Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Letellier, P. , Ewing, D. F. , Goodby, J. W. , Haley, J. , Kelly, S. M. and Mackenzie, G.(1997) 'The effect of hydrogen bonding, molecular shape, dipole moments, and chain length on the mesomorphism of some D-glucose and D-glucosamine derivatives', Liquid Crystals, 22: 5, 609 — 620
To link to this Article: DOI: 10.1080/026782997209027
URL: http://dx.doi.org/10.1080/026782997209027

LIQUID CRYSTALS, 1997, VOL. 22, NO. 5, 609–620

The effect of hydrogen bonding, molecular shape, dipole moments, and chain length on the mesomorphism of some D-glucose and D-glucosamine derivatives

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(*Received 23 September 1996; accepted 10 January 1997*)

Diverse 4-substituted-benzyl 1-*O* -α- and β-D-glucopyranosides, 4-substituted-benzyl 2-deoxy-2-trifluoroacetamido-α- and β-D-glucopyranosides and 4-substituted-benzyl 2-acetamido-2-deoxy-α- and β-D-glucopyranosides have been synthesized. They were prepared directly by a one-step alkylation of commercially available carbohydrate starting materials. The 4-substituted-benzyl 2-deoxy-2-trifluoroacetamido-α- and β-D-glucopyranosides were cleaved to yield the corresponding free amines. The influence of hydrogen bonding, terminal dipole moments, molecular shape and chain length on the thermotropic mesomorphic behaviour of these benzyl-substituted carbohydrate amphiphiles is discussed. Comparisons between the mesomorphic behaviour of the new benzyl-substituted carbohydrates and that of the related phenyl-substituted carbohydrates, as well as the non-aromatic *n*-alkyl D-glucosides, are made. Although the new carbohydrates do not exhibit lyotropic phase behaviour, the 4-substituted-benzyl 2-deoxy-2-trifluoroacetamido-α- and β-D-glucopyranosides have been found to gel water at very low sugar concentrations.

1. Introduction

Although the anomalous melting behaviour of pure glycolipids with long aliphatic chains has been noted on several occasions over the last 150 years [1–5], it is not until relatively recently that they have been recognized and characterized as undoubted liquid crystals [6–14] with lamellar smectic A [8, 13, 14], discotic or cubic [15–17] structures. Many glycolipids exhibit amphotropic behaviour [18], in that they possess 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.

Modified derivatives of naturally occurring monosaccharides are the subject of increasing interest as solvents for non-denatured proteins [21, 22], antibacterial and antiviral agents [23–25], surfactants [26], artificial blood [27], drug delivery systems [28], optically active building blocks for chiral nematic and ferroelectric liquid crystals [29, 30], etc. In addition to commercial applications, the structural and biological functions of monosaccharides, oligosaccharides and polysaccharides in the organization and function of cell membranes are being increasingly studied [31, 32]. In all of these investigations it is becoming increasingly clear that the molecular shape of the carbohydrate moiety, as determined by its constitution, configuration and degree and strength of hydrogen bonding with neighbouring molecules, plays a decisive role in the self-assembling of supramolecular aggregates with a defined function [33–35].

Although a large number of modified monosaccharides and oligosaccharides exhibiting thermotropic and lyotropic liquid crystal properties has been synthesized, especially in the last five years [33–43], it is important to investigate systematic changes in carbohydrate structure to maximize the amount of useful information to be derived from these studies. The results obtained from the study of monosaccharides are easier to interpret than those from oligosaccharides due to the lower number and complexity of variable parameters, such as conformation, reactive sites and intramolecular interactions. Therefore, it was decided to synthesize a diverse series of 4-substituted-benzyl glucopyranosides including 2-deoxy derivatives having acetamido and trifluoroacetamido groups in this position. β-D-glucopyranosides can provide the necessary structural diversity in order to study the relationship between molecular shape, chain length, dipole moments and degree of aromaticity and liquid crystalline behaviour [35]. D-Glucose derivatives were chosen because comparisons with known systems

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0267–8292/97 $12·00

could be readily facilitated since most available thermal data in the literature refer to glucose derivatives [11, 12, 36–43]. This is partially due to the ready availability and low cost of D-glucose, which is the most prevalent monosaccharide in nature. In order to facilitate convenient access to the desired products, we have developed a highly efficient synthesis from commercially available D-acetylglucosamine and D-glucose in a one step reaction without the necessity for laborious protection/deprotection steps [35].

2. Synthesis

A direct glycosidation of commercially available 2-acetamido-2-deoxy-D-glucose with the relevant benzyl bromide using sodium hydride as base and *N*,*N*′-dimethylformamide as solvent yielded the desired 4-substituted-benzyl 2-acetamido-2-deoxy-α- and β-D-glucopyranosides (**12**α/β and **18**α/β–**21**α/β) in one-step instead of the usual reaction pathways requiring protection/deprotection [35]. The pure α- and β-anomers were separated from the anomeric mixture (see table 1) by column chromatography, and purified separately (see § 5).

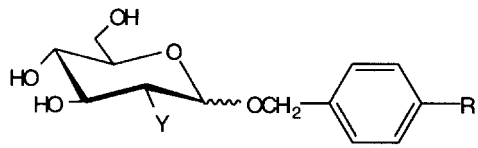
The pyranose form was obtained exclusively. The required benzyl bromides were either commercially available or were prepared from the corresponding 4-substituted benzoic acids by reduction with lithium aluminium hydride [44] to the benzyl alcohol and subsequent bromination using dibromotriphenyl phosphine [45]. The 4-substituted-benzyl β-D-glucopyranosides were prepared analogously starting from D-glucose. The β-anomers preferentially crystallized out from solutions of the anomeric mixtures in ethyl acetate, thus generating the pure 4-substituted-benzyl β-D-glucopyranosides (**8**β, **9**β and **13**β–**17**β) usually in good yield (≈20–60%). A similar reaction using 2-deoxy-2-trifluoroacetamido-D-glucose yielded the corresponding 4-decyloxybenzyl 2-deoxy-2-trifluoroacetamido-α- and β-D-glucopyranosides (**11**α and **11**β) respectively. These were deprotected to give the free amines, 4-decyloxybenzyl 2-amino-2-deoxy-α- and β-D-glucopyranosides (**10**α and **10**β), respectively, by cleavage in the presence of potassium carbonate.

3. Phase characterization

3.1. *Phase characterization by thermal optical microscopy*

For the carbohydrates which exhibit thermotropic liquid crystal mesophases, the same mesomorphic behaviour is found. Upon cooling from the isotropic liquid, a liquid crystal phase forms spontaneously as *bâtonnets*. These coalesce quickly in the bulk to form focal-conic domains. As the sample is cooled further, the carbohydrate molecules in the focal-conic domains adhere more

Table 1. Yield and anomeric ratio for the 4-substituted-benzyl α- and β-D- glucopyranosides (**8**α/β, **9**α/β and **13**α/β–**17**α/β), 4-decyloxybenzyl 2-amino-2-deoxy-α- and β-D-glucopyranoside (**10**α and **10**β), 4-decyloxybenzyl 2-deoxy-2-trifluoroacetamido-α- and β-D-glucopyranoside (**11**α/β) and 4-substituted-benzyl 2-acetamido-2-deoxy-α- and β-D-glucopyranoside (**12**α/β and **18**α/β–**21**α/β).



Carbohydrate	*Y*	*R*	Yield	α/β ratio
8α/β	OH	OC_7H_{15}	18	1:14[a]
9α/β	OH	$OC_{10}H_{21}$	18	1:10[a]
10α	NH_2	$OC_{10}H_{21}$		α
10β	NH_2	$OC_{10}H_{21}$	92	β
11α/β	$NHCOCF_3$	$OC_{10}H_{21}$	20	1:4[b]
12α/β	NHAc	$OC_{10}H_{21}$	14	1:2[b]
13α/β	OH	H	48	1:10[a]
14α/β	OH	CH_3	46	1:18[a]
16α/β	OH	F	63	1:10[a]
17β	OH	CF_3	47	β[a]
18α/β	NHAc	H	62	1:3·8[a]
19α/β	NHAc	F	65 (49)	1:1·77[a] (1:2[b])
20α/β	NHAc	CH_3	71	1:7·6[a]
21α/β	NHAc	CF_3	63 (44)	1:5[a] (1:2·5[b])

[a] α/β ratio determined by NMR.
[b] α/β ratio of isolated product.

to the glass surface of sample slides due to hydrogen bonding and 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). Around air bubbles and at the edge of the preparation focal-conic defects remain. The simultaneous presence of both homeotropic and focal-conic textures indicates that the mesophase is calamitic smectic A* in type [8, 13, 14, 33]. The notation smectic A* is used to describe the thermotropic phases exhibited by these compounds simply because the materials are all optically active and the A* phases formed by them must have reduced symmetries [33]. The use of nylon coated microscope slides and cover-slips produced an unoriented focal-conic defect texture that persisted across the whole of the preparation. 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. Ready mechanical displacement of the material in this texture indicates that the relative viscosity of the phase is low for a system that is expected to be extensively hydrogen-bonded.

Homeotropic textures for all of the materials were readily obtained using well cleaned glass slides, which were free from dust and grease. The formation of a homeotropic texture indicates that the mesophase is uniaxial. However, conoscopic studies were unable to reveal whether or not the phase possessed negative or positive birefringence. This may well be due to the inherently low birefringence of the materials, which will not exhibit a well-defined or clear conoscopic interference pattern.

3.2. *Miscibility studies*

A number of miscibility studies were carried out in order to establish the identities of the thermotropic mesophases exhibited by the carbohydrates **8**β–**10**β with thermotropic liquid crystal character. Miscibility studies were carried out using the previously classified material octyl β-D-glucopyranoside as the standard. Co-miscibility between the liquid crystal phases of the carbohydrates **8**β–**10**β) was established with the smectic A_d^* phase of the standard material. Thus, the thermotropic phases of the three compounds were found to have the same identity, and were all classified as smectic A_d^*.

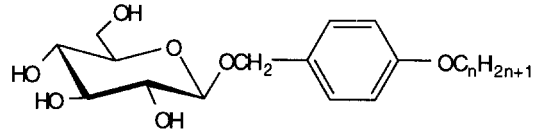
3.3. *Phase characterization by differential scanning calorimetry*

The enthalpy values for the various transitions of the 4-heptyloxybenzyl β-D-glucopyranose (**8**β) and 4-decyloxybenzyl β-D-glucopyranose (**9**β) are given in table 2. In addition, the temperature for recrystallisation for **8**β is also given as this could not be determined accurately from thermal optical microscopy. Comparisons of the enthalpy data can also be drawn from consideration of figures 1 and 2, respectively, which show the first heating and cooling thermograms for 4-heptyloxybenzyl β-D-glucopyranose (**8**β) and 4-decyloxybenzyl β-D-glucopyranose (**9**β). The decyl homologue **9**β is seen to exhibit a much broader SmA* temperature range than that observed for the corresponding heptyl homologue **8**β. The decyl homologue **9**β also exhibits a lower melting point enthalpy than that observed for the corresponding heptyl homologue **8**β. This is consistent with the fact that although the heptyl homologue **8**β recrystallizes, the decyl homologue **9**β appears to form a glass with a second order transition at about 65°C. The clearing point enthalpies are relatively small in comparison with 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. These results are consistent with a previous finding that there may be a relationship between the size of the melting enthalpy, the melting point and whether or not the material exhibits a glass transition on cooling [33]. Furthermore, it should be noted that the peaks for the phase transitions are relatively sharp, indicating a high degree of purity for the materials. The first heating and cooling thermograms for 4-(decyloxy)benzyl 2-amino-2-deoxy-β-D-glucopyranose (**10**β) is shown in figure 3. The value for T_{SmA*} on heating is 3°C lower than that obtained by microscopy. It is clear from this observation and from the irregularity of the base line, as well as from the absence of a clear melting peak, that substantial decomposition had taken place on heating and no valid data could be ascertained.

3.4. *Lyotropic mesomorphism*

No lyotropic phases could be observed for the carbohydrate derivatives prepared under the conditions described in § 5. They were either very sparingly soluble or formed optically clear solutions. However, the 4-decyloxybenzyl 2-deoxy-2-trifluoroacetamido-α- and β-D-glucopyranosides (**11**α and **11**β) were found to gel water at very low concentrations ($\approx$1%). The results of further studies of this interesting behaviour will be published at a later date.

Table 2. Transition temperatures and enthalpies for the melting points and clearing points of 4-heptyloxybenzyl β-D-glucopyranoside (**8**β) and 4-decyloxybenzyl β-D-glucopyranoside (**9**β).



		Melting		Clearing		Recryst	
Carbohydrate	n	T/°C	ΔH/J g^{-1}	T/°C	ΔH/J g^{-1}	T/°C	ΔH/J g^{-1}
8β	7	122	79·900	147	4·477	84	−66·549
9β	10	117	61·726	166	3·155	—	—

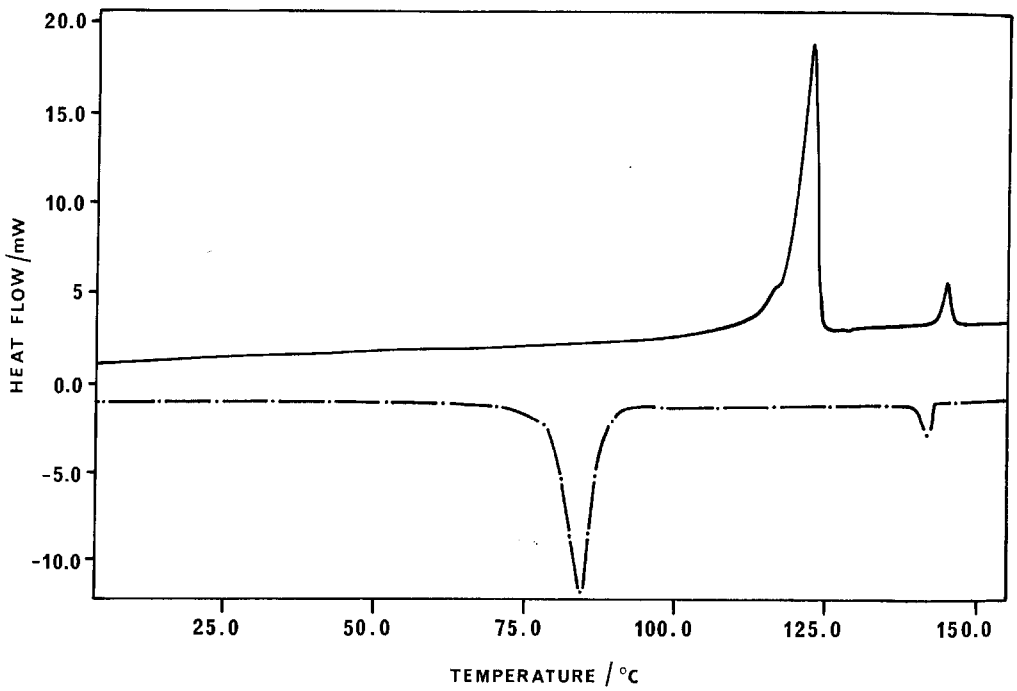


Figure 1. Differential scanning thermograms as a function of temperature for the first heating and cooling cycle for 4-heptyloxybenzyl β-D-glucopyranoside (**8**β); scan rate 10°C min^{-1}.

4. Discussion of the transition temperatures

The transition temperatures for the decyl 2-deoxy-β-D-glucopyranoside (**1**β) [37, 38], decyl 2-amino-2-deoxy-β-D-glucopyranoside (**2**β) [39], decyl 2-deoxy-2-fluoro-β-D-glucopyranoside (**3**β) [37, 38], decyl β-D-glucopyranoside (**4**β) [10, 18, 40] and decyl 2-acetamido-2-deoxy-β-D-glucopyranoside (**5**β) [41] collated in table 3 clearly show the effect of hydrogen bonding on the melting point (T_m) and the smectic A*–isotropic liquid transition temperature T_{SmA*}. The nature of the substituent Y varies, while its configuration and the position and configuration of the hydroxy groups and the configuration at the anomeric centre (β) remain constant. The decyl homologue was chosen because of its broad enantiotropic smectic A* phase. It has been clearly demonstrated that the tendency to form liquid crystal phases and the absolute value of the transition temperatures depend directly on the degree of molecular association due to groups available for hydrogen bonding, their number, configuration and position [33–35]. Therefore, as the 2-deoxy-β-D-glucopyranoside (**1**β) has only three hydroxy groups, it is not surprising that T_{SmA*} is lower than the other values for T_{SmA*} collected in table 1 for the carbohydrates **2**β–**5**β which have four groups capable of hydrogen bonding. Although the amino group of the 2-deoxy-2-amino-β-D-glucopyranoside (**2**β) has two hydrogen atoms available for hydrogen bonding, these bonds are weaker due to the lower

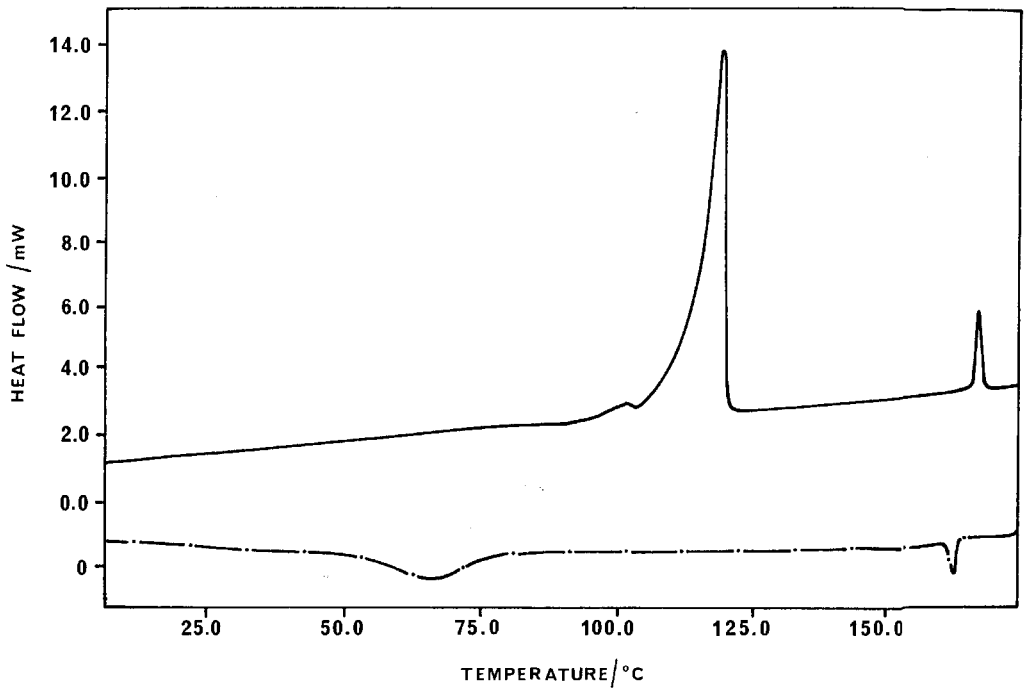


Figure 2. Differential scanning thermograms as a function of temperature for the first heating and cooling cycle for 4-decyloxybenzyl β-D-glucopyranoside (**9**β); scan rate 10°C min^{-1}.

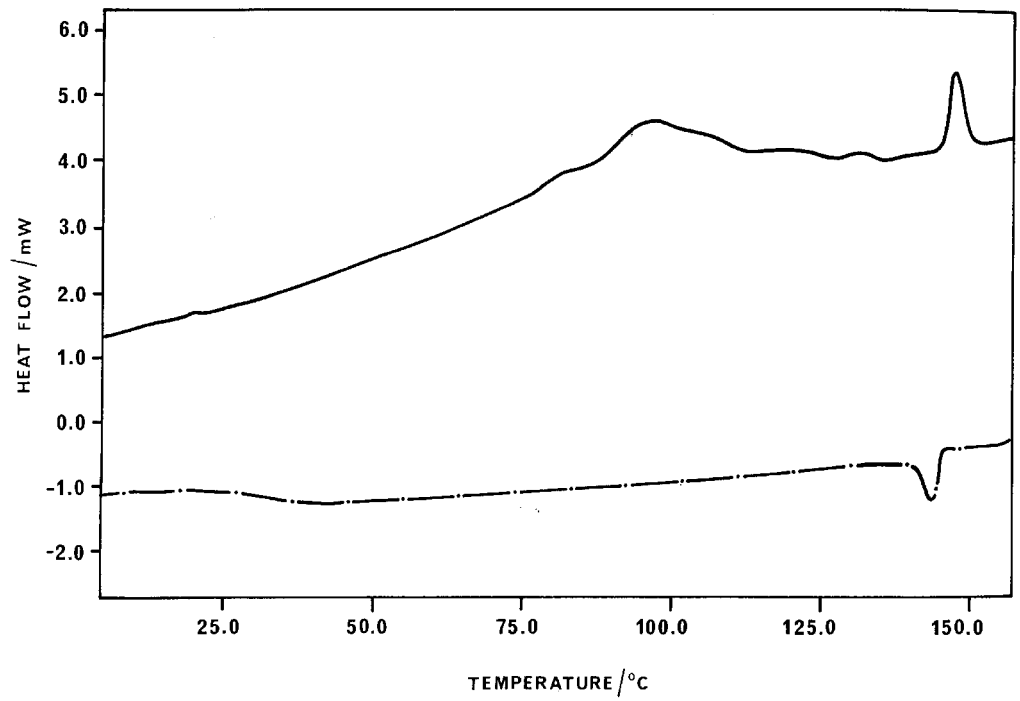
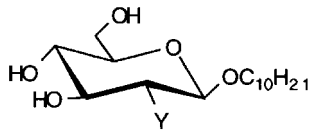


Figure 3. Differential scanning thermograms as a function of temperature for the first heating and cooling cycle for 4-decyloxybenzyl 2-amino-2-deoxy-β-D-glucopyranoside (**10**β); scan rate 10°C min^{-1}.

electronegativity of nitrogen compared with that of oxygen. Additionally, only one hydrogen bond with a hydroxy group of a neighbouring molecule can be formed. This leads to only a slightly higher value for T_{SmA*}. The fluorine atom in 2-deoxy-2-fluoro-β-D-glucopyranoside (**3**β) can act as a hydrogen bond acceptor.

Table 3. Transition temperatures for decyl 2-deoxy-β-D-glucopyranoside (**1**β), decyl 2-amino-2-deoxy-β-D-glucopyranoside (**2**β), decyl 2-deoxy-2-fluoro-β-D-glucopyranoside (**3**β), decyl β-D-glucopyranoside (**4**β) and 2-acetamido-2-deoxy-β-D-glucopyranoside (**5**β).



Carbohydrate	*Y*	Cr–SmA/I/°C	SmA–I/°C	Reference
1β	H	100	91[a]	[37, 38]
2β	NH_2	119	97[a]	[39]
3β	F	89	127	[37, 38]
4β	OH	76	138	[10, 18, 40]
5β	NHAc	93	186	[41]

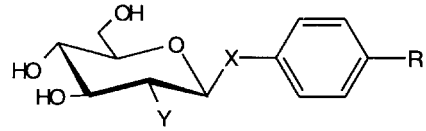
[a] Monotropic transition temperature.

This gives rise to four hydrogen bonds between two adjacent carbohydrate head groups resulting in a high value for T_{SmA*}. However, the presence of four equivalent hydroxy groups capable of hydrogen bonding in the D-glucopyranoside **4**β) gives rise to an even higher T_{SmA*}. This value is only superseded by that for the 2-acetamido-2-deoxy-β-D-glucopyranoside (**5**β). The hydrogen bond between an hydroxy group and the hydrogen atom of an amide group is especially strong and gives rise to the highest T_{SmA*}.

The effect of hydrogen bonding and molecular shape is shown in table 4. All the D-glucopyranosides **6**β–**9**β exhibit enantiotropic SmA* phases. The added degree of polarizability due to the oxygen atom attached to the phenyl ring of compound **7**β compared with compound **6**β leads to only a moderate increase (+10°C) in T_{SmA*} [42]. This is in contrast to the large increases generally found for non-amphiphilic liquid crystals. However, the kink in the molecular structure introduced by the benzyl link in compound **8**β gives rise to a much lower T_{SmA*} compared with that of the directly linked diacetal **7**β. That this is not due to the small difference in alkoxy chain length (one CH_2 unit) is clearly shown by the transition temperatures for the corresponding decyloxy homologue **9**β. The replacement of the hydroxy group in glucopyranoside **9**β to yield the D-glucosamine derivative **10**β results in a lower T_{SmA*}. This is probably due to weaker hydrogen bonds between the amine function and the hydroxy groups of neighbouring molecules. In contrast, the much stronger hydrogen bonding in the amides **11**β and **12**β results in a substantially higher T_m. The degree of supercooling is limited (10°C) so that no monotropic mesophases could be observed. The importance of the anomeric configuration is demonstrated by comparison of the transition temperatures (T_m, 160°C, decomposition) of the 4-decyloxybenzyl 2-amino-2-deoxy-α-D-glucopyranoside (**10**α) and those (T_m, 124°C, T_{SmA*}, 150°C) of the 4-decyloxybenzyl 2-amino-2-deoxy-β-D-glucopyranoside (**10**β). Despite substantial supercooling of the former no mesophase could be observed, which is perhaps due to the significant degree of decomposition observed at the melting point.

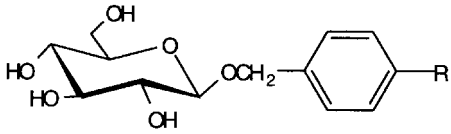
The 4-substituted-benzyl β-D-glucopyranosides **8**β, **9**β and **13**β–**17**β in table 5 are arranged in order of increasing dipole moment associated with the bond between the terminal substituent *R* and the phenyl ring. It is seen that even a relatively high value of the dipole moment and, implicitly, the dielectric anisotropy, for the trifluoro-substituted D-glucopyranoside **17**β does not give rise to observable mesomorphism. However, increasing the length of the terminal chain from methyl to hexyloxy

Table 4. Transition temperatures for 4-octylphenyl β-D-glucopyranoside (**6**β), 4-heptyloxyphenyl β-D-glucopyranoside (**7**β), 4-heptyloxybenzyl β-D-glucopyranoside (**8**β), 4-decyloxybenzyl β-D-glucopyranoside (**9**β), 4-decyloxybenzyl 2-amino-2-deoxy-β-D-glucopyranoside (**10**β), 4-decyloxybenzyl 2-deoxy-2-trifluoacetamido-β-D-glucopyranoside (**11**β) and 4-decyloxybenzyl 2-acetamido-2-deoxy-β-D-glucopyranoside (**12**β).



Carbohydrate	*X*	*Y*	*R*	Cr–SmA/I/°C	SmA–I/°C	Reference
6β	O	OH	C_8H_{17}	108	192	[42]
7β	O	OH	OC_7H_{15}	107	202	[42]
8β	OCH_2	OH	OC_7H_{15}	122	147	
9β	OCH_2	OH	$OC_{10}H_{21}$	117	166	
10β	OCH_2	NH_2	$OC_{10}H_{21}$	124	150	
11β	OCH_2	$NHCOCF_3$	$OC_{10}H_{21}$	209	—	
12β	OCH_2	NHAc	$OC_{10}H_{21}$	190	—	

Table 5. Transition temperatures for the 4-substituted-benzyl β-D-glucopyranosides **8**β, **9**β and **13**β–**17**β.

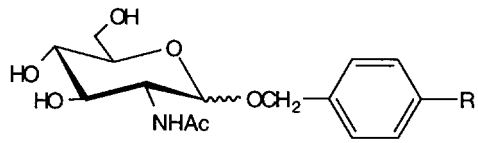


Carbohydrate	*R*	Cr–SmA/I/°C	SmA–I/°C	Reference
13β	H	122	—	
14β	CH_3	158	—	
15β	OC_6H_{13}	115	127	[43]
8β	OC_7H_{15}	122	147	
9β	$OC_{10}H_{21}$	117	166	
16β	F	129	—	
17β	CF_3	133	—	

results in the formation of an enantiotropic SmA* phase. The homologues **8**β and **9**β with even longer chain lengths show higher T_{SmA*}. This shows clearly that steric factors and the ratio of the size of the hydrophilic head group to the hydrophilic hydrocarbon chain are much more important in determining the thermotropic as well as the lyotropic mesomorphism of amphotropic compounds.

The thermal data for the 4-substituted-benzyl 2-acetamido-2-deoxy-α-D-glucopyranosides **12**α and **18**α–**21**α and the 4-substituted-benzyl 2-acetamido-2-deoxy-β-D-glucopyranosides **12**β and **18**β–**21**β are collated in table 6. These indicate that the negative effects of the benzyl link and strong hydrogen bonding due to the amide group result in high melting materials with a

Table 6. Melting points for the 4-substituted-benzyl 2-acetamido-2-deoxy-α-D-glucopyranosides **12**α and **18**α–**21**α, and 4-substituted-benzyl 2-acetamido-2-deoxy-β-D-glucopyranosides **12**β and **18**β–**21**β.



Carbohydrate	*R*	Cr–I/°C
18α	H	170
19α	F	197
20α	CH_3	211
21α	CF_3	228
12α	$OC_{10}H_{21}$	176
18β	H	207
19β	F	178
20β	CH_3	225
21β	CF_3	240 (dec)
12β	$OC_{10}H_{21}$	190

minimum of supercooling. The consequence of this is that even the 4-decyloxybenzyl 2-acetamido-2-deoxy-α- and β-D-glucopyranosides (**12**α and **12**β) do not exhibit observable mesomorphism. Even though T_m of the α anomer is often lower (≈10°C, on average) than that of the β anomer in this series, no monotropic mesophases could be observed.

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 using DMSO-d_6 as solvent 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 indicated the stereochemistry of the anomeric centre (e.g. for compound **12**α: $\delta_H^1 = 4{\cdot}7$, $J_{1,2} = 3{\cdot}5$ Hz, $\delta_C{}^{13} = 95{\cdot}6$; compound **12**β: $\delta_H^1 = 4{\cdot}33$, $J_{1,2} = 8$ Hz, $\delta_C^{13} = 100{\cdot}4$).

The purities of the compounds were determined by thin layer chromatography (TLC), high performance liquid chromatography (HPLC), elemental analysis (C, H, N) and differential scanning calorimetry (DSC). 4 × 8 cm precoated TLC plates, SiO_2 SIL G/UV_{254}, layer thickness 0·25 mm (Machery-Nagel, Düren, Germany) were utilized.

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 a solvent. All temperatures were measured externally unless otherwise stated.

Mesophase identification and the transition temperatures of the carbohydrates prepared were determined by optical microscopy using either a Zeiss Universal or a Olympus 2 polarizing light microscope in conjunction with a Mettler FP 82 microfurnace and FP 80 Central Processor. Homeotropic sample preparations suitable for phase characterization 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 by using nylon coated slides. Nylon coating of the slides (~200–300 Å thick) was obtained 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 1 h, 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.

Differential scanning calorimetry was used to determine enthalpies of transition and to confirm the phase transition temperatures determined by optical microscopy. Differential scanning thermograms (scan rate $10° \text{ min}^{-1}$) 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 differential scanning calorimetry show some discrepancies of about 1–3°C. Discrepancies 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 various rates depending on the rate of heating, the time spent at an elevated temperature and the 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 obtained 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.

Investigations of the lyotropic phase behaviour were carried out either at room temperature by simply allowing crystals of the test material to dissolve in water, thereby creating a concentration gradient supporting mesophase formation, or by partially filling flat capillary tubes with each individual compound and allowing water to run into the tube by capillary action to yield specimens with a concentration gradient along the length of the capillary tube. If the crystals did not dissolve in water at room temperature, the specimens were heated in the microfurnance at a temperature below 100°C.

5.2. *General glycosidation procedure*

Soldium hydride (1·3 mol eq) and the benzyl bromide derivative (1·5 mol eq) were added to a solution of the sugar in DMF, (10 mmol cm^{-3}). The resultant suspension was then stirred at room temperature until it became clear. A few drops of methanol were added to destroy any excess of sodium hydride and the solvent was removed under reduced pressure. The residue was dissolved in butanol/ethyl acetate (60 cm^3, 1:1, v/v) and washed with water (2×20 cm^3). The combined aqueous layers were then extracted with butanol/ethyl acetate (20 cm^3, 1:1, v/v). The combined organic phases were evaporated down under reduced pressure and the residue purified by column chromatography on silica gel using chloroform/methanol (9:1, v/v) as eluent. The crude anomeric mixtures of simple D-glucopyranosides were separated by fractional crystallization from ethyl acetate. The β-anomer was found to crystallize out preferentially from this solution. The 2-deoxy-D-glucopyranosides were separated by column chromatography; the α-anomer was found to be the first product to be eluted followed by the β-anomer.

5.3. *General cleavage procedure*

Potassium carbonate (3 eq) was added to a solution of either 4-decyloxybenzyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**11**α) or 4-decyloxybenzyl 2-acetamido-2-deoxy-β-D-glucopyranoside (**11**β) in methanol/water. After heating under reflux for 2 h, the solution was filtered and then the solvent removed under reduced pressure. The residue was dissolved in ethyl acetate (40 cm^3) and then washed with water (3×15 cm^3). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure to afford the 4-decyloxybenzyl 2-amino-2-deoxy-α-D-glucopyranoside (**10**α) or the 4-decyloxybenzyl 2-amino-2-deoxy-β-D-glucopyranoside (**10**β) respectively.

5.4. *Characterization results for individual compounds*

5.4.1. *4-Heptyloxybenzyl* β-D-*glucopyranoside* (**8**β)

^{1}H NMR: 0·85 (3H, t, alkyl), 1·21–1·43 (8H, m, alkyl), 1·69 (2H, q, alkyl), 2·96–3·17 (4H, m, H-2, H-3, H-4, H-5), 3·46 (1H, m, $J_{5,6'} = 3$ Hz, H-6′), 3·68 (1H, dd, $J_{6,6'} =$ 12 Hz, $J_{5,6} = 6$ Hz, H-6), 3·94 (2H, t, $J = 7{\cdot}5$ Hz, R–C<u>H</u>$_2$–OPh), 4·19 (1H, d, $J_{1,2} = 7{\cdot}8$ Hz, H-1), 4·49 (1H, d, $J_{CH2} = 12$ Hz, C<u>H</u>$_2$Ph), 4·53 (1H, t, $J_{OH,H\text{-}6} = J_{OH,H\text{-}6'} =$ 6 Hz, OH-6), 4·74 (1H, d, $J_{CH2} = 12$ Hz, C<u>H</u>$_2$Ph), 4·90, 4·94, 5·06 (3H, 3d, $J_{OH,CH} = 5$ Hz, 3 OH), 6·87 and 7·28 (4H, 2d, Phenyl). ^{13}C NMR: 13·9, 22·0, 25·5, 28·4, 28·7,

31·2 (alkyl), 61·1 (C-6), 69·1, 70·1, 76·7, 76·9, (C-2–C-5), 101·7 (C-1), 67·3 (R$\underline{C}$H$_2$OPh), 73·4 ($\underline{C}$H$_2$Ph), 113·9, 129·3, 129·6, 158·1, (Phenyl). Elemental analysis for $C_{20}H_{32}O_7$; calcd: C 62·48, H 8·39; found: C 62·17, H 8·60 per cent . $[\alpha]_D^{25}$ −41·2 (DMSO, c=2·847).

5.4.2. *4-Decyloxybenzyl* β-D-*glucopyranoside* (**9**β)

^{1}H NMR: 0·85 (3H, t, alkyl), 1·21–1·43 (14H, m, alkyl), 1·67 (2H, q, alkyl), 2·96–3·18 (4H, m, H-2, H-3, H-4, H-5), 3·46 (1H, m, $J_{5,6'}$=3 Hz, H-6′), 3·69 (1H, dd, $J_{6,6'}$=12 Hz, $J_{5,6}$=6 Hz, H-6), 3·93 (2H, t, J=7·5 Hz, R–C$\underline{H}_2$–OPh), 4·19 (1H, d, $J_{1,2}$=7·8 Hz, H-1), 4·48 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·51 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$= 6 Hz, OH-6), 4·72 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·88,4·92, 5·05 (3H, 3d, $J_{OH,CH}$=5 Hz, 3 OH), 6·86 and 7·28 (4H, 2d, Phenyl). ^{13}C NMR: 14·0, 22·1, 25·5, 28·5, 28·7, 31·4 (alkyl), 61·2 (C-6), 69·2, 70·2, 8·8, 77·0, (C-2–C-5), 101·8 (C-1), 67·4 (R$\underline{C}$H$_2$OPh), 73·5 ($\underline{C}$H$_2$Ph), 114·0, 129·4, 129·7, 158·1, (Phenyl). Elemental analysis for $C_{23}H_{38}O_7$; calcd: C 57·77, H 6·71; found: C 57·75, H 6·81 percent $[\alpha]_D^{25}$ −32·5 (DMSO, c=1·399).

5.4.3. *4-Decyloxybenzyl 2-amino-2-deoxy*-α-D-*glucopyranoside* (**10**α)

^{1}H NMR: 0·86 (3H, t, alkyl), 1·21–1·43 (14H, m, alkyl), 1·68 (2H, q, alkyl), 2·43 (1H, dd, $J_{1,2}$=4 Hz, $J_{2,3}$=9·5 Hz, H-2), 3·00–3·75 (7H, m, H-3, H-4, H-5, H-6, H-6′, NH$_2$), 3·94 (2H, t, RC$\underline{H}_2$OPh), 4·33 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·53 (1H, OH-6), 4·59 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·72 (1H, d, $J_{1,2}$=4 Hz, H-1), 4·92 (2H, 2 OH), 6·89 and 7·26 (4H, 2d, $J_{OH,O}$=8 Hz, Phenyl). ^{13}C NMR: 13·9, 22·1, 25·5, 28·6, 28·7, 28·9, 29·0, 31·3 (alkyl), 56·1 (C-2), 60·9 (C-6), 67·6, 70·3, 74·8 (C-3–C-5), 97·7 (C-1), 67·4 (R$\underline{C}$H$_2$OPh), 73·4 ($\underline{C}$H$_2$Ph), 114·1, 129·3, 129·6, 158·2, (Phenyl).

5.4.4. *4-Decyloxybenzyl 2-amino-2-deoxy*-β-D-*glucopyranoside* (**10**β)

^{1}H NMR: 0·85 (3H, t, alkyl), 1·25–1·45 (14H, m, alkyl), 1·50 (2H, q, alkyl); 1·66 (2H, q, alkyl), 2·40 (1H, t, $J_{1,2}$=$J_{2,3}$=8 Hz, H-2), 3·05 (2H, m, H-3, H-4), 3·33 (1H, H-5), 3·48 (1H, H6′), 3·70 (1H, dd, $J_{6,6'}$=12 Hz, $J_{5,6}$=5 Hz, H-6), 3·93 (2H, t, J=7·5 Hz, RC$\underline{H}_2$OPh), 4·12 (1H, d, $J_{1,2}$=8 Hz, H-1), 4·46 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·53 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=6 Hz, OH-6), 4·73 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·98, 5·02 (2H, 2 OH), 6·57 and 7·25 (4H, 2d $J_{OH,O}$=8 Hz, Phenyl). ^{13}C NMR: 13·9, 22·1, 25·5, 28·7, 28·8, 28·9, 29·0, 31·3 (alkyl), 57·3 (C-2), 61·1 (C-6), 69·2, 70·1, 77·2 (C-3–C-5), 102·6 (C-1), 67·3 (R$\underline{C}$H$_2$OPh), 76·5 ($\underline{C}$H$_2$Ph), 114·1, 129·4, 129·7, 158·1, (Phenyl). Elemental analysis for $C_{23}H_{39}NO_6$; calcd: C 64·94; H 9·24, N 3·29; found: C 64·87, H 9·35, N 3·11 per cent. $[\alpha]_D^{25}$ −42·2 (DMSO, c=1·021).

5.4.5. *4-Decyloxybenzyl 2-deoxy-2-trifluoroacetamido*-α-D-*glucopyranoside* (**11**α)

^{1}H NMR: 0·86 (3H, t, alkyl), 1·25–1·45 (14H, m, alkyl), 1·69 (2H, q, alkyl), 3·18 (1H, m, H-5), 3·49 (3H, m, H-3, H-4, H-6′), 3·71 (2H, m, H-2, H-6), 4·36 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·59 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$= 6 Hz, OH-6), 4·59 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·74 (1H, d, $J_{1,2}$=3·5 Hz, H-1), 4·93, 5·14 (2H, 2d, $J_{OH,CH}$= 5 Hz, 2 OH), 6·87 and 7·23 (4H, 2d, Phenyl), 9·50 (1H, d, $J_{NH,H-2}$=8 Hz, N$\underline{H}$CO). ^{13}C NMR: 13·9, 22·1, 25·5, 28·6, 28·7, 28·7, 28·9, 29·0, 31·3 (alkyl), 54·9 (C-2), 60·6 (C-6), 67·4, 69·5, 70·7 (C-3–C-5), 94·3 (C-1), 67·5 (R$\underline{C}$H$_2$OPh), 73·1 ($\underline{C}$H$_2$Ph), 114·1, 129·2, 158·2, (Phenyl), 109·5, 113·8, 118·0, 122·2, ($\underline{C}$F$_3$CO), 155·8, 156·3, 156·8, 157·3 (CF$_3\underline{C}$O). Elemental analysis for $C_{25}H_{41}F_3NO_7$; calcd: C 57·57, H 7·34, N 2·68; found: C 57·57, H 7·36, N 2·59 percent. $[\alpha]_D^{25}$ +130·0° (DMSO, c=1·148).

5.4.6. *4-Decyloxybenzyl 2-deoxy-2-trifluoroacetamido*-β-D-*glucopyranoside* (**11**β)

^{1}H NMR: 0·86 (3H, t, alkyl), 1·21–1·43 (14H, m, alkyl), 1·68 (2H, q, alkyl); 3·12 (2H, m, H-3, H-4), 3·38 (3H, m, H-2, H-5, H-6′), 3·73 (1H, dd, $J_{6,6'}$=12 Hz, $J_{5,6}$=5 Hz, H-6), 3·92 (2H, t, J=7·5 Hz, R–C$\underline{H}_2$–OPh), 4·44 (1H, d, $J_{1,2}$=8 Hz, H-1), 4·44 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·62 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=6 Hz, OH-6), 4·69 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 5·12, 5·19 (2H, 2d, $J_{OH,CH}$=5 Hz, 2 OH), 6·85 and 7·15 (4H, 2d, Phenyl), 9·19 (1H, d, $J_{NH,H-2}$=9 Hz, N$\underline{H}$CO). ^{13}C NMR: 13·9, 22·1, 25·5, 28·7, 28·7, 29·0, 29·0, 31·3 (alkyl), 56·2 (C-2), 60·9 (C-6), 69·4, 70·6, 77·2 (C-3–C-5), 99·3 (C-1), 67·3 (R$\underline{C}$H$_2$OPh), 73·1 ($\underline{C}$H$_2$Ph), 114·0, 128·9, 129·4, 158·1, (Phenyl), 109·8, 114·0, 118·3, 122·5, ($\underline{C}$F$_3$CO), 155·4, 156·0, 156·5, 157·0 (CF$_3\underline{C}$O). Elemental analysis for $C_{25}H_{41}F_3NO_7$; calcd: C 57·57, H 7·34, N 2·68; found: C 57·70, H 7·46, N 2·62 per cent. $[\alpha]_D^{23}$ −22·1 (DMSO, c=1·548).

5.4.7. *4-Decyloxybenzyl 2-acetamido-2-deoxy*-α-D-*glucopyranoside* (**12**α)

^{1}H NMR: 0·86 (3H, t, alkyl), 1·22–1·42 (14H, m, alkyl), 1·68 (2H, q, alkyl), 1·83 (3H, s, C$\underline{H}_3$CO), 3·15 (1H, m, H-5), 3·48 (3H, m, H-3, H-4, H-6′), 3·66 (2H, m, H-2, H-6), 3·93 (2H, t, J=7·5 Hz, R–C$\underline{H}_2$–OPh), 4·33 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·55 (1H, t, $J_{OH,H-6}$= $J_{OH,H-6'}$=6 Hz, OH-6), 4·58 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·73 (1H, d, $J_{OH,CH}$=5 Hz, OH), 4·74 (1H, d, $J_{1,2}$=3·5 Hz, H-1), 5·02 (H, d, $J_{OH,CH}$=5 Hz, OH), 6·88 and 7·26 (4H, 2d, Phenyl), 7·78 (1H, d, $J_{NH,H-2}$=8 Hz, N$\underline{H}$CO). ^{13}C NMR: 14·0, 22·1, 25·5, 28·4, 28·8, 28·8, 28·9, 29·0, 31·3 (alkyl), 22·5 ($\underline{C}$H$_3$CO), 53·7 (C-2), 60·8 (C-6), 67·4, 70·6, 70·9 (C-3–C-5), 95·6 (C-1), 67·4 (R$\underline{C}$H$_2$OPh), 73·0 ($\underline{C}$H$_2$Ph), 114·1, 129·2, 129·6, 158·1, (Phenyl), 169·4 (CH$_3\underline{C}$O). Elemental analysis for $C_{25}H_{41}NO_6$; calcd: C

64·21, H 8·84; N 2·99; found: C 64·22, H 9·03, N 2·89 per cent. $[\alpha]_D^{25}$ +123·7 (MeOH, c=0·609).

5.4.8. *4-Decyloxybenzyl 2-acetamido-2-deoxy*-β-*D-glucopyranoside* (**12**β)

^{1}H NMR: 0·85 (3H, t, alkyl), 1·21–1·43 (14H, m, alkyl), 1·69 (2H, q, alkyl), 1·79 (3H, s, C$\underline{H}_3$CO), 3·08 (2H, m, H-3, H-4), 3·28 (1H, m, H-5), 3·42–3·52 (2H, m, H-2, H-6′), 3·71 (1H, dd, $J_{6,6'}$=11 Hz, $J_{5,6}$=5 Hz, H-6), 3·93 (2H, t, J=7·5 Hz, R–C$\underline{H}_2$–OPh), 4·33 (1H, d, $J_{1,2}$=8 Hz, H-1), 4·42 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·56 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=6 Hz, OH-6), 4·69 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·90, 4·99 (2H, 2d, $J_{OH,CH}$=5 Hz, 2 OH), 6·86 and 7·18 (4H, 2d, Phenyl), 7·67 (1H, d, $J_{NH,H-2}$=9 Hz, N$\underline{H}$CO). ^{13}C NMR: 13·9, 22·1, 25·5, 28·4, 28·7, 28·8, 28·9, 29·0, 31·3 (alkyl), 23·1 (C$\underline{H}_3$CO), 55·4 (C-2), 61·2 (C-6), 69·1, 70·7, 77·4 (C-3–C-5), 100·4 (C-1), 67·35 (R$\underline{C}$H$_2$OPh), 74·2 ($\underline{C}$H$_2$Ph), 114·0, 128·9, 129·8, 158·4, (Phenyl), 170·0 (CH$_3\underline{C}$O). Elemental analysis for $C_{25}H_{41}NO_6$; calcd: C 64·21, H 8·84, N 2·99; found: C 64·15, H 8·96; N, 2·91 per cent. $[\alpha]_D^{25}$ −32·3° (DMSO, c=0·667).

5.4.9. *4-Benzyl* β-*D-glucopyranoside* (**13**β)

^{1}H NMR: 3·00–3·20 (4H, m, H-2, H-3, H-4, H-5), 3·45 (1H, m, H-6′), 3·69 (1H, dd, $J_{6,6'}$=12 Hz, $J_{5,6}$=6 Hz, H-6), 4·23 (1H, d, $J_{1,2}$=8 Hz, H-1), 4·53 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=5 Hz, OH-6), 4·58 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·83 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·92,4·97, 5·12 (3H, 3d, $J_{OH,CH}$=5 Hz, 3 OH), 7·25–7·42 (5H, m, Phenyl). ^{13}C NMR: 61·1 (C-6), 69·4, 70·1, 76·7, 77·0, (C-2–C-5), 102·1 (C-1), 73·5 ($\underline{C}$H$_2$Ph), 127·3, 127·6, 128·1, 138·1 (Phenyl). Elemental analysis for $C_{13}H_{18}O_6$; calcd: C 57·77, H, 6·71; found: C 57·75, H 6·81 per cent. $[\alpha]_D^{27}$ −50·8 (DMSO, c=1·697).

5.4.10. *4-Methylbenzyl* β-*D-glucopyranoside* (**14**β)

^{1}H NMR: 2·28 (3H, s, C$\underline{H}_3$Ph), 2·99–3·17 (4H, m, H-2, H-3, H-4, H-5), 3·45 (1H, m, H-6′), 3·70 (1H, dd, $J_{6,6'}$=12 Hz, $J_{5,6}$=6 Hz, H-6), 4·19 (1H, d, $J_{1,2}$=8 Hz, H-1), 4·54 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=5 Hz, OH-6), 4·53 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·77 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·93,4·97, 5·10 (3H, 3d, $J_{OH,CH}$=5 Hz, 3 OH), 7·14 and 7·27 (4H, 2d, Phenyl). ^{13}C NMR: 61·1 (C-6), 69·3, 70·1, 76·8, 77·0, (C-2–C-5), 101·9 (C-1), 20·8 ($\underline{C}$H$_3$Ph), 73·5 ($\underline{C}$H$_2$Ph), 127·8, 128·7, 135·0, 136·5, (Phenyl). Elemental analysis for $C_{14}H_{20}O_6$; calcd: C 59·14, H 7·09; found: C 59·06, H 7·15 per cent. $[\alpha]_D^{24}$ −34·4° (DMSO, c=1·401).

5.4.11. *4-Fluorobenzyl* β-*D-glucopyranoside* (**16**β)

^{1}H NMR: 3·00–3·20 (4H, m, H-2, H-3, H-4, H-5), 3·45 (1H, m, H-6′), 3·68 (1H, dd, $J_{6,6'}$=13 Hz, $J_{5,6}$=6 Hz, H-6), 4·22 (1H, d, $J_{1,2}$=8 Hz, H-1), 4·54 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=5 Hz, OH-6), 4·54 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·78 (1H, d, J_{CH2}=12 Hz, C$\underline{H}_2$Ph), 4·93,4·98, 5·12 (3H, 3d, $J_{OH,CH}$=5 Hz, 3 OH), 7·15–7·68 (4H, m, Phenyl). ^{13}C NMR: 61·1 (C-6), 68·8, 70·1, 76·7, 77·0, (C-2–C-5), 102·0 (C-1), 73·5 ($\underline{C}$H$_2$Ph), 114·7, 115·0, 129·5, 129·6, 134·3, 134·3, 159·7, 163·3 (Phenyl). Elemental analysis for $C_{13}H_{17}FO_6$; calcd: C 54·16, H 5·94; found: C 54·15, H 5·81 per cent. $[\alpha]_D^{27}$ −26·3 (DMSO, c=2·003).

5.4.12. *4-Trifluoromethylbenzyl* β-*D-glucopyranoside* (**17**β)

^{1}H NMR: 3·00–3·20 (4H, m, H-2, H-3, H-4, H-5), 3·46 (1H, m, $J_{5,6'}$=3 Hz, H-6′), 3·70 (1H, dd, $J_{6,6'}$=12 Hz, $J_{5,6}$=6 Hz, H-6), 4·26 (1H, d, $J_{1,2}$=7·8 Hz, H-1), 4·55 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=6 Hz, OH-6), 4·70 (1H, d, J_{CH2}=13 Hz, C$\underline{H}_2$Ph), 4·92 (1H, d, J_{CH2}=13 Hz, C$\underline{H}_2$Ph), 4·93,4·98, 5·18 (3H, 3d, $J_{OH,CH}$=5 Hz, 3 OH), 7·63 and 7·70 (4H, 2d, Phenyl). ^{13}C NMR: 61·1 (C-6), 68·7, 70·1, 76·7, 77·0, (C-2–C-5), 102·3 (C-1), 73·52 ($\underline{C}$H$_2$Ph), 125·0, 125·0, 127·8, 143·2, (Phenyl), 118·3, 122·3, 126·3, 130·3 ($\underline{C}$F$_3$Ph). Elemental analysis for $C_{14}H_{17}F_3O_6$; calcd: C 49·71, H 5·07; found: C 49·65, H 5·18 per cent. $[\alpha]_D^{24}$ −41·0° (DMSO, c=1·401).

5.4.13. *4-Benzyl 2-acetamido-2-deoxy*-α-*D-glucopyranoside* (**18**α)

^{1}H NMR: 1·83 (3H, s, C$\underline{H}_3$CO), 3·16 (1H, m, H-5), 3·42–3·58 (3H, m, H-3, H-4, H-6′), 3·62–3·74 (2H, m, H-2, H-6), 4·41 (1H, d, J_{CH2}=13 Hz, C$\underline{H}_2$Ph), 4·57 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=6 Hz, OH-6), 4·67 (1H, d, J_{CH2}=13 Hz, C$\underline{H}_2$Ph), 4·71 (1H, d, $J_{1,2}$=4 Hz, H-1), 4·77, 5·04 (2H, 2d, $J_{OH,CH}$=5 Hz, 2 OH), 7·22–7·38 (5H, m, Phenyl), 7·85 (1H, d, $J_{NH,H-2}$=8 Hz, N$\underline{H}$CO). ^{13}C NMR: 23·1 (C$\underline{H}_3$CO), 55·4 (C-2), 61·1 (C-6), 69·4, 70·7, 77·0, (C-3–C-5), 100·7 (C-1), 74·2 ($\underline{C}$H$_2$Ph), 127·1, 127·3, 128·1, 138·1, (Phenyl), 169·0 (CH$_3\underline{C}$O). Elemental analysis for $C_{15}H_{21}O_6$, 0·4 H_2O; calcd: C 56·54, H 6·90, N 4·39; found: C 56·54, H 6·90, N 4·39 per cent. $[\alpha]_D^{29}$ +118 (DMSO, c=2·898).

5.4.14. *4-Benzyl 2-acetamido-2-deoxy*-β-*D-glucopyranoside* (**18**β)

^{1}H NMR: 1·81 (3H, s, C$\underline{H}_3$CO), 3·10 (2H, m, H-3, H-4), 3·31 (1H, m, H-5), 3·44–3·57 (2H, m, H-2, H-6′), 3·72 (1H, dd, $J_{6,6'}$=12 Hz, $J_{5,6}$=5 Hz, H-6), 4·36 (1H, d, $J_{1,2}$=8 Hz, H-1), 4·51 (1H, d, J_{CH2}=13 Hz, C$\underline{H}_2$Ph), 4·58 (1H, t, $J_{OH,H-6}$=$J_{OH,H-6'}$=6 Hz, OH-6), 4·78 (1H, d, J_{CH2}=13 Hz, C$\underline{H}_2$Ph), 4·93, 5·02 (2H, 2d, $J_{OH,CH}$=5 Hz, 2 OH), 7·22–7·38 (5H, m, Phenyl), 7·73 (1H, d, $J_{NH,H-2}$=9 Hz, N$\underline{H}$CO). ^{13}C NMR: 23·1 (C$\underline{H}_3$CO), 55·4 (C-2), 61·1 (C-6), 69·4, 70·7, 77·0, (C-3–C-5), 100·7 (C-1), 74·2 ($\underline{C}$H$_2$Ph), 127·1, 127·3, 128·1, 138·1, (Phenyl), 169·0 (CH$_3\underline{C}$O). Elemental analysis for $C_{15}H_{21}O_6$, 0·15 H_2O;

calcd: C 57·55, H 6·86, N 4·47; found: C 57·56; H 6·88, N 4·32 per cent. $[\alpha]_D^{27} - 50{\cdot}2$ (DMSO, $c = 2{\cdot}811$).

5.4.15. *4-Fluorobenzyl 2-acetamido-2-deoxy-α-D-glucopyranoside* (**19**α)

^{1}H NMR: 1·83 (3H, s, C$\underline{H}_3$CO), 3·15 (1H, m, H-5), 3·30–3·53 (3H, m, H-3, H-4, H-6′), 3·65 (2H, m, H-2, H-6), 4·39 (1H, d, $J_{CH2} = 12$ Hz, C$\underline{H}_2$Ph), 4·56 (1H, t, $J_{OH,H-6} = J_{OH,H-6'} = 6$ Hz, OH-6), 4·63 (1H, d, $J_{CH2} = 12$ Hz, C$\underline{H}_2$Ph), 4·68 (1H, d, $J_{1,2} = 3{\cdot}8$ Hz, H-1), 4·75, 5·04 (2H, 2d, $J_{OH,CH} = 5$ Hz, 2 OH), 7·16 (2H, t, Phenyl)-7·41 (2H, dd, $J_{aro} = 8$ Hz, $J_{H-F} = 6$ Hz Phenyl), 7·84 (1H, d, $J_{NH,H-2} = 8$ Hz, N$\underline{H}$CO). ^{13}C NMR: 22·7 (C$\underline{H}_3$CO), 53·9 (C-2), 61·1 (C-6), 67·3, 70·7, 71·0, (C-3–C-5), 96·1 (C-1), 73·3 (C$\underline{H}_2$Ph), 115·0, 115·3, 129·8, 129·9, 134·3, 134·3, 16·0, 163·6, (Phenyl), 170·1 (CH$_3$C$\underline{O}$). Elemental analysis for $C_{15}H_{20}FNO_6$; calcd: C 54·71, H 6·12, N 4·25; found: C 54·76, H 6·09, N 4·16 per cent. $[\alpha]_D^{25} + 132{\cdot}8$ (MeOH, $c = 2{\cdot}018$).

5.4.16. *4-Fluorobenzyl 2-acetamido-2-deoxy-β-D-glucopyranoside* (**19**β)

^{1}H NMR: 1·81 (3H, s, C$\underline{H}_3$CO), 3·23–3·55 (5H, m, H-2, H-3, H-4, H-5, H-6′); 3·72 (1H, dd, $J_{6,6'} = 12$ Hz, $J_{5,6} = 5$ Hz, H-6), 4·34 (1H, d, $J_{1,2} = 8$ Hz, H-1), 4·49 (1H, d, $J_{CH2} = 12$ Hz, C$\underline{H}_2$Ph), 4·59 (1H, t, $J_{OH,H-6} = J_{OH,H-6'} = 6$ Hz, OH-6), 4·76 (1H, d, $J_{CH2} = 12$ Hz, C$\underline{H}_2$Ph), 4·94, 5·30 (2H, 2d, $J_{OH,CH} = 5$ Hz, 2 OH), 7·15 (2H, t, $J_{aro} = J_{H-F} = 8$ Hz, Phenyl), 7·33 (2H, dd, Phenyl), 7·55 (1H, d, $J_{NH,H-2} = 9$ Hz, N$\underline{H}$CO). ^{13}C NMR: 23·1 (C$\underline{H}_3$CO), 55·4 (C-2), 61·1 (C-6), 68·7, 70·7, 77·1, (C-3–C-5), 100·6 (C-1), 74·2 (C$\underline{H}_2$Ph), 114·8, 115·1, 129·3, 129·4, 134·3, 134·4, 159·7, 163·3, (Phenyl), 169·2 (CH$_3$C$\underline{O}$). Elemental analysis for $C_{15}H_{20}FNO_6$; calcd: C 54·71, H 6·12, N 4·25; found: C 54·66, H 6·13, N 4·11 per cent. $[\alpha]_D^{25} - 32{\cdot}2$ (MeOH, $c = 1{\cdot}150$).

5.4.17. *4-Methylbenzyl 2-acetamido-2-deoxy-α-D-glucopyranoside* (**20**α)

^{1}H NMR: 1·83 (3H, s, C$\underline{H}_3$CO), 2·29 (3H, s, C$\underline{H}_3$Ph), 3·15 (1H, m, H-5), 3·41–3·57 (3H, m, H-3, H-4, H-6′), 3·61–3·72 (2H, m, H-2, H-6), 4·37 (1H, d, $J_{CH2} = 12{\cdot}5$ Hz, C$\underline{H}_2$Ph), 4·55 (1H, t, $J_{OH,H-6} = J_{OH,H-6'} = 6$ Hz, OH-6), 4·62 (1H, d, $J_{CH2} = 12{\cdot}5$ Hz, C$\underline{H}_2$Ph), 4·67 (1H, d, $J_{1,2} = 3{\cdot}5$ Hz, H-1), 4·73, 5·01 (2H, 2d, $J_{OH,CH} = 5$ Hz, 2 OH), 7·14 and 7·25 (4H, 2d, Phenyl), 7·79 (1H, d, $J_{NH,H-2} = 8$ Hz, N$\underline{H}$CO). ^{13}C NMR: 20·8 (C$\underline{H}_3$Ph), 22·5 (C$\underline{H}_3$CO), 53·7 (C-2), 60·9 (C-6), 67·5, 70·6, 70·9, (C-3–C-5), 95·7 (C-1), 73·1 (C$\underline{H}_2$Ph), 127·6, 128·7, 124·8, 136·6, (Phenyl), 169·4 (CH$_3$C$\underline{O}$). Elemental analysis for $C_{16}H_{23}FNO_6$; calcd: C 59·06; H 7·12; N 4·30; found: C 58·96, H 7·21, N 4·06 per cent. $[\alpha]_D^{27} + 163{\cdot}9$ (MeOH, $c = 1{\cdot}730$).

5.4.18. *4-Methylbenzyl 2-acetamido-2-deoxy-β-D-glucopyranoside* (**20**β)

^{1}H NMR: 1·81 (3H,s, C$\underline{H}_3$CO), 2·29 (3H, s, C$\underline{H}_3$Ph), 3·08 (2H, m, H-3, H-4), 3·28 (1H, m, H-5), 3·48 (2H, m, H-2, H-6′), 3·71 (1H, dd, $J_{6,6'} = 12$ Hz, $J_{5,6} = 5$ Hz, H-6), 4·33 (1H, d, $J_{1,2} = 8$ Hz, H-1), 4·46 (1H, d, $J_{CH2} = 12{\cdot}5$ Hz, C$\underline{H}_2$Ph), 4·57 (1H, t, $J_{OH,H-6} = J_{OH,H-6'} = 6$ Hz, OH-6), 4·73 (1H, d, $J_{CH2} = 12{\cdot}5$ Hz, C$\underline{H}_2$Ph), 4·91, 4·99 (2H, 2d, $J_{OH,CH} = 5$ Hz, 2 OH), 7·13 and 7·17 (4H, 2d, Phenyl), 7·69 (1H, d, $J_{NH,H-2} = 9$ Hz, N$\underline{H}$CO). ^{13}C NMR: 20·7 (C$\underline{H}_3$Ph), 23·1 (C$\underline{H}_3$CO), 55·4 (C-2), 61·1 (C-6), 69·2, 70·7, 77·0, (C-3–C-5), 100·5 (C-1), 74·2 (C$\underline{H}_2$Ph), 127·3, 128·7, 135·0, 136·4, (Phenyl), 169·0 (CH$_3$C$\underline{O}$). Elemental analysis for $C_{16}H_{23}FNO_6$; calcd: C 58·41; H 7·17; N 4·25; found: C 58·61, H 7·14, N 3·92 per cent. $[\alpha]_D^{22} - 50{\cdot}0$ (DMSO, $c = 2{\cdot}54$).

5.4.19. *4-Trifluoromethylbenzyl 2-acetamido-2-deoxy-α-D-glucopyranoside* (**21**α)

^{1}H NMR: 1·83 (3H, s, C$\underline{H}_3$CO), 3·15 (1H, m, H-5), 3·27–3·77 (5H, m, H-2, H-3, H-4, H-6, H-6′), 4·52 (1H, d, $J_{CH2} = 12{\cdot}5$ Hz, C$\underline{H}_2$Ph), 4·57 (1H, t, $J_{OH,H-6} = J_{OH,H-6'} = 6$ Hz, OH-6), 4·73 (1H, d, $J_{1,2} = 3{\cdot}5$ Hz, H-1), 4·75 (1H, d, $J_{CH2} = 12{\cdot}5$ Hz, C$\underline{H}_2$Ph), 4·78, 5·06 (2H, 2d, $J_{OH,CH} = 5$ Hz, 2 OH), 7·56 and 7·72 (4H, 2d, Phenyl), 7·91 (1H, d, $J_{NH,H-2} = 8$ Hz, N$\underline{H}$CO). ^{13}C NMR: 22·6 (C$\underline{H}_3$CO), 53·8 (C-2), 60·8 (C-6), 67·0, 70·6, 70·9, (C-3–C-5), 96·3 (C-1), 73·3 (C$\underline{H}_2$Ph), 125·0, 125·0, 125·1, 125·1, 127·9, 143·0, (Phenyl), 169·6 (CH$_3$C$\underline{O}$),118·3, 122·3, 126·3, 130·3 (C$\underline{F}_3$Ph). Elemental analysis for $C_{16}H_{20}F_3NO_6$; calcd: C 50·66, H 5·31; N 3·69; found: C 50·56, H 5·32, N 3·54 per cent. $[\alpha]_D^{27} + 226{\cdot}6$ (MeOH, $c = 1{\cdot}193$).

5.4.20. *4-Trifluoromethylbenzyl 2-acetamido-2-deoxy-β-D-glucopyranoside* (**21**β)

^{1}H NMR: 1·83 (3H, s, C$\underline{H}_3$CO), 3·12 (2H, m, H-3, H-4), 3·35 (1H, m, H-5), 3·51 (2H, m, H-2, H-6′), 3·72 (1H, dd, $J_{6,6'} = 12$ Hz, $J_{5,6} = 5$ Hz, H-6), 4·37 (1H, d, $J_{1,2} = 8$ Hz, H-1), 4·62 (1H, t, $J_{OH,H-6} = J_{OH,H-6'} = 6$ Hz, OH-6), 4·63 (1H, d, $J_{CH2} = 13$ Hz, C$\underline{H}_2$Ph), 4·88 (1H, d, $J_{CH2} = 13$ Hz, C$\underline{H}_2$Ph), 4·98, 5·04 (2H, 2d, $J_{OH,CH} = 5$ Hz, 2 OH), 7·50 and 7·70 (4H, 2d, Phenyl), 7·75 (1H, d, $J_{NH,H-2} = 9$ Hz, N$\underline{H}$CO). ^{13}C NMR: 23·1 (C$\underline{H}_3$CO), 55·3 (C-2), 61·1 (C-6), 68·6, 70·64, 77·1, (C-3–C-5), 100·9 (C-1), 74·1 (C$\underline{H}_2$Ph), 125·0, 125·0, 125·1, 125·1, 127·6, 143·2 (Phenyl), 118·4, 122·4, 126·3, 130·3 (C$\underline{F}_3$Ph), 169·2 (CH$_3$C$\underline{O}$). Elemental analysis for $C_{16}H_{20}F_3NO_6$; calcd: C 50·66; H 5·31; N 3·69; found: C 50·57; H 5·42, N 3·53 per cent. $[\alpha]_D^{25} - 39{\cdot}3$ (MeOH, $c = 1{\cdot}886$).

We gratefully aknowledge the EPSRC for support of a postdoctorate (P. L.) and an Advanced Fellowship (S. M. K.). Mrs B. Worthington (^{1}H NMR), Mr

R. Knight (IR) and Mr A. D. Roberts (MS) are thanked for their assistance.

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