-14	5	10*
-13	79	67
-12	90	90
-11	65	64
-10	68	68
-9	76	65
-8	81	80
-7	159	134
-6	142	149
-5	144	140
-4	68	73
-3	46	45
-2	101	110
-1	61	53
0	163	145
1	230	202
2	86	61
3	5	10*
4	42	41
5	149	127
6	79	86
7	7	17*
8	7	4*
9	106	111
10	7	20*
11	81	94
12	57	59
13	71	91
30ℓ		
-14	49	47
-13	110	99
-12	6	9*
-11	95	103
-10	62	65
-9	79	92
-8	68	61
-7	141	115
-6	88	80
-5	6	19*
-4	132	128
-3	131	119
-2	68	55
-1	58	58
0	135	132
1	84	77
2	71	60
3	195	217
4	152	133
5	54	43
6	166	134
7	88	81
8	57	46
9	56	57
10	53	57
11	79	75
12	28	30
13	35	45
31ℓ		
-13	5	6*
-12	122	99
-11	65	58
-10	33	25
-9	90	86
-8	40	48
-7	7	12*
-6	47	51
-5	37	39
-4	305	292
-3	68	57
-2	128	121
-1	129	108
0	160	156
1	170	155
2	319	285
3	172	176
4	71	72
5	115	123
6	103	85
7	134	110
8	84	88
9	84	86
10	6	11*
11	45	44
12	56	68
32ℓ		
-13	49	55
-12	27	31
-11	50	51
-10	50	44
-9	79	85
-8	7	7*
-7	135	123
-6	65	59
-5	7	13*
-4	131	119
-3	104	89
-2	38	40
-1	42	39
0	7	14*
1	86	98
2	81	74
3	39	38
4	131	108
5	88	83
6	39	42
7	81	96
8	40	43
9	50	55
10	99	90
11	52	52
33ℓ		
-11	55	58
-10	6	11*
-9	74	69
-8	68	91
-7	140	136
-6	47	48
-5	86	80
-4	65	72
-3	7	19*
-2	90	80
-1	148	159
0	65	64
1	35	26
2	93	81
3	81	78
4	7	15*
5	101	111
6	117	101
7	55	41
8	30	40
9	104	103
10	14	28
34ℓ		
-10	23	36
-9	65	73
-8	114	112
-7	110	93
-6	120	119
-5	34	43
-4	59	54
-3	140	134
-2	56	44
-1	7	17*
0	86	92
1	71	69
2	7	18*
3	42	35
4	81	83
5	122	111
6	28	39
7	65	55
35ℓ		
-7	16	23
-6	4	11*
-5	5	11*
-4	45	46
-3	5	18*
-2	47	49
-1	54	56
0	71	77
1	28	27
2	56	55
3	29	37
4	45	41

and have confirmed the original work of McDonald & Beevers (1952) in which it was suggested that the C(1)O(1) bond was significantly shortened. This shortening of the C(1)O(1) bond has been reported for other carbohydrates and their derivatives, as for example β-D-arabinose (Hordvik, 1961), β-D-glucose (Ferrier, 1963), cellobiose (Jacobson, Wunderlich & Lipscomb, 1961) and in particular methyl β-D-xylopyranoside (Brown, 1965). It appears that such a reduction in bond length also occurs in methyl 1-thio-β-D-xyloside. Thus the mean of the two anomeric carbon–sulphur bonds is $1{\cdot}80_0$ Å, which is noticeably shorter than the mean of $1{\cdot}82_7$ Å for the methyl carbon–sulphur bonds.

Bond angles on atoms directly associated with the ring are, in general, close to tetrahedral but several differ from the mean (109·2°) by three times their standard deviations. Only for the C(2)C(3)C(4) angle, however, is there agreement between the two molecules and in this case the large angle is probably significant. At the same time it may be noted that the angles at the ring oxygen atoms, O(5) and O′(5) are normal (109·7°). These points are discussed below with refdrence to the system of hydrogen bonds in the crystal and the packing of the methyl groups.

Broadly speaking, a crystal of methyl 1-thio-β-D-xylopyranoside is composed of parallel, infinite plates in which the molecules are cross-linked by a network of fairly strong intermolecular hydrogen bonds (Fig. 1).

Table 4(*a*). *Bond lengths and standard deviations*

	Length	σ		Length	σ
S —C(1)	1·796 Å	0·011	S′ —C′(1)	1·806 Å	0·013
S —C(6)	1·823	0·015	S′ —C′(6)	1·834	0·013
C(1)–C(2)	1·531	0·015	C′(1)–C′(2)	1·555	0·017
C(2)–C(3)	1·536	0·015	C′(2)–C′(3)	1·548	0·016
C(3)–C(4)	1·503	0·015	C′(3)–C′(4)	1·524	0·015
C(4)–C(5)	1·531	0·016	C′(4)–C′(5)	1·536	0·016
C(5)–O(5)	1·429	0·013	C′(5)–O′(5)	1·427	0·015
C(2)–O(2)	1·428	0·013	C′(2)–O′(2)	1·416	0·014
C(3)–O(3)	1·420	0·013	C′(3)–O′(3)	1·424	0·013
C(4)–O(4)	1·433	0·014	C′(4)–O′(4)	1·417	0·014
C(1)–O(5)	1·451	0·014	C′(1)–O′(5)	1·438	0·015

Mean values S–C 1·814 Å C–C 1·533 Å C–O 1·428 Å

Table 4(*b*). *Bond angles and standard deviations*

	Angle	σ		Angle	σ
C(6)SC(1)	98·4°	0·6	C′(6)S′C′(1)	98·1°	0·6
SC(1)O(5)	108·5	0·7	S′C′(1)O′(5)	107·6	0·8
SC(1)C(2)	110·6	0·8	S′C′(1)C′(2)	109·9	0·8
C(1)C(2)C(3)	110·5	0·9	C′(1)C′(2)C′(3)	109·0	0·9
C(2)C(3)C(4)	112·9	0·9	C′(2)C′(3)C′(4)	113·3	0·9
C(3)C(4)C(5)	109·9	0·9	C′(3)C′(4)C′(5)	110·1	0·9
O(5)C(1)C(2)	108·8	0·9	O′(5)C′(1)C′(2)	108·3	0·9
O(5)C(5)C(4)	109·3	0·9	O′(5)C′(5)C′(4)	110·7	0·9
O(2)C(2)C(1)	106·6	0·8	O′(2)C′(2)C′(1)	109·8	0·9
O(2)C(2)C(3)	109·6	0·8	O′(2)C′(2)C′(3)	107·0	0·9
O(3)C(3)C(2)	107·3	0·8	O′(3)C′(3)C′(2)	108·3	0·9
O(3)C(3)C(4)	110·9	0·9	O′(3)C′(3)C′(4)	107·4	0·9
O(4)C(4)C(3)	108·1	0·9	O′(4)C′(4)C′(3)	109·4	0·9
O(4)C(4)C(5)	107·8	0·9	O′(4)C′(4)C′(5)	106·5	0·9
C(1)O(5)C(5)	109·7	0·8	C′(1)O′(5)C′(5)	110·1	0·9

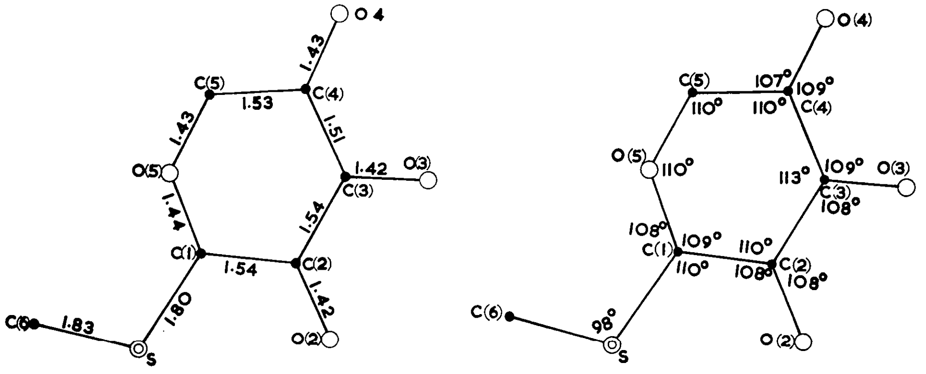

Fig. 2. Mean bond angles and bond lengths.

The bonding between the plates, on the other hand, is by forces such as van der Waals which are much weaker.

The intermolecular bonding suggested here is based on the observed oxygen–oxygen distances and it is assumed that intramolecular bonding between oxygens on contiguous carbon atoms may be neglected. With this assumption the non-equivalent molecules *A* and *B* (Fig. 1) are connected by a system of hydrogen bonds arranged to form two helical chains, *p* and *q*, the axes of which are parallel to [100]; chain *p* involves O′(2), O(3) and O′(4), whilst *q* involves O(2), O′(3) and O(4). Also marked on Fig. 1 are the positions of the hydroxyl protons, suggested by an $(F_o - F_c)$ synthesis from which high angle reflexions ($2 \sin \theta/\lambda \geq 1{\cdot}05$) were omitted. If these sites are basically correct then the directions of the hydrogen bond chains are defined as O′(2)–H ··· O′(4)–H ··· O(3)–H ··· O′(2) for *p* and O(2)–H ··· O′(3)–H ··· O(4)–H ··· O(2) for *q*. Thus each hydroxyl group acts as both a hydrogen bond donor and a hydrogen bond acceptor.

The oxygen–oxygen bond distances are listed in Table 5 and may be separated into two groups: the first centred at 2·73 Å, the second at 2·70 Å. These distances are normal for this class of compound but are grouped at the lower end of the range of 2·68 Å to 3·04 Å found in other monosaccharides (Jeffrey & Rosenstein, 1964). A study of the polarized infrared spectra of single crystals of methyl 1-thio-β-D-xylopyranoside confirms that there are hydrogen bonds present of at least two different strengths (Michell, 1965).

Table 5. *Hydrogen bond distances*

O′(4)–O′(2)	2·738 Å
O(4) –O(2)	2·722
O(3) –O′(2)	2·718
O′(3)–O(2)	2·703
O′(4)–O(3)	2·701
O(4) –O′(3)	2·699

It was mentioned above that the ring angles C(2)-C(3)C(4), (112·9°), and C′(2)C′(3)C′(4), (113·3°) are significantly larger than tetrahedral. This particular distortion of the molecule may arise as a consequence of the hydrogen bonding between the hydroxyl groups on C(2), C(3) and C(4). A departure of this angle from tetrahedral has been found also in methyl β-D-xylopyranoside (Brown, 1965) which similarly has the hydrogen bonding confined to the oxygens on C(2), C(3) and C(4). Moreover, both the glycoside and its sulphur homologue have approximately normal bond angles at the ring oxygen, which is contrary to what is found for a number of other carbohydrates (Jeffrey & Rosenstein, 1964). In neither material does the ring oxygen act as a hydrogen bond acceptor.

In the isolated molecule of methyl 1-thio-β-D-xyloside the methyl group is free to rotate around the S–C(1) bond. In the crystal both molecules in the asymmetric unit occur with the methyl group on the side of the S–C(1) bond nearest the ring oxygen and in the general plane of the molecule (Fig. 1). The molecular packing within the crystal, however, does not provide the same environment for both the methyl groups (Fig. 3). Thus C′(6) has as neighbours a single atom C(6) and three atom pairs, $C(6^{III})$–S^{III}, $C(5^{I})$–$O(5^{I})$, $C(5^{II})$–$O(5^{II})$: each pair is covalently bonded and contains one divalent atom. C(6), on the other hand, has but one such pair O′(5)–C′(5) although there are two single atoms, C′(6) and S^{III}. The variation in the nature of the packing may be used to explain qualitatively the difference in the thermal parameters of the two atoms, C(6) and C′(6) (Table 2).

The methyl carbon atom C′(6) is approximately equidistant from the two adjacent ring oxygen atoms $O(5^{I})$ and $O(5^{II})$ with distances 3·39 and 3·40 Å respectively, which agree well with the sum of the accepted van der Waals radii of oxygen (1·40 Å) and the methyl group (2·0 Å) (Pauling, 1960). The observed distances between C′(6) and $C(5^{II})$, $C(5^{I})$ and $C(6^{I})$ are 4·06, 3·39 and 3·62 Å respectively, although the contact distance expected in each is approximately 4·0 Å: on the assumption that the methylene radius is 2·0 Å. The shorter of the two anomalous distances corresponds to the sum of the van der Waals radii of carbon (1·4 Å) and a methyl group. As the atom $C(5^{I})$ lies approximately on the axis of the C′(6)–S′ bond, a close approach such as that found is feasible if two

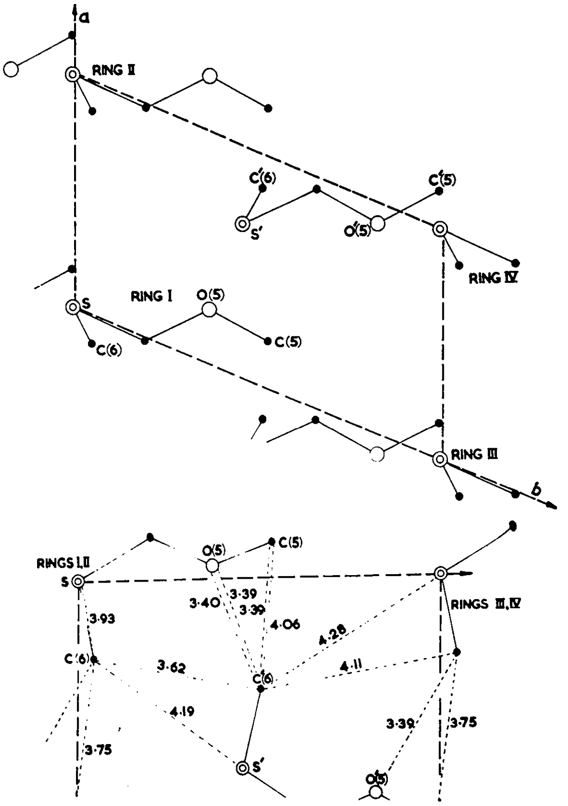

Fig. 3. Contact distances and packing of the methyl groups.

of the protons on C′(6) straddle the O(5^I)–C(5^I) bond. The other proton is located then between the methylene protons of C(5^I) and directed towards C(6^{IV}). A similar meshing of the C(6) protons with the O′(5)–C′(5) bond and the methylene protons of C′(5) is necessary to account for the short distances of 3·39 Å and 3·75 Å between C(6^{IV}) and O′(5) and C′(5). If this arrangement of the methyl protons is basically correct, then the approach distance between C′(6) and C(6^I), and C′(6) and C(6^{II}), should be approximately 4·4 Å and 3·7 Å, if the proton van der Waals radius is taken as 1·2 Å. The observed distances are 4·11 Å and 3·62 Å respectively.

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Crystal and Molecular Structure of L-α-Glycerylphosphorylcholin

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The crystal structure of L-α-glycerylphosphorylcholin – the basic unit of the lecithins – has been determined and refined to an *R* value of 0·062 by anisotropic least-squares treatment.

Introduction

Our X-ray studies of lipids in the solid state have been undertaken to contribute to the knowledge of the structure of important biological systems with partly ordered lipid molecules such as cell membranes and the myelin sheath of nerves. Phosphatides with zwitterion structure (lecithins, cephalins, sphingomyelins) are important components in such systems. In order to obtain accurate structural information on the polar regions in the lecithins, we have performed a single-crystal analysis of the basic unit, glycerylphosphorylcholin (GPC).

Experimental

Optically active L-α-GPC ($C_8H_{20}O_6NP$) was synthesized according to Baer & Kates (1948). The compound was purified by four recrystallizations of its $CdCl_2$ complex. GPC was recovered by dissolving the complex in water and passing the solution through an ion exchanger (Tattrie & McArthur, 1958) and finally dried in vacuum over phosphorus pentoxide.

Crystals of GPC were obtained from ethanol (99·5%). They grow in long prisms and are often twinned. As GPC is very hygroscopic the crystals had to be handled in a water-free atmosphere and mounted in glass capillaries for the X-ray work.

The crystals are monoclinic ($P2_1$) with the following cell dimensions (Cu $K\alpha$ radiation): $a=10·10$, $b=7·71$, $c=16·62$ Å, $\beta=102·7°$.

A reasonable value for the calculated density of the crystals, 1·320 g.cm^{-3}, is obtained if there are four molecules per cell. The Patterson series also conforms with two molecules per asymmetric unit.