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Carbohydrate Research 311 (1998) 89–94

CARBOHYDRATE RESEARCH

Note

Synthesis of 1,2-*O*-isopropylidene-3,5-*O*-propylidene-α–D-glucofuranose as a convenient precursor of both 6-*O*-alkyl and 6-*O*-glycidyl-D-glucose amphiphiles

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Received 3 December 1997; accepted 10 July 1998

Abstract

1,2-*O*-Isopropylidene-3,5-*O*-propylidene-α-D-glucofuranose (**3**) was synthesized by conversion of 3-*O*-allyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) into its 3-*O*-prop-1-enyl isomer (**2**), followed by rapid acid-catalysed intramolecular acetalation in an aprotic solvent. The diacetal **3** was used as the precursor of 6-*O*-alkyl and 6-*O*-glucidyl-D-glucose amphiphiles, which show thermotropic and lyotropic liquid-crystalline properties.

Keywords: Allyl isomerisation; 1,2-*O*-Isopropylidene-3,5-*O*-propylidene-α-D–glucofuranose; 6-*O*-Alkyl-D-glucose; 6-*O*-Glycidyl-D-glucose; CMC; Liquid crystal

Regiospecific derivatisation of D-glucose at C-6 requires appropriately protected intermediates. Such conversions are readily effected in the following examples: (*i*) regioselective 6-*O*-acylation [1,2]; (*ii*) substitution of 6-deoxy-6-iodo-D-glucofuranose to form corresponding carbamic esters and *N*-alkylamines [3]. The 6-iodo intermediate fails to give 6-*O*-alkyl derivatives. Such a reaction can be achieved from 1,2-*O*-isopropylidene-3,5-*O*-acetalated-α-D-glucofuranoses [4] obtained in low yield by selective acetalation of 1,2-*O*-isopropylidene-α-D-glucofuranose. Other substrates may be either 3-*O*-alkyl-5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose [5] or the methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside [6], obtained by long multistep process.

We present here a route to 1,2-*O*-isopropylidene-3,5-*O*-propylidene-α-D-glucofuranose (**3**) that allows all types of regiospecific derivatisation of D-glucose at C-6. Thus **3** was used to synthesize both 6-*O*-alkyl and 6-*O*-glucidyl-D-glucoses as new amphiphiles.

1,2-*O*-Isopropylidene-3,5-*O*-propylidene-α-D-glucofuranose (**3**) was prepared from 3-*O*-allyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) in 68% yield following Scheme 1. The first step (*a*) involved isomerisation of the 3-*O*-allyl group to the corresponding 3-*O*-prop-1-enyl group. Similar

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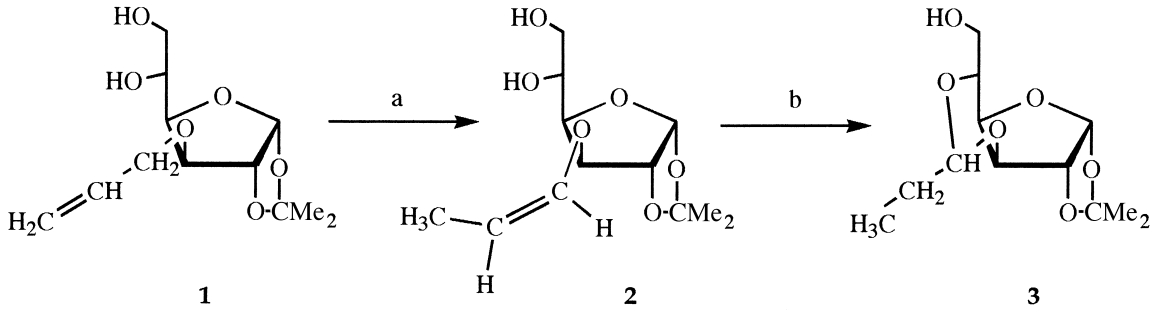
0008-6215/98/$—see front matter
PII S0008-6215(98)00207-9



1 2 3

Scheme 1.

isomerisation of *O*-allyl derivatives has been reported with transition metal catalysts [7] or with potassium *t*-butoxide in dimethyl sulfoxide [8–11]. The latter method, applied to compound **1**, gave the ether **2** in 56% yield, whereas the yield was 80% using potassium hydroxide in toluene–dimethyl sulfoxide. The prop-1-enyl group in the ether **2** had the *Z* configuration ($J_{H,H}$ 6.0 Hz). The key step (*b*) was an intramolecular acetalation. In aqueous acid solution, compound **2** gave both the diacetal **3** and 1,2-*O*-isopropylidene-α-D-glucofuranose (**3′**). It has been reported that the *O*-prop-1-enyl group can be hydrolysed with 0.1 M HCl in 9:1 acetone–water [9]. If the acid was introduced in an anhydrous aprotic solvent such as dichloromethane, only the diacetal **3** was obtained (Table 1). It is noteworthy that the intramolecular acetalation in the aprotic solvent is rapid (5 min), even at low acid concentration.

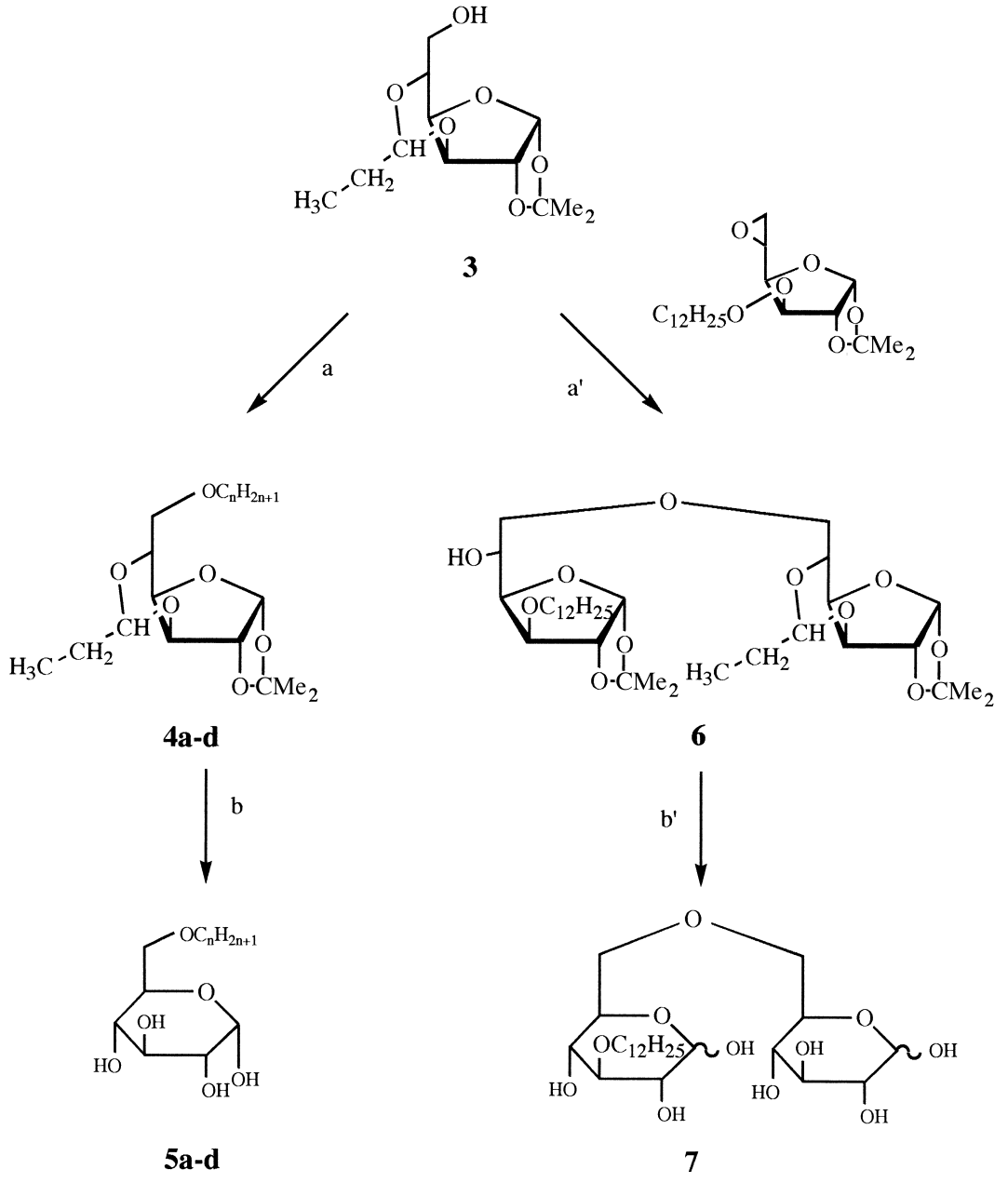
O-Alkylation of diacetal **3** was achieved with *n*-alkyl bromide and potassium hydroxide in 4:1 toluene–dimethyl sulfoxide at room temperature to give derivatives of type **4** in 80–97% yield (Scheme 2). Subsequent deprotection in 9:1 trifluoroacetic acid–water at room temperature gave the corresponding type **5** compounds (Table 2). It is emphasized that all the samples were isolated as pure α anomers, whereas those previously reported [6] are α, β anomeric mixtures. Condensation of diacetal **3** with 5,6-anhydro-3-*O*-*n*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose [5] in the presence of potassium hydroxide in 1:1 toluene–dimethyl sulfoxide at 40 °C gave the ether-linked disaccharide 6-*O*-(6-deoxy-1,2-*O*-isopropylidene-3,5-*O*-propylidene-α-D-glucofuranos-6-yl)-3-*O*-*n*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**6**) in 66% yield (Scheme 2). Examination of the crude product by HPLC showed small amounts of trisaccharide and tetrasaccharide derivatives. Deprotection of derivative **6**, using the same conditions as used for type **4** derivatives gave 6-*O*-(6-deoxy-D-glucopyranos-6-yl)-3-*O*-*n*-dodecyl-D-glucopyranose (**7**) in 44% yield. NMR spectra showed that the disaccharide **7** existed exclusively as the pyranose form, in 3:2 α, β ratio. We expect to apply the described reaction to alternative substrates (3-*O*-alkyl-5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose, 5,6-anhydro-3-*O*-*n*-alkyl-1,2-*O*-isopropylidene-α-D-galactofuranose, and 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose) to obtain a range of 6-*O*-glycidyl-D-glucose derivatives.

Table 1
Solvent influence on the acid-catalysed intramolecular acetalation of compound **2** at room temperature

HCl (M)	Solvent	Time (min)	**3**:**3′** Distribution[a]	Yield **3** (%)
0.2	EtOH	120	20:80	18
0.2	1,4-Dioxane–water (4:1)	240	20:80	19
0.2	CH_2Cl_2	5	100:0	84
0.05	CH_2Cl_2	5	100:0	85
0.02	CH_2Cl_2	5	100:0	85

[a] 1,2-*O*-isopropylidene-α-D-glucofuranose (**3′**).

The amphiphilic character of **5a–d** and **7** was emphasized by a preliminary study of both the critical micelle concentration (CMC) and the mesophasic transitions. 6-*O*-Alkyl-α-D-glucopyranoses (**5a–d**) have low CMC values in water at 25 °C (close to 5×10^{-4} molL^{-1}), without significant change being observed upon varying the alkyl chain length. In contrast, with the 3-*O*-alkyl-D-glucose isomers [12], CMC values vary from 10.4 10^{-4} molL^{-1} for the **5b** analog, to 2.3 10^{-4} molL^{-1} for the **5d** analog. However in the two series, the surface tension (γ) at these concentrations is close to 28–30 mN m^{-1}. All of the compounds **5a–d** and **7** gave thermotropic and lyotropic liquid crystals. In the thermotropic liquid-crystal study, we



Scheme 2.

observed (Table 3) that the solid–liquid-crystal transition temperature (T_m) of the 6-*O*-alkyl-α-D-glucopyranoses (**5**) increase upon increasing the alkyl chain-length from $n=6$ to $n=12$ carbon atoms (**5a–5d**). A similar alkyl chain-length effect was noted with the 1-*O*-alkyl-D,L-xylitol series [13]. The disaccharidic compound **7** shows lower phase–transition temperatures and a shorter liquid-crystal temperature-range than the monosaccharidic compound **5d**, which has the same hydrophobic chain (*n*–dodecyl). Moreover, for all of the monosaccharide compounds **5a–d** the temperature of the transition lyotropic solid–liquid crystal varies from 42 to 65 °C, whereas the corresponding temperature for the disaccharide compound **7** is lower than 20 °C; the isotropization temperature is always above 95 °C. In this preliminary study, lyotropic liquid crystals are generated by water–crystal contact. Control of the water concentration will allow rationalization of these results.

Table 2
Preparation of 6-*O*-alkyl-D-glucose diacetal derivatives **4a–d** and corresponding deacetalated compounds **5a–d**

O-Alkylation[a]		Deacetalation[b]		
Product	Yield (%)	Product	α, β, Yield (%)	Isolated pure α, Yield (%)
4a	80	**5a**	85	33
4b	96	**5b**	82	41
4c	96	**5c**	84	64
4d	97	**5d**	81	73

[a] $C_nH_{2n+1}Br$ (1.2 equiv), KOH (2.4 equiv), 4:1 toluene–Me_2SO, RT, 3 days.
[b] 9:1 Cf_3CO_2H–H_2O, RT, 7 h.

1. Experimental

General methods.—Melting points were determined on an electrothermal automatic apparatus, and are uncorrected. Optical rotations, for solutions in $CHCl_3$ or MeOH, were measured with a digital polarimeter JASCO model DIP-370 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. 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).

Table 3
Thermotropic phase-transition temperatures (°C) for 6-*O*-alkyl-α-D-glucopyranoses (**5a–d**) and 6-*O*-glucidyl-D-glucopyranoses (**7**)

Product	Microscopy		DSC[a]	
	Tm[b] ( )[d]	Ti[c] ( )[d]	Tm[b] ( )[d]	Ti[c] ( )[d]
5a	65.5	129.2	59.3	127.6
5b	78.2 (83.0)	148.0 (153.0)	76.0 (89.2)	145.8 (160.5)
5c	82.0 (84.0)	146.3 (155.0)	82.0	148.0
5d	95.5 (93.0)	137.3 (163.0)	91.0	131.4
7	—	—	87.1	121.8

[a] Measured at 2 °C min^{-1}.
[b] Melting temperature (solid–liquid crystal transition).
[c] Isotropization temperature (liquid crystal–isotropic liquid transition).
[d] Literature data, for α, β anomer mixtures [6].

Surface tension, critical micelle concentration (CMC) and phase transition determinations.—For CMC studies, an initial aqueous solution (S_0) of each compound was prepared at 25 °C, corresponding to the concentration C_0. Several samples were obtained by diluting S_0 in the concentration range C_0:$C_0/2$, $C_0/4$, $C_0/10$, $C_0/50$, $C_0/100$, and $C_0/200$. The surface tension (γ) of each sample was measured by the Wilhelmy plate method [11], after a period of more than 1 h in the thermostated cell (25 °C). The critical micelle concentration (CMC) was determined from a plot of $\gamma = f(\log C)$. The classical slope change coordinates gave, respectively, the CMC and the corresponding γ values.

Phase-transition temperatures were determined by DSC (Differential Scanning Calorimetry) using a Mettler FP85 furnace and by thermal polarized-light microscopy using an Olympus BX50 polarizing transmitted light, instrument equipped with a Mettler FP82 microfurnace. Both Mettler devices were recorded on an FP90 central processor. For thermotropic liquid-crystals, the transition temperatures, noted T_m (solid → liquid crystal) and T_i (liquid crystal → isotropic liquid) are T_{onset} measured at 2 °C min^{-1} by DSC. For lyotropic liquid-crystals, transition temperatures were determined by simply allowing crystals of the test material to dissolve in water, thereby creating a concentration gradient which supports mesophase formation.

1,2-O-Isopropylidene-3-O-prop-1-enyl-α-D-glucofuranose (**2**).—To a solution of 3-*O*-allyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) [5] (40 g, 154 mmol) in 1:1 toluene–Me_2SO (200 g L^{-1}) was added powdered KOH (34.5 g, 616 mmol). After 4 h at 100 °C, the mixture was filtered and water was added. The organic phase was separated, dried (Na_2SO_4) and concentrated under diminished pressure. 1,2-*O*-Isopropylidene-3-*O*-prop-1-enyl-α-D-glucofuranose (**2**) was isolated after purification by column chromatography with 4:1 hexane–acetone (32 g, 80%): mp 67–68 °C; $[\alpha]_D^{24}$ +17.3° (*c* 1.0, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ143.7 (C-α); 111.9 (*C*-iso), 105.0 (C-1), 103.6 (C-β), 83.5, 82.7, 79.9 (C-2, C-3, C-4), 68.8 (C-5), 64.3 (C-6), 26.1 and 26.6 (CH_3-iso), 9.1 (C-γ). ^1H NMR ($CDCl_3$): δ6.00 (dq, 1 H, H-β), 5.88 (d, 1 H, J_{1-2} 3.7 Hz, H−1), 4.51 (2d, 2 H, J_{2-3} 0 Hz, H-2 and H−α), 4.24 (d, 1 H, $J_{3,4}$ 2.9 Hz, H-3), 4.12 (dd, 1 H, $J_{4,5}$ 8.5 Hz, H-4), 3.90 (m, 1 H, J_{5-6b} 5.1 Hz, H-5), 3.80 (dd, 1 H, J_{6a-6b} 9.0 Hz, H-6), 3.69 (dd, 1 H, H-6b), 1.50 (d, 3 H, H-γ), 1.45 and 1.26 (2s, CH_3-iso). Anal. Calcd for

$C_{12}H_{20}O_6$ (260.86): C, 55.25; H, 7.73. Found: C, 55.19; H, 7.78.

1,2-O-*Isopropylidene-3,5*-O-*propylidene*-α-D-*glucofuranose* (**3**).—To a solution of **2** (10 g, 38.5 mmol) in CH_2Cl_2 (100 g L^{-1}) was added dropwise 1.8 mL of 36 M HCl. After 5 min at room temperature, the mixture was neutralized with satd aq NH_4Cl. The organic phase was separated, washed with water (twice), dried (Na_2SO_4) and concentrated under diminished pressure. 1,2-*O*-Isopropylidene-3,5-*O*-propylidene-α-D-glucofuranose (**3**) was isolated by crystallization of the crude product from 3:7 diethylether–hexane (8.5 g, 85%); mp 98–102 °C; $[\alpha]_D^{24}$ +12.1°(*c* 1.3, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 111.7 (C-iso), 104.8 (C-1), 95.3 (C-α), 83.8, 77.2, 73.3 (C-2, C-3, C-4), 72.7 (C-5), 61.2 (C-6), 27.7 (C-β), 26.0 and 26.6 (CH_3-iso), 8.0 (C-γ). ^1H NMR ($CDCl_3$): δ 5.95 (d, 1 H, J_{1-2} 3.7 Hz, H-1), 4.70 (t, 1 H, H-α), 4.52 (d, 1 H, J_{2-3} 0 Hz, H-2), 4.18 (d, 1 H, J_{3-4} 2.1 Hz, H-3), 4.17 (dd, 1 H, J_{4-5} 2.1 Hz, H-4), 3.90 (m, 1 H, J_{5-6a} 3.2 Hz, J_{5-6b} 4.9 Hz, H-5), 3.75 (dd, 1 H, J_{6a-6b} 11.9 Hz, H-6a), 3.71 (dd, 1 H, H-6b), 1.57 (dq, 2 H, H-β), 1.45 and 1.26 (2s, CH_3-iso), 0.88 (t, 3 H, H-γ). Anal. Calcd for $C_{12}H_{20}O_6$ (260.86): C, 55.25; H, 7.73. Found: C, 55.32; H, 7.68.

6-O-*Alkyl-1,2*-O-*isopropylidene-3,5*-O-*propylidene*-α-D-*glucofuranose* (**4**).—To a solution of **3** (10 g, 38.5 mmol) and 1.2 equiv of $C_nH_{2n+1}Br$ ($n = 6$, 8, 10, 12) in 4:1 toluene–Me_2SO (100 g L^{-1}) was added powdered KOH (5.2 g, 92.3 mmol). After 3 days at room temperature, 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 6-*O*-alkyl-1,2-*O*-isopropylidene-3,5-*O*-propylidene-α-D-glucofuranose (**4**) was isolated after purification by column chromatography with 49:1 hexane–acetone (Table 4). ^{13}C NMR ($CDCl_3$): δ 111.9 (C-iso), 104.7 (C-1), 96.7 (C-α), 84.0 (C-2), 77.5 (C-4), 73.5 (C-3), 72.1 (C-5, C-6), 71.6 (C-α′), 31.8 to 22.0 (CH_2′ and C-β), 26.0 and 26.6 (CH_3-iso), 14.0 (C-ω′), 8.0 (C-γ). ^1H NMR ($CDCl_3$): δ 5.95 (d, 1 H, J_{1-2} 3.7 Hz, H-1), 4.85 (t, 1 H, $J_{\alpha,\beta}$ 5.2 Hz, H-α), 4.50 (d, 1 H, J_{2-3} 0 Hz, H-2), 4.23 (d, 1 H, J_{3-4} 1.9 Hz, H-3), 4.16 (m, 1 H, J_{5-6b} 4.5 Hz, H-5), 4.03 (m, 1 H, J_{4-5} 1.2 Hz, H-4), 3.71 (dd, 1 H, J_{5-6a} 4.2 Hz, H-6a), 3.62 (dd, 1 H, J_{6a-6b} 10.4 Hz, H-6b), 3.38 (t, 2 H, H-α′, H-α″), 1.21→1.54 (CH_2chain, CH_3-iso), 0.83 (CH_3-ω′, CH_3-γ).

6-O-*Alkyl*-α-D-*glucopyranose* (**5**).—6-*O*-Alkyl-1,2-*O*-isopropylidene-3,5–*O*-propylidene-α-D-glucofuranose (**4**) (2 g) were added to a stirred solution of 9:1 CF_3COOH–H_2O (100 g L^{-1}). After 7 h at room temperature, the solution was concentrated to dryness under diminished pressure. The desired products were crystallized from diethyl ether (Table 4). NMR showed that only the α pyranose form crystallized. ^{13}C NMR ($CDCl_3$): δ 94.1 (C-1), 75.9 (C-3), 74.9 (C-2), 72.9 (C-4), 72.7 (C-5), 72.4 (C-6), 72.2 (C-α′), 32.1 → 22.9 (CH_2chain), 14.3 (C-ω′). ^1H NMR ($CDCl_3$): δ 5.88 (d, 1 H, J_{1-2} 3.6 Hz, H-1), 4.83 (m, 1 H, H-5), 4.72 (dd, 1 H, J_{3-4} 9.1 Hz, H-3), 4.26 (m, 1 H, J_{5-6b} 2.0 Hz, H-6b), 4.20 (dd, 1 H, J_{2-3} 9.5 Hz, H-2), 4.12 (dd, 1 H, J_{4-5} 9.4 Hz, H-4), 4.07 (m, 1 H, J_{6a-6b} 10.3 Hz, H-6a), 3.60 (m, 2 H, H-α′, H-α″), 1.21 → 1.64 (CH_2chain), 0.83 (CH_3-ω′).

6-O-*(6-Deoxy-1,2*-O-*isopropylidene-3,5*-O-*propylidene*-α-D-*glucofuranos-6-yl)-3*-O-n-*dodecyl-1,2*-O-*isopropylidene*-α-D-*glucofuranose* (**6**).—To a solution of **3** (2.4 g, 9 mmol) and 3-*O*-dodecyl-5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose [5] (1.1 g, 3 mmol) in 1:1 toluene–Me_2SO (100 g L^{-1})

Table 4
Physicochemical and microanalytical data for compounds **4a–d** and **5a–d**

Product	Yield (%)	Mp[a] (°C)	$[\alpha]_D^{25}$	Formula	Calcd		Found	
					C	H	C	H
4a	80	Oil	6.8° (c 1.4)[b]	$C_{18}H_{32}O_6$ (344.45)	62.77	9.36	62.63	9.42
4b	96	Oil	6.4° (c 1.2)[b]	$C_{20}H_{36}O_6$ (372.50)	64.49	9.74	64.55	9.82
4c	96	Oil	5.0° (c 1.2)[b]	$C_{22}H_{40}O_6$ (400.55)	65.97	10.07	66.11	10.12
4d	97	Oil	3.5° (c 1.3)[b]	$C_{24}H_{44}O_6$ (428.6 1)	67.26	10.35	67.15	10.41
5a	33	65.5	49.30° (c 1.3)[c]	$C_{12}H_{24}O_6$ (264.32)	54.53	9.15	54.64	9.21
5b	41	78.2	45.9° (c 1.2)[c]	$C_{14}H_{28}O_6$ (292.37)	57.51	9.65	57.59	9.71
5c	64	82.0	41.8° (c 1.2)[c]	$C_{16}H_{32}O_6$ (320.42)	59.98	10.07	60.09	10.12
5d	73	95.5	37.4° (c 1.0)[c]	$C_{18}H_{36}O_6$ (348.48)	62.04	10.41	61.95	10.38

[a] Measured by thermal microscopy.
[b] In $CHCl_3$.
[c] in MeOH (stabilized during 5 days).

was added powdered KOH (0.56 g, 10 mmol). After 40 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 6-*O*-(6-deoxy-1,2-*O*-isopropylidene-3,5-*O*-propylidene-α-D-glucofuranos-6-yl)-3-*O*-*n*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**6**) was isolated after purification by column chromatography with 4:1 hexane–acetone (1.25 g, 66%): $[\alpha]_D^{24}$ −15.7° (*c* 1.0, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 111.6 (C-iso), 105.0 (C-1), 104.8 (C-1′), 96.4 (C-α′), 83.9 (C-2′), 82.6 (C-3), 82.1 (C-2), 79.5 (C-4), 77.3 (C-4′), 73.5 (C-6), 73.2 (C-3′), 71.9 (C-5′, C-6′), 70.6 (C-αchain-), 68.0 (C-5), 31.8 to 22.6 (CH_2chain and C-β′), 26.0 to 26.7 (CH_3-iso), 14.0 (C-ωchain), 7.9 (C-γ′). ^1H NMR ($CDCl_3$): δ 5.93 (d, 1 H, J_{1-2} 3.7 Hz, H-1′), 5.83 (d, 1 H, J_{1-2} 3.7 Hz, H-1), 4.74 (m, 1 H, H-α′), 4.49 (1 H, H-2′), 4.48 (1 H, H-2), 4.21 (1 H, H-5′), 4.19 (1 H, H-4′), 4.03 (2 H, H-4, H-5), 3.98 (1 H, H-3′), 3.89 (1 H, H-3), 3.75 (2 H, H-6′), 3.63 (2 H, H-6), 3.59 and 3.44 (2 H, H-α), 1.56 to 1.20 (21 H, H-β′ and chain), 1.42 (d, 3 H, H-γ′), 1.26 and 1.20 (4s, CH_3-iso), 0.83 (3 H,C-ω). Anal. Calcd for $C_{33}H_{58}O_{11}$ (630.0): C, 62.86; H, 9.21. Found: C, 63.08; H, 9.27.

6-O-*(6-Deoxy*-D-*glucopyranos-6-yl)-3*-O-*dodecyl*-D-*glucopyranose* (**7**).—This material was prepared from the ether-linked **6** (1.35 g, 2.14 mmol) using the same deprotection method as for the type **4** compound, but dring 25 min instead of 7 h (0.48 g, 44); mp 87.1 °C. On account of the complexity of the NMR spectra, only chemical shifts of C-1 and C-3 are given; 98.8 (C-1β), 94.0 (C-1α), 87.1 (C-3β), 84.2 (C-3α). Anal. Calcd for $C_{24}H_{46}O_{11}$ (510.0): C, 56.47; H, 9.02. Found: C, 56.29; H, 9.15.

Acknowledgements

The authors thank the Conseil Régional de Picardie, the Centre de Valorisation des Glucides and the Ministère de la Recherche for financial support. We thank Professor G. Mackenzie for his critical comments.

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