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The stereochemistry of glycolipids. A key for understanding membrane functions?

V. Vill[a]; Volkmar Vill[bc]; Thomas Böcker[b]; Joachim Thiem[b]; Fred Fischer[c]
[a] Institut für Organische Chemie, Universität Hamburg, D-20146 Hamburg 13, Germany [b] Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Orléansring 23, D-4400 Münster, F.R. Germany [c] Physikalisches Institut der Westfälischen Wilhelms-Universität Wilhelm-Klemm-Strasse 10, D-4400 Münster, F.R. Germany

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The stereochemistry of glycolipids. A key for understanding membrane functions?

V. VILL

Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg 13, Germany

A Commentary on the paper "Studies on liquid-crystalline glycosides" by Volkmar Vill, Thomas Böcker, Joachim Thiem and Fred Fischer. First published in *Liquid Crystals*, **6**, 349-356 (1989).

Why are the components of membranes chiral? Why do plants use galactolipids, bacteria glucolipids and animals phospholipids for the formation of membranes? Which biological processes are controlled directly by the structure of the membrane? How can viruses, bacteria and/or toxins penetrate through the membrane into the cell? How can we create drug delivery systems specific for the target and not the drug? How do transmembrane proteins interact to cooperate? Can we modify membranes to prevent infections? What is the function of liquid crystals in Nature?

These complex questions are located in a triangle between chemistry, physics and biology. The chemical structure results in the physical properties of these structures which, in turn, dictate biological functions. The long range order of the molecules results in the liquid-crystalline cell membrane, which is still difficult to understand fully. A common place in science is the analysis of the interactions of single molecules, for example a substrate molecule interacts with the active site of a protein. These types of interaction can be readily observed, measured and visualized. In contrast, the properties of membranes are collective phenomena. Liquid crystals are formed by average interactions that can only be analyzed by special experimental methods and need imagination to be understood.

The liquid crystal research group around Vill (then at the University of Münster now at the University of Hamburg) started in 1986 to use carbohydrates for liquid crystal applications. The first paper [1] focused on the use of the chirality of sugars to create highly twisted chiral nematic phases. It described, for the first time, the use of dianhydrosorbitol as a chiral dopant. Today, this material is well-known as one of the most efficient chiral dopants for selective reflection in chiral nematic phases, referred to in hundreds of papers and patents [2]. The Hamburg group was able to demonstrate that sugars are good precursors for all kind of monophilic chiral phases such as the chiral nematic, blue phases, ferroelectric and TGBA phases. They developed methods for the quantification of structure/property relationships for liquid crystals; for example, the analysis tools of the database LiqCryst [3]. This resulted in an understanding of monophilic materials. However, amphiphilic liquid crystals and their biological functions appear to be the major challenge of the future.

G.A. Jeffrey described in 1986 a small list of liquid-crystalline alkyl glycosides which mainly show smectic A phases [4]. Chiral phases were not observed even though all of the mesogenic molecules were chiral. Then, we were concerned to understand the influence of sugar head groups on these phases and presented sets of new glycosides, which allow a systematic analysis focussing on:

- various diastereomers: α and β, *gluco* and *galacto*
- various polarities: hexoses, uronic acids
- mono-, di- and trisaccharides

The compounds presented in the 1989 *Liquid Crystals* paper were mainly smectic A materials [5], because we were too shy to publish the more exciting results. In fact, we had already discovered thermotropic cubic phases in our first set of compounds, which were published later including the X-ray data [6].

The subsequent papers dealt more with naturally occurring glycolipids and their biophysical properties; these opened a vast research area and lead to important results. During this research we were able to answer some of the questions raised in the first paragraph.

(a) The bicontinous cubic phase of glycoglycero lipids and lecithins can be induced by small impurities and this can provide an explanation for passive endocytosis; for example, toxins can pass through

*Email: Vill@liqcryst.chemie.uni-hamburg.de

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membranes because of a phase transition from a lamellar phase to a bicontinuous phase (a pore in a membrane is a seed crystal for the cubic phase). The plant lipids, galactolipids, have properties which are less temperature dependent than those of lecithins and glucolipids; that is plants use galactolipids because they do not have a constant body temperature and so the membrane has to work over a range of temperatures.

(b) The chirality and complexity of glycolipids is essential for biological processes. We have observed a strong helical twisting power of glycolipids in micellar solutions, the formation of lyotropic chiral nematic phases and chiral recognition in phase diagrams.

(c) Today, we understand the smectic A_d phase of carbohydrate liquid crystals as an uncorrelated smectic C phase. The tilt direction within the phase is correlated between hydrophobic layers but not between the sugar head groups.

(d) The chirality of membrane molecules reduces the symmetry and allows directed interactions of proteins both inside and through the membrane.

The 1989 *Liquid Crystals* paper [5] gives examples of liquid crystal applications for carbohydrate chemists and demonstrates the value of carbohydrate starting materials to researchers in the field. In other words, the paper was an initial stimulation to a growing research area.

Even today, research areas are divided into opposite areas: either life science or material science, either physics or chemistry, either fundamental science or application. Liquid crystal research is not limited to any one of these areas, it is really interdisciplinary in all of its aspects. The central issue is the understanding of the molecular properties.

References

[1] V. Vill, F. Fischer, J. Thiem. *Z. Naturforsch.*, **43a**, 1119 (1988).

[2] K.-H. Etzbach, P. Delavier, K. Siemensmeyer, G. Wagenblast, L. Laupichler, V. Vill. (BASF), *Ger. Offen*. DE-OS 4.342.280 (11.12.1993/14.06.1995), *Chem. Abstr*., **123**, 83352.

[3] *LiqCryst 4.6 Advanced-Database of Liquid Crystals*, V. Vill, Fujitsu Kyushu System (FQS) Ltd, Fukuoka, Japan, 2005; LCI Publisher, Hamburg, 2005, http://liqcryst.chemie.uni-hamburg.de.

[4] G.A. Jeffrey. *Acc. Chem. Res.*, **19**, 168 (1986).

[5] V. Vill, Th. Böcker, J. Thiem, F. Fischer. *Liq. Cryst.*, **6**, 349 (1989).

[6] S. Fischer, H. Fischer, S. Diele, G. Pelzl, K. Jankowsky, R.R. Schmidt, V. Vill. *Liq. Cryst.*, **17**, 855 (1994).

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Studies on liquid-crystalline glycosides

VOLKMAR VILL*, THOMAS BÖCKER†, JOACHIM THIEM† and FRED FISCHER‡

†Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Orléansring 23, D-4400 Münster, F.R. Germany

‡Physikalisches Institut der Westfälischen Wilhelms-Universität Wilhelm-Klemm-Strasse 10, D-4400 Münster, F.R. Germany

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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 described [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?

*Corresponding author. Email: Vill@liqcryst.chemie.uni-hamburg.de

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 readily, however, this could be achieved by annealing at 60°C for 24 hours. The b-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

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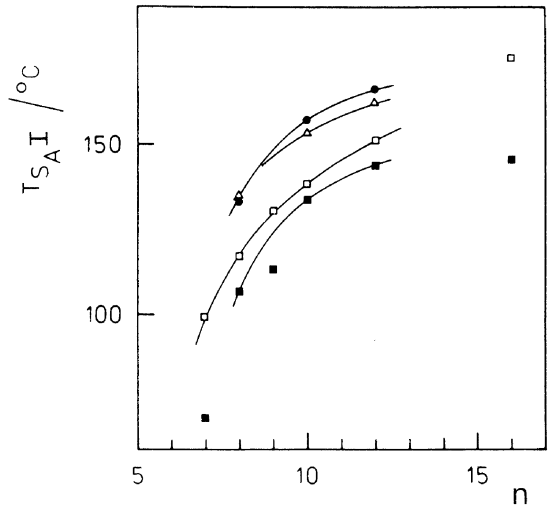


Figure 1. Liquid-crystalline monosaccharide glycosides (the graphs make use of the data for n=8, 10 and 12). □, α-Glc (**1**); ■, β-Glc (**2**); △, α-Man (**3**); •, β-Gal (**4**).

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

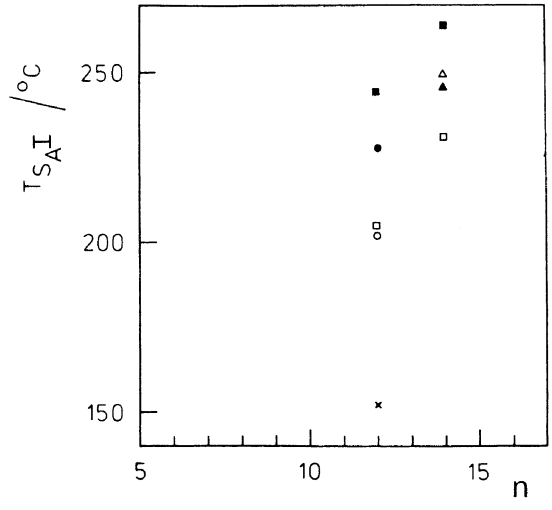
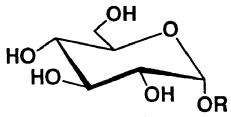


Figure 2. Liquid-crystalline di- and trisaccharide glycosides. □, α-Mal (**8**); ■, β-Mal (**9**); △, α-Lac (**10**); ▲, β-Lac (**11**); ×, Isomal (**12**); ○, α-Trio (**13**), •, β-Trio (**14**).

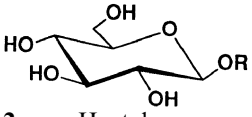
Liquid crystalline glycosides.

α-D-Glucopyranosides



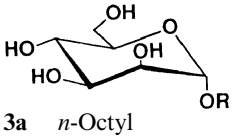
1a	*n*-Heptyl					C	53°C	S_A	99°C	I	[8]
1b	*n*-Octyl					C	71.8°C	S_A	118°C	I (*a*)	–
1c	*n*-Nonyl					C	65°C	S_A	130°C	I	[8]
1d	*n*-Decyl					C	76°C	S_A	138°C	I	[8]
1e	*n*-Dodecyl					C	77°C	S_A	151°C (*b*)	I	[8]
1f	*n*-Hexadecyl					C	108°C	S_A	175°C	I	[10]

β-D-Glucopyranosides



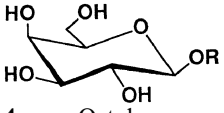
2a	*n*-Heptyl			C2	56°C	C1	59°C	S_A	69°C	I	[11]
2b	*n*-Octyl					C	67.1°C	S_A	106.4°C (*c*)	I	[1]
2c	*n*-Nonyl			C2	51°C	C1	68°C	S_A	113°C	I	[11]
2d	*n*-Decyl			C2	64.9°C	C1	70.3°C	S_A	135.5°C	I	[1]
2e	*n*-Dodeycl	C3	54.8	C2	63.2°C	C1	80.4°C	S_A	143.4°C	I	[1]
2f	*n*-Hexadecyl			C2	78°C	C1	110°C	S_A	145°C	I	[7]

α-D-Mannopyranosides



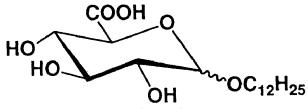
3a	*n*-Octyl					C	55.0°C	S_A	133.9°C	I	
3b	*n*-Decyl					C	64.7°C	S_A	152.7°C	I	
3e	*n*-Dodecyl					C	74.2°C	S_A	161.7°C	I	

β-D-Galactopyranosides



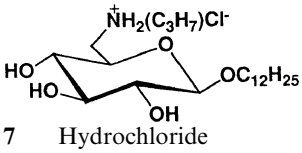
4a	*n*-Octyl					C	98.3°C	S_A	132.9°C	I	
4b	*n*-Decyl			C2	82°C	C1	93.5°C	S_A	157.3°C	I	
4c	*n*-Dodecyl			C2	55°C (*d*)	C1	99.4°C	S_A	165.7°C	I	

(D-Glucopyranoside) uronic acid



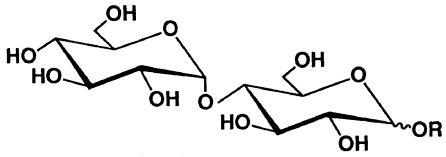
5a	α-*n*-Dodecyl					C	65°C (*d*)	S_A	173°C	I	
6b	β-*n*-Dodecyl					C	83°C (*d*)	S_A	177°C	I	

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



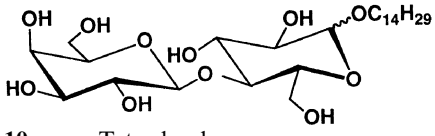
7	Hydrochloride					C	– (*e*)	S_A	174°C	Z(*f*)	

D-Maltosides



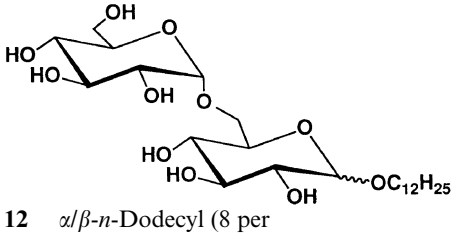
8a	α-*n*-Dodecyl	C	82°C (*d*)	S_A	205°C	I
8b	α-*n*-Tetradecyl	C	102.5°C	S_A	231°C	I
9a	β-*n*-Dodecyl	C	80°C (*d*)	S_A	244°C	I
9b	β-*n*-Tetradecyl	C	86°C (*d*)	S_A	264°C	I

D-Lactosides



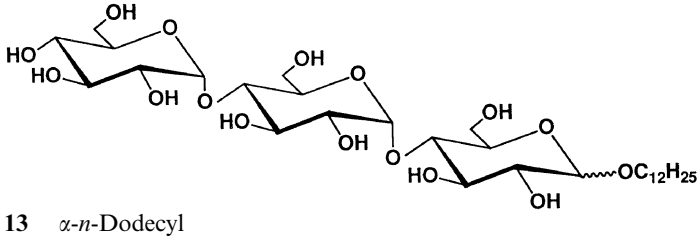
10	α-*n*-Tetradecyl	C	173°C	S_A	>249°C	Z (*b*)
11	β-*n*-Tetradecyl	C	183°C	S_A	246°C	I

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.

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 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 lacto-sides, 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 ± 10°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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References

[1] J.W. Goodby. *Molec. Crystals liq. Crystals*, **110**, 205 (1984).
[2] G.A. Jeffrey. *Accts chem. Res.*, **19**, 168 (1986).
[3] G.W. Gray, P.A. Winsor. *Liquid Crystals and Plastic Crystals*. John Wiley & Sons (1974).
[4] G.W. Gray, J.W. Goodby. *Smectic Liquid Crystals*. Leonard Hill (1984).
[5] M.A. Marcus, P.L. Finn. *Molec. Crystals liq. Crystals Lett.*, **2**, 159 (1985).
[6] K. Praefke. *DFG-Kolloquium 'Anisotrope Fluide'*. Berlin. 12 (1988).
[7] E. Fischer, B. Helferich. *Justus Liebigs Annln Chem.*, **383**, 68 (1911).
[8] E. Barrell, B. Grant, M. Oxsen, E.T. Samalski, P.C. Moews, J.R. Knox, R.R. Gaskill, J.L. Haberfeld. *Org. Coat. Plast. Chem.*, **40**, 67 (1979).
[9] D.L. Dorset, J.P. Rosenbusch. *Chem. Phys. Lipids*, **29**, 299 (1981).
[10] P.Q. Pfeffer. *J. org. Chem.*, **41**, 2925 (1976).
[11] G.A. Jeffrey, S. Bhattacharyee. *Carbohydr. Res.*, **115**, 53 (1983).
[12] G.M. Brown, P. Dubreuil, F.M. Ichhaporia, J.E. Desnoyers. *Can. J. Chem.*, **48**, 2525 (1970).
[13] G. Geiseler. *Z. Chem.*, **18**, 1 (1978).
[14] M.A. Marcus. *Molec. Crystals liq. Crystals Lett.*, **3**, 85 (1986).
[15] B. Pfannemüller, W. Welte, E. Chin, J.W. Goodby. *Liq. Crystals*, **1**, 357 (1986).
[16] M. Schafheutle. *DFG-Doktoranden-Kolloquium 'Anisotrope Fluide'*. Berlin. 3 (1988).
[17] M.L. Wolfrom, A. Thompson. *Meth. Carbohydr. Chem.*, **2**, 211 (1962).