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Studies on liquid-crystalline glycosides

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A number of α- and β-glycosides with long chain aliphatic alcohols as aglycones were prepared, and the liquid-crystalline properties of the various mono-, di, and trisaccharide series compared. Further, the first liquid-crystalline glycosides of glucuronic acid and of an amino sugar hydrochloride were detected. It may be concluded that the clearing points increase with (*a*) a larger number of hydrogen bonds, (*b*) a rope-like, space-filling structure, and (*c*) a balanced molecular weight ratio between the polar and apolar parts of the molecule. In all of the cases studied so far only smectic A phases were observed.

1. Introduction

Recently thermotropic liquid-crystalline phases of amphiphilic carbohydrate derivatives have been desribed [1, 2]. Owing to a rigid mesogenic unit and a cylindrical molecular structure classical calamitic liquid crystals exhibit mesomorphic properties [3]. In addition to phases without periodic density modulations (N, Ch, S_D, BP) others with layer structures of various order (S_A . . . S_K) have been observed [4]. Obviously liquid-crystalline carbohydrate derivatives do not need the mesogenic units, and so the amphiphilic molecular structure is decisive for their existance. For most of the compounds studied previously only one liquid-crystalline phase with a layered structure was observed. This could be mixed with the lyotropic lamellar phase [5], and so was identified as a S_A phase [1]. Quite recently, however, forked amphiphiles such as long chain dithioacetales of sugars were reported to exhibit discotic mesophases [6].

The present contribution focuses on the preparation of several glycosides and a study of their properties in order to answer the questions:

are higher ordered or tilted smectic phases formed in addition to S_A phases? and

are there correlations between stereochemistry and mesomorphic properties?

2. General part

A series of data for α- and β-glucopyranosides have been reported in the literature [1, 7–11]. Throughout, β-derivatives with equatorial substituents showed the lowest clearing points of all the hexopyranosides, for α-anomers enhanced clearing points were observed, but these were still notably lower than those of the corresponding *manno* and *galacto* derivatives.

Previously the α-mannopyranosides **3b** and **3c** were reported to show double melting points [12]. Despite their rather high clearing points they did not crystallize

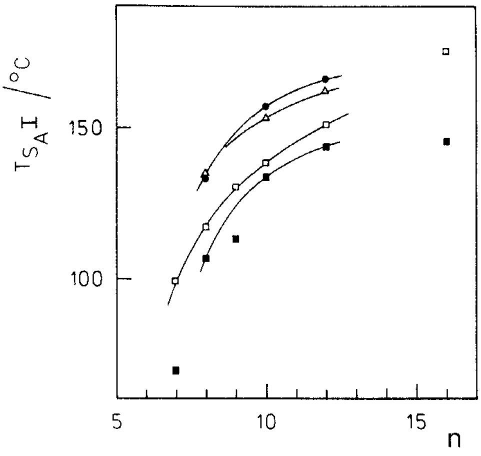


Figure 1. Liquid-crystalline monosaccharide glycosides (the graphs make use of the data for n = 8, 10 and 12). □, α-Glc (**1**); ■, β-Glc (**2**); △, α-Man (**3**); ●, β-Gal (**4**).

readily, however, this could be achieved by annealing at 60°C for 24 hours. The β-galactopyranosides **4a**–**4b** crystallized very well, and showed high clearing points similar to the α-manno derivatives **3a**–**3c**. There is ample evidence that all four homologeous series show similar patterns (cf. figure 1). For a given chain length of the aglyone the clearing points varied over a range of approximately 40°C, owing to the individual constitution of the six-membered ring with its differently arranged hydroxy, hydroxymethylene, and alkoxy groups. In all of these cases the liquid-crystalline phases showed a simple fan-shaped texture as well as the homeotropic texture, and so were identified as S_A phases. The melting point of the dodecyl mannopyranoside **3c** could be supercooled well below room temperature. In this case the phase could be observed over a range of more than 160°C, that is from 161·7° to below 0°C.

Previously evidence was presented that hydrogen bonding is a dominant factor for the formation of structures in liquid-crystalline phases [5]. This does not imply a simple conception of individual oligomeric structures, however, clusters with fluctuating bonds are formed which exist even above temperatures of 200°C [13]. Consequently, by deuteriation this motion should be retarded and an increase in the clearing point expected via the kinetic isotopic effect. To prove this assumption octyl galactopyranoside **4a** was dissolved in D_2O and lyophilized; this process was repeated several times to ensure a complete H/D exchange. Whereas **4a** showed a clearing point T_c = 132·9°C the clearing point of deuteriated **4a** was increased slightly to T_c = 134·0°C. Even though this finding could indicate a kinetic isotopic effect the small difference ΔT_c of 1·1°C may have other interpretations.

Orientation studies on the S_A phases of these amphiphilic compounds were performed which showed properties other than those of ordinary S_A phases. Using glass plates cleaned with chromic sulphuric acid a homeotropic orientation resulted with fan-shaped textures at the edge of air bubbles. The amount of fan-shaped texture increased in going from the octyl to the dodecyl derivative. Following coating with polyamides (Ultramide) and scratching the glass plates simple fan-shaped textures and no homogeneous textures with the director parallel to the plates (i.e. a planar texture) were formed. Homeotropic orientations were obtained by shearing the cells or by coating the glass plates with cetyl ammonium bromide (CTAB). Formation of planar textures could not be achieved with any of these compounds.

The reason for the different clearing points can be understood following inspection of the volume required by the rotating molecule. Generally, for axial hydroxy groups the molecule becomes shorter (4-OH or 1-OR) or narrower (2-OH or 3-OH). On going from β-Gal (4-OH axial) to β-Glc (4-OH equatorial) and α-Man (2-OH axial) to α-Glc (2-OH equatorial) and α-Glc (1-OR axial) to β-Glc (1-OR equatorial) the volumes increase and the clearing points decrease respectively. This effect is largest at C4, and smallest at C1, the anomeric centre. In both cases the axial groups reduce the molecular size, however, in the latter case the axially positioned aglycone increases the total volume requirement because of the aliphatic chain. The glucuronic acid glycosides **5** and **6** showed considerably enhanced clearing points with respect to the corresponding glucose derivatives **1e** and **2e**, and this can be related to their increased polarity as well as their pronounced hydrogen bonding ability.

An ionic hydrochloride structure is present in the 6-propylamino derivative **7**. This compound is already liquid-crystalline at room temperature with a clearing point of 174°C. In the isotropic phase it decomposed quickly, supposedly by attack of the nucleophile Cl^- at the sugar ring, particularly at the anomeric centre (C1). Whereas all other known hydrochlorides are crystalline and decompose on melting, compound **7** represents the first liquid-crystalline carbohydrate hydrochloride. In contrast, the basic amine, n-dodecyl 6-deoxy-6-propylamino-β-D-glucopyranoside, did not show any liquid-crystalline phases and formed a syrup at room temperature. Obviously, introduction of an apolar propyl amino group into the polar region of the molecule interfered with the formation of hydrogen bonds. Again, this effect was compensated for by the ionic structure of the hydrochloride **7**.

The 1→4 interglycosidically linked disaccharides **8a** to **11** showed markedly higher clearing points than the monosaccharids **1a** to **4c** (cf. figure 2, table). Compound **9a** (*n*-dodecyl β-D-maltoside) was described previously [14]. A purchased, crystalline material was reported to have a melting point of 102°C and a clearing point at 245°C with decomposition. However, our synthesized material showed a clearing point of 244°C without decomposition. Further lyotropic liquid crystals of **9a** and its miscibility with dodecyl β-D-glucopyranoside (**2e**) were demonstrated [14]. These

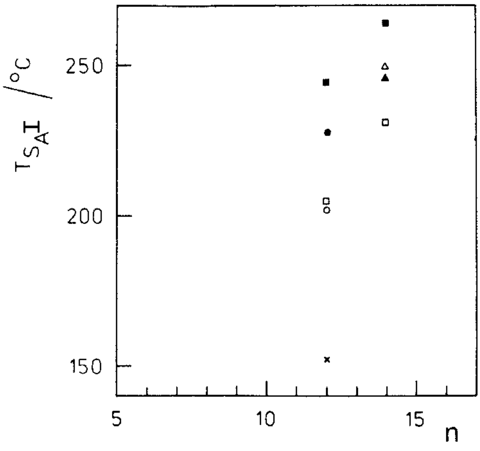
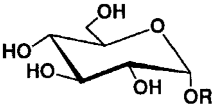


Figure 2. Liquid-crystalline di- and trisaccharide glycosides. □, α-Mal (**8**); ■, β-Mal (**9**); △, α-Lac (**10**); ▲, β-Lac (**11**); x, Isomal (**12**); ○, α-Trio (**13**), ●, β-Trio (**14**).

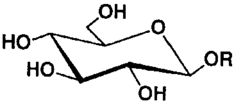
Liquid crystalline glycosides.

α-D-Glucopyranosides



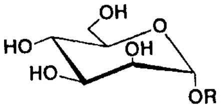
1a	*n*-Heptyl	C	53°C	S_A	99°C	I	[8]
1b	*n*-Octyl	C	71·8°C	S_A	118°C	I (*a*)	–
1c	*n*-Nonyl	C	65°C	S_A	130°C	I	[8]
1d	*n*-Decyl	C	76°C	S_A	138°C	I	[8]
1e	*n*-Dodecyl	C	77°C	S_A	151°C (*b*)	I	[8]
1f	*n*-Hexadecyl	C	108°C	S_A	175°C	I	[10]

β-D-Glucopyranosides



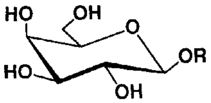
2a	*n*-Heptyl		C2	56°C	C1	59°C	S_A	69°C	I	[11]
2b	*n*-Octyl				C	67·1°C	S_A	106·4°C (*c*)	I	[1]
2c	*n*-Nonyl		C2	51°C	C1	68°C	S_A	113°C	I	[11]
2d	*n*-Decyl		C2	64·9°C	C1	70·3°C	S_A	135·5°C	I	[1]
2e	*n*-Dodeycl	C3 54·8	C2	63·2°C	C1	80·4°C	S_A	143·4°C	I	[1]
2f	*n*-Hexadecyl		C2	78°C	C1	110°C	S_A	145°C	I	[7]

α-D-Mannopyranosides



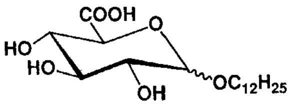
3a	*n*-Octyl	C	55·0°C	S_A	133·9°C	I
3b	*n*-Decyl	C	64·7°C	S_A	152·7°C	I
3e	*n*-Dodecyl	C	74·2°C	S_A	161·7°C	I

β-D-Galactopyranosides



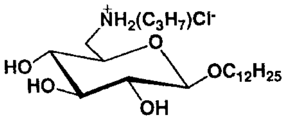
4a	*n*-Octyl			C	98·3°C	S_A	132·9°C	I
4b	*n*-Decyl	C2	82°C	C1	93·5°C	S_A	157·3°C	I
4c	*n*-Dodecyl	C2	55°C (*d*)	C1	99·4°C	S_A	165·7°C	I

(D-Glucopyranoside) uronic acid



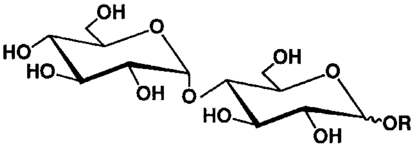
5a	α-*n*-Dodecyl	C	65°C (*d*)	S_A	173°C	I
6b	β-*n*-Dodecyl	C	83°C (*d*)	S_A	177°C	I

n-Dodecyl 6-deoxy-6-propylamino-β-D-glucopyranoside



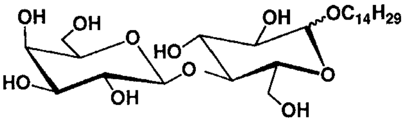
7	Hydrochloride	C	– (*e*)	S_A	174°C	Z (*f*)

D-Maltosides



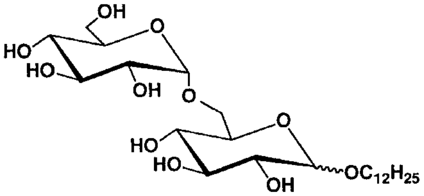
8a α-*n*-Dodecyl	C	82°C(*d*)	S_A	205°C	I
8b α-*n*-Tetradecyl	C	102·5°C	S_A	231°C	I
9a β-*n*-Dodecyl	C	80°C(*d*)	S_A	244°C	I
9b β-*n*-Tetradecyl	C	86°C(*d*)	S_A	264°C	I

D-Lactosides



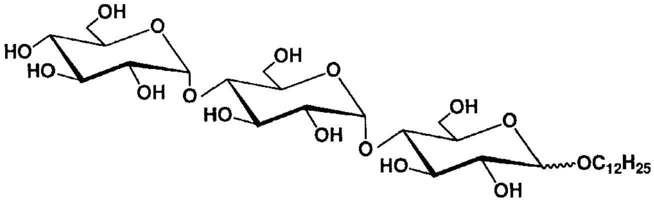
10 α-*n*-Tetradecyl	C	173°C	S_A	> 249°C	Z(*b*)
11 β-*n*-Tetradecyl	C	183°C	S_A	246°C	I

D-Isomaltoside



12 α/β-*n*-Dodecyl (8 per cent α)	C	118°C(*d*)	S_A	152°C	I

D-Maltotriosides



13 α-*n*-Dodecyl	C	143°C(*d*)	S_A	202°C	I
14 β-*n*-Dodecyl	C	135°C(*d*)	S_A	228°C	I

(*a*) Reported [9]: C2 52°C C1 71·8°C S_A 117°C I.

(*b*) We observed T_c = 148·9°C.

(*c*) We observed T_c = 107·6°C.

(*d*) Following lyophilization these compounds formed non-crystalline solids. Thus, no exact melting point could be determined. Probably, the real melting points will be higher.

(*e*) Not detected; liquid-crystalline at room temperature.

(*f*) Decomposition at the clearing point.

observations, as well as the high clearing point, clearly relate to the pressure of a large number of hydrogen bonds.

Altogether, the findings in the 1→4-linked disaccharide series are more difficult to evaluate. On the one hand in comparison to the monosaccharide derivatives the geometrical properties are more complicated, and on the other hand the number of compounds for comparison is still limited. For the given constitution the clearing points varied over a range of about 40°C owing to the various configurations.

For the maltosides the β-anomer showed the higher clearing point, in the lactosides, however, the α-anomer. The average clearing points of α- and β-anomers in both series turned out to be almost similar. The increase of the clearing points on going from the dodecyl to the tetradecyl glycoside amount to approximately 20°C in contrast to about 10°C for the corresponding monosaccharide derivatives.

Whereas the 1→4 linked disaccharide derivatives are linear the isomeric 1→6 linked isomaltoside **12** is angular. Even though both may form the same amount of hydrogen bonds the clearing point of **12** was about 100°C below that of the corresponding 1→4 linked compound **9a**. Again, the bulky molecule **12** requires a considerably larger volume than its stretched isomer **9a**. However, this effect cannot be explained by an increased flexibility of **12** in contrast to **9a**. As reported previously, both the rather flexible alkyl gluconamides as well as alkyl gluconates showed higher clearing points than the corresponding alkyl glucopyranosides [15]. Again, this result is in accord with the assumption of a much smaller volume for the former compounds. Similar to calamitic liquid crystals with rod-like structures these amphiphilic mesogens show stretched, round, space-filling shapes. In contrast, however, they can be completely flexible resembling rope-like structures.

The maltotriosides **13** and **14** showed high clearing points similar to those of the disaccharides **8a** and **9a**. Obviously, the clearing point is increased considerably with the length of the alkyl chain. Longer chain trisaccharide glycosides should exhibit higher clearing points than the corresponding disaccharide derivatives. Assuming the number of hydrogen bonds to be solely responsible for the range of the clearing points, these would be expected to be about 300°C for the trisaccharide glycosides.

According to these findings higher clearing points resulted if polar and apolar parts of the glycosides showed a balanced molecular weight ratio. Within a certain series with a given number of hydroxy groups the clearing points increased with the chain length of the alcohol until the molecular weight ratio of the sugar and the aglycone approach unity. Further, for a given ratio of both parts of the molecule the clearing points should increase with the number of hydroxy groups (C_7-mono- < C_{14}-di- < C_{21}-trisaccharide glycoside).

3. Conclusions

These observations lead us to following conclusions. The clearing points of alkyl glycosides increased with a large number of hydrogen bonds between the carbohydrate moietes [14], a rope-like structure, which contributes to a reduced volume required by the rotating molecule, and a delicately balanced ratio between the number of polar hydroxy groups and the length of the alkyl chain. Tilted phases were not observed with any of these derivatives and are generally not favoured for amphiphilic compounds. However, their occurrence cannot be excluded, in particular because of the recent demonstration of tilted lamellar phases with ferroelectric properties [16].

4. Experimental part

All transition temperatures were determined optically. The clearing points of compounds **3a**–**7** were measured on a special hot stage with an Olympus BH polarizing microscope (error ± 0·1°C). Because of the higher temperatures those of the oligosaccharides **8a**–**14** were determined on a Kofler hot stage microscope (error ± 1·0°C).

4.1. *Synthesis of alkyl glycosides* (*General procedure*)

The disaccharide or monosaccharide (10 mmol) was treated with anhydrous sodium acetate (16 (10) mmol) and acetic anhydride (20 (12·5) ml) heated to 120 (100)°C for 4 hours and worked up as usual [17] to give the β-anomer of the peracetylated saccharide.

The peracetylated β-saccharide (10 mmol) was dissolved in anhydrous dichloromethane (80 ml) and stirred with molecular sieves 4 Å (4 g) under a nitrogen atmosphere. The solution was treated with tin tetrachloride (10 mmol) and immediately after with the alcohol component (1·2 mmol) dissolved in anhydrous dichloromethane (20 ml).

The preparation of β-glycosides required a reaction time of 2–4 hours, that of the α-glycosides approximately 48 h. After that time the mixture was poured into saturated sodium hydrogen carbonate solution (100 ml), the organic layer separated, the aqueous phase extracted with dichloromethane (40 ml), the combined organic phases washed twice with water (40 ml), filtered over Celite and evaporated *in vacuo*. The resulting syrup was dried in high *vacuo* and purified by flash chromatography [6 cm column, silica gel 60 (Merck), n-hexane/ethyl acetate]. The resulting material was deacetylated by treatment with sodium methoxide in anhydrous methanol (40 ml) under reflux and subsequently neutralized with ion exchange resin (Amberlite IR 120 H^+).

Finally, this mixture was separated into the anomers using a strongly basic anion exchange resin (Dowex 1 × 2, OH^-) and elution with methanol. Detection was on RP 18 with acetonitrile/water, 9 : 1. The resulting material was evaporated *in vacuo* and following solution in water lyophilized to give a colourless amorphous solid. Yields: 30–55 per cent based on the starting saccharide for the three stage process, including purifications.

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