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Crystal structures and thermotropic properties of alkyl α-D-glucopyranosides and their hydrates

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Abstract

Thermotropic properties and crystal structures of alkyl α-D-glucopyranosides and their hydrates were estimated by X-ray, DSC and thermogravimetric measurements (TGA). Monohydrates rapidly lose their crystal water several degrees below the melting point of the anhydrous glucopyranosides. The melting points of the monohydrates measured in DSC pressure cells (chain length longer than seven) are lower, and the clearing points higher than those of the anhydrous glucosides. Layer distances of smectic and crystalline phases of anhydrous compounds were established. Melting points, densities and layer distances of the crystalline anhydrous glucopyranosides display strong even–odd effects. The strong decrease of these effects in the case of the monohydrates can be elucidated by the results of X-ray crystal structure analysis. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Alkyl α-D-glucopyranoside monohydrates; X-ray; Single crystal; DSC; TGA

1. Introduction

Fischer and Helfrich [1] published in 1911 a ‘double melting point’ for alkylglucosides. Noller and Rockwell [2] characterised this as transition to a liquid crystalline phase. Transition temperatures [1,3–12], enthalpies [4–6,10] and layer distances (distance of two identical layers) of the thermotropic [5,9,10,13] and crystalline phase [5,9,13] have been published for β anomers but less so for α anomers. The liquid crystalline phase was found to be type smectic A in all cases [5,9,10,13,14]. Below the melting point crystal–crystal transitions were found in some cases, especially for β anomers [1,6,9,10,12].

There are only a few papers that deal with hydrates of alkylglucopyranosides. Straathof et al. [15] described the crystallisation of octyl α-D-glucopyranoside monohydrate from the crude reaction products of the Fischer synthesis upon addition of petroleum ether and its DSC behaviour [16]. The monohydrates of heptyl to decyl α-D-glucopyranosides can be directly obtained by crystallisation, from water at room temperature, of the α/β mixtures (Fischer synthesis) [17]. Focher et al. [6] found a lower melting point of hydrated octyl α-D-glucopyranoside (stored at 90% relative humidity) relative to the anhydrous compound.

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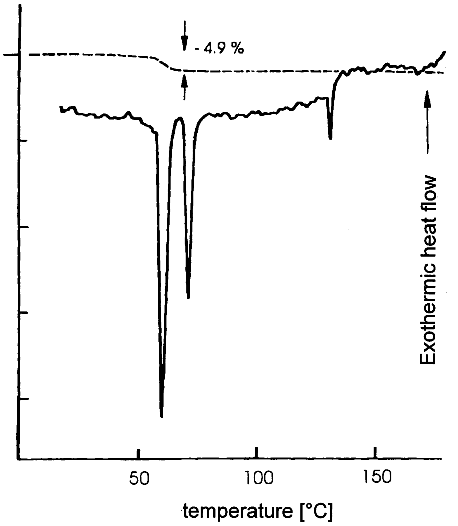

Fig. 1. TGA of nonyl α-D-glucopyranoside: solid line, heat flow; dotted line, mass loss.

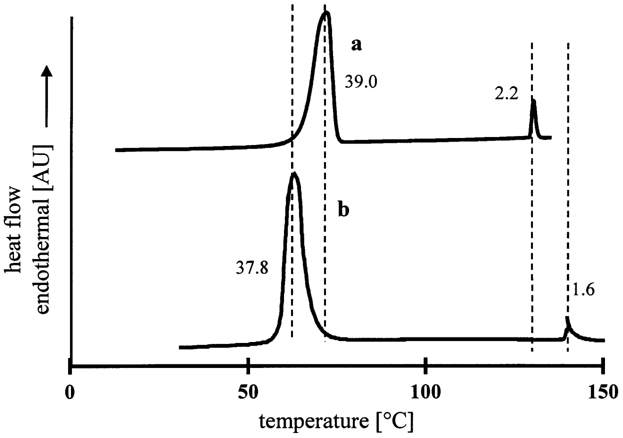

Fig. 2. Differential scanning calorimetry. (a) Anhydrous nonyl α-D-glucopyranoside $dT/dt = 10$ °C min^{-1}; (b) nonyl α-D-glucopyranosid monohydrate $dT/dt = 5$ °C min^{-1}. Numbers indicate endothermic transition enthalpies in kJ mol^{-1}.

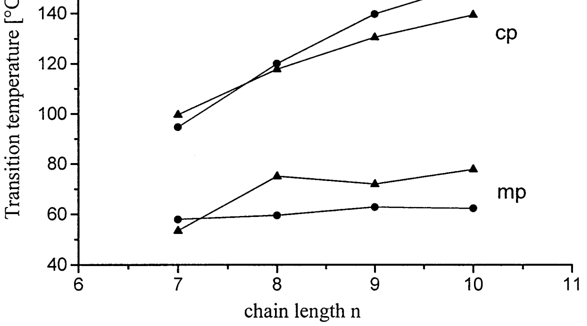

Fig. 3. Clearing point cp and melting point mp of heptyl to decyl α-D-glucopyranosides: ▲, anhydrous compounds; ●, monohydrates.

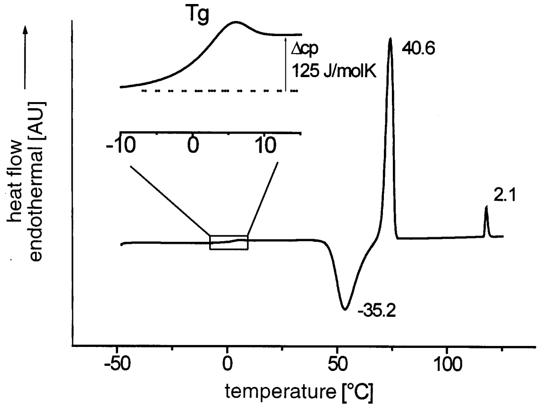

Fig. 4. Second heating differential scanning calorimetry curve of octyl α-D-glucopyranoside with glass transition at 0 °C and recrystallisation at 53.5 °C. $dT/dt = 10$ °C min^{-1}. Numbers indicate endothermic transition enthalpies in kJ mol^{-1}.

Prade and et al. [18] made the general statement that a certain content of water could lead to lower melting and higher clearing points.

The first structural description of an alkyl α-D-glucopyranoside (decyl α-D-glucopyranoside) was published in 1976 by Moews and Knox [19]. The structures of the anhydrate [20], monohydrate [21] and hemihydrate [21] of octyl α-D-glucopyranoside followed in 1987 and 1988, hexyl α-D-glucopyranoside and heptyl α-D-glucopyranoside monohydrate in 1998 [17]. In contrast, only the methyl β-D-glucopyranoside hemihydrate [22] and a mixture of the octyl α/β-D-glucopyranoside (equal ratio) [23] have been published.

In this paper the structures of heptyl and nonyl α-D-glucopyranoside, decyl α-D-glucopyranoside monohydrate and hexyl α-D-glucopyranoside hemihydrate and new data on the liquid crystal behaviour of the α compounds and their monohydrates are presented. The reason for the extended even–odd effects of physical properties of the anhydrous crystal and their strong decrease in the case of the monohydrate and the liquid phase is discussed.

2. Experimental

Materials.—Mixtures of α:β (7:3) alkyl α-D-glucopyranosides were obtained by Fischer synthesis. Monohydrates of heptyl to decyl α-glucopyranosides were separated from these

Table 1
Transition temperatures and enthalpy values for anhydrous alkyl α-D-glucopyranosides

n [a]	Tg (mp)	Transitions								Lit.
		Glass temperature		Recrystallisation [b]		Melting point		Clearing point		
		Tg (°C)	Δc_p (J mol^{-1} °C)	t_{max} (°C)	ΔH (kJ mol^{-1})	Mp (°C)	ΔH (kJ mol^{-1})	Cp (°C)	ΔH (kJ mol^{-1})	
7	0.80	−12.4	120			53.4	28.7	99.6	1.4	
						51.5	26.15	97.9	1.21	[4]
8	0.78	0.0	125	53.5	−35.2	75.1	40.6	117.8	2.1	
						73	46.4	117	1.8	[6]
						71.8	36.82	117	2.05	[5]
						54.9	35.27	120.1	1.77	[4]
						69		116		[8]
						57 [c]	10.2	120 [c]	0.3	[16]
9	0.79	+1.1	92			71.9	39.0	130.4	2.2	
						57.0	33.35	128.0	1.88	[4]
10	0.79	−1.4	122	56.3	−33.4	77.8	46.2	139.4	2.2	
						70.3	38.07	134.2	0.70	[4]
11				60.2	−22.5	80.6	47.0	145.9	2.1	
12						81	61.5	149	2.4	[6]
13				32.1, 38.5	−6.7, −17.8	86.1	58.3	150.6	2.0	
14				46.3 [d]	−34.5	84.9	60.8	150.5	1.8	

[a] n = chain length.

[b] Crystallisation in second heating curve.

[c] Estimated from published DSC curve.

[d] Crystallisation in first cooling curve.

mixtures by crystallisation from water [17]; all anhydrous glucopyranosides were crystallised from organic solvents [17,24].

Preparation of single crystals for X-ray measurements.—Approximately 0.5–1.0 wt% of anhydrous heptyl or nonyl α-D-glucopyranosides were dissolved in EtOAc (distilled) at about 70 °C. The sample tubes were slowly cooled to room temperature and stored for 3–5 days. When no crystallisation was observed after this time, the cap of the reagent tube was slightly opened to allow slow evaporation. Single crystals were typically obtained within 2 weeks. Decyl α-D-glucopyranoside monohydrate and hexyl α-D-glucopyranoside hemihydrate were crystallised from EtOAc saturated with water.

DSC.—For differential-scanning calorimetric (DSC) measurements of the anhydrous glucopyranosides a Perkin–Elmer DSC 7 instrument was used. In total 5–10 mg (lyophilised) were examined in sealed aluminium pans with a scan rate of 10 K min^{-1}. The monohydrates (recrystallised from water) were measured in steel pressure vessels with a Setaram DSC 141 instrument. The scan rate was 5 K min^{-1}. Indium was used for calibration of both instruments.

TGA.—Thermogravimetric analysis (TGA) was performed in a Seteram TGA 92–16.18 unit. The heating rate was 10 K min^{-1} and the helium stream flow 20 ml min^{-1}.

X-ray investigations on thermotropic phases.—For this purpose a Guinier camera (Huber Diffraktionstechnik, Rimsting) and for calibration a self-constructed small-angle X-ray camera of the institute in Halle were used.

Structure analysis.—All structures were analysed at 296 K on a Siemens P4 diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 71.073$ pm); the intensity of the primary beam was controlled by monitoring three reference reflections every 100 reflec-

Table 2
Transition temperatures and enthalpy values for alkyl α-D-glucopyranoside monohydrates

n [a]	Melting point		Clearing point		Lit.
	Mp (°C)	ΔH (kJ mol^{-1})	Cp (°C)	ΔH (kJ mol^{-1})	
7	57.9	26.4	94.7	0.6	
8	59.5	30.3	120.0	1.2	
	73 [b]	11.2	117 [b]	0.4	[16]
9	62.8	37.8	139.7	1.6	
10	62.3	34.5	151.7	1.8	

[a] n = chain length.

[b] Estimated from published curve from literature.

Table 3
Single-crystal data of alkyl α-D-glucopyranosides [a]

Chain length n	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	Z	D_x (g cm^{-3})	Lit.
Anhydrous								
6	5.115(2)	7.589(2)	17.795(4)	96.11(3)	686.8(4)	2	1.278	[17]
7	6.127(2)	7.239(2)	17.045(3)	92.00(3)	755.6(3)	2	1.223	
8	5.140(2)	7.604(2)	19.939(4)	92.18(2)	778.7(2)	2	1.25	[20]
9	6.110(2)	7.248(2)	19.325(2)	95.69(2)	851.6(4)	2	1.195	
10	5.153(2)	7.626(4)	22.125(7)	90.95(4)	869.3	2	1.220	[19]
Hemihydrate								
6	15.160(4)	5.016(2)	19.063(5)	101.58(2)	1420.1(8)	4	1.278	
8	15.190(5)	5.136(3)	19.944(7)	92.74(3)	1554.2(10)	4	1.288	[21]
Monohydrate								
7	18.304(4)	4.971(2)	19.620(4)	115.11(3)	1616.4(8)	4	1.218	[17]
8	17.896(2)	5.154(1)	18.303(2)	90.30(1)	1688.2(4)	4	1.221	[21]
10	17.818(7)	5.140(2)	20.968(7)	92.49(3)	1918.7(12)	4	1.172	

[a] The unit cells with $Z = 2$ belong to the space group $P2_1$, with $Z = 4$ to $C2$.

Table 4
Data pertaining to the crystal structure determination

	Heptyl α-D-glucopyranoside	Nonyl α-D-glucopyranoside	Decyl α-D-glucopyranoside-monohydrate	Hexyl α-D-glucopyranoside-hemihydrate
M (g mol^{-1})	278.35	306.40	338.44	273.33
Crystal dimensions (mm)	0.40 × 0.20 × 0.15	0.50 × 0.25 × 0.12	0.50 × 0.20 × 0.15	0.60 × 0.15 × 0.04
Collected reflections	4038	4551	3864	3727
2θ Range (°)	3–55	3–50	3–50	3–55
Independent	3464	3903	3360	3253
$F_o \geq 2\sigma(F_o)$	3351	3741	2726	2655
Parameters	173	191	209	171
R/R_w [$w^{-1} = \sigma^2(F_o)$]	0.052/0.053	0.056/0.058	0.081/0.093	0.084/0.106
Max/min residual electron density (e Å^{-3})	0.65/−0.30	0.66/−0.35	0.35–0.33	0.74/−0.66

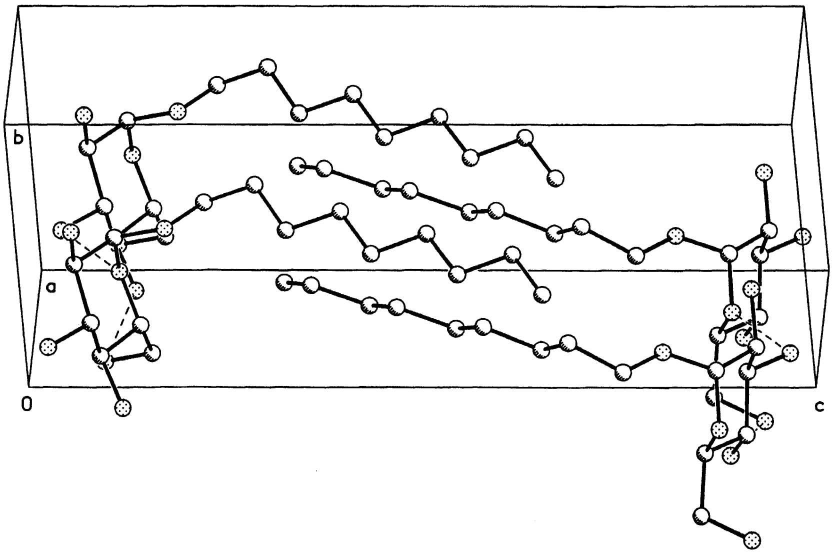

Fig. 5. Crystal structure of nonyl α-D-glucopyranoside.

tions. The structures were solved by direct methods and refined against F by full-matrix least-squares using the program package SHELXTL V.4.2 [25]. The positions of the hydrogen atoms were geometrically calculated and refined with fixed U values (0.08 Å^2) applying the riding model. All non-hydrogen atoms were refined anisotropically.

The X-ray diffraction patterns were obtained with an Enraf–Nonius PDS 120 diffractometer using Cu K_α radiation ($\lambda = 154.059$ pm).

3. Results and discussion

DSC and thermogravimetry.—A typical thermogravimetric curve of the monohydrates is shown in Fig. 1.

Transition temperatures of the monohydrates were unexpectedly different for DSC and thermogravimetry (Figs. 1 and 2). In the DSC pressure vessels only a negligible amount of water must be evaporated to maintain the equilibrium pressure of the monohydrates. In TGA, the monohydrates lose their crystal water several degrees below the melting point and consequently the second and third TGA peak represent the melting and clearing point of the anhydrous glucopyranosides, respectively.

The transition points of the monohydrates and of the anhydrous compounds are collected as a function of the chain length (Fig. 3). The melting points of the anhydrous glucosides display remarkable even–odd effects [4,14,18], which are typical of many crystalline compounds [26–28]. This effect is less pronounced for the monohydrates.

The monohydrates of octyl to decyl α-D-glucopyranoside have lower melting but higher clearing points than the anhydrous compounds. Heptyl α-D-glucopyranoside display the opposite characteristics. The melting process of anhydrous heptyl (50.4–53.4 °C) and tetradecyl α-D-glucopyranoside (80.8–84.9 °C) is characterised by two overlapping peaks, whose origin was not clarified. A crystal–crystal transition could be taken into account. The thermotropic phases can be strongly supercooled and glass transitions at the temperature *T*g are observed. *T*g divided by the melting point mp is 0.79 ± 0.01 (Fig. 4 and Table 1), as expected for typical macromolecules [29].

Recrystallisation on heating is observed for octyl, decyl, undecyl and tridecyl α-D-glucopyranosides, but not for heptyl, nonyl and dodecyl α-D-glucopyranosides (Fig. 4 and Table 1). The recrystallisation of tetradecyl α-D-glucopyranoside is so fast that it occurs at the cooling curve about 40 °C below the melting point. The differences in melting enthalpies of the anhydrous glucosides and monohydrates are low for compounds with an odd number of carbon atoms (seven: 2.3 kJ mol^{-1} and nine: 1.2 kJ mol^{-1}) and high for those with even numbers (eight: 10.3 kJ mol^{-1} and ten: 11.7 kJ mol^{-1}) (Tables 1 and 2). This indi-

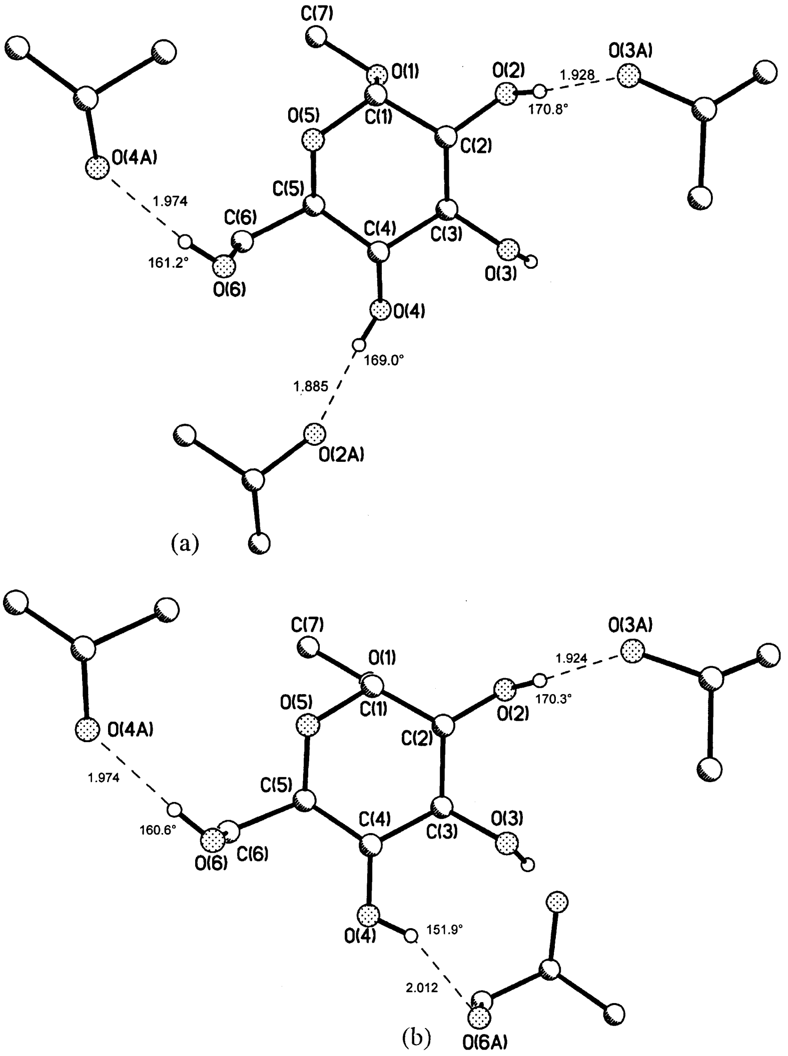

Fig. 6. Hydrogen bonding in the crystal structure of heptyl α-D-glucopyranoside (a) and of nonyl α-D-glucopyranoside (b). The H···O distances are given in Å. For the purpose of clarity, only the first carbon atom of the alkyl chain is shown.

Table 5
Chain arrangement of the different crystal structures

Compounds	Even	Odd
Anhydrous	all-trans conformation chain direction and chain planes are parallel whole molecule is stretched	single gauche conformation at O1C7–C8C9 chain planes perpendicular to each other but chain directions parallel chain directions nearly perpendicular to the sugar group
Hemihydrate	n [a] = 6 single gauche conformation at O1C7–C8C9 chain planes perpendicular to each other, chain directions parallel n [a] = 8 all-trans conformation chain direction and chain planes parallel whole molecule is stretched	unknown until now
Monohydrate	chain planes parallel chain directions crossed	chain planes parallel chain directions crossed

[a] n = chain length.

cates that the anhydrous glucopyranosides with even carbon atoms should have the highest lattice energy.

Crystal structures.—Table 3 shows the essential data of the crystal structures. For comparison, all known glucopyranosides are included. Refinement data are listed in Table 4. Hydrogen bondings are represented in Figs. 6, 9 and 11. The crystal structure of the alkyl α-D-glucopyranosides contains alternating bilayers of sugar groups and layers of interdigitizing hydrocarbon chains with characteristically different chain arrangements. The chains are slightly curved and tilted. In a good approximation, all carbon atoms of a chain are located in a single plane (chain plane). The different arrangement of the chains can be described using the chain planes and the directions of the chains (Table 5).

Heptyl and nonyl α-D-glucopyranosides. Anhydrous heptyl and nonyl α-D-glucopyranosides (Fig. 5) form platelets in the space group $P2_1$, as well as hexyl, octyl and decyl α-D-glucopyranosides [17,19,20]. The directions of alkyl chains are ordered parallel to each other. However, there are remarkable differences in the orientation of the chain planes between the compounds with even and odd numbers of carbon atoms (Table 5). The single gauche conformation (Table 6) of the anhydrous compounds with odd numbers of carbon atoms permits shorter layer distances (see Fig. 12) and lower densities (Fig. 7). The densities of the hydrocarbon chains calculated from the linear slope of the molar volume, V_m, as a function of the chain length (Fig. 7) are similar for compounds with even ($\rho = 1.003$ g cm^{-3}) and odd numbers of carbon atoms ($\rho = 0.986$ g cm^{-3}). It should be emphasised that these values are very close to the density of crystalline polyethylene ($\rho = 1.004$ g cm^{-3}) [30].

Decyl α-D-glucopyranoside monohydrate. Decyl α-D-glucopyranoside monohydrate crystallises as needles in the space group $C2$ like all other monohydrates [17,21]. Interestingly, the structures of the monohydrates and anhydrous glucosides are quite different. The incorporation of water results in an arrangement of the sugar groups different from that

Table 6
Torsion angle τ (°) (O1C7–C8C9) of alkyl α-D-glucopyranosides

Chain length n	Anhydrous	Hemihydrate
6	175.7(0.3)	
7	59.4(0.4)	−72.5
8	4.4(0.4) [20]	180 [a] [21]
9	60.1(0.4)	
10	180 [a] [19]	

[a] The alkyl chains are fully extended, but no exact values are given in the literature.

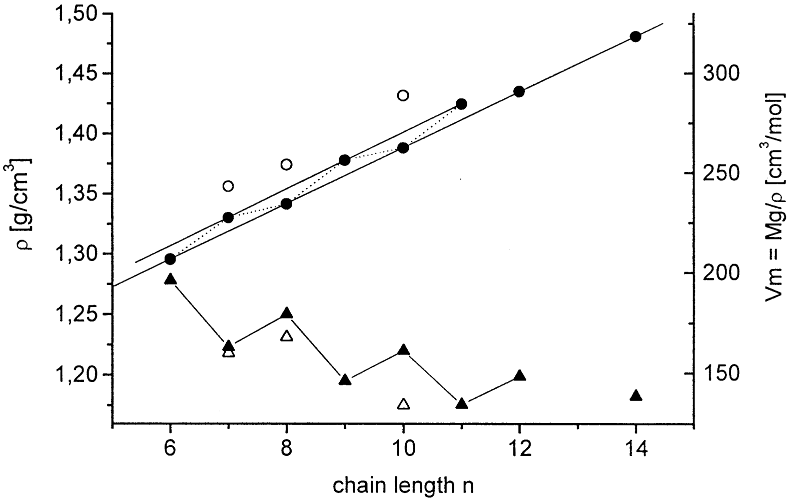

Fig. 7. Molar volume ● and density ▲ of the alkyl α-D-glucopyranosides and their monohydrates (open symbols).

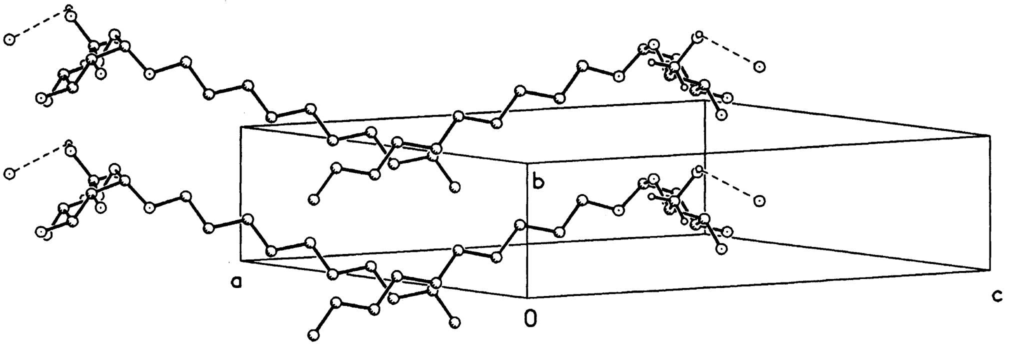

Fig. 8. Crystal structure of decyl α-D-glucopyranoside monohydrate. For the purpose of clarity not all molecules of the unit cell are shown.

of the anhydrous glucosides. The driving force arises from the strong hydrogen-bridging bonds (Fig. 9). The conformation is nearly independent of the chain length and the even–odd effect disappears. This means that the hydrogen-bond-stabilised conformation of these sugar groups in the crystal forces the chains into a less favourable packing with crossed chain directions (137° for decyl α-D-glucopyranoside monohydrate) (Fig. 8).

Hexyl α-D-glucopyranoside hemihydrate. In contrast, this hemihydrate is formed by crystallisation from aqueous ethyl acetate. The crystals are needles in the space group *C*2. Although hexyl and octyl α-D-glucopyranoside hemihydrate crystallise in the same space group, there are characteristic differences in the conformation of the chains, which are displayed in Tables 5 and 6 (Figs. 10 and 11).

Layer distances.—Bilayer structures with head-to-head sugar groups have been reported for the thermotropic phases and the crystalline phases [5,9,10,13,14,17,19–21] of the alkyl α and β-D-glucopyranosides (Table 7). The different crystallisation properties of α and β glucosides become more obvious upon comparison of the layer distances in the crystalline and the liquid crystalline state for both anomers. The layer distances of the α anomers were calculated from crystal data by $d = c\sin\beta$ (d, layer distance; c, cell axis c; β, monoclinal angle); those of the β anomers are known only from X-ray powder patterns [5,9,10,13] (Fig. 12).

A characteristic feature of the anhydrous alkyl α-D-glucopyranosides is the distinct even–odd effect in the crystalline phase. The α anomers display the smallest layer distances because of their interdigitated alkyl chains. The high layer distances and slope of the crystalline β anomers is because the chains are not interdigitated [13], and so no even–odd effect is observed. The big differences between the layer distances of the α and β glucosides decrease in the liquid crystalline phase. The nearly complete disappearance of the even–odd effect can be explained by the fluid structure of the chains in the liquid crystalline phases. The even–odd effect of the monohydrates is very small, because of their low chain order.

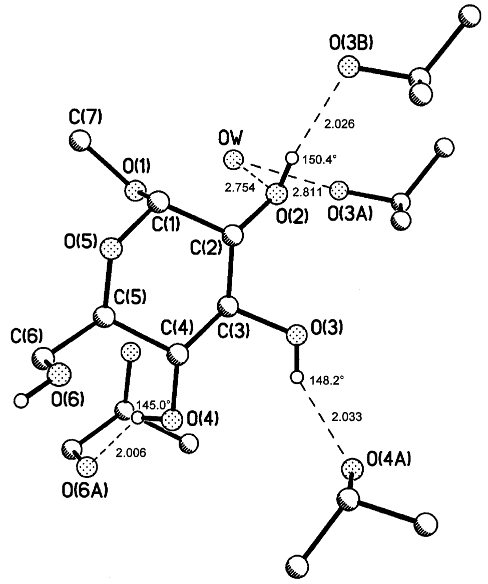

Fig. 9. Hydrogen bonding in the crystal structure of decyl α-D-glucopyranoside monohydrate. The H···O distances are given in Å. For the purpose of clarity only the first carbon atom of the alkyl chain is shown.

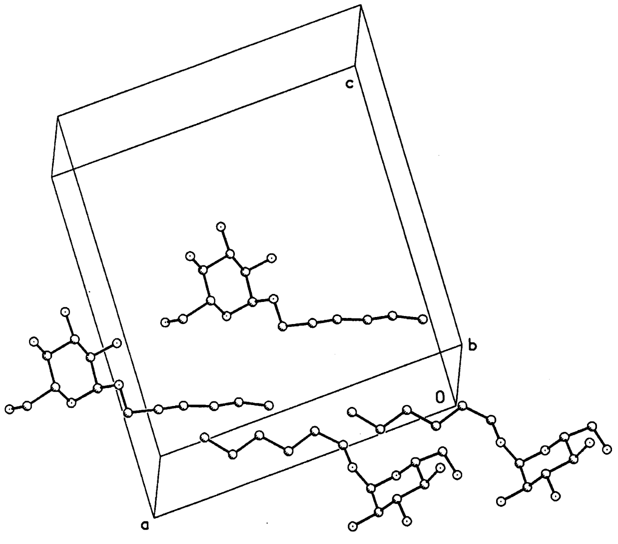

Fig. 10. Crystal structure of hexyl α-D-glucopyranoside hemihydrate. For the purpose of clarity not all molecules of the elementary cell are shown.

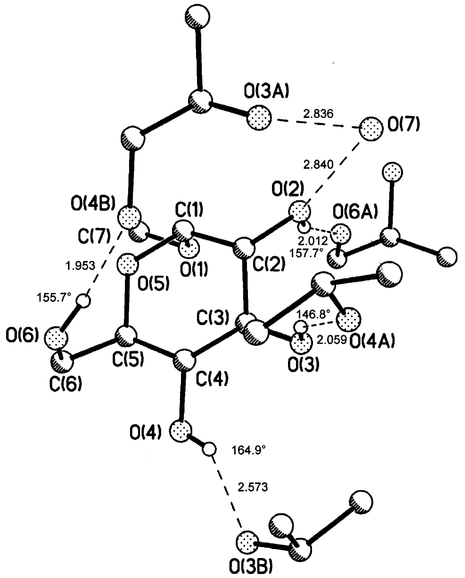

Fig. 11. Hydrogen bonding in the crystal structure of hexyl α-D-glucopyranoside hemihydrate. The H···O distances are given in Å. For the purpose of clarity only the first carbon atom of the alkyl chain is shown.

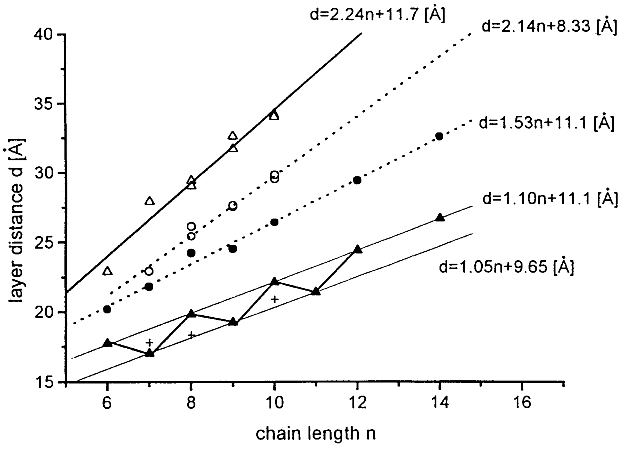

Fig. 12. Layer distances *d* as a function of the chain length *n*. Open symbols, alkyl β-D-glucopyranosides [5,9,10,13]; full symbols, alkyl α-D-glucopyranosides; ▲ crystalline phase, ● liquid crystalline phase, + monohydrates.

4. Supplementary material

Tables of atomic coordinates, bond lengths, and bond angles have been deposited at the Cambridge Crystallographic Data Centre. These tables may be obtained on request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on quoting CCDC-135427 for nonyl α-D-glucopyranoside, CCDC-135428 for decyl α-D-glucopy-

Table 7
Layer distances *d* of alkyl α- and β-D-glucopyranosides both in crystalline and thermotropic phase

Chain length *n*	Alkyl α-D-glucopyranosides		Alkyl β-D-glucopyranosides	
	Crystalline (Å)	Liquid crystal (Å)	Crystalline (Å)	Liquid crystal (Å)
Anhydrous				
6	17.7 [17]	20.2	22.9 [13]	
7	17.03	21.8	27.9 [9]	22.9 [9]
				22.9 [10]
8	19.92	24.2	29.4 [9]	26.1 [9]
	19.8 [5]	23.3 [5]	29.4 [5]	26.1 [10]
	19.7 [13]		29.0 [13]	25.4 [13]
	19.9 [20]			
9	19.2	24.5	32.6 [9]	27.6 [9]
			31.7 [13]	27.6 [10]
				27.5 [13]
10	22.1 [19]	26.4	34.0 [9]	29.5 [9]
			34.2 [13]	29.5 [10]
				29.8 [13]
11	21.40			
12	24.41	29.4		
14	26.65	32.6		
Monohydrate				
7	17.8 [17]			
8	18.3 [21]			
10	20.9			

ranoside monohydrate, CCDC-135429 for heptyl α-D-glucopyranoside and CCDC-13430 for hexyl α-D-glucopyranoside hemihydrate.

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References

[1] E. Fischer, B. Helferich, *Justus Liebigs Ann. Chem.*, 383 (1911) 68–91.

[2] C.R. Noller, W.C. Rockwell, *J. Am. Chem. Soc.*, 60 (1938) 2076–2077.

[3] G.M. Brown, P. Dubreuil, F.M. Ichhaporia, J.E. Desnoyers, *Can. J. Chem.*, 48 (1970) 2525–2531.

[4] E. Barrall, B. Grant, M. Oxsen, E.T. Samulski, P.C. Moews, J.R. Knox, R.R. Gaskill, J.L. Haberfeld, *Org. Coat. Plast. Chem.*, 40 (1979) 67–74.

[5] D.L. Dorset, J.P. Rosenbusch, *Chem. Phys. Lipids*, 29 (1981) 299–307.

[6] B. Focher, G. Savelli, G. Torri, *Chem. Phys. Lipids*, 53 (1990) 141–155.

[7] B. Pfannemüller, W. Welte, E. Chin, J.W. Goodby, *Liq. Cryst.*, 4 (1986) 357–370.

[8] P. Sakya, J.M. Seddon, V. Vill, *Liq. Cryst.*, 23 (1997) 409–424.

[9] G.A. Jeffrey, S. Bhattacharjee, *Carbohydr. Res.*, 115 (1983) 53–58.

[10] J.W. Goodby, *Mol. Cryst. Liq. Cryst.*, 110 (1984) 205–219.

[11] D.E. Koeltzow, A.D. Urfer, *J. Am. Oil Chem. Soc.*, 61 (1984) 1651–1655.

[12] H. Kiwada, H. Niimura, Y. Fujisaki, S. Yamada, Y. Kato, *Chem. Pharm. Bull.*, 33 (1985) 753–759.

[13] D.L. Dorset, *Carboydr. Res.*, 206 (1990) 193–205.

[14] G.A. Jeffrey, L.M. Wingert, *Liq. Cryst.*, 12 (1992) 179–202.

[15] A.J.J. Straathof, H. van Bekkum, A.P.G. Kieboom, *Starch/Stärke*, 40 (1988) 229–234.

[16] A.J.J. Straathof, H. van Bekkum, A.P.G. Kieboom, *Starch/Stärke*, 40 (1988) 438–440.

[17] V. Adasch, B. Hoffmann, W. Milius, G. Platz, *Carbohydr. Res.*, 314/3-4 (1998) 177–187.

[18] H. Prade, R. Miethchen, V. Vill, *J. Prakt. Chem.*, 337 (1995) 427–440.

[19] P.C. Moews, J.R. Knox, *J. Am. Chem. Soc.*, 98 (1976) 6628–6633.

[20] G.A. Jeffrey, Y. Yeon, *Carbohydr. Res.*, 169 (1987) 1–11.

[21] H. van Koningsveld, J.C. Jansen, A.J.J. Straathof, *Acta Crystallogr., Sect. C*, 44 (1988) 1054–1057.

[22] G.A. Jeffrey, S. Takagi, *Acta Crystallogr., Sect. B*, 33 (1977) 738–742.

[23] G.A. Jeffrey, Y. Yeon, *Carbohydr. Res.*, 237 (1992) 45–55.

[24] C.G. Biliaderis, D.J. Prokopowich, M.R. Jacobson, J.N. BeMiller, *Carbohydr. Res.*, 280 (1996) 157–169.

[25] G.M. Sheldrick, SHELXTL PLUS V.4.2, Crystallographic System, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1992.

[26] A. Blumstein, O. Thomas, *Macromolecules*, 15 (1982) 1264–1267.

[27] J.-I. Jin, S. Antoun, C. Ober, R.W. Lenz, *Br. Polym. J.*, 12 (1980) 132–146.

[28] A.C. Griffin, S.J. Havens, *J. Polym. Sci., Polym. Phys. Ed.*, 19 (1981) 951–969.

[29] F.W. Billmeyer Jr., *Textbook of Polymer Science*, Interscience Publishers, Wiley, New York, 1962, pp. 212–213.

[30] H.-G. Elias, *Makromoleküle*, fifth ed., Hüthig & Wepf Verlag, Basel-Heidelberg, 1990, p. 746.