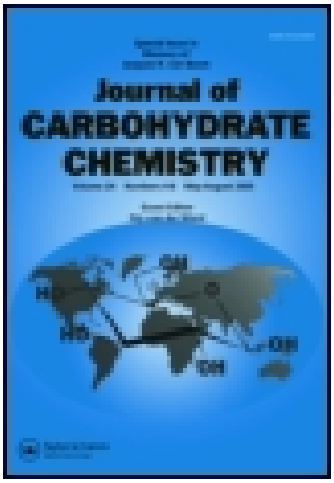


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lcar20

Synthesis of O-Alkyl D-Xylitols with Potential Luquid-Crystalline Properties

Benali Harmouch [a], Paul Godé [a], Gérard Goethals [a], John Goodby [b], Julie Haley [b], Stephen Kelly [b], Phillipe Letellier [b], Grahame Mackenzie [b], Patrick Martin [a], Gino Ronco [a], Marcus Watson [b] & Pierre Villa [a]

[a] Laboratoire de Chimie Organique et Cinétique, Faculté des Sciences, Université de Picardie-Jules Verne , 33, rue Saint-Leu, 80039, Amiens, France

[b] The School of Chemistry, The University of Hull , Hull, HU6 7RX, England

Published online: 20 Aug 2006.

J. CARBOHYDRATE CHEMISTRY, 16(4&5), 479-497 (1997)

SYNTHESIS OF *O*-ALKYL D-XYLITOLS WITH POTENTIAL LIQUID - CRYSTALLINE PROPERTIES [1]

Benali Harmouch,[a] Paul Godé,[a] Gérard Goethals,[a] John Goodby,[b] Julie Haley,[b] Stephen Kelly,[b] Phillipe Letellier,[b] Grahame Mackenzie,[b] Patrick Martin,[a] Gino Ronco,[a] Marcus Watson[b] and Pierre Villa[a*]

a) Laboratoire de Chimie Organique et Cinétique, Faculté des Sciences, Université de Picardie-Jules Verne, 33, rue Saint-Leu, 80039 Amiens (France)
b) The School of Chemistry, The University of Hull, Hull HU6 7RX (England)

Final Form December 24, 1996

ABSTRACT

A general synthetic approach to enantiomerically pure x-*O*-alkyl-D-xylitols has been developed from D-xylose. These products provide access to new thermotropic liquid crystals.

INTRODUCTION

Recently, we have been concerned with a systematic and fundamental investigation into the effects of the linking group (positioned between the sugar unit and the aliphatic chain in mono-substituted systems) on the lyotropic and thermotropic properties of acyclic systems.[2] For this purpose, we chose to study the self-assembling behaviour of alkyl substituted xylitols

where the aliphatic chain was attached to the xylitol moiety *via* ether, ester and thioether linkages (see structure **I** in Figure 1). From this investigation, we were able to show that the efficiency for forming thermotropic phases followed the pattern,

$$-SR > -OCOR > -OR$$

whereas, surprisingly, the reverse sequence appeared to be the case for lyotropic phases.

In this current study, we report the synthesis of x-*O*-alkyl-D-xylitols (structure **II**) and first results on the effects on the self-assembling properties of moving the position of a dodecyl chain.

RESULTS AND DISCUSSION

The xylitol amphiphile derivatives x-*O*-alkyl-D-xylitol in which R is an alkyl chain (n-C_8H_{17} or n-$C_{12}H_{25}$) linked to the xylitol moiety at the x position (x = 1, 2, 3 or 4) by the oxygen atom, were synthesized following Scheme 1. The precursors x-*O*-alkyl-D-xylose (**3, 6, 9** and **14**) were prepared by regiospecific functionalization of D-xylose. Their reduction gave the corresponding alditol derivatives **15-18**.

Preparation of x-*O*-Alkyl-D-xylose 3, 6, 9, 14. Products **3** were prepared *via* derivatization of the anhydro derivative of D-xylose **1**,[3,4] using alkyl alcohol, potassium hydroxide in toluene-dimethylsulphoxide to give 5-*O*-alkyl-1,2-*O*-isopropylidene-α-D-xylofuranose **2**.[5,6] Treatment of **2** with sulphuric acid (0.3M) in dioxane-water gave 5-*O*-alkyl-D-xylofuranose **3a** (76%) and **3b** (65%) as a mixture of anomers α, β (**3a** α/β = 3/2 ; **3b** α/β = 2/3, NMR ^{13}C in C_5D_5N).

The 2-substituted product **6**, was prepared *via* derivatization of the monoacetal of methyl β-D-xylofuranoside derivative **4**,[7,8] using alkyl bromide in toluene-dimethylsulphoxide and potassium hydroxide to yield the methyl 2-*O*-alkyl-3,5-*O*-isopropylidene-β-D-xylofuranoside **5a** (86%) and **5b** (80%). Subsequently **5** was deprotected with aqueous acetic acid to give 2-*O*-alkyl-D-xylopyranose **6a** (58%) and **6b** (56%).

The 3-substituted product **9**, was prepared from the trityl monoacetal **7** [9] *via* the same synthetic procedure as for the preparation of **5** to give **8a** (85%) and **8b** (83%). Compound **8** was deprotected using a similar procedure

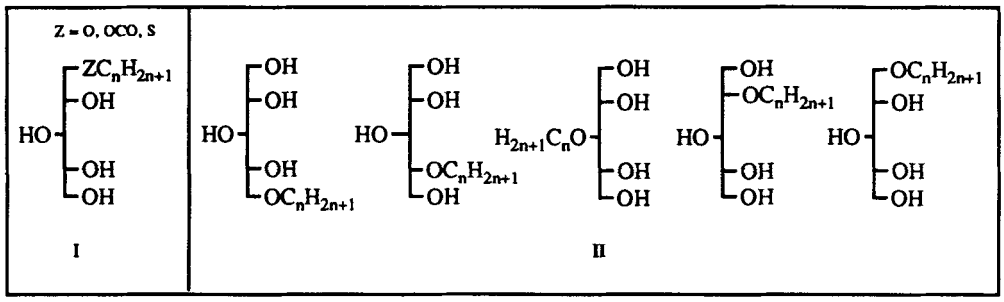


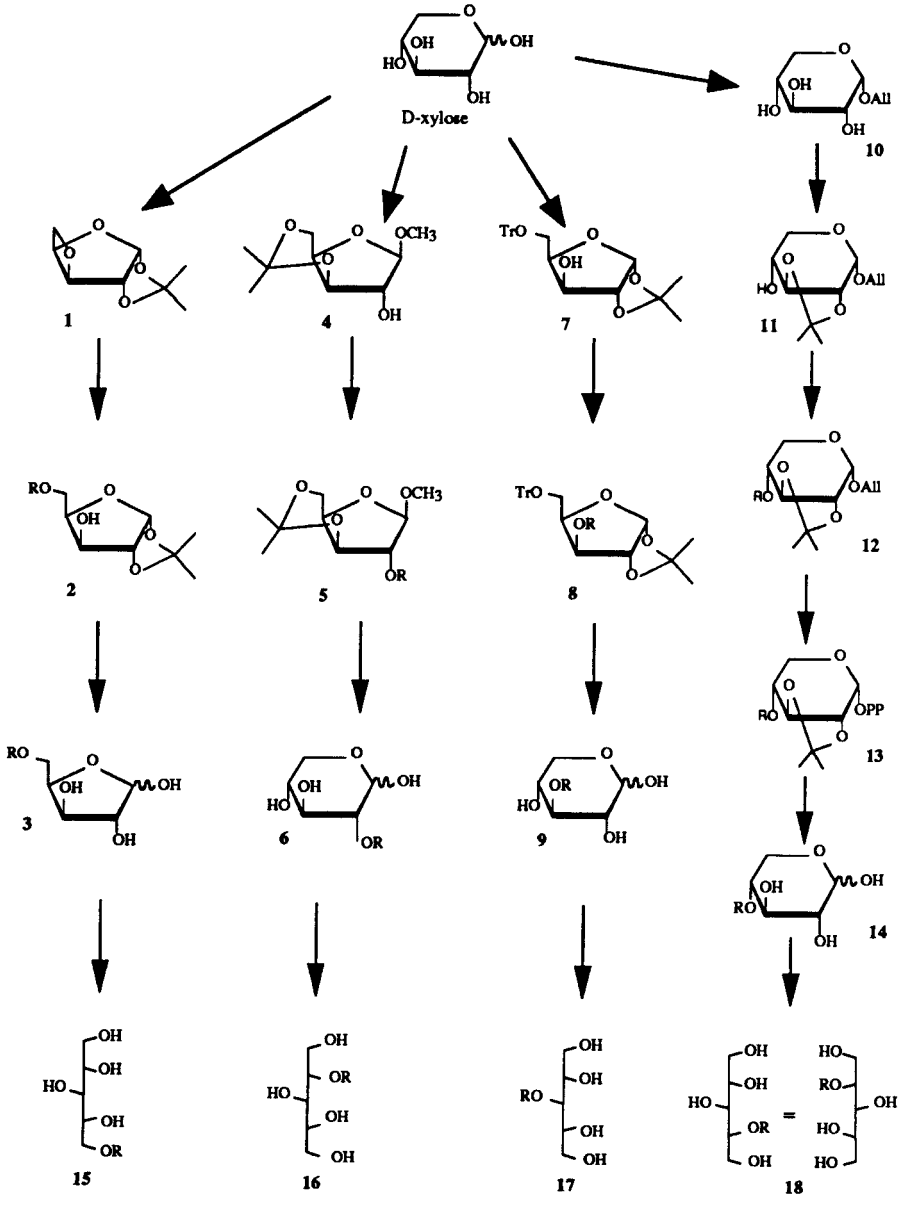
Figure 1. Structure I and structure II.

as for the preparation of **3** to give 3-*O*-alkyl-D-xylopyranose **9a** (78%) and **9b** (70%).

The 4-substituted product **14**, was prepared in a five step synthetic procedure starting from D-xylose, which was first treated with acetyl chloride[10] and allyl alcohol to give allyl α-D-xylopyranoside **10** in 55% yield. The product **10** was then protected using methoxypropene[11] and a trace of toluene sulphonic acid in dimethylformamide to give **11** (70%), which with the alkyl bromide and potassium hydroxide gave the corresponding alkyl products **12a** (79%) and **12b** (76%), respectively. Treatment of **12a** and **12b** with potassium *tert*-butoxide[12] in toluene-dimethylsulphoxide gave propenyl 4-*O*-alkyl-2,3-*O*-isopropylidene-α-D-xylopyranoside **13a** (94%) and **13b** (86%) respectively. These products were subsequently deprotected to yield **14a** (77%) and **14b** (70%).

Preparation of x-*O*-Alkyl-xylitol 15-18. The x-*O*-alkyl-D-xylose **3, 6, 9, 14** were subjected to reduction using sodium borohydride in methanol to give final products **15-18.**

Transition Temperatures. Most mono-substituted acyclic liquid-crystalline sugars exhibit chiral smectic A* phases.[13] However, the relationship between the position of aliphatic substitution, the overall stereochemistry of the system and the thermotropic liquid crystal transition temperatures has not been investigated in detail. In this present study we have chosen to examine this relationship through characterization of a family of *n*-dodecyl xylitols, structures **15b-18b.**



Scheme 1

The *n*-dodecyl chain was moved from the 1-position to the 5-position for the xylitol moiety, thereby allowing us to directly compare the transition temperatures of the individual materials (Figure 2).

Initial results show, surprisingly, that compound **17b**, which has the poorest degree of molecular anisotropy, i.e., it is the shortest and broadest compound of the four, has the highest transition temperatures. Conversely, the longest and narrowest compounds, have the lowest isotropization points. This effect seems due to internal hydrogen bonding in compound **17b** which allows for the formation of a more rigid structure with respect to the carbohydrate moiety.

The transition temperatures were found to vary almost linearly with position, i.e., for **15b** to **17b**. Moreover, we observed that compounds **16** and **18** which have the alkyl chain at the C-2 and C-4 position show both nearly the same phase transition and the same isotropization temperatures. We observed the same phenomenon with the 5-*O*-alkyl-D-xylitol (**15**) and its racemate 1-*O*-alkyl-D,L-xylitol.[2] This suggests that in this series, the location of the alkyl chain is important in determining phase transition and isotropization temperatures but not the stereochemistry of the carbohydrate moiety. Both of these first results obtained are atypical of liquid crystal systems. In noncarbohydrate systems it is well-known that changing the location of the aliphatic chain can result in large non-linear variations in transition temperature, and where multiple chiral centres are concerned, the position of attachment of a terminal aliphatic chain can result in large variations in phase type and transition temperatures. Thus it is rather striking, for the systems under investigations, that the transition temperatures vary linearly with the position of alkyl chain attachment and that the stereochemistry of substitution does not affect either phase type or transition temperature. This indicates that the thermotropic liquid crystal properties of substitute sugars are quite unlike those of conventional thermotropic non-amphiphilic liquid crystals. Studies of the liquid-crystalline properties of these materials will be reported in detail elsewhere.

EXPERIMENTAL

General methods. Melting points were determined on an electrothermal apparatus, and are uncorrected. NMR spectra were recorded with a Bruker WB-300 instrument for solutions in $CDCl_3$ or C_5D_5N (internal

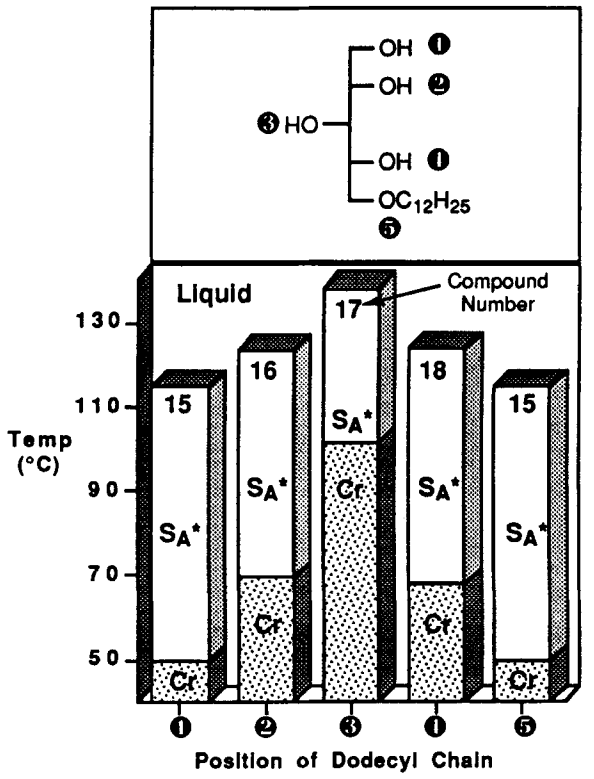


Figure 2. Variation in transition temperatures as a function of position of the dodecyl chain for compounds **15b-18b**.

Me_4Si). Reactions were monitored by either HPLC (Waters 721), using the reverse phase columns RP-18 (Merck) or CPG (Girdel) with an OV 17 column. In some cases, the purity was controlled by HPLC with the reverse phase column PN 27-196 (Waters). Column chromatography was performed on Silica Gel (60 mesh, Matrex) by gradient elution with hexane-acetone or hexane-THF (in each case the ratio of silica gel to product mixture to be purified was 30:1). The purity of compounds was verified by chromatography and NMR.

Phase identification and determination of phase transition temperatures were carried out, concomitantly, by thermal polarised light microscopy using either a Zeiss Universal or a Leitz Laborlux 12 Pol

polarizing transmitted light microscope equipped with a Mettler FP82 microfurnace in conjunction with an FP80 Central Processor. Homeotropic sample preparations suitable for phase characterisation were prepared simply by using very clean glass microscope slides (washed with water, acetone, water, concentrated nitric acid, water and dry acetone), whereas homogeneous defect textures were obtained by using nylon coated slides. Nylon coating of the slides (~200-300 Å thick) was obtained by dipping clean slides into a solution of nylon (6/6) in formic acid (1% m/v). The nylon solution was allowed to drain off the slides over a period of 1h, and then they were baked dry, free from solvent, in an oven at 100 °C for a period of 3 h. The slides were not buffed, as is usual for preparing aligned samples, but instead they were used untreated so that many defects would be created when the liquid crystal formed on the surface of the slide on cooling from the liquid phase.

Synthesis of Precursors x-O-Alkyl-D-xylose (3, 6, 9, 14)

Synthesis of 5-O-Alkyl-D-xylofuranose (3).

5-*O*-Alkyl-1,2-*O*-isopropylidene-α-D-xylofuranose (2). Finely powdered potassium hydroxide (6 equiv) and the anhydro derivative **1**[3,4] (1 equiv) were added to a stirred solution of the appropriate alcohol (3 equiv) in 1:1 toluene-Me_2SO, at 80 °C. After 95% conversion (CPG monitoring), the mixture was filtered and the filtrate neutralized with saturated aq NH_4Cl. The organic phase was separated, washed with water (twice), dried (Na_2SO_4), and concentrated under reduced pressure. The desired products were isolated after purification by column chromatography with 97:3 hexane-acetone.

5-*O*-*n*-Octyl-1,2-*O*-isopropylidene-α-D-xylofuranose (2a). Likewise, **1** (30 g, 0.17 mol) and octyl alcohol (68.1 g, 0.52 mol), after 8 h, yielded 32.7 g (63.5%) of **2a**. mp 41-43 °C. $[\alpha]_D^{20}$ 1.2° (*c* 1.2, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 0.83 (t, $J_{\omega,\omega-1}$ = 6.8 Hz, 3H, Hω); 1.22 (m, $(CH_2)_5$); 1.27 and 1.44 (2 s, 6H, C*Me*$_2$); 1.54 (m, $J_{\alpha,\beta}$ = 6.6 Hz, 2H, Hβ); 3.43 (dt, $J_{\alpha,\alpha'}$ = 9.3 Hz, $J_{\alpha,\beta}$ = 6.8 Hz, 1H, Hα'); 3.51 (dt, 1H, Hα); 3.85 (dd, $J_{5a,5b}$ = 11.1 Hz, $J_{4,5b}$ = 3.2 Hz, 1H, H-5b); 3.91 (dd, $J_{4,5a}$ = 3.7 Hz, 1H, H-5a); 4.01 (d, $J_{3,4}$ = 2.9 Hz, $J_{2,3}$ = 0.0 Hz, 1H, H-3); 4.16 (ddd, 1H, H-4); 4.47 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-2); 5.93 (d, 1H, H-1). ^{13}C NMR (75 MHz) δ: 13.1 (Cω); 21.6-30.8 ($(CH_2)_5$); 25.2 and 25.8 (C*Me*$_2$); 28.4 (Cβ); 68.3 (C-5); 71.7 (Cα); 75.7 (C-3); 76.8 (C-4); 84.5 (C-2); 103.9 (C-1); 110.5 (*C*Me$_2$).

5-*O*-*n*-Dodecyl-1,2-*O*-isopropylidene-α-D-xylofuranose (2b). Likewise, **1** (30 g, 0.17 mol) and dodecyl alcohol (97.4 g, 0.52 mol), after 12 h, yielded 45 g (73.5%) of **2b**. mp 62-64 °C. $[\alpha]_D^{20}$ 0.8° (*c* 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 0.82 (t, $J_{\omega,\omega-1}$ = 6.8 Hz, 3H, Hω); 1.20 (m, $(CH_2)_9$); 1.27-1.43 (2 s, 6H, CMe_2); 1.52 (m, $J_{\alpha,\beta}$ = 6.6 Hz, 2H, Hβ); 3.42 (dt, $J_{\alpha,\alpha'}$ = 9.4 Hz, , 1H, Hα'); 3.51 (dt, 1H, Hα); 3.83 (dd, $J_{5a,5b}$ = 11.1 Hz, 1H, H-5b); 3.89 (dd, $J_{4,5b}$ = 3.3 Hz, 1H, H-5a); 3.98 (d, $J_{3,4}$ = 2.9 Hz, 1H, H-3); 4.15 (dd, $J_{4,5a}$ = 3.5 Hz, 1H, H-4); 4.45 (d, $J_{2,3}$ = 0.0 Hz, 1H, H-2); 5.92 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 13.0 (Cω); 22.5-31.7 ($(CH_2)_9$); 25.1 and 25.8 (CMe_2); 30.9 (Cβ); 68.2 (C-5); 71.6 (Cα); 75.7 (C-3); 76.9 (C-4); 84.5 (C-2); 103.9 (C-1); 110.5 (CMe_2).

5-*O*-Alkyl-D-xylofuranose (3). 5-*O*-alkyl-1,2-*O*-isopropylidene-α-D-xylofuranose **2** (100 $g.L^{-1}$) was added, at 50 °C, to a stirred solution of H_2SO_4 (0.3M) in 4:1 dioxane-H_2O. After a 97% conversion (HPLC monitoring), the solution was cooled and neutralized with saturated aq NaOH and solid $NaHCO_3$. The filtrate was evaporated to dryness under reduced pressure, and the desired products were isolated after purification by column chromatography with 1:1 hexane-acetone.

5-*O*-*n*-Octyl-D-xylofuranose (3a). Likewise, **2a** (5 g, 16.5 mmol), after 55 min, yielded 3.3 g (75%) of **3a**. α/β = 3/2 (NMR ^{13}C in C_5D_5N). mp 41-43 °C. $[\alpha]_D^{20}$ 9.4° (*c* 1.0, CH_3OH).

Anal. Calcd for $C_{13}H_{26}O_5$ (262.35) : C, 59.52; H, 9.99. Found: C, 59.36; H, 10.06.

Anomeric derivative α. ^1H NMR (300 MHz, C_5D_5N) δ: 0.86 (t, $J_{\omega,\omega-1}$ = 6.8 Hz, 3H, Hω); 1.21-1.36 (m, $(CH_2)_5$); 1.64 (m, 2H, Hβ); 3.59 (m, 2H, Hα); 4.09 (dd, $J_{5a,5b}$ = 10.4 Hz, $J_{4,5b}$ = 6.4 Hz, 1H, H-5b); 4.21 (dd, $J_{4,5a}$ = 4.6 Hz, 1H, H-5a); 4.70 (d, $J_{1,2}$ = 4.0 Hz, 1H, H-2); 4.90 (dd, $J_{2,3}$ = 2.8 Hz, 1H, H-3); 4.98 (m, $J_{3,4}$ = 4.0 Hz, 1H, H-4); 6.15 (d, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.2 (Cω); 22.9-32.0 ($(CH_2)_6$); 70.9 (C-5); 71.4 (Cα); 77.4 (C-3); 78.5 (C-2); 78.8 (C-4); 97.9 (C-1).

Anomeric derivative β. ^1H NMR (300 MHz, C_5D_5N) δ: 0.86 (t, $J_{\omega,\omega-1}$ = 6.8 Hz, 3H, Hω); 1.21-1.36 (m, $(CH_2)_5$); 1.64 (m, 2H, Hβ); 3.59 (m, 2H, Hα); 4.19 (dd, $J_{5a,5b}$ = 10.4 Hz, $J_{4,5b}$ = 6.4 Hz, 1H, H-5b); 4.32 (dd,$J_{4,5a}$ = 4.9 Hz, 1H, H-5a); 4.79 (dd, $J_{3,4}$ = 4.4 Hz, 1H, H-3); 4.86 (d, $J_{2,3}$ = 2.8 Hz, 1H, H-2); 4.98 (m, 1H, H-4); 5.97 (s, $J_{1,2}$ = 0 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.2 (Cω); 22.9-32.0 ($(CH_2)_6$); 71.4 (C-5); 71.7 (Cα); 77.4 (C-3); 81.7 (C-4); 82.5 (C-2); 104.5 (C-1).

5-*O*-*n*-Dodecyl-D-xylofuranose (3b). Likewise, **2b** (5 g, 13.9 mmol), after 50 min, yielded 2.8 g (63%) of **3b**. α/β = 2/3 (NMR ^{13}C in C_5D_5N). mp 41-45 °C. $[\alpha]_D^{20}$ 12.9° (*c* 1.0, CH_3OH).

Anal. Calcd for $C_{17}H_{34}O_5$ (318.46) : C, 64.12; H, 10.76. Found: C, 64.36; H, 10.98.

Anomeric derivative α. ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.87 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.21-1.35 (m, $(CH_2)_9$); 1.67 (m, 2H, Hβ); 3.62 (m, 2H, Hα); 4.10 (dd, $J_{5a,5b}$ = 10.2 Hz, $J_{4,5b}$ = 6.3 Hz, 1H, H-5b); 4.20 (dd, $J_{4,5a}$ = 6.6 Hz, 1H, H-5a); 4.69 (dd, $J_{2,3}$ = 2.7 Hz, 1H, H-2); 4.90 (dd, $J_{3,4}$ = 4.3 Hz, 1H, H-3); 4.98 (m, $J_{4,5b}$ = 6.3 Hz, 1H, H-4); 6.15 (d, $J_{1,2}$ = 3.8 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.2 (Cω); 22.9-32.1 ($(CH_2)_{10}$); 70.7 (C-5); 71.7 (Cα); 77.6 (C-3); 78.5 (C-2); 78.7 (C-4); 97.6 (C-1).

Anomeric derivative β. ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.87 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.21-1.35 (m, $(CH_2)_9$); 1.67 (m, 2H, Hβ); 3.62 (m, 2H, Hα); 4.22 (dd, $J_{4,5a}$ = 4.2 Hz, 1H, H-5b); 4.33 (dd, $J_{5a,5b}$ = 10.2 Hz, 1H, H-5a); 4.79 (dd, $J_{2,3}$ = 2.0 Hz, $J_{3,4}$ = 4.4 Hz, 1H, H-3); 4.85 (d, $J_{1,2}$ = 0.0 Hz, 1H, H-2); 4.89 (m, $J_{4,5b}$ = 4.8 Hz, 1H, H-4); 5.96 (s, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.2 (Cω); 22.9-32.1 ($(CH_2)_{10}$); 71.3 (C-5); 71.7 (Cα); 77.4 (C-3); 81.7 (C-4); 82.4 (C-2); 104.4 (C-1).

Synthesis of 2-O-Alkyl-D-xylopyranose (6).

Methyl 2-*O*-Alkyl-3,5-*O*-isopropylidene-β-D-xylofuranoside (5). Finely powdered potassium hydroxide (2.4 equiv) and alkyl bromide (1.2 equiv) were added to a stirred solution of monoacetal **4**[8] (1 equiv) in 4:1 toluene-Me_2SO, at room temperature. After 95% conversion (CPG monitoring), the mixture was filtered and the filtrate neutralized with saturated aq NH_4Cl. The organic phase was separated, washed with water (twice), dried (Na_2SO_4), and evaporated to dryness under reduced pressure. The desired products were isolated after purification by column chromatography with 19:1 hexane-acetone.

Methyl 2-*O*-*n*-Octyl-3,5-*O*-isopropylidene-β-D-xylofuranoside (5a). Likewise, **4** (10 g, 49 mmol) and octyl bromide (11.3 g, 58.8 mmol), after 18 h, yielded 13.3 g (86%) of **5a**. oil. $[\alpha]_D^{20}$ -51.8° (*c* 1.6, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.84 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.16 (s, $(CH_2)_5$); 1.34-1.36 (2 s, 6H, CMe_2); 1.53 (q, 2H, Hβ); 3.40 (s, 3H, OMe); 3.46 (t, 2H, Hα); 3.75 (s, $J_{2,3}$ = 0.0 Hz, 1H, H-2); 3.81 (dd, $J_{5a,5b}$ = 12.3 Hz, 1H, H-5b); 3.94 (dd, $J_{5b,4}$ = 4.9 Hz, 1H, H-5a); 4.12 (m, $J_{5a,4}$ = 4.3 Hz, 1H, H-4); 4.13 (d, $J_{3,4}$ = 4.2 Hz, 1H, H-3); 4.86 (s, $J_{1,2}$ = 0.0 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 13.0 (Cω); 20.0-30.9 ($(CH_2)_6$); 25.1-26.1 (CMe_2); 54.4 (OMe); 60.0 (C-5); 69.3 (Cα); 72.3 (C-4); 73.7 (C-3); 87.3 (C-2); 97.3 (CMe_2); 107.5 (C-1).

Methyl 2-*O*-*n*-Dodecyl-3,5-*O*-isopropylidene-β-D-xylofuranoside (5b). Likewise, **4** (10 g, 49 mmol) and dodecyl bromide (14.6 g, 58.8 mmol), after 21 h, yielded 14.6g (80%) of **5b**. oil. $[\alpha]_D^{20}$ -44.9° (*c* 1.1, $CHCl_3$). ^{1}H NMR (300 MHz,

$CDCl_3$) δ: 0.84 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.16 (s, $(CH_2)_9$); 1.34-1.36 (2 s, 6H, CMe_2); 1.52 (q, 2H, Hβ); 3.38 (s, 3H, OMe); 3.47 (t, 2H, Hα); 3.76 (m, $J_{2,3}$ = 0.0 Hz, 1H, H-2); 3.80 (dd, $J_{5a,5b}$ = 12.1 Hz, 1H, H-5b); 3.94 (dd, $J_{5b,4}$ = 4.8 Hz, 1H, H-5a); 4.12 (dt, $J_{5a,4}$ = 4.4 Hz, 1H, H-4); 4.14 (d, $J_{3,4}$ = 4.3 Hz, 1H, H-3); 4.87 (s, $J_{1,2}$ = 0.0 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 13.0 (Cω); 20.0-30.9 ($(CH_2)_{10}$); 25.0-26.2 (CMe_2); 54.2 (OMe); 59.8 (C-5); 69.4 (Cα); 72.2 (C-4); 73.6 (C-3); 87.2 (C-2); 97.3 (CMe_2); 107.6 (C-1).

2-*O*-Alkyl-D-xylopyranose (6). Methyl 2-*O*-alkyl-3,5-*O*-isopropylidene-β-D-xylofuranoside **5** (100 $g.L^{-1}$) was added to a stirred solution of 4:1 CH_3COOH-H_2O. After a 97% conversion (HPLC monitoring) at 100 °C, the solution was concentrated to dryness under reduced pressure. The desired products were isolated after purification by column chromatography with 1:1 hexane-acetone.

2-*O*-*n*-Octyl-D-xylopyranose (6a). Likewise, **5a** (7 g, 22.1 mmol), after 1.5 h, yielded 3.4 g (58%) of **6a**. α/β = 47/53 (NMR ^{13}C in C_5D_5N). mp 70-85 °C. $[\alpha]_D^{20}$ 25.3° (*c* 1.0, CH_3OH).

Anal. Calcd for $C_{13}H_{26}O_5$ (262.35) : C, 59.52; H, 9.99. Found: C, 59.76; H, 10.16.

Anomeric derivative α. ^1H NMR (300 MHz, C_5D_5N) δ: 0.86 (t, $J_{\omega,\omega-1}$ = 6.8 Hz, 3H, Hω); 1.22-1.75 (m, $(CH_2)_6$); 3.73 (dd, $J_{4,5a}$ = 10.4 Hz, 1H, H-5a); 3.76 (dd, $J_{2,3}$ = 9.3 Hz, 1H, H-2); 3.93-4.39 (m, 2H, Hα and Hα'); 4.18 (dd, $J_{5a,5b}$ = 10.4 Hz, 1H, H-5b); 4.29 (m, $J_{4,5b}$ = 5.7 Hz, 1H, H-4); 4.70 (dd, $J_{3,4}$ = 8.4 Hz, 1H, H-3); 5.90 (d, $J_{1,2}$ = 3.1 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.2 (Cω); 22.9-32.0 ($(CH_2)_6$); 62.8 (C-5); 71.1 (Cα); 71.5 (C-4); 74.2 (C-3); 82.4 (C-2); 92.0 (C-1).

Anomeric derivative β. ^1H NMR (300 MHz, C_5D_5N) δ: 0.87 (t, $J_{\omega,\omega-1}$ = 6.8 Hz, 3H, Hω); 1.22-1.85 (m, $(CH_2)_6$); 3.69 (dd, $J_{2,3}$ = 8.2 Hz, 1H, H-2); 3.73 (dd, $J_{5a,5b}$ = 10.4 Hz, 1H, H-5b); 3.93-4.39 (m, 2H, Hα and Hα'); 4.14 (dd, $J_{3,4}$ = 9.0 Hz, 1H, H-3); 4.29 (m, $J_{4,5b}$ = 10.4 Hz, 1H, H-4); 4.39 (dd, $J_{4,5a}$ = 5.6 Hz, 1H, H-5a); 5.21 (d, $J_{1,2}$ = 7.5 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.2 (Cω); 22.9-32.0 ($(CH_2)_6$); 67.2 (C-5); 71.9 (C-4); 73.1 (Cα); 77.9 (C-3); 84.9 (C-2); 99.3 (C-1).

2-*O*-*n*-Dodecyl-D-xylopyranose (6b). Likewise, **5b** (7 g, 22.1 mmol), after 2 h, yielded 3.4 g (56%) of **6b**. α/β = 45/55 (NMR ^{13}C in C_5D_5N). mp 78-81 °C. $[\alpha]_D^{20}$ 21.9° (*c* 1.3, CH_3OH).

Anal. Calcd for $C_{17}H_{34}O_5$ (318.46) : C, 64.12; H, 10.76. Found: C, 64.46; H, 11.04.

Anomeric derivative α. ^1H NMR (300 MHz, C_5D_5N) δ: 0.86 (t, $J_{\omega,\omega-1}$ = 6.4 Hz, 3H, Hω); 1.22-1.72 (m, $(CH_2)_{10}$); 3.74 (dd, $J_{4,5a}$ = 10.3 Hz, 1H, H-5a); 3.75 (dd, $J_{2,3}$ = 9.3 Hz, 1H, H-2); 3.96-4.42 (m, 2H, Hα and Hα'); 4.22 (dd, $J_{5a,5b}$ = 10.6

Hz, 1H, H-5b); 4.24 (m, $J_{4,5b}$ = 5.3 Hz, 1H, H-4); 4.64 (dd, $J_{3,4}$ = 8.8 Hz, 1H, H-3); 5.88 (d, $J_{1,2}$ = 3.1 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.5 (Cω); 23.2-31.1 ($(CH_2)_{10}$); 63.1 (C-5); 71.4 (Cα); 71.7 (C-4); 74.5 (C-3); 82.6 (C-2); 92.3 (C-1).

Anomeric derivative β. ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.86 (t, $J_{\omega,\omega-1}$ = 6.4 Hz, 3H, Hω); 1.22-1.72 (m, $(CH_2)_{10}$); 3.66 (dd, $J_{2,3}$ = 8.1 Hz, 1H, H-2); 3.96-4.42 (m, 2H, Hα and Hα'); 3.74 (dd, $J_{5a,5b}$ = 10.6 Hz, 1H, H-5b); 4.11 (dd, $J_{3,4}$ = 8.5 Hz, 1H, H-3); 4.24 (m, $J_{4,5b}$ = 10.6 Hz, 1H, H-4); 4.37 (dd, $J_{4,5a}$ = 5.6 Hz, 1H, H-5a); 5.19 (d, $J_{1,2}$ = 7.4 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.5 (Cω); 23.2-31.2 ($(CH_2)_{10}$); 67.4 (C-5); 72.2 (C-4); 73.3 (Cα); 78.1 (C-3); 85.0 (C-2); 99.5 (C-1).

Synthesis of 3-O-Alkyl-D-xylopyranose (9).

5-*O*-Trityl-3-*O*-alkyl-1,2-*O*-isopropylidene-α-D-xylofuranose (8). This material was prepared from the trityl monoacetal 7[9] using the same method as for the synthesis of compound **5**, but at 60 °C instead of room temperature. The desired products were isolated after purification by column chromatography with 23:2 hexane-acetone.

5-*O*-Trityl-3-*O*-*n*-octyl-1,2-*O*-isopropylidene-α-D-xylofuranose (8a). Likewise, **7** (10 g, 23.1 mmol) and octyl bromide (5.4 g, 27.8 mmol), after 20 h, yielded 10.7 g (85%) of **8a**. mp 112-114 °C. $[\alpha]_D^{20}$ -37.1° (*c* 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.21-1.41 (m, $(CH_2)_6$); 1.32 and 1.53 (2 s, 6H, C*Me*$_2$); 3.31 (dd, $J_{5a,5b}$ = 9.3 Hz, 1H, H-5b); 3.39-3.52 (2 dt, 2H, Hα); 3.47 (dd, $J_{4,5b}$ = 7.2 Hz, 1H, H-5a); 3.87 (d, $J_{3,4}$ = 2.9 Hz, 1H, H-3); 4.37 (m, $J_{4,5a}$ = 6.7 Hz, 1H, H-4); 4.51 (d, $J_{2,3}$ = 0 Hz, 1H, H-2); 5.87 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1); 7.19-7.31 (9H, Hmeta, Hpara); 7.45-7.47 (6H, Hortho). ^{13}C NMR (75 MHz) δ: 13.2 (Cω); 21.7-30.9 ($(CH_2)_6$); 25.3 and 25.9 (C*Me*$_2$); 59.9 (C-5); 69.8 (Cα); 78.4 (C-4); 81.3 (C-3); 81.5 (C-2); 104.0 (C-1); 110.5 (CMe_2); 126.0-127.8 (Corth, Cmeta, Cpara); 143.0 (Cipso).

5-*O*-Trityl-3-*O*-*n*-dodecyl-1,2-*O*-isopropylidene-α-D-xylofuranose (8b). Likewise, **7** (10 g, 23.1 mmol) and dodecyl bromide (6.9 g, 27.8 mmol), after 17 h, yielded 11.5 g (83%) of **8b**. mp 58-70 °C. $[\alpha]_D^{20}$ -25.9° (*c* 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.21-1.38 (m, $(CH_2)_{10}$); 1.31 and 1.52 (2 s, 6H, C*Me*$_2$); 3.28 (dd, $J_{5a,5b}$ = 9.1 Hz, 1H, H-5b); 3.31-3.49 (2 dt, 2H, Hα); 3.46 (dd, $J_{4,5b}$ = 7.2 Hz, 1H, H-5a); 3.85 (d, $J_{3,4}$ = 2.3 Hz, 1H, H-3); 4.34 (m, $J_{4,5a}$ = 6.2 Hz, 1H, H-4); 4.49 (d, $J_{2,3}$ = 0 Hz, 1H, H-2); 5.85 (d, $J_{1,2}$ = 3.8 Hz, 1H, H-1); 7.20-7.30 (9H, Hmeta, Hpara); 7.42-7.45 (6H, Hortho). ^{13}C NMR (75 MHz) δ: 13.2 (Cω); 21.7-31.0 ($(CH_2)_{10}$); 25.3 and 25.9 (C*Me*$_2$); 59.9 (C-5); 69.8

(Cα); 78.5 (C-4); 81.3 (C-3); 81.5 (C-2); 104.0 (C-1); 110.5 (CMe_2); 126.0-127.8 (Corth, Cmeta, Cpara); 143.0 (Cipso).

3-*O*-Alkyl-D-xylopyranose (9). This material was prepared from the monoacetal **8** using the same method as for the synthesis of compound **3**, but at solvent reflux temperature instead of 50 °C. The desired products were isolated after purification by column chromatography with 1:1 hexane-acetone.

3-*O*-*n*-Octyl-D-xylopyranose (9a). Likewise, **8a** (6 g, 11.0 mmol), after 78 min, yielded 2.2 g (78%) of **9a**. α/β = 50/50 (NMR ^{13}C in C_5D_5N). After recrystallization in 9:1 ethyl ether-acetone only **9a**β was isolated. mp 90-107 °C. $[\alpha]_D^{20}$ 9.7° (*c* 1.2, CH_3OH). ^1H NMR (300 MHz, C_5D_5N) δ: 0.86 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.21-1.42 (m, $(CH_2)_6$); 3.77 (dd, $J_{5ax,5eq}$ = 10.5 Hz, 1H, H-5eq); 3.83 (t, $J_{3,4}$ = 8.3 Hz, 1H, H-3); 4.08-4.34 (2 dt, 2H, Hα); 4.08 (dd, $J_{2,3}$ = 8.9 Hz, 1H, H-2); 4.26 (ddd, $J_{4,5ax}$ = 5.6 Hz, 1H, H-4); 4.36 (dd, $J_{4,5eq}$ = 10.5 Hz, 1H, H-5ax); 5.23 (d, $J_{1,2}$ = 7.5 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.2 (Cω); 22.9-32.0 ($(CH_2)_6$); 67.3 (C-5); 70.8 (C-4); 73.4 (Cα); 76.3 (C-2); 86.8 (C-3); 99.6 (C-1).

Anal. Calcd for $C_{13}H_{26}O_5$ (262.35) : C, 59.52; H, 9.99. Found: C, 59.78; H, 10.16.

3-*O*-*n*-Dodecyl-D-xylopyranose (9b). Likewise, **8b** (6 g, 10.0 mmol), after 70 min, yielded 2.2 g (70%) of **9b**. α/β = 44/56 (NMR ^{13}C in C_5D_5N).

Anomeric derivative **9b**β was isolated like **9a**β. mp 95-115 °C. $[\alpha]_D^{20}$ 13.5° (*c* 1.5, CH_3OH). ^1H NMR (300 MHz, C_5D_5N) δ: 0.86 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.21-1.42 (m, $(CH_2)_{10}$); 4.32 (dd, $J_{5ax,5eq}$ = 10.8 Hz, 1H, H-5eq); 3.82 (t, $J_{3,4}$ = 7.9 Hz, 1H, H-3); 4.06-4.28 (2 dt, 2H, Hα); 4.49 (dd, $J_{2,3}$ = 9.2 Hz, 1H, H-2); 4.19 (ddd, $J_{4,5ax}$ = 10.5 Hz, 1H, H-4); 4.36 (dd, $J_{4,5eq}$ = 10.5 Hz, 1H, H-5ax); 5.19 (d, $J_{1,2}$ = 7.4 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.7 (Cω); 23.3-32.5 ($(CH_2)_{10}$); 67.7 (C-5); 71.2 (C-4); 73.8 (Cα); 76.7 (C-2); 87.3 (C-3); 100.0 (C-1).

Anal. Calcd for $C_{17}H_{34}O_5$ (318.46) : C, 64.12; H, 10.76. Found: C, 64.38; H, 11.98.

Synthesis of 4-O-Alkyl-D-xylopyranose (14).

Allyl α-D-Xylopyranoside (10). Acetyl chloride[10] (50 mL, 0.7 mol) and D-xylopyranose (50 g, 0.3 mol) were added with stirring to allyl alcohol (200 mL, 2.9 mol), at 0 °C. After 15 h (95% conversion HPLC monitoring), at room temperature, the mixture was cooled and neutralized with solid $NaHCO_3$. The solution was filtered (Celite) with the aid of 4:1 ethyl ether-THF, and the resulting filtrate was concentrated under reduced pressure. Allyl α-D-xylopyranoside **10** was isolated after purification by column chromatography with 1:4 hexane-acetone yielded 34.9 g (55%). mp 106-109 °C, $[\alpha]_D^{20}$ 159.5°

(*c* 1.0, CH_3OH). ^1H NMR (300 MHz, C_5D_5N) δ: 3.42 (dd, $J_{2,3}$ = 9.0 Hz, 1H, H-2); 4.00-4.32 (m, 4H, H-3, H-4, H-5); 4.01-4.24 (m, 2H, C*H*$_2$-CH=); 5.15-5.33 (m, 2H, CH_2=); 5.19 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1); 5.84-5.96 (m, 1H, CH=). ^{13}C NMR (75 MHz) δ: 63.7 (C-5); 66.8 (-CH_2-CH=); 71.6 (C-4); 73.9 (C-2); 75.7 (C-3); 100.3 (C-1); 117.1 (=CH_2); 135.5 (CH=).

Allyl 2,3-*O*-Isopropylidene-α-D-xylopyranoside (11). Methoxypropene (5.5 g, 76.9 mmol) and TsOH[11] (10 mg) were added to a stirred solution of allyl α-D-xylopyranoside (**10**) (4 g, 21.1 mmol) in dimethylformamide (40 mL) at 0 °C. After 1 h (the reaction was complete CPG monitoring) at room temperature, the solution was cooled and neutralized with solid $NaHCO_3$. The filtrate was concentrated under reduced pressure, and allyl 2,3-*O*-isopropylidene-α-D-xylopyranoside (**11**) was isolated after purification by column chromatography with 23:2 hexane-acetone. yielded 3.4 g (70%). mp 74-76 °C. $[\alpha]_D^{20}$ 146.6° (*c* 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 1.39 and 1.43 (2s, 6H, C*Me*$_2$); 3.27 (dd, $J_{5a,5b}$ = 11.0 Hz, 1H, H-5b); 3.39 (dd, $J_{2,3}$ = 9.3 Hz, $J_{1,2}$ = 3.0 Hz, 1H, H-2); 3.69 (dd, $J_{4,5a}$ = 4.9 Hz, 1H, H-5a); 3.91 (m, $J_{4,5b}$ = 10.0 Hz, 1H, H-4); 3.94 (dd, $J_{3,4}$ = 5.7 Hz, 1H, H-3); 4.01-4.24 (m, 2H, C*H*$_2$-CH=); 5.08 (d, 1H, H-1); 5.15-5.33 (m, 2H, CH_2=); 5.84-5.96 (m, 1H, CH_2-C*H*=). ^{13}C NMR (75 MHz) δ: 25.4 and 25.8 (C*Me*$_2$); 61.7 (C-5); 67.7 (-CH_2-CH=); 69.1 (C-4); 74.8 (C-2); 76.2 (C-3); 95.1 (C-1); 109.7 (C*Me*$_2$); 116.2 (=CH_2); 132.8 (CH=).

Allyl 4-*O*-Alkyl-2,3-*O*-isopropylidene-α-D-xylopyranoside (12). This material was prepared from the monoacetal **11** using the same method as for the synthesis of compound **5**. The desired products were isolated after purification by column chromatography with 47:3 hexane-acetone.

Allyl 4-*O*-*n*-Octyl-2,3-*O*-isopropylidene-α-D-xylopyranoside (12a). Likewise, **11** (1.5 g, 6.5 mmol) and octyl bromide (1.5 g, 7.8 mmol), after 18 h, yielded 1.8 g (79%) of **12a**. oil. $[\alpha]_D^{20}$ 100.4° (*c* 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 0.82 (t, $J_{\omega,\omega-1}$ = 6.7 Hz, 3H, Hω); 1.23 (m, $(CH_2)_5$); 1.38 and 1.40 (2 s, 6H, C*Me*$_2$); 1.50 (m, $J_{\alpha,\beta}$ = 6.7 Hz, 2H, Hβ); 3.31 (dd, $J_{5a,5b}$ = 11.1 Hz, 1H, H-5b); 3.34 (dd, $J_{1,2}$ = 3.0 Hz, $J_{2,3}$ = 9.4 Hz, 1H, H-2); 3.43 (dt, 1H, $H_{\alpha'}$); 3.58 (ddd, $J_{4,5a}$ = 5.2 Hz, $J_{4,5b}$ = 10.9 Hz, 1H, H-4); 3.65 (dt, 1H, H_α); 3.72 (dd, 1H, H-5a); 3.93 (dd, $J_{3,4}$ = 9.4 Hz, 1H, H-3); 4.02-4.18 (m, 2H, -C*H*$_2$-CH=); 5.05 (d, 1H, H-1); 5.10-5.30 (m, 2H, =CH_2); 5.80-5.93 (m, 1H, -CH=). ^{13}C NMR (75 MHz) δ: 13.1 (Cω); 21.6-30.8 ($(CH_2)_6$); 25.5 and 26.0 (C*Me*$_2$); 60.2 (C-5); 67.5 (-CH_2-CH=); 69.5 (Cα); 74.9 (C-2); 75.6 (C-3); 76.2 (C-4); 94.9 (C-1); 109.3 (CMe_2); 116.2 (=CH_2); 132.8 (-CH=).

Allyl 4-*O*-*n*-Dodecyl-2,3-*O*-isopropylidene-α-D-xylopyranoside (12b). Likewise, **11** (1.5 g, 6.5 mmol) and dodecyl bromide (1.9 g, 7.8 mmol), after 21 h, yielded 2.0 g (76%) of **12b**. mp 29-31 °C. $[\alpha]_D^{20}$ 93.7° (*c* 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 0.84 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.22 (m, $(CH_2)_9$); 1.39 and 1.42 (2s, 6H, C*Me*$_2$); 1.51 (m, $J_{\alpha,\beta}$ = 6.8 Hz, 2H, Hβ); 3.31 (dd, $J_{4,5b}$ = 10.6 Hz, 1H, H-5b); 3.39 (dd, $J_{1,2}$ = 3.0 Hz, $J_{2,3}$ = 9.6 Hz, 1H, H-2); 3.46 (dt, 1H, $H_{\alpha'}$); 3.60 (ddd, $J_{4,5a}$ = 5.2 Hz, 1H, H-4); 3.66 (dt, 1H, H_α); 3.74 (dd, $J_{5a,5b}$ = 11.0 Hz, 1H, H-5a); 3.94 (dd, $J_{3,4}$ = 9.5 Hz, 1H, H-3); 4.03-4.17 (m, 2H, -C*H*$_2$-CH=); 5.06 (d, 1H, H-1); 5.12-5.31 (m, 2H, =CH_2); 5.83-5.89 (m, 1H, -CH=). ^{13}C NMR (75 MHz) δ: 13.1 (Cω); 21.7-30.9 ($(CH_2)_{10}$); 25.5 and 26.0 (C*Me*$_2$); 60.2 (C-5); 67.6 (-CH_2-CH=); 69.5 (Cα); 75.0 (C-2); 75.7 (C-3); 76.3 (C-4); 95.0 (C-1); 109.3 (CMe_2); 116.2 (=CH_2); 132.8 (-CH=).

Propenyl 4-*O*-Alkyl-2,3-*O*-isopropylidene-α-D-xylopyranoside (13). Potassium *tert*-butoxide (2 equiv) was added to a stirred solution of allyl 4-*O*-alkyl-2,3-*O*-isopropylidene-D-xylopyranoside **12** in 1:1 toluene-Me_2SO (100 $g.L^{-1}$). After the reaction was complete (CPG monitoring) at 100 °C, the mixture was filtered and the filtrate neutralized with saturated aq NH_4Cl. The organic phase was separated, washed with water (twice), dried (Na_2SO_4), and concentrated under reduced pressure. The desired products were isolated after purification by column chromatography with 47:3 hexane-acetone.

Propenyl 4-*O*-*n*-Octyl-2,3-*O*-isopropylidene-α-D-xylopyranoside (13a). Likewise, **12a** (2 g, 5.8 mmol) and *t*BuOK (1.3 g, 11.7 mmol), after 50 h, yielded 1.9 g (94%) of **13a**. oil. $[\alpha]_D^{20}$ 74.2° (*c* 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 0.82 (t, $J_{\omega,\omega-1}$ = 6.8 Hz, 3H, Hω); 1.23 (m, $(CH_2)_6$); 1.39 and 1.42 (2s, 6H, C*Me*$_2$); 1.55-1.58 (m, 3H, C*H*$_3$-CH=); 3.29 (dd, $J_{5a,5b}$ = 11.1 Hz, 1H, H-5b); 3.38 (dd, $J_{2,3}$ = 9.5 Hz, 1H, H-2); 3.45 (dt, $J_{\alpha,\alpha'}$ = 9.4 Hz, $J_{\alpha,\beta}$ = 6.8 Hz, 1H, $H_{\alpha'}$); 3.60 (ddd, $J_{3,4}$ = 9.4 Hz, 1H, H-4); 3.66 (dt, 1H, H_α); 3.75 (dd, $J_{4,5a}$ = 5.2 Hz, 1H, H-5a); 3.98 (dd, $J_{2,3}$ = 9.5 Hz, 1H, H-3); 4.53-4.62 (m, 1H, CH_3-C*H*=); 5.20 (d, $J_{1,2}$ = 2.9 Hz, 1H, H-1); 6.05-6.08 (m, 1H, O-CH=). ^{13}C NMR (75 MHz) δ: 8.3 (CH_3-CH=); 13.1 (Cω); 25.3 and 25.9 (C*Me*$_2$); 21.6-30.8 ($(CH_2)_5$); 29.0 (Cβ); 60.7 (C-5); 69.6 (Cα); 74.7 (C-2); 75.6 (C-3); 76.0 (C-4); 95.4 (C-1); 103.6 (CH_3-CH=); 109.7 (CMe_2); 140.5 (O-CH=).

Propenyl 4-*O*-*n*-Dodecyl-2,3-*O*-isopropylidene-α-D-xylopyranoside (13b). Likewise, **12b** (2 g, 5.0 mmol) and *t*BuOK (1.1 g, 10.4 mmol), after 60 h, yielded 1.7 g (86%) of **13b**. oil. $[\alpha]_D^{20}$ 59.8° (*c* 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 0.84 (t, $J_{\omega,\omega-1}$ = 6.0 Hz, 3H, Hω); 1.22 (m, $(CH_2)_{10}$); 1.42 and 1.44 (2 s, 6H, C*Me*$_2$); 1.55-1.58 (m, 3H, C*H*$_3$-CH=); 3.31 (dd, $J_{5a,5b}$ = 11.2 Hz, 1H, H-5b);

3.40 (dd, $J_{2,3}$ = 9.5 Hz, 1H, H-2); 3.50 (dt, $J_{\alpha,\alpha'}$ = 9.2 Hz, $J_{\alpha,\beta}$ = 6.8 Hz, 1H, $H_{\alpha'}$); 3.63 (ddd, $J_{4,5a}$ = 5.2 Hz, 1H, H-4); 3.70 (dt, 1H, H_{α}); 3.77 (dd, $J_{4,5a}$ = 5.2 Hz, 1H, H-5a); 4.00 (dd, $J_{3,4}$ = 9.5 Hz, 1H, H-3); 4.53-4.62 (m, 1H, CH_3-C*H*=); 5.22 (d, $J_{1,2}$ = 2.9 Hz, 1H, H-1); 6.05-6.08 (m, 1H, O-CH=). ^{13}C NMR (75 MHz) δ: 8.2 (CH_3-CH=); 13.0 (Cω); 25.3 and 25.9 (C*Me*$_2$); 21.6-30.9 ((CH_2)$_9$); 29.0 (Cβ); 60.8 (C-5); 69.7 (Cα); 74.8 (C-2); 75.7 (C-3); 76.0 (C-4); 95.5 (C-1); 103.6 (CH_3-CH=); 109.7 (CMe_2); 140.5 (O-CH=).

4-*O*-Alkyl-D-xylopyranose (14). Propenyl 4-*O*-alkyl-2,3-*O*-isopropylidene-α-D-xylopyranoside **13** (100 g.L^{-1}) was added to a stirred solution of H_2SO_4 (0.2M) in 4:1 dioxane-H_2O. After the reaction was complete (HPLC monitoring) at 50 °C, the solution was cooled and neutralized with saturated aq NaOH and solid $NaHCO_3$. The filtrate was concentrated under reduced pressure, and 4-*O*-alkyl-D-xylopyranose **14** was isolated after purification by column chromatography with 1:1 hexane-acetone.

4-*O*-*n*-Octyl-D-xylopyranose (14a). Likewise, **13a** (1.5 g, 4.4 mmol), after 48 min, yielded 0.9 g (77%) of **14a**. α/β = 6/4 (NMR ^{13}C in C_5D_5N). After recrystallization in 9:1 hexane-ethyl ether only **14a**α was isolated from the mixture. mp 66-96°C. $[\alpha]_D^{20}$ 40.7° (*c* 1.1, CH_3OH). ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.86 (t, $J_{\omega,\omega-1}$ = 6.5 Hz, 3H, Hω); 1.21 (m, (CH_2)$_5$); 1.67 (m, $J_{\alpha,\beta}$ = 6.7 Hz, 2H, Hβ); 3.79 (m, $J_{4,5eq}$ = 5.5 Hz, 2H, H-4 and $H_{\alpha'}$); 3.94 (dt, $J_{\alpha,\alpha'}$ = 9.1 Hz, 1H, Hα); 4.12 (d, $J_{2,3}$ = 8.7 Hz, 1H, H-2); 4.14 (dd, $J_{5eq,5ax}$ = 10.7 Hz, 1H, H-5eq); 4.39 (dd, $J_{4,5ax}$ = 10.7 Hz, 1H, H-5ax); 4.64 (dd, $J_{3,4}$ = 8.8 Hz, 1H, H-3); 5.84 (d, $J_{1,2}$ = 0.0 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.2 (Cω); 22.9-32.0 ((CH_2)$_5$); 30.8 (Cβ); 60.7 (C-5); 71.4 (Cα); 74.2 (C-3); 74.5 (C-2); 80.0 (C-4); 94.5 (C-1).

Anal. Calcd for $C_{13}H_{26}O_5$ (262.35) : C, 59.52; H, 9.99. Found: C, 59.66; H, 10.12.

4-*O*-*n*-Dodecyl-D-xylopyranose (14b). Likewise, **13b** (1.5 g, 3.8 mmol), after 45 min, yielded 0.8 g (70%) of **14b**. α/β = 7/3 (NMR ^{13}C in C_5D_5N). Anomeric derivative **14b**α was isolated like **14a**α. mp 90-125°C. $[\alpha]_D^{20}$ 25.6° (*c* 1.2, CH_3OH). ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.87 (t, $J_{\omega,\omega-1}$ = 6.7 Hz, 3H, Hω); 1.23 (m, (CH_2)$_9$); 1.61 (m, $J_{\alpha,\beta}$ = 6.6 Hz, 2H, Hβ); 3.76 (m, $J_{4,5ax}$ = 10.6 Hz, 2H, H-4 and $H_{\alpha'}$); 3.91 (dt, $J_{\alpha,\alpha'}$ = 9.2 Hz, 1H, Hα); 4.08 (d, $J_{2,3}$ = 8.7 Hz, 1H, H-2); 4.11 (dd, $J_{4,5eq}$ = 4.4 Hz, 1H, H-5eq); 4.35 (dd, $J_{5ax,5eq}$ = 10.6 Hz, 1H, H-5ax); 4.59 (dd, $J_{3,4}$ = 8.7 Hz, 1H, H-3); 5.79 (s, $J_{1,2}$ = 0.0 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 14.7 (Cω); 23.3-32.5 ((CH_2)$_9$); 31.2 (Cβ); 61.0 (C-5); 71.8 (Cα); 74.6 (C-3); 74.8 (C-2); 80.4 (C-4); 94.5 (C-1).

Anal. Calcd for $C_{17}H_{34}O_5$ (318.46) : C, 64.12; H, 10.76. Found: C, 64.38; H, 11.04.

Synthesis of Alditols 15 to 18

General method for the reduction of the x-*O*-Alkyl-D-xyloses to Alditols 15 to 18. Each xylose derivative **3, 6, 9, 14** (50 $g.L^{-1}$) was dissolved in methanol and treated with sodium borohydride (6 equiv) at room temperature for 16 h. The sodium borohydride excess was destroyed by treatment with formic acid for 5 h at room temperature and the solution was concentrated under reduced pressure. Cationic Resin H^+ was added to a solution of the crude products in 1:1 MeOH-H_2O. After 15 min the mixture was filtered and the filtrate was concentrated under reduced pressure. The desired products were isolated subsequently after purification by column chromatography with 1:9 hexane-THF.

5-*O*-*n*-Octyl-D-xylitol (15a). Likewise, **3a** (5.0 g, 19.0 mmol) yielded 2.6 g (52%) of **15a**. oil. $[\alpha]_D^{20}$ 1.0° (*c* 1.2, CH_3OH).^1H NMR (300 MHz, C_5D_5N) δ: 0.82 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.16 (m, $(CH_2)_5$); 1.56 (m, $J_{\alpha,\beta}$ = 6.6 Hz, 2H, Hβ); 3.49 (t, 2H, Hα); 3.97 (dd, $J_{4,5b}$ = 6.3 Hz, 1H, H-5b); 4.04 (dd, $J_{4,5a}$ = 5.1 Hz, $J_{5a,5b}$ = 9.8 Hz, 1H, H-5a); 4.29 (dd, $J_{1b,2}$ = 5.8 Hz, 1H, H-1b); 4.35 (dd, $J_{1a,2}$ = 5.2 Hz, $J_{1a,1b}$ = 10.8 Hz, 1H, H-1a); 4.41 (dd, $J_{3,4}$ = 3.5 Hz, 1H, H-3); 4.51 (m, $J_{2,3}$ = 3.5 Hz, 1H, H-2); 4.56 (m, 1H, H-4). ^{13}C NMR (75 MHz) d: 14.5 (Cω); 23.2-32.3 ($(CH_2)_5$); 30.6 (Cβ); 64.8 (C-1), 71.9 (Cα); 72.5 (C-3); 72.6 (C-4); 73.8 (C-5); 74.6 (C-2)
Anal. Calcd for $C_{13}H_{28}O_5$ (264.36) : C, 59.06; H, 10.68. Found: C, 59.27; H, 10.58.

5-*O*-*n*-Dodecyl-D-xylitol (15b). Likewise, **3b** (5.0 g, 15.7 mmol) yielded 2.8 g (56%) of **15b**. mp 50-111 °C. $[\alpha]_D^{20}$ 1.2° (*c* 1.0, CH_3OH). ^1H NMR (300 MHz, C_5D_5N) δ: 0.84 (t, $J_{\omega,\omega-1}$ = 6.4 Hz, 3H, Hω); 1.20 (m, $CH_2)_9$); 1.56 (m, $J_{\alpha,\beta}$ = 6.6 Hz, 2H, Hβ); 3.48 (t, 2H, Hα); 3.94 (dd, $J_{4,5b}$ = 6.3 Hz, 1H, H-5b); 4.02 (dd, $J_{4,5a}$ = 5.2 Hz, $J_{5a,5b}$ = 10.2 Hz, 1H, H-5a); 4.26 (dd, $J_{1b,2}$ = 5.8 Hz, 1H, H-1b); 4.31 (dd, $J_{1a,2}$ = 5.2 Hz, $J_{1a,1b}$ = 10.9 Hz, 1H, H-1a); 4.37 (dd, $J_{3,4}$ = 3.5 Hz, 1H, H-3); 4.48 (m, $J_{2,3}$ = 3.5 Hz, 1H, H-2); 4.55 (m, 1H, H-4). ^{13}C NMR (75 MHz, C_5D_5N) δ: 14.6 (Cω); 23.2-32.4 ($(CH_2)_9$); 30.5 (Cβ); 64.8 (C-1); 72.0 (Cα); 72.5 (C-3); 72.6 (C-4); 73.9 (C-5); 74.7 (C-2).
Anal. Calcd for $C_{17}H_{36}O_5$ (320.47) : C, 63.71; H, 11.32. Found: C, 63.51; H, 11.21.

2-*O*-*n*-Octyl-D-xylitol (16a). Likewise, **6a** (2.0 g, 7.6 mmol) yielded 1.0 g (50%) of **16a**. mp 47-80 °C. $[\alpha]_D^{20}$ 3.0° (*c* 1.1, CH_3OH). ^1H NMR (300 MHz, C_5D_5N) δ: 0.82 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.15 (m, $(CH_2)_5$); 1.59 (m, $J_{\alpha,\beta}$ = 6.7 Hz, 2H, Hβ); 3.71 (dt, $J_{\alpha,\alpha'}$ = 9.1 Hz, 1H, Hα'); 3.86 (dt, 1H, Hα); 4.06 (ddd, $J_{2,3}$ = 4.6 Hz, 1H, H-2); 4.26 (dd, $J_{4,5b}$ = 6.0 Hz, $J_{5a,5b}$ = 10.9 Hz, 1H, H-5b); 4.30 (dd, $J_{1b,2}$ = 4.5 Hz, 1H, H-1b); 4.34 (dd, $J_{4,5a}$ = 5.2 Hz, 1H, H-5a); 4.39 (dd, $J_{1a,2}$ = 4.8

Hz, $J_{1a,1b}$ = 11.5 Hz, 1H, H-1a); 4.53 (ddd, $J_{3,4}$ = 3.5 Hz, 1H, H-4); 4.56 (dd, $J_{2,3}$ = 4.6 Hz, 1H, H-3). ^{13}C NMR (75 MHz, C_5D_5N) δ:14.6 (Cω); 23.3-32.4 ($(CH_2)_5$); 31.1 (Cβ); 61.9 (C-1); 65.2 (C-5); 71.3 (Cα); 72.3 (C-3); 73.1 (C-4); 83.2 (C-2).
Anal. Calcd for $C_{13}H_{28}O_5$ (264.36) : C, 59.06; H, 10.68. Found: C, 59.30; H, 10.75.

2-*O*-*n*-Dodecyl-D-xylitol (16b). Likewise, **6b** (2.0 g, 6.3 mmol) yielded 1.1 g (57%) of **16b**. mp 69-120 °C. $[\alpha]_D^{20}$ 3.2° (*c* 1.1, CH_3OH). ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.85 (t, $J_{\omega,\omega-1}$ = 6.7 Hz, 3H, Hω); 1.19 (m, $(CH_2)_9$); 1.61 (m, $J_{\alpha,\beta}$ = 6.7 Hz, 2H, Hβ); 3.72 (dt, $J_{\alpha,\alpha'}$ = 9.1 Hz, 1H, H-α'); 3.88 (dt, 1H, H-α); 4.09 (ddd, $J_{2,3}$ = 4.6 Hz, $J_{1a,2}$ = 4.6 Hz, 1H, H-2); 4.29 (dd, $J_{5a,5b}$ = 10.7 Hz, $J_{4,5b}$ = 6.0 Hz, 1H, H-5b); 4.32 (dd, $J_{1a,1b}$ = 11.3 Hz, $J_{1b,2}$ = 4.5 Hz, 1H, H-1b); 4.36 (dd, $J_{4,5a}$ = 5.0 Hz, 1H, H-5a); 4.42 (dd, 1H, H-1a); 4.57 (ddd, $J_{3,4}$ = 3.5 Hz, 1H, H-4); 4.60 (dd, 1H, H-3). ^{13}C NMR (75 MHz, C_5D_5N) δ:14.6 (Cω); 23.3-31.1 ($(CH_2)_9$); 31.1 (Cβ); 61.9 (C-1); 65.2 (C-5); 71.4 (Cα); 72.4 (C-3); 73.2 (C-4); 83.2 (C-2).
Anal. Calcd for $C_{17}H_{36}O_5$ (320.47) : C, 63.71; H, 11.32. Found: C, 64.03; H, 11.34.

3-*O*-*n*-Octyl-*meso*-xylitol (17a). Likewise, **9a** (6.0 g, 22.9 mmol) yielded 3.3 g (55%) of **17a**. mp 110.5 °C. ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.84 (t, $J_{\omega,\omega-1}$ = 6.8 Hz, 3H, Hω); 1.17-1.32 (m, $(CH_2)_5$); 1.66 (m, $J_{\alpha,\beta}$ = 6.6 Hz, 2H, Hβ); 3.96 (t, 2H, Hα); 4,21 (t, $J_{2,3}$ = $J_{3,4}$ = 3.8 Hz, 1H, H-3); 4.33-4.39 (m, 4H, H-1 and H-5); 4.66 (m, 2H, H-2 and H-4). ^{13}C NMR (75 MHz, C_5D_5N) δ; 14.6 (Cω); 23.2-32.4 ($(CH_2)_5$); 31.3 (Cβ); 64.6 (C-1, C-5); 73.4 (Cα); 73.7 (C-2, C-4); 81.5 (C-3).
Anal. Calcd for $C_{13}H_{28}O_5$ (264.36) : C, 59.06; H, 10.68. Found: C, 59.10; H, 10.21.

3-*O*-*n*-Dodecyl-*meso*-xylitol (17b). Likewise, **9b** (6.0 g, 18.8 mmol) yielded 3.4 g (53%) of **17b**. mp 101-137 °C. ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.84 (t, $J_{\omega,\omega-1}$ = 6.7 Hz, 3H, Hω); 1.19-1.35 (m, $(CH_2)_9$); 1.61 (m, $J_{\alpha,\beta}$ = 6.5 Hz, 2H, Hβ); 3.93 (t, 2H, Hα); 4.18 (dd, $J_{2,3}$ = $J_{3,4}$ = 3.8 Hz, 1H, H-3); 4,30-4.34 (m, 4H, H-1, and H-5); 4.62 (m, $J_{1,2}$ = $J_{4,5}$ = 5,4 Hz, 2H, H-2 and H-4). ^{13}C NMR (75 MHz, C_5D_5N) δ: 14.6 (Cω); 23.3-32.4 ($(CH_2)_9$); 31.3 (Cβ); 64.6 (C-1, C-5); 73.3 (Cα); 73.6 (C-2, C-4); 81.5 (C-3).
Anal. Calcd for $C_{17}H_{36}O_5$ (320.47) : C, 63.71; H, 11.32. Found: C, 63.57; H, 11.33.

4-*O*-*n*-Octyl-D-xylitol (18a). Likewise, **14a** (1.0 g, 3.8 mmol) yielded 0.6 g (56%) of **18a**. mp 48-82 °C. $[\alpha]_D^{20}$ -1.1° (*c* 1.3, CH_3OH). ^{1}H NMR (300 MHz, C_5D_5N) δ: 0.82 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.15 (m, $(CH_2)_5$); 1.59 (m, $J_{\alpha,\beta}$ = 6.7 Hz, 2H, Hβ); 3.71 (dt, $J_{\alpha,\alpha'}$ = 9.0 Hz, 1H, Hα'); 3.87 (dt, 1H, Hα); 4.06 (ddd, $J_{4,5b}$ = 4.6 Hz, 1H, H-4); 4.27 (dd, $J_{1b,2}$ = 6.0 Hz, 1H, H-1b); 4.31 (dd, $J_{5a,5b}$ = 11.6 Hz, 1H, H-5b); 4.34 (dd, $J_{1a,1b}$ = 10.7 Hz, $J_{1a,2}$ = 5.0 Hz, 1H, H-1a); 4.40 (dd, $J_{4,5a}$ = 4.7 Hz, 1H, H-5a); 4.54 (ddd, $J_{2,3}$ = 3.5 Hz, 1H, H-2); 4.57 (dd, $J_{3,4}$ = 4.6 Hz, 1H, H-3).

^{13}C NMR (75 MHz, C_5D_5N) δ: 14.6 (Cω); 23.2-32.4 ($(CH_2)_5$); 31.1 (Cβ); 61.9 (C-5); 65.2 (C-5); 71.3 (Cα); 72.3 (C-3); 73.1 (C-2); 83.3 (C-4).
Anal. Calcd for $C_{13}H_{28}O_5$ (264.36) : C, 59.06; H, 10.68. Found: C, 58.82; H, 10.57.

4-*O*-*n*-Dodecyl-D-xylitol (18b). Likewise, **14b** (1.0 g, 3.1 mmol) yielded 0.5 g (55%) of **18b**. mp 67-123 °C. $[\alpha]_D^{20}$ -1.2° (*c* 1.0, CH_3OH). ^1H NMR (300 MHz, C_5D_5N) δ: 0.81 (t, $J_{\omega,\omega-1}$ = 6.6 Hz, 3H, Hω); 1.17 (m, $(CH_2)_9$); 1.57 (m, $J_{\alpha,\beta}$ = 6.7 Hz, 2H, Hβ); 3.68 (dt, $J_{\alpha,\alpha'}$ = 9,1 Hz, 1H, Hα'); 3.84 (dt, 1H, Hα); 4.03 (ddd, $J_{4,5b}$ = 4.6 Hz, 1H, H-4); 4.23 (dd, $J_{1b,2}$ = 5.9 Hz, 1H, H-1b); 4.29 (dd, $J_{4,5b}$ = 4.6 Hz, $J_{5a,5b}$ = 11.5 Hz, 1H, H-5b); 4.31 (dd, $J_{1a,1b}$ = 10.6 Hz, $J_{1a,2}$ = 5.0 Hz, 1H, H-1a); 4.36 (dd, $J_{4,5a}$ = 4.5 Hz, 1H, H-5a); 4.51 (ddd, $J_{2,3}$ = 3.4 Hz, 1H, H-2); 4.53 (dd, $J_{3,4}$ = 4.6 Hz, 1H, H-3). ^{13}C NMR (75 MHz, C_5D_5N) δ: 14.7 (Cω); 23.3-32.5 ($(CH_2)_9$); 31.1 (Cβ); 61.9 (C-5); 65.2 (C-1); 72.4 (C-3); 73.1 (C-2); 83.3 (C-4).
Anal. Calcd for $C_{17}H_{36}O_5$ (320.47) : C, 63.71; H, 11.32. Found: C, 63.60; H, 11.30.

ACKNOWLEDGMENTS

We would like to thank the Biopôle de Picardie, as well the Ministère Français des Affaires Etrangères and the British Council (Alliance) for financial support of this research work.

REFERENCES

1. Presented at the *XVIIIth International Carbohydrate Symposium*, Milan, Italy, July 21-26 (1996).
2. J. Goodby, J. Haley, M. Watson, G. Mackenzie, S. Kelly, P. Letellier, O. Douillet, P. Godé, G. Goethals, G. Ronco and P. Villa, *Liq. Cryst.*, (in press).
3. R. Whistler, T. Luttenegger and R. Rawell, *J. Org. Chem.*, **33** (1), 396 (1968).
4. P. Martin, Ph. D. Thesis, Université de Picardie-Jules Verne, Amiens, France, (1993).
5. P. Martin, J.Y. Conan, B. Harmouch, D. Postel, G. Ronco, C. Rouch and P. Villa, *Chem. Lett.*, **1**, 141 (1994).
6. P. Martin, B. Harmouch, D. Postel, G. Ronco, L. Spychala and P. Villa, *Carbohydr. Res.*, **254**, 325 (1994).
7. M. Thomé, M. Giudicelli, D. Picq and D. Anker, *J. Carbohydr. Chem.*, **10** (5), 923 (1991).
8. B. Baker, R. Schaub and J. Williams, *J. Am. Chem. Soc.*, **77**, 7 (1955).
9. W. Sowa, *Can. J. Chem.*, **46**, 1586 (1968).

10. K. Takeo, M. Nakagen, Y. Teramoto and Y. Nitta, *Carbohydr. Res.*, **201**, 261 (1990).
11. J. Naleway, C. Raetz and L. Anderson, *Carbohydr. Res.*, **179**, 199 (1988).
12. G. Price and W. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961).
13. J. Goodby, *Mol. Cryst. Liq. Cryst.*, **110**, 205 (1984).