

Selective Synthesis of Aliphatic Ethylene Glycol Sulfonate Surfactants

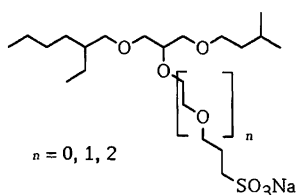
Odd R. Gautun,^a Per H.J. Carlsen,^{a,†} Trygve Maldal,^b Olav Vikane^b and Eimund Gilje^b

^aInstitute of Organic Chemistry, University of Trondheim-NTH, N-7034 Trondheim, Norway and ^bStatoil, PETEK, N-4035 Stavanger, Norway

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The selective synthesis of a series of components in a commercial surfactant mixture was studied. The general structure of the surfactant was a glycerol-based double chain monosulfonate molecule, with a C₈-Guerbert alcohol, 2-ethylhexanol, at C-1, a pentyloxy group at C-3 and a 3-oxypropane-1-sulfonic acid or an ethoxylated 3-oxypropane-1-sulfonic acid side chain at the C-2 position. The main chain alcohol was obtained by a base catalyzed reaction of 2-ethylhexyl glycidyl ether with a pentyl alcohol. High C-3 selectivity was obtained. Two methods were used for the construction of the ethoxylated side chain at the C-2. A sequence consisting of *O*-allylation followed by ozonolysis and sodium borohydride work-up gave good yields of the desired ethoxylated homologs. A shorter, more efficient method involved the reaction with 1,2-ethylene sulfate. This method gave the ethoxylated homologs with high selectivity and in high yields. *O*-Propane sulfonation was accomplished by the reaction of the appropriate alkoxides with 1,3-propane sulfone. The pure sodium sulfonates were isolated in good overall yields by continuous extraction with hexane or diethyl ether.

Surfactants are potentially useful in the enhanced oil recovery, (EOR), processes, as they reduce surface tension, and microemulsion systems composed of oil, water and eventually cosurfactants are formed.¹ Most commercial surfactants are complex mixtures. Polyethoxylated alkyl sulfonates are important commercial surfactants. A typical example of a branched sulfonate² can be described by the general formula:



The properties of a surfactant mixture will depend on its composition as well as the structures and properties of the individual surfactant molecules. For the study of the efficiency of a surfactant system, i.e. in a structure-activity relationship (SAR) study, the pure components will be required. This will also be necessary for the purpose of identifying the components in the product mixtures.

[†] To whom correspondence should be addressed.

We report here the selective synthesis of a series of reference materials of the general formula shown above, together with a number of potential byproducts. The surfactant properties of these compounds have also been studied.

Results and discussion

This surfactant is a glycerol-based double chain monosulfonate molecule, with a C₈-Guerbert alcohol,³ 2-ethylhexanol, at C-1, a pentyloxy group at C-3 and an 3-oxypropane-1-sulfonic acid or an ethoxylated 3-oxypropane-1-sulfonic acid side chain at the C-2 position. Thus the surfactants consisted of a family of molecules with ethylenoxy, (EO) units in the C-2 side-chain, where *n* in Fig. 1 is an integer, here varying from 0 to 2. For brevity the number of EO units will be denoted EO_{*n*}. The surfactant system may also contain byproducts due to the sulfonation procedure in the commercial processes. Potential byproducts may contain isopentyl or 2-ethylhexyl groups at the glycerol 3-position.

The 1,3-*O*-dialkylglycerols **1a–1c** were prepared with high selectivity in a base catalyzed nucleophilic ring opening reaction of the commercially available 2-ethylhexyl glycidyl ether, **9**, with the appropriate alcohols, affording the desired compounds **1a–1c** in 79, 69 and 61 % iso-

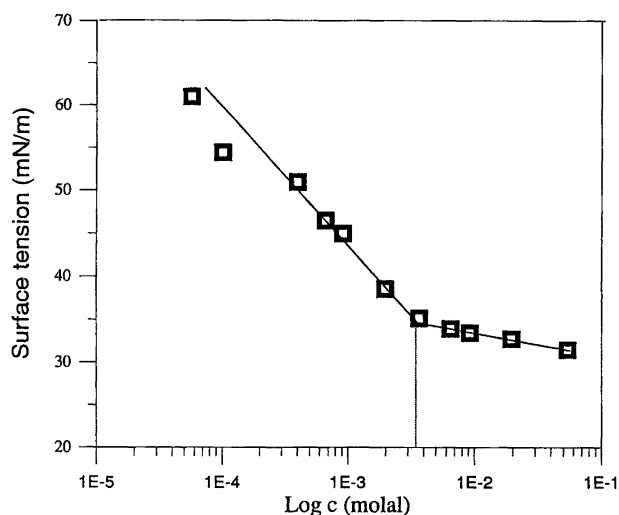
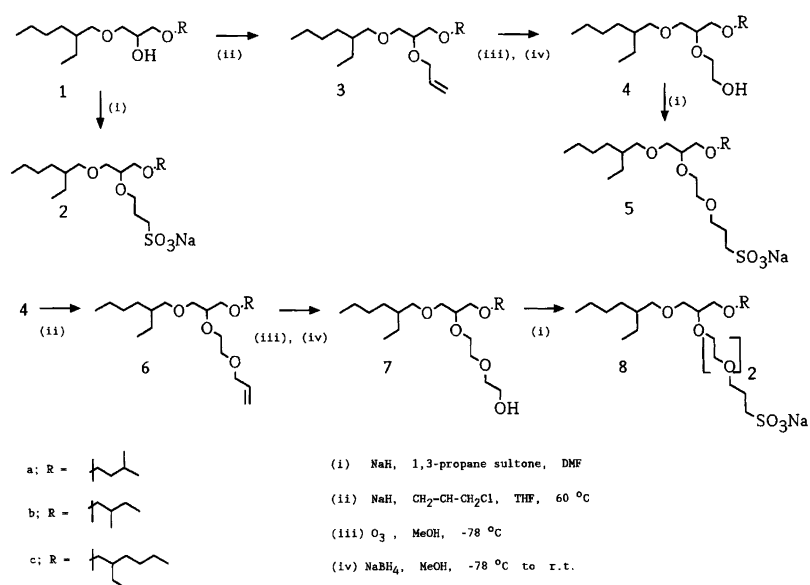


Fig. 1. Plot of surface tension vs. log *c* for compound **8b**.

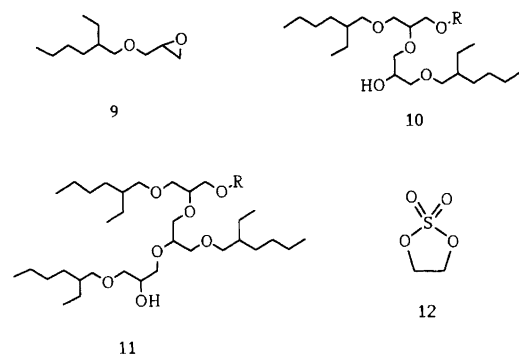
lated yields, respectively. This regioselectivities with respect to reaction at the C-3 carbon of this epoxide were in all cases shown to be better than 99 % by GLC analysis. These results were further confirmed by PDC oxidation of **1a** and **1b** in *N,N*-dimethylformamide, DMF,⁴ as the corresponding ketones were the exclusive products. No formation of carboxylic acids could be detected. On the other hand, byproducts, e.g. compounds **10** and **11** in Scheme 2, were formed due to polycondensation of 2-ethylhexylglycidyl ether with the primary products, **1**. This problem was, however, minimized by using 3-methyl-1-butanol, 2-methyl-1-butanol or 2-ethyl-1-hexanol (ROH), respectively, as solvents for the reactions (ratio ROH: epoxide 9: 1). The desired, pure products were easily isolated by distillation.

Ethoxylation. Introduction of the ethylenoxy (EO) groups in the side chain may be accomplished by reacting the appropriate alcohols with ethylene oxide in the presence of an acidic catalyst. However, these reactions were not selective. The primary products will react with excess ethylene oxide, yielding a wide distribution of EO homologs, together with varying amounts of undesired by products such as polyethylene glycols (PEG), dioxane etc.⁵ For optimal selectivity, this type of ethoxylation reaction was therefore ruled out. The selective introduction of the EO moiety yielding products **4a** and **4b**, involved initial *O*-allylation followed by ozonolysis and sodium borohydride work-up (Scheme 1). Under these reaction conditions, the pure EO₁ alcohols **4a** and **4b** were obtained after distillation in 72 and 67 % overall yields from **1a** and **1b**, respectively. The reaction sequence was repeated using alcohols **4a** and **4b** giving the pure EO₂ products **7a** and **7b** in 60 and 69 % distilled yields, respectively. No effort was made to optimize the yields. The synthetic procedures described here appeared to be general, selective and yielding the EO-homologs in satisfactory yields.

An alternative ethoxylation procedure, based on the use of cyclic sulfates, was developed. 1,2-Cyclic sulfites and 1,2-cyclic sulfates in their reactivity behave much like epoxide synthons.⁶ Few examples of the synthetic utilization of cyclic sulfates are found, presumably owing to a lack of good methods for their preparation. However, a simple, one-pot procedure for the conversion of diols to cyclic sulfites was recently reported, which in a subsequent Ru-catalyzed oxidation was converted to the cyclic sulfates in good yields, (64–97 %).⁷ The stoichiometric oxidant was sodium metaperiodate. However, we found that sodium hypochlorite was a convenient, inexpensive alternative to periodate. Reacting the ethylene sulfate, **12**, with nucleophiles readily formed the β-substituted ethyl sulfates in high yields. These in turn were easily hydro-



Scheme 1.



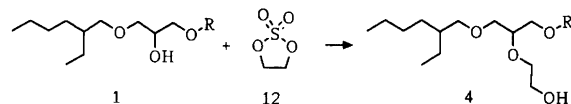
Scheme 2.

lyzed to the corresponding hydroxy compounds either by reflux with HCl/water^{8,9} or at low temperature using catalytic amounts of sulfuric acid in dry dioxane.¹⁰ We have studied these methods for the selective introduction of the EO₁-unit (Scheme 3).

Reacting, e.g., **1a** with ethylene sulfate⁶ in acetonitrile in the presence of NaH gave pure **4a** in 65% distilled yield. Ethylene sulfate was superior to ethylene oxide for controlled EO chain extension, owing to higher reactivity and an intrinsic protecting sulfate group preventing EO polycondensation. Attempts to use the commercially available ethylene sulfite for the EO extension reaction failed, probably because of nucleophilic attack of the hard alkoxy anion at the sulfite S atom.¹¹

Propylsulfonation. The surfactant molecules **2a–2c** ($n = 0$), **5a** and **5b** ($n = 1$) and **8a** and **8b** ($n = 2$) were subsequently prepared by reaction of the appropriate sodium alkoxides of alcohols **1**, **4** or **7** with 1,3-propane sultone in DMF. The sodium sulfonates were all isolated from aqueous solutions by continuous extraction with hexane or diethyl ether as white waxy products. In some cases these products were also recrystallized from ethanol-water without any improvement of purity.

The purities of the products were in all cases better than 96% as determined by GLC analysis. Purities of the sodium sulfonates were determined by HPLC. Spectroscopic properties of all products were in agreement with



Scheme 3.

the proposed structures. HH- and HC-COSY NMR techniques was used for the structural assignment of the NMR data. The assignments are reported in some details in the experimental section for the individual products. Numbering of the atoms in the molecules was based on standard nomenclature. Atoms in the side chains were denoted with primed and double primed numbers.

The critical micellar concentrations (CMC) were determined using two different experimental techniques, from the concentration dependency of the surface tensions and the conductivity respectively of the surfactant solutions. Thus, the CMC values can be found from a plot of the surface tension or the conductivity vs. the log of the surfactant concentrations, c . A typical example is shown in Fig. 1 for compound **8b**. The measured CMC values for a series of surfactants as well as their ability to lower surface tension, γ_{cmc} , are summarized in Table 1. In this table is also shown the calculated numbers for the hydrophile–lipophile balance,¹² (HLB-number).

From a CMC point of view, these pure sulfonate molecules were moderately active surfactants. There appeared to be a reasonable correlation between the CMC values and the calculated HLB numbers.¹³ As expected, the CMC values decreased with increasing EO-numbers as well as with increasing size of the hydrophobic alkyl groups. The conformational properties of the molecules may have an effect on the structure of the interfacial layers as indicated by the small but distinct differences in CMC values for compounds **2a/2b**, **5a/5b** and **8a/8b**. These molecules are different only in the positions of the methyl groups in the pentyl side chains. The differences in measured CMC values as determined by the two different methods can be ascribed to slight variations in the experimental techniques.

Table 1.

Surfactant	CMC ^a /10 ³ mol kg ⁻¹	γ_{CMC}^b mN m ⁻¹	CMC ^c /10 ³ mol kg ⁻¹	CMC (average) /10 ³ mol kg ⁻¹	EO, n	MW	HLB
2a	7.7	31.2	8.4	8;1	0	418	12.9
2b	7.1	33.2	6.4	6.8	0	418	12.9
2c	1.1	32.2	3.0	2.0	0	461	11.5
5a	5.0	32.4	* ^d	* ^d	1	463	13.2
5b	4.3	32.2	6.5	5.2	1	463	13.2
8a	6.4	30.8	5.2	5.8	2	507	14.5
8b	3.2	34.9	* ^d	2.3	2	507	14.5

^a CMC as determined by surface tension measurements. ^b Surface tension at CMC. ^c CMC as determined by conductivity measurements. ^d CMC values were not determined owing to low solubility of the substrate.

Experimental

General. NMR spectra (^1H , ^{13}C , DEPT, $^1\text{H}^1\text{H}$ and $^1\text{H}^{13}\text{C}$ COSY) were recorded on a Jeol JNM-EX400 FT NMR system, using CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard. IR spectra were obtained on a Nicolet 20-SXC FT-IR. Mass spectra were recorded on a AEI MS-902 spectrometer. GLC measurements were performed on a Perkin-Elmer Autosystem equipped with a non-polar CP-Sil 5CB capillary column (25 m) and a semi-polar CP-Sil 19CB capillary column (25 m). HPLC was performed with a Perkin Elmer instrument, consisting of a pump (Binary LC pump 250), RI (LC-30) and UV detectors and a LC 600 Autosampler injector with a 10 μl sampling loop. Signals from both detectors were processed with a Perkin Elmer Nelson computer (model 1020). The column used was an Apex Prepsil ODS 8 μ (Jones Chromatography, 25 cm \times 4.6 mm i.d.). A mixture of MeOH–H $_2$ O (3: 2), added NH $_4$ Ac (50 mg l $^{-1}$ eluent), was used as mobile phase.

Critical micelle concentrations (CMC) were determined for the surfactants in distilled water at 25 $^\circ\text{C}$ by two methods. Thus, CMC was determined on a Lauda tensiometer by measurements of the surface tension changes vs. the log of the surfactant concentrations, c . The surface tension measurements were performed by the Wilhelmy vertical plate technique,¹⁴ using a 19.9 \times 10.0 mm platinum blade. Before the measurements the blade was cleaned by successive washing with distilled water, acetone and ethanol and heating in a propane flame to evaporate traces of solvents. Measurements were taken until the change in surface tension was less than 0.2 mN m $^{-1}$. The CMC values were determined as the point of intersect between the two linear segments of the γ vs. $\log c$ curve. The γ_{cmc} value is the surface tension at the CMC.

The CMC values were also determined from the changes in conductivity, λ , with respect to the surfactant concentrations. The conductivity was measured with a Wayne–Kerr autobalance precision bridge B642, at a frequency of 10 4 rad $^{-1}$. The conductivity electrodes (Philips PW 9512) were calibrated using KCl solutions in the concentration range 0–1 mol m $^{-3}$. The CMC values were determined as the point of intersect between the two linear segments of the conductivity, λ vs. the molal surfactant concentrations, c .

11-Ethyl-2-methyl-5,9-dioxa-7-pentadecanol (1a). Sodium hydride (6.00 g, 0.25 mol) was dissolved in 3-methyl-1-butanol (1 l, 9.18 mol) under a nitrogen atmosphere at room temperature. 2-Ethylhexyl glycidyl ether, **9**, (223 ml, 1.07 mol) was then added to this mixture over a period of 10 min, and the resulting mixture was stirred at room temperature for 2 days. The reaction mixture was washed with brine (900 ml), and dried over anhydrous MgSO $_4$. Excess 3-methyl-1-butanol was distilled off under reduced pressure. Distillation of the crude product

(b.p. 128–134 $^\circ\text{C}$ at 0.03 mmHg) yielded 231.75 g (79 %) of pure **1a** (99 %, GLC).

^1H NMR (400 MHz, CDCl_3): δ 0.87 (app. t, $J_{14,15} = J_{1',2'} = 7.8$ Hz, 6 H, CH $_3$ -15/2'), 0.90 (d, $J_{1,2} = 6.8$ Hz, 6 H, CH $_3$ -1), 1.22–1.41 (m, 8 H, CH $_2$), 1.45–1.54 (m, 3 H, H-3/11), 1.69 (hep., $J_{1,2} = J_{2,3} = 6.8$ Hz, 1 H, H-2), 2.46 (br. s, 1 H, OH), 3.30–3.37 (m, 2 H, H-10), 3.40–3.52 (m, 6 H, H-4/6/8), 3.93 (app. pent., $J_{6,7} = J_{7,8} = 5$ Hz, 1 H, H-7) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 11.1, 14.1 and 22.6 (CH $_3$), 23.1 and 23.9 (CH $_2$), 25.1 (CH), 29.1, 30.6 and 38.5 (CH $_2$), 39.6 and 69.5 (CH), 70.0, 72.0, 72.1 and 74.4 (CH $_2$) ppm; IR (neat): 3457 (broad), 2960, 2930, 2870, 1469, 1385, 1370, 1114 cm $^{-1}$; MS [m/z (% rel. int.):] 274 (0.05, M^+), 256 (13), 129 (10), 128 (7), 113 (41), 112 (22), 101 (28), 87 (9), 83 (8), 75 (10), 72 (13), 71 (100), 70 (47), 69 (49), 58 (17), 57 (100), 56 (11), 55 (26).

9-Ethyl-5-(5-methyl-2-oxa-1-hexyl)-4,7-dioxa-1-tridecane-sulfonic acid, sodium salt (2a). Compound **1a** (20.00 g, 0.0729 mol) was added to a slurry containing sodium hydride (3.54 g, 0.148 mol) in dry DMF (100 ml) and stirred for 30 min at room temperature, under a nitrogen atmosphere. Then 1,3-propane sultone (10.62 g, 0.0869 mol) was then added to the reaction mixture over a period of 3 min. During the addition of the sultone, a strong exothermic reaction accompanied by foaming was observed. After stirring for 3 h, water (6 ml) was added to deactivate any excess of sodium hydride. The mixture was concentrated under reduced pressure and the residue dissolved into a solution containing sodium hydroxide (15 g), brine (100 ml) and water (100 ml). This mixture was subjected to continuous extraction with ether (or hexane). The organic phase was then concentrated under reduced pressure. After azeotropic distillation in benzene and subsequent evaporation of the solvent under reduced pressure, **2a** was isolated in a quantitative yield as a pure white waxy product (98 %, HPLC).

^1H NMR (400 MHz, CDCl_3): δ 0.84–0.92 (m, 6 H, CH $_3$), 0.89 (d, $J_{5',6'} = 6.4$ Hz, 6 H, CH $_3$ -6'), 1.22–1.41 (m, 8 H, CH $_2$), 1.43–1.54 (m, 3 H, H-9/4'), 1.60–1.72 (m, 1 H, H-5'), 1.98–2.06 (m, 2 H, H-2), 2.96 (app. t, $J_{1,2} = 7.5$ Hz, 2 H, H-1), 3.26–3.33 (m, 2 H, H-8), 3.41–3.49 (m, 5 H, H-6/1'/3'), 3.50–3.55 (m, 2 H, H-5 and H-6/1'), 3.65 (app. t, $J_{2,3} = 6$ Hz, 2 H, H-3) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 11.0, 14.1, 22.67 and 22.73 (CH $_3$), 23.1 and 23.8 (CH $_2$), 25.1 (CH), 25.4, 29.1, 30.5 and 38.3 (CH $_2$), 39.5 (CH), 47.9, 68.8, 70.0, 70.3, 70.4, 74.36 and 74.41 (CH $_2$), 77.7 (CH) ppm; IR (KBr): 3472 (br.), 2958, 2929, 2872, 1465, 1213, 1192, 1115, 1054, 735, 620, 531 cm $^{-1}$.

9-Ethyl-5-(5-methyl-2-oxa-1-hexyl)-4,7-dioxa-1-tridecene (3a). Compound **1a** (75.08 g, 0.274 mol) was added to a slurry containing sodium hydride (7.82 g, 0.326 mol) in dry THF (200 ml) and stirred for 5 min at room temperature, under a nitrogen atmosphere. Allyl chloride (25.09 g, 0.327 mol) was then added, and the reaction

mixture was heated (60 °C) with stirring for 18 h. Then another portion of allyl chloride (5.00 g, 0.065 mol) was added. After being stirred and heated (60 °C) for another 4 h, the reaction mixture was cooled to room temperature, and water (50 ml) was added to deactivate any excess of sodium hydride. The reaction mixture was dissolved in dichloromethane (500 ml), and washed with brine (500 ml). The aqueous phase was extracted with more dichloromethane (500 ml) and the combined organic phase was dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure and the crude product was distilled under reduced pressure, (b.p. 117–120 °C at 0.08 mmHg). The yield of pure **3a** was 76.88 g (89 %), (98.8 % by GLC).

¹H NMR (400 MHz, CDCl₃): δ 0.85–0.92 (m, 6 H, CH₃), 0.89 (d, *J*_{5',6'} = 6.8 Hz, 6 H, CH₃-6'), 1.24–1.42 (m, 8 H, CH₂), 1.43–1.53 (m, 3 H, H-9/4'), 1.69 (hep., *J*_{4',5'} = *J*_{5',6'} = 6.8 Hz, 1 H, H-5'), 3.27–3.36 (m, 2 H, H-8), 3.43–3.53 (m, 6 H, H-6/1'/3'), 3.65 (p, *J*_{5,6} = *J*_{1',5} = 5.3 Hz, 1 H, H-5), 4.15 (app. d, *J*_{2,3} = 5 Hz, 2 H, H-3), 5.14 (app. dd, *J*_{1,2} = 10 Hz, *J*_{1,1} = 1.4 Hz, 1 H, H-1), 5.28 (app. dd, *J*_{1,2} = 17 Hz, *J*_{1,1} = 1.4 Hz, 1 H, H-1), 5.92 (app. ddt, *J*_{1,2} = 17 Hz, *J*_{1,2} = 10 Hz, *J*_{2,3} = 5 Hz, 1 H, H-2) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.08, 11.11, 14.1, 22.64 and 22.70 (CH₃), 23.1 and 23.9 (CH₂), 25.1 (CH), 29.1, 30.6 and 38.5 (CH₂), 39.6 (CH), 70.0, 71.1, 71.30, 71.36 and 74.4 (CH₂), 77.1 (CH), 116.6 and 135.4 (alkene) ppm; IR (neat): 2958, 2928, 2871, 1466, 1380, 1367, 1116, 995, 921 cm⁻¹; MS [*m/z* (% rel. int.)]: 314 (3, *M*⁺), 256 (4), 145 (9), 129 (17), 113 (14), 112 (9), 101 (8), 71 (100), 70 (14), 69 (13), 58 (7), 57 (41).

8-Ethyl-4-(5-methyl-2-oxa-1-hexyl)-3,6-dioxo-1-dodecanol (4a). A solution containing **3a** (30.02 g, 95.45 mmol) in 200 ml of MeOH was cooled to -78 °C in a dry ice/acetone bath and treated with ozone until a consistent blue colour was achieved. Then an excess of sodium borohydride (10.0 g, 0.26 mol) was added in small portions. The resulting mixture was allowed to reach room temperature. After stirring over night at this temperature, the solvent was removed under reduced pressure. The residue was dissolved in ether (200 ml) and washed with water (100 ml). The aqueous phase was then extracted with ether (3 × 100 ml) and the combined organic phases dried over anhydrous MgSO₄. Filtration, evaporation and distillation under reduced pressure (b.p. 133–137 °C at 0.08 mmHg) gave 24.76 g (81 %) of pure **4a** (98 % by GLC).

¹H NMR (400 MHz, CDCl₃): δ 0.84–0.95 (m, 6 H, CH₃), 0.90 (d, *J*_{5',6'} = 6.8 Hz, 6 H, CH₃-6'), 1.24–1.41 (m, 8 H, CH₂), 1.45–1.53 (m, 3 H, H-8/4'), 1.69 (hep., *J*_{4',5'} = *J*_{5',6'} = 6.8 Hz, 1 H, H-5'), 3.24–3.32 [br. s, 1 H, OH (?)], 3.33 (d, *J*_{7,8} = 6.3 Hz, 2 H, H-7), 3.43–3.51 (m, 6 H, H-5/1'/3'), 3.67–3.70 (m, 2 H, H-1 or H-2), 3.72–3.78 (m, 3 H, H-4 and H-1 or H-2) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.1, 14.1 and 22.6 (CH₃), 23.1 and 23.8 (CH₂), 25.1 (CH), 29.1, 30.5 and 38.4 (CH₂), 39.6 (CH), 62.2, 70.2, 71.5, 71.7, 72.3 and 74.6 (CH₂), 78.7

(CH) ppm; IR (neat): 3461 (broad), 2958, 2928, 2872, 1466, 1380, 1113 cm⁻¹; MS [*m/z* (% rel. int.)]: 318 (0.04, *M*⁺), 256 (13), 129 (8), 128 (6), 127 (5), 113 (16), 112 (9), 105 (15), 101 (7), 89 (8), 88 (11), 87 (30), 71 (100), 70 (17), 69 (12), 58 (9), 57 (33).

Ethylene sulfate, 12. To a stirred solution containing 10.8 g, 0.1 mol, of ethylene sulfite, in 100 ml of tetrachloromethane (or dichloromethane) was added 5 ml of a 1 % RuO₄ / CCl₄ solution, and 45 ml of a 15 % sodium hypochlorite solution was then added over a 30 min period. The reaction was exothermic and cooled in a water-ice bath. After being stirred at room temperature for ca. 1 h the mixture had a consistent yellow-green color. The organic layer was separated, and the aqueous phase was extracted with CCl₄. The organic layers were combined, a drop of methanol was added and then the layers were dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, leaving behind the crude product, **12**, as a white crystalline product (m.p. 98–99 °C) which was used without further purification. The yield was 9.1 g, 73 %. The spectroscopic properties were in agreement with those of an authentic sample.

Ethoxylation of alcohols with cyclic sulfates. General procedure. To a solution containing 0.020 mol of the appropriate alcohol in 40 ml of acetonitrile under a nitrogen atmosphere, 0.24 g of NaH was added and stirred at room temperature for ca. 30 min. Then a solution containing 3.50 g (0.028 mol) of ethylene sulfate, **12**, in 15 ml of acetonitrile was added over a 2 min period, and the reaction mixture was stirred for 1 h and refluxed for 30 min. The solvent was then evaporated leaving behind the crude sulfate, which was hydrolyzed by reflux for 2 h in 40 ml of 1M HCl, yielding the desired ethoxylated product in an essential quantitative yield. The ethoxylated products were distilled under reduced pressure.

12-Ethyl-8-(5-methyl-2-oxa-1-hexyl)-4,7,10-trioxa-1-hexadecanesulfonic acid, sodium salt (5a). A mixture containing **4a** (13.6 g, 43.0 mmol) and sodium hydride (2.50 g, 104.2 mmol) in dry DMF (200 ml) was stirred under an N₂ atmosphere and then heated to 60 °C in an oil bath. Then 10.0 g 1,3-propane sultone (81.97 mmol) in dry DMF (50 ml) was added over a period of 10 min. The resulting reaction mixture was kept at 60 °C for 1 h, then allowed to cool to room temperature, and stirred overnight. The work up was performed according to the procedure given for **2a**, yielding 19.86 g (106 %) of **5a** of 96 % purity (HPLC).

¹H NMR (400 MHz, CDCl₃): δ 0.81–0.91 (m, 6 H, CH₃), 0.90 (d, *J*_{5',6'} = 6.8 Hz, 6 H, CH₃-6'), 1.23–1.40 (m, 8 H, CH₂), 1.43–1.55 (m, 3 H, H-12/4'), 1.62–1.73 (m, 1 H, H-5'), 2.00–2.20 (m, 2 H, H-2), 2.90–3.00 (m, 2 H, H-1), 3.31 (app. d, *J*_{11,12} = 5.4 Hz, 2 H, H-11), 3.43–3.53 (m, 6 H, H-9/1'/3'), 3.53–3.59 (m, 4 H, H-3 and H-5 or H-6), 3.59–3.65 (m, 1 H, H-8), 3.70–3.78 (m, 2 H, H-5 or H-6) ppm; ¹³C NMR (100 MHz, CDCl₃): δ

11.1, 14.1 and 22.7 (CH₃), 23.1, 23.8 and 25.0 (CH₂), 25.1 (CH), 29.1, 30.5 and 38.4 (CH₂), 39.5 (CH), 47.9 (CH₂), 69.2, 69.9, 70.0, 70.6, 70.7 and 74.4 (CH₂), 78.1 (CH) ppm; IR (KBr): 3459 (broad), 2958, 2929, 2871, 1466, 1195, 1116, 1052, 795, 618, 531 cm⁻¹.

12-Ethyl-8-(5-methyl-2-oxa-1-hexyl)-4,7,10-trioxa-1-hexadecene (6a). Compound **6a** was prepared from **4a** and allyl chloride according to the procedure described for **3a**. The crude product was distilled under reduced pressure, b.p. 134–138°C (0.08 mmHg), yielding 21.29 g (78.7 %) of **6a**, (96 % pure by GLC).

¹H NMR (400 MHz, CDCl₃): δ 0.85–0.90 (m, 6 H, CH₃), 0.89 (d, $J_{5',6'} = 6.4$ Hz, 6 H, CH₃-6'), 1.25–1.42 (m, 8 H, CH₂), 1.43–1.51 (m, 3 H, H-12/4'), 1.69 (hept., $J_{4',5'} = J_{5',6'} = 6.8$ Hz, 1 H, H-5'), 3.31 (app. d, $J_{11,12} = 5.9$ Hz, 2 H, H-11), 3.44–5.53 (m, 6 H, H-9/1'/3'), 3.59 (app. t, $J_{5,6} = 5$ Hz, 2 H, H-5 or H-6), 3.65 (p, $J_{8,9} = J_{1',8} = 5.4$ Hz, 1 H, H-8), 3.78 (app. t, $J_{5,6} = 5$ Hz, 2 H, H-5 or H-6), 4.02 (app. d, $J_{2,3} = 5.9$ Hz, 2 H, H-3), 5.16 (app. dd, $J_{1,2} = 10$ Hz, $J_{1,1} = 2$ Hz, 1 H, H-1), 5.26 (app. dd, $J_{1,2} = 17$ Hz, $J_{1,1} = 2$ Hz, 1 H, H-1), 5.91 (app. ddt, $J_{1,2} = 17$ Hz, $J_{1,2} = 10$ Hz, $J_{2,3} = 5.9$ Hz, 1 H, H-2) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.1, 14.1, 22.64 and 22.68 (CH₃), 23.1 and 23.9 (CH₂), 25.1 (CH), 29.1, 30.6 and 38.6 (CH₂), 39.6 (CH), 69.8, 69.9, 70.0, 71.1, 71.3, 72.2, 74.4 (CH₂), 78.5 (CH), 116.8 and 135.0 (alkene) ppm; IR (neat): 2963, 2925, 2860, 1468, 1381, 1370, 1115, 996, 924 cm⁻¹; MS [m/z (% rel. int.)]: 358 (19, M^+), 275 (2), 257 (16), 256 (77), 215 (10), 145 (58), 143 (8), 129 (32), 128 (18), 127 (23), 119 (7), 113 (40), 112 (32), 103 (8), 101 (10), 87 (39), 86 (9), 85 (22), 84 (13), 83 (11), 75 (8), 73 (60), 72 (7), 71 (100), 70 (35), 69 (11), 58 (19), 57 (31).

11-Ethyl-7-(5-methyl-2-oxa-1-hexyl)-3,6,9-trioxa-1-pentadecanol (7a). Compound **7a** was prepared from **6a** according to the procedure described for **4a** (ozone, sodium borohydride). Distillation of the crude product (b.p. 153–158°C at 0.07 mmHg) yielded 15.40 g (76 %) of **7a**, as a colourless liquid, (94 % pure by GLC).

¹H NMR (400 MHz, CDCl₃): δ 0.81–0.91 (m, 6 H, CH₃), 0.90 (d, $J_{5',6'} = 6.3$ Hz, 6 H, CH₃-6'), 1.25–1.40 (m, 8 H, CH₂), 1.43–1.53 (m, 3 H, H-11/4'), 1.68 (hept., $J_{4',5'} = J_{5',6'} = 6.8$ Hz, 1 H, H-5'), 2.70 (br. s, 1 H, OH), 3.31 (app. d, $J_{10,11} = 5.9$ Hz, 2 H, H-10), 3.44–3.53 (m, 6 H, H-8/1'/3'), 3.59–3.62 (m, 2 H, H1 or H2 or H4 or H5), 3.65–3.73 (m, 5 H, H7 and H1/2 or H4/5), 3.77–3.79 (m, 2 H, H1 or H2 or H4 or H5) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.1, 14.1, 22.64 and 22.68 (CH₃), 23.1 and 23.9 (CH₂), 25.1 (CH), 29.1, 30.6 and 38.4 (CH₂), 39.6 (CH), 61.8, 69.8, 70.1, 70.8, 71.1, 71.2, 72.5 and 74.5 (CH₂), 78.5 (CH) ppm; IR (neat): 3457 (br), 2957, 2928, 2871, 1466, 1380, 1367, 1118 cm⁻¹; MS [m/z (% rel. int.)]: 362 (0.1, M^+), 276 (3), 275 (17), 257 (16), 256 (90), 233 (11), 170 (10), 149 (69), 145 (7), 143 (10), 133 (27), 132 (9), 131 (77), 129 (19), 128 (20), 127 (19), 119 (11), 113 (38), 112 (34), 107 (12), 101 (11), 89 (94),

88 (16), 87 (59), 71 (100), 70 (36), 69 (10), 58 (19), 57 (30).

15-Ethyl-11-(5-methyl-2-oxa-1-hexyl)-4,7,10,13-tetraoxa-1-nonadecanesulfonic acid, sodium salt (8a). Compound **8a** was prepared from **7a** and 1,3-propane sultone according to the procedure described for **5a**, as a white waxy product in 89 % isolated yield (7.36 g). The purity was 98 % by HPLC.

¹H NMR (400 MHz, CDCl₃): δ 0.85–0.90 (m, 6 H, CH₃), 0.89 (d, $J_{5',6'} = 6.4$ Hz, 6 H, CH₃-6'), 1.22–1.41 (m, 8 H, CH₂), 1.42–1.53 (m, 3 H, H-15/4'), 1.68 (app. hept., $J_{5',6'} = 6.8$ Hz, 1 H, H-5'), 1.98–2.10 (m, 2 H, H-2), 2.89–2.97 (m, 2 H, H-1), 3.31 (app. d, $J_{14,15} = 5.9$ Hz, 2 H, H-14), 3.43–3.51 (m, 6H, H-12/1'/3'), 3.51–3.66 (m, 9 H, H-11 and OCH₂), 3.75 (app. t, $J = 5$ Hz, 2 H, OCH₂) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.1, 14.1 and 22.7 (CH₃), 23.1 and 23.8 (CH₂), 25.1 (CH and CH₂), 29.1, 30.5 and 38.5 (CH₂), 39.6 (CH), 48.0, 69.6, 69.7, 70.0, 70.3, 70.5, 70.8, 70.9 and 74.4 (CH₂), 78.3 (CH) ppm; IR (KBr): 2957, 2929, 2871, 1466, 1197, 1117, 1059, 620 cm⁻¹.

11-Ethyl-3-methyl-5,9-dioxa-7-pentadecanol (1b). Compound **1b** was prepared from 2-methyl-1-butanol and 2-ethylhexyl glycidyl ether according to the procedure given for **1a**. The crude product was distilled at b.p. 132–140°C (0.07 mmHg) yielding 176.62 g (69 %) of **1b** of 96.4 % purity (GLC).

¹H NMR (400 MHz, CDCl₃): δ 0.85–0.91 (m, 12 H, CH₃), 1.08–1.19 (m, 1 H, H-2), 1.26–1.54 (m, 10 H, 4 × CH₂ and H-2/11), 1.59–1.71 (m, 1 H, H-3), 2.50 (br. s, 1 H, OH), 3.21–3.26 (m, 1 H, H-4), 3.30–3.38 (m, 3 H, H-4/10), 3.41–3.50 (m, 4 H, H-6/8), 3.90–3.97 (m, 1 H, H-7) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.1, 11.3, 14.1 and 16.6 (CH₃), 23.1, 23.9, 26.2, 29.1 and 30.6 (CH₂), 34.9, 39.6 and 69.5 (CH), 72.1, 74.4 and 76.8 (CH₂) ppm; IR (neat): 3460 (br), 2980, 2940, 2880, 1476, 1383, 1115 cm⁻¹; MS [m/z (% rel. int.)]: 274 (0.06, M^+), 257 (2), 256 (9), 113 (18), 112 (8), 71 (100), 70 (17), 58 (10), 57 (45), 55 (9).

9-Ethyl-5-(4-methyl-2-oxa-1-hexyl)-4,7-dioxa-1-tridecane-sulfonic acid, sodium salt (2b). Compound **2b** was prepared from **1b** and 1,3-propane sultone according to the procedure described for **2a**. This afforded a white waxy product, identified as **2b** in 74 % yield (35.56 g).

¹H NMR (400 MHz, CDCl₃): δ 0.85–0.90 (m, 12 H, CH₃), 1.06–1.15 (m, 1 H, H-5'), 1.24–1.53 (m, 8 H, 4 × CH₂ and H-9/5'), 1.64 (app. hex., 1 H, $J_{3',4'} = J_{4',5'} = J_{4',1'} = 6.3$ Hz, H-4'), 1.97–2.05 (m, 2 H, H-2), 2.92–2.98 (m, 2 H, H-1), 3.15–3.35 (m, 4 H, H-8/3'), 3.42–3.55 (m, 5 H, H-5/6/1'), 3.65 (app. t, $J_{2,3} = 5.5$ Hz, H-3) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.0, 11.3, 14.1, 16.55 and 16.61 (CH₃), 23.1, 23.8, 25.5, 26.2, 29.1 and 30.5 (CH₂), 34.75, 34.80 and 39.5 (CH), 47.9, 68.9, 70.4, 70.57, 70.63, 74.36, 74.43 and 76.8 (CH₂), 77.7 (CH)

ppm; IR (KBr): 2958, 2929, 2874, 2861, 1617, 1465, 1214, 1194, 1114, 1055 cm^{-1} .

9-Ethyl-5-(4-methyl-2-oxa-1-hexyl)-4,7-dioxa-1-tridecene (3b). Compound **3b** was prepared from **1b** and allyl chloride according to the procedure given for **3a**. The product was purified by distillation. Yield 42.77 g (93 %) as a colourless liquid, 98.8 % pure (GLC), b.p. 112–122°C at 0.05 mmHg.

^1H NMR (400 MHz, CDCl_3): δ 0.85–0.91 (m, 12 H, CH_3), 1.07–1.18 (m, 1 H, H-5'), 1.22–1.53 (m, 10 H, 4 \times CH_2 and H-9/5'), 1.59–1.68 (m, 1 H, H-4'), 3.18–3.24 (m, 1 H, H-3'), 3.27–3.35 (m, 3 H, H-8/3'), 3.44–3.52 (m, 4 H, H-6/1'), 3.65 (app. p, $J_{5,6} = J_{5,1'} = 5$ Hz, 1H, H-5), 4.15 (app. d, $J_{2,3} = 5$ Hz, 2 H, H-3), 5.14 (app. dd, $J_{1,2} = 10$ Hz, $J_{1,1'} = 2$ Hz, 1 H, H-1), 5.27 (app. dd, $J_{1,2} = 17$ Hz, $J_{1,1'} = 2$ Hz, 1 H, H-1), 5.94 (app. ddt, $J_{1,2} = 17$ Hz, $J_{1,2} = 10$ Hz, $J_{2,3} = 5$ Hz, 1 H, H-2) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 11.08, 11.12, 11.3, 14.1, 16.55 and 16.61 (CH_3), 23.1, 23.9, 26.2, 29.1 and 30.6 (CH_2), 34.9 and 39.6 (CH), 71.32, 71.38, 74.5 and 76.9 (CH_2), 77.2 (CH), 116.6 and 135.5 (alkene) ppm; IR (neat): 2960, 2930, 2874, 2860, 1463, 1379, 1112, 995, 921 cm^{-1} ; MS [m/z (% rel. int.)]: 314 (2, M^+), 257 (2), 256 (6), 129 (10), 113 (17), 112 (10), 101 (12), 75 (20), 71 (100), 70 (11), 58 (12).

8-Ethyl-4-(4-methyl-2-oxa-1-hexyl)-3,6-dioxa-1-dodecanol (4b). Compound **4b** was prepared from **3b** according to the procedure given for **4a** (ozone, sodium borohydride). Distillation of the crude product (b.p. 133–135°C at 0.08 mmHg) gave 22.05 g (72 %) of **4b** as a colourless liquid, 94 % pure (GLC).

^1H NMR (400 MHz): δ 0.86–0.91 (m, 12 H, CH_3), 1.08–1.19 (m, 1 H, H-5'), 1.22–1.54 (m, 10 H, 4 \times CH_2 and H-8/5'), 1.61–1.69 (m, 1 H, H-4'), 3.23–3.25 (m, 1 H, H-3'), 3.30–3.34 (m, 3 H, H-7/3'), 3.42–3.50 (m, 4 H, H-5/1'), 3.67–3.71 (m, 2 H, H-1), 3.71–3.79 (m, 3 H, H-2/4) ppm; ^{13}C NMR (100 MHz): δ 11.0, 11.3, 14.1 and 16.6 (CH_3), 23.1, 23.8, 26.2, 29.1 and 30.5 (CH_2), 34.9 and 39.6 (CH), 62.2, 71.7, 72.3, 74.6 and 77.0 (CH_2), 78.7 (CH) ppm; IR (neat): 3453, 2960, 2930, 2874, 1737, 1462, 1379, 1111 cm^{-1} ; MS [m/z (% rel. int.)]: 316 (0.06, M^+), 258 (2), 257 (18), 256 (100), 231 (7), 129 (10), 128 (17), 127 (11), 113 (35), 112 (25), 105 (53), 89 (23), 88 (26), 87 (31), 71 (69), 70 (22), 59 (69), 58 (21), 57.

12-Ethyl-8-(4-methyl-2-oxa-1-hexyl)-4,7,10-trioxa-1-hexadecanesulfonic acid, sodium salt (5b). Compound **5b** was prepared in a quantitative yield (32.5 g), as a white waxy product, from **4b** according to the procedure given for **5a**. The purity was 97 % by HPLC.

^1H NMR (400 MHz, CDCl_3): δ 0.85–0.91 (m, 12 H, CH_3), 1.08–1.17 (m, 1 H, H-5'), 1.20–1.54 (m, 10 H, 4 \times CH_2 and H-12/5'), 1.64 (app. hex., $J_{3,4'} = J_{4',5'} = J_{4',1'} = 6.3$ Hz, 1 H, H-4'), 2.00–2.09 (m, 2 H, H-2), 2.92–2.98 (m, 2 H, H-1), 3.19–3.25 (m, 1 H, H-3'), 3.28–3.34 (m, 3 H, H-11/3'), 3.50–3.76 (m, 11 H, H-3/5/6/8/

9/1') ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 11.06, 11.10, 11.3, 14.1, 16.55 and 16.59 (CH_3), 23.1, 23.8, 25.0, 26.2, 29.1 and 30.5 (CH_2), 34.76, 34.80 and 39.5 (CH), 48.0, 69.3, 70.0, 70.79, 70.83, 70.87, 74.40, 74.43 and 76.8 (CH_2), 78.2 (CH) ppm; IR (KBr): 3468, 2960, 2930, 2873, 2862, 1464, 1210, 1194, 1115, 1057, 621 (m), 532 (m) cm^{-1} .

12-Ethyl-8-(4-methyl-2-oxa-1-hexyl)-4,7,10-trioxa-1-hexadecene (6b). Compound **6b** was prepared from **4b** and allyl chloride according to the procedure given for **3a**. Distillation of the crude product (b.p. 131°C at 0.04 mmHg) yielded 4.10 g (17 %) of **6b**, as a colourless liquid, 96 % pure (GLC).

^1H NMR (400 MHz, CDCl_3): δ 0.85–0.90 (m, 12 H, CH_3), 1.06–1.18 (m, 1 H, H-5'), 1.25–1.53 (m, 10 H, 4 \times CH_2 and H-12/5'), 1.63 (app. hex., $J_{3,4'} = J_{4',5'} = J_{4',1'} = 6.3$ Hz, 1 H, H-4'), 3.18–3.24 (m, 1 H, H-3'), 3.28–3.32 (m, 1 H, H-3'), 3.31 (d, $J_{11,12} = 5.9$ Hz, 2 H, H-11), 3.44–3.53 (m, 4 H, H-9/1'), 3.59 (app. dd, $J = 4.9$ Hz, $J = 3.9$ Hz, 2 H, H-5 or H-6), 3.65 (p, $J_{8,9} = J_{8,1'} = 5.4$ Hz, 1 H, H-8), 3.78 (app. dd, $J = 4.9$ Hz, $J = 3.9$ Hz, 2 H, H-5 or H-6), 4.02 (ddd, $J_{2,3} = 5.9$ Hz, $J_{1,3} = J_{1,3} = 1.5$ Hz, 2 H, H-3), 5.16 (ddt, $J_{1,2} = 10.3$ Hz, $J_{1,1} = J_{1,3} = 1.5$ Hz, 1 H, H-1), 5.27 (ddt, $J_{1,2} = 17.3$ Hz, $J_{1,1} = J_{1,3} = 1.5$ Hz, 1 H, H-1), 5.91 (ddt, $J_{1,2} = 17.1$ Hz, $J_{1,2} = 10.3$ Hz, $J_{2,3} = 5.9$ Hz, 1 H, H-2) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 11.08, 11.11, 11.3, 14.1, 16.57 and 16.61 (CH_3), 23.1, 23.9, 26.2, 29.1 and 30.6 (CH_2), 34.9 and 39.6 (CH), 69.82, 69.90, 71.3, 72.2, 74.4 and 76.9 (CH_2), 78.5 (CH), 116.8 and 135.0 (alkene) ppm; IR (neat): 2960, 2930, 2874, 2861, 1463, 1112, 922 cm^{-1} ; MS [m/z (% rel. int.)]: 358 (7, M^+), 257 (4), 256 (17), 145 (21), 129 (8), 113 (13), 112 (8), 87 (32), 86 (7), 85 (13), 84 (7), 83 (8), 75 (10), 73 (31), 71 (100), 70 (15), 58 (13), 57 (60), 55 (16).

11-Ethyl-7-(4-methyl-2-oxa-1-hexyl)-3,6,9-trioxa-1-pentadecanol (7b). Compound **7b** was prepared from **6b** according to the procedure given for **4a** (ozone, sodium borohydride). Distillation of the crude product (b.p. 147–150°C at 0.05 mm Hg) gave 6.20 g (69 %) of 98.5 % pure **7b** (GLC).

^1H NMR (400 MHz, CDCl_3): δ 0.85–0.90 (m, 12 H, CH_3), 1.07–1.18 (m, 1 H, H-5'), 1.22–1.53 (m, 10 H, 4 \times CH_2 and H-11/5'), 1.64 (app. hex., $J_{3,4'} = J_{4',5'} = J_{4',1'} = 6.3$ Hz, 1H, H-4'), 2.62 (br. s, 1 H, OH), 3.18–3.23 (m, 1 H, H-3'), 3.27–3.32 (m, 1H, H-3'), 3.31 (d, $J_{10,11} = 5.9$ Hz, 2 H, H-10), 3.42–3.53 (m, 4 H, H-8/1'), 3.59–3.62 (m, 2 H, H1 or H2 or H4 or H5), 3.65–3.69 (m, 3 H, H-7 and H1 or H2 or H4 or H5), 3.69–3.72 (m, 2 H, H1 or H2 or H4 or H5), 3.76–3.80 (m, 2 H, H1 or H2 or H4 or H5) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 11.1, 11.3, 14.1, 16.53 and 16.57 (CH_3), 23.1, 23.9, 26.2, 29.1 and 30.6 (CH_2), 34.9 and 39.6 (CH), 61.8, 69.9, 70.8, 71.3, 72.5, 74.5 and 76.9 (CH_2), 78.5 (CH) ppm; IR (neat): 3435, 2959, 2929, 2874, 1462, 1379, 1113 cm^{-1} ; MS [m/z (% rel. int.)]: 344 (0.3, $M^+ - \text{H}_2\text{O}$), 275 (2), 256

(27), 171 (11), 149 (27), 131 (26), 129 (10), 113 (14), 112 (11), 89 (50), 87 (51), 75 (9), 71 (100), 70 (16), 59(10), 58 (16), 57 (68), 55 (17).

15-Ethyl-11-(4-methyl-2-oxa-1-hexyl)-4,7,10,13-tetraoxa-1-nonadecanesulfonic acid, sodium salt (8b). Compound **8b** was prepared from **7b** and 1,3-propane sultone according to the procedure given for **5a** (8.7 g), 93 % pure (HPLC).

¹H NMR (400 MHz, CDCl₃): δ 0.84–0.92 (m, 12 H, CH₃), 1.07–1.18 (m, 1 H, H-5'), 1.25–1.53 (m, 10 H, 4 × CH₂ and H-15/5'), 1.63 (app. hex., $J_{3',4'} = J_{4',5'} = J_{4',11'} = 6.4$ Hz, 1 H, H-4'), 1.97–2.06 (m, 2 H, H-2), 2.90–2.98 (m, 2 H, H-1), 3.18–3.24 (m, 1 H, H-3'), 3.27–3.33 (m, 1 H, H-3'), 3.30 (d, $J_{14,15} = 5.9$ Hz, 2 H, H-14), 3.45–3.65 (m, 13 H, 4 × OCH₂ and H-11/12/1'), 3.70–3.78 (m, 2 H, OCH₂) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.1, 11.4, 14.1 and 16.6 (CH₃), 23.1, 23.8, 24.9, 26.2, 29.1 and 30.5 (CH₂), 34.9 and 39.6 (CH), 47.9, 69.6, 69.7, 69.9, 70.1, 70.3, 70.5, 71.0, 74.38, 74.41 and 76.8 (CH₂), 78.2 (CH) ppm; IR (KBr): 3455, 2960, 2929, 2874, 1618, 1464, 1420, 1216, 1193, 1116, 1061 cm⁻¹.

5,13-Diethyl-7,11-dioxa-9-heptadecanol (1c). **1c** was prepared from 2-ethyl-1-hexanol and 2-ethylhexyl glycidyl ether according to the procedure given for **1a**. Distillation of the crude product (b.p. 134–146 °C at 0.3 mmHg) yielded 15.52 g (31 %) of **1c**, as a colourless liquid, 97 % pure (GLC).

¹H NMR (400 MHz, CDCl₃): δ 0.86–0.91 (m, 12 H, CH₃), 1.22–1.43 (m, 16 H, 8 × CH₂), 1.51 (app. hex., $J = 6$ Hz, 2 H, H-5/13), 2.43 (d, $J_{9,OH} = 4.4$ Hz, 1 H, OH), 3.30–3.38 (m, 4 H, H-6/12), 3.41–3.49 (m, 4 H, H-8/10), 3.93 (app. hex., $J_{8,9} = J_{9,10} = J_{9,OH} = 4.9$ Hz, 1 H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 11.1 and 14.1 (CH₃), 23.1, 23.9, 29.1 and 30.6 (CH₂), 39.6 and 69.5 (CH), 72.1 and 74.4 (CH₂) ppm; IR (neat): 3583, 3458, 2959, 2927, 2866, 1464, 1379, 1325, 1254, 1217, 1110, 1010, 870, 770, 728 cm⁻¹; MS [m/z (% rel. int.)]: 316 (0.05, M⁺), 298 (10), 113 (40), 112 (19), 71 (72), 70 (14), 69 (11), 58 (11), 57 (100), 56 (10), 55 (17), 43 (39).

9-Ethyl-5-(4-ethyl-2-oxa-1-octyl)-4,7-dioxa-1-tridecanesulfonic acid, sodium salt (2c). Compound **2c** was prepared from **1c** and 1,3-propane sultone according to the procedure shown for **2a**. After work up, pure **2c** (HPLC) was isolated in 68 % yield (40 g) as a white waxy product.

¹H NMR (400 MHz, CDCl₃): δ 0.86 (t, $J = 7.3$ Hz, 6 H, CH₃), 0.89 (t, $J = 6.8$ Hz, 6 H, CH₃), 1.20–1.43 (m, 16 H, 8 × CH₂), 1.48–1.54 (m, 2 H, H-9/4'), 1.96–2.06 (m, 2 H, H-2), 2.93–3.00 (m, 2 H, H-1), 3.25–3.34 (m,

4 H, H-8/3'), 3.43–3.54 (m, 5 H, H-5/6/1'), 3.63–3.69 (m, 2 H, H-3) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.01, 11.06 and 14.2 (CH₃), 23.2, 23.8, 25.5, 29.1 and 30.5 (CH₂), 39.43 and 39.47 (CH), 47.9, 68.9, 70.5, 74.41 and 74.47 (CH₂), 77.7 (CH) ppm; IR (KBr): 2960, 2930, 2865, 1465, 1213, 1194, 1113, 1055, 619 cm⁻¹.

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