Carbohydrate Liquid Crystals even at Ambient Temperature

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The dialkyl dithioacetals of D-glucose, L-rhamnose, D-mannose, D-galactose, D-arabinose, D-xylose, and D-lyxose have been prepared, and with the exception of rhamnose, all exhibit liquid crystalline behaviour; the transition points for phase changes are strongly dependent on stereochemistry.

Various monosaccharides and derivatives thereof condensed with functional groups bearing long alkyl chains exhibit liquid crystalline (LC) behaviour.[1] The staggering capacity for structural variation in carbohydrates suggests they may be a valuable source of liquid crystals.[2] We report here for some aldose derivatives, the complex relationship between configuration and the display of LC behaviour.

The dialkyl dithioacetals (**1**)—(**7**), derived from, respectively, D-glucose, L-rhamnose, D-mannose, D-galactose, D-arabinose, D-xylose, and D-lyxose show promise as LC sources. The desired derivatives were obtained by treatment of the sugar (20—30 mmol) with 2 equiv. of n-alkylthiol (in 10 ml conc. HCl–1 g $ZnCl_2$–2 g $CaCl_2$) for 0.5—8 h (depending on the compound) at room temperature or in an ice bath.[3]† Data for twelve derivatives of D-glucose (**1**) are given in Table 1. These compounds all exhibit LC behaviour. Differential scanning calorimetry (d.s.c.) was used to determine thermal behaviour; a large endothermal transition at the melting point followed by a far smaller endothermal transition at the clearing point were observed. In several cases one or more

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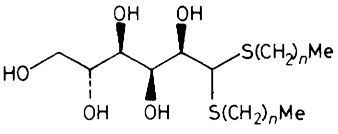
† All new compounds were fully characterized by spectroscopic methods and gave satisfactory elemental analyses and/or exact mass spectra.

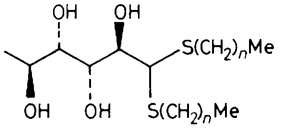
Table 1. Liquid crystalline behaviour of dialkyl dithioacetals (**1**) derived from D-glucose.

D-Glucose dialkyl dithioacetal (**1**)	M.p./°C	S_A-Iso/°C[a]
D-Glucose dibutyl dithioacetal	127—127.5	
D-Glucose dipentyl dithioacetal	115—116	
D-Glucose dihexyl dithioacetal	103—103.5	[b]
D-Glucose diheptyl dithioacetal	101.5	103.5 (102)
D-Glucose dioctyl dithioacetal	100	117 (115.5)
D-Glucose dinonyl dithioacetal	99.5—100.5	130.5 (129.5)
D-Glucose didecyl dithioacetal	97.5	132.5 (131.5)
D-Glucose diundecyl dithioacetal	98—98.5	138 (135)
D-Glucose didodecyl dithioacetal	97	136 (134.5)
D-Glucose ditridecyl dithioacetal	97.5—98.0	142 (139.5)
D-Glucose ditetradecyl dithioacetal	93—94	138 (135)
D-Glucose dipentadecyl dithioacetal	97.5	133.5 (131.5)

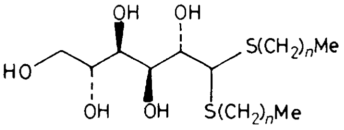
[a] Values in parentheses observed upon cooling. [b] Simultaneous crystallization and liquid crystal formation observed upon cooling.



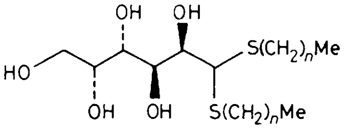
(**1**)



(**2**)



(**3**)



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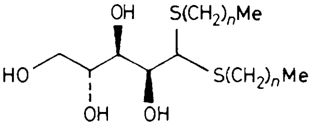

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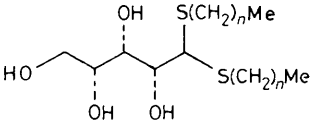
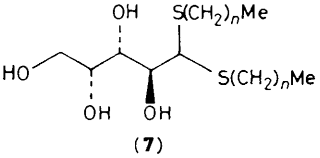


(**6**)



(**7**)

crystal-to-crystal transitions occurred. Supercooling of the LC phase was considerable in all samples and a smectic A phase was formed (determined by microscopic examination).[4] Fairly typical behaviour for an homologous series was observed.[5]

Table 2. Liquid crystalline behaviour of dioctyl dithioacetals of sugars (**2**)—(**7**).

Aldose dioctyl dithioacetal	M.p./°C	S_A-Iso/°C
D Glucose dioctyl dithioacetal (**1**)	100	117 (115.5)
L-Rhamnose dioctyl dithioacetal (**2**)	113—114	
D-Mannose dioctyl dithioacetal (**3**)	113.5—114.0	144.5 (143.5)
D-Galactose dioctyl dithioacetal (**4**)	112.5—113.5	142 (140.5)
L-Arabinose dioctyl dithioacetal (**5**)	88	103.5 (100)
D-Xylose dioctyl dithioacetal (**6**)	*ca.* Room temp.	110 (107)
D-Lyxose dioctyl dithioacetal (**7**)	64	104 (102)

Table 3. Liquid crystalline behaviour of some dialkyl dithioacetals (**6**) derived from xylose.

D-Xylose dialkyl dithioacetal	M.p./°C	S_A-Iso/°C
D-Xylose dihexyl dithioacetal	<Room temp.	61 (59)
D-Xylose diheptyl dithioacetal	<Room temp.	78.5 (76)
D-Xylose dioctyl dithioacetal	*ca.* Room temp.	110 (107)
D-Xylose didodecyl dithioacetal	~30	188 (185)[a]

[a] Decomposition begins at the clearing point.

To our knowledge these are the first acyclic carbohydrate derivatives with more than one alkyl chain reported to exhibit LC characteristics.[6] Other open chain carbohydrate mesogens have been found to be prone to decomposition (caramelization), which seems to occur more rapidly in the LC phase.[7] No evidence of such behaviour has been found; these compounds can be taken through numerous heating–cooling cycles without observable deterioration.

For the C_6 alkyl chain the LC phase is monotropic, whereas for C_7 and higher chains enantiotropic behaviour is seen. From preliminary *X*-ray data for the C_8 derivative, the width of the smectic layers is 26 Å, somewhat less than two molecular lengths.‡ This is consistent with the usual model for the smectic A_d phase, which entails interdigitated head-to-head orientation of the polar groups with the hydrophobic tails directed outwards.[1]

Data for the dioctyl dithioacetals of the sugars (**2**)—(**7**) are given in Table 2. Note that the dithioacetal derived from L-rhamnose (**2**), 6-deoxy-L-mannose, fails to exhibit LC behaviour. The nonpolar methyl end group may prevent formation of the interdigitated head-to-head bimolecular layers characteristic of carbohydrate derivatives exhibiting mesogenic behaviour.

However, the dioctyl dithioacetal of the C_5 monosaccharide, xylose (**6**), is liquid crystalline at room temperature and is mesomorphic over a wide temperature range. Data for four xylose derivatives of different chain lengths are given in Table 3. All derivatives show a remarkably broad LC range and the phases are smectic. Note that xylose in the extended chain conformation drawn is the only pentose studied that may have all of its hydroxyl groups oriented in roughly the same direction (all *gauche* arrangement of the hydroxyl groups). This stereochemical aspect may well be necessary for the lowering of the transition temperature for the crystalline–LC change of phase.

The accuracy of Jeffrey's prediction that a vast store of liquid crystalline materials can be derived from carbohydrates seems clear.[1] We have also observed, for instance, that 1-deoxy-1-alkylamino-D-alditols as well as alkyl thioglucosides

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‡ Powder diffraction data were obtained at the Department of Solid State Physics of the University of Groningen.

exhibit a broad range of LC behaviour. Again the stereochemistry of the carbohydrate moiety has a strong effect on the observed transition temperatures. Investigations of the effect of configurational and structural variations on the temperature range of liquid crystal formation are continuing.

Added in proof: It has come to our attention that similar work has been published idependently by W. V. Dahlhoff, *Z. Naturforsch, Teil B*, 1987, **426**, 661; (*Chem. Abstr.*, **108**, 38208k).

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