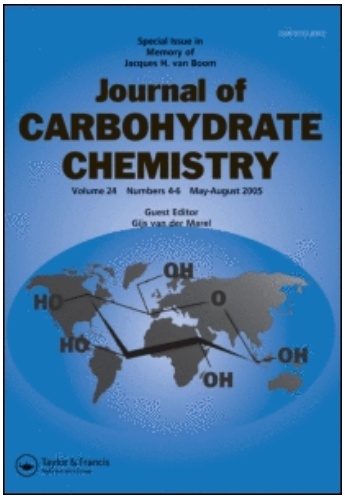


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# SYNTHESIS OF NEW DIMERIC AMPHIPHILES. INFLUENCE OF ANOMERIC CONFIGURATION AND SPACER FUNCTIONALITY ON INTERFACIAL PROPERTIES

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## ABSTRACT

The synthesis of new dimeric carbohydrate-based surfactants was performed connecting two butyl glucopyranosides with a spacer through ester and ether linkages. Critical micellar concentrations were determined to study the influence of anomeric configuration and spacer functionality on surfactant properties.

## INTRODUCTION

Dimeric or gemini surfactants are defined as surfactants made up of two amphiphilic moieties connected at the level of the head polar groups, or of the alkyl chains but still very close to the head groups, by a spacer group which can be hydrophilic or hydrophobic, rigid or flexible.[1] They have dynamic properties and form structures including aggregates and micelles[2] that are drastically different from those of monomeric surfactants.

Among the parameters influencing the interfacial properties of gemini surfactants, are the hydrophilic/lipophilic ratio, the ionic or nonionic nature of polar heads, and the length of hydrophobic chains (see reference 3 for reviews). However, to our knowledge, no reports regarding subtle differences determined by the spacial orientation of substituents or the position of the linkage between monomeric units have been published. Carbohydrate-based dimeric amphiphiles allow a great variability of structures and on the other hand are environmentally compatible.

We have already described the synthesis of dimeric surfactants from butyl α-D-glucopyranoside (**1**), using three different spacers (flexible and rigid) to link the sugar moieties through *O*-2 or *O*-6 with ester linkages.[3,4] The improved surfactant properties of these new compounds became evident from their critical micellar concentration (CMC), ten-fold smaller than that of their parent surfactant. In that previous work, we found that a simple change in the position of linking from *O*-6 to *O*-2 of the parent alkyl glucoside leads to products with different properties such as water solubility and CMC values. Those changes are presumably due to a change in the preferred conformation of the molecule, allowing for better alignment of polar and nonpolar groups and thus improving micelle shape.[5]

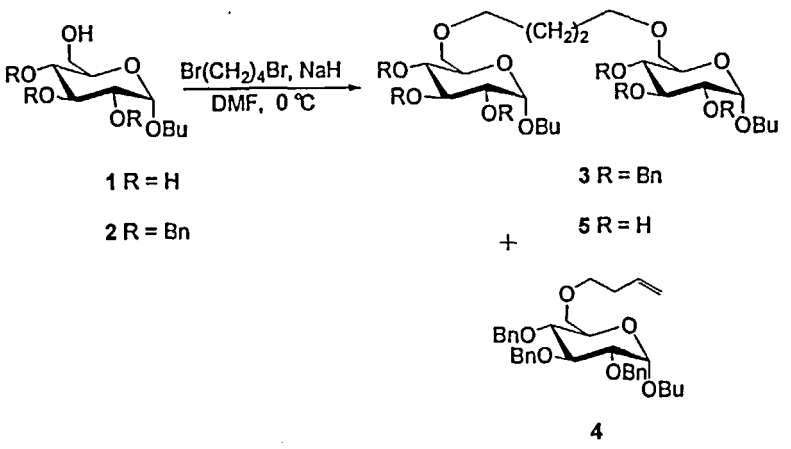


Since it is known that anomeric configuration affects the surfactant properties of alkyl glycosides, we were prompted to study its influence in this new type of dimeric surfactant. Additionally, the spacer may be linked through a variety of functional groups to the carbohydrate. We now report on the synthesis of model compounds that allow us to better rationalize the influence of subtle structural differences on the physicochemical properties of carbohydrate-based dimeric surfactants.

## RESULTS AND DISCUSSION

Ester linked dimeric amphiphiles were synthesized as the first examples due to the known biodegradability of this kind of linkage. A change of functionality which will introduce differences in polarity and hydrophobicity is performed joining the spacer through an ether.

The synthesis of an ether-linked gemini surfactant is shown in Scheme **1**. Butyl α-D-glucopyranoside (**1**) was converted into butyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside



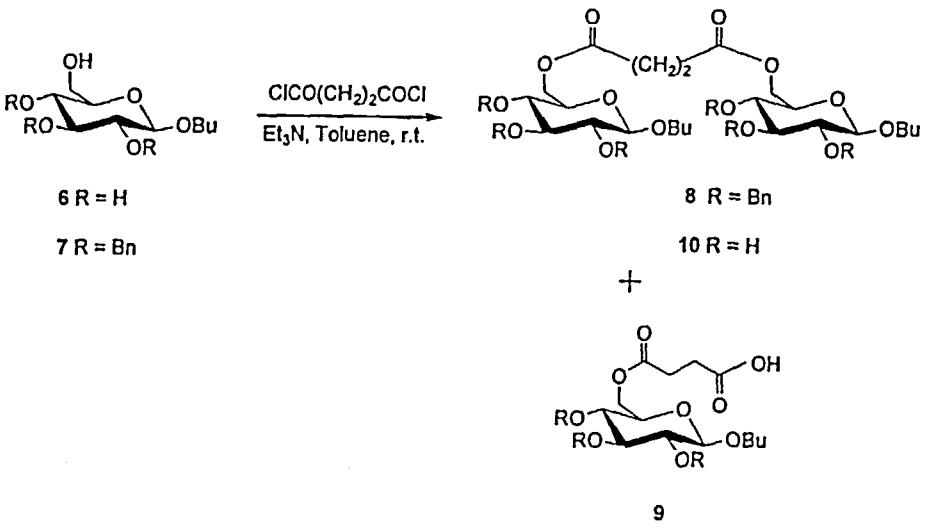

**Scheme 1**



(**2**) as reported.[5] Compound **2** was reacted with sodium hydride and 1,4-dibromobutane. The expected product of coupling bis-*O*-(butyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yl)-1,4-butanediol (**3**) was obtained, together with large quantities of starting material. The addition of more NaH/dibromobutane improved the yield of **3** to 29 %, but a by-product (**4**) was also formed, as a result of the elimination of the primary bromide on the mono-ether product. Hydrogenolysis of the benzyl groups on **3** gave the bis-*O*-(butyl α-D-glucopyranosid-6-yl)-1,4-butanediol (**5**) in 93 % yield.

Butyl β-D-glucopyranoside (**6**)[5] was also tritylated at *O*-6, benzylated, and detritylated to give butyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**7**) in 54 % overall yield as a crystalline compound. The reaction of **7** with succinyl chloride/triethylamine gave the dimeric product bis-(butyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosid-6-yl) succinate (**8**, 50 % yield) together with a slight quantity of the monomeric substituted succinic acid **9** (13 %). Catalytic hydrogenolysis of **8** led to bis-(butyl β-D-glucopyranosid-6-yl) succinate (**10**) in 98 % yield (Scheme **2**).

Interfacial properties of these new dimeric products are shown in Table **1**, together with those of bis-(butyl α-D-glucopyranosid-6-yl) succinate (**11**)[5] and the corresponding monomers, which have been included for comparison. As seen from Table 1, surfactant properties of dimeric (or gemini) compounds are largely superior to those of monomeric alkyl glucosides, confirming our previous results.[5]




**Scheme 2**

Table 1. Interfacial Properties of Compounds **1**, **5**, **6**, **10**, and **11**[5] in Water at 25 °C Measured by the Maximum Bubble Pressure Method.

| Product | Config. | CMC (mM) | $\gamma_{CMC}$ (mN/m) | $C_{20}$ (mM) | Spacer | Linked through |
|---|---|---|---|---|---|---|
| **1** | α | 77.2 | 47.8 | 59.3 | — | — |
| **5** | α | 5.6 | 37.7 | 2.1 | $(CH_2)_4$ | O-6 |
| **6** | β | 110.3 | 42.2 | 64.0 | — | — |
| **10** | β | 12.9 | 46.8 | 7.8 | succinyl | O-6 |
| **11** | α | 8.7 | 42.0 | 3.3 | succinyl | O-6 |

It is known that in general α glycosides show improved surfactant properties over the isomeric β compounds.[5] As expected, butyl α-D-glucopyranoside (**1**) has a lower and thus, better, CMC value than does butyl β-D-glucopyranoside (**6**, Table 1).

The corresponding dimers (**10**, **11**) show a similar behaviour. Moreover, the ratio of CMC values for compounds **10** and **11** is about 1.5, and a similar ratio is obtained when we compare compounds **6** and **1**. This result would suggest an intrinsic influence of anomeric configuration on surfactant properties, in spite of the monomeric or dimeric nature of the

molecule. The anomeric configuration determines the spacial orientation of the butyl chain, and therefore the tridimensional arrangement of polar and nonpolar moieties of the surfactant.

The situation is different for the ether-linked **5**, since the replacement of an ester by an ether led to a product with a slightly lower hydrophilic character than that of compound **11**. The difference in CMC values between both compounds is significant, suggesting that a less polar spacer improves the surfactant properties of the molecule. Similar differences are also observed when $\gamma_{CMC}$ (surface tension at CMC) and the efficiency of adsorption $C_{20}$ (the molar surfactant concentration in the aqueous phase required to decrease the surface tension of the solvent by 20 mN/m) are compared. This improvement cannot only be assigned to the lowering of the hydrophilic/lipophilic ratio, since there is no direct relationship between this ratio and CMC values.[3] Therefore, these findings could be better explained on the basis of the increased rotational degrees of freedom of the $C_6$-O-C bonds in ether **5** when compared to ester **11**, bearing a $sp^2$ carbon. This fact may be reflected in the conformation finally adopted by the molecules.



## EXPERIMENTAL

**General methods.** Melting points (mp) were determined with a Fisher-Johns mp apparatus and are uncorrected. Optical rotations were measured at 20 ± 2 °C with a Perkin Elmer Model 241 digital polarimeter, using a 10 cm, 1 mL cell. $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker AC 200. IR spectra were recorded with a FT-spectrometer. Mass spectra were obtained with a JMS-700 spectrometer.

**Surface Properties.** Surface tension ($\gamma$) of each solution of surfactants was calculated from the maximum pressure required to form a bubble at the bottom of the capillary tube just touching the liquid surface, using the Laplace equation $\Delta P = 2.\gamma/r$, where $\Delta P$ is a difference of pressure registered in the manometer and r is the capillary radius (maximum bubble pressure method).[7]

The apparatus was calibrated using 20 different pure liquids of known surface tension, from which the capillary radius can be easily determined as the slope of the curve $\Delta P$ vs. $\gamma$. Using linear regression data a value of r = 0.078 ± 0.001 mm and a correlation

coefficient 0.9997, was estimated. Systematic errors in the equipment can be calculated from errors in the radius, ΔP and temperature, where the maximum error in γ is 1.24 mN/m. The relative error for a typical surface tension value of 35 mN/m is 3.5 %.

Critical micelle concentration (CMC) was taken as the concentration at the point of intersection of the two linear portions of the γ vs. concentration plots. The slope of the linear portions of each curve in the plot was determined by the method of least mean squares, using confidence intervals of linear regression of SigmaPlot® 4.01. Error in CMC is about 10 %.[8] As an example, a value of 8.1 x $10^{-3}$ M was obtained for sodium dodecyl sulfate (SDS), according to literature (8.2 x $10^{-3}$ M).[9] In our previus report,[5] the method of least mean squares was not used to determine the slope of the linear portion of the γ vs. concentration plot.



**Bis-*O*-(butyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yl)-1,4-butanediol (3).** Butyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (2),[5] 105.0 mg (0.21 mmol), was dissolved in DMF (0.8 mL), and them 1,4-dibromobutane (0.015 mL, 0.12 mmol) and sodium hydride 55 % in mineral oil (12 mg, 0.27 mmol) were added at 0 °C. The reaction mixture was kept overnight in the dark at room temperature and 1,4-dibromobutane and sodium hydride were added again as before. This addition was repeated after 24 h. The reaction was quenched with methanol (2 mL). After solvent evaporation, preparative thin-layer chromatography on silica gel (3:1 cyclohexane-ethyl acetate) afforded **2** (32.4 mg, 29 % yield) as a syrup: $[\alpha]_D$ + 33.8 ° (*c* 1.3, $CHCl_3$ ); IR (film) $\nu_{max}$ ($cm^{-1}$): 2929.3 (CH), 1070.4 (OC), 733.1, 696.4 (Ph);$^1$H NMR: δ 7.35-7.25 (m, 30 H, Ph), 5.01-4.53 (m, 14 H, $CH_2$Ph, H-1), 3.97 (t, 2 H, *J* 9.1 Hz, H-3), 3.76-3.31 (m, 18 H, H-2, H-4, H-5, H-6, $CH_2O$, $OCH_2(CH_2)_2CH_2O$), 1.66-1.52 (m, 8 H, $CH_2CH_2O$, $OCH_2(CH_2)_2CH_2O$), 1.35 (m, 4 H, $CH_2$), 0.90 (t, 6 H, *J* 7.3 Hz, $CH_3$). $^{13}$C NMR: δ 139.0 (Ph), 128.3-127.5 (Ph), 96.9 (C-1), 82.12 (C-3), 80.2 (C-2), 77.9 (C-4), 75.6, 75.1, 73.1 ($CH_2$Ph), 71.3 (C-5), 70.1 ($OCH_2(CH_2)_2CH_2O$), 69.4 ($CH_2O$), 67.8 (C-6), 31.2 ($CH_2$), 19.4 ($CH_2$), 13.9 ($CH_3$).

CIMS ($NH_3$): Calcd for $C_{66}H_{86}O_{12}N$: *m/z* 1084.6150. Found: 1084.6179.

Butyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-butenyl)-α-D-glucopyranoside (**4**) was also eluted as a byproduct (20.0 mg, 17.0 %): $[\alpha]_D$ + 26.1 ° (*c* 1.1, $CHCl_3$ ); IR (film) $\nu_{max}$ ($cm^{-1}$): 2935.5 (CH), 1650.2 (C=C), 1109.2 (OC), 736.6, 696.5 (Ph); $^1$H NMR: δ 7.35-7.25 (m, 15 H, Ph), 5.80 (m, 1 H, $J_{cis}$ 10.2 Hz, $J_{trans}$ 17.2 Hz, H-3'), 5.11-4.57 (m, 9 H, $CH_2$Ph,

H-1, H-4'a, H-4'b), 3.98 (t, 1 H, *J* 9.1 Hz, H-3), 3.79-3.34 (m, 9 H, H-2, H-4, H-5, H-6a, H-6b, H-1', $CH_2O$), 2.33 (dd, 2 H, $J_{allylic}$ < 1 Hz, *J* 6.7 Hz, $J_{gem}$ 13.5 Hz, H-2'), 1.62 (m, 2 H, $CH_2$), 1.36 (m, 2 H, $CH_2$), 0.92 (t, 3 H, *J* 7.3 Hz, $CH_3$). $^{13}C$ NMR: δ 138.5 (C-3'), 135.1 (Ph), 128.0-127.5 (Ph), 116.4 (C-4'), 96.9 (C-1), 82.2 (C-3), 80.2 (C-2), 77.8 (C-4), 75.7, 75.1, 73.1 ($CH_2Ph$), 71.0 (C-5), 70.1 (C-1'), 69.4 ($CH_2O$), 67.9 (C-6), 34.1 (C-2'), 31.5 ($CH_2$), 19.4 ($CH_2$), 13.9 ($CH_3$).

**Bis-*O*-(butyl α-D-glucopyranosid-6-yl)-1,4-butanediol (5).** Compound **3** (48.0 mg, 0.045 mmol) in 1:1 methanol-ethyl acetate (12 mL) was kept under a hydrogen atmosphere at 50 psi over Pd/C 10 % for 9 h. The mixture was filtered, and solvent evaporation gave pure **4** (22.0 mg, 93 % yield), as a colorless glass: $[\alpha]_D$ + 89.2 ° (*c* 1.1, MeOH); IR (film) $\nu_{max}$ ($cm^{-1}$): 3357.9 (OH), 2931.6 (CH), 1047.5 (OC); $^1H$ NMR (methanol-d): δ 4.75 (d, 2 H, $J_{1,2}$ 3.7 Hz, H-1), 3.78-3.23 (m, 20 H, H-2, H-3, H-4, H-5, H-6, $CH_2O$, $OCH_2(CH_2)_2CH_2O$), 1.67-1.56 (m, 8 H, $CH_2CH_2O$, $OCH_2(CH_2)_2CH_2O$), 1.38 (m, 4 H, $CH_2$), 0.94 (t, 6 H, *J* 7.3 Hz, $CH_3$ ). $^{13}C$ NMR: δ 100.1 (C-1), 75.2 (C-3), 73.6 (C-5*), 72.6 (C-2*), 72.4 (C-4), 72.0 ($OCH_2(CH_2)_2CH_2O$), 71.3 (C-6), 32.8 ($CH_2$), 27.4 ($OCH_2(CH_2)_2CH_2O$), 20.5 ($CH_2$), 14.3 ($CH_3$). (* May be interchanged).

FABMS (Na): Calcd for $C_{24}H_{46}O_{12}Na$: *m/z* 549.2887. Found: 549.2878.

**Butyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (7).** Butyl β-D-glucopyrano-side (**6**) was tritylated by the method of Chaudhary *et al.*[10] To a solution of **6** (1.14 g, 4.83 mmol) in DMF (12.5 mL), trityl chloride (2.10 g, 7.53 mmol), triethylamine (1.5 mL, 10.76 mmol), and DMAP (49 mg, 0.33 mmol) were added. The mixture was stirred at 35 °C for 40 h, poured into ice-water, and extracted with dichloromethane (2 x 100 mL). After washing with satd ammonium chloride and brine, the dichloromethane solution was dried (sodium sulfate), filtered and concentrated to a syrup. After drying overnight over $P_2O_5$, the residue was dissolved in DMF (20 mL). Benzyl bromide (2.1 mL, 17.68 mmol) and NaH (55 % in mineral oil, 820 mg, 18.85 mmol) were added at 0 °C. After stirring 24 h at room temperature, methanol (3 mL) was added. After 30 min, chloroform (150 mL) was added and the solution was washed with brine (4 x 80 mL), dried and concentrated. To the solid residue obtained, ethanol (50 mL) and pyridinium chloride (420 mg, 3.64 mmol) were added. The mixture was refluxed for 2 h, and the solvent was evaporated. The crude residue was purified by flash chromatography on silica gel (10:0 to 8:2 cyclohexane-ethyl acetate) to give pure **7** (1.31 g, 54 % yield over 3 steps) as a white

solid: mp 67 °C (hexane-dichloromethane); $[\alpha]_D$ + 0.9 ° (*c* 0.9, $CHCl_3$); IR (film) $\nu_{max}$ ($cm^{-1}$): 3398.4 (OH), 1090.3 (OC), 749.7, 695.8 (Ph); $^1H$ NMR: δ 7.35-7.25 (m, 15 H, Ph), 4.96-4.60 (m, 6 H, $CH_2Ph$), 4.43 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.92 (m, 2 H, *J* 6.4 Hz, $J_{gem}$ 9.5 Hz, $CH_2CH_aO$), 3.66 (t, 1 H, $J_{2,3}$ 8.8 Hz, H-3), 3.61-3.49 (m, 2 H, H-4, $CH_2CH_bO$), 3.44-3.31 (m, 4 H, H-2, H-5, H-6a, H-6b), 1.61 (m, 2 H, $CH_2$), 1.43 (m, 2 H, $CH_2$), 0.93 (t, 3 H, *J* 7.3 Hz, $CH_3$). $^{13}C$ NMR: δ 138.6-138.0 (Ph), 128.4-126.8 (Ph), 103.1 (C-1), 84.5 (C-3), 82.3 (C-2), 77.6 (C-4), 75.5, 75.0, 74.8 ($CH_2Ph$, C-5), 69.9 ($CH_2O$), 62.0 (C-6), 31.8 ($CH_2$), 19.2 ($CH_2$), 13.8 ($CH_3$).

Anal. Calcd for $C_{31}H_{38}O_6$: C 73.48, H 7.56. Found: C 73.26, H 7.83.

**Bis-(butyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosid-6-yl) succinate (8).** Compound 7 (133.0 mg, 0.263 mmol) was dissolved in toluene (0.6 mL) and triethylamine (0.044 mL, 0.32 mmol) and succinyl chloride (0.017 mL, 0.16 mmol) were added. The reaction mixture was kept overnight at room temperature and concentrated. Preparative thin-layer chromatography on silica gel (75:25 cyclohexane-ethyl acetate) afforded **8** (72.0 mg, 50 % yield) as a white solid: mp 102 °C; $[\alpha]_D$ +8.1 ° (*c* 0.5, $CHCl_3$ ); $^1H$ NMR: δ 7.31-7.25 (m, 30 H, Ph), 4.96-4.52 (m, 12 H, $CH_2Ph$), 4.37 (d, 2 H, $J_{1,2}$ 7.7 Hz, H-1 and 1'), 4.35 (dd, 2 H, $J_{5,6a}$ 2.1 Hz, $J_{6a,6b}$ 12.6 Hz, H-6a and 6'a), 4.21 (dd, 2 H, $J_{5,6b}$ 4.0 Hz, H-6b and 6'b), 3.91 (dt, 2 H, *J* 6.3 Hz, $J_{gem}$ 9.5 Hz, $CH_2CHaO$), 3.65-3.47 (m, 8 H, H-2 and 2', H-4 and 4', H-5 and H-5', $CH_2CHbO$), 3.42 (dd, 2 H, $J_{2,3}$ 8.0 Hz, $J_{3,4}$ 9.2 Hz, H-3 and H-3'), 2.60 (s, 4 H, $CH_2COO$-), 1.59 (m, 4 H, $CH_2$), 1.39 (m, 4 H, $CH_2$), 0.91 (t, 6 H, *J* 7.3 Hz, $CH_3$). $^{13}C$ NMR: δ 171.8 (COO-), 138.4-137.8 (Ph), 128.4-127.6 (Ph), 103.6 (C-1 and 1'), 84.7 (C-3 and 3'), 82.2 (C-2 and 2'), 77.6 (C-4 and 4'), 75.6, 75.0, 74.8 ($CH_2Ph$), 72.8 (C-5 and 5'), 69.9 ($CH_2O$), 63.4 (C-6 and 6'), 31.7 ($CH_2COO$-, $CH_2$), 19.2 ($CH_2$), 13.8 ($CH_3$). IR (film) $\nu_{max}$ ($cm^{-1}$): 1738.7 (C=O), 1069.7 ($OCH_2$), 735.7, 698.0 (Ph).

CIMS ($NH_3$): Calcd for $C_{66}H_{82}O_{14}N$: *m/z* 1112.5735. Found: 1112.5728.

Further elution afforded 4-(butyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosid-6-yl) succinic acid (**9**) (21.0 mg, 13 %): mp 52 °C; $[\alpha]_D$ +1.4 ° (*c* 0.8, $CHCl_3$ ); $^1H$ NMR: δ 7.34-7.25 (m, 15 H, Ph), 4.97-4.53 (m, 6 H, $CH_2Ph$), 4.37 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.34 (dd, 1 H, $J_{5,6a}$ 2.0 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.24 (dd, 1 H, $J_{5,6b}$ 4.0 Hz, H-6b), 3.91 (dt, 1 H, *J* 6.4 Hz, $J_{gem}$ 9.6 Hz, $CH_2CHaO$), 3.66-3.48 (m, 4 H, H-2, H-4, H-5, $CH_2CHbO$), 3.43 (dd, 1 H, $J_{2,3}$ 8.2 Hz, $J_{3,4}$ 9.0 Hz, H-3), 2.65 (m, 4 H, $CH_2COO$-), 1.61

(m, 2 H, $CH_2$), 1.43 (m, 2 H, $CH_2$), 0.91 (t, 3 H, *J* 7.3 Hz, $CH_3$). $^{13}C$ NMR: δ 181.3 (COOH), 171.8 (COO-), 138.5-137.8 (Ph), 128.5-127.6 (Ph), 103.7 (C-1), 84.7 (C-3), 82.2 (C-2), 77.6 (C-4), 75.7, 75.0, 74.8 ($CH_2Ph$), 72.8 (C-5), 69.9 ($CH_2O$), 63.5 (C-6), 31.8 ($CH_2$), 28.7 (*C*$H_2$COO-), 19.2 ($CH_2$), 13.8 ($CH_3$). IR (film) $\nu_{max}$ ($cm^{-1}$): 3485.2 (OH), 1739.5 (COOR), 1714.2 (COOH), 1069.5 ($OCH_2$), 736.8, 698.5 (Ph).

Anal. Calcd for $C_{35}H_{42}O_9$: C 69.29, H 6.98. Found: C 69.04, H 6.95.

**Bis-(butyl β-D-glucopyranosid-6-yl) succinate (10).** Compound **8** (65.0 mg, 0.059 mmol) in 1:1 methanol-ethyl acetate was kept under a hydrogen atmosphere at 3.3 atm over Pd/C 10 % for 7 to give pure **10** (32.0 mg, 98 % yield), as a syrup: $[\alpha]_D$ -2.4 ° (*c* 0.3, MeOH); $^1H$ NMR (methanol-d): δ 4.35 (dd, 2 H, $J_{5,6a}$ 2.2, $J_{6a,6b}$ 11.7 Hz, H-6a and 6'a), 4.19-4.10 (m, 4 H, H-1 and H-1', H-6b and 6'b), 3.76 (dt, 2 H, *J* 6.6 Hz, $J_{gem}$ 9.9 Hz, $CH_2CHaO$), 3.48 (m, 2 H, $CH_2CHbO$), 3.35 (m, 2 H, H-5 and 5'), 3.28-3.19 (m, 4 H, H-2 and 2', H-4 and 4'), 3.09 (dd, 2 H, $J_{2,3}$ 8.0 Hz, $J_{3,4}$ 9.1 Hz, H-3 and H-3'), 2.59 (s, 4 H, $CH_2COO$-), 1.51 (m, 4 H, $CH_2$), 1.33 (m, 4 H, $CH_2$), 0.86 (t, 6 H, *J* 7.3Hz, $CH_3$ ). $^{13}C$ NMR: δ 173.9 (COO-), 104.4 (C-1 and 1'), 78.0 (C-3 and 3'), 75.2 (C-5 and 5'), 75.0 (C-2 and 2'), 71.7 (C-4 and 4'), 70.7 ($CH_2O$), 65.0 (C-6 and 6'), 32.9 ($CH_2COO$-), 29.9 ($CH_2$), 20.2 ($CH_2$), 14.2 ($CH_3$). IR (film) $\nu_{max}$ ($cm^{-1}$): 3392.8 (OH), 1734.2 (C=O).

FABMS (+Na): Calcd for $C_{28}H_{42}O_{14}Na$: *m/z* 577.2472. Found: 577.24



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