Synthesis and Physico-Chemical Properties of Novel Biocompatible Alkyl D-Mannopyranosiduronate Surfactants Derived from Alginate

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Keywords: Alginate / Bioorganic chemistry / Mannuronic acid / Micelles / Surfactants

The present article describes the preparation and the physico-chemical properties of novel biocompatible surfactants derived from alginate for applications in detergents and cosmetics. Controlled acid hydrolysis of commercially available alginate from *Laminaria digitata* gives saturated oligo-mannuronates on a multigram scale. Subsequent one-pot acid glycosidic bond hydrolysis, esterification and stereocontrolled Fischer glycosylation in butanol with the related oligouronates efficiently provides *n*-butyl (*n*-butyl α-D-mannopyranosiduronate) (**3**). Double-tailed amphiphiles were next obtained from this key intermediate **3** by transesterification/transglycosylation processes in fatty alcohols. Aqueous basic and acid treatments furnished anionic or neutral single-tailed surfactants. These original alginate-derived amphiphiles exhibit attractive surface-tension and foaming properties.

Introduction

The development of surfactants based on natural renewable resources is a concept that is gaining recognition in the detergent and cosmetics industries.[1–3] This new class of biocompatible and biodegradable surfactants is a response to the increasing consumer demand for products that are both greener and more powerful. In order to achieve these objectives, it is necessary to use renewable, low-cost raw materials that are available in large quantities and to design molecular structures that show improved performance, favourable ecotoxicological properties and reduced environmental impact. Within this context, sugar-based surfactants[4] represent a significantly growing market, although only a few substances, such as alkyl polyglycosides,[5] sucrose esters[6] and sorbitan esters, are produced on an industrial scale.[7] These amphiphilic compounds are based on fatty alcohols derived from natural soybean, palm, sunflower or coconut oils and carbohydrate raw materials extracted from sugar cane, beet or cereals.

The industrial processes for the synthesis of alkyl polyglycosides involve Fischer glycosidation of monohydrate D-glucose with fatty alcohols from C_8 to C_{16} to afford a mixture of 1-*O*-alkyl mono-, di-, tri- and oligoglycosides.[5] Sucrose esters, as a mixture of mono- and polysubstituted compounds, are produced by a transesterification reaction of the primary hydroxyl group of the glucose moiety and methyl esters of fatty acids.[6] Sorbitan esters are built up from two basic ingredients: sorbitol and fatty esters.[7] They are manufactured by both internal ether formation and esterification reaction leading to the synthesis of anhydrohexitol esters.

As part of our program dealing with the synthesis of surfactants from totally *O*-unprotected uronic acids,[8,9] we describe here the preparation of a new class of glycosiduronates derived from alginate, which is the main polysaccharide of brown seaweed. The lack of D-mannopyranosiduronic acid in a monomeric form could explain the absence of publications dealing with mannuronic acid derived surfactants, contrary to the glucuronic, galacturonic or iduronic series.[8,9] Mannofuranurono-6,3-lactone is the only commercially available monomeric sugar derived from alginate. We recently published the synthesis of alkyl β-D-mannofuranurono-6,3-lactones for structural characterisations of alkyl uronates in a mannofuranosidic form.[10]

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Results and Discussion

Preparation of *n*-Alkyl (*n*-Alkyl α-D-Mannopyranosiduronate)s

Alginate is a heteropolysaccharide composed of (1,4)-linked β-D-mannuronic acid and α-L-guluronic acid residues;[11] it is the main polysaccharide of brown algae.[12–14] Several authors have described the preparation of oligomannuronates by acid and/or enzymatic depolymerisations,[15–22] but very few works deal with mannuronic acid in the monomeric form, probably because of the difficulty to hydrolyse the α- or β-(1,4) links in alginates. Haug and co-workers have described the partial acid depolymerisation of alginate to give homopolymer blocks of D-mannuronic acid (MM) and of L-guluronic acid (GG) with a degree of polymerisation (DP) of approximately 20, in addition to heterogeneous blocks of both uronic acids (MG; Figure 1).[15–17] The three types of blocks were separated by fractionated precipitation in accordance with their pH-dependant solubility in water (Table 1). Due to the difficulty of hydrolysing the (1,4) linkages of the homopolymeric blocks with an acid, very few groups have succeeded in preparing saturated oligouronates containing less than five osidic units. Shimokawa[23] and Matsubara[24] have reported the preparation of DP1–DP9 or DP1–DP12 saturated oligoguluronate mixtures in 11–12% yields. Nevertheless, there is no related methodology in the literature for the synthesis of these oligouronic acids on a multigram scale and with a low average DP and restricted polydispersity.

Table 1. Physical state of blocks as a function of pH.

Physical state of blocks	pH < 2	2 < pH < 3	3 < pH
Precipitates	MM GG	GG	–
Solubles	MG	MG MM	MG GG MM

We first investigated the synthesis of sodium mannuronate polymers **1** by applying Haug's methodology on a semi-industrial scale. The algae used as raw materials for the production of commercial alginates led to polysaccharides with different uronic acid compositions: *L digitata*, *Ascophyllum nodosum* and *Macrocystis pyrifera* are known to contain mannuronate-enriched alginates, whereas those present in *L. hyperborea* are characterised by a lower mannuronate/guluronate ratio. Preliminary laboratory tests on various commercially available alginates permitted us to select S20NS alginate from *Laminaria digitata* (higher M/G ratio, lower composition in MG blocks) for the pilot-plant transfer, thus allowing the preparation of sodium polymannuronates **1** with an average degree of polymerisation of 16 and on a hundred gram scale[25] in a 23% yield (see Experimental Section).

We then treated these polymannuronates **1** with acid in order to reduce the degree of polymerisation. Due to the insolubility of MM blocks at pH lower than 2.85, the reaction was performed at pH 3; heating to 100 °C for 8 h led to a mixture of oligomannuronates with an average DP of 5 (Scheme 1). Separation of oligouronic acids was generally performed by a high-performance liquid chromatography ion-pair method, although the use of this powerful analytical approach in the case of charged oligomers could not be easily extended to a multigram scale. We therefore focused our attention on the development of other separation methodologies with the aim of reducing the polydispersity of our uronate mixtures. The most efficient purification method was found to be an ultrafiltration process with a 3500 D cell-membrane cut-off which permitted both elimination of the highest oligomers and the isolation of several grams of enriched DP 2–4 saturated uronates **2** (Figure 2) in the presence of sodium chloride.

The absence of published results concerning the use of oligomannuronates in organic chemistry conduced us to study the reactivity of such compounds in organic solvents

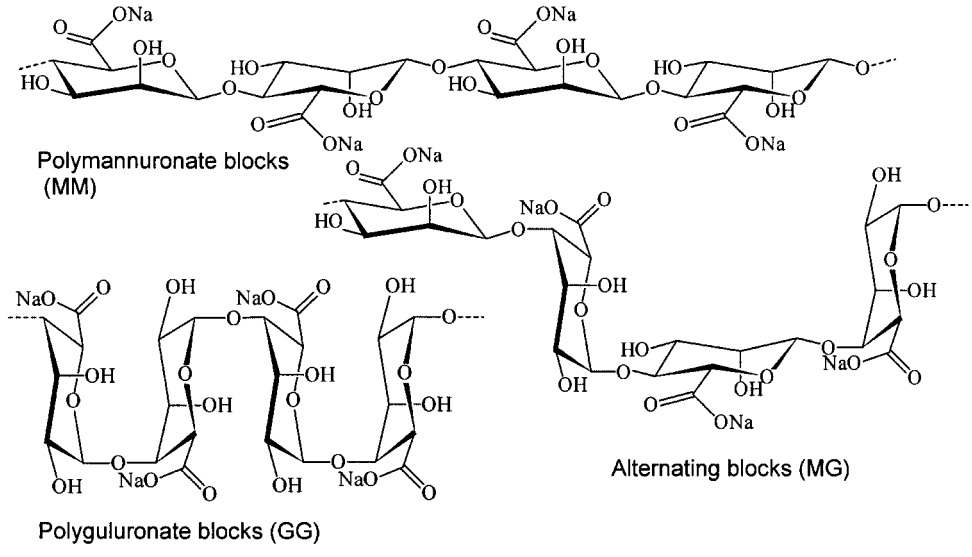
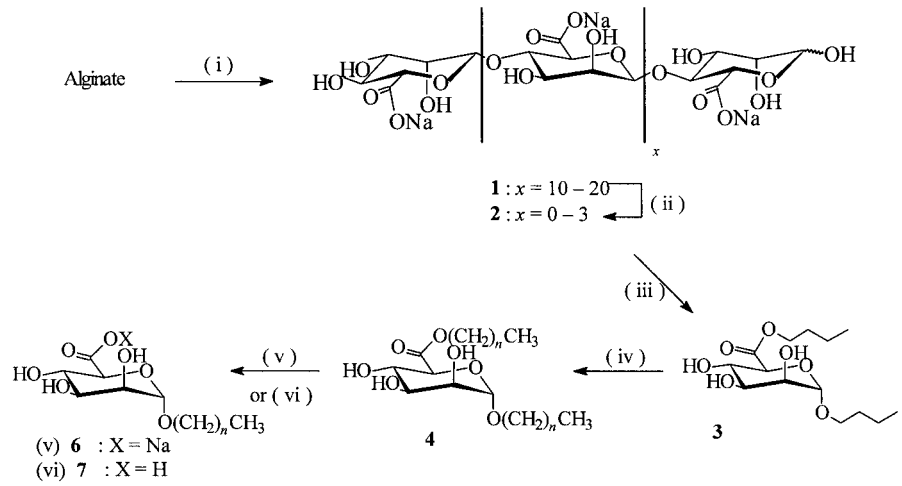


Figure 1. Structure of blocks of alginates.



Scheme 1. Stereoselective synthesis of α-D-mannuronate derivatives: (i) aq. HCl, pH 0.9, 23%; (ii) aq. HCl, pH 3.0, 89%; (iii) MSA, BuOH, 112–115 °C, 50%; (iv) MSA, $CH_3(CH_2)_nOH$, 65 °C, 2–5 mbar [**4a** (*n* = 7): 67%; **4b** (*n* = 9): 58%; **4c** (*n* = 11): 70%; **4d** (*n* = 13): 61%; **4e** (*n* = 15): 58%]; (v) aq. 0.1 N NaOH, CH_2Cl_2 [**6a** (*n* = 7): 90%; **6b** (*n* = 9): 88%; **6c** (*n* = 11): 89%]; (vi) aq. 0.1 N NaOH, CH_2Cl_2 then aq. 5% HCl, 0 °C [**7a** (*n* = 7): 90%; **7b** (*n* = 9): 88%; **7c** (*n* = 11): 89%; **7d** (*n* = 13): 88%].

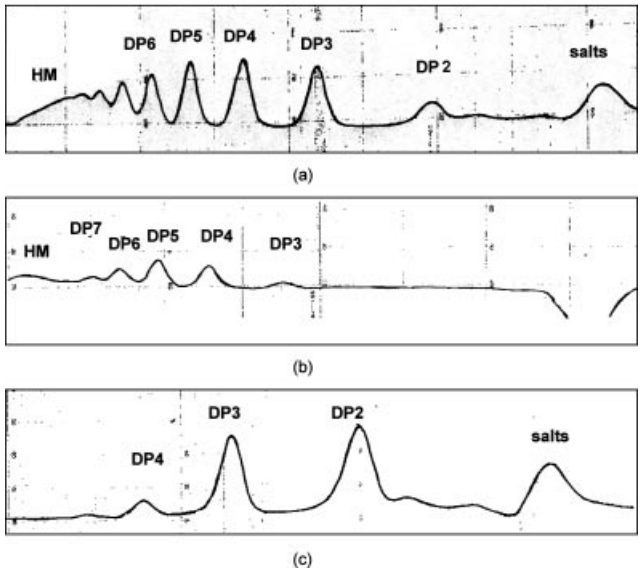


Figure 2. Ultrafiltration (UF) process with a 3500 D cell-membrane cut-off for the production of sodium oligomannuronates **2** with an average degree of polymerisation of 3: (a) starting oligo-mannuronate mixture before UF; (b) retentate after UF; (c) permeate after UF.

with numerous chemicals. We were confronted with i) the low dispersion of the substrates and the products in the reaction mixture, ii) the unreactivity of the substrates, mainly due to their insolubility in non-aqueous media, iii) the difficulties in product purification and analysis, and finally iv) the total lack of structural data for mannopyranosiduronates. In order to overcome these problems, our strategy involved the use of a short alcohol as the solvent to make the dispersion of sodium uronates easier, as well as acidic conditions to favour hydrolysis, esterification and/or glycosylation reactions. Treatment of saturated uronates **2** with methanesulfonic acid (MSA, 4 equiv.) in butanol at 112–115 °C provided *n*-butyl (*n*-butyl α-D-mannopyranosiduronate) (**3**) as a result of three simultaneous reactions (Scheme 1).[26] Firstly, the acid hydrolysis of the β-(1,4) linkages of the oligomers gave uronates in a monomeric form, thereby reducing the number of reaction products. Secondly, acidification of the carboxylate functions followed by esterification with butanol afforded the corresponding butyl esters. Finally, Fischer glycosylation with the short alcohol stereoselectively provided alkyl glycoside **3** in a pyranosidic form and with an α-configuration (50% overall yield). Monomer **3** was purified by flash chromatography, isolated as a pure α-anomer, and then easily characterised on the grounds of signals identified by COSY and heteronuclear ^1H-^{13}C experiments. The low-field resonance (δ = 100.5 ppm) observed for the anomeric carbon is indicative of an α-configuration.

At this stage, we envisaged the preparation of glycosidic surfactants incorporating longer hydrophobic alkyl chains in order to bring a more amphiphilic character to the glycosides. Firstly, simultaneous transesterification and transglycosylation were carried out in dodecanol, at 65 °C, in the presence of methanesulfonic acid and at low pressure (2–5 mbar) in order to eliminate the butanol formed in the reaction (Scheme 1). The main product was *n*-dodecyl (*n*-dodecyl α-D-mannopyranosiduronate) (**4c**), which is the thermodynamically more stable and kinetically formed product. A minor compound was identified as the *n*-dodecyl D-mannofuranurono-6,3-lactone **5c** (Figure 3), which has

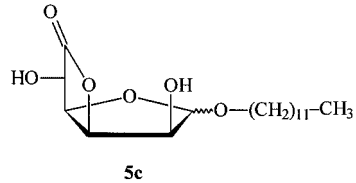


Figure 3. Structure of *n*-dodecyl D-mannofuranurono-6,3-lactone **5c**.

previously been synthesised from commercial D-mannofuranurono-6,3-lactone.[10] The kinetics of the reaction was then evaluated by GC after derivatisation of the crude mixture by silylation, and by parallel syntheses using a Büchi Syncore Reactor: this study permitted us to define the best reaction conditions concerning amounts of MSA, concentration of dodecanol (DodOH) and time conversion (Figures 4 and 5). The best yield we were able to obtain for the synthesis of compound **4c** was 74% when momoner **3** was treated with 1 equiv. of MSA and 8 equiv. of dodecanol, at 65 °C for 6 h. A small amount of uncharacterised by-products (5%) and lactone **5c** (15% yield) were detected by GC in addition to an unidentified intermediate (Figure 5) which disappeared with the formation of the desired compound **4c**. In the second step, these optimised conditions were reproduced for the synthesis of compounds **4a**,**b** and **4d**,**e**

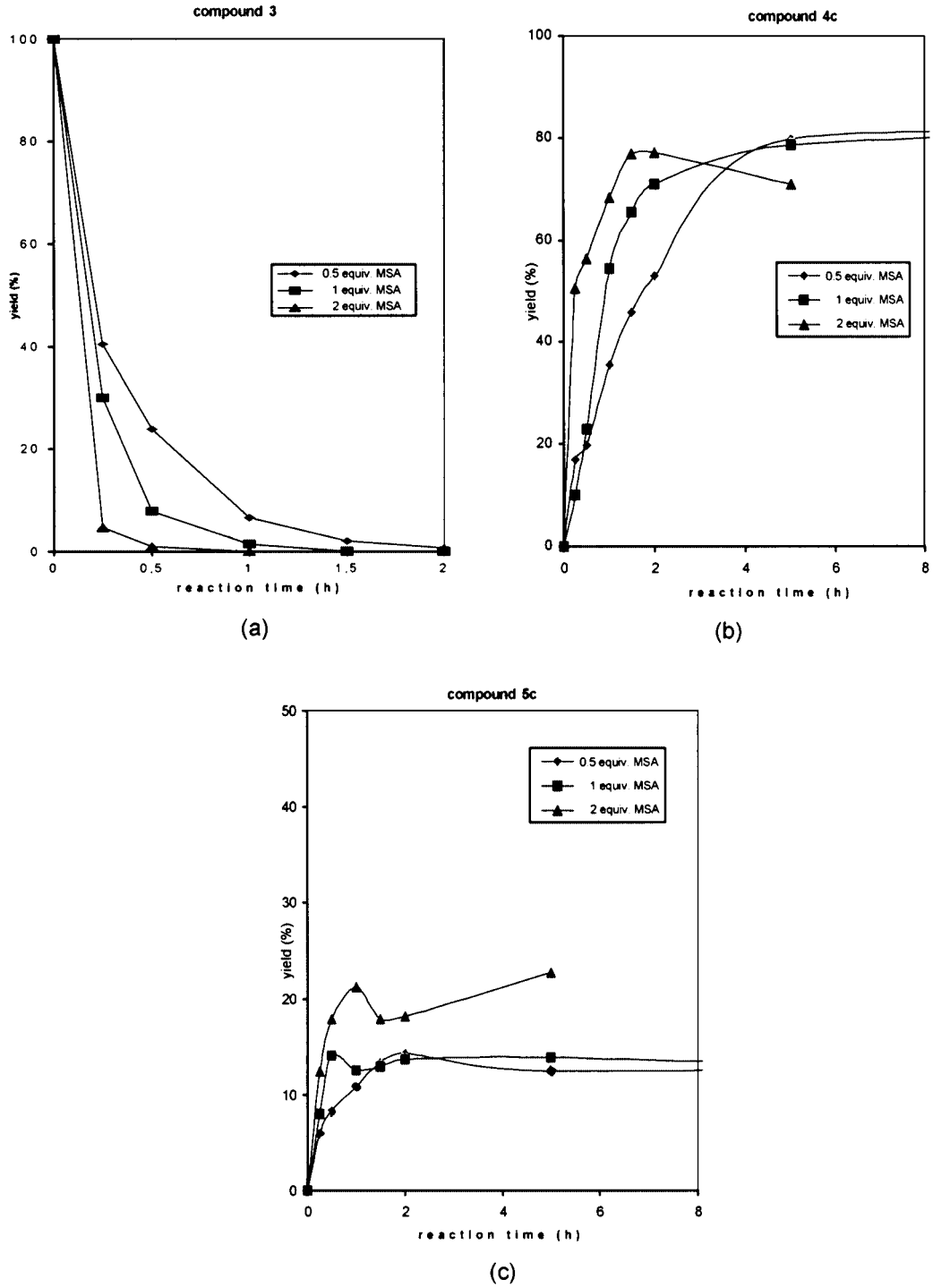


Figure 4. Influence of the MSA amount used [0.5 equiv. (♦), 1 equiv. (■), 1.5 equiv. (▲)] on the kinetics of the transesterification-transglycosylation reactions of compound **3** (8 equiv. dodecanol: DodOH): (a) disappearance of starting compound **3**; (b) formation of compound **4c**; (c) formation of lactone **5c**.

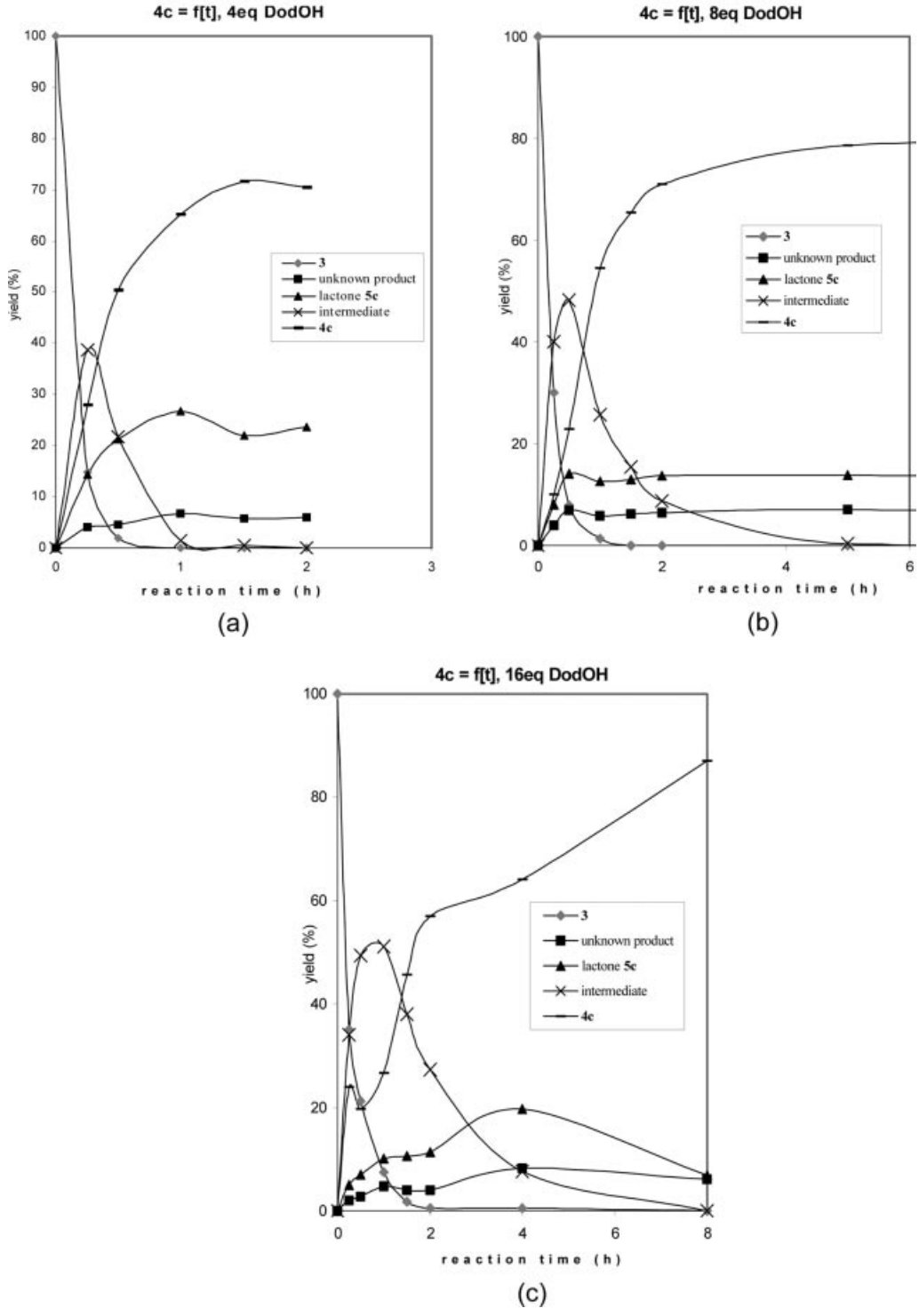


Figure 5. Influence of the dodecanol amount used on the kinetics of the transesterification-transglycosylation reactions of compound **3** (1 equiv. MSA). Yields of starting compound **3** (♦), desired compound **4c** (–), lactone **5c** (▲) as well as unknown product (■) and reaction intermediate (X) are represented as a function of the reaction time: (a) 4 equiv. DodOH; (b) 8 equiv. DodOH; (c) 16 equiv. DodOH.

from the corresponding long-chain alcohols: these surfactants, which possess two lipophilic chains, were successfully isolated in 58–67% yields.

Our last goal was to transform these esters into sodium α-D-mannopyranosiduronates **6** and their corresponding acid forms **7**. Compounds **4a**–**c** were therefore saponified in high yields (0.1 N NaOH, 1.1 equiv., in water/CH_2Cl_2; 1 h) into sodium uronates **6a**–**c** (compound **6d** not prepared). The formation of the carboxylic acids was achieved by successive basic (0.1 N NaOH, 1.1 equiv., in water/CH_2Cl_2; 1 h)

and acidic (aq. 1 N HCl at 0 °C until pH 1) treatment of compounds **4a**–**d** to give the corresponding α-D-mannopyranosidic acids **7a**–**d**. The result reported here is of much interest as this is one of the very few examples where *O*-glycosiduronic acids have been synthesised without protecting groups and with a high stereocontrol. These compounds represent a new class of carbohydrate-based surfactants in their neutral or anionic forms derived, for the first time to the best of our knowledge, from alginate as a raw material.

Physicochemical Properties of Sodium (*n*-Alkyl α-D-Mannopyranosiduronates) 6 and (*n*-Alkyl α-D-Mannopyranosiduronic Acids) 7

Surfactants are amphiphilic molecules that tend to partition preferentially at the interface between fluid phases, such as at air/water interfaces.[27,28] The formation of such ordered molecular films at an interface lowers the interfacial tension and is responsible for the unique properties of surfactant molecules. One of the most widely used indexes for evaluating surfactant activity is the critical micelle concentration (CMC). The CMC is in effect the solubility of a surfactant within an aqueous phase, or the minimum surfactant concentration required for reaching the lowest interfacial or surface-tension values γ. At concentrations above the CMC, surfactants associate readily to form micelles. The CMC value is estimated from the inflection point in the γ vs. log C curve. The surface tension of aqueous solutions of anionic and neutral single-tailed compounds **6a**, **6c** and **7c**,**d** in water was measured with a drop tensiometer. A syringe with a U-shaped needle was lowered into a sample cell containing an aqueous solution of surfactant, and an air bubble was produced from the syringe. The dynamic surface tension was measured by filming the rising bubble and analysing the contour of the bubble according to axiasymmetric drop-shape analysis (ADSA) with a Tracker instrument from IT Concept.[29] The surface tension was thus determined at room temperature for several concentrations of surfactants in pure water (Figure 6).

As shown in Figure 6 and Table 2, four different surfactants differing in their hydrophilic moiety (anionic or non ionic) and the lengths of the linear hydrophobic chain were studied. Compounds with C_{14}–C_{18} fatty chains were not soluble enough in water at room temperature to exhibit surface-tension properties under standard conditions. The data also include values obtained with industrial non-ionic surfactants, such as alkylpolyglucoside (APG) and polyethylene glycol (PEG) derivatives possessing a dodecyl alkyl chain, in order to carry out a comparison.

Compounds **6a**, **6c** and **7c**,**d** reduce the surface tension to values (29–30 mN m^{-1}) that compare favourably with those obtained with commercial non-ionic surfactants (PEG, APG).[30] The surface tensions were found to be independent of the sugar residue hydrophilicity and the hydrophobic character of the alkyl chains, unlike the CMC values. In all cases, carboxylate derivatives exhibited higher CMC values than their neutral counterparts. This is clearly due to the presence of the negative charge, which renders the amphiphile more soluble in water. As expected, the CMC values decrease with increasing alkyl chain length.

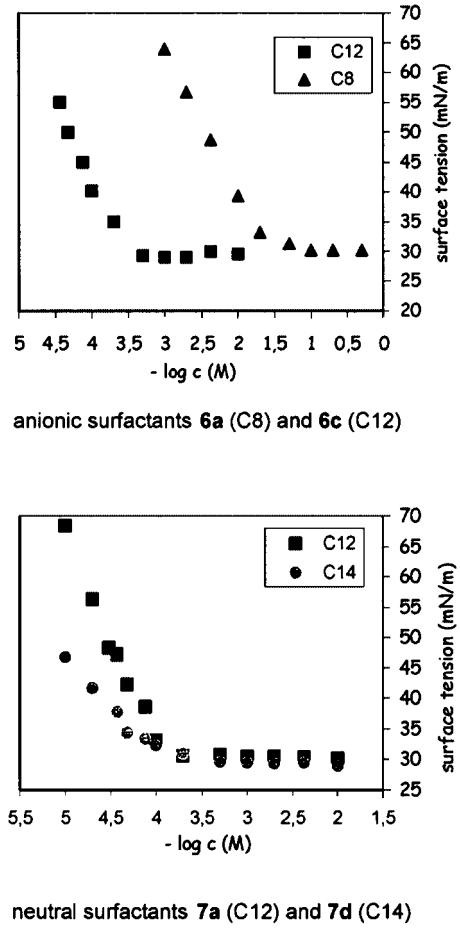


Figure 6. Surface tension curves of aqueous solutions of anionic and neutral single-tailed compounds **6a** (▲), **6c** (■), **7c** (■) and **7d** (●).

Table 2. CMC and surface-tension values of anionic and neutral single-tailed compounds **6a, 6c** and **7c**,**d** in comparison with standard neutral surfactants PEG and APG.

Compounds	CMC [mmol L^{-1}]	CMC [g L^{-1}]	γCMC [mN m^{-1}]
6a (C8)	1.62	0.49	30.2
6c (C12)	0.28	0.11	29.5
7c (C12)	0.13	0.05	30.5
7d (C14)	0.16	0.06	29.7
PEG	0.08	0.04	33
APG	0.26	0.09	30

Good foaming behaviour is also an attractive property for the use of surfactants in body-cleansing products, such as shower gels and foam baths or hair shampoos. Ether sulfates are the most important class of surfactants used for cosmetic cleansing formulations. The foaming behaviour of the C_{12} sodium alkyl α-D-mannuronate **6c** and the C_{12}–C_{14} acid forms **7c**,**d** was evaluated in comparison with a sodium dodecyl sulfate (SDS) reference. Foam was formed by bubbling air into a round-bottomed flask containing an aqueous solution of surfactant, and it was continuously transfer-

red into a beaker until a given volume of foam was reached.[31–34] The air flow was then stopped and the foam stability was recorded. The foaming performance was then evaluated as the time required to obtain the desired volume (2 L) of foam, and the foam stability corresponds to the foam residual volume observed with time. Surfactant concentrations of 0.1 or 0.2 g L^{-1} were chosen for studies above CMC (Table 3).

Table 3. Time required to obtain 2 L of foam for compounds **6c** and **7c**,**d** in comparison with SDS.

Compounds	C (g L^{-1})	t (min)
6c (C12)	0.1	–[a]
7c (C12)	0.1	3
7d (C14)	0.2	12
SDS	1	1.5

[a] Collapse of the foam occurred before its transfer into the beaker.

Anionic surfactant **6c** did not exhibit good foaming properties in so far as the foam rapidly collapsed before its transfer into the beaker. It is noteworthy that mannuronic acids **7c**,**d** are high-foaming anionic surfactants that are comparable with the ether sulfate derivative. In particular, similar values are observed for surfactant **7c** and SDS both in regard to foam performance (Table 3) and foam stability (Figure 7).

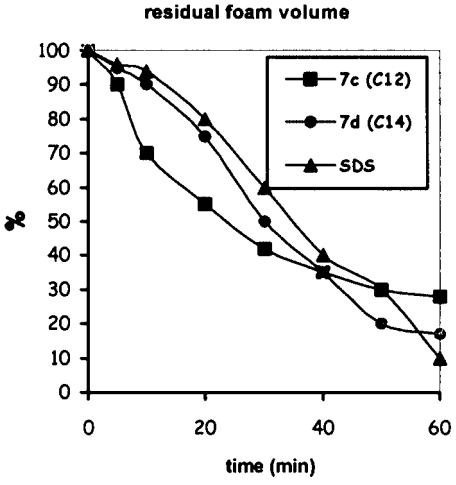


Figure 7. Foam stability with time for mannuronic acids **7c** (■) and **7d** (●) in comparison with SDS (▲).

Conclusions

In conclusion, we have shown that alginate is an attractive starting material for the preparation of novel biocompatible alkyl D-mannopyranosiduronate surfactants. Controlled acid hydrolysis processes efficiently produce oligo- and mono-mannuronate derivatives with a high stereocontrol at the anomeric position. The monosaccharidic form is a precursor of single- and double-tailed amphiphiles upon transesterification/transglycosylation reactions and aqueous acid and/or basic treatments. Neutral and anionic compounds possessing a C_8–C_{14} aliphatic chain have been found to be high-foaming and surface-active surfactants, respectively. Studies that are now in progress are aimed at examining the physico-chemical properties of the double-tailed amphiphiles. The variability of these compounds in terms of hydrophilic-hydrophobic balance, permits us to envisage additional applications such as oil-in-water and water-in-oil emulsions. Preliminary results show that very stable emulsions can be obtained with vegetable (sunflower) and mineral (paraffin) oil and fatty ester (capric/caprylic esters) formulations including these new synthetic amphiphiles.[34] Furthermore, with the aim of reducing the cost of these surfactants (price of alginates: 11–12 Euros per kg), additional procedures were recently carried out directly on brown seaweeds (<0.2 Euros per kg), to provide oligomannuronates **2** in quite satisfactory yields (12.5%).[25,34] These promising results may allow the production of these novel alkyl D-mannopyranosiduronate surfactants with an overall cost compatible with their potential application markets.

Experimental Section

General Remarks: Alginate from *Laminaria digitata* was purchased from Degussa; all other commercially available chemicals were used without further purification. *N*,*N*-Dimethylformamide (DMF) and dichloromethane were dried over phosphorus pentoxide and distilled, while tetrahydrofuran was dried with sodium/benzophenone before distilling. TLC analyses were conducted on precoated non-activated plates (E. Merck 60 F_{254}) with detection by UV absorption (254 nm), when applicable, and charring with 5% H_2SO_4 or 60 g/L PMA in EtOH. For column chromatography, E. Merck 60H (5–40 μm) silica gel was used. Optical rotations were determined with a Perkin–Elmer 341 polarimeter at 20 °C in a 1-dm cell. Melting points were determined on a Reichert microscope and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ or CD_3OD at 298 K. Chemical shifts are given in ppm (δ) measured downfield from $SiMe_4$ at $\delta = 0$ ppm using the residual solvent signal as secondary reference; coupling constants (J) are given in Hertz (Hz). Microanalyses were performed by the Service de Microanalyses de l'ICSN (Gif-sur-Yvette, France). GC analysis was performed on a GC 8000 TOP CEInstruments gas chromatograph and the separation was achieved on a Alltech AT1 column, 30 m × 0.25 mm i.d., 0.25-μm film thickness. Helium was used as a carrier gas and the inlet pressure was set to 75 kPa. The injections were done at 180 °C and the temperature detector was fixed at 300 °C. The GC oven temperature program was as follows: 150 °C initial column temperature, 1 min at 150 °C, 3 °C min^{-1} to 300 °C, for 25 min. Silylation was performed as follows: 20 mg of the reaction mixture was dissolved in 1 mL of dry pyridine and 200 μL of hexamethyldisilazane and 100 μL of chlorotrimethylsilane were added. The mixture was stirred at room temperature for 15 min before the removal of pyridine. The residue was dissolved in diethyl ether (0.5 mL) and filtered through cotton. The resulting solution (0.5 μL) was then used for injection into the GC. Parallel syntheses were performed on a Büchi Syncore Reactor using samples containing 500 mg of starting compound **3**. CMC values were measured with a Tracker instrument, IT Concept drop tensiometer.

Sodium Polymannuronates 1: Sodium alginate (500 g) from *Laminaria digitata* was progressively added to water (37.6 L) and the solution was vigorously stirred overnight. The solution was heated to 95 °C and aq. HCl (1.52 kg of conc. HCl diluted in 10.4 L of

water) was slowly added before stirring at 95–100 °C for 2 h. After cooling, the removal of two thirds of the liquid phase and the centrifugation of the rest of the suspension (9000 g, 20 °C, 35 min) led to a precipitate composed of MM and GG blocks. The homopolymers were suspended in water (17 L), stirred for 1 h and solubilized by addition of aq. 0.1 N NaOH (29 L) until pH 4.5. After acidification to pH 2.85 with aq. 0.025 N HCl (22.4 L) and stirring overnight, diatomaceous earth (kieselguhr, 2 kg) was added and the mixture was stirred for 15 min. The subsequent suspension was filtered and the filtrate was neutralised with aq. 0.1 N NaOH (7.0 kg). Ultrafiltration of the solution (8000 D, 300 L of water) and lyophilisation led to sodium polymannuronates **1** with an average degree of polymerisation of 16 (123 g, 23%).

Sodium Oligomannuronates 2: Aqueous 1 N HCl was added to a solution of sodium polymannuronates **1** (30.0 g) in water (3 L) until pH 3.00. The mixture was refluxed for 8 h before cooling and neutralisation with aq. 1 N NaOH. After ultrafiltration through Amicon cell (3500 D), lyophilisation led to a mixture of sodium oligomannuronates **2** with an average degree of polymerisation of 3 (26.7 g, 89%), in addition to sodium chloride salts (25%).

***n*-Butyl (*n*-Butyl α-D-Mannopyranosiduronate) 3:** Methanesulfonic acid (5.07 mL, 78.12 mmol, 4 equiv.) was added to a suspension of sodium oligomannuronates **2** (3.75 g, 19.53 mmol CO_2Na, 1 equiv.) in butanol (190 mL). The mixture was vigorously stirred at 112–115 °C for 8 h and the water formed in the reaction was progressively eliminated by azeotropic evaporation. After cooling to room temperature, the reaction mixture was neutralised with aq. 1 N NaOH (55 mL), concentrated under reduced pressure (50 °C, 80 mbar) and dried under vacuum. The residue was vigorously stirred in CH_2Cl_2 (200 mL) and insoluble salts were eliminated by filtration through celite. The filtrate was concentrated and the crude oil was chromatographed (CH_2Cl_2/MeOH, 95:5) to afford **3** as a colourless oil (3 g) in 50% yield. TLC: R_f (CH_2Cl_2/CH_3OH, 9:1) = 0.41. $[\alpha]_D^{20}$ = +45.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89, 0.90 (2t, ^3J = 7.3 Hz, 6 H, 2CH_3), 1.29–1.40 (m, 2 H, CH_2CH$_3$), 1.47–1.57 (m, 2 H, OCH$_2$CH_2), 1.60–1.68 (m, 2 H, OCH$_2$CH_2), 3.41 (dt, ^3J = 6.8, 9.7 Hz, 1 H, OCHH), 3.67 (dt, ^3J = 6.9 Hz, 1 H, OCHH), 3.79 (bd, ^3J = 7.4 Hz, 1 H, 3-H), 3.90 (br. s, 1 H, 2-H), 3.98 (t, ^3J = 9.7 Hz, 1 H, 4-H), 4.03 (d, J = 9.7 Hz, 1 H, 5-H), 4.17 (t, ^3J = 6.7 Hz, 2 H, OCH$_2$), 4.85 (s, 1 H, 1-H) ppm.^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.7, 13.8 (2 CH_3), 19.0, 19.3 (2 CH$_2$CH$_3$), 30.4 (OCH$_2$$CH_2$), 31.4 (OCH$_2$$CH_2$), 65.7 (OCH$_2$), 68.0 (OCH$_2$), 68.6 (C-4), 70.4 (C-2), 71.2 (C-3), 71.5 (C-5), 100.5 (C-1), 171.0 (CO) ppm. $C_{14}H_{26}O_7$ (306.36) + 0.25H_2O: calcd. C 54.09, H 8.59; found C 54.37, H 8.61.

General Procedure for *n*-Alkyl (*n*-Alkyl α-D-Mannopyranosiduronate) 4: Compound **3** (100 mg, 0.3264 mmol) was heated in fatty alcohol (8 equiv.) at 65 °C for 15 min under vacuum before adding methanesulfonic acid (1 equiv.). The reaction medium was stirred at 65 °C for 6 h under vacuum (2–5 mbar) and then neutralised by triethylamine at room temperature. The crude oil was purified by silica gel chromatography with CH_2Cl_2/CH_3OH, (99:1–95:5) to yield **4**.

***n*-Octyl (*n*-Octyl α-D-Mannopyranosiduronate) (4a):** Transglycosidation and transesterification with octanol (340 mg) afforded **4a** as a colourless oil (91.5 mg, 67%). TLC: R_f (CH_2Cl_2/CH_3OH, 9:1) = 0.34. $[\alpha]_D^{20}$ = +34.7 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87 (t, ^3J = 6.8 Hz, 6 H, 2 CH_3), 1.20–1.35 (m, 20 H, 10 CH_2), 1.51–1.58 (m, 2 H, OCH$_2$CH_2), 1.63–1.68 (m, 2 H, OCH$_2$CH_2), 3.41 (dt, ^3J = 6.6, 9.2 Hz, 1 H, OCHH), 3.66 (dt, ^3J = 6.9 Hz, 1 H, OCHH), 3.80–3.85 (m, 1 H, 3-H), 3.92 (s, 1 H, 2-H), 4.00 (t, ^3J = 9.5 Hz, 1 H, 4-H), 4.05 (d, J = 9.5 Hz, 1 H, 5-H), 4.17 (t, ^3J = 6.7 Hz, 2 H, OCH$_2$), 4.87 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1 (2 CH_3), 22.7 (2 CH$_2$CH$_3$), 25.8, 26.1, 28.4, 29.2–29.4, 31.8, 31.9 (10 CH_2), 66.0 (OCH$_2$), 68.4 (OCH$_2$), 68.6 (C-4), 70.4 (C-2), 71.2 (C-3), 71.4 (C-5), 100.5 (C-1), 171.1 (CO) ppm. $C_{22}H_{42}O_7$ (418.57) + 0.5H_2O: calcd. C 61.80, H 10.14; found C 61.78, H 10.13.

***n*-Decyl (*n*-Decyl α-D-Mannopyranosiduronate) (4b):** Transglycosidation and transesterification with decanol (411 mg) afforded **4b** as a pasty solid (89.8 mg, 58%). M.p. 41 °C (Et_2O). TLC: R_f (CH_2Cl_2/CH_3OH, 9:1) = 0.36. $[\alpha]_D^{20}$ = +31.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87 (t, ^3J = 6.8 Hz, 6 H, 2 CH_3), 1.20–1.34 (m, 28 H, 14 CH_2), 1.50–1.58 (m, 2 H, OCH$_2$CH_2), 1.62–1.68 (m, 2 H, OCH$_2$CH_2), 3.42 (dt, ^3J = 6.6, 9.3 Hz, 1 H, OCHH), 3.65 (dt, ^3J = 6.9 Hz, 1 H, OCHH), 3.79–3.86 (m, 1 H, 3-H), 3.92 (s, 1 H, 2-H), 4.00 (t, ^3J = 9.6 Hz, 1 H, 4-H), 4.05 (d, J = 9.6 Hz, 1 H, 5-H), 4.16 (t, ^3J = 6.8 Hz, 2 H, OCH$_2$), 4.87 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1 (2 CH_3), 22.7 (2 CH$_2$CH$_3$), 25.8, 26.1, 28.4, 29.2–29.5, 31.8, 31.9 (14 CH_2), 66.0 (OCH$_2$), 68.4 (OCH$_2$), 68.6 (C-4), 70.4 (C-2), 71.2 (C-3), 71.4 (C-5), 100.5 (C-1), 171.1 (CO) ppm. $C_{26}H_{50}O_7$ (474.68) + H_2O: calcd. C 63.38, H 10.64; found C 63.73, H 10.28.

***n*-Dodecyl (*n*-Dodecyl α-D-Mannopyranosiduronate) (4c):** Transglycosidation and transesterification with dodecanol (484 mg) afforded **4c** as a crystalline solid (128 mg, 74%). M.p. 55 °C (Et_2O). TLC: R_f (CH_2Cl_2/CH_3OH, 9:1) = 0.37. $[\alpha]_D^{20}$ = +28.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 (t, ^3J = 6.7 Hz, 6 H, 2 CH_3), 1.20–1.32 (m, 36 H, 18 CH_2), 1.50–1.59 (m, 2 H, OCH$_2$CH_2), 1.61–1.69 (m, 2 H, OCH$_2$CH_2), 3.40 (dt, ^3J = 6.6, 9.4 Hz, 1 H, OCHH), 3.64 (dt, ^3J = 6.9 Hz, 1 H, OCHH), 3.78–3.83 (m, 1 H, 3-H), 3.91 (s, 1 H, 2-H), 3.99 (t, ^3J = 9.7 Hz, 1 H, 4-H), 4.04 (d, J = 9.7 Hz, 1 H, 5-H), 4.15 (t, ^3J = 6.9 Hz, 2 H, OCH$_2$), 4.85 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1 (2 CH_3), 22.7 (2 CH$_2$CH$_3$), 25.8, 26.1, 28.4, 29.4–29.7, 32.0 (18 CH_2), 66.0 (OCH$_2$), 68.4 (OCH$_2$), 68.6 (C-4), 70.4 (C-2), 71.2 (C-3), 71.4 (C-5), 100.5 (C-1), 171.1 (CO) ppm. $C_{30}H_{58}O_7$ (530.79): calcd. C 67.89, H 11.01; found C 67.54, H 10.84.

***n*-Tetradecyl (*n*-Tetradecyl α-D-Mannopyranosiduronate) (4d):** Transglycosidation and transesterification with tetradecanol (557 mg) afforded **4d** as a crystalline solid (117 mg, 61%). M.p. 64 °C (Et_2O). TLC: R_f (CH_2Cl_2/CH_3OH, 9:1) = 0.39. $[\alpha]_D^{20}$ = +25.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87 (t, ^3J = 6.8 Hz, 6 H, 2 CH_3), 1.20–1.35 (m, 44 H, 22 CH_2), 1.46–1.60 (m, 2 H, OCH$_2$CH_2), 1.62–1.71 (m, 2 H, OCH$_2$CH_2), 3.43 (dt, ^3J = 6.6, 9.7 Hz, 1 H, OCHH), 3.67 (dt, ^3J = 6.9 Hz, 1 H, OCHH), 3.81–3.85 (m, 1 H, 3-H), 3.92 (s, 1 H, 2-H), 4.01 (t, ^3J = 9.5 Hz, 1 H, 4-H), 4.06 (d, J = 9.5 Hz, 1 H, 5-H), 4.18 (t, ^3J = 6.8 Hz, 2 H, OCH$_2$), 4.88 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.2 (2 CH_3), 22.8 (2 CH$_2$CH$_3$), 25.9, 26.2, 28.5, 29.4–29.8, 32.0 (22 CH_2), 66.1 (OCH$_2$), 68.5 (OCH$_2$), 68.8 (C-4), 70.4 (C-2), 71.2 (C-3), 71.2 (C-5), 100.4 (C-1), 171.1 (CO) ppm. $C_{34}H_{66}O_7$ (586.90) + 0.25H_2O: calcd. C 69.05, H 11.33; found C 69.06, H 11.27.

***n*-Hexadecyl (*n*-Hexadecyl α-D-Mannopyranosiduronate) (4e):** Transglycosidation and transesterification with hexadecanol (630 mg) afforded **4e** as an amorphous solid (116 mg, 58%). M.p. 70 °C (Et_2O). TLC: R_f (CH_2Cl_2/CH_3OH, 9:1) = 0.41. $[\alpha]_D^{20}$ = +22.2 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87 (t, ^3J = 6.6 Hz, 6 H, 2 CH_3), 1.19–1.35 (m, 52 H, 26 CH_2), 1.51–1.59 (m, 2 H, OCH$_2$CH_2), 1.61–1.71 (m, 2 H, OCH$_2$CH_2), 3.44 (dt, ^3J = 6.3, 9.7 Hz, 1 H, OCHH), 3.68 (dt, ^3J = 6.8 Hz, 1 H, OCHH), 3.83–3.87 (m, 1 H, 3-H), 3.92 (s, 1 H, 2-H), 4.00 (t, ^3J = 9.3 Hz, 1 H, 4-H), 4.06 (d, J = 9.3 Hz, 1 H, 5-H), 4.18 (t, ^3J =

6.5 Hz, 2 H, OCH_2), 4.88 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.2 (2 CH_3), 22.8 (2 CH_2CH_3), 25.9, 26.2, 28.5, 29.4–29.9, 32.0 (26 CH_2), 66.1 (OCH_2), 68.5 (OCH_2), 68.9 (C-4), 70.4 (C-2), 71.1 (C-3), 71.2 (C-5), 100.3 (C-1), 171.1 (CO) ppm. $C_{38}H_{74}O_7$ (614.01): calcd. C 70.98, H 11.60; found C 70.85, H 11.67.

General Procedure for the Synthesis of Sodium *n*-Alkyl α-D-Mannopyranosiduronate 6: Aqueous 0.1 N NaOH (1.1 equiv.) was slowly added to a solution of *n*-alkyl (*n*-alkyl α-D-mannopyranosiduronate) **4a**–**c** (1 equiv.) in CH_2Cl_2. After stirring for 1 h at room temperature, the reaction medium was concentrated under reduced pressure at 30 °C and the residue was diluted with hot CH_3OH. Silica gel was added and the mixture was concentrated under reduced pressure and dried under vacuum. The residue was suspended in hot CH_2Cl_2, filtered and rinsed several times with CH_2Cl_2 until total elimination of the formed fatty alcohol. The silica gel was finally rinsed with 2-propanol/EtOAc/H_2O (6:3:1). After concentration and drying, purification by dialysis at 100 D afforded sodium *n*-alkyl α-D-mannopyranosiduronates **6**.

Sodium *n*-Octyl α-D-Mannopyranosiduronate (6a): Yield: 90%. TLC: R_f (EtOAc/2-propanol/H_2O, 6:3:1) = 0.22. $[\alpha]_D^{20}$ = +1.3 (*c* = 0.1, CH_3OH). ^1H NMR (400 MHz, D_2O, 25 °C): δ = 1.11 (t, ^3J = 6.8 Hz, 3 H, CH_3), 1.53 (s, 10 H, 5 CH_2), 1.78–1.83 (m, 2 H, OCH_2CH_2), 3.64 (dt, ^3J = 6.9, 9.4 Hz, 1 H, OCH*H*), 3.94 (dt, ^3J = 6.6 Hz, 1 H, OC*H*H), 3.97 (d, ^3J = 9.4 Hz, 1 H, 5-H), 4.03 (dd, ^3J = 3.0, 9.5 Hz, 1 H, 3-H), 4.07 (t, 1 H, 4-H), 4.10–4.12 (m, 1 H, 2-H), 5.08 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, D_2O, 25 °C): δ = 14.5 (CH_3), 23.2 (CH_2CH_3), 26.8–32.4 (5 CH_2), 68.7 (OCH_2), 70.0 (C-4), 71.0 (C-2), 71.4 (C-3), 73.0 (C-5), 100.6 (C-1), 177.5 (CO) ppm.

Sodium *n*-Decyl α-D-Mannopyranosiduronate (6b): Yield: 88%. TLC: R_f (EtOAc/2-propanol/H_2O, 6:3:1) = 0.23. $[\alpha]_D^{20}$ = +3.2 (*c* = 0.25, CH_3OH). ^1H NMR (400 MHz, D_2O, 25 °C): δ = 1.11 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.53 (s, 14 H, 7 CH_2), 1.78–1.84 (m, 2 H, OCH_2CH_2), 3.65 (dt, ^3J = 6.9, 9.5 Hz, 1 H, OCH*H*), 3.94 (dt, ^3J = 6.6 Hz, 1 H, OC*H*H), 3.99 (d, ^3J = 9.5 Hz, 1 H, 5-H), 4.04 (m, 1 H, 3-H), 4.08 (t, ^3J = 9.6 Hz, 1 H, 4-H), 4.11–4.13 (m, 1 H, 2-H), 5.08 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, D_2O, 25 °C): δ = 14.5 (CH_3), 23.3 (CH_2CH_3), 26.8–32.5 (7 CH_2), 68.7 (OCH_2), 70.0 (C-4), 71.0 (C-2), 71.5 (C-3), 73.1 (C-5), 100.7 (C-1), 177.6 (CO) ppm.

Sodium *n*-Dodecyl α-D-Mannopyranosiduronate (6c): Yield: 89%. TLC: R_f (EtOAc/2-propanol/H_2O, 6:3:1) = 0.23. $[\alpha]_D^{20}$ = +8.1 (*c* = 0.25, CH_3OH). ^1H NMR (400 MHz, D_2O, 25 °C): δ = 1.12 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.54 (s, 18 H, 9 CH_2), 1.79–1.86 (m, 2 H, OCH_2CH_2), 3.66 (dt, ^3J = 6.9, 9.4 Hz, 1 H, OCH*H*), 3.95 (dt, ^3J = 6.6 Hz, 1 H, OC*H*H), 4.00 (d, ^3J = 9.5 Hz, 1 H, 5-H), 4.05 (dd, ^3J = 3.1, 9.4 Hz, 1 H, 3-H), 4.09 (t, 1 H, 4-H), 4.11–4.13 (m, 1 H, 2-H), 5.09 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, D_2O, 25 °C): δ = 14.5 (CH_3), 23.3 (CH_2CH_3), 26.9–32.6 (9 CH_2), 68.8 (OCH_2), 70.1 (C-4), 71.2 (C-2), 71.6 (C-3), 73.2 (C-5), 100.8 (C-1), 177.5 (CO) ppm.

General Procedure for the Synthesis of Sodium *n*-Alkyl α-D-Mannopyranosiduronic Acids 7: Aqueous 0.1 N NaOH (1.1 equiv.) was slowly added to a solution of *n*-alkyl (*n*-alkyl α-D-mannopyranosiduronate) **4** (1 equiv.) in CH_2Cl_2. After stirring for 1 h at room temperature, the organic solvent was removed under reduced pressure and the residue was acidified at 0 °C with aq. 1 N HCl until pH 1. The aqueous phase was then extracted with ethyl acetate, the combined organic phases were concentrated under reduced pressure and the residue was dissolved in methanol at 30 °C. Silica gel was then added and the mixture was concentrated under reduced pressure and dried under vacuum. The residue was suspended in hot CH_2Cl_2, filtered and rinsed several times with CH_2Cl_2 until total elimination of the formed fatty alcohol. The silica gel was finally rinsed with 2-propanol/EtOAc/H_2O (6:3:1). After concentration and drying, purification by dialysis at 100 D afforded *n*-alkyl α-D-mannopyranosiduronic acids **7**.

***n*-Octyl α-D-Mannopyranosiduronic Acid (7a):** Yield: 90%. TLC: R_f (EtOAc/2-propanol/H_2O, 6:3:1) = 0.41. $[\alpha]_D^{20}$ = +39.4 (*c* = 1, CH_3OH). ^1H NMR (400 MHz, CD_3OD, 25 °C): δ = 0.91 (t, ^3J = 6.8 Hz, 3 H, CH_3), 1.24–1.40 (m, 10 H, 5 CH_2), 1.57–1.59 (m, 2 H, OCH_2CH_2), 3.45 (dt, ^3J = 6.2, 9.4 Hz, 1 H, OCH*H*), 3.71–3.73 (m, 2 H, OC*H*H, 3-H), 3.78 (d, ^3J = 1.4 Hz, 1 H, 2-H), 3.87 (t, ^3J = 9.3 Hz, 1 H, 4-H), 3.99 (d, ^3J = 9.4 Hz, 1 H, 5-H), 4.80 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 14.5 (CH_3), 23.6 (CH_2CH_3), 27.1–33.1 (5 CH_2), 69.0 (OCH_2), 69.7 (C-4), 71.4 (C-2), 72.0 (C-3), 73.4 (C-5), 101.8 (C-1), 173.3 (CO) ppm. $C_{14}H_{26}O_7$ (306.36): calcd. C 54.88, H 8.56; found C 54.72, H 8.62.

***n*-Decyl α-D-Mannopyranosiduronic Acid (7b):** Yield: 88%. TLC: R_f (EtOAc/2-propanol/H_2O, 6:3:1) = 0.43. $[\alpha]_D^{20}$ = +37.6 (*c* = 1, CH_3OH). ^1H NMR (400 MHz, CD_3OD, 25 °C): δ = 0.91 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.24–1.41 (m, 14 H, 7 CH_2), 1.57–1.60 (m, 2 H, OCH_2CH_2), 3.45 (dt, ^3J = 6.2, 9.3 Hz, 1 H, OCH*H*), 3.71–3.74 (m, 2 H, OC*H*H, 3-H), 3.79 (d, ^3J = 1.4 Hz, 1 H, 2-H), 3.89 (t, ^3J = 9.2 Hz, 1 H, 4-H), 4.00 (d, ^3J = 9.3 Hz, 1 H, 5-H), 4.80 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 14.5 (CH_3), 23.7 (CH_2CH_3), 27.2–33.1 (7 CH_2), 69.1 (OCH_2), 69.8 (C-4), 71.4 (C-2), 72.0 (C-3), 73.4 (C-5), 101.8 (C-1), 173.2 (CO) ppm. $C_{16}H_{30}O_7$ (334.41): calcd. C 57.46, H 9.04; found C 57.30, H 9.16.

***n*-Dodecyl α-D-Mannopyranosiduronic Acid (7c):** Yield: 89%. TLC: R_f (EtOAc/2-propanol/H_2O, 6:3:1) = 0.42. $[\alpha]_D^{20}$ = +35.1 (*c* = 1, CH_3OH). ^1H NMR (400 MHz, CD_3OD, 25 °C): δ = 0.90 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.25–1.40 (m, 18 H, 9 CH_2), 1.58–1.60 (m, 2 H, OCH_2CH_2), 3.46 (dt, ^3J = 6.1, 9.3 Hz, 1 H, OCH*H*), 3.70–3.73 (m, 2 H, OC*H*H, 3-H), 3.80 (d, ^3J = 1.5 Hz, 1 H, 2-H), 3.89 (t, ^3J = 9.2 Hz, 1 H, 4-H), 4.00 (d, ^3J = 9.3 Hz, 1 H, 5-H), 4.81 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 14.5 (CH_3), 23.7 (CH_2CH_3), 27.2–33.0 (9 CH_2), 69.1 (OCH_2), 69.8 (C-4), 71.6 (C-2), 72.1 (C-3), 73.5 (C-5), 101.9 (C-1), 173.3 (CO) ppm. $C_{18}H_{34}O_7$ (362.47): calcd. C 59.64, H 9.46; found C 59.20, H 9.61.

***n*-Tetradecyl α-D-Mannopyranosiduronic Acid (7d):** Yield: 88%. TLC: R_f (EtOAc/2-propanol/H_2O, 6:3:1) = 0.40. $[\alpha]_D^{20}$ = +33.2 (*c* = 1, CH_3OH). ^1H NMR (400 MHz, CD_3OD, 25 °C): δ = 0.90 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.23–1.40 (m, 22 H, 11 CH_2), 1.57–1.60 (m, 2 H, OCH_2CH_2), 3.45 (dt, ^3J = 6.1, 9.3 Hz, 1 H, OCH*H*), 3.71–3.73 (m, 2 H, OC*H*H, 3-H), 3.81 (d, ^3J = 1.4 Hz, 1 H, 2-H), 3.89 (t, ^3J = 9.3 Hz, 1 H, 4-H), 4.00 (d, ^3J = 9.3 Hz, 1 H, 5-H), 4.82 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 14.5 (CH_3), 23.6 (CH_2CH_3), 27.1–33.0 (11 CH_2), 69.1 (OCH_2), 69.8 (C-4), 71.5 (C-2), 72.0 (C-3), 73.5 (C-5), 101.9 (C-1), 173.2 (CO) ppm. $C_{20}H_{38}O_7$ (390.52): calcd. C 61.51, H 9.81; found C 61.50, H 9.75.

Acknowledgments

We thank Mr. P. Golven and Mr. Y. Lelong for excellent technical assistance, Dr. A. Heyraud for preparative HPLC studies, the French Association Nationale pour la Recherche et Technologie (ANRT) and the Ministère de l'Education Nationale de la Recherche et de la Technologie for a grant to M.R.

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Received: January 12, 2005

