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Discotic peracylated glycosides

V. Vill[a]; J. Thiem[a]
[a] Institut für Organische Chemie der Universität Hamburg, Hamburg 13, Germany

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PRELIMINARY COMMUNICATION

Discotic peracylated glycosides

by V. VILL and J. THIEM*
Institut für Organische Chemie der Universität Hamburg,
Martin-Luther-King-Platz 6, D-2000 Hamburg 13, Germany

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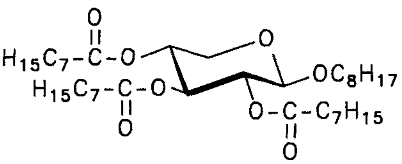
Easily accessible peracylated glycosides show columnar discotic phases. The mesomorphic properties of the cellobiosides studied are interpreted as resulting from the polarity contrast between the sugar nucleus and the alkyl side chains.

Hexasubstituted benzene derivatives, the first discotic liquid crystals, were described by Chandrasekhar *et al.* [1]. Recently Kohne *et al.* demonstrated that hexasubstituted cyclohexanes, such as the peracylated *scyllo* inositols, formed discotic mesophases [2, 3]. However, in studies of the corresponding peracylated glucose derivatives **4** and **5** no mesophases were detected [2]. This was rationalized in terms of the unfavourable space filling properties of the molecules resulting from the lack of side chains as well as an unspecified stereoelectronic effect of the ring oxygen. In contrast to this Zimmermann *et al.* reported at the same time monotropic discotic phases for the peracylated sugar derivatives **4** and **6** [4].

According to our interpretation of these results the stereoelectronic effects are of dominant importance. In fact, the strong anomeric effect of the ester groups should be considered [5]. This supports the arrangement of such anomeric substituents in a preferred axial position. Consequently, the population of the all-equatorial conformation is somewhat reduced. Furthermore, stabilizing *gauche* interactions between all of the ester groups cannot be obtained to the same extent as observed with *scyllo* inositols [5]. In the present contribution we have studied glycosides which do not carry an

Table 1.



No	Phase transitions
1	C 38·2°C I

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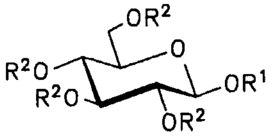
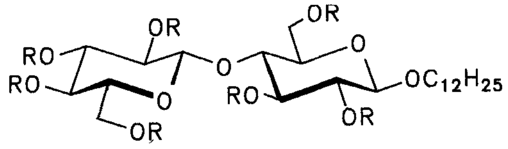
* Author for correspondence.

Table 2.



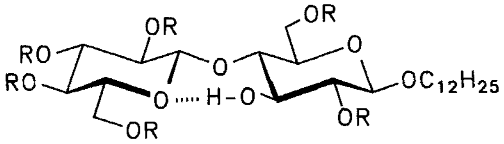
No.	R^1	R^2	Phase transitions	References
2	$C_{10}H_{21}$	CO–$C_{11}H_{23}$	C ? P 56°C I	———
3	$C_{12}H_{25}$	CO–$C_{11}H_{23}$	C ? P 59·8°C I	———
4	CO–C_9H_{19}	CO–C_9H_{19}	———	C 40°C D 32·5°C I [4] C 39·5°C I [2]
5	CO–$C_{15}H_{31}$	CO–$C_{15}H_{31}$	———	C 73·5° I [2] C 68°C sint. 72°C I [11]
6	CO–$C_{17}H_{35}$	CO–$C_{17}H_{35}$	———	C 72°C sint. 78°C I [11] C ? D ? I [4]
7	$C_{10}H_{21}$	CO–C_6H_4–$OC_{12}H_{15}$	C ? I	———
8	CH_3	CO–$C_6H_2(OAc)_3$	———	C 110°C X 160°C I [7]

Table 3.



No.	R	Phase transitions
9	$C_{11}H_{23}$	C 74°C D 92·7°C I
10	C_6H_4–$OC_{12}H_{25}$	C ? D 120°C I

Table 4.



No.	R	Phase transitions
11	C_6H_4–$OC_{12}H_{25}$	C ? D 145°C I

Figure 1. Phase transitions of peracylated glycosides.

acyloxy but rather an alkyloxy group at the anomeric centre. Thus, the influence of the anomeric effect should be considerably reduced and hence alter the gross structural appearance of the molecules.

The peracylated octyl-β-D-xylopyranoside **1** with only four wing groups and no substituted methylene group at C–5 does not form any mesophase. The crystalline material forms needles which melt at 38·2°C. Owing to the large ^{3}J coupling constants in the ^{1}H NMR ($J_{1,2}=7·0$; $J_{2,3}=9·0$; $J_{4,5e}=9·1$ Hz) a preferential all-equatorial

$^4C_1(D)$ chair conformation is obvious, however, this does not exclude completely some contribution from the inverted $^1C_4(D)$ chair as well as from other conformations.

In contrast, both the peracylated decyl- and dodecyl-β-D-glucopyranosides **2** and **3** form a highly viscous anisotropic paste which shows all of the properties of a mesophase. It cannot be supercooled and recrystallized but precipitates in a waxy form from various solvent mixtures. Without breaking the contours it can be spread, shows homeotropic and spherolytic textures but does not form any of the known discotic textures. It is assumed that this phase compares to the well-established discotic phases as does the α-phase of lipids to the smectic phases. In keeping with this similarity, like the α-phase, it does not allow aromatic functions to be incorporated into the molecule. Thus, the *p*-alkoxybenzoylated glucopyranoside **7** forms a tough sirup without a mesophase. All attempts to achieve crystallization of **7** by using several different solvents or by tempering at various temperatures failed. Following our studies we believe that Zimmermann *et al.* [4] most likely observed corresponding phases in their derivatives **4** and **6** and considered them to be normal columnar discotic phases, whereas Kohne *et al.* [2] assigned them to be crystalline.

A previously rather intensely studied class of compounds featuring corresponding structural requirements are the tannins, the gallic acid esters of glucopyranosides. For a series of tannins melting anomalies were observed and reported [6]. In fact, as early as 1923 Karrer *et al.* [7] described the anomalous melting of methyl-tetrakis(triacetylgalloyl)-β-D-glucopyranoside (**8**) in almost the same words as used previously by Fischer *et al.* [8] for hexadecyl-β-D-glucopyranoside: at 110°C the compound melts to form a paste, between 125–135°C the viscosity increases and small drops are formed; at 150–160°C the (isotropic) liquid is obtained. Thus, this most likely represents the first report of a discotic liquid crystal. It may be assumed that the gallic acid esters improve the required space filling properties [2] of the molecule owing to the three additional substituents at the aromatic partial structure.

Whereas all of glucopyranosides **2**–**6** show only highly ordered mesophases the perlauroyl cellobioside **9** gives rise to a simple columnar discotic phase with textures resembling reflections on steel cylinders (see figure 2). With respect to the extended form of the molecule which seems to be more flexible than the corresponding glucose derivatives this finding is quite unexpected. A perfect disc form as expected for discotic compounds is by no means at hand, however, the different amphiphilic character on

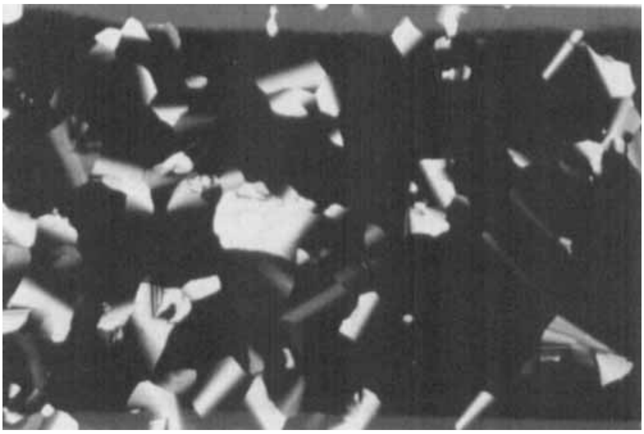


Figure 2. Texture of the discotic phase of **9**, 91·5°C, 0·5 × 1·0 mm², crossed nicols.

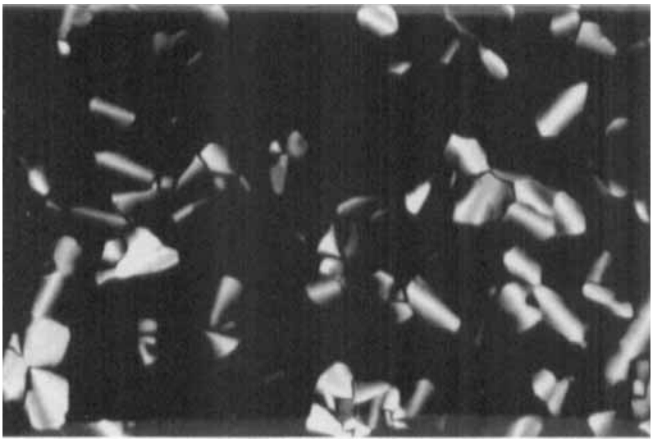


Figure 3. Texture of the discotic phase of **10**, 25·0°C, $0{\cdot}25 \times 0{\cdot}5\,\mathrm{mm}^2$, crossed nicols.

going from the polar nucleus to the hydrophobic side chains seems to be responsible for the formation of the mesophase. It can be assumed that this particular structural form is preferentially expressed by the formation of a discotic phase.

By acylation [9] of dodecyl-β-D-cellobioside with an even larger excess of acylating agent the hepta-(**10**) as well as the hexa-(*p*-dodecyloxy)benzoates (**11**) could be obtained and easily separated by chromatography. Even though for compound **10** 242 proton signals with varying intensity were observed the structural assignment based on ^{1}H NMR COSY experiments was unequivocal. Starting for **10** with the protons H–1 (δ 4·56) and H–1′(δ 4·85) which show doublets ($J_{1,2} = J_{1',2'} = 8{\cdot}0$ Hz) via crosspeaks all the remaining ring protons are easily detected. Internally, the assignment is verified because the H–4 (δ 4·16) at the interglycosidic linkage appears about 1 ppm upfield from H–4′ (δ 5·27). In contrast to the data of **10** compound **11** shows only one deviation in that H–3 (δ 4·00) is observed at rather higher field indicating the unacylated position. This finding corresponds to considerations which render the 3-OH group to be sterically congested, and further the mobile hydrogen may form a bridge to the ring oxygen of the non-reducing ring. Previously Vazquez *et al.* [10] has indicated a corresponding hindrance of the 3-position in connection with degradation studies of heptabenzoylated cellobiodsides.

Both compounds **10** and **11** form columnar discotic phases (see figure 3) similar to the laurate **9**. The hexaester derivative **11** shows a 25°C enhanced clearing point in comparison to the heptaester **10** perhaps because of an intramolecular hydrogen bridge which seems to stabilize the disc form.

The novel compounds **1–3**, **7** and **9–11** were prepared by acylation of the corresponding unblocked glycosides [12] in pyridine [9]. They were purified chromatographically, and the compounds were recrystallized from ethanol. Characterizations were by ^{1}H NMR spectroscopy and C,H combustion analysis. The transition temperatures were determined optically. The clearing points were measured on a Mettler hot stage FP 82 with an Olympus BH polarizing microscope (error ±0·1°C). Identification of phases was based on typical textures.

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