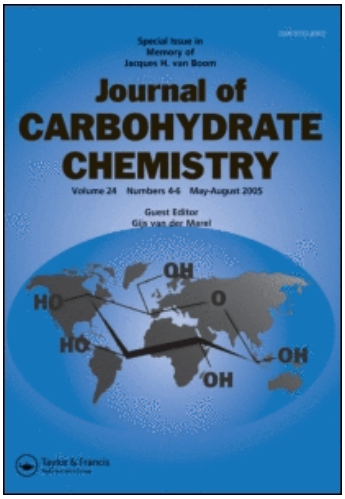

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Synthesis of Ether-Linked Di- and Trisaccharide Derivatives Part II- Functionalization and Potential Applications of Ether-Linked Di- and Trisaccharides Containing d-Glucose

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SYNTHESIS OF ETHER-LINKED DI- AND TRISACCHARIDE DERIVATIVES

Part II- FUNCTIONALIZATION AND POTENTIAL APPLICATIONS OF ETHER-LINKED DI- AND TRISACCHARIDES CONTAINING D-GLUCOSE

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ABSTRACT

We have prepared three series of functionalized disaccharides of the type A(6->n)B and a trisaccharide with the formula A-*O*-B-*O*-C, in which A = D-glucose (or its derivatives) and both B and C are any of D-fructose, D-galactose, D-glucose, xylitol and glycerol (or their derivatives). These compounds resulted from the regiospecific functionalization of either A or B and either the partial or total deprotection of either 6-*O*-(3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl)-3-*O*-alkyl-1,2-*O*-isopropylidene-α-D-glucofuranose or its analogues of type **1** described in part I.[1] We also report results on surface activity and biological properties of some of the molecules prepared.

INTRODUCTION

We have previously described[1] the synthesis of disaccharide substrates with an ether junction having the general formula A(6->n)B. Such compounds are obtained by condensation of an acetal derivative of

B (SuOH) with 3-*O*-alkyl-5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose corresponding to the structure **1** (Scheme 1).

These products can give access to numerous compounds according to functionalizations on, for example, either the site C-5-OH of the D-glucose A unit or unit B (SuOH). One of the functionalizations could be the introduction of a third saccharide unit according to the methodology described in the first part.[1] Either partial or total removal of acetal functions permits regulation of hydrophilicity in accordance with the envisaged applications of the products.

The work reported herein concerns:

- either the partial or total deprotection of type **1** compounds having a lipophilic group R_1 on site C-3 of the D-glucose unit A;

- the derivatisation at site C-5 of the D-glucose unit A, by conversion to either an ether or ester, involving either an alkylated or fluoroalkylated chain R_2, and conversion to the corresponding partially or totally deacetonated products;

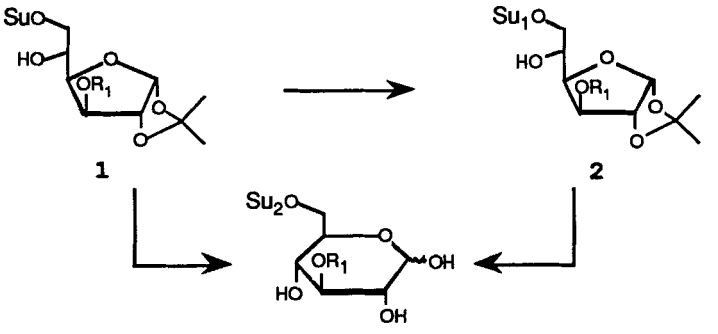
- the introduction on unit B = D-glucose, of either an ester or thioether, involving an alkylated chain R_3 and the attachment of a third D-glucose unit C leading to a trisaccharide compound with the general formula: A-*O*-B-*O*-C;

- surface activity and biological properties of some of the A(6->n)B molecules.

RESULTS and DISCUSSION

A- *Hydrolysis of compounds of type* ***1*** *leading to products of types* ***2*** *and* ***3***.

The deprotection of type **1** compounds was effected according to the relevant sequence of reactions outlined in Scheme 1. Type **2** compounds were obtained in good yields by partial hydrolysis of type **1** derivatives, at 50 °C in a solution of 0.2 N H_2SO_4 in ethanol-water (19:1). Using such conditions, the deprotection of unit B led to **2a** and **2b** (involving deprotection of the 5,6-*O*-isopropylidene group of unit B = D-glucose); **2c** (involving total deprotection of the unit B = xylitol); **2d** (involving deprotection of unit B = glycerol). These products have interesting potential applications; for example, product **2a** is known to be an antagonist of calcium membrane channels[2] and **2b** was found to show



2a: R_1=*n*-C_8H_{17}; Su_1 = 3-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-3-yl

2b: R_1=*n*-$C_{12}H_{25}$; Su_1 = 3-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-3-yl

2c: R_1=*n*-$C_{12}H_{25}$; Su_1 = 1-deoxy-DL-xylit-1-yl

2d: R_1=*n*-$C_{12}H_{25}$; Su_1 = 1-deoxyglycer-1-yl

3a: R_1=*n*-C_8H_{17}; Su_2 = 3-deoxy-D-glucopyranos-3-yl

3b: R_1=*n*-$C_{12}H_{25}$; Su_2 = 3-deoxy-D-glucopyranos-3-yl

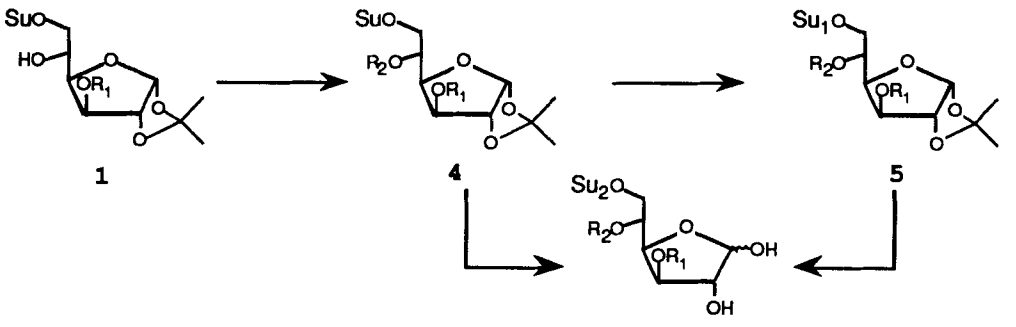
3c: R_1=*n*-C_8H_{17}; Su_2 = 6-deoxy-D-galactos-6-yl

3d: R_1=*n*-$C_{12}H_{25}$; Su_2 = 6-deoxy-D-galactos-6-yl

SCHEME 1

surfactant properties (γ = 33.2 mN/m, CMC = $4.87.10^{-4}$ M at 25 °C). Surfactant properties were also observed for **2c** and **2d** each of which have the same alkyl chain as **2b** and either an equal or a greater number of free OH groups. Also, type **2** compounds have been used in this study as intermediates for further regiospecific derivatisations at the C-6 site of unit B as described in paragraph C.

Products of type **3** were obtained from either type **1** or type **2** substrates by full hydrolysis of type **1** derivatives, at 70 °C in 1 N H_2SO_4 and dioxane-water (3:1); the yields ranged from 45% to 60%. Using these conditions, we did not observe the formation of monosaccharide derivatives. This result illustrates the resistance of ether junction to forcing acid hydrolysis. When the alkyl chain R_1 had more than 8 carbon atoms, the products obtained were found to possess surfactant properties (γ = 33.7 mN/m; CMC = $4.82.10^{-4}$ M at 25 °C for **3b**).



4a: R_1=R_2=*n*-C_8H_{17};	Su = 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl
4b: R_1=CH_2-CH=CH_2; R_2=*n*-C_8H_{17};	Su = 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl
4c: R_1=CH_2-CH=CH_2; R_2=*n*-C_8H_{17};	Su = 1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranos-1-yl
4d: R_1=R_2=*n*-$C_{12}H_{25}$;	Su = 3-deoxy-1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranos-3-yl
4e: R_1=R_2=*n*-$C_{12}H_{25}$;	Su = 1-deoxy-2,3:4,5-di-*O*-isopropylidene-DL-xylit-1-yl
4f: R_1=*n*-$C_{12}H_{25}$; R_2=$CH_2SC_2H_4C_4F_9$;;	Su = 1-deoxy-2,3:4,5-di-*O*-isopropylidene-DL-xylit-1-yl
4g: R_1=*n*-$C_{12}H_{25}$; R_2=$COC_2H_4C_8F_{17}$;	Su = 1-deoxy-2,3:4,5-di-*O*-isopropylidene-DL-xylit-1-yl
5a: R_1=R_2=*n*-$C_{12}H_{25}$;	Su_1 = 3-deoxy-1,2-*O*-isopropylidene-β-D-fructopyranos-3-yl
5b: R_1=R_2=*n*-$C_{12}H_{25}$;	Su_1 = 1-deoxy-DL-xylit-1-yl
5c: R_1=*n*-$C_{12}H_{25}$; R_2=$COC_2H_4C_8F_{17}$;	Su_1 = 1-deoxy-DL-xylit-1-yl
6a: R_1=R_2=*n*-$C_{12}H_{25}$;	Su_2 = 3-deoxy-D-glucopyranos-3-yl
6a: R_1=R_2=*n*-$C_{12}H_{25}$;	Su_2 = 1-deoxy-DL-xylit-1-yl

SCHEME 2

B- *Disaccharide compounds of type* ***4***, ***5*** *and* ***6*** *with two substituents on the D-glucose unit A.*

Compounds of type **1** were found to be easily converted to derivatives having a second substituent at site C-5 of unit A, in accordance with the sequence outlined in Scheme 2.

The first step was the introduction of the R_2 group leading to type **4** compounds. This was effected by either etherification with the corresponding alkyl bromides in toluene-DMSO in the presence of KOH[3] or esterification with the corresponding acid chloride in toluene in the presence of TEA:[4] compounds of type **4** were obtained in yields ranging from 55 to 82%.

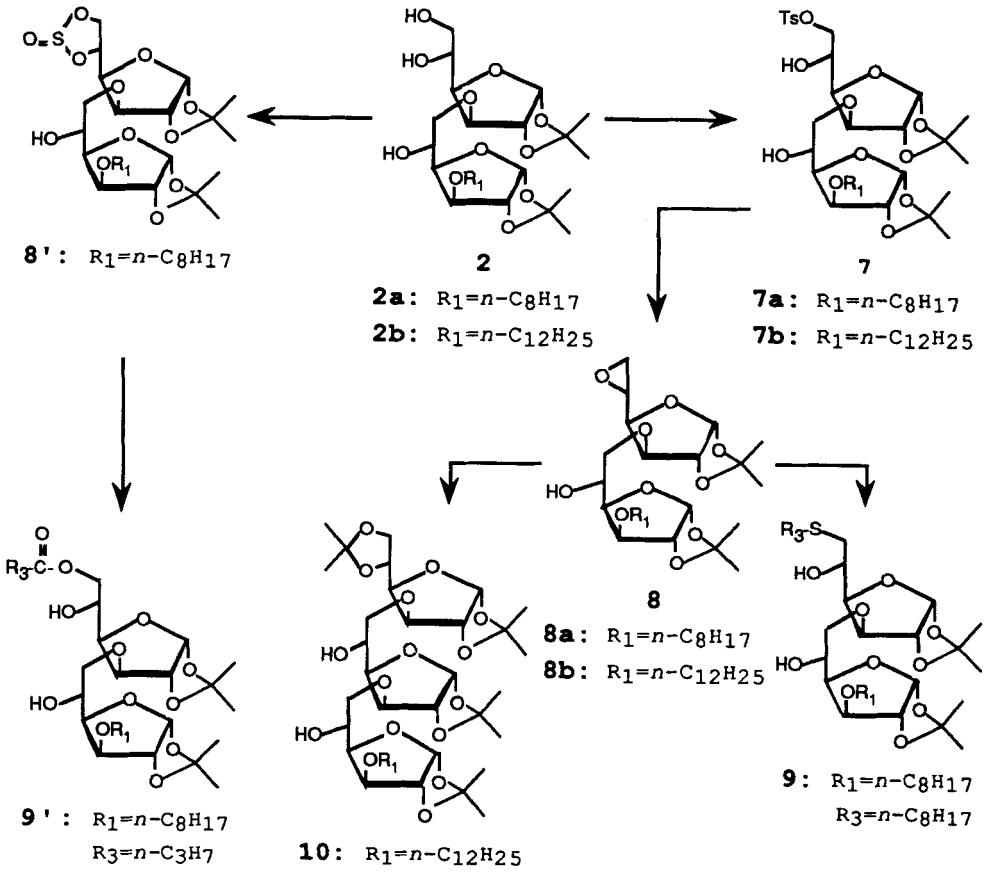
Products of type **5** (involving selective deprotection of unit B) were prepared using the conditions previously described for type **2** products: **5a, 5b** and **5c,** are characterized by two lipophilic groups R_1 and R_2 on the D-glucose unit and two or four free OH groups on the B unit.

Products of type **6** (involving total deprotection of the two saccharide units) were obtained using the conditions described for the synthesis of products of type **3**. In these products, unit A has necessarily a glucofuranose configuration whereas those of type **3** can take the glucopyranose configuration. Also prepared, were compounds **6a** and **6b** which are composed of two D-glucose units linked together and a D-glucose unit linked to a xylitol unit respectively. These products were found to be more hydrophilic than their precursors which are of type **5** (6 free OH groups instead of 4).

*C- Compounds of type **9, 9'** and **10** resulting from the attachment of either an alkyl substituent (R_3) or a monosaccharide on unit B.*

Deprotection of compounds of types **1** and **4** liberates two OH groups, as in the case of either **2a** and **2b** (SuOH = 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) or **2d** (2,3-*O*-isopropylidene-glycerol), a substituent R_3 identical to R_1, R_2 or a third glucide unit (C) can be readily introduced on to unit B. Scheme 3 identifies some of the di- and trisaccharides obtained by etherification, thioetherification and esterification, respectively, of the disaccharides **2a** and **2b** (A = B = D-glucose).

Regiospecific substitutions on the second D-glucose unit (B) require appropriate activation of compounds of either type **2a** or **2b**. This was achieved by conversion to either the anhydro derivatives **8** or cyclic sulfite derivative **8'**. Anhydro derivatives **8** were obtained with overall yields higher than 60% using the conditions described in Part I.[1] The **8a** derivative (R_1 = *n*-C_8H_{17}) led regiospecifically to the thioether **9** in 70% yield, by addition of the corresponding thiol in the presence of LiCl in toluene.



SCHEME 3

Similarly **8b** (R_1 = n-$C_{12}H_{25}$) was condensed with diacetone glucose (2 equiv) in toluene-DMSO (1:1) using KOH as the base (5 equiv) to afford the trisaccharide derivative **10** in 61% yield. The ^{13}C NMR signals for C-6 and C-5 were found to be similar to those observed for compounds of type **1** (Δ 0.7-1.2 ppm (C-5) and Δ 0.6-0.9 ppm(C-6)). Such evidence was supportive of the structure assigned to **10**. The latter reaction also gave two products, in small proportions: one probably resulted from the condensation of compound **10** with substrate **8b** and the other from the intramolecular attack of C-5-O^- group on carbon C-6 of the anhydro site of **8b**.

The 5,6-cyclic sulfite **8'** was obtained in 71% yield by reaction of thionyl chloride with the compound **2a**.[5-7] The resultant compound **8'** led

regiospecifically to the butyric ester **9'** in 88% yield, by treatment with sodium butyrate at 110 °C in toluene-DMSO (1:1). This product **8'** is analogous to 3-*O*-butanoyl- and 6-*O*-butanoyl-1,2-*O*-isopropylidene-α-D-glucofuranose[8] which were found to exhibit antitumour activity resulting from latent release[9] of *n*-butyric acid at the tumour site.[10] Other esters of the type **9'** were also prepared by direct esterification of the type **2** compounds with more bulky acylating agents.

CONCLUSIONS

This work has shown that type **1** disaccharides can be efficiently used to synthesize a variety of regiospecifically substituted disaccharides, involving either the same type or another type of glucidic unit. Also, the ether junction in such derivatives is particularly resistant to severe hydrolytic conditions.

Facile methods were used to introduce substituents by the formation of esters or thioethers having alkyl or fluoroalkyl chains. All type **1** compounds investigated could be derivatised at site C-5 of unit A = D-glucose, with the introduction of a group R_2 by either direct esterification or etherification. A selective deacetalation strategy has been devised for unit B (B = D-glucose or glycerol for example), such that the substituent R_3 can be regiospecifically introduced. This route was shown to give trisaccharide compounds of type A-*O*-B-*O*-C, in the case where R_3 is a derivative of a glucide unit C.

Surfactant properties were observed for compounds **2b** and **3b** (A = B = D-glucose); each has the same lipophilic chain (R_1 = *n*-$C_{12}H_{25}$) but differ by having 3 and 7 free OH groups respectively. Similar properties were observed for the other type **2** and type **3** compounds. It is noteworthy that for these compounds, the choice of unit B and the number of free hydroxyls made available by deprotection of acetal groups allows control of hydrophilicity within the respective series of products. Thus the number (p) of free OH groups can be: p=3 for **2a**, **2b** and **2d**; p=5 for **2c**, p=7 for **3a**, **3b**, **3c** and **3d**. Such flexibility affords a large choice of potential applications. Compounds of types **4** and **5** also have amphipathic character which is a requirement for surfactant applications. Furthermore, it is known that the localization of hydrophobic groups, of the type R_1 and R_2, on the same glucidic unit can lead to the formation of vesicles.[11]

Some of the products described herein possess interesting biological properties. We have observed that **2a** is an antagonist of calcium membrane channels and the butyric ester **9'** has potential antitumour activities.

EXPERIMENTAL

General Procedures. Reactions were monitored by either HPLC (Waters 721), using either of the reverse phase columns RP-18 (Merck) or PN 27-196 (Waters) or GLC (Girdel) with either of the columns OV 17 or SE 30. Preparative chromatography was performed on silica gel (Matrex 60 mesh) with a hexane-acetone gradient. Specific rotations were determined with a JASCO-DIP 970 polarimeter (Prolabo) and melting points with an electrothermal automatic apparatus. ^{13}C NMR spectra were recorded using a Brücker WP 300 spectrometer. The ^{13}C signal assignment of the C_2, C_3, C_4 carbons of the D-glucose moiety for compounds **2-10,** as well as that of the C_1 carbons when both monosaccharide units are D-glucose, can result in problems of interpretation because the chemical shifts are very close.

Type **1** disaccharide derivatives,namely, **6-O-(3-deoxy-1,2:5,6-di-O-isopropylidene-α-D-glucofuranos-3-yl)-3-O-alkyl-1,2-O-isopropylidene-α-D-glucofuranose (1a** (R1=*n*-C_8H_{17}); **1'a** (R1=*n*-$C_{12}H_{25}$)), **6-O-(6-deoxy-1,2:3,4-di-O-isopropylidene-α-D-galacto-pyranos-6-yl)-3-O-alkyl-1,2-O-α-D-(1b** (R1=*n*-C_8-H_{17}); **1'b** (R1=*n*-$C_{12}H_{25}$)), **6-O-(1-deoxy-2,3:4,5-di-O-isopropylidene-β-D-fructo-pyranos-1-yl)-3-O-dodecyl-1,2-O-isopropylidene-α-D-glucofura-nose (1c), 6-O-(3-deoxy-1,2:4,5-di-O-isopropylidene-β-D-fruc-topyranos-3-yl)-3-O-dodecyl-1,2-O-isopropylidene-α-D-glucofu-ranose (1d), 6-O-(1-deoxy-2,3:4,5-di-O-isopropylidene-DL-xylit-1-yl)-3-O-dodecyl-1,2-O-isopropylidene-α-D-glucofuran-ose (1e) 6-O-(1-deoxy-2,3-O-isopropylidene-DL-glycer-1-yl)-3-O-dodecyl-1,2-O-isopropylidene-α-D-glucofuranose (1f),** were synthesized in accordance with the method described in part I.[1]

6-O-(3-deoxy-1,2-O-isopropylidene-α-D-glucofuranos-3-yl)-1,2-O-isopropylidene-3-O-octyl-α-D-glucofuranose (2a). Compound **1a** (34.5 g, 60 mmol) was added to a stirred 0.2 N sulfuric acid solution in ethanol-water (19:1) (300 mL) at 50 °C. The reaction was monitored by HPLC until 95% of conversion was observed and then sodium hydroxide was added

to effect neutralization. The residue yielded, after silica gel column eluted with hexane-acetone (7:3), 25.9 g (81%) of **2a** as a syrup; $[\alpha]_D^{25}$ -35.1° (*c* 1.2, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (105.1), C_2 (82.1), C_3 (82.1), C_4 (79.9), C_5 (69.2), C_6 (72.8), $C_{1'}$ (105.4), $C_{2'}$ (82.0), $C_{3'}$ (82.5), $C_{4'}$ (80.1), $C_{5'}$ (68.0), $C_{6'}$ (64.5), 2xCMe_2 (2x111.8), 4xCH_3 (26.0-26.7), C_α (70.6), C_β (31.7), 5xCH_2 (29.5-22.5), CH_3 (14.1).

Anal. Calcd for $C_{26}H_{46}O_{11}$ (534.6): C, 57.45; H, 8.88. Found: C, 57.75; H, 8.78.

6-*O*-(3-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-3-yl)-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (2b). The above procedure was applied to **1'a** (31.1 g, 49.3 mmol) to yield 21.8 g (75%) of **2b** as a syrup, after elution on a silica gel column with hexane-acetone (3:1); $[\alpha]_D^{25}$ -36.9° (*c* 1.1, $CHCl_3$). The ^{13}C NMR spectrum of the glucosyl moieties was identical to that of **2a**.

Anal. Calcd for $C_{30}H_{54}O_{11}$ (590.7): C, 61.00; H, 9.21. Found: C, 60.78; H, 9.52.

6-*O*-(1-deoxyxylit-1-yl)-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (2c). Likewise, **1e** (2.2 g, 3.65 mmol) gave 1.6 g (84%) of **2c** as a syrup, after elution on a silica gel column with acetone; $[\alpha]_D^{25}$ -15.9° (*c* 1.0, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.5), C_2 (81.4), C_3 (81.1), C_4 (79.7), C_5 (66.3), C_6 (73.5), $C_{1'}$ (69.7), $C_{2'}$ (72.1), $C_{3'}$ (72.1), $C_{4'}$ (70.4), $C_{5'}$ (62.6), CMe_2 (110.5), 2xCH_3 (25.9-26.5), C_α (72.7), C_β (31.2), 9xCH_2 (29.5-22.0), CH_3 (13.8).

Anal. Calcd for $C_{26}H_{50}O_{10}$ (522.7): C, 59.75; H, 9.64. Found: C, 59.65; H, 9.70.

6-*O*-(1-deoxyglycer-1-yl)-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (2d). Likewise, **1f** (3.4 g, 6.76 mmol) gave 2.3 g (74%) of **2d** as a syrup, after elution on a silica gel column with hexane-acetone (7:3); $[\alpha]_D^{25}$ -20.4° (*c* 1.3, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.0), C_2 (81.2), C_3 (81.2), C_4 (78.4), C_5 (66.7), C_6 (71.7), $C_{1'}$ (69.7), $C_{2'}$ (70.0), $C_{3'}$ (62.7), CMe_2 (110.7), 2xCH_3 (25.2-25,1), C_α (72.4), C_β (30.9), 9xCH_2 (29.5-22.5), CH_3 (13.1).

Anal. Calcd for $C_{24}H_{46}O_8$ (462.6): C, 62.31; H, 10.02. Found: C, 62.55; H, 9.95.

6-*O*-(3-deoxy-D-glucopyranos-3-yl)-3-*O*-octyl-D-glucopyranose (3a). Compound **1a** (2.6 g, 4.52 mmol) was added to a stirred 1 N sulfuric acid solution in dioxane-water

(3:1) (300 mL) at 70 °C. The reaction was monitored by HPLC until 95% of conversion was observed. Sodium hydroxide solution was then added to effect neutralization. The residue yielded, after elution on a silica gel column with acetone-ethanol (4:1), 1.4 g (68%) of **3a**: mp 84-89 °C; $[\alpha]_D^{25}$ +25.2° (*c* 1.3, CH_3OH). The ^{13}C NMR showed C_1; $C_{1'}$: 96.9; 96.8 for β-anomers, C_1; $C_{1'}$: 92.3; 92.1 for α-anomers.

Anal. Calcd for $C_{20}H_{38}O_{11}$ (454.5): C, 52.85; H, 8.43. Found: C, 53.10; H, 8.28.

6-*O*-(3-deoxy-D-glucopyranos-3-yl)-3-*O*-dodecyl-D-glucopyranose (3b). The above procedure was applied to **1'a** (2.2 g, 3.49 mmol) to yield 0.94 g (53%) of **3b** after elution on a silica gel column with acetone-ethanol (4:1): mp 155-195 °C; $[\alpha]_D^{25}$ +40.1° (*c* 1.1, CH_3OH). The ^{13}C NMR spectrum of the glucosyl moieties was identical to that of **3a**.

Anal. Calcd for $C_{24}H_{42}O_{11}$ (510.6): C, 56.90; H, 8.35. Found: C, 56.50; H, 8.45.

6-*O*-(6-deoxy-D-galactos-6-yl)-3-*O*-octyl-D-glucopyranose (3c). Likewise, **1b** (3.5 g, 6.1 mmol) gave 1.45 g (52%) of **3c** after elution on a silica gel column with acetone-ethanol (4:1): mp 147-150 °C; $[\alpha]_D^{25}$ +26.5° (*c* 1.3, CH_3OH). The ^{13}C NMR showed C_1 (96.7 β-anomer; 92.1 α-anomer), $C_{1'}$ (97.2 β-pyranic anomer; 92.1 α-pyranic anomer; 95.5 α-furanic anomer).

Anal. Calcd for $C_{20}H_{38}O_{11}$ (454.5): C, 52.85; H, 8.43. Found: C, 52.49; H, 8.55.

6-*O*-(6-deoxy-D-galactos-6-yl)-3-*O*-dodecyl-D-glucopyranose (3d). Likewise, **1'b** (3.5 g, 5.556 mmol) gave 1.2 g (42%) of **3d** after elution on a silica gel column with acetone-ethanol (4:1): mp 210-220 °C; $[\alpha]_D^{25}$ +37.1° (*c* 1.3, CH_3OH). The ^{13}C NMR spectrum of the glycosyl moieties was identical to that of **3c**.

Anal. Calcd for $C_{24}H_{42}O_{11}$ (510.6): C, 56.90; H, 8.35. Found: C, 56.50; H, 8.45.

6-*O*-(3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl)-3,5-di-*O*-octyl-1,2-*O*-isopropylidene-α-D-glucofuranose (4a). Powdered KOH (2.7 g, 48.2 mmol), anhydrous Na_2SO_4 and *n*-bromooctane (4.6 g, 23.96 mmol) were added to a stirred solution of **1a** (11.5 g, 20 mmol) in toluene-DMSO (1:1) (120 mL). After 10 h at 50 °C, the mixture was filtered and neutralized with a saturated solution of NH_4Cl. The aqueous phase was extracted with toluene and the solvent evaporated

under vacuum. The residue was purified on a silica gel column eluted with hexane-acetone (97:3) to yield 10.9 g (80%) of **4a** as a syrup; $[\alpha]_D^{25}$ -32.9° (*c* 1.0, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.1), C_2 (81.6), C_3 (80.8), C_4 (80.8), C_5 (77.7), C_6 (69.2), $C_{1'}$ (104.0), $C_{2'}$ (81.5), $C_{3'}$ (80.8), $C_{4'}$ (74.4), $C_{5'}$ (71.4), $C_{6'}$ (66.1), 3xCMe_2 (110.6; 110.6; 107.8), 6xCMe_2 (25.8; 25.1), 2xC_α (70.4), 2xC_β (30.8); 5xCH_2 (29.3-21.6), CH_3 (13.0).

Anal. Calcd for $C_{37}H_{66}O_{11}$ (686.9): C, 64.69; H, 9.68. Found: C, 64.90; H, 9.61.

6-*O*-(3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl)-3-*O*-allyl-1,2-*O*-isopropylidene-5-*O*-octyl-α-D-glucofuranose (4b). The above procedure was applied to the allyl derivative **1'a** (2 g, 3.98 mmol) and *n*-bromooctane (0.9 g, 4.7 mmol) to yield 1.5 g (61%) of **4b** as a syrup, after elution on a silica gel column with hexane-acetone (9:1); $[\alpha]_D^{25}$ +30.8° (*c* 1.1, $CHCl_3$). The ^{13}C NMR spectrum of the glucosyl moieties was identical to that of **4a** R_1= CH_2-CH=CH_2: C_α (71.1), C_β (133.9), C_γ (117.1).

Anal. Calcd for $C_{32}H_{54}O_{11}$ (614.7): C, 62.52; H, 8.85. Found: C, 62.80; H, 8.75.

6-*O*-(1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranos-1-yl)-3-*O*-allyl-5-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (4c). Likewise, **1c** (1.38 g, 2.2 mmol) and allyl bromide (0.32 g, 2.6 mmol) gave 0.9 g (61%) of **4c** as a syrup, after elution on a silica gel column with hexane-acetone (41:4); $[\alpha]_D^{25}$ -31.4° (*c* 0.8, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (105.0), C_2 (81.8), C_3 (81.8), C_4 (79.05), C_5 (75.4), C_6 (73.6), $C_{1'}$ (72.9), $C_{2'}$ (102.6), $C_{3'}$ (69.8), $C_{4'}$ (70.2), $C_{5'}$ (71.0), $C_{6'}$ (60.9), 3xCMe_2 (111.4; 108.8; 108.4), 6xCH_3 (26.7-24.0), C_α (70.2), C_β (31.7), 9xCH_2 (29.5-22.6), CH_3 (13.9), $C_{\alpha'}$ (71.7), $C_{\beta'}$ (135.2), $C_{\gamma'}$ (115.8).

Anal. Calcd for $C_{36}H_{62}O_{11}$ (670.9): C, 64.45; H, 9.31. Found: C, 64.18; H, 9.42.

6-*O*-(3-deoxy-1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranos-3-yl)-3,5-di-*O*-dodecyl-1,2-*O*-isopropylidene -α-D-glucofuranose (4d). Likewise, **1d** (2.4 g, 3.8 mmol) and dodecyl bromide (1.14 g, 4.6 mmol) gave 1.87 g (62%) of **4d** as a syrup, after elution on a silica gel column with hexane-acetone (19:1). $[\alpha]_D^{25}$ -53.6° (*c* 0.7, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ:

C_1 (105.0), C_2 (81.8), C_3 (81.8), C_4 (78.8), C_5 (75.7), C_6 (72.1), $C_{1'}$ (71.8), $C_{2'}$ (104.4), $C_{3'}$ (77.6), $C_{4'}$ (77.7), $C_{5'}$ (73.6), $C_{6'}$ (60.2), 3x*C*Me$_2$ (111.8; 111.3; 108.7), 6x*C*H$_2$ (28.5-25.9), 2xC_α (70.5; 70.1), 2xC_β (31.8); 18x*C*H$_2$ (30.3-22.5), 2x*C*H$_3$ (13.9).

Anal. Calcd for $C_{45}H_{82}O_{11}$ (799.1): C, 67.63; H, 10.34. Found: C, 67.80; H, 10.22.

6-*O*-(1-deoxy-2,3:4,5-di-*O*-isopropylidene-DL-xylit-1-yl)-3,5-di-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (4e). Likewise, **1e** (2.1 g, 3.48 mmol) and dodecyl bromide (1.3 g, 5.24 mmol) gave 2.2 g (82%) of **4e** as a syrup, after elution on a silica gel column with hexane-acetone (49:1); $[\alpha]_D^{25}$ -14.7° (*c* 1.4, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.0), C_2 (80.8), C_3 (80.7), C_4 (77.8), C_5 (77.5), C_6 (71.6), $C_{1'}$ (70.9), $C_{2'}$ (75.6; 75.3), $C_{3'}$ (74.7), $C_{4'}$ (74.2), $C_{5'}$ (64.8), 3x*C*Me$_2$ (110.5; 2x108.5), 6x*C*H$_2$ (24.3-26.6), 2xC_α (69.9), 2xC_β (30.9), 5x*C*H$_2$ (29.5-21.7), *C*H$_3$ (13.9).

Anal. Calcd for $C_{44}H_{82}O_{11}$ (771.1): C, 68.53; H, 10.72. Found: C, 68.61; H, 10.70.

6-*O*-(1-deoxy-2,3:4,5-di-*O*-isopropylidene-DL-xylit-1-yl)-3-*O*-dodecyl-1,2-*O*-isopropylidene-5-*O*-(methyl-thio-[(F-butyl)-ethyl])-α-D-glucofuranose (4f). Likewise at room temperature, **1e** (4.1 g, 6.8 mmol) and methyl-thio-(F-butyl)ethyl bromide (3.04 g, 8 mmol) gave 3.3 g (54%) of **4f** as a syrup, after elution on a silica gel column with hexane-acetone (17:3); $[\alpha]_D^{25}$ -10.5° (*c* 1.4, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (103.9), C_2 (80.7), C_3 (80.4), C_4 (77.7), C_5 (73.1), C_6 (72.0), $C_{1'}$ (70.9), $C_{2'}$ (77.4), $C_{3'}$ (75.1), $C_{4'}$ (74.4), $C_{5'}$ (64.7), 3x*C*Me$_2$ (110.6; 108.5; 108.5), 6x*C*H$_2$ (24.3-26.6), C_α (72.2), C_β (30.8), -*O*-*C*H$_2$-S (68.9), *C*H$_2$-CF$_2$ (30.2), -S-*C*H$_2$ (21.6).

Anal. Calcd for $C_{39}H_{63}O_{10}F_9S$ (894.9): C, 52.34; H, 7.09; F, 19.10. Found: C, 52.50; H, 7.19; F: 19.19.

6-*O*-(1-deoxy-2,3:4,5-di-*O*-isopropylidene-DL-xylit-1-yl)-3-*O*-dodecyl-5-*O*-[(F-octyl)-propionyl]-1,2-*O*-isopropylidene-α-D-glucofuranose (4g). (F-octyl)-propionyl chloride (3.25 g, 6.26 mmol) was added to a stirred solution of **1e** (3.2 g, 5.3 mmol) in toluene in the presence of TEA at 60 °C. After 4 h, the mixture was extracted and yielded, after silica gel column chromatography (hexane-acetone 97:3); 4.4 g (77%) of **4g** as a syrup. $[\alpha]_D^{25}$ -9.7° (*c* 1.5, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.2), C_2 (80.7), C_3

(80.6), C_4 (77.7), C_5 (69.0), C_6 (70.6), $C_{1'}$ (69.6), $C_{2'}$ (76.9; 76.6), $C_{3'}$ (75.4; 75.3), $C_{4'}$ (74.8; 74.7), $C_{5'}$ (64.7), 3xCMe_2 (110.7; 108.6; 108.6), 6xCH_2 (25.9-26.6), C_α (69.6), C_β (330.9), 5xCH_2 (29.5-21.6), CH_3 (13.0), C=O (166.7), CH_2CF_2 (25.0).

Anal. Calcd for $C_{43}H_{61}O_{11}F_{17}$ (1076.9): C, 47.96; H, 5.66; F, 29.99. Found: C, 48.21; H, 5.60; F, 30.08.

6-*O*-(3-deoxy-1,2-*O*-isopropylidene-β-D-fructopyranos-3-yl)-3,5-di-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (5a). The method described for the synthesis of **2a** applied to **4d** (1.73 g, 2.16 mmol) gave 1.2 g (72%) of **5a** as a syrup, after elution on a silica gel column with hexane-acetone (7:3); $[\alpha]_D^{25}$ -75.6° (*c* 0.8, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (105.4), C_2 (81.9), C_3 (81.4), C_4 (78.6), C_5 (74.9), C_6 (71.8), $C_{1'}$ (71.3), $C_{2'}$ (104.7), $C_{3'}$ (77.5), $C_{4'}$ (70.9), $C_{5'}$ (69.1), $C_{6'}$ (63.4), 2xCMe_2 (112.1; 111.8), 4xCH_3 (27.0-25.8), 2xC_α (69.8; 70.3), 2xC_β (31.8), 18xCH_2 (30.0-22.6), 2xCH_3 (13.9).

Anal. Calcd for $C_{42}H_{78}O_{11}$ (759): C, 66.46; H, 10.35. Found: C, 66.66; H, 10.25.

6-*O*-(1-deoxyxylit-1-yl)-3,5-di-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (5b). Likewise, **4e** (3.7 g, 4.8 mmol) gave 2.5 g (75%) of **5b** as a syrup, after elution on a silica gel column with hexane-acetone (13:7); $[\alpha]_D^{25}$ -24.6° (*c* 1.1, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.8), C_2 (81.6), C_3 (81.6), C_4 (78.6), C_5 (74.9), C_6 (72.5), $C_{1'}$ (70.3), $C_{2'}$ (71.3), $C_{3'}$ (70.4), $C_{4'}$ (70.7), $C_{5'}$ (63.8), CMe_2 (111.6), 2xCH_3 (25.9-26.5), C_α (70.1), C_β (31.8), 9xCH_2 (29.5-22.5), CH_3 (13.9).

Anal. Calcd for $C_{38}H_{71}O_{10}$ (691): C, 66.05; H, 10.79. Found: C, 66.15; H, 10.78.

6-*O*-(1-deoxyxylit-1-yl)-3-*O*-dodecyl-5-*O*-[(F-octyl)-propionyl]-1,2-*O*-isopropylidene-α-D-glucofuranose (5c). Likewise, **4g** (1.4 g, 1.3 mmol) gave 0.8 g (62%) of **5c** as a syrup, after elution on a silica gel column with hexane-acetone (3:7); $[\alpha]_D^{25}$ -9.0° (*c* 1.2, CH_3OH). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.6), C_2 (80.9), C_3 (80.9), C_4 (76.5), C_5 (69.8), C_6 (72.8), $C_{1'}$ (69.5), $C_{2'}$ (72.1), $C_{3'}$ (70.3), $C_{4'}$ (70.3), $C_{5'}$ (62.6), CMe_2 (110.9), 2xCH_3 (25.8-26.3), C_α (69.3), C_β (31.2), 5xCH_2 (29.0-21.7), CH_3 (12.8), C=O (169.2), CH_2CF_2 (25.2).

Anal. Calcd for $C_{37}H_{53}O_{11}F_{17}$ (996.8): C, 44.58; H, 5.36; F, 32.40. Found: C, 44.90; H, 5.25; F, 32.28.

6-*O*-(3-Deoxy-D-glucopyranos-3-yl)-3,5-di-*O*-octyl-D-glucofuranose (6a). The method described for the synthesis of **3a** applied to **4a** (4 g, 5.82 mmol) gave 2.1 g (64%) of **6a** after elution on a silica gel column with acetone; $[\alpha]_D^{25}$ +17.5° (*c* 1.1, CH_3OH). The ^{13}C NMR spectrum showed C_1 (103.4 β-anomer; 97.2 α-anomer), $C_{1'}$ (96.7 β-anomer; 92.2 α-anomer).

Anal. Calcd for $C_{24}H_{42}O_{11}$ (566.7): C, 59.34; H, 9.60. Found: C, 59.09; H, 9.75.

6-*O*-(1-deoxy-DL-xylit-1-yl)-3,5-di-*O*-dodecyl-D-glucofuranose (6b). Likewise, **4e** (4.5 g, 5.83 mmol) gave 2.6 g (68%) of **6b** after elution on a silica gel column with acetone-ethanol (4:1); $[\alpha]_D^{25}$ -14.0° (*c* 1.2, CH_3OH). The ^{13}C NMR spectrum showed C_1 (103.4 β-anomer; 97.2 α-anomer).

Anal. Calcd for $C_{35}H_{70}O_{10}$ (650.9): C, 64.98; H, 10.84. Found: C, 64.69; H, 10.78.

6-*O*-(3-deoxy-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-glucofuranos-3-yl)-1,2-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranose (7a). Compound **7a** was synthesized, in accordance with the method described in Part I[1] for monosaccharides, from *p*-toluenesulphonyl chloride (8 g, 42 mmol) and **2a** (18.7 g, 35 mmol). After purification, 18 g (75%) of **7a** were obtained as a syrup; $[\alpha]_D^{25}$ -21.8° (*c* 1.2, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (105.1), C_2 (81.9), C_3 (81.6), C_4 (79.2), C_5 (67.8), C_6 (72.5), $C_{1'}$ (104.7), $C_{2'}$ (83.2), $C_{3'}$ (81.8), $C_{4'}$ (79.4), $C_{5'}$ (66.7), $C_{6'}$ (72.0), 2xCMe_2 (111.5; 111.6), 4xCH_3 (25.9; 26.8), C_α (70.3), C_β (31.5), 5xCH_2 (29.3-22.3), CH_3 (13.9), C'_1 (144.4), C_{ortho} (129.5), C_{meta} (127.7), C_{para} (132.5), CH_3 (21.2).

Anal. Calcd for $C_{33}H_{52}O_{13}S$ (688.6): C, 57.55; H, 7.61. Found: C, 57.85; H, 7.49.

6-*O*-(3-deoxy-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-glucofuranos-3-yl)-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (7b). Likewise, *p*-toluenesulphonyl chloride (7.6 g, 39.9 mmol) and **2b** (19.5 g, 33 mmol) yielded 18 g (73%) of **7b** as a syrup, after elution on a silica gel column with hexane-acetone mixture (4:1); $[\alpha]_D^{25}$ -24.6° (*c* 1.2, $CHCl_3$). The ^{13}C NMR spectrum of the glucosyl moieties was identical to that of **7a**.

Anal. Calcd for $C_{37}H_{60}O_{13}S$ (744.8): C, 59.66; H, 8.12. Found: C, 60.01; H, 8.02.

6-*O*-(5,6-anhydro-3-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-3-yl)-1,2-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranose

(8a). Compound **8a** was synthesized in accordance with the method described in Part I[1] for monosaccharides, from NaOH (2.3 g, 57.5 mmol) and **7a** (16.5 g, 23.9 mmol). After 1 h at room temperature, the resulting residue was chromatographed on a silica gel column eluted with hexane-acetone (24:1) to yield 11.7 g (95%) of **8a** as a syrup; $[\alpha]_D^{25}$ -44.0° (*c* 1.0, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.9), C_2 (83.2), C_3 (82.1), C_4 (81.0), C_5 (67.9), C_6 (72.3), $C_{1'}$ (104.7), $C_{2'}$ (82.2), $C_{3'}$ (81.8), $C_{4'}$ (79.2), $C_{5'}$ (47.9), $C_{6'}$ (46.6), 2xCMe_2 (111.2; 111.4), 4xCH_3 (25.8-26.4), C_α (70.3), C_β (31.5), 5xCH_2 (29.5-22.2), CH_3 (13.7).

Anal. Calcd for $C_{26}H_{44}O_{10}$ (516.6): C, 60.45; H, 8.58. Found: C, 60.60; H, 8.39.

6-*O*-(5,6-anhydro-3-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-3-yl)-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (8b). Likewise, NaOH (2.2 g, 55 mmol) and **7b** (17.2 g, 23 mmol) yielded 12.2 g (92%) of **8b** as a syrup, after elution on a silica gel column with hexane-acetone mixture (97:3); $[\alpha]_D^{25}$ -46.1° (*c* 1.0, $CHCl_3$). The ^{13}C NMR spectrum of the glucosyl moieties was identical to that of **8a**.

Anal. Calcd for $C_{30}H_{52}O_{10}$ (572.7): C, 62.91; H, 9.15. Found: C, 63.19; H, 9.08.

6-*O*-(3-deoxy-1,2-*O*-isopropylidene-5,6-sulfite-α-D-glucofuranos-3-yl)-1,2-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranose (8'). Thionyl chloride (1.8 g, 15 mmol) was slowly added to a stirred solution of **2a** (4 g, 7.48 mmol) in ethyl acetate (40 mL) in the presence of TEA (3.03 g, 30 mmol). After 1 h at 0 °C, the mixture was filtered, concentrated and then extracted with a mixture of toluene-water (1:1) (40 mL). The organic phase was concentrated to give a residue which yielded, after elution with hexane-acetone (9:1), 3.1 g (71%) of **8'** as a syrup; $[\alpha]_D^{25}$ -52.3° (*c* 1.0, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (105.3), C_2 (82.5), C_3 (81.1), C_4 (79.6), C_5 (68.1), C_6 (72.9), $C_{1'}$ (105.1), $C_{2'}$ (82.3), $C_{3'}$ (82.0), $C_{4'}$ (78.9), $C_{5'}$ (76.8), $C_{6'}$ (68.7), 2xCMe_2 (112.2; 111.6), 4xCH_3 (26.1-26.7), C_α (70.6); C_β (31.7), 5xCH_2 (29.7-22.6), CH_3 (13.9).

Anal. Calcd for $C_{26}H_{44}O_{12}S$ (580.6): C, 53.78; H, 7.64. Found: C, 54.02; H, 7.56.

6-*O*-(3,6-dideoxy-1,2-*O*-isopropylidene-6-*S*-octyl-α-D-glucofuranos-3-yl)-1,2-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranose (9). Powdered LiCl (0.3 g, 6.7 mmol) and 1-octanethiol

(1.5 g, 10.3 mmol) were added to a stirred solution of **8a** (3.3 g, 6.39 mmol) in toluene (30 mL). After 48 h at 110 °C, the mixture was filtered and the filtrate concentrated under vacuum. The residue was purified on a silica gel column eluted with hexane-acetone (93:7) to yield 3 g (72%) of **9** as a syrup; $[\alpha]_D^{25}$ -20.4° (*c* 1.5, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (105.2), C_2 (82.2), C_3 (82.1), C_4 (79.6), C_5 (68.2), C_6 (72.9), $C_{1'}$ (105.5), $C_{2'}$ (83.9), $C_{3'}$ (82.1), $C_{4'}$ (79.8), $C_{5'}$ (67.3), $C_{6'}$ (36.8), 2xCMe_2 (111.7; 111.5), 4xCH_3 (25.9-26.6), C_α (70.6), C_β (31.7), $C_{\alpha'}$ (32.6), 10xCH_2 (29.5-22.5), 2xCH_3 (13.9).

Anal. Calcd for $C_{34}H_{62}O_{10}S$ (652.8): C, 61.61; H, 9.43. Found: C, 61.81; H, 9.40.

6-*O*-(6-*O*-butanoyl-3-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-3-yl)-1,2-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranose (9'). Sodium butanoate (0.96 g, 8.7 mmol) was added to a stirred solution of **8'** (2.35 g, 4 mmol) in toluene-DMSO (1:1) (25 mL). After 4 h at 110 °C, the mixture was filtered and the filtrate concentrated under vacuum. The residue was purified on a silica gel column eluted with hexane-acetone (22:3) to yield 2.05 g (84%) of **9'** as a syrup; $[\alpha]_D^{25}$ -32.6° (*c* 1.1, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (105.1), C_2 (82.2), C_3 (82.1), C_4 (79.6), C_5 (68.2), C_6 (72.9), $C_{1'}$ (105.5), $C_{2'}$ (83.9), $C_{3'}$ (82.1), $C_{4'}$ (79.8), $C_{5'}$ (67.5), $C_{6'}$ (66.5), 2xCMe_2 (111.8; 111.7), 4xCH_3 (25.9-26.6), C_α (70.7), C_β (31.8), 5xCH_2 (29.7-22.6), CH_3 (14.1), *C*=O (174.1), $C_{\alpha'}$ (36.1), $C_{\beta'}$ (18.4), CH_3 (13.7).

Anal. Calcd for $C_{30}H_{52}O_{12}$ (604.7): C, 59.58; H, 8.67. Found: C, 59.27; H, 8.69.

6-*O*-[6-*O*-(3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl)-3-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-3-yl]-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranose (10). Powdered KOH (2.3 g, 41.1 mmol) and **8b** (4.6 g, 8.03 mmol) were added to a stirred solution of diacetone glucose (4.2 g, 16.2 mmol) in toluene-DMSO (1:1) (60 mL). After 24 h at 40 °C, the mixture was extracted with toluene and the organic phases concentrated under vacuum. The resulting crude product gave:

- 1.1 g of a mixture of three products containing 40% of **10** determined by HPLC analysis after elution with hexane-acetone (22:3);

- 4.2 g (61%) of **10** as a syrup after elution with hexane-acetone (9:1); $[\alpha]_D^{25}$ -25.4° (*c* 1.7, $CHCl_3$). ^{13}C NMR ($CDCl_3$) δ: C_1 (104.1), C_2 (83.2), C_3 (81.3), C_4 (79.0), C_5 (67.1), C_6 (72.4), $C_{1'}$ (104.4), $C_{2'}$ (82.9), $C_{3'}$ (81.3), $C_{4'}$ (79.2), $C_{5'}$ (67.4), $C_{6'}$ (72.9), $C_{1''}$ (104.6), $C_{2''}$ (81.6), $C_{3''}$ (81.3), $C_{4''}$ (80.5), $C_{5''}$ (71.8), $C_{6''}$ (66.7), 4xCMe_2 (2x110.7; 110.8; 108.3), 8xCH_3 (25.8-26.7), C_α (69.8), C_β (30.9), 9xCH_2 (28.8-21.7); CH_3 (13.1).

Anal. Calcd for $C_{42}H_{72}O_{16}$ (833): C, 60.56; H, 8.71. Found: C, 60.42; H, 8.76.

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