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THE CRYSTAL STRUCTURE OF HEPTYL 1-THIO-α-D-GLUCOPYRANOSIDE, A MEMBER OF A NEW HOMOLOGOUS SERIES OF MESOGENIC CARBOHYDRATE DERIVATIVES

HENK A. VAN DOREN*, RALPH VAN DER GEEST

Netherlands Institute for Carbohydrate Research-TNO, Rouaanstraat 27, 9723 CC Groningen (The Netherlands)

FRÉ VAN BOLHUIS,

Crystal & Molecular Structure Centre, University of Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

RICHARD M. KELLOGG, AND HANS WYNBERG

Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

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ABSTRACT

The crystal structure of heptyl 1-thio-α-D-glucopyranoside, $C_{13}H_{26}O_5S$, is monoclinic, space group $P2_1$, with $Z = 2$, $a = 6.013(1)$, $b = 7.324(1)$, $c = 17.536(4)$ Å, $\beta = 98.21(2)°$, $V = 764.4$ Å^3, $D_{calc} = 1.279$ g.cm^{-3}. The crystal involves a bilayer head-to-head molecular packing with interdigitizing alkyl chains. The carbohydrate moieties are hydrogen-bonded in finite chains which include all the oxygen atoms and which are linked[1] into a network by the minor component of the three-center bond from HO-6. The crystal structure is transformed into a smectic A liquid crystal phase at 96.8° (ΔH 34.6 kJ.mol^{-1}) that shows a periodicity of 23.1 Å. The clearing point is at 138.3° (ΔH 2.2 kJ.mol^{-1}).

INTRODUCTION

A homologous series of alkyl 1-thio-α-D-glucopyranosides (*n*-propyl to *n*-dodecyl) was synthesized[2] as part of our research[3] into the scope and limitations of mesogenic behavior in carbohydrate derivatives. One of the most significant factors in determining the liquid crystalline behavior of this type of compound is the formation of hydrogen-bonded layers of carbohydrate moieties, with the hydrophobic alkyl chains pointing outward in a parallel fashion. As visualized by Jeffrey[4], the alkyl chains are the first to "melt", whereas the hydrogen-bonded layers of the carbohydrate moieties remain intact, thus forming the backbone of the (SA_d) liquid

*Author for correspondence.

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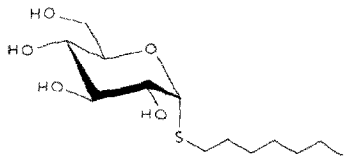
crystalline phase. This model implies that the determination of the crystal structure of these compounds will yield detailed information on the structure of the liquid crystalline phase.

EXPERIMENTAL

*Heptyl 1-thio-α-*D*-glucopyranoside*[2] (**1**). — M.p. 96.8°, $[\alpha]_D^{20}$ +239° (*c* 1, methanol) was recrystallized several times from ethanol to yield colorless crystals of sufficient quality and size for X-ray structure determination.



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The thermal behavior of **1** was investigated quantitatively with a Perkin–Elmer differential scanning calorimeter (DSC 7) and visually with a Mettler FP 82 hot-stage mounted on a Nikon microscope. The crystals melted at 96.8° to give a viscous anisotropic phase followed by transition to the isotropic liquid phase at

TABLE I

CRYSTAL STRUCTURE AND REFINEMENT DATA FOR HEPTYL 1-THIO-α-D-GLUCOPYRANOSIDE

	$C_{13}H_{26}O_5S$
Molecular weight	294.41
Crystal type	monoclinic
Space group	$P2_1$, $Z = 2$
Cell dimensions a(Å)	6.013(1)
b(Å)	7.324(1)
c(Å)	17.536(4)
β(deg)	98.21(2)
V(Å^3)	764.4
Crystal dimensions (mm)	0.40 × 0.35 × 0.25
D_{calc} (g.cm^{-3})	1.279
Radiation	graphite-monochromated MoK_α
Cell dimensions based on 25 reflections	$10.2 \leq \theta \leq 22.7°$
μ_{calc} (cm^{-1})	2.15
Intensity measured by	2814 reflections, 2814
$\theta/2\theta$ scans on Nonius	unique, 2644 with $I > 3\sigma(I)$
CAD4-F diffractometer	used in analysis
Final agreement factors:	
$R=\Sigma\|\|F_o\| - \|F_c\|\|/\varepsilon\|F_o\|$	0.030
$R_w=[\varepsilon w(\|F_o\| - \|F_c\|)^2/\varepsilon w\|F_o\|^2]^{1/2}$	0.039
G (goodness of fit)	1.6
No. of parameters	215

TABLE II

POSITIONAL PARAMETERS[a] AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR HEPTYL 1-THIO-α-D-GLUCOPYRANOSIDE AT 130 K

Atom	x	y	z	$B(Å^2)^b$
S-1	0.70697(8)	0.915	0.23766(3)	1.065(7)
O-2	0.8840(3)	0.8298(2)	0.09097(9)	1.24(3)
O-3	1.0564(2)	1.1742(2)	0.04647(8)	1.02(2)
O-4	0.9317(2)	1.4754(2)	0.13659(9)	1.15(3)
O-5	0.4654(2)	1.1536(2)	0.14020(8)	0.89(2)
O-6	0.3593(3)	1.5409(2)	0.10459(9)	1.35(3)
C-1	0.5813(3)	0.9826(3)	0.1404(1)	0.93(3)
C-2	0.7580(3)	0.9951(3)	0.0857(1)	0.89(3)
C-3	0.9134(3)	1.1592(3)	0.1049(1)	0.78(3)
C-4	0.7777(3)	1.3345(3)	0.1090(1)	0.82(3)
C-5	0.6098(3)	1.3050(3)	0.1660(1)	0.84(3)
C-6	0.4650(3)	1.4699(3)	0.1761(1)	1.13(3)
C-7	0.4527(4)	0.9355(4)	0.2822(1)	1.62(4)
C-8	0.4901(4)	0.8648(4)	0.3648(1)	1.62(4)
C-9	0.2988(4)	0.9240(4)	0.4080(1)	1.68(4)
C-10	0.3179(4)	0.8513(4)	0.4902(1)	1.69(4)
C-11	0.1338(4)	0.9250(5)	0.5333(1)	1.67(4)
C-12	0.1425(4)	0.8521(4)	0.6150(1)	2.07(5)
C-13	−0.0426(4)	0.9292(6)	0.6563(1)	2.54(5)
H-1	0.476	0.890	0.123	
H-2	0.685	1.012	0.034	
H-2′	0.936	0.807	0.043	
H-3	1.001	1.142	0.154	
H-3′	1.209	1.166	0.070	
H-4	0.698	1.366	0.060	
H-4′	0.863	1.590	0.123	
H-5	0.697	1.282	0.215	
H-6	0.557	1.562	0.202	
H-6′	0.352	1.436	0.206	
H-6″	0.209	1.498	0.096	
H-7′	0.410	1.060	0.282	
H-7	0.336	0.867	0.253	
H-8	0.628	0.912	0.390	
H-8′	0.497	0.735	0.364	
H-9	0.161	0.882	0.380	
H-9′	0.297	1.054	0.410	
H-10	0.460	0.886	0.517	
H-10′	0.307	0.722	0.488	
H-11	−0.007	0.893	0.505	
H-11′	0.148	1.054	0.536	
H-12	0.284	0.883	0.644	
H-12′	0.128	0.723	0.613	
H-13″	−0.014	1.055	0.667	
H-13	−0.183	0.917	0.624	
H-13′	−0.046	0.864	0.703	

[a]Estimated standard deviations, given in parentheses, refer to the least significant digit. [b]Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) × [a2 × B(1,1) + b2 × B(2,2) + c2 × B(3,3) + ab(cosγ) × B(1,2) + ac(cosβ) × B(1,3) + bc(cosα) × B(2,3)].

TABLE III

BONDS LENGTHS IN HEPTYL 1-THIO-α-D-GLUCOPYRANOSIDE

Bond	*Length (Å)*[a]	*Bond*	*Length (Å)*[a]
C-1–C-2	1.533(3)	C-1–S	1.831(2)
C-2–C-3	1.530(3)	S–C-7	1.819(3)
C-3–C-4	1.528(3)		
C-4–C-5	1.534(3)	C-7–C-8	1.524(3)
C-5–C-6	1.514(3)	C-8–C-9	1.528(3)
		C-9–C-10	1.526(3)
C-1–O-5	1.433(3)	C-10–C-11	1.525(3)
C-2–O-2	1.424(3)	C-11–C-12	1.523(3)
C-3–O-3	1.433(3)	C-12–C-13	1.521(4)
C-4–O-4	1.424(3)		
C-5–O-5	1.441(2)		
C-6–O-6	1.421(3)		

[a]Estimated standard deviations, given in parentheses, refer to the least significant digit.

138.3°. On cooling, a liquid crystalline phase was formed that was largely pseudoisotropic with areas of focal conic fan texture.

A Guinier powder X-ray photograph showed a strong, fairly sharp, single line that corresponded to a d-spacing of 23.1 Å. The combined data are indicative of a smectic A_d phase.

The diffraction data were measured[5] at 130 K on a Nonius CAD4-F diffractometer interfaced to a PDP/11-23 with graphite-monochromated MoK_α-radiation in the θ–2θ scan mode. Scaling factors and Lorentz and polarization corrections were applied, but no absorption corrections were made.

The structure was solved by direct methods; computer software: SDP/PDP[6]. The positions of the H-atoms were revealed from a single difference Fourier-map

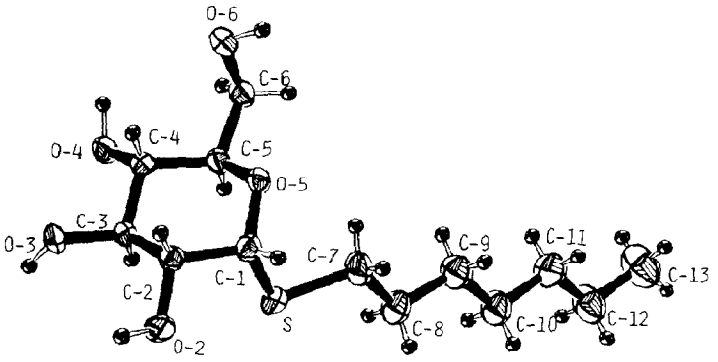

Fig. 1. Atomic notations and thermal ellipsoids at 50% probability for heptyl 1-thio-α-D-glucopyranoside (**1**).

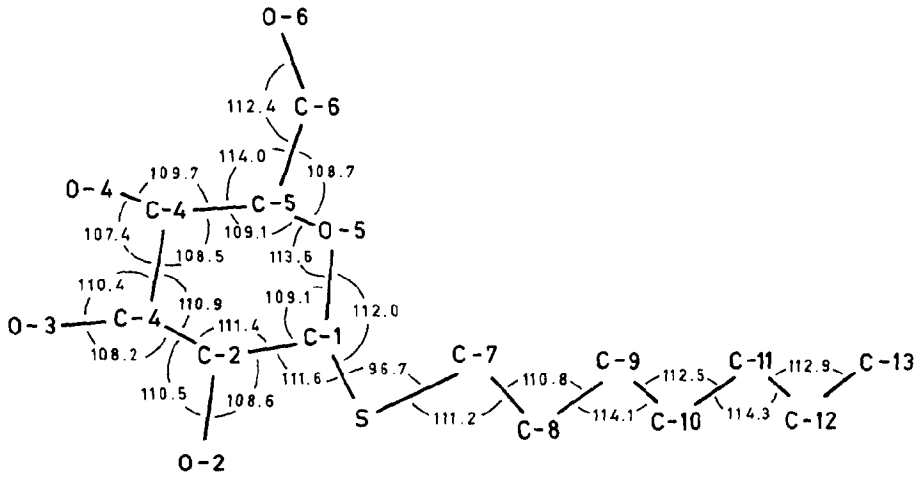

Fig. 2. Valence-bond angles (°) of heptyl 1-thio-α-D-glucopyranoside (**1**) at 130 K; maximum estimated standard deviations are ±0.2°.

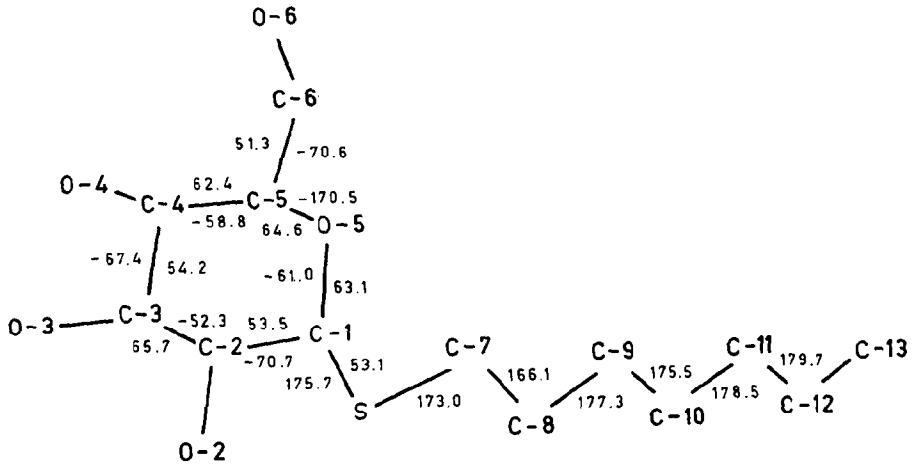

Fig. 3. Torsion angles (°) of heptyl 1-thio-α-D-glucopyranoside (**1**) at 130 K; maximum estimated standard deviations are ±0.2°.

based on all the non-hydrogen atoms. Refinement was carried out in a block-diagonal least-squares procedure using anisotropic temperature factors for the non H-atoms and isotropic fixed temperature factors (B = 5.0 Å^2) for the H-atoms. In the final refinements, the H-atoms were constrained to their corresponding atoms at a distance of 0.95 Å. Crystal and refinement data* are given in Table I. The

*Lists of general temperature factor expressions, observed and calculated structure factors, *etc.* are deposited with, and can be obtained from, Elsevier Science Publishers, B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/424/*Carbohydr. Res.*, 194 (1989) 79–86.

atomic notation and thermal ellipsoids are shown in Fig. 1, atomic positional parameters are listed in Table II, and valence bond lengths in Table III. Valence-bond angles and torsion angles are shown in Figs. 2 and 3.

DISCUSSION

The molecular packing of **1**, shown in Fig. 4, is similar to that of other long-chain alkyl pyranosides[7-9]. The carbohydrate moieties form hydrogen-bonded double layers. The hydrocarbon chains extend from these layers and interdigitize with the alkyl chains of the next layer. There are four obvious hydrogen bonds. These and other close hydrogen–oxygen contacts are compiled in Table IV.

Further analysis of the packing, kindly provided by Professor G. A. Jeffrey (University of Pittsburgh), reveals the character of the hydrogen bonding. Finite chains originate at HO-6 and terminate at O-5. This is type II hydrogen bonding in the classification proposed[10] for pyranoses and pyranosides. These finite chains are linked into a network by the minor component of the three-center bond originating from HO-6 as shown in Fig. 5, where the O–H covalent bond lengths have been normalized to 0.97 Å to correct for the charge density effect[11,12].

It is difficult to compare the crystal structure of **1** with that of octyl α-D-gluco-pyranoside[7], because the hydrogen bonding of the latter is influenced by the

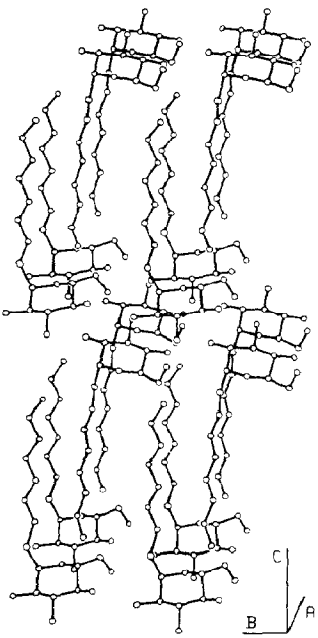

Fig. 4. Molecular packing in the crystal of heptyl 1-thio-α-D-glucopyranoside (**1**).

TABLE IV

CLOSE OXYGEN/HYDROGEN CONTACTS IN HEPTYL 1-THIO-α-D-GLUCOPYRANOSIDE

Atom 1	*Atom 2*	*Distance (Å)*[a]	*Atom 1*	*Atom 2*	*Distance (Å)*[a]
O-2	H(O-3)	3.038(2)	O-4	H(O-2)	2.931(2)
O-2	H(O-4)	1.854(2)	O-4	H(O-6)	1.909(2)
O-3	H(O-2)	2.784(2)[b]	O-5	H(O-3)	1.837(1)
O-3	H(O-2)	1.854(2)	O-5	H(O-6)	3.001(1)[b]
O-3	H(O-6)	2.644(2)	O-6	H(O-3)	2.931(2)
O-3	H(O-6)	3.052(1)	O-6	H(O-4)	3.067(2)
			O-6	H(O-4)	3.024(2)[b]

[a]Numbers in parentheses are estimated standard deviations in the least significant digits. [b]Denotes intramolecular contacts.

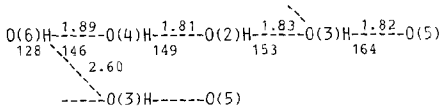

Fig. 5. Hydrogen bonding in heptyl 1-thio-α-D-glucopyranoside (**1**); distances in Å, angles in degrees.

presence of water in the crystal. Comparison of the crystal structure of **1** with that of the 2-epimer heptyl 1-thio-α-D-mannopyranoside[8] reveals some striking differences. The glycosidic torsion angle (O-5–C-1–S–C-7) is significantly smaller (53.1° *vs.* 67.7°), and the torsion angles in the heptyl chain are further removed from the ideal all-*trans* conformation, most notably S–C-7–C-8–C-9, which has a torsion angle of 166.1°. The angle between the plane of the ring and the alkyl chain is larger for **1** than for the thiomannopyranoside. This difference is also reflected in the d-spacing of the liquid crystalline layers (23.1 Å in **1** *vs.* 20–21 Å for heptyl 1-thio-α-D-mannopyranoside). With access to crystal data for other closely related compounds, it may become possible to correlate carbohydrate configuration to thermal behavior.

ACKNOWLEDGMENT

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