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N-Acyl-β-D-glycopyranosylamines and 2-alkylamido-2-deoxy-α/β-D-glucopyranoses: relationship between molecular structure and mesomorphism

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A variety of *N*-acyl-β-D-glucopyranosylamines, *N*-acyl-β-D-mannopyranosylamines and 2-alkylamido-2-deoxy-α/β-D-glucoses has been prepared regiospecifically and in good yield in a one step reaction of the appropriate acid chloride with D-mannosylamine, 2-amino-2-deoxy-D-glucopyranose (prepared in one step from glucose and mannose according to literature methods) and D-glucosamine liberated *in situ* from the commercially available hydrochloride. The dependence of the liquid crystal transition temperatures and mesophase formation on the degree and nature of intermolecular hydrogen bonding has been studied by choosing two different carbohydrate cores and by attaching aliphatic terminal chains *via* an amide linkage in two different positions. Comparison is made with related compounds reported in the literature. Whereas the *N*-acyl-β-D-mannopyranosylamines and *N*-acyl-β-D-glucopyranosylamines possess wide-range smectic A* phases, the corresponding 2-alkylamido-2-deoxy-β-D-glucopyranoses do not exhibit observable mesomorphism. Although some homologues of the compounds synthesized have already been reported in the literature, their liquid crystalline behaviour was not reported. These investigations confirm the general view that it is the number and type of hydrogen bonding groups on the carbohydrate moiety and the aliphatic chain length that primarily determine thermotropic mesophase behaviour, as well as the absolute values of the transition temperatures.

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1. Introduction

Over the last 150 years glycolipids with long aliphatic chains have been reported to exhibit unusual melting behaviour or double melting points [1–5]. It is now clear that these carbohydrates were actually liquid crystals exhibiting lamellar smectic A [6–14], columnar discotic [8, 13, 14] or cubic [15–17] mesophases. Furthermore, glycolipids often possess amphotropic behaviour [18], as they exhibit liquid crystalline properties both on melting the pure material to generate a thermotropic mesophase and also in the presence of solvents, e.g. with water to produce lyotropic mesophases [19, 20], which are also temperature dependent.

Derivatives of naturally occurring monosaccharides have been used as solvents for non-denatured proteins [21, 22], antibacterial and antiviral agents [23–25], surfactants [26], artificial blood [27], drug delivery systems [28], and as optically active building blocks for chiral nematic and ferroelectric liquid crystals [29, 30]. There is also increasing interest [31, 32] in the structural and biological role of monosaccharides, oligosaccharides and polysaccharides in the organization and function of cell membranes. It is becoming increasingly clear that both the molecular shape of the carbohydrate moiety and the degree and strength of hydrogen bonding with next-neighbour molecules play a decisive role in determining the type of order and the transition temperatures [33–36] of any liquid crystalline mesophase formed. This becomes apparent from evaluation of the large number of modified monosaccharides and oligosaccharides, which have been synthesized recently, especially in the last five years [33–43], and which exhibit thermotropic and lyotropic liquid crystalline behaviour.

The preparation from readily available starting materials [44] using a one-step methodology is reported for a limited number of readily accessible carbohydrates incorporating an amide linkage. The amides were selected to allow a study of the effect on the mesomorphic behaviour of introducing an additional site for hydrogen bonding next to the core. This structural feature was introduced at two different positions in the core

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carbohydrate. Initial investigations have shown that this feature can lead to higher melting (T_m) and clearing points (T_{SmA*I}) than those observed for related compounds such as esters. The amide linkage also seems to play an important role in the supramolecular structure of diverse glycoconjugates [45]. There are only a small number of liquid crystalline carbohydrates with an amide linkage reported in the literature [18, 46–49] and the present work should contribute to understanding their mesomorphic behaviour.

This investigation of carbohydrates incorporating an amide linkage has been extended to include an alicyclic moiety as a structural feature in order to determine the effect of rigidity in the terminal chain on the mesomorphism of amphiphilic liquid crystals. Previous investigations have shown that cyclohexyl carbohydrate derivatives exhibit mesomorphism at elevated temperatures [42].

D-Glucose and D-mannose derivatives were chosen for these investigations, since comparisons with known systems could be readily facilitated as most thermal data reported in the literature refer to glucose derivatives [11, 12, 36–43].

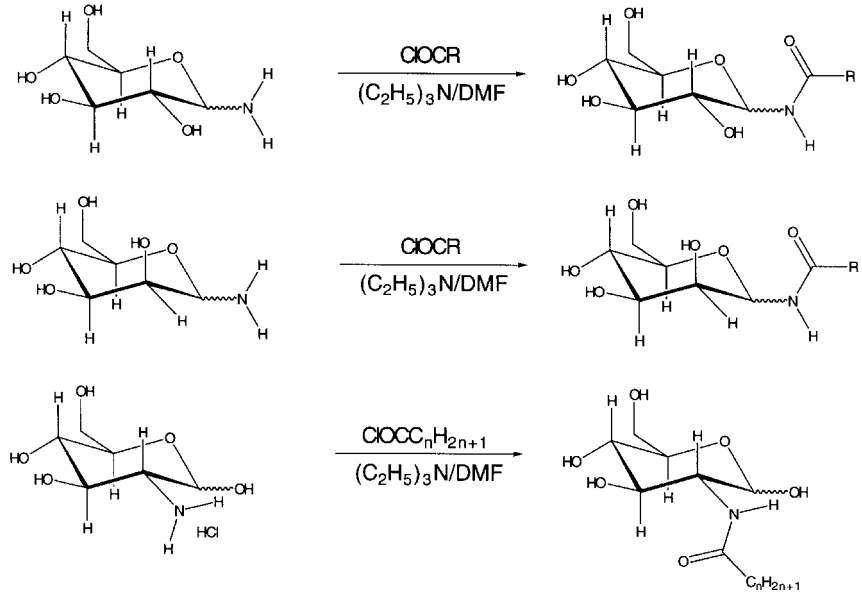
2. Synthesis

A direct acylation of D-mannopyranosylamine and D-glucopyranosylamine, prepared according to a literature method [44] in one step from glucose and mannose, with the appropriate acid chlorides using triethylamine as base and *N*,*N*-dimethylformamide as solvent yielded the desired *N*-acyl-β-D-glycosylamines (**1–12** and **17**) in good yield and purity (scheme). The required acid chlorides were either commercially available or were prepared from the corresponding carboxylic acids by reaction with thionyl chloride. Good selectivity for *N*-acylation was achieved without the necessity of using thiadiazole reagents [45]. This acylation reaction was stereospecific producing the β-anomers only, in all cases. The anomeric configuration is easily established for the glucose derivatives on the basis of a value of $J_{1,2}=9$ Hz. In the mannose derivatives the corresponding value, $J_{1,2}<0{\cdot}5$ Hz, suggests that the dihedral angle between H-1 and H-2 is *c.* 90°. This is to be expected for the β-anomer, a consequence of ring distortion due to interaction between the substituents at positions 1 and 2. A value of $J_{1,2}=1{\cdot}25$ Hz has been reported for di-β-D-mannopyranosylamine [50]. The β-configuration is further confirmed by the shift of C-5 (77·3). The corresponding 2-alkylamido-2-deoxy-β-D-glucopyranoses (**13–16**) were prepared analogously starting from 2-amino-2-deoxy-D-glucopyranose liberated *in situ* from the commercially available hydrochloride (scheme). The products were each isolated as an anomeric mixture, which was not separated. Elemental analysis is reported for the mixture, whereas ^{1}H NMR data for both anomers were extracted from the spectra of the anomeric mixture.

3. Phase characterization

3.1. *Phase characterization by thermal optical microscopy*

All the thermotropic mesophases are of the same type and exhibit the same behaviour. Bâtonnets are observed



Scheme

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on cooling from the isotropic liquid; these coalesce quickly in the bulk to form focal-conic domains. As the sample is cooled further, the hydrophilic end of the carbohydrate molecules adheres more strongly to the glass surface via hydrogen bonding. Thus, most of the resultant texture becomes homeotropic and optically extinct. This indicates that the phase is optically uniaxial (if the mesophase were biaxial then a residual birefringence for the sample would be observed). However, focal-conic defects can still be observed around air bubbles and at the edges of the sample. This optical behaviour, i.e. the simultaneous presence of both homeotropic and focal-conic textures, indicates that the mesophase is a calamitic smectic A* phase [8, 13, 14, 33]. The notation smectic A* is used to describe the smectic A phase exhibited by these compounds as they are optically active and, therefore, the A* phases formed by them must have reduced symmetry [33]. An unoriented focal-conic defect texture that persisted across the whole of the preparation was found for preparations on nylon coated microscope slides and cover-slips. The elliptical and hyperbolic lines of optical discontinuity characteristic of focal-conic defects could be clearly observed. The characterization of these defects classifies the mesophase as being smectic A* with a layered structure where the long axes of the molecules are on average orthogonal to the layer planes, and the in-plane and out-of-plane positional ordering of the molecules is short range.

Homeotropic textures for all of the enantiotropic phases were obtained on dust and grease free glass slides. Although this implies that the mesophase is uniaxial, conoscopic observations could not distinguish between negative and positive birefringence. This may well be explained by the low birefringence of most of these materials, which do not exhibit a well-defined or clear conoscopic interference pattern.

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3.2. *Miscibility studies*

Co-miscibility between the liquid crystal phases of the carbohydrates (**1–12**) with the smectic A*$_d$ phase of the standard material octyl β-D-glucopyranoside was observed. Thus, the thermotropic phases of these carbohydrates can be classified as smectic A*$_d$.

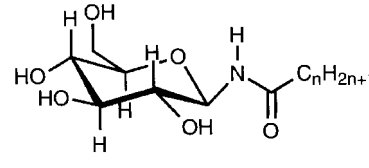
3.3. *Phase characterization by differential scanning calorimetry*

The enthalpy values for the various transitions of the *N*-acyl-β-D-glucopyranosylamines (**1–6**) and *N*-acyl-β-D-mannopyranosylamines (**7–12**) are given in tables 1 and 2. Comparisons of the enthalpy data can also be drawn from consideration of figure 1 respectively, which shows the first heating thermograms for the *N*-acyl-β-D-glucopyranosylamines (**1–6**) and from figure 2 for the corresponding *N*-acyl-β-D-mannopyranosylamines (**7–12**). The glucose series (**1–6**) is seen to exhibit a much broader SmA* temperature range at higher temperatures than that observed for the corresponding mannose series (**7–12**) [figure 3]. A high degree of thermal decomposition is observed for the latter above the clearing point. The clearing point enthalpies are relatively small in comparison to the melting enthalpies, and the values measured are of a similar magnitude to those found in conventional liquid crystal systems which exhibit SmA* to isotropic liquid transitions. The peaks for the phase transitions are relatively sharp, indicating a high degree of purity for the materials.

4. Discussion of the transition temperatures.

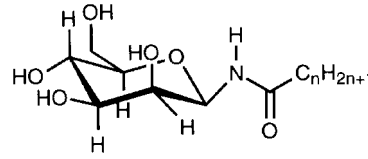
The liquid crystalline transition temperatures of the *N*-acyl-β-D-glucopyranosylamines (**1–6**) are collated in table 1. Both the melting point (T_m) [51] and smectic A*–isotropic liquid transition temperature (T_{SmA*I}) are high, and a broad SmA* phase is observed for most

Table 1. Transition temperatures and enthalpies of transition for the *N*-acyl-β-D-glucopyranosylamines (**1–6**).



Compound	*n*	Cr–SmA*/I/°C	ΔH/Jg^{-1}	SmA*–I/°C	ΔH/Jg^{-1}
(**1**)	8	183		—	
(**2**)	9	187	103·8	207	7·2
(**3**)	11	182	106·4	223	6·5
(**4**)	13	181	79·4	230	4·8
(**5**)	15	182	85·0	233	1·7
(**6**)	17	170	70·4	220	0·2

Table 2. Transition temperatures and enthalpies of transition for the *N*-acyl-β-D-mannopyranosylamines (**7**–**12**).



Compound	*n*	Cr–SmA*/I/°C	ΔH/Jg^{-1}	SmA*–I/°C	ΔH/Jg^{-1}
(**7**)	8	194		—	
(**8**)	9	192		—	
(**9**)	11	188	100	198	4·9
(**10**)	13	176	97·0	213	3·2
(**11**)	15	165	92·4	209	1·5
(**12**)	17	180	83·2	216	0·1

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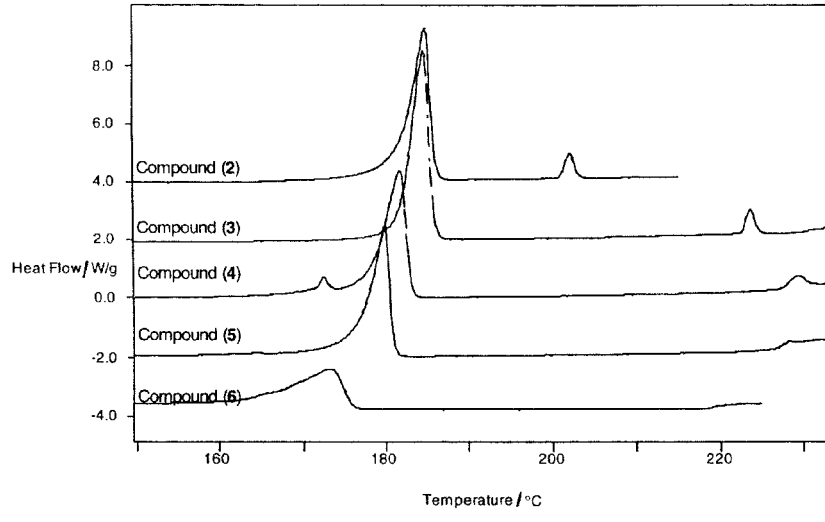

Figure 1. Differential scanning thermograms as a function of temperature for the first heating cycle for the *N*-acyl-β-D-glucopyranosylamines (**2**–**6**), scan rate 10°C min^{-1}.

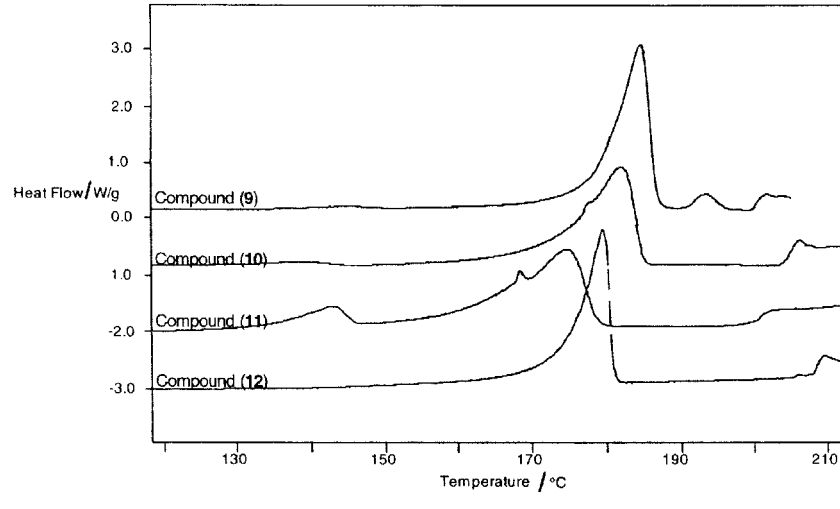

Figure 2. Differential scanning thermograms as a function of temperature for the first heating cycle for the *N*-acyl-β-D-mannopyranosylamines (**9**–**12**), scan rate 10°C min^{-1}.

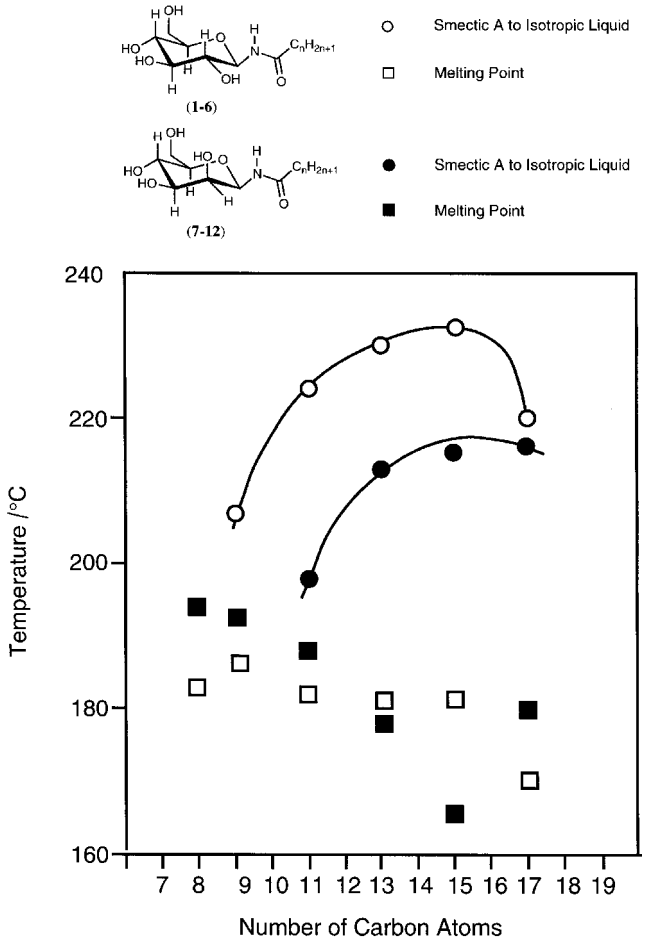

Figure 3. Plot of the transition temperatures of the *N*-acyl-β-D-glucopyranosylamines (**1–6**) and the *N*-acyl-β-D-mannopyranosylamines (**7–12**) against the number of the carbon atoms (*n*) in the alkyl part of the acyl terminal chain.

homologues after a critical chain length is reached ($n=9$). The maximum differences in the absolute values of T_m and T_{SmA*I} are not great (17°C and 23°C, respectively) on increasing the chain length significantly ($n=8$–17), i.e. they show a relatively small dependence on chain length. This is typical of many liquid crystalline carbohydrate homologous series, and suggests that a minimum ratio of the hydrophobic to hydrophilic parts is necessary for mesophase formation; thereafter an increase in this ratio does not affect the transition temperatures greatly. This behaviour is markedly different from that observed for most non-amphiphilic thermotropic liquid crystals, where a much stronger dependence on chain length and transition temperatures is generally observed.

The mesomorphic behaviour of the homologous series of *N*-acyl-β-D-mannopyranosylamines (**7–12**) is different from that of the corresponding *N*-acyl-β-D-glucopyranosylamines (**1–6**) [table 2 and figure 3]. T_m and T_{SmA*I} are lower in general (−10°C and −10°C, on average, respectively) for the mannose derivatives and a longer chain length is required for mesophase formation ($n=11$). However, T_{SmA*I} then increases sharply and reaches almost the same values as those observed for the corresponding *N*-acyl-β-D-glucopyranosylamines (**5** and **6**) with the same chain lengths ($n=16$ and 18), i.e. the temperature dependence is markedly different for both series within a narrow temperature range. The unusually low T_{SmA*I} of compound **6** ($n=17$) could be due to impurity. However, this interpretation is not consistent with the good values obtained for the elemental analysis and the clean ^{1}H NMR spectrum; it may well be due to thermal decomposition at this high temperature. This may also be responsible for the slightly lower T_{SmA*I} of compound **11** ($n=15$) compared with the values for compounds **10** and **12** ($n=13$ and 17) with shorter and longer chains.

It seems reasonable to suggest that the high T_m and T_{SmA*I} of the amides (**1–12**) is due primarily to a high degree of hydrogen bonding between adjacent carbohydrate cores with a minimum of interdigitation of the aliphatic chains (figure 4) as suggested [10–12] for the bilayer lamellar structure of the thermotropic SmA* phase in the absence of more than trace amounts of water. A bilayer structure with intercalated aliphatic chains for the crystalline state of various alkyl glycosides has been found by X-ray measurements at room temperature [8–10]. However, there is no general correlation between the crystal structure of a solid and the supramolecular organization of a thermotropic liquid crystalline phase formed from it under the action of heat. The rotation volumes of the fluid aliphatic chains at elevated temperatures would fill the spaces between the carbohydrate moieties. Peaks in the DSC thermograms are indicative of chain melting at temperatures lower than the melting point (figures 1 and 2). The carbonyl (CO) and amino (NH) parts of the amide linkage are assumed to adopt a *trans*-conformation as suggested for related *N*-alkylribonamides [49, 50]. Liquid crystalline carbohydrates with various aromatic and alicyclic cores have been synthesized [52] in order to allow an unambiguous determination of the thermotropic SmA* bilayer structure by X-ray studies. These studies of representative homologues of the compounds, i.e. *N*-octadecanoyl-β-D-glucopyranosylamine (**5**) and *N*-octadecanoyl-2-amino-2-deoxy-β-D-glucopyranose (**17**) in the crystalline and liquid crystalline state appear to confirm this interpretation [53].

Changing the position of the alkylamido group from the 1-position in the *N*-acyl-β-D-glucopyranosylamines (**1–6**) to the 2-position in the corresponding 2-alkylamido-2-deoxy-β-D-glucopyranoses (**13–16**) results in an increased T_m and the disappearance of

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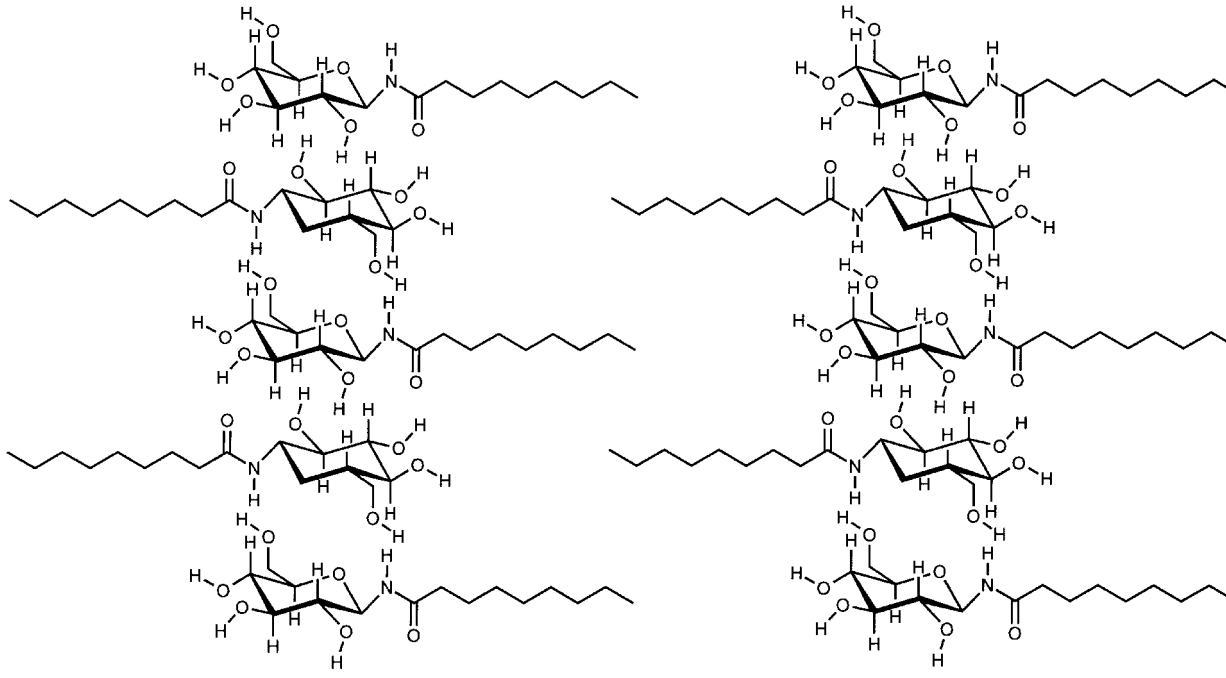

Figure 4. Possible bilayer structure for the smectic A* phase of the carbohydrates (**1–12**).

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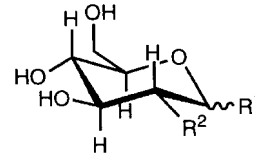
thermotropic mesomorphism (table 3). The T_m values reported for these compounds in the literature [54] are lower than those reported here. Unfortunately, the expected monotropic behaviour for the compounds (**13–16**) could not be observed owing to the very limited degree of supercooling observed during microscopy and DSC measurements. It may well be that a substituent in position 2 disrupts the degree of hydrogen bonding between nearest neighbours and substantially changes the molecular conformation. Steric interactions and electrostatic repulsion between the carbonyl oxygen atom and the hydroxyl oxygen atom at the anomeric centre probably cause a degree of rotation around the amide (CO–NH) linkage, leading to a non-linear conformation of the hydrophobic alkyl chain and the hydrophilic carbohydrate core. Whatever the actual conformation of the chain and bilayer structure, it is clear that the degree and form of hydrogen bonding and the overall conformation of the 2-alkylamido-2-deoxy-β-D-glucopyranoses (**13–16**) should be considerably different from that of the corresponding *N*-acyl-β-D-glucopyranosylamines (**1–6**) and that this combination of factors is not conducive to mesophase formation. X-ray studies of representative homologues (**5** and **17**) of these two types

Table 3. Transition temperatures for the *N*-acyl-β-D-glucopyranosylamines (**1, 3, 4** and **5**) and the 2-alkylamido-2-deoxy-α/β-D-glucopyranoses (**13–16**).



Compound	*n*	R^1	R^2	Cr–SmA*/I/°C	SmA*–I/°C
(**1**)	8	$NHOCC_nH_{2n+1}$	OH	183	—
(**3**)	11	$NHOCC_nH_{2n+1}$	OH	182	235
(**4**)	13	$NHOCC_nH_{2n+1}$	OH	181	230
(**5**)	17	$NHOCC_nH_{2n+1}$	OH	170	220
(**13**)	8	OH	$NHOCC_nH_{2n+1}$	214	—
(**14**)	11	OH	$NHOCC_nH_{2n+1}$	210	—
(**15**)	13	OH	$NHOCC_nH_{2n+1}$	216	—
(**16**)	17	OH	$NHOCC_nH_{2n+1}$	197	—

of compound appear to confirm this interpretation as neither show intercalation of the carbohydrate core nor the alkyl chains in the crystalline state [53].

The liquid crystal transition temperatures of *N-trans*-4-pentylcyclohexanecarbonyl-β-D-glucopyranosylamine (**17**) and the corresponding *N*-nonanoyl-β-D-glucopyranosylamine (**2**) are collated in table 4. The *N-trans*-4-pentylcyclohexanecarbonyl-β-D-glucopyranosylamine (**17**) does not exhibit an observable mesophase. This is also due in large part to the added rigidity of the *trans*-1, 4-disubstituted cyclohexane ring compared with that of the corresponding purely aliphatic chain which can adopt many non-linear conformations, especially at such high temperatures. The high value for T_m and only moderate degree of supercooling does not allow a mesophase to be observed. T_m could also be expected to be high for the above reasons. The limited number of similar known carbohydrates incorporating a *trans*-1, 4-disubstituted cyclohexane ring do exhibit enantiotropic SmA* phase at temperatures above those of the corresponding alkyl glycosides of approximately the same length [42].

Comparison of the transition temperatures of the dodecyl β-D-glucopyranoside (**18**) [3] and *N*-dodecanoyl-β-D-glucosylamine (**3**) (table 5) demonstrates clearly the effect of additional hydrogen bonding and the reduced conformational freedom attributable to the amide linkage. Both the melting and clearing points of the amide (**3**) are significantly higher than those of the ether (**18**) of equal chain length at the anomeric position on the same sugar. However, whereas the ether (**18**) has four groups capable of forming hydrogen bonds with nearest neighbours, the amide (**3**) has five. This interpretation is reinforced by consideration of the thermal data collated in table 6 for the 6-*O*-octadecyl-β-D-galactopyranose (**19**) [55] and the 6-deoxy-octadecanamido-β-D-galactopyranose (**20**) [46]. Both the melting and clearing points of the amide (**20**) are higher than those of the corresponding ether (**19**), although the differences are not so marked as those observed for the ether (**18**) and amide (**3**) in table 5. That these differences in transition temperatures can be attributed to the amide linkage as a whole and not just, for example, to higher polarizability due to the additional carbonyl group present in the amide linkage is demonstrated clearly by the data collated in table 7. Although the transition temperatures of the tertiary amine (**21**) [56] are indeed higher than those of the corresponding

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Table 4. Transition temperatures for the *N*-nonanoyl-β-D-glucopyranosylamine (**2**) and the *N-trans*-4-pentylcyclohexanecarbonyl-β-D-glucopyranosylamine (**17**).

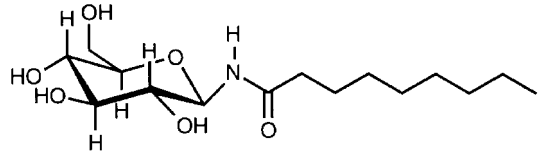
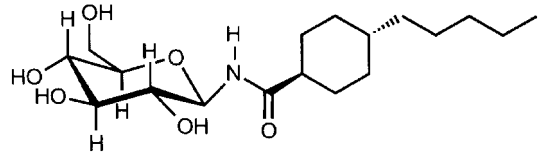
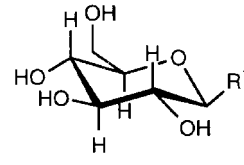
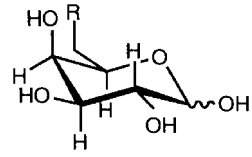
Compound	Structure	Cr–SmA*/I/°C	SmA*–I/°C
(**2**)		187	207
(**17**)		259	—

Table 5. Transition temperatures for the dodecyl β-glucopyranoside (**18**) and the *N*-dodecanoyl-β-D-glucosylamine (**3**).



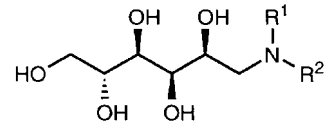
Compound	*R*	Cr–SmA*/°C	SmA*–I/°C	Reference
(**18**)	$-O-CH_2-C_{11}H_{23}$	80	142	[3]
(**3**)	$-NH-CO-C_{11}H_{23}$	182	235	

Table 6. Transition temperatures for the 6-*O*-octadecyl-β-D-galactopyranose (**19**) and the 6-octadecamido-β-D-galactopyranose (**20**).



Compound	*R*	Cr–SmA*/°C	SmA*–I/°C	Reference
(**19**)	–O–CH_2–$C_{17}H_{35}$	119	164	[55]
(**20**)	–NH–CO–$C_{17}H_{35}$	134	197	[46]

Table 7. Transition temperatures for the 1-(tetradecylmethylamino)-1-deoxy-D-glucitol (**21**), the *N*-tetradecanoyl-*N*-methyl-1-amino-1-deoxy-D-glucitol (**22**) and the 1-tetradecyl-D-gluconamide (**23**).



Compound	R^1	R^2	Cr–SmA*/°C	SmA*–I/°C	Reference
(**21**)	CH_3	–CH_2–$C_{13}H_{27}$	92	106	[56]
(**22**)	CH_3	–CO–$C_{13}H_{27}$	100	147	[18, 47]
(**23**)	H	–CO–$C_{12}H_{25}$	159	189	[18, 47]

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tertiary amide (**22**) [18, 47], where a methylene group (CH_2) has been replaced by a carbonyl function (C=O), the transition temperatures of the secondary amide (**23**) [18, 47], which is capable of additional hydrogen bonding due to the hydrogen atom (R^1=H) instead of the methyl group (R^1=CH_3) are considerably higher than those of both the amine (**21**) and the amide (**22**). The absence of the methyl group in the amide (**23**) could also be a factor giving rise to a high clearing point, due a lower degree of steric hindrance attributable to the methyl group in the amine (**21**) and the amide (**22**).

5. Experimental

5.1. *Characterization*

The structures of the intermediate and final products were determined by ^{1}H NMR and ^{13}C NMR spectroscopy (JEOL JNM-GX 270 spectrometer), mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer), and infrared spectroscopy (Perkin Elmer 457 grating spectrophotometer). ^{1}H chemical shifts were measured for solutions in DMSO-d_6 relative to $(CH_3)_4Si$ and ^{13}C chemical shifts relative to the solvent (δ 39·5). The ^{1}H and ^{13}C NMR data clearly showed the pyranose form for the derivatized monosaccharides and also indicate the stereochemistry of the anomeric centre (e.g. for compound **13**α: for H-1 δ=4·92, $J_{1,2}$=4·0 Hz, for C-1 δ=90·6; compound **13**β: for H-1 δ=4·52, $J_{1,2}$=6 Hz, for C-1 δ=95·6).

The purity of the compounds was determined by thin layer chromatography (TLC), high performance liquid chromatography (HPLC), elemental analysis (C, H, N) and differential scanning calorimetry (DSC); 4 × 8 cm^2 precoated TLC plates, SiO_2 SIL G/UV_{254}, layer thickness 0·25 mm (Machery-Nagel, Düren, Germany) were utilized. Melting points were determined with a Buchi apparatus and are uncorrected. Optical rotations were recorded at room temperature on $CHCl_3$ solutions with a Perkin-Elmer 241 polarimeter using a 1 dm cell.

Column chromatography was carried out using silica gel 60 (230–400 mesh ASTM). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were carried out under N_2 unless water was present as a reagent or solvent. All temperatures were measured externally unless otherwise stated.

Mesophase identification and the determination of transition temperatures of the carbohydrates prepared were determined by optical microscopy using either a Zeiss Universal or an Olympus BH-2 polarizing light microscope in conjunction with a Mettler FP 52 microfurnace and FP 5 Central Processor. Homeotropic sample preparations suitable for phase characterization

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were prepared simply by using very clean glass microscope slides (washed with water, acetone, water, concentrated nitric acid, water and dry acetone), whereas homogeneous defect textures were obtained using nylon coated slides. Nylon coating of the slides (~200–300 Å thick) was carried out by dipping clean slides into a solution of nylon (6/6) in formic acid (1% wt/vol). The nylon solution was allowed to drain off the slides over a period of 1h, and then they were baked dry, free from solvent, in an oven at 100°C for a period of 3 h. The slides were not buffed, as is usual for preparing aligned samples; instead they were used untreated so that many defects would be created when the liquid crystal formed on the surface of the slide on cooling from the liquid phase.

DSC was used to determine enthalpies of transition and to confirm the phase transition temperatures determined by optical microscopy. Differential scanning thermograms (scan rate 10° min^{-1}) were obtained using a Perkin Elmer DSC 7 PC system operating on DOS software. The results obtained were standardized with respect to indium (measured onset 156·68°C, ΔH 28·47 $J g^{-1}$, literature value 156·60°C, ΔH 28·45 $J g^{-1}$), nitrotoluene (measured onset 51·17°C, ΔH 118·49 $J g^{-1}$, literature value 51·63°C, ΔH 122·58 $J g^{-1}$) and benzil (measured onset 94·42°C, ΔH 108·52 $J g^{-1}$, literature value 94·87°C, ΔH 92·68 $J g^{-1}$).

Comparison of the transition temperatures determined by optical microscopy and DSC shows some discrepancies of about 1–3°C. These may be due to two factors; firstly, the two methods use instruments which are calibrated in different ways, and secondly, and more importantly, the carbohydrates tend to decompose at elevated temperatures at a rate which depends on the rate of heating, time spent at an elevated temperature and nature of the supporting substrate, e.g. the materials decomposed more quickly in aluminium DSC pans than on glass microscope slides.

Phase diagrams were constructed by determining the phase transition temperatures of individual binary mixtures of a test material mixed with a standard compound of known phase transition sequence. The binary mixtures were produced by weighing out each individual test material and a known standard material (octyl β-D-glucopyranoside [10, 18, 40]) on a microscope slide and mixing them thoroughly while in their liquid states [33]. The cooled samples were introduced into the microscope microfurnace and the phase transition temperatures and classification of phase type were assessed in the usual manner. Typically, when the test and standard materials were mixed on a microscope slide while in their liquid states, some decomposition occurred thereby resulting in lower transition temperatures. In all cases recrystallization temperatures were not determined because the binary mixtures supercooled to room temperature in their liquid crystalline states.

5.2. *General procedure for the synthesis of N-acyl-β-D-glycopyranosylamines*

A solution of acid chloride (1·0 mol eq.) in DMF (10 cm^3) was added dropwise to a solution of glycopyranosylamine (2·0 g, 1·5 mol eq.) and triethylamine (5 cm^3) in DMF (20 cm^3). After stirring for 1 h at room temperature the solvent was removed under reduced pressure and the residue extracted into a mixture of butanol/water (150 cm^3; 2:1 v/v). The organic layer was then washed with water (2 × 50 cm^3). The remaining butanol was evaporated under reduced pressure to give a white solid, which was washed with boiling acetone, and then filtered off and dried to afford the desired glycopyranosylamine.

For each class of compound, the NMR data were essentially the same for individual members of the class and representative data only are given below. Elemental analysis data for all compounds are given in table 8.

N-Alkanoyl-β-D-glucopyranosylamines (**1–6**). ^{1}H NMR (DMSO/TMS): δ=0·86 (t, 3H, J=6·5 Hz, Me), 2·08 (t, 2H, J=7·5 Hz, alkyl), 2·98–3·21 (m, 4H, H-2, H-3, H-4, H-5), 3·40 (m, 1H, $J_{5,6}$=5 Hz, $J_{6,6'}$=12 Hz, H-6), 3·6 (m, 1H, $J_{5,6'}$=5 Hz, H-6′), 4·45 (t, 1H, 6-OH), 4·72, 4·74, 4·82 (3 × d, 3H, 3 × OH), 4·68 (t, 1H, $J_{1,2}=J_{1,NH}$=9 Hz, H-1), 8·23 (d, 1H, NH). ^{13}C NMR: δ=60·92 (C-6), 69·99 (C-4), 72·45, 77·56, 78·47 (C-2, C-3, C-5), 79·41 (C-1), 172·52 (CO).

N-Alkanoyl-β-D-mannopyranosylamines (**7–12**). ^{1}H NMR (DMSO/TMS): δ=0·85 (t, 3H, J=7 Hz, Me), 2·13 (t, 2H, J=7·5 Hz, alkyl), 3·04 (t, J=7·5 Hz, H-3), 3·25 – 3·44 (m, 3H, H-4, H-5, H-6), 3·52 (s, 1H, H-2), 3·65 (dd, 1H, $J_{5,6}$=6 Hz, $J_{6,6'}$=12 Hz, H-6′), 4·43 (t, 1H, 6-OH), 4·71, 4·74, 4·82 (3 × d, 3H, 3 × OH), 5·02 (d, 1H, $J_{1,NH}$= 9Hz, H-1), 7·94 (d, 1H, NH). ^{13}C NMR: δ=61·33 (C-6), 66·74 (C-4), 70·78 (C-2), 74·03 (C-3), 77·31 (C-5), 79·00 (C-1), 171·90 (CO).

5.3. *General procedure for the synthesis of 2-alkanamido-2-deoxy-α,β-D-glucopyranoses*

2-Amino-2-deoxy-D-glucopyranose hydrochloride (2 g) was treated with a freshly prepared sodium methoxide solution in methanol. The resultant suspension was stirred for 15 min at room temperature, filtered to remove inorganic material and then evaporated. A solution of acid chloride (1·0 mol eq.) in DMF (10 cm^3) was added dropwise to a solution of the resultant glycosylamine residue (1·5 mol eq.) and triethylamine (5 cm^3) in DMF (20 cm^3). After stirring for 1 h at room temperature the solvent was removed under reduced pressure and the residue extracted into a mixture of butanol (100 cm^3) and water (50 cm^3). The organic layer was then washed with water (2 × 50 cm^3). The remaining butanol was

Table 8. Elemental analysis data for the compounds (**1–17**).

		Calculated			Found		
Compound	Formula	C	H	N	C	H	N
(**1**)	$C_{15}H_{29}NO_6$	56·41	9·15	4·38	56·21	9·42	4·35
(**2**)	$C_{16}H_{31}NO_6$	57·63	9·37	4·19	57·46	9·58	4·08
(**3**)	$C_{18}H_{35}NO_6$	59·81	9·76	3·87	60·01	10·16	3·80
(**4**)	$C_{20}H_{39}NO_6$	61·67	10·09	3·59	61·53	10·50	3·57
(**5**)	$C_{22}H_{43}NO_6$	63·28	10·38	3·35	63·56	10·94	3·27
(**6**)	$C_{24}H_{47}NO_6$	64·68	10·63	3·14	65·27	11·15	3·02
(**7**)	$C_{15}H_{29}NO_6$	56·41	9·15	4·38	56·65	9·46	4·36
(**8**)	$C_{16}H_{31}NO_6$	57·63	9·37	4·19	57·49	9·55	4·14
(**9**)	$C_{18}H_{35}NO_6$	59·81	9·76	3·87	60·09	10·14	3·83
(**10**)	$C_{20}H_{39}NO_6$[a]	60·82	10·11	3·54	60·77	10·50	3·53
(**11**)	$C_{22}H_{43}NO_6$	63·28	10·38	3·35	63·46	10·32	3·40
(**12**)	$C_{24}H_{47}NO_6$[a]	63·91	10·64	3·10	63·82	10·99	3·16
(**13**)	$C_{15}H_{29}NO_6$	56·41	9·15	4·38	56·27	9·42	4·35
(**14**)	$C_{18}H_{35}NO_6$	59·81	9·76	3·87	59·78	10·16	3·74
(**15**)	$C_{20}H_{39}NO_6$	61·67	10·05	3·59	60·61	10·42	3·52
(**16**)	$C_{24}H_{47}NO_6$[a]	63·91	10·64	3·10	63·89	10·88	3·17
(**17**)	$C_{18}H_{33}NO_6$	60·15	9·25	3·89	60·54	9·39	3·83

[a]With 0·3 molecules of water of crystallisation.

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then evaporated under reduced pressure and the residue purified by column chromatography. The mixture of α and β isomers obtained in this way was further purified by washing with boiling acetone and then dried to afford the desired glucosylamine.

Representative NMR data only are given below for the anomeric mixtures. Elemental analysis data are given in table 8.

2-Alkanamido-2-deoxy-α-D-glucopyranoses (**13**α–**16**α). ^{1}H NMR (DMSO/TMS): δ=0·85 (t, 3H, J=7 Hz, Me), 2·08 (t, 2H, J=7·5 Hz, alkyl), 3·01–3·71 (m, 6H, H-2.H-3, H-4, H-5, H-6, H-6′), 4·41 (t, 1H, 6-OH), 4·56, 4·88 (2 × d, 2H, 2 × OH), 4·92 (t, 1H, $J_{1,2}=J_{1,OH}$=4 Hz, H-1), 6·38 (d, 1H, 1-OH), 7·49 (d, 1H, NH).

2-Alkanamido-2-deoxy-α-D-glucopyranoses (**13**β–**16**β). ^{1}H NMR (DMSO/TMS): δ=0·85 (t, 3H, J=7 Hz, Me), 2·08 (t, 2H, J=7·5 Hz, alkyl), 3·01–3·71 (m, 6 H, H-2.H-3, H-4, H-5, H-6, H-6′), 4·42 (t, 1H, 6-OH), 4·52 (t, 1H, $J_{1,2}=J_{1,OH}$=6 Hz, H-1), 4·56, 4·77 (2 × d, 2H, 2 × OH, 6·45 (d, 1H, 1-OH), 7·63 (d, 1H, NH). ^{13}C NMR: δ= 61·13 (C-6), 57·09 (C-2), 70·89, 74·36, 76·77 (C-3–C-5), 95·60 (C-1), 172·74 (CO).

N-(trans-4-Pentylcyclohexanecarbonyl)-β-D-glucopyranosylamine (**17**). ^{1}H NMR (DMSO/TMS): δ= 0·8–1·8 (m, 20H, alkyl), 2·08 (t, 2H, J=7·5 Hz, alkyl), 2·98–3·21 (m, 4H, H-2.H-3, H-4, H-5), 3·40 (m, 1H, $J_{5,6}$=5 Hz, $J_{6,6'}$=12 Hz), 3·61 (m, 1H, $J_{5,6'}$=6 Hz, H-6′), 4·45, 4·76, 4·85, 5·00 (4H, 4 × OH), 4·66 (t, 1H, $J_{1,2}=J_{1,NH}$=9 Hz, H-1), 8·19 (d, 1H, NH). 13C NMR: δ= 60·92 (C-6), 70·01 (C-4), 72·42, 77·58, 78·49 (C-2, C-3, C-4, C-5), 79·46 (C-1), 176·56 (CO).

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