Liquid-Crystalline D-Glucose Dialkyl Acetals and Dodecyl D-Glucofuranosides

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Two new systems of liquid crystalline glucose derivatives **5a–d**, **6a**, **b** are prepared, studied and compared with reference compounds. The α- and β-D-dodecyl glucofuranosides **6a**, **b** show smectic A phases. The clearing points of the furanosides are of the same magnitude as those of the pyranosides. The alkyl glucose acetals **5a–d** show columnar discotic phases. The clearing points are about 30°C lower than those of the corresponding thioacetals.

In the past few years there has been great interest in amphiphilic liquid crystalline carbohydrate derivatives[1]. The knowledge of this new class of mesogenic compounds is rather small, and the influence of structure variation is not well understood compared to that of the numerous and well-known monophilic liquid crystals. The conformation and configuration as well as the formation of hydrogen bonds and the stiffness of the molecular shape play an important role for the mesogenic properties of carbohydrates.

Thus, carbohydrate derivatives normally only show disordered liquid–crystalline phases with simple goemetry like the smectic A phase[2], hexagonal columnar-discotic D_{hd} phase[3a,4] or cubic phase[5,6].

The alkyl β-D-glucopyranosides[2] were chosen as reference compounds for the smectic mesogens. A systematic variation of this group of compounds was performed in the following manner: Change of the configuration of the sugar moiety[7] and the position of the alkyl chain[8], preparation of acyclic D-glucitols[9a,b], and replacement of OH groups by ionic[10] and amino groups[11]. Reference compounds for the discotic mesogens are the glucose dialkyl dithioacetals[3a,b,12].

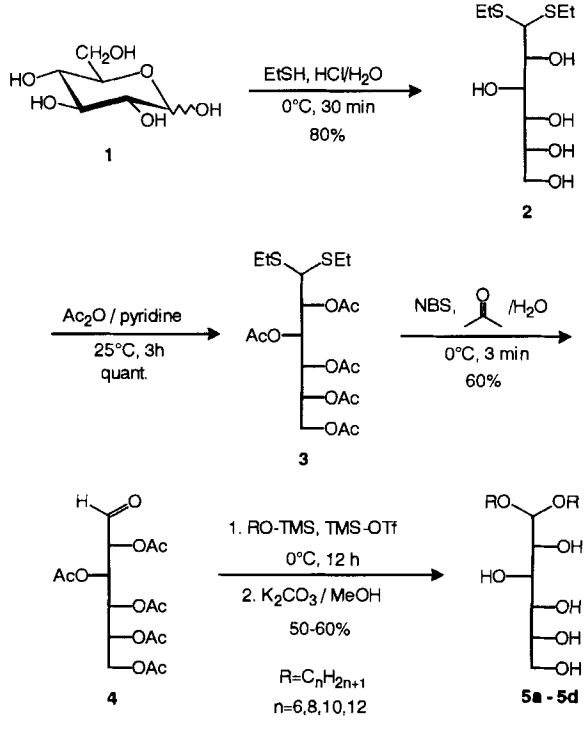
We now present the results of our investigation of the liquid–crystalline phases of D-glucose dialkyl acetals with a C_6–C_{12} chain and dodecyl D-glucofuranosides as new carbohydrate modifications, which provide some information about the effect of conformational stiffness on the mesogenic properties of carbohydrates and allow a direct comparison with the characteristics of the D-glucose dialkyl dithioacetals.

Results and Discussion

Synthesis of Liquid-Crystalline Carbohydrates 5a–6b

The synthesis of D-glucose dialkyl acetals (Scheme 1) and dodecyl D-glucofuranosides (Scheme 2) was performed in the following way. The treatment of D-glucose with ethanethiol gave the D-glucose diethyl dithioacetal **2**[13] which was acetylated[14] to afford the pentaacetate **3**. Oxidative desulfurization of **3** with *N*-bromosuccinimide[15] yielded 2,3,4,5,6-penta-*O*-acetyl-*aldehydo*-D-glucose (**4**) with a free aldehyde moiety. Reaction of **4** with the trimethylsilyl ethers of hexanol, octanol, decanol or dodecanol, in the presence of a catalytic amount of trimethylsilyl triflate according to the procedure described by Noyori[16], yielded the corresponding peracetylated D-glucose dialkyl acetals which were deprotected without further purification to give the desired D-glucose dialkyl acetals **5a-d**. The products were recrystallized twice from ethyl acetate to afford a white, crystalline powder.

Scheme 1



Dodecyl α- and β-D-glucofuranoside (**6a,b**) were prepared by treating the D-glucose didodecyl acetal **5d** with

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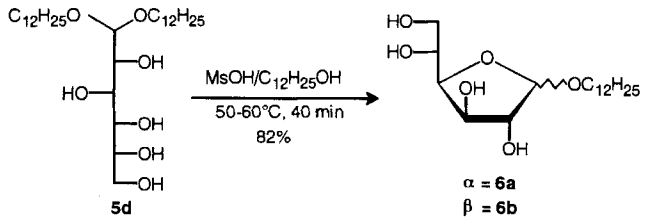
Scheme 2



dodecanol/methanesulfonic acid (Scheme 2). The resulting anomers were separated by preparative TLC and purified by recrystallization from ethyl acetate.

The structures of **6a,b** were determined by comparing their ^{1}H-NMR spectra and optical rotations with those of the known methyl furanosides (Table 1).

Table 1. Relevant coupling constants (^{1}H NMR), melting points and optical rotations of glucofuranosides

	Methyl-α-D-glucofuranoside	Methyl-β-D-glucofuranoside	Dodecyl-α-D-glucofuranoside (**6a**)[a]	Dodecyl-β-D-glucofuranoside (**6b**)[a]
$^3J_{1\text{-H},2\text{-H}}$	4.5 Hz[b]	1.1 Hz[b]	4.5 Hz	0.5 Hz
$^3J_{2\text{-H},3\text{-H}}$	3.3 Hz[b]	1.0 Hz[b]	3.5 Hz	1.1 Hz
$^3J_{3\text{-H},4\text{-H}}$	4.7 Hz[b]	4.6 Hz[b]	5.0 Hz	4.5 Hz
m.p.	63°C[c]	–	69.5°C	74.4°C
$[\alpha]_D^{20}$	+115°[c] (c = 2.0, H_2O)	−78°[c] (c = 3.0, H_2O)	+76° (c = 0.5, MeOH)	−50.8° (c = 0.5, MeOH) (α:β ≈ 5:95)

[a] This work; [D_4]methanol, 500 MHz. – [b] Ref.[17]; D_2O, 220 MHz. – [c] Ref.[18].

Liquid-Crystalline Properties of the Glucofuranosides 6a,b

The dodecyl glucofuranosides show smectic A phases like the pyranosides. The α anomer **6a** melts at 69.5°C and clears at 114.2°C; the β anomer **6b** melts at 74.4°C and clears at 147.2°C. In the supercooled liquid-crystalline phase of **6b** a reversible change of texture occurs at 10°C, corresponding to a metastable crystalline or a highly ordered smectic phase.

Table 2 shows a comparison of the properties of **6a** and **6b** with those of realated compounds. This led us to draw the following conclusions:

(i) The clearing points of the furanosides are of the same magnitude as those of the pyranosides. Thus, the flexibility of the five-membered furanose ring compared to the rather stiff six-membered pyranose ring does not lead to a decrease of the clearing points.

(ii) As found for the glucopyranosides the α-D-glucofuranoside has a lower clearing point than the β anomer. However, in the case of the pyranosides this effect is rather small, whereas for the glucofuranosides the difference of the clearing points of the anomers is more than 30°C.

(iii) The β-D-glucofuranoside **6b** has a clearing point by 50°C higher than the corresponding *manno* derivativel[19]. In the case of the α-D-pyranosides the *manno* derivative has the higher clearing point.

Table 2. Clearing points of dodecyl D-glycosides **6a** and **6b** and related compounds

Sugar	Phase transitions	Source
α-D-Mannopyranoside	Cr 74.2 S_A 161.7 I	[7]
β-D-Mannofuranoside	Cr 55.8 S_A 97.2 I	[19]
1-*O*-Substituted D-mannitol	Cr 111.2 S_A 167 I	[20]
α-D-Glucopyranoside	Cr 81.4 S_A 149.5 I	This work[a]
β-D-Glucopyranoside	Cr 80.4 S_A 144.9 I	This work[b]
α-D-Glucofuranoside	Cr 69.5 S_A 114.2 I	This work
β-D-Glucofuranoside	Cr 74.4 S_A 147.8 I[c]	This work

[a] Reported: Cr 81 S_A 149 I[21]. – [b] Reported: Cr 80.4 S_A 143.4 I[2]. – [c] Unknown monotropic phase below room temperature, S_B or Cr_2.

Liquid-Crystalline Properties of the Glucose Dialkyl Acetals 5a–d

All compounds have nearly the same melting point of 90–93°C (Table 3). Three of them exhibit a columnar-discotic D_{hd} phase which is mixable with the liquid-crystalline phase of the glucose didodecyl dithioacetals[3a]. The clearing points rise with the chain length from 82.1°C (octyl) to 118.5°C (dodecyl). Thus, the acetals behave like the corresponding thioacetals showing the same liquid-crystalline phases and the same dependence of the chain length, but the clearing points are about 30°C lower.

Table 3. Phase transitions of glucose acetals and thioacetals

Compound	Chain	Phase transitions[a]	c.p. of Dithioacetals[b]	Contact with H_2O, 80°C
5a	C_6	(82) Cr 90.2 I	82.5	isotropic solution
5b	C_8	(58) Cr 92.4 D_{hd} 82.1 I	118.9	cubic mesophase
5c	C_{10}	(60) Cr 93.1 D_{hd} 101.7 I	132.5	discotic mesophase
5d	C_{12}	(62) Cr 93.6 D_{hd} 118.5 I	136	unsoluble

[a] The values in brackets are the temperatures of recrystallization. – [b] Transition temperatures of the corresponding dithioacetals, taken from the literature[3b,25,26].

It had already been shown that in the case of smectic carbohydrate-derived liquid crystals sulfur as linking atom between hydrophilic and hydrophobic parts of the molecule causes higher clearing points than oxygen. This was demonstrated for α-D-thioglucosides[22], 1-thioglycerides[23a], 1-alkylthio-1-deoxy-D-glucitols[23b] and thioesters of galacturonic acid[24]. In this work we found a similar influence of sulfur on the discotic phases.

Conclusions

The conformational flexibility of amphiphilic liquid-crystalline carbohydrates has only a small influence on the type and the clearing point of the mesogenic phase. Open-chain compounds and compounds with rigid or flexible rings exhibit nearly the same clearing points. In contrast, the configuration at the stereogenic centers of the sugar moiety is highly important. Thus, inversion of one OH group could

change the clearing points by 50°C as found for the liquid-crystalline furanosides. Compounds with sulfur as linking atom between hydrophilic and hydrophobic molecular parts show higher clearing points than the corresponding oxygen derivatives.

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Experimental

Optical rotations: Perkin-Elmer 241 polarimeter, sodium lamp (589 nm, D line). – ^1H and ^{13}C NMR: Bruker and Varian instruments, $CDCl_3$ as solvent. – IR: Bruker ifs 25 FT-IR spectrometer, KBr pellets. – FAB-MS: Finnigan MAT 95 system with 3-nitrobenzaldehyde as matrix. – Elemental analyses: Analytical laboratory of the university. – Transition temperatures: Polarizing microscope Olympus BH equipped with a Mettler FP 82 heating stage; the assignments of the liqud-crystalline phases are based on characteristic textures and contact preparations with reference compounds.

D-Glucose Diethyl Dithioacetal (**2**): From 20.0 g (111 mmol) of D-glucose (**1**) 25.0 g (80%) of D-glucose diethyl dithioacetal (**2**) was obtained as a colorless powder; m.p. 127°C (ref.[13] 127.5°C). – MS (DCI, NH_3); *m/z* (%): 70.1 (100), 303.6 (38) [$M^+ + NH_3$].

2,3,4,5,6-Penta-O-acetyl-D-glucose Diethyl Dithioacetal (**3**): 14.3 g (50.0 mmol) of **2** was acetylated with pyridine/acetanhydride to give 24.8 g (ca. 99%) of crude **3** which was used without further purification.

2,3,4,5,6-Penta-O-acetyl-D-glucose (**4**): 4.97 g (10.0 mmol) of 2,3,4,5,6-penta-*O*-acetyl-D-glucose diethyl dithioacetal (**3**) and 4.45 g (25.0 mmol) of *N*-bromosuccinimide gave 2.34 g (69%) of **4** by using the method of Miljkovic et al.[15]; m.p. 116.5°C (ref.[13] 116.5°C).

Dodecyl Trimethylsilyl Ether: TMSCl (35.0 g, 30.0 ml, 0.32 mol) was mixed with triethylamine (32.6 g, 45.0 ml, 0.32 mol), and the mixture was centrifuged[27]. To 60 ml of this mixture dodecanol (10.0 ml, 44.5 mmol) was added in portions under Ar. The mixture was stirred for 1 h. After quenching with 30 ml of methanol, the solution was concentrated and the residue extracted three times with pentane. The combined extracts were concentrated to give 11.0 g (95%) of a colorless liquid. The product was used without further purification. – IR (film): No OH band. – ^1H NMR (C_6D_6): δ = 0.12 [br. s, 9H, $Si(CH_3)_3$], 0.91 (m_c, 3H, CH_3), 1.28 (br. s, 18H, 3- to 11-H), 1.58 (m_c, 2H, 2-H), 3.55 (t, *J* = 6.3 Hz, 2H, 1-H).

In a similar way, the following compounds were prepared: hexyl trimethylsilyl ether, octyl trimethylsilyl ether, decyl trimethylsilyl ether.

D-Glucose Didodecyl Acetal (**5d**): To a stirred solution of dodecyl trimethylsilyl ether (1.37 g, 5.32 mmol) and 2,3,4,5,6-penta-*O*-acetyl-D-glucose (**4**, 0.90 g, 2.22 mmol) in dichloromethane (10 ml) was added TMSOTf (90 µl, 0.10 mmol) in portions under Ar at −35°C. The mixture was stirred at the same temperature for additional 12 h, then the reaction was quenched with 0.5 ml of a mixture of dry triethylamine and dry methanol (1:1, v/v). After concentration of the reaction mixture, the residue was dissolved in dry methanol (5.0 ml), and the solution was stirred with K_2CO_3 (80 mg) for 30 min at room temperature while the product precipitated. The whole mixture was poured into ice-cold water (20 ml), and the product was filtered off, dried in vacuo and recrystallized twice from ethyl acetate to give 670 mg (56%) of **5d** as white crystals; $[\alpha]_D^{20}$ = +10.4 (*c* = 0.5, methanol). – ^1H NMR ([D_4]methanol/TMS): δ = 0.90 (m, 6H, CH_3), 1.32 (br. s, 18H, 3'- to 11'-H), 1.60 (m, 4H, 2'-H), 3.5–3.8 (m, 9H, 1'-H, 2- to 6-H), 3.98 (dd, *J* = 2.5 Hz, *J* = 2.5 Hz, 1H, 3-H), 4.55 (d, *J* = 6.7 Hz, 1H, 1-H). – ^{13}C NMR ([D_5]pyridine/TMS): δ = 14.30 (C-12'), 22.96, 26.59, 26.63, 29.82, 29.95, 30.42, 30.54, 32.19 (C-2' to -11'), 65.07 (C-6), 66.99, 68.27 (C-1'), 69.60, 73.01, 75.11, 75.93 (C-2 to -5), 104.0 (C-1). – MS (FAB, 3-nitrobenzaldehyde, NaCl); *m/z* (%): 349 (100) [$M^+ - C_{12}H_{25}OH$ + H], 557 (50) [M^+ + Na], 534 (100) [M^- − H]. – IR (KBr): $\tilde{\nu}$ = 3384 cm^{-1} (OH), 2958, 2920, 2852 m (CH_2), 1470 (CH_2/CH_3), 1390 (CH_3), 1266 (OH), 1132, 1122, 1108, 1088, 1064, 1032 (C–O), 718 (CH_2). – $C_{30}H_{62}O_7$ (534.82): calcd. C 67.37, H 11.68; found C 67.29, H 11.56.

D-Glucose Didecyl Acetal (**5c**): According to the procedure used for the preparation of **5d**, the reaction of **4** (830 mg, 2.12 mmol) with decyl trimethylsilyl ether (1.17 g, 5.09 mmol) yielded 570 mg (56%) of **5c**; $[\alpha]_D^{20}$ = +11.6 (*c* = 0.5, methanol). – $C_{26}H_{54}O_7$ (478.7): calcd. C 65.23, H 11.37; found C 65.32, H 11.40.

D-Glucose Dioctyl Acetal (**5b**): According to the procedure used for the preparation of **5d**, the reaction of **4** (613 mg, 1.57 mmol) with octyl trimethylsilyl ether (736 mg, 3.77 mmol) yielded 398 mg (60%) of **5b**; $[\alpha]_D^{20}$ = +12.6 (*c* = 0.5, methanol). – $C_{22}H_{46}O_7$ (422.6): calcd. C 62.53, H 10.97; found C 62.72, H 10.92.

D-Glucose Dihexyl Acetal (**5a**): According to the procedure used for the preparation of **5d**, the reaction of **4** (580 mg, 1.50 mmol) with hexyl trimethylsilyl ether (630 mg, 3.60 mmol) yielded 316 mg (58%) of **5a**; $[\alpha]_D^{20}$ = +14.8 (*c* = 0.5, methanol). – $C_{18}H_{38}O_7$ (366.5): calcd. C 58.99, H 10.45; found C 59.08, H 10.55.

Dodecyl α- and β-D-Glucofuranosides (**6a** and **6b**): 411 mg (0.77 mmol) of 2,3,4,5,6-Penta-*O*-acetyl-D-glucose (**5d**) was mixed with 8.0 ml of a solution of 64.8 µl of methanesulfonic acid and 131 g of dodecanol, and the mixture was stirred for 40 min at 50–60°C [TLC control, silica gel, dichloromethane/methanol (1:1), R_f(acetal) = 0.43, R_f(α-furanoside) = 0.33, R_f(β-furanoside) = 0.28]. After neutralization with triethylamine (0.5 ml), stirring was continued for additional 5 min. The main amount of dodecanol was evaporated at 80–100°C by bulb-to-bulb vacuum distillation. Chromatography on 25 g of silica gel [*tert*-butyl methyl ether/petroleum ether (1:1), dichloromethane/methanol (1:1)] afforded 265 mg (99%) of the crude furanosides. Partial separation of the anomers was achieved by flash chromatography on 60 g of silica gel 60 Merck, 7734 with dichloromethane/methanol (9:1); pure anomers were separated by preparative TLC [Woelm Pharma, F254, 0.25 mm; dichloromethane/methanol (9:1)], followed by recrystallisation from ethyl acetate. – $C_{18}H_{36}O_6$ (348.48): calcd. C 62.04, H 10.41; found C 61.94, H 10.39.

α *Anomer:* $[\alpha]_D^{20}$ = +76.0 (*c* = 0.5, methanol). – ^1H NMR ([D_4]methanol/TMS): δ = 0.885 (m_c, 3H, 12'-H), 1.3 (m, 18H, 3'- to 11'-H), 1.612 (m_c, 2H, 2'-H), 3.498 (dt, *J* = 6.5 Hz, *J* = 9.5 Hz, 1H, 1'-H_a), 3.580 (dd, *J* = 6.5 Hz, *J* = 11.5 Hz, 1H, 6-H_a), 3.733 (dt, *J* = 6.5 Hz, *J* = 9.5 Hz, 1H, 1'-H_b), 3.760 (dd, *J* = 3.5 Hz, *J* = 11.5 Hz, 1H, 6-H_b), 3.838 (ddd, *J* = 3.5 Hz, *J* = 6.5 Hz, *J* = 7.5 Hz, 1H, 5-H), 3.980 (dd, *J* = 3.5 Hz, *J* = 4.5 Hz, 1H, 2-H), 4.022 (dd, *J* = 5.0 Hz, *J* = 7.5 Hz, 1H, 4-H), 4.226 (dd, *J* = 3.5 Hz, *J* = 5.0 Hz, 1H, 3-H), 5.015 (d, *J* = 4.5 Hz, 1H, 10-H). – ^{13}C NMR ([D_4]methanol/TMS): δ = 14.43 (C-12'), 23.72, 27.19, 30.47, 30.56, 30.74, 30.79, 33.06 (C-2' to -11'), 64.90 (C-6), 69.83 (C-1'), 72.06, 77.70, 79.13, 79.28 (C-2 to -5), 103.1 (C-1). – MS (FAB, 3-nitrobenzaldehyde, NaCl); *m/z* (%): 349 (100) [M^+ + H], 371 (45) [M^+ + Na], 698 (20) [2 M^+ + H], 347 (90) [M^- − H], 501 (100), 499 (20) [M^- + 3-NBA − H], 696 (20) [2 M^- − H]. – IR (KBr): $\tilde{\nu}$ = 3380–3500 cm^{-1} (OH), 2936, 2916, 2868, 2852 (CH_2), 1472

(CH_2/CH_3), 1374, 1356 (CH_3), 1242 (OH), 1126, 1084, 1046, 1016 (C–O), 718 (CH_2).

β *Anomer:* ^{1}H NMR ([D$_4$]methanol/TMS): δ = 0.90 (m_c, 3H, 12'-H), 1.3 (m, 18H, 3'- to 11'-H), 1.57 (m_c, 2H, 2'-H), 3.392 (dt, J = 6.5 Hz, J = 9.5 Hz, 1H, 1'-H_a), 3.634 (dd, J = 6.0 Hz, J = 11.5 Hz, 1H, 6-H_a), 3.688 (dt, J = 6.5 Hz, J = 9.5 Hz, 1H, 1'-H_b), 3.796 (dd, J = 3.0 Hz, J = 11.5 Hz, 1H, 6-H_b), 3.924 (ddd, J = 3.0 Hz, J = 6.0 Hz, J = 7.5 Hz, 1H, 5-H), 4.012 (dd, J = 0.5 Hz, J = 1.5 Hz, 1H, 2-H), 4.082 (dd, J = 4.5 Hz, J = 9.0 Hz, 1H, 4-H), 4.102 (dd, J = 1.0 Hz, J = 4.5 Hz, 1H, 3-H), 4.836 (d, J = 0.5 Hz, 1H, 1-H). – IR (KBr): $\tilde{\nu}$ = 3374 cm^{-1} (OH), 2918, 2852 (OH), 1466 (CH_2/CH_3), 1382, 1336 (CH_3), 1272, 1226 (OH), 1168, 1104, 1084, 1028 (C–O), 722 (CH_2).

The pyranosides were prepared according to the procedure reported in ref.[7].

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