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Synthesis and characterization of thermotropic amphiphilic liquid crystals: semiperfluoroalkyl-β-D-glucopyranosides

Huy Loc Nguyen[a]; James Dedier[a]; Huu Tinh Nguyen[b]; Gilles Sigaud[b]
[a] Laboratoire de Chimie des Substances Végétales (LCSV), Institut du Pin, Université Bordeaux I, 351 cours de la Libération, 33405 Talence Cédex, France, [b] Centre de Recherche Paul Pascal, CNRS, Université Bordeaux I, avenue Albert Schweitzer, 33600 Pessac, France,

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Synthesis and characterization of thermotropic amphiphilic liquid crystals: semiperfluoroalkyl-β-D-glucopyranosides

HUY LOC NGUYEN, JAMES DEDIER
Laboratoire de Chimie des Substances Végétales (LCSV), Institut du Pin,
Université Bordeaux I, 351 cours de la Libération, 33405 Talence Cédex, France

HUU TINH NGUYEN* and GILLES SIGAUD
Centre de Recherche Paul Pascal, CNRS, Université Bordeaux I,
avenue Albert Schweitzer, 33600 Pessac, France

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As part of our study of the mesomorphic properties of glucopyranosides containing fluorinated chains, this paper focuses on an investigation of the liquid crystalline behaviour of non-aromatic compounds. The synthesis of eight single-tailed materials which contain a semiperfluoroalkyl chain linked to the polar glucose head group is described. Using polarized optical microscopy, DSC and X-ray diffraction all the materials were found to show only monomesomorphism, a smectic A phase with bimolecular layers. The thermal behaviour is discussed in comparison with the previously reported data on the series of parent compounds.

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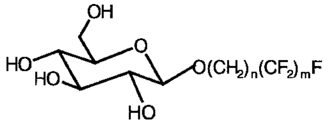
1. Introduction

Carbohydrate amphiphiles have a large field of application due to their biological activity and surfactant properties: many compounds are now commercially available for reconstitution of membrane proteins and solubilization. Several compounds are also used as non-ionic surfactants in biodegradable detergents [1–4]. The hydrophilic moieties of these amphiphiles are naturally occurring mono-, di-, oligo-, or poly-saccharides to which can be attached aliphatic or aromatic hydrophobic parts in a variety of ways [5–7].

Moreover, the thermotropic liquid crystalline properties displayed by many of the compounds have enlarged their field of interest. The first reports published in 1938 [8] and 1979 [9] drew attention to this potential research area in carbohydrates. Since then, systematic studies were essentially concentrated on monocyclic systems—monoacyclic carbohydrates in which the sugar is connected to a simple hydrocarbon chain by different linkages (ether, ester, amide, amino, thio or carbon groups) in various positions [10–28].

Since 1980, perfluoroalkyl substituted carbohydrates have also been studied for many potential uses in medical and pharmaceutical research because of their effective properties as non-coagulating surfactants and emulsifiers [29]. Moreover, thermotropic mesomorphic behaviour for a few perfluoroalkylated amphiphiles has been reported recently for the first time by Miethchen [30–32]. In a previous paper [33] we extended these observations to a series of semiperfluoroalkyloxyphenyl- and perfluoroalkylphenyl-β-D-glucopyranosides and showed that they exhibit smectic A phases with a bimolecular layer arrangement. In the present paper we continue by reporting the synthesis of a complete series of semiperfluoroalkyl-β-D-glucopyranosides, varying the length of the hydrogenous part with respect to the fluorinated part of the chain, as shown in the following structure.



GluO-H_nF_m series
n: number of methylenes.
m: number of fluoromethylenes.

The mesomorphic behaviour of these products has been characterized using polarized light microscopy and differential scanning calorimetry (DSC) and the results are compared with those already reported by Hein and Miethchen [31] on a few members of this family. X-ray diffraction has also been used on some of the compounds to confirm the phase assignment.

2. Synthesis of the compounds

2.1. *Compound characterization*

All chemical reactions were monitored by thin layer chromatography (TLC; $4 \times 8\,\mathrm{cm}^2$ pre-coated plates SiO_2/UV 254, layer thickness 0.25 mm) and the spots were located under a UV lamp (254 nm), with I_2, or

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*Author for correspondence; e-mail: tinh@crpp.u-bordeaux.fr

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by spraying with a 5% aqueous solution of sulphuric acid followed by heating. Purification was achieved by gradient column chromatography on silica gel (254 nm, 60 mesh, Aldrich) using a heptane/ethyl acetate mixture as eluent.

The structures of the compounds were determined by ^{1}H, ^{13}C, HH-COSY and HC-COSY NMR spectroscopy (Bruker-250 MHz) and FTIR (Nicolet 210) spectroscopy. NMR spectra were recorded using the solvents $CDCl_3$ or DMSO. The purities of the final compounds were checked by TLC, elemental analysis (CHN) and DSC. Melting points were determined by microscopic observation.

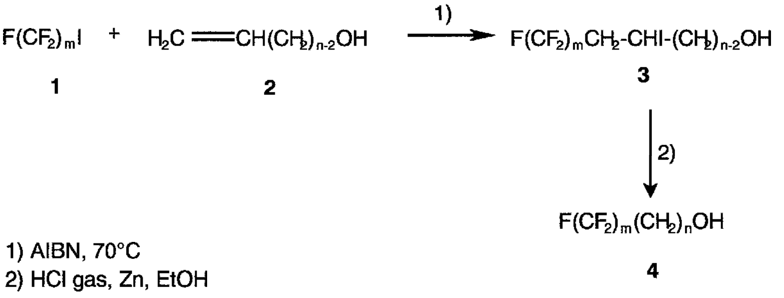
2.2. *Synthesis*

The synthesis of the amphiphilic compounds with various lengths of the perfluoroalkyl and hydrogenous alkyl units involves two parts. First, for the synthesis of the chains very few fluorine-containing chains are commercially available. Most of the semiperfluoro alcohols used in this work have been prepared by first carrying out radical additions of perfluoroalkyl iodides to alcen-1-ols. Then the iodine was removed by Zn reduction in the presence of hydrogen chloride gas to form the desired products as presented in scheme 1. The synthesis of the semiperfluoro alcohols with $n = 4$ to 6, and $m = 4$ to 6 is described in [33].

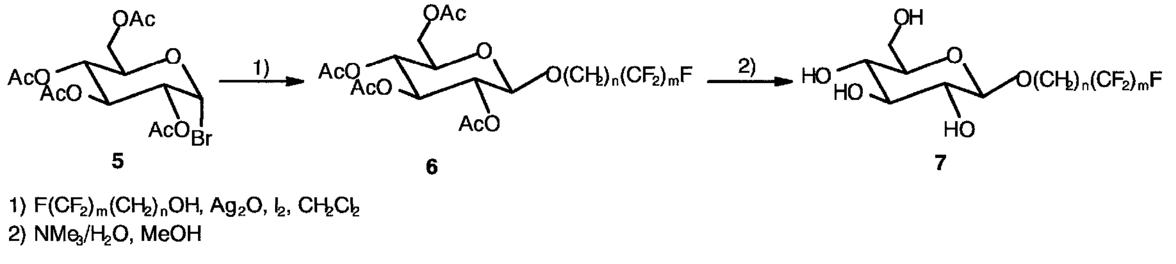
Secondly, the *n*-semiperfluoroalkyl-β-D-glucopyranosides were prepared by glycosidation of the semiperfluoro alcohols with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide, compound **5**, [34, 35] under the conditions of Konigs–Knorr [36] improved by Liefländer *et al.* [37] to minimize the risk of racemization. As a result of the careful conduct of this key step, all products **6** in the series were obtained in a highly pure stereochemical form. However some of the products were isolated in poor yield caused by the low reactivities of some of the semiperfluoro alcohols and the purification steps involved. Finally, the acetyl groups of the products **6** were easily removed by trimethylamine in water/methanol solution to give the amphiphilic compounds **7** in quantitative yields.

2.2.1. *Semiperfluoroalkyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranosides,* **6**

A solution of 5 mmol of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **5** in 15 ml of dry CH_2Cl_2 was added dropwise to a suspension of 5 mmol of the semiperfluoro alcohol, 10 mmol of Ag_2O, 10 g of drierite (pre-dried at 400°C for about 2 h) and 5 mmol of iodine in 15 ml of dry CH_2Cl_2. The mixture was stirred vigorously at room temperature for 24 h and then filtered. The solid removed was washed with CH_2Cl_2 and the combined filtrate and washings were evaporated to give a viscous liquid. The pure product was isolated by chromatography on silica gel (heptane/ethyl acetate, 1 : 1) and crystallized from ethanol; yield 20–60%. IR (cm^{-1}, neat): 2958, 1754, 1234, 1035. ^{1}H NMR ($CDCl_3$, δ/ppm): 5.25–4.99 (m, $H_4 + H_3 + H_2$), 4.52 (d, 8 Hz, $H_{1\beta}$), 4.3–4.11 (m, $2H_6$), 3.95–3.89 (m, H of $-CH_2O-$), 3.73–3.66 (m, H_5), 3.53–3.49 (m, H of $-CH_2O-$), 2.2–2.0 (m, $R_fCH_2- + 4\ CH_3$), 1.8–1.6 (m, CH_2 groups). ^{13}C NMR



Scheme 1. Synthesis of the semiperfluoro alcohols.



Scheme 2. Synthesis of the *n*-semiperfluoroalkyl-β-D-glucopyranosides.

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($CDCl_3$, δ/ppm): 170–169 (4 COO–), 100 (C_1), 72.8 (C_3), 71.8 (C_5), 71.2 (C_2), 69.1 (C_6), 68.4 (C_4), 61.9 ($-CH_2O-$), 31 (t, R_fCH_2-), 20.6 (4 CH_3), 30–15 (CH_2 groups).

2.2.2. *Semiperfluoroalkyl-β-D-glucopyranosides, 7*

2 mmol of acetylated semiperfluoroalkyl-β-D-glucopyranoside was deprotected quantitively with a mixture of 2 ml of a 45 wt % solution of Me_3N in water and 8 ml of MeOH. After stirring at room temperature for 24 h, the solvent was evaporated, controlling the temperature carefully. The desired products **7** were obtained by crystallization from MeOH/MeCN (1:2); yield 60–90%. IR (cm^{-1}, neat): 3353, 2944, 2863, 1382, 1243, 1197, 1076. ^1H NMR ($CDCl_3$, δ/ppm): 4.97–4.9 (m, 3 OH), 4.47–4.43 (t, OH), 4.12 (d, 7.63 Hz, $H_{1\beta}$), 3.81–3.77 (m, H of $-CH_2O-$), 3.69–3.62 (m, H_6), 3.55–3.37 (m, H_6 + H of $-CH_2O-$), 3.2–2.8 (m, $H_3 + H_4 + H_5 + H_2$), 2.4–2.3 (m, R_fCH_2-), 2.0–1.5 (CH_2 groups). ^{13}C NMR ($CDCl_3$, δ/ppm): 102.7 (C_1), 76.8 (d, $C_3 + C_4$), 73.4 (C_5), 70 (C_2), 68 (CH_2O-), 61 (C_6), 29.5 (t, R_fCH_2-), 30.6–16.7 (CH_2 groups).

3. Mesomorphic properties

Phase identification and the determination of phase transition temperatures were first carried out by polarized light microscopy using a Zeiss Ortholux microscope equipped with a Mettler FP52 hot stage. Homeotropic alignment of samples was commonly observed on clean glass microscope slides (washed with acetone, chloroform, water, sulphochromic acid solution, water and acetone), whereas planar defect textures could be obtained using surfactant coated slides. Coating of the slides was carried out by dipping clean slides into a solution of 2 wt % polyimide in ethanol. The solution was allowed to drain from the slides which were then baked free from solvent in an oven at 200°C for 75 min.

Differential scanning thermograms were recorded at the same rates (5°C min^{-1} for heating and 2°C min^{-1} for cooling) for all compounds using a Perkin Elmer DSC7. Additional X-ray scattering experiments, using a Guinier chamber and powder samples, were performed on a few compounds to confirm definitely the nature of the mesophases assumed to be similar for all materials.

Microscopic observations performed on compounds **8**–**15** with untreated clean slides showed very uniform homeotropic textures on cooling from the isotropic state. On the other hand, the same compounds on coated slides and at a slow cooling rate all developed fan-shaped textures. This is a clear indication of a direct transition from the isotropic liquid to an enantiotropic smectic A phase (figure 1). Only a slight continuous change of texture or no change at all was observed on further cooling to room temperature.

There was complete agreement between the DSC thermal events and the changes observed by textural analysis. Analysis of the thermograms showed that materials **8**–**15** display sharp melting peaks on heating, confirming the satisfactory chemical purity as given by elemental and NMR analysis. Upon cooling, the mesomorphic state is recovered, but only compounds **8**, **9** and **13** return to the solid state via clear exothermic peaks. The other compounds were presumed to stay in a glassy state. Some products however probably decomposed slightly in the vicinity of the isotropic phase as a result of their high clearing temperatures. The results based on both techniques are summarized in the table.

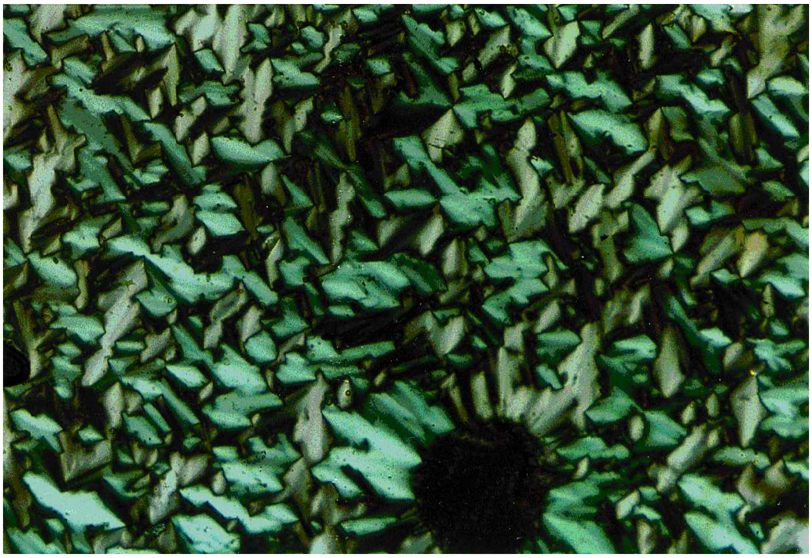

Figure 1. Focal-conic texture; compound **8**, 150°C; cooling from the isotropic phase.

Table. Phase behaviour of the semiperfluoroalkyl-β-D-glucopyranosides (compounds **8**–**15**) from DSC and polarized light microscopy. The data in italics for compounds **16** and **17** are from Hein *et al.* [31]. The temperature in brackets indicates a monotropic transition.

Compound	T_{melting}/°C	$\Delta H_{\text{melting}}$/J g^{-1}	T_{clearing}/°C	$\Delta H_{\text{clearing}}$/J g^{-1}	Ref.
GluO-H_2F_6 8	137.6	68.4	196.9	3.2	
GluO-H_2F_8 9	148.4	66.2	219.4	2.2	
GluO-H_3F_4 *16*	*148*	—	(*140*)	—	[31]
GluO-H_3F_6 *17*	*155*	—	*180*	—	[31]
GluO-H_4F_4 10	104.1	42.8	148.0	2.1	
GluO-H_4F_6 11	118	42.2	179.2	1.4	
GluO-H_5F_4 12	113.9	60.5	146.7	1.0	
GluO-H_5F_6 13	124.4	62.5	176.4	1.3	
GluO-H_6F_4 14	91.2	36.5	155.1	0.7	
GluO-H_6F_6 15	76.0	33.4	148.5	1.5	

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X-ray patterns were obtained for compounds **14** and **15**. They are similar and show two Bragg reflections of comparable intensities corresponding to the fundamental wave vector and its first harmonic. The layer thicknesses deduced from the q-vectors of the fundamental Bragg peaks are, respectively, 32 and 36 Å which provide evidence for a bimolecular arrangement within the layers (the layer spacing is slightly less than twice the molecular length, see figure 2).

4. Discussion and conclusion

The results obtained with the compounds analysed in this paper are fully consistent with all the data previously recorded on various series of glucopyranosides whether fluorinated or not. The transition temperatures of the compounds **16** and **17** which have been independently studied agree with those of the other members of the series. Our measurements confirm that all these amphiphiles exhibit only a smectic A phase with a bimolecular organization within the layers, as far as their thermotropic behaviour is concerned.

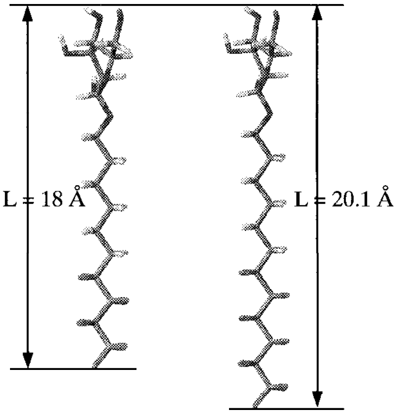

Figure 2. Stereomodels in the most extended conformation for compounds **14** and **15**.

As can be seen in figures 3 and 4 (in which the evolution of the melting and clearing temperatures has been plotted as a function of the length of the non-fluorinated part of the chain, H_n, for a given constant length of the fluorinated part, F_4 and F_6) fluorination increases the temperature of clarification at low n values. However, when a sufficiently long chain is attained ($n + m = 12$) there is no difference between the semi-perfluorinated and the fully hydrogenous compounds. Thus it seems that the specific interactions attributable to the fluorine, and which stabilize the smectic state, tend to disappear progressively. One can remark that this effect is not seen when a phenyl ring is incorporated between the pyranoside core and the chain.

A phase diagram study between the H_{12} and H_6F_6 (or H_8F_4) compounds would be helpful to clarify whether a tail to tail arrangement of the perfluoroalkyl chains in the hydrophobic region could explain this behaviour, but the H_{12} compound is not available at the present time.

These observations also apply to the melting temperatures which are different and higher in the fluorinated compared with hydrogenous compounds at low n values, but merge when the number of carbons in the chain reaches 12 (figure 4). Finally, one can also note the characteristic even–odd evolution of the melting temperatures based on the length of the hydrogenous part which has been already noted in several different series of semiperfluorinated mesogens [38].

Thus, the study of this series of semiperfluoroalkyl-β-D-glucopyranosides, following our earlier study of the semiperfluoroalkyloxyphenyl-β-D-glucopyranosides [33], has shown, through a similar comparison with previously reported data on a series of alkyl-β-D-glucopyranosides, that the temperatures of transition of the smectic A phase are sensitive to fluorination, but its bilayered structure is not. However, the enhancement of the clarification

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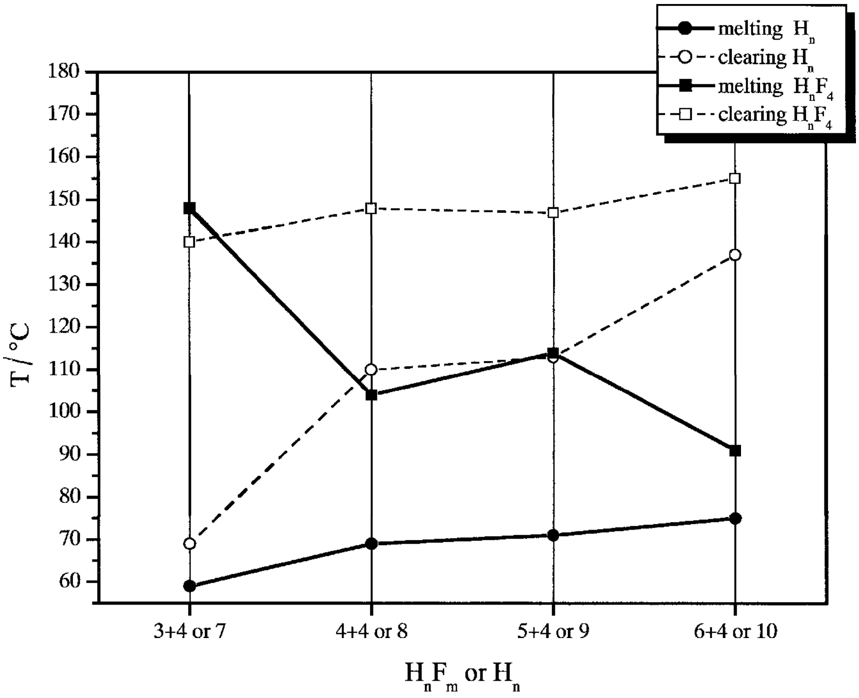

Figure 3. Phase transition temperatures as a function of the number of carbons in the terminal chains: semiperfluoroalkyl-β-D-glucopyranosides with constant $m = 4$ and *n*-alkyl-β-D-glucopyranosides.

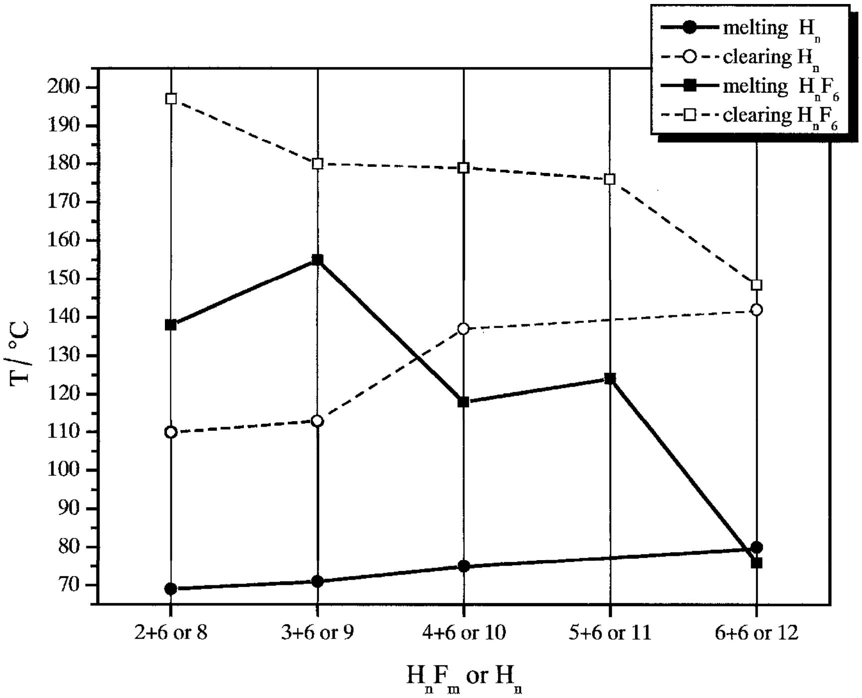

Figure 4. Phase transition temperatures as a function of the number of carbons in the terminal chains: semiperfluoroalkyl-β-D-glucopyranosides with constant $m = 6$ and *n*-alkyl-β-D-glucopyranosides.

temperatures due to fluorination of the chain does not extend beyond the point where the aliphatic and fluorinated parts balance, in contrast to the case when the glucopyranoside molecule incorporates a phenyl ring. This seems to confirm that in such polyphilic molecules, the amphipatic interactions among the aromatic and fluorinated parts are stronger than those among the fluorinated and aliphatic parts.

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