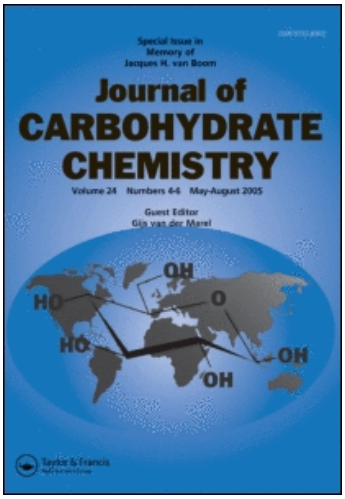

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LIQUID CRYSTALLINE 6-DEOXY GLYCOSIDES

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ABSTRACT

Octyl and dodecyl fucosides were synthesized by the tin tetrachloride catalyzed reaction of fucose tetraacetate 7 and the corresponding alcohol. Separation of the reaction mixture afforded pyranosides and furanosides. The liquid crystalline properties of compounds 6, 11 and 14 were determined, and for the last a new phase is observed and discussed. Beyond the classical rules for liquid crystalline behavior, molecular principles which serve as a basis for a broader interpretation of all different mesophases are proposed. The synthesized derivatives are considered to represent a novel organisational type of liquid crystalline compounds, for which the concept "monolayer with frustrated chain end" is suggested.

INTRODUCTION

Recently, the liquid crystalline properties of alkyl glycosides, first described years ago,[1-3] were fully appreciated,[4-7] and now there is an increasing interest in the properties of similar compounds. The principles that are

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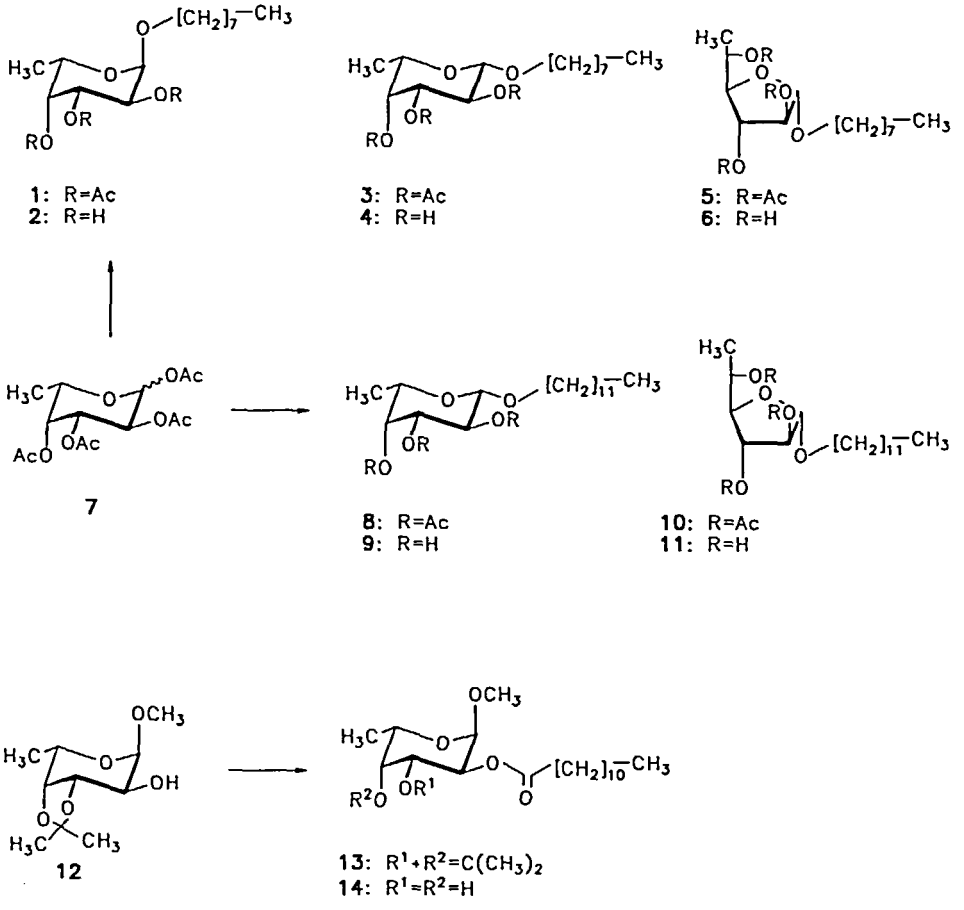
important for amphiphilic liquid crystals are different from those for classical non amphiphilic compounds,[8] which we would like to call "monophilic".

In the case of amphiphilic ionic alkali salts of carboxylic acids [9,10] liquid crystalline phases are observed only at high temperatures. Compared to those phases which are difficult to characterize, mesophases of carbohydrates are easy to study.[5] Carbohydrate derivatives are not only interesting for their liquid crystalline properties, but also serve as model compounds for molecular interactions. Further, they show surfactant properties,[11,12] which are also of technical interest. Analogous compounds are found in plasma membrane, and are involved in a variety of important biological processes.[13]

RESULTS AND DISCUSSION

Synthesis of Compounds. The long chain L-fucosides **1** - **6** and **8** - **11** were synthesized by direct glycosylation of the tetraacetate **7** using tin tetrachloride as a catalyst.[14,15] The glycosyl donor **7** was prepared by acetylation with acetic anhydride and sodium acetate under reflux to yield an anomeric mixture of acetates, in which the ß-isomer predominated (more than 80 %). A 1,2-*trans* orientation of acetyl groups is necessary for the glycosylation step. Tin tetrachloride induced the cleavage of the 1-acetoxy group, which leads to the acetoxonium ion, and this undergoes nucleophilic attack by the alcohol. This glycosylation reaction may be controlled, because under kinetic conditions enhanced ß-glycoside yields are obtained, whereas longer reaction times lead to α-glycosides as major products.[16] The influence of the reaction conditions on the anomeric ratio was not tested. However, it was shown that glycosylation of **7** with octanol at room temperature yielded the same ratio of fucosides after 3 h as after 24 h; namely, approximately a 1 : 1 : 1 mixture of pyranosides **1** and **3** and the furanoside **5**. The analoguous reaction with dodecanol afforded the furanoside **10**, accompanied by the ß-pyranoside **8**, whereas no α-glycoside was formed.



SCHEME 1

While it was easy to determine the structures of the α- and ß-pyranosides by interpreting the coupling constants $^{3}J_{1,2}$ in the proton NMR spectra, this does not really proof the ß-configuration of the furanosides 6 and 11, though the small values of 1.6 and 1.9 Hz, respectively, give rise to a trans-orientation of H-1 and H-2. Further information was obtained by a gated decoupling NMR experiment. The hetero coupling constants ^{1}J(C-1,H-1), 170.2 Hz for 6 and 170.3 Hz for 11, confirm the ß-configuration of the furanosides after comparison with analogous literature data.[17]

It has often been shown that the course of the glycosylation not only depends on the configuration of the anomeric center but also at other ring positions, especially at C-4. The tin tetrachloride catalyzed glycosylation gives i.e. lower yields in the case of *galacto* configurated sugars than for *gluco* configurated derivatives.[16] Formation of furanosides under these conditions has not yet been reported.

Yields of glycosylations were not especially high. This may be due to the *galacto* configuration, and is also observed in the simple Fischer reaction of L-fucose. Low glycosylation yields in the fucose series may be due to the complex formation of both anomeric furanosides and pyranosides, which could be demonstrated during Fischer glycosylation of fucose in boiling methanol.[18]

The procedure applied leads to three isomeric products, which are expected to be interesting for studies of their liquid crystalline properties. To facilitate purification by flash chromatography, reacetylation of the reaction mixture was done to completely acetylate the excess of alcohol. After chromatography the mixture was deprotected by Zemplén deacetylation, either directly or after HPLC separation (hexane/ethyl acetate, 7 : 1, 5 % methanol). Further purification of the unprotected glycosides was performed on a strongly basic anion exchange resin column, which separates glycosides according to their different pK_a-values.[19]

The long chain esterified methyl fucoside 13 was obtained from 12 [20] by reaction with lauroyl chloride in pyridine. Cleavage of the 3,4-O-isopropylidene group led to 14 which was recrystallized from n-hexane.

Models for Molecular Arrangement and Liquid Crystalline Behavior

The two basic reasons which have to be considered for the development of mesomorphic phases are the molecular form on the one hand and on the other hand the internally contrasting characteristics, (i.e. different polarities, different hydrophilicity, or different shape) and this we like to call "intramolecular contrast". A favorable molecular form causes a closely packed arrangement of the mesophase,[21]

while the intramolecular contrast leads to ordered phases by separating certain parts of the molecule.[22] This in turn affords a rise in attractive interactions.

According to these two principles, thermotropic liquid crystals are devided into amphiphilic and monophilic liquid crystals. In the group of amphiphilic liquid crystals the intramolecular contrast causes the formation of the mesophase, whereas stereochemistry has only modulating influence. In contrast, for monophilic (not amphiphilic) liquid crystal species, stereochemistry is responsible for the formation of the mesophase, and electronic effects have only a minor modulating influence. The dominant structural element of monophilic liquid crystals is the mesogenic group.[8]

In contrast, the formation of amphiphilic liquid crystals is based on the interaction of different and clearly separated parts within the molecules (e.g. hydrophilic, lipophilic, fluorophilic). According to number, form, position and length of fragments, layer,[5] columnar,[23] and cubic[24,25] structures are formed which, in the case of thermotropic liquid crystals, are called smectic, discotic, and cubic phases. They find their lyotropic counterparts[26] in lamellar, middle, and cubic phases.

The formation of liquid crystalline phases during cooling of amphiphilic carbohydrate derivatives finds an analogy in the separation of solvent mixtures of polyols and paraffins, except for the following difference: there is no macroscopic separation into two phases, but some sort of "micro separation" on a molecular scale.[22] This is why the molecular regions with different polarities are clearly separated.

Recently, Praefcke et al.[23] and van Doren et al.[27] demonstrated that the formation of a mesophase in the case of discotic amphiphiles is prevented by removal of a hydroxy group from the central hydrophilic region. To reconsider the conditions for the appearance of liquid crystalline properties, especially for smectic phases, the 6-deoxy glycosides 2, 4, 6, 9 and 11 were synthesized and examined.

Observed Liquid Crystalline Properties and Discussion

Until now, smectic phases formed by amphiphilic substances have only been observed as interdigitated bilayers,[5] and these are of little relevance for any technical application. Highly polar unidirectional orientated smectic monolayer phases, however, give promise of displaying interesting electric, and especially ferroelectric properties.

As was expected, the fucopyranosides 2, 4 and 9 show no liquid crystalline properties, even when compound 4 was supercooled below 0°C. However, alkyl pentosides such as 15, with the same number of hydroxy groups form smectic S_A phases. The clearing temperature of the octyl ß-xylopyranoside 15 is 84.9°C and the melting point is reported[28] to be 92°C. In contrast to the fucopyranosides the furanosides 6 and 11 show S_A phases. Their clearing points (see Table 1) are rather high, and this can hardly be explained by the classical bilayer model (Figure 1). The terminal methyl groups are positioned exactly in the hydrophilic center of the molecule and thus formation of hydrogen bonds is restricted (see Figure 1, handicapped bilayer structure). The 5-methyl group represents a small lipophilic area ("frustrated end") which cannot form an ordered region within the mesophase. Instead, the methyl group may combine with the longer alkyl chain at C-1 to form a lipophilic region (Figure 2, polar monolayer). Preliminary physical experiments show that the orientation of this phase may be changed by an alternating electric field.

The 2-lauroyl derivative 14 shows a new phase (M in Table 1), which is not miscible with either the smectic phases of alkyl glycosides, nor the α-phase of glycerides.The form of this molecule does not comply with the demands for classical amphiphilic phases such as S_A or discotic phases. The mesophase of 14 shows a viscosity comparable to ordered smectic or discotic phases, it is optically uniaxial, and this is consistent with the properties of columnar discotic liquid crystals. The texture of this material has not previously been described for thermotropic liquid crystals.

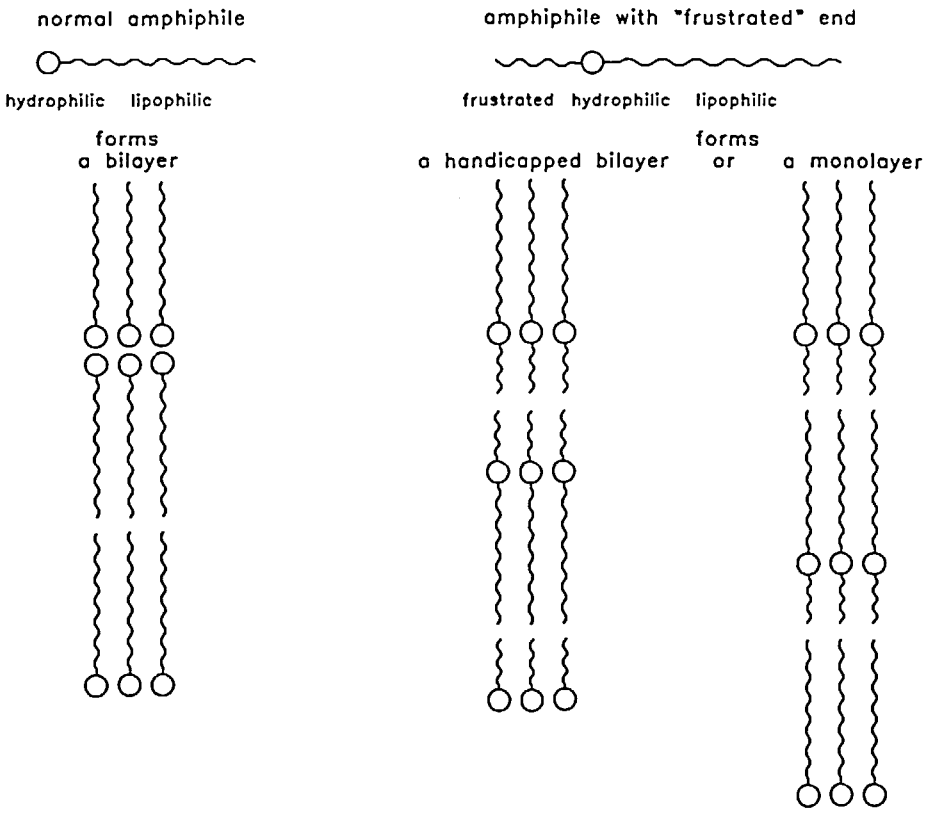
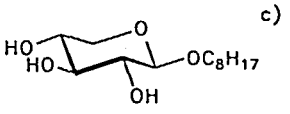
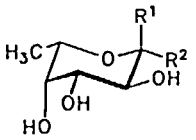
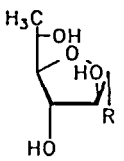
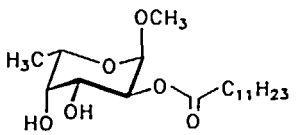


FIGURE 1. Supramolecular Structure as Conception for Smectic A Phase of Fucose Glycosides.

However, in some cases similar patterns have been reported for lyotropic middle phases.[29] With a cover slide textures are observed which are composed of many fine-grained, hardly resolvable lines. Without a cover slide a texture is observed which looks like strokes of a brush (van Gogh manner). Uniaxial growth of the phase is characteristic, and thus some similarity to discotic phases can be assumed.

Compound 14 can be divided into three regions of different polarity (see Figure 2). The new phase may be explained by aggregation of the polar parts of the molecule into columns, which are surrounded in the outer sphere by the semipolar regions. The area between these columns is filled by the flexible nonpolar hydrocarbon chains.

TABLE 1. Properties of Liquid Crystalline L-Fucose Glycosides.

Compounds	Phase transitions [a) b)]
 c) **15**	(80) K 91.9 (S_A 84.9) I
	
2 R^1 = OC_8H_{17}, R^2 = H	(62) K 113.6 I
4 R^1 = H, R^2 = OC_8H_{17}	(<20) K 62.0 I
9 R^1 = H, R^2 = $OC_{12}H_{23}$	(<20) K 75.6 I
	
6: R=OC_8H_{17}	K 75.2 (S_A ca.20) I
11: R=$OC_{12}H_{23}$	K 89.5 (S_A 49.5) I
	
14	K 61.5 (M 54.2) I

Abbreviations:
a) Number in parentheses: solidification temperature, K: crystalline, S_A: smectic A, M: unknown mesophase, I: isotropic phase (normal fluid).
b) Temperatures in °C.
c) Kindly provided by Dr.P.Rollin, LCBA, University of Orléans; compare ref.28).

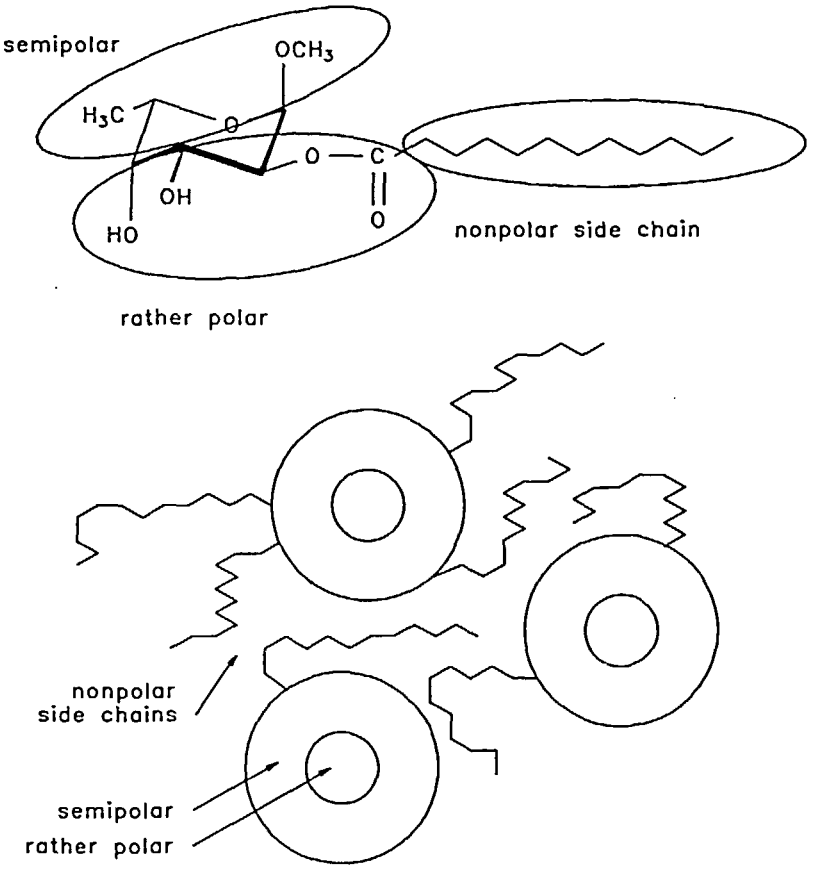


FIGURE 2. Proposal for the Spatial Assignment according to the Three Regions of Different Polarity of Compound 14. (Top: Polarity-Structural-Function Assignment; Bottom: View from Above of Assumed Packing of 14.)

These results show that novel liquid crystalline phenomena can be discovered and interpreted beyond well-established classical models for liquid crystalline behavior.

EXPERIMENTAL

General Methods. Reactions were monitored by TLC on silica gel 60 GF_{254} (Merck) or on reversed phase RP-18 GF_{254} (Merck) with detection by charring with sulfuric acid. Flash chromatographic purifications were performed on silica gel 60 (230-400 mesh). HPLC separations were performed with Knauer

equipment on a Knauer Nucleosil 100 column (diameter 32 mm). Anion exchange resin separations were performed on Dowex 1x2 p.A. (200-400 mesh, Cl^- form, Serva) after transformation into the OH^- form, eluting with methanol. Melting points were determined with an Olympus polarization microscope. Optical rotations were measured with a Perkin-Elmer polarimeter 241 (Na-D wave length). ^1H-NMR spectra were recorded at 300 (Bruker AM 360) or 400 MHz (Bruker WM 400). Microanalyses were performed by the microanalytical laboratory of the Organisch-Chemisches Institut, Universität Münster.

Liquid Crystalline Properties. The phase transitions were observed with an Olympus polarization microscope BH, equipped with a Mettler heating table FP 82.

Octyl 2,3,4-Tri-O-acetyl-6-deoxy-α- and ß-L-galactopyranoside (1) and (3) and Octyl 2,3,5-Tri-O-acetyl-6-deoxy-ß-L-galactofuranoside (5) . Compound 7 (9.0 g, 27.1 mmol) was dissolved in anhydrous dichloromethane (200 mL), stirred with molecular sieve (4 Å, 10 g) for 15 min, and treated with tin tetrachloride (3.5 mL, 29.9 mmol) and 1-octanol (4.5 mL, 28.6 mmol). Stirring was continued for 3 h at room temperature, and then the mixture was neutralized with sodium hydrogen carbonate solution, extracted with dichloromethane, dried (MgSO4) and evaporated. The crude product was reacetylated (10 mL anhydrous pyridine, 2 mL acetic anhydride) and then coevaporated with toluene to yield 5.4 g (50 %) of a yellow syrup. This mixture was separated by HPLC (hexane/ethyl acetate, 12 : 1, 1 % methanol) to give 2.18 g (20 %) α-octyl pyranoside (1), 1.50 g (14 %) ß-octyl pyranoside (3), and 1.48 g (14 %) ß-octyl furanoside (5) as colourless syrups, which were identified by proton NMR spectra.

1: ^1H NMR ($CDCl_3$) δ 0.83 (t, 3H, alkyl CH_3), 1.09 (d, $J_{5,6}$=6.6 Hz, 3H, 6-H), 1.22 (m_c, 10 H, alkyl H), 1.52 (m_c, 2H, $OCH_2\underline{CH_2}$), 1.93, 2.03, 2.10 (each s, 3H, $OCOC\underline{H_3}$), 3.34 (ddd ≈ m_c, OCH, aliph.chain), 3.61 (ddd ≈ m_c, OCH', aliph.chain), 4.10 (bq, $J_{4,5}$=1.2 Hz, $J_{5,6}$=6.6 Hz, 5-H), 5.01 (dd, $J_{1,2}$=3.7 Hz, $J_{2,3}$=10.8 Hz, 2-H), 5.06 (d, $J_{1,2}$=3.7 Hz, 1-H), 5.24 (dd, $J_{3,4}$=3.4 Hz, $J_{4,5}$=1.2 Hz, 4-H), 5.30 (dd, $J_{2,3}$=10.8 Hz, $J_{3,4}$=3.4 Hz, 3-H).

3: ^1H NMR ($CDCl_3$) δ 0.84 (t, 3H, alkyl CH_3), 1.18 (d,

$J_{5,6}$=6.6 Hz, 3H, 6-H), 1.23 (m_c, 10 H, alkyl H), 1.52 (m_c, 2H, $OCH_2C\underline{H}_2$), 1.94, 2.00, 2.12 (each s, 3H, $OCOCH_3$), 3.41 (m_c, $OC\underline{H}$, aliph.chain) 3.75 (dq, $J_{4,5}$= 1.1 Hz, $J_{5,6}$=6.6 Hz, 5-H), 3.85 (m_c, $OC\underline{H}'$, aliph.chain), 4.38 (d, $J_{1,2}$=8.0 Hz, 1-H), 4.98 (dd, $J_{2,3}$=10.6 Hz, $J_{3,4}$=3.3 Hz, 3-H), 5.14 (dd, $J_{1,2}$=8.0 Hz, $J_{2,3}$=10.6 Hz, 2-H), 5.19 (dd, $J_{3,4}$=3.3 Hz, $J_{4,5}$=1.1 Hz, 4-H).

5: ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, alkyl CH_3), 1.23(m_c, 10H, alkyl H), 1.27 (d, 3H, $J_{5,6}$=6.6 Hz, 6-H), 1.56 (m_c, 2H, $OCH_2C\underline{H}_2$), 2.05, 2.06, 2.07 (each s, 3H, $OCOC\underline{H}_3$), 3.42 (ddd ≈ m_c, OCH, aliph.chain), 3.64 (ddd ≈ m_c, OCH', aliph.chain), 4.04 (dd, $J_{3,4}$=5.9 Hz, $J_{4,5}$=4.3 Hz, 4-H), 4.97 (m, 3H, 1-H, 2-H, 3-H), 5.12 (dq, $J_{4,5}$=4.3 Hz, $J_{5,6}$=6.6 Hz, 5-H).

Deprotection of the acetylated octyl glycosides 1, 3 and 5. The sugar (2 mmol) was dissolved in anhydrous methanol (20 mL), treated with a small amount of solid sodium methanolate until the reaction was complete, neutralized (Amberlite IR 120, H^+), filtered, concentrated and purified by flash chromatography (chloroform/methanol, 5 : 1).

Octyl 6-Deoxy-α-L-galactopyranoside (2). The acetylated sugar 1 (1.5g, 3.72 mmol) was deprotected, purified and recrystallized from methanol to yield 550 mg (54 %) of 2, m p 113.7°C. - $[\alpha]D^{20}$ - 123.4° (c 1.1, methanol). - ^{1}H NMR (d_4-MeOH) δ 0.89 (t, 3H, alkyl CH_3), 1.20 (d, $J_{5,6}$=6.6 Hz, 3H, 6-H), 1.31 (m_c, 10 H, alkyl H), 1.61 (m_c, 2H, $OCH_2C\underline{H}_2$), 3.43 (m_c, $OC\underline{H}$, aliph. chain), 3.65 (m_c, 2H, 4-H, $OC\underline{H}'$, aliph. chain), 3.72 (m_c, 2H, 2-H, 3-H), 3.93 (dq, $J_{4,5}$=0.8 Hz, $J_{5,6}$=6.6 Hz, 5-H), 4.74 (d, $J_{1,2}$=2.0 Hz, 1-H).

Anal. Calcd for C_{14} H_{28} O_5 (276.4): C, 60.84; H, 10.21. Found: C, 60.70; H, 10.22.

Octyl 6-Deoxy-β-L-galactopyranoside (4). The acetylated sugar 3 (1.1 g, 2.73 mmol) was deprotected to give 545 mg (72 %) of 4 after chromatography and crystallization from n-hexane, m p 67°C. $[\alpha]D^{25}$ + 19.9° (c 1.0, methanol).- ^{1}H NMR (d_4 - MeOH) δ 0.89 (t, 3H, alkyl CH_3), 1.26 (d, $J_{5,6}$=6.7 Hz, 6-H), 1.32 (m, 10 H, alkyl H), 1.60 (m, 2H, $OCH_2C\underline{H}_2$), 3.44 (m_c, 2H, 2-H, 4-H), 3.50 (m, OCH, aliph.chain), 3.58 (m, 2H, 3-H, 5-H), 3.82 (m, OCH', aliph.chain), 4.16 (m, 1-H).

Anal. Calcd for C_{14} H_{28} O_5 (276.4): C, 60.84; H, 10.21. Found: C, 60.48; H, 10.43.

Octyl 6-Deoxy-ß-L-galactofuranoside (6). The acetylated sugar 5 (1.2 g, 2.98 mmol) was deprotected to give 500 mg (61 %) of 6 after chromatography, m p 75°C, $[\alpha]D^{25}$ +94.3° (c 1.0, methanol). - ^{1}H NMR (d_4 - MeOH) δ 0.89 (t, 3H, alkyl CH_3), 1.24 (d, $J_{5,6}$=6.6 Hz, 3H, 6-H), 1.29 (m, 10 H, alkyl H), 1.56 (m, 2H, $OCH_2C\underline{H}_2$), 3.41 (m, OCH, aliph. chain), 3.69 (dd, $J_{3,4}$=6.3 Hz, $J_{4,5}$=4.8 Hz, 4-H), 3.70 (m, OCH', aliph.chain), 3.83 (m, $J_{5,6}$=6.6 Hz, $J_{4,5}$=4.8 Hz, 5-H), 3.85 (dd, $J_{2,3}$=3.6 Hz, $J_{3,4}$=6.3 Hz, 3-H), 3.94 (dd, $J_{1,2}$=1.6 Hz, $J_{2,3}$=3.5 Hz, 2-H), 4.84 (d, $J_{1,2}$=1.6 Hz, 1-H). -^{13}C NMR (d_4-MeOH) δ 14.4 (alkyl CH_3), 19.8 (C-6), 23.6, 27.2, 30.3, 30.4, 30.6, 32.9 (alkl C), 68.3 (C-5), 68.7 (OC alkyl), 79.3 (C-3), 83.5 (C-2), 88.2 (C-4), 109.1 (C-1); ^1J(C-1,H-1)=170.2 Hz.

Anal. Calcd for C_{14} H_{28} O_5 (276.4): C, 60.84; H, 10.21. Found: C, 61.01; H, 10.45.

Dodecyl 6-Deoxy ß-L-galactopyranoside (9) and Dodecyl 6-Deoxy-ß-L-galactofuranoside (11). Compound 7 (10.0 g,30.1 mmol) was dissolved in anhydrous dichloromethane (300 mL) and stirred with molecular sieves (4 Å, 10 g) for 15 min. The solution was treated with tin tetrachloride (3.5 mL, 29.90 mmol) and 1-dodecanol (8.4 mL, 45.1 mmol) and stirred at room temperature for 48 h. It was neutralized with sodium hydrogen carbonate solution, extracted with dichloromethane, the extract was concentrated and purified by flash chromatography (n-hexane/ethyl acetate, 4 : 1) to yield 6.2 g (13.52 mmol) of the glycoside mixture. The crude mixture was dissolved in anhydrous methanol (60 mL) and treated with solid sodium methanolate. After deacetylation was complete, the solution was neutralized (Amberlite, IR 120 H^+), filtered and concentrated. The product mixture (4.2 g, 12.63 mmol) was detected on RP-18 -plates (acetonitrile/water 90 : 10). Two main products were separated after purification on an anion exchange resin column to yield 1.0 g (10 % based on tetraacetate 7) of pyranoside 9 and 2.39 g (24 % based on tetraacetate 7) of furanoside 11.

9: m p 75.6°C, $[\alpha]D^{25}$ + 13.2° (c 1.0, in methanol). ^{1}H NMR (d_4-MeOH) δ 0.89 (t, 3H, alkyl $C\underline{H}_3$), 1.25 (d, $J_{5,6}$=6.5 Hz, 3H, 6-H), 1.29 (m, 18H, alkyl H), 1.60 (m, 2H, $OCH_2C\underline{H}_2$), 3.44 (m,

2H, 2-H, 4-H), 3.50 (m, OCH, aliph. chain), 3.59 (m, 2H, 3-H, 5-H), 3.82 (m, OCH', aliph.chain), 4.16 (m, 1-H).

Anal. Calcd for $C_{18}H_{36}O_5$ (332.5): C, 65.02; H, 10.91. Found: C, 65.44; H, 10.90.

11: m p 90°C, $[\alpha]D^{25}$ + 72.05° (c 1.0, methanol). ^{1}H-NMR (d_4-MeOH) δ 0.89 (t, 3H, alkyl CH_3), 1.23 (d, $J_{5,6}$=6.6 Hz, 6-H), 1.29 (m, 18 H, alkyl H), 1.58 (m, 2H, OCH_2H_2), 3.41 (m, OCH, aliph.chain), 3.67 (dd, $J_{3,4}$=6.4 Hz, $J_{4,5}$=4.8 Hz, 4-H), 3.70 (m, OCH', aliph.chain), 3.81 (m, $J_{4,5}$=4.8 Hz, $J_{5,6}$=6.6 Hz, 5-H), 3.83 (dd, $J_{2,3}$=3.5 Hz, $J_{3,4}$=6.4 Hz, 3-H), 3.92 (dd, $J_{1,2}$=1.9 Hz, $J_{2,3}$=3.5 Hz, 2-H), 4.83 (d, $J_{1,2}$=1.9 Hz, 1-H).- ^{13}C NMR (d_4-MeOH): δ = 14.5 (alkyl CH_3), 19.9 (C-6), 23.8-33.1 (m, alkyl C), 68.4 (C-5), 68.8 (OC alkyl), 79.4 (C-3), 83.8 (C-2), 88.2 (C-4), 109.2 (C-1); ^1J(C-1,H-1)= 170.3 Hz.

Anal. Calcd for $C_{18}H_{36}O_5$ (332.5): C, 65.02; H, 10.91. Found: 65.09; H, 11.10.

Compounds 9 and 11 were also characterized by proton NMR data of the acetylated derivatives 8 and 10.

Dodecyl 2,3,4-Tri-O-acetyl-6-deoxy-ß-L-galactopyranoside (8).

^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, alkyl CH_3), 1.19 (d, $J_{5,6}$=6.6 Hz, 3H, 6-H), 1.22 (m, 18 H, alkyl H), 1.53 (m, 2H, OCH_2CH_2), 1.95, 2.01, 2.14 (each s, 3H, $OCOCH_3$), 3.41 (m, OCH, aliph.chain), 3.76 (dq, $J_{5,6}$=6.6 Hz, $J_{4,5}$=1.1 Hz, 5-H), 3.86 (m, OCH', aliph.chain), 4.38 (d, $J_{1,2}$=8.1 Hz, 1-H), 4.98 (dd, $J_{2,3}$=10.7 Hz, $J_{3,4}$=3.7 Hz, 3-H), 5.15 (dd, $J_{1,2}$=8.1 Hz, $J_{2,3}$=10.7 Hz, 2-H), 5.19 (dd, $J_{3,4}$=3.7 Hz, $J_{4,5}$=1.1 Hz, 4-H).

Dodecyl 2,3,5-Tri-O-acetyl-6-deoxy-ß-L-galactofuranoside (10). ^{1}H NMR ($CDCl_3$) δ 0.84 (t, 3H, alkyl CH_3), 1.22 (m, 18H, alkyl H), 1.28 (d, $J_{5,6}$=6.6 Hz, 3H, 6-H), 1.56 (m, 2H, OCH_2CH_2), 2.05, 2.06, 2.07 (each s, 3H, $OCOCH_3$), 3.42 (m, OCH, aliph.chain), 3.63 (m, OCH', aliph.chain), 4.04 (dd, $J_{3,4}$=5.8 Hz, $J_{4,5}$=4.2 Hz, 4-H), 4.97 (m, 3H, 1-H, 2-H, 3-H), 5.12 (m, $J_{4,5}$=4.2 Hz, $J_{5,6}$=6.6 Hz, 5-H).

Methyl 6-Deoxy-2-O-dodecanoyl-3,4-O-isopropylidene-α-L-galactopyranoside (13). A solution of 12[19] (490 mg, 2.1 mmol) in anhydrous pyridine (20 mL) was treated with lauroyl chloride (dodecanoyl chloride, 0.6 mL, 2.6 mmol). This mixture was stirred at room temperature for 24 h, then

diluted with water, extracted with dichloromethane and concentrated with toluene to yield 800 mg (208 mmol, 99 %) of an orange syrup. The crude product was pure enough to be used in the next step. Purification was performed on silica gel (toluene/ethylacetate, 4 : 1, v/v) to obtain analytical data. $[\alpha]D^{20}$ -98.9° (c 1.0, chloroform). ^1H NMR ($CDCl_3$) δ 0.86 (t, 3H, alkyl CH_3), 1.23 (mc, 16 H, alkyl H), 1.32 (s, 3H, $OCCH_3$), 1.35 (d, $J_{5,6}$=6.6 Hz, 3H, 6-H), 1.50 (s, 3H, $OCCH_3$), 1.61 (m_c, 2H, $OCOCH_2C\underline{H}_2$), 2.36 (t, 2H, $OCOC\underline{H}_2$),3.34 (s, 3H, OCH_3), 4.06 (m_c, 2H, 4-H, 5-H), 4.27 (dd, $J_{2,3}$=8.2 Hz, $J_{3,4}$=5.2 Hz, 3-H), 4.78 (d, $J_{1,2}$=3.6 Hz, 1-H), 4.89 (dd, $J_{1,2}$=3.6 Hz, $J_{2,3}$=8.2 Hz, 2-H).

Anal. Calcd for $C_{12}H_{40}O_5$ (384.6): C, 68.71; H, 10.48. Found: C, 68.34; H, 10.46.

Methyl 6-Deoxy-2-O-dodecanoyl-α-L-galactopyranoside (14). A solution of 13 (200 mg, 0.52 mmol) in 50 % acetic acid (10 mL) was stirred for 3.5 h at 80°C. The mixture was concentrated with toluene and purified on silica gel (hexane/ethyl acetate, 1 : 1) to yield 130 mg of 14 (73 %) as colorless crystals, m p 62°C, $[\alpha]D^{20}$ -82.4° (c 1.0, chloroform). - ^1H NMR ($CDCl_3$) δ 0.84 (t, 3H, alkyl CH_3), 1.21 (m_c, 16 H, alkyl H), 1.26 (d, $J_{5,6}$=6.6 Hz, 3H, 6-H), 1.59 (m_c, 2H, $OCOCH_2C\underline{H}_2$), 2.36 (t, 2H, $OCOC\underline{H}_2$), 2.82 and 2.93 (d, 3-OH, 4-OH), 3.34 (s, 3H, OCH_3), 3.78 (m_c, 4-H), 3.94 (m_c, 2H, 3-H, 5-H), 4.81 (d, $J_{1,2}$=3.8 Hz, 1-H), 4.95 (dd, $J_{1,2}$=3.8 Hz, $J_{2,3}$=10.4 Hz, 2-H).- ^{13}C NMR ($CDCl_3$) : δ = 13.97 (s, alkyl CH_3), 15.98 (s, C-6), 24.84 - 34.19 (m, alkyl C), 55.20 (s, OCH_3), 65.46 and 68.43 (s, C-3, C-5), 71.21 (s, C-2), 72.22 (s, C-4), 97.35 (s, C-1), 174.42 (s, C=0).

Anal. Calcd for $C_{19}H_{36}O_5$ (344.5): C, 66.24; H, 10.53. Found: C, 66.29; H, 10.34.

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