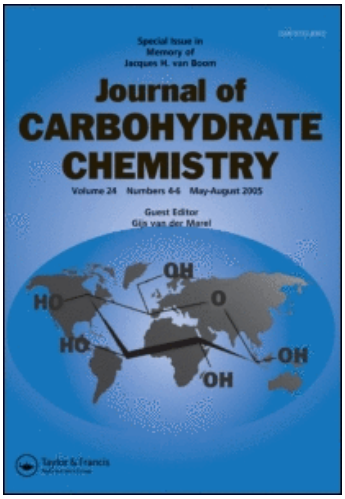

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Synthesis of Enantiomerically Pure Alkylated d-Erythritols and d-Threitols from d-Xylose—Structural Influences on Their Mesophasic Behavior

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ABSTRACT

1-*O*-Alkyl and 2-*O*-alkyl-D-threitol enantiomers were derived from 5-*O*-alkyl and 5-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranoses. The analogous erythritol derivatives were also obtained from the same precursors via analogous D-ribose monoacetals. Mesophasic behavior studies of these alditols and their alkylated D-ribose and D-xylose precursor, showed that the relative orientation of alkyl and OH groups appeared to be the main structural factor affecting the thermotropic and lyotropic phase transition temperatures.

INTRODUCTION

The study of the relationship between the molecular structure of carbohydrates and their thermotropic and lyotropic properties is of fundamental interest, since monosaccharides are important for the organization and function of cell membranes.[1] They also have practical applications as antibacterial and antiviral agents,[2] surfactants[3] and drug delivery systems.[4]

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In a preliminary mesophase study of racemic 1-*O*-*n*-alkyl-D,L-erythritols and threitols[5,6] we observed that all the threitol derivatives having an alkyl chain with 8 to 12 carbon atoms, exhibited smectic A* phases, whereas for the erythritol analogs, this mesophase was only observed with the dodecyl chain. To investigate the structural influences on mesophasic behavior, we synthesized enantiomerically pure 1-*O*-alkyl and 2-*O*-alkyl-D-erythritols and the analogous threitol derivatives, from D-xylose. We studied both their thermotropic and lyotropic phase transition temperatures and compared them to their corresponding D-ribose and D-xylose derivatives.

RESULTS AND DISCUSSION

Synthesis

All the compounds described were synthesized from D-xylose via 5-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**1**) and the corresponding 5-*O*-alkyl analogs **2**[7] (Scheme 1).

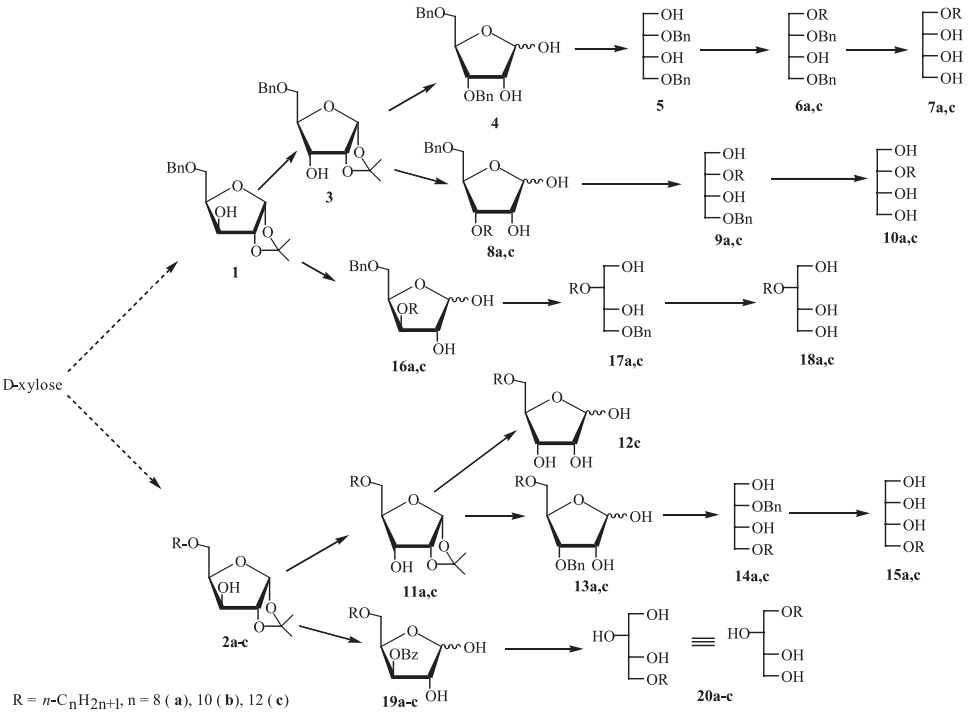
To obtain the D-erythritol derivatives, the D-xylose monoacetals **1** and **2** were first converted into the corresponding D-ribose derivatives **3** and **11** by DCC–Me_2SO oxidation and subsequent stereospecific $NaBH_4$ reduction. Then, three parallel routes involving etherification at the C-3 position and oxidative $NaIO_4$ degradation led, respectively, to the 1-*O*-alkyl-D-erythritols **7a,c**, 2-*O*-alkyl-D-erythritols **10a,c**, 5-*O*-alkyl-D-ribofuranose **12c** and 4-*O*-alkyl-D-erythritols **15a,c** (identical to 1-*O*-alkyl-L-erythritols) (Table 1).

The xylose monoacetals **1** and **2** have the required configuration to obtain, respectively, the 2-*O*-*n*-alkyl-D-threitols **18a,c** and 1-*O*-*n*-alkyl-D-threitols **20a–c** by similar routes (Table 2).

Mesophasic Behavior

We noted that all the compounds studied show both thermotropic (smectic A*) and lyotropic (lamellar) liquid crystalline behavior; moreover, some of them show a solid → solid transition. Table 3 reports the temperatures of the transitions solid → solid (S_1–S_2), solid → thermotropic liquid crystal (Mp), thermotropic liquid crystal → isotro-isotropic liquid (Cp), solid–water → lyotropic liquid crystal (T_1) and lyotropic liquid crystal → isotropic liquid (T_2).

A relationship between structure and liquid crystalline behavior was observed. Thus: 1) all the transition temperatures increase by increasing the alkyl chain length from 8 to 12 carbon atoms as with the reported 1-*O*-alkyl-D,L-xylitols[9] and 6-*O*-alkyl-α-D-galactopyranoses;[10] 2) a previous study[5] of primary dodecyl alditols (racemates of 1-*O*-dodecylglycerol, erythritol, threitol, xylitol, 6-*O*-dodecyl-D-galactitol and 1-*O*-dodecyl-D-mannitol) showed a linear relationship between Cp and the number of free OH groups and similar Cp values for the related erythritol-threitol (73.9–71.0°C) and galactose–mannitol derivatives (166.7–167.0°C). This appeared fortuitous, since Table 3 results show differences in Mp and T_1 values, between the erythritol and threitol series. Moreover, transition temperatures are affected by the alkyl chain position in



Scheme 1. Synthesis of pure alkylated D-erythritol and D-threitol enantiomers.

each series of racemic and enantiomerically pure products. To simplify interpretation of the data, we considered only the pure enantiomers because racemates can undergo specific interactions between D and L structures.

The structural features which influence phase transition temperatures were first examined with the corresponding *O*-dodecyl-D-riboses and D-xyloses[11] which constitute a representative model. The results shown in Table 4 indicate that the dodecyl α-D-xylopyranoside, which has its alkyl chain and neighbouring OH group in a *cis* configuration, has a lower phase transition temperature than compounds where the configuration is *trans*, as in the case of the octyl β-D-xylopyranoside (in spite of a shorter alkyl chain), and the 3-*O*-dodecyl and 4-*O*-dodecyl-D-xylopyranoses. This suggests that the steric hindrance of an alkyl chain having a *cis* orientation relative to the neighbouring OH groups reduces intermolecular hydrogen bonding and thereby crystal stability. Similar hindrance can occur with both 1-*O*-alkyl and 2-*O*-alkyl-D-erythritol configurations which have a lower temperature transition than their corresponding alkylated D-threitols which do not show the ''*cis* alkyl chain effect.''

We also observed that compounds with two *cis* neighbouring hydroxyls exhibit intramolecular hydrogen bonding which reduces competitive intermolecular hydrogen bonding and, by consequence, crystal stability. This phenomenon is consistent with the observation that both the 5-*O*-dodecyl-D-ribofuranose (*cis* C_2–OH, C_3–OH) and 4-*O*-dodecyl-α-D-xylopyranose (*cis* C_1–OH, C_2–OH) have lower transition temperatures than the 5-*O*-dodecyl-D-xylofuranose and 3-*O*-dodecyl-β-D-xylopyranose, respectively

Table 1. Physicochemical and microanalytical data of D-erythritol derivatives.

Compound	Yield (%)	α:β	$[\alpha]_D^{25}$ $CHCl_3$	Mp (°C)	Formula	Calcd C	Calcd H	Found C	Found H
6a	80		− 16 (*c* 0.9)	oil	$C_{26}H_{38}O_4$	75.33	9.24	75.27	9.21
6c	85		− 18 (*c* 0.9)	oil	$C_{30}H_{46}O_4$	76.55	9.85	76.61	9.88
7a	91		26 (*c* 0.8)	29.5	$C_{12}H_{26}O_4$	61.51	11.18	61.47	11.21
7c	93		37 (*c* 0.6)	51.0	$C_{16}H_{34}O_4$	66.17	11.80	66.23	11.76
8a	96	11:9	40 (*c* 0.7)	72.8	$C_{20}H_{32}O_5$	68.15	9.15	68.09	9.18
8c	90	3:2	32 (*c* 1.1)	78.1	$C_{24}H_{40}O_5$	70.55	9.87	70.62	9.92
9a	88		86 (*c* 1.0)	oil	$C_{19}H_{32}O_4$	70.34	9.94	70.27	9.91
9c	92		76 (*c* 1.2)	oil	$C_{23}H_{40}O_4$	72.59	10.59	72.53	10.62
10a	95		17 (*c* 1.1)[a]	oil	$C_{12}H_{26}O_4$	61.51	11.18	61.56	11.15
10c	94		7 (*c* 0.8)[a]	42.2	$C_{16}H_{34}O_4$	66.17	11.80	66.09	11.84
11a	92		33 (*c* 1.0)[a]	oil	$C_{16}H_{30}O_5$	63.55	10.00	63.62	9.97
11c	83		29 (*c* 1.1)[a]	66.6	$C_{20}H_{38}O_5$	67.00	10.68	67.10	10.71
13a	93	3:17	35 (*c* 0.6)	63.3	$C_{20}H_{32}O_5$	68.15	9.15	68.21	9.12
13c	94	3:22	22 (*c* 1.1)	71.5	$C_{24}H_{40}O_5$	70.55	9.87	70.62	9.92
14a	85		− 25 (*c* 1.1)	oil	$C_{19}H_{32}O_4$	70.34	9.94	70.30	9.91
14c	81		− 34 (*c* 1.1)	36.6	$C_{23}H_{40}O_4$	72.59	10.59	72.64	10.62
15a	87		− 25 (*c* 0.8)[a]	43.0	$C_{12}H_{26}O_4$	61.51	11.18	61.47	11.10
15c	100		− 34 (*c* 0.7)[a]	60.4	$C_{16}H_{34}O_4$	66.17	11.80	66.09	11.84

[a]Measured in MeOH.

Table 2. Physicochemical and microanalytical data of D-threitol derivatives.

Compound	Yield (%)	α:β	$[\alpha]_D^{25}$ $CHCl_3$	Mp (°C)	Formula	Calcd C	Calcd H	Found C	Found H
16a	81	13:7	− 7 (*c* 1.4)	oil	$C_{20}H_{32}O_5$	68.15	9.15	68.21	9.02
16c	82	16:9	− 27 (*c* 1.7)	oil	$C_{24}H_{40}O_5$	70.55	9.87	70.49	9.90
17a	83		− 12 (*c* 0.9)	oil	$C_{19}H_{32}O_4$	70.33	9.94	70.39	9.78
17c	82		− 11 (*c* 1.0)	oil	$C_{23}H_{40}O_4$	72.59	10.59	72.67	10.52
18a	91		− 16 (*c* 1.0)[a]	31.5	$C_{12}H_{26}O_4$	61.51	11.18	61.77	11.39
18c	93		− 33 (*c* 0.7)[a]	50.5	$C_{16}H_{34}O_4$	66.17	11.80	66.25	11.96
19a	65	3:2	25 (*c* 1.2)	oil	$C_{20}H_{30}O_6$	65.55	8.25	65.60	8.19
19b	70	14:11	22 (*c* 1.3)	oil	$C_{22}H_{34}O_6$	66.98	8.69	67.05	8.73
19c	73	7:3	8 (*c* 1.1)	oil	$C_{24}H_{38}O_6$	68.22	9.65	68.29	9.70
20a	83		3 (*c* 1.0)[a]	32.1	$C_{12}H_{26}O_4$	61.51	11.18	61.58	11.22
20b	83		27 (*c* 0.7)[a]	44.8	$C_{14}H_{30}O_4$	64.09	11.52	64.21	11.63
20c	81		17 (*c* 1.0)[b]	56.9	$C_{16}H_{34}O_4$	66.17	11.80	67.05	12.02

[a]Measured in MeOH.
[b]Measured in C_5H_5N.

Table 3. Phase transition temperatures (°C) of pure alkylated D-erythritol and D-threitol enantiomers and corresponding racemics.

Compound ($R = n\text{-}C_nH_{2n+1}$)	n	Thermotropy (DSC)			Lyotropy[c]	
		S_1-S_2[a]	Mp	Cp	T_1	T_2
1-OR-D-erythritol	8 (**7a**)		29.5	47.3	< RT	91.2
	12 (**7c**)	31.8	51.0	63.8	35.7	103.0
4-OR-D-erythritol	8 (**15a**)		43.0[b]	50.7[b]	< RT	97.5
(≡ 1-OR-L-erythritol)	12 (**15c**)		60.4[b]	64.0[b]	38.0	132.0
1-OR-D,L-erythritol[5,6]d	8		54.9	–	42.0	89.0
	12		68.5	73.9	47.0	105.0
2-OR-D-erythritol	8 (**10a**)		8.7	30.2	< RT	66.0
	12 (**10c**)		42.2	74.1	34.7	107.0
2-OR-D,L-erythritol[6]d	8		– 9.2	8.1	< RT	< RT
	12	32.9	38.5	76.4	42.0	109.0
1-OR-D-threitol	8 (**20a**)	7.3	32.1	54.8	< RT	90.4
	10 (**20b**)	8.4	44.8	63.6	< RT	109.0
	12 (**20c**)	43.0	56.9	66.6	33.0	110.8
1-OR-D,L-threitol[5,6]d	8		32.3	52.9	< RT	102.5
	10	42.2	42.4	63.2	< RT	113.7
	12	41.8	58.2	71.0	< RT	123.8
2-OR-D-threitol	8 (**18a**)		31.5	44.1	< RT	70.3
	12 (**18c**)		50.5	84.2	33.4	112.0
2-OR-L-threitol[8]	8		20	62		Not tested
	9		29	52		
	10		32	65		
2-OR-D,L-threitol[6]d	8		13.7	53.5	< RT	73.0
	12		41.9	87.3	< RT	107.0

[a]Solid–Solid transition.
[b]By microscopy (no separated peaks by DSC).
[c]By microscopy.
[d]Corrected Ref. [2] values with freshly lyophilized samples.

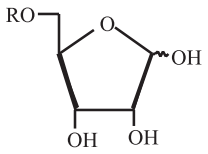
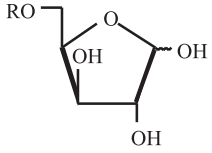
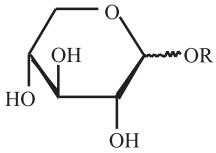
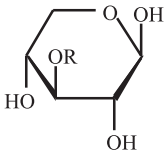
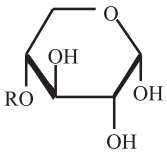
(Table 4). The above interpretation can be applied to both the 2-*O*-alkyl-D-erythritols and 2-*O*-alkyl-D-threitols which show lower transition temperatures than the corresponding 1-*O*-alkyl derivatives : the first series, with two *cis* OH groups near the hydrophobic tail, is less favourable to establish intermolecular hydrogen bonding than the second series with three successive OH groups.

Thus, the relative orientation of alkyl and OH groups appeared to be the main structural factor affecting the phase transition temperatures in the herein studied glycoamphiphilic compounds.

EXPERIMENTAL

General methods. Melting points were determined on an electrothermal automatic apparatus, and are uncorrected. Optical rotations, for solutions in $CHCl_3$

Table 4. Phase transition temperatures (°C) of x-*O*-alkyl-D-riboses and D-xyloses.

				Thermotropy		Lyotropy	
Entry	Compound	R	α:β	Mp	Cp	T_1	T_2
1		$C_{12}H_{25}$	1:3	60.0	104.8	35.0	110.0
2		$C_{12}H_{25}$[11]	2:3	69.8	106.5	42	142
3		C_8H_{17}[11]	β	67.1	99.8	46	99.5
		$C_{12}H_{25}$[11]	α	65.1[a]		35	93
4		$C_{12}H_{25}$[11]	β	100.9[a]		55	119
5		$C_{12}H_{25}$[11]	α	95.5	124.5	63	122

[a]No thermotropic liquid crystals.

or MeOH, were measured with a digital polarimeter JASCO model DIP-370, using a sodium lamp at 25°C. NMR spectra were recorded with a Bruker WB-300 instrument for solutions in $CDCl_3$ or Me_2SO-d_6 (internal Me_4Si). Elemental analyses were performed by the Service Central de Micro-Analyse du Centre National de la Recherche Scientifique (Vernaison, France). Reactions were monitored by either HPLC (Waters 721), using either the reverse phase columns RP-18 (Merck) or PN 27-196 (Waters), or CPG (Girdel) with either the columns OV 17 or SE 30. Analytical TLC was performed on Merck aluminium backed silica gel (Silica Gel F254). Column chromatography was performed on silica gel (60 mesh, Matrex) by gradient elution with hexane–acetone (in each case the ratio of silica gel to product mixture to be purified, was 30:1).

Liquid crystalline properties. Phase transition temperatures were determined by DSC using a Mettler FP85 microfurnace and/or by thermal polarized optic microscopy using an Olympus BX50. For thermotropic liquid crystals, transition temperatures, noted Mp (solid γ liquid crystal) and Cp (liquid crystal γ isotropic liquid) were T_{onset} measured at 10 or 2°C.mn^{-1} by DSC. All the products were freshly lyophilized before the study. For lyotropic liquid crystals, transition temperatures, noted as T_1 (liquid crystal appearance) and T_2 (liquid crystal disappearance) were determined by simply allowing crystals of the test material to dissolve in water, thereby creating a concentration gradient which supported mesophase formation.

5-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-ribofuranose (3). To a stirred solution of 5-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**1**)[7] (28 g, 100 mmol) and DCC (g, 300 mmol) in 3:2 AcOEt–Me_2SO (230 mL), at 0°C was added dropwise a solution of H_3PO_4 in Me_2SO (400 g.L^{-1}). After 3 h at room temperature, the mixture was cooled to 0°C and a solution of oxalic acid in MeOH (300 g.L^{-1}) was added dropwise. After 15 min, the mixture was filtered and the filtrate concentrated under diminished pressure. The crude product was dissolved in AcOEt, washed with water, dried (Na_2SO_4) and concentrated under diminished pressure. The crude ketose (27 g, 97 mmol) was reduced with $NaBH_4$ (194 mmol) in 4:1 EtOH–H_2O (270 mL). After 1 h at room temperature, formic acid (10 mL) was added and the solution was stirred for 3 h. The mixture was filtered and the filtrate concentrated under diminished pressure. The desired product was isolated after purification by column chromatography with 19:1 hexane–acetone (24 g, 86%); mp 81.3°C, $[\alpha]_D$ + 107° (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.30 → 7.23 (Ph), 5.79 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 4.59 → 4.54 (m, 4H, *CH*$_2$–Ph), 4.52 (t, 1H, $J_{2,3}$ = 4.2 Hz, H-2), 3.90 → 3.85 (m, 2H, H-3 H-4), 3.75 (dd, 1H, $J_{4,5}$ = 2.1 Hz, H-5), 3.60 (dd, 1H, $J_{4,5'}$ = 4.2 Hz, $J_{5,5'}$ = 10.9 Hz, H-5a′), 2.48 (1H, OH), 1.52 → 1.33 (2s, 6H, C*Me*$_2$). ^{13}C NMR ($CDCl_3$) δ 137.9, 128.3, 127.7, 127.6 (Ph), 112.5 (*C*Me2), 104.1 (C-1), 79.9 (C-4), 78.4 (C-2), 73.5 (*CH*$_2$–Ph), 71.7 (C-3), 68.7 (C-5), 26.5, 26.4 (C*Me*$_2$).

Anal. Calcd for $C_{15}H_{20}O_5$ (280.32): C, 64.27; H, 7.19. Found: C, 64.30; H, 7.17.

3,5-Di-*O*-benzyl-D-ribofuranose (4). To a stirred solution of **3** (9.8 g, 35 mmol) in 4:1 toluene–Me_2SO (100 mL) was added powdered KOH (4.7 g, 84 mmol) and benzyl bromide (42 mmol). After 24 h at 40°C, the mixture was filtered and the filtrate neutralized with satd aq NH_4Cl. The organic phase was separated, washed with water (twice), dried (Na_2SO_4) and concentrated under diminished pressure. The desired product was isolated after purification by column chromatography with 9:1 hexane–acetone (11.7 g, 90%) and deprotected in 0.6N HCl in 4:1 dioxane–H_2O (220 mL) at 50°C. After 3 h, the mixture was cooled, neutralized with solid $NaHCO_3$, filtered and the filtrate concentrated under diminished pressure. The desired product was isolated after purification by column chromatography with 7:3 hexane–acetone (9.8 g, 94%), α/β 3:2; mp 79.8°C, $[\alpha]_D$ + 27° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) of **4** δ 7.34 → 7.23 (Ph), 5.24 (d, 1H, $J_{1\alpha,2\alpha}$ = 4.2 Hz, H-1α), 5.21 (s, 1H, H-1β), 4.59 → 4.42 (m, 4H, *CH*$_2$–Ph), 4.25 → 4.14 (m, 3H, H-3β, H-4α, H-4β), 4.10 (q, 1H, $J_{2\alpha,3\alpha}$ = 5.8 Hz, H-2α), 4.00 (d, 1H, $J_{2\beta,3\beta}$ 4.7 Hz, H-2β), 3.93 (dd, 1H, $J_{3\alpha,4\alpha}$ = 3.8 Hz, H-3α), 3.60 (dd, 1H, $J_{5b\beta,4\beta}$ = 3.0 Hz, H-5bβ), 3.49 (dd, 1H, $J_{5a\beta,4\beta}$ = 4.2 Hz, $J_{5a\beta,5b\beta}$ = 10.3 Hz, H-5aβ), 3.47 → 3.41 (m, 2H, H-5aα, H-5bα). ^{13}C NMR ($CDCl_3$) of **4** δ 137.8, 136.9,

128.6, 127.6 (Ph), 102.4 (C-1β), 96.9 (C-1α), 80.8 (C-4β), 80.2 (C-4α), 78.2 (C-3β), 77.8 (C-3α), 74.4 (C-2β), 72.9, 73.5 (CH_2–Ph), 69.8 (C-5β), 69.6 (C-5α).

2,4-Di-*O*-benzyl-D-erythritol (5). To a solution of **4** (5 g, 15 mmol) in ethanol (120 mL) was added dropwise at 0°C, an aqueous solution of $NaIO_4$ (150 mL). After 1 h at room temperature, the mixture was filtered and the filtrate concentrated under diminished pressure and the concentrate dissolved in CH_2Cl_2 (100 mL). The organic phase was washed with water twice, dried (Na_2SO_4) and concentrated under diminished pressure. The crude aldehyde was reduced under the conditions used for **3**. The desired product was isolated after purification by column chromatography with 3:2 hexane–acetone (4.1 g, 90%); oil, $[\alpha]_D$ + 21° (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) of **5** δ 7.35 → 7.23 (Ph), 4.60 (d, 1H, $J_{a,b}$ = 11.8 Hz, H-a (CH_2–Ph)), 4.53 (d, 1H, H-a′ (CH_2–Ph)), 4.50 (d, 1H, H-b (CH_2–Ph)), 4.48 (d, 1H, H-b′ (CH_2–Ph)), 3.92 (m, 1H, $J_{2,3}$ 6.9 Hz, H-3), 3.83 → 3.74 (m, 2H, $J_{1a,2}$ = 4.2 Hz, H-1a, H-1b), 3.63 (dd, 1H, $J_{4a,4b}$ = 9.6 Hz, $J_{3,4b}$ = 3.7 Hz, H-4b), 3.55 (dd, 1H, $J_{3,4a}$ = 5.7 Hz, H-4a), 3.49 (dt, 1H, $J_{1b,2}$ = 4.2 Hz, H-2). ^{13}C NMR ($CDCl_3$) of **5** δ 137.9, 128.4, 127.9 (Ph), 78.9 (C-2), 73.4, 72.2 (2CH_2–Ph), 71.0 (C-4), 70.7 (C-3), 61.4 (C-1).

1-*O*-*n*-Alkyl-2,4-di-*O*-benzyl-D-erythritols (6a,c). Compound **5** was selectively alkylated under the conditions used for the acetal precursor of **4**. The desired product was isolated after purification by column chromatography with 9:1 hexane–acetone (Table 1). ^{1}H NMR ($CDCl_3$) of **6c** δ 7.30 → 7.23 (Ph), 4.71 → 4.48(m, 4H, CH_2–Ph), 3.92 (dd, 1H, H-4b), 3.69 → 3.59 (m, 5H, H-1a, H-1b, H-2, H-3, H-4a), 3.45 (m, 1H, H-α′), 3.40 (dt, 1H, H-α), 1.57 → 1.25 (CH_2 alkyl chain), 0.86 (t, 3H, H-ω). ^{13}C NMR ($CDCl_3$) of **6c** δ 137.7, 128.4, 127.8, 127.8 (Ph), 77.8 (C-2), 73.3, 72.5 (CH_2–Ph), 71.2 (C-α), 70.9 (C-4), 70.7 (C-3), 31.8 → 22.6 (CH_2 alkyl chain), 14.0 (C-ω).

1-*O*-*n*-Alkyl-D-erythritols (7a,c). A methanol solution of **6** (100 g.L^{-1}) and Pd/C 10%, was stirred under a H_2 atmosphere (1 atm) at 25°C. After 10 h, the catalyst was filtered off and the filtrate concentrated under diminished pressure. The desired product was isolated after purification by column chromatography with 2:3 hexane–acetone (Table 1). ^{1}H NMR (C_5D_5N) of **7c**: δ 4.43 (m, 1H, $J_{3,4b}$ = 6 Hz, H-4b), 4.42 (m, 1H, $J_{1a,2}$ = 6.6 Hz, H-2), 4.35 (dd, 1H, J_{4a-4b} = 12 Hz, J_{3-4a} = 5 Hz H-4a), 4.34 (m, 1H, H-3), 4.15 (dd, 1H, $J_{1b,2}$ = 3.1 Hz, H-1b), 3.99 (dd, 1H, $J_{1a,1b}$ = 9.7 Hz, H-1a), 3.54 (dt, 1H, $J_{\alpha,\alpha'}$ = 9.3 Hz, H-α′), 3.50 (dt, 1H, $J_{\alpha,\beta}$ = 6.5 Hz, H-α), 1.51 → 1.23 (CH_2 alkyl chain), 0.87 (t, 3H, $J_{\omega,\omega-1}$ = 6.6 Hz, H-ω). ^{13}C NMR (C_5D_5N) of **7c** δ 73.9 (C-1), 73.6 (C-2), 72.4 (C-3), 71.4 (C-α), 64.7 (C-4), 31.8 → 22.7 (CH_2 alkyl chain), 14.0 (C-ω).

3-*O*-*n*-Alkyl-5-*O*-benzyl-D-ribofuranoses (8a,c). Compound **3** was alkylated under the conditions used for **6a,c**. The product was isolated in 90% yield after purification by column chromatography with 9:1 hexane–acetone, and deprotected under the conditions used for **4**. The desired products were isolated by crystallization of the crude product from 3:7 diethyl ether–hexane (Table 1). ^{1}H NMR ($CDCl_3$) of **8a** δ 7.31 → 7.20 (Ph), 5.23 → 5.20 (m, 2H, H-1α, H-1β), 4.64 → 4.41 (m, 4H, CH_2–Ph), 4.18 → 3.55 (m, 5H, H-3α, H-3β, H-4α, H-4β, H – 2), 3.75 (d, 1H, H-2), 3.57 → 3.35 (m, 8H, 4H-5, 4H-α), 1.54 → 1.24 (CH_2 alkyl chain), 0.85 (t, 3H, $J_{\omega,\omega-1}$ = 6.6 Hz, H-ω). ^{13}C NMR ($CDCl_3$) of **8a** δ 137.8 → 127.5 (Ph), 102.5 (C-1β),

97.0 (C-1α), 80.9, 79.9 (C-3α, C-3β), 78.7 (C-2), 74.4, 70.4 (C-4α, C-4β), 73.5 (2CH_2–Ph), 71.4 (C-α(α)), 71.2 (C-α(β)), 70.0 (C-5β), 69.7 (C-5α), 31.7 → 22.5 (CH_2 alkyl chain), 14.0 (C-ω).

2-*O*-*n*-Alkyl-4-*O*-benzyl-D-erythritols (9a,c). Compounds **8a,c** were subjected to $NaIO_4$ oxidative degradation and subsequent reduction under the conditions used for **5**. The desired products were isolated after purification by column chromatography (Table 1). ^{1}H NMR ($CDCl_3$) of **9c** δ 7.32 → 7.23 (Ph), 4.56 (d, 1H, $J_{a,b}$ 11.8 Hz, H-b (CH_2–Ph)), 4.51 (d, 1H, H-a (CH_2–Ph)), 3.88 (m, 1H, $J_{2,3}$ = 6.9 Hz, H-3), 3.79 → 3.69 (m, 2H, H-1a, H-1b), 3.63 (dd, 1H, $J_{4a,4b}$ = 9.3 Hz, $J_{3,4b}$ = 3.6 Hz, H-4b), 3.56 (dd, 1H, H-4a), 3.51 (dt, 1H, $J_{\alpha,\beta}$ = 6.7 Hz, H-α′), 3.40 (dt, 1H, $J_{\alpha,\alpha'}$ = 9.3 Hz, H-α), 3.32 (m, 1H, H-2), 1.52 → 1.23 (CH_2 alkyl chain), 0.85 (t, 3H, $J_{\omega,\omega-1}$ = 6.6 Hz, H-ω). ^{13}C NMR ($CDCl_3$) of **9c** δ 137.7, 128.4, 127.8, 127.8 (Ph), 79.2 (C-2), 73.4 (CH_2–Ph), 70.9 (C-4), 70.7 (C-3), 70.5 (C-α), 61.4 (C-1), 31.8 → 22.6 (CH_2 alkyl chain), 14.0 (C-ω).

2-*O*-*n*-Alkyl-D-erythritols (10a,c). Compounds **9a,c** were debenzylated under the conditions used for **7**. The desired products were isolated by crystallization of the crude product from diethyl ether (Table 1). ^{1}H NMR (C_5D_5N) of **10c** δ 4.24 (m, 1H, $J_{3,4b}$ = 4.5 Hz, H-3), 4.18 → 4.11 (m, 2H, H-1a, H-1b), 4.08 (dd, 1H, $J_{4a,4b}$ = 11.0 Hz, H-4b), 4.03 (dd, 1H, $J_{3,4a}$ = 6.2 Hz, H-4a), 3.73 → 3.66 (m, 2H, H-2, H-α′), 3.65 (dt, 1H, $J_{\alpha,\alpha'}$ = 9.3 Hz, H-α), 1.60 → 1.18 (m, CH_2 alkyl chain), 0.83 (t, 3H, $J_{\omega,\omega-1}$ = 6.6 Hz, H-ω). ^{13}C NMR (C_5D_5N) of **10c** δ 82.6 (C-2), 73.4 (C-3), 71.2 (C-α), 64.9 (C-4), 62.5 (C-1), 32.5 → 23.3 (CH_2 alkyl chain), 14.7 (C-ω).

1,2-*O*-Isopropylidene-5-*O*-*n*-alkyl-α-D-ribofuranoses (11a,c). 5-*O*-*n*-Alkyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**2a–c**)[7] was oxidized and then reduced under the conditions used for **3**. The desired product was isolated after purification by column chromatography (Table 1). ^{1}H NMR ($CDCl_3$) of **11a** δ 5.78 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 4.51 (d, 1H, $J_{2,3}$ = 4.2 Hz, H-2), 3.88 (m, 1H, $J_{3,4}$ = 4.0 Hz, H-4), 3.85 (m, 2H, $J_{4,5a}$ = 4.4 Hz, $J_{4,5b}$ = 2.3 Hz, $J_{5a,5b}$ = 10.9 Hz, H-5a, H-5b), 3.45 (dt, 1H, $J_{\alpha\alpha',\beta\beta'}$ = 5.1 Hz, H-α′), 3.41 (dt, 1H, $J_{\alpha,\alpha'}$ = 9.3 Hz, H-α), 1.56 → 1.22 (CH_2 alkyl chain),), 0.83 (t, 3H, $J_{\omega,\omega-1}$ = 6.7 Hz, H-ω). ^{13}C NMR ($CDCl_3$) of **11a** δ 112.5 (CMe_2), 104.1 (C-1), 79.7 (C-4), 78.3 (C-2), 71.9 (C-α), 71.7 (C-3), 69.2 (C-5), 31.7 → 22.5 (CH_2 alkyl chain), 26.4 (CMe_2), 14.0 (C-ω).

5-*O*-*n*-Dodecyl-D-ribofuranose (12c). Compound **11c** (5 g, 14 mmol) was deprotected under the conditions used for **4**. After extraction and concentration, the crude product was recrystallized in 2:1 hexane–acetone (4.1 g, 92%); α/β = 1/3, mp 60°C, $[\alpha]_D$ − 8° (*c* 0.6, C_5H_5N). ^{1}H NMR (C_5D_5N) δ 5.96 (s, 1H, H-1β), 5.79 (s, 1H, H-1α), 4.77 (m, 1H, $J_{2\beta,3\beta}$ = 4.6 Hz, $J_{3\beta,4\beta}$ = 5.5 Hz, H-3β), 4.70 (m, 1H, $J_{4\beta,5a\beta}$ = 6.3 Hz, H-4β), 4.59 (d, 1H, H-2β), 4.46 (d, 1H, $J_{2\alpha,3\alpha}$ = 4.5 Hz, H-2α), 3.99 (dd, 1H, $J_{4\beta,5b\beta}$ = 3.2 Hz, H-5bβ), 3.90 (dd, 1H, $J_{5a\beta,5b\beta}$ = 10.3 Hz, H-5aβ), 3.78 (dd, 1H, $J_{5a\alpha,5b\alpha}$ = 10.6 Hz, H-5bα), 3.70 (dd, 1H, $J_{4\alpha,5a\alpha}$ = 4.7 Hz, H-5aα), 3.57 → 3.44 (m, H-α), 1.59 → 1.19 (m, CH_2 alkyl chain), 0.83 (t, 3H, $J_{\omega,\omega-1}$ = 6.3 Hz, H-ω). ^{13}C NMR (C_5D_5N) δ 102.4 (C-1β), 96.8 (C-1α), 81.7 (C-4β), 76.0 (C-2β), 73.0 (C-5β), 72.0 (C-3β), 71.2 (C-2α), 71.0 (C-5α), 70.6 (C-α), 31.0 → 21.8 (CH_2 alkyl chain), 13.2 (C-ω).

Anal. Calcd for $C_{17}H_{34}O_5$ (318.46): C, 64.12; H, 10.76. Found: C, 64.28; H, 10.89.

5-*O*-*n*-Alkyl-3-*O*-benzyl-D-ribofuranoses (13a,c). Compounds **11a,c** were benzylated in the conditions used for **6a,c**. The products were isolated in 92% yield after purification by column chromatography with 9:1 hexane–acetone, and deprotected under the conditions used for **4**. The desired products were isolated by crystallization of the crude product from 3:7 diethyl ether–hexane (Table 1). ^{1}H NMR (Me_2SO–d_6) of **13c** δ 7.34 → 7.25 (Ph), 4.99 (s, 1H, H-1β), 4.63 (d, 1H, H-b (*CH*$_2$–Ph)), 4.43 (d, 1H, H-a (*CH*$_2$–Ph)), 3.93 (m, 1H, H-4β), 3.85 (m, 1H, H-2β), 3.78 (m, 1H, H-3β), 3.42 → 3.34 (m, 4H, H-5aβ, H-5bβ, H − α, H − α′), 2.50 (s, 2OH), 1.45 → 1.23 (CH_2 alkyl chain), 0.83 (t, 3H, H-ω). ^{13}C NMR (Me_2SO–d_6) of **13c** δ 138.3, 128.0, 127.4, 127.3 (Ph), 101.9 (C-1α), 96.0 (C-1β), 78.9 (C-3β), 78.7 (C-4β), 72.9 (C-α, C-2β), 70.8 (*CH*$_2$–Ph), 70.4 (C-5β), 31.2 → 22.0 (CH_2 alkyl chain), 13.8 (C-ω).

4-*O*-*n*-Alkyl-2-*O*-benzyl-D-erythritols (14a,c). Compounds **13a,c** were subjected to $NaIO_4$ oxidative degradation and subsequent reduction under the conditions used for **5**. The desired products were isolated after purification by column chromatography (Table 1). ^{1}H NMR ($CDCl_3$) of **14c** δ 7.31 → 7.23 (Ph), 4.63 (d, 1H, $J_{a,b}$ = 11.6 Hz, H-b (*CH*$_2$–Ph)), 4.55 (d, 1H, H-a (*CH*$_2$–Ph)), 3.89 (m, 1H, $J_{3,4b}$ = 3.7 Hz, H-3), 3.79 (t, 2H, $J_{1,2}$ = 4.8 Hz, $J_{1,OH}$ = 5.1 Hz, 2H-1), 3.56 (dd, 1H, $J_{4a,4b}$ = 9.7 Hz, H-4b), 3.49 (dd, 1H, $J_{3,4a}$ = 5.5 Hz, H-4a), 3.47 (m, 1H, H-2), 3.40 (t, 2H, $J_{\alpha,\beta}$ = 6.5 Hz, H-α), 1.53 → 1.21 (CH_2 alkyl chain), 0.84 (t, 3H, $J_{\omega,\omega-1}$ = 6.6 Hz, H-ω). ^{13}C NMR ($CDCl_3$) of **14c** δ 137.9, 128.4, 127.8, 127.8 (Ph), 78.9 (C-2) ; 72.2 (*CH*$_2$–Ph), 71.6 (C-α), 71.2 (C-4), 70.7 (C-3), 61.4 (C-1), 31.7 → 22.6 (CH_2 alkyl chain), 14.0 (C-ω).

4-*O*-*n*-Alkyl-D-erythritols (15a,c). Compounds **14a,c** were debenzylated under the conditions used for **7a,c**. The desired products were isolated after purification by column chromatography (Table 1). ^{1}H NMR (C_5D_5N) of **15c** δ 4.39 (m, 2H, $J_{1b,2}$ = 6.2 Hz, H-1b, H-3), 4.29 (m, 2H, $J_{1a,2}$ = 5.1 Hz, $J_{1a,1b}$ = 12.5 Hz, H-1b, H-2), 4.11 (dd, 1H, $J_{4b,3}$ = 2.6 Hz, H-4b), 3.96 (dd, 1H, $J_{4a,3}$ = 6.6 Hz, $J_{4a,4b}$ = 9.6 Hz, H-4a), 3.53 (dt, 1H, $J_{\alpha,\alpha'}$ = 9.3 Hz, H-α′), 3.49 (dt, 1H, $J_{\alpha\alpha',\beta\beta'}$ = 6.6 Hz, H-α), 1.59 → 1.19 (CH_2 alkyl chain), 0.82 (t, 3H, $J_{\omega,\omega-1}$ = 6.6 Hz, H-ω). ^{13}C NMR (C_5D_5N) of **15c** δ 74.1 (C-4), 73.9 (C-3), 72.7 (C-2), 71.7 (C-α), 65.0 (C-1), 32.1 → 22.9 (CH_2 alkyl chain), 14.2 (C-ω).

3-*O*-*n*-Alkyl-5-*O*-benzyl-D-xylofuranoses (16a,c). The 5-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**1**)[7] was alkylated under the conditions used for **6a,c**. The products were isolated in 95% yield after purification by column chromatography with 9:1 hexane–acetone, and deprotected under the conditions used for **4**. The desired products were isolated after purification by column chromatography (Table 2). ^{1}H NMR (C_5D_5N) of **16c** δ 7.30 → 7.23 (Ph), 5.42 (d, 1H, $J_{1\alpha,2\alpha}$ = 4.5 Hz, H-1α), 5.01 (s, 1H, H-1β), 4.61 → 4.37 (m, 4H, H-2β, CH_2–Ph, H-4β), 4.12 (d, 1H, H-4α), 4.03 (q, 1H, $J_{2\alpha,3\alpha}$ = 5.0 Hz, H-2α), 3.81 → 3.76 (m, 2H, H-3α, H-3β), 3.74 → 3.50 (m, 2H, H-5a, H-5b), 3.40 → 3.29 (m, 2H, 2H-α alkyl chain), 1.48 → 1.23 (CH_2 alkyl chain), 0.85 (t, 3H, $J_{\omega,\omega-1}$ = 6.5 Hz, H-ω). ^{13}C NMR (C_5D_5N) of **16c** δ 138.0, 128.3, 127.7, 127.6 (Ph), 103.3 (C-1β), 96.0 (C-1α), 84.1 (C-3α), 83.2 (C-3β), 80.1 (C-2α), 78.7 (C-4α), 77.6 (C-4β), 75.4 (C-2β), 73.4 (*CH*$_2$–Ph), 71.2 (C-α(β)), 70.4 (C-α(α)), 68.9 (C-5α, C-5β), 31.8 → 22.6 (CH_2 alkyl chain), 14.0 (C-ω).

2-*O*-*n*-Alkyl-4-*O*-benzyl-D-threitols (17a,c). Compounds **16a,c** were subjected to $NaIO_4$ oxidative degradation and subsequent reduction under the conditions used for **5**. The desired products were isolated after purification by column chromatography (Table 2). ^{1}H NMR ($CDCl_3$) of **17c** δ 7.30 → 7.23 (Ph), 4.52 (m, 2H, H-a, H-b (*CH*$_2$–Ph), 3.90 (m, 1H, $J_{2,3}$ = 5.3 Hz, H-3), 3.76 (m, 2H, H-1b, H-α′), 3.62 (m, 1H, $J_{1a,2}$ = 4.3 Hz, $J_{1a,1b}$ = 11.8 Hz, H-1a), 3.59 (dd, 1H, H-4b), 3.56 (dd, 1H, $J_{3,4a}$ = 5.6 Hz, H-4a), 3.45 (dt, 2H, $J_{\alpha,\alpha'}$ = 9.3 Hz, $J_{\alpha,\beta}$ = 6.8 Hz, H-α), 3.45 → 3.39 (m, 1H, $J_{1b,2}$ = 4.7 Hz, H-2), 1.30 → 1.22 (CH_2 alkyl chain), 0.85 (t, 3H, $J_{\omega,\omega-1}$ = 6.6 Hz, H-ω). ^{13}C NMR ($CDCl_3$) of **17c** δ 137.7, 128.4, 127.8 (Ph), 79.5 (C-2), 73.0 (*C*H$_2$–Ph), 71.0 (C-α), 70.8 (C-4), 70.5 (C-3), 61.5 (C-1), 31.8 → 22.3 (CH_2 alkyl chain), 14.0 (C-ω).

2-*O*-*n*-Alkyl-D-threitols ≡ 3-*O*-*n*-alkyl-D-threitols (18a,c). Compounds **17a,c** were debenzylated under the conditions used for **7**. The desired products were isolated after purification by column chromatography (Table 2). ^{1}H NMR (C_5D_5N) of **18c** δ 4.52 (m, 1H, $J_{3,4b}$ = 5.1 Hz, H-3), 4.30 → 4.22 (m, 3H, H-1a, H-1b, H-4a), 4.40 (dd, 1H, J_{4a-4b} = 11.2 Hz, H-4b), 4.03 (ddd ; 1H, $J_{2,3}$ = 3.4 Hz, H-2), 3.90 (dt, 1H, $J_{\alpha\alpha',\beta\beta'}$ = 9.0 Hz, H-α′), 3.74 (dt, 1H, $J_{\alpha,\beta}$ = 6.7 Hz, H-α), 3.22 (s, 1H, OH), 1.67 → 1.16 (CH_2 alkyl chain), 0.83 (t, 3H, H-ω). ^{13}C NMR (C_5D_5N) of **18c** δ 82.1 (C-2), 73.2 (C-3), 71.8 (C-α), 64.0 (C-1), 61.8 (C-4), 32.0 → 22.9 (CH_2 alkyl chain), 14.2 (C-ω).

5-*O*-*n*-Alkyl-3-*O*-benzoyl-D-xylofuranoses (19a–c). To a solution of 5-*O*-*n*-alkyl-1,2-*O*-isopropylidene-α-D-xylofuranose **2a–c** in pyridine (200 g.L^{-1}) was added dropwise a solution of benzoyl chloride (1 equiv) in CH_2Cl_2 (200 g.L^{-1}) at 0°C. After 24 h at room temperature, the mixture was filtered and the filtrate concentrated under diminished pressure. The desired products were isolated in 98% yield after purification by column chromatography with 9:1 hexane–acetone and deprotected under the conditions used for **4**. The desired products were isolated after purification by column chromatography (Table 2). ^{1}H NMR (C_5D_5N) of **19aα** δ 8.32 → 7.33 (Ph), 6.41 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 6.54 (dd, 1H, $J_{3,4}$ = 6.2 Hz, H-3), 6.00 (d, 1H, H-2), 5.17 (m, 1H, $J_{4,5a}$ = 5.0 Hz, $J_{4,5b}$ = 5.1 Hz, H-4), 3.90 (dd, 1H, $J_{5a,5b}$ = 10.2 Hz, H-5a), 3.74 (dd, 1H, H-5b), 1.56 → 1.15 (CH_2 alkyl chain), 0.83 (t, 3H, $J_{\omega,\omega-1}$ = 6.5 Hz, H-ω). ^{13}C NMR (C_5D_5N) of **19aα** δ 166.5 (CO), 134.1 → 129.2 (Ph), 95.4 (C-1), 79.4 (C-2), 77.2 (C-3), 75.7 (C-4), 72.2 (C-α), 70.1 (C-5), 32.3 → 23.2 (CH_2 alkyl chain), 14.6 (C-ω). ^{1}H NMR (C_5D_5N) of **19aβ** δ 8.32 → 7.33 (Ph), 6.23 (d, 1H, $J_{3,4}$ = 5.4 Hz, H-3), 6.08 (s, 1H, H-1), 6.02 (m, 1H, H-2), 5.08 (m, 1H, $J_{3,4}$ = 5.4 Hz, H-4), 3.94 (dd, 1H, $J_{4,5a}$ = 6.0 Hz, $J_{5a,5b}$ = 10.4 Hz, H-5a), 3.77 (dd, 1H, H-5b), 1.56 → 1.15 (CH_2 alkyl chain), 0.83 (t, 3H, $J_{\omega,\omega-1}$ = 6.5 Hz, H-ω). ^{13}C NMR (C_5D_5N) of **19aβ** δ 166.5 (CO), 134.1 → 129.2 (Ph), 102.0 (C-1), 83.7 (C-2), 80.0 (C-4), 77.2 (C-3), 72.1 (C-α), 70.9 (C-5), 32.3 → 23.2 (CH_2 alkyl chain), 14.6 (C-ω).

1-*O*-*n*-Alkyl-D-threitols ≡ 4-*O*-*n*-alkyl-D-threitols (20a–c). Compounds **19a–c** were subjected to $NaIO_4$ oxidative degradation and subsequent reduction under the conditions used for **5**. The desired products were isolated after purification by column chromatography (Table 2). ^{1}H NMR (C_5D_5N) of **20a** δ 4.49 (m, 1H, $J_{1a,2}$ = 6.4 Hz, H-2), 4.36 (m, 1H, J_{3-4a} = 5.5 Hz, H-3), 4.31 (dd, 1H, $J_{3,4b}$ = 5.0 Hz, H-4a), 4.25 (dd, 1H, $J_{4a,4b}$ = 9.7 Hz, H-4b), 4.02 (dd, 1H, $J_{1b,2}$ = 5.4 Hz, H-1a), 3.93 (dd, 1H, $J_{1a,1b}$ = 9.5 Hz, H-1b), 3.50 (t, 3H, $J_{\alpha,\beta}$ = 6.5 Hz, H-α), 1.62 → 1.17

(CH_2 chain), 0.83 (t, 3H, $J_{\omega,\omega-1}$ = 6.6 Hz, H-ω). ^{13}C NMR (C_5D_5N) of **20a** δ 73.9 (C-1), 73.3 (C-3), 71.6 (C-5, C-α), 71.2 (C-2), 64.5 (C-4), 32.0 → 22.9 (CH_2 alkyl chain), 14.2 (C-ω).

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