Pergamon

Tetrahedron 55 (1999) 12711–12722

TETRAHEDRON

New Dimeric Surfactants from Alkyl Glucosides

Mariano J. L. Castro, José Kovensky and Alicia Fernández Cirelli*

Centro de Investigaciones en Hidratos de Carbono (CIHIDECAR, CONICET)
Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires,
Ciudad Universitaria, Pabellón II, 3er. Piso, 1428 Buenos Aires, Argentina

Received 13 May 1999; accepted 1 September 1999

Abstract: Carbohydrate containing dimeric (or gemini) surfactants were synthesized starting from D-glucose. Three different spacers (glutaryl, succinyl and terephthaloyl) were used to link the sugar moieties through *O*-2 or *O*-6. The critical micellar concentration (CMC) for these new compounds was ten-fold smaller than that of their monomeric counterpart.

Keywords: Dimers - esters - glycosides - surfactants

INTRODUCTION

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

The interesting properties of dimeric surfactants prompted us to design and synthesize a new type of amphiphilic molecules, composed by two alkyl glucosides linked through a spacer. We have already described a first example where two molecules of butyl-α-D-glucopyranoside are linked through a flexible spacer at C-6.[3] The use of ecologically safe surfactants such as alkyl glycosides as monomers is mainly due to their biodegradability, and the fact that they can be easily prepared starting from renewable raw materials as carbohydrates and long hydrocarbon chain alcohols.

In this paper, we report the synthesis of dimeric surfactants from butyl-α-D-glucopyranoside (**1**), using three different spacers to link the sugar moieties through *O*-2 or *O*-6. The improved surfactant properties of

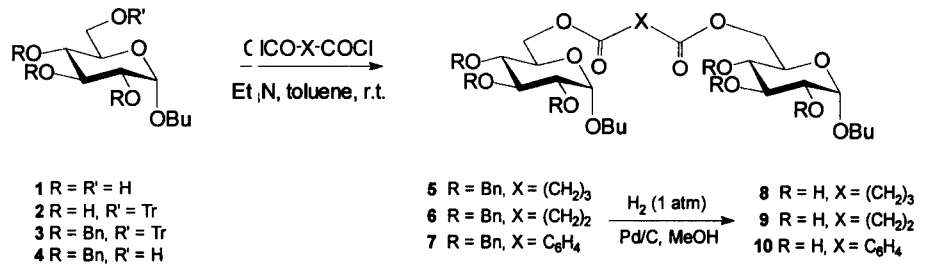
* Author to whom correspondence should be addressed. E-mail: afc@rec.uba.ar
Dedicated to Professor Pierre Sinaÿ on the occasion of his 62nd birthday.

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00786-3

these new compounds become evident from their critical micellar concentration (CMC), ten-fold smaller than that of their constituting parent surfactant.

RESULTS AND DISCUSSION

Dimeric surfactants were prepared from suitable protected butyl glucopyranosides to avoid mixture of products. The synthetic sequence developed for the preparation of 1,5-bis-[6-*O*-(*n*-butyl-α-D-glucopyranosid)] glutarate (**8**)[3] was used with different acyl dichlorides to study the influence of the linker on the surfactant properties. Butyl-α-D-glucopyranoside (**1**) was protected as the 6-*O*-trityl ether **2** and benzylated to give **3**. Butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**4**) was cleanly obtained (89 % yield) in neutral conditions by heating **3** with pyridinium chloride in ethanol (Scheme 1).



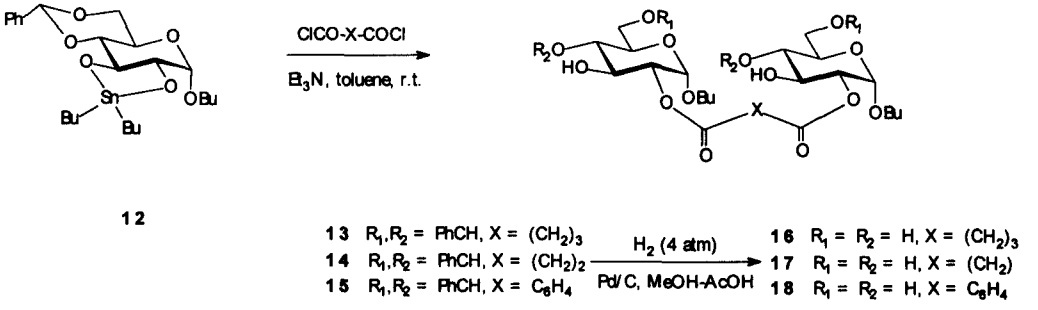
Scheme 1

In the key coupling step, compound **4** was treated with three different diacyl dichlorides: glutaryl, succinyl and terephthaloyl dichlorides to give 1,5-bis-[6-*O*-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] glutarate (**5**, 38 % yield), 1,4-bis-[6-*O*-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] succinate (**6**, 44 % yield), and bis-[6-*O*-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] terephthalate (**7**, 70 % yield), respectively. Yields are related to the stability of the corresponding dichloride, since long reaction times are needed for the condensation. Methanol was added to quench the reaction. Monosaccharide containing by-products: methyl [6-O-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] succinate and methyl [6-O-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] terephthalate were identified from the reaction mixtures.

Hydrogenation of the benzyl groups in compounds **5**, **6** and **7** lead to the target compounds 1,5-bis-[6-*O*-(*n*-butyl-α-D-glucopyranosid)] glutarate (**8**), 1,4-bis-[6-*O*-(*n*-butyl-α-D-glucopyranosid)] succinate (**9**) and bis-[6-*O*-(*n*-butyl-α-D-glucopyranosid)] terephthalate (**10**), respectively.

Structural characterization was performed spectroscopically and is described in Experimental. Symmetric dimeric structure became evident through the simple NMR spectra obtained, and MS allowed us to confirm the molecular weight.

Since physicochemical properties depend on the conformation of the surfactants, compounds linked through *O*-2 were prepared, using the same acylchlorides as linkers. The sequence performed is shown in Scheme 2. Butyl-α-D-glucopyranoside (**1**) was converted to its 4,6-*O*-benzylidene acetal **11** (70 % yield) which was then heated with dibutyltin oxide in toluene to give the *n*-Butyl-2,3-*O*-stannylidene-4,6-*O*-benzylidene-α-D-glucopyranoside (**12**). When this reaction was performed in a microwave oven[4] the reaction time was 10 minutes.



Scheme 2

The stannylidene **12** was then treated with the three diacyl dichlorides leading selectively to the dimers coupled at *O*-2: 1,5-bis-[2-O-(*n*-butyl-4,6-*O*-benzylidene-α-D-glucopyranosid)] glutarate (**13**), 1,4-bis-[2-O-(*n*-butyl-4,6-*O*-benzylidene-α-D-glucopyranosid)] succinate (**14**) and bis-[2-O-(*n*-butyl-4,6-*O*-benzylidene-α-D-glucopyranosid)] terephthalate (**15**). Reaction was monitored by t.l.c. until no further changes were observed. After purification, compounds **13**, **14** and **15** were obtained in 35-40 % yield.

The preferential esterification at O-2 of alkyl α-D-hexopyranosides in the absence of steric effects has been known for some time. The enhanced reactivity at O-2 in the stannylidene **12** may be explained on the basis of stereoelectronic effects associated with dimeric structures, as already stated by David and Hanessian[5].

Substitution at *O*-2 was confirmed by NMR. The resonance for H-2 in compounds **13** (4.77 ppm), **14** (4.77 ppm), and **15** (5.04 ppm) was shifted to lower fields when compared with H-2 in *n*-butyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**11**). A shift of 0.15-0.28 ppm was also observed for H-1. On the other hand, the resonance for C-1 in compounds **13** (96.5 ppm), **14** (96.4 ppm), and **15** (96.6 ppm) was shifted upfield when compared with C-1 in compound **11**, while the resonance for C-2 was shifted downfield (0.3-0.5 ppm).

After the hydrogenation step 1,5-bis-[2-O-(*n*-butyl-α-D-glucopyranosid)] glutarate (**16**), 1,4-bis-[2-O-(*n*-butyl-α-D-glucopyranosid)] succinate (**17**) and bis-[2-O-(*n*-butyl-α-D-glucopyranosid)] terephthalate (**18**) were obtained.

In a preliminary examination of surfactant properties, the surface tension (γ) and critical micellar concentration (CMC) of compounds **8**, **9**, **16**, **17** and **18** were measured in water at 25 °C (Table 1). The terephthalate **10** was insoluble in water. Properties of butyl-α-D-glucopyranoside (**1**) were determined for comparison.

It is evident from the data that compounds **8**, **9**, **16**, **17** and **18** have CMC values 1-2 orders of magnitude smaller than the single chain compound **1** and comparable to that of conventional surfactants although they bear a short hydrophobic chain (C-4). The surface tension at the CMC (γ_{CMC}) is similar for all compounds. The differences observed fall within the range of experimental error. Regards surfactant efficiency, dimeric compounds have C_{20} values (the molar surfactant concentration in the aqueous phase required to decrease the surface tension of the solvent by 20 mN/m) 1-2 orders of magnitude smaller than butyl α-D-glucopyranoside.

The number of compounds in consideration is small to allow a meaningful correlation of structural effects on both γ and CMC values. Nevertheless, it is interesting to note that for the succinyl derivatives **9** and **17**, a change in the position of attachment from O-6 to O-2, lead to a product with a four-fold lower CMC. However, no significative change in CMC value has been observed between the glutarates **8** and **16.** A comparison between terephthalates **10** and **18** is not possible since compound **10** is insoluble in water. Preliminary Molecular Modelling[6] showed a very ordered conformation for the succinate **17** and terephthalate **18**, with the two alkyl chains parallel to each other and orthogonal to the plane formed by the carbohydrates moieties and the linker (Figure 1). This arrangement could improve intermolecular interactions and therefore the formation of micelles and explain the improved surfactant properties of **17** as well as the water solubility of **18**, since sugar moieties should be more exposed to the solvent.

Glutaryl spacer does not allow parallelism between alkyl chains in spite of the position of linkage, leading more extended conformations. In ionic gemini surfactants it has been reported[7] that for hydrophobic methylene spacers, the CMC goes through a maximum with increasing spacer carbon number at about 5-6. A short spacer is expected to impose a reduced intermonomeric head group separation influencing the distribution of distances between the polar heads in the interface, the spontaneous curvature of the surfactant layer, and in turn the shape of aggregates formed by these surfactants. With larger spacers a progressive penetration of the spacer into the aggregate hydrophobe core is also expected since the spacer is too hydrophobic to remain in the aqueous phase.[8] This effect appears evident if we compare CMC values for compounds **8** and **9** and for compounds **16** and **17**. In the last example, the difference is more significative since the linkage through O-2 allows a more ordered disposition of the alkyl chains in the latter compound and a greater exposition of the polar head groups.

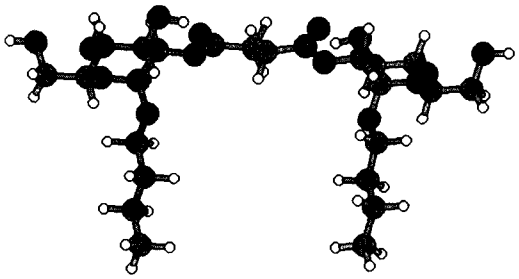


Fig. 1. Optimized structure of 1,4-bis-[2-*O*-(*n*-butyl-α-D-glucopyranosid] succinate **17** calculated by AM1 method

The improved surfactant properties of the new amphiphilic compounds here reported show the higher efficiency of dimeric (or gemini) surfactants compared with their monomeric counterpart. Further studies concerning micelle type and the structure adopted at the air-liquid interface would be necessary to rationalize the influence of subtle structural differences on the physical properties of these amphiphiles, but they are out of the scope of this report.

Table1. Surfactants Properties of Compounds **1**, **8**, **9**, **16**, **17**, and **18** in Water at 25°C Measured by the Bubble Method.

Product	CMC (mM)	γ_{CMC} (mN/m)	C_{20} (mM)	Spacer	Linked through
1	75.0	47.8	66.0	—	—
8	8.0	49.5	5.0	glutaryl	O-6
9	6.0	46.7	3.0	succinyl	O-6
16	7.0	50.7	5.0	glutaryl	O-2
17	1.5	49.8	1.3	succinyl	O-2
18	6.0	49.5	9.0	terephthaloyl	O-2

EXPERIMENTAL

General.

^{1}H NMR and ^{13}C NMR spectra were recorded at 200.13 MHz and 50.13 MHz, respectively, in $CDCl_3$ or CD_3OD. TLC was carried out on precoated aluminum plates (0.1 mm) of silicagel 60 F-254; detection was performed by exposure to UV light and by spraying the plates with 5 % (v/v) H_2SO_4 in ethanol followed by heating. IR spectra were recorded with a FT-spectrometer. Melting points are uncorrected.

***n*-Butyl-6-*O*-trityl-α-D-glucopyranoside (2).** *n*-Butyl-α-D-glucopyranoside **(1)** was prepared form D-glucose as previously reported.[3] Compound **1** (1.0 g, 4.23 mmol) was dissolved in anhydrous pyridine (8.0 mL), and trytil chloride (3.0 g) was added. After 5 days at room temperature, the solvent was evaporated and the residue was purified by silica gel column chromatography (4:1 cyclohexane-ethyl acetate) to give **2** (1.02 g, 50 % yield), as a syrup, which crystallized from ethanol-water: m.p. 60 °C, $[\alpha]_D$ +50.1 ° (c 0.7, $CHCl_3$); ^{1}H NMR: δ 7.47-7.19 (m, 15 H, Ph), 4.86 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 3.78-3.35 (m, 8 H, H-2, H-3, H-4, H-5, H-6a, H-6b, CH_2O), 1.62 (m, 2 H, CH_2), 1.39 (m, 2 H, CH_2), 0.94 (t, 3 H, *J* 7.4 Hz, CH_3). ^{13}C NMR: δ 143.9, 128.7, 127.8, 127.0 (Ph), 98.0 (C-1), 86.8 (*C*Ph_3), 74.7 (C-3), 72.2, 71.5 (C-2, C-5), 70.4 (C-4), 67.9 (CH_2O), 64.0 (C-6), 31.5 (CH_2), 19.3 (CH_2), 13.8 (CH_3). IR (film) ν_{max} (cm^{-1}): 3380.5 (OH), 1723.2 (Ph_3C), 758.3, 7529.4 (Ph). *Anal.* Calcd. for $C_{29}H_{34}O_6$: C 72.77, H 7.17. Found: C 72.58, H 7.05.

***n*-Butyl-2,3,4-tri-*O*-benzyl-6-*O*-trityl-α-D-glucopyranoside (3).** Compound **2** (1.0 g, 2.09 mmol) was dissolved in DMF (14.0 mL). Sodium hydride (80 % in mineral oil, 260.0 mg, 8.36 mmol) and benzyl bromide (1.0 mL, 8.42 mmol) were added at 0 °C. After stirring overnight at room temperature, methanol (10 mL), and after 30 min, chloroform (50 mL) were added. The organic layer was separated and washed with water, dried (Na_2SO_4), filtered and the solvent evaporated to a syrup, that was directly used for the next step. A small fraction (100 mg) was purified by preparative layer chromatography (93:7 cyclohexane-ethyl acetate) to give pure **3**, as a syrup: $[\alpha]_D$ +24.1 ° (c 1.0, $CHCl_3$); ^{1}H NMR: δ 7.50-7.16 (m, 30 H, Ph), 5.02-4.69 (m, 6 H, $J_{1,2}$ 3.6 Hz, CH_2Ph, H-1), 4.30 (d, 1 H, J_{gem} 10.4 Hz, C*H*Ph), 4.00 (t, 1 H, $J_{3,4}$ 9.2 Hz, H-4), 3.85-3.48 (m, 6 H, H-2, H-3, H-5, H-6a, CH_2O), 3.22 (dd, 1 H, $J_{5,6b}$ 5.0, $J_{6a,6b}$ 10.0 Hz, H-6b), 1.66 (m, 2 H, CH_2), 1.40 (m, 2 H, CH_2), 0.95 (t, 3 H, *J* 7.3Hz, CH_3). ^{13}C NMR: δ 144.1-138.1 and 128.9-127.0 (Ph), 96.7 (C-1), 86.4 (*C*Ph_3), 82.4 (C-3), 80.6 (C-2), 78.5 (C-4), 76.0, 75.1, 73.2 (*C*H_2Ph), 70.5 (C-5), 67.8 (CH_2O), 62.9 (C-6), 31.7 (CH_2), 19.6 (CH_2), 14.0 (CH_3). IR (film) ν_{max} (cm^{-1}): 1736.0 (Ph_3C), 748.8, 696.2 (Ph) *Anal.* Calcd. for $C_{50}H_{52}O_6$: C 80.17, H 7.00. Found: C 79.88, H 6.78.

***n*-Butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (4).** A mixture of crude **3**, ethanol (40 mL) and pyridinium chloride (185.0 mg,1.60 mmol) was refluxed for 2 h. After solvent evaporation, the crude mixture was chromatographed on silica gel (9:1 cyclohexane-ethyl acetate) giving **4** (950.0 mg, 89 % yield from **2**), as a syrup: $[\alpha]_D$ +53.3 ° (c 1.0, $CHCl_3$); ^1H NMR: δ 7.36-7.24 (m, 15 H, Ph), 5.02-4.60 (m, 9 H, $J_{1,2}$ 3.6 Hz, CH_2Ph, H-6a, H-6b, H-1), 4.01 (t, 1 H, $J_{3,4}$ 9.2 Hz, H-4), 3.72-3.33 (m, 6 H, H-2, H-3, H-5, CH_2O), 1.63 (m, 2 H, CH_2), 1.38 (m, 2 H, CH_2), 0.92 (t, 3 H, *J* 7.3Hz, CH_3). ^{13}C NMR: δ 129.8-126.3 (Ph), 97.0 (C-1), 82.0 (C-3), 80.5 (C-2), 77.7 (C-4), 75.7-73.2 (*C*H_2Ph), 70.8 (C-5), 68.1 (CH_2O), 62.0 (C-6), 31.6 (CH_2), 19.5 (CH_2), 14.0 (CH_3). IR (film) ν_{max} (cm^{-1}): 3484.0 (OH), 736.8, 698.2 (Ph). *Anal.* Calcd. for $C_{31}H_{38}O_6$: C 73.48, H 7.56. Found: C 73.21, H 7.29.

1,5-bis-[6-*O*-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] glutarate (5). 180.0 mg (0.36 mmol) of **4** were dissolved in toluene (3.0 mL). Triethylamine (0.060 mL, 0.43 mmol) and glutaryl chloride (0.030 mL, 0.23 mmol) were added. After overnight at room temperature, methanol (1 mL) was added. After solvent evaporation, preparative layer chromatography on silica gel (75:25 cyclohexane-ethyl acetate) afforded **5** (75.0 mg, 38 % yield) as a syrup. Data for this compound have been already reported.[3]

1,4-bis-[6-*O*-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] succinate (6). 145.0 mg (0.29 mmol) of **4** were dissolved in toluene (0.5 mL). Triethylamine (0.044 mL, 0.32 mmol) and succinyl chloride (0.020 mL, 0.17 mmol) were added. After overnight at room temperature, more triethylamine (0.022 mL, 0.16 mmol) and succinyl chloride (0.010 mL, 0.09 mmol) were added and the mixture was stirred for another 16 h at room temperature. Methanol (1 mL) was then added, and after solvent evaporation, preparative layer chromatography on silica gel (75:25 cyclohexane-ethyl acetate) afforded **6** (70.0 mg, 44 % yield) as a syrup: $[\alpha]_D$ 33.3 ° (c 1.2, $CHCl_3$); ^1H NMR: δ 7.33-7.26 (m, 30 H, Ph), 5.13-4.52 (m, 14 H, J_{gem} 12.1 Hz, $J_{1,2}$ 3.7 Hz, CH_2Ph, H-1 and 1'), 4.26 (d, 4 H, H-6 and 6'), 4.00 (t, 2 H, $J_{3,4}$ 9.1 Hz, H-4 and 4'), 3.83 (m, 2 H, H-5 and 5'), 3.66-3.36 (m, 8 H, H-2 and 2', H-3 and 3', CH_2O), 2.58 (s, 4 H, CH_2COO-), 1.58 (m, 4 H, CH_2), 1.38 (m, 4 H, CH_2), 0.91 (t, 6 H, *J* 7.2Hz, CH_3). ^{13}C NMR: δ 171.9 (COO-), 138.8-137.,9 (Ph), 128.4-127.6 (Ph), 96.8 (C-1 and 1'), 82.0 (C-3 and 3'), 80.2 (C-2 and 2'), 76.4 (C-4 and 4'), 75.7, 75.1, 73.1 (CH_2Ph), 68.6 (C-5 and 5'), 68.0 (CH_2O), 63.4 (C-6 and 6'), 31.5 (*C*H_2COO-, CH_2), 19.4 (CH_2), 13.8 (CH_3). FAB-MS: 1094 (M+). IR (film) ν_{max} (cm^{-1}): 1740.0 (C=O), 738.3, 698.8 (Ph). *Anal.* Calcd. for $C_{66}H_{78}O_{14}$: C 72.37, H 7.18. Found: C 72.77, H 7.30.

Methyl [6-*O*-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] succinate was isolated as a minor product, C.i.M.S.: Calcd. for $C_{36}H_{48}O_9N$ ($M+NH_4^+$): m/z 638.3329. Found: 638.3324.

Bis-[6-*O*-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] terephthalate (7). 250.0 mg (0.49 mmol) of **4** were dissolved in toluene (1.0 mL). Triethylamine (0.076 mL, 0.54 mmol) and terephthaloyl chloride (0.060 mg, 0.30 mmol) were added. After overnight at room temperature, methanol (1 mL) was added. After solvent evaporation, preparative layer chromatography on silica gel (75:25 cyclohexane-ethyl acetate) afforded **7** (196.0 mg, 70 % yield) as a syrup: $[\alpha]_D$ +83.5 ° (*c* 1.05, $CHCl_3$); ^1H NMR: δ 8.00 (s, 4 H, Ph), 7.43-7.19 (m, 30 H, Ph), 5.06-4.40 (m, 18 H, J_{gem} 12.1, $J_{1,2}$ 3.7 Hz, CH_2Ph, H-1 and 1', H-6 and 6'), 4.10-4.01 (t, 2 H, $J_{3,4}$ 9.2 Hz, H-4 and 4'), 3.95 (m, 2 H, H-5 and 5'), 3.69-3.36 (m, 8 H, H-2 and 2', H-3 and 3', CH_2O), 1.63 (m, 4 H, CH_2), 1.36 (m, 4 H, CH_2), 0.91 (t, 6 H, *J* 7.3Hz, CH_3). ^{13}C NMR: δ 165.3 (COO-), 138.6-137.7 (Ph), 129.5-127.6 (Ph), 96.8 (C-1 and 1'), 82.1 (C-3 and 3'), 80.3 (C-2 and 2'), 76.4 (C-4 and 4'), 75.8, 75.1, 73.1 (CH_2Ph), 68.7 (C-5 and 5'), 68.1 (CH_2O), 64.0 (C-6 and 6'), 31.4 (CH_2), 19.4 (CH_2), 13.8 (CH_3). IR (film) ν_{max} (cm^{-1}): 1729.4 (C=O), 742.2, 702.7 (Ph). *Anal.* Calcd. for $C_{70}H_{78}O_{14}$: C 73.53, H 6.88. Found: C 73.27, H 6.67.

Methyl [6-*O*-(*n*-butyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)] terephthalate was isolated as a minor product, C.i.M.S.: Calcd. for $C_{40}H_{48}O_9N$ ($M+NH_4^+$): m/z 686.3329. Found: 686.3318.

1,5-bis-[6-*O*-(*n*-butyl-α-D-glucopyranosid)] glutarate (8). Compound **5** (75.0 mg, 0.07 mmol) in methanol was hydrogenated at 1 atm over Pd/C 10 % for 24 h, to give pure **8** (53.0 mg, quantitative), as a syrup: $[\alpha]_D$ +56 ° (*c* 1.02, $CHCl_3$). ^1H and ^{13}C NMR data have been already reported.[3] IR (film) ν_{max} (cm^{-1}): 3401.3 (OH), 1732.4 (C=O). C.i.M.S.: Calcd. for $C_{25}H_{48}O_{14}N$ ($M+NH_4^+$): m/z 586.3075. Found: 586.3060.

1,4-bis-[6-*O*-(*n*-butyl-α-D-glucopyranosid)] succinate (9). Compound **6** (75.5 mg, 0.07 mmol) in methanol was hydrogenated at 1 atm over Pd/C 10 % for 24 h. The crude residue was purified by flash chromatography on silica gel (10:0 to 10:1 ethyl acetate-methanol) to give pure **9** (34.0 mg, 89 % yield), as a syrup: $[\alpha]_D$ +65 ° (*c* 0.76, $CHCl_3$); ^1H NMR (methanol-d): δ 4.79 (d, 2 H, $J_{1,2}$ 3.7 Hz, H-1 and 1'), 4.42 (dd, 2 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 11.7 Hz, H-6a and 6'a), 4.24 (dd, 2 H, $J_{5,6b}$ 6.0, $J_{6a,6b}$ 11.7 Hz, H-6b and 6'b), 3.83-3.25 (m, 12 H, H-2 and 2', H-3 and 3', H-4 and 4', H-5 and 5', 2 CH_2O), 2.70 (s, 4 H, 2 CH_2COO-), 1.72-1.60 (m, 4 H, 2 CH_2), 1.53-1.42 (m, 4 H, 2 CH_2), 0.99 (t, 6 H, *J* 7.3Hz, 2 CH_3). ^{13}C NMR: δ 173.9 (COO-), 100.2 (C-1 and 1'), 75.1 (C-3 and 3'), 73.5 (C-5 and 5'), 72.0 (C-2 and 2'), 71.2 (C-4 and 4'), 69.1 (CH_2O), 65.3 (C-6 and 6'), 32.8 (CH_2COO-), 30.0 (CH_2), 20.4 (CH_2), 14.2 (CH_3). IR (film) ν_{max} (cm^{-1}): 3400.0 (OH), 1734.8 (C=O). C.i.M.S.: Calcd. for $C_{24}H_{46}O_{14}N$ ($M+NH_4^+$): m/z 572.2918. Found: 572.2927.

Bis-[6-*O*-(*n*-butyl-α-D-glucopyranosid)] terephthalate (10). Compound **7** (120.0 mg, 0.105 mmol) in methanol was hydrogenated at 1 atm over Pd/C 10 % for 24 h. The crude residue was purified by flash chromatography on silica gel (8:1 ethyl acetate-methanol) to give pure **10** (58.0 mg, 92 % yield), as a syrup:

$[\alpha]_D$ +68 ° (*c* 1.6, MeOH); ^{1}H NMR (methanol-d): δ 8.24 (broad s, 4 H, Ph), 4.91-4.78 (m, 4 H, H-1 and 1', H-6a and 6'a), 4.58 (dd, 2 H, $J_{5,6b}$ 6.2, $J_{6a,6b}$ 11.2 Hz, H-6b and 6'b), 4.08-4.00 (m, 2 H, H-4 and 4'), 3.81 (t, 4 H, 2 CH_2O), 3.64-3.44 (m, 6 H, H-2 and 2', H-3 and 3', H-5 and 5'), 1.73-1.70 (m, 4 H, 2 CH_2), 1.56-1.41 (m, 4 H, 2 CH_2), 1.02 (t, 6 H, *J* 7.2 Hz, 2 CH_3). ^{13}C NMR: δ 166.8 (COO-), 135.4 and 130.6 (Ph), 100.2 (C-1 and 1'), 75.1 (C-3 and 3'), 73.5 (C-5 and 5'), 72.2 (C-2 and 2'), 71.3 (C-4 and 4'), 69.1 (CH_2O), 66.0 (C-6 and 6'), 32.7 (CH_2), 20.4 (CH_2), 14.2 (CH_3). IR (film) ν_{max} (cm^{-1}): 3380.5 (OH), 1723.2 (C=O), 729.4 (Ph). FAB-M.S. (+Na): Calcd. for $C_{28}H_{42}O_{14}Na$: m/z 625.2472. Found: 625.2470.

***n*-Butyl-4,6-*O*-benzylidene-α-D-glucopyranoside (11).** A mixture of **1** (1.60 g, 6.77 mmol), benzaldehyde dimethyl acetal (1.43 mL, 9.50 mmol), and camphorsulfonic acid (220 mg) in dry chloroform (35 mL), was heated at 85 °C for 4 h.[9] Sodium carbonate (900 mg) was added, and the heating was maintained for another 30 min. The mixture was filtered, and the solvent evaporated. Column chromatography on silica gel (7:3 cyclohexane-ethyl acetate) gave pure **11** (1.54 g, 70 % yield), as a white solid: m.p. 103 °C; $[\alpha]_D$ +97.2 ° (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 7.52-7.25 (m, 5 H, Ph), 5.53 (s, 1 H, CHPh), 4.88 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.27 (m, 1 H, H-6a, $J_{5,6}$ 8.9, $J_{6,6}$ 3.6 Hz), 3.97-3.42 (m, 7 H, H-2, H-3, H-4, H-5, H-6b, CH_2O), 1.62 (m, 2 H, CH_2), 1.40 (m, 2 H, CH_2), 0.95 (t, 3 H, *J* 7.3Hz, CH_3). ^{13}C NMR: δ 137.2, 129.2, 128.3, 126.2 (Ph), 101.9 (CHPh), 98.8 (C-1), 81.0 (C-2), 73.0, 71.9, 69.0 (C-3, C-4, C-5), 68.5 (CH_2O), 62.6, (C-6), 31.6 (CH_2), 19.4 (CH_2), 13.9 (CH_3). IR (film) ν_{max} (cm^{-1}): 3405.0 (OH), 746.9, 696.5 (Ph). FAB-M.S.: Calcd. for $C_{17}H_{24}O_6$: m/z 325.1651. Found: 325.1635.

***n*-Butyl-2,3-*O*-stannylidene-4,6-*O*-benzylidene-α-D-glucopyranoside (12).**

Method A. A mixture of **11** (450.0 mg, 1.39 mmol), toluene (42 mL) and dibutyltin oxide (370.0 mg, 1.49 mmol) was heated at 150 °C for 18 h in a flask with a Dean-Stark adaptor. The reaction was monitored by IR (OH band at 3500 cm^{-1}). After solvent evaporation, compound **12** was used for the next step without further purification.

Method B.[4] A mixture of **11** (203.0 mg, 0.63 mmol), toluene (25 mL) and dibutyltin oxide (163.6 mg, 0.66 mmol) in an erlenmeyer flask adapted with a small air-condenser, was placed in a microwave oven (119 watt). The oven was then turned on for 1 minute. After 30 seconds, it was turned on again for 1 min. The sequence was repeated to totalize 10 minutes, when the IR spectrum indicated the end of the reaction. After solvent evaporation, compound **12** was used for the next step without further purification.

1,5-bis-[2-O-(*n*-Butyl-4,6-*O*-benzylidene-α-D-glucopyranosid)] glutarate (13). Compound **12** (180 mg) was dissolved in toluene (0.5 mL). Triethylamine (0.049 mL, 0.35 mmol) and glutaryl chloride (0.025 mL, 0.19 mmol) were added. After overnight at room temperature, methanol (0.4 mL) was added. After solvent

evaporation, preparative layer chromatography on silica gel (65:35 toluene-ethyl acetate) afforded **13** (45.9 mg, 37 % yield from **11**) as a syrup: $[\alpha]_D$ +119.9. ° (*c* 2.00, $CHCl_3$); ^1H NMR: δ 7.48-7.25 (m, 10 H, Ph), 5.53 (s, 2 H, CHPh), 5.03 (d, 2 H, $J_{1,2}$ 3.8 Hz, H-1), 4.77 (dd, 2 H, $J_{2,3}$ 9.5Hz, H-2), 4.26 (dd, 2 H, $J_{6,6}$ 4.0 Hz, $J_{5,6}$ 9.3 Hz, H-6a), 4.17 (t, 2 H, H-3), 3.83 (dd, 2 H, H-6b), 3.78-2.99 (m, 8 H, H-4, H-5, CH_2O), 2.45 (t, 4 H, *J* 6.7 Hz, CH_2COO-), 2.02 (m, 2 H, C*H*$_2CH_2COO$-), 1.55 (m, 4 H, CH_2), 1.37 (m, 4 H, CH_2), 0.92 (t, 6 H, *J* 7.3Hz, CH_3). ^{13}C NMR: δ 172.7 (COO-), 137.1 (Ph), 129.2-126.2 (Ph), 101.9 (CHPh), 96.5 (C-1 and 1'), 81.5 (C-2 and 2'), 74.8 (C-3 and 3'), 68.9, 68.6 (C-4 and 4', C-5 and 5'), 68.2 (CH_2O), 62.1, (C-6 and 6'), 32.6 (CH_2COO-), 31.4 (CH_2), 20.1 (*C*H_2CH_2COO-), 19.2 (CH_2), 13.8 (CH_3). IR (film) ν_{max} (cm^{-1}): 3469.7 (OH), 1732.6 (C=O), 754.3, 700.2 (Ph). *Anal.* Calcd. for $C_{41}H_{56}O_{14}$: C 63.72, H 7.30. Found: C 63.41, H 7.43.

1,4-bis-[2-O-(*n*-Butyl-4,6-*O*-benzylidene-α-D-glucopyranosid)] succinate (14). Compound **12** (206 mg) was dissolved in toluene (0.6 mL). Triethylamine (0.067 mL, 0.48 mmol) and succinyl chloride (0.033 mL, 0.22 mmol) were added. After overnight at room temperature, methanol (0.4 mL) was added. After solvent evaporation, preparative layer chromatography on silica gel (7:3 toluene-ethyl acetate) afforded **14** (48.0 mg, 35 % yield from **11**) as a syrup: $[\alpha]_D$ +103.8 ° (*c* 1.13, $CHCl_3$); ^1H NMR: d 7.51-7.25 (m, 10 H, Ph), 5.54 (s, 2 H, CHPh), 5.03 (d, 2 H. $J_{1,2}$ 3,7 Hz, H-1), 4.77 (dd, 2 H, $J_{2,3}$ 9,5 Hz, H-2), 4.30-4.15 (m, 4 H, $J_{6,6}$ 4,2 Hz, $J_{5,6}$ 9,6 Hz, H-6a, H-3), 3.84 (dd, 2 H, H-6b), 3.78-3.56 (m, 8 H, H-4, CH_2O, H-5), 2.73 (s, 4 H, CH_2COO), 1.58 (m, 4 H, CH_2), 1.40 (m, 4 H, CH_2), 0.93 (t, 6 H, *J* 7.2Hz, CH_3). ^{13}C NMR: δ 171.8 (COO-), 137.1 (Ph), 129.2-126.3 (Ph), 102.0 (CHPh), 96.4 (C-1 and 1'), 81.4 (C-2 and 2'), 74.3 (C-3 and 3'), 68.9, 68.6(C-4 and 4', C-5 and 5'), 68.3 (CH_2O), 62.2 (C-6 and 6'), 31.4 (CH_2), 29.3 (*C*H_2COO-), 19.2 (CH_2), 13.8 (CH_3). IR (film) ν_{max} (cm^{-1}): 3445.6 (OH), 1738.5 (C=O), 754.4, 699.6 (Ph). *Anal.* Calcd. for $C_{40}H_{50}O_{14}$: C 63.31, H 7.17. Found: C 63.11, H 7.35.

Bis-[2-O-(*n*-Butyl-4,6-*O*-benzylidene-α-D-glucopyranosid)] terephthalate (15). Compound **12** (139 mg) was dissolved in toluene (0.5 mL). Triethylamine (0.040 mL, 0.29 mmol) and terephthaloyl chloride (31 mg, 0.153 mmol) were added. After overnight at room temperature, methanol (0.5 mL) was added. After solvent evaporation, preparative layer chromatography on silica gel (3:2 toluene-ethyl acetate) afforded **15** (41.0 mg, 42 % yield from **11**) as a syrup: $[\alpha]_D$ +132.4. ° (*c* 1.11, $CHCl_3$); ^1H NMR: d 8.14 (s, 4 H, Ph), 7.53-7.25 (m, 10 H, Ph), 5.57 (s, 2 H, CHPh), 5.16 (d, 2 H, $J_{1,2}$ 3.8 Hz, H-1), 5.04 (dd, 2 H, $J_{2,3}$ 9.5Hz, H-2), 4.37 (t, 2 H, $J_{3,4}$ 9.4 Hz, H-3), 4.32 (dd, 2 H, $J_{6,6}$ 4.4 Hz, $J_{5,6}$ 9.8 Hz, H-6a), 3.92 (dd, 2 H, H-6b), 3.78 (t, 2 H, H-4), 3.61 (t, 4 H, *J* 9.5 Hz, CH_2O), 3.39 (m, 2 H, H-5), 1.52 (m, 4 H, CH_2), 1.30 (m, 4 H, CH_2), 0.83 (t, 6 H, *J* 7.3Hz, CH_3). ^{13}C NMR: d 165.4 (COO-), 137.1 (Ph), 129.8-126.3 (Ph), 102.0 (CHPh), 96.6 (C-1 and 1'), 81.6 (C-2 and 2'), 74.6 (C-3 and 3'), 68.9 (C-4 and 4', C-5 and 5'), 68.3 (CH_2O), 62.2, (C-6 and 6'), 31.4

(CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (film) ν_{max} (cm^{-1}): 3469.0 (OH), 1721.4 (C=O), 731.8, 699.6 (Ph). *Anal.* Calcd. for $C_{42}H_{50}O_{14}$: C 64.77, H 6.47. Found: C 65.14, H 6.91.

1,5-bis-[2-O-(*n*-Butyl-α-D-glucopyranosid)] glutarate (16). Compound **13** (94.3 mg, 0.12 mmol) in 2:1:1 ethyl acetate-methanol-acetic acid was hydrogenated at 4 atm over Pd/C 10 % for 5 h, to give pure **16** (68.8 mg, 95 % yield), as a syrup: $[\alpha]_D$ +117.2 ° (*c* 1.34, MeOH); ^{1}H NMR (methanol-d): δ 4.96 (d, 2 H, $J_{1,2}$ 3.7 Hz, H-1 and 1'), 4.58 (dd, 2 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.9 Hz, H-2 and 2'), 3.88-3.55 (m, 8 H, H-3 and 3', H-6a and 6'a, H-6b and 6'b, CH_2O), 3.51-3.31 (m, 6 H, H-4 and 4', H-5 and 5', CH_2O), 2.48 (t, 4 H, *J* 7.0 Hz, 2 CH_2COO-), 2.03-1.93 (m, 2 H, C*H*$_2$$CH_2COO$-), 1.64-1.51 (m, 4 H, 2 CH_2), 1.46-1.29 (m, 4 H, 2 CH_2), 0.94 (t, 6 H, *J* 7.3Hz, 2 CH_3). ^{13}C NMR: δ 174.5 (COO-), 97.0 (C-1 and 1'), 75.1 (C-2 and 2'), 73.4 (C-3 and 3'), 72.3 (C-5 and 5'), 71.7 (C-4 and 4'), 68.7 (CH_2O), 62.4 (C-6 and 6'), 33.9 (CH_2COO-), 32.5 (CH_2), 21.2 (CH_2CH_2COO-), 20.3 (CH_2), 14.2 (CH_3). IR (film) ν_{max} (cm^{-1}): 3420.0 (OH), 1733.4 (C=O). FAB-M.S. (+LiCl): Calcd. for $C_{25}H_{44}O_{14}Li$: m/z 575.2892. Found: 575.2888.

1,4-bis-[2-O-(*n*-Butyl-α-D-glucopyranosid)] succinate (17). Compound **14** (132.7 mg, 0.17 mmol) in 2:1:1 ethyl acetate-methanol-acetic acid was hydrogenated at 4 atm over Pd/C 10 % for 5 h, to give pure **17** (93.2 mg, 96 % yield), as a syrup: $[\alpha]_D$ +134.4 ° (*c* 1.29, MeOH); ^{1}H NMR (methanol-d): δ 4.95 (d, 2 H, $J_{1,2}$ 3.7 Hz, H-1 and 1'), 4.58 (dd, 2 H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.0 Hz, H-2 and 2'), 3.89-3.30 (m, 14 H, H-3 and 3', H-4 and 4', H-5 and 5', H-6a and 6'a, H-6b and 6'b, 2 CH_2O), 2.70 (s, 4 H, 2 CH_2COO-), 1.61-1.36 (m, 8 H, 4 CH_2), 0.95 (t, 6 H, *J* 7.2Hz, 2 CH_3). ^{13}C NMR: δ 174.0 (COO-), 100.1 (C-1 and 1'), 75.2 (C-2 and 2'), 73.6 (C-3 and 3'), 71.9 (C-4 and 4', C-5 and 5'), 68.8 (CH_2O), 62.8 (C-6 and 6'), 32.8 (CH_2), 29.9 (CH_2COO-), 20.4 (CH_2), 14.2 (CH_3). IR (film) ν_{max} (cm^{-1}): 3419.6 (OH), 1733.2 (C=O). C.i.M.S.: Calcd. for $C_{24}H_{46}O_{14}N$ ($M+NH_4^+$): m/z 572.2918. Found: 572.2923.

1,4-bis-[2-O-(*n*-Butyl-α-D-glucopyranosid)] terephthalate (18). Compound **15** (99.4 mg, 0.128 mmol) in 2:1:1 ethyl acetate-methanol-acetic acid was hydrogenated at 4 atm over Pd/C 10 %. After 5 h, solvent evaporation gave **18** (69.2 mg, 90 % yield), as a syrup: $[\alpha]_D$ 112.8 ° (*c* 0.94, MeOH); ^{1}H NMR (methanol-d): δ 8.19 (s, 4 H, Ph), 5.12 (d, 2 H, $J_{1,2}$ 4.0 Hz, H-1 and 1'), 4.84 (dd, 2 H, $J_{1,2}$ 4.0, $J_{2,3}$ 9.9 Hz, H-2 and 2'), 4.02 (dd, 2 H, $J_{3,4}$ 9.1, $J_{2,3}$ 9.9 Hz, H-3 and 3'), 3.88-3.63 (m, 8 H, H-4 and 4', H-6a and 6'a, H-6b and 6'b, CH_2O), 3.50-3.29 (m, 4 H, H-5 and 5', CH_2O), 1.59-1.24 (m, 8 H, 4 CH_2), 0.82 (t, 6 H, *J* 7.3Hz, 2 CH_3). ^{13}C NMR: δ 166.8 (COO-), 135.3 and 130.8 (Ph), 97.1 (C-1 and 1'), 76.1 (C-2 and 2'), 73.6 (C-3 and 3'), 72.5 (C-5 and 5'), 71.8 (C-4 and 4'), 68.7 (CH_2O), 62.5 (C-6 and 6'), 32.5 (CH_2), 20.3 (CH_2), 14.0 (CH_3). IR (film)

ν_{max} (cm^{-1}): 3431.2 (OH), 1718.0 (C=O), 732.3 IR (film) ν_{max} (cm^{-1}): 3469.2 (OH), 1732.6 (C=O), 754.3, 700.2 (Ph). FAB-M.S. (+Na): Calcd. for $C_{28}H_{42}O_{14}Na$: m/z 625.2472. Found: 625.2477.

Surfactant properties.

Air-water surface tensions were measured at 25 °C by in a special adapted tensiometer based in the bubble presure method.[10] Calibration was performed against a range of standard liquids; excellent agreement with the literature values was found.[11] Critical micellar concentrations (CMC) for compounds **1**, **8**, **9**, **16**, **17** and **18** were determined by extrapolation of surface tension vs. concentration curves. All compounds showed the typical graphics, with an abrupt change in slope at the zone corresponding to CMC.

Acknowledgements.

This work was carried out with the financial contribution of UBA (Universidad de Buenos Aires) and CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas). Elemental analyses were performed by UMYMFOR (CONICET). M. Castro thanks UBA for a fellowship. J. Kovensky and A. Fernández Cirelli are Research Members of CONICET.

REFERENCES

1. a. Zana, R.; Benrraou, M.; Rueff, R. *Langmuir* **1991**, *7*, 1072-1075.
   b. Menger, F. M.; Littau, C. A. *J. Am. Chem. Soc.* **1991**, *113*, 1451-1452.
   c. Menger, F. M.; Littau, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 10083-10090.
2. a. Karaborni, S.; Esselink, K.; Hilbers, P. A. J.; Smit, B.; Karthauser, J.; van Os, N. M.; Zana, R. *Science* **1994**, *266*, 254-256.
   b. Hue, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324-1327.
   c. Perez, L.; Torres, J. L.; Manresa, A.; Solans, C.; Infante, M. R. *Langmuir* **1996**, *12*, 5296-5301.
3. Castro, M. J. L.; Kovensky, J.; Fernández Cirelli, A. *Tetrahedron Lett.* **1997**, *38*, 3995-3998.
4. a. Morcuende, A.; Valverde, S.; Herradón, B. *Synlett.* **1994**, 89-95.
   b. Herradón, B.; Morcuende, A.; Valverde, S. *Synlett.* **1995**, 455-458.
5. David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 643-663.
6. Hyperchem 5.0, AMPAC version 5.0, Semichem Inc., 7128 Summit. The parameters of the AM1 method belong to Dewar, M. J. S.; Zoebisch, E. F.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902-3909.
7. Holmberg K. *Novel Surfactants. Preparation, applications, and biodegradability*; Surfactant Science Series Vol. 74, Marcel Dekker Inc.,1998; pp. 255-256.
8. a. Zana, R.; Talmon, Y. *Nature* **1993**, 362, 228- 230.
   b. Danino, D.; Talmon, Y.; Zana, R. *Langmuir* **1995**, 11, 1448-56.
9. Ferro, V.; Mocerino, M.; Stick R. V.; Tilbrook, D. M. G. *Aust. J. Chem.* **1988**, *41*, 813-815.
10. Becher, P. *Emulsions, Theory and Practice*; Litton Educational Publishing, 1965; pp. 355-356.
11. Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1997-1998; pp. **6**- 135-138.