

The Crystal Structure of Methyl 1-Thio- α -D-ribopyranoside

By R. L. GIRLING* AND G. A. JEFFREY

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15213, U.S.A.

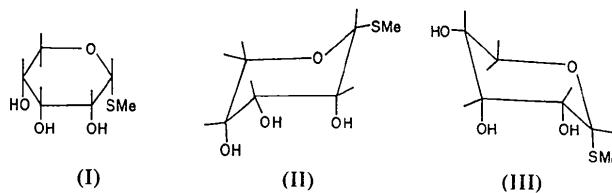
(Received 20 September 1972; accepted 9 November 1973)

The crystal structure of methyl 1-thio- α -D-ribopyranoside, $C_6H_{12}O_4S$, has been determined by direct methods. The space group is $P2_12_12_1$, with four molecules in a unit cell, $a = 8.696(2)$, $b = 12.83(3)$, $c = 7.335(2)$ Å. The structure was refined to $R = 0.028$ for 830 independent reflections measured with Ni-filtered Cu $K\alpha$ radiation. The absolute configuration was confirmed. The molecule has the 1C_4 chair conformation, thereby permitting the formation of a *syn-axial* intramolecular hydrogen bond with an $H \cdots O$ distance of 2.1 Å and $O-H \cdots O$ angle of 142° . The intermolecular hydrogen-bonding forms buckled ribbons extending in the c direction which link the molecules into columns, separated by van der Waals interactions.

Introduction

Originally isolated as comparatively rare natural products (Horton & Hutson, 1963), the thiosugars have recently become more important as synthetic intermediates (Paulson & Todt, 1968), possible precursors of nucleosides (Whistler, Nayak & Perkins, 1970), and potential enzymatic inhibitors (Claeyssens & De Bruyne, 1965). Methyl 1-thio- α -D-ribopyranoside (I) is a member of a series of mono and dithiosubstituted ribopyranosides prepared and supplied in the crystalline form by Dr N. A. Hughes of the University of Newcastle upon Tyne, England. The α -D-ribopyranoses are conformationally interesting because both the 1C_4 (II) and 4C_1 (III) chair conformers give rise to *syn-axial* interactions which are believed to play an important role in determining conformational stability. Theoretical calculations and experimental observations by p.m.r. on α and β -D-ribopyranose indicate that both conformers are present in aqueous solution (Stoddart, 1971). The influence of intramolecular hydrogen bonding on the con-

formational equilibrium in solution of a related compound, methyl 2-deoxy- α -ribopyranoside, has been discussed recently by Lemieux (1971).



The object of this investigation was primarily to determine the molecular conformation in the crystalline state of (I) and it is the first of a systematic study of the structural and conformational characteristics of several mono- and dithioribopyranosides. The influence of configuration, the anomeric effect, and intramolecular hydrogen bonding on the conformation of the pyranosides has been reviewed recently by Stoddart (1971); this study is aimed at examining to what degree these various conformational determining factors are influenced by the substitution of the ring or anomeric oxygen by a sulfur atom.

* Present address: Biology Division, Bldg. 202, Argonne National Laboratory, Argonne, Illinois 60440, U.S.A.

Table 1. Atomic positional and thermal parameters with e.s.d.'s for methyl 1-thio- α -D-ribopyranoside

Positional parameters are expressed as fractions of the lattice translations. Thermal parameters are defined by the expression: $T = \exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Non-hydrogen parameters $\times 10^4$, hydrogen parameters $\times 10^3$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	1398 (1)	1924 (8)	9541 (1)	163 (1)	68 (1)	138 (2)	-7 (1)	24 (2)	11 (1)
C(1)	2638 (5)	2333 (3)	7716 (5)	120 (7)	55 (3)	108 (7)	3 (3)	4 (6)	6 (4)
C(2)	2811 (5)	3523 (3)	7747 (5)	114 (6)	53 (2)	107 (7)	-5 (3)	-18 (5)	-7 (3)
C(3)	3748 (5)	3866 (3)	6094 (5)	114 (5)	50 (2)	132 (6)	-1 (4)	18 (6)	2 (3)
C(4)	3020 (4)	3447 (3)	4345 (5)	112 (5)	61 (3)	112 (8)	-1 (3)	15 (6)	0 (4)
C(5)	2906 (5)	2274 (3)	4509 (6)	156 (7)	57 (3)	118 (3)	-3 (4)	19 (7)	-19 (4)
C(6)	1884 (8)	552 (4)	9598 (11)	234 (12)	68 (3)	381 (17)	5 (5)	91 (13)	68 (7)
O(2)	1356 (4)	4033 (2)	7831 (4)	118 (4)	59 (2)	116 (5)	15 (3)	15 (4)	-7 (3)
O(3)	3921 (5)	4963 (2)	6127 (4)	198 (6)	49 (2)	121 (5)	-15 (3)	8 (5)	3 (3)
O(4)	1516 (4)	3867 (2)	4151 (4)	143 (5)	71 (2)	112 (6)	12 (2)	-7 (5)	24 (3)
O(5)	1976 (2)	1948 (2)	6030 (3)	130 (4)	49 (2)	107 (4)	-12 (2)	-2 (3)	-11 (2)

Table 1 (*cont.*)

Hydrogen atoms positional parameters are $\times 10^3$.

<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(2)	111 (5)	413 (3)	693 (5)
H(3)	390 (4)	519 (2)	470 (4)
H(4)	138 (4)	412 (2)	346 (4)
H(5)	378 (4)	202 (2)	787 (4)
H(6)	337 (3)	371 (2)	886 (4)
H(7)	480 (3)	350 (2)	632 (4)
H(8)	365 (4)	362 (2)	338 (4)
H(9)	394 (4)	195 (2)	470 (5)
H(10)	244 (3)	204 (3)	348 (4)
H(11)	150 (6)	31 (4)	1057 (8)
H(12)	298 (5)	50 (3)	973 (7)
H(13)	89 (7)	26 (4)	834 (9)

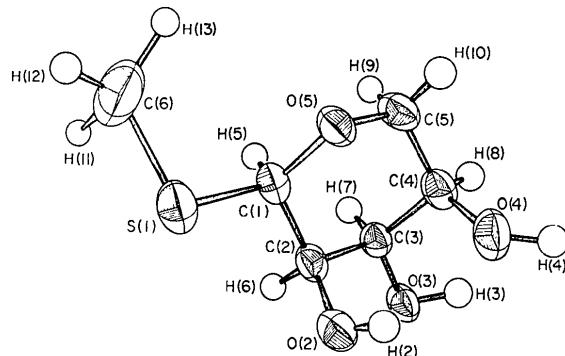


Fig. 1. Methyl 1-thio- α -D-ribopyranoside, showing the thermal ellipsoids at the 50% probability and the atomic nomenclature.

Crystal data

Methyl 1-thio- α -D-ribopyranoside, C₆H₁₂O₄S, M. W. 180.2, m.p. 155–6°C

Colorless needles, orthorhombic, $P_{2}1_22_1$ from systematic extinctions $h00$ absent for h odd, $0k0$ absent for k odd, $00l$ absent for l odd.

$$a \equiv 8.696(2), b \equiv 12.83(3), c \equiv 7.335(2) \text{ \AA}, Z \equiv 4$$

$$D_m = 1.476 \text{ g cm}^{-3} \text{ (flotation)}, D_x = 1.472 \text{ g cm}^{-3},$$

Experimental

The crystal used for data collection was selected from the specimen supplied by Professor Hughes, who had recrystallized it from a mixture of ethanol and ethyl acetate. It was a needle, $0.09 \times 0.13 \times 0.43$ mm, elongated in the c direction. The data were measured with Ni-filtered Cu $K\alpha$ radiation on a Picker FACS I diffractometer at room temperature. Cell dimensions calculated from film data were used as initial values in a best least-squares fit (Shiono, 1970) to the 2θ values for 20 reflections obtained by manually adjusting the setting angles until 50 % of the total beam intensity was obtained in each of the half windows. The intensities of 830 symmetry-independent reflections were measured using a $\theta/2\theta$ scan, with variable scan width, $1^\circ/\text{min}$ scan rate, and a 10 sec background count on each side of the reflection. Three reflections were used to monitor crystal alignment and crystal decomposition; the X-ray intensities varied less than 2 % and these small variations were used as scale factors in the data processing.

Table 2. Observed and calculated structure factors

Columns are: h index, $10|F_{\text{obs}}|$, $10|F_{\text{calc}}|$. Asterisks indicate unobserved reflections.

1187	1199	0	0	401	3	458	455	7	162	163	1	426	416	6	15*	93	2	170	159	0	138	136	208	208	218	22	0	9	73	72	1	12
1188	1190	0	0	402	3	459	456	7	163	164	1	427	417	6	15*	94	2	171	160	0	139	137	209	209	219	23	0	9	74	73	1	12
1189	1191	0	0	403	3	460	457	7	164	165	1	428	418	6	15*	95	2	172	161	0	140	138	210	210	220	24	0	9	75	74	1	12
1190	1192	0	0	404	3	461	458	7	165	166	1	429	419	6	15*	96	2	173	162	0	141	139	211	211	221	25	0	9	76	75	1	12
1191	1193	0	0	405	3	462	459	7	166	167	1	430	420	6	15*	97	2	174	163	0	142	140	212	212	222	26	0	9	77	76	1	12
1192	1194	0	0	406	3	463	460	7	167	168	1	431	421	6	15*	98	2	175	164	0	143	141	213	213	223	27	0	9	78	77	1	12
1193	1195	0	0	407	3	464	461	7	168	169	1	432	422	6	15*	99	2	176	165	0	144	142	214	214	224	28	0	9	79	78	1	12
1194	1196	0	0	408	3	465	462	7	169	170	1	433	423	6	15*	100	2	177	166	0	145	143	215	215	225	29	0	9	80	79	1	12
1195	1197	0	0	409	3	466	463	7	170	171	1	434	424	6	15*	101	2	178	167	0	146	144	216	216	226	30	0	9	81	80	1	12
1196	1198	0	0	410	3	467	464	7	171	172	1	435	425	6	15*	102	2	179	168	0	147	145	217	217	227	31	0	9	82	81	1	12
1197	1199	0	0	411	3	468	465	7	172	173	1	436	426	6	15*	103	2	180	169	0	148	146	218	218	228	32	0	9	83	82	1	12
1198	1200	0	0	412	3	469	466	7	173	174	1	437	427	6	15*	104	2	181	170	0	149	147	219	219	229	33	0	9	84	83	1	12
1199	1201	0	0	413	3	470	467	7	174	175	1	438	428	6	15*	105	2	182	171	0	150	148	220	220	230	34	0	9	85	84	1	12
1200	1202	0	0	414	3	471	468	7	175	176	1	439	429	6	15*	106	2	183	172	0	151	149	221	221	231	35	0	9	86	85	1	12
1201	1203	0	0	415	3	472	469	7	176	177	1	440	430	6	15*	107	2	184	173	0	152	150	222	222	232	36	0	9	87	86	1	12
1202	1204	0	0	416	3	473	470	7	177	178	1	441	431	6	15*	108	2	185	174	0	153	151	223	223	233	37	0	9	88	87	1	12
1203	1205	0	0	417	3	474	471	7	178	179	1	442	432	6	15*	109	2	186	175	0	154	152	224	224	234	38	0	9	89	88	1	12
1204	1206	0	0	418	3	475	472	7	179	180	1	443	433	6	15*	110	2	187	176	0	155	153	225	225	235	39	0	9	90	89	1	12
1205	1207	0	0	419	3	476	473	7	180	181	1	444	434	6	15*	111	2	188	177	0	156	154	226	226	236	40	0	9	91	90	1	12
1206	1208	0	0	420	3	477	474	7	181	182	1	445	435	6	15*	112	2	189	178	0	157	155	227	227	237	41	0	9	92	91	1	12
1207	1209	0	0	421	3	478	475	7	182	183	1	446	436	6	15*	113	2	190	179	0	158	156	228	228	238	42	0	9	93	92	1	12
1208	1210	0	0	422	3	479	476	7	183	184	1	447	437	6	15*	114	2	191	180	0	159	157	229	229	239	43	0	9	94	93	1	12
1209	1211	0	0	423	3	480	477	7	184	185	1	448	438	6	15*	115	2	192	181	0	160	158	230	230	240	44	0	9	95	94	1	12
1210	1212	0	0	424	3	481	478	7	185	186	1	449	439	6	15*	116	2	193	182	0	161	159	231	231	241	45	0	9	96	95	1	12
1211	1213	0	0	425	3	482	479	7	186	187	1	450	440	6	15*	117	2	194	183	0	162	160	232	232	242	46	0	9	97	96	1	12
1212	1214	0	0	426	3	483	480	7	187	188	1	451	441	6	15*	118	2	195	184	0	163	161	233	233	243	47	0	9	98	97	1	12
1213	1215	0	0	427	3	484	481	7	188	189	1	452	442	6	15*	119	2	196	185	0	164	162	234	234	244	48	0	9	99	98	1	12
1214	1216	0	0	428	3	485	482	7	189	190	1	453	443	6	15*	120	2	197	186	0	165	163	235	235	245	49	0	9	100	99	1	12
1215	1217	0	0	429	3	486	483	7	190	191	1	454	444	6	15*	121	2	198	187	0	166	164	236	236	246	50	0	9	101	100	1	12
1216	1218	0	0	430	3	487	484	7	191	192	1	455	445	6	15*	122	2	199	188	0	167	165	237	237	247	51	0	9	102	101	1	12
1217	1219	0	0	431	3	488	485	7	192	193	1	456	446	6	15*	123	2	200	189	0	168	166	238	238	248	52	0	9	103	102	1	12
1218	1220	0	0	432	3	489	486	7	193	194	1	457	447	6	15*	124	2	201	190	0	169	167	239	239	249	53	0	9	104	103	1	12
1219	1221	0	0	433	3	490	487	7	194	195	1	458	448	6	15*	125	2	202	191	0	170	168	240	240	250	54	0	9	105	104	1	12
1220	1222	0	0	434	3	491	488	7	195	196	1	459	449	6	15*	126	2	203	192	0	171	169	241	241	251	55	0	9	106	105	1	12
1221	1223	0	0	435	3	492	489	7	196	197	1	460	450	6	15*	127	2	204	193	0	172	170	242	242	252	56	0	9	107	106	1	12
1222	1224	0	0	436	3	493	490	7	197	198	1	461	451	6	15*	128	2	205	194	0	173	171	243	243	253	57	0	9	108	107	1	12
1223	1225	0	0	437	3	494	491	7	198	199	1	462	452	6	15*	129	2	206	195	0	174	172	244	244	254	58	0	9	109	108	1	12
1224	1226	0	0	438	3	495	492	7	199	200	1	463	453	6	15*	130	2	207	196	0	175	173	245	245	255	59	0	9	110	109	1	12
1225	1227	0	0	439	3	496	493	7	200	201	1	464	454	6	15*	131	2	208	197	0	176	174	246	246	256	60	0	9	111	110	1	12
1226	1228	0	0	440	3	497	494	7	201	202	1	465	455	6	15*	132	2	209	198	0	177	175	247	247	257	61	0	9	112	111	1	12
1227	1229	0	0	441	3	498	495	7	202	203	1	466	456	6	15*	133	2	210	199	0	178	176	248	248	258	62	0	9	113	112	1	12
1228	1230	0	0	442	3	499	496	7	203	204	1	467	457	6	15*	134	2	211	200	0	179	177	249	249	259	63	0	9	114	113	1	12
1229	1231	0	0	443	3	500	497	7	204	205	1	468	458	6	15*	135	2	212	201	0	180	178	250	250	260	64	0	9	115	114	1	12
1230	1232	0	0	444	3	501	498	7	205	206	1	469	459	6	15*	136	2	213	202	0	181	179	251	251	261	65	0	9	116	115	1	12
1231	1233	0	0	445	3	502	499	7	206	207	1	470	460	6	15*	137	2	214	203	0	182	180	252	252	262	66	0	9	117	116	1	12
1232	1234	0	0	446	3	503	500	7	207	208	1	471	461	6	15*	138	2	215	204	0	183	181	253	253	263	67	0	9	118	117	1	12
1233	1235	0	0	447	3	504	501	7	208	209	1	472	462	6	15*	139	2	216	205	0	184	182	254	254	264	68	0	9	119	118	1	12
1234	1236	0	0	448	3	505	502	7	209	210	1	473	463	6	15*	140	2	217	206	0	185	183	255	255	265	69	0	9	120	119	1	12
1235	1237	0	0	449	3	506	503	7	210	211	1	474	464	6	15*	141	2	218	207	0	186	184	256	256	266	70	0	9	121</			

There were 143 reflections less than two standard deviations above background and these were considered unobserved. The data were corrected for L_p (Shiono, 1970) and absorption (Craven, 1963; Busing & Levy, 1957), and reduced to structure amplitudes.

Structure determination and refinement

The structure factors were scaled and normalized by the use of a Wilson plot. Additional renormalization of special groups of E 's to assist in phase determination was carried out using a program by Shiono (1970). Several sets of three origin-defining and one enantiomorph-determining reflection were selected and used in a tangent-refinement procedure (Hall, 1967). The resulting E maps, calculated from the 132 highest E values, failed to reveal the structure, but the addition of a fifth phase to the tangent refinement gave an E map with peaks corresponding to all but one non-hydrogen atom. The initial structure-factor agreement, $R=0.29$, was reduced to 0.05 by the addition of the missing atom and anisotropic refinement, using a block-diagonal least-squares program on an IBM 1130 (Shiono, 1970). At this stage, all the hydrogen atoms were unambiguously located from a difference map. Anomalous dispersion corrections (Cromer & Liberman, 1970) for S and O atoms were added and a full-matrix least-squares refinement of all heavy atoms anisotropically and hydrogen atoms isotropically gave a final R of 0.028 and wR of 0.023, where $w=1/(\sin \theta/\lambda)$. The weighting approximates in this case to the average $1/\sigma F$ for a given range of $\sin \theta$, thus the strong reflections, which are subject to multiple reflection and extinction effects, are not overweighted. The function minimized was $\sum w(|F_o| - K|F_c|)^2$ where K is a single scale factor. No observed data point was removed or 'weighted' zero during the refinement.

The absolute configuration of the sugar was determined by two methods; a Bijvoet pair comparison, and a refinement of D and L isomers for $+h+k+l$ data (Ibers & Hamilton, 1964). The intensities of the Bijvoet pairs were recorded by hand-centering the reflections and counting for 20 sec at the maximum peak height. The ratio of the observed and calculated intensities below clearly indicates the D isomer.

h	k	l	$I(hkl)$ $I(\bar{h}\bar{k}\bar{l})$	Obs.	Calc. for D isomer
7	7	1		0·72	0·79
4	10	2		0·66	0·76
4	6	1		0·85	0·78
3	1	2		1·27	1·31
3	11	1		0·73	0·74
2	10	3		0·68	0·76
1	3	4		0·69	0·71
1	4	1		1·31	1·54
1	5	1		1·18	1·22

Refinement of $+h+k+l$ reflections for the D ($R=0.028$) and L ($R=0.035$) isomers rejected the L at greater than 99.5% confidence level using Hamilton's (1965) R -value significance test. The final atomic positional and thermal parameters are given in Table 1 and the structure factors in Table 2. The atomic numbering and thermal ellipsoids are shown in Fig. 1.

Description of the structure

The molecule (I), shown in Fig. 1, has the 1C_4 , or $1C$, ring conformation (II) with the two axial oxygen atoms O(2), O(4), linked by an intramolecular hydrogen bond, as previously reported by Girling & Jeffrey (1971). Although there may be other factors involved, the preference over the more usual 4C_1 conformer (III) can therefore be ascribed simply to the greater strength of

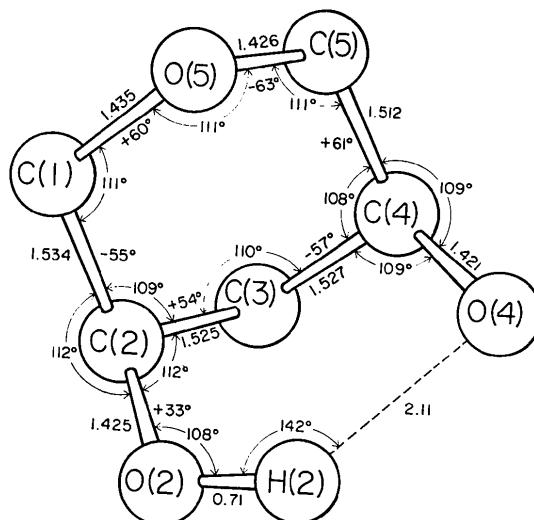


Fig. 2. Fused-ring system formed by the intramolecular hydrogen bond; it consists of two six-membered rings in the chair conformation and an eight-membered ring in the 'tub' form. Torsion angles and valence angles are in $^\circ$, distances are in \AA . The standard deviations are 0.005 \AA and 0.5° , except for those involving hydrogens, where they are 0.1 \AA and $\sim 5^\circ$.

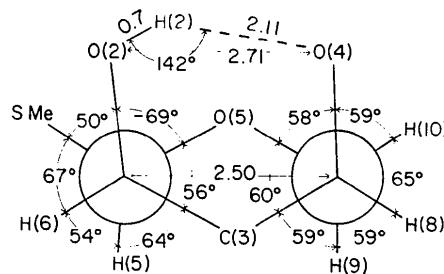


Fig. 3. The intramolecular hydrogen bonding in methyl 1-thio- α -D-ribopyranoside, viewed in the direction of the C(2) \rightarrow C(1), C(4) \rightarrow C(5) bonds. The standard deviations are given in Fig. 2.

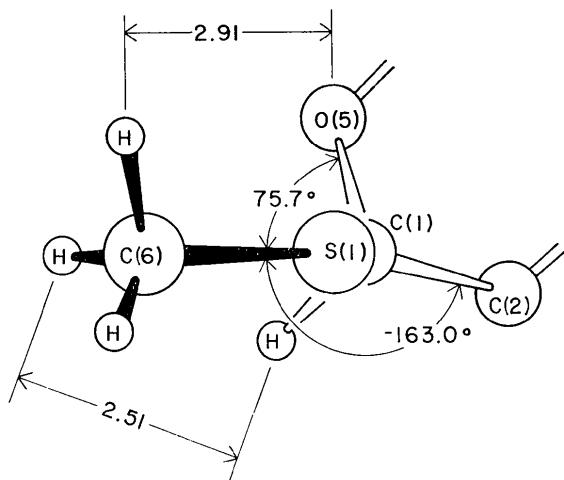


Fig. 4. Torsional angles and closest intramolecular contacts (\AA) of the methyl group viewed down the $S(1)\text{--}C(1)$ bond, in methyl 1-thio- α -D-ribopyranoside.

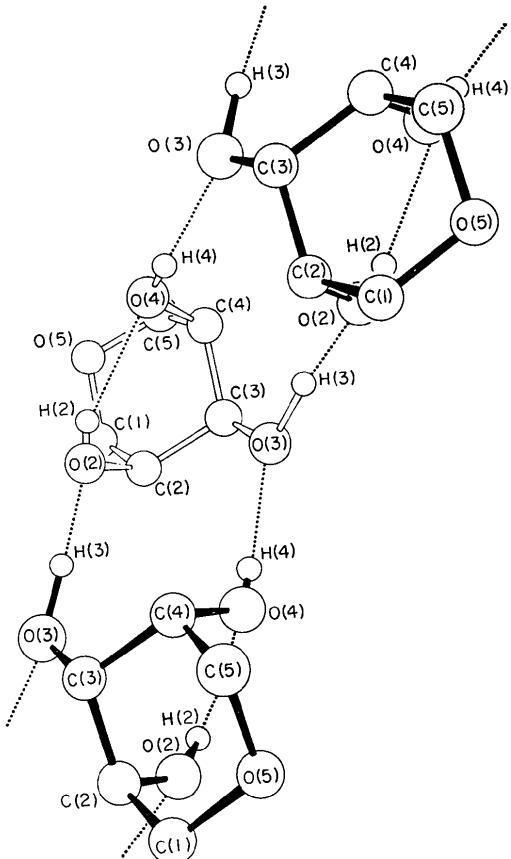


Fig. 5. Hydrogen bonding, represented by dotted lines, in the crystal structure of methyl 1-thio- α -D-ribopyranoside. View is the ac plane with c direction approximately parallel to the direction of the hydrogen bonding. The $S\text{-CH}_3$ and the methylene hydrogens have been omitted to simplify the diagram.

the $O\text{-H}\cdots O$ intramolecular hydrogen bond compared with the alternative *syn-axial* $O\text{-H}\cdots S$ bond which would be possible with (III). The intramolecular hydrogen bond, shown in Fig. 4, has also been observed in methyl 1,5-dithio- α -D-ribopyranoside (Girling & Jeffrey, 1971), which also has the 1C_4 ring conformation. It is transannular to the pyranose ring, forming the fused ring system shown in Fig. 3, which would limit conformational change should it persist in the solution. Evidence that it can persist is cited by Lemieux & Levine (1964), Lemieux & Pavia (1969), Lemieux (1971) and others (Kabayama & Patterson, 1958; Foster, Harrison, Lehmann & Webber, 1963) to show that *syn-axial* intramolecular hydrogen bonds are important factors in determining the population of conformers in non-hydrolytic solvents, where competitive intermolecular hydrogen-bonding with the solvent species cannot occur. In 2-C-methyl β -L-ribopyranoside in CCl_4 solution, for example, the band at 3512 cm^{-1} in the IR spectrum has been assigned to this $2,4\text{-}(\text{OH})_2$ hydrogen-bonding interaction (Ferrier, Overend, Rafterty, Wall & Williams, 1963).

The effect of this intramolecular bond formation on the pyranose ring geometry can be obtained by comparison with a model ring based on substituting an oxygen for methylene in the cyclohexane molecular structure (Stoddart, 1971; Davies & Hassel, 1963) or with the 'best' pyranoid ring suggested by Arnott & Scott (1972), or with the mean observed ring-torsional angles in aldopyranoses (Jeffrey, 1972). All three results give *syn-axial* $O(2)\cdots O(4)$ separations of $2.65\text{--}2.70 \text{ \AA}$ with $C(2)\cdots C(4)$ distances in the pyranose ring of $2.50\text{--}2.55 \text{ \AA}$. The observed distances for $O(2)\cdots O(4)$ and $C(2)\cdots C(4)$ of $2.71(1)$ and $2.50(1) \text{ \AA}$ in this structure indicate that the formation of the intramolecular hydrogen bond brings about no significant deformation of the pyranose ring (see Fig. 3 and Table 3). This is in contrast to epi-inositol (Jeffrey & Kim, 1971) and methyl 5-thio- α -D-ribopyranoside (Jeffrey & Girling, 1972), where the *syn-axial* $O\text{-O}$ interactions without intramolecular H-bonding result in an $O\cdots O$ separation of nearly 3.0 \AA with an accompanying distortion of the pyranose ring.

Table 3. Torsional angles for methyl 1-thio- α -D-ribopyranoside

(Ring angles are given in Fig. 3.)	
$O(4)\text{-}C(4)\text{-}C(5)\text{-}O(5)$	$-58.5 (0.5)^\circ$
$O(4)\text{-}C(4)\text{-}C(3)\text{-}O(3)$	-61.3
$O(4)\text{-}C(4)\text{-}C(3)\text{-}C(2)$	$+62.0$
$O(3)\text{-}C(3)\text{-}C(4)\text{-}C(5)$	-179.9
$O(3)\text{-}C(3)\text{-}C(2)\text{-}O(2)$	$+56.2$
$O(3)\text{-}C(3)\text{-}C(2)\text{-}C(1)$	-179.5
$O(2)\text{-}C(2)\text{-}C(3)\text{-}C(4)$	-69.9
$O(2)\text{-}C(2)\text{-}C(1)\text{-}O(5)$	$+69.0$
$O(2)\text{-}C(2)\text{-}C(1)\text{-}S(1)$	-50.5
$S(1)\text{-}C(1)\text{-}C(2)\text{-}C(3)$	-174.5
$S(1)\text{-}C(1)\text{-}O(5)\text{-}C(5)$	-179.6
$C(6)\text{-}S(1)\text{-}C(1)\text{-}O(5)$	$+75.2$
$C(6)\text{-}S(1)\text{-}C(1)\text{-}C(2)$	-163.3

Since the formation of the *syn-axial* intramolecular hydrogen bond is so consistent with unstrained pyranose ring geometry, one might ask why it is not more commonly observed in the crystal structures of pyranose sugars. In solution, these bonds are believed to be formed only where there is a lack of competition from other suitable hydrogen-bonding groups, as in non-hydrolytic solvents (Stoddart, 1971). Similarly, in the solid state, the hydrogen bonding function of the hydroxyl groups is generally fully utilized in intermolecular cohesion and intramolecular hydrogen bonding appears to be secondary. The reason may be that the bond energy for an intramolecular bond is less than for a comparable intermolecular bond because of less favorable H···O distances and O-H···O bond angles which are constrained in pyranose sugars to be about 2.0 Å and 140°, as compared with the commonly observed intermolecular hydrogen bond distances of 1.7–1.8 Å and 170–180°.

The bond distances and bond angles, which differ from $109.5 \pm 0.5^\circ$, for methyl 1-thio- α -D-ribopyranoside are given in Table 4. They do not differ significantly from those expected from other carbohydrate structure determinations and from the results of Mathieson & Poppleton (1966) for methyl 1-thio- β -D-xylopyranoside. Although S(1)-C(1) is 0.013 Å shorter than S(1)-C(6), this observation is of marginal significance in relation to the anomeric bond shortening effect (Berman, Chu & Jeffrey, 1967). The estimated standard deviation of the S(6) parameters is relatively large because of the greater thermal motion of the aglycone group.

Table 4. Bond distances and angles (other than 109.5°) for methyl 1-thio- α -D-ribopyranoside

S(1)-C(1)	1.796 (3) Å	C(1)-S(1)-C(6)	99°
S(1)-C(6)	1.809 (6)	O(5)-C(1)-S(1)	108
C(1)-C(2)	1.534 (5)	C(3)-C(4)-C(5)	108
C(2)-C(3)	1.525 (5)	C(4)-C(5)-O(5)	111
C(3)-C(4)	1.527 (5)	C(5)-O(5)-C(1)	111
C(4)-C(5)	1.512 (5)	O(5)-C(1)-C(2)	111
C(2)-O(2)	1.425 (4)	C(1)-C(2)-O(2)	112
C(3)-O(3)	1.416 (4)	C(3)-C(2)-O(2)	112
C(4)-O(4)	1.421 (4)	C(4)-C(3)-O(3)	114
C(5)-O(5)	1.426 (4)		
C(1)-O(5)	1.435 (4)		
Intramolecular H-bond			
O(2)···O(4)	2.709 (7) Å	O(2)-H(2)···O(4)	142°
H(2)···O(4)	2.1 (1)		
O(2)-H(2)	0.7 (1)		

The methyl group torsion angle C(6)-S(1)-C(1)-O(5) is 15° greater than the ideal 60° for normal +*synclinal* orientation of an aglycone bond. This additional twist is in the direction such as to increase the H···O(5) non-bonding distance at the expense of the H···H distance, as shown in Fig. 4.

The hydrogen bonding, shown in Fig. 5, is compara-

tively simple. It consists of infinite chains with a sequence of one intra- and two intermolecular bonds, → O(2)H → O(4)H → O(3)H → O(2)H →, forming a two stranded ribbon which extends in the c direction. This ribbon of hydrogen bonds links successive molecules related by the screw axes parallel to c in a buckled column one molecule wide along a and two molecules in the b direction, as shown in Fig. 6. The nonpolar groups are on the exterior of these columns and their intermolecular contacts correspond to van der Waals forces as shown by the intermolecular non-bonded distances given in Table 5; none are significantly less than the sum of the van der Waals radii. The thermal motion of the non-hydrogen atoms reflects the unidirectional character of the hydrogen bonding by having larger r.m.s. components in the a and b directions than in the c direction.

This research was supported by the U. S. Public Health Service, National Institutes of Health Grant No. GM-11293.

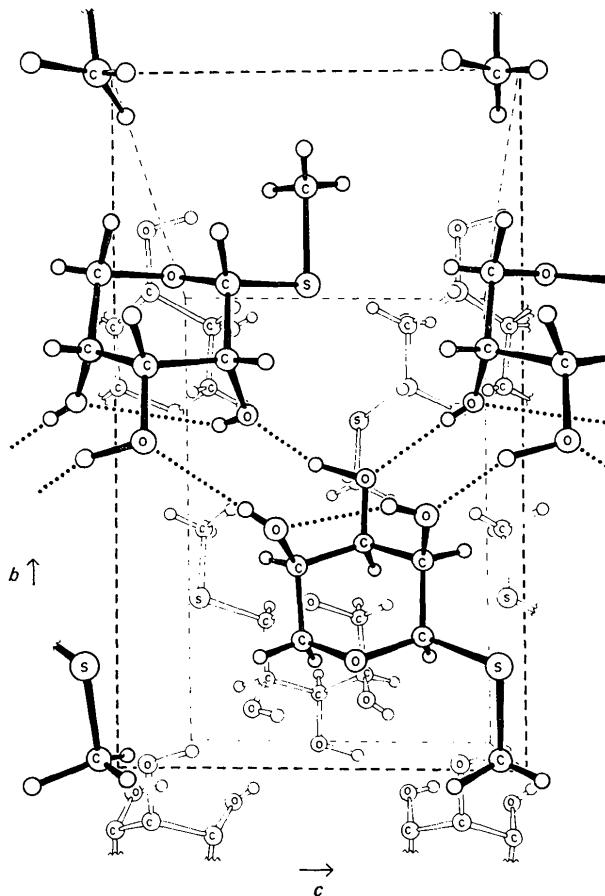


Fig. 6. A perspective view of the molecular packing in the crystal structure of methyl 1-thio- α -D-ribopyranoside. The dotted lines indicate the ribbons of the hydrogen bonds which link the molecules into columns extending in the c direction.

Table 5. Intermolecular approaches in methyl 1-thio- α -D-ribopyranoside less than 3.5 Å for non-hydrogen atoms and less than 3.0 Å involving hydrogen atoms

Intermolecular H-bonds

O(2) ··· O(3)	2.748 (8) Å
O(3) ··· O(4)	2.703 (8)
H(4) ··· O(3)	2.1 (1)
H(3) ··· O(2)	2.0 (1)
O(2) ··· H(3)	1.7 (1)
O(4)-H(4) ··· O(3)	178°
O(3)-H(3) ··· O(2)	174

Van der Waals distances

O(2) ··· C(4)	3.46 (1) Å	H(2) ··· H(3)	2.2 (2) Å
O(2) ··· O(4)	3.41 (1)	H(2) ··· H(13)	2.3 (2)
O(3) ··· C(2)	3.49 (1)	H(2) ··· H(9)	2.6 (2)
O(5) ··· C(3)	3.39 (1)	H(3) ··· H(4)	2.9 (2)
O(5) ··· C(4)	3.50 (1)	H(3) ··· H(6)	2.5 (2)
		H(3) ··· H(12)	2.8 (2)
C(2) ··· H(3)	2.6 (1)	H(3) ··· H(13)	2.9 (2)
C(5) ··· H(7)	2.9 (1)	H(4) ··· H(5)	2.9 (2)
O(2) ··· H(13)	2.7 (1)	H(4) ··· H(6)	2.8 (2)
O(3) ··· H(12)	2.8 (1)	H(4) ··· H(9)	2.9 (2)
O(4) ··· H(9)	2.6 (1)	H(7) ··· H(10)	2.4 (2)
O(5) ··· H(7)	2.6 (1)	H(8) ··· H(13)	2.8 (2)

References

- ARNOTT, S. & SCOTT, W. E. (1972). *J. Chem. Soc. Perkin Trans. II*, pp. 324–335.
 BERMAN, H. M., CHU, S. S. C. & JEFFREY, G. A. (1967). *Science*, **157**, 1576–1577.
 BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
 CLAEYSSENS, M. & DE BRUYNE, C. K. (1965). *Naturwissenschaften*, **52**, 515.
 CRAVEN, B. M. (1963). Tech. Rpt. No. 45, Crystallography Laboratory, Univ. of Pittsburgh, Pittsburgh, Pa.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1896.
 DAVIES, M. & HASSEL, O. (1963). *Acta Chem. Scand.* **17**, 1181.
 FERRIER, R. J., OVEREND, W. G., RAFFERTY, G. A., WALL, H. M. & WILLIAMS, N. R. (1963). *Proc. Chem. Soc.* p. 133.
 FOSTER, A. B., HARRISON, R., LEHMANN, J. & WEBBER, J. M. (1963). *J. Chem. Soc.* pp. 4471–4477.
 GIRLING, R. L. & JEFFREY, G. A. (1971). *Carbohydr. Res.* **18**, 339–341.
 HALL, S. R. (1967). *Direct Phasing Methods*. UWAC-17. The Univ. of Western Australia, revised for IBM 7090 by H. M. BERMAN.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
 HORTON, D. & HUTSON, D. H. (1963). *Advanc. Carbohydr. Chem.* **18**, 123–199.
 IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781–782.
 JEFFREY, G. A. (1972). *Conformational Studies in the Solid State: Extrapolation to Molecules in Solution*. Chapter in Amer. Chem. Soc. Advances in Chemistry Series. In the press.
 JEFFREY, G. A. & GIRLING, R. L. (1972). Unpublished work.
 JEFFREY, G. A. & KIM, H. S. (1971). *Acta Cryst.* **B27**, 1812–1817.
 KABAYAMA, M. A. & PATTERSON, D. (1958). *Canad. J. Chem.* **36**, 563–573.
 LEMIEUX, R. U. (1971). *Pure Appl. Chem.* **25**, 527–548.
 LEMIEUX, R. U. & LEVINE, S. (1964). *Canad. J. Chem.* **42**, 1473–1480.
 LEMIEUX, R. U. & PAVIA, A. A. (1969). *Canad. J. Chem.* **47**, 4441–4446.
 MATHIESON, A. McL. & POPPLETON, B. J. (1966). *Acta Cryst.* **21**, 72–79.
 PAULSEN, H. & TODT, K. (1968). *Advanc. Carbohydr. Chem.* **23**, 206–216.
 SHIONO, R. (1970). Tech. Rpts. 48 and 49, Department of Crystallography, Univ. of Pittsburgh, Pittsburgh, Pa.
 STODDART, J. F. (1971). *Stereochemistry of Carbohydrates*. Chapter 3, pp. 58–87 New York: Wiley-Interscience.
 WHISTLER, R. L., NAYAK, U. G. & PERKINS, A. W. (1970). *J. Org. Chem.* **35**, 519–521.

Acta Cryst. (1973). **B29**, 1011

Structure du m-Crésol

PAR CLAUDETTE BOIS

Université Paris VI, Laboratoire de Recherches de Chimie Systématique, 24 rue Lhomond, Paris 5e, France

(Reçu le 29 novembre 1972, accepté le 8 janvier 1973)

Crystals of m-cresol are monoclinic, with 24 molecules in a unit cell of dimensions $a=25.90$, $b=6.20$, $c=33.06$ Å, $\beta=133.9^\circ$, space group $P2_1/c$. The structure, determined from three-dimensional single-crystal X-ray data registered at -100°C , has been automatically solved by direct methods. The structure was refined to a final R of 7.6% for 3835 reflexions. The molecules are linked by hydrogen bonds to form eight chains parallel to the b direction.

Ce travail qui vient terminer l'étude structurale des résols (Bois, 1970, 1972) s'intègre dans une étude plus générale des xylénols et des résols, entreprise au laboratoire.

Etude expérimentale

La température de solidification du m-crésol est de 11°C , mais il présente une importante surfusion. Nous