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Sulfonated surfactants obtained from furfural

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Furfural obtained from pentose containing biomass such as hemicelluloses is subjected to photooxygenation. The resulting hydroxyfuranone obtained in high yields undergoes acetalization with fatty alcohols. Using $NaHSO_3$, surfactants are obtained by addition of a sulfonate group to α,β-unsaturated carboxyl or carbonyl compounds. Addition occurred either at the C=C double bond (**6**) or at the aldehyde function (**7**). Compared to conventional surfactants of this type, the resulting compounds possess similar good detergent properties. In the case of compound family **6** and when compared to the corresponding alkylsulfate and alkylsulfonate surfactants, even lower critical micelle concentrations (CMC) are observed. Biodegradation of the new surfactants was determined according to the OECD Test guideline 301 F. Compounds of family **6** are biodegradable. Biodegradation of compounds of family **7** stopped after 10 days.

Introduction

The limited resources of fossil hydrocarbons on the one hand and the search for new chemical compounds for various applications on the other focus the interest of chemists on biomass as a renewable feedstock for fine chemistry.[1–5] In this context, carbohydrates play an important role.[6] They represent about 75% of the approximately 180 billion tons of biomass produced each year by nature. Hemicelluloses and pentoses constitute a class of carbohydrates which is now also intensively studied as a feedstock for fine chemistry.[7]

Thus, furfural obtained from pentose containing biomass is a valuable synthon for fine chemistry. Currently, about 300 000 tons per year[8] are produced mainly by cyclodehydration of pentoses.[9–12] In the context of process optimisation, various mechanisms of this dehydration have been reported.[9,12–14] Many transformations of furfural into intermediates for the chemical industry have been reported with the aim to replace fossil based resources.[4,6,7,10] In the context of furfural chemistry, we are particularly interested in using oxidation products of furfural such as furanones (α,β-unsaturated butyrolactones). Recently, we published transformations of such compounds into zwitterionic surfactants. Michael addition and condensation with fatty amines and furanones was applied to the synthesis of a new family of Gemini type surfactants possessing two hydrophobic moieties.[15] We also used the photochemically induced radical addition of tertiary amines to the olefinic double bond as a key step.[16,17] Such photochemical reactions fulfil particularly well requirements of sustainable chemistry.[18,19] A combination of renewable resources and sustainable methods for synthesis opens up new prospects in this context. Hitherto, various strategies have been used to synthesize surfactants from renewable resources.[20] In the present article, we focus on the synthesis of new families of surfactants carrying a sulfonate group as an anionic hydrophilic moiety. The major advantage of sulfonates is their almost complete dissociation thus leaving a highly polar anion as the hydrophilic moiety.[21–23]

Results and discussion

Synthesis of sulfonate surfactants

We started our investigations with the photooxygenation of furfural to 5-hydroxy-2[5*H*]-furanone **1** (Scheme 1). This reaction is well known and is generally performed in high yields.[9,24–26] The transformation is also performed under mild reaction conditions with visible artificial or sun light and oxygen or air is used as an oxidant.[19,27] The endoperoxide intermediate **2** is generated by addition of singlet oxygen. Singlet oxygen is produced *via* photochemical sensitization.[28] Due to the low excitation energy of oxygen, the sensitization can also be performed with visible light using dyes as a sensitizer. This oxygen species is highly polarizible and electrophilic. It easily attacks olefinic double bonds. Generally, the formation of a perepoxide intermediate is discussed.[29] Often, the formation of endoperoxides such as **2** in the

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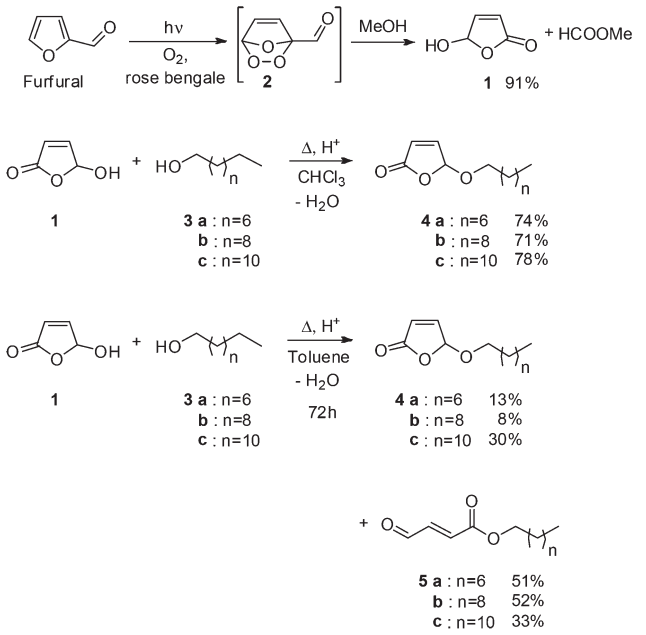
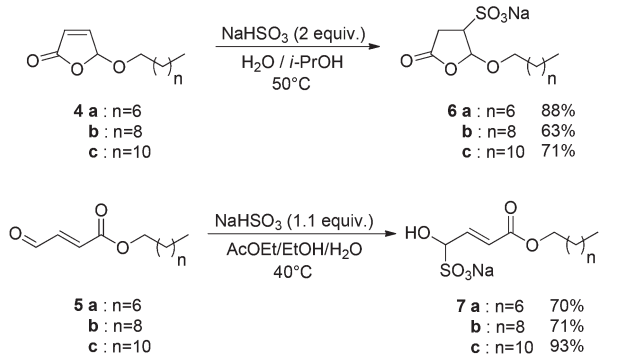
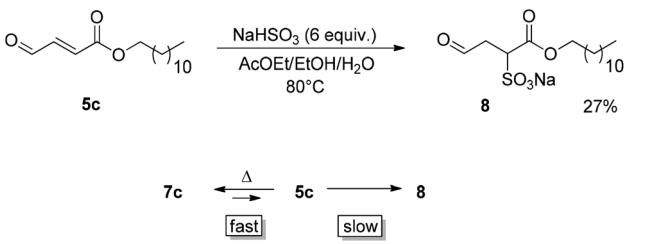


Scheme 1 Synthesis of alkoxyfuranones.



Scheme 2 Addition of a sulfonate function.



Scheme 3 Addition of a sulfonate function to the α,β-unsaturated aldehyde **5c**.

transformation of dienes is in competition with other typical products from the photooxygenation.[30] The perepoxide intermediates may therefore also play a role in the formation of endoperoxide **2**. Since the reaction is carried out in alcohols as a solvent such as methanol, the addition of a solvent molecule to the aldehyde function of **2** induces a fragmentation and hydroxyfuranone **1** and methylformiate are generated. In order to add a hydrophobic moiety, compound **1** was transformed with fatty alcohols **3a–c**. Thus the 5-alkoxy-2[5*H*]-furanones **4a–c** were obtained in high yields in an acetalization reaction by azeotropic destillation.[16] This reaction was also performed with toluene. Prolonged heating under these conditions leads to the formation of the open form **5a–c** possessing an α,β-unsaturated aldehyde function. In the present study, only compound **5c** was isolated while **5a,b** were precipitated as bisulfite adducts (see below).

Compounds **4a–c** and **5a–c** are hydrophobic. In order to attach a hydrophilic moiety and to confer on them surfactant properties, we transformed these compounds with $NaHSO_3$ (Scheme 2). In a Michael reaction the HSO_3^- was added to the α,β-unsaturated lactone.[22,31,32] Thus, compounds **6a–c** have been obtained in good yields. When the open ring derivatives **5a–b** were treated under similar conditions, 1,2-addition of the HSO_3^- anion to the aldehyde function of the α,β-unsaturated carbonyl compound occurred and the resulting hydroxyl sulfonates **7a–c** were isolated in good yields. Such compounds are generally obtained as a precipitate. In contrast to the previous 1,4-addition of bisulfite, the latter reaction has frequently been reported in the literature.[33]

This latter reaction is reversible and in the case of transformations of α,β-unsaturated aldehydes, the concomitant 1,4-addition (Michael reaction) was studied.[32] We wonder whether this competition plays a role in the transformations of compounds **5a–c** with $NaHSO_3$. Indeed, when compound **5c** was heated for a long period (5 days) in the presence of a larger excess of $NaHSO_3$ (6 equiv.), compound **8** was formed in moderate yields (Scheme 3). Obviously, the transformation of **5c** into **7c** is fast but reversible. In order to maintain a sufficient stationary concentration of **5c**, heating at higher temperature (80 °C) is necessary (compare Scheme 2). The 1,4-addition leading to **8** is slower and needs a larger excess of $NaHSO_3$. This excess is also necessary to compensate the low stationary concentration of **5c**. Further aldehyde chemical modification in **8** could lead to new families of surfactants with particular properties.

Determination of physicochemical characteristics

Surfactant properties such as surface tension reduction, micelles formation (determination of the critical micelle concentration (CMC)) or adsorption at the liquid–gas interface have been studied for compound family **6a,b,c**. This study has been carried out as previously reported for other furfural derived surfactants.[15,16] The results are reported in Table 1. Due to the Krafft point of the compound **6c**, physicochemical properties were determined at 50 °C. At this point, it has to be noted that the stability in aqueous solution of compound **6c** has been investigated using NMR spectroscopy. After heating the solution at 50 °C for one hour, no product degradation was detected.

The surfactant concentration at which micellization starts is known as the critical micelle concentration. This value is one of the most important properties of surfactant solutions, because the micelle formation affects both the surface or

Table 1 Surfactant properties of furfural derived anionic sulfonates **6a,b,c** (Scheme 2) at pH 7

Entry	Compound	n	T [°C]	CMC [mM]	pC_{20}	γCMC [mN m^{-1}]	A [Å^2]	Krafft point [°C]
1	**6a**	6	25	28.72	2.562	29.1	89.0	Nd
2	**6b**	8	25	5.81	3.224	29.0	80.6	31
3	**6c**	10	50	0.81	3.935	28.1	65.8	43–45

interfacial tension reduction and the properties of the surfactants such as the solubilization and detergency. The CMC was detected by the break of the curve of the surface tension with the concentration of the surfactant in solution, measured by the Wilhelmy plate method.[34] The efficiency of a surfactant in reducing surface tension is measured by the C_{20} value, the surfactant concentration needed to reduce the surface tension by 20 mN m^{-1}, and the CMC values. The pC_{20} (negative logarithm), rather than the concentration itself is most often used since these values can more easily be related to the corresponding standard free enthalpy ΔG^0 needed for the transfer of the surfactant from the bulk liquid phase to the interphase. The effectiveness is also measured by the surface tension reached at the CMC.[21] The Gibbs equation (eqn (1)) shows the relationship between the surface excess (Γ in mol m^{-2}) and the slope of the plot of the surface tension (γ in N m^{-1}) *versus* the logarithm of the surfactant concentration. In our case, the ionic surfactant in the absence of any other solutes in the solution was studied. Then a multiplying factor 2 in the denominator was added to the Gibbs equation,[21]

$$\Gamma = -\frac{1}{2RT}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln C}\right)_T \quad (1)$$

The reciprocal of this value gives the surface area occupied by a mole of adsorbed molecules. Division by Avogadro's number converts this into the area per molecule at the interface.

As expected, the CMC decreases 10^2 times with increasing the length of the hydrophobic chain of the surfactants by 4 methylene groups. We have also validated that this family of surfactants follows the well known empirical equation observed by Klevens (eqn (2)) between the log CMC and the number of carbon atoms n in the hydrophobic chain (Fig. 1).[35]

$$\log \mathrm{CMC} = A - Bn \quad (2)$$

Although the value of 0.388 found for B is slightly high, it is still in accordance with the general rule (B = log 2) for the ionic surfactants. Moreover, the value of 1.59 found for A is also in accordance with the value obtained for other anionic surfactants.[21]

In the same manner, it was shown that the efficiency factor pC_{20} is a linear function of the number of carbon atoms in a straight-chain hydrophobic group, increasing as the number of carbon atoms increases (Fig. 2).[21]

It is important to point out the high effectiveness of this family of surfactants as interesting surface tension reductions were observed at the CMC in the same range as those observed for conventional anionic surfactants.[21] These results indicate an efficient adsorption at the interface. The area per molecule at surface saturation decreases with increasing length of the hydrophobic chain of the surfactants and is particularly pronounced for the compound **6c**. The physicochemical characteristics of compounds **6a,b,c** were compared to anionic surfactants such as sodium alkylsulfate, sodium alkylsulfonate and sodium alkylbenzenesulfonate.[21] Table 2 describes the properties of these conventional surfactants. First, we observe that compounds **6a,b,c** have lower CMC than the corresponding alkylsulfate and alkylsulfonate surfactants (Table 1, entry 1 and Table 2, entries 1 and 6; Table 1, entry 2 and Table 2 entries 2 and 7; Table 1 entry 3 and Table 2 entries 3 and 8) confirming that the lactone ring behaves as a part of the hydrophobic tail. Indeed, taking into consideration the four additional carbons of the lactone ring, the CMC values measured for compounds **6a,b,c** were in the same range than the values of the corresponding alkylsulfate and alkylsulfonate surfactants (Table 1, entry 1 and Table 2, entries 3 and 8; Table 1, entry 2 and Table 2 entries 4 and 11; Table 1 entry 3 and Table 2 entries 5 and 12). Despite the presence of oxygen atoms, we conclude that the lactone ring is more hydrophobic

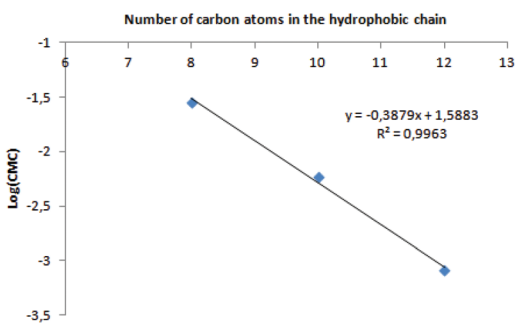


Fig. 1 Log(CMC) as a function of the number of carbon atoms in the hydrophobic chain.

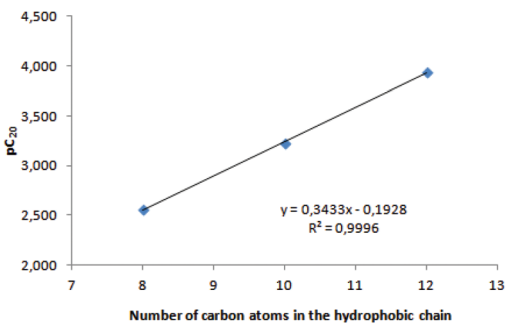


Fig. 2 pC_{20} as a function of the number of carbon atoms in the hydrophobic chain.

Table 2 Physicochemical properties of conventional anionic surfactants

Entry	Family	Molecular structure	Temperature [°C]	CMC [mM]	pC_{20}	Γm [mol cm^{-2} 10^{-10}]	A [Å^2]
1	Sodium alkylsulfonate	$C_8H_{17}SO_3Na$	40	160	—	—	—
2		$C_{10}H_{21}SO_3Na$	25	43	1.69	3.22	52
			40	40	1.66	3.05	54
3		$C_{12}H_{25}SO_3Na$	25	12.4	2.36	2.93	57
			40	11.4	2.33	2.73	60
4		$C_{14}H_{29}SO_3Na$	40	2.5	—	—	—
5		$C_{16}H_{33}SO_3Na$	50	0.7	—	—	—
6	Sodium alkylsulfate	$C_8H_{17}SO_4Na$	40	140	—	—	—
7		$C_{10}H_{21}SO_4Na$	27	—	1.89	2.9	57
			40	33	—	—	—
8		$C_{12}H_{25}SO_4Na$	25	8.2	2.51	3.16	53
			40	8.6	—	—	—
9		$C_{12}H_{25}(OC_2H_4)_1SO_4Na$	25	3.9	2.75	2.92	57
10		$C_{12}H_{25}(OC_2H_4)_2SO_4Na$	25	2.9	2.92	2.62	63
11		$C_{14}H_{29}SO_4Na$	25	2.1	3.1	3.0	56
			40	2.2	—	—	—
12		$C_{16}H_{33}SO_4Na$	40	0.58	3.70	—	—
13	Sodium alkylbenzene sulfonate	p-$C_8H_{17}C_6H_4SO_3Na$	25	—	—	3.0	55
			35	15	—	—	—
14		p-$C_{10}H_{21}C_6H_4SO_3Na$	50	3.1	—	—	—
			70	—	2.53	3.9	43
15		p-$C_{12}H_{25}C_6H_4SO_3Na$	60	1.2	—	—	—
			70	—	3.10	3.7	45

than the corresponding sulfated ethoxylates (Table 1, entry 3 and Table 2, entries 5, 8, 9, 10 and 12). Moreover, we noticed that CMC of compounds **6a,b,c** were in the same range as the values of alkylbenzenesulfonate with the same number of carbon atoms in the hydrophobic chain (Table 1, entry 1 and Table 2, entry 13; Table 1, entry 2 and Table 2, entry 14; Table 1, entry 3 and Table 2, entry 15).

We also studied physicochemical behavior of compounds of family 7. Unfortunately, the more hydrophobic one **7c** was not stable in warm water. The reversible addition of the bisulfite function to aldehyde may explain the weak chemical stability of compound **7c**. Thus we only focused our investigation on compounds **7a** and **7b** (Fig. 3).

It is first important to point out that in the range of concentrations studied here, the shorter tailed surfactant did not aggregate. This behavior is typical for hydrotrope surfactants. For compound **7b**, we observed a CMC of 5.76 mM and a surface tension at CMC of 28.8 mN m^{-1}. These values are very close to those observed for a similar polar head surfactant **6b** that was built up with the same hydrophobic chain. However, we observed a striking difference between the two molecules as **7b** possesses an area per molecule of 182 Å^2. This probably means that **7b** is spreading out while absorbing at the interface.

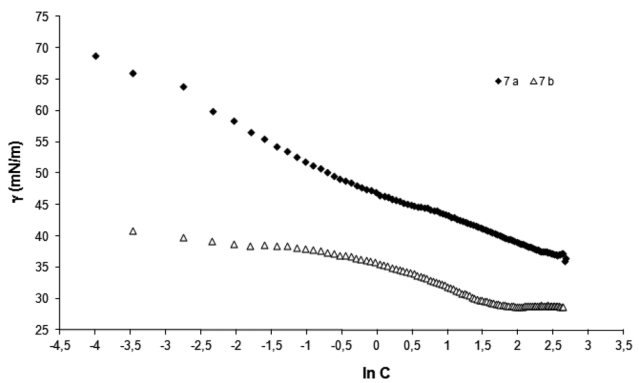


Fig. 3 Evolution of surface tension as a function of ln(*C*) for compounds **7a** and **7b**.

Biodegradability of the surfactants

Biodegradability is an important item in the field of surfactants and standards have been defined by international institutions such as the OECD. The biodegradation of our surfactants was determined according to the OECD Test guideline 301 F[36] which is particularly demanding. This test uses a manometric respirometer to follow the consumption of oxygen during 28 days in a closed flask containing 30 to 60 mg l^{-1} of the test substance and inoculums coming from a sewage plant. The percentage of biodegradation is obtained by dividing the resulting biological oxygen demand (BOD) by the theoretical oxygen demand (ThOD) of the test substance. As in one of our previous studies[15] on zwitterionic compounds, three replicates were performed for each surfactant. The results are presented in Table 3. According to the E.U. directive (Commission Regulation (EC) No. 907/2006 of 20 June 2006),[37] surfactants of the family **6** are considered as biodegradable as degradation reaches 60% after 28 days. Thus, all compounds **6a,b,c** are classified as biodegradable. We notice that surfactants of the family **6** show better biodegradation than conventional linear alkylbenzene sulfonate (LAS) (Table 3, entry 7).[7,38] Significant biodegradation is already observed after 10 days. Moreover, the short latency during the biodegradation of compounds **6a,b,c** compared to conventional surfactants may indicate a low toxicity of these molecules. For compounds of family **7**, the biodegradation remained below the 60% level at

Table 3 Biodegradation according to the OECD Test guideline 301 F[36]

Entry	Surfactants	*n*	Biodegradation after 28 days [%]	Biodegradation after 10 days [%]	Latency (<10%) [days]
1	**6a**	6	74	49	2
2	**6b**	8	78	56	2
3	**6c**	10	67	52	2
4	**7a**	6	37.5	33	2
5	**7b**	8	50	41	2
6	**7c**	10	26	26	3
7	LAS	12	60	20	8

28 days. It is also important to point out that for **7c**, the biodegradation process seems to stop after 10 days. We actually question the potential antimicrobial effect of these compounds. The unsaturated bond of the polar head or the possible toxicity of metabolites generated during the biodegradation might explain the low biodegradation level.

Furthermore, α,β-unsaturated aldehydes are formed during degradation. These compounds formed by the release of HSO_3^- anions may be toxic (see above).

Conclusions

Starting from furfural obtained from pentose containing biomass, we have developed a synthetic approach to new families of sulfonate containing surfactants. The ecologically friendly photooxygenation of furfural with air is used as a key step. In particular, the introduction of the sulfonate group is carried out under mild conditions, either by Michael addition of HSO_3^- to α,β-unsaturated lactones or by addition to an aldehyde function. The resulting compounds of family **6** possess interesting surfactant activities when compared to conventional compounds such alkyl sulfates or alkyl sulfonates. These compounds are also biodegradable.

In perspective, avoiding purification by chromatography or extraction with halogenated solvents will increase the sustainability of the synthesis.

Experimental part

General

NMR spectra were recorded with a Bruker AC 250 (250 MHz for ^{1}H and 62 MHz for ^{13}C). Chemical shifts are given in ppm relatively to TMS using residual solvent signals as secondary references. IR spectra were recorded on a Nicolet AVATAR 320 FT-IR. MS and HRMS were obtained on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode (EV = 30 V, 80 °C, flow of injection 5 ml min^{-1}). Atom absorption spectroscopy was carried out with a Variant Liberty 2 (ICPAES). Preparative chromatography was carried out with silica gel 60A from Carlo Erba Reactifs-SDS. TLC was carried out with Kieselgel 60F254 plates from Merck. 5-Hydroxy-2[5*H*]-furanone **3** has been synthesized as previously described.[26]

Synthesis of alkoxyfuranones 4a–c[16]

Compound 4a. A solution of 5-hydroxy-2[5*H*]-furanone **1** (10 g, 0.1 mol), 1-octanol **3a** (13.6 g, 0.105 mol) and *p*-toluenesulfonic acid (570 mg, 3 mol%) in chloroform (50 ml) was heated under reflux for 1 h. After evaporation of the solvent, the residue was neutralized with a saturated Na_2CO_3 solution. The alkoxyfuranone **4a** was extracted with CH_2Cl_2. The organic solution was dried with $MgSO_4$. After evaporation of the solvent, the residue was distilled under high vacuum. Yield: 15.7 g (74%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.18 (dd, J = 4.6, 1.5 Hz, 1H), 6.19 (dd, J = 4.5, 1.4 Hz, 1H), 5.89 (d, J = 1.2 Hz, 1H), 2.59–3.88 (m, 2H), 1.55–1.66 (m, 2H), 1.24 (m, 10H), 0.83 (dt, J = 4.8, 6.8 Hz, 3H) ppm; ^{13}C NMR (62 MHz, $CDCl_3$): δ = 170.66, 150.50, 125.03, 103.49, 70.74, 31.84, 29.53, 29.34, 29.25, 25.93, 22.70, 14.15 ppm.

Compound 4b. This compound was synthesized following the same procedure as for compound **4a** at the same molar scale. Yield: 17.1 g (71%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.20 (d, J = 5.6 Hz, 1H), 6.22 (d, J = 5.6 Hz, 1H), 5.91 (s, 1H), 3.85 (ddd, J = 8.8, 6.6, 2.2 Hz, 1H), 3.65 (ddd, J = 9.1, 6.8, 2.3 Hz, 1H), 1.61 (m, 2H), 1.25 (m, 14 H), 0.86 (dt, J = 4.8, 6.8 Hz, 3H) ppm; ^{13}C NMR (62 MHz, $CDCl_3$): δ = 170.61, 150.49, 124.98, 103.47, 70.68, 31.92, 29.56, 29.51 (2×), 29.34 (2×), 25.90, 22.71, 14.14 ppm.

Compound 4c. This compound was synthesized following the same procedure as for compound **4a** at the same molar scale. Yield: 20.91 g (78%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.19 (dd, J = 5.7, 0.9 Hz, 1H), 6.21 (dd, J = 5.7, 1.0 Hz, 1H), 5.91 (d, J = 1.0 Hz, 1H), 3.84 (ddd, J = 9.2, 6.6, 2.5 Hz, 1H), 3.65 (ddd, J = 9.1, 6.7, 2.4 Hz, 1H), 1.62 (qint, J = 6.7 Hz, 2H), 1.24 (m, 18H), 0.86 (dt, J = 4.8, 6.1 Hz, 3H) ppm; ^{13}C NMR (62 MHz, $CDCl_3$): δ = 170.62, 150.48, 125.01, 103.47, 70.71, 31.97, 29.69 (2×), 29.63 (2×), 29.58, 29.52, 29.38, 25.92, 22.74, 14.17 ppm.

Synthesis of α,β-unsaturated aldehydes 5a–c

The α,β-unsaturated aldehydes **5a–c** were obtained when the acetalization of 5-hydroxy-2[5*H*]-furanone **1** was performed in toluene instead of chloroform and upon prolonged heating (compare Scheme 1). The aldehydes were not isolated and the yields were determined by spectroscopy. They have been transformed *in situ* into the bisulfite adducts **7a–c** (see below, compare Scheme 2).

Compound **5c** was also prepared separately. A solution of 5-hydroxy-2[5*H*]-furanone **1** (15 g, 0.15 mol), 1-dodecanol **3c** (29.5 g, 0.158 mol) and *p*-toluenesulfonic acid (285 mg, 1 mol %) in chloroform (70 ml) was heated under reflux for 1 h using a Dean–Stark distilling trap. After evaporation of the solvent, the residue was neutralized with a saturated Na_2CO_3 solution. The alkoxyfuranone **3a** was extracted with CH_2Cl_2. The organic solution was dried with $MgSO_4$. After evaporation of the solvent, the residue was distilled under high vacuum. Yield: 14.5 g (36%); mp. 29–30 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.76 (d, J = 7.5 Hz, 1H), 6.85 (dd, J = 15.9, 7.5 Hz, 1H), 6.71 (d, J = 15.9 Hz, 1H), 4.22 (t, J = 6.6 Hz, 2H), 1.68 (quin, J = 6.4 Hz, 2H), 1.25 (m, 18H), 0.86 (dt, J = 5.4, 6.7 Hz, 3H) ppm; ^{13}C NMR (62 MHz, $CDCl_3$): δ = 192.63, 165.02, 140.41, 139.61, 66.03, 32.03, 29.74 (2×), 29.67, 29.61, 29.46, 29.32, 28.59, 25.98, 22.81, 14.24 ppm; IR (film): ν = 2957, 2926, 2856, 2732, 1730, 1703 cm^{-1}; Elemental analysis: calcd (%) for $C_{16}H_{28}O_3$ (268.20): C 71.60, H 10.52; found: C 71.40, H 10.66; TOFMSES$^+$ [M + Na$^+$] = 291.1936 (calcd 291.1936).

Synthesis of sulfonates 6a–c

Compound 6a. A solution of alkoxyfuranone **4a** (14.8 g, 70 mmol) in isopropanol (310 ml) is added to a solution of $NaHSO_3$ (14.5 g, 140 mmol) in water (230 ml). The resulting mixture was heated at 50 °C for 28 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate–methanol 90/10). Yield: 19.53 g (88%); mp. 236–237 °C.

^{1}H NMR (250 MHz, [d$_6$]DMSO): δ = 5.53 (s, 1H), 3.58 (ddd, J = 9.6, 6.5, 3.0 Hz, 2H), 3.11 (dd, J = 9.3, 1.3 Hz, 1H), 2.90 (dd, J = 18.4, 9.5 Hz, 1H), 2.50 (dd, J = 18.2, 2.4 Hz, 1H), 1.51 (m, 2H), 1.24 (m, 10H), 0.84 (dt, J = 5.6, 6.7 Hz, 3H) ppm; ^{13}C NMR (62 MHz, [d$_6$]DMSO): δ = 175.43, 105.06, 68.85, 59.21, 31.25, 30.40, 28.94, 28.73, 28.66, 25.43, 22.10, 13.98 ppm; IR (KBr): ν = 3598, 3461, 3010, 2956, 2956, 2854, 1768, 1636 cm^{-1}; Elemental analysis: calcd (%) for $C_{12}H_{21}NaO_6S$ (316.35): C 45.56, H 6.69, S 10.14; found: C 44.25, H 6.86, S 10.58; TOFMSES$^-$ [M − Na$^+$] = 293.1049 (calcd 293.59).

Compound 6b. A solution of alkoxyfuranone **4b** (15.3 g, 64 mmol) in isopropanol (285 ml) is added to a solution of $NaHSO_3$ (13.3 g, 127 mmol) in water (210 ml). The resulting mixture was heated at 50 °C for 28 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate–methanol 90/10). Yield: 13.77 g (63%); mp. 236–237 °C.

^{1}H NMR (250 MHz, [d$_6$]DMSO): δ = 5.52 (s, 1H), 3.58 (ddd, J = 9.6, 6.6, 3.0 Hz, 2H), 3.11 (dd, J = 9.4, 1.1 Hz, 1H), 2.90 (dd, J = 18.4, 9.5 Hz, 1H), 2.50 (dd, J = 18.1, 2.4 Hz, 1H), 1.51 (m, 2H), 1.24 (m, 14H), 0.85 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (62 MHz, [d$_6$]DMSO): δ = 175.43, 105.06, 68.85, 59.21, 31.32, 30.40, 28.99 (2×), 28.77 (2×), 28.73, 25.44, 22.13, 13.99 ppm; IR (KBr): ν = 3597, 3460, 3011, 2955, 2922, 2852, 1768, 1636 cm^{-1}; Elemental analysis: calcd (%) for $C_{14}H_{25}NaO_6S$ (344.40): C 48.82, H 7.32, S 9.31; found: C 46.79, H 7.15, S 8.91; TOFMSES$^-$ [M − Na$^+$] = 321.1372 (calcd 321.1370).

Compound 6c. A solution of alkoxyfuranone **4c** (4.6 g, 17.2 mmol) in isopropanol (77 ml) is added to a solution of $NaHSO_3$ (3.58 g, 34.4 mmol) in water (57 ml). The resulting mixture was heated at 50 °C for 28 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate–methanol 90/10). Yield: 4.5 g (71%); mp. 237–238 °C.

^{1}H NMR (250 MHz, [d$_6$]DMSO): δ = 5.52 (s, 1H), 3.58 (ddd, J = 9.4, 6.3, 3.0 Hz, 2H), 3.10 (dd, J = 9.5, 0.8 Hz, 1H), 2.90 (dd, J = 18.4, 9.5 Hz, 1H), 2.49 (dd, J = 18.4, 2.5 Hz, 1H), 1.50 (m, 2H), 1.23 (m, 16H), 0.85 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (62 MHz, [d$_6$]DMSO): δ = 175.43, 105.07, 68.85, 59.21, 31.32, 30.41, 29.03 (4×), 28.95, 28.74 (2×), 25.43, 22.12, 13.96 ppm; IR (KBr): ν = 3593, 3455, 3007, 2955, 2918, 2851, 1769, 1636 cm^{-1}; Elemental analysis: calcd (%) for $C_{16}H_{29}NaO_6S$ (372.45): C 51.60, H 7.85, S 9.61; found: C 49.56, H 7.96, S 8.95; TOFMSES$^-$ [M − Na$^+$] = 349.1684 (calcd 349.1685).

Synthesis of hydroxysulfonates 7a–c

Compound 7a. A mixture of ethyl acetate (38 ml), ethanol (23 ml), water (7.5 ml), $NaHSO_3$ (5.0 g, 47.8 mmol) and **5a**/**4a** in a ratio of 4 : 1 (11.34 g, 53.5 mmol) was heated to 40 °C for 2 h. The mixture was filtered and the solid was washed with ethanol and dried at air. Yield 9.5 g (70%) Compound **4a** (2.2 g) was recovered from the liquid phase.

^{1}H NMR (250 MHz, [d$_6$]DMSO): δ = 6.83 (dd, J = 15.9, 5.1 Hz, 1H), 5.83 (m, 2H), 4.51 (s, broaden, 1H), 3.87 (t, J = 6.8 Hz, 2H), 0.81 (m, 12H), 0.65 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (62 MHz, [d$_6$]DMSO): δ = 166.21, 146.51, 120.61, 83.18, 64.19, 31.61, 29.01 (2×), 28.57, 25.82, 22.47, 14.33 ppm; IR (KBr): ν = 3513, 2957, 2923, 2853, 1716, 1176 cm^{-1}; Elemental analysis: calcd (%) for $C_{12}H_{21}NaO_6S$ (316.35): C 45.56, H 6.69, S 10.14; found: C 32.28, H 4.80, S 15.86 (the sample contained $NaHSO_3$ which was added in excess to the reaction mixture); TOFMSES$^+$ [M + Na$^+$] = 339.08.

Compound 7b. A mixture of ethyl acetate (46 ml), ethanol (27 ml), water (9 ml), $NaHSO_3$ (6.0 g, 57.4 mmol) and **5b**/**4b** in a ratio of 6 : 1 (15.42 g, 64.2 mmol) was heated to 40 °C for 2.5 h. The mixture was filtered and the solid was washed with ethanol and dried at air. Yield 12.7 g (71%). Compound **4b** (2.0 g) was recovered from the liquid phase.

^{1}H NMR (250 MHz, [d$_6$]DMSO): δ = 7.08 (dd, J = 15.6, 5.1 Hz, 1H), 6.19 (m, 2H), 4.73 (d, broaden, J = 5.1 Hz, 1H), 4.10 (t, J = 6.7 Hz, 2H), 1.12 (m, 16H), 0.89 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (62 MHz, [d$_6$]DMSO): δ = 166.22, 146.01, 120.54, 83.21, 64.18, 31.67, 29.34 (2×), 29.07, 28.57, 25.81, 22.49, 14.34 ppm; IR (KBr): ν = 3449, 2957, 2922, 2850, 1717, 1175 cm^{-1}; Elemental analysis: calcd (%) for $C_{14}H_{25}NaO_6S$ (344.40): C 48.82, H 7.32, S 9.31; found: C 37.31, H 5.30, S 13.93 (the sample contained $NaHSO_3$ which was added in excess to the reaction mixture); TOFMSES$^+$ [M + Na$^+$] = 367.11.

Compound 7c. A mixture of ethyl acetate (32 ml), ethanol (19 ml), water (6 ml), $NaHSO_3$ (4.16 g, 40.0 mmol) and **5c**/**4c** in a ratio of 4 : 3 (12.0 g, 44.7 mmol) was heated to 40 °C for 2.5 h. The mixture was filtered and the solid was washed with ethanol and dried at air. Yield 5.25 g (94%). Compound **4b**

(5.6 g) and dodecanol **3c** (2.4 g) were recovered from the liquid phase after evaporation and flash chromatography (eluent: ethyl acetate–ethanol 3/7).

^{1}H NMR (250 MHz, [d_6]DMSO): δ = 7.30 (dd, J = 15.8, 5.1 Hz, 1H), 6.40 (m, 2H), 4.94 (s, broaden, 1H), 4.32 (t, J = 6.0 Hz, 2H), 1.32 (m, 20H), 1.10 (t, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (62 MHz, [d_6]DMSO): δ = 163.86, 144.25, 118.19, 80.87, 61.82, 29.35, 26.06 (3×), 26.77 (2×), 26.73, 26.24, 23.47, 20.15, 11.99 ppm; IR (KBr): ν = 3499, 2956, 2921, 2849, 1717, 1175 cm^{-1}; Elemental analysis: calcd (%) for $C_{16}H_{29}NaO_6S$ (372.45): C 51.60, H 7.85, S 9.61; found: C 40.71, H 6.07, S 13.11; (the sample contained $NaHSO_3$ which was added in excess to the reaction mixture); TOFMSES$^-$ [M + Na$^+$] = 395.1484 (calcd 395.1481).

Synthesis of sulfonate 8

A solution of α,β-unsaturated aldehyde **5c** (268 mg, 1.0 mmol) in isopropanol (4.5 ml) is added to a solution of $NaHSO_3$ (624 mg, 6.0 mmol) in water (3 ml). The resulting mixture was heated at 80 °C for 5 days. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate–methanol 95/5). Yield: 100 mg (27%); mp. 228–229 °C.

^{1}H NMR (250 MHz, [d_6]DMSO): δ = 9.72 (s, 1H), 4.40 (m, 1H), 4.17 (m, 2H), 3.34 (m, 2H), 1.61 (m, 2H), 1.25 (m, 18H), 0.86 (dt, J = 5.5, 6.5 Hz, 3H) ppm; ^{13}C NMR (62 MHz, [d_6]-DMSO): δ = 201.14, 168.52, 64.20, 59.53, 43.24, 31.37, 29.09 (3×), 28.79 (2×), 28.13, 25.37, 25.03, 22.18, 13.99 ppm; IR (KBr): ν = 3437, 2958, 2924, 2853, 1724, 1642 cm^{-1}; Elemental analysis: calcd (%) for $C_{16}H_{29}NaO_6S$ (372.45): C 51.60, H 7.85, S 9.61; found: C 51.46, H 7.54, S 9.23; TOFMSES$^-$ [M + Na$^+$] = 395.1488 (calcd 395.1481).

Physicochemical characterizations

Solution preparation and materials. All solutions were prepared using water that was completely deionized (Millipore) and filtered (0.22 mm). Hydrochloric acid, 0.1 N in solution, was supplied by VWR (France) and sodium hydroxide (0.1 N) by Labosi (France).

Surface tension, CMC and area/molecule. The plot of the surface tensions (γ) against ln C of aqueous surfactant solutions was recorded by a Wilhelmy-type surface balance (Krüss K100MK2) equipped with a dosimeter (700 dosino, Metrohm). Measurements were conducted at 25 ± 0.5 °C.

Biodegradability

Biodegradability was performed following the OECD 301F standard, which requires the biological oxygen consumption (BOC) and the theoretical oxygen demand (ThOD). The ThOD (in mg of oxygen per mg of the product) corresponds to the amount of oxygen necessary to oxidize the compound into its final oxidation products. Sodium acetate was used as a reference. With the average number of each element in the structure and the molar weight (MW) of the compound, the ThOD can be calculated according to the first equation (eqn (3)) when no nitrification occurs.

$$\mathrm{ThOD} = \frac{2\mathrm{C} + 0.5(\mathrm{H} - \mathrm{Cl} - 3\mathrm{N}) + 3\mathrm{S} + 2.5\mathrm{P} + 0.5\mathrm{Na} - \mathrm{O}}{\mathrm{MW}} \times 16 \quad (3)$$

The biological oxygen consumption (BOC) was determined by means of an IBUK respirometer, which identifies the oxygen consumption all along the degradation process. Experiments were conducted at 20 °C over a period of 28 days in a medium containing various mineral substances (sodium and potassium phosphates, ammonium, calcium and iron chlorides, magnesium sulfate) and bacteria collected from a local wastewater treatment plant. The starting pH was 7.4. The percentage of biodegradation or biodegradability (B [%]) values is obtained according to the subsequent equation (eqn (4)):

$$B[\%] = \frac{\mathrm{BOC}}{\mathrm{ThOD}} \times 100 \quad (4)$$

The reliability of the experiment depends on 3 parameters. The first one is the degradation of the reference molecule (sodium acetate). Its degradation has to reach 60% after 14 days. Secondly, the mineral medium has to exhibit oxygen consumption below 60 mg l^{-1} (ideally between 20 and 30 mg l^{-1}) after 28 days. Finally, after 28 days the pH should be between 6 and 8.5.

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