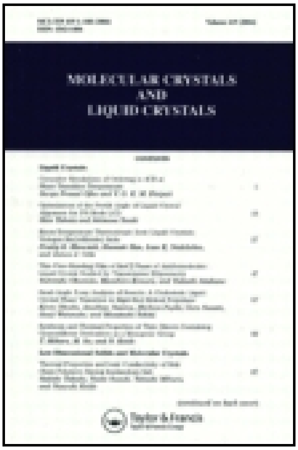

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Liquid Crystal Phases Exhibited by Some Monosaccharides

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LIQUID CRYSTAL PHASES EXHIBITED BY SOME MONOSACCHARIDES

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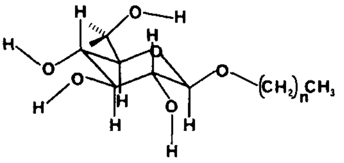
Recently some mono-alkylated derivatives of β-D-glucopyranoside and thio-α-D-mannopyranoside were shown to exhibit liquid crystal properties. The structure of the phase produced by these materials was described as being of a layered smectic type. However, a full classification of the phase was not given. The present investigation defines the phase as smectic A with a bilayer structuring. The lamellar spacings previously found for the phase agree with calculated values for a bilayer ordering in which the carbohydrate moieties overlap to produce an extensively hydrogen bonded structure. The phase was found to be immiscible with the A phases of conventional smectogens because the hydrogen bonding necessary for phase formation is disrupted in binary mixtures.

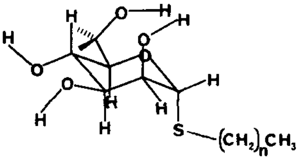
1. INTRODUCTION

The n-alkyl-1-O-β-D-glucopyranosides (I) and the n-alkyl-1-thio-α-D-mannopyranosides (II) have been shown to exhibit liquid crystal phases by X-ray diffraction and calorimetric investigations.[1-3]



(I)

n-ALKYL-1-O-β-D-GLUCOPYRANOSIDE



(II)

n-ALKYL-1-THIO-α-D-MANNOPYRANOSIDE

The n-alkyl-1-O-β-D-glucopyranosides possess a single liquid crystal mesophase which was suggested to be of a smectic nature. Powder diffraction X-ray studies of this phase produced a single diffuse ring of scattering similar to those obtained for smectic A phases.[4] The formation of liquid crystal phases by the first group of materials (I) was associated with crystal structures in which the carbohydrate moieties are extensively hydrogen bonded with the alkyl chains being intercalated.[2]

In this study the optical textures of the phases exhibited by the n-alkyl-1-O-β-D-glucopyranosides and their miscibilities with common thermeotropic liquid crystals were investigated. The phase was found to produce microscopic textures typical of the smectic A phase, however, it was found to be immiscible with the A phases of other common liquid crystals.

2. RESULTS

Transition temperatures obtained by differential scanning calorimetry and thermal optical microscopy for the n-alkyl-1-O-β-D-glucopyranosides (Sigma) studied were found to be in general agreement with those published previously.[2,3] Table 1 lists the transition temperatures and the enthalpies of transition obtained by differential scanning calorimetry, and fig. 1 shows a plot of the transition temperatures as a function of increasing terminal alkyl chain length.

Table 1

n-alkyl	crystal 1	crystal 2	crystal 3	mesophase	Liquid
n-heptyl+	• 56	• 69	• -	• -	•
n-octyl	• 67.07	• -	• -	• 106.38	•
ΔH	(13.31)			(1.37)	
n-nonyl+	• 51	• 68	• -	• 113	•
n-decyl	• 64.85	• 70.26	• -	• 133.53	•
ΔH	(combined	12.50)		(1.12)	
n-dodecyl	• 54.81	• 63.15	• 80.4	• 143.38	•
ΔH	(11.56)	(3.86)	(17.18)	(1.03)	

† results from refs., 2 and 3
ΔH values in cal/g, temperatures in °C.

Figure 2 shows a typical trace of a heating and cooling cycle obtained for n-dodecyl-1-O-β-D-glucopyranoside. The transition peaks were found to be extremely sharp with little hysteresis occuring for the mesophase to isotropic liquid phase change, indicating that the recrystallized material was relatively pure. The cooling cycles of all of the members studied showed little or no enthalpy for the transition back to the solid. However, in many cases there was a slight rise in the baseline of the cycle suggesting that the material had set into a glassy solid. This was confirmed by examination of the textures by thermal optical microscopy; little or no change was shown by the texture on cooling to room temperature, however, difficulty in the mechanical

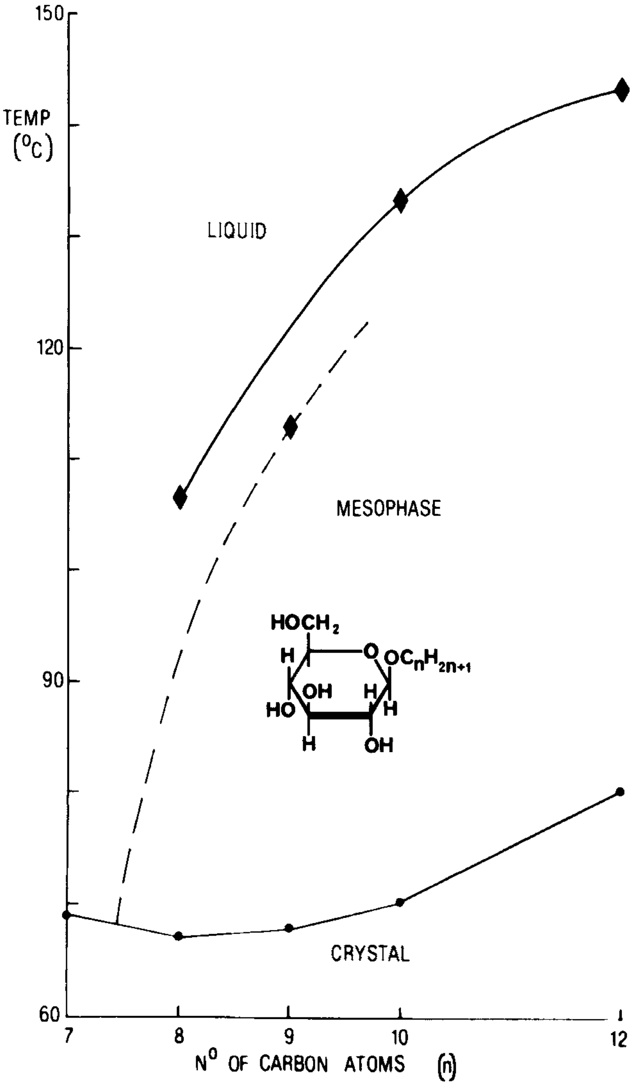


FIGURE 1: Plot of the transition temperatures against the number of carbon atoms (n) in the n-alkyl chain of the n-alkyl-1-O-β-D-glucopyranosides. Key ♦, mesophase-liquid; ● crystal-mesophase.

displacement of the cover-slip indicated that the phase had indeed solidified. Paramarphosis of the optical texture of the mesophase had occurred and the pattern had been carried into the solid state. DSC heating and cooling cycles showed that each compound only exhibited one truly reversible phase change indicating that just one liquid crystal phase was present. This was confirmed by thermal microscopy as no textural changes were observed on cooling to the crystal once the texture for the phase had been formed from the isotropic liquid.

Thermal optical microscopic observations of the alkylated sugars showed that the mesophase formed from the isotropic liquid possessed two textural forms, a homeotropic and a focal-conic fan texture. Indeed, the only texture observed when the materials were placed between clean, but untreated, glass plates was the homeotropic texture. However, at the isotropic liquid to mesophase transition bâtonnets were observed, but they were transient and gave way rapidly to the formation of the homeotropic texture. Conoscopy of the phase in this texture failed to produce an interference figure, this may have been due to the thinness and weak birefringence of the specimen. Attempts were also made to pull a free-standing film of the n-dodecyl homologue in order to produce a thick, homeotropically aligned specimen for conoscopic observations. The mesophase, however, was unlike other smectic A (or C) phases because it proved too viscous to be drawn and no film could be generated. All further attempts to produce an identifiable interference figure failed.

The alkylated sugars produced homogeneous textures in cells prepared for homogeneously aligned smectic applications. The surfaces of the cell were treated with a polymer (nylon-6) and rubbed in one direction.[5] The glass plates were then glued together along two edges with an epoxy-resin using 25 µm spacers in the glued-sealing area. The cell was filled by capillary action while the saccharide was in its liquid phase. On cooling the material from the isotropic phase, the mesophase separated in the form of bâtonnets (plate 1) which coalesced to form a focal-conic fan texture (plate 2)

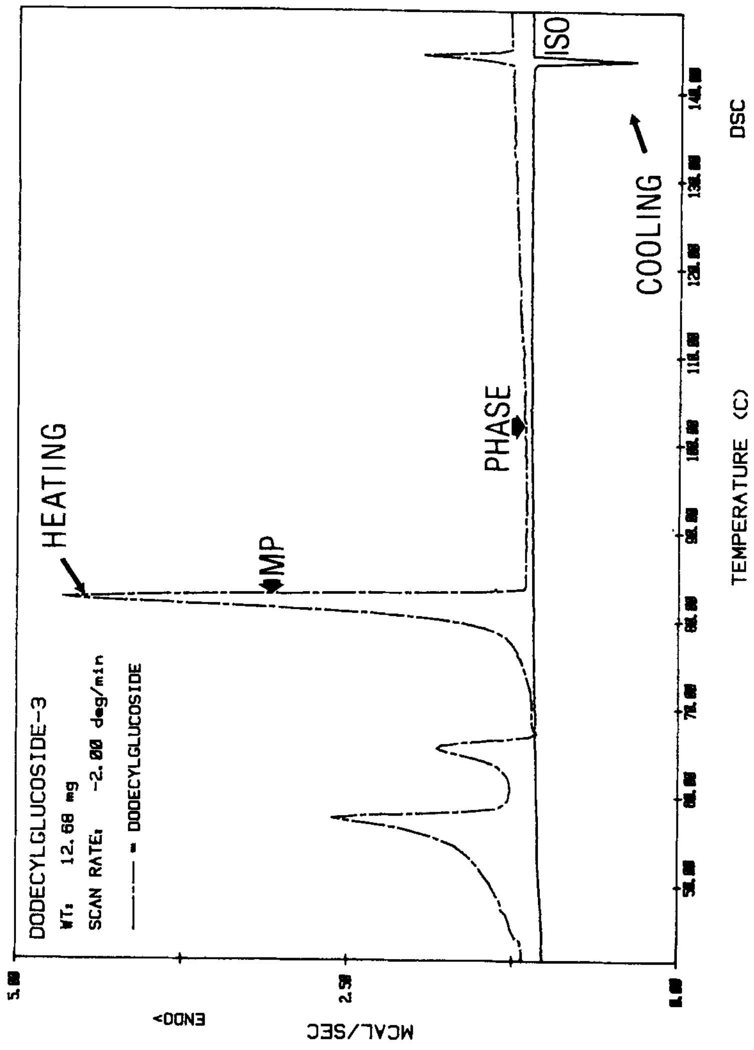


FIGURE 2: The heating and cooling cycles by DSC for n-dodecyl-1-O-β-D-glucopyranoside

characterized by elliptical and hyperbolic lines of optical discontinuity. These two types of texture (fan and homeotropic) are typical of those formed by the smectic A phase.[6] Of the other phases, the crystal and hexatic B's are the only ones capable of formation of a homeotropic texture, however both form mosaics and not fans on cooling from the isotropic liquid.[6] Alternatively, as these materials are optically active they could possibly exhibit a C* phase which is characterized by focal-conic and pseudo-homeotropic textures.[7] The absense of a conoscopic figure could indicate the presence of a C* phase, however in this case one would also expect pitch bands and breakages in the fans neither of which is present.[7] Thus, the strongest candidate in the classification of the phase exhibited by these sugars is the S_A modification.

Interestingly, although the phase was obtained in a homogeneous texture for treated glass surfaces, the phase remained unaligned. This is in stark contrast to conventional thermeotropic smectic A materials which generally align very well on a rubbed polymer (nylon) surface.[5] This is probably due to strong hydrogen bonding occurring between the amide linkage of the surfactant and the hydroxyl functions of the carbohydrate moiety of the liquid crystal. The numerous hydroxyl functions of the saccharide group can hydrogen bond in various ways to the surfactant generating different orientations of the molecule at the surface which results in no alignment.

Miscibility studies with a variety of conventional smectogens provided no firm conclusions to the identity of the phase exhibited by the carbohydrates. All examinations of the test substances with known standards showed an incompatibility between the materials in binary mixtures. One compound tended to 'pool' in the other indicating an incompatibility rather than a phase immiscibility. The standard materials employed were, n-hexyl 4′-n-pentyloxybiphenyl-4-carboxylate,[8] 65OBC (A, Bhex, and E phases), N-(4-n-butyloxybenzylidene)-4′-n-octylaniline,[9] 4O.8 (A and Bcryst phases), 4′-n-octyl-4-cyanobiphenyl,[10] 8CB (N and Ad phases), and (±)-4-(2′-methylbutyl)phenyl 4′-n-octylbiphenyl-4-carboxylate,[11] 8SI (N, A, C, I, J, and G phases). The lack of miscibility between these standards and the test saccharides is probably due to disruption of the hydrogen bonding in the phase of the saccharide by the introduction of a foreign material. Once this is broken the monomers of the sugar no longer have a liquid crystal nature,and there is an incompatibility between the aromatic portions of the standard and the carbohydrate moiety of the test compound causing the materials to segregate.

3. DISCUSSION

The positive results obtained in the characterization of the phase exhibited by the n-alkyl-1-O-β-D-glucopyranosides are few, and therefore a definite classification of the phase would be rather tenuous. A full description of the phase can only be accomplished by the X-ray diffraction of aligned samples. This will be difficult because the phase cannot be easily aligned either by surfactants or by free-standing film techniques.[12] Thus, magnetically oriented samples may provide the best method of investigating their phase structure.

Powder diffraction studies by Jeffrey and Bhattacharjee[2] show that the phase is probably of the A or C type. Their diffractograms show a diffuse ring of scattering which is commonly associated with A and C phases; sharper and more numerous rings typical of the ordered smectic phases are not observed. The lamellar spacings measured were found to be greater than the average molecular length of the corresponding monomer suggesting that the phase is constituted of bilayers. Calculations from Dreiding molecular models show that for an exact overlap between the carbohydrate moieties for alternating molecules, a lamellar spacing for the phase is obtained which on average is approximately 2Å longer than those measured by X-ray diffraction. Table 2 lists the experimental and calculated d spacings. It is usual for the lamellar spacing in the A phase to be shorter than the actual molecular length ($d \sim 0.9\ell$). Thus the small discrepancies between dcalc. and dexpt. for this structure would seem to indicate an orthogonal (A_d) and not a tilted (C) structure for the phase.

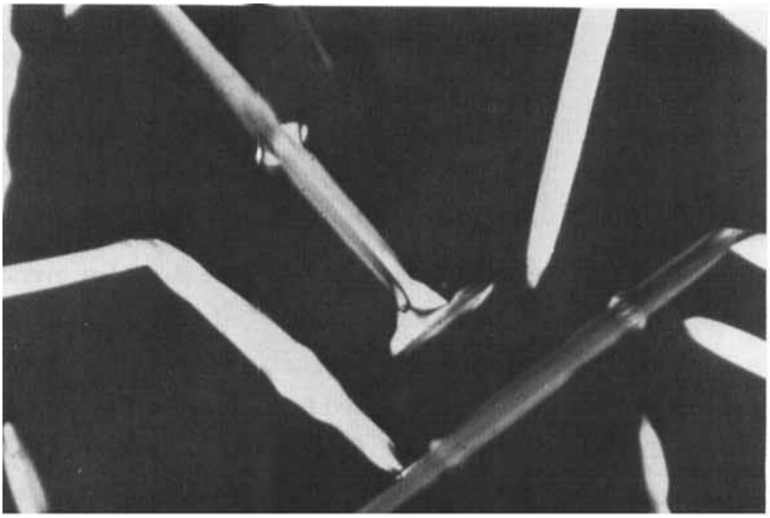


PLATE 1: The mesophase separating from the isotropic liquid in the form of bâtonnets. The material is n-dodecyl-1-O-β-D-glucopyranoside.

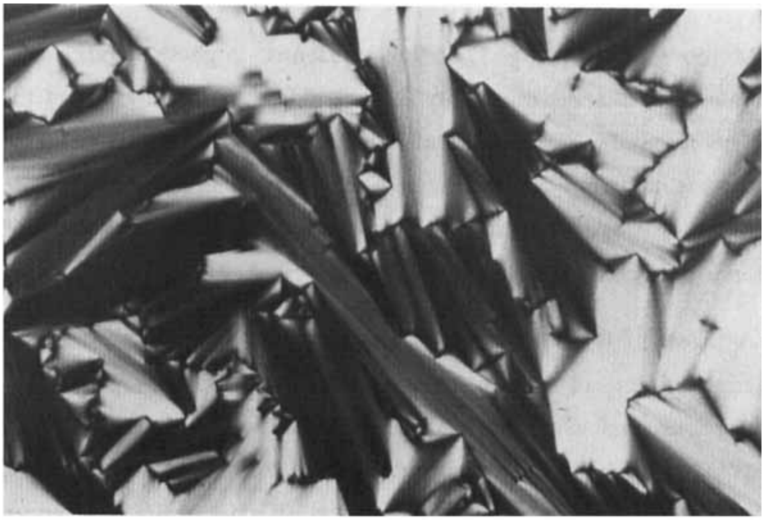


PLATE 2: The focal-conic texture of n-dodecyl-1-O-β-D-glucopyranoside. The glass supports have been treated with rubbed nylon in order to produce a homogeneous texture.

Table 2

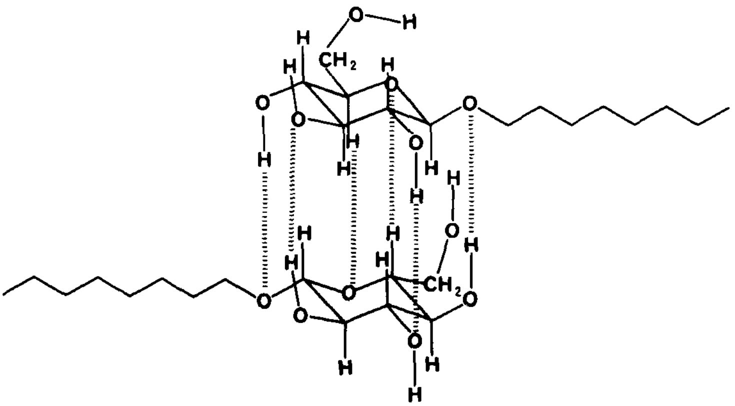
n-alkyl	dexpt Å	dcalc† Å
n-heptyl	22.9	24.6
n-octyl	26.1	27.1
n-nonyl	27.6	29.5
n-decyl	29.5	32.2

† dcalc ± 0.5Å

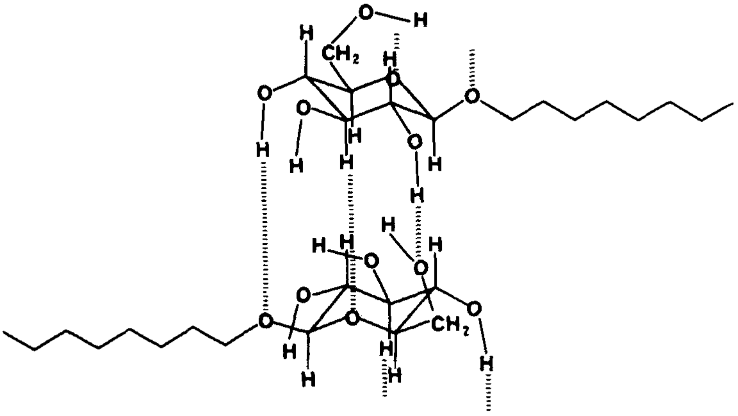
Two possibilities for the structure of the phase involving overlapping carbohydrate groups can be postulated, a stacked chair structure and an alternating chair structure, see fig. 3. The stacked chair structure shows good hydrogen bonding overlap of the hydroxyl functions while they are not quite so well fitted in the alternating chair form. In the layer the molecules are hydrogen bonded together giving some rigidity to the in-plane ordering, unlike the situation in a conventional A phase. There is also hydrogen bonding between the stacks of these columns of carbohydrate chairs, and overall the in-plane structuring will be "mechanically stiff." Hence it is difficult to pull a free standing film of these materials.

Moreover, the hydrogen bonding is essential to phase stability and once it is broken, as in some miscibility studies, the temperature range of the phase will be reduced. Similarly if all of the hydroxyl groups are alkylated or acylated eliminating the hydrogen bonding element no phase is observed. Thus the hydrogen bonding invoked by the structure of the carbohydrate group is paramount in phase formation.

A phase of this type can still be classed as S_{A_d}[13] because it involves a random ordering of the molecules that are on average perpendicular to the layer planes and which have an interdigitated bilayer structure. Similarly, other materials have been classified by code letter even though they are not necessarily miscible with other members of that miscibility group. For instance, fig. 4, shows the structures of two cyano compounds which have been classified structurally. The B phase of n-propyl dicydohexyl - carbonitrile[14]



(a) STACKED CHAIR STRUCTURE



(b) ALTERNATING CHAIR STRUCTURE

FIGURE 3: The stacking structures of the alkylated carbohydrates.

is not miscible with conventional B phases because the dipolar interaction of the two cyano groups is broken when molecules which have differing interactions are introduced into the system. Similarly, the C phases of the 4-n-alkoxyphenyl 4′-cyanobenzoates are also immiscible with the C phases of materials which do not possess terminal cyano groups, simply because the overlapping polarized structure is disrupted.[15] Other systems also exist which show a marked similarity to the way in which the n-alkyl-1-O-β-D-glucopyranosides require hydrogen bonding to stabilize the structure. For example, diisobutylsilanediol[16] exhibits a discotic phase in which the discs are constituted of two hydrogen bonded diisobutylsilanediol molecules. The discs are held together in stacks by hydrogen bonding to form a columnar structure, see fig. 5. It is interesting to note in this case that if the size of the alkyl substituents attached to the silicon atom are varied then the phase is lost. The diisobutyl groups are the only substituents which possess enough alkyl character and still permit strong hydrogen bonding between two molecules in order to form a discotic mesophase. Thus, the phase of this material, like the saccharides, is very sensitive to small changes in molecular structure. These two types of material are closely related in that the molecular stacks (columns or in-plane structure) are held together by hydrogen bonding.

The n-alkyl-1-thio-α-D-mannopyranosides[1] have also been shown to exhibit liquid crystal phases. In this case the n-alkyl chain joins the carbohydrate ring system in an axial position such that the alkyl chain in its all-*trans* conformation dips below the equator of the ring. The phase structure will probably be of a tilted type for a core interaction similar to that of the glucosides, or else the phase may be orthogonal with the core pairs rotated through 90° in comparison to the glucosides. The phases of the mannosides could therefore be of a different class to the glucosides, and it would be interesting therefore to study the miscibility of these two types of sugar.

The phase of the n-alkyl-1-O-β-D-glucopyranosides is tentively classed as S_{Ad}, however, it is not miscible with other more typical members of this group (unless they also have hydrogen bonded structures). These materials therefore form a new subset of the Ad type.

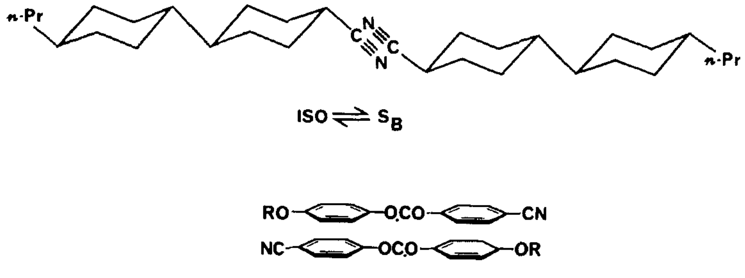
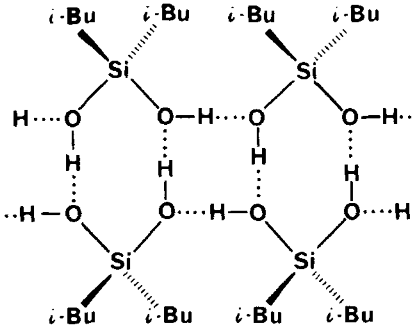


FIGURE 4



DIISOBUTYLSILANEDIOL

FIGURE 5

4. EXPERIMENTAL

The materials were purchased from Sigma and purified by recrystallization from ethanol. Their purities were checked by HPLC using a reverse phase column and acetonitrile as eluant. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC 4 equiped with a thermal analysis data station (TADS). Thermal optical microscopy was performed on a Zeiss universal polarizing microscope employing a Mettler FP52 hot-stage in conjunction with a FP5 control unit.

5. CONCLUSION

The phase exhibited by the n-alkyl-1-O-β-D-glucopyranosides has been tentitively classed as A in type, but a helical smectic C* structuring although unlikely cannot be totally ruled out at present. A full classification must await further detailed structural studies on aligned specimens. If the phase is of the A type it will probably have an interdigitated bilayer structure and will be classed as Ad. However, its immiscibility with other phases of this type, because of the breakdown in hydrogen bonding, would mean that the phase is a separate subset of Ad.

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