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Henk A. van Doren; Anna M. van der Heijden; A. T. J. W. De Goede; Fred van Rantwijk; Herman van Bekkum

Online publication date: 06 August 2010

To cite this Article van Doren, Henk A. , van der Heijden, Anna M. , De Goede, A. T. J. W. , van Rantwijk, Fred and van Bekkum, Herman(2000) 'Mesogenic ketohexose and aldopentose derivatives: anomalous behaviour of the alkyl D-fructopyranosides', Liquid Crystals, 27: 1, 63 — 68
To link to this Article: DOI: 10.1080/026782900203227
URL: http://dx.doi.org/10.1080/026782900203227

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LIQUID CRYSTALS, 2000, VOL. 27, NO. 1, 63–68

Mesogenic ketohexose and aldopentose derivatives: anomalous behaviour of the alkyl D-fructopyranosides

HENK A. VAN DOREN*

TNO Nutrition and Food Research Institute, P.O. Box 360, 3700 AJ Zeist, The Netherlands

ANNA M. VAN DER HEIJDEN, A. T. J. W. DE GOEDE, FRED VAN RANTWIJK and HERMAN VAN BEKKUM

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
e-mail: A.M.vanderHeijden@stm.tudelft.nl, F.vanRantwijk@stm.tudelft.nl

(*Received 5 November 1998; in final form 12 July 1999; accepted 28 July 1999*)

The thermotropic and lyotropic behaviour of a number of alkyl ketopyranosides, alkyl ketofuranosides, an alkyl pentopyranoside and an alkyl pentofuranoside were studied. With the exception of the alkyl β-D-fructopyranosides, all the compounds display the expected smectic A* phases. The three alkyl fructopyranoside homologues studied (octyl, decyl and dodecyl) display a novel, rather viscous mesophase (monotropic), the nature of which is as yet unclear. The unknown phase is not a smectic A phase, because a phase transition from smectic A* to phase X is observed for both the decyl and the dodecyl derivative. The lyotropic behaviour of all the compounds in this study is quite similar to that reported earlier for other monoalkylated monosaccharide derivatives, except that the unknown phase X is again observed for the fructopyranoside derivatives.

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1. Introduction

Many liquid crystalline (LC) monoalkyl monosaccharide derivatives have been reported in the literature [1, 2]. So far, the mesophase exhibited by these compounds is, without a single exception, smectic A* (SmA*)† [3]. Based on this observation alone, there would appear to be little need to synthesize new but similar derivatives. However, monoalkylated monosaccharides are amphiphilic molecules with an application potential in the surfactant field and they may also have interesting biological properties. Therefore, various new classes of derivatives are still being prepared. In our laboratory one project has entailed the acid catalysed alkylation of ketoses and pentoses. The synthesis and purification of these products has been described in detail elsewhere [4, 5]. The present work is concerned with the thermotropic and lyotropic LC behaviour of medium chain alkyl β-D-fructopyranosides (**1**), alkyl α-L-sorbopyranosides (**2**), alkyl β-D-fructofuranosides (**3**), alkyl β-D-ribofuranosides (**4**) and alkyl β-D-arabinopyranosides (**5**) with the structures shown in figure 1.

* Author for correspondence.

† The asterisk serves to indicate that the mesophases are made up of chiral molecules; chiral supramolecular architecture of the lamellar layers has not been observed.

2. Experimental

2.1. *General*

GC analysis was performed on a Hewlett Packard (HP) 5890, Series II chromatography, equipped with a 7673 auto-injected and a Chrompack 50 m × 0.32 mm CP-Sil 5 CB, 0.12 column. The carrier gas was nitrogen at a flow rate of 1.5 ml min^{-1}. Temperature program: 60°C (5 min) to 300°C (10°C min^{-1}). Peaks were detected using flame ionization detection (FID) and were integrated on a HP 3396A integrator. Tetradecane was used as internal standard. Samples were prepared by withdrawing 20 µl samples of the reaction mixture and treating them with 0.5 ml of a trimethylsilylating reagent consisting of a mixture of pyridine (104 ml), *N*,*N*-bis(trimethylsilyl)trifluoroacetamide (26 ml), and trimethylsilyl chloride (13 ml).

Separation of the different reaction products was performed by using a Millipore-Waters Delta Prep 4000 preparative chromatography system equipped with two 25 × 100 mm 7 Symmetry C18 cartridges in a 25 × 10 Radial Compression unit and an extension tube, a Waters differential refractometer R401 and a Waters fraction collector.

NMR spectra were recorded using a 300 MHz Varian Unity Inova spectrometer or a 400 MHz Varian-VXR

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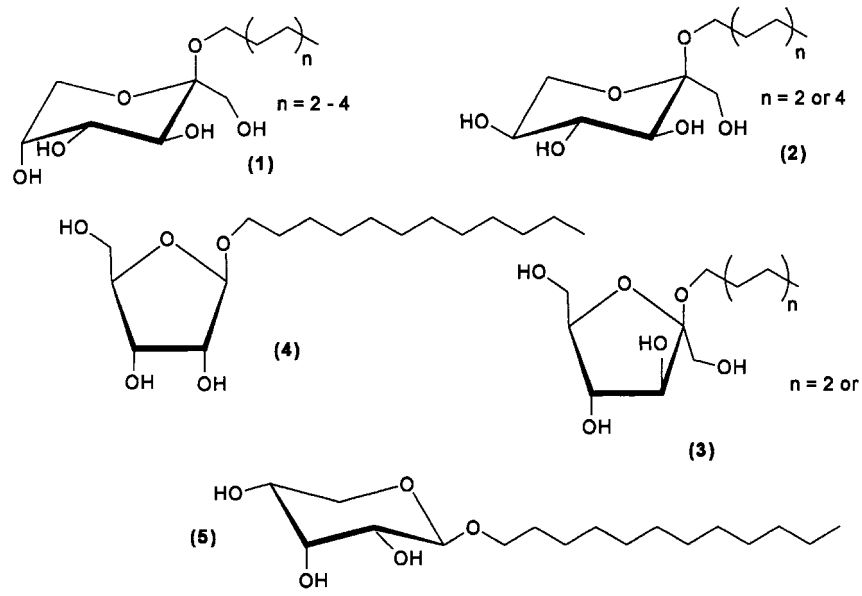

Figure 1. Structures of alkyl glycosides studied.

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400S spectrometer; optical rotations were measured using a Perkin Elmer 241 polarimeter at 598 nm.

Thermomicroscopy was performed with a Mettler FP 800 system; the hot stage was mounted on a Nikon polarization microscope equipped with a Minolta 7000 camera, using a first order red plate and a Kodak Ektacolor Gold Professional (20 DIN-160 ASA) film. Quantitative thermal analyses were performed using a Perkin Elmer PC Series DSC 7. The values reported are those from the first heating/cooling scans. For the measurements of the Krafft temperatures, large volume DSC pans were filled with *c.* 3 mg of anhydrous compound and 50 µl of water.

Silica-alumina cracking catalyst Ketjencat HA-HPV (25 wt % Al_2O_3) was a gift from Akzo-Nobel Chemicals, Amsterdam. All reagents and solvents were purchased from any of the large research chemical suppliers and were used without further purification, unless indicated otherwise.

2.2. *Synthesis*

The Fischer alkylation of fructose can be performed by mildly acidic catalysts such as amorphous silica–alumina or mesoporous molecular sieves [4, 5]. The alkyl β-D-fructopyranosides (**1**) could be crystallized selectively from the reaction mixture by the addition of diethyl ether. The alkyl β-D-fructofuranosides (**3**) were obtained by chromatographic separation, while the corresponding α-fructofuranosides were not stable in the pure form.

The successful alkylation of fructose encouraged us to attempt the application of a cracking catalyst for the Fischer alkylation of other monosaccharides such as L-sorbose, D-ribose and D-arabinose. All products were obtained by selective crystallization from the reaction mixture by adding diethyl ether. No further optimization was attempted.

2.2.1. *Synthesis of alkyl fructosides*

D-Fructose (3.0 g, 16.7 mmol) was treated with 1-octanol (42 ml, 266.7 mmol) and the suspension was stirred and heated to 80°C under vacuum. Subsequently silica–alumina catalyst (HA-HPV, 3 g, activated by heating at 430°C for 24 h) was added and water was scavenged using zeolite KA (10 g) in a Soxhlet apparatus as described earlier [4]. The reaction was monitored using GC. After 24 h, the reaction was stopped and the catalyst removed by filtration. The filtrate was diluted with 400 ml of dimethyl ether and cooled to − 8°C when the octyl β-D-fructopyranoside precipitated. Recrystallization from water afforded the pure pyranoside. The analytical data have been described [4]. The same procedure was followed for the decyl and the dodecyl fructopyranoside [4].

For the isolation of the octyl and dodecyl β-D-fructofuranosides, the reaction mixtures were separated using preparative HPLC. The exact procedure and the analytical data are reported elsewhere [5].

2.2.2. *Synthesis of other dodecyl saccharides*

The same reaction procedure was followed as for the synthesis of dodecyl fructoside: 3.0 g of monosaccharide (16.7 mmol for L-sorbose; 20 mmol for D-ribose and D-arabinose) were treated with 1-dodecanol (49.6 g, 267 mmol) in the presence of 3.0 g HA-HPV catalyst. Reactions were monitored by GC. After 24 h the reaction was stopped and the reaction mixture was filtered

through a glass filter. Upon addition of 200 ml of diethyl ether, precipitation of product followed. The isolated products were analysed as described earlier [4].

2.2.3. *Synthesis of a α-L-octyl sorboside*

Octyl L-sorboside was synthesized using the same procedure as for the octyl α-D-fructoside. L-Sorbose (3.0 g, 16.7 mmol) was treated with 1-octanol (42 ml, 266.7 mmol) and the suspension was stirred and heated to 80°C under vacuum. Subsequently silica–alumina catalyst (HA-HPV, 3 g, activated by heating at 430°C for 24 h) was added and water was scavenged using zeolite KA (10 g) in a Soxhlet apparatus. The reaction was monitored using GC. After 24 h the reaction was stopped and the catalyst removed by filtration. The filtrate was diluted with 400 ml of diethyl ether and cooled to − 8°C whereon the octyl α-L-sorbopyranoside precipitated. Recrystallization from water afforded the pure pyranoside, $[\alpha]_D$ − 61.8° (*c.* 1.0, methanol). ^{13}C NMR (75 MHz, CD_3OD) δ 14.11 (CH_3), 22.68 (CH_2), 26.13 (CH_2), 29.33 (CH_2), 29.55 (CH_2), 30.08 (CH_2), 31.90 (CH_2), 61.01 (C), 62.28, 62.87 (C1, C6), 69.76, 72.27, 74.76, (C3, C4, C5) 100.00 (C2). Anal: calc. for $C_{14}H_{28}O_6$ (292.36), C 57.51, H 9.65, O 32.8; found C 57.01, H 9.65, O 33.3%.

3. Results and discussion

3.1. *Thermotropic liquid crystalline behaviour*

The thermotropic LC behaviour was studied by means of polarization microscopy and differential scanning calorimetry (DSC). The melting and clearing temperatures and the corresponding enthalpies are given in table 1.

With the exception of the alkyl β-D-fructopyranosides and dodecyl arabinopyranoside, all the derivatives studied behave in the expected fashion, i.e. a SmA* phase is formed upon melting. Dodecyl arabinopyranoside has only a monotropic phase. With DSC, no mesophase is observed in a cooling run at 5 K min^{-1}, but when the isotropic phase is supercooled at the same cooling rate on a clear glass microscope slide, a SmA* phase is observed at *c.* 81°C, followed almost immediately by crystallization. The clearing point of the other pentose derivative, dodecyl β-D-ribofuranoside, is also rather low, much lower than those of the corresponding hexose-based alkyl glucosides, mannosides and galactosides [6].

Although a crystal-to-crystal transition is frequently observed during the first heating run of monoalkyl monosaccharide derivatives, the behaviour of the alkyl β-D-fructopyranosides is unusually complex. A total of six endothermal peaks is observed in the DSC first heating run for octyl β-D-fructopyranoside, the first four having a ΔH of less than 5 kJ mol^{-1}. The two highest temperature peaks are not fully resolved. On cooling only one exothermal peak is observed (115.1–114.4°C, ΔH − 23 kJ mol^{-1}). When the melting process is examined in a hot stage mounted on a polarization microscope, no changes in the birefringence of the crystal are observed up to a temperature of 126°C. At this stage the birefringence fades and the sample melts into a viscous weakly birefringent mesophase, which becomes more fluid at 130°C and converts to the isotropic liquid phase at 131.5°C (see also [7]). On controlled cooling of the isotropic phase, the mesophase reappears at 129.5°C. Swirling motions are observed in the sample (especially when uncovered droplets are studied) and a wavy, hairy texture is formed, which coalesces to the pattern shown for the dodecyl β-D-fructopyranoside in figure 2. Further cooling does not lead to any more changes in the texture, even after prolonged standing at ambient temperature, although the viscosity becomes much higher. The mesophase formed (called here

Table 1. The melting and clearing temperatures and enthalpies of several alkylated ketohexoses and aldopentoses from DSC measurements.

Compound	m.p./°C	$\Delta H_{melting}$/kJ mol^{-1}	c.p./°C SmA_d–I	$\Delta H_{clearing}$/kJ mol^{-1}
Octyl sorbopyranoside	78.4–81.5	30.7	125.7–126.5	2.14
Dodecyl sorbopyranoside	91.1–94.7	43.9	151.0–151.8[a]	2.33
Octyl β-D-fructofuranoside	< 25			
Dodecyl β-D-fructofuranoside	47.1–50.5[b]	36.9	155.7–156.9	2.39
Octyl β-D-fructopyranoside	125.2–129.6[c]	34.2	—	—
Decyl β-D-fructopyranoside	130.6–132.2	33.1	(122.0–121.1)[d]	(1.76)
Dodecyl β-D-fructopyranoside	127.0–129.8	29.1	131.6–132.3	1.89
Dodecyl β-D-ribofuranoside	95.7–96.9	41.8	98.4–98.8	1.43
Dodecyl β-D-arabinopyranoside	115.8–117.1	44.4	(∼ 81)[d,e]	—

[a] Decomposition sets in immediately above the clearing point.
[b] Broad melting peak composed of three unresolved maxima.
[c] Double peak (Cr–X–I).
[d] Values between brackets indicate monotropic transitions.
[e] Observed visually with a hot stage mounted on the polarization microscope.

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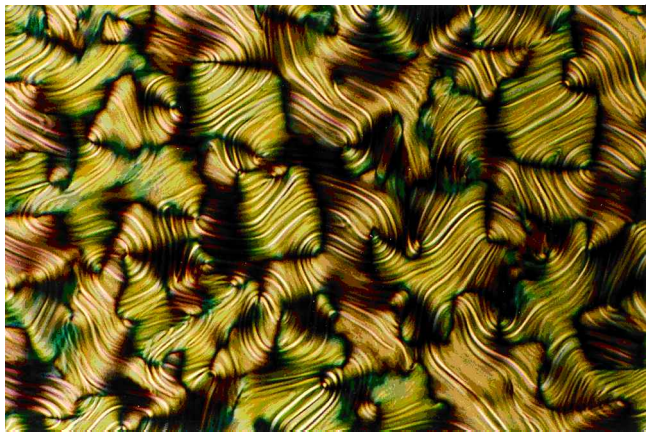
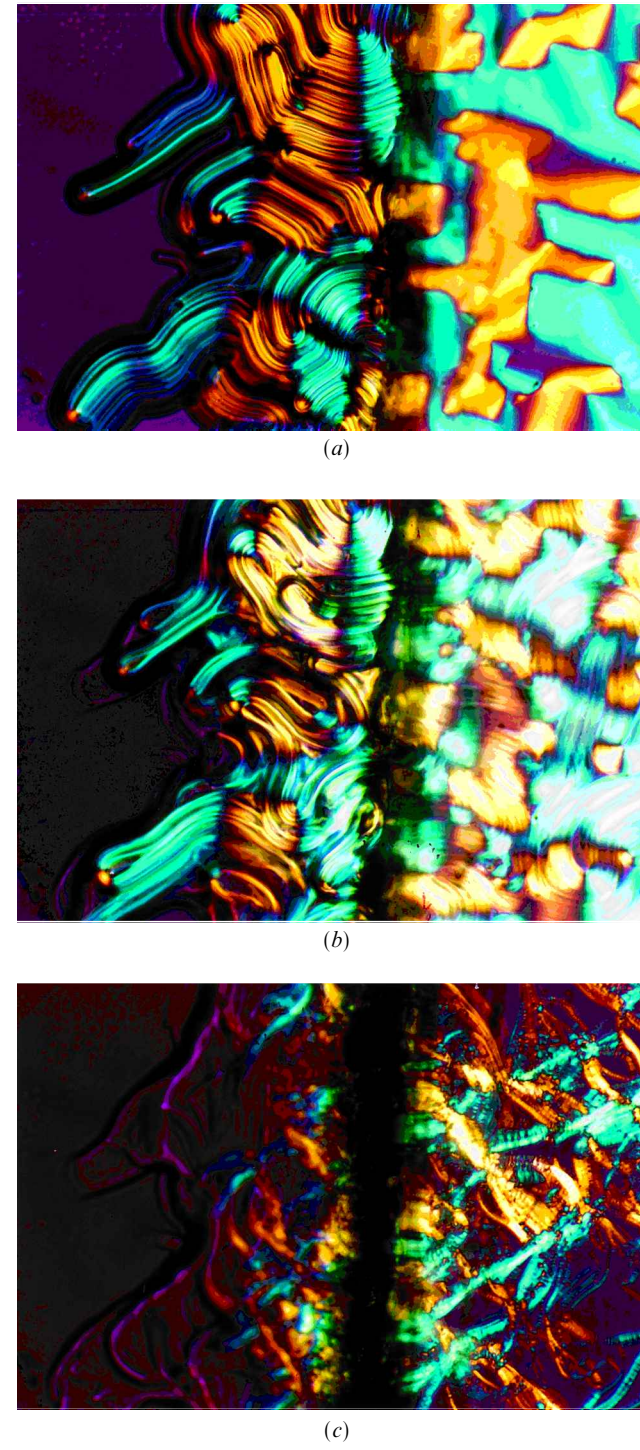


Figure 2. Paramorphotic solid phase of dodecyl β-D-fructopyranoside with the texture of the unknown phase X.

phase X) is much more viscous than the SmA* phase usually observed and the pattern is not familiar. When an isotropic sample is cooled very rapidly by taking the microscope slide out of the hot stage, no mesophase formation is observed and rapid crystallization ensues.

Decyl β-D-fructopyranoside exhibits a similar DSC pattern. Four small peaks are observed and the large high temperature peak has a double shoulder. The cooling run shows one tiny peak at 121°C (ΔH − 1.76 kJ mol^{-1}) and a large one at 118.6°C (ΔH − 26 kJ mol^{-1}). Two weak, very broad, endothermal transitions are also discernable with peaks at *c.* 55°C and *c.* 18°C, respectively. The enthalpy found for the highest temperature peak is not unusual for an I–SmA* transition in monosaccharide derivatives. When the compound is studied in the polarization microscope, the solid material appears to melt into the isotropic liquid without any intermediate phases. Upon slow cooling, at *c.* 131°C, the same swirling motions and phase texture are observed as for the phase X of the octyl derivative. On rapid cooling from the isotropic state, the transient formation of a SmA* phase is observed (bâtonnets) prior to crystallization of the sample.

The DSC heating curve of dodecyl β-D-fructopyranoside exhibits three exothermal transitions, a sharp Cr–Cr transition with the peak at 64.5°C (ΔH 22.4 kJ mol^{-1}), followed by Cr–SmA* and SmA*–I transitions with peaks at 129.8°C (ΔH 29.1 kJ mol^{-1}) and 132.3°C (ΔH *c.* 1.8 kJ mol^{-1}), respectively. The cooling curve features three endothermal transitions, with peaks at 131.7°C (I–SmA*, ΔH − 1.89 kJ mol^{-1}), 117.2°C (SmA*–X, ΔH − 25.4 kJ mol^{-1}), and 51.4°C (broad, X–Cr?, ΔH − 12.1 kJ mol^{-1}), respectively. With the exception of the presence of the enantiotropic SmA* phase, the dodecyl derivative behaves no differently from its octyl and decyl homologues. The phase transition from phase X to SmA* on heating is shown in figure 3. The texture of



(*a*)

(*b*)

(*c*)

Figure 3. (*a*) Texture of phase X of dodecyl β-D-fructopyranoside at 130°C partly covered with a cover slip; (*b*) the same preparation at 131.5°C showing phase X changing to SmA*; (*c*) the SmA* phase of the preparation at 132°C.

the X phase is identical to the textures formed by the lower homologues, and its formation is not observed in a rapid cooling run. It is most likely a higher ordered

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smectic phase, but the texture is quite different from, e.g., the SmB or E phases observed earlier in amphiphilic derivatives. No paramorphotic behaviour has been observed; the texture of the X phase appears to be independent of the orientation of the SmA* phase it arises from. Although a columnar phase cannot be ruled out completely, it appears to be highly unlikely. Even the long chain glycerol ethers (having a very small 'carbohydrate' head group) form smectic phases and, so far, a second alkyl chain has always been required to obtain a columnar mesophase.

The anomalous behaviour of the alkyl β-D-fructopyranosides may well arise from the fact that the fructopyranoside headgroup has two very distinct sides. The 'top' side of the pyranoside ring is rather hydrophobic with three adjacent *cis*-methine protons present (C-4, -5, -6), whereas three of the four hydroxyl groups, as well as the ring-oxygen are on the extremely hydrophilic 'bottom' side. This specific orientation complicates the formation of the three dimensional hydrogen-bonded network required for the stabilization of the SmA* bilayers [3], especially since the only hydroxyl group pointing to the top side is almost certainly involved in a stable intramolecular hydrogen bond (6-membered ring) with the oxygen at C-1. Lower SmA*–I transition temperatures result (compare Galema *et al.* [8]), and in this specific case a new type of aggregation is apparently induced.

3.2. *Lyotropic liquid crystalline behaviour*

Although studied to a lesser extent than the thermotropic behaviour, carbohydrate amphiphiles often form lyotropic mesophases when mixed with water (see for instance [9–13]). Stable lyotropic mesophases can only be formed above the Krafft temperature, i.e. the temperature at which the solubility of the amphiphile is sufficient to form aggregates in dilute solution. The Krafft temperature can also be viewed as the melting point of an amphiphile (or its hydrate) in water and, therefore, it can be determined by heating a small amount of sample dispersed in an excess of water in a sealed aluminum DSC-cup. A qualitative determination of the lyotropic mesophases which form at various temperatures and concentrations is conveniently achieved by controlled heating of a contact preparation of the sample and water on a microscope slide. Table 2 shows the Krafft temperatures and the lyotropic mesophases observed for each compound.

Based on our experience with a large number of carbohydrate-derived amphiphiles [14, 15], we would expect the octyl derivatives to form spherical or worm-like micelles in dilute solution, which, at higher concentrations, aggregate to form an I_1 phase (an optically isotropic mesophase consisting of closely-packed spherical micelles) or an H_1 phase (the 'normal' hexagonal mesophase consisting of worm-like micelles, which are ordered in a hexagonal pattern), respectively. This is exactly

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Table 2. The Krafft temperatures and corresponding enthalpies of several ketohexose and aldopentose derivatives and the lyotropic mesophases observed in contact preparations with water.

Compound	T_{Krafft}/°C[a]	$\Delta H_{melting}$/kJ mol^{-1}	Lyotropic mesophases[b]
Octyl α-L-sorbopyranoside	20[c]	?[c]	H_1 (39)[d]–V_1 (60)–L_α
Dodecyl α-L-sorbopyranoside	57	38.5	[~40] cr hydr (58)–[58] V_1–[60] L_α
Octyl β-D-fructofuranoside	< 10[e]	—	H_1 (55)–V_1–L_α
Dodecyl β-D-fructofuranoside	39	41.2	I_1 (58)–H_1 (40)–V_1 (75)–L_α (95)
Octyl β-D-fructopyranoside	48	24.1	[~35] cr hydr (49)–[70] L_α[f]
Decyl β-D-fructopyranoside	51[g]	29.0	[~43] cr hydr (53)–[53] V_1–[58] L_α[f]
Dodecyl β-D-fructopyranoside	59	42.5	[~47] cr hydr (58)–[58] V_1–L_α–X
Dodecyl β-D-ribofuranoside	60	43.8	L_α (myelin figures)
Dodecyl β-D-arabinopyranoside	> 100[e]	—	—

[a] Measured as an endothermic transition in a DSC heating run (2–4 mg of sample in 50 µl of H_2O).

[b] Lyomesophase with highest water content mentioned first; temperatures in square brackets indicate the appearance of a phase and round brackets indicate the disappearance of a phase. If a phase is not preceded by a number in square brackets, it appears immediately at T_{Krafft}. If there is no number in round brackets following a phase, this phase persists up to *c* 100°C, the upper limit of this type of experiment.

[c] A sharp peak is observed at 20°C, followed by an extremely broad, irregularly shaped peak.

[d] At 30°C the H_1-band starts to become narrower; a second optically isotropic phase seems to appear where the hexagonal texture has faded.

[e] No transitions observed by means of DSC.

[f] When the sample is cooled, the L_α-band changes texture and the same phase X is formed as that described for the thermotropic experiments.

[g] The DSC scan shows three endothermal transitions (19°C, 3 kJ mol^{-1}; 43°C, 10 kJ mol^{-1}; 51°C, 29 kJ mol^{-1}). The second peak probably signifies the formation of a crystalline hydrate.

what is found for octyl α-L-sorbopyranoside and octyl β-D-fructofuranoside. Octyl β-D-fructopyranoside, on the other hand, behaves quite differently. Well below the Krafft temperature, water starts to penetrate the sample and recrystallization to a hydrated form takes place. At the Krafft temperature this hydrate melts and the sample slowly dissolves, apparently without the formation of lyotropic mesophases. At approximately 70°C, a lamellar phase is formed, which is stable to 100°C. When the sample is cooled again, the lamellar region undergoes a transition to a phase that has the same appearance as phase X observed in the thermotropic experiments.

Dodecyl derivatives of monosaccharides are likely to form vesicular aggregates in dilute solution. Aggregation of these would lead to a lamellar (L_α) phase. The cubic (V_1) phase, which is often observed as an intermediate phase between the hexagonal and lamellar phases, can also be formed. When the lamellar phase is formed at the interface with the bulk aqueous phase, a beautiful phenomenon is likely to occur, namely the formation of myelin figures [10]. Myelin figures are long, worm-like protrusions that appear to grow into the aqueous phase. In myelin figures the lamellae are present as concentric cylinders. Myelin figures are indeed observed in a contact preparation of dodecyl ribofuranoside, but not in the other three compounds. Dodecyl arabinopyranoside has a Krafft temperture of higher than 100°C, and no mesophase formation is observed. After melting of the crystalline hydrate, dodecyl fructopyranoside exhibits a cubic and a lamellar phase as well as the X phase which is also observed in the thermotropic experiments. The contact preparation of the dodecyl fructofuranoside reveals a behaviour that indicates the presence of micellar aggregates in aqueous solution rather then vesicles. This means that the effective hydrated head group size of dodecyl fructofuranoside must be relatively large, probably due to the two CH_2OH groups attached to the furanose ring.

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4. Conclusions

A study of the thermotropic and lyotropic behaviour of several monoalkylated aldopentose and ketohexose derivatives has led to the discovery of a novel type of mesophase, observed only in the case of alkyl β-D-fructopyranosides and formed by anhydrous as well as hydrated samples. The nature of the phase remains unclear. Based on the shape of the molecules, one would expect the phase to be lamellar in nature. Powder X-ray experiments could probably shed more light on the structure and identity of phase X.

The authors wish to thank Mr A Sinnema and Dr J. A. Peters for recording the NMR spectra. Dr J. W. J. Gielen (Unichema International) and Dr H. W. C. Raaijmakers (Coöperatie Cosun U.A.) are thanked for fruitful discussions. Financial support by the Dutch Foundation for Technological Research SON-STW is gratefully acknowledged.

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