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Liquid-Crystalline Behaviour in the n-Alkyl Gluconamides and Other Related Carbohydrates

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Liquid-crystalline behaviour in the *n*-alkyl gluconamides and other related carbohydrates

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Many alkyl derivatives of carbohydrates are used as detergents for cell wall membranes. This study describes the liquid-crystalline properties of a number of these systems. The combination of a hydrophilic carbohydrate moiety and a hydrophobic aliphatic substituent leads to the formation of both thermotropic and lyotropic liquid-crystal mesophases. Materials with this structural combination are suspected to form interdigitated bilayer smectic A phases. The central core region of the layer is held together by dynamic hydrogen-bonding between the neighbouring carbohydrate moieties, whereas the terminal aliphatic chains create fluidity between layers.

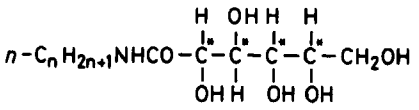
1. Introduction

Thermotropic liquid-crystal mesophases were recently discovered and classified in carbohydrate systems [1–4]. Generally, materials which exhibit these properties are alkyl derivatives of carbohydrates in their cyclic pyranose forms. However, it was recently shown that *n*-octyl gluconate, which has an open chain structure, also exhibits liquid-crystalline properties [5].

The formation of liquid-crystalline phases in carbohydrate systems appears to be promoted by the different interactions of the two chemically dissimilar portions of the molecular structures of these compounds. The carbohydrate moieties interact strongly through hydrogen-bonding, whereas the alkyl chains interact only weakly through van der Waals forces. This produces a bilayer structure similar to that for interdigitated smectic A (A_d) phases [2], except that the bilayer in this case is held together by hydrogen-bonding within the layer planes rather than by strong dipolar interactions, as in for example the 4-*n*-alkyl-4′-cyanobiphenyls [6]. Consequently, the hydrogen-bonded form of the phase is more viscous than the dipolar variation. The two modifications also appear to be immiscible because of the breakdown of the hydrogen-bonding of the carbohydrate containing species caused by mixing with non-hydrogen-bonding dipolar aromatic molecules [2].

In this study the liquid-crystalline properties of the *n*-alkyl gluconamides, an open chain carbohydrate system, are described. The results obtained are compared with those for cyclic derivatives and mixed (open chain and cyclic ring) structures.

Table 1. Transition temperatures† determined for the *n*-alkyl gluconamides



n	K_1		K_2		K_3		S		Iso
6	●	119·7	●		—		—	155·6	●
ΔH‡		(1·08)						(33·64)	
7	●	79·2	●	96	(●	150·4)	●	156·4†	●
ΔH		(2·15)		(7·49)		‖		(36·76)	
8	●	72	●	87·4	●	158·2	●	159·1†	●
ΔH		§		(9·79)		(33·5)		(0·51)	
9	●	83·5	●	99·36	●	159·5	●	174·9†	●
ΔH		§		(9·46)		(33·75)		‖	
10	●	74·6	●	91·15	●	156·9	●	182†	●
ΔH		(4·54)		(7·58)		(31·09)		‖	
11	●	77·2	●	99·4	●	156·7	●	190·2†	●
ΔH		(3·18)		(7·72)		(35·21)		‖	
12	●	80·5	●	94·4	●	155	●	189†	●
ΔH		(2·31)		(8·18)		(28·61)		‖	
18	●	111	●	151	—		●	196·7†	●
ΔH		(1·92)		(32·7)				‖	

† The clearing points were determined by thermal optical microscopy, the other temperatures were obtained from D.S.C.

‡ Values obtained in cal/g; 1 cal is equivalent to 4·184 J.

§ Too small to measure.

‖ Decomposition in the liquid-crystal phase, therefore the enthalpy could not be measured.

2. Experimental

The synthesis of the materials was reported previously [7]. Their structures and purities were determined by infra-red spectroscopy and elemental analysis. The sample of *n*-octyl-α-D-glucopyranoside was kindly provided by Dr. M. Garavito, Biozentrum, Basel (Switzerland). The liquid-crystalline behaviour of the carbohydrates was investigated by thermal, polarized-light microscopy employing a Zeiss Universal microscope in conjunction with a Mettler FP52 microfurance and FP5 control unit, and by differential scanning calorimetry using a Perkin–Elmer DSC-4-TADS instrument. Homogeneously aligned specimens of the liquid-crystal phases were obtained in cells constructed of nylon 6–10 coated glass plates separated by 10 μm spacers [8].

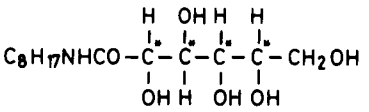
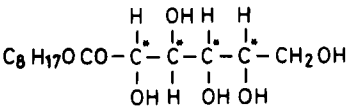
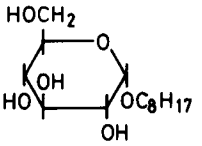
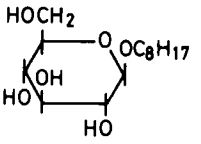
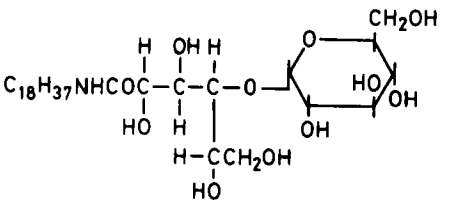
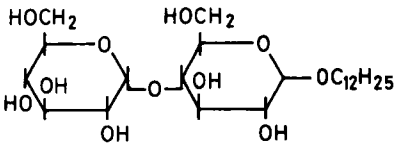
3. Results

The results obtained for the melting behaviour of the materials investigated are given in tables 1 and 2. Table 1 gives the transition temperatures and enthalpies for the *n*-alkyl gluconamides. Table 2 lists the transition temperatures for a number of related materials. The transition temperatures obtained for the *n*-alkyl gluconamides are shown as a function of increasing terminal alkyl chain length in figure 1. The results obtained for the various properties of these compounds are summarized as follows.

3.1. *Melting behaviour*

Generally the *n*-alkyl gluconamides studied melted in a complex manner through two or three crystal phases into a liquid crystal and then to the liquid, or alternatively

Table 2.

Compound	m.p./°C	cl. pt./°C
	158·2	159·1
n-octyl gluconamide		
	160·1	160·0
n-octyl gluconate		
	72·3	116·3
n-octyl-1-O-α-D-glucopyranoside		
	67·1	106·4
n-octyl-1-O-β-D-glucopyranoside		
	109·5	> 207 (Decomp)
n-octadecyl maltobionamide		
	102	> 245
n-dodecyl maltoside		

directly to the liquid. The first crystal phase (K_1) usually appears highly birefringent between crossed-polarizers, however the subsequent crystal phases (K_2) and (K_3) lose most of the coloured birefringence on heating, producing a monotone crystalline texture. Melting into the liquid-crystal phase produces an oily-streak texture (figure 2) accompanied by homeotropic areas bounded by the streaks. Differential scanning

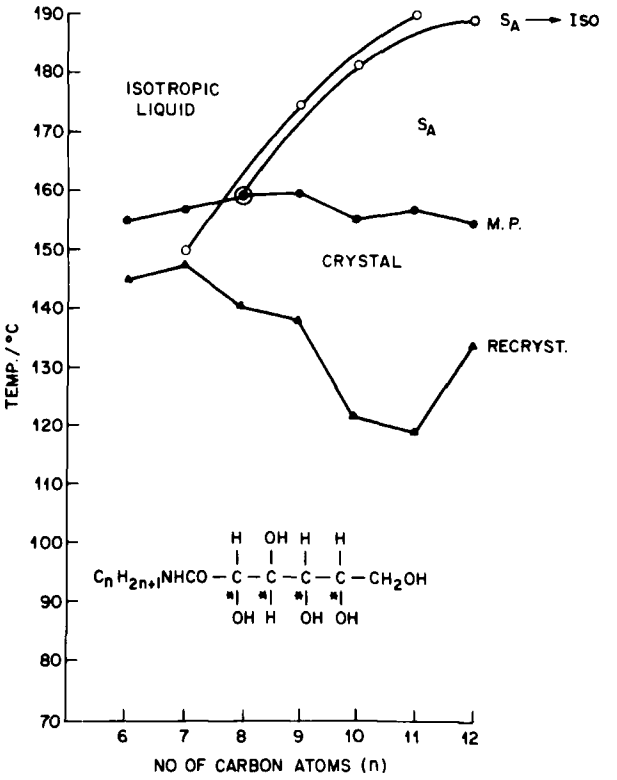


Figure 1. Plot of the transition temperatures versus increasing *n*-alkyl chain length for the *n*-alkyl gluconamides. Key: ●, crystal to isotropic liquid or smectic A; ○, smectic A to isotropic liquid; △, isotropic liquid or smectic A to crystal on cooling.

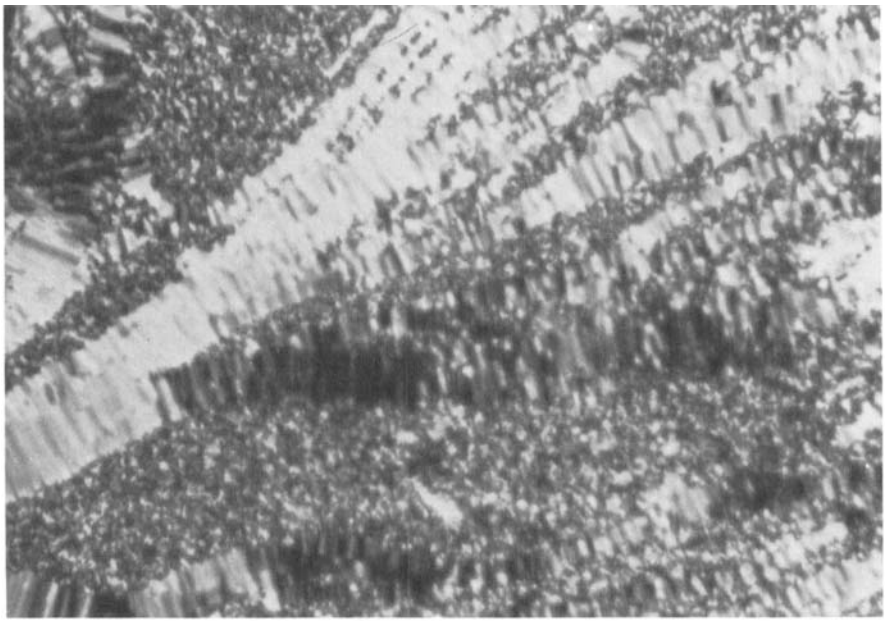


Figure 2. The oily-streak texture of *n*-undecyl gluconamide formed on melting from the crystalline state.

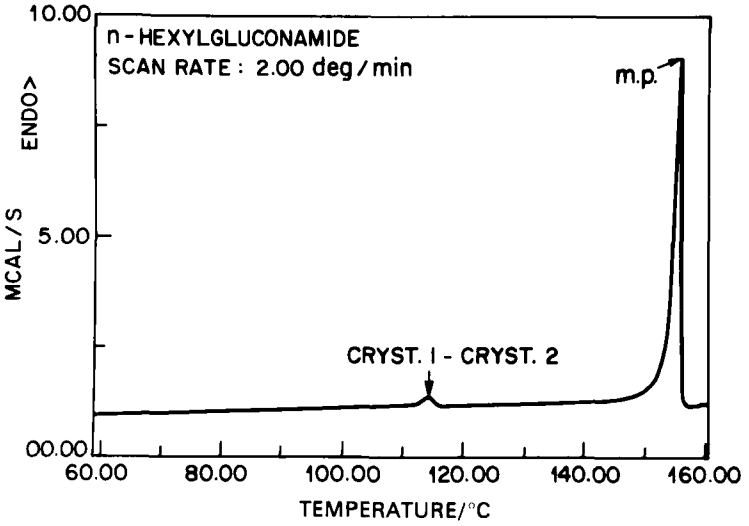


Figure 3. D.S.C. trace for the first heating cycle of *n*-hexyl gluconamide; 1 cal is equivalent to 4·184 J.

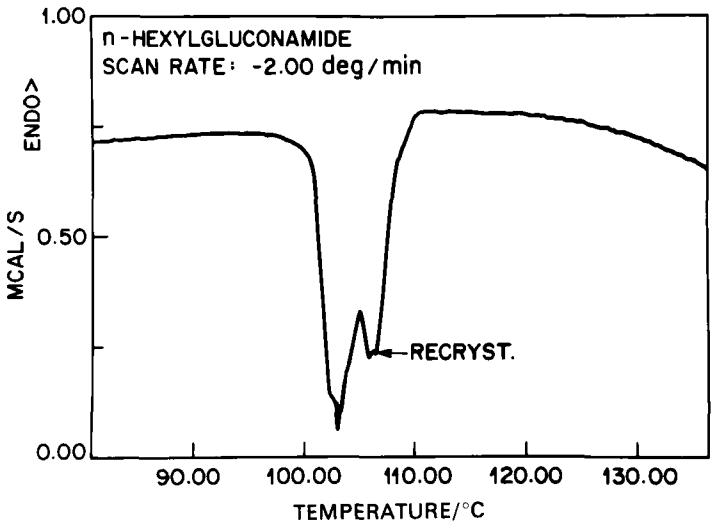


Figure 4. D.S.C. trace for the cooling cycle of *n*-hexyl gluconamide.

calorimetry confirmed the optical studies and showed that enthalpy values for the crystal–crystal phase changes were in the region of 2 to 7 cal/g, whereas the melting points were normally greater than 30 cal/g. The enthalpy values for the liquid crystal–isotropic liquid clearing points could not be obtained because of excessive decomposition (caramelization). A number of heating and cooling cycles obtained by differential scanning calorimetry are shown in figures 3 to 9 inclusive. It is interesting to note that the transition temperatures, enthalpy peak size, and peak shape for *n*-octyl gluconamide (figure 5) are very similar to those reported previously for *n*-octyl gluconate [5].

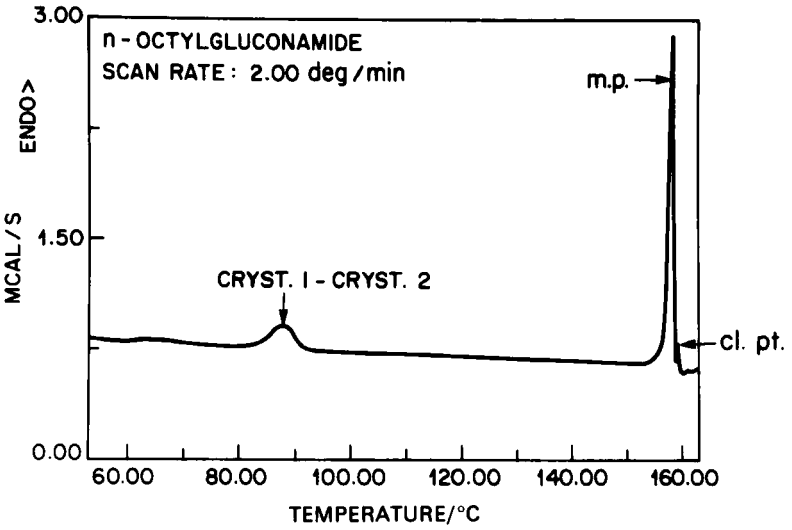


Figure 5. D.S.C. trace for the first heating cycle of *n*-octyl gluconamide.

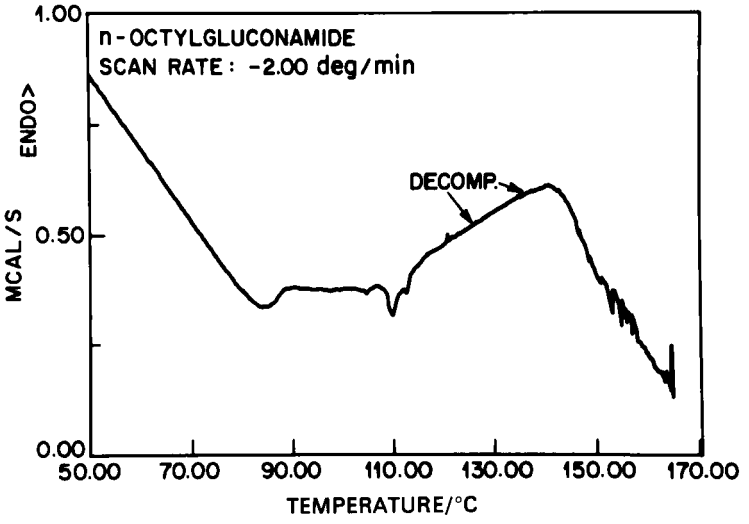


Figure 6. D.S.C. trace for the cooling cycle of *n*-octyl gluconamide.

3.2. *Thermal decomposition processes*

Thermal decomposition through caramelization showed some interesting comparisons between material classes. First, within an homologous series, for example the *n*-alkyl gluconamides or the *n*-alkyl-1-O-β-D-glucopyranosides, decomposition was more rapid in materials that exhibited liquid-crystal phases than in those that did not (figure 10). Comparison between figures 3 to 9 for *n*-hexyl, *n*-octyl, and *n*-undecyl gluconamides exemplifies this process. In figure 3 for the *n*-hexyl member, a normal melting point is obtained, recrystallization (figure 4) occurs fairly readily on cooling and no liquid-crystal phase is observed. The *n*-octyl homologue (figure 5) exhibits a short temperature-range liquid-crystal phase. The heating cycle clearly shows a peak for the liquid-crystal–isotropic liquid phase change occurring just after the melting

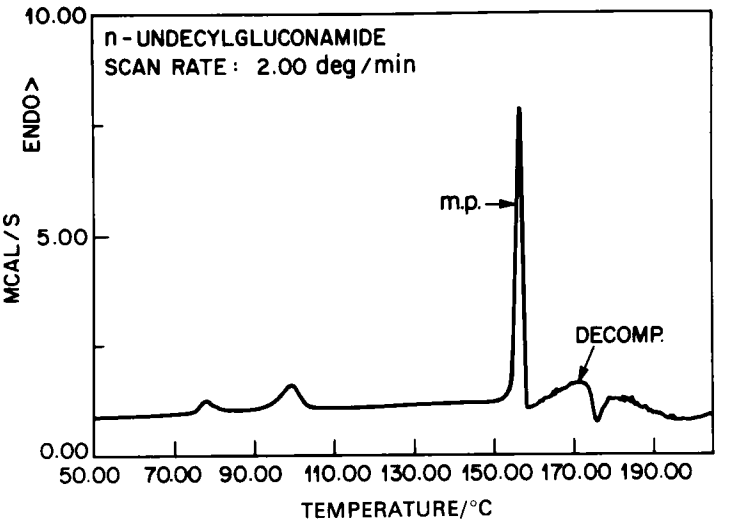


Figure 7. D.S.C. trace for the first heating cycle of *n*-undecyl gluconamide.

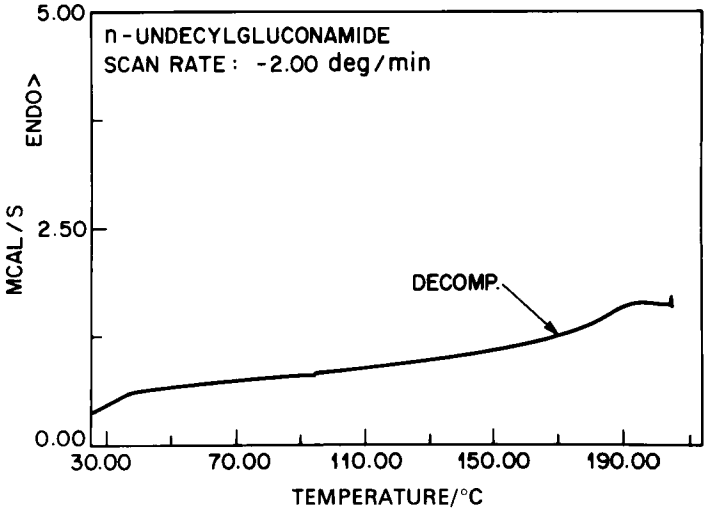


Figure 8. D.S.C. trace for the cooling cycle of *n*-undecyl gluconamide.

point on heating. The cooling cycle (figure 6) however is erratic due to decomposition. Finally the *n*-undecyl member exhibits a wider temperature-range liquid-crystal phase than the other two homologues, but in this case decomposition is initiated in the heating cycle at the phase change to the liquid crystal. At this point the trace (figure 7) becomes erratic and meaningless. Cooling of this sample produces no enthalpy peaks (figure 8) because the specimen had completely decomposed after being heated to the isotropic liquid. Decomposition through caramelization is more rapid in the liquid-crystal phase than either the crystal or the amorphous liquid. The upper clearing point temperatures were obtained from thermal optical microscopy by rapidly heating the specimen and observing an appropriate area that had not undergone much decomposition.

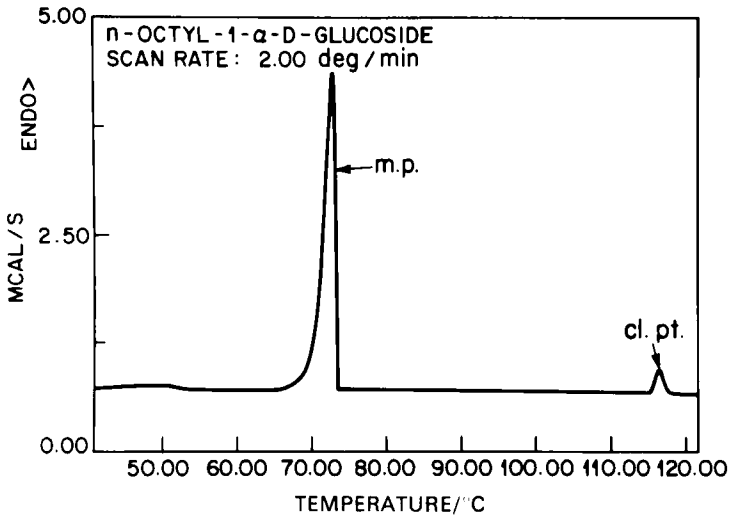


Figure 9. D.S.C. trace for the first heating cycle of *n*-octyl-1-O-α-D-glucopyranoside.

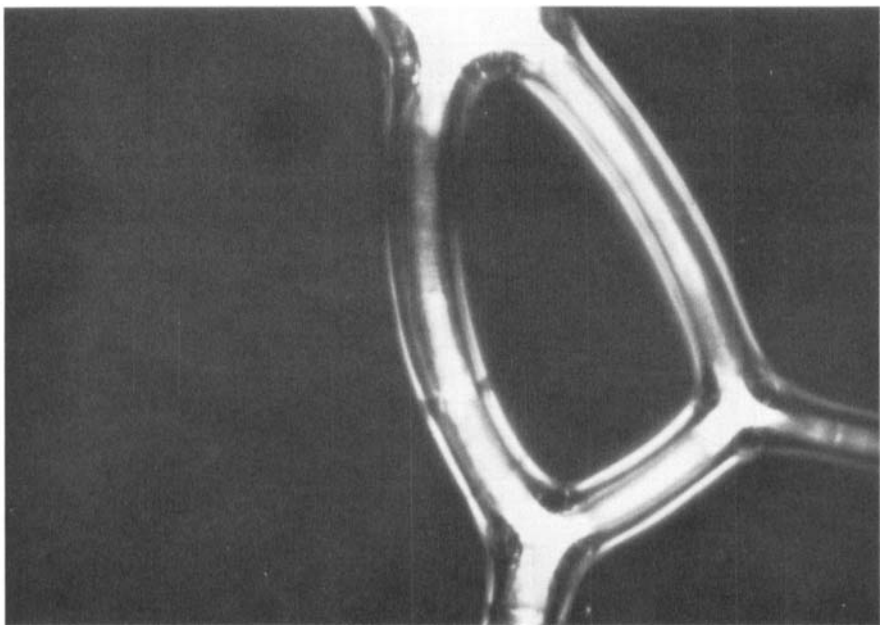


Figure 10. Decomposition of *n*-undecyl gluconamide by caramelization; the liquid-crystalline phase forms a webbing pattern of focal-conic-like defects bounding areas of decomposed gaseous material and air.

Second, decomposition occurs much more rapidly in the open chain sugars than it does in the cyclic pyranoside analogues. For example, *n*-octyl-1-O-α-D-glucopyranoside can be cycled up and down in temperature by differential scanning calorimetry with little decomposition. Figure 9 shows the heating cycle for this compound, the trace through the wide temperature range of the liquid-crystal phase is normal unlike those obtained for the gluconamides. Similarly in a study of the maltoside and maltobionamide, the maltoside was relatively stable whereas the maltobionamide rapidly degraded once it was heated to the liquid-crystal phase.

Figure 11. Contact preparation between *n*-nonyl gluconamide (left-hand side) and *n*-dodecyl-1-O-β-D-glucopyranoside (right-hand side), showing that the two materials are continuously miscible in their liquid-crystal phases.

3.3. *Liquid-crystalline behaviour*

The transition temperatures of the *n*-alkyl gluconamides are depicted in figure 1 as a function of increasing alkyl chain length. The liquid-crystal phase, which is common to certain members of this homologous series, is injected at the *n*-heptyl homologue where it is observed as a monotonic phase. Injection at the *n*-heptyl homologue is typical for carbohydrate systems. The liquid crystal to isotropic liquid transition temperatures rise rapidly with increasing chain length, whereas the melting points of the individual members remain at a relatively constant value of between 150 and 160°C. The recrystallization temperatures, however, start to fall at the point of injection of the liquid-crystal phase. This may be due to increased decomposition of the samples that exhibit liquid-crystal phases.

The isotropic liquid–liquid-crystal phase transition temperatures alternate along the series with the odd members lying on the upper temperature curve shown in figure 1. The alternation is in the same sense as the N to I, or S_A to N or I sequencing pattern commonly observed for liquid-crystalline systems [9].

The identification of the liquid-crystal phase exhibited by the compounds shown in both tables 1 and 2 was made from textural observations. The phase was initially shown by miscibility studies to be the same as the one exhibited by the *n*-alkyl-1-O-β-D-glucopyranosides (see figure 11). Textural investigations were then made on selected members of the two groups. The results obtained were found to be common to those materials studied. When observed between clean glass slides and crossed polarizers the materials melted to give an oily-streak texture (figure 2). The streaks appeared to be composed of focal-conic domains oriented laterally to the long axis of the streak. In most cases the oily-streaks bounded areas that were essentially homeotropic.

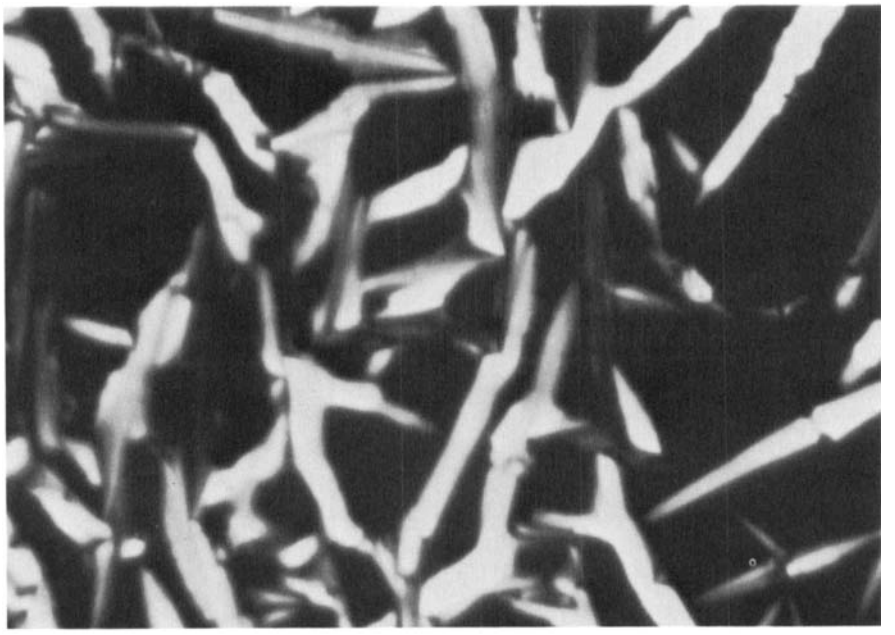


Figure 12. The smectic phase of *n*-undecyl gluconamide separating in the form of bâtonnets on cooling the isotropic liquid.

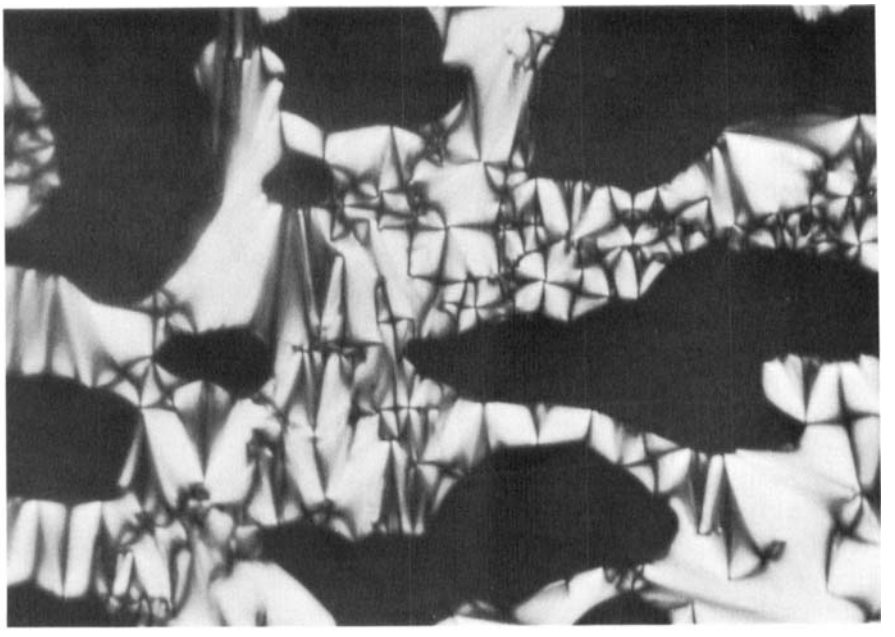


Figure 13. Coalescence of the bâtonnets of *n*-undecyl gluconamide to form a smectic A focal-conic texture. The formation of hyberbolic and elliptical lines of optical discontinuity can be seen clearly as black crosses in the texture.

Unfortunately a conoscopic figure for these regions could not be obtained, possibly because of the weak birefringent nature of the materials. Classical textures of the mesophase suitable for phase identification were obtained in glass cells, where the plate separation was 10 μm and the internal surfaces had been coated with a nylon

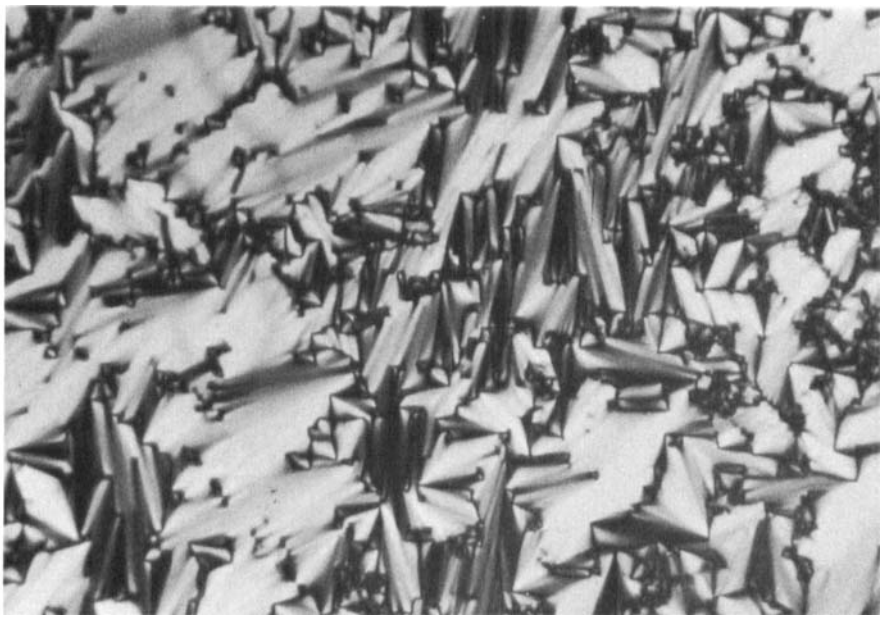


Figure 14. The focal-conic texture of the smectic A phase of *n*-undecyl gluconamide.

6–10 surfactant [8]. The liquid-crystal mesophase nucleated in the form of bâtonnets (figure 12). These coalesced (figure 13) to produce a classical focal-conic domain texture with clearly defined confocal elliptical–hyperbolic defects typical of the smectic A phase [10] (figure 14).

The cholesteric, S_A and S_C phases form focal-conic defects on cooling from the isotropic liquid, however, the S_A phase is the only one to form a corresponding homeotropic texture. The combination of these two observations classifies the mesophase as smectic S_A, but of an unknown subgroup. Attempts were made through miscibility studies to categorize the S_A subgroup. Initially the mesophases of the *n*-alkyl-1-O-β-D-glucopyranosides, the *n*-alkyl-1-O-α-D-glucopyranosides, the *n*-alkyl gluconates, the *n*-alkyl gluconamides, the *n*-alkyl maltosides, and the *n*-alkyl maltobionamides were shown to be of the same miscibility group. Attempts to classify the subgroup with known, previously classified material outside of carbohydrate systems failed. Structural studies on the *n*-alkyl-1-O-β-D-glucopyranosides suggest that the mesophase is composed of an interdigitated bilayer [1, 2], which is an S_{A_d} classification. Consequently it is expected, because of the miscibility between the carbohydrates studied, that the mesophase exhibited is of the S_{A_d} type for the other homologous series.

4. Discussion

The results show that the several carbohydrate systems studied exhibit a single mesophase of the smectic A type. The subgroup classification is probably S_{A_d} which has an interdigitated bilayer structure. This result appears to be irrespective of whether the carbohydrate molecules have the cyclic pyranose or open chain configuration. Consequently, the drive to form a liquid-crystalline structure is probably derived from a desire for the hydrophilic parts of the molecules to pack strongly

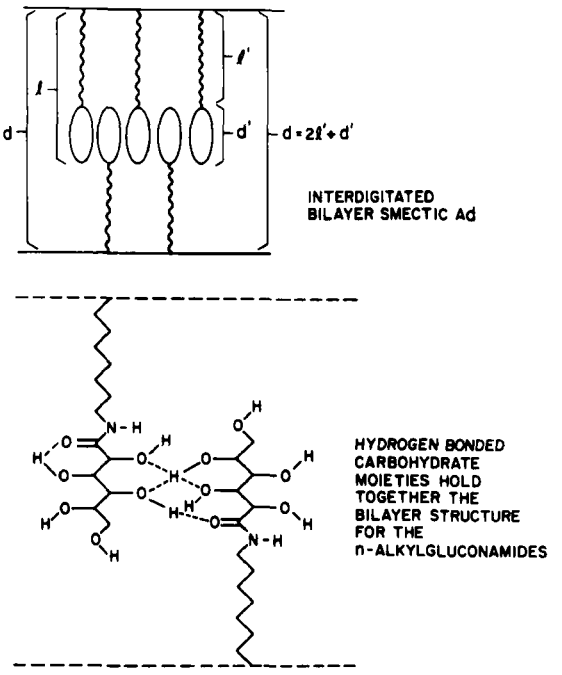


Figure 15. A hypothetical model for the layer structure of the *n*-alkyl derivatives of carbohydrates. The hydrogen-bonded ordering within the layers is shown for *n*-octyl gluconamide. Note, this is only one of the many possible orientations and conformations of the molecules in this dynamic smectic state.

together to give a disordered hydrogen-bonded structure. The weaker interacting hydrophobic aliphatic regions probably form a liquid-like barrier between the layers of hydrogen-bonded cores as shown in figure 15 for the *n*-alkyl gluconamides. This would give a lamellar spacing which on average would be equal to twice the hydrophobic aliphatic chain length plus the length of the carbohydrate moiety, i.e. a lamellar spacing between one and two times the molecular length. This is a proposed model for the mesophases of monoalkyl carbohydrates. However, it should be remembered that in this smectic phase the molecules are in a dynamic state. The aliphatic chains are relatively fluid, and the hydrogen-bonding that holds the cores together often breaks and reforms as the molecules undergo reorientational motion.

Table 2 lists a number of interesting comparisons; first the *n*-octyl gluconamide and *n*-octyl gluconate have similar phase sequences and transition temperatures. In liquid-crystal systems where the cores are not hydrogen-bonded the progression from an ester linkage to a hydrogen-bonding amide would produce great differences in transition temperatures and phase type. In this case, however, the amide inter and intra-molecular hydrogen-bonding is only a small fraction of the total hydrogen-bonding in the system. Therefore, the effect of the extra hydrogen-bonding due to the amide linkage is minimal, thus the two molecules become almost iso-structural and consequently have similar phase behaviour.

Second, the 1-o-β and the 1-o-α pyranosides have similar phase transition temperatures [11]. The alkylated axial α position has a slightly higher transition temperature than the equatorial β position. In non-hydrogen-bonded liquid-crystal systems this would produce great differences in phase behaviour with the axial analogue being

more likely to have a poorer tendency to form mesophases. In carbohydrate systems, however, it does not appear to matter greatly if the hydrophobic terminal chain is axial or not with respect to the hydrogen-bonded core. This may be due to the carbohydrate cores packing at a slight angle to one another so that each position is equally favoured, or that the hydrogen-bonding is so strong and the aliphatic interaction so weak that the transitions are dependent first on a melting of aliphatic chains (crystal to liquid crystal), and then on a melting of the carbohydrate cores (liquid crystal to isotropic liquid).

Third, the transition temperatures of materials with open chain carbohydrate cores are often higher than those with closed ring structures, except when decomposition occurs rapidly.

Fourth, monosaccharide and disaccharide systems have similar relationships to transition temperature behaviour as di- and tri-aromatic ring systems in non-carbohydrate liquid crystals. For example, *n*-dodecyl-1-O-β-D-glucopyranoside has a clearing point of 144°C, but for *n*-dodecyl maltoside it is greater than 245°C. However, the transition temperatures appear to be only slightly affected if one carbohydrate moiety has an open chain structure. For example, the clearing points for *n*-octadecyl gluconamide and *n*-octadecyl maltobionamide are only 10°C apart. The lack of a great difference in clearing point values for these two materials may be due to the fact that the maltobionamide degrades at a faster rate, and thus the true clearing point temperature was never obtained. Additionally, the maltobionamide has a closed carbohydrate ring attached to the fourth carbon atom and not to the terminal carbon atom of the open chain carbohydrate. Hence the overall structure is broader and shorter than the linear structure. This in turn lowers the clearing point in comparison to a fully extended structure. Thus it is possible in the light of the above considerations that a mixed system (open chain and closed ring glucose) can also act as a double ring core structure.

Lastly the decomposition process (caramelization) occurs more rapidly in the liquid-crystalline mesophase than in either the solid or the liquid, and for carbohydrates in their open chain structure rather than a pyranose structure. The structural format for the crystalline state of a number of these materials is a head-to-tail interlayer packing [1, 5,12] with the molecules overlapping with each other and the same way up. In the liquid the molecules are randomly ordered, but in the liquid crystal they have a head-to-tail overlap of the carbohydrate residues. This antiparallel arrangement of the carbohydrate residues (as shown in figure 15) (unlike that in the crystal where they are parallel) may be instrumental in the decomposition process. Thus it is possible that caramelization is initiated by an intermolecular process where the carbohydrate residues are in an antiparallel open chain format.

5. Conclusions

The *n*-alkyl gluconamides were found to exhibit liquid-crystalline phases which are miscible with those of the *n*-alkyl-1-O-β-D-glucopyranosides. The phases are classified as smectic S_A, tentatively as S_{A_d} where the carbohydrate cores overlap to produce a bilayer structure.

Comparative studies show that the liquid-crystal phase transitions are relatively insensitive to changes in central linkages, position of hydrophobic terminal chains, and to mixing open carbohydrate structures with closed ring pyranose structures.

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Note added in proof.—Concurrent to our investigations on the *n*-alkyl gluconamides an X-ray study has been carried out by Drs. D. Bayens-Volant and C. David on the smectic phases of some of these materials. In a personal communication they indicated that the S_A phase is composed of layers where the lamellar spacing is approximately equal to the molecular length, thus classifying the system as smectic A_1. Consequently, in mixtures of these materials with the glucopyranosides there must be an $S_{A_d} - S_{A_1}$ phase transition in the phase diagram.

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