Boyd, G. V., Monteil, R. L., Lindley, P. F. & Mahmoud, M. M. (1978). *J. Chem. Soc. Perkin Trans.* 1, pp. 1351–1360.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure.* London and New York: Plenum.

Germain, G., Main, P. & Woolfson, M. M. (1974). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Kupchan, S. M., Hemingway, R. J., Werner, D. & Karim, A. (1969). *J. Org. Chem.* **34**, 3903–3908.

Lee, K.-H., Ibuka, T., Kim, S.-H., Vestal, B. R. & Hall, I. H. (1975). *J. Med. Chem.* **18**, 812–817.

Sternhell, S. (1969). *Q. Rev. Chem. Soc.* **23**, 236–270.

Acta Cryst. (1981). B**37**, 1465–1467

Methyl 1-Thio-β-D-galactopyranoside at 123 K

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Abstract. $C_7H_{14}O_5S$, orthorhombic, $P2_12_12_1$, at 123 K [293 K] a = 7·759 (4) [7·810 (2)], b = 8·952 (4) [9·010 (2)], c = 13·172 (5) [13·223 (4)] Å, V = 914·9 [930·4] Å^3, Z = 4, D_x = 1·524 [1·498] Mg m^{-3}, D_m = [1·494] Mg m^{-3}. The intensities of 3134 symmetry-independent reflections were measured with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å), of which 2821 have $I > 2\sigma$. The structure was solved using *MULTAN* and refined anisotropically for the non-hydrogen atoms and isotropically for H atoms to R = 0·046, R_w = 0·049 by full-matrix least squares. The pyranose ring is a normal $^4C_1$ chair. The thioglycosidic torsion angle of −99° is larger than that observed in the methyl β-pyranosides. The ring C–O bond lengths are 1·429 (2) and 1·440 (2) Å. The C–S bond lengths are 1·806 (1) and 1·811 (3) Å. The hydrogen bonding consists of an infinite chain with a side-loop, which involves an intermolecular and two bifurcated interactions.

Introduction. Methyl 1-thio-β-D-galactopyranoside, from Sigma Chemical Co., was recrystallized from an ethanol–water solution at room temperature. A CAD-4 diffractometer was used for data collection with a crystal 0·72 × 0·48 × 0·24 mm, cut from a larger specimen. The unit-cell parameters were determined by a least-squares fit of $\sin^2\theta$ values for 34 reflections with 34° < 2θ < 48°. No corrections were made for absorption ($\mu_{\mathrm{Mo}K\alpha}$ = 0·53 mm^{-1}) or extinction. The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) from 152 reflections with $|E| >$ 1·78. The 14 non-hydrogen atoms were revealed on the E map and refined isotropically to R = 0·09. The methylene H atoms were then placed at calculated positions and the remaining H atom positions were obtained from a difference map. C, O and S atomic parameters were refined anisotropically, and H atom parameters isotropically by full-matrix least squares (Busing, Martin & Levy, 1962) to final agreement factors of R = 0·046, R_w = 0·049, S = 1·66. H(4) and the methyl hydrogens H(71), H(72) and H(73) were poorly defined and their parameters were not refined. The function refined was $\sum w||F_o| - k|F_c||^2$, with $w^{-1} = \sigma_c^2$ from counting statistics. Only the strongest reflection, 013, appeared to be strongly affected by extinction, with $F_o = 0{\cdot}81F_c$. The atomic scattering factors used for C, O and S were those of Cromer & Waber (1965) and for H those of Stewart, Davidson & Simpson (1965). The atomic parameters are given in Table 1.[*] The atomic notation and thermal ellipsoids are shown in Fig. 1 and the molecular dimensions are given in Fig. 2. Fig. 3 gives a stereoview of the unit-cell contents.

Discussion. The pyranose ring has the normal $^4C_1$ conformation, with Cremer & Pople (1975) puckering parameters of Q = 0·598 Å, θ = 4·86°, φ = 16·4°. The thioglycosidic torsion angle, O(5)–C(1)–S–C(7), of −99·4 (2)° is larger than that in methyl β-galacto-

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35912 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors for the title compound at 123 K*

Values are $\times 10^5$ for the S atom, $\times 10^4$ for C and O atoms, and $\times 10^3$ for H atoms. Estimated standard deviations given in parentheses refer to the least significant digit.

	x	y	z	B_{eq}/B_{iso} (Å^2)†	X—H (Å)
S	16187 (6)	−7183 (5)	3092 (3)	1·32 (2)	
C(1)	1551 (2)	386 (2)	−837 (1)	0·96 (4)	
C(2)	160 (2)	1606 (2)	−781 (1)	0·91 (4)	
C(3)	176 (2)	2463 (2)	−1787 (1)	0·92 (4)	
C(4)	1984 (2)	3032 (2)	−2035 (1)	0·91 (4)	
C(5)	3266 (2)	1736 (2)	−1992 (1)	0·91 (4)	
C(6)	5098 (2)	2251 (2)	−2193 (1)	1·16 (5)	
C(7)	1897 (4)	−2566 (2)	−226 (2)	3·37 (10)	
O(2)	−1506 (1)	953 (1)	−668 (1)	1·33 (4)	
O(3)	−1055 (2)	3633 (1)	−1807 (1)	1·52 (4)	
O(4)	2430 (1)	4184 (1)	−1327 (1)	1·15 (4)	
O(5)	3204 (1)	1045 (1)	−1005 (1)	1·02 (3)	
O(6)	6246 (1)	1010 (2)	−2256 (1)	1·46 (4)	
H(1)	125 (3)	−29 (3)	−138 (2)	1·4 (4)	0·97 (3)
H(2)	40 (3)	228 (2)	−23 (2)	0·6 (4)	0·96 (2)
H(3)	−18 (3)	167 (3)	−233 (2)	0·9 (4)	1·04 (3)
H(4)*	198	346	−274	0·6	1·00
H(5)	292 (2)	94 (2)	−251 (2)	0·3 (3)	1·02 (2)
H(61)	554 (3)	298 (3)	−165 (2)	1·1 (4)	1·03 (3)
H(62)	510 (3)	290 (2)	−288 (1)	0·3 (3)	1·08 (2)
H(71)*	83	−280	−72	6·0	1·07
H(72)*	310	−265	−55	6·0	1·03
H(73)*	184	−331	34	6·0	1·00
HO(2)	−180 (4)	97 (3)	−11 (2)	2·0 (5)	0·77 (3)
HO(3)	−103 (4)	413 (4)	−128 (2)	3·0 (6)	0·82 (3)
HO(4)	296 (4)	477 (3)	−163 (2)	2·3 (6)	0·78 (3)
HO(6)	689 (4)	104 (3)	−176 (2)	2·7 (6)	0·82 (3)

* Unrefined.

† For non-H atoms $B_{eq} = \frac{4}{3}\sum \beta_{ii} a_i^2$.

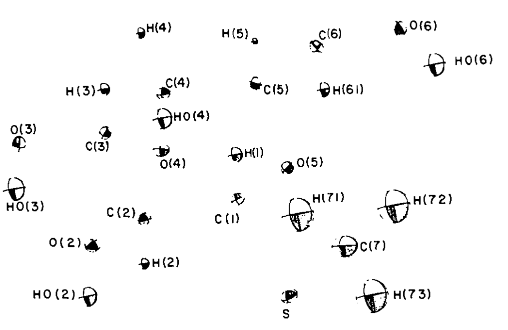
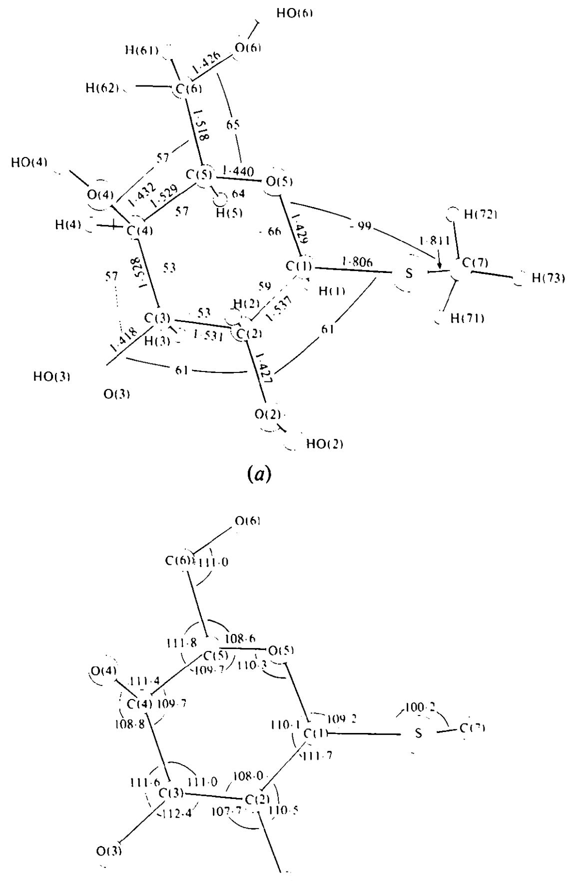


Fig. 1. Methyl 1-thio-β-D-galactopyranoside at 123 K: atomic notation and thermal ellipsoids at 50% probability (Johnson, 1976).



(*a*)

(*b*)

Fig. 2. Molecular dimensions of methyl 1-thio-β-D-galactopyranoside. (*a*) Bond lengths (Å) and selected torsion angles (°), (*b*) bond angles (°). The σ's for the bond lengths are 0·002 Å, except for C(1)—S, 0·001 Å, and C(7)—S, 0·003 Å. The σ's for the valence and torsion angles are 0·2°.

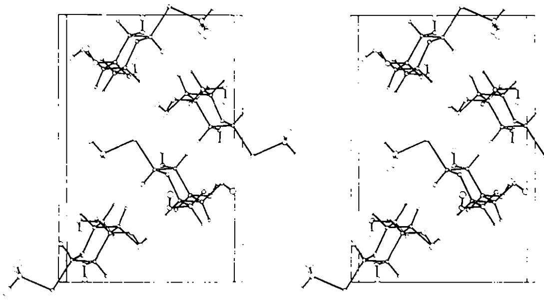


Fig. 3. Stereoview of the unit-cell contents in the structure of methyl 1-thio-β-D-galactopyranoside. **c** is vertical and **b** is horizontal.

pyranoside (−77°, Takagi & Jeffrey, 1978), and the other methyl β-pyranosides (Jeffrey, Pople & Radom, 1972). Glycosidic torsion angles around −100° have been observed, however, in some disaccharides (Jeffrey, Pople & Radom, 1974), where they can be associated with steric effects or intra-residue hydrogen bonding. In 1-thio pyranosides, the larger angle could be a manifestation of a different torsion potential associated with the '*exo*-anomeric effect' in a thioacetal residue. The primary alchol group has the *gauche*/*trans* conformation as in methyl β-D-galactopyranoside. The ring C—C bond lengths vary over the commonly observed range, 1·528 (2) to 1·537 (2) Å. The C—OH

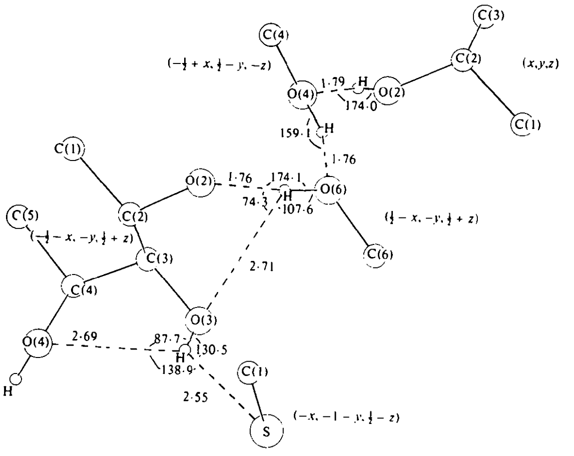


Fig. 4. Hydrogen bonding in the crystal structure of methyl 1-thio-β-D-galactopyranoside. The H···O values are obtained with normalized O—H covalent bond distances of 0·97 Å.

bond lengths range from 1·418 (2) to 1·432 (2) Å. The two ring C—O bonds differ by 0·011 Å, which is barely significant. They are 0·008 Å longer than those in methyl β-galactopyranoside. The two C—S bond lengths differ by 0·005 (3) Å, which is also barely significant, although a similar difference was observed in methyl 1-thio-α-D-ribopyranoside (1·796, 1·809 Å; Girling & Jeffrey, 1973). The geometry of the hydrogen bonding is shown in Fig. 4. It consists of an infinite chain, with a spiral, represented schematically below.

```
      ···O(2)–H···O(4)–H···O(6)–
                           |
          S···H–O(3)···H···O(2)–H
                 ⋮
        O(2)–H···O(4)–H···O(6)–
                           |
                           H
```

The O(6)H and O(3)H bonds are bifurcated, although the O(6)H···O(3) bonding is very weak. O(3)—H makes a weak bifurcated hydrogen bond, which is intramolecular to O(4) and intermolecular to S. The H is close to the plane of the two O and S atoms to which it is bonded, as shown by the sum of the *X*—H—*Y* angles.

The nearest intermolecular neighbors to the ring oxygen O(5) are H(O2) at 2·956 Å and H(O3) at 2·960 Å. The former might be regarded as a very weak component of a bifurcated interaction, making an angle of 115° with O(2)–H(O2) and of 71° with H(O2)···O(4). The three angles about H(O2) add up to 360° so that H(O2) is in the plane of the three oxygens O(2), O(4) and O(5), *cf.* Ceccarelli, Jeffrey & Taylor (1981). The latter could similarly be the weak component of a trifurcated interaction which makes an angle of 141° with O(3)–H(O3), 106° with H(O3)···O(4) and 57° with H(O3)···S.

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References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Ceccarelli, C., Jeffrey, G. A. & Taylor, R. (1981). *J. Mol. Struct.* **70**, 255–271.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Girling, R. L. & Jeffrey, G. A. (1973). *Acta Cryst.* B**29**, 1006–1011.

Jeffrey, G. A., Pople, J. A. & Radom, L. (1972). *Carbohydr. Res.* **25**, 117–131.

Jeffrey, G. A., Pople, J. A. & Radom, L. (1974). *Carbohydr. Res.* **38**, 81–95.

Johnson, C. K. (1976). *ORTEP* II. Report ORNL-3158. Oak Ridge National Laboratory, Tennessee.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Takagi, S. & Jeffrey, G. A. (1978). *Acta Cryst.* B**34**, 2006–2010.