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A convenient synthesis of alkyl D-glycofuranosiduronic acids and alkyl D-glycofuranosides from unprotected carbohydrates

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Abstract

O-Glycosylation of a variety of long chain alcohols with totally unprotected uronic acids (D-glucuronic and D-galacturonic acids) and neutral carbohydrates (D-glucose, D-galactose, D-mannose and D-glucofuranurono-6,3-lactone), performed in heterogeneous media and promoted by Lewis acids (ferric chloride or boron trifluoride diethyl etherate), afforded alkyl D-glycofuranosiduronic acids and alkyl D-glycofuranosides, respectively, in high yields. Both chemoselectivity and anomeric stereoselectivity were enhanced by complexing agents, i.e. calcium or barium chloride. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Glycosylation; Unprotected carbohydrates; Alkyl D-glycofuranosiduronic acids; Alkyl D-glycofuranosides

1. Introduction

Despite significant advances in the last decades, the chemical synthesis of *O*-glycosides requires a number of time-consuming protection, activation and deprotection steps [1]. In this context, direct synthesis of tautomerically and anomerically pure alkyl glycosides and glycosiduronic acids from *O*-unprotected sugars represents an interesting challenge in carbohydrate chemistry. The Fischer glycosylation of alcohols is the most commonly used method for preparing simple glycosides [2] but the reaction invariably produces mixtures of α,β-glycopyranosides and the corresponding furanosides owing to: (i) tautomeric equilibria and (ii) in situ anomerizations. In the case of the uronic acids, esterification also competes with glycoside formation [3].

In a preliminary report, we have described a rapid and simple method for the preparation of alkyl D-glycosides and of alkyl D-glycosiduronic acids from the corresponding unprotected carbohydrates [4]. We have also found that, depending

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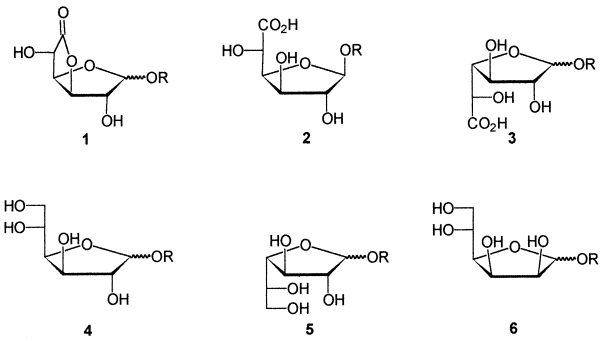
on the promoter and on the reaction conditions, either alkyl pyranosides or the furanoid isomers were obtained in moderate to good yields [4]. In this paper, we have generalized this methodology and we report herein full experimental details for the diastereocontrolled preparation of long chain alkyl glycosides exclusively in the furanosidic cyclic form starting from D-glucuronic and D-galacturonic acids (D-GlcA and D-GalA, respectively), D-glucofuranurono-6,3-lactone (''D-glucurone''), D-glucose (D-Glc), D-galactose (D-Gal) and D-mannose (D-Man).

2. Results and discussion

The synthesis of tautomerically and anomerically well defined alkyl *O*-glycosides from unprotected carbohydrates requires: (i) reaction of the alcohol with the sugar faster than self-condensation of the donor and (ii) control of the equilibria involving the substrates, the intermediates and the products, including control of the α/β stereoselectivity in the case of the products.

Reaction of D-GlcA with 1-octanol (2 equiv) and ferric chloride (2 equiv) in tetrahydrofuran at room temperature for 24 h afforded almost exclusively the octyl β-D-glucofuranurono-6,3-lactone **1a**β in moderate yield (50%). This methodology similarly afforded the unsaturated glycoside **1e**β. These results compare favorably with the recently described acid catalyzed glycosidation of D-glucurone, which yielded alkyl D-glucofuranurono-6,3-lactones in the range of 20–30% yield and modest diastereoselectivities [5]. We therefore attempted the direct glycosidation of D-glucurone with several long chain saturated alcohols. After experimentation, we found that the best results were attained when the reactions were performed in refluxing tetrahydrofuran for 1 h in the presence of boron trifluoride diethyl etherate (3 equiv). Lactonic compounds **1b–d** were thus isolated in 76–93% yields and high diastereoselectivities (α/β = 1:4.4–10.1). Both α and β anomers were easily purified by column chromatography. The application of this methodology to 1,12-dodecanediol is noteworthy since the monoglycosylated derivative **1f**β was exclusively obtained. The assignment of the structures of compounds **1**α and **1**β was established by comparison with published data [5] and was confirmed by specific rotation data (Table 1) which shows that α-anomers are much more dextrorotatory than β-anomers in accord with Hudson's rules [6].



a : R = $CH_3(CH_2)_7$-
b : R = $CH_3(CH_2)_9$-
c : R = $CH_3(CH_2)_{11}$-
d : R = $CH_3(CH_2)_{13}$-
e : R = CH_2=$CH(CH_2)_9$-
f : R = $HO(CH_2)_{12}$-

Lactonic compounds **1b,c**β could be hydrolysed under mild conditions (0.25 M sodium hydroxide in water-acetone, 0 °C for 1 h) and the resulting sodium (alkyl β-D-glucofuranosid)uronates were acidified, thus affording crystalline alkyl β-D-glucofuranosiduronic acids **2b,c** in 90% yields and without ring expansion neither β-elimination processes [7]. Compounds **2b,c** could be recrystallized from methanol–diethyl ether and were fully characterized (see Experimental section). Relactonization occurred within a few weeks at room temperature but use of the sodium salts of the acids allowed measurement of ^{1}H NMR spectra.

In the D-galacturonic acid series, the stereochemistry is not favorable for five-membered ring lactone formation. Indeed, the coupling of D-GalA with methanol as an acceptor under homogeneous conditions afforded mixtures of methyl D-galacturonates and methyl (methyl D-galactosid)uronates in the pyranoid and furanoid forms regardless of

Table 1
Specific rotation data for decyl D-glycofuranosiduronic acids and decyl D-glycofuranosides

Compound	$[\alpha]_D^{20}$ (°)	c (g/100 mL), Solvent
1bα	+90.9	0.63, THF
1bβ	−46.0	0.78, CH_2Cl_2
2bβ	−50.7	0.85, MeOH
4bα	+81	1.0, THF
4bβ	−64	1.0, THF
5bα	+54	1.0, THF
5bβ	−80	1.0, THF
6bα	+79	1.0, THF
6bβ	−59	1.0, MeOH

the promoter, proving that esterification of the carboxyl group of D-GalA proceeded faster than glycosylation, in accord with previous results [8]. We found a reversed chemoselectivity towards acetal formation when the reaction was performed in heterogeneous media at room temperature by using tetrahydrofuran as the solvent for the acceptor (0.85 equiv) and ferric chloride (3 equiv) as the promoter. Methyl D-galactosiduronic acids were thus isolated in ca. 70% overall yield as a mixture of α,β-furanoid and α,β-pyranoid compounds.

In order to ascertain wether this glycosylation was applicable for the stereoselective synthesis of tautomerically pure alkyl D-galactofuranosiduronic acids, we next explored the Lewis acid-promoted glycosidation of D-GalA in the presence of alkaline-earth cations. Sugar acids are expected to hold strong complexing ability since calcium complexes of polysaccharides containing uronic acids are probably implicated inter alia in calcium storage and calcium dependent cell–cell adhesion [9]. Indeed, when the reaction of D-GalA with a variety of alcohols (2 equiv) was performed in tetrahydrofuran in the presence of ferric chloride (3 equiv) and calcium chloride (2 equiv) at room temperature for 48–72 h, alkyl D-galactofuranosiduronic acids **3a–f** were obtained in good yield and high β-selectivity (typically $\beta/\alpha = 9{:}1$). It was also found that increasing the amount of calcium chloride slowed down both the reaction rate and the anomerization of the initially formed alkyl α-D-galactofuranosiduronic acid into the β-anomer. Pure materials **3**β were isolated after work-up by simple crystallization from dichloromethane or diethyl ether–light petroleum. The furanoid form and the β-configuration of compounds **3a–f** were established by NMR spectroscopy and corroborated by specific rotation measurements (Table 1). The ^{1}H and ^{13}C chemical shifts and the low coupling constants ($J_{1,2}$ 2.7 Hz) corresponded well with the known values for methyl (methyl β-D-galactofuranosid)uronate [10]. To the best of our knowledge, alkyl D-galactofuranosiduronic acids are obtained here for the first time from *O*-unprotected D-GalA. These results highlight the potential of calcium cations to form complexes with D-galacturonic acid intermediates and/or products under the reaction conditions. Because complexation phenomena inhibit both esterification and formation of the thermodynamically more stable pyranoid isomers, we propose that calcium ions may coordinate at least to O-5 and the carboxy group. Moreover, when an anomeric mixture of **3c**α,β, was submitted to acidic conditions, i.e. ferric chloride in tetrahydrofuran, **3c**α anomerized into **3c**β without ring expansion nor release of dodecanol. Therefore, this experiment shows that anomerization of the α-furanoside may occur through endocyclic bond cleavage followed by recyclization, thus giving mainly the thermodynamically more stable β-D-galactofuranosiduronic acid.

These results encouraged us to investigate the preparation of neutral alkyl hexofuranosides starting from D-Glc, D-Gal and D-Man in heterogeneous media by using ferric chloride as the promoter [11] and the appropriate earth-cation as additive. However, the absence of any carboxyl group in neutral aldoses should be a priori less favorable. Nevertheless, it has been previously shown that Fischer glycosylation of methanol in the presence of a strong acid may be affected by the addition of selected cations to the reaction mixture [12].

The reaction of D-Glc with 1-octanol (1.5 equiv) in dichloromethane for 24 h at room temperature in the presence of ferric chloride (3 equiv) exclusively afforded the kinetically favored octyl α-D-glucofuranoside **4a**α in a low 15% yield. When the same reaction was performed in tetrahydrofuran or in 1,4-dioxane, the yield could be largely enhanced (72%) but compound **4a** was isolated as a mixture of anomers ($\alpha/\beta = 1{:}1.4$). After experimentation, we found that barium chloride (2 equiv) in 1,4-dioxane did not affect the overall yield of octyl D-glucofuranosides **4a** but interestingly increased the β/α ratio (3.3:1). The best conditions found for 1-octanol were thus extended to a variety of saturated and unsaturated alcohols and to 1,12-dodecanediol. The expected alkyl D-glucofuranosides **4b,c,e,f** were obtained in good yields and typical α/β ratios of 1:2.5–3. After work-up, both anomers of **4b,c,e** were separated by column chromatography and recrystallized from ethyl acetate-light petroleum. 2D-COSY ^{1}H NMR and ^{1}H–^{13}C correlation spectra allowed the complete assignment of the NMR signals for both anomers. The broad singlet for H-1 ($J_{1,2} < 1.0$ Hz) and the lowest field signal (δ 109.9 ppm) for C-1 dictate the β-configuration while the α-anomer is characterized inter alia by a larger $J_{1,2}$ value (i.e. 4.2 Hz) and by an upfield resonance for the anomeric carbon (δ 103.5 ppm). All chemical shifts and spin–spin

coupling values are in good agreement with those corresponding to known methyl and alkyl D-glucofuranosides [5,6b,10,13] and $[\alpha]_D$ values (Table 1) corroborate these results.

The application of this methodology to D-galactose and to D-mannose was also examined. With D-Gal, in the presence of ferric chloride (3 equiv) and 1-octanol (1.5 equiv) in tetrahydrofuran, octyl D-galactofuranoside **5a** was isolated in 60% yield (α/β = 1:2.3) after 48 h at room temperature. However, the diastereoselectivity was improved in the presence of calcium chloride (1 equiv) and the α/β ratio reached typically 1:3.8–4.9. After work-up, pure **5a**β crystallized out of the α, β-mixture from diethyl ether. A similar feature was observed for **5b**β obtained by galactosylation of 1-decanol. The assignment of the β-D-galactofuranosidic structure was made on the basis of a small coupling constant between H-1 and H-2 ($J_{1,2} < 2$ Hz) and the chemical shift of C-1 (δ 110.0 ppm). The present work therefore complements the preparation of decyl α-D-galactofuranoside **5b**α through anomeric *O*-alkylation of D-Gal recently proposed by Klotz and Schmidt [14].

Similarly, reaction of D-Man with 1-octanol (1.5 equiv) in the presence of ferric chloride (3 equiv) and calcium chloride (2 equiv) in tetrahydrofuran at room temperature for 40 h afforded octyl D-mannofuranoside **6a** in a moderate-40% yield and diastereoselectivity (α/β = 2.6:1). On the other hand, under analogous conditions but in the absence of any additive, octyl and decyl D-mannofuranosides **6a** and **6b** were isolated in 58 and 54% yields, respectively. The glycosylation was highly diastereoselective since the α-anomers were obtained almost exclusively in α/β ratios typically greater than 19:1. Moreover, **6a,b**α were isolated without chromatographic purification by simple crystallization from diethyl ether. The chemical shift of the anomeric center (δ 110.0 ppm) and the positive optical rotation (Table 1) allowed us to establish unequivocally the 1,2-*trans* linkage of alkyl α-D-mannofuranosides **6**α [6].

In conclusion, glycosylation of long chain alcohols with neutral carbohydrates and uronic acids in heterogeneous media and in the presence of ferric chloride makes a useful approach for transformation of unprotected sugars directly into the corresponding alkyl D-glycofuranosides. Anomeric control in furanoside formation may be gained by use of selected alkaline-earth cations. Alkyl glycofuranosides described here are useful as surfactants or liquid crystals [15] and as building blocks for original glycofuranosyl donors in oligosaccharide synthesis [16,17].

3. Experimental

General methods.—D-Galacturonic acid was purchased from ARD (Pomacle, France) while all other chemicals were commercially available. Tetrahydrofuran (THF) and 1,4-dioxane were dried over sodium/benzophenone and distilled. All reactions were performed under nitrogen. TLC-analyses were conducted on precoated non activated plates (E. Merck 60 F_{254}) and compounds were visualized using a 5% soln of H_2SO_4 in EtOH followed by heating. For column chromatography, E. Merck 60H (5–40 μm) Silica Gel was used. All melting points (mp) were determined on a Reichert microscop and are uncorrected. Clearing points (cp) for the thermotropic compounds [15] were determined by differential scanning calorimetry using a Perkin–Elmer DSC 7 PC system operating on DOS software. IR spectra were recorded on a IRFT Nicolet 205 spectrometer. Optical rotations were measured on a Polartronic D polarimeter at 20 °C using a 1-dm cell. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker ARX 400 spectrometer at 400 and 100 MHz, respectively. Chemical shift data is given in δ-units measured downfield from Me_4Si and elemental analyses were performed by the Service de Microanalyse de l'ENSCR (Rennes, France).

General procedure for the preparation of n-*alkyl* β-D-*glucofuranosidurono-6,3–lactones* (**1**β) *from* D-*glucuronic acid.*—To a suspension of D-glucuronic acid (3.88 g, 20 mmol) in THF (40 mL) at 0 °C were successively added 40 mmol of alcohol and, portionwise, 6.48 g (40 mmol) of $FeCl_3$. After several hours at room temperature, the reaction media was concentrated and partitioned between EtOAc (80 mL) and 5% aq HCl (20 mL). The organic layer was washed with the acidic soln until discolouration and with H_2O, dried ($MgSO_4$) and concentrated under reduced pressure. The crude oil was purified by column chromatography and recrystallized.

n-*Octyl* β-D-*glucofuranosidurono-6,3-lactone* (**1a**β).—The glycosylation of *n*-octanol (5.20 g,) for 24 h afforded, after column chromatography (1:1 light petroleum–Et_2O, then Et_2O and 9:1 Et_2O–MeOH) and recrystallization from Et_2O-*n*-hexane,

1aβ (2.88 g, 50%) as a white solid; TLC (19:1 CH_2Cl_2–MeOH): R_f 0.50; mp 72–73 °C (Et_2O-*n*-hexane), lit. 71–73 °C [5]; $[\alpha]_D^{20}$ −53° (*c* 0.78, CH_2Cl_2), lit. −41.9° (acetone) [5]; IR (HCB): ν 1785 and 1803 (C=O), and 3350 cm^{-1} (OH); ^1H NMR ($CDCl_3 + D_2O$); δ5.08 (s, 1 H, H-1); 4.95 (dd, 1 H, $J_{4,5}$ 6.7 Hz, $J_{4,3}$ 4.8 Hz, H-4); 4.80 (d, 1 H, H-3); 4.34 (d, 1 H, H-2); 4.28 (d, 1 H, H-5); 3.62 (td, ^2J 9.4 Hz, ^3J 6.7 Hz, 1 H, OCH_2); 3.37 (td, 1 H, ^3J 6.6 Hz, OCH_2); 1.50–1.45 (m, 2 H, OCH_2CH_2); 1.25–1.20 (m, 10 H, CH_2); 0.82 (t, 3 H, *J* 6.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 175.6 (C-6); 109.0 (C-1); 83.5 (C-3); 77.3 (C-2); 77.2 (C-4); 69.2 (C-5); 69.1 (OCH_2); 31.8, 29.3, 29.2, 25.9, 22.6 (CH_2); 14.0 (CH_3); *m*/*z* (CI, NH_3): 306 (100%, $[M+NH_4]^+$). Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.31; H, 8.39; O, 33.30. Found: C, 58.42; H, 8,50; O, 33.37.

10′-Undecenyl β-D-*glucofuranosidurono-6,3-lactone* (**1e**β).—The glycosylation of 10-undecen-1-ol (6.80 g) afforded, after 3 days at room temperature, work-up and chromatographic purification (1:1 light petroleum–Et_2O then Et_2O), 3.28 g (10 mmol, 50%) of **1e**β which was recrystallized from EtOAc; TLC (19:1 CH_2Cl_2–MeOH): R_f 0.55; mp 75–76 °C (Et_2O–light petroleum); $[\alpha]_D^{20}$ −48.4° (*c* 1.6, $CHCl_3$); IR (HCB): ν 1777 (C=O), and 3350 cm^{-1} (OH); ^{13}C NMR ($CDCl_3$): δ 175.4 (C-6); 139.1 ($CH=CH_2$); 114.1 ($CH_2=CH$); 109.0 (C-1); 83.5 (C-3); 77.3 (C-2); 77.1 (C-4); 69.1 (C-5, OCH_2); 33.7, 29.4, 29.3, 29.1, 28.9, 25.6 (CH_2); *m*/*z* (CI, NH_3) 346 (100%, $[M+NH_4]^+$). Anal. Calcd for $C_{17}H_{28}O_6$: C, 62.17; H, 8.59; O, 29.23. Found: C, 62.16; H, 8.79; O, 29.12.

General procedure for the preparation of n-*alkyl* D-*glucofuranosidurono-6,3-lactones* (**1**) *from* D-*glucofuranurono-6,3-lactone*.—To a suspension of D-glucofuranurono-6,3-lactone (1 equiv) in dry THF were added the appropriate alcohol (2 equiv) and $BF_3{\cdot}Et_2O$ (3 equiv). The reaction media was heated at reflux until homogeneity. After solvent removal, the residue was diluted in EtOAc (80 mL). The organic layer was successively washed with 5% aq HCl (2×30 mL), H_2O, dried ($MgSO_4$) and concentrated. The crude oil was purified by chromatography (1:1 light petroleum–Et_2O, then Et_2O and finally 9:1 Et_2O–MeOH).

n-*Decyl* D-*glucofuranosidurono-6,3-lactone* (**1b**).—The glycosylation of *n*-decanol (4.74 g, 30 mmol) by D-glucofuranurono-6,3-lactone (2.64 g, 30 mmol) in THF (30 mL) afforded, after chromatographic separation, 0.52 g (1.6 mmol, 11%) of **1b**α which was recrystallized from Et_2O, and 3.80 g (12 mmol, 80%) of **1b**β, which was recrystallized from EtOAc–Et_2O (α/β = 1:7.3); TLC (19:1 CH_2Cl_2–MeOH): R_f 0.70 (**1b**α), 0.55 (**1b**β); **1b**α: mp 95–96 °C (Et_2O), lit. 95–96 °C [5]; $[\alpha]_D^{20}$ +90.9° (*c* 0.63, THF), lit. +92.7° (acetone) [5]; IR (HCB): ν 1766 (C=O), and 3440 cm^{-1} (OH); ^{13}C NMR ($CDCl_3$): δ 174.4 (C-6); 102.7 (C-1); 84.7 (C-3); 76.3 (C-2); 76.0 (C-4); 70.3 (C-5); 69.8 (OCH_2); 31.9, 29.5, 29.3, 26.0, 22.6 (CH_2); 14.0 (CH_3); *m*/*z* (CI, NH_3) 334 (100%, $[M+NH_4]^+$); **1b**β: mp 83–84 °C (EtOAc–Et_2O), lit. 81–83 °C [5]; cp 90–91 °C; $[\alpha]_D^{20}$ −46.0° (*c* 0.78, CH_2Cl_2), lit. −38.5° (acetone) [5]; IR (HCB): ν 1776 and 1804 (C=O), and 3350 cm^{-1} (OH); ^{13}C NMR ($CDCl_3$): δ 175.5 (C-6); 109.1 (C-1); 83.5 (C-3); 77.3 (C-2); 77.2 (C-4); 69.2 (C-5, OCH_2); 31.9, 29.6, 29.4, 29.3, 29.2, 25.9, 22.7 (CH_2); 14.1 (CH_3); *m*/*z* (CI, NH_3) 334 (100%, $[M+NH_4]^+$). Anal. Calcd for $C_{16}H_{28}O_6$: C, 60.74; H, 8.92; O, 30.34. Found: C, 60.74; H, 8.96; O 30.14.

n-*Dodecyl* D-*glucofuranosidurono-6,3-lactone* (**1c**).—The glycosylation of *n*-dodecanol (5.58 g, 30 mmol) by D-glucofuranurono-6,3-lactone (2.64 g, 30 mmol) in THF (30 mL) afforded, after chromatographic separation, 0.40 g (1.2 mmol, 8%) of **1c**α which was recrystallized from Et_2O, and 4.39 g (12.7 mmol, 85%) of **1c**β which was recrystallized from EtOAc–Et_2O (α/β = 1:10.1); TLC (19:1 CH_2Cl_2–MeOH): R_f 0.70 (**1c**α), R_f 0.56 (**1c**β); **1c**α: mp 98–99 °C (Et_2O), lit. 95–97 °C [5]; $[\alpha]_D^{20}$ +86.3° (*c* 0.56, THF), lit. +81.5° (acetone) [5]; IR (HCB): ν 1766 (C=O), and 3440 cm^{-1} (OH); ^{13}C NMR ($CDCl_3$): δ 174.3 (C-6); 102.7 (C-1); 84.7 (C-3); 76.3 (C-2); 76.0 (C-4); 70.3 (C-5); 69.9 (OCH_2); 31.9, 29.6, 29.5, 29.3, 26.0, 22.7 (CH_2); 14.0 (CH_3); *m*/*z* (CI, NH_3): 362 (100%, $[M+NH_4]^+$); **1c**β: mp 92 °C (EtOAc–Et_2O), lit. 88–89 °C [5]; cp 116.5–117 °C; $[\alpha]_D^{20}$ −37.9° (*c* 0.68, $CHCl_3$), lit. −35.6° (acetone) [5]; IR (HCB) ν 1785 and 1803 (C=O), and 3350 cm^{-1} (OH); ^{13}C NMR ($CDCl_3$): δ 174.8 (C-6); 109.2 (C-1); 83.4 (C-3); 77.6 (C-2); 77.1 (C-4); 69.4 (OCH_2); 69.2 (C-5); 32.0, 29.7, 29.6, 29.4, 26.0, 22.7 (CH_2); 14.2 (CH_3); *m*/*z* (CI, NH_3) 362 (100%, $[M+NH_4]^+$); HRMS: *m*/*z* 344 $[M]^+$ (Calcd for $C_{18}H_{32}O_6$: 344.21987; Found: 344.2208). Anal. Calcd for $C_{18}H_{32}O_6$: C, 62.76; H, 9.37; O, 27.87. Found: C, 62.41; H, 9.54; O, 27.72.

n-*Tetradecyl* D-*glucofuranosidurono-6,3-lactone* (**1d**).—The glycosylation of *n*-tetradecanol (6.42 g, 30 mmol) by D-glucofuranurono-6,3-lactone (2.64 g, 15 mmol) in THF (30 mL) afforded, after

chromatographic separation, 0.76 g (2 mmol, 14%) of **1d**α which was recrystallized from MeOH–Et_2O, and 3.45 g (9.3 mmol, 62%) of **1d**β which was recrystallized from Et_2O–EtOAc (α/β = 1:4.4); TLC (19:1 CH_2Cl_2–MeOH): R_f 0.72 (**1d**α), 0.57 (**1d**β); **1d**α: mp 99–100 °C (Et_2O–MeOH); $[\alpha]_D^{20}$ +77.1° (*c* 1.0, THF); IR (HCB): ν 1767 (C=O), and 3440 cm^{-1} (OH); ^{13}C NMR ($CDCl_3$): δ 174.2 (C-6); 102.8 (C-1); 84.7 (C-3); 76.4 (C-2); 76.0 (C-4); 70.4 (C-5); 69.9 (OCH_2); 32.0, 29.7, 29.4, 26.0, 22.7, (CH_2); 14.1 (CH_3); *m/z* (CI, NH_3) 390 (100%, $[M+NH_4]^+$); **1d**β: mp 97–98 °C (EtOAc–Et_2O); cp 130 °C; $[\alpha]_D^{20}$ −37.6° (*c* 0.74, $CHCl_3$); IR (HCB): ν 1785 and 1803 (C=O), and 3350 cm^{-1} (OH); ^1H NMR ($CDCl_3 + D_2O$): δ 5,02 (s, 1 H, H-1); 4.92 (dd, 1 H, $J_{4,5}$ 6.8 Hz, $J_{4,3}$ 4.9 Hz, H-4); 4.78 (d, 1 H, H-3); 4.35 (s, 1 H, H-2); 4.27 (d, 1 H, H-5); 3.60 (dt, 1 H, ^2J 9.3 Hz, ^3J 6.9 Hz, OCH_2); 3.35 (dt, ^3J 6.9 Hz, 1 H, OCH_2); 1.48–1.40 (m, 2 H, OCH_2CH_2); 1.26–1.18 (m, 22 H, CH_2); 0.81 (t, 3 H, *J* 6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 174.3 (C-6); 109.3 (C-1); 83.2 (C-3); 77.8 (C-2); 76.3 (C-4); 69.5 (OCH_2); 69.2 (C-5); 32.0, 29.8, 29.7, 29.6, 29.4, 29.3, 26.0, 22.8 (CH_2); 14.1 (CH_3); *m/z* (CI, NH_3) 390 (100%, $[M+NH_4]^+$). Anal. Calcd for $C_{20}H_{36}O_6$: C, 64.49; H, 9.74; O, 25.77. Found: C, 64.54; H, 9.87; O, 25.75.

12′-Hydroxy-n-*dodecyl* β-D-*glucofuranosiduronо-6,3-lactone* (**1f**β).—The glycosylation of 1,12-dodecanediol (6.06 g, 30 mmol) by D-glucofuranurono-6,3-lactone (2.64 g, 15 mmol) in THF (30 mL) afforded, after chromatographic purification, 2.65 g (7.4 mmol, 50 %) of pure **1f**β which was recrystallized from EtOAc; TLC (19:1 CH_2Cl_2-MeOH): R_f 0.30; mp 107–108 °C (Et_2O–MeOH); $[\alpha]_D^{20}$ −31.9° (*c* 0.94, THF); IR (HCB): ν 1760 (C=O), 3375 (OH), and 3520 cm^{-1} (OH); ^{13}C NMR (CD_3OD): δ 177.8 (C-6); 111.1 (C-1); 85.4 (C-3); 80.0 (C-2); 79.2 (C-4); 71.2 (C-5); 70.0 (OCH_2); 63.7 (CH_2OH); 34.4, 31.4, 31.3, 31.0, 27.8, 27.6 (CH_2); *m/z* (CI, NH_3) 378 (100%, $[M+NH_4]^+$), 361 (40, $[M+H]^+$). Anal. Calcd for $C_{18}H_{32}O_7$: C, 59.98; H, 8.95; O, 31.07. Found: C, 59.68; H, 8.85; O, 31.04.

General procedure for the synthesis of alkyl β-D-*glucofuranosiduronic acids* (**2**).—To a stirred solution of **1**β (10 mmol) in Me_2CO (20 mL) at 0 °C was added 0.5 N aq NaOH (20 mL). After 1 h at 0 °C, the soln was partitioned between Et_2O (40 mL) and H_2O (10 mL). The resulting aq layer was acidified (aq HCl) and extracted with EtOAc (3×20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The target acid **2** was finally purified by recrystallization.

n-*Decyl* β-D-*glucofuranosiduronic acid* (**2b**).—3.16 g (10 mmol) of **1b**β afforded 3.01 g (90%) of **2b**β which was recrystallized from Et_2O-MeOH; TLC (3:2 EtOAc–MeOH): R_f 0.35; mp 93–94 °C (Et_2O–MeOH); cp 104–105 °C; $[\alpha]_D^{20}$ −50.7° (*c* 0.85, MeOH); IR (HCB): ν 1750 (C=O), and 3380 cm^{-1} (OH); ^1H NMR (CD_3OD + NaOD): δ 4.87 (s, 1H, H-1); 4.57 (dd, 1 H, $J_{4,5}$ 3.1 Hz, $J_{4,3}$ 5.8 Hz, H-4); 4.41 (d, 1 H, H-5); 4.22 (d, 1 H, H-3); 4.12 (s, 1 H, H-2); 3.80 (dt, 1 H, ^2J 9.5 Hz, ^3J 6.5 Hz, OCH_2); 3.50 (dt, 1 H, ^3J 6.7 Hz, OCH_2); 1.50–1.45 (m, 2 H, OCH_2CH_2); 1.20–1.15 (m, 14 H, CH_2); 0.80 (t, 3 H, *J* 6.5 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 176.5 (C-6); 110.3 (C-1); 84.3 (C-4); 82.1 (C-2); 78.1 (C-3); 72.0 (C-5); 70.0 (OCH_2); 33.8, 31.4, 31.3, 31.2, 27.9, 24.4 (CH_2); 15.2 (CH_3); *m/z* (CI, NH_3) 335 (100%, $[M+H]^+$). Anal. Calcd for $C_{16}H_{30}O_7$: C, 57.47; H, 9.04; O, 33.49. Found: C, 57.46; H, 9.04; O, 33.18.

n-*Dodecyl* β-D-*glucofuranosiduronic acid* (**2c**).—3.44 g (10 mmol) of **1c**β yielded 3.26 g (90%) of **2c**β which was recrystallized from Et_2O–MeOH; TLC (3:2 EtOAc–MeOH): R_f 0.35; mp 99–100 °C (EtOAc–MeOH); cp 120 °C; $[\alpha]_D^{20}$ −46.2° (*c* 0.87, MeOH); IR (HCB): ν 1750 (C=O), and 3380 cm^{-1} (OH); ^{13}C NMR (CD_3OD): δ 176.6 (C-6); 110.4 (C-1); 84.4 (C-4); 82.3 (C-2); 78.2 (C-3); 72.1 (C-5); 70.0 (OCH_2); 33.8, 31.5, 31.3, 31.2, 28.0, 24.4 (CH_2); 15.2 (CH_3); *m/z* (CI, NH_3) 363 (100%, $[M+H]^+$). Anal. Calcd for $C_{18}H_{34}O_7$: C, 59.64; H, 9.46; O, 30.90. Found: C, 59.81; H, 9.60; O, 30.74.

General procedure for the synthesis of alkyl β-D-*galactofuranosiduronic acids* (**3b**).—To a suspension of D-galacturonic acid (4.24 g, 20 mmol) in THF (30 mL) were successively added, at 0 °C, $CaCl_2$ (4.44 g, 40 mmol), the appropriate alcohol (2 equiv) and, in small portions, $FeCl_3$ (9.72 g, 60 mmol). The reaction mixture was vigorously stirred at room temperature for 1–3 days. After removal of the solvent, the residue was partitioned between Et_2O (80 mL) and 5% aq HCl (20 mL). The organic layer was successively washed with aq HCl until discolouration, NaOH (0.5 N, 40 mL) and NaOH (0.1 N, 30 mL). The basic aq layers were combined, extracted with Et_2O (3×20 mL), acidified (HCl, 5N) and extracted with EtOAc (3×20 mL). The latter three organic extracts were washed with H_2O (10 mL), dried ($MgSO_4$) and concentrated. The residue was finally subjected to crystallization.

n-*Octyl* β-D-*galactofuranosiduronic acid* (**3a**β).—The glycosylation of *n*-octanol (5.20 g, 40 mmol) for 2 days afforded, after crystallization from Et_2O–light petroleum, **3a**β (3.67 g, 60%) as a white powder; TLC (3:2 EtOAc–MeOH +1% Me_4NOH): R_f 0.40; mp 87–89 °C (Et_2O–light petroleum); cp 100–101 °C; $[\alpha]_D^{20}$ −67° (*c* 1.2, MeOH); ^{13}C NMR (CD_3OD): δ 176.2 (C–6); 110.1 (C-1); 85.6 (C-4); 84.0 (C-2); 78.7 (C-3); 71.1 (C-5); 69.8 (OCH_2); 33.7, 31.4, 31.2, 31.1, 27.9, 24.4 [$(CH_2)_6CH_3$]; 15.2 (CH_3); *m*/*z* (CI, NH_3) 324 (100%, $[M+NH_4]^+$), 194 (9, $[M-C_8H_{17}+H]^+$). Anal. Calcd for $C_{14}H_{26}O_7$: C, 54.88; H, 8.56; O, 36.56. Found: C, 54.72; H, 8.62; O, 36.74.

n-*Decyl* β-D-*galactofuranosiduronic acid* (**3b**β).—The glycosylation of *n*-decanol (6.32 g, 40 mmol) for 2 days afforded, after crystallization from Et_2O–light petroleum or pure CH_2Cl_2, **3b**β (4.68 g, 70%) as a white powder; TLC (3:2 EtOAc–MeOH +1% Me_4NOH): R_f 0.43; mp 92–93 °C (Et_2O–light petroleum); cp 136–138 °C; $[\alpha]_D^{20}$ −65° (*c* 1, MeOH); ^1H NMR [$(CD_3)_2SO+D_2O$]: δ 4.72 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1); 4.09 (d, 1 H, $J_{5,4}$ 2.0 Hz, H-5); 4.02 (dd, 1 H, $J_{4,3}$ 7.7 Hz, H-4); 3.95 (dd, 1 H, $J_{3,2}$ 5.2 Hz, H-3); 3.78 (dd, 1 H, H-2); 3.52 (dt, 1 H, ^2J 9.8 Hz, ^3J 6.8 Hz, OCH_2); 3.32 (dt, 1 H, ^3J 6.7 Hz, OCH_2); 1.52–1.47 (m, 2 H, OCH_2CH_2); 1.32–1.23 (m, 14 H, [$(CH_2)_7CH_3$]); 0.88 (t, 3 H, *J* 6.9 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 176.1 (C-6); 110.1 (C-1); 85.7 (C-4); 83.9 (C-2); 78.7 (C-3); 71.1 (C-5); 69.8 (OCH_2); 33.7, 31.4, 31.2, 31.1, 27.9, 24.4 [$(CH_2)_8CH_3$]; 15.2 (CH_3); *m*/*z* (CI, NH_3) 352 (100%, $[M+NH_4]^+$), 194 (10, $[M-C_{10}H_{21}+H]+$). Anal. Calcd for $C_{16}H_{30}O7$: C, 57.46; H, 9.04; O, 33.49. Found: C, 57.30; H, 9.16; O, 33.29.

n-*Dodecyl* β-D-*galactofuranosiduronic acid* (**3c**β).—The glycosylation of *n*-dodecanol (7.44 g, 40 mmol) for 2 days afforded, after crystallization from Et_2O or CH_2Cl_2, **3c**β (4.71 g, 65%) as a white powder; TLC (3:2 EtOAc–MeOH +1% Me_4NOH): R_f 0.45; mp 100–101 °C (Et_2O); cp 143–145 °C; $[\alpha]_D^{20}$ −61.9° (*c* 0.6, MeOH); ^{13}C NMR (CD_3OD): δ 176.1 (C-6); 110.1 (C-1); 85.7 (C-4); 83.9 (C-2); 78.7 (C-3); 71.9 (C-5); 69.7 (OCH_2); 33.8, 31.4, 31.3, 31.2, 27.0, 24.4 [$(CH_2)_{10}CH_3$]; 15.2 (CH_3); *m*/*z* (CI, NH_3) 380 (100%, $[M+NH_4]^+$). Anal. Calcd for $C_{18}H_{34}O_7$: C, 59.64; H, 9.46; O, 30.90. Found: C, 59.20; H, 9.61; O, 30.59.

n-*Tetradecyl* β-D-*galactofuranosiduronic acid* (**3d**β).—The glycosylation of *n*-tetradecanol (8.56 g, 40 mmol) for 2 days afforded, after crystallization from CH_2Cl_2, **3d**β (5.07 g, 65%) as a white powder; TLC (3:2 EtOAc–MeOH +1% Me_4NOH): R_f 0.48; mp 103–104 °C (CH_2Cl_2); cp 145–147 °C; $[\alpha]_D^{20}$ −49° (*c* 0.9, MeOH); ^{13}C NMR (CD_3OD): δ 176.2 (C-6); 110.1 (C-1); 85.7 (C-4); 84.0 (C-2); 78.3 (C-3); 71.1 (C-5); 69.8 (OCH_2); 33.8, 31.5, 31.3, 31.2, 28.0, 24.5 [$(CH_2)_{12}CH_3$]; 15.2 (CH_3); *m*/*z* (CI, NH_3) 408 (100%, $[M+NH_4]^+$), 391 (8, $[M+H]^+$). Anal. Calcd for $C_{20}H_{38}O_7$: C, 61.51; H, 9.81; O, 28.68. Found: C, 61.50; H, 9.75; O, 28.85.

10′-Undecenyl β-D-*galactofuranosiduronic acid* (**3e**β).—The glycosylation of 10-undecen-1-ol (6.80 g, 40 mmol) for 3 days afforded, after crystallization from Et_2O–petroleum ether, **3e**β (4.10 g, 60%) as a white powder; TLC (3:2 EtOAc–MeOH +1% Me_4NOH): R_f 0.45; mp 84–85 °C (Et_2O–petroleum ether); cp 124–125 °C; $[\alpha]_D^{20}$ −55° (*c* 0.9, MeOH); ^{13}C NMR (CD_3OD): δ 176.2 (C-6); 140.8 ($CH=CH_2$); 115.4 ($CH_2=CH$); 110.1 (C-1); 85.6 (C-4); 84.0 (C-2); 78.7 (C–3); 71.1 (C-5); 69.8 (OCH_2); 35.6, 31.4, 31.3, 31.2, 30.9, 30.8, 27.9 [$(CH_2)_8CH=CH_2$]; *m*/*z* (CI, NH_3) 364 (100%, $[M+NH_4]^+$), 192 (12, $[M-C_{11}H_{21}+H]^+$). Anal. Calcd for $C_{17}H_{30}O_7$: C, 58.94; H, 8.73; O, 32.33. Found: C, 58.78; H, 8.63; O, 32.19.

12′-Hydroxy-dodecyl β-D-*galactofuranosiduronic acid* (**3f**β).—The glycosylation of 1,12–dodecanediol (8.08 g, 40 mmol) for 3 days afforded, after crystallization from Et_2O–light petroleum, **3f**β (3.80 g, 50%) as a white powder; TLC (3:2 EtOAc–MeOH +1% Me_4NOH): R_f 0.50; mp 95–96 °C (Et_2O–light petroleum); $[\alpha]_D^{20}$ −42° (*c* 1.1, MeOH); ^{13}C NMR (CD_3OD): δ 176.2 (C-6); 110.1 (C-1); 85.6 (C-4); 84.0 (C-2); 78.7 (C-3); 71.1 (C-5); 69.8 (OCH_2); 63.8 (CH_2OH); 34.4, 31.4, 30.9, 28.0, 27.8 [$(CH_2)_{11}CH_2OH$]; *m*/*z* (CI, NH_3) 396 (30%, $[M+NH_4]^+$), 220 (100, $[C_{12}H_{26}O_2+NH_4]^+$), 194 (47, $[M-C_{12}H_{25}O+H]^+$). Anal. Calcd for $C_{18}H_{34}O_8$: C, 57.12; H, 9.06; O, 33.82. Found: C, 56.98; H, 9.02; O, 33.75.

Synthesis of n-*octyl* α-D-*glucofuranoside* (**4a**α) *in* CH_2Cl_2.—To a suspension of D–glucose (3.60 g, 20 mmol) in CH_2Cl_2 (30 mL) at 0 °C were added 1-octanol (3.90 g, 30 mmol) and, portionwise, $FeCl_3$ (9.72 g, 60 mmol). The reaction mixture was stirred at room temperature for 24 h, diluted with CH_2Cl_2 (50 mL), washed with 5% aq HCl and H_2O. The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (19:1 CH_2Cl_2–MeOH) followed by recrystallization from EtOAc–light petroleum yielded **4a**α (0.87 g, 15%); TLC (9:1 CH_2Cl_2–MeOH):

R_f 0.22; mp 48–49 °C (EtOAc–light petroleum); cp 55 °C; $[\alpha]_D^{20}$ +89 ° (*c* 1.1, MeOH); ^{1}H NMR (CD_3OD): δ 5.02 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1); 4.23 (dd, 1 H, $J_{3,4}$ 5.0 Hz, $J_{3,2}$ 4.0 Hz, H-3); 4.03 (dd, 1 H, $J_{4,5}$ 7.6 Hz, H-4); 3.99 (dd, 1 H, H-2); 3.85 (ddd, 1 H, $J_{5,6}$ 6.4 Hz, $J_{5,6'}$ 3.5 Hz, H-5); 3.77 (dt, 1 H, $J_{6',6}$ 11.3 Hz, H-6′); 3.75 (dt, 1 H, ^2J 9.7 Hz, ^3J 6.8 Hz, OCH_2); 3.59 (dd, 1 H, H-6); 3.51 (dt, 1 H, ^3J 6.6 Hz, OCH_2); 1.67–1.58 (m, 2 H, OCH_2CH_2); 1.42–1.31 (m, 10 H, CH_2); 0.91 (t, 3 H, *J* 6.7 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 103.5 (C-1); 79.6 (C-2, C-4); 78.1 (C-3); 72.5 (C-5); 70.3 (OCH_2); 65.5 (C-6); 33.5 (OCH_2CH_2); 31.3, 31.0, 30.9, 27.7, 24.2 [$(CH_2)_5CH_3$]; 15.2 (CH_3); *m*/*z* (CI, NH_3) 310 (100%, $[M+NH_4]^+$), 293 (4, $[M+H]^+$), 180 (32, $[M-C_8H_{17}O+NH_3]^+$). Anal. Calcd for $C_{14}H_{28}O_6$: C, 57.51; H, 9.65; O, 32.84. Found: C, 57.40; H, 9.83; O, 32.96.

General procedure for the synthesis of alkyl D-*glucofuranosides* (**4**) *in 1,4–dioxane*.—To a suspension of D-glucose (3.60 g, 20 mmol) in dry 1,4-dioxane (30 mL) at 0 °C were added 9.80 g (40 mmol) of $BaCl_2$ (9.80 g, 40 mmol), 30 mmol of the appropriate alcohol and, by small portions, 9.72 g (60 mmol) of $FeCl_3$. After 24 h at room teperature and removal of the solvent, the residue was partitioned between EtOAc (100 mL) and 5% aq HCl (20 mL). The organic layer was washed with the acidic soln until discolouration and the aq layers thus obtained extracted with EtOAc (3×20 mL). The combined organic extracts were then washed with H_2O (3×15 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The target compounds were finally purufied by chromatography eluting with 19:1 CH_2Cl_2–MeOH and recrystallized.

n-*Octyl* D-*glucofuranoside* (**4a**).—The glycosylation of 1-octanol (3.90 g) afforded 0.71 g (12%) of **4a**α and 2.38 g (41%) of **4a**β (α/β = 1:3.3); TLC (9:1 CH_2Cl_2–MeOH): R_f 0.22 (**4a**α) 0.16 (**4a**β); **4a**β: mp 53–55 °C (EtOAc), lit. 52–54 °C [5]; cp 94 °C; $[\alpha]_D^{20}$ −65 ° (*c* 1.0, MeOH), lit. −71.5 ° (acetone) [5]; ^{1}H NMR (CD_3OD): δ 4,85 (d, 1 H, $J_{1,2}$ 0.6 Hz, H-1); 4.12–4.07 (m, 2 H, H-3, H-4); 4,02 (broad s, 1 H, H-2); 3.96–3.81 (m, 1 H, H-5); 3.81 (dd, 1 H, $J_{6',6}$ 11.5 Hz, $J_{6',5}$ 3.7 Hz, H-6′); 3.70 (dt, 1 H, ^2J 9.6 Hz, ^3J 6.7 Hz, OCH_2); 3.64 (dd, 1 H, $J_{6,5}$ 6.0 Hz, H-6); 3.40 (dt, 1 H, ^3J 6.5 Hz, OCH_2); 1.60–1.53 (m, 2 H, OCH_2CH_2); 1.38–1.31 (m, 10 H, CH_2); 0.91 (t, 3 H, *J* 6.7 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 109.9 (C-1); 82.7 (C-4); 81.8 (C-2); 77.3 (C-3); 71.8 (C-5); 69.3 (OCH_2); 65.3 (C-6); 33.0 (OCH_2CH_2); 30.6, 30.5, 30.4, 27.7, 23.7 [$(CH_2)_5CH_3$]; 14.5 (CH_3); *m*/*z* (CI, NH_3) 310 (100%, $[M+NH_4]^+$), 293 (7, $[M+H]^+$), 180 (49, $[M-C_8H_{17}O+NH_3]^+$). Anal. Calcd for $C_{14}H_{28}O_6$: C, 57.51; H, 9.65. Found: C, 57.45; H, 9.65.

n-*Decyl* D-*glucofuranoside* (**4b**).—The glycosylation of *n*-decanol (4.74 g) afforded 1.43 g (22%) of **4b**α and 3.69 g (58%) of **4b**β (α/β = 1:2.6); TLC (9:1 CH_2Cl_2–MeOH): R_f 0.34 (**4b**α), 0.28 (**4b**β); **4b**α: mp 64–65 °C (EtOAc); cp 94 °C; $[\alpha]_D^{20}$ +81 ° (*c* 1.0, THF); ^{1}H NMR (CD_3OD): δ 4.91 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1); 4.07 (dd, 1 H, $J_{3,4}$ 5.1 Hz, $J_{3,2}$ 4.0 Hz, H-3); 3.93 (dd, 1 H, $J_{4,5}$ 7.6 Hz, H-4); 3.89 (dd, 1 H, H-2); 3.73 (ddd, 1 H, $J_{5,6}$ 6.4 Hz, $J_{5,6'}$ 3.5 Hz, H-5); 3.65 (dt, 1 H, $J_{6',6}$ 11.4 Hz, H-6′); 3.63 (dt, 1 H, ^2J 9.7 Hz, ^3J 6.8 Hz, OCH_2); 3.48 (dd, 1 H, H–6); 3.40 (dt, 1 H, ^3J 6.7 Hz, OCH_2); 1.55–1.52 (m, 2 H, OCH_2CH_2); 1.49–1.26 (m, 14 H, CH_2); 0.80 (t, 3 H, *J* 6.8 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 103.8 (C-1); 80.0 (C-4 or C-2); 79.8 (C-2 or C-4); 78.4 (C-3); 72.8 (C-5); 70.6 (OCH_2); 65.7 (C-6); 33.8 (OCH_2CH_2); 31.5, 31.3, 31.2, 27.9, 24.3 [$(CH_2)_7CH_3$]; 15.2 (CH_3); *m*/*z* (CI, NH_3) 338 (100%, $[M+NH_4]^+$), 321 (4, $[M+H]^+$), 180 (6, $[M-C_{10}H_{21}O+NH_3]^+$). Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.97; H, 10.07; O, 29.96. Found: C, 60.22; H, 10.22; O, 29.91; **4b**β: mp 69–71 °C (EtOAc), lit. 67–68 °C [5]; cp 130 °C; $[\alpha]_D^{20}$ −64 ° (*c* 1.0, THF), lit. −66.8 ° (acetone) [5]; ^{1}H NMR (CD_3OD): δ 4.87 (broad s, 1 H, H-1); 4.14–4.11 (m, 2 H, H-3, H-4); 4.05 (broad s, 1 H, H-2); 3.98–3.94 (m, 1 H, H-5); 3.84 (dd, 1 H, $J_{6',6}$ 11.5 Hz, $J_{6',5}$ 3.7 Hz, H-6′); 3.67 (dt, 1 H, ^2J 9.6 Hz, ^3J 6.7 Hz, OCH_2); 3.64 (dd, 1 H, $J_{6,5}$ 6.0 Hz, H-6); 3.40 (dt, ^3J 6.5 Hz, 1 H, OCH_2); 1.62–1.57 (m, 2 H, OCH_2CH_2); 1.35–1.31 (m, 14 H, CH_2); 0.94 (t, 3 H, *J* 6.7 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 110.6 (C-1); 83.4 (C-4); 82.6 (C-2); 78.3 (C-3); 72.7 (C-5); 70.1 (OCH_2); 66.0 (C-6); 33.7 (OCH_2CH_2); 31.4, 31.2, 31.1, 27.9, 24.3 [$(CH_2)_7CH_3$]; 15.1 (CH_3); *m*/*z* (CI, NH_3) 338 (100%, $[M+NH_4]^+$), 321 (7, $[M+H]^+$), 180 (16, $[M-C_{10}H_{21}O+NH_3]^+$). Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.97; H, 10.07; O, 29.96; Found: C, 60.10; H, 10.38, O, 29.75.

10′-Undecenyl D-*glucofuranoside* (**4e**).—The glycosylation of 10-undecen-1-ol (5.10 g) afforded 1.10 g (16%) of **4e**α as a colourless oil and 2.56 g (39%) of **4e**β as a colourless oil, (α/β = 1:2.6); TLC (9:1 CH_2Cl_2–MeOH): R_f 0.59 (**4e**α) 0.50 (**4e**β); **4e**α: $[\alpha]_D^{20}$ +62 ° (*c* 1.0, MeOH); ^{1}H NMR (CD_3OD): δ 5.80 (ddt, 1 H, J_{cis} 17.2 Hz, J_{trans}

10.1 Hz, ^3J 6.7 Hz, $CH_2=CH$); 5.01 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1); 4.97 (broad dd, 1 H, ^2J 1.3 Hz, $CH_2=CH$); 4.91 (broad d, 1 H, $CH_2=CH$); 4.23 (dd, 1 H, $J_{3,4}$ 5.3 Hz, $J_{3,2}$ 3.9 Hz, H-3); 4.02 (dd, 1 H, $J_{4,5}$ 7.5 Hz, H-4); 3.98 (dd, 1 H, H-2); 3.86–3.82 (m, 1 H, H-5); 3.78–3.71 (m, 2 H, OCH_2, H-6′); 3.60 (dd, 1 H, $J_{6,6'}$ 11.3 Hz, $J_{6,5}$ 6.4 Hz, H-6); 3.48 (dt, 1 H, ^2J 9.6 Hz, ^3J 6.7 Hz, OCH_2); 2.04 (q, 2 H, $CH_2CH=CH_2$); 1.63–1.58 (m, 2 H, OCH_2CH_2); 1.38–1.31 (m, 12 H, CH_2); ^{13}C NMR (CD_3OD): δ 140.1 ($CH_2=CH$); 114.7 ($CH_2=CH$); 103.1 (C-1); 79.2 (C-4); 79.1 (C-2); 77.6 (C-3); 72.0 (C-5); 69.8 (OCH_2); 64.8 (C-6); 34.9 (OCH_2CH_2); 30.7, 30.6, 30.5, 30.2, 30.1, 27.2 [$(CH_2)_7$]; *m/z* (CI, NH_3) 350 (100%, $[M+NH_4]^+$), 333 (18, $[M+H]+$), 180 (53, $[M-C_{11}H_{21}O+NH_3]^+$); **4e**β: $[\alpha]_D^{20}$ −50° (*c* 1.0, MeOH); ^{1}H NMR (CD_3OD) δ 5.80 (ddt, 1 H, J_{cis} 17.0 Hz, J_{trans} 10.2 Hz, ^3J 6.7 Hz, $CH_2=CH$); 4,91 (broad dd, 1 H, ^2J 0.9 Hz, $CH_2=CH$); 4,84 (m, 1 H, H-1); 4.11–4.07 (m, 2 H, H-3, H-4); 4.02 (broad s, 1 H, H-2); 3.95–3.90 (m, 1 H, H-5); 3.80 (dd, 1 H, $J_{6',6}$ 11.5 Hz, $J_{6',5}$ 2.9 Hz, H-6′); 3.69 (dt, 1 H, ^2J 9.5 Hz, ^3J 6.7 Hz, OCH_2); 3.64 (dd, $J_{6,5}$ 5.9 Hz, 1 H, H-6); 3.39 (dt, 1 H, ^3J 6.6 Hz, OCH_2); 2.04 (q, 2 H, $CH_2CH=CH_2$); 1.61–1.53 (m, 2 H, OCH_2CH_2); 1.40–1.30 (m, 12 H, CH_2); ^{13}C NMR (CD_3OD): δ 140.1 ($CH_2=CH$); 114.7 ($CH_2=CH$); 109.9 (C-1); 82.7 (C-4); 81.8 (C-2); 77.3 (C-3); 71.8 (C-5); 69.3 (OCH_2); 65.2 (C-6); 34.9 (OCH_2CH_2); 30.7, 30.6, 30.5, 30.2, 30.1, 27.2 [$(CH_2)_7$]; *m/z* (CI, NH_3) 350 (100%, $[M+NH_4]^+$), 333 (36, $[M+H]^+$), 180 (50, $[M-C_{10}H_{21}O+NH_3]^+$).

12′-Hydroxy-n-*dodecyl* D-*glucofuranoside* (**4f**).—The glycosylation of 1,12-dodecanediol (6.06 g) afforded, after chromatography (4:1 CH_2Cl_2–MeOH) and recrystallization from EtOAc, 2.70 g (37%) of **4f** as an inseparable mixture of anomers. The $\alpha:\beta$ ratio was determined by ^{1}H NMR from the signals corresponding to the anomeric protons (α/β = 1:1.5); TLC (4:1 CH_2Cl_2–MeOH): R_f 0.67 (**4f**α), 0.63 (**4f**β); **4f**α: ^{1}H NMR (CD_3OD) for the anomeric proton: δ 5.04 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1); ^{13}C NMR (CD_3OD): δ 103.7 (C-1); 79.9 (C-4); 79.8 (C-2); 78.4 (C-3); 72.7 (C-5); 70.5 (OCH_2); 65.6 (C-6); 64.0 (CH_2OH); 34.3 (OCH_2CH_2); 31.6, 27.5, 27.9 [$(CH_2)_9$]; **4f**β: ^{1}H NMR (CD_3OD) for the anomeric proton: δ 4.75 (s, 1 H, H-1); ^{13}C NMR (CD_3OD): δ 110.6 (C-1); 83.3 (C-4); 82.4 (C-2); 78.0 (C-3); 72.5 (C-5); 70.0 (OCH_2); 66.0 (C-6); 63.7 (CH_2OH); 34.3 (OCH_2CH_2); 31.7, 27.9, 27.5 [$(CH_2)_9$].

General procedure for the synthesis of alkyl D-*galactofuranosides* (**5**).—This procedure is similar to that described above for D-glucose but using D-galactose (3.60 g, 20 mmol), the appropriate alcohol (30 mmol), $CaCl_2$ (2.22 g, 20 mmol) and $FeCl_3$ (9.72 g, 60 mmol) in THF (30 mL). After 48 h at room temperature and work-up, pure **5a,b**β crystallized out of the crude oil from Et_2O. The filtrate was next concentrated and purified by chromatography eluting with 19:1 CH_2Cl_2–MeOH.

n-*Octyl* D-*galactofuranoside* (**5a**).—The glycosylation of 1-octanol (3.90 g) afforded 0.56 g (10%) of **5a**α and 2.71 g (46%) of **5a**β (α/β = 1:4.9); TLC (9:1 CH_2Cl_2–MeOH): R_f 0.22 (**5a**α) 0.16 (**5a**β); **5a**α: mp 50–52 °C (EtOAc); cp 61 °C; $[\alpha]_D^{20}$ +57° (*c* 1.0, MeOH); ^{1}H NMR (CD_3OD): δ 4.84 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1); 4.09 (dd, 1 H, $J_{3,2}$ 7.7 Hz, $J_{3,4}$ 6.8 Hz, H-3); 3.94 (dd, 1 H, H-2); 3.80 (dt, 1 H, ^2J 9.5 Hz, ^3J 6.9 Hz, OCH_2); 3.72 (dd, $J_{4,5}$ 5.0 Hz, 1 H, H-4); 3.65–3.53 (m, 3 H, H-5, H-6, H-6′); 3.46 (dt, 1 H, ^3J 6.7 Hz, OCH_2); 1.63–1.60 (m, 2 H, OCH_2CH_2); 1.32–1.28 (m, 10 H, CH_2); 0.89 (t, 3 H, *J* 6.8 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 103.5 (C-1); 84.3 (C-4); 79.5 (C-2); 77.1 (C-3); 75.2 (C-5); 70.5 (OCH_2); 64.9 (C-6); 33.2 (OCH_2CH_2); 31.5, 31.3, 31.2, 28.3, 28.0, 24.3 [$(CH_2)_5CH_3$]; 15.2 (CH_3); *m/z* (CI, NH_3) 310 (100%, $[M+NH_4]^+$), 293 (3, $[M+H]^+$), 180 (29, $[M-C_8H_{17}O+NH_3]^+$). Anal. Calcd for $C_{14}H_{28}O_6$: C, 57.51; H, 9.65. Found: C, 57.37; H, 9.84; **5a**β: mp 98–99 °C (EtOAc); cp 127 °C; $[\alpha]_D^{20}$ −91° (*c* 1.0, THF); ^{1}H NMR (CD_3OD, 50 °C) for the anomeric proton: δ 4.86 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1); ^{13}C NMR (CD_3OD): δ 110.0 (C-1); 84.9 (C-4); 84.0 (C-2); 79.5 (C-3); 73.2 (C-5); 69.6 (OCH_2); 65.4 (C-6); 33.7 (OCH_2CH_2); 31.4, 31.2, 31.1, 27.9, 24.4 [$(CH_2)_5CH_3$]; 15.2 (CH_3); *m/z* (CI, NH_3) 310 (100%, $[M+NH_4]^+$), 293 (2, $[M+H]^+$), 180 (10, $[M-C_8H_{17}O+NH_3]^+$). Anal. Calcd for $C_{14}H_{28}O_6$: C, 57.51; H, 9.65; O, 32.84. Found: C, 57.64; H, 9.68; O, 32.51.

n-*Decyl* D-*galactofuranoside* (**5b**).—The glycosylation of 1-decanol (4.74 g) afforded 0.74 g (12%) of **5b**α and 2.78 g (43%) of **5b**β (α/β = 1:3.8); TLC (9:1 CH_2Cl_2–MeOH): R_f 0.42 (**5b**α) 0.35 (**5b**β); **5b**α: mp 63–65 °C (EtOAc); cp 102 °C; $[\alpha]_D^{20}$ +54° (*c* 1.0, THF), lit. +50.9° (*c* 1, MeOH) [13]; ^{1}H NMR (CD_3OD): δ 4.85 (m, H-1, HDO); 4.08 (dd, 1 H, $J_{3,2}$ 7.7 Hz, $J_{3,4}$ 6.8 Hz, H-3); 3,94 (dd, 1 H, $J_{2,1}$ 4.5 Hz, H-2); 3.79 (dt, 1 H, ^2J 9.5 Hz, ^3J 6.9 Hz, OCH_2); 3.72 (dd, 1 H, $J_{4,5}$ 5.0 Hz, H-4); 3.54–3.51 (m, 3 H, H-5, H-6, H-6′); 3.45 (dt, 1 H, ^3J 6.7 Hz,

OCH_2); 1.63–1.58 (m, 2 H, OCH_2CH_2); 1.40–1.30 (m, 14 H, CH_2); 0.89 (t, 3 H, J 6.6 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 103.5 (C-1); 84.2 (C-4); 79.5 (C-2); 77.1 (C-3); 75.1 (C-5); 70.4 (OCH_2); 64.9 (C-6); 33.8 (OCH_2CH_2); 31.4, 31.3, 31.2, 27.9, 24.5 [$(CH_2)_7CH_3$]; 15.3 (CH_3); m/z (CI, NH_3) 338 (100%, $[M+NH_4]^+$), 321 (2, $[M+H]^+$), 180 (19, $[M-C_{10}H_{21}O+NH_3]^+$). Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.97; H, 10.07; O, 29.96. Found: C, 60.35; H, 10.27; O, 29.58; **5b**β: mp 102–103 °C (EtOAc); cp 153 °C; $[\alpha]_D^{20}$ −80° (c 1.0, THF); ^1H NMR (CD_3OD): δ 4.85 (m, H-1, HOD); 4.00 (dd, 1 H, $J_{3,4}$ 6.6 Hz, $J_{3,2}$ 3.9 Hz, H-3); 3.96 (dd, 1 H, $J_{2,1}$ 1.8 Hz, H-2); 3.90 (dd, 1 H, $J_{4,5}$ 3.2 Hz, H-4); 3.73–3.67 (m, 2 H, H-5, OCH_2); 3.68 (broad d, $J_{6,6'}$ 6.1 Hz, 2 H, H-6, H–6′); 3.41 (dt, 1 H, ^2J 9.6 Hz, ^3J 6.6 Hz, OCH_2); 1.60–1.54 (m, 2 H, OCH_2CH_2); 1.40–1.30 (m, 14 H, CH_2); 0.90 (t, 3 H, J 6.7 Hz, CH_3); ^{13}C NMR (CD_3OD); δ 110.1 (C-1); 85.0 (C-4); 84.1 (C-2); 79.5 (C-3); 73.2 (C-5); 69.6 (OCH_2); 65.4 (C-6); 33.8 (OCH_2CH_2); 31.5, 31.3, 31.2, 28.0, 24.5 [$(CH_2)_7CH_3$]; 15.2 (CH_3); m/z (CI, NH_3) 338 (100%, $[M+NH_4]^+$), 180 (20, $[M-C_{10}H_{21}O+NH_3]^+$). Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.97; H, 10.07; O, 29.96. Found: C, 59.81; H, 10.32; O, 29.23.

12′-Hydroxy-n-*dodecyl* D-*galactofuranoside* (**5f**).—The glycosylation of 1,12-dodecanediol (5.34 g) afforded, after chromatography (4:1 CH_2Cl_2–MeOH) and recrystallization from EtOAc, a mixture of inseparable anomers of **5f** (2.70 g, 37%). NMR data was determined from the mixture of both anomers; TLC (4:1 CH_2Cl_2–MeOH): R_f 0.63 (**5f**α), 0.56 (**5f**β); **5f**α: ^1H NMR (CD_3OD, 50 °C) for the anomeric proton: δ 4.86 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1); ^{13}C NMR (CD_3OD): δ 103.5 (C-1); 84.2 (C-4); 79.5 (C-2); 77.1 (C-3); 75.1 (C-5); 64.9 (C-6); 63.7 (CH_2OH); 34.4 (OCH_2CH_2); 31.4, 27.9, 27.6 [$(CH_2)_9$]; **5f**β: ^1H NMR (CD_3OD, 50 °C) for the anomeric proton: δ 4.85 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1); ^{13}C NMR (CD_3OD) δ 110.0 (C-1); 84.9 (C–4); 84.0 (C-2); 79.5 (C-3); 75.2 (C-5); 69.6 (OCH_2); 65.4 (C-6); 63.7 (CH_2OH); 34.4 (OCH_2CH_2); 31.4, 27.9, 27.6 [$(CH_2)_9$]. Anal. Calcd for $C_{18}H_{36}O_7$: C, 59.29; H, 9.97; O, 30.74. Found: C, 59.59; H, 9.89; O, 30.54.

General procedure for the synthesis of alkyl D-*mannofuranosides* (**6**).—This procedure is similar to that described above starting from D-mannose (3.60 g, 20 mmol), the appropriate alcohol (30 mmol) and $FeCl_3$ (9.72 g, 60 mmol) in THF (70 mL). After 48 h at room temperature and work-up, pure **6a,b**α crystallized out of the crude residue from Et_2O. The filtrate was next concentrated and purified by chromatography eluting with 19:1 CH_2Cl_2–MeOH.

n-*Octyl* D-*mannofuranoside* (**6a**).—The glycosylation of 1-octanol (3.90 g) yielded 0.16 g (3%) of **6a**β and 3.20 g (55%) of **6a**α (α/β = 20:1); TLC (9:1 CH_2Cl_2–MeOH): R_f 0.59 (**6a**β) 0.52 (**6a**α); **6a**β: mp 42–43 °C (Et_2O), lit. 38 °C [18]; $[\alpha]_D^{20}$ −75° (c 1.0, MeOH), lit. −71.3° (c 4, MeOH) [18]; ^1H NMR (CD_3OD): δ 4.86 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1); 4.17 (dd, 1 H, $J_{3,2}$ 4.9 Hz, $J_{3,4}$ 3.6 Hz, H-3); 4.06 (t, 1 H, H-2); 3.93–3.89 (m, 2 H, H-4, H-5); 3.80–3.77 (m, 1 H, H-6′); 3.70 (dt, 1 H, ^2J 9.7 Hz, ^3J 6.8 Hz, OCH_2); 3,42 (dt, 1 H, ^3J 6.6 Hz, OCH_2); 1.62–1.56 (m, 2 H, OCH_2CH_2); 1.35–1.25 (m, 10 H, CH_2); 0.90 (t, 3 H, J 6.8 Hz, CH_3); ^{13}C NMR (CD_3OD): δ 103.7 (C-1); 82.1 (C-4); 74.7 (C-2); 72.6, 72.7 (C-3, C-5); 70.4 (OCH_2); 65.5 (C-6); 33.7 (OCH_2CH_2); 31.5, 31.3, 31.1, 28.0, 24.4 [$(CH_2)_5CH_3$]; 15.2 (CH_3); m/z (CI, NH_3) 310 (100%, $[M+NH_4]^+$), 293 (29, $[M+H]^+$), 180 (63, $[M-C_8H_{17}O+NH_3]^+$); **6a**α: mp 98–99 °C (Et_2O–MeOH); cp 100 °C; $[\alpha]_D^{20}$ +80° (c 1.1, THF); ^1H NMR (CD_3OD): δ 4,89 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1); 4.26 (dd, 1 H, $J_{3,2}$ 4.9 Hz, $J_{3,4}$ 4.0 Hz, H-3); 3.99 (dd, 1 H, H-2); 3.92–3.91 (m, 2 H, H-4, H-5); 3.78–3.75 (m, 1 H, H-6′); 3.66 (dt, 1 H, ^2J 9.6 Hz, ^3J 6.6 Hz, OCH_2); 3.59–3.55 (m, 1 H, H-6); 3.41 (dt, 1 H, ^3J 6.6 Hz, OCH_2); 1.62–1.53 (m, 2 H, OCH_2CH_2); 1.37–1.22 (m, 10 H, CH_2); 0.90 (t, 3 H, J 6.8 Hz, CH_3); ^{13}C NMR (CD_3OD) δ 110.0 (C-1); 81.4 (C-4); 79.1 (C-2); 73.5 (C-3); 72.4 (C-5); 70.3 (OCH_2); 65.7 (C-6); 33.8 (OCH_2CH_2); 31.6, 31.3, 31.2, 28.0, 24.5 [$(CH_2)_5CH_3$]; 15.2 (CH_3); m/z (CI, NH_3) 310 (100%, $[M+NH_4]^+$), 293 (5, $[M+H]^+$), 180 (54, $[M-C_8H_{17}O+NH_3]^+$). Anal. Calcd for $C_{14}H_{28}O_6$: C, 57.51; H, 9.65; O, 32.84. Found: C, 57.47; H, 9.52; O, 32.72;.

n-*Decyl* D-*mannofuranoside* (**6b**).—The glycosylation of 1-decanol (4.74 g) afforded 0.10 g (2%) of **6b**β and 3.35 g (52%) of **6b**α (α/β = 30.5:1); TLC (CH_2Cl_2–MeOH): R_f 0.55 (**6b**β) 0.49 (**6b**α); **6b**β: mp 43–44 °C (Et_2O), lit. 45 °C [18]; $[\alpha]_D^{20}$ −59.0° (c 1.0, MeOH), lit. −60.4° (c 1.4, MeOH) [18]; ^{13}C NMR (CD_3OD): δ 103.7 (C-1); 82.0 (C-4); 74.6 (C-2); 72.6, 72.5 (C–3, C-5); 70.4 (OCH_2); 65.4 (C-6); 33.7 (OCH_2CH_2); 31.4, 31.3, 31.1, 28.2, 27.9, 24.4 (CH_2); 15.3 (CH_3); **6b**α: mp 100–101 °C (EtOAc); cp 127 °C; $[\alpha]_D^{20}$ +79° (c 1.0, THF); ^{13}C NMR (CD_3OD): δ 109.2 (C-1); 80.6 (C-4); 78.4 (C-2); 72.8 (C-3); 71.6 (C-5); 69.5 (OCH_2); 64.9 (C-6);

33.1 (OCH_2CH_2); 30.9, 30.8, 30.7, 30.6, 30.5, 27.3, 23.8 [$(CH_2)_7CH_3$]; 14.5 (CH_3); *m/z* (CI, NH_3) 338 (100%, $[M+NH_4]^+$), 321 (2, $[M+H]^+$), 180 (48, $[M-C_{10}H_{21}O+NH_3]^+$). Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.96; H, 10.07. Found: C, 59.73; H, 10.49.

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