Synthesis of Branched-Chain Alkyl Glucosides and Their Liquid Crystal Behaviour

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Abstract

Although glycolipids exist in nature, they can also be synthesized either chemically or enzymatically. Due to their role in the nervous system and biomembranes, natural glycolipids are extensively studied by researchers, especially biochemists, but their liquid crystal state is not well understood. In this paper, starting from glucose and a series of branched-chain alcohols, novel alkyl glycosides have been synthesized. These compounds have been structurally elucidated using standard spectroscopic techniques like hydrogen (^{1}H) NMR, carbon-13 (^{13}C) NMR, and infra-red- (IR) and also using high resolution mass spectrometry (HRMS). Their thermotropic liquid crystalline properties were investigated using polarizing microscopy and differential scanning calorimetry. It was found that the shorter carbon chain analogues gave the smectic A phase while the longer ones gave only the columnar phase. The results were compared with those of the straight chain counterparts.

I. Introduction

Research work on the behaviour of the synthetic straight-chain alkyl glycosides have been reported extensively in the literature [1], unlike those of the branched-chain alkyl glycosides. Nevertheless there were some recent papers on the biological functions of the natural branched-chain alkyl glycosides isolated from Carribbean marine sponges "*Plakortis Simplex*" [2,3]. Synthesis and liquid crystal studies of glycosides have been carried out previously for example for three derivatives of umbelliferyl β-D-glucoside which have a coumarin unit (Fig 1a). Their smectic A (Sm A) formation is influenced by the steric factor [4]. 4-Alkyloxyphenyl-β-D-glycopyranosides (methoxy to decyloxy and dodecyloxy) had also been synthesized (Fig 1b) [5] and their thermotropic and lyotropic phase behaviour were investigated. The compounds with the shortest alkoxy substituents have no liquid crystal properties. The butoxy derivative displays a monotropic Sm A while the higher homologues display enantiotropic Sm A phases. For lyotropic phases (hexagonal, cubic and lamellar), only the compounds with alkoxy chains longer than butoxy show such phases [5].

Investigation of the influence of anomeric linkage, configuration, ring size and flexibility as well as electric charges on the phase behaviour have been carried out for some long chain alkyl glycosides with monosaccharide head groups, for example hexadecyl-β-D-glycopyranosides (Fig 1c), were carried out [6].

In pharmaceutical research, perfluoroalkyl substituted carbohydrates are well known for their non-coagulating surfactants and emulsifying properties. Some of these materials and their related analogues have been synthesized for example with a semiperfluoro alkyl chain linked to the polar glucose head group (Fig 1d) [7].

A study on the synthetic glycolipids/water system was made where the problem of the high Krafft temperature was overcomed [8]. Partial phase diagrams and liquid crystalline mesophases of a series of 6-*O*-acyl-α,β-D-glycopyranoses were studied in heavy water as well as their surface properties e.g. critical micellar concentration (cmc). Also the minimum area/molecule at the air-water interface (a_{min}) was investigated in water at a certain temperature [9].

Our work involved the synthesis of novel branched-chain alkyl glycosides whose general structure is given in Fig 2. The aim of the synthesis is to study the effect of branching on the volume of lipophilic parts and the increase of lipophilicity, which in turn may lead to the observation of special liquid crystaline phases. The results were then compared with those of the straight chain glucosides from the available literature [10-14].

The synthesis of the straight chain alkyl glycosides can be performed by several methods, such as the reaction between 1-nonanol and glucose in dioxane [15] to produce nonyl glucoside using *p*-toluenesulfonic acid monohydrate as the reagent. We used the method described in [1] which have been recently modified [16], and which allowed the possibility to obtain both α- and β-anomers from the same starting materials, depending on the reaction conditions (e.g. temperature). The method involves three stages: first the peracetylation to protect the -OH groups of the sugar using acetic anhydride, second the glycosidation or the alkylation where the peracetylated sugar acts as a glycosyl donor. A Lewis acid catalyst (boron trifluoride) is used to

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catalyze the displacement of the acetoxy group at the first carbon (C-1). Finally the sugar headgroup was deacetylated using sodium methylate as catalyst, Fig 3 shows the overall synthetic scheme.

II Results

1. Techniques

Thin-layer chromatography was performed on silica gel (Merck GF_{254}) coated on aluminium plates. The detection was effected by immersing these plates into 5% $KMnO_4$ solution. Column chromatography was performed using silica gel 230-400 mesh. For glycosidation reactions, nitrogen was introduced to the reaction flask to maintain water free reaction conditions. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer, spectrum 2000. Nuclear magnetic resonance spectra were recorded on a Bruker AMX-400 Lambda spectrometer. High resolution mass spectra were measured using Kartos MS80. Identification of optical texture was carried out by using an Olympus BH-2 polarising microscope with Mettler FP82 Hotstage and Mettler FP80 Central processor while the transition temperatures were recorded by both optical polarizing microscopy and differential scanning calorimetry with a Mettler Toledo, DSC 821^e with Sample Robot TSO 8O1RO.

2. Procedure

Synthesis of β-D-glucose pentaacetate

To a stirred solution of β-glucose (10 mmol) and acetic anhydride (60 mmol) at 0^oC a solution of one drop of sulphuric acid in 5 ml of acetic anhydride was added drop by drop under stirring. The temperature of the solution was then increased gradually up to 60 ^oC . The reaction was left stirring for two hours then the reaction mixture was poured slowly into ice. After all ice was melted, dichloromethane was added and the mixture was stirred for three hours. Using separating funnel, the separated dichloromethane layer was received slowly into a concentrated sodium bicarbonate solution. The aqueous phase was extracted twice with dichloromethane and the combined organic extracts were washed with water, dried over magnesium sulphate, filtered and evaporated. The residue was recrystalized from ethanol.

Synthesis of alkyl glycopyranosides

To a stirred solution of peracetylated glucose (10 mmol) and alcohol (14 mmol) in dry dichloromethane (100 ml) under nitrogen atmosphere, boron trifluoride etherate (14 mmol) was added *via* syringe. The solution was stirred for six hours at room temperature after which it was quenched with saturated hydrogen carbonate solution. The aqueous phase was extracted twice with dichloromethane and the combined organic extracts were washed with water, dried over magnesium sulfate, filtered and evaporated to give the crude extract. The extract was then purified by column chromatography using petroleum ether and ethyl acetate as the solvent system to give the desired product.

Deacetylation of alkyl glycopyranoside tetraacetate

The product from the previous stage was dissolved in dry methanol (1mmol in 20 ml) under nitrogen; a catalytic amount of sodium metal was added to the solution. The reaction was

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stirred for two hours. The progress of the reaction was monitored using TLC (i.e. by the disappearance of starting materials). After the completion of the reaction, the solution was neutralised with H^+ resin and filtered through celite. Concentration of the filtrate under reduced pressure gave the required product as white crystals.

3. Spectroscopic Results

Comp (1) (2′-Ethyl-n-hexyl)-β-D-glycopyranoside $C_{14}H_{28}O_6$
Yield 97%
HRMS measured value 292.3776, expected value 292.3674
^{1}H-NMR (400 MHz, MeOH d_4):
δ = 4.12 (d, 1 H, H-1), 3.76 (dd, 1 H, H-αa), 3.73 (dd, 1 H, H-6a), 3.56 (dd, 1 H, H-6b), 3.32 – 3.12 (m, 4 H, H-3, H-4, H-5, H-αb), 3.06 (dd, 1 H, H-2), 1.44 (mc, 1 H, H-β), 1.36 – 1.15 (m, 8H, H-4CH_2), 0.85 - 0.75 (m, 6 H, 2CH_3) ppm.
J: $^3J_{H1,H2}$ = 7.63 Hz, $^3J_{H2,H3}$ = 8.65 Hz, $^3J_{H5,H6a}$ = 2.03 Hz, $^3J_{H5,H6b}$ = 4.06 Hz, $^2J_{H6a,H6b}$ = 11.69 Hz.

Comp (2) (2′-Ethyl-n-hexyl)-2,3,4,5-tetra-*O*-acetyl-β-D-glycopyranoside $C_{22}H_{36}O_{10}$
Yield 37%
HRMS measured value 460.5285, expected value 460.5138
^{1}H-NMR (400 MHz, $CDCl_3$ + TMS):
δ = 5.14 (dd, 1H, H-3), 5.02 (dd, 1H, H-4), 4.92 (dd, 1H, H-2), 4.40 (d, 1H, H-1), 4.20 (dd, 1H, H-6a), 4.08 (dd, 1H, H-6b), 3.75 (dd, 1H-H-αa), 3.62 (ddd, 1H, H-5), 3.25 (dd, 1H, H-αb), 2.02, 1.96, 1.95, 1.94 (each: s, 3H, , H-4AcO), 1.43 (mc, 1H, H-βCH) 1.34-1.15 (m, 8H, H-4CH_2), 0.84-0.74 (m, 6H, H-2CH_3)
J = $^3J_{H1,H2}$ = 8.20 Hz, $^3J_{H2,H3}$ = 9.42 Hz, $^3J_{H3,H4}$ = 9.51 Hz, $^3J_{H3,H5}$ = 9.68 Hz, $^3J_{H5,H6a}$ = 4.83 Hz, $^3J_{H5,H6b}$ = 5.11 Hz, $^2J_{H6a,H6b}$ = 12.01 Hz.
^{13}C-NMR (100 MHz, $CDCl_3$ + TMS):
δ = 170.69, 170.29, 169.36, 169.18 (C=O, OAc), 101.11 (C-1), 77.28 (C-3), 76.65 (C-5), 76.45 (C-2), 71.31 (C-α), 68.53 (C-4), 61.99 (C-6), 39.21 (C-β), 30.30, 30.04, 29.63, 28.80 (C-CH_2), 22.96, 20.69, 20.58, 20.55 (CH_3-OAc), 14.01(C-CH_3)

Comp (3) (2′-n-Butyl-n-octyl)-β-D-glycopyranoside $C_{18}H_{36}O_6$
Yield 95%
HRMS measured value 348.4765, expected value 348.4734
^{1}H-NMR (400 MHz, MeOH d_4):
δ = 4.11 (d, 1 H, H-1), 3.76 (dd, 1 H, H-αa), 3.71 (dd, 1 H, H-6a), 3.57 (dd, 1 H, H-6b), 3.32 – 3.15 (m, 4 H, H-3, H-4, H-5, H αb), 3.07 (dd, 1 H, H-2), 1.70 (mc, 1 H, H-β), 1.30– 1.13 (m, 16H, H-CH_2), 0.83 - 0.76 (m, 6 H, 2CH_3) ppm.

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J: $^{3}J_{H1,H2}$ = 7.88 Hz, $^{3}J_{H2,H3}$ = 8.90 Hz, $^{3}J_{H5,H6a}$ = 3.56 Hz, $^{3}J_{H5,H6b}$ = 4.34 Hz, $^{2}J_{H6a,H6b}$ = 11.70 Hz.

Comp (4) (2′-n-Butyl-n-octyl)-2,3,4,5-tetra-*O*-acetyl-β-D-glycopyranoside $C_{26}H_{44}O_{10}$
Yield 34%
.**HRMS** measured value 516.6273, expected value 516.6198

^{1}H-NMR (400 MHz, $CDCl_3$ + TMS):

δ = 5.12 (dd, 1H, H-3), 5.02 (dd, 1H, H-4), 4.90 (dd, 1H, H-2), 4.39 (d, 1H, H-1), 4.20 (dd, 1H, H-6a), 4.06 (dd, 1H, H-6b), 3.73 (mc, 1H-H-αa), 3.62 (ddd, 1H, H-5), 3.22 (mc, 1H, H-αb), 2.02, 1.96, 1.95, 1.94 (each: s, 3H, H-4AcO), 1.43 (mc, 1H, H-βCH), 1.19-1.14 (m, 16H, H-8CH_2), 0.82-0.76 (m, 6H, H-2CH_3)

J = $^{3}J_{H1,H2}$ = 8.13Hz, $^{3}J_{H2,H3}$ = 9.46 Hz, $^{3}J_{H3,H4}$ = 9.47 Hz, $^{3}J_{H3,H5}$ = 9.56 Hz $^{3}J_{H5,H6a}$ = 2.84 Hz, $^{3}J_{H5,H6b}$ = 5.09 Hz, $^{2}J_{H6a,H6b}$ = 11.96 Hz.

^{13}C-NMR (100 MHz, $CDCl_3$ + TMS):

δ = 170.88, 170.30, 169.37, 169.16 (C=O, OAc), 102.00 (C-1), 77.28 (C-3), 76.96 (C-5), 76.65 (C-2), 71.65 (C-α), 68.53 (C-4), 61.96 (C-6), 39.00 (C-β), 30.30, 30.04, 29.88, 29.55, 29.49, 29.63, 28.80 (C-CH_2), 22.61, 20.59, 20.93, 20.65 (CH_3-OAc), 14.00(C-CH_3)

Comp (5) (2′-n-Hexyl-n-decyl)-β-D-glycopyranoside $C_{22}H_{44}O_6$
Yield 96%

^{1}H-NMR (400 MHz, MeOH d_4):

δ = 4.11 (d, 1 H, H-1), 3.72 (dd, 1 H, H-αa), 3.70 (dd, 1 H, H-6a), 3.56 (dd, 1 H, H-6b), 3.32 – 3.12 (m, 4 H, H-3, H-4, H-5, H- αa), 3.07 (dd, 1 H, H-2), 1.49 (mc, 1 H, H-β), 1.25 – 1.12 (m, 24 H, H-12CH_2), 0.82 – 0.76 (m, 6 H, H-2CH_3) ppm.

J: $^{3}J_{H1,H2}$ = 7.63 Hz, $^{3}J_{H2,H3}$ = 8.65 Hz, $^{3}J_{H5,H6a}$ = 3.56 Hz, $^{3}J_{H5,H6b}$ = 5.36 Hz, $^{2}J_{H6a,H6b}$ = 11.96 Hz.

Comp (6) (2′-n-Hexyl-n-decyl)-2,3,4,5-tetra-*O*-acetyl-β-D-glycopyranoside $C_{30}H_{52}O_{10}$
Yield 41%
HRMS measured value 572.7262, expected value 572.7258

^{1}H-NMR (400 MHz, $CDCl_3$ + TMS):

δ = 5.13 (dd, 1H, H-3), 5.02 (dd, 1H, H-4), 4.92 (dd, 1H, H-2), 4.39 (d, 1H, H-1), 4.20 (dd, 1H, H-6a), 4.07 (dd, 1H, H-6b), 3.74 (mc, 1H-H-αa), 3.62 (ddd, 1H, H-5), 3.25 (dd, 1H, H-αb), 2.02, 1.96, 1.95, 1,94 (each: s, 3H, H-4AcO), 1.43 (mc, 1H, H-βCH) 1.36-1.16 (m, 24H, H-12CH_2), 0.83-0.74 (m, 6H, H-2CH_3)

J = $^{3}J_{H1,H2}$ = 8.15 Hz, $^{3}J_{H2,H3}$ = 9.50 Hz, $^{3}J_{H3,H4}$ = 9.61 Hz, $^{3}J_{H4,H5}$ = 9.58 Hz, $^{3}J_{H5,H6a}$ = 4.82 Hz, $^{3}J_{H5,H6b}$ = 5.12 Hz, $^{2}J_{H6a,H6b}$ = 11.96 Hz.

^{13}C-NMR (100 MHz, $CDCl_3$ + TMS):

δ = 170.63, 170.26, 169.34, 169.20 (C=O, OAc), 101.09 (C-1), 77.32 (C-3), 76.67 (C-5), 76.45 (C-2), 71.33 (C-α), 68.55 (C-4), 62.00 (C-6), 37.95 (C-β), 37.95, 31.83, 31.80, 31.06, 30.85, 30.01, 29. 63, 29.55, 29.28, 26.70, 26.57, 26.52 (C-CH_2), 22.61, 20.91, 20.65, 20.53 (CH_3-OAc), 14.03(C-CH_3)

Comp (7) (2′-n-Octyl-n-dodecyl)-β-D-glycopyranoside $C_{26}H_{52}O_6$
Yield 93%
HRMS measured value 460.6742, expected value 460.6854
^{1}H-NMR (400 MHz, MeOH d_4):

δ = 4.11 (d, 1 H, H-1), 3.75 (dd, 1 H, H-αa), 3.70 (dd, 1 H, H-6a), 3.57 (dd, 1 H, H-6b), 3.35 – 3.10 (m, 4 H, H-3, H-4, H-5, H- αb), 3.07 (dd, 1 H, H-2), 1.50 (mc, 1 H, H-βCH), 1.22 – 1.16 (m, 32 H, H-16CH_2), 0.85 - 0.76 (m, 6 H, H-2CH_3) ppm.

J: $^3J_{H1,H2}$ = 7.62 Hz, $^3J_{H2,H3}$ = 9.54 Hz, $^3J_{H5,H6a}$ = 1.91 Hz, $^3J_{H5,H6b}$ = 5.34 Hz, $^2J_{H6a,H6b}$ = 11.83 Hz.

Comp (8) (2′-n-Octyl-n-dodecyl)-2,3,4,5-tetra-*O*-acetyl-β-D-glycopyranoside $C_{34}H_{60}O_{10}$
Yield 45%
HRMS measured value 628.8251, expected value 628.8318
^{1}H-NMR (400 MHz, $CDCl_3$ + TMS):

δ = 5.14 (dd, 1H, H-3), 5.02 (dd, 1H, H-4), 4.92 (dd, 1H, H-2), 4.40 (d, 1H, H-1), 4.21 (dd, 1H, H-6a), 4.06 (dd, 1H, H-6b), 3.73 (mc, 1H-H-αa), 3.60 (ddd, 1H, H-5), 3.23 (mc, 1H, H-αb), 2.02, 1.96, 1.95, 1.94 (each: s, 3H, H-4AcO), 1.43 (mc, 1H-βCH) 1.35-1.15 (m, 32H, H-16CH_2), 0.84-0.75 (m, 6H, H-2CH_3)

J = $^3J_{H1,H2}$ = 8.12 Hz, $^3J_{H2,H3}$ = 9.52Hz, $^3J_{H3,H4}$ = 9.49 Hz, $^3J_{H4,H5}$ = 9.63 Hz, $^3J_{H5,H6a}$ = 4.80 Hz, $^3J_{H5,H6b}$ = 5.15 Hz, $^2J_{H6a,H6b}$ = 12.01 Hz.

^{13}C-NMR (100 MHz, $CDCl_3$ + TMS):
δ = 170.65, 170.31, 169.29, 169.18 (C=O, OAc), 101.00 (C-1), 77.28 (C-3), 76.65 (C-5), 76.45 (C-2), 71.31 (C-α), 68.53 (C-4), 61.99 (C-6), 39.21 (C-β), 30.30, 30.04, 29.63, 28.80 (C-CH_2), 22.96, 20.69, 20.58, 20.55 (CH_3-OAc), 14.01(C-CH_3)

Comp (9) (2′-n-Decyl-n-tetradecyl)-β-D-glycopyranoside $C_{30}H_{60}O_6$
Yield 96%
HRMS measured value 516.7731, expected value 516.7914
^{1}H-NMR (400 MHz, MeOH d_4):

δ = 4.31 (d, 1 H, H-1), 3.94 (dd, 1 H, H-αa), 3.90 (dd, 1 H, H-6a), 3.76 (dd, 1 H, H-6b), 3.51 – 3.30 (m, 4 H, H-3, H-4, H-5, H-αb), 3.26 (dd, 1 H, H-2), 1.70 (mc, 1 H, H-βCH), 1.53 – 1.31 (m, 40 H, H-20CH_2), 1.01 - 0.96 (m, 6 H, H- 2CH_3) ppm.

J: $^{3}J_{H1,H2}$ = 7.63 Hz, $^{3}J_{H2,H3}$ = 9.54 Hz, $^{3}J_{H5,H6a}$ = 1.91 Hz, $^{3}J_{H5,H6b}$ = 5.34 Hz, $^{2}J_{H6a,H6b}$ = 11.83 Hz.

Comp (10) (2′-n-Decyl-n-tetradecyl)-2,3,4,5-tetra-*O*-acetyl-β-D-glycopyranoside $C_{38}H_{68}O_{10}$.
Yield 40%
HRMS measured value 684.9239, expected value 684.9378
^{1}H-NMR (400 MHz, $CDCl_3$ + TMS):

δ = 5.13 (dd, 1 H, H-3), 5.02 (dd, 1 H, H-4), 4.92 (dd, 1 H, H-2), 4.38 (d, 1 H, H-1), 4.20 (dd, 1 H, H-6a), 4.06 (dd, 1 H, H-6b), 3.73 (dd, 1 H, H-αa), 3.61 (ddd, 1 H, H-5), 3.22 (dd, 1 H, H-αb), 2.01, 1.96, 1.95, 1.93 (each: s, 3 H, H-4AcO), 1.52 – 1.44 (m, 1 H, H-βCH), 1.27 – 1.14 (m, 40 H, 20CH_2), 0.84 – 0.79 (m, 6 H, H-2CH_3) ppm.

J = $^{3}J_{H1,H2}$ = 8.14 Hz, $^{3}J_{H2,H3}$ = 9.54 Hz, $^{3}J_{H3,H4}$ = 9.67 Hz, $^{3}J_{H4,H5}$ = 9.66 Hz, $^{3}J_{H5,H6a}$ = 4.04 Hz, $^{3}J_{H5,H6b}$ = 5.09 Hz, $^{2}J_{H6a,H6b}$ = 12.21 Hz.

^{13}C-NMR (100 MHz, MeOH d_4):

δ = 103.69 (C-1), 77.12 (C-3), 76.80 (C-2), 74.09 (C-4), 72.97 (C-α), 70.62 (C-5), 61.73 (C-6), 38.56 (C-β), 38.35, 38.13, 38.01, 37.77, 37.71, 37.49, 37.28, 38.43, 32.00, 31.10, 30.02, 29.70, 29.68, 29.64, 29.40, 26.74, 22.66 (C-CH_2), 13.37 (CH_3) ppm. 30.45, 30.11, 30.08, 29.35, 27.32, 27.08, 23.09 (C-CH_2), 21.34, 21.24, 21.08, 20.99 (CH_3-OAc), 13.37 (C-CH_3).

III. Discussion

Glycolipids form complex supramolecular structures due to their amphiphilic nature, both in solvent (lyotropic) as well as in the pure form (thermotropic). Supramolecular structures are not unique to glycolipids since other types of liquid crystal material can also form complex morphologies. These type of compounds are classified as amphotropic liquid crystals [17]. The common phases displayed are the micellar, hexagonal or columnar and the smectic or lamellar phases. In addition, other more complex morphological structures (the bicontinuous and discontinuous cubic phases) are gaining attention and interest, since these have some biological relevance. For example in processes like membrane fusion and membrane traffic, as can be found during exocytosis or virus cell fusion in the course of infection. The generic mesophase behaviour of glycolipids for thermotropic and lyotropic phases is shown in Fig 4.

Compounds 1, 3, 5, 7 and 9 are branched glucosides (Fig 5). From the polarizing microscopy work, compounds 1, 3 and 5 gave a smectic A phase since they showed steps and fan-shape textures (Fig 6 a), while compound 7 and 9 gave a columnar phase, identified by their characteristic texture (Fig 6 b). Although these compounds appear to be solid at the room temperature, they are actually in the liquid crystal glassy state since on heating they melt immediately into the liquid crystal (both smectic A and columnar) phases but on cooling these anisotropic liquid phases remain even below ambient. Therefore we did not record their melting temperatures but only their transition temperatures into the isotropic phase (or the clearing

temperatures) were determined (see Table 1). These behaviors are expected for branched-chain glucosides since the branching has the effect of increasing disorder (hence lowering of the melting temperatures) in a similar manner as found by Minden et al. (2002) [18] for the methyl branched glycosyl diacylglycerols.

OPM studies also revealed that compounds 1, 3 and 5 have similar phase behavior, since their clearing temperatures (smectic A to isotropic) are almost the same: 55 ^{o}C, 57 ^{o}C and 55 ^{o}C respectively. On the other hand the clearing temperatures for compounds 7 and 9 (columnar to isotropic) are much higher: 72^{o}C and 95 ^{o}C respectively.

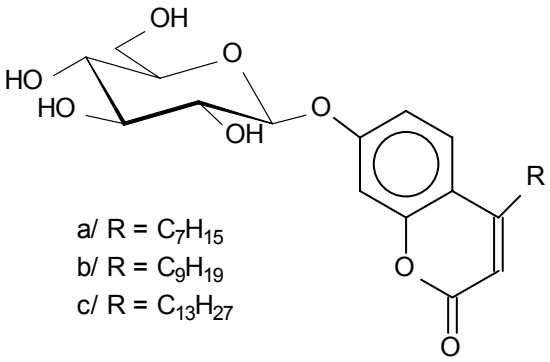
Compound 2, (peracetylated glucoside with eight carbon atoms in the tail) is crystalline at room temperature unlike the case of peracetylated straight chain alkyl glucosides which are all liquid at the same temperature [1]. Compounds 4, 6, 8 and 10 are all syrupy at room temperature (Fig 5).

In general the transition temperature data from the differential scanning calorimetry DSC confirmed those clearing temperatures values obtained by OPM within 2-3 degrees.

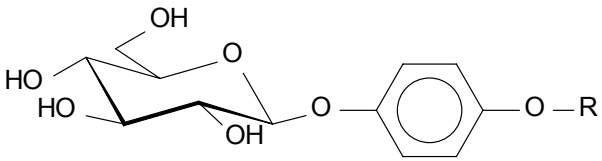
Our results are compared with those of the straight-chained alkyl glucosides as shown in Table 1. The data for the straight-chained glucosides are taken from the literature [10-13]. Straight chain alkyl glucosides only give liquid crystal phases when there are eight or more carbon atoms in the alkyl chain, while compound 1 (of the branched chain series) with six carbon atoms in the main chain is a smectic A liquid crystal. In general the melting and clearing temperatures for the straight chain alkyl glucosides are much higher than those of the branched chain analogues. The straight chain alkyl glucosides also gave only smectic A phases while the branched series gave a columnar phase when the number of carbon atoms in the main straight chain is 12 and more.

The branching of the alkyl chain, in general, increases disorder in the lipophilic region of the smectic layers which can be explained by the geometric packing theory of the alkyl chain [19]; hence it markedly reduces the clearing temperatures. This result is consistent with those found for the Guerbet alcohol surfactants which are known for their low temperature detergent properties [20]. As the branches increase in length (and hence size) (for compounds 7 and 9), the overall structure of the glucosides becomes more cone-shaped (rather than rod-shaped as for the straight chained counterpart). Hence these cone-shaped structures favor the formation of the columnar phase.

To conclude, we have synthesized ten branched-chain alkyl glycosides, which showed liquid crystal phase behaviour (both the smectic A and columnar phases). These results were compared with those of the straight chain alkyl glycosides, which gave only the smectic A phase. The branched chain deacetylated alkyl glucosides also gave lower melting and clearing temperatures compared to their straight chain counterparts. Hence they have the potential to be used in applications as low temperature surfactants. Future studies on these compounds are necessary and these include the determination of the phase diagrams both for the thermotropic and lyotropic systems in order to further explore their potential in technical and biological applications.

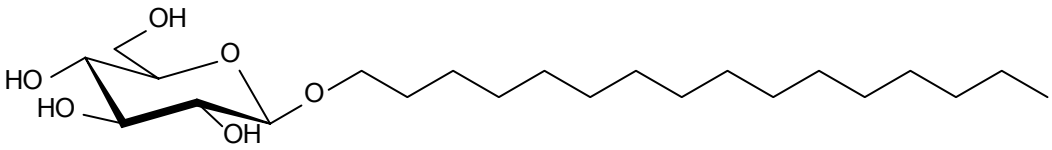


a The molecular structure of 4-alkyl derivatives of umbelliferyl β-D-glucoside

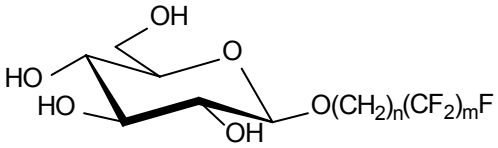


1-12 R = CH_3....$C_{10}H_{21}$ and $C_{12}H_{25}$

b 4-alkyoxyphenyl--β-D-glycopyranosides



c Hexadecyl--β-D-glycopyranoside



n: No of methylene groups, m: No of flouromethylene groups

d Perfluoroalkyl glycoside series

Figure 1: Some examples of alkyl glucosides

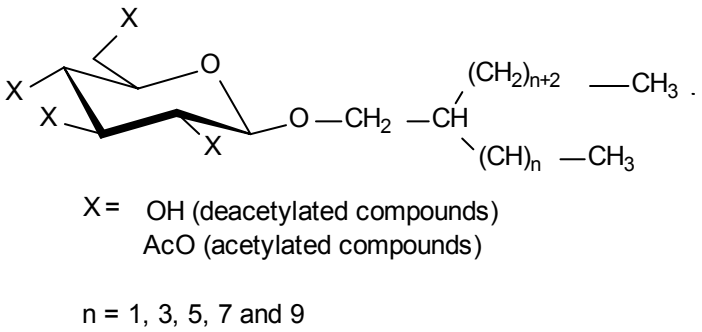


Figure 2: General structures for branched chain alkyl β-D-glucosides

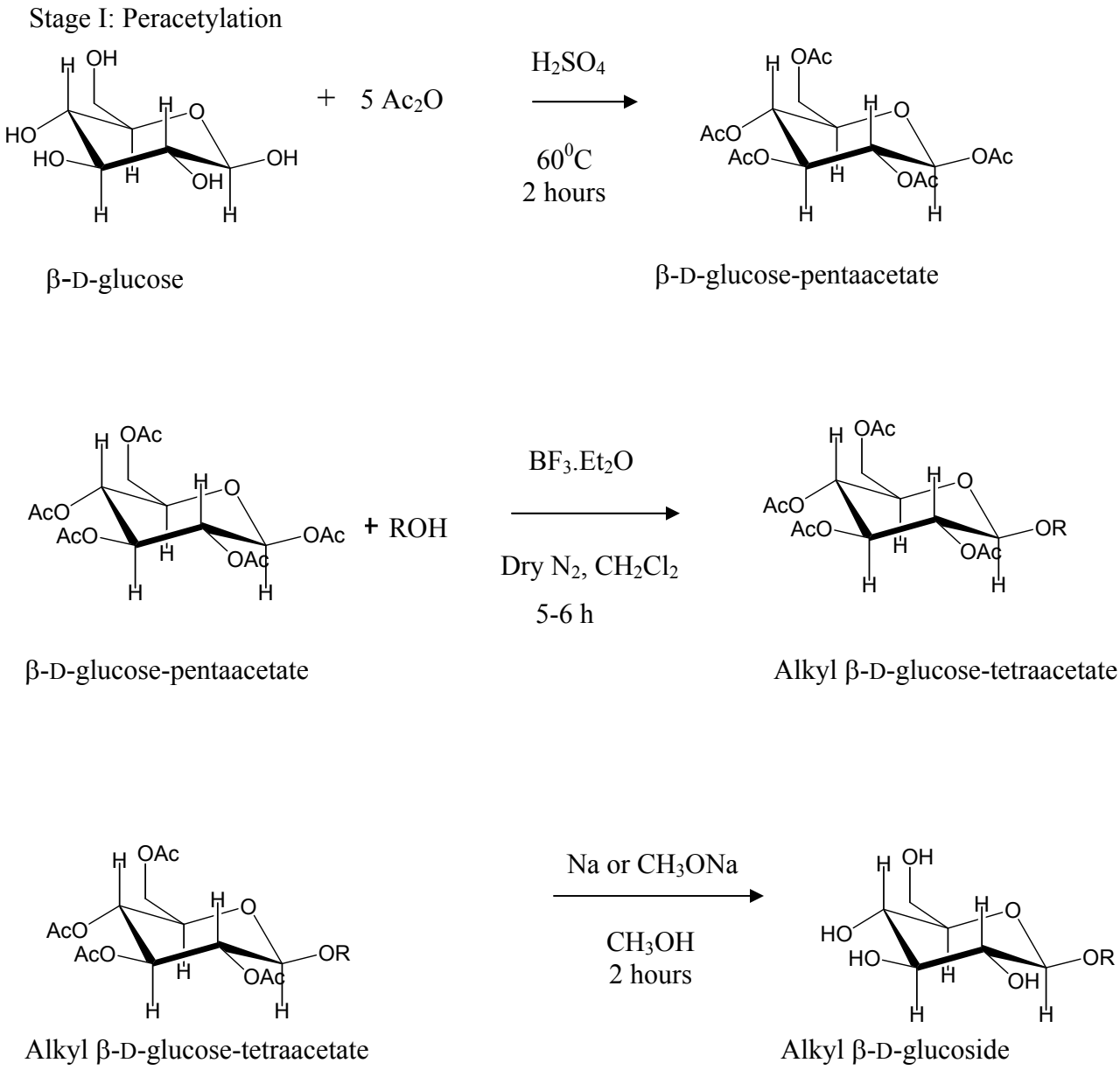


Figure 3: Chemical synthetic scheme for branched-chain alkyl glucosides.

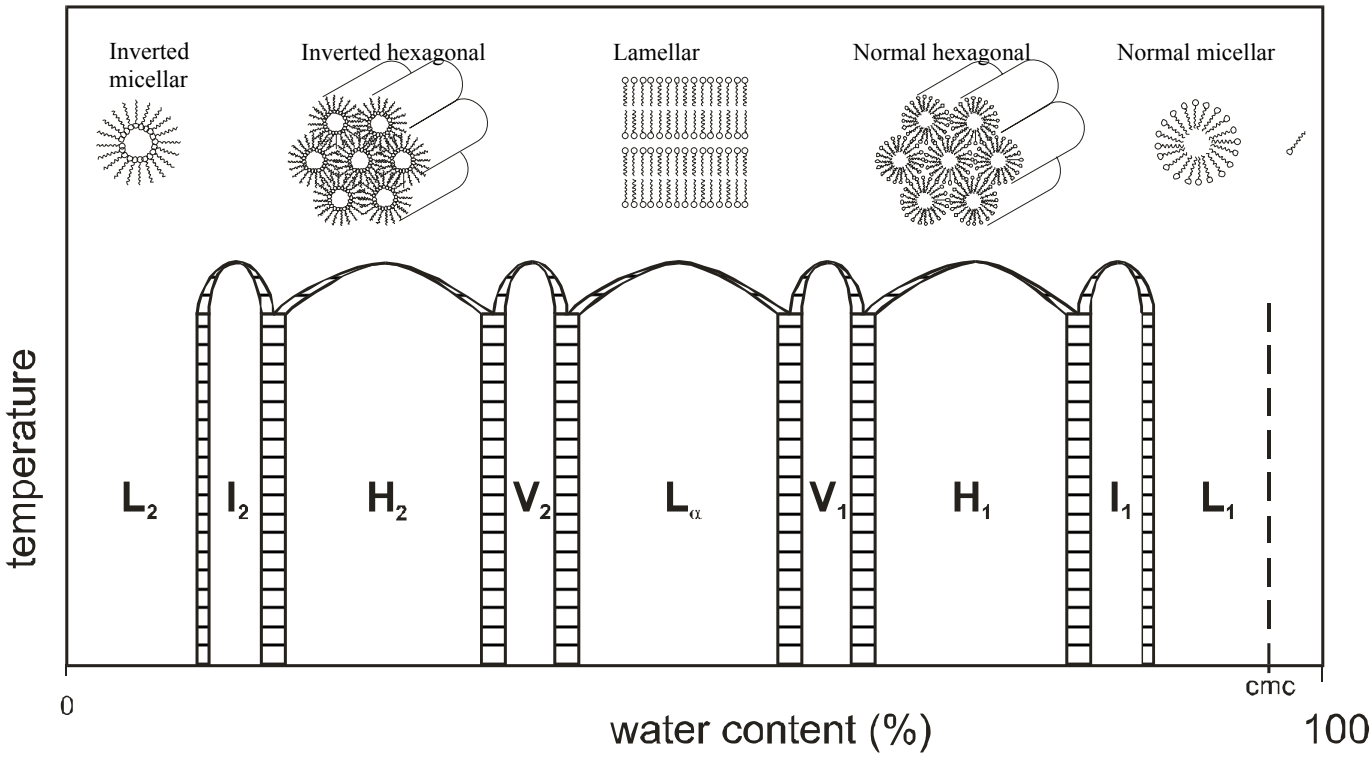


Figure 4: generic phase behaviour of lyotropic and thermotropic liquid crystal system.

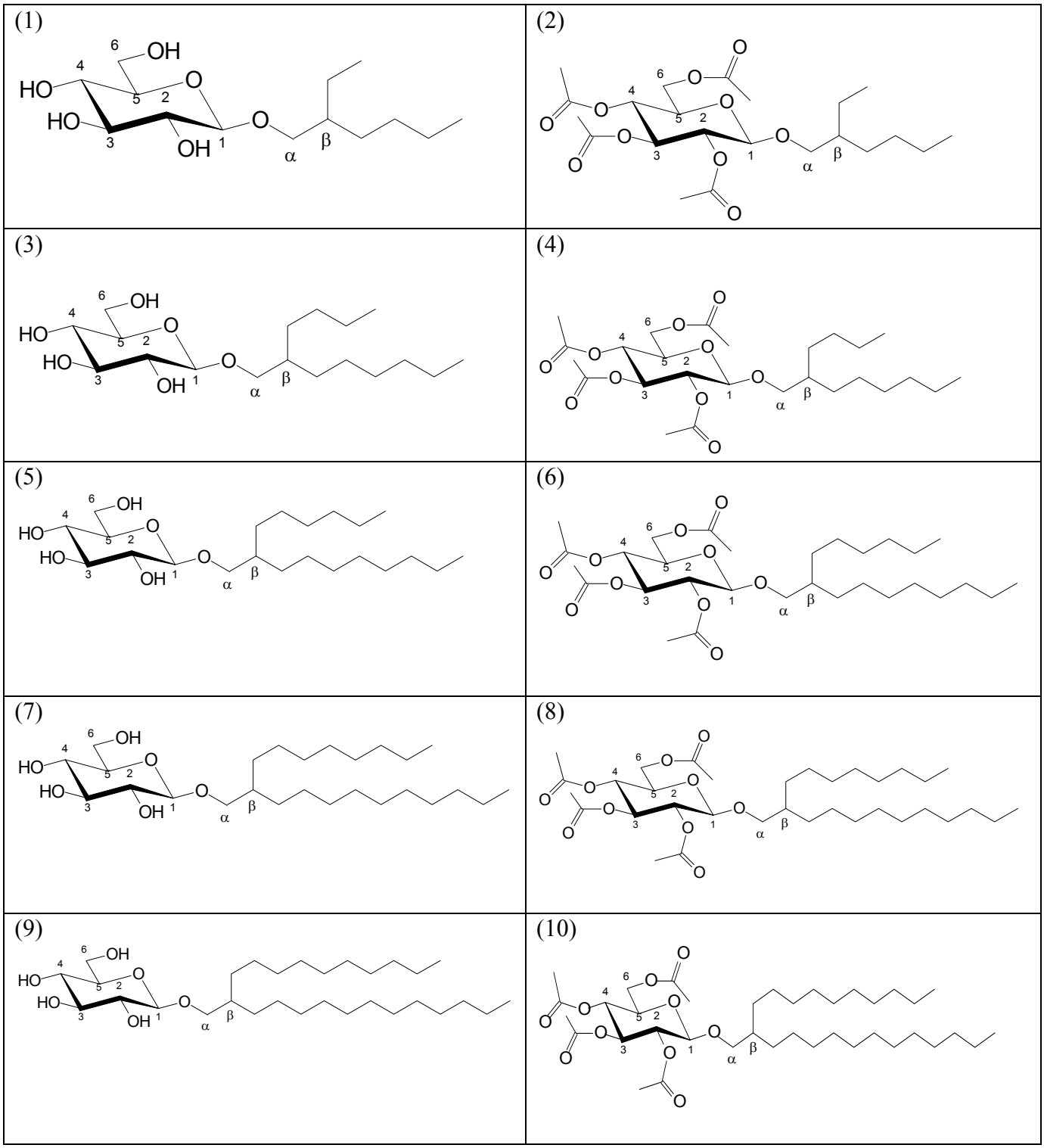
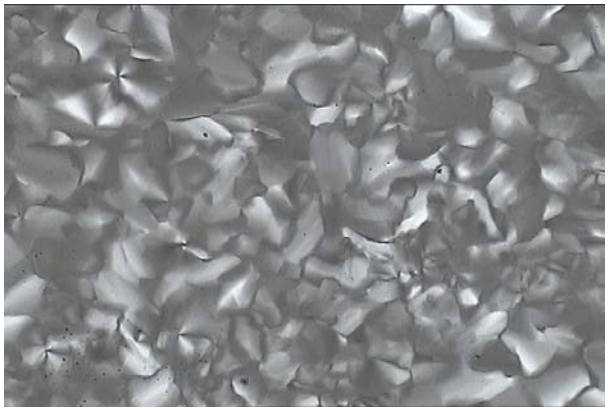
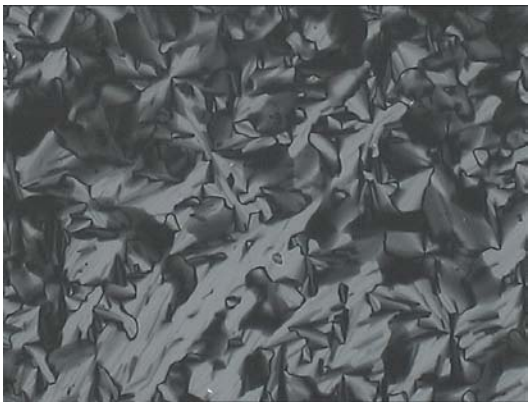


Figure 5: List of synthesized branched chain alkyl glucosides



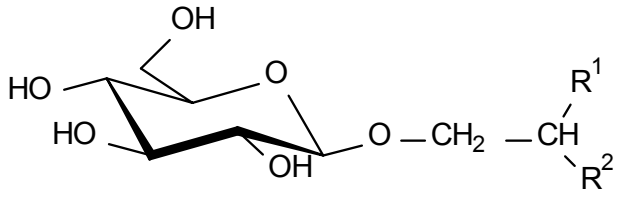
a Smectic A texture for compound (5) at 30^0C



Compound (7) Compound (9)

b Columnar phase for compound (7) and compound (9) at 60^0

Figure 6: Polarizing microscopic textures of some branched chain alkyl glucosides.



$R^1 = C_nH_{2n+1}$; n = 4,6,8,10 and 12
R^2 = H for straight chained glucosides
= C_mH_{2m+1} (m = 2,4,6,8 and 10) for branched-chain alkyl glucosides

Table1
General structure for straight chain ($R^2$is H) and branched chain glucosides ($R^2 \neq$H). Cr denotes a crystal phase, SmA is smectic A,and Col columnar phases respectively; iso stands for the isotropic phase.

n	Transition temperatures for branched-chain glucosides	Transition temperatures for straight chain glucosides when R^2 is H	
			Ref.
4	Cr ? SmA 57 iso	Cr 90 iso	[10]
6	Cr ? SmA 55 iso	Cr 67 SmA 106 iso	[11]
8	Cr ? SmA 57 iso	Cr 64.9 SmA 170 iso	[11]
10	Cr ? Col 72 iso	Cr 80 SmA 144 iso	[12]
12	Cr ? Col 95 iso	Cr ? SmA 155 iso	[13]

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