Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Non-Amphiphilic Carbohydrate Liquid Crystals Containing an Intact Monosaccharide Moiety

E. Smits [a] , J. B.F.N. Engberts [a] , R. M. Kellogg [a] & H. A. Van Doren [b]
[a] Universrty of Groningen, Laboratory for Organic and Molecular Inorganic Chemistry, Nijenborgh 4, 9747, AG Groningen, the Netherlands
[b] Netherlands Institute for Carbohydrate Research, Rouaanstraat 27, 9723, CC Groningen, the Netherlands
Version of record first published: 23 Sep 2006.

To cite this article: E. Smits , J. B.F.N. Engberts , R. M. Kellogg & H. A. Van Doren (1995): Non-Amphiphilic Carbohydrate Liquid Crystals Containing an Intact Monosaccharide Moiety, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 260:1, 185-199

To link to this article: http://dx.doi.org/10.1080/10587259508038691

Mol. Cryst. Liq. Cryst. 1995, Vol. 260, pp. 185–199
Reprints available directly from the publisher
Photocopying permitted by license only

Non-Amphiphilic Carbohydrate Liquid Crystals Containing an Intact Monosaccharide Moiety

E. SMITS, J.B.F.N. ENGBERTS, R.M. KELLOGG
University of Groningen, Laboratory for Organic and Molecular Inorganic Chemistry, Nijenborgh 4, 9747 AG Groningen, the Netherlands

H.A. VAN DOREN*
Netherlands Institute for Carbohydrate Research, Rouaanstraat 27, 9723 CC Groningen, the Netherlands

A chiral rigid moiety which forms the basis of a new class of non-amphiphilic carbohydrate liquid crystals has been developed. This moiety contains a fully intact glucopyranose ring embedded in a trans-decalin structure. The original carbohydrate is substituted so that only two hydroxyl groups are left, resulting in derivatives with reduced hydrophilicity. The substituents R and X-R' on the 4,6-*O*-ylidene ß-D-glucopyranoside are in the equatorial position and can be varied extensively, using straightforward synthetic procedures. Investigations as to the requirements for R and X-R' for inducing liquid-crystalline behavior have shown that at least one of the substituents should contain a large, polarizable aromatic moiety. An aromatic Schiff base fulfils this requirement.

Keywords: *Schiff base, monosaccharide, smectic A phase, liquid crystals, carbohydrate.*

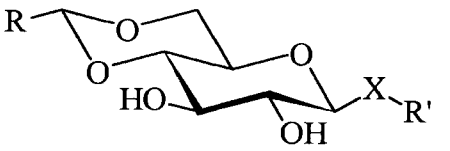
INTRODUCTION

Carbohydrate liquid crystals usually consist of monosaccharide derivatives with one or more alkyl chains.[1] Although the molecules themselves are chiral, amphiphilic carbohydrate liquid crystals do not form chiral mesophases. This is most likely the result of the amphiphilic character of the derivatives. The type of mesophase formed in amphiphilic mesogens is governed by the overall molecular shape.[2,3] For mono-alkylated derivatives

* Author for correspondence

such as alkyl 1-thio-(α-and-ß)-D-glucopyranosides[4,5] and 4,6-*O*-alkylidene-D-glucopyranosides[6] only smectic A phases have been observed. Vill et al.[7] reported on compounds in which several of the free hydroxyl groups of the monosaccharide had been eliminated. These derivatives of deoxy sugars indeed showed cholesteric and blue phases. However, in the approach of Vill et al.,[7] the original sugar moiety is stripped of its hydroxyl groups.

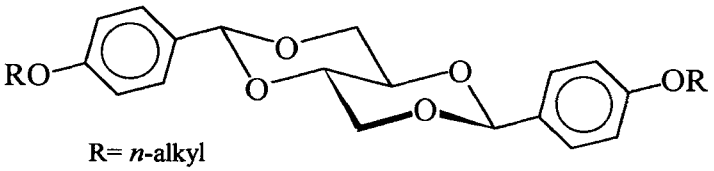
We were of the opinion that a simple monosaccharide can function as the core of a new class of calamitic mesogens when it is embedded in the following trans-decalin structure.



I

R = alkyl, 4-alkoxyphenyl, aromatic Schiff base
X-R'= thioalkyl, oxyaryl, oxy(4-alkylphenyl)

This can be achieved with a glucopyranose ring substituted at the anomeric centre, and protected at the 4,6-position. Rigidity is guaranteed in the trans-decalin structure. The hydrophilicity is reduced since only the 2,3-hydroxyl groups are left free (and these can, if so desired, be functionalized). Both the R and X-R' groups on the rigid 'trans-decalin' ring system **I** are in the equatorial position, and can be varied extensively and independently. In contrast, the structurally similar nematogenic and smectogenic *trans*-1,3,5,7-tetraoxadecalin derivatives prepared by Kohne et al.[8] have identical substituents on both sides of the symmetrical rigid core, which renders these compounds achiral.



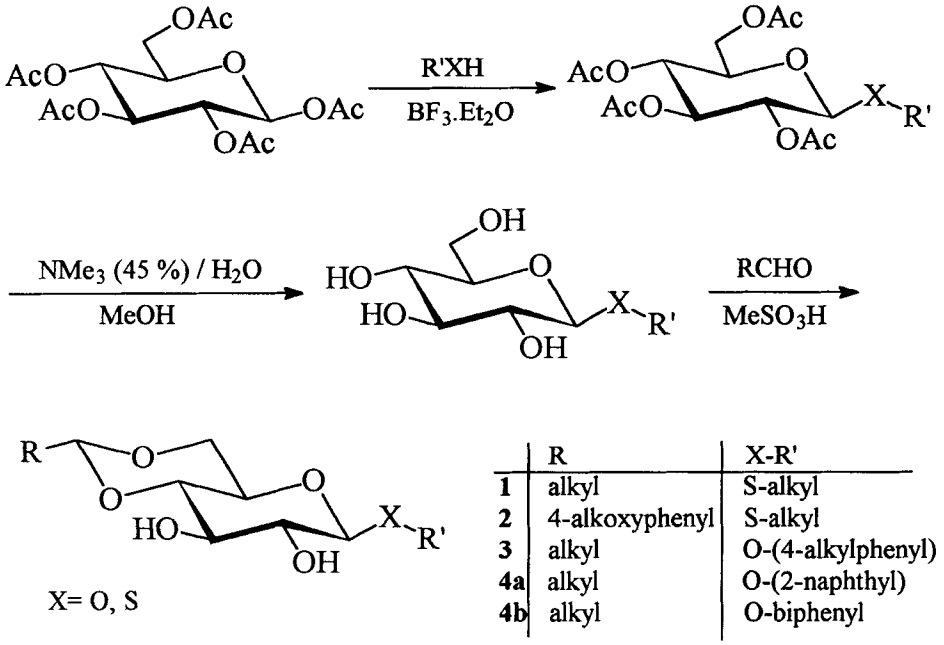
R= *n*-alkyl

trans-1,3,5,7-tetraoxadecalin derivatives prepared by Kohne et al. [8]

We were fairly confident that I, which can be constructed in a straightforward synthetic reaction sequence, could be the basis for a new class of mesogens. But what would be the requirements for R, and X-R' with respect to inducing (chiral) mesogenic behavior?

SYNTHESIS

The carbohydrate derivatives based on I were prepared by the general route depicted in Scheme 1. The first step is the formation of an n-alkyl 1-thio-glucopyranoside or an aryl glucopyranoside. The *n*-alkyl 1-thio-ß-D-gluco-pyranosides were prepared by reaction of ß-D-glucose pentaacetate with an alkanethiol in the presence of 5 equivalents of the Lewis acid boron trifluoride etherate as described by Van Doren et al.[4] The ß-products are isolated almost exclusively when the reaction is quenched after 15 min. Longer reaction times lead to considerable amounts of α-product. The acetylated compounds were purified by crystallization and subsequently were deprotected by means of trimethylamine in aqueous methanol. The aryl ß-D-glucopyranosides were obtained by glycosidation of a substituted phenol. This reaction was performed using 1 equivalent of boron trifluoride etherate in anhydrous dichloromethane.[9] The reaction mixture was stirred at room temperature for 48 h, after work-up the ß-product was obtained. By means of this procedure a wide variety of aryl ß-D-glucopyranosides was prepared and isolated in anomerically pure form after recrystallization from ethanol (yield: 40 - 80 % depending on the nature of the substituent in the phenol). If the α-anomer is the desired product, the reagents must be refluxed in chloroform for 6 hours. The use of boron trifluoride etherate instead of stannic chloride[10] results in milder reaction conditions, easier work-up procedures, higher yields and good control over the configuration at the anomeric centre. There is no need for the preparation of reactive glucosyl donors (*e.g.*, 2,3,4,6-tetra-*O*-acetyl-1-*O*-trifluoroacetyl-α-D-glucopyranose[11]),



	R	X-R'
1	alkyl	S-alkyl
2	4-alkoxyphenyl	S-alkyl
3	alkyl	O-(4-alkylphenyl)
4a	alkyl	O-(2-naphthyl)
4b	alkyl	O-biphenyl

Scheme 1

since ß-D-glucose pentaacetate is used as the starting material.

The 1,3-dioxane ring is formed in an acid-catalyzed equilibrium reaction of the 1-substituted-ß-D-glucopyranoside with an aldehyde. Various catalyst/solvent mixtures and methods to shift the equilibrium in favor of the product have been reported in the literature. Miethchen et al.[6,12] performed the reaction with glucose and an aldehyde in *N,N*-dimethyl-formamide (DMF) with methanesulfonic acid. The yields did not exceed 60 %. However, the authors reported that the reaction time (30 h) can be reduced considerably by sonication of the reaction mixture. Bergonzi et al.[13] prepared ylidene derivatives in 52 - 78 % yield using boron trifluoride etherate as a catalyst in dimethyl sulfoxide at 65°C. Anomerization of the starting material methyl α-D-glucopyranoside is a serious disadvantage of the latter method. Pyridinium tosylate in refluxing benzene with azeotropic

removal of water is an alternative successfully applied by Dahlhoff.[14] In our hands the methanesulfonic acid-catalyzed reaction in ethyl acetate at room temperature or at 50°C proved to be the most successful procedure for the preparation of aliphatic ylidene derivatives. With deactivated aldehydes such as 4-alkoxybenzaldehydes, the highest yields (28% after purification by column chromatography on silica gel and recrystallization) were obtained with methanesulfonic acid in DMF.

For the preparation of the Schiff base derivatives, terephthalic dialdehyde is first substituted with an *n*-alkyl 1-thio-ß-D-glucopyranoside on one side and in a subsequent step with a 4-*n*-alkylaniline. The reaction conditions for obtaining monosubstituted terephthalic dialdehyde derivatives have not yet been optimized. In order to obtain the Schiff bases the reagents were dissolved in ethanol, a catalytic amount of acetic acid was added and the crystalline product was isolated after 15 min.[15]

RESULTS AND DISCUSSION

The first derivatives prepared on the basis of **I** were compounds with R= alkyl and X-R'= thioalkyl. The products (**1a-f**) are crystalline materials but unfortunately did not show mesogenic behavior (the melting points are listed in Table 1). The vast majority of liquid-crystalline substances contain two or more aromatic rings, and polar bridging or terminal groups.[16] Aromatic character was introduced into the side chains of **I** in two ways:

- Aromatic substituents like naphthyl, biphenyl or 4-alkoxyphenyl were linked via sulphur or oxygen at the anomeric center, the substituent R still being an alkyl group.
- Reaction of 1-substituted-ß-D-glucopyranosides with aromatic aldehydes provides derivatives with aromatic character on the other side of **I**.

The compounds **2a-c**, **3a**, **4a** and **4b** were synthesized but no mesophases were observed (Table 1).

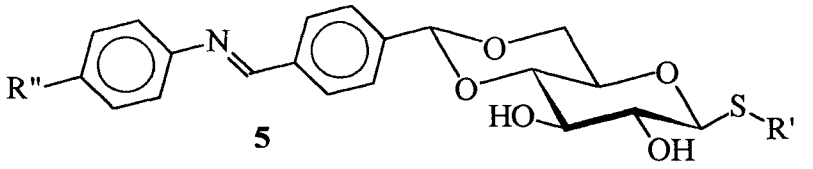
Table 1. Phase transition temperatures of 1-substituted 4,6-O-ylidene glucopyranoside derivatives.

	R	X-R'	melting points (°C)[a,b]	
1a	$CH_3(CH_2)_4$	S-$(CH_2)_5CH_3$	(64.6)	68.5
1b	$CH_3(CH_2)_5$	S-$(CH_2)_6CH_3$		67.7
1c	$CH_3(CH_2)_6$	S-$(CH_2)_7CH_3$		66.2
1d	$CH_3(CH_2)_8$	S-$(CH_2)_9CH_3$		62.2
1e	$CH_3(CH_2)_{10}$	S-$(CH_2)_{11}CH_3$		63.5
1f	$CH_3(CH_2)_{10}$	S-$(CH_2)_4CH_3$		75.5
1g	$CH_3(CH_2)_3$	S-$(CH_2)_{11}CH_3$		63.9
2a	$CH_3(CH_2)_7$-O-C_6H_4	S-$(CH_2)_7CH_3$	(97.5)	102.2
2b	$CH_3(CH_2)_9$-O-C_6H_4	S-$(CH_2)_9CH_3$	(72.6)	97.1
2c	$CH_3(CH_2)_{11}$-O-C_6H_4	S-$(CH_2)_{11}CH_3$	(90.3)	102.2
3a	$CH_3(CH_2)_6$	O-C_6H_4-$(CH_2)_7CH_3$		170.0
4a	$CH_3(CH_2)_6$	O-(2-naphthyl)		191.1
4b	$CH_3(CH_2)_6$	O-biphenyl		189.0

a) Measured with DSC. b) Values in parentheses indicate crystal-crystal transitions.

These results indicate that more polarizability is needed in order to induce liquid-crystalline behavior. The aromatic and highly polarizable Schiff base functionality, being an excellent moiety for inducing liquid-crystallinity,[16,17] was subsequently chosen as a substituent on **I**. The following series of compounds (**5a-f**) represents the first non-amphiphilic rod-like carbohydrate derivatives with a fully intact glucopyranose ring that exhibit liquid-crystalline behavior. Table 2 shows the melting and clearing points of some members of this so called SBTS-series (derived from its constituent structural units: Schiff Base, Terephthalic dialdehyde, 1-alkyl *S*-ß-D-gluco-pyranoside). On the basis of polarization microscopy the mesophase of the products was assigned as smectic A.

Table 2 *Phase transition temperatures of the Schiff-base derivatives*



5

	R"	R'	phase transitions (°C)
5a	CH_3-O	$(CH_2)_4CH_3$	not mesogenic[a]
5b	$CH_3(CH_2)_3$	$(CH_2)_4CH_3$	S_A + additional mesophase?[a]
5c	$CH_3(CH_2)_3$	$(CH_2)_4CH_3$	S_A + additional mesophase?[a]
5d	$CH_3(CH_2)_7$	$(CH_2)_7CH_3$	**K** ca.90 S_A 157.5 **I**
5e	$CH_3(CH_2)_7$	$(CH_2)_9CH_3$	**K** 129.3 S_A 159.8 **I**
5f	$CH_3(CH_2)_{11}$	$(CH_2)_9CH_3$	**K** 127.3 S_A 157.5 **I**

[a]Compounds not sufficiently pure for definite assignment of phase behavior.

When a sample of compound **5f** is cooled from the isotropic state, bâtonnets are formed at the isotropic to liquid-crystalline transition. Further cooling gives the typical focal-conic fan-like texture shown in Figure 2.

Generally homologous series of rod-like liquid-crystalline compounds with long alkyl chains show smectic phases.[16] On introduction of shorter alkyl chains a nematic phase may be formed in addition to the smectic phase(s). The latter usually disappear(s) for very short-chain derivatives. Short-chain derivatives of the SBTS series, which were expected to form a nematic or cholesteric phase, were synthesized. Much to our disappointment, the compounds **5b** and **5c** appear to give only a smectic A phase, whereas the *p*-anisidine derivative **5a** did not show any mesogenic behavior at all.

We contend that members of the SBTS-series may be considered as non-amphiphilic derivatives, although it should be noted that two vicinal hydroxyl groups are generally sufficient for a molecule to display amphiphilic character. Tschierske et al.[18] reported calamitic propane-1,2-diol

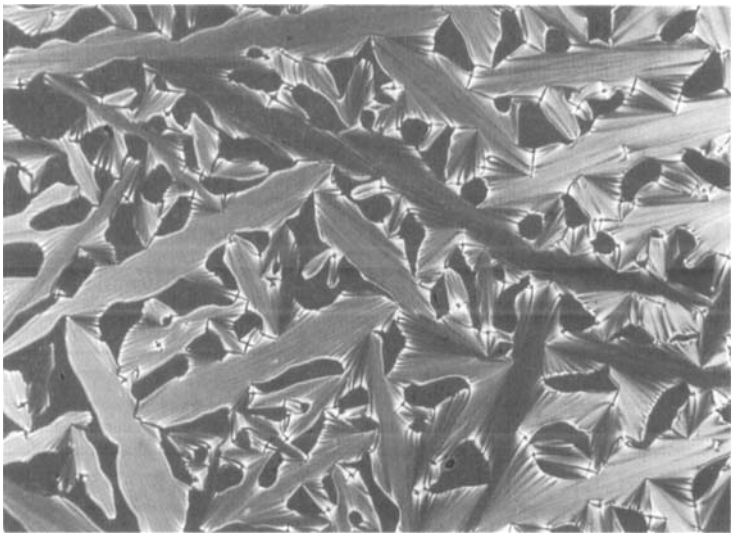


Figure 2. Smectic A phase of **5f**. *157°C.* See Color Plate XII.

derivatives incorporating mesogenic structural units. These mesogens are considered to be amphiphilic and indeed the liquid-crystalline phases are stabilized by the addition of water. These molecules contain distinct hydrophobic and hydrophilic sites which make them structurally similar to the classical carbohydrate amphiphiles, the mesophase of which is determined by the shape of the molecule.[2,3] In spite of their amphiphilic character these derivatives do form tilted smectic phases. Recently, Tschierske et al.[19] reported the observation of chiral mesophases in dihydroxyalkyl-substituted cyanobiphenyls. In our Schiff base derivatives the two hydroxyl functions are located in the rigid core of a large hydrophobic molecule. Formation of aggregates in contact preparations with water has not been observed. Miscibility studies of the Schiff base derivative **5f** with classical carbohydrate liquid crystals (undecyl 1-thio-α-D-glucopyranoside, 4,6-*O*-dodecylidene D-glucitol and 4,6-*O*-(4-dodecyloxybenzylidene) D-gluco-

pyranose) showed that the mesophase of the SBTS series does not mix with the smectic A_d phase of amphiphilic mesogens. We therefore regard the derivatives of I as non-amphiphilic and expect characteristics reminiscent of calamitic liquid crystals.

To obtain more insight in the scope and limitations of these novel materials, we are currently expanding the number of derivatives containing I as a chiral core. Compounds in which R= 4-alkoxyphenyl and X-R'= *O*-(4-alkylphenyl) seem to have promising characteristics.

CONCLUSIONS

The present series of Schiff bases provides the first example of non-amphiphilic carbohydrate derivatives with a fully intact glucopyranose structure, that form (smectic A) liquid-crystalline phases. It shows that a simple monosaccharide can function as the basic structural unit of calamitic mesogens, when its hydrophilicity is sufficiently reduced. The advantage of the rigid chiral core I is that its substituents R and X-R' can easily be varied to include a wide range of derivatives. At least one of the substituents on I should contain a large polarizable aromatic group in order to induce liquid-crystalline behavior. We are currently investigating the structural requirements for the synthesis of carbohydrate liquid crystals that do form *chiral* mesophases.

EXPERIMENTAL

General - All reagents and solvents were purchased form any one of the large chemical suppliers and were used without further purification. The structure of all products was confirmed by NMR-spectroscopy. In the final products, no impurities were observed by NMR. Where determined,

elemental analysis revealed at least 99% purity. NMR spectra were recorded on a 300 MHz Varian VTR-300 spectrometer. Chemical shifts are related to $CHCl_3$ or CD_3OD. Thermomicroscopy was performed with the Mettler FP 800 system, the hot stage was mounted on a Nikon microscope. Quantitative thermal analyses were performed using a Perkin Elmer PC Series DSC 7.

n-Alkyl 1-thio-2,3,4,6-tetra-O-acetyl-ß-D-glucopyranosides were synthesized by reaction of ß-D-glucose pentaacetate with an alkanethiol in chloroform in the presence of 5 equivalents of boron trifluoride etherate.[4] The ß-product was obtained by quenching the reaction after 15 min. Longer reaction times lead to considerable amounts of α-product. The products were purified by crystallization from hexane or ethanol.

The NMR data of *n*-decyl 1-thio-2,3,4,6-tetra-*O*-acetyl-ß-D-glucopyranoside are given as an example: ^{1}H NMR ($CDCl_3$) δ 0.86 (t,3H,H-10'); 1.24 (br m,14H,H-3'/9'); 1.57 (2H,H-2'); 1.99, 2.01, 2.04, 6.26 (4 × s,12H,$COCH_3$); 3.68 (m, H-1'); 3.69 (ddd,1H,H-5); 4.10 (dd,1H, $J_{5,6a}$=2.4 Hz, $J_{6a,6b}$=12.5 Hz); 4.22 (dd,1H, $J_{5,6b}$=4.9 Hz); 4.47 (d,1H,H-1, $J_{1,2}$=10 Hz); 5.01 (dd,1H); 5.06 (dd,1H); 5.20 (dd,1H). ^{13}C NMR δ 13.9 (C-10"); 20.4, 20.5 (4C,acetyl); 22.5 (C-1'); 28.6, 28.9, 29.1, 29.3, 29.4, 29.8, 31.7 (C-2'/9'); 62.0 (C-1'); 68.1, 69.7, 73.7, 75.6 (C-2/5); 83.4 (C-1); 169.1, 169.2, 170.0, 170.4 (4C,acetyl).

n-Alkyl 1-thio-ß-D-glucopyranosides. The acetylated alkyl glucosides were deprotected with trimethylamine in aqueous methanol. The reagent was prepared by mixing a 45% solution of trimetylamine in water was mixed with 4 volumes of methanol. After 24 h the solvent was evaporated and the remaining syrup was crystallized from methanol/acetonitrile.

The NMR data of *n*-decyl 1-thio-ß-D-glucopyranoside are given as a typical example: ^{1}H NMR (CD_3OD) δ 0.94 (t,3H,CH_3); 1.34 (m,14 H,H-3'/9'); 1.67 (m,2H,H-2'), 2.74 (m,2H,H-1'); 3.33 (m,4H,H-2,3,4,5); 3.70 (dd,1H,H-6a, $J_{5,6a}$=5.2 Hz, $J_{6a,6b}$=12.1 Hz); 3.90 (dd,1H,H-6b, $J_{5,6b}$=2.1 Hz); 4.40 (d,1H,H-1, $J_{1,2}$=9.5 Hz). ^{13}C NMR δ 14.5 (C-10'), 23.7 (C-1'), 30.0, 30.3,

30.4, 30.7, 30.8, 31.0, 33.0 C-2'/9'); 62.9 (C-6); 71.4, 74.3, 79.5, 81.9 (C-2/5); 87.1 (C-1).

Naphthyl or (4'-substituted-phenyl) 2,3,4,6-tetra-O-acetyl ß-D-glucopyranosides. Typically 7.8 g (20 mmol) of ß-D-glucose pentaacetate and 2.9 g (20 mmol) of ß-naphthol was dissolved in 40 ml of dry dichloromethane. Molecular sieves (4 Å) were added. A 50 % (w/w) solution of boron trifluoride etherate (5.6 ml, 1 equivalent) was added. The reaction mixture was stirred at room temperature for 48 h and then poured into 100 ml of 5 % sodium bicarbonate solution. The organic layer was separated, washed with sodium bicarbonate and once with water, dried over magnesium sulphate and concentrated. The crude product was recrystallized from ethanol. Yield 69 % (compared to 32 % obtained from a stannic chloride catalyzed reaction), m.p.= 129-130°C.

NMR data for (2-naphthyl) 2,3,4,6-tetra-*O*-acetyl ß-D-glucopyranoside: ^{1}H NMR ($CDCl_3$) δ 2.02 (3 × s,12H,acetyl); 3.86 (m,1H,H-5); 4.16 (dd,1H); 4.27 (dd,1H); 5.17 (m,2H); 5.29 (m,2H); 7.13, 7.31-7.45, 7.69-7.77 (m,7H, naphthyl). ^{13}C NMR δ 20.3, 20.4, 20.4, 20.5 (4C,acetyl), 61.9 (C-6), 68.2, 71.1, 71.9, 72.6 (C-2/5), 98.9 (C-1); 111.3, 118.6, 124.5, 126.4, 126.8, 127.5, 129.5 (7C, aromatic C-H); 130.0, 133.9 (C-9',10'); 154.4 (C-2'); 169.0, 169.2, 169.9, 170.3 (4C, acetyl).

Naphthyl or (4'-substituted-phenyl) ß-D-glucopyranosides were obtained by deprotection of the corresponding acetylated precursors with trimethyl amine in aqueous methanol. The glucopyranosides were recrystallized from methanol.

NMR data of naphthyl ß-D-glucopyranoside. ^{1}H NMR (CD_3OD) δ 3.31 (dd,1H); 3.47 (m,3H); 3.74 (dd,1H); 3.93 (dd,1H); 5.07 (d,1H,H-1, $J_{1,2}$6.8 Hz); 7.27-7.49, 7.75, 7.78 (m,7H, naphthyl). ^{13}C NMR δ 62.5 (C-6); 71.4, 75.0, 78.0, 78.2 (C-2-5); 102.4 (C-1); 112.0, 119.9, 125.2, 127.3, 128.2, 128.5, 130.3 (7C, aromatic C-H); 131.2, 135.8 (C-9'-10'); 156.8 (C-2').

4,6-O-alkylidene n-alkyl 1-thio-ß-D-glucopyranosides (**1**). *n*-Alkyl 1-thio-ß-D-glucopyranoside (2 mmol) and alkanal (4 mmol) were dissolved in 20 ml of ethyl acetate and stirred for 48 h with 0.1 ml of methanesulfonic acid. The reaction mixture was neutralized with 3 ml of saturated $NaHCO_3$ solution. The organic layer was separated, dried over magnesium sulphate and concentrated. The product was separated from the excess of alkanal by column chromatography on silica gel with chloroform followed by 10 % methanol in chloroform as eluent. The alkanal is eluted from the column before the reaction product. The colorless product was recrystallized from methanol.

NMR data of 4,6-O-decylidene *n*-decyl 1-thio-ß-D-glucopyranoside (**1d**). ^1H NMR ($CDCl_3$): δ 0.87, (t,3H,H-10'); 1,25 (m,28H,H-3'/9'); 1.59-1.65 (m,4H,H-2', 2"); 2.69 (t,2H,H-1'); 3,31 (ddd,2H,H-6); 3,42, 3.50, 3.72 (3×dd, 3H,H-2/4); 4.14 (ddd,1H,H-5); 4.37 (d,1H,H-1); 4.52 (t,2H,H-1"); 2.79, 3.04 (2× br s, OH). ^{13}C NMR δ 14.0 (C-10' and C-10"); 22.58 (C-1'); 24.0, 28.7, 29.1, 29.2, 29.3, 29.4, 29.5, 30.0, 30.5, 31.8, 34.1 (C-2'/9' and C-2"/9"); 68.0 (C-6); 70.7, 73.1, 74.4, 79.7 (C-2/5); 86.7 (C-1); 102.7 (C-1"). Elemental analysis: calculated: %C 65.78, H 10.62, S 6.75. Found: %C 65.60, H 10.48, S 6.63.

Elemental analysis of 4,6-*O*-octylidene *n*-octyl 1-thio-ß-D-glucopyranoside (**1c**): calculated: %C 63.12 %H 10.11; found: %C 63.56 %H 10.23.

Elemental analysis of 4,6-*O*-hexylidene *n*-hexyl 1-thio-ß-D-glucopyranoside (**1a**): calculated: %C 59.64, %H 9.45; found: %C 59.99, %H 9.53.

NMR data of 4,6-*O*-octylidene (ß-naphthyl) ß-D-glucopyranoside (**4a**). ^1H NMR ($CDCl_3$) δ 0.76 (t,1H,H-8"); 1.16 (br m,8H,H-4"/7"); 1.30 (m,2H,H-3"); 1.56 (m,2H,H-2"); 3.23 (dd,1H); 3.35 (m,1H,H-5); 3.46 (dd,1H); 3.56 (dd,1H); 3.64 (dd,1H); 4.10 (dd,1H); 4.46 (t,1H,H-1"); 5.00 (d,1H,H-1, $J_{1,2}$=7.6 Hz). ^{13}C NMR ($CDCl_3$,CD_3OD) δ 13.6 (C-8"); 22.27, 23.7, 28.8, 29.1, 31.4, 34.0 (C-2"-7"); 68.0 (C-6); 66.6, 73.1, 74.2, 79.8 (C-2-5); 101.6 (C-1); 102.6 (C-1"); 111.5, 118.7, 124.2, 126.2, 126.9, 127.3, 129.3 (aromatic C-H); 129.9, 134.0 (C-9'-10'); 154.7 (C-2'). Elemental analysis: calculated: %C

69.21, %H 7.74 found: %C 68.84, %H 7.79.

4,6-O-(4'-alkoxybenzylidene) n-alkyl 1-thio-ß-D-glucopyranosides (**2**) were prepared according to the procedure described by Miethchen et al.[12]

NMR data of 4,6-*O*-(dodecyloxybenzylidene) *n*-dodecyl 1-thio-ß-D-glucopyranoside (**2c**): ^{1}H ($CDCl_3$) δ 0.84 (t,6H,H-12' and H-12"); 1.24 (br m,36H,H-3'-11' and H-3"-11"); 1.58 (m,2H); 1.73 (m,2H); 2.67 (m,2H,H-1'); 3.2-3.4 (br m, 2H); 3.64 (m,2H); 3.85 (t, 2H,H-1"); 4.21 (ddd,1H,H-5); 3.34 (d,1H,H-1); 5.44 (s,1H, acetal); 6.85 (d,2H); 7.37 (d,2H). ^{13}C NMR δ 14.0 (C-12' and C-12"); 22.5 (C1'); 25.9, 28.7, 29.1, 29.2, 29.3, 29.4, 29.5, 29.9, 30.4, 31.8 (C-2'-11' and C-2"-11"); 67.9 (C-6); 68.4 (C-1"); 70.4, 73.1, 74.4, 80.2 (C-2-5); 86.6 (C-1); 101.7 (C,benzylidene); 114.1, 127.4 (4C,aromatic C-H); 129.0 (C, aromatic); 159.7 (aromatic C-O).

Elemental analysis of 4,6-*O*-(octyloxybenzylidene) *n*-octyl 1-thio-ß-D-glucopyranoside (**2a**): calculated: %C 66.98, %H 9.22; found %C 66.60, %H 9.27.

4,6-O-(4"-formylbenzylidene) n-alkyl 1-thio-ß-D-glucopyranoside. Typically, 5 mmol of *n*-alkyl 1-thio-ß-D-glucopyranoside and 5 mmol of terephthalic dialdehyde were dissolved in 20 ml of ethyl acetate. After addition of 0.1 ml of methanesulfonic acid, the reaction mixture was stirred for 24 h. 30 ml of ethyl acetate was added and the mixture was heated in a water bath to obtain a clear solution. The reaction mixture was neutralized by the addition of 5 ml of saturated $NaHCO_3$ solution, the organic layer was separated, dried over magnesium sulphate and concentrated. The crude reaction product, containing mono- and di- substituted product as well as unreacted aldehyde and *n*-alkyl 1-thio-ß-D-glucopyranoside, was purified by means of column chromatography using silica gel and chloroform and a chloroform methanol (9:1) mixture. The product was recrystallized from ethanol.

NMR data of 4,6-*O*-(4"-formylbenzylidene) *n*-pentyl 1-thio-ß-D-glucopyranoside. ^{1}H NMR ($CDCl_3$): δ 0.90 (t,3H,H-5'); 1.34 (4H,m,H-3',4'); 1.64 (m,2H,H2'); 2.71 (t,2H,H-1'); 3.48 (dd,1H); 3.51 (dd,1H); 3.69 (dd,1H); 3.77

(dd,1H); 3.83 (dd,1H); 4.35 (dd,1H,H-6a, $J_{6a,6b}$=10.6 Hz, $J_{6a,5}$=4.8 Hz); 4.44 (d,1H,H-1, $J_{1,2}$9.5 Hz); 5.59 (s,1H,benzylidene); 7.66 (d,2H); 7.87 (d,2H); 10.00 (s,1H,aldehyde). ^{13}C NMR 13.8 (C-5'); 22.1 (C-1'); 29.6, 30.6, 30.8 (C-2'-4'); 68.5 (C-6); 70.3, 73.3, 74.4, 80.3 (C-2-5); 86.8 (C-1); 100.7 (C,benzylidene); 127.0; 129.6 (aromatic C-H); 136.7, 142.8 (C-1",4"); 191.8 (C,aldehyde).

4,6-O-(4-[N-(4-n-alkylphenyl)-imino]-benzylidene)-n-alkyl-1-thio-ß-D-gluco-pyranosides (**5**). 0.5 mmol of 4,6-*O*-(4"-formylbenzylidene) *n*-alkyl 1-thio-ß-D-glucopyranoside and 0.5 mmol of 4-alkylaniline (or 4-anisidine) were dissolved in 3 ml of ethanol, two drops of acetic acid as catalyst were added. After 15 min. the Schiff base precipitated, was filtered of with suction and was recrystallized from ethanol.

NMR data of 4,6-*O*-(4-[N-(4-*n*-dodecylphenyl)-imino]-benzylidene)-*n*-decyl-1-thio-ß-D-glucopyranoside (**5f**). ^{1}H NMR ($CHCl_3$) δ 0.91 (t,3H,2×CH_3); 1.29 (br m, 32H,16×CH_3); 1.65 (m,4H,2×CH_2); 2.64 (m,2H,CH_2); 2.74 (t,2H,CH_2): 2.83 (br s,1H,)H); 3.15 (br s,1H,OH); 3.52 (dd,1H); 3.55 (dd,1H); 3.61 (dd, 1H); 3.80 (dd,1H); 3.85 (dd,1H); 4.38 (dd,1H,H-6, J_{5-6}= 4.8 Hz, J_{6a-6b}=10.6 Hz); 4.46 (d,1H,H-1, J_{1-2}=8.88 Hz; 5.60 (s,1H, benzylidene); 7.19 (2×d,4H,aniline); 7.60 (d,2H); 7.91 (d,2H); 8.48 (s,1H,imino). ^{13}C NMR δ 14.0 (2×CH_3); 22.5 (C-S); 28.8, 29.0, 29.2, 29.4, 29.5. 30.0, 30.6, 31.4, 31.8, 35.4 (CH_2, alkyl chains); 68.5 (C-6); 70.4, 73.2, 74.4, 80.3 (C-2/5); 86.8 (C-1); 101.3 (C-H,benzylidene); 120.7, 12.6, 128.5, 129.0 (4 × aromatic C-H); 137.0, 139.5, 141.0, 149.2 (4 aromatic C); 158.7 (C-H, imino).

ACKNOWLEDGEMENT

This research project was supported by the 'Centrale Beleids Ruimte', a special fund of the University of Groningen.

REFERENCES

1. G.A. Jeffrey, L.M. Wingert, *Liq. Cryst.*, **12**, 179 (1992).
2. H.A. van Doren, L.M. Wingert, *Mol. Cryst. Liq. Cryst.*, **198**, 381 (1991).
3. H.A. van Doren, L.M. Wingert, *Recl. Trav. Chim. Pays-Bas,* **113**, 260 (1994).
4. H.A. van Doren, R. van der Geest, R. M. Kellog, H. Wynberg, *Carbohydr. Res.*, **194**, 71 (1989).
5. S.A. Galema, J.B.F.N. Engberts, H.A. van Doren, submitted for publication in *Carbohydr. Res.*
6. J. Thiem, V. Vill, R. Mietchen, D. Peters, *J. Prakt. Chem.*, **333**, 173 (1991).
7. P. Pudlo, J. Thiem, V. Vill, *Chem. Ber.*, **123**, 1129 (1990).
8. B. Kohne, K. Praefcke, R.S. Omar, F. Frolow, *Z. Naturforsch.*, **41b**, 736 (1986).
9. S. Mabic, C. Benezra, J.P. Lepoittevin, *Tetrahedron Lett.*, **34**, 4531 (1993).
10. L. M. Wingert, G.A. Jeffrey, J. Baker, D.C. Baker, *Liq. Cryst.*, **13**, 467 (1993).
11. Z.J. Li, L.N. Cai, M.S. Cai, *Synth. Commun.*, **22**, 2121 (1992).
12. R. Miethchen, D. Peters *Z. Chem.*, **28**, 298 (1988).
13. E. Bergonzi, R. Bernetti, C. Boffi, V. Brocca, E.A. Cleveland, *Die Stärke*, **12**, 386 (1964).
14. W.V. Dahlhoff, K. Riehl, P. Zugenmaier, *Liebigs Ann. Chem.*, 1063, (1993).
15. M. Marcos, J.L. Serrano, T. Sierra, M. J. Giménez, *Chem. Mater.*, **5**, 1332 (1993).
16. H. Kelker, R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980, p 47.
17. Y.Y. Hsu, D. Dolphin, *Mol. Cryst. Liq. Cryst.*, **42**, 327 (1977).
18. C. Tschierske, A. Lunow, D. Joachimi, F. Hentrich, D. Girdziunaite, H. Zaschke, A Mädicke, G. Brezesinski, F. Kuschel. *Liq. Cryst.,* **9**, 821 (1991).
19. D. Joachimi, C. Tschierske, H. Müller, J.H. Wendorff, L. Scheinder, R. Kleppinger, *Angew. Chem. Int. Ed. Engl.*, **32**, 1165 (1993).