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Structure and Conformational Analysis of Methyl α-Thiomaltoside,* $C_{13}H_{24}O_{10}S$

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Abstract

This paper deals with the crystal and molecular structure of methyl α-thiomaltoside, which is the first structure ever reported for a thio-disaccharide system. The crystal structure of the title compound has been established by direct methods from 4777 independent reflections and refined to a final R value of 0·042. The crystal belongs to the monoclinic system, space group $P2_1$ and has a unit cell of dimensions $a = 14·196$ (4), $b = 4·846$ (1), $c = 12·410$ (3) Å, $\beta = 110·12$ (10)°, with $Z = 2$, $V = 801·1$ Å^3; $M_r = 372·4$, $D_m = 1·54$ (1), $D_x = 1·543$ Mgm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·17 mm^{-1}, $F(000) = 396$, room temperature. The two glucose residues have the $^4C_1$ conformation and are $\alpha(1\rightarrow4)$ linked. The structural features at the glycosidic bridge are: C(1)–S(1) = 1·826 (1), C(4′)–S(1) = 1·828 (1) Å, C(1)–S(1)–C(4′) = 100·3 (1)°. Comparison with other sulphur-containing molecular segments has been performed. The conformational angles φ = O(5)–C(1)–S(1)–C(4′) and ψ = C(1)–S(1)–C(4′)–C(5′) at the glycosidic linkage have the values 89 and −116·8° respectively. The observed conformational behaviour has been analysed with the aid of a conformational analysis investigation. The primary hydroxyl group in the non-reducing residue is in the *gt* conformation, whereas a *gg* orientation is observed for the corresponding hydroxyl in the reducing residue. There is no intramolecular hydrogen bond, and the structure is maintained by an extensive network of hydrogen bonds.

Introduction

The understanding of the structural basis for the action of glycanases and, more generally, of proteins continues to be of interest (Pincus & Scheraga, 1981; Warshel, 1981). In the field of polyosidase–oligosaccharide complexes, 1-thioglycosides have appeared to be good substrate analogues (Monod, 1956; Boos, Schaedel & Wallenfelds, 1967; Rafestin, Obrenovitch, Oblin & Monsigny, 1974; Steers, Cuatrecasas & Pollard, 1971; Claeyssens, Kersters-Hilderson, Van Wauve & De Brugue, 1970). This potentiality is also

* Methyl 4-*S*-α-D-glucopyranosyl-4-thio-α-D-glucopyranoside.
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true for the induction, as well as for the purification, of glycanases (Blanc-Muesser, Defaye, Driguez & Ohleyer, 1981; Rho, Desrochers, Jurasek, Driguez & Defaye, 1982). A comparative study of the enzymic behaviour of nitrophenyl maltosides and maltotriosides, along with their corresponding thio analogues, showed no significant difference in their binding at the α-amylase binding site, as estimated by their Michaelis constants K_m (Blanc-Muesser, Defaye, Driguez, Marchis-Mourens & Seigner, 1982). Recently a modified maltotriose molecule, where the replacement of the O atom of an α-(1→4) linkage by an S atom (thereby preventing the substrate analogue from complete enzymic hydrolysis), was shown to be an excellent candidate in providing an isomorphous derivative of crystalline α-amylase (Payan, Haser, Pierrot, Frey, Astier, Abadie, Duée & Buisson, 1980). The investigation of the crystal structure of the title compound was undertaken in order to determine the characteristic geometry induced by an S atom at the glycosidic linkage, and thereby to elucidate the overall changes, if any, occurring between thiomaltoside and the equivalent α-(1→4)-*O* linked disaccharide.

Experimental

X-ray investigation

Methyl α-thiomaltoside was prepared following the route described by Blanc-Muesser, Defaye & Driguez (1982) which succeeds a previous report on the stereoselective syntheses of 1-thioglycosides (Blanc-Muesser, Defaye & Driguez, 1978).

Crystals grown from a supersaturated aqueous solution. Twenty reflections used for measuring lattice parameters. D_m measured by flotation in a mixture of anhydrous CCl_4 and cyclohexane. Philips PW1100 diffractometer, θ–2θ scan mode, Ni-filtered Mo radiation. 4777 independent reflections up to $\theta = 40°$; 4685 with $I > 2{\cdot}5\sigma(I)$. Three standard reflections ($\bar{3}\bar{1}1$, $\bar{2}04$, 120): 4% intensity decrease during data collection. Absorption ignored, crystal dimensions $0{\cdot}30 \times 0{\cdot}20 \times 0{\cdot}25$ mm. Scattering factors from *International Tables for X-ray Crystallography* (1962). Intensities corrected for Lorentz–polarization effects.

The structure was solved by application of *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The E map computed with the best set of phases revealed the S atom only. Successive Fourier calculations revealed the remaining nonhydrogen atoms. Several cycles of full-matrix least-squares refinement with *ORFLS* (Busing, Martin & Levy, 1962) led to a conventional R value of 0·059. The H atoms were located and included in the refinement with isotropic temperature factors. The final R values for all observed and measured reflections were 0·044 and 0·042, respectively. Quantity minimized: $w(F_o - F_c)^2$, each reflexion being assigned a weight $w = 1/\sigma^2(F)$ derived from $\sigma(I)$. At the end of the refinement, $(\Delta/\sigma)_{ave} < 0.2$. A final electron density map showed no significant residual density, the extreme fluctuations being −0·15, +0·20 e Å^{-3}.*

Conformational analysis

The potential energy was calculated by including the partitioned contributions arising from the van der Waals, torsional and hydrogen-bond contributions. The van der Waals interactions were evaluated by using 6–12 potential functions, with the parameters proposed by Scott & Scheraga (1966*a*, *b*). As for the non-bonded interactions involving the S atom, the following parameters were used: atomic polarizability $x_S = 3{\cdot}06 \times 10^{-24}$ cm^3, number of polarizable electrons $N_S = 14{\cdot}8$, the van der Waals radius being $R_S = 1{\cdot}85$ Å. Following recent PCILO and MNDO calculations on thio-sugar analogues (Tvaroska, 1982) a threefold intrinsic torsional potential was used for rotations around the C(1)–S(1) and S(1)–C(4′) bonds, with barriers of 2·1 kJ mol^{-1}. Hydrogen-bond energies (when included in the calculation) were computed by an empirical expression: $V_{HB} = 33{\cdot}14(R - 2{\cdot}55)(R - 3{\cdot}05)$, where R is the distance between O atoms, which should lie between 2·55 and 3·05 Å. The crystal structure coordinates were used, except for the hydrogen positions which were recalculated using the information derived from a neutron diffraction investigation on oligosaccharides (Gress & Jeffrey, 1977). The energy maps were computed as a function of φ and ψ at intervals of 5°. With respect to the relative energy minimum, iso-energy contours were drawn by interpolation of 4·2 kJ mol^{-1}. The 50 kJ mol^{-1} contour was selected as the outer limit.

Results and discussion

Atomic positional parameters are shown in Table 1. A stereoscopic view of the methyl α-thiomaltoside molecule is shown in Fig. 1 (*PITMOS*; Dheu & Pérez, 1980). The numbering of the atoms, shown in Fig. 2, proceeds from the non-reducing end (unprimed atoms) to the reducing end (primed atoms); the C atom of the methyl group has been labelled C*M*(1′). The bond distances and angles are given in Tables 2 and 3 respectively.

The mean C–C distance of 1·526 Å and the mean C–O bond length of 1·423 Å are in good agreement with the values of 1·525 and 1·430 Å given by Berman & Kim (1968) for the ideal pyranose ring. However, a significant lengthening of the intracyclic C(5)–O(5) bond is observed.

* Lists of structure factors, anisotropic thermal parameters H-atom parameters and distances involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP39112 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional parameters with their e.s.d.'s in parentheses* ($\times 10^5$ *for* S, $\times 10^4$ *for* O *and* C) *and* B_{eq} *values* (Å^2)

$$B_{eq} = \tfrac{4}{3}(\beta_{11}/a^{*2} + \beta_{22}/b^{*2} + \beta_{33}/c^{*2}).$$

	x	y	z	B_{eq}
S(1)	18673 (4)	−39630	22308 (4)	1·85
C(1)	1620 (1)	−6951 (4)	2990 (1)	1·46
C(2)	805 (1)	−6387 (4)	3518 (1)	1·51
C(3)	1196 (1)	−4449 (4)	4541 (1)	1·65
C(4)	2150 (1)	−5621 (5)	5406 (1)	1·90
C(5)	2915 (1)	−6175 (5)	4820 (1)	1·69
C(6)	3860 (1)	−7592 (6)	5616 (2)	2·23
O(2)	−94 (1)	−5361 (4)	2703 (1)	2·16
O(3)	468 (1)	−4180 (4)	5094 (1)	2·61
O(4)	2578 (1)	−3743 (6)	6320 (1)	3·18
O(5)	2490 (1)	−8004 (3)	3862 (1)	1·67
O(6)	4577 (1)	−7997 (4)	5069 (1)	2·57
C(1′)	2811 (1)	−5728 (5)	−871 (1)	1·91
C(2′)	1714 (1)	−6234 (4)	−1026 (1)	1·68
C(3′)	1423 (1)	−4793 (4)	−96 (1)	1·53
C(4′)	2165 (1)	−5688 (4)	1078 (1)	1·54
C(5′)	3246 (1)	−5126 (5)	1149 (2)	1·82
C(6′)	4030 (2)	−6139 (7)	2254 (2)	2·54
C*M*(1′)	3930 (2)	−2331 (8)	−1055 (3)	3·69
O(1′)	2929 (1)	−2943 (4)	−1099 (1)	2·52
O(2′)	1107 (1)	−5366 (4)	−2151 (1)	2·12
O(3′)	419 (1)	−5523 (4)	−234 (1)	2·36
O(5′)	3435 (1)	−6559 (4)	231 (1)	2·03
O(6′)	3909 (2)	−8972 (6)	2466 (2)	3·50

Table 2. *Bond distances* (Å) *and their e.s.d.'s in methyl α-thiomaltoside*

S(1)–C(1) 1·826 (1)			
C(1)–C(2)	1·538 (2)	C(1)–O(5)	1·427 (2)
C(2)–C(3)	1·522 (2)	C(2)–O(2)	1·418 (2)
C(3)–C(4)	1·519 (2)	C(3)–O(3)	1·430 (2)
C(4)–C(5)	1·524 (2)	C(4)–O(4)	1·418 (2)
C(5)–C(6)	1·528 (2)	C(5)–O(5)	1·439 (2)
		C(6)–O(6)	1·418 (2)
S(1)–C(4′) 1·828 (1)			
C(1′)–C(2′)	1·522 (2)	C(1′)–O(1′)	1·401 (2)
C(2′)–C(3′)	1·523 (2)	C(1′)–O(5′)	1·408 (2)
C(3′)–C(4′)	1·538 (2)	C(2′)–O(2′)	1·429 (2)
C(4′)–C(5′)	1·531 (2)	C(3′)–O(3′)	1·421 (2)
C(5′)–C(6′)	1·520 (2)	C(5′)–O(5′)	1·436 (2)
		C(6′)–O(6′)	1·419 (2)
		C*M*(1′)–O(1′)	1·434 (2)

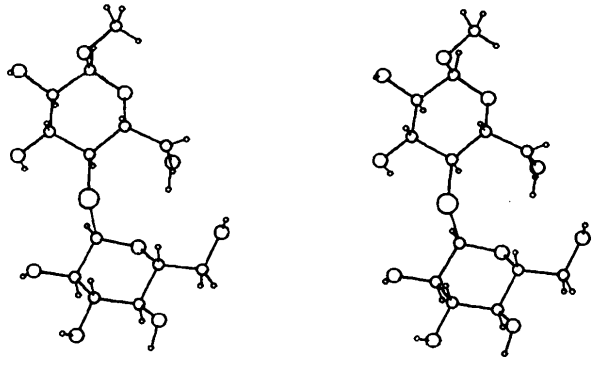

Fig. 1. Stereoscopic view of methyl α-thiomaltoside.

Table 3. *Bond angles* (°) *and their e.s.d.'s in methyl α-thiomaltoside*

C(1)–S(1)–C(4′)	100·3 (1)	C(2′)–C(1′)–O(1′)	108·5 (1)
S(1)–C(1)–C(2)	112·6 (1)	C(2′)–C(1′)–O(5′)	110·6 (1)
S(1)–C(1)–O(5)	113·9 (1)	O(1′)–C(1′)–O(5′)	113·1 (1)
C(2)–C(1)–O(5)	108.8 (1)	C(1′)–C(2′)–C(3′)	111·3 (1)
C(1)–C(2)–C(3)	110·7 (1)	C(1′)–C(2′)–O(2′)	108·8 (1)
C(1)–C(2)–O(2)	112·5 (1)	C(3′)–C(2′)–O(2′)	112·1 (1)
C(3)–C(2)–O(2)	111·0 (1)	C(2′)–C(3′)–C(4′)	108·2 (1)
C(2)–C(3)–C(4)	109·8 (1)	C(2′)–C(3′)–O(3′)	108·5 (1)
C(2)–C(3)–O(3)	109·9 (1)	C(4′)–C(3′)–O(3′)	112·1 (1)
C(4)–C(3)–O(3)	108·1 (1)	S(1)–C(4′)–C(3′)	110·2 (1)
C(3)–C(4)–C(5)	109·7 (1)	S(1)–C(4′)–C(5′)	111·8 (1)
C(3)–C(4)–O(4)	111·0 (1)	C(3′)–C(4′)–C(5′)	110·5 (1)
C(5)–C(4)–O(4)	108·4 (1)	C(4′)–C(5′)–C(6′)	113·8 (1)
C(4)–C(5)–C(6)	112·5 (1)	C(4′)–C(5′)–O(5′)	109·0 (1)
C(4)–C(5)–O(5)	109·7 (1)	C(6′)–C(5′)–O(5′)	106·3 (1)
C(6)–C(5)–O(5)	106·4 (1)	C(5′)–C(6′)–O(6′)	112·4 (1)
C(5)–C(6)–O(6)	111·6 (1)	C(1′)–O(1′)–C*M*(1′)	112·2 (1)
C(1)–O(5)–C(5)	114·4 (1)	C(1′)–O(5′)–C(5′)	113·9 (1)

The internal C–C–C ring angles are close to tetrahedral (range 108·2–111·3°, mean 110°) whereas the exocyclic C(4)–C(5)–C(6) exhibit a significant opening with values of 112·5° and 113·8°. The endocyclic C–C–O bond angles (range 108·8–110·6°) have an average value of 109·5°. The endocyclic C–O–C vary very little and average 114·1°. The exocyclic C–C–O angles show a wide variation from 108·4 to 112·5°, average 110·2°.

The C–H bond lengths range between 0·93 (5) and 1·09 (5) Å, mean value 0·99 Å. The average O–H distance is 0·89 Å, with a range of 0·74 (5) to 1·04 (5) Å.

The torsion angles around the pyranose ring are given in Table 4. The expected $^4C_1$ conformation is found for both residues. The ring conformation in this structure is similar to that found in other glucose residues.

The conformation of the primary hydroxyl group at C(6) is described by the torsion angles O(5)–C(5)–C(6)–O(6) and C(4)–C(5)–C(6)–O(6). According to the terminology proposed by Sundaralingam (1968), the conformation about C(5)–C(6) in the unprimed residue is *gauche–trans*, whereas that in the non-reducing residue is *gauche–gauche*. These observed orientations agree with the general rules that were derived from a large survey of the occurrence of stable conformers as displayed by the primary hydroxyl groups in glucopyranoses (Marchessault & Pérez, 1979).

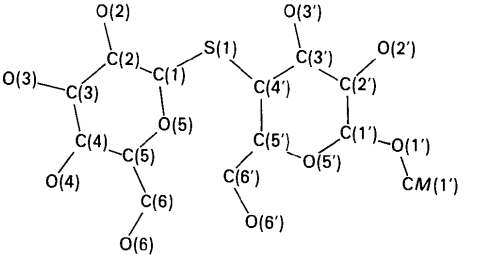

Fig. 2. Numbering of the atoms in methyl α-thiomaltoside.

Table 4. *Torsion angles* (°) *in methyl α-thiomaltoside* (*e.s.d.* 1·5°)

Torsion about the glycosidic bond		
O(5)–C(1)–S(1)–C(4′)	89·0	
H(1)–C(1)–S(1)–C(4′)	−25·6	
C(1)–S(1)–C(4′)–C(5′)	−116·8	
C(1)–S(1)–C(4′)–H(4′)	3·6	
Endocyclic torsion angles		
	Unprimed residue	Primed residue
O(5)–C(1)–C(2)–C(3)	55·8	56·0
C(1)–C(2)–C(3)–C(4)	−55·1	−53·6
C(2)–C(3)–C(4)–C(5)	55·2	54·8
C(3)–C(4)–C(5)–O(5)	−56·8	−57·5
C(4)–C(5)–O(5)–C(1)	61·1	60·9
C(5)–O(5)–C(1)–C(2)	−59·9	−60·1
Exocyclic torsion angles		
S(1)–C(1)–C(2)–O(2)	53·4	55·4 [O(1′)]
O(2)–C(2)–C(3)–O(3)	60·4	62·4
O(3)–C(3)–C(4)–O(4)	−65·2	−61·6 [S(1)]
O(4)–C(4)–C(5)–C(6)	63·7	61·0 [S(1)]
O(5)–C(5)–C(6)–O(6)	62·0	−66·0
C(4)–C(5)–C(6)–O(6)	−117·8	53·9
O(5′)–C(1′)–O(1′)–C*M*(1′)	61·2	
H(1′)–C(1′)–O(1′)–C*M*(1′)	−55·1	

Table 5. *Geometry in some acetal and thio-acetal molecular fragments* (Å *and* deg)

$\theta = 60°$		$\theta = 180°$	
111·7		107·3	
C(5)···O(5)···C(1)···O(1)···C	(*a*)	C(5)···O(5)···C(1)···O(1)···C	(*a*)
1·438 1·417 1·409		1·439 1·428 1·387	
111·9	(*b*)		
C(5)···O(5)···C(11)···S(1)···C	(*c*)		
1·446 1·446 1·799	(*d*)		
	(*e*)	108·8	(*g*)
	(*f*)	C(5)···O(5)···C(1)···S(1)···C	(*h*)
		1·441 1·435 1·804	(*i*)
			(*j*)
112·9		108·7	
C(5)···S(5)···C(1)···O(1)···C	(*k*)	C(5)···S(5)···C(1)···O(1)···C	(*k*)
1·810 1·850 1·392	(*l*)	1·796 1·842 1·396	(*m*)
113·6		114·5	
C(5)···S(5)···C(1)···S(1)···C	(*n*)	C(5)···S(5)···C(1)···S(1)···C	(*n*)
1·788 1·826 1·789		1·815 1·810 1·805	

References: (*a*) Pérez & Marchessault (1978); (*b*) Carter, Ruble & Jeffrey (1982); (*c*) Girling & Jeffrey (1973*a*); (*d*) Ducruix & Pascard-Billy (1972); (*e*) Partharsarathy & Davis (1967); (*f*) this work; (*g*) Beale, Stephenson & Stevens (1972); (*h*) Mathieson & Poppleton (1966); (*i*) Atkinson, Ruble & Jeffrey (1981); (*j*) Takagi & Jeffrey (1978); (*k*) Girling & Jeffrey (1973*b*); (*l*) Clegg (1981); (*m*) Miler-Srenger, Stora & Hughes (1981); (*n*) Girling & Jeffrey (1974).

Geometry of the glycosidic linkage

The present results establish the geometry induced by an S atom on an α-(1→4) type of junction between glucopyranose units. The C(1)–S(1) bond length is 1·826 (1) Å, the S(1)–C(4′) distance being 1·828 (1) Å. Another important parameter is the valence angle τ = C(1)–S(1)–C(4′) whose value is 100·3 (1)°. As a net result, the non-bonded C(1)···C(4′) distance in thiomaltoside is 2·805 (2) Å, which is about 0·35 Å larger than in the case of an α-(1→4)-*O* glycosidic linkage. The C–S distances observed in this work fall in the range 1·755 to 1·846 Å previously observed in thiocarbohydrates (Takagi & Jeffrey, 1978). Despite the relative paucity of available crystallographic data about the magnitude of C–S–C angles, it appears that the observed value of 100·3° is larger than usual. Therefore, as in *O*-glycosides, there would be a significant opening of the valence angle at the glycosidic linkage.

The glycosidic linkage represents a molecular segment where two electronegative atoms (*X* and *Y*) bearing lone pairs of electrons are linked to the anomeric C atom. The electronic structure of this arrangement affects the geomery and conformation of the molecule, the resulting consequences being termed the anomeric and *exo*-anomeric effect (Lemieux & Chu, 1969; Lemieux, Pavia, Martin & Watanabe, 1969). Table 5 is presented to elucidate any structural correlation arising from substitution of the O atom by S in the following acetal sequence: C(5)–*X*(5)–C(1)–*Y*(1)–C (*X* and *Y* being either O or S atoms) as a function of the conformation about the torsion angle C(5)–*X*(5)–C(1)–*Y*(1). Apart from the well known differences occurring in the C(5)–O(5)–C(1)–O(1)–C sequence, no significant relation between the C–*X* and C–*Y* bond length and the torsion angle can be found. However, a systematic coupling of *X*(5)–C(1)–*Y*(1) bond angles to torsion angle is observed. The conformation θ = 180° (β anomeric configuration) results in smaller values than those found for θ = 60° (α anomeric configuration).

Conformation about the glycosidic linkage

The relative orientation of contiguous pyranosides is described by the torsion angles around the glycosidic bonds C(1)–S(1) and S(1)–C(4′); these angles are denoted as the conformational angles φ, ψ. In the solid-state conformation φ = O(5)–C(1)–S(1)–C(4′) = 89·0° and ψ = C(1)–S(1)–C(4′)–C(5′) = −116·8°. The conformational behaviour of thiomaltoside is best understood by the study of the available space in terms of low-energy regions. As shown above, the primary hydroxyl group can assume different stable conformations. In order to investigate the effect of the side-group orientation on the conformation of methyl α-thiomaltoside, the primary hydroxyl groups were systematically set to the two preferred non-eclipsed orientations: *gauche–gauche* and *gauche–trans*. The four energy maps corresponding to all possible combinations were calculated and compared. In all cases, the outer-limit contour encompasses a similar area and the calculated energy minima occur for similar values of φ, ψ. No significant variation can be observed, and it must be concluded that the relative orientations of the primary hydroxyl groups do not have any drastic influence on the conformational property of the thiomaltoside backbone. A similar conclusion was also derived for α-(1→4)-*O*

linked glucopyranoses (Pérez, Roux, Revol & Marchessault, 1979).

The energy maps shown in Figs. 3 and 4 were established with the primary hydroxyl groups having the orientation found in the crystal structure. The energy map in Fig. 3(*b*) was computed by taking into account non-bonded interactions and torsion potential only. Two distinct regions of the (φ, ψ) space define the low-energy domains; the overall shape and the geographical occurrences are similar to those found for maltose. In the low-energy area spanning $\psi = -80$ to $\psi = -190°$ are found both calculated ($\varphi = 45$, $\psi = -160°$) and crystallographic energy minima; the latter lies within the 2·1 kJ mol^{-1} region. It is noticeable that the 16·8 kJ mol^{-1} energy contour delimits a zone that encompasses more than 80% of the available surface. The introduction of an energy contribution arising from intramolecular hydrogen bonding results in a significant alteration of the low-energy region (Fig. 3*a*). The calculated energy minimum is now shifted to $\varphi = 95°$ and $\psi = -110°$. Close examination of the two interactions involved with this minimum discloses the occurrence of two intramolecular hydrogen bonds between O(5) and O(6′) and O(6) and O(6′). However, such a bonding scheme is not observed in the crystal structure. It is therefore puzzling to observe that a slight shift of 10° in φ and ψ from the crystallographic minimum would have induced a more stable intramolecular energy. In fact packing forces do override such an occurrence in producing a more stable three-dimensional arrangement.

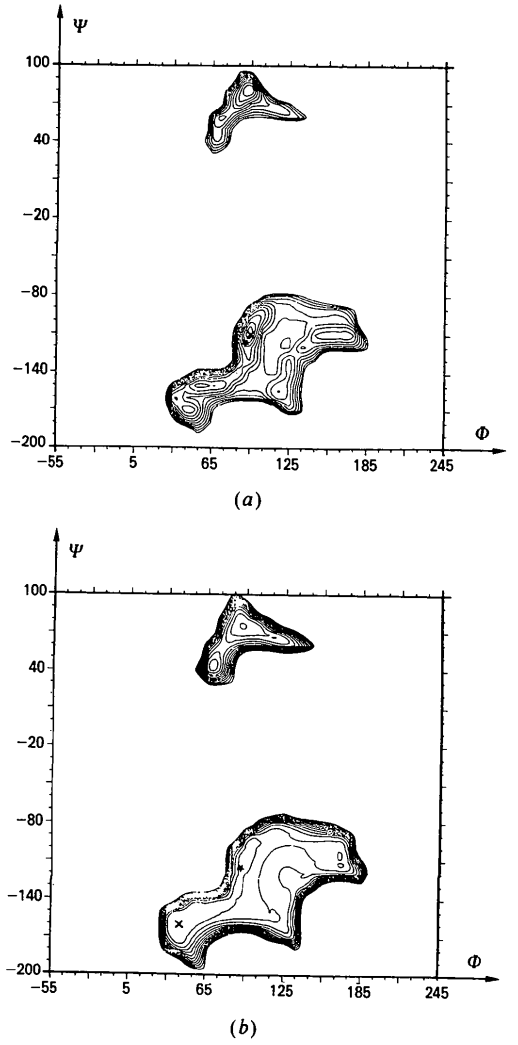

Fig. 3. Energy diagram computed for methyl α-thiomaltoside. Contours were drawn by interpolation of energy computed at 5° in φ and ψ. The asterisk indicates the observed crystalline conformation, whereas × indicates the calculated absolute minimum. (*a*) The hydrogen-bond contribution has been considered. (*b*) The hydrogen-bond contribution has been omitted.

In some cases, α-(1→4)-*O*-linked disaccharides exhibit an intramolecular hydrogen bond between atoms O(2) and O(3′) belonging to contiguous residues; this is found for α-maltose (Takusagawa & Jacobson, 1978), methyl β-maltopyranoside (Chu & Jeffrey, 1967) and α-maltose monohydrate (Gress & Jeffrey, 1977). In the structure of methyl α-thiomaltoside, such a feature is not found, since the distance O(2)···O(3′) is 3·956 (2) Å. Nevertheless, the occurrence of such an intramolecular hydrogen bond could be possible as shown in Fig. 4. Therefore, the observed lack of intramolecular hydrogen bonding cannot be attributed to the substitution of the O atom by S at the glycosidic linkage.

Molecular packing

The packing of the molecules in the unit cell is shown in Fig. 5. The molecules are extended along the *a* axis and display an antiparallel arrangement. The small value of *b* necessarily causes the molecule to be parallel to (010). The three-dimensional arrangement results from intermolecular hydrogen bonds,

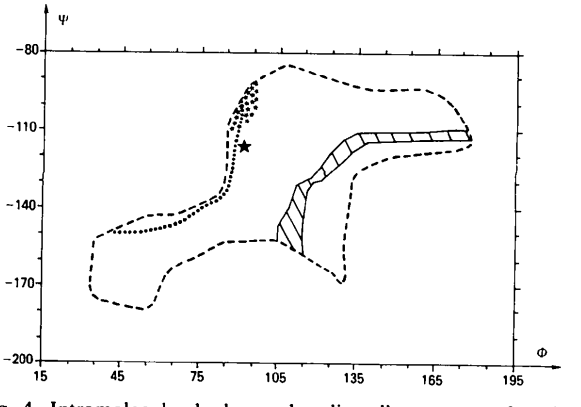

Fig. 4. Intramolecular hydrogen-bonding diagram as a function of rotations of 5° in φ and ψ. The 33·6 kJ mol^{-1} energy contour was selected as the outer limit. Shaded area: O(2)···O(3′), asterisks: O(5)···O(6′), dotted line O(6)···O(6′).

Table 6. *Hydrogen bonding in methyl α-thiomaltoside*

i	*j*	*k*	D_{ik} (Å)	D_{jk} (Å)	θ_{ijk} (°)
O(2)–H(O2)···O(2′)[(i)]			2·778 (2)	1·96 (5)	170 (2)
O(2′)–H(O2′)···O(2)[(i)]			2·778 (2)	2·06 (5)	167 (2)
O(3)–H(O3)···O(3)[(ii)]			2·735 (2)	1·87 (5)	164 (2)
O(3′)–H(O3′)···O(3′)[(i)]			2·846 (2)	1·96 (5)	147 (2)
O(6)–H(O6)···O(6)[(iii)]			2·736 (2)	1·91 (5)	177 (2)

Symmetry code: none x, y, z; (i) $-x, -1/2+y, -z$; (ii) $-x, 1/2+y, 1-z$; (iii) $1-x, 1/2+y, 1-z$.

whose geometrical characteristics are given in Table 6. It is worth noticing that all secondary hydroxyl groups are involved in hydrogen bonding with neighbouring secondary hydroxyl groups; each acts both as a donor and an acceptor. Conversely, the primary hydroxyl groups of neighbouring molecules face each other and also interact through hydrogen bonds. However, this is not true for the hydroxyl group O(6′).

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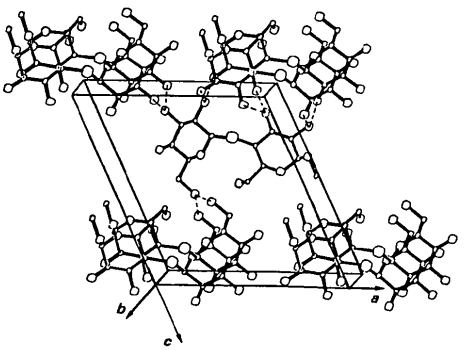

Fig. 5. Packing of the molecules of methyl α-thiomaltoside.

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