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Some novel disaccharide-derived liquid crystals

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Some novel disaccharide-derived amphiphiles, in which the hydrophobic long chain alkyl group and an α -D-glucose moiety are separated by a hydrophilic five carbon spacer or a hydrophobic furan residue, were investigated as to their mesomorphic properties using DSC, thermomicroscopy and various X-ray methods. All compounds exhibit a smectic A phase, characterized by aggregation to a bilayered S_{Ad} structure. The layer thickness d , measured by X-ray, correlates with the presence of polar and non-polar moieties, adjoining molecules interacting via hydrogen bonding. Based on the known structural concepts for sugar-derived liquid crystals, a model is suggested to account for the observed S_{Ad} layer arrangement. The mesomorphic behaviour of two *N*-alkanoyl derivatives of (glucosyloxymethylfuryl)methylamine, i.e. species in which sugar and long chain fatty acid are separated by a quasi-aromatic furan residue, is unusual, as different X-ray methods invariably give the same odd d -value indicative of a smectic layer thickness of three to four molecules.

1. Introduction

Amphiphiles composed of a single long chain *n*-alkyl or acyl moiety and a pyranoid or acyclic monosaccharide portion (in either glycoside, ester, or amide linkage) have increasingly become accessible within the last decade [1–5]. They invariably form smectic A_d mesophases believed to be head-to-head bilayers with interdigitizing alkyl chains in the case of cyclic sugar residues, in contrast to head-to-tail monolayers with non-interweaved alkyl chains, when the saccharidic portions are acyclic [2, 3].

Amongst the large number of saccharide amphiphiles with a single alkyl chain, those derived from the readily accessible disaccharides maltose, lactose, and cellobiose are comparatively few: the α - [5] and the β -anomers [4, 5] of *n*-dodecyl and *n*-tetradecyl maltoside, both anomers of *n*-tetradecyl lactoside [5] and the *n*-alkyl β -D-cellobiosides with chain lengths of 7–18 [6]; also the octadecyl maltobionamide [4], the *n*-dodecyl glycosides of β -D-isomaltulose [5] and α -D-gentiobiose [7] have been studied. Despite their interesting liquid crystalline properties, there is no clear picture at present of the way in which their mesophase behaviour is influenced in enlarging the hydrophilic sugar portions, i.e. on proceeding from long chain *n*-alkyl monosaccharides to

analogues with two pyranoid residues or to compounds in which one monosaccharide is pyranoid and the second acyclic. This led us to study a number of model compounds derived from the disaccharide isomaltulose, a D-glucopyranosyl- α (1 \rightarrow 6)-D-fructose, which has recently become accessible on an industrial scale [8], and in which the fructose portion can readily be converted into the next lower D-arabinonic acid [9] or, by a twofold dehydration, into a furan residue [10]. Subsequent amidation or esterification [9, 10] leads to the terminally glucosylated *N*-(1-alkyl)-D-arabinonamides **1–3**, and the quite novel amphiphiles **4–6**, in which glucosyl and *n*-alkyl portions are separated by a quasi-aromatic furan moiety (figure 1):

The liquid crystalline behaviour of these model compounds is the subject of this communication.

2. Experimental

The acquisition of the isomaltulose-derived compounds **1–6** was effected as follows: (a) amidation of methyl (α -D-glucopyranosyl)-D-arabinonate [9] with *n*-octyl-(\rightarrow **1**), *n*-dodecyl-(\rightarrow **2**), and *n*-octadecylamine (\rightarrow **3**), as detailed in [9] for **2**; (b) DCC-induced esterification of α -GMF-carboxylic acid [10] with dodecanol (\rightarrow **4**) [10]; (c) amidation of α -GMF-amine [10] with the acid chlorides of capric and lauric acid, respectively (\rightarrow **5** and

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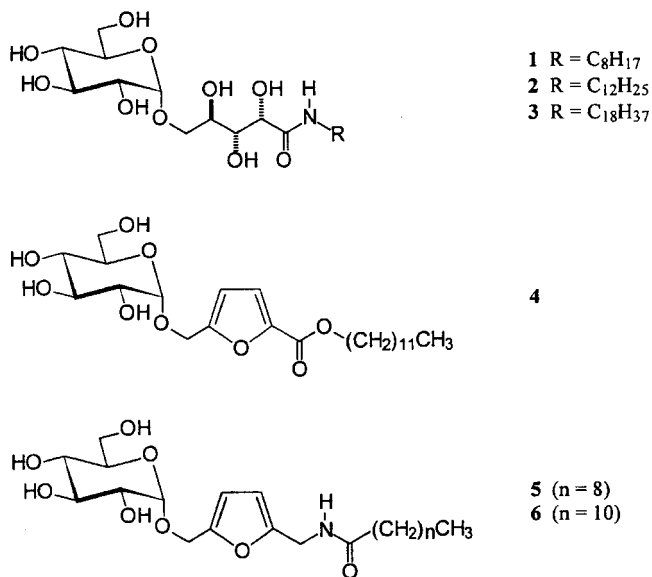


Figure 1. Chemical structures of the *N*-(1-octyl)- (**1**), *N*-(1-dodecyl)- (**2**), and *N*-(1-octadecyl)- derivatives (**3**) of 5-*O*-(α -D-glucosyl)-D-arabinonamide, of the dodecyl ester of 5-(α -D-glucosyloxymethyl)furanic acid (**4**), and the *N*-decanoyl (**5**) and *N*-dodecanoyl derivatives (**6**) of 2-aminomethyl-5-(α -D-glucosyloxymethyl)furan (abbreviated: GMF-amides).

6) [10]. To assure their dryness, they were kept over CaCl₂ *in vacuo*. The phase behaviour was determined by DSC (Dupont Thermal Analyser 990) and thermomicroscopy (Leitz Orthoplan Pol, Mettler FP 800) supported with S-VHS video equipment (Panasonic, Sony). X-ray investigations were performed using either flat

Table 1. Phase transitions of isomaltulose-derived amphiphiles **1–6**

Compound	Mesomorphic data			/K	
1	Cr	336	S _{A_d}	406	I
2	Cr	326	S _{A_d}	473	I
3	Cr	373	S _{A_d}	423	I
4	Cr	309	S _{A_d}	408	I
5	Cr	343	S _X	415	I
6	Cr	320	S _X	416	I

film technique or a position sensitive detector (Stoe PSD). Compounds **5** and **6** were examined additionally by small angle X-ray scattering (SAXS) using synchrotron radiation (polymer beamline A2, Hasylab, Hamburg, Germany). An image-plate was taken as a two-dimensional detector. In all cases thin capillaries ($\varnothing=1$ mm) containing the samples were examined first at room temperature in the estimated mesophase range,

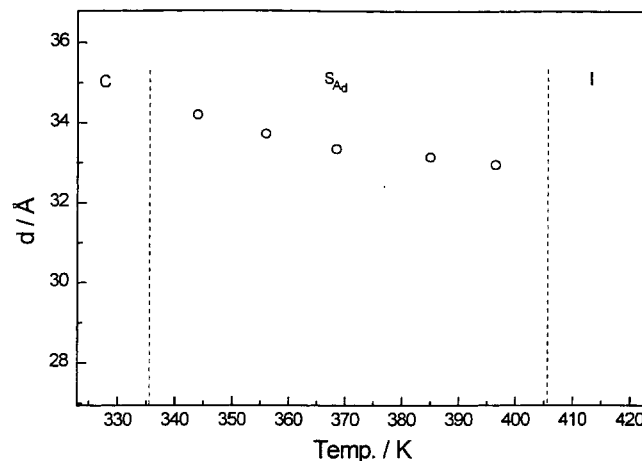
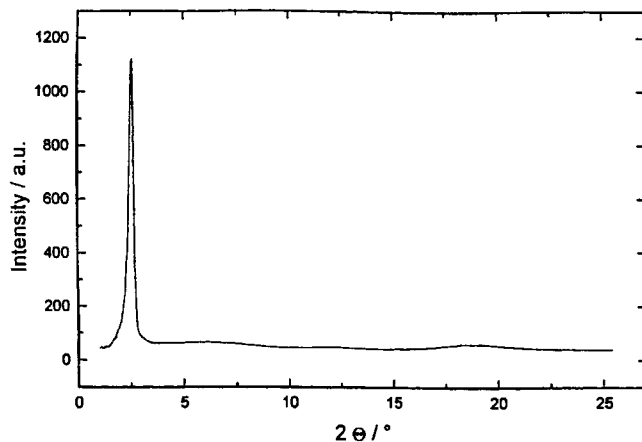


Figure 2. *N*-(1-Octyl)-5-*O*-(α -D-glucosyl)-D-arabinonamide (**1**). (a) 2θ versus intensity plot; (b) change of the *d*-value with temperature.

Table 2. Estimated molecular extensions and X-ray-derived *d*-values (in Å) of amphiphiles **1–6**

Compound	Molecular length	Aglycon length	Aliphatic chain length	X-ray <i>d</i> -value
1	22.8	18.2	11.1	33.7
2	28.0	23.4	16.1	44.0
3	34.8	30.2	23.0	52.3
4	26.6	21.9	15.4	38.1
5	22.5	18.0	11.1	79.1
6	25.4	20.6	14.1	98.9

as well as in the isotropic liquid. The temperature accuracy was within ± 0.5 K.

The phase transitions obtained and the X-ray derived d -values are listed in tables 1 and 2, respectively. As all the compounds, under the microscope, showed either oily streak or mottled mosaic textures independent of heating rates and starting temperatures, the textures were in most cases not helpful for phase characterization. Therefore, DSC curves were recorded at different heating rates (2, 5, 10 K min⁻¹) in order to observe the phase transitions, with a fresh sample for each measurement, because melts from a previous scan supercooled to room temperature.

3. Results and discussion

From the observed textures, a smectic phase could be detected for each of the six compounds, but there was no direct relationship between melting and clearing with regard to the aliphatic chain length (cf. table 1). Compounds **4–6**, due to their central furan residue, have three hydroxyl groups less than compounds **1–3**, and therefore their smectic–isotropic transition temperatures are lower, most notably for the ester **4**, which, unlike **5** and **6**, is not capable of intermolecular hydrogen bonding via amide NH-protons. Such melting and clearing behaviour has been observed previously [2] in a homologous series of *N*-alkylglycopyranosylamines with aliphatic chain lengths from C₇–C₁₆, with neither an odd–even effect nor any other relation between chain length and the transition temperatures being found; rather the data

seemed to be statistically distributed around certain values. Accordingly, the common trend that longer aliphatic chains raise the phase transition temperatures in a homologous series does not apply to compounds **1–6**, since obviously an additional structural or interaction parameter is influencing the bulk properties and the phase transition behaviour.

Most of the known thermotropic monosaccharide amphiphiles possess an S_{A_d} phase [1,3], and a similar behaviour was expected for compounds **1–6**. Table 2 lists the molecular extensions and the X-ray-derived layer thicknesses d . The 2θ versus intensity scan of **1** within the mesophase (346 K) reveals a sharp signal in the small angle region ($d=34$ Å) and a diffuse one at $d=4.6$ Å (see figure 2).

The layer thickness d , within the smectic phase range, decreases with increasing temperature, hence strongly indicating the presence of a smectic lamellar structure. As the d -values of compounds **1–4** are between the lengths of one and two molecules, the formation of bilayers is unequivocal. Using the measured d -value and the individual molecular extension, the degree of overlap within the bilayer can be calculated and lies around 75% (**1**: 74%, **2**: 79%, **3**: 75%, **4**: 72%). The compound with the largest overlap (**2**) possesses the highest clearing point, and the order of overlap agrees with the related nematic–isotropic transition temperatures observed to be **2** > **3** > **1** > **4**. The extensions of the hydrophilic parts of the molecules are always in the same range, but the polarity and the capability for hydrogen bond formation

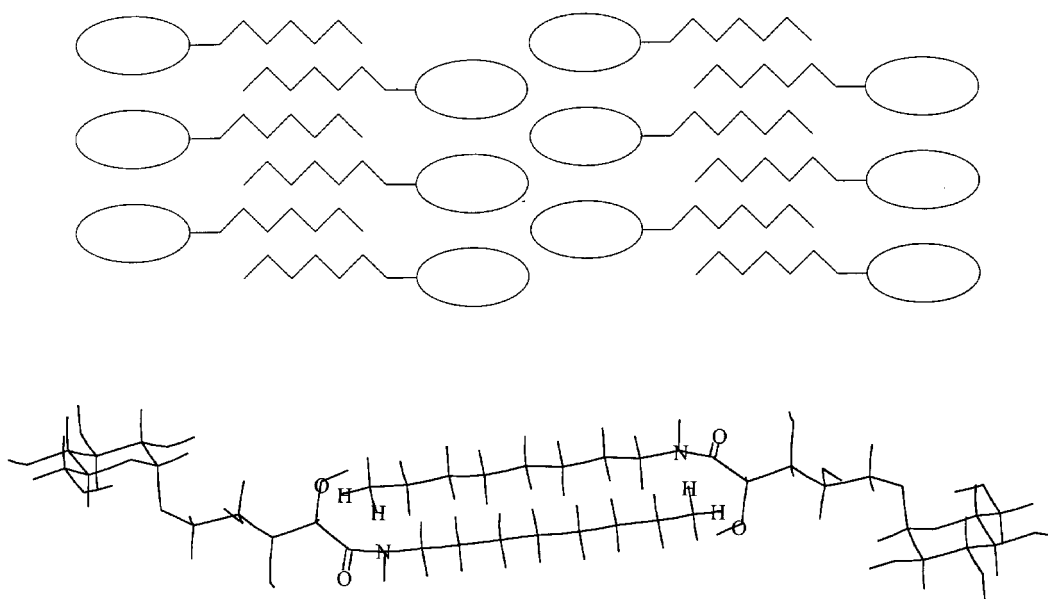


Figure 3. Schematic drawings of *N*-(1-octyl)-5-*O*-(α -D-glucosyl)-D-arabinonamide (**1**). (a) model for the S_{A_d} phase (head-to-head layer arrangement) according to [2]; (b) conceivable dimer formation ($d=33.7$ Å), hydrogen-bonded interaction centres being labelled.

with neighbouring molecules are different due to the presence of either hydroxyl, ester, or amide groups.

Structural models have been suggested for monosaccharide amphiphiles with a single alkyl chain [3]. The most appropriate assumption appears to involve the alignment of the aliphatic chains similarly to those of rod-like mesogens, with optimized van der Waals interaction and hydrogen bridges between the sugar parts, whereby the hydrophilic pyranoside portions are arranged as in lyotropic bilayer systems (see figure 3).

This concept appears to correlate best with the data obtained for compounds **1–3**, i.e. the regions with the aliphatic moieties form the core of the mesophase bilayer, the glucopyranose portions being on the outside, quite similarly to lamellar phases, i.e. interaction with the next smectic layer via hydrogen bonding (see figure 3, top and bottom entry) is small.

In the case of GMF-amides **5** and **6**, the experimental layer thicknesses are substantially larger than those calculated (table 2), corresponding to about 3–4 times the molecular length. Although the established models mentioned cannot account for this, the wide angle reflections in the X-ray investigations give strong evidence for a smectic phase. Conceivably, one smectic layer thickness could consist of four molecules in an enhanced kind of molecular self-organization. The reason for this unusual finding (particularly in view of the standard data for compounds **1–3**, and **4**) remains to be elucidated; clarification is expected from detailed synchrotron measurements presently being performed.

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