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Liquid Crystals

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Chemoenzymatic synthesis of discotic liquid crystals

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PRELIMINARY COMMUNICATIONS

Chemoenzymatic synthesis of discotic liquid crystals

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Acylations at the 6-position of alkyl glycosides were obtained using the esterification potential of lipases. Thus, sugars with two alkyl chains result showing columnar discotic phases. The correlation between the configuration of the sugar moieties and the different clearing points can be understood on the basis of simple stereochemical assumptions.

The liquid-crystalline properties of amphiphilic compounds derived from alkylated carbohydrates have been investigated for some years. Mono-alkylated derivatives such as alkyl glycosides form smectic phases nearly exclusively [1–3]. However, dialkyl mercaptans as examples of dialkylated derivatives exhibit discotic mesophases [4] if the alkyl chains are positioned close to each other under an acute angle that allows the molecule to adopt a discus segment-like shape (see figure 1). Recently de Nijs *et al.* [5] reported on the unidentified mesophase of octyl 6-O-octanoyl-α-D-glucopyranoside. Because the alkyl chains of this molecule form an obtuse angle, at first glance it is not possible to decide whether smectic or discotic phases are more favourable. Further, the presence of a novel mesophase with such a disadvantageous molecular structure must also be considered. In order to study and clarify the situation we have prepared some octyl 6-O-dodecanoyl-glycopyranosides by the chemoenzymatic approach.

The chemoenzymatic synthesis of these compounds was carried out in two steps. The preparation of the octyl glycosides can be easily achieved using the method described by Böcker *et al.* [6]. The subsequent enzymatic esterification with molten dodecanoic acid was performed at 70°C without any cosolvent in the presence of porcine pancreas lipase, following the procedure of Adelhorst *et al.* [7]. In contrast, the approach of de Nijs *et al.* [5], using the ethyl ester of the fatty acid and tetrahydrofuran as cosolvent was not very effective in our hands. In particular the separation of the ethyl ester is difficult to achieve. On the other hand the dodecanoic acid and the adduct could be separated in one chromatographic step by use of basic alumina. The yields range between 30 and 50 per cent, and the structures were assigned unequivocally by ^{13}C and ^{1}H NMR. The transition temperatures were measured on a Mettler hot stage FP 82 with an Olympus BH polarizing microscope, and the identification of phases was based on typical textures.

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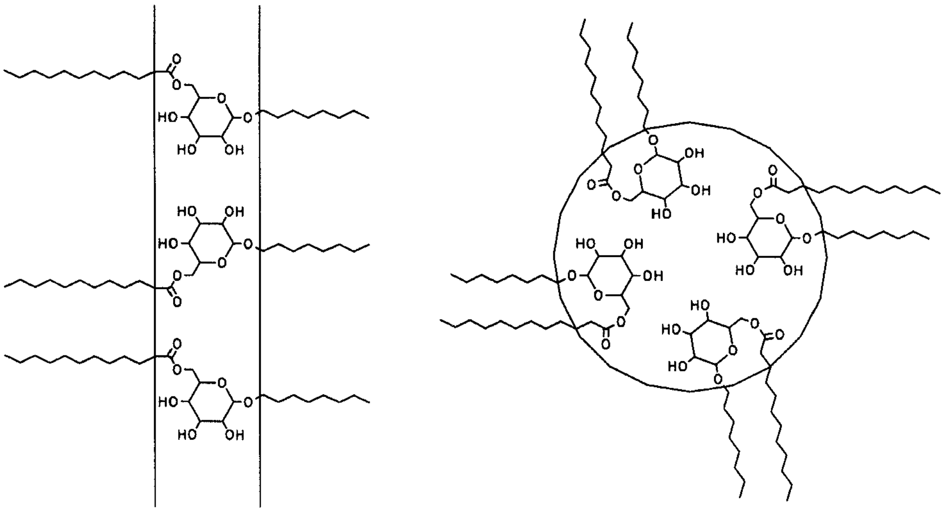
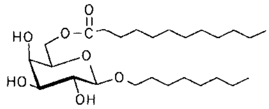
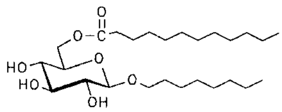
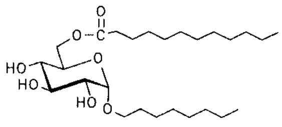
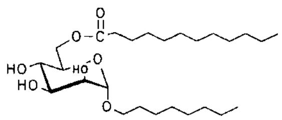


Figure 1. Possible arrangements of alkyl 6-O-acyl-glycopyranosides. Left side: smectic phase; right side: discotic phase.

Liquid-crystalline properties of alkyl 6-O-acyl-glycopyranosides.

1 β-galacto C 91·7°C D 84·8°C I	
2 β-gluco C 71·0°C D 87·7°C I	
3 α-gluco C 57·2°C M 20·2°C I	
4 α-manno C <0°C M 5°C I	

All of the compounds prepared show liquid-crystalline phases (see the table) but the clearing points vary considerably and obviously are strongly dependent on the configuration. Both β-glycosides **1** and **2** form columnar discotic mesophases (see figure 2) with high clearing points above 80°C. However, the α-glycosides **3** and **4** show clearing points below 20°C. Presumably, these mesophases are also of a discotic nature, although any definite textures could not yet be assigned. For compounds with identical configurations at the anomeric centre the all equatorial orientation of the OH groups results in a slightly higher clearing point than in the corresponding cases with one axial

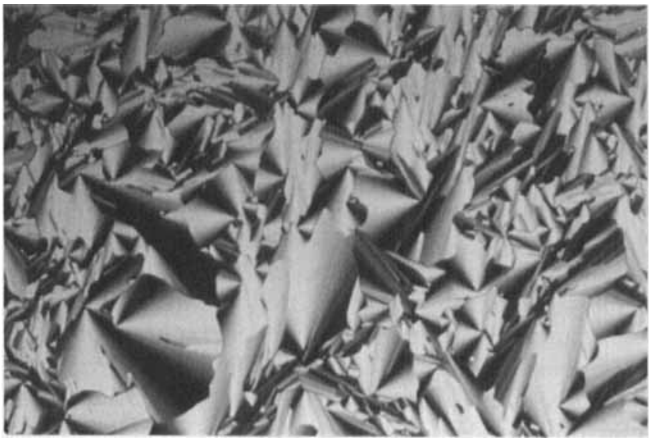


Figure 2. The optical texture of the discotic mesophase of **2**; area≈0·6 × 1 mm^2, at 35°C, crossed nicols, with cover slide.

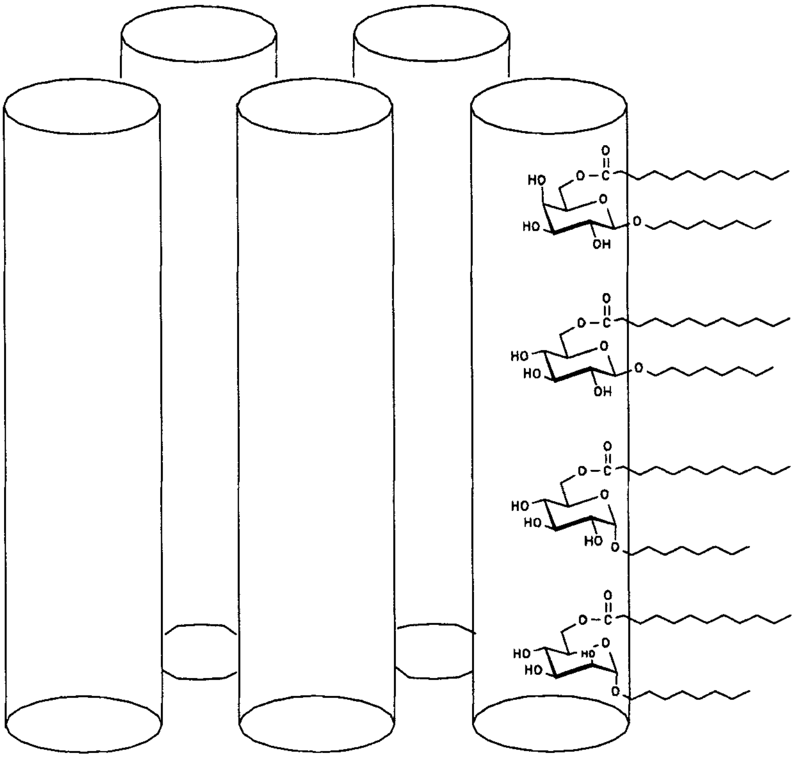


Figure 3. A model of the discotic phase.

OH group (T_c: **2** > **1**, **3** > **4**). Additionally, in the case of compound **2**, the mesophase was also confirmed by X-ray diffraction. We observed a D_{hd} phase with an inter column distance of 31·45 Å. There is no hint of further order inside the columns.

These liquid-crystalline properties can be explained by a simple model (see figure 3). The driving force for the formation of the mesophases of these compounds resides in the tendency of the hydrophilic and hydrophobic parts of the molecules to separate from each other. The surface between these areas constitutes a cylindrical jacket. Along this bent plane the amphiphilic molecules have a two dimensional freedom of movement and of rotation related to the longitudinal axis. With the compounds **1** and **2** carrying equatorial aglycons the alkyl groups enclose a smaller angle than with those carrying an axial aglycon (**3**, **4**). Therefore, both compounds **1** and **2** are advantageously packed within the mesophase and enjoy a higher freedom of movement (higher entropy), because an acute triangle rotates more easily than an obtuse one.

Obviously, compounds with axial OH groups show nearly the same clearing points as the related derivatives with equatorial OH groups. Thus, it can be concluded that in the mesophase hydrogen bridges are built up in a horizontal as well as in a vertical direction with almost identical preference. Owing to these findings the postulate of defined multimers as in the case of dialkyl mercaptans [4] obviously cannot be generalized. In fact, we rather prefer our interpretation which could certainly be applied to this case as well.

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