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Preliminary communication
Liquid crystalline cardanyl β-D-glucopyranosides

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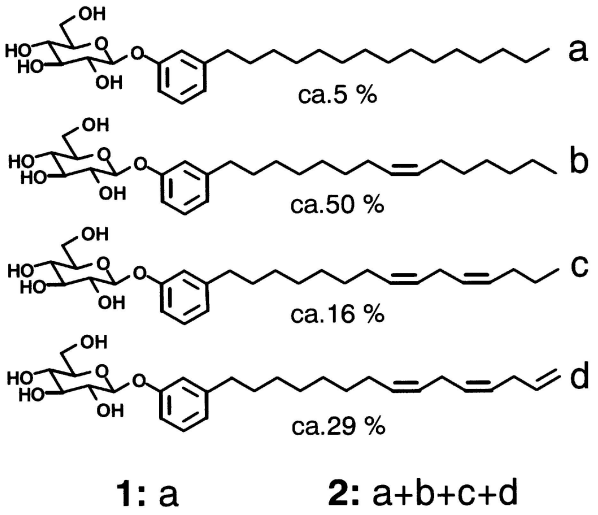
Two novel aryl glycosides were synthesized, which varied in the extent of unsaturation in the lipophilic part, from plant/crop-based renewable resource materials. Their liquid crystalline properties were characterized by optical polarizing microscopy, differential scanning calorimetry and X-ray diffraction. All the mesophases are identified as lamellar in structure.

The self-assembly of amphiphilic molecules to give nanostructured materials is of current interest in organic materials science [1–4]. One such example are carbohydrate amphiphiles, which have a wide field of applications due to their biological activity and surfactant properties [5, 6]. In the course of our work on the synthesis of new carbohydrate amphiphiles from renewable resources as chiral building blocks for molecular self-assembly, we had access to cardanyl glucosides, which showed excellent self-assembly properties in aqueous solutions leading to nanotube formation [7]. We were also interested in examining the anticipated thermotropic properties of these glucolipids with varying unsaturation in the side chain. Variation of the carbohydrate head group on the phase behaviour and mesophase formation has been investigated intensively, while the effect of unsaturation in the lipophilic part on the mesogenic properties has received little attention [8–12]. Furthermore, we propose the direct use of industrial by-product, cardanol [13] (obtained from *Anacardium occidentale L*, a renewable resource and a mixture of four components) for the synthesis of liquid crystalline aryl glycolipids. The significance of this molecule is its origin from a natural material and hence its extremely low cost; also, it possesses a flexible segment in its structure.

The synthesis of glucopyranosides **1** and **2** (see the scheme) has been reported earlier [7], and relevant information is given later in this communication; their structures were verified by elemental analysis and NMR spectroscopy. The liquid crystal properties of these compounds were studied using a polarizing optical microscopy (POM) (Olympus BX50) equipped with a heating stage (Mettler FP-90), and the optical images were recorded by a 3-CCD video camera (Olympus CS520MD). The thermal behaviour of the glycolipids was characterized by differential scanning calorimetry (DSC, Seiko 6100, heating and cooling rate 1.0°C min^{-1}). Phase identification was made by comparing the observed textures with those reported in the literature [14, 15]. X-ray diffraction (XRD) was also used to confirm the phase assignments. All powder XRD patterns were taken on a Rigaku diffractometer (Type 4037) using graded



Scheme. Structure of cardanyl glucosides **1** and **2**.

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d-space elliptical side-by-side multiplayer optics monochromated CuK_α radiation (40 kV, 30 mA) and imaging plates (R-Axis IV). For the lyotropic samples, the glycolipids **1** and **2** were fully hydrated with excess water.

Table 1 summarizes the thermal phase behaviour of the glucolipids **1** and **2** examined by means of DSC and POM. In the present study, DSC results revealed that both lipids show a similar phase transition profile, although the unsaturated mixture lipid **2** gives lower phase transition temperatures. Both dry lipids exhibited thermotropic behaviour; on heating, a crystal melts into a liquid crystal, which is finally converted into an isotropic liquid. The transition temperatures of dry lipid **2** were found to be 20 to 30°C lower than those of the saturated counterpart **1**.

The fully hydrated lipid **1** showed a gel to liquid crystalline phase transition at 77.8°C. Above this temperature, maltese crosses and oily streaks (see the figure) were observed by microscopy, indicating that the phase is a lamellar liquid crystal. For the hydrated lipid **2**, the chain unsaturation leads to a much lower phase transition temperature. The liquid crystal phase of the hydrated lipid **2** appeared just above room temperature (above 33°C); the introduction of C=C double bonds in the chain is effective in decreasing the phase transition temperature (by approximately 45°C). Small angle XRD confirmed that both compounds form lamellar phases, both thermotropically and lyotropically. The *d*-spacing values of the diffraction lines are listed in table 2. For the samples, the evaluated spacing ratios were essentially 1 : 1/2 : 1/3 : 1/4. This clearly indicates the phase types are lamellar.

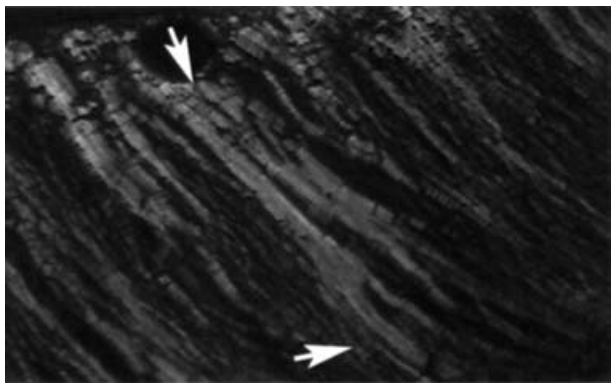

Figure. Lyotropic mesophases of fully-hydrated glucolipid **1**; oily streaks above 90°C (white arrow), magnification 10×.

Cardanyl glucosides **1** and **2** were synthesized in two steps from penta-O-acetyl β-D-glucose and the corresponding phenol as reported earlier [7]. The glycosidic bond was formed in a Lewis acid-catalysed (borontrifluoride etherate) reaction at room temperature to give the β-product exclusively. The acetylated β-glucopyranosides were purified by recrystallization from ethanol and deprotected quantitatively using trimethylamine in aqueous methanol. The crude products were purified by silica gel column chromatography and recrystallization in methanol. 3′*n*-Pentadecylphenyl-β-D-glucopyranoside **1**: m.p. 143.5°C (optical microscopy), $[\alpha]_D^{25} - 36.72°$ (c = 0.222, EtOH). ^{1}H NMR (DMSO, d_6): 0.88 (t, 3H, Me), 1.26 (m, 24H, CH_2), 1.58 (m, 2H, C**H**$_2$CH$_2$Ar), 2.56 (m, or t, 2H, CH_2Ar), 3.13–3.69 (m, H_2, H_3, H_4, H_5 and H_6), 4.82 (d, 1H, H_1, $J_{1,2} = 7.3$), 6.78 (d, 2H), 6.80–6.88 (d, 1H), 7.17–7.19 (t, 1H). ELAN: $C_{27}H_{46}O_6$ calc. C 69.493, H 9.935; found C 68.993, H 9.876%. Cardanyl-β-D-glucopyranoside **2**: m.p. 123.0°C (optical microscopy), $[\alpha]_D^{25} - 36.26°$ (c = 0.215, EtOH). ^{1}H NMR (DMSO, d_6): 0.88 (t, 3H, Me), 1.25 (m, 10H, CH_2), 1.58 (m, 2H, C**H**$_2$CH$_2$Ar), 2.0 (C**H**$_2$CH=CH$_2$), 2.56 (m, or t, 2H, CH_2Ar), 2.78 (CH=CHC**H**$_2$CH=CH), 3.13–3.69

Table 1. Thermal phase transitions of dry and fully-hydrated glucolipids **1** and **2**, examined by DSC and POM.

Sample	Phase transition (DSC)[a]	ΔH/kcal mol^{-1}	Observed birefringent texture (microscopy)
1 (dry)	Cr $\xrightarrow{142.7°C}$ LC $\xrightarrow{145°C^b}$ I Cr $\xleftarrow{131°C}$ LC $\xleftarrow{138.9°C}$ I	$\Delta H_{total} = 5.31^c$	Conical fan texture at 142.7°C on heating.
2 (dry)	Cr $\xrightarrow{119.0°C}$ LC $\xrightarrow{121.7°C}$ I Cr $\xleftarrow{102.7°C}$ LC $\xleftarrow{115.0°C}$ I	$\Delta H_{total} = 3.03^c$	Conical fan texture at 115°C on cooling.
1 (fully hydrated)	G $\xrightarrow{77.8°C}$ LC	$\Delta H_{gel\text{-}liquid} = 13.68$	Maltese cross at 81°C, oily streak at 90°C.
2 (fully hydrated)	G $\xrightarrow{33.0°C}$ LC	$\Delta H_{gel\text{-}liquid} = 0.70$	Water penetration at 33°C and birefringent texture appeared.

[a] Scanning rates = 1.0°C min^{-1}. Cr = a crystalline phase, LC = a liquid crystalline phase, I = an isotropic liquid phase, G = a gel phase (a hydrated solid phase). The phase transition temperatures were taken from the peak maxima of the transition peaks.
[b] Value from the microscope measurement.
[c] The enthalpy values reported are combined values for LC transition and melting.

Table 2. Small-angle XRD lines of dry and fully-hydrated glucolipids **1** and **2**.

Experimental conditions[a]		*d*-spacing values of diffraction lines[b]				The ratio of *d*-spacing values	Phase type
		d_1	d_2	d_3	d_4	$d_1 : d_2 : d_3 : d_4$	
Glucolipid ***1***							
dry solid	25°C	3.84	1.92	1.27	0.94	1 : 0.500 : 0.331 : 0.240	lamellar
dry LC	143°C	4.12	2.05	—	1.02	1 : 0.498 : — : 0.248	lamellar
hydrated LC	85°C	4.44	2.24	—	—	1 : 0.505 : — : —	lamellar
Glucolipid ***2***							
dry solid	25°C	3.90	1.95	1.3	0.98	1 : 0.500 : 0.330 : 0.250	lamellar
dry LC	120°C	3.97	2.00	—	0.99	1 : 0.504 : — : 0.250	lamellar
hydrated LC	50°C	4.26	2.11	1.39	—	1 : 0.495 : 0.326 : —	lamellar

[a] LC = liquid crystalline phase.
[b] d_1, d_2, d_3 and d_4 denote *d*-spacing values of first, second, third and fourth diffraction lines for lamellar structures.

(m, H_2, H_3, H_4, H_5 and H_6), 4.82 (d, 1H, H_1, $J_{1,2} = 7.3$), 5.34–5.42 (vinyl bond), 6.79 (d, 2H), 6.80–6.89 (d, 1H), 7.19–7.20 (t, 1H). ELAN: $C_{27}H_{42}O_6$ calc. C 70.099, H 9.150; found C 70.386, H 9.441%.

The amphiphilic 4-alkylphenyl glucopyranosides with short alkyl chains [9] and 4-alkoxyphenyl glucopyranosides with C_{10} and C_{12} chains [11] showed thermotropic LC behaviour and mesophase sequence, crystal–smectic A phase–isotropic liquid, and this is similar to the behaviour of the *n*-alkylglucopyranosides containing C_{18} alkyl chains. However, the introduction of chain unsaturation is effective in decreasing the melting temperature of the amphiphilic alkylglucopyranosides [12]. These compounds, saturated with water, form lamellar liquid crystalline (lyotropic) phases above the T_c values. Variation of the alkyl chain length or the introduction of a rigid spacer unit (a phenyl ring) also has a large effect on the polymorphism of the lyotropic LC behaviour. Interestingly, 4-alkoxyphenyl glucosides [11 *b*] form ribbon aggregates below T_m in water. In the present work, a system with 3-alkylphenyl glucopyranosides having a C_{15} alkyl chain showed similar LC behaviour both in thermotropic and lyotropic mesophase formation.

In the cardanyl glucolipid systems, we have shown that the introduction of double bonds in the lipophilic part significantly decreases the phase transition temperatures, although the lipids show a common pattern in their phase transitions. Furthermore, the lipids **1** and **2** could form nanofibres and nanotubes in controlled conditions in water [7]. The extended study of the fractionation of cardanyl glucoside **2** into individual components is in progress, to investigate detailed characteristics of this class of materials. The present study has also demonstrated that we could synthesize new liquid crystalline alkylphenyl glycosides from renewable plant/crop-based resources, which provides a cheap and environmentally sustainable approach to new building blocks in organic materials chemistry.

References

[1] Kunitake, T., 1992, *Angew. Chem. Int. Ed.*, **31,** 709.
[2] Schnur, J. M., 1993, *Science*, **262,** 1669.
[3] Fuhrhop, J.-H., and Koning, J., 1994, *Membranes and Molecular Assemblies: The Synkinetic Approach*, edited by J. F. Stoddart (Cambridge: The Royal Society of Chemistry).
[4] Shimizu, T., 2002, *Macromol. Rapid Commun.*, **23,** 311.
[5] Feiters, M. C., and Nolte, R. J. M., 2000, *Advances in Supramolecular Chemistry*, edited by G. W. Gokel (JAI Press Inc.), pp. 41–156.
[6] Boullanger, P., 1998, *Top Curr. Chem.*, **187,** 275.
[7] John, G., Masuda, M., Okada, Y., Yase, K., and Shimizu, T., 2001, *Adv. Mater.*, **13,** 715.
[8] Tschierske, C., Lunow, A., and Zaschke, H., 1990, *Liq. Cryst.*, **8,** 885.
[9] Wingert, L. M., Jeffrey, G. A., Jahangir, and Baker, D. C., 1993, *Liq. Cryst.*, **13,** 467.
[10] Ewing, D. F., Goodby, J. W., Haley, J. A., Kelly, S. M., Letellier, P., and Mackenzie, G., 1997, *Liq. Cryst.*, **23,** 759.
[11] (*a*) Van Doren, H. A., Smits, E., Pestman, J. M., Engberts, J. B. F. N., and Kellogg, R. M., 2000, *Chem. Soc. Rev.*, **29,** 183; (*b*) Smits, E., Engberts, J. B. F. N., Kellogg, R. M., and van Doren, H. A., 1997, *Liq. Cryst.*, **23,** 481.
[12] Vill, V., von Minden, H. M., Koch, M. H. J., Seydel, U., and Brandenburg, K., 2000, *Chem. Phys. Lipids*, **104,** 75.
[13] Tyman, J. H. P., 1979, *Chem. Soc. Rev.*, **8,** 499.
[14] Demus, D., and Richter, L., 1978, *Textures of Liquid Crystals* (Weinheim: Verlag Chemie).
[15] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals-Textures and Structures* (Glasgow-London: Leonard Hill).
[16] Vill, V., Bocker, T., Thiem, J., and Fischer, F., 1989, *Liq. Cryst.*, **6,** 349.
[17] Pfannemuller, B., Welte, W., Chin, E., and Goodby, J. W., 1986, *Liq. Cryst.*, **1,** 357.