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# Effect of the C-2 hydroxyl group on the mesomorphism of alkyl glycosides: synthesis and thermotropic behavior of alkyl 2-deoxy-D-*arabino*-hexopyranosides

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ABSTRACT

A homologous series of alkyl 2-deoxy-α-D-*arabino*-hexopyranosides and alkyl 2-deoxy-β-D-*arabino*-hexopyranosides were synthesized, upon glycosylation of 1-alkanols (from $C_8$ to $C_{18}$ alkanols) with ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-D-*arabino*-hexopyranoside, followed by a deprotection. The thermotropic behavior of these new types of alkyl glycosides was investigated. It was observed that the β-anomers of these alkyl glycosides, bearing nonyl to tetradecyl alkyl chain are mesomorphic, exhibiting monotropic smectic A phase. In contrast, the α-anomers are all non-mesomorphic. An effort to identify the liquid crystalline behavior of binary mixtures of the α- and β-anomers was undertaken and it was found that mixtures containing equimolar amounts of the anomers exhibited mesomorphic behavior. A fine balance of the hydrophilic and hydrophobic components within the molecule is also found to be important for the alkyl 2-deoxy glycosides to form the mesophase.



## 1. Introduction

Amphiphilic sugars are known to exhibit liquid crystalline behavior owing to their amhiphilicity (van Doren et al., 2000; Vill and Hashim, 2002; Jeffrey, 1986; Paleos and Tsiourvas, 1995; Goodby et al., 1998, 2007; Tschierske, 1998). Cell membrane bound glycolipids are examples *par excellence* of the lyotropic behavior of the amphiphilic sugars and their importance in biological functions (Abraham and Pascher, 1997; Wolken and Brown, 1980). A driving force for the mesophase formation in these molecules is the phase segregation, leading to aggregates, possessing distinct lipophilic and hydrophilic regions (Boullanger, 1997; van Doren and Wingert, 1994). Amphiphilic sugars possess an abundance of chiral centers and their liquid crystalline phases are generally smectic or columnar and/or cubic phases (Molinier et al., 2003, 2006, 2007). The absence of macroscopic chirality in the amphiphilic sugars and glycolipids could be attributed to the strong hydrogen bonding network between the hydroxyl groups of the sugar moiety, which force a layering with head to head arrangement of the molecules. It was shown recently that features that affect hydrogen bonding network can lead to the formation of chiral mesophases in sugar-based bolaamphiphiles (Abraham et al., 2005; Das et al., 2008).

Hexdecyl β-D-glucopyranoside is an early example of the glycolipids exhibiting liquid crystalline properties (Fischer and Helferich, 1911; Noller and Rockwell, 1938). The homologous series of both alkyl α-D-glucopyranosides and alkyl β-D-glucopyranosides exhibit the smectic A (SmA) phase and the SmA to isotropic transition temperature increases with increasing alkyl chain length (Goodby, 1984; Pfeffer et al., 1976; Jeffrey and Bhattacharjee, 1983). With detailed information available currently on the mesomorphic behavior of only the normal alkyl glycosides, it is pertinent to investigate the mesomorphic behavior on alkyl glycosides that lack one or more hydroxyl group in their hydrophilic sugar component. This report presents the results of the studies on alkyl glycosides, wherein 2-deoxy sugar constitutes the hydrophilic segment. Several homologues of the alkyl α-D-*arabino*-hexopyranosides and alkyl β-D-*arabino*-hexopyranosides series are synthesized and the thermotropic behavior of these new alkyl glycosides is assessed with the aid of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

## 2. Results and discussion

### 2.1. Synthesis

The synthesis of alkyl 2-deoxyglucosides was initiated from ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-D-*arabino*-hexopyranoside (Paul and Jayaraman, 2004). The alkyl 2-deoxyglucosides were

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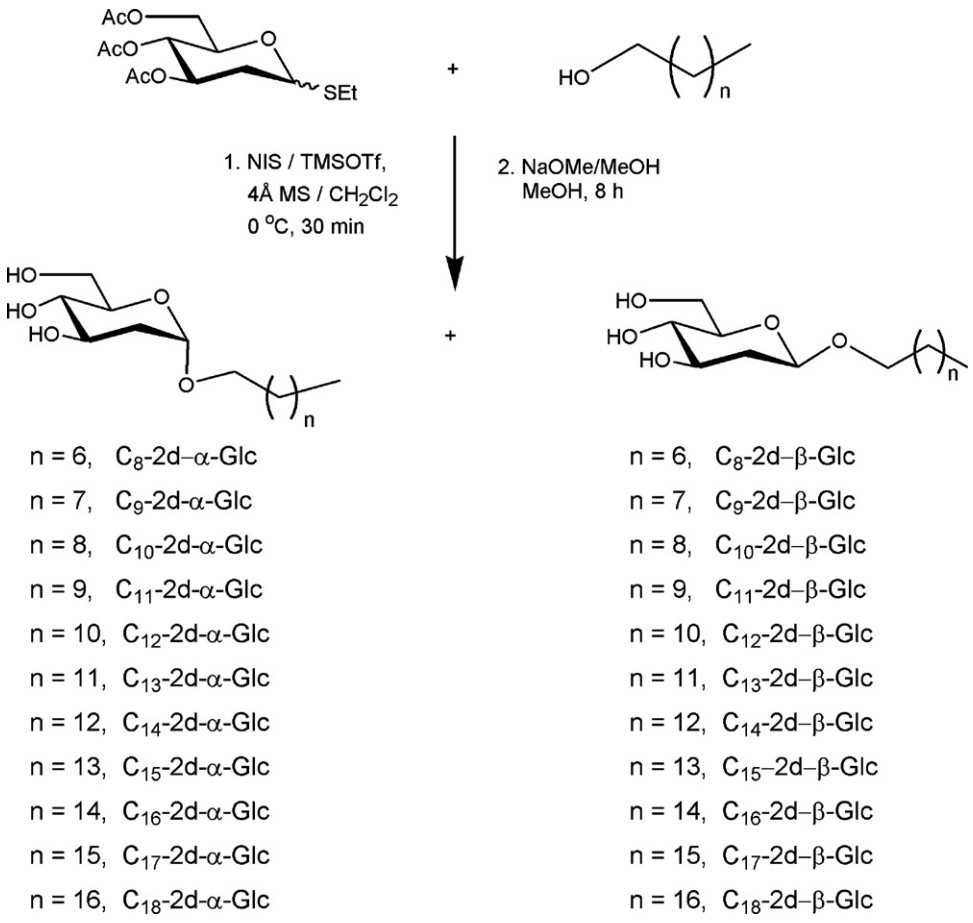


**Scheme 1.** Synthesis of alkyl 2-deoxy-D-*arabino*-hexopyranosides ($C_n$-2d-α/β-Glc).

prepared by the glycosylation of 1-alkanols with the above glycosyl donor in the presence of *N*-iodosuccinimide (NIS)/trimethylsilyl trifluoro-methanesulfonate (TMSOTf), followed by the deprotection of the acetate protecting groups (Scheme 1). The glycosylation led to almost equal amounts of both the α- and the β-anomers. The alkyl 2-deoxy-α- and β-D-*arabino*-hexopyranosides ($C_n$-2d-α-Glc and $C_n$-2d-β-Glc) were characterized by physical methods to confirm their constitutions.

### 2.2. Thermal behavior

The mesomorphic behavior of these new alkyl glycosides was investigated by POM and DSC techniques. Among the alkyl 2-deoxy-β-glucosides ($C_n$-2d-β-Glc), compounds $C_9$–$C_{14}$ ($n$ = 9–14) exhibited a monotropic SmA phase. Upon slow cooling from the isotropic state, a fan-shaped texture was observed (Fig. 1). When the sample exhibiting the undisturbed fan-shaped focal conic pattern was pressed, a near complete homeotropic alignment was observed, thereby suggesting the texture to be a SmA phase. The observed SmA texture is seen commonly for the sugar mesogens (Gray and Goodby, 1984; Zur et al., 1998; Jayaraman et al., 2007). The compounds $C_9$-2d-β-Glc, $C_{11}$-2d-β-Glc and $C_{13}$-2d-β-Glc exhibited an endothermic peak in the heating cycle and two exothermic peaks in the cooling cycle. The higher temperature peak corresponded to the I–SmA transition, whereas the low temperature peak in the cooling cycle was due to the SmA–Cr transition. A representative DSC thermogram is shown in Fig. 2. The even numbered compounds $C_{10}$-2d-β-Glc, $C_{12}$-2d-β-Glc and $C_{14}$-2d-β-

**Fig. 1.** The fan-shaped texture of the SmA phase obtained upon slow cooling of the isotropic liquid of $C_{13}$-2d-β-Glc (left) and binary mixture $C_{12}$-2d-α,β-Glc (1:1) (right).

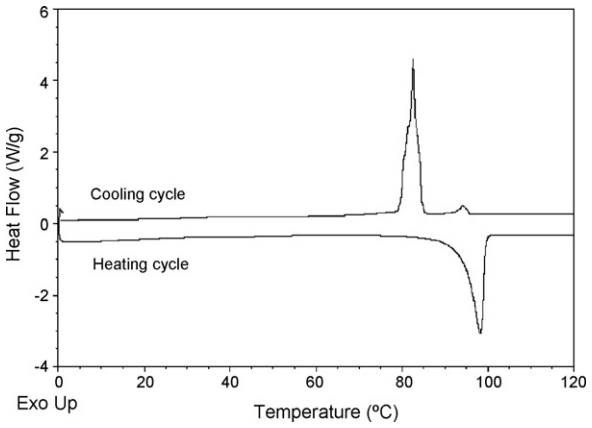


**Fig. 2.** DSC thermogram for $C_{11}$-2d-α-Glc at a heating and cooling rate is 5 °C min$^{-1}$ during the second cycle.

Glc also exhibited a fan-shaped texture of SmA phase for a narrow temperature range (<2 °C), immediately prior to the crystallization. Perhaps this low thermal stability of the phase prevented its signature being seen in the DSC. The metastable nature of the SmA phase was evident from the fact that the phase was monotropic for the odd numbered homologues. Also, the mesophase of odd chain length compounds were more stable than the even chain length derivatives. It is important to note that the melting and the isotropic to SmA transition temperatures do not seem to have a systematic variation with the alkyl chain lengths. The corresponding α-anomers, namely, alkyl 2-deoxy-α-D-glucosides ($C_n$-2d-α-Glc) were all non-mesomorphic. The phase transition temperatures and the associated enthalpies are presented in Table 1. The melting points of the α-anomers are slightly more than the corresponding β-anomers.

The binary mixtures of alkyl 2-deoxy-α-D-glucosides and alkyl 2-deoxy-β-D-glucosides in equimolar ratio exhibited SmA phase, similar to that of the pure β-derivatives in the cooling cycle. The texture of SmA phase for $C_{12}$-2d-α,β-Glc (1:1) is presented in Fig. 1. The phase transition temperatures and associated enthalpies are presented in Table 2. The thermograms of all the binary mixtures showed an endothermic peak followed by a weaker transition in the heating cycle of the thermograms, perhaps suggesting the appearance of the SmA phase, a feature that could not be, however, confirmed in the polarizing microscopy observations. In the cooling cycle of the thermogram, two exothermic peaks were observed. The peak with lower enthalpy was due to I–SmA transition and the peak with higher enthalpy corresponded to SmA–Cr transition. The DSC thermogram of $C_{15}$-2d-α,β-Glc (1:1), obtained at a rate of 5 °C min$^{-1}$, is shown in Fig. 3. It is observed that while the I–SmA phase transition temperature was weakly affected by the rate of cooling, the crystallization (SmA–Cr) temperature showed a very strong dependence. Fig. 4 shows the temperatures for the transitions I–SmA and SmA–Cr phases as a function of the cooling rate. The crystallization temperature reached a limiting value at a cooling rate of ~15 °C min$^{-1}$. A similar dependence of the SmA–Cr transition temperature on the cooling rate was reported for the monotropic liquid crystalline polyester (Bashir et al., 1998).

**Table 1**
Transition temperatures and enthalpies of transitions for alkyl 2-deoxy-α/β-D-*arabino*-hexopyranosides[a]

| Compounds | Transition temperature (°C) [enthalpy (J/g)] |
|---|---|
| $C_8$-2d-α-Glc | Cr 107.9 [132.1] I 95.7 [131.7] Cr |
| $C_8$-2d-β-Glc | Cr 83.1 [80.6] I 71.5 [80.4] Cr |
| $C_9$-2d-α-Glc | Cr 104.3 [114.4] I 90.9 [113.5] Cr |
| $C_9$-2d-β-Glc | Cr 91.9 [97.0] I 83.9 [5.2] SmA 72.11 [91.3] Cr |
| $C_{10}$-2d-α-Glc | Cr 111.4 [160.7] I 100.3 [160.6] Cr |
| $C_{10}$-2d-β-Glc | Cr 97.7 [118.1] I 88.1 SmA 86.5 [118.0] Cr[b] |
| $C_{11}$-2d-α-Glc | Cr 109.0 [174.8] I 82.7 [172.9] Cr |
| $C_{11}$-2d-β-Glc | Cr 99.2 [87.0] I 93.8 [3.9] SmA 86.5[82.5] Cr |
| $C_{12}$-2d-α-Glc | Cr 110.4 [153.5] I 96.4 [148.7] Cr |
| $C_{12}$-2d-β-Glc | Cr 103.7 [148.4] I 99.5 SmA 97.6 [147.6] Cr[b] |
| $C_{13}$-2d-α-Glc | Cr 113.2 [181.8] I 98.2 [181.6] Cr |
| $C_{13}$-2d-β-Glc | Cr 104.0 [125.6] I 98.9 [3.7] SmA 91.4 [120.6] Cr |
| $C_{14}$-2d-α-Glc | Cr 113.6 [158.5] I 93.1 [150.1] Cr |
| $C_{14}$-2d-β-Glc | Cr 106.1 [123.6] I 97.2 SmA 92.4 [119.0] Cr[b] |
| $C_{15}$-2d-α-Glc | Cr 116.3 [190.3] I 102.2 [181.9] Cr |
| $C_{15}$-2d-β-Glc | Cr 108.4 [123.4] I 97.1 [121.4] Cr |
| $C_{16}$-2d-α-Glc | Cr 117.0 [181.9] I 100.2 [181.3 Cr |
| $C_{16}$-2d-β-Glc | Cr 109.2 [146.5] I 99.1 [137.9] Cr |
| $C_{17}$-2d-α-Glc | Cr 117.9 [157.4] I 103.7 [157.3] Cr |
| $C_{17}$-2d-β-Glc | Cr 111.3 [131.3] I 104.2 [127.1] Cr |
| $C_{18}$-2d-α-Glc | Cr 119.0 [212.0] I 92.3 [209.1] Cr |
| $C_{18}$-2d-β-Glc | Cr 110.2 [145.0] I 100.9 [136.6] Cr |

[a] The heating/cooling rate is 5 °C min$^{-1}$, during the second cycle.
[b] Both the I–SmA and SmA–Cr transitions merged together. The I–SmA transition temperature was determined with the aid of POM.

**Table 2**
Transition temperatures and enthalpies of transitions for the binary mixtures of alkyl 2-deoxy-α/β-D-*arabino*-hexopyranosides[a]

| Binary mixtures | Transition temperature (°C) [enthalpy (J/g)] |
|---|---|
| $C_9$-2d-α,β-Glc (1:1) | Cr 80.0 [131.3][b] SmA 87.2 I 72.4 [5.3] SmA 39.1 [79.1] Cr |
| $C_{10}$-2d-α,β-Glc (1:1) | Cr 83.7 [136.8][b] SmA 93.7 I 82.3 [5.9] SmA 46.9 [102.4] Cr |
| $C_{11}$-2d-α,β-Glc (1:1) | Cr 86.2 [113.6][b] SmA 94.5 I 86.2 [4.6] SmA 58.9 [97.1] Cr |
| $C_{12}$-2d-α,β-Glc (1:1) | Cr 88.4 [107.6][b] SmA 97.3 I 85.0 [4.0] SmA 56.8 [91.0] Cr |
| $C_{13}$-2d-α,β-Glc (1:1) | Cr 93.1 [137.1][b] SmA 95.2 I 94.0 [4.2] SmA 68.6 [128.1] Cr |
| $C_{14}$-2d-α,β-Glc (1:1) | Cr 94.9 [138.4][b] SmA 102.6 I 92.0 [3.7] SmA 73.5 [133.2] Cr |
| $C_{15}$-2d-α,β-Glc (1:1) | Cr 95.7 [125.5][b] SmA 104.6 I 92.3 [3.0] SmA 76.7 [120.8] Cr |
| $C_{16}$-2d-α,β-Glc (1:1) | Cr 98.5 [160.2][b] SmA 105.5 I 94.1 [2.8] SmA 77.9 [140.8] Cr |
| $C_{17}$-2d-α,β-Glc (1:1) | Cr 100.4 [145.8][b] SmA 106.5 I 92.1 [2.4] SmA 81.0 [142.5] Cr |
| $C_{18}$-2d-α,β-Glc (1:1) | Cr 102.1 [169.1][b] SmA 106.7 I 93.2 [2.3] SmA 81.7 [146.3] Cr |

[a] The heating and cooling rate is 5 °C min$^{-1}$, during the second cycle.
[b] The Cr–SmA and SmA–I transitions are merging together. The enthalpies are given for the combined transitions.

The crystal structure of the binary mixtures of octyl α-D-glucoside and octyl β-D-glucoside in equimolar ratio is known previously (Jeffrey and Yeon, 1992). In the crystalline state, both the α- and β-derivatives arrange in an alternate fashion. A similar possibility could be considered with the binary mixtures of the 2-deoxy glycosides. The mesomorphism of the binary mixtures could be due to the formation of dimers of the α- and β-anomers. The thermal behavior of the binary mixtures of $C_{13}$-2d-α-Glc and $C_{13}$-2d-β-Glc, as well as $C_{15}$-2d-α-Glc and $C_{15}$-2d-β-Glc, in different molar ratios, from 10 mol% to 90 mol%, was also investigated. As the amount of

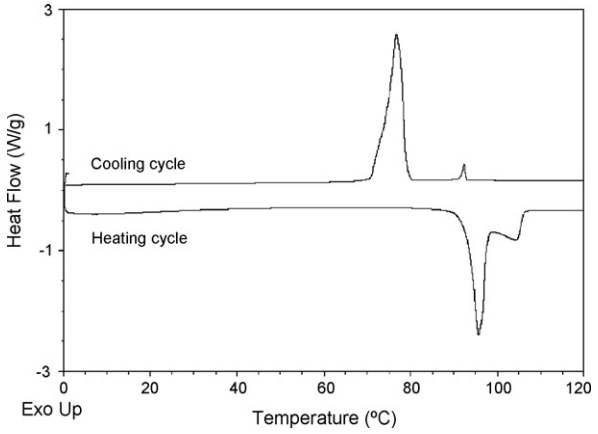


**Fig. 3.** DSC thermogram for $C_{15}$-2d-α,β-Glc (1:1), at a heating and cooling rate is 5 °C min$^{-1}$ during the second cycle.

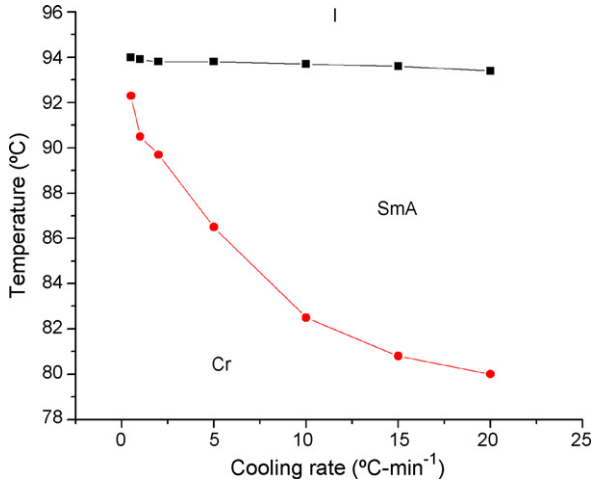


**Fig. 4.** Plot of transition temperature versus cooling rate for $C_{11}$-2d-β-Glc.

the α-anomer increased in the pure β-anomer for $C_{13}$-2d-Glc, the mesophase range increased and it reached a maximum at 50 mol%. Further increase in the α-component reduced the mesophase range and above 80 mol%, the mesophase ceased to exist. For $C_{15}$-2d-Glc, where both α- and β-anomers were not liquid crystalline, 25 mol% of α-anomer induced a mesomorphism in the pure β-anomer. As the component of the α-anomer increased, the mesomorphic range increased, with a maximum at 50 mol%. The corresponding phase diagrams are presented in Fig. 5. At higher concentrations of the α-anomer, the mesomorphic range decreased. These results show that both the α- and the β-anomers are able to induce the mesomorphism in the counterpart anomer equally. Importantly, the results suggest that not only the hydroxyl group of the sugar moiety, but also the anomeric configuration plays a role in the mesophase formation.

There are few reports on the mesomorphic behavior of the binary mixtures of thermotropic carbohydrate mesogens. The binary mixtures of the α- and the β-anomers of *n*-alkyl D-glucopyranosides were studied to describe the molecular packing and co-solubility in the crystalline and the liquid crystalline phases (Dorset, 1990). A cubic phase could be induced in the binary mixture, with one component forming the columnar phase in its pure state and the other component forming the lamellar phase (von Minden et al., 2002; Feng et al., 2003). The stability of the induced cubic phase was temperature- as well as concentration-dependent. The binary mixtures of the glycoglycerolipids with phospholipids have been studied to determine the glycolipid–phospholipid miscibility in the solid and liquid crystalline states (Koynova et al., 1988). Also, the head group orientations of alkyl glycolipids at a lipid bilayer interface have been studied in detail (Sanders and Prestegard, 1992).

The liquid crystalline behavior of the normal alkyl glucosides is well known (Goodby, 1984; Pfeffer et al., 1976; Jeffrey and Bhattacharjee, 1983). The alkyl glucosides, in both the α- and the β-anomeric configurations, exhibit enantiotropic SmA phase, with alkyl chain lengths from $C_7$ to $C_{16}$. In this case, the SmA–I transition temperature increases with increasing alkyl chain length (Vill et al., 1989). The clearing points of α-glucosides are also found to be more than the corresponding β-anomers and the mesomorphic range of α-anomers is more generally (Goodby et al., 2007). The difference between the alkyl glucosides and the compounds studied herein is the absence of the hydroxyl group at C-2 of the sugar moiety in the later. The mesomorphism in carbohydrates is primarily due to the microphase segregation of hydrophilic and hydrophobic moieties (Boullanger, 1997; van Doren and Wingert, 1994). The molecules form a bilayer structure, as the hydrophilic sugar head groups held together by the strong hydrogen bonding, and the hydrophobic alkyl chain tails by the weak van der Waals forces (van Doren and Wingert, 1991). The crystal structure of the alkyl α-D-glucoside reveals that the molecules form a bilayer structure, both in the crystalline state as well as in the mesophase (Moews and Knox, 1976; Jeffrey and Yeon, 1987; van Koningsveld et al., 1988; Adasch et al., 1998; Hoffmann et al., 2000). The alkyl 2-deoxy glucosides studied herein are devoid of the hydroxyl group at C-2. The observation that the mesomorphism exists not only in short temperature ranges, but also is dependent on the anomeric configuration can be accounted due to the absence of the hydroxyl group at C-2 in these alkyl 2-deoxy glucosides. These observations are in contrast to the mesophase behavior of normal alkyl glycosides that show greater mesophase stabilities for the α-anomers. The α-anomers of the alkyl 2-deoxy glycosides studied herein destabilize the mesophase formation, either due to an extremely narrow temperature range at which the mesophase evolves, or due to an altered molecular arrangement, which does not allow the mesophase formation. The fact that the binary mixtures of the α- and β-anomers exhibit the SmA phase indicate a possible reduction in the melting temperatures and the crystallization tendencies of the α-anomers, so as to allow the smectic phase formation in the binary mixtures. A number of examples can be seen wherein an induced mesophase evolves in the binary mixtures, including glycolipids (Tschierske, 1998, 2001; von Minden et al., 2002; Paleos and Tsiourvas, 1995).

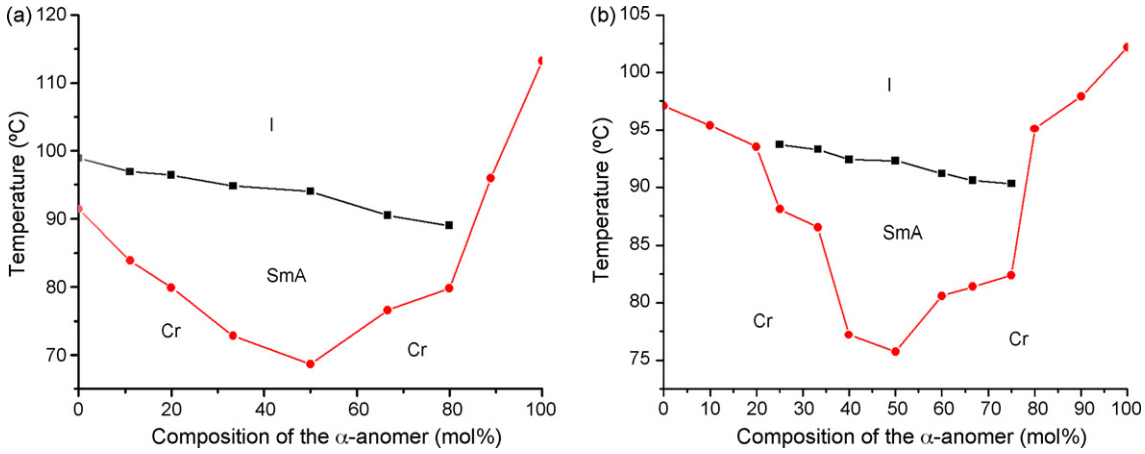


**Fig. 5.** Phase diagrams for the binary mixtures of (a) $C_{13}$-2d-α-Glc and $C_{13}$-2d-β-Glc and (b) $C_{15}$-2d-α-Glc and $C_{15}$-2d-β –Glc.

## 3. Conclusion

A new homologous series of alkyl 2-deoxy-D-*arabino*-hexopyranosides, in pure α- and β-anomeric forms, is synthesized. Only the β-anomers with alkyl chain lengths between $C_9$ and $C_{14}$ exhibited a monotropic SmA phase. None of the α-anomer was liquid crystalline. Mesophase could, however, be induced by mixing either of the anomers of same alkyl chain lengths and the mesophase range was found to reach a maximum at ∼50 mol%. In particular, this study uncovers that the presence of the C-2 hydroxyl group is crucial for the normal alkyl glycosides to exhibit mesophase in a wide temperature range, for both the anomeric forms of the glycosides. The absence of the C-2 hydroxyl group in the present alkyl glycosides restricted their thermotropic behavior. The present study illustrates that the C-2 hydroxyl group plays a significant role in the mesophase formation of alkyl glycosides.

## 4. Experimental

### 4.1. General

Chemicals were purchased from commercial sources and were used without further purification. The following alkyl 2-deoxy glycosides are known previously: octyl 2-deoxy-α/β-D-*arabino*-hexopyranoside (Liu and Still, 1993; Kim et al., 2005); tetradecyl 2-deoxy-α/β-D-*arabino*-hexopyranoside (Sanders and Prestegard, 1992). Solvents were dried and distilled using literature procedure (Perrin and Armarego, 1988). Analytical TLC was performed on commercial Merck plates, coated with silica gel $GF_{254}$ (0.25 mm), with a detection by charring after immersion in 5% $H_2SO_4$/EtOH. Silica gel (100–200 mesh) was used for column chromatography. Microanalyses were performed on an automated C, H, N analyzer. High resolution mass spectra were obtained from Q-TOF instruments by an electrospray ionization (ESI) technique. $^1$H and $^{13}$C NMR spectral analysis were performed on a Jeol 300 and 75 MHz, respectively, or a Bruker 400 and 100 MHz, respectively. The mesophases were characterized by using a Mettler FP82HT hot stage and central processor, in conjunction with a Litz DMRXP polarizing microscope. The transition temperatures and transition enthalpies were determined by differential scanning calorimetry (DSC Q100, TA Instruments).

### 4.2. General procedure for the synthesis of alkyl 2-deoxy-α/β-D-*arabino*-hexopyranosides

A mixture of ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-D-*arabino*-hexopyranoside (Paul and Jayaraman, 2004) (0.3–0.5 g, 1 molar equiv.), NIS (1.2 molar equiv.), 1-alkanol (1.2 molar equiv.) and 4 Å MS in $CH_2Cl_2$ (10 mL) was stirred at 0 °C for 15 min. A solution of TMSOTf (0.1 molar equiv.) in $CH_2Cl_2$ was added and allowed to stir for 30 min at 0 °C, under $N_2$ atmosphere. The reaction mixture was filtered through a celite pad, the filtrate diluted with $CH_2Cl_2$, washed with aq. $NaHCO_3$ (3 × 50 mL), aq. $Na_2S_2O_3$ (5%, 3 × 50 mL), aq. NaCl (3 × 50 mL) and dried ($Na_2SO_4$). The solution was concentrated and subjected to column chromatography ($SiO_2$). Alkyl 2-deoxy-3,4,6-tri-*O*-acetyl-D-*arabino*-hexopyranosides were separated (EtOAc/pet. ether). A methanolic solution of NaOMe (0.5 M, 1 mL) was added to a solution of tri-*O*-acetyl-2-deoxyglucosides in MeOH and stirred for 8 h at room temperature. The reaction mixture was neutralized with AcOH/MeOH (1:9, v/v), concentrated, and the crude product purified by column chromatography ($SiO_2$, 5% MeOH/$CHCl_3$), to afford alkyl 2-deoxy-α-D-*arabino*-hexopyranosides and alkyl 2-deoxy-β-D-*arabino*-hexopyranosides, each in ∼30–35% yield, as white solids.

#### 4.2.1. Octyl 2-deoxy-α-D-arabino-hexopyranoside ($C_8$-2d-α-Glc)

$[\alpha]_D^{25}$ = 106.4 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 4.86 (d, 1H, *J* = 5.01 Hz, –OH), 4.74 (d, 1H, *J* = 5.01, H-1), 4.73 (d, 1H, *J* = 4.80 Hz, –OH), 4.40 (t, 1H, *J* = 5.90 Hz, –OH), 3.61 (m, 1H, H-3), 3.52 (m, 1H, H-$6_a$), 3.46 (m, 1H, H-$6_b$), 3.29 (m, 2H, –$OCH_2$), 3.24 (m, 1H, H-5), 3.02 (m, 1H, *J* = 5.01 Hz, H-4), 1.85 (dd, 1H, *J* = 12.84, *J* = 5.01 Hz, H-$2_e$), 1.47 (m, 2H, –$CH_2$–), 1.41 (dd, 1H, *J* = 12.84, *J* = 3.48 Hz, H-$2_a$), 1.22 (bs, 10H, –$CH_2$–), 0.84 (t, 3H, *J* = 6.94 Hz, –$CH_3$). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 96.4, 73.0, 71.7, 68.0, 66.0, 61.0, 38.0, 31.2, 28.9, 28.8, 28.7, 25.8, 22.1, 13.9. ESI-MS: *m/z* calcd for $C_{14}H_{28}O_5Na$: 299.1834; found: 299.1836. Anal. calcd for $C_{14}H_{28}O_5$: C, 60.84; H, 10.21; found: C, 60.65; H, 9.83%.

#### 4.2.2. Octyl 2-deoxy-β-D-arabino-hexopyranoside ($C_8$-2d-β-Glc)

$[\alpha]_D^{25}$ = −22.5 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 4.84 (t, 2H, *J* = 4.54 Hz, –OH), 4.44 (t, 1H, *J* = 5.90 Hz, –OH), 4.41 (dd, 1H, *J* = 9.71, 1.45 Hz, H-1), 3.74 (m, 2H, –$OCH_2$), 3.65 (ddd, 1H, *J* = 12.10, 5.90, 1.71 Hz, H-3), 3.44 (m, 1H, *J* = 5.90 Hz, H-4), 3.34 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 2.99 (m, 1H, H-5), 1.91 (ddd, 1H, *J* = 12.10, 4.94, 1.45 Hz, H-$2_e$), 1.46 (m, 2H, *J* = 6.03 Hz, –$CH_2$), 1.23 (m, 11H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.52 Hz, –$CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 100.1, 75.4, 71.8, 71.5, 69.9, 61.9, 38.8, 31.8, 29.6, 29.4, 29.3, 26.0, 22.7, 14.1. ESI-MS: *m/z* calcd for $C_{14}H_{28}O_5Na$: 299.1834; found: 299.1825. Anal. calcd for $C_{14}H_{28}O_5$: C, 60.84; H, 10.21; found: C, 60.76; H, 10.16%.

#### 4.2.3. Nonyl 2-deoxy-α-D-arabino-hexopyranoside ($C_9$-2d-α-Glc)

$[\alpha]_D^{25}$ = 96.7 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 4.85 (d, 1H, *J* = 5.04 Hz, –OH), 4.76 (d, 1H, *J* = 5.04 Hz, H-1), 4.73 (d, 1H, *J* = 4.84 Hz, –OH), 4.41 (t, 1H, *J* = 5.86 Hz, –OH), 3.60 (m, 1H, H-3), 3.52 (m, 1H, H-$6_a$), 3.46 (m, 1H, H-$6_b$), 3.29 (m, 2H, –$OCH_2$), 3.24 (m, 1H, H-5), 3.01 (m, 1H, *J* = 5.04, H-4), 1.86 (dd, 1H, *J* = 12.85, 5.04 Hz, H-$2_e$), 1.47 (m, 2H, –$CH_2$), 1.41 (dd, 1H, *J* = 12.85, 3.53 Hz, H-$2_a$), 1.23 (bs, 12H, –$CH_2$), 0.84 (t, 3H, *J* = 6.41 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ: 96.4, 73.1, 71.7, 68.1, 66.1, 61.0, 38.0, 31.3, 29.1, 29.0, 28.9, 28.7, 25.8, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{15}H_{30}O_5Na$: 313.1978; found: 313.1990. Anal. calcd for $C_{15}H_{30}O_5$: C, 62.04; H, 10.41; found: C, 61.92; H, 10.16%.

#### 4.2.4. Nonyl 2-deoxy-β-D-arabino-hexopyranoside ($C_9$-2d-β-Glc)

$[\alpha]_D^{25}$ = −28.3 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 4.84 (t, 2H, *J* = 4.49 Hz, –OH), 4.45 (t, 1H, *J* = 5.91 Hz, –OH), 4.41 (dd, 1H, *J* = 9.62, 1.42 Hz, H-1), 3.73 (m, 2H, –$OCH_2$), 3.66 (ddd, 1H, *J* = 12.0, 5.91, 1.86 Hz, H-3), 3.45 (m, 1H, *J* = 5.91 Hz, H-4), 3.35 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 3.00 (m, 1H, H-5), 1.92 (ddd, 1H, *J* = 12.0, 4.85, 1.42 Hz, H-$2_e$), 1.46 (m, 2H, *J* = 5.81 Hz, –$CH_2$), 1.23 (m, 13H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.26 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ: 99.2, 77.0, 71.6, 70.7, 68.1, 61.2, 38.9, 31.3, 29.2, 29.0, 28.9, 28.7, 25.6, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{15}H_{30}O_5Na$: 313.1991; found: 313.1990. Anal. calcd for $C_{15}H_{30}O_5$: C, 62.04; H, 10.41; found: C, 61.98; H, 10.02%.

#### 4.2.5. Decyl 2-deoxy-α-D-arabino-hexopyranoside ($C_{10}$-2d-α-Glc)

$[\alpha]_D^{25}$ = 86.7 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 4.84 (d, 1H, *J* = 5.02 Hz, –OH), 4.75 (d, 1H, *J* = 5.02, H-1), 4.73 (d, 1H, *J* = 4.83 Hz, –OH), 4.41 (t, 1H, *J* = 5.95 Hz, –OH), 3.62 (m, 1H, H-3), 3.53 (m, 1H, H-$6_a$), 3.46 (m, 1H, H-$6_b$), 3.29 (m, 2H, –$OCH_2$), 3.24 (m, 1H, H-5), 3.02 (m, 1H, *J* = 5.02, H-4), 1.85 (dd, 1H, *J* = 12.84, 5.02 Hz, H-$2_e$), 1.47 (m, 2H, –$CH_2$), 1.41 (dd, 1H, *J* = 12.84, 3.48 Hz, H-$2_a$), 1.22 (bs, 14H, –$CH_2$), 0.84 (t, 3H, *J* = 6.97 Hz, –$CH_3$). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 96.5, 73.1, 71.7, 68.1, 66.1, 61.1, 38.1, 32.1, 31.4, 29.1, 28.8, 26.8, 25.9, 22.2, 21.2, 14.1. ESI-MS: *m/z* calcd for $C_{16}H_{32}O_5Na$:

327.2147; found: 327.2144. Anal. calcd for $C_{16}H_{32}O_5$: C, 63.13; H, 10.16; found: C, 63.09; H, 10.23%.

*4.2.6. Decyl 2-deoxy-β-D-arabino-hexopyranoside (C10-2d-β-Glc)*

$[\alpha]_D^{25} = -28.8$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.85 (t, 2H, *J* = 4.46 Hz, –OH), 4.45 (t, 1H, *J* = 5.83 Hz, –OH), 4.40 (dd, 1H, *J* = 9.58, 1.43 Hz, H-1), 3.72 (m, 2H, $-OCH_2$), 3.67 (ddd, 1H, *J* = 12.01, 5.83, 1.83 Hz, H-3), 3.45 (m, 1H, *J* = 5.83 Hz, H-4), 3.33 (m, 2 H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 3.02 (m, 1H, H-5), 1.92 (ddd, 1H, *J* = 12.01, 4.98, 1.43 Hz, H-$2_e$), 1.46 (m, 2H, *J* = 5.84 Hz, $-CH_2$), 1.22 (m, 15H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.16 Hz, $-CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 100.1, 75.5, 71.4, 71.3, 69.8, 61.6, 38.8, 31.9, 29.6, 29.5, 29.3, 26.0, 22.7, 14.1. ESI-MS: *m/z* calcd for $C_{16}H_{32}O_5Na$: 327.2147; found: 327.2141. Anal. calcd for $C_{16}H_{32}O_5$: C, 63.13; H, 10.16; found: C, 63.20; H, 10.53%.

*4.2.7. Undecyl 2-deoxy-α-D-arabino-hexopyranoside (C11-2d-α-Glc)*

$[\alpha]_D^{25} = 86.8$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.84 (d, 1H, *J* = 5.06 Hz, –OH), 4.76 (d, 1H, *J* = 5.06 Hz, H-1), 4.72 (d, 1H, *J* = 4.89 Hz, –OH), 4.42 (t, 1H, *J* = 5.93 Hz, –OH), 3.60 (m, 1H, H-3), 3.53 (m, 1H, H-$6_a$), 3.46 (m, 1H, H-$6_b$), 3.29 (m, 2H, $-OCH_2$), 3.25 (m, 1H, H-5), 3.01 (m, 1H, *J* = 5.06 Hz, H-4), 1.86 (dd, 1H, *J* = 12.74, 5.06 Hz, H-$2_e$), 1.47 (m, 2H, $-CH_2$), 1.41 (dd, 1H, *J* = 12.74, 3.54 Hz, H-$2_a$), 1.23 (bs, 16H, $-CH_2$), 0.84 (t, 3H, *J* = 6.47 Hz, $-CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 96.4, 73.1, 71.7, 68.1, 66.1, 38.0, 31.3, 29.1, 29.0, 28.9, 28.7, 25.8, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{17}H_{34}O_5Na$: 341.2304; found: 341.2304. Anal. calcd for $C_{17}H_{34}O_5$: C, 64.12; H, 10.76; found: C, 64.21; H, 10.51%.

*4.2.8. Undecyl 2-deoxy-β-D-arabino-hexopyranoside (C11-2d-β-Glc)*

$[\alpha]_D^{25} = -25.2$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.87 (t, 2H, *J* = 4.44 Hz, –OH), 4.48 (t, 1H, *J* = 5.93 Hz, –OH), 4.41 (dd, 1H, *J* = 9.58, 1.43 Hz, H-1), 3.71 (m, 2H, $-OCH_2$), 3.66 (ddd, 1H, *J* = 11.98, 5.93, 1.83 Hz, H-3), 3.44 (m, 1H, *J* = 5.93 Hz, H-4), 3.46 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 3.01 (m, 1H, H-5), 1.94 (ddd, 1H, *J* = 11.98, 4.90, 1.43 Hz, H-$2_e$), 1.45 (m, 2H, *J* = 5.86 Hz, $-CH_2$), 1.22 (m, 17H, H-$2_a$ and methylene), 0.83 (t, 3H, *J* = 6.52 Hz, $-CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 99.3, 77.1, 71.7, 70.7, 68.2, 61.3, 38.9, 31.4, 29.3, 29.1, 29.0, 28.8, 25.7, 22.2, 14.1. ESI-MS: *m/z* calcd for $C_{17}H_{34}O_5Na$: 341.2304; found: 341.2293. Anal. calcd for $C_{17}H_{34}O_5$: C, 64.12; H, 10.76; found: C, 63.99; H, 10.47%.

*4.2.9. Dodecyl 2-deoxy-α-D-arabino-hexopyranoside (C12-2d-α-Glc)*

$[\alpha]_D^{25} = 84.8$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.85 (d, 1H, *J* = 5.10 Hz, –OH), 4.75 (d, 1H, *J* = 5.10 Hz, H-1), 4.72 (d, 1H, *J* = 4.82 Hz, –OH), 4.40 (t, 1H, *J* = 5.94 Hz, –OH), 3.61 (m, 1H, H-3), 3.53 (m, 1H, H-$6_a$), 3.46 (m, 1H, H-$6_b$), 3.29 (m, 2H, $-OCH_2$), 3.24 (m, 1H, H-5), 3.02 (m, 1H, *J* = 5.10 Hz, H-4), 1.85 (dd, 1H, *J* = 12.84, 5.10 Hz, H-$2_e$), 1.47 (m, 2H, $-CH_2$), 1.41 (dd, 1H, *J* = 12.84, 3.48 Hz, H-$2_a$), 1.22 (bs, 18H, $-CH_2$), 0.84 (t, 3H, *J* = 6.94 Hz, $-CH_3$). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$: 96.6, 73.2, 71.8, 68.3, 66.3, 61.2, 38.1, 31.5, 29.2, 29.0, 28.9, 26.0, 22.3, 14.2. ESI-MS: *m/z* calcd for $C_{18}H_{36}O_5Na$: 355.2460; found: 355.2449. Anal. calcd for $C_{18}H_{36}O_5$: C, 65.03; H, 10.91; found: C, 64.94; H, 10.86%.

*4.2.10. Dodecyl 2-deoxy-β-D-arabino-hexopyranoside (C12-2d-β-Glc)*

$[\alpha]_D^{25} = -29.8$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.85 (t, 2H, *J* = 4.48 Hz, –OH), 4.48 (t, 1H, *J* = 5.91 Hz, –OH), 4.41 (dd, 1H, *J* = 9.61, 1.44 Hz, H-1), 3.72 (m, 2H, $-OCH_2$), 3.67 (ddd, 1H, *J* = 11.86, 5.91, 1.87 Hz, H-3), 3.44 (m, 1H, *J* = 5.91 Hz, H-4), 3.39 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 2.99 (m, 1H, H-5), 1.93 (ddd, 1H, *J* = 11.86, 4.90, 1.44 Hz, H-$2_e$), 1.45 (m, 2H, *J* = 5.85 Hz, $-CH_2$), 1.22 (m, 19H, H-$2_a$ and methylene), 0.83 (t, 3H, *J* = 6.22 Hz, $-CH_3$). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$: 100.1, 75.5, 71.7, 71.4, 69.9, 61.8, 38.8, 31.9, 29.7, 29.6, 29.5, 29.4, 26.0, 22.7, 14.1. ESI-MS: *m/z* calcd for $C_{18}H_{36}O_5Na$: 355.2460; found: 355.2460. Anal. calcd for $C_{18}H_{36}O_5$: C, 65.03; H, 10.91; found: C, 65.00; H, 10.83%.

*4.2.11. Tridecyl 2-deoxy-α-D-arabino-hexopyranoside (C13-2d-α-Glc)*

$[\alpha]_D^{25} = 81.0$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.85 (d, 1H, *J* = 5.05 Hz, –OH), 4.75 (d, 1H, *J* = 5.05 Hz, H-1), 4.73 (d, 1H, *J* = 4.88 Hz, –OH), 4.41 (t, 1H, *J* = 5.92 Hz, –OH), 3.60 (m, 1H, H-3), 3.53 (m, 1H, H-$6_a$), 3.44 (m, 1H, H-$6_b$), 3.29 (m, 2H, $-OCH_2$), 3.24 (m, 1H, H-5), 3.01 (m, 1H, *J* = 5.05 Hz, H-4), 1.85 (dd, 1H, *J* = 12.80, 5.05 Hz, H-$2_e$), 1.47 (m, 2H, $-CH_2$), 1.41 (dd, 1H, *J* = 12.80, 3.54 Hz, H-$2_a$), 1.22 (bs, 20H, $-CH_2$), 0.84 (t, 3H, *J* = 6.98 Hz, $-CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 96.4, 73.1, 71.7, 68.1, 66.1, 61.0, 38.0, 29.1, 29.0, 28.9, 28.8, 25.8, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{19}H_{38}O_5Na$: 369.2617; found: 369.2617. Anal. calcd for $C_{19}H_{38}O_5$: C, 65.86; H, 11.05; found: C, 65.86; H, 11.19%.

*4.2.12. Tridecyl 2-deoxy-β-D-arabino-hexopyranoside (C13-2d-β-Glc)*

$[\alpha]_D^{25} = -23.5$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.84 (t, 2H, *J* = 4.54 Hz, –OH), 4.44 (t, 1H, *J* = 5.92 Hz, –OH), 4.41 (dd, 1H, *J* = 9.71, 1.45 Hz, H-1), 3.74 (m, 2H, $-OCH_2$), 3.65 (ddd, 1H, *J* = 12.20, 5.92, 1.71 Hz, H-3), 3.44 (m, 1H, *J* = 5.92 Hz, H-4), 3.34 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 2.99 (m, 1H, H-5), 1.91 (ddd, 1H, *J* = 12.20, 4.94, 1.45 Hz, H-$2_e$), 1.46 (m, 2H, *J* = 6.03 Hz, $-CH_2$), 1.23 (m, 21H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.52 Hz, $-CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 99.2, 77.0, 71.6, 70.6, 68.1, 61.2, 38.9, 31.3, 29.2, 29.1, 29.0, 28.9, 28.7, 25.6, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{19}H_{38}O_5Na$: 369.2617; found: 369.2617. Anal. calcd for $C_{19}H_{38}O_5$: C, 65.86; H, 11.05; found: C, 65.58; H, 11.17%.

*4.2.13. Tetradecyl 2-deoxy-α-D-arabino-hexopyranoside (C14-2d-α-Glc)*

$[\alpha]_D^{25} = 73.8$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.86 (d, 1H, *J* = 5.09 Hz, –OH), 4.77 (d, 1H, *J* = 5.09 Hz, H-1), 4.74 (d, 1H, *J* = 4.85 Hz, –OH), 4.47 (t, 1H, *J* = 5.91 Hz, –OH), 3.62 (m, 1H, H-3), 3.54 (m, 1H, H-$6_a$), 3.51 (m, 1H, H-$6_b$), 3.28 (m, 2H, $-OCH_2$), 3.23 (m, 1H, H-5), 3.02 (m, 1H, *J* = 5.09 Hz, H-4), 1.85 (dd, 1H, *J* = 12.80, 5.09 Hz, H-$2_e$), 1.46 (m, 2H, $-CH_2$), 1.41 (dd, 1H, *J* = 12.80, 3.51 Hz, H-$2_a$), 1.21 (bs, 22H, $-CH_2$), 0.83 (t, 3H, *J* = 6.98 Hz, $-CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 96.5, 73.1, 71.8, 68.1, 66.1, 61.1, 38.1, 31.3, 29.1, 28.9, 28.8, 25.9, 22.2, 14.0. ESI-MS: *m/z* calcd for $C_{20}H_{40}O_5Na$: 383.2773; found: 383.2756. Anal. calcd for $C_{20}H_{40}O_5$: C, 66.63; H, 11.18; found: C, 66.52; H, 11.25%.

*4.2.14. Tetradecyl 2-deoxy-β-D-arabino-hexopyranoside (C14-2d-β-Glc)*

$[\alpha]_D^{25} = -23.3$ (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.83 (m, 2H, –OH), 4.44 (t, 1H, *J* = 5.87 Hz, –OH), 4.41 (dd, 1H, *J* = 9.67, 1.47 Hz, H-1), 3.74 (m, 2H, $-OCH_2$), 3.67 (ddd, 1H, *J* = 11.71, 5.87, 1.87 Hz, H-3), 3.45 (m, 1H, *J* = 5.87 Hz, H-4), 3.36 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 3.00 (m, 1H, H-5), 1.92 (ddd, 1H, *J* = 11.71, 4.97, 1.47 Hz, H-$2_e$), 1.45 (m, 2H, *J* = 6.32 Hz, $-CH_2$), 1.22 (m, 23H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.52 Hz, $-CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 99.2, 77.0, 71.7, 70.7, 68.1, 61.2, 38.9, 31.3, 29.2, 29.0, 28.9, 28.7, 25.6, 22.1, 13.9. ESI-MS: *m/z* calcd for $C_{20}H_{40}O_5Na$: 383.2773; found: 383.2759. Anal. calcd for $C_{20}H_{40}O_5$: C, 66.63; H, 11.18; found: C, 67.04; H, 11.16%.

*4.2.15. Pentadecyl 2-deoxy-α-D-arabino-hexopyranoside ($C_{15}$-2d-α-Glc)*

$[\alpha]_D^{25}$ = 76.0 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.85 (d, 1H, *J* = 5.12 Hz, –OH), 4.75 (d, 1H, *J* = 5.12 Hz, H-1), 4.72 (d, 1H, *J* = 4.82 Hz, –OH), 4.40 (t, 1H, *J* = 5.94 Hz, –OH), 3.61 (m, 1H, H-3), 3.53 (m, 1H, H-$6_a$), 3.46 (m, 1H, H-$6_b$), 3.29 (m, 2H, –$OCH_2$), 3.24 (m, 1H, H-5), 3.02 (m, 1H, *J* = 5.12 Hz, H-4), 1.85 (dd, 1H, *J* = 12.84, 5.12 Hz, H-$2_e$), 1.47 (m, 2H, –$CH_2$), 1.41 (dd, 1H, *J* = 12.84, 3.48 Hz, H-$2_a$), 1.22 (bs, 24 H, –$CH_2$), 0.84 (t, 3H, *J* = 6.94 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 96.4, 73.1, 71.7, 68.1, 66.1, 61.0, 38.0, 31.3, 29.1, 28.9, 28.8, 25.8, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{21}H_{42}O_5Na$: 397.2930; found: 397.2915. Anal. calcd for $C_{21}H_{42}O_5$: C, 67.34; H, 11.30; found: C, 67.29; H, 11.24%.

*4.2.16. Pentadecyl 2-deoxy-β-D-arabino-hexopyranoside ($C_{15}$-2d-β-Glc)*

$[\alpha]_D^{25}$ = −24.2 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.84 (t, 2H, *J* = 4.41 Hz, –OH), 4.44 (t, 1H, *J* = 5.85 Hz, –OH), 4.41 (dd, 1H, *J* = 9.68, 1.44 Hz, H-1), 3.74 (m, 2H, –$OCH_2$), 3.66 (ddd, 1H, *J* = 12.0, 5.85, 1.69 Hz, H-3), 3.45 (m, 1H, *J* = 5.85 Hz, H-4), 3.36 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 2.99 (m, 1H, H-5)1.92 (ddd, 1H, *J* = 12.0, 5.14, 1.44 Hz, H-$2_e$), 1.45 (m, 2H, *J* = 6.48 Hz, –$CH_2$), 1.22 (m, 25H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.47 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 99.2, 77.0, 71.6, 70.7, 68.1, 61.2, 38.9, 31.3, 29.2, 29.1, 29.0, 28.9, 28.7, 25.6, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{21}H_{42}O_5Na$: 397.2930; found: 397.2917. Anal. calcd for $C_{21}H_{42}O_5$: C, 67.34; H, 11.30; found: C, 67.49; H, 11.25%.

*4.2.17. Hexadecyl 2-deoxy-α-D-arabino-hexopyranoside ($C_{16}$-2d-α-Glc)*

$[\alpha]_D^{25}$ = 68.2 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.83 (d, 1H, *J* = 5.03 Hz, –OH), 4.76 (d, 1H, *J* = 5.03 Hz, H-1), 4.70 (d, 1H, *J* = 4.77 Hz, –OH), 4.39 (t, 1H, *J* = 5.94 Hz, –OH), 3.61 (m, 1H, H-3), 3.53 (m, 1H, H-$6_a$), 3.46 (m, 1H, H-$6_b$), 3.29 (m, 2H, –$OCH_2$), 3.27 (m, 1H, H-5), 3.01 (m, 1H, J = 5.03 Hz, H-4), 1.85 (dd, 1H, *J* = 12.77, 5.03 Hz, H-$2_e$), 1.47 (m, 2H, –$CH_2$), 1.41 (dd, 1H, *J* = 12.77, 3.52 Hz, H-$2_a$), 1.22 (bs, 26H, –$CH_2$), 0.84 (t, 3H, *J* = 6.98 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 96.4, 73.1, 71.7, 68.0, 66.0, 61.0, 37.9, 31.3, 29.0, 28.9, 28.8, 28.7, 25.8, 22.1, 13.9. ESI-MS: *m/z* calcd for $C_{22}H_{44}O_5Na$: 411.3086; found: 411.3084. Anal. calcd for $C_{22}H_{44}O_5$: C, 68.00; H, 11.41; found: C, 68.32; H, 11.27%.

*4.2.18. Hexadecyl 2-deoxy-β-D-arabino-hexopyranoside ($C_{16}$-2d-β-Glc)*

$[\alpha]_D^{25}$ = −19.0 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.84 (t, 2H, *J* = 4.88 Hz, –OH), 4.43 (t, 1H, *J* = 5.83 Hz, –OH), 4.41 (dd, 1H, *J* = 9.44, 1.37 Hz, H-1), 3.74 (m, 2H, –$OCH_2$), 3.66 (ddd, 1H, *J* = 12.29, 5.83, 1.82 Hz, H-3), 3.44 (m, 1H, *J* = 5.83 Hz, H-4), 3.36 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue peak), 2.99 (m, 1H, H-5), 1.92 (ddd, 1H, *J* = 12.29, 5.00, 1.37 Hz, H-$2_e$), 1.46 (m, 2H, *J* = 6.43 Hz, –$CH_2$), 1.22 (m, 27H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.45 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 99.2, 77.0, 71.6, 70.7, 68.1, 61.2, 38.9, 31.3, 30.7, 29.2, 29.1, 29.0, 28.9, 28.7, 25.6, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{22}H_{44}O_5Na$: 411.3086; found: 411.3087. Anal. calcd for $C_{22}H_{44}O_5$: C, 68.00; H, 11.41; found: C, 67.86; H, 11.36%.

*4.2.19. Heptadecyl 2-deoxy-α-D-arabino-hexopyranoside ($C_{17}$-2d-α-Glc)*

$[\alpha]_D^{25}$ = 68.3 (*c* 1, MeOH/$CHCl_3$, 1:3, v/v). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.84 (d, 1H, *J* = 5.01 Hz, –OH), 4.77 (d, 1H, *J* = 5.01 Hz, H-1), 4.73 (d, 1H, *J* = 4.82 Hz, –OH), 4.41 (t, 1H, *J* = 5.94 Hz, –OH), 3.61 (m, 1H, H-3), 3.53 (m, 1H, H-$6_a$), 3.45 (m, 1H, H-$6_b$), 3.29 (m, 2H, –$OCH_2$), 3.23 (m, 1H, H-5), 3.01 (m, 1H, *J* = 5.01 Hz, H-4), 1.85 (dd, 1H, *J* = 12.84, 5.01 Hz, H-$2_e$), 1.48 (m, 2H, –$CH_2$), 1.41 (dd, 1H, *J* = 12.84, 3.47 Hz, H-$2_a$), 1.22 (bs, 28H, –$CH_2$), 0.84 (t, 3H, *J* = 6.96 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 96.4, 72.9, 71.8, 68.0, 66.0, 61.0, 37.9, 31.1, 29.1, 29.0, 28.9, 28.8, 28.7, 28.5, 25.6, 21.9, 13.8. ESI-MS: *m/z* calcd for $C_{23}H_{46}O_5Na$: 425.3243; found: 425.3260. Anal. calcd for $C_{23}H_{46}O_5$: C, 68.61; H, 11.51; found: C, 68.83; H, 11.51%.

*4.2.20. Heptadecyl 2-deoxy-β-D-arabino-hexopyranoside ($C_{17}$-2d-β-Glc)*

$[\alpha]_D^{25}$ = −24.2 (*c* 1, MeOH). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.84 (m, 2H, –OH), 4.44 (t, 1H, *J* = 5.86 Hz, –OH), 4.41 (dd, 1H, *J* = 9.67, 1.54 Hz, H-1), 3.74 (m, 2H, –$OCH_2$), 3.67 (ddd, 1H, *J* = 12.17, 5.86, 1.87 Hz, H-3), 3.45 (m, 1H, *J* = 5.86 Hz, H-4), 3.36 (m, 2H, H-$6_a$ and H-$6_b$, overlapped with DMSO residue), 3.00 (m, 1H, H-5), 1.92 (ddd, 1H, *J* = 12.17, 4.97, 1.54 Hz, H-$2_e$), 1.45 (m, 2H, *J* = 6.32 Hz, –$CH_2$), 1.22 (m, 29H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.45 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 99.1, 76.9, 71.7, 70.6, 67.9, 61.2, 38.8, 31.1, 29.1, 28.9, 28.8, 28.7, 28.5, 25.4, 21.9, 13.7. ESI-MS: *m/z* calcd for $C_{23}H_{46}O_5Na$: 425.3243; found: 425.3256. Anal. calcd for $C_{23}H_{46}O_5$: C, 68.61; H, 11.51; found: C, 68.63; H, 11.40%.

*4.2.21. Octadecyl 2-deoxy-α-D-arabino-hexopyranoside ($C_{18}$-2d-α-Glc)*

$[\alpha]_D^{25}$ = 61.3 (*c* 1, MeOH/$CHCl_3$, 1:3, v/v). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.86 (d, 1H, *J* = 5.03 Hz, –OH), 4.77 (d, 1H, *J* = 5.03 Hz, H-1), 4.74 (d, 1H, *J* = 4.85 Hz, –OH), 4.41 (t, 1H, *J* = 5.93 Hz, –OH), 3.61 (m, 1H, H-3), 3.53 (m, 1H, H-$6_a$), 3.46 (m, 1H, H-$6_b$), 3.29 (m, 2 H, –$OCH_2$), 3.23 (m, 1H, H-5), 3.01 (m, 1H, *J* = 5.03 Hz, H-4), 1.85 (dd, 1H, *J* = 12.83, 5.03 Hz, H-$2_e$), 1.47 (m, 2H, –$CH_2$), 1.41 (dd, 1H, *J* = 12.83, 3.52 Hz, H-$2_a$), 1.22 (bs, 30H, –$CH_2$), 0.84 (t, 3H, *J* = 6.94 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 96.5, 73.1, 71.8, 68.1, 66.1, 61.1, 38.1, 31.3, 29.1, 28.9, 28.8, 25.9, 22.2, 14.0. ESI-MS: *m/z* calcd for $C_{24}H_{48}O_5Na$: 439.3399; found: 439.3399. Anal. calcd for $C_{24}H_{48}O_5$: C, 69.19; H, 11.61; found: C, 69.29; H, 11.66%.

*4.2.22. Octadecyl 2-deoxy-β-D-arabino-hexopyranoside ($C_{18}$-2d-β-Glc)*

$[\alpha]_D^{25}$ = −18.0 (*c* 1, MeOH/$CHCl_3$, 1:3, v/v). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 4.84 (t, 2H, *J* = 4.66, –OH), 4.43 (t, 1H, *J* = 5.81 Hz, –OH), 4.40 (dd, 1H, *J* = 9.41, 1.38 Hz, H-1), 3.74 (m, 2H, –$OCH_2$), 3.67 (ddd, 1H, *J* = 12.15, 5.81, 1.83 Hz, H-3), 3.44 (m, 1H, *J* = 5.81 Hz, H-4), 3.35 (m, 2H, H-$6_a$ and H-$6_b$, oerlapped with DMSO residue), 2.99 (m, 1H, H-5), 1.92 (ddd, 1H, *J* = 12.15, 5.11, 1.38 Hz, H-$2_e$), 1.45 (m, 2H, *J* = 6.4 Hz, –$CH_2$), 1.22 (m, 31H, H-$2_a$ and methylene), 0.84 (t, 3H, *J* = 6.31 Hz, –$CH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 99.2, 77.0, 71.6, 70.7, 68.1, 61.2, 38.9, 31.3, 29.2, 29.0, 28.9, 28.7, 25.6, 22.1, 14.0. ESI-MS: *m/z* calcd for $C_{24}H_{48}O_5Na$: 439.3399; found: 439.3399. Anal. calcd for $C_{24}H_{48}O_5$: C, 69.19; H, 11.61; found: C, 69.21; H, 11.84%).

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