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Carbohydrate Research 343 (2008) 839–847
Carbohydrate RESEARCH

Synthesis of sugar-based chelating surfactants for metal removal from wastewater

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Received 2 October 2007; received in revised form 27 December 2007; accepted 14 January 2008
Available online 26 January 2008

Abstract—Four chelating surfactants were synthesized in a few steps from octyl D-glucosides. Their main interfacial properties were determined, and their flotation properties were evaluated on a laboratory scale using Fe(III) as a model contaminant metal. The performance on metal extraction was mainly dependent on the complexing functional group, but the surfactant efficiency was also important.

Keywords: Surfactant; Chelate; Metal; Flotation

1. Introduction

Remediation of wastewater and soils is an important task for environmental processing. Various remediation techniques have been reported for heavy-metal removal from polluted materials: precipitation, liquid–liquid extraction, electroremediation, phytoremediation, and flotation.[1,2] In the flotation procedure, surfactants are used to remove metals from an aqueous solution. After complexation, air is bubbled and metals are removed from the solution by isolation of the foam. For collecting specific metal ions, complexing agents as amidoxime-type surfactants, hydroxamic acid-type surfactants, and EDTA-type surfactants have been prepared and used in flotation experiments.[3] Floatability has been shown to be related to the hydrophilic–lipophilic balance (HLB),[4] and good performances were obtained by adding a nonionic surfactant to the complexing agent solution.

Environmental compatibility requires biodegradable surfactants with good chelating properties for the treatment of polluted effluents. Alkyl glycosides are widely used nonionic surfactants presenting excellent biodegradability and the absence of toxic effects.[5] They are readily prepared from renewable materials as fatty alcohols and carbohydrates, and they are gradually replacing the other known nonionic surfactants derived from the petrochemical industry.

In this paper, we report on the synthesis of a new type of chelating surfactants based on octyl glucosides modified by the introduction of a complexing function. Carboxylic and hydroxamic acids have been chosen for their known properties as metal collectors. Critical micellar concentrations were determined. Flotation experiments in a laboratory scale have been performed with Fe(III) solutions as a model contaminant metal.

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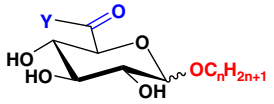
doi:10.1016/j.carres.2008.01.015

2. Results and discussion

2.1. Synthesis

The structures proposed are alkyl glucosides in which the primary hydroxyl group of glucose has been transformed in a chelating functional group.



Long-chain alkyl glucosides have been synthesized from pentaacetate **1** (Scheme 1) under microwave irradiation.[6] This heating system proceeds in very short reaction times and in very good yields. The α:β ratio changes with microwave conditions. In our hands, octyl glucopyranosides are obtained in 3 min in a 70% yield and a 70:30 α:β ratio. The octyl chain has been selected because a good compromise between flotation and water solubility can be expected from its interfacial properties.[7]

Separation of anomers could be performed on the protected glucosides **2a**–**b**, which were then deacetylated in Zemplèn conditions to give pure octyl D-glucopyranosides **3a** and **3b**.

Different conditions for selective oxidation of the primary alcohol have been evaluated. Catalytic TEMPO in acetonitrile–phosphate buffer (pH 6.7) using $NaClO_2$–NaClO as the regenerating oxidant system[8] led to the desired glucuronic acid derivative in 89% yield when tested on 100 mg, but the workup and purification on higher quantities were problematic and prevented the scale-up of the procedure. The use of air and Pt/C (50 °C, pH 9, 48 h)[9] gave only 36% yield.

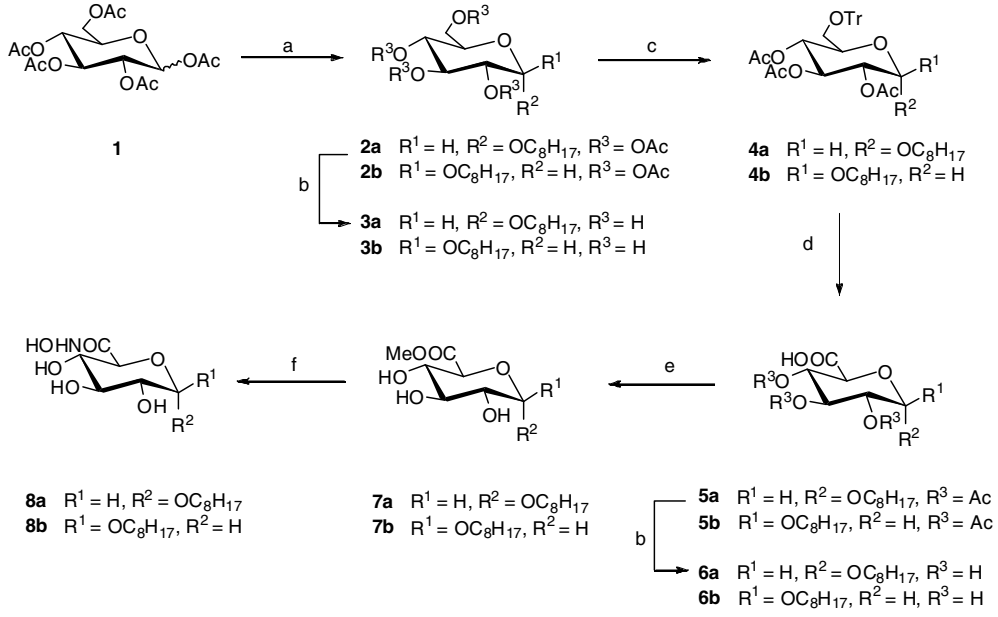
On the other hand, selective protection of the primary position as a trityl ether, followed by acetylation and oxidation with the system CrO_3(cat)/H_5IO_6 afforded the desired octyl glucopyranosiduronates **5a** and **5b** in 70% and 55% yields, respectively, for the three steps.

Reaction of **5a**–**b** with NH_2OBn·HCl and NEt_3 was performed with two different coupling agents: BOP and DCC; however, the corresponding hydroxamate derivatives were obtained in only modest yields (50–55%). Using NH_2OTBS higher yields were obtained (up to 78%), but results were not always reproducible, and tedious workup was necessary to eliminate the excess of silyl byproducts.

Finally, after deacetylation conversion to the corresponding methyl esters **6a** and **6b**, reaction with aqueous hydroxylamine led smoothly to **8a** and **8b** in 87% and 67% yield, respectively. The most suitable synthetic route is shown in Scheme 1. Therefore, a set of chelating surfactants have been easily synthesized from D-glucose in a few steps.

2.2. Interfacial properties

In a preliminary examination of surfactant properties, air–water surface tensions (γ) were measured at 25 °C in a specially adapted tensiometer based on the bubble pressure method[10] and plotted versus log C to get critical micellar concentrations (CMC) of compounds **6a**, **6b**,



Scheme 1. Reagents and conditions: (a) octanol, $ZnCl_2$, microwave (60 W), 3 min; (b) NaMeO, MeOH; (c) TrCl, pyridine, then Ac_2O; (d) CrO_3 (cat), H_5IO_6, aq CH_3CN, 30 min; (e) MeOH, H_2SO_4, reflux overnight; (f) aq NH_2OH, rt, 16 h.

Table 1. Interfacial properties of new complexing surfactants

Compound	CMC (mM)	γ_{CMC} (mN/m)	C_{20} (mM)	HLB
6a	13.1 ± 1.8	29.5 ± 0.7	3.0 ± 0.4	13.4
6b	15.6 ± 1.5	31.3 ± 0.7	5.6 ± 0.4	13.4
8a	20.7 ± 1.3	36.6 ± 0.7	9.3 ± 0.2	13.7
8b	20.6 ± 2.6	32.9 ± 0.7	5.4 ± 0.4	13.7
Octyl α-D-glucopyranoside[6]	10.0 ± 1.1	36.4 ± 0.7	2.2 ± 0.2	13.1

8a, and **8b**. The values obtained are shown in Table 1, together with the corresponding values of octyl α-D-glucopyranoside for comparison.

It is evident from the data that compounds **6a**, **6b**, **8a**, and **8b** have CMC values 1.3–2.0-fold higher than octyl α-D-glucopyranoside and 10-fold higher than octyl polyglucoside butyl ether (0.9 mM).[11] One of the reasons of this behavior is the difference of the HLB value between compounds **6a**, **6b**, **8a**, and **8b** (from 13.4 to 13.7), octyl α-D-glucopyranoside (13.1), and octyl polyglucoside butyl ether (11.6).

According to the literature, when the alkyl chain in the surfactant is fixed and the polar head lipophilicity is increased, the CMC value will be reduced (from 10 mM for octyl-α-D-glucopyranoside to 0.9 mM for its butyl ether counterparts). However, when the alkyl tail is fixed and the polar head is modified in order to increase its hydrophilicity, the CMC value will be increased (e.g., from 4.9 mM for $C_8H_{17}OC_2H_4OH$ to 9.9 mM for $C_8H_{17}(OC_2H_4)_6OH$).[12]

The surface tension at CMC (γ_{CMC}) is a useful measure of the effectiveness of the surfactants to reduce the surface tension of the solvent, and it is the lowest value of surface tension that the surfactant–solvent system can reach. Compound **6a** is the most effective surfactant, and compound **8a** has the highest γ_{CMC} value, it being the least effective one. Meanwhile, about the same γ_{CMC} values were obtained for compounds **6b** and **8b**.

On the other hand, the efficiency of a surfactant can be measured by C_{20} value, the molar surfactant concentration in the aqueous phase required to decrease the surface tension of the solvent by 20 mN/m.[13] Compounds **6a**, **6b**, **8a**, and **8b** showed C_{20} values higher than octyl α-D-glucopyranoside; therefore, the new surfactants prepared are less efficient to reduce the surface tension. The C_{20} value is a fundamental parameter to get a proper surfactant for optimal flotation performances, because the flotation tests are performed at about this concentration. Compound **6a** showed the best value, and compound **8a** showed the worst value, while compounds **6b** and **8b** showed intermediate efficiency.

It is interesting to note that while compounds **6a** and **6b** bearing carboxylic acid groups displayed CMC and γ_{CMC} values lower than hydroxamic acid derivatives **8a** and **8b**, C_{20} values showed a completely different behavior. Compounds with a different polar head as **6b** and **8b** presented similar surfactant efficiency (5.62 and 5.37, respectively). Although the number of compounds in consideration is small to establish a general correlation between structure and CMC, γ_{CMC}, and/or C_{20}, the surfactant properties displayed by this family (Table 1) allow us to compare the flotation properties of compounds with different polar head and C_{20} (**6a** and **8a**), and compounds with different polar head but similar C_{20} (**6b** and **8b**).

2.3. Removal of Fe(III) from aqueous solutions by flotation

Flotation experiments were performed with aqueous solutions containing metallic pollutants. Calculated HLB values are 13.4 and 13.7 for carboxylic and hydroxamic acid derivatives (Table 1), respectively; therefore, appropriate flotation properties can be expected.[3]

Fe(III) was chosen as the model metal contaminant, because a visual evidence of the extraction with compounds **8a** and **8b** may be expected, due to the colored complex formed between Fe(III) and the hydroxamic acid function. Besides, since iron recovery is of interest in the treatment of electroplating wastewater, a method using oxidizing bacteria has recently been reported.[14] On the other hand, ferric ions are often used in excess to precipitate other pollutant species (arsenic, chromium) from groundwater,[15] and the remaining Fe(III) must be removed.

Flotation experiments were performed with the device shown in Figure 1.

Briefly, the solution containing the surfactant and Fe(III) was introduced in the flotation column and air is bubbled from the bottom. The foam was recovered through the lateral tube, and Fe(III) was determined in the foam and in the residual liquid.

Fe(III) concentrations were determined by ICP using a 1:20 dilution and reading at two different wavelengths: 239 and 259 nm. A matrix effect being observed for the surfactant, the determination was performed using the method of measured additions. The results obtained for our chelating surfactants are summarized in Table 2.

Compounds **8a** and **8b** with a hydroxamic acid polar head have shown better performance of iron extraction than compounds **6a** and **6b** with carboxylic acid polar head, as expected. However, further analysis evidences subtle differences among these compounds. Considering

Figure 1.

Table 2. Fe(III) removal from aqueous solutions by chelating surfactants

Compound	Foam [Fe(III)] (mg/L)	Liquid [Fe(III)] (mg/L)	Ratio $[Fe(III)]_{foam}/[Fe(III)]_{liquid}$
6a	9.5 ± 0.2	7.8 ± 0.3	1.2 ± 0.05
6b	7.4 ± 0.9	7.8 ± 1.1	0.9 ± 0.2
8a	13.4 ± 1.0	6.0 ± 0.9	2.2 ± 0.4
8b	13.2 ± 0.9	4.2 ± 0.3	3.1 ± 0.3
Sodium laurate[a]	—	—	—

[a] A precipitate appeared and no enough foam was formed.

the β-glycosides, the iron recovery of the hydroxamic acid derivative **8b** is 3.4-fold higher than that of carboxylic acid **6b** (3.1 and 0.9, respectively). On the other hand, for the α-glycosides the iron recovery of compound **8a** is only 1.8-fold higher than that of **6a** (2.2- and 1.2-fold, respectively). This different behavior may be related to the surfactant efficiency (C_{20} values) of these compounds. For couple **8b/6b**, the increment in iron recovery directly shows the effect of the chelating polar head, since both surfactants have similar C_{20} values (5.6 and 5.4, respectively, as shown in Table 1). For the α derivatives, however, the situation is different, as compound **8a** (with better polar head features than **6a**) is less efficient to reduce the surface tension (C_{20} values are 9.3 and 3.0, respectively). Therefore, these results suggest that the polar head trapping capability of a surfactant is not the unique parameter determining the flotation properties, and the efficiency in reducing the surface tension must also be considered in order to obtain adequate performances.

In conclusion, a new family of compounds with metal-chelating properties was synthesized in a few steps from octyl D-glucosides. The metal recovery was dependent on the complexing functional group of the surfactant. In addition, the C_{20} value was the main interfacial property for flotation performance with Fe(III) solutions. Further studies regarding the influence of polar head and interfacial properties in the flotation experiences are in progress in our laboratory in order to rationalize the design and the synthesis of these chelating surfactants.

3. Experimental

3.1. General methods

All chemicals were purchased from Sigma, Aldrich, or Akros and were used without further purification. Melting points were determined with a Büchi 535 apparatus. Optical rotations were measured with a Perkin–Elmer Model 343 polarimeter using a sodium lamp at 20 °C. Optical rotation ($[\alpha]_D$) values are given in 10^{-1} deg cm^2 g^{-1}. High-resolution electrospray-ionization mass spectra in the positive-ion mode were obtained on a Q-TOF Ultima Global hybrid quadrupole/time-of-flight instrument (Waters–Micromass, Manchester, UK), equipped with a pneumatically assisted electrospray (Z-spray) ion source and an additional sprayer (Lock Spray) for the reference compound. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AC 300 spectrometer. All new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by ^{1}H–^{1}H and ^{1}H–^{13}C correlation experiments. Inductively-coupled plasma-atomic emission spectrometry (ICP) was performed in a Perkin–Elmer Optima 2000 Dual View, using the following conditions: Ar flux plasma 1.5 L/min, nebulization 0.5 L/min, auxiliary 0.7 L/min, RF 1500 W, wavelengths (Fe) 239.562 and 259.393 nm. Infrared spectra were recorded on a Nicolet O.M.N.I. sampler Avatar 320.FTIR spectrometer. UV/vis spectra were recorded on a JASCO Model 7850. Microwave irradiation was performed in a CEM-Discover® System.

3.2. Octyl 2,3,4,6-tetra-*O*-acetyl-α,β-D-glucopyranoside (2a,b)

A mixture of 1,2,3,4,6-penta-*O*-acetyl-D-glucopyranose (**1**, 3.9 g, 10.0 mmol), 1-octanol (3.25 mL, 20.2 mmol), and $ZnCl_2$ (1.4 g, 10.0 mmol) in a 100-mL flask was stirred under argon in the microwave reactor. The following conditions were used: $T = 115$ °C, $P = 60$ W, ramp time = 3 min, holdtime = 3 min. After cooling, the brown oil obtained was filtered through silica gel (eluant EtOAc). After solvent evaporation, the mixture was reacetylated using pyridine (4.1 mL) and Ac_2O (5.0 mL). After stirring overnight at rt, MeOH (10 mL) was added, and the mixture was stirred for 10 min. The solution was diluted with EtOAc (100 mL) and washed with water (5 × 100 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated to a syrup. Flash chromatography on silica gel (1:4 to 2:3 EtOAc–cyclohexane) gave **2a** (2.55 g, 55% yield) and **2b** (0.81 g, 18% yield).

3.2.1. Octyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (2a). Oil, R_f 0.7 (1:1 EtOAc–cyclohexane); $[\alpha]_D^{20}$ +34 (*c* 0.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.36 (t, 1H, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.94 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.92 (t, 1H, $J_{3,4}$ 9.8 Hz, $J_{4,5}$ 10.2 Hz, H-4), 4.72 (dd, 1H, $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 10.2 Hz, H-2), 4.15 (dd, 1H, $J_{5,6a}$ 4.5 Hz, $J_{6a,6b}$ 12.2 Hz, H-6a), 3.96 (dd, 1H, $J_{5,6b}$ 2.2 Hz, $J_{6a,6b}$ 12.2 Hz, H-6b), 3.90 (ddd, 1H, $J_{4,5}$ 10.2 Hz, $J_{5,6a}$ 4.5 Hz, $J_{5,6b}$ 2.2 Hz, H-5), 3.57 (td, 1H, $J_{1'a,1'b}$ 9.7 Hz, $J_{1'a,2'}$ 6.5 Hz, H-1′a), 3.31 (td, 1H, $J_{1'a,1'b}$ 9.7 Hz, $J_{1'b,2'}$ 6.5 Hz, H-1′b), 1.96, 1.93, 1.91, 1.89 (4s, 3H each, 4CH_3), 1.48 (quint, 2H, $J_{1',2'}$ 6.5 Hz, $J_{2',3'}$ 6.5 Hz, H-2′), 1.25–1.12 (m, 10H, H-3′ to H-7′), 0.76 (t, 3H, $J_{7',8'}$ 6.8 Hz, H-8′). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.2, 169.70, 169.68, 169.2 (4C=O), 95.3 (C-1), 70.6 (C-2), 69.9 (C-3), 68.3 (C-1′, C-4), 66.8 (C-5), 61.6 (C-6), 31.5, 28.9, 25.7, 22.3 (C-2′ to C-7′), 20.3 (2*C*H_3–CO), 20.24, 20.22 (2*C*H_3–CO), 13.7 (C-8′).

3.2.2. Octyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (2b). White crystals (cyclohexane), mp 51.5–53 °C, mp (lit.[16]) 53–54 °C, R_f 0.64 (1:1 EtOAc–cyclohexane); $[\alpha]_D^{25}$ −17 (*c* 1.02, $CHCl_3$), $[\alpha]_D^{25}$ (lit.[14]) −21.7 (*c* 1.0, MeOH); IR (ATR in cm^{-1}): 2922, 2874, 2854 (ν_{CH}), 1743 ($\nu_{C=O}$), 1472, 1428, 1368, 1257, 1223, 1167, 1133, 1091, 1038. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.13 (t, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 9.6 Hz, H-3), 5.00 (t, 1H, $J_{3,4}$ 9.6 Hz, $J_{4,5}$ 9.9 Hz, H-4), 4.90 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 9.6 Hz, H-2), 4.43 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.20 (dd, 1H, $J_{5,6a}$ 4.7 Hz, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.05 (dd, 1H, $J_{5,6b}$ 2.4 Hz, $J_{6a,6b}$ 12.3 Hz, H-6b), 3.79 (td, 1H, $J_{1'a,1'b}$ 9.6 Hz, $J_{1'a,2'}$ 6.3 Hz, H-1′a), 3.63 (ddd, 1H, $J_{4,5}$ 9.9 Hz, $J_{5,6a}$ 4.7 Hz, $J_{5,6b}$ 2.4 Hz, H-5), 3.40 (td, 1H, $J_{1'a,1'b}$ 9.6 Hz, $J_{1'b,2'}$ 6.7 Hz, H-1′b), 2.00, 1.96, 1.94, 1.92 (4s, 3H each, 4 CH_3), 1.48 (m, 2H, 2H-2′), 1.28–1.08 (m, 10H, H-3′ to H-7′), 0.79 (t, 3H, $J_{7',8'}$ 7.0 Hz, H-8′). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.5, 170.2, 169.3, 169.1 (4C=O), 100.7 (C-1), 72.7 (C-3), 71.5 (C-5), 71.2 (C-2), 70.1 (C-1′), 68.3 (C-4), 61.8 (C-6), 31.7, 29.2, 29.1 (2C), 25.7, 22.5 (C-2′–C-7′), 20.6, 20.5 (4*C*H_3–CO), 13.9 (C-8′).

3.3. Octyl α-D-glucopyranoside (3a)

Compound **2a** (2.5 g, 5.4 mmol) was dissolved in dry MeOH (8 mL). A solution of 1 M NaOMe in MeOH (2.7 mL) was added, and the mixture was stirred under N_2 at rt until total disappearance of starting materials and intermediates (3 h). Amberlyst IR-120 (H^+) was added, and the mixture was stirred until the pH reached 5. The resin was filtered off, and the solution was evaporated to dryness leading to compound **3a** (quantitative yield), as a gum, R_f 0.53 (1:9 MeOH–EtOAc); $[\alpha]_D^{20}$ +117 (*c* 1.0, MeOH); $[\alpha]_D^{23}$ (lit.[17]) +117.9 (*c* 1.0, MeOH); IR (ATR in cm^{-1}): 3600–3000 (ν_{OH}), 2952, 2922, 2847 (ν_{CH}), 1655, 1637, 1459, 1410, 1379, 1352, 1145, 1112, 1086, 1050, 1024, 1002. ^{1}H NMR (300 MHz, CD_3OD): δ 4.78 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 3.79 (dd, 1H, $J_{5,6a}$ 2.4 Hz, $J_{6a,6b}$ 11.8 Hz, H-6a), 3.72 (td, 1H, $J_{1'a,1'b}$ 9.6 Hz, $J_{1'a,2'}$ 6.9 Hz, H-1′a), 3.66 (dd, 1H, $J_{5,6b}$ 5.4 Hz, $J_{6a,6b}$ 11.8 Hz, H-6b), 3.65 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 9.3 Hz, H-3), 3.57 (ddd, 1H, $J_{4,5}$ 9.8 Hz, $J_{5,6a}$ 2.4 Hz, $J_{5,6b}$ 5.4 Hz, H-5), 3.44 (td, 1H, $J_{1'a,1'b}$ 9.6 Hz, $J_{1'b,2'}$ 6.4 Hz, H-1′b), 3.40 (dd, 1H, $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.31 (dd, 1H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.8 Hz, H-4), 1.62 (m, 2H, H-2′), 1.30 (m, 10H, H-3′ to H-7′), 0.89 (t, 3H, $J_{7',8'}$ 6.8 Hz, H-8′). ^{13}C NMR (75.5 MHz, CD_3OD): δ 100.0 (C-1), 75.0 (C-3), 73.50, 73.45 (C-2, C-5), 71.7 (C-4), 69.1 (C-1′), 62.5 (C-6), 33.0, 30.6, 30.5, 30.3, 27.3, 23.7 (C-2′ to C-7′), 14.5 (C-8′).

3.4. Octyl β-D-glucopyranoside (3b)

Compound **2b** was deacetylated under Zemplèn conditions as for **3a** to give compound **3b** (quantitative yield), as a gum: R_f 0.55 (1:9 MeOH–EtOAc); $[\alpha]_D^{20}$ −30 (*c* 1.0, MeOH); $[\alpha]_D^{25}$ (lit.[14]) −30.3 (*c* 1.0, MeOH); IR (ATR in cm^{-1}): 3600–2950 (ν_{OH}), 2923, 2854 (ν_{CH}), 1645, 1463, 1378, 1160, 1112, 1085, 1027, 919, 894. ^{1}H NMR (300 MHz, CD_3OD): δ 4.25 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 3.90 (dt, 1H, $J_{1'a,1'b}$ 9.6 Hz, $J_{1'a,2'}$ 6.8 Hz, H-1′a), 3.86 (dd, 1H, $J_{5,6a}$ 1.7 Hz, $J_{6a,6b}$ 11.9 Hz, H-6a), 3.67 (dd, 1H, $J_{5,6b}$ 5.2 Hz, $J_{6a,6b}$ 11.9 Hz, H-6b), 3.53 (td, 1H, $J_{1'b,2'}$ 6.8 Hz, H-1′b), 3.43–3.23 (m, 3H, H-3, H-4, H-5), 3.18 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 8.9 Hz, H-2), 1.62 (quint, 2H, $J_{1'a,2'}$ 6.8 Hz, $J_{2',3'}$ 6.8 Hz, H-2′), 1.45–1.23 (m, 10H, H-3′ to H-7′), 0.89 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, CD_3OD): δ 104.3 (C-1), 78.0 (C-3), 77.8 (C-5), 75.0 (C-2), 71.5 (C-4), 70.9 (C-1′), 62.7 (C-6), 33.0, 30.7, 30.5, 30.4, 27.1, 23.7 (C-2′ to C-7′), 14.4 (C-8′).

3.5. Octyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranoside (4a)

A solution of **3a** (4.4 g, 15 mmol) and trityl chloride (8.5 g, 30 mmol) in pyridine (40 mL) was stirred at 80 °C for 2 h. After cooling, Ac_2O (48 mL) was added, and the mixture was stirred overnight at rt. MeOH (96 mL) was added, and after stirring for 10 min the solution was diluted with EtOAc (100 mL) and washed with water (3 × 100 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated to a syrup. Flash chromatography on silica gel (5:9.5 to 1:4 EtOAc–cyclohexane) gave **4a** (8.14 g, 84% yield) as a colorless syrup: R_f 0.53 (3:7 EtOAc–cyclohexane); $[\alpha]_D^{20}$ +99 (*c* 1.1, EtOH); FTIR (cm^{-1}): 2926, 2852 (ν_{-CH}), 1752 ($\nu_{C=O}$), 1491, 1449 ($\nu_{C=C}$), 1367, 1244, 1222, 1035 (ν_{C-O-C}), 900, 765, 747, 709. ^1H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, 6H, J_{ortho} 7.1 Hz, H_o-Ar), 7.29–7.16 (m, 9H, H-Ar_m, H-Ar_p), 5.47 (t, 1H, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 9.3 Hz, H-3), 5.15 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.09 (t, 1H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 10.2 Hz, H-4), 4.92 (dd, 1H, $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 10.2 Hz, H-2), 4.00 (ddd, 1H, $J_{4,5}$ 10.2 Hz, $J_{5,6a}$ 2.1 Hz, $J_{5,6b}$ 5.2 Hz, H-5), 3.79 (td, 1H, $J_{1'a,1'b}$ 9.7 Hz, $J_{1'a,2'}$ 6.6 Hz, H-1′a), 3.47 (td, 1H, $J_{1'a,1'b}$ 9.7 Hz, $J_{1'b,2'}$ 6.6 Hz, H-1′b), 3.20 (dd, 1H, $J_{5,6a}$ 2.1 Hz, $J_{6a,6b}$ 10.3 Hz, H-6a), 3.12 (dd, 1H, $J_{5,6b}$ 5.2 Hz, $J_{6a,6b}$ 10.3 Hz, H-6b), 2.04, 1.97, 1.72 (3s, 3H each, $3CH_3$), 1.63 (m, 2H, H-2′), 1.42–1.21 (m, 10H, H-3′ to H-7′), 0.87 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.0 (2C=O) 169.1 (C=O), 143.5 (C_i-Ph), 128.5 (C_m-Ph), 127.6 (C_o-Ph), 126.8 (C_p-Ph), 95.2 (C-1), 86.4 (*C*Ph_3), 71.1 (C-2), 70.5 (C-3), 69.1 (C-4), 68.5 (C-5), 68.1 (C-1′), 61.9 (C-6), 31.6, 29.1, 25.9, 22.5, (C-2′ to C-7′), 20.54, 20.50, 20.3 (3*C*H_3–CO), 13.9 (C-8′).

HRESIMS (+Na): calcd for $C_{39}H_{48}O_9Na$: *m*/*z* 683.3196. Found: 683.3214.

3.6. Octyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (4b)

Compound **3b** (3.85 g, 13.2 mmol) was reacted as for the preparation of **4a** to give **4b** (6.40 g, 74% yield) as a colorless syrup: R_f 0.5 (3:7 EtOAc –cyclohexane); $[\alpha]_D^{20}$ +33 (*c* 1.0, EtOH); FTIR (cm^{-1}): 2951, 2930, 2849 (ν_{-CH}), 1757 ($\nu_{C=O}$), 1491, 1449 ($\nu_{C=C}$), 1373, 1244, 1217 (ν_{C-O-C}), 1046, 900, 766, 748, 704. ^1H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, 6H, $J_{o,m}$ 7.0 Hz, H-Ar_o), 7.30–7.17 (m, 9H, H-Ar_m, H-Ar_p), 5.20 (t, 1H, $J_{3,4}$ 9.4 Hz, $J_{4,5}$ 9.4 Hz, H-4), 5.16 (t, 1H, $J_{2,3}$ 9.4 Hz, $J_{3,4}$ 9.4 Hz, H-3), 5.08 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.4 Hz, H-2), 4.52 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.95 (td, 1H, $J_{1'a,1'b}$ 9.6 Hz, $J_{1'a,2'}$ 6.3 Hz, H-1′a), 3.57 (m, 2H, H-1′b, H-5), 3.27 (dd, 1H, $J_{5,6a}$ 2.1 Hz, $J_{6a,6b}$ 10.4 Hz, H-6a), 3.10 (dd, 1H, $J_{5,6b}$ 4.5 Hz, $J_{6a,6b}$ 10.4 Hz, H-6b), 2.03, 1.97, 1.71 (3s, 3H each, $3CH_3$), 1.65 (m, 2H, H-2′), 1.39–1.21 (m, 10H, H-3′ to H-7′), 0.87 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.2, 169.2, 168.7 (3C=O), 143.5 (C_i-Ph), 128.5 (C_m-Ph), 127.6 (C_o-Ph), 126.8 (C_p-Ph), 100.6 (C-1), 86.4 (*C*Ph_3), 73.11, 73.09 (C-3, C-5), 71.5 (C-2), 69.6 (C-1′), 68.7 (C-4), 61.9 (C-6), 31.6, 29.4, 29.1, 26.7, 25.8, 22.5 (C-2′ to C-7′), 20.48, 20.46, 20.2 (3*C*H_3-CO), 13.9 (C-8′).

HRESIMS (+Na): calcd for $C_{39}H_{48}O_9Na$: *m*/*z* 683.3196. Found: 683.3210.

3.7. Octyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosiduronic acid (5a)

First, an oxidant solution was prepared by dissolving H_5IO_6 (11.4 g, 50 mmol) and CrO_3 (23 mg, 0.23 mmol) in wet CH_3CN (0.75% water v/v) to a volume of 114 mL. The oxidant solution (72 mL) was added to a solution of **4a** (8.15 g, 12.6 mmol) in wet acetonitrile (40 mL, 0.75% water v/v) in 30 min at rt. The mixture was stirred at rt for 1.5 h. Completion of the reaction was confirmed by TLC (9:1 dichloromethane–MeOH). After filtration on silica gel, CH_3CN was removed by evaporation. The residue was dissolved in CH_2Cl_2, dried (Na_2SO_4), filtered, and concentrated to a syrup. Flash chromatography on silica gel (1:1 EtOAc–cyclohexane, then 9:1 CH_2Cl_2–MeOH) gave **5a** (4.61 g, 85% yield) as a colorless syrup: R_f 0.21 (9:1 CH_2Cl_2–MeOH); $[\alpha]_D^{20}$ +99 (*c* 1.1, EtOH); FTIR (cm^{-1}): 2927, 2853 (ν_{-CH}), 1752 ($\nu_{C=O}$), 1608, 1431, 1369, 1221, 1166, 1043 (ν_{C-O-C}), 981, 901. ^1H NMR (300 MHz, $CDCl_3$): δ 9.03 (m, 1H, CO_2H), 5.54 (t, 1H, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 9.3 Hz, H-3), 5.21 (t, 1H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 10.2 Hz, H-4), 5.17 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.88 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.2 Hz, H-2), 4.36 (d, 1H, $J_{4,5}$ 10.2 Hz, H-5), 3.75 (td, 1H, $J_{1'a,1'b}$ 9.9 Hz, $J_{1'a,2'}$ 6.6 Hz, H-1′a), 3.46 (td, 1H, $J_{1'a,1'b}$ 9.9 Hz, $J_{1'b,2'}$ 6.6 Hz, H-1′b), 2.07, 2.04, 2.03 (3s, 3H each, $3CH_3$), 1.61 (quint, 2H, $J_{1',2'}$ 6.6 Hz, $J_{2',3'}$ 6.6 Hz, H-2′), 1.35–1.25 (m, 10H, H-3′ to H-7′), 0.89 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 171.3 (C-6), 170.2, 170.1, 169.9 (3C=O), 95.6 (C-1), 70.5 (C-2), 69.5, 69.4 (C-3, C-4), 69.1 (C-1′), 67.5 (C-5), 31.6, 29.0, 25.8, 22.5 (C-2′ to C-7′), 20.48, 20.42, 20.36 (3*C*H_3–CO), 13.9 (C-8′).

HRESIMS (+Na): calcd for $C_{20}H_{32}O_{10}Na$: *m*/*z* 455.1893. Found: 455.1886.

3.8. Octyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosiduronic acid (5b)

Compound **4b** (3.87 g, 5.9 mmol) was reacted as for the preparation of **5a** to give **5b** (6.4 g, 74% yield) as white crystals (cyclohexane): mp 129.5–131.8 °C; R_f 0.18 (9:1 CH_2Cl_2–MeOH); $[\alpha]_D^{20}$ +34 (*c* 1.0; EtOH); FTIR (cm^{-1}): 3500–2860 (ν_{OH}), 2935, 2872, 2860 (ν_{-CH}), 1741 ($\nu_{C=O}$), 1700 ($\nu_{C=O}$), 1438, 1384, 1369, 1266, 1243, 1201, 1081, 1063, 1030 (ν_{C-O-C}), 981, 701. ^1H NMR (300 MHz, $CDCl_3$): δ 9.50 (m, 1H, CO_2H), 5.26

(m, 2H, H-3, H-4), 5.01 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 9.3 Hz, H-2), 4.59 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 4.10 (d, 1H, $J_{4,5}$ 9.6 Hz, H-5), 3.91 (td, 1H, $J_{1'a,1'b}$ 9.6 Hz, $J_{1'a,2'}$ 6.4 Hz, H-1′a), 3.49 (td, 1H, $J_{1'a,1'b}$ 9.6 Hz, $J_{1'b,2'}$ 6.8 Hz, H-1′b), 2.05, 2.04, 2.03 (3s, 3H each, $3CH_3$), 1.56 (m, 2H, H-2′), 1.32–1.21 (m, 10H, H-3′ to H-7′), 0.88 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.8 (C-6), 170.3, 169.7, 169.3 (3C=O), 100.7 (C-1), 70.5 (C-1′), 72.1, 71.9, 71.2, 69.2 (C-2 to C-5), 31.7, 29.2, 25.7, 22.6 (C-2′ to C-7′), 20.6 ($2CH_3$–CO), 20.5 (CH_3–CO), 14.0 (C-8′). HRESIMS (+Na): calcd for $C_{20}H_{32}O_{10}Na$: m/z 455.1893. Found: 455.1910.

3.9. Octyl α-D-glucopyranosiduronic acid (6a)

Compound **5a** (1.58 g, 3.65 mmol) was deacetylated under Zemplèn conditions as before to give compound **6a** (1.14 g, 98% yield) as a white solid: mp >250 °C (dec); R_f 0.78 (6:4 CH_2Cl_2–MeOH); $[\alpha]_D^{20}$ 63 (c 1.0, MeOH); IR (ATR in cm^{-1}): 3650–3000 (ν_{OH}), 2954, 2924, 2856 (ν_{CH}), 1729, 1463, 1259, 1197, 1153, 1046, 987. ^{1}H NMR (300 MHz, CD_3OD): δ 4.98 (br s, 1H, H-1), 3.95 (d, 1H, $J_{4,5}$ 10.1 Hz, H-5), 3.72 (m, 2H, H-3, H-1′a), 3.48 (m, 3H, H-2, H-4, H-1′b), 1.63 (m, 2H, H-2′), 1.31 (m, 10H, H-3′ to H-7′), 0.90 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, CD_3OD): δ 177.0 (C-6), 100.4 (C-1), 74.6 (C-3), 73.6, 72.8 (C-2, C-4), 72.3 (C-5), 69.9 (C-1′), 33.0, 30.6, 30.4, 27.3, 23.7 (C-2′ to C-7′), 14.4 (C-8′). Spectroscopic data are in accord with those previously described.[18]

3.9.1. Oxidation with TEMPO. A solution of compound **3a** (104.3 mg, 0.36 mmol), TEMPO (39.8 mg, 0.25 mmol) in CH_3CN (1.9 mL) and 0.67 M phosphate buffer (pH 6.7) was heated to 35 °C under vigorous magnetic stirring. $NaClO_2$ (80.8 mg, 0.89 mmol, 20% aq solution) and immediately after that NaClO (2.1 M solution, 3.8 μL, 8.0 μM) were added. After stirring for 4 days at 35 °C, $Na_2S_2O_3$ (0.5 M solution, 0.35 mL) was added. The mixture was acidified to pH 1 with HCl (37%) and then concentrated. MeOH was added, and the mixture was filtered through silica gel and concentrated. Flash chromatography on silica gel (9:1 to 7:3 CH_2Cl_2–MeOH) gave compound **6a** (98.6 mg, 89% yield).

3.9.2. Oxidation with O_2, Pt/C. To a solution of compound **3a** (5.30 g, 18.1 mmol) in 3:1 water–dioxane (186 mL), Pt/C (5%, 7.43 g) was added. The pH was adjusted to 9–10 with 40% NaOH. The mixture was heated 36 h at 50 °C under vigorous magnetic stirring while air was bubbled and the pH maintained between 8.5 and 11. After cooling, the mixture was filtered and DOWEX 50 × 8 (H^+) resin was added until the pH became acidic. After filtration, evaporation, and flash chromatography on silica gel (9:1 to 6:4 CH_2Cl_2–MeOH, then MeOH), compound **6a** (1.99 g, 36% yield) was obtained.

3.10. Octyl β-D-glucopyranosiduronic acid (6b)

Compound **5b** (179 mg, 0.415 mmol) was deacetylated under Zemplèn conditions as before to give compound **6b** (91.8 mg, 51% yield) as a white solid: mp 217.7–221.2 °C; R_f 0.78 (6:4 CH_2Cl_2–MeOH); $[\alpha]_D^{20}$ −27 (c 0.95, MeOH); IR (ATR in cm^{-1}): 3650–2975 (ν_{OH}), 2925, 2856 (ν_{CH}), 1731, 1645, 1490, 1444, 1374, 1210, 1161, 1086, 1026, 930. ^{1}H NMR (300 MHz, CD_3OD): δ 4.31 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.96 (dt, 1H, $J_{1'a,1'b}$ 9.4 Hz, $J_{1'a,2'}$ 6.9 Hz, H-1′a), 3.71 (d, 1H, $J_{4,5}$ 9.1 Hz, H-5), 3.57–3.44 (m, 3H, H-1′b, H-3, H-4), 3.26 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 8.9 Hz, H-2), 1.63 (quint, 2H, $J_{1'a,2'}$ 6.9 Hz, $J_{2',3'}$ 6.9 Hz, H-2′), 1.30 (m, 10H, H-3′ to H-7′), 0.90 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, CD_3OD): δ 177.5 (C-6), 104.3 (C-1), 77.7 (C-3[†]), 76.1(C-5), 74.7 (C-2), 73.5 (C-4[†]), 71.4 (C-1′), 33.0, 30.8, 30.7, 30.5, 27.1, 23.7 (C-2′ to C-7′), 14.5 (C-8′).

HRESIMS (sodium salt, +Na): calcd for $C_{14}H_{25}O_7Na_2$: m/z 351.1396. Found: 351.1394.

3.10.1. Oxidation with O_2, Pt/C. Compound **3b** (410 mg, 1.4 mmol) was reacted as for the preparation of **6a** to give **6b** (165 mg, 39% yield).

3.11. Octyl (methyl α-D-glucopyranosiduronate) (7a)

To a solution of **6a** (572.7 mg, 1.89 mmol) in MeOH (20 mL) a drop of concd H_2SO_4 was added, and the mixture was refluxed overnight. After concentration, flash chromatography on silica gel (9:1 CH_2Cl_2–MeOH) gave **7a** (544.7 mg, 90% yield), as a colorless oil, which was directly used for the next step.

3.12. Octyl (methyl β-D-glucopyranosiduronate) (7b)

Compound **6b** (536.2 mg, 1.75 mmol) was reacted as for the preparation of **7a** to give **7b** (399.1 mg, 71% yield) a colorless oil, which was directly used for the next step.

3.13. Octyl *N*-hydroxy-α-D-glucopyranosiduronamide (8a)

To a solution of **7a** (354.0 mg, 1.1 mmol) in MeOH (10 mL), 50% aq NH_2OH (1.45 mL) was added. After stirring 16 h at rt, the mixture was concentrated to a syrup. Flash chromatography on silica gel (9:1 to 1:4 EtOAc–MeOH) afforded pure **8a** (310.2 mg, 87% yield) as a colorless oil: R_f 0.09 (9:1 EtOAc–MeOH); $[\alpha]_D^{20}$ −35 (c 0.99, EtOH); FTIR (cm^{-1}): 3460–3173 (ν_{OH},

[†] Assignments may be interchanged.

ν_{NH}), 2917, 2851 (ν_{-CH}), 1650 ($\nu_{C=O}$), 1561, 1466, 1356, 1149, 1035, 831. ^{1}H NMR (300 MHz, CD_3OD): δ 4.82 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 3.91 (d, 1H, $J_{4,5}$ 9.7 Hz, H-5), 3.69 (dt, 1H, $J_{1'a,1'b}$ 9.7 Hz, $J_{1'a,2'}$ 6.9 Hz, H-1′a), 3.65 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 8.9 Hz, H-3), 3.53 (dd, 1H, $J_{3,4}$ 8.9 Hz, $J_{4,5}$ 9.7 Hz, H-4), 3.46 (dd, 1H, $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 9.6 Hz, H-2), 3.44 (dt, 1H, $J_{1'a,1'b}$ 9.7 Hz, $J_{1'a,2'}$ 6.6 Hz, H-1′b), 1.64 (m, 2H, H-2′), 1.30 (m, 10H, H-3′ to H-7′), 0.90 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, CD_3OD): δ 169.0 (C-6), 100.6 (C-1), 74.5 (C-3), 73.3 (C-4), 72.9 (C-2), 71.5 (C-5), 69.8 (C-1′), 33.0, 30.6, 30.4, 27.2, 23.7 (C-2′ to C-7′), 14.5 (C-8′).

HRESIMS (+Na): calcd for $C_{14}H_{27}NO_7Na$: m/z 344.1685. Found: 344.1688.

3.14. Octyl *N*-hydroxy-β-D-glucopyranosiduronamide (8b)

Compound **7b** (544.7 mg, 1.70 mmol) was reacted as for the preparation of **8a** to give **8b** (366.1 mg, 67% yield) as a white solid: mp >175 °C (dec); R_f 0.09 (9:1 EtOAc–MeOH); $[\alpha]_D^{20}$ +79 (c 0.99, EtOH); FTIR (cm^{-1}): 3500–3000 (ν_{OH}), 3341 (ν_{NH}), 2923, 2855 (ν_{-CH}), 1679 ($\nu_{C=O}$), 1505, 1459, 1352, 1256, 1148, 1084, 1032, 800. ^{1}H NMR (300 MHz, CD_3OD): δ 4.28 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.83 (dt, 1H, $J_{1'a,1'b}$ 9.4 Hz, $J_{1'a,2'}$ 6.9 Hz, H-1′a), 3.71 (d, 1H, $J_{4,5}$ 9.1 Hz, H-5), 3.57–3.44 (m, 3H, H-1′b, H-3, H-4), 3.26 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 8.9 Hz, H-2), 1.63 (quint, 2H, $J_{1'a,2'} = J_{2',3'}$ 6.9 Hz, H-2′), 1.30 (m, 10H, H-3′ to H-7′), 0.90 (t, 3H, $J_{7',8'}$ 6.7 Hz, H-8′). ^{13}C NMR (75.5 MHz, CD_3OD): δ 168.1 (C-6), 104.8 (C-1), 77.6 (C-3), 75.5 (C-4 or C-5), 74.6 (C-2), 72.8 (C-4 or C-5), 71.1 (C-1′), 33.0, 30.8, 30.6, 30.4, 27.1, 23.7 (C-2′ to C-7′), 14.4 (C-8′).

HRESIMS (+Na): calcd for $C_{14}H_{27}NO_7Na$: m/z 344.1685. Found: 344.1675.

3.15. Determination of interfacial properties

Air–water surface tensions were measured at 25 °C in a specially adapted tensiometer based on the bubble pressure method.[19] Calibration was performed against a range of standard liquids,[9] and excellent agreement with literature values was found.[20] Critical micellar concentration (CMC) was determined by extrapolation of surface tension versus log concentration plots. All compounds exhibited the typical plots, with an abrupt change in slope at the zone corresponding to the CMC. Other interfacial properties were calculated according to known methods.[21]

3.16. Flotation experiments

A 0.35 mM solution of $FeCl_3$ in milli-Q water (solution 1) was prepared, and the Fe(III) concentration was determined by ICP using a 1:20 dilution and reading at two different wavelengths: 239 and 259 nm. Values of 18.3 ± 0.1 ppm and 18.6 ± 0.3 ppm, respectively, were obtained. Separately, a 1.75 mM solution of the surfactant (solution 2) in milli-Q water was prepared. For the flotation experiment, 7 mL of solution 1 and 7 mL of solution 2 were mixtured to give solution 3, corresponding to a 5.0 chelatant–metal ratio. A 4-mL aliquot of solution 3 was introduced in the flotation column. Air was bubbled from the bottom of the column for 2 min. The foam produced was recovered through the lateral tube. At the end of this time 1.5–2 mL of each phase was collected, and the concentrations were determined by ICP. A matrix effect being observed for the surfactant, the determination was performed using the method of measured additions:

Sample	Mother solution (μL)	Standard Fe(III) solution (1000 ppm, μL)	2% HNO_3 (mL)
1	250	0	4.750
2	250	25	4.725
3	250	50	4.700
4	250	75	4.675

The values of intensity read for each 5-mL sample were plotted versus Fe(III) concentration added, and the original concentration (considering the dilution 1:20) was obtained by extrapolation to $I = 0$. Flotation experiments were performed in duplicates, whereas Fe(III) concentrations were calculated as average values from triplicate ICP determinations.

Acknowledgments

The authors are indebted to DGA (fellowship to N.F.), Universidad de Buenos Aires, Centre National de la Recherche Scientifique (CNRS), and the Ministère délégué à l'Enseignement Supérieur et à la Recherche for financial support. This work was also supported by a Binational Cooperation France-Argentina, CNRS, and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.01.015.

References

1. (a) Woller, N.; Subklew, G.; Schwuger, M. J. *Colloids Surf., A* **1996**, *117*, 189–200; (b) Schwuger, M. J.; Subklew,

G.; Woller, N.. *Colloids Surf., A* **2001**, *186*, 229–242; (c) Mulligan, C. N.; Yong, R. N.; Gibbs, B. F. *Eng. Geol.* **2001**, *60*, 193–207.
2. Lemlich, R. *Adsorptive Bubble Separation Techniques*; Academic Press: New York, 1972.
3. Koide, Y.; Takamoto, H.; Matsukawa, K.; Yamada, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3364–3369.
4. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley & Sons: New York, 1989, pp 325–329.
5. Steber, J.; Guhl, W.; Stelter, N.; Schröder, F. R. In Hill, K., von Rybinski, W., Stoll, G., Eds.; Alkyl Polyglycosides. Technology, Properties and Applications; VCH: Weinheim, 1997; pp 177–187.
6. Limousin, C.; Cléophax, J.; Patit, A.; Loupy, A.; Lukacs, G. *J. Carbohydr. Chem.* **1997**, *16*, 327–342.
7. Castro, M. J. L.; Kovensky, J.; Fernández Cirelli, A. *Langmuir* **2002**, *18*, 2477–2482.
8. Barbier, M.; Breton, T.; Servat, K.; Grand, E.; Kokoh, B.; Kovensky, J. *J. Carbohydr. Chem.* **2006**, *25*, 253–266.
9. Ripke, N.; Thiem, J.; Böcker, T. European Patent 0326673 A2, 1988.
10. Castro, M. J. L.; Ritacco, H.; Kovensky, J.; Fernández Cirelli, A. *J. Chem. Educ.* **2001**, *78*, 347–348.
11. Rhode, O.; Weuthen, M.; Nickel, D. In Hill, K., von Rybinski, W., Stoll, G., Eds.; Alkyl Polyglycosides. Technology, Properties and Applications; VCH: Weinheim, 1997; pp 139–149.
12. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley & Sons: New York, 1989, pp 128–129.
13. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley & Sons: New York, 1989, pp 84–85.
14. Park, D.; Lee, D. S.; Park, J. M.; Chun, H. D.; Park, S. K.; Jitsuhara, I.; Miki, O.; Kato, T. *Ind. Eng. Chem. Res.* **2005**, *44*, 1854–1859.
15. Berg, M.; Luzi, S.; Trang, P. T. K.; Viet, P. H.; Giger, W.; Stüben, D. *Environ. Sci. Technol.* **2006**, *40*, 5567–5573.
16. Noller, C. R.; Rockwell, W. C. *J. Am. Chem. Soc.* **1938**, *60*, 2076–2077.
17. Brown, G. M.; Dubreuil, P.; Ichhaporia, F. M.; Desnoyers, J. E. *Can. J. Chem.* **1970**, *48*, 2525–2531.
18. Menger, F. M.; Binder, W. H.; Keiper, J. S. *Langmuir* **1997**, *13*, 3247–3250.
19. (a) Becher, P. *Emulsions, Theory and Practice*; Litton Educational Publishing: New York, 1965; (b) Fainerman, V. B.; Miller, R. In *The Maximum Bubble Pressure Tensiometry. Drops and Bubbles in Interfacial Research*; Moëbius, D., Miller, R., Eds.; Elsevier Science: New York, 1998; p 279.
20. Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1997–1998, pp 6–135.
21. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley & Sons: New York, 1989, pp 108–239.