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Amphiphilic carbohydrate-based mesogens incorporating structural features of calamitic liquid crystals

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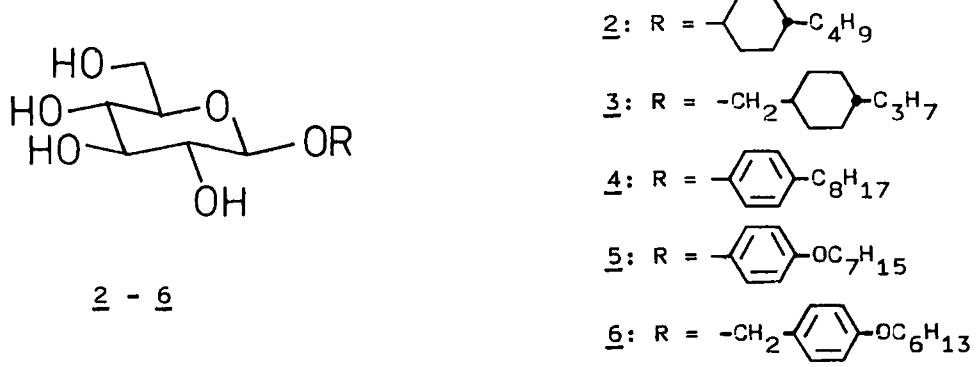
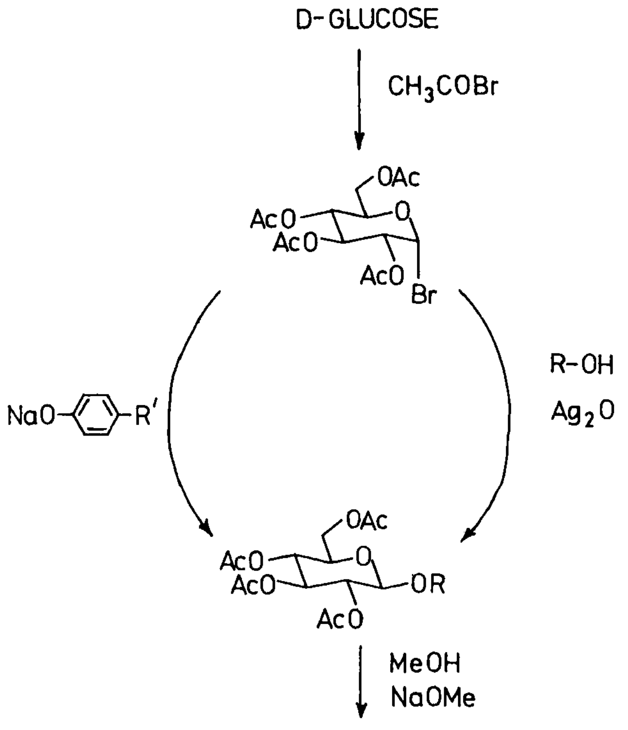
Several examples of liquid-crystalline carbohydrate derivatives incorporating a carbocyclic ring in the side chain are reported and the influence of structural variations discussed. The mesophase observed for all compounds described is smectic A and the mesophase stability is strongly affected by the linking unit between the carbocyclic and carbohydrate moieties.

Various amphiphilic carbohydrate derivatives with functional groups bearing long alkyl chains exhibit liquid-crystalline behaviour [1–8]. Indeed it has been stated that these compounds may be a valuable source for a large number of liquid crystals [1]. Most of the mesogenic carbohydrate derivatives described hitherto consist of a carbohydrate unit linked with one or more *n*-alkyl chains. The formation of liquid-crystalline phases in these carbohydrate systems is promoted by the different interactions of the two chemically dissimilar portions of the molecular structures. Thus the carbohydrate moieties interact through hydrogen bonding, whereas the alkyl chains interact through van der Waals forces [1, 7].

It has recently been stated that the *n*-alkane-1,2-diols are parent compounds for a large family of liquid-crystalline carbohydrate derivatives [9]. Since the appropriate introduction of rigid structural units into the *n*-alkyl chain of the liquid-crystalline *n*-alkane-1,2-diols gives rise to higher clearing temperatures [10] it was of special interest to combine structural features of calamitic mesogens with those of carbohydrate-based liquid crystals. The only reported example of a carbohydrate mesogen with a carbocyclic moiety in the side chain was *N*-4′-*n*-butylphenyl-D-ribonamide [5]. Here we report on efforts to incorporate the trans-1,4-cyclohexylene unit and the 1,4-phenylene unit into the *n*-alkyl chain of mesogenic 1-*O*-*β*-D-alkylglucopyranosides:



Scheme.



2 - 6

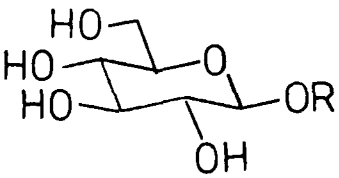
Synthesis of the 1-*O*-β-D-glucopyranosides **2–6**.

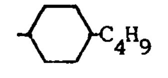
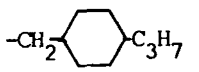
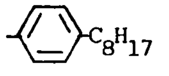
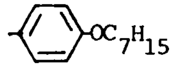
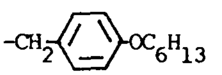
The synthesis of 1-*O*-trans-4'-*n*-butylcyclohexyl-β-D-glucopyranoside **2**, 1-*O*-trans-4'-*n*-propylcyclohexylmethyl-β-D-glucopyranoside **3**, 1-*O*-4'-*n*-octylphenyl-β-D-glucopyranoside **4**, 1-*O*-4'-*n*-heptyloxy-β-D-glucopyranoside **5**, and 1-*O*-4'-*n*-hexyloxyphenylmethyl-β-D-glucopyranoside **6** was readily achieved by glucosylation of acetobromoglucose [11], followed by deprotection of the hydroxy groups using standard procedures (yields 70–80 per cent) [12], as shown in the figure.

It was found by polarizing microscopy that the carbohydrate derivatives **2–6** exhibit stable smectic A mesophases above the melting point (focal conic texture with large homeotropic areas). The transition temperatures of the freshly synthesized β-glucopyranosides, together with those of the comparable *n*-alkyl derivatives **1** are given in the table. The results obtained can be summarized as follows. All cyclohexyl substituted derivatives exhibit higher clearing temperatures, when compared with the related *n*-alkyl derivatives **1.1** [1, 6, 8]. The mesophase stability is also significantly increased by the introduction of a 1,4-phenylene unit. As usually observed for non-amphiphilic calamitic mesogens [13], the clearing temperature of the alkoxy substituted derivative **5** is elevated in comparison with the *n*-alkyl derivative **4**. This indicates the significance of attractive and repulsive interactions between the hydrophobic moieties for the self-assembly of carbohydrate amphiphiles.

However a significant depression of the clearing temperature is observed if an additional methylene group is introduced between the glycosidic oxygen atom and the phenyl group (compound **6**). Even though an even numbered linking unit (–CH$_2$–O–) between the carbohydrate moiety and the rigid core is created, which is expected to

Transition temperatures for the compounds **1**–**6**†.



Compound‡	R	m.p./ °C	c.p.§/ °C	Reference
1.1	$-C_8H_{17}$	69	110	[1, 6]
2		137	167	
3		125	147	
1.2	$-C_{12}H_{25}$	80	142	[1, 6]
4		108	192	
5		107	202	
6		115	127	

† Determined by polarizing microscopy.

‡ Satisfactory C,H-analyses were obtained for **2**–**6**.

§ Clearing point.

|| ^{1}H NMR (200 MHz, DMSO-d_6, ppm): 0·89 (t, J = 6 Hz, 3 H, $-CH_3$); 1·23 (s, broad, 10 H, $-CH_2-$); 1·51 (m, broad, 2 H, $-CH_2-CH_2-$ar); 3·0–3·7 (m, 8 H, $-CH_2-$ar, $-CH_2OH$, $=CH-OH$); 4·54 (t, J = 4·7 Hz, 1 H, $-CH_2-OH$); 4·78 (d, J = 7·2 Hz, 1 H, H-1); 5·00 (d, J = 4·7 Hz, 1 H, -OH); 5·06 (d, J = 3·5 Hz, 1 H, -OH); 5·26 (d, J = 3·7 Hz, 1 H, -OH); 6·91 (d, J = 8·4 Hz, 2 H, H-ar); 7·07 (d, J = 8·5 Hz, 2 H, H-ar). ^{13}C NMR (20 MHz, DMSO-d_6, ppm): 14·38 (CH_3); 23·63 (CH_2); 30·21 (CH_2); 30·33 (CH_2); 30·50 (CH_2); 32·78 (CH_2); 32·95 (CH_2); 36·05 (CH_2); 62·57 (CH_2OH); 71·42 (CH–O); 74·94 (CH–O); 78·02 (2 C, CH–O); 102·61 (C-2); 117·75 (2 C, CH-ar); 130·18 (2 C, CH-ar); 137·99 (C-ar); 157·17 (C-ar).

stabilize the liquid-crystalline phases, the mesophase stability is significantly diminished in this way. We would explain this behaviour in the following way. First, the mesophase stability of the glucosides seems to be influenced only slightly by the geometry of this linking unit. This is evident from the comparison of the cyclohexyl substituted 1-*O*-*β*-glucosides **2** and **3**, where the oxymethylene bridged compound **3** exhibits a slightly lower clearing temperature. It is also known that 1-*O*-*β*-pyranosides and 1-*O*-*α*-pyranosides have similar transition temperatures, whereas the axial *α*-alkylated pyranosides have higher clearing temperatures than the equatorial *β*-alkylated [1].

It appears that an angle between the dissimilar portions of these mesogens slightly improves the packing of the carbohydrate units and the hydrogen bonding between them. Secondly, the intramolecular flexibility of the CH_2–ar bond in compound **6** is significantly greater than that of the O–ar bond in compound **5**, due to loss of conjugation with the aromatic π-system. This behaviour is well known for calamitic mesogens, where the intramolecular flexibility has a strong effect on the transition temperatures [14–16]. From our results it appears that the introduction of structural features of calamitic mesogens into the side chain of amphiphilic carbohydrate liquid crystals gives rise to greater mesophase stability, if these structural units are known to stabilize non-amphiphilic mesogens. Thereby, the geometry of the linkage between carbocyclic and carbohydrate moiety seems not to matter greatly.

We conclude by noting that the introduction of calamitic mesogenic units into carbohydrate amphiphiles greatly increases the potential number of carbohydrate liquid crystals and allows for greater control of their thermal properties.

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