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An homologous series of 6-*O*-*n*-alkyl-α-D-galactopyranoses: synthesis and thermotropic mesomorphic properties

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An homologous series of 6-*O*-*n*-alkyl-α-D-galactopyranoses has been prepared. The length of the terminal chains has been varied systematically and the effect on the liquid crystal transition temperatures studied. Most homologues of the series exhibit enantiotropic smectic A* phases. X-ray analysis indicates a lamellar structure for the smectic A* phase with hydrogen-bonded carbohydrate cores at the layer centre, either with no interdigitation of the tilted terminal alkyl chains but with a high degree of chain melting, or with some degree of chain intercalation. The 6-*O*-*n*-alkyl-α-D-galactopyranoses possess clearing points at higher temperatures than those of the corresponding *n*-alkyl α-D-galactopyranosides. The introduction of a higher degree of hydrogen bonding by the replacement of the oxygen atom in the ether linkage between the chain and the carbohydrate ring by an amide linkage leads to higher transition temperatures. The dependence of the liquid crystalline behaviour on the position of the same alkyl substituent and the nature of the sugar in the pyranose form, as well as on the anomeric configuration of the liquid crystalline carbohydrates with four hydroxy groups, is reported.

1. Introduction

The study of the relationship between the molecular structure of carbohydrates and their thermotropic and lyotropic properties is of fundamental interest, since monosaccharides, oligosaccharides and polysaccharides are important for the organization and function of cell membranes [1, 2]. They also have practical applications as solvents for non-denatured proteins [3, 4], as antibacterial and antiviral agents [5–7], surfactants [8], artificial blood [9], drug delivery systems [10] and have been used as optically active building blocks for chiral nematic and ferroelectric liquid crystals [11, 12]. Although many substituted liquid crystalline carbohydrates with alkyl chains attached by ester, ether or thioether linkages are known [13–38], thermal data for complete homologous series are rare [39, 40], since it is known that liquid crystalline properties are generally found for carbohydrates after a critical alkyl chain length has been exceeded (≈3–8 methylene units, depending on the form of the sugar). However, since most practical applications of carbohydrates involve aqueous solutions, suspensions or gels and as the solubility, surface tension, critical micelle concentration, lyotropic phase formation, etc. are all dependent on the hydrophilic–lipophilic ratio [41], it is important to synthesize homologous series for systematic investigations of their physical properties. Most thermal data for liquid crystalline carbohydrate derivatives to be found in the literature are for glucose, perhaps due to its ready availability and cheapness. However, investigations of the physical properties of other carbohydrates, such as galactose [42–44] in the pure state [42–44] and as components of aqueous solutions [45], indicate that they may exhibit a more advantageous property spectrum compared with that of glucose derivatives. It has also been reported that substituted sugars in the pyranose form with axial hydroxy groups, such as galactose, exhibit higher clearing points than those sugars such as glucose with only equatorial hydroxy groups with the same substituents, such as alkyl chains [42–44]. Therefore, we report here on the dependence of the liquid crystalline behaviour on chain length for an almost complete homologous series ($n=2$, 3, 5–16, 18) of 6-*O*-*n*-alkyl-D-galactopyranoses. Comparisons with the related *n*-alkyl-D-galactopyranosides [42] enable the dependence of the transition temperatures on the position of the alkyl substituent and the nature of the anomeric configuration of the carbohydrates to be determined. The lyotropic properties of these new galactose derivatives is currently being investigated and will be reported later.

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2. Synthesis

The 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**) were prepared by alkylation of 1,2: 3,4-di-*O*-isopropylidene-α-D-galactopyranose using appropriate ω-bromoalkanes and potassium hydroxide to produce the intermediate 6-*O*-*n*-alkyl-1,2: 3,4-di-*O*-isopropylidene-α-D-galactopyranoses, followed by deprotection using trifluoroacetic acid [46, 47] (see the scheme). The conditions for the deacetalization were chosen to permit anomeric integrity to be maintained. The yields and elemental analyses for the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**) are collated in table 1; the NMR data are collected in table 2. The butyl homologue could not be obtained in a sufficiently pure form to be reported despite several attempts at synthesis and purification. The synthesis of the 6-*O*-octyl-α/β-D-mannopyranose (**19**) will be reported elsewhere.

3. Phase characterization

3.1. *Phase characterization by thermal optical microscopy*

All the compounds prepared, apart from the first two homologues which are non-mesomorphic, possess thermotropic mesophases of the same type and exhibit the same behaviour during optical microscopy. Bâtonnets are observed on cooling from the isotropic liquid, and these coalesce quickly in the bulk to form focal-conic domains. As the sample is cooled further, the hydrophilic end of the carbohydrate molecules adhere 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. simultaneous presence of both homeotropic and focal-conic textures, indicates that the mesophase is a calamitic smectic A* phase (SmA*) [15, 20, 21, 28]. The notation SmA* 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 [28]. 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, conoscopy 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, or by the thin sample preparations and use of long working-distance objectives and a condenser.

3.2. *Miscibility studies*

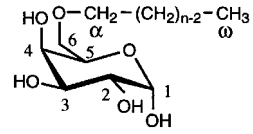
Co-miscibility between the liquid crystal phases of the carbohydrates **1–15** with the smectic A_d^* phase of the

Table 1. Yields and elemental analyses for the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**).

					Calculated/%		Found/%	
Compound	n[a]	Yields[b]/%	Formula	MW	C	H	C	H
1	2	66	$C_8H_{16}O_6$	208·21	46·15	7·75	46·68	7·75
2	3	82	$C_9H_{18}O_6$	222·24	48·64	8·16	48·36	8·16
3	5	74	$C_{11}H_{22}O_6$	250·29	52·78	8·86	51·27	8·53
4	6	70	$C_{12}H_{24}O_6$	264·32	54·53	9·15	54·08	9·35
5	7	82	$C_{13}H_{26}O_6$	278·34	56·09	9·41	55·21	9·85
6	8	88	$C_{14}H_{28}O_6$	292·37	57·51	9·65	57·42	10·17
7	9	84	$C_{15}H_{35}O_6$	306·40	58·80	9·87	59·25	10·47
8	10	84	$C_{16}H_{32}O_6$	320·42	59·97	10·06	58·99	10·56
9	11	89	$C_{17}H_{34}O_6$	334·45	61·05	10·24	60·55	10·45
10	12	91	$C_{18}H_{36}O_6$	348·48	62·03	10·41	63·37	11·17
11	13	87	$C_{19}H_{38}O_6$	362·51	62·95	10·56	62·25	11·25
12	14	86	$C_{20}H_{40}O_6$	376·53	63·79	10·70	64·10	11·41
13	15	92	$C_{21}H_{42}O_6$	390·56	64·58	10·84	64·41	11·18
14	16	93	$C_{22}H_{44}O_6$	404·59	65·31	10·96	65·50	11·66
15	18	94	$C_{24}H_{48}O_6$	432·64	66·62	11·18	66·59	11·92

[a] Number of carbon atoms in the *n*-alkyl chain.
[b] Calculated starting from 6-*O*-*n*-alkyl-1,2: 3,4-di-*O*-isopropylidene-α-D-galactose.

Table 2. NMR data for the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**) in Me_2SO-d6 at 300 K.

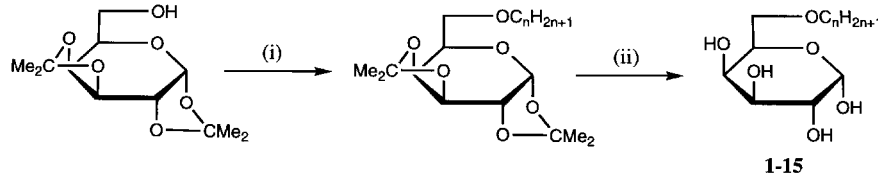


^{13}C *NMR chemical shifts*

	Galactose moiety						Alkyl chain		
Parameter	C1	C2	C3	C4	C5	C6	α-CH_2	($n-2$)-CH_2	ω-CH_3
δ (ppm)	92·5	69·2	68·5	69·4	68·3	70·1	70·3	21·9–31·2	13·8

^{1}H *NMR chemical shifts*

	Galactose moiety							Alkyl chain		
Parameter	H1	H2	H3	H4	H5	H6a	H6b	α-CH_2	($n-2$)-CH_2	ω-CH_3
δ (ppm)	4·91 t	3·47 dd	3·52 dd	3·62 m	3·91 t	3·35 m	3·50 m	3·33 t	1·23 m	0·84 t
J (Hz)	$J_{1,2}$ 3·6	$J_{2,3}$ 10·1	$J_{3,4}$ 3·3	$J_{4,5}$ 3·2	$J_{5,6a}$ 5·9	$J_{6a,6b}$ 10·6	$J_{6b,5}$ 5·2	$J_{\alpha\beta}$ 7·3	—	$J_{\omega\omega-1}$ 5·8



(i) $BrC_nH_{2n+1}/KOH/Me_2SO$
(ii) CF_3COOH/H_2O

Scheme

standard material octyl β-D-glucopyranoside [15, 17] was observed utilizing optical microscopy. Thus, the thermotropic phases of these carbohydrates can be classified as smectic A_d^*, see X-ray studies (§ 3.4).

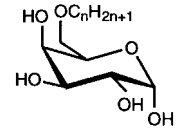
3.3. *Phase characterization by differential scanning calorimetry*

The enthalpy values for the melting (T_m) and clearing points (T_{SmA^*I}) of the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**) are collated in table 3. Typical heating thermograms for the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**) are shown in figures 1 and 2, for the decyl and tetradecyl homologues **10** and **12**, respectively. It is clear from the thermograms that the transitions T_m and T_{SmA^*I} are both first order transitions. The decomposition observed for many homologues at T_{SmA^*I} is shown clearly in figure 2, whereas T_{SmA^*I} in figure 1 shows relatively little decomposition. However, T_{SmA^*I} measured on cooling is often lower due to thermal decomposition. There is also a greater tendency to form a glassy state on cooling rather than to recrystallize. 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, although the variations are quite large (1·16–7·88 J g^{-1}) for T_{SmA^*I} and much larger than the percentage change for T_m (72·7–127·8 J g^{-1}). The peaks for the phase transitions are relatively sharp indicating a high degree of purity for the materials (confirmed by the elemental analyses and NMR data, see tables 1 and 2, respectively). Neither a melting nor clearing a point for the ethyl and propyl homologues **1** and **2** could be detected. A glass transition temperature was found for both compounds below 0°C (see table 3 and figure 3).

3.4. *X-ray analysis*

The experimental results obtained by X-ray analysis, as described in the § 5, for 6-*O*-decyl-α-D-galactopyranose (**8**) are shown in figure 4. Elevation of the temperature leads to a loss of the values observed for the diffraction maxima, indicative of a loss of liquid crystalline ordering

Table 3. Transition temperatures and enthalpies of transition for the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**).



Compound	*n*	T_p/°C	Cr–SmA*/I/°C	ΔH/J g^{-1}	SmA*-I/°C	ΔH/J g^{-1}
1	2	−2	—		—	
2	3	−18	—		—	
3	5		114	14·5	123	4·82
4	6		106	101·4	145	8·80
5	7		113	110·7	168	7·88
6	8		113	117·1	169	7·75
7	9		120	91·7	176	2·94
8	10		117	72·7	172	1·87
9	11		127	128·6	176	4·16
10	12		119	127·8	171	3·70
11	13		129	141·9	174	2·4
12	14		114	118·1	169	6·92
13	15		127	138·2	170	2·06
14	16		121	127·1	167	1·58
15	18		119	125·6	164	1·16

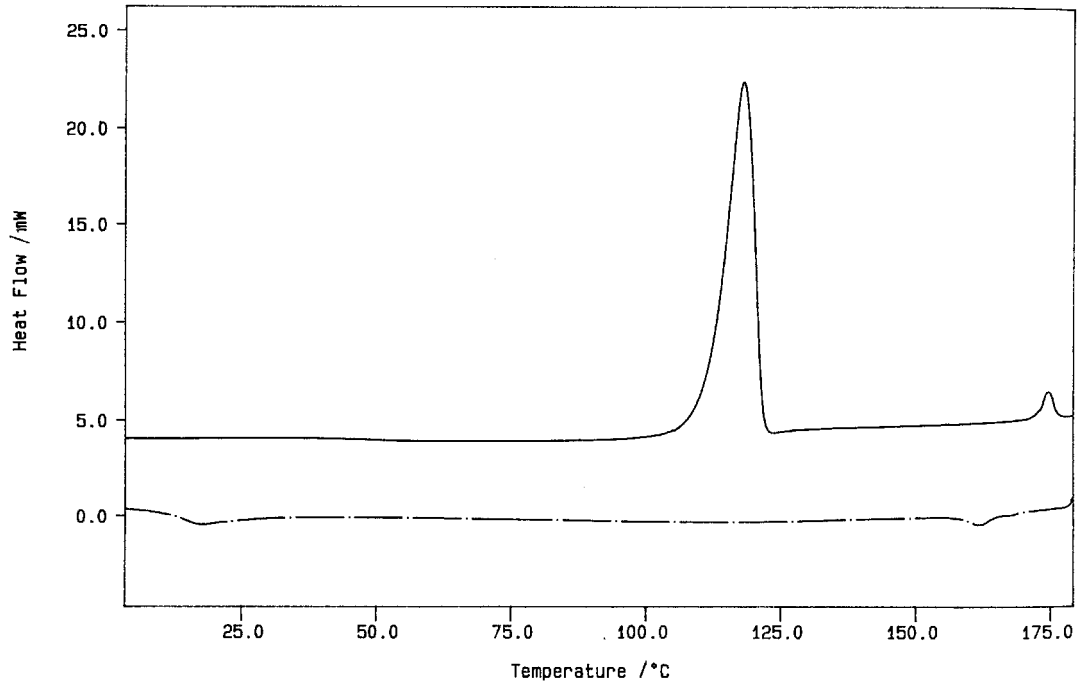


Figure 1. Differential scanning thermograms for the first heating and cooling cycle for 6-*O*-dodecyl-α-D-galactopyranose (**10**), scan rate 10°C min^{-1}.

with increasing temperature. Between 122 and 176°C the *d*-spacing decreases between 31·4 to 28·8 Å. Above that temperature the material reaches its isotropic liquid state leading to the absence of small angle intensity maxima.

The spacing of 31·4 Å at 122°C indicates that, compared with the overall length of one molecule of 16·2 Å, as obtained *via* molecular modelling of one molecule in the gas phase at 0 K using the CERIUS 2.0 (MSI) software (shown in figure 5) a bilayer structure of two molecular lengths appears to be present in the crystalline state. These calculations are for one molecule only and

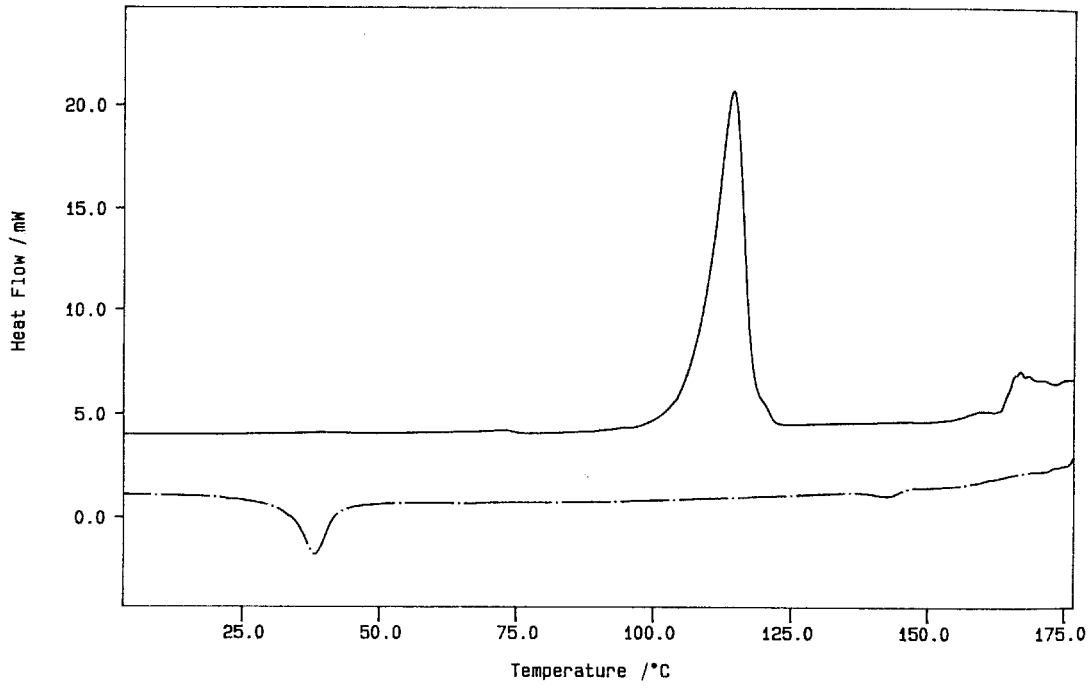


Figure 2. Differential scanning thermograms for the first heating and cooling cycle for 6-*O*-tetradecyl-α-D-galactopyranose (**12**), scan rate 10°C min^{-1}.

clearly do not take into account intermolecular interactions such as hydrogen bonding. However, they do give an indication of the shape of the lowest energy conformation of the molecules under investigation, as would Dreiding models. The experimentally observed values agree with a structure where the carbohydrate groups are set in a bipolar arrangement and where the alkyl chains are not intercalated.

The large reduction of the *d*-spacing with rising temperature above 122°C in the liquid crystalline state is in contrast to the behaviour usually observed for calamitic thermotropic liquid crystals, although some reduction in the *d*-spacing with increasing temperature is common due to effective melting of the terminal part of the aliphatic chain giving rise to conformationally isotropic regions. There are two molecular arrangements which would readily allow for such behaviour. One possibility is that the positions of the bipolar carbohydrate head groups become less well defined with respect to each other with rising temperature, and that some interdigitation occurs. This would lead to a reduction of the *d*-spacing and to an overall expansion in the axes describing the plane of the smectic layering. A similar effect could be achieved by an increase of the amount of *gauche* conformations present in the alkyl chain, reducing the length of the smectic layering and accounting for the decrease of ordering observed. As both processes seem to be equally possible, and do not exclude each other, the presence of both should be assumed, leading overall to a phase structure of the material as proposed earlier [19] (figure 6). Thermal decomposition at these elevated temperatures during the X-ray measurements cannot be totally excluded and may also contribute to some extent to the observed variations in the *d*-spacings.

4. Discussion of the transition temperatures

After a critical length of the alkyl chain ($n=5$) of the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1**–**15**) has been reached, most homologues exhibit high T_m and T_{SmA^*I} (see table 3 and figure 3). Therefore, a broad SmA* phase is observed for most homologues. T_m shows a certain degree of alternation and a general tendency to increase with increasing chain length. For short alkyl chains ($n=$ 1 and 2) only a glass transition temperature could be observed. These two homologues are liquids at room temperature, although D-(+)-galactose itself is a high melting solid ($T_m=165$–168°C). T_{SmA^*I} also increases from very low values for short alkyl chain lengths, but then reaches a maximum before decreasing gradually as the chain becomes longer. These plots are typical for various series of non-amphiphilic liquid crystals and show the normal pattern of alternation in T_{SmA^*I} for odd and even homologues, although the dependence of the various shapes of such plots on molecular structure has not yet been adequately explained. Although many series

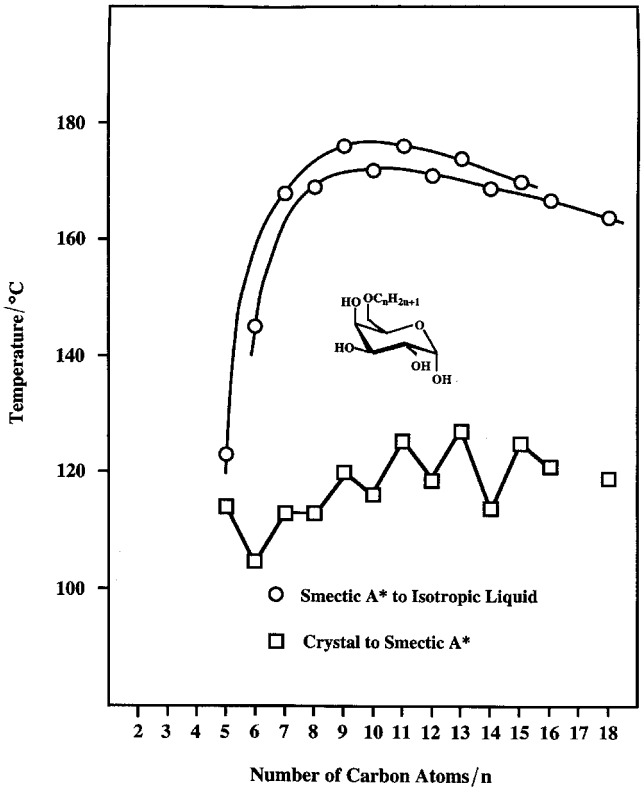


Figure 3. Plot of the transition temperatures of the 6-*O*-alkyl-α-D-galactopyranoses (**1–15**) against the number of the carbon atoms (n) in the alkyl terminal chain.

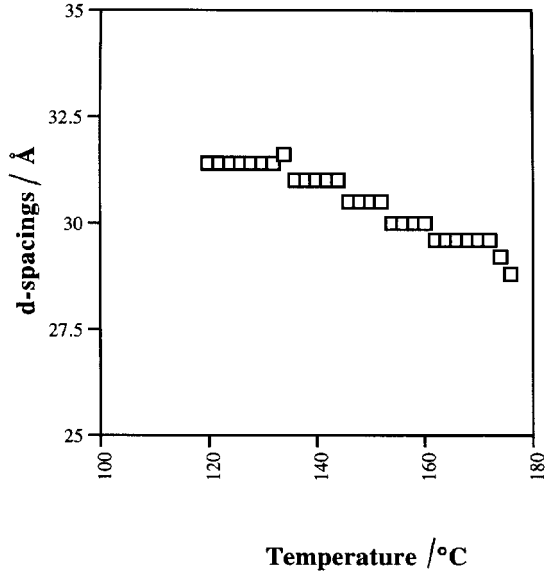


Figure 4. The d-spacings of 6-*O*-decyl-α-D-galactopyranose (**8**) at a heat scan rate of 2°C min^{-1}.

of amphiphilic carbohydrate derivatives with liquid crystalline behaviour have been reported, these generally consist of too few homologues for alternation to be observed or have not been plotted against chain length as a figure. It is evident for the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**), that short alkyl chains disrupt the packing arrangements required for both the crystalline and liquid crystalline states as the first two homologues ($n=1$ and 2) of the series are both isotropic liquids at room temperature. Only after a certain critical value of the ratio of hydrophobic chain length to hydrophilic core, i.e. the hydrophobic/hydrophilic ratio, has been reached are solids formed and mesomorphism is observed. The critical value of this ratio is different for these two competing states and seems to be almost irrelevant for the crystalline state once the critical value has been exceeded. The presence of five hydroxy groups in D-(+)-galactose leads to additional hydrogen bonding, a more symmetrical molecular shape and a higher degree of polarity than in the 6-*O*-*n*-alkyl-α-D-galactopyranoses (**1–15**), which is probably responsible for the high T_m.

It can be seen from table 4 that the highest value for T_{SmA*I} of the carbohydrates **6** and **16–21** with an alkyl substituent of the same length (octyl) in different positions of the carbohydrates in the pyranose form is observed for the 6-*O*-octyl α-D-galactopyranose (**6**). Except for the 6-*O*-octyl-β-D-glucopyranoside (**16**), the T_{SmA*I} of the other glycopyranoses **17–21** are similar. This is another example of the β-anomer exhibiting a lower T_{SmA*I} than that of the corresponding α-anomer [42]. This suggests that the alkyl chain in the 6-position and the configuration of the hydroxy groups in galactose allow a particularly advantageous conformation for liquid crystal formation. This could be due to a quasi 6-membered ring being formed due to hydrogen bonding between the hydroxy group in position four and the oxygen atom in position 6. Although this quasi 6-membered ring would not contribute directly to the intermolecular hydrogen bonding network required for mesophase stability, it could well give rise to a molecular conformation that retains its shape at elevated temperatures and/or exhibits an efficient packing arrangement. Either of these factors would lead to a higher clearing point for galactose derivatives. Although comparisons are rendered somewhat difficult due to different anomers and anomer mixtures being present (α for **6**, **17** and **20**; β for **16** and **18**; α/β for **19** and **21**), the thermal data in table 4 do suggest that T_{SmA*I} is highest for galactose and lowest for glucose, with mannose exhibiting intermediate values. This is consistent with earlier observations, which postulated that substituted sugars in the pyranose form, such as mannose and galactose, with more axial hydroxy groups than glucose, have smaller

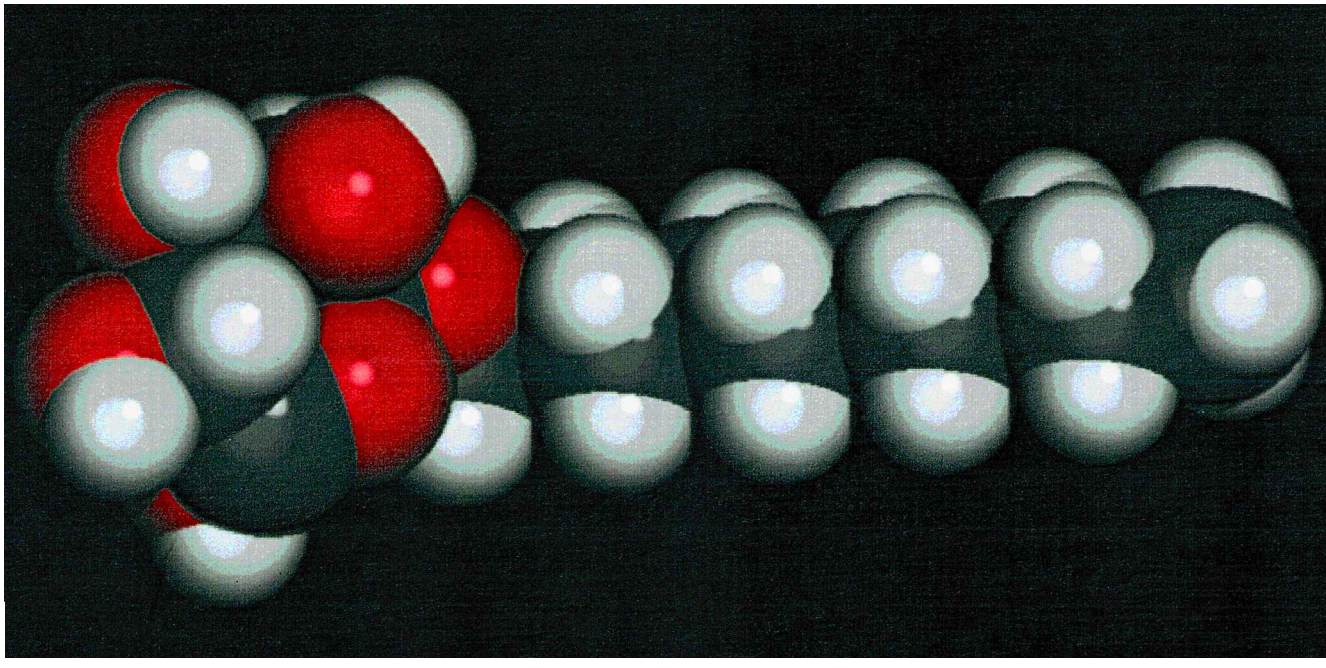


Figure 5. A model of 6-*O*-decyl-α-D-galactopyranose (**8**) as obtained by CERIUS 2.0.

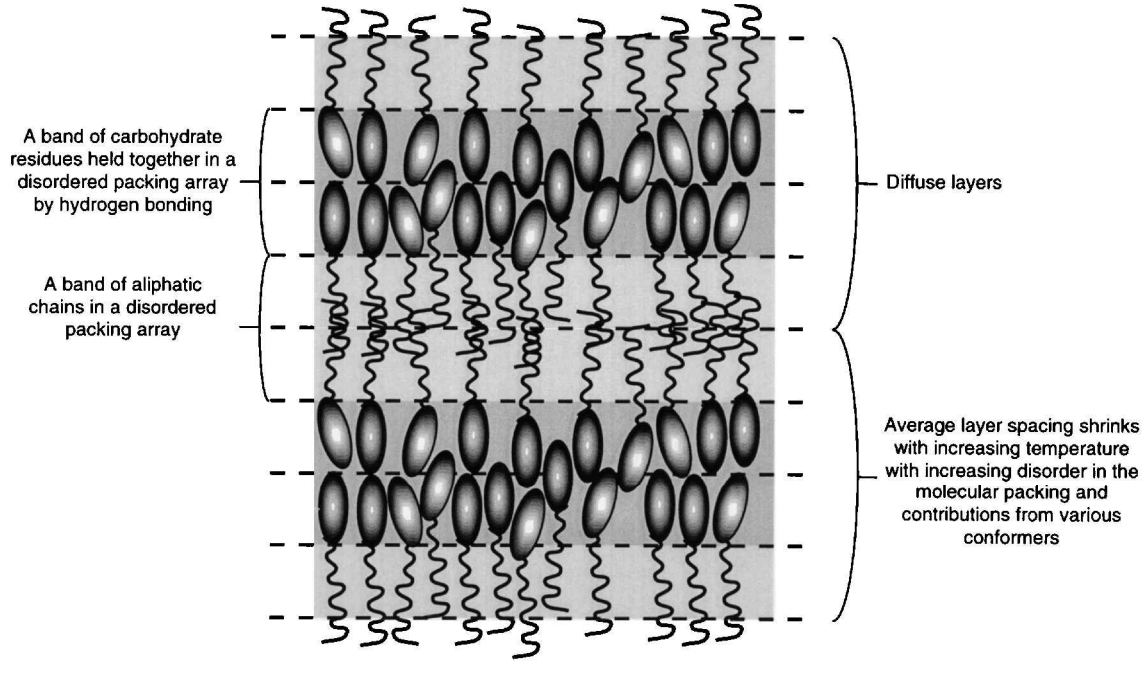


Figure 6. A schematic representation of the SmA* phase of 6-*O*-decyl-α-D-galactopyranose (**8**).

rotation volumes and therefore a high T_{SmA*I} [42]. The galactose derivative **18** is in the middle of the table because it is a β-anomer.

The thermal data listed in table 5 indicate that the presence of an additional site for hydrogen bonding in the 6-*O*-octadecanoylamido-6-deoxy-D-galactose (**22**) [43], 6-hexadecansulphonamido-6-deoxy-D-galactose (**23**) [43] and 6-(9- or 10-chloro-octadecanoylamido)-6-deoxy-D-galactose (**24**) [43] compared with the ether 6-*O*-octadecyl-α-D-galactopyranose (**15**) with comparable chain lengths, leads to significantly higher T_{SmA*I}. This is also attributable to a higher degree of polarity of the hydrophilic part of the carbohydrate [43]. The replacement of a hydrogen atom by a chlorine atom in

Table 4. Transition temperatures for the carbohydrates **6** and **16–21**.

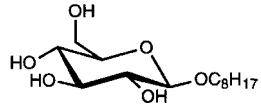
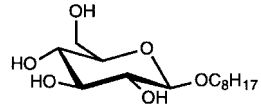
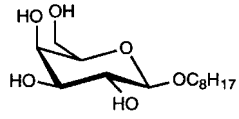
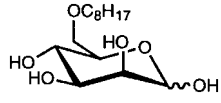
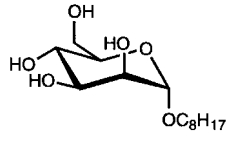
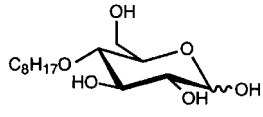
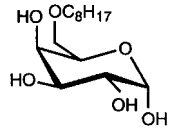
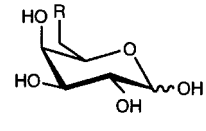
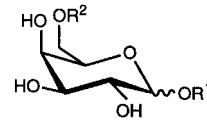
Compound	Structure	Cr–SmA*/°C	SmA*-I/°C	References
16		67	108	[17, 20]
17		68	125	[25]
18		98	133	[42]
19		86	135	
20		55	134	[42]
21		110	140	[48]
6		113	169	

Table 5. Transition temperatures for 6-*O*-octadecyl-α-D-galactopyranose (**15**) and 6-*O*-octadecanoylamido-6-deoxy-D-galactose (**22**), 6-hexadecansulphonamido-6-deoxy-D-galactose (**23**) and 6-(9- or 10-chlorooctadecanoylamido)-6-deoxy-D-galactose (**24**).



Compound	*R*	Cr–SmA*/°C	SmA*-I/°C	References
15	$OC_{18}H_{37}$	119	164	
22	$NHCOC_{17}H_{35}$	134	197	[43]
23	$NHSOC_{16}H_{33}$	142	235	[43]
24	$NHCOC_{17}H_{34}Cl$	133	196	[43]

Table 6. Transition temperatures for the *n*-alkyl β-D-galactopyranosides **17**, **25** and **26**, and the 6-*O*-*n*-alkyl-α-D-galactopyranoses **6**, **8** and **10**.



Compound	R^1	R^2	Cr–SmA*/°C	SmA*-I/°C	References
17	C_8H_{17}	H	98	133	[42]
25	$C_{10}H_{21}$	H	94	157	[42]
26	$C_{12}H_{25}$	H	99	166	[42]
6	H	C_8H_{17}	113	169	
8	H	$C_{10}H_{21}$	123	169	
10	H	$C_{12}H_{25}$	119	171	

a position in the middle of the chain of 6-*O*-octadecanoylamido-6-deoxy-D-galactose (**22**) to yield the 6-(9- or 10-chloro-octadecanoylamido)-6-deoxy-D-galactose (**24**) changes T_{SmA*I} hardly at all. This has parallels with behaviour found for non-amphiphilic liquid crystals.

The thermal data collected in table 6 indicate that the 6-position in galactose promotes liquid crystalline behaviour more than the same chain in the anomeric position (see above), although comparison is complicated by the presence of different anomers. However, it is evident that a different temperature dependence can be observed for each series and that care must be taken in comparing transition temperatures of just one homologue for two different series of carbohydrates.

5. Experimental

5.1. *Characterization*

NMR spectra were recorded using a Bruker WP-300 and using the solvents $CDCl_3$, Me_2SO or C_5D_5N (internal standard Me_4Si). Reactions were monitored by either HPLC (Waters 721), using either of the reverse phase columns RP-18 (Merck) or PN 27–196 (Waters) or CPG (Girdel) with the columns OV 17 or SE 30. The structures of the compounds were determined by ^1H and ^{13}C NMR spectroscopy.

The purity of the compounds was determined by thin layer chromatography (TLC), high performance liquid chromatography (HPLC), elemental analysis (CHN) 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. Melting points were determined with a Buchi apparatus and are uncorrected. Optical rotations were recorded at room temperature with $CHCl_3$ solutions and a Perkin-Elmer 241 polarimeter using a 1 dm cell.

Column chromatography was performed on silica gel (60 mesh, Matrex) by gradient elution with hexane–acetone (in each case the ratio of silica gel to product mixture to be purified was 30:1). 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 determination of the transition temperatures of the carbohydrates prepared were determined by optical microscopy using either a Zeiss Universal or a Leitz Laborlux 12 Pol 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 by using 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 the slides were dried at 100°C for 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 smectic A* phase formed on the surface of the slide on cooling from the isotropic liquid.

Differential scanning calorimetry was used to determine the enthalpies of transition and to confirm the phase transition temperatures determined by optical microscopy. Differential scanning thermograms (scan rate 10°C min^{-1}) were obtained using a Perkin Elmer DSC 7 operating on 7 series/UNIX software. The results obtained were standardized with respect to indium (measured onset 156·65°C, ΔH 28·42 J g^{-1}, literature values 156·60°C, ΔH 28·45 J g^{-1}), 4-nitrotoluene (measured onset 51·25°C, ΔH 119·23 J g^{-1}, literature values

51·63°C, ΔH 122·58 J g^{-1}) and benzil (measured onset 94·53°C, ΔH 99·87 J g^{-1}, literature values 94·87°C, ΔH 92·68 J g^{-1}).

Comparison of the transition temperatures determined by optical microscopy and DSC show some discrepancies of about 1–3°C. This 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, 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. However, where the differences in the *melting points* as determined by these two techniques were greater then 1–3°C, the DSC values are given since no decomposition was observed on melting.

In order to characterize the solid state of these materials further, compound 6-*O*-decyl-α-D-galactopyranose (**8**) was investigated using X-ray diffraction. The tendency of carbohydrates to decompose at high temperatures required an experimental set-up allowing for the recording of sufficient data before degradation of the sample set in. Thus high flux synchrotron radiation was employed, using the experimental set-up of station 8.2 at Daresbury Laboratories, described elsewhere [49–51]. Samples were prepared as polycrystalline powders in Lindemann tubes and maintained at a controlled temperature allowing for the recording of diffraction data whilst performing a temperature scan of 2°C min^{-1} in the temperature range of 120 to 180°C. The selected experimental set-up was limited to the recording of data relating to lattice constants greater than 17·8 Å. The use of wet rat-tail collagen as calibration standard leads to a systematic error of 3% of the observed *d*-spacings [52]. The wavelength of radiation used was 1·54 Å.

5.2. *General synthetic procedures*

5.2.1. *6-O-n-alkyl-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoses*

Finely powdered potassium hydroxide (2·4 equiv.) and the appropriate bromoalkane (1·2 equiv.) were added to a stirred solution of the 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (1 equiv.) in 4:1 toluene–Me_2SO (100 g l^{-1}) at room temperature. After 98% conversion (10–36 h), the mixture was filtered and the filtrate neutralized with saturated aqueous NH_4Cl solution. The organic phase was separated off, washed with water (twice), dried (Na_2SO_4) and the solvent removed under reduced pressure. The desired products were isolated after purification by column chromatography on silica gel (solvent mixture hexane:acetone 49:1 v/v) in 85 to 95% yields.

5.2.2. *6-O-n-alkyl-α-D-galactopyranoses (**1–15**)*

The appropriate 6-*O*-*n*-alkyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (500 g l^{-1}) was added to a stirred solution of CF_3COOH and H_2O 9:1(v/v) at room temperature. Cold diethyl ether was added after 15 min and the solution was cooled to −20°C. The desired products were filtered off, sucked dry, washed with diethyl ether (twice) and recrystallized from THF to give the 6-*O*-*n*-alkyl-α-D-galactopyranose (**1–15**). The yields, elemental analyses and NMR data are collated in tables 1 and 2, respectively.

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