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

Amphiphilic and mesogenic carbohydrates XIII. Perfluoroalkylated amphiphilic liquid crystals with inositol and carbohydrate head groups

Dirk Schwäbisch[a]; Susanne Wille[a]; Martin Hein[a]; Ralf Miethchen Corresponding author[a]
[a] Department of Organic Chemistry, University of Rostock, D-18051 Rostock, Germany

Online publication date: 12 May 2010

To cite this Article Schwäbisch, Dirk , Wille, Susanne , Hein, Martin and Miethchen Corresponding author, Ralf(2004) 'Amphiphilic and mesogenic carbohydrates XIII. Perfluoroalkylated amphiphilic liquid crystals with inositol and carbohydrate head groups', Liquid Crystals, 31: 8, 1143 — 1150
To link to this Article: DOI: 10.1080/02678290410001724782
URL: http://dx.doi.org/10.1080/02678290410001724782

LIQUID CRYSTALS, VOL. 31, NO. 8, AUGUST 2004, 1143–1150

Amphiphilic and mesogenic carbohydrates XIII. Perfluoroalkylated amphiphilic liquid crystals with inositol and carbohydrate head groups†, ‡

DIRK SCHWÄBISCH, SUSANNE WILLE, MARTIN HEIN and RALF MIETHCHEN*

Department of Organic Chemistry, University of Rostock, Albert-Einstein-Str. 3a, D-18051 Rostock, Germany

(*Received 19 February 2004; accepted 7 April 2004*)

New perfluoroalkylated amphiphiles based on carbohydrates (D-xylose, D-ribose, D-glucose) and on *myo*-inositol were synthesized and their thermotropic liquid crystalline behaviour was investigated. The introduction of perfluoroalkyl groups was carried out by radical addition of 1-iodoperfluoroalkanes to *O*- and *C*-allyl-substituted sugar and inositol derivatives.

1. Introduction

In addition to acyclic polyols, carbonic, phosphonic and sulphonic acids, carbohydrates have also often been used as polar head groups of amphiphilic liquid crystals. The latter are readily available and well suited as chiral building blocks. The number of reviews describing carbohydrate derived liquid crystals indicates the increased interest in this topic [1–5].

It has been shown by this group that perfluoroalkylated single-tailed sugar-amphiphiles form more stable liquid crystalline phases than their hydrocarbon counterparts. This is due to a higher intramolecular contrast between the hydrophilic and hydrophobic molecular parts and the higher stiffness of perfluoroalkyl chains compared with their alkyl analogues [6, 7]. A good example of this is the fact that even perfluorobutyl-substituted carbohydrate derivatives tend to form stable liquid crystalline SmA-phases [8]. In a recent review, the mesogenic properties of perfluoroalkylated carbohydrates are discussed in more detail [9].

Here, we report the influence of different hydrophilic head groups on the mesomorphic behaviour of perfluoroalkyl-substituted amphiphiles and the effects on the thermal behaviour when the perfluoroalkyl chain is linked to different positions of the hydrophilic head group. In addition, *C*-glycosidic and *O*-glycosidic derivatives are compared. For this, allylated D-xylose, D-ribose, D-glucose and *myo*-inositol derivatives were perfluoroalkylated using the well known dithionite method of perfluoroalkylation [10–12].

*Author for correspondence;
e-mail: ralf.miethchen@chemie.uni-rostock.de

†For part XII see ref.[19].

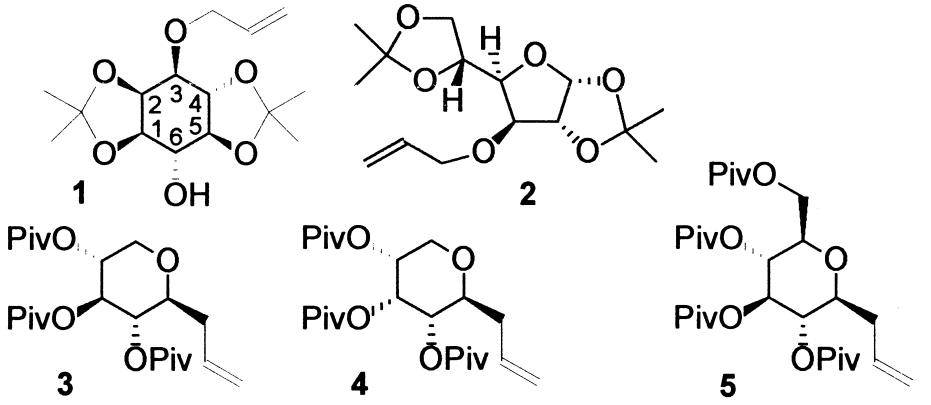
‡Dedicated to Prof. Dr. G.-V. Röschenthaler on the occasion of his 60th birthday

2. Experimental

The starting materials for the desired amphiphilic target compounds are 3-*O*-allyl-1,2:4,5-di-*O*-isopropylidene-DL-*myo*-inositol (**1**), 3-*O*-allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**), 3-(2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl) propene (**3**), 3-(2,3,4-tri-*O*-pivaloyl-β-D-ribopyranosyl) propene (**4**), and 3-(2,3,4,6-tetra-*O*-pivaloyl-β-D-glucopyranosyl) propene (**5**). They were synthesized by well known methods. Thus, the allylated inositol derivative **1** was generated by a modified procedure of Liu and coworkers [13] using a mixture of barium oxide and barium hydroxide octahydrate as base (scheme 1). It was confirmed by several multidimensional NMR investigations that the sterically more hindered hydroxy group in position 3 of the ring was exclusively allylated. The 3-*O*-allyl derivative **2** is easily available by alkylation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose with allyl bromide in the presence of sodium hydride [14]. The allylated *C*-glycosides **3**–**5** were obtained from the corresponding per-*O*-pivaloylated sugars by treatment with allyltrimethylsilane in the presence of boron trifluoride according to a procedure reported by Giannis and Sandhoff for acetylated precursors [15]. Pivaloylated starting materials gave higher yields then acetylated educts.

The allyl derivatives **1**–**5** were perfluoroalkylated by dithionite-mediated addition of the corresponding 1-iodoperfluoroalkane and the crude products obtained

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001724782



Scheme 1. Allylated starting materials **1**–**5**.

were subsequently hydrodeiodinated by treatment with $Pd/C/H_2$ or Bu_3SnH/AIBN (scheme 2). The tributyltin hydride method worked better in the case of *C*-glycosidic-linked addition products, especially with the pivaloylated glucose derivatives. Certainly, the products **7b** and **7c** were already synthesized by Huang and Xie [10], but the data published by these authors are imprecise and no values for phase transition temperatures are given.

Finally, the amphiphilic target compounds were generated by deprotection of the compounds **6a**–**d**, **7a**–**d**, **8a**–**c**, **9b**, and **10b, c**. The isopropylidene groups of **6a**–**d** and **7a**–**d** were removed with aqueous trifluoroacetic acid yielding compounds **11a**–**d** and **12a**–**d**, respectively. Depivaloylation was achieved by heating the compounds **8a**–**c**, **9b** and **10b, c** in a methanolic solution of potassium *t*-butylate (scheme 2). The 3-*O*-alkylated amphiphiles **16a**–**d** (scheme 3) were generated from the corresponding diisopropylidene precursor [16].

3. Results and discussion

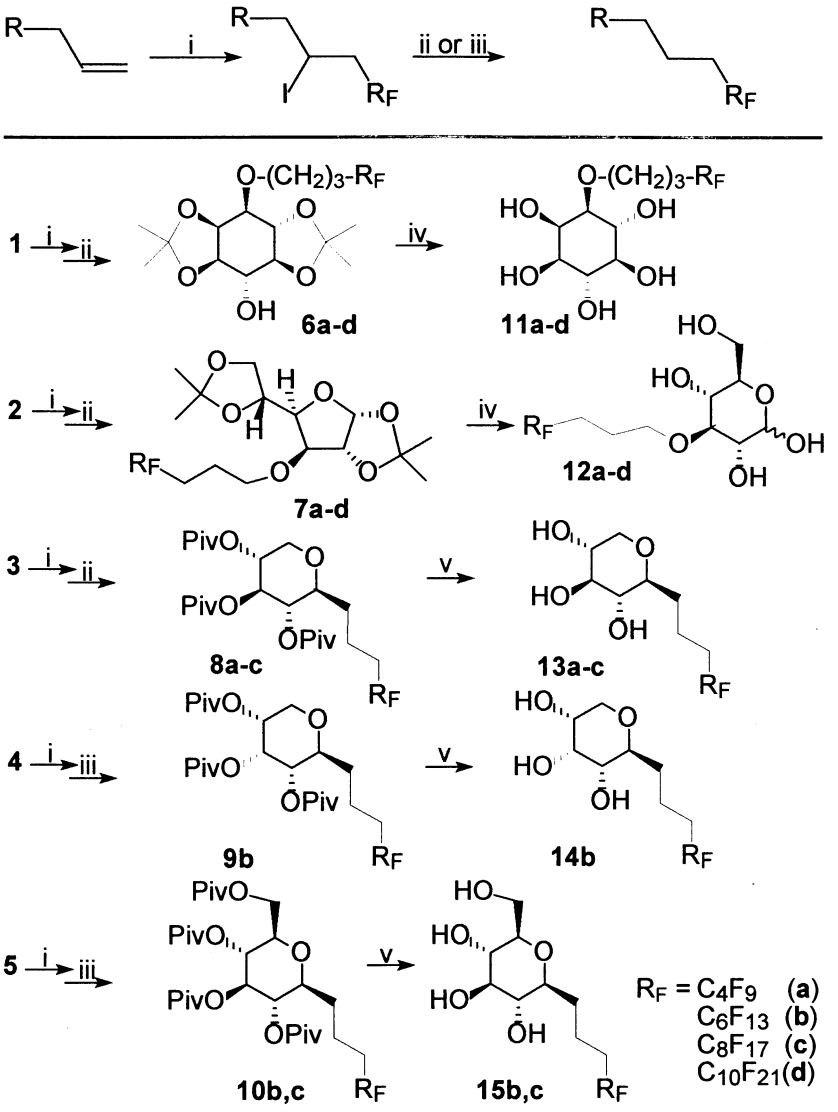
The amphiphilic compounds **11**–**15** form smectic A phases with typical fan-shaped textures. In some cases these compounds tend to form homeotropic alignments, but nevertheless 'stepped drops' are observed, for samples without cover slides. A comparison of the thermal data of the perfluoroalkylated amphiphiles **12a**–**d** with those of their hydrocarbon counterparts **16a**–**d** shows that the fluorinated mesogens form the more stable liquid crystalline phases, i.e. show higher clearing points (figure 1). The higher stability of the phases seen for the fluorinated amphiphiles results from the higher stiffness (loss of conformational freedom) of perfluoroalkyl chains compared with alkyl chains. A second effect is the higher tendency of these amphiphiles to separate into hydrophilic and hydrophobic regions (higher intramolecular contrast). The comparison of the thermal data of the 3-*O*-perfluoroalkylpropyl-D-glucoses **12a**–**d** with the regioisomeric perfluoroalkylpropyl β-D-glucopyranosides **17a**–**d** [18–20] (scheme 3) reveals higher clearing temperatures for the glycosides indicating higher mesophase stabilities (figure 2).

It has already been shown that amphiphilic alkyl glucosides show higher clearing temperatures than the regioisomeric 3-*O*-alkyl-D-glucoses [17]. This results from differences in the hydrogen bonding network within the hydrophilic region of the bilayer and on the pyranoidic and furanoidic forms of **12a**–**d** being in equilibrium, respectively. As expected, the inositol derivatives **11a**–**d** form more stable supramolecular phases than the tetrahydroxy derivatives **12a**–**d**, because, among other factors, the fifth free hydroxy group additionally increased the hydrogen bond network (figure 3).

All four homologues **11a**–**d** show enantiotropic mesogenic behaviour and form smectic A phases. The assignment of the phase proved to be difficult, because the compounds (like **12a**–**d**) tend to align homeotropically. It is noteworthy, that the two higher homologues **11c**,**d** and the higher glucose homologues **12b**–**d** decompose close to their clearing temperatures. It follows from this that the measured thermal data of these mesogens are affected by small amounts of impurities.

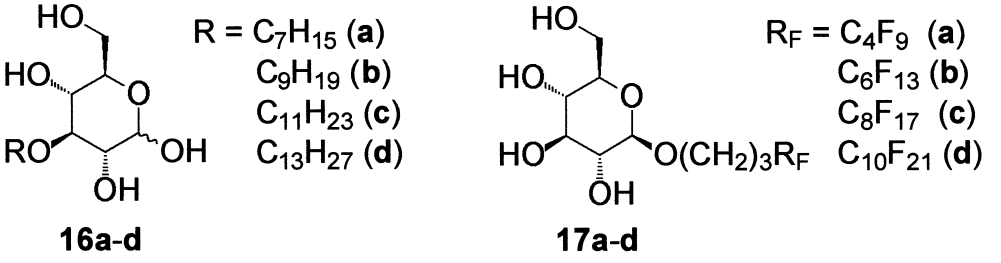
The *C*-glycosidic amphiphiles **13**–**15** form, with the exception of the perfluorohexyl derivative **14b**, enantiotropic SmA phases. The monotropic phase transition of **14b** (the SmA phase appears only on supercooling) compared with the *xylo*-derivative **13b**, indicates that **13b** forms a more effective hydrogen bond network within its bilayer, which arises from the stereochemical advantage of the OH group at C-atom 3.

As expected, compared with the pentose-based mesogens, *gluco*-configured liquid crystals have higher clearing points. In particular, the comparison between



Scheme 2. Perfluoroalkylation, hydrodeiodination, and deprotection of the allylated precursors **1**–**5**; i = 1-iodoperfluoroalkane, $Na_2S_2O_4$; $NaHCO_3$, H_2O/MeCN, 0°C → rt, 1–3 h; ii = H_2, Pd/C, MeOH, EtOAc, Et_3N, rt, 4 h; iii = Bu_3SnH, AIBN, toluene, 80°C, 1–2 h; iv = 80% TFA; v = MeOH, tertBuOK.

the *xylo*-derivatives **13b** and **13c** with **15b**,**c** indicates that this stabilization is essentially caused by the additional hydroxy group. Much more interesting is the comparison of the liquid crystalline properties of *O*- and *C*-fluoroalkylated glucosides. The table shows that the *C*-glycosides have an increased mesophase



Scheme 3. 3-*O*-Alkylglucoses **16a**–**d** [17] and 3-perfluoroalkylpropyl glucosides **17a**–**d** [18–20].

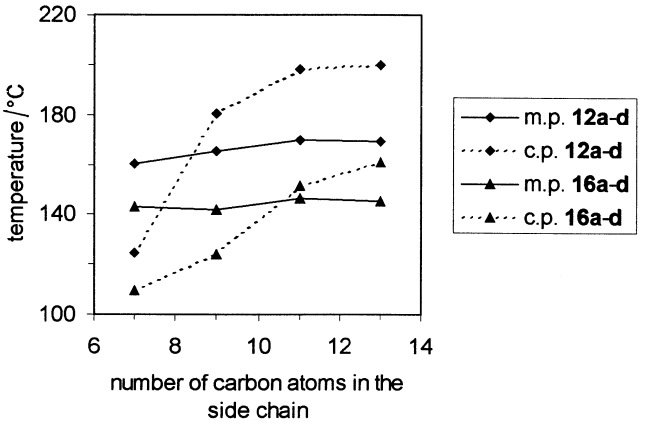


Figure 1. Thermal data for perfluoroalkylated amphiphiles **12a–d** and their hydrocarbon analogues **16a–d** (m.p. = melting point, c.p. = clearing point).

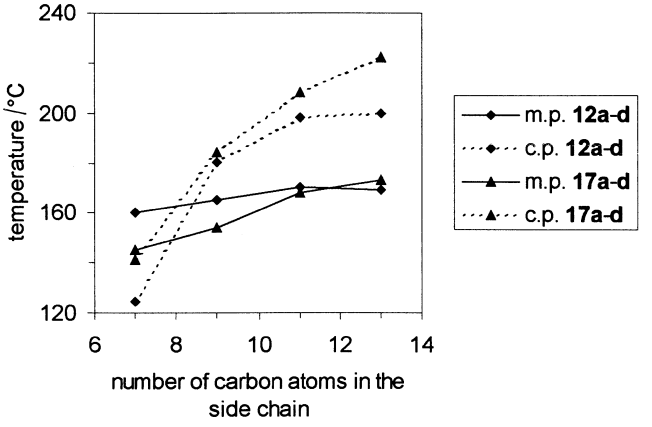


Figure 2. Thermal data for compounds **12a–d** and fluoroalkylated glycosides **17a–d** (m.p. = melting point, c.p. = clearing point).

stability over the *O*-glycosides with an identical perfluoroalkylpropyl chain. Thus, *O*-glycoside **17b** ($R_F = C_6F_{13}$) clears at 184°C, whereas the clearing temperature of *C*-glycoside **15b** ($R_F = C_6F_{13}$) is observed at 207°C. This behaviour may possibly be explained by the different number of spacer atoms between head group and perfluoroalkyl chain. The missing oxygen atom should decrease the flexibility of the side chain causing a higher stabilization of the mesophase. Furthermore, differences in geometry and the odd-even effect may contribute to the stabilization.

4. Conclusions

The introduction of a perfluoroalkylpropyl to replace an alkyl chain in amphiphlic liquid crystals leads to a remarkable stabilization of the resulting mesophases. Changes in the regio- (compare **12a–d** with **17a–d**) or

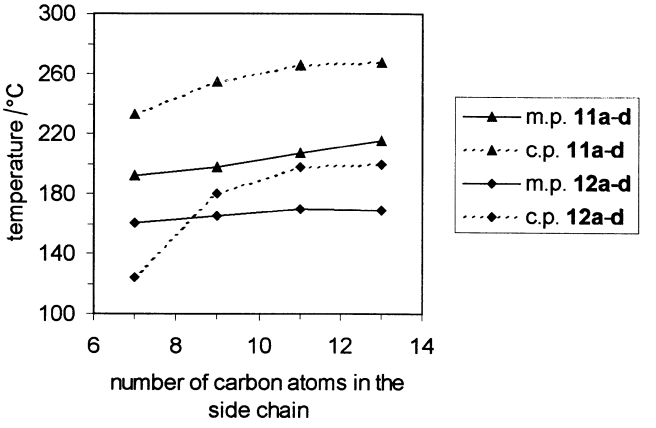


Figure 3. Thermal data for the inositol derivatives **11a–d** and the amphiphilic glucose derivatives **12a–d** (m.p. = melting point, c.p. = clearing point).

Table 1. Thermal data for the fluoroalkylated *C*-glycosides **13–15**.

Compound	Phase transitions: transition points (°C) determined by polarizing microscopy.
13a	Cr 96, SmA 104.5, I
13b	Cr 120, SmA 123, I
13c	Cr 140, SmA 148, I
14b	(SmA 104–108) Cr 108, I
15b	Cr 147, SmA 207–208, I
15c	Cr 151–153, SmA 224–227, I

stereo-chemistry (compare **13b** with **14b**) of the polar head group have a strong influence on the mesophase stability.

The *C*-glucosidic amphiphiles **15b**,**c** show the most stable thermotropic mesophases of all the glucose derivatives investigated by ourselves. Furthermore, the increased thermal stability of these compounds is noticeable, especially, when compared with perfluoroalkylated thioglycosides [19, 20].

5. Synthesis protocols

The reactions were followed by thin layer chromatography using precoated alumina sheets (Merck 60, F254); detection was effected by spraying with 10% methanolic sulphuric acid solution and subsequent thermal treatment or by spraying with 5% methanolic molybdophosphoric acid and subsequent thermal treatment. Silica Gel 60 (0.062–0.2 mm, Merck) and Silica Gel 60 (40–63 μm, Merck), respectively, were used for column chromatographic separations. All solvents were purified and dried using standard procedures [21]. Melting and clearing points were determined with a

Leitz Laborlux 12 Pol microscope equipped with a Mettler FP 90 hot stage. Additional DSC measurements were carried out using Perkin-Elmer DSC 7 and Mettler TA-3000 differential scanning calorimeters. For the identification of mesophases we compared the optical textures (polarizing microscope) with textures from the literature [22]. Optical rotations were measured on a polarimeter Polar LμP (IBZ Messtechnik) and the NMR spectra were recorded on a Bruker AC-250 and an AVANCE 500 using TMS and CCl_3F as internal standards, respectively. NMR data are given for only one example in a homologous series (significant differences within a homologous series are only observable for ^{19}F NMR data). Chemicals: 1-iodoperfluoroalkanes (ABCR), sodium dithionite (Fluka), palladium on charcoal (FLUKA), trifluoroacetic acid (ABCR), tributylstannane (FLUKA).

5.1. *Perfluoroalkylations*

In a typical procedure, to a cooled (0°C) and stirred solution of 1.33 mmol of the allyl compound in 6 ml acetonitrile and 3 ml water, 360–680 mg (4.3–8.1 mmol) of sodium bicarbonate were added at 0°C under argon. Then 3.33 mmol of the appropriate 1-iodoperfluoroalkane and 420–470 mg (2.4–2.7 mmol) of sodium dithionite were added and the mixture allowed to warm slowly to room temperature. After completion of the reaction (approx. 1.5 h, tlc control) 100 ml of diethyl ether were poured into the reaction mixture. The resulting solution was washed with brine and water (50 ml of each), before drying over sodium sulphate. For the products containing acid-sensitive isopropylidene protecting groups, 2 ml of triethylamine were added to the solution. After filtration the solution was evaporated to dryness under reduced pressure. The resulting crude product was used without further purification for the hydrodeiodination step which was carried out according to §5.2 (for starting materials **1**–**3**) and 5.3 (for starting materials **4**,**5**).

5.2. *Catalytic hydrodeiodination*

The crude product (see §5.1) was dissolved in a mixture of 10 ml ethanol and 10 ml ethyl acetate, and after addition of some drops of triethylamine (derivatives with isopropylidene protecting groups) or 100 mg of sodium acetate (derivatives with pivaloyl protecting groups) and 40 mg palladium on charcoal (10%) the iodine was cleaved off in a hydrogen atmosphere (1 atm) overnight (at least 3.5 h). After removal of the charcoal the solution was concentrated and the resulting product purified via column chromatography.

5.3. *Radical hydrodeiodination*

The crude addition product (see §5.1) was dissolved or suspended in 25 ml of abs. toluene. Then 0.1 mol eq AIBN (α,α′-azobisisobutyronitrile) and 1.2 mol eq Bu_3SnH were added and the mixture was heated at 80°C for 1–2 h. After complete conversion (tlc control) 25 ml of a concentrated aqueous KF solution were added and the mixture stirred for 30 min to convert the Bu_3SnCl into the insoluble Bu_3SnF. The solution was filtered, the solid washed twice with toluene and the organic phase separated. After washing with water and brine the organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure. The residue was purified by column chromatography.

6a: 77% colourless crystals, m.p. 99°C (MeOH/H_2O). Anal. for $C_{19}H_{25}F_9O_6$ (520.39): calc. C 43.85, H 4.84; found C 44.01, H 4.85%. ^1H NMR (250 MHz, $(CD_3)_2CO$): δ 4.54 (m, $^3J_{1,2}=5$ Hz, $^3J_{2,3}=3.7$ Hz, 1H, H-2); 4.53 (m, $^3J_{6,OH}=4.6$ Hz, 1H, OH); 3.99 (dd, $^3J_{1,6}=6.7$ Hz, 1H, H-1); 3.89–3.73 (m, 5H, H-3, H-4, H-6, OCH_2); 3.34 (m, $^3J_{4,5}=10.7$ Hz, 1H, H-5); 2.51–2.25 (m, 2H, CH_2); 1.96–1.83 (m, 2H, CH_2); 1.43 (s, 3H, CH_3); 1.37 (s, 3H, CH_3); 1.36 (s, 3H, CH_3); 1.29 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $(CD_3)_2CO$): δ 111.8, 109.8 (2 acetal-C); 83.3 (C-1); 80.0 (C-5); 77.7, 77.4, 76.8 (C-2, C-3, C-4); 74.9 (C-6); 68.4 (OCH_2); 28.5 (CH_3); 28.3 (CH_2); 27.3, 27.2, 26.2 (3 CH_3), 21.7 (CH_2). ^{19}F NMR (235 MHz, $(CD_3)_2CO$): δ −81.7 (t, $J_{F,F}=11$ Hz, CF_3); −114.7 (s (br), CF_2); −124.8 (s (br), CF_2); −126.4 (s (br), CF_2).

6b: 76% colourless crystals, m.p. 101°C (MeOH/H_2O). Anal. for $C_{21}H_{25}F_{13}O_6$ (620.40): calc. C 40.66, H 4.06; found C 40.66, H 4.11%.

6c: 81% colourless crystals, m.p. 115°C (MeOH/H_2O). Anal. for $C_{23}H_{25}F_{17}O_6$ (720.42): calc. C 38.35, H 3.50; found C 38.39, H 3.37%.

6d: 56% colourless crystals, m.p. 129°C (MeOH/H_2O). Anal. for $C_{25}H_{25}F_{21}O_6$ (820.44): calc. C 36.60, H 3.07; found C 36.62, H 2.90%.

7a: 66% colourless oil. Anal. for $C_{19}H_{25}F_9O_6$ (520.38): calc. C 43.85, H 4.84; found C 43.90, H 4.52%. ^1H NMR (250 MHz, $CDCl_3$): δ 5.86 (d, $^3J_{1,2}=3.7$ Hz, 1H, H-1); 4.51 (d, $^3J_{2,3}=3.7$ Hz, 1H, H-2); 4.25 (ddd, $^3J_{4,5}=8.5$ Hz, $^3J_{5,6a}=5.8$ Hz, $^3J_{5,6b}=5.6$ Hz, 1H, H-5); 4.08 (t, 1H, H-4); 4.06 (dd, $^2J_{6a,6b}=8.6$ Hz, 1H, H-6a); 3.97 (dd, 1H, H-6b); 3.87 (m, 1H, H-3); 3.74 (m, 1H, OCH_2a); 3.57 (m, 1H, OCH_2b); 3.22 (m, 2H, CH_2); 2.57 (m, 2H, CH_2); 1.48, 1.40 (2s, 6H, 2 CH_3); 1.30 (s, 6H, 2 CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ 111.9, 109.1 (2 acetal-C); 105.3 (C-1); 82.3, 82.1, 81.2, 72.2 (C-2, C-3, C-4, C-5); 68.8 (OCH_2); 67.5 (C-6); 27.7 (t, $^2J_{C,F}=22.2$ Hz, CH_2); 26.8 (2 CH_3); 26.2, 25.0 (2 CH_3); 26.7 (CH_2). ^{19}F NMR (235 MHz, $CDCl_3$): δ −80.8 (t, $^3J_{F,F}=10$ Hz, CF_3);

−114.4 (t, $^3J_{F,F}=12$ Hz, CF_2); −124.2 (m, CF_2); −125.9 (t, $^3J_{F,F}=13$ Hz, CF_2).

7b: 65% colourless oil. Anal. for $C_{21}H_{25}F_{13}O_6$ (620.40): calc. C 40.66, H 4.06; found C 40.68, H 4.20%.

7c: 60% colourless oil. Anal. for $C_{23}H_{25}F_{17}O_6$ (720.42): calc. C 38.35, H 3.50; found C 38.36, H 3.55%.

7d: 22% colourless oil. Anal. for $C_{25}H_{25}F_{21}O_6$ (820.43): calc. C 36.60, H 3.07; found C 36.73, H 3.21%.

8a: 58% colourless crystals, m.p. 79–82°C (heptane). Anal. for $C_{27}H_{39}F_9O_7$ (646.58): calc. C 50.16, H 6.08; found C 50.45, H 6.13%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.27 (t, $^3J_{3',4'}=9.5$ Hz, 1H, H-3′); 4.95 (ddd, $^3J_{4',5'a}=5.7$, $^3J_{4',5'b}=10.4$ Hz, 1H, H-4′); 4.88 (t, $^3J_{2',3'}=9.5$ Hz, 1H, H-2′); 4.06 (dd, $^2J_{5'a,5'b}=11.0$ Hz, 1H, H-5′a); 3.34 (ddd, $^3J_{1',3a}=3.4$, $^3J_{1',3b}=7.8$, $^3J_{1',2'}=9.8$ Hz, 1H, H-1′); 3.22 (t, 1H, H-5′b); 2.17–1.91 (m, 2H, H-1a, H-1b); 1.91–1.73 (m, 1H, H-3a); 1.73–1.60 (m, 1H, H-3b); 1.60–1.42 (m, 1H, H-2a, H-2b); 1.14, 1.13, 1.11 (3s, 27H, 3 $C(CH_3)_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ 177.7, 177.6, 177.3 (3 C–O); 78.4 (C-1′); 73.3 (C-3′); 71.7 (C-2′); 69.7 (C-4′); 67.1 (C-5′); 39.1 (3 $\underline{C}(CH_3)_3$); 31.2 (C-3); 30.9 (t, $^2J_{C\text{-}1,F}=$ 22.6 Hz, C-1); 27.5, 27.4 (3 $C(\underline{C}H_3)_3$); 16.5 (C-2). ^{19}F NMR (235 MHz, $CDCl_3$): $\delta=-80.8$ (s (br), CF_3); −114.3 (m, CF_2); −124.3 (s (br), CF_2); −125.8 (m, CF_2).

8b: 49% colourless crystals, m.p. 53–54°C (heptane). Anal. for $C_{29}H_{39}F_{13}O_7$ (746.60): calc. C 46.65, H 5.27; found C 46.80, H 5.30%.

8c: 45% colourless crystals, m.p. 53°C (heptane). Anal. for $C_{31}H_{39}F_{17}O_7$ (846.61): calc. C 43.98, H 4.64; found C 44.34, H 4.72%.

9b: 81% colourless crystals, m.p. 80–81°C (heptane). Anal. for $C_{29}H_{39}F_{13}O_7$ (746.60): calc. C 46.65, H 5.27; found C 46.11, H 5.28%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.62 (t, $^3J_{3',4'}=2.6$ Hz, 1H, H-3′); 4.96 (dq, $^3J_{4',5'a}=$ 5.4, $^3J_{4',5'b}=10.8$ Hz, 1H, H-4′); 4.70 (dd, $^3J_{2',3'}=2.7$, $^3J_{1',2'}=10.0$ Hz, 1H, H-2′); 3.85 (dd, $^2J_{5'a,5'b}=10.6$ Hz, 1H, H-5′a); 3.70–3.59 (m, 1H, H-1′); 3.59 (t, 1H, H-5′b); 2.20–1.77 (m, 2H, H-1a, H-1b); 1.76–1.48 (m, 2H, H-3a, H-3b); 1.48–1.28 (m, 2H, H-2a, H-2b); 1.26, 1.13, 1.12 (3 s, 27H, 3 $C(CH_3)_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ 176.9, 176.8, 176.7 (3 C–O); 73.3 (C-1′); 70.2, 67.7, 67.0 (C-2′, C-3′, C-4′); 63.6 (C-5′); 39.1, 38.7 (3 $\underline{C}(CH_3)_3$); 30.7 (t, $^2J_{C\text{-}1,F}=21.5$ Hz, C-1); 29.1 (C-3); 27.3, 27.0 (3 $C(\underline{C}H_3)_3$); 16.3 (C-2). ^{19}F NMR (235 MHz, $CDCl_3$): δ −80.6 (s, CF_3), −114.1, −121.8, −122.7, −123.4, −126.0 (5 s (br), 5 CF_2).

10b: 53% colourless crystals, m.p. 117–118°C (heptane). Anal. for $C_{35}H_{49}F_{13}O_9$ (860.74): calc. C 48.84, H 5.74; found C 48.96, H 6.02%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.38 (t, $^3J_{3',4'}=9.7$ Hz, 1H, H-3′); 5.07 (dd, $^3J_{1',2'}=6.1$, $^3J_{2',3'}=9.8$ Hz, 1H, H-2′); 5.00 (dd, $^3J_{4',5'}=9.8$ Hz, 1H, H-4′); 4.24–4.12 (m, 1H, H-1′); 4.07 (d, $^3J_{5',6'a}=2.2$, $^2J_{6'a,6'b}=12.3$ Hz, 1H, H-6′a); 4.04 (d, $^3J_{5',6'b}=5.9$ Hz, 1H, H-6′b); 3.77 (ddd, 1H, H-5′); 2.23–1.89 (m, 3H, H-3a, H-1a, H-1b); 1.89–1.70 (m, 1H, H-3b); 1.70–1.33 (m, 2H, H-2a, H-2b); 1.19, 1.15, 1.11 (3 s, 36H, 4 $C(CH_3)_3$). ^{13}C NMR (63 MHz, $CDCl_3$): δ 178.1, 177.2, 177.0, 176.6 (4 C–O); 72.2, 70.6, 69.9, 69.0, 68.5 (C-1′, C-2′ C-3′, C-4′, C-5′); 62.7 (C-6′); 38.7 (4 $\underline{C}(CH_3)_3$); 30.3 (t, $^2J_{C\text{-}1,F}=22.3$ Hz, C-1); 27.1, 27.0 (4 $C(\underline{C}H_3)_3$); 24.4 (C-3); 16.1 (C-2). ^{19}F NMR (235 MHz, $CDCl_3$): δ −80.6 (s, CF_3); −114.0, −121.7, −122.7, −123.3, −125.9 (5s (br), 5 CF_2).

10c: 38% colourless crystals, m.p. 116–118°C (heptane). Anal. for $C_{37}H_{49}F_{17}O_9$ (960.76): calc. C 46.26, H 5.14; found C 46.33, H 5.40.

5.4. *Removal of isopropylidene groups*

A suspension of 0.96 mmol of the diisopropylidene-protected compound in 50 ml aqueous trifluoroacetic acid was stirred at room temperature. When the starting material was dissolved stirring was continued for 2 h. The solvent was then evaporated off and remaining residues were codistilled with ethanol and toluene (3 times each). The resulting crude product was recrystallized from ethyl acetate.

11a: 98% colourless crystals, m.p. 192°C-SmA-233°C (EtOAc). Anal. for $C_{13}H_{17}F_9O_6$ (440.26): calc. C 35.47, H 3.89; found C 35.57, H 3.92%. ^{1}H NMR (250 MHz, $(CD_3)_2SO$): δ 4.59 (m, 2H, 2 OH); 4.52 (d, $^3J_{H,OH}=3.5$ Hz, 1H, OH); 4.47 (d, $^3J_{2,OH}=3.5$ Hz, 1H, OH-2); 4.40 (d, $^3J_{1,OH}=5.4$ Hz, 1H, OH-1); 3.86 (m, $^3J_{1,2}=^3J_{2,3}=2.3$ Hz, 1H, H-2); 3.57 (m, 2H, OCH_2); 3.46–3.31 (m, 2H, H-6, H-4 or H-5); 3.09 (dd, $^3J_{1,2}=2.3$ Hz, $^3J_{1,6}=9.5$ Hz, 1H, H-1); 2.92 (m, 2H, H-3, H-4 or H-5); 2.36 (m, 2H, CH_2); 1.76 (m, 2H, CH_2). ^{13}C NMR (63 MHz, $(CD_3)_2SO$): δ 80.1, 75.1, 72.3, 71.5, 69.1, 69.0 (C-1 – C-6); 67.7 (OCH_2); 27.4 (t, $^2J_{C,F}=22$ Hz, CH_2); 21.0 (CH_2). ^{19}F NMR (235 MHz, $(CD_3)_2SO$): δ −80.8 (s, CF_3); −113.7 (s, CF_2); −124.1 (s, CF_2); −125.9 (s, CF_2).

11b: 98% colourless crystals, m.p. 198°C-SmA-254°C (EtOAc). Anal. for $C_{15}H_{17}F_{13}O_6$ (540.27): calc. C 33.35, H 3.17; found C 33.49, H 3.27%.

11c: 98% colourless crystals, m.p. 207°C-SmA-266°C (EtOAc). Anal. for $C_{17}H_{17}F_{17}O_6$ (640.29): calc. C 31.89, H 2.68; found C 31.99, H 2.88%.

11d: 97% colourless crystals, m.p. 216°C-SmA-267°C (EtOAc). Anal. for $C_{19}H_{17}F_{21}O_6$ (740.30): calc. C 30.83, H 2.31; found C 30.80, H 2.31%.

12a: 87% colourless crystals, m.p. 160°C (EtOAc). Anal. for $C_{13}H_{17}F_9O_6$ (420.26): calc. C 35.47, H 3.89;

found C 35.22, H 3.75%. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ 6.86 (d, $^3J_{OH,1}=6.3$ Hz, 1H, OH-1); 4.83 (m, 2H, OH-3, OH-4); 4.46 (t, $^3J_{OH,6}=5.7$ Hz, 1H, OH-6), 4.72 (t, $^3J_{1,2}=6.9$ Hz, 1H, H-1), 3.69–3.61 (m, 3H, OCH_2, H-6a); 3.41 (m, $^3J_{5,6b}=6.0$ Hz, 1H, H-6b); 3.09 (m, 2H, H-3, H-5); 2.95 (m, 2H, H-2, H-4); 2.46–2.23 (m, 2H, CH_2); 1.79–1.69 (m, 2H, CH_2). ^{13}C NMR (63 MHz, $(CD_3)_2SO$): δ 96.8 (C-1); 85.2 (C-2 or C-4); 76.6 (C-3 or C-5); 74.5 (C-2 or C-4); 70.2 (OCH_2); 69.6 (C-3 or C-5); 61.0 (C-6); 27.0 (t, $^2J_{C,F}=22$ Hz, CH_2); 20.8 (CH_2). ^{19}F NMR (235 MHz, $(CD_3)_2SO$): δ −81.2 (t, $^3J_{F,F}=10$ Hz, CF_3); −114.4 (m, CF_2); −124.1 (m, CF_2); −125.8 (m, CF_2).

12b: 88% colourless crystals, m.p. 165°C-SmA-180°C (EtOAc). Anal. for $C_{15}H_{17}F_{13}O_6$ (540.27): calc. C 33.35, H 3.17; found C 33.37, H 3.05%.

12c: 87% colourless crystals, m.p. 170°C-SmA-195°C (EtOAc). Anal. for $C_{17}H_{17}F_{17}O_6$ (640.29): calc. C 31.89, H 2.68; found C 31.89, H 2.75%.

12d: 88% colourless crystals, m.p. 169°C-SmA-200°C decomp.(EtOAc). Anal. for $C_{19}H_{17}F_{21}O_6$ (740.30): calc. C 30.83, H 2.31; found C 31.03, H 2.12%.

5.5. *Removal of pivaloyl groups*

The pivaloylated compound (0.3–0.5 mmol) was dissolved in 10 ml of abs. methanol and then KO^{t}Bu (1/10 mol eq per pivaloyl group to remove) was added. The mixture was stirred for 1–2 days at 50°C. After complete conversion (tlc control) the solution was cooled to rt and neutralized by addition of IR-120 cation exchange resign (H^+ form). After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography. Further purification was achieved by recrystallization from acetonitrile/methanol mixtures.

13a: 70% colourless crystals, m.p. 96°C-SmA-104.5°C (toluene). Anal. for $C_{12}H_{15}F_9O_4$ (394.23): calc. C 36.56, H 3.84; found C 37.12, H 3.91%. ^{1}H NMR (250 MHz, CD_3OD): δ 3.83 (dd, $^3J_{4',5'a}=5.3$, $^2J_{5'a,5'b}=10.9$ Hz, 1H, H-5′a); 3.40 (ddd, $^3J_{3',4'}=8.9$, $^3J_{4',5'b}=10.5$ Hz, 1H, H-4′); 3.25–3.17 (m, $^3J_{2',3'}=8.5$ Hz, 1H, H-3′); 3.14–2.95 (m, 3H, H-1′, H-2′, H-5′b); 2.27–2.00 (m, 2H, H-1a, H-1b); 2.00–1.71 (m, 2H, H-3a, H-3b); 1.71–1.54 (m, 1H, H-2a); 1.54–1.36 (m, 1H, H-2b). ^{13}C NMR (63 MHz, CD_3OD): δ 81.3, 79.9, 75.4, 71.3 (C-1′, C-2′, C-3′, C-4′); 71.1 (C-5′); 32.2 (C-3); 31.7 (t, $^2J_{C\text{-}1,F}=22$ Hz, C-1); 17.5 (t, $^3J_{C\text{-}2,F}=4$ Hz, C-2). ^{19}F NMR (235 MHz, CD_3OD): δ −79.3 (s, CF_3); −112.3, −122.2, −123.9 (3s, 3 CF_2).

13b: 72% colourless crystals, m.p. 120°C-SmA-123°C (acetonitrile/methanol). Anal. for $C_{14}H_{15}F_{13}O_4$ (494.24): calc. C 34.02, H 3.06; found C 34.25, H 3.07%.

13c: 86% colourless crystals, m.p. 140°C-SmA-148°C (acetonitrile/methanol). Anal. for $C_{16}H_{15}F_{17}O_4$ (594.26): calc. C 32.34, H 2.54; found C 32.91, H 2.29%.

14b: 86% colourless crystals, m.p. 108°C (toluene). Anal. for $C_{14}H_{15}F_{13}O_4$ (494.24): calc. C 34.02, H 3.06; found C 34.34, H 2.93%. ^{1}H NMR (250 MHz, CD_3OD): δ 3.98 (t, $^3J_{2',3'}=2.6$ Hz, 1H, H-3′); 3.64–3.52 (m, $^3J_{3',4'}=2.7$ Hz, 2H, H-4′, H-5′a); 3.51–3.31 (m, 2H, H-1′, H-5′b); 3.16 (dd, $^3J_{1',2'}=9.6$ Hz, 1H, H-2′); 2.28–2.02 (m, 2H, H-1a, H-1b); 1.95–1.71 (m, 2H, H-3a, H-3b); 1.70–1.53 (m, 1H, H-2a); 1.49–1.29 (m, 1H, H-2b). ^{13}C NMR (63 MHz, CD_3OD): δ 75.6 (C-1′); 72.7, 72.4, 69.1 (C-2′, C-3′, C-4′); 66.5 (C-5′); 32.2 (C-3); 31.9 (t, $^2J_{C\text{-}1,F}=21.8$ Hz, C-1); 17.6 (C-2). ^{19}F NMR (235 MHz, CD_3OD): δ −78.2 (s, CF_3); −111.3, −118.8, −119.7, −120.4, −123.2 (5s (br), 5 CF_2).

15b: 93% colourless crystals, m.p. 147°C-SmA-208°C (acetonitrile/methanol). Anal. for $C_{15}H_{17}F_{13}O_5$ (524.27): calc. C 34.36, H 3.27; found C 34.86, H 3.32%. ^{1}H NMR (250 MHz, CD_3OD): δ 3.87 (m, $^3J_{1',3a}=4.7$, $^3J_{1',2'}=9.6$ Hz, 1H, H-1′); 3.75 (dd, $^3J_{5',6'a}=2.4$, $^2J_{6'a,6'b}=11.7$ Hz, 1H, H-6a); 3.64–3.52 (m, 2H, H-2′, H-6b); 3.47 (t, $^3J_{3',4'}=8.9$ Hz, 1H, H-3′); 3.36 (ddd, $^3J_{5',6'b}=5.6$, $^3J_{4',5'}=8.2$ Hz, 1H, H-5′); 3.21 (dd, $^3J_{3',4'}=9.4$ Hz, 1H, H-4′); 2.33–2.07 (m, 2H, H-1a, H-1b); 1.87–1.53 (m, 4H, H-3a, H-3b, H-2a, H-2b). ^{13}C NMR (63 MHz, CD_3OD): δ 77.0 (C-1′); 75.2 (C-3′); 74.6 (C-5′); 73.0 (C-2′); 72.3 (C-4′); 63.1 (C-6′); 31.5 (t, $^2J_{C\text{-}1,F}=22$ Hz, C-1); 25.0 (C-3); 17.9 (C-2). ^{19}F NMR (235 MHz, CD_3OD): δ −79.0 (s, CF_3); −112.1, −119.6, −120.6, −121.2, −124.1 (5s (br), 5 CF_2).

15c: 62% colourless crystals, m.p. 153°C-SmA-227°C (acetonitrile/methanol). Anal. for $C_{17}H_{17}F_{17}O_5$ (624.29): calc. C 32.71, H 2.74; found C 32.99, H 2.78%.

References

[1] Prade, H., Miethchen, R., and Vill, V., 1995, *J. prakt. Chem.*, **237,** 427.

[2] Paleos, C. M., and Tsiourvas, D., 1995, *Angew. Chem. int. Ed. Engl.*, **134,** 1696.

[3] Goodby, J. W., Watson, M. J., MacKenzie, G., Kelly, S. M., Bachir, S., Bault, P., Gode, P., Goethals, G., Martin, P., Ronco, G., and Villa, P., 1998, *Liq. Cryst.*, **25,** 139.

[4] Goodby, J. W., Mehl, G. H., Saez, I. M., Tuffin, R. P., Mackenzie, G., Auzely-Velty, R., Benvegnu, T., and Plusquellec, D., 1998, *Chem. Commun.*, 2057.

[5] Veber, M., Cheylan, E., Czernecki, S., and Xie, J., 1996, *Liq. Cryst.*, **21,** 197.

[6] Kissa, E., 1994, *Fluorinated Surfactants – Synthesis, Properties, Applications* (New York: M. Dekker).

[7] Riess, J. G., 1995, *J. Liposome Res.*, **5,** 413.

[8] Zur, C., Miller, A. O., and Miethchen, R., 1998, *Liq. Cryst*, **24,** 695.

[9] MIETHCHEN, R., and HEIN, M., 2000, *Carbohydr. Res.*, **327,** 169.
[10] HUANG, W. Y., and XIE, Y., 1991, *Chin. J. Chem.*, **9,** 351; *Chem. Abstr.*, 1992, **116**, 106596.
[11] HUANG, W.Y., and WU, F. H., 1999, *Israel J. Chem.*, **39,** 167.
[12] PLENKIEWICZ, H., DMOWSKI, W., and LIPINSKI, M., 2001, *J. fluorine Chem.*, **111,** 227.
[13] LIU, C., THOMAS, N. F., and POTTER, B. V., 1993, *Chem. Commun.*, **22,** 1687.
[14] TAKAHASHI, S., KUZUHARA, H., and NAKAJIMA, M., 2001, *Tetrahedron*, **57,** 6915.
[15] GIANNIS, A., and SANDHOFF, K., 1985, *Tetrahedron Lett*, **26,** 1479.
[16] BÉCAERT, T., VANLEMMENS, P., VILLA, P., LAHYANI, A., LEHOUELLEUR, J., POSTEL, D., RONCO, G., and BRULÉ, G., 1996, *Bol. Chim. Farm.*, **135,** 204.
[17] MIETHCHEN, R., HOLZ, J., PRADE, H., and LIPTÁK, A., 1992, *Tetrahedron*, **48,** 3061.
[18] HEIN, M., and MIETHCHEN, R., 1998, *Tetrahedron Lett.*, **39,** 6679.
[19] HEIN, M., MIETHCHEN, R., and SCHWÄBISCH, D., 1999, *J. fluorine Chem.*, **98,** 55.
[20] HEIN, M., MIETHCHEN, R., SCHWÄBISCH, D., and SCHICK, CHR., 2000, *Liq. Cryst.*, **27,** 163.
[21] LEONHARD, J., LYGO, B., and PROCTER, G., 1996, *Praxis der organischen Chemie* (Weinheim: VCH).
[22] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Leipzig: Deutscher Verlag für Grundstoffindustrie, 2. Aufl.).