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Interfacial aspects of the catalysis of the synthesis of amphiphilic sucrose ethers from 1,2-epoxydodecane and 1,2-epoxydodecan-3-ol in water

Mathieu Danel, Juliette Gagnaire, Yves Queneau*

Laboratoire de Sucrochimie, UMR 143 CNRS, c/o Béghin-Say, CEI, BP 2132, 27 boulevard du 11 Novembre 1918, 69603 Villeurbanne Cedex, France

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Dedicated to Professor Gérard Descotes for his accomplishments in the field of carbohydrate chemistry and for his continuous efforts for the development of sucrochemistry

Abstract

The addition of sucrose on two fatty epoxides, 1,2-epoxydodecane and 1,2-epoxydodecan-3-ol, has been studied in DMSO and water. The study of the kinetics of the reaction showed that the 1,2-epoxydodecan-3-ol is more reactive for both interfacial and electronic reasons. In water, the induction time normally necessary is dramatically reduced with an immediate emulsification of the mixture which is beneficial to the interfacial formation of sucrose ethers. The comparison of the reaction in DMSO allowed to estimate the assistance of the α-hydroxyl group through intramolecular hydrogen bonding in 1,2-epoxydodecan-3-ol, revealing that both aspects are involved in the catalysis of the reaction in aqueous medium.

Keywords: Sucrose; Surfactant; Epoxide; Ethers; Water

1. Introduction

Sucrose derivatisation by grafting a fatty chain can provide non-ionic surfactants that have good properties as mild and for some of them as fully biodegradable emulsifying agents [1]. Although their synthesis is easy in polar organic solvents which are able to solubilise both the sucrose and the fatty reagent [2,3], there is a need for new cleaner processes taking into account the possible use of these compounds in the food and cosmetic fields. Synthesis in water or without solvent [4–7] implies the formation of new interfaces, liquid–liquid or solid–liquid, that will influence the reactivity. The aim of our work is to explore the effect of the heterogeneity of the medium on the synthesis of sucrose ethers obtained by addition of sucrose on fatty epoxides in water.

In a preceding work [6,7], we showed that it is possible to synthesise sucrose α-hydroxydodecylethers in water by reacting sucrose and 1,2-epoxydodecane (Fig. 1). The kinetics of the reaction showed that interfacial phenomena occurred during the synthesis, due to the fact that the epoxide and the aqueous phase containing the sucrose are not miscible. An induction time was observed corresponding to the time needed for the formation of the first surface-active species. The progressive emulsification of the mixture resulted in the acceleration of the interfacial reactions, namely the

* Corresponding author. Tel.: +33-4-7244-2989; fax: +33-4-7244-2991.
E-mail address: queneau@univ-lyon1.fr (Y. Queneau).

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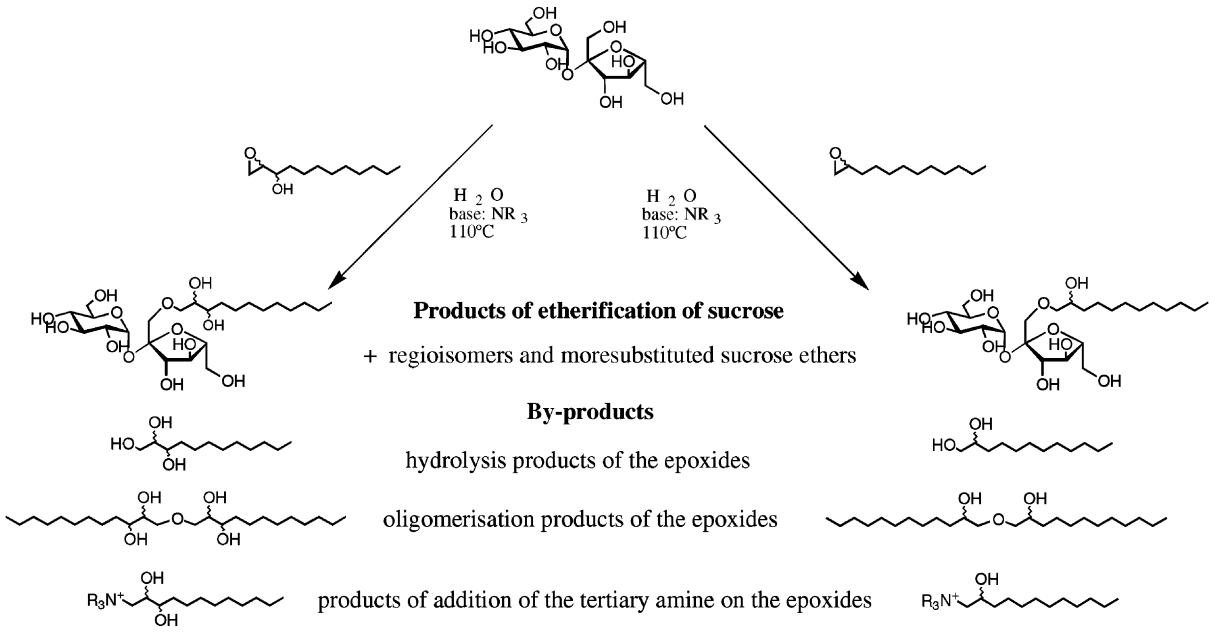

Fig. 1. Reaction scheme.

formation of sucrose ethers as well as the hydrolysis product of the epoxide. We have shown how important was the presence of a tertiary amine as basic catalyst, being soluble in both phases. It was also shown that the addition of surfactant additives resulted, depending on their structure, in a modulation of the induction time, the reaction maximum rate, the competition between etherification and hydrolysis of the epoxide (and its further oligomerisation), and on the average degree of substitution (DS) of the sucrose ethers. The purpose of this work is to evaluate the influence of a less hydrophobic epoxide on all these parameters. By comparing the reactivity of 1,2-epoxydodecan-3-ol and 1,2-epoxydodecane both in water and in DMSO (Fig. 1), it was tried to differentiate between the interfacial aspects and the electronic activation which is provided by the possible intramolecular hydrogen bonding of the α-hydroxy epoxide linkage (Fig. 6). New and more hydrophilic sucrose ethers were thus obtained. The regioisomeric distribution of the monosubstituted sucrose ethers was also investigated in order to corroborate our past observations on the relative reactivity of sucrose hydroxyl groups in water.

2. Experimental

2.1. Preparation of the 1,2-epoxydodecan-3-ol

Dodec-1-en-3-ol. To a solution of vinyl magnesium chloride (15 wt.% in THF, 22.9 ml, 38.4 mmol) in anhydrous THF (100 ml) under nitrogen and cooled at 0 °C, was added dropwise a solution of *n*-decanal (6.0 ml, 32.0 mmol) in THF (40 ml). After 1 h at 0 °C, the mixture was warmed to room temperature and stirred for 2 h. The mixture was then poured into iced water (100 ml) and 1 N HCl was added until complete solubilisation of the precipitate. Diethyl ether (100 ml) was added and the aqueous layer was further extracted with diethyl ether (2 × 50 ml). The combined organic layers were dried on sodium sulphate, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (hexane/ethyl acetate 9/1, Rf 0.32), to give 4.9 g of the allylic alcohol as an oil (82% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.87 (t, 3H, $J_{11–12}$ = 6.6 Hz, Me); 1.20–1.50 (m, 16H, $(CH_2)_8$); 2.07 (s, 1H, OH); 4.06 (dd, 1H, $J_{2–3}$ = 6.2 Hz, $J_{3–4}$ = 12.5 Hz, H-3); 5.07 (ddd, 1H, $J_{1a–1b}$ =

1.5 Hz, $J_{1a-2} = 10.3$ Hz, $J_{1a-3} = 1.5$ Hz, H-1a); 5.19 (ddd, 1H, $J_{1b-2} = 17.3$ Hz, $J_{1b-3} = 1.5$ Hz, H-1b); 5.84 (ddd, 1H, H-2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 14.5 (Me); 23.1, 25.7, 29.7, 29.9, 30.0, 32.3, 37.4 ($(CH_2)_8$); 73.6 (C-3); 114.8 (C-1); 141.8 (C-2).

1,2-Epoxydodecan-3-ol. To a solution of the allylic alcohol (5.9 g, 31.8 mmol) in anhydrous dichloromethane (120 ml) under nitrogen and cooled at 0 °C, was added the *meta*-chloroperbenzoic acid (11.8 g, 47.8 mmol). After 30 min at 0 °C, the mixture was warmed to room temperature and stirred for 15 h. The reaction mixture was then washed with a 0.3 M NaOH solution (2×200 ml) and the aqueous layer was extracted with diethylether (2×50 ml). The combined organic layers were dried on magnesium sulphate, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (hexane/ethyl acetate 4/1, Rf 0.29) to give 4.9 g of 1,2-epoxydodecan-3-ol (77% yield) as a 3:2 mixture of *threo*/*erythro* isomers (NMR). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): *threo*: 0.83 (t, 3H, $J_{11-12} = 6.6$ Hz, Me); 1.16–1.59 (m, 16H, $(CH_2)_8$); 2.32 (d, 1H, $J_{3-OH} = 5.5$ Hz, OH); 2.63–2.70 and 2.74–2.80 (m, 2H, H-1); 2.90–2.98 (m, 1H, H-2), 3.36 (ddd, 1H, $J_{2-3} = 5.5$ Hz, $J_{3-4} = 11.0$ Hz, H-3); *erythro*: 0.83 (t, 3H, $J_{11-12} = 6.6$ Hz, Me); 1.16–1.59 (m, 16H, $(CH_2)_8$); 2.15 (d, 1H, $J_{3-OH} = 2.6$ Hz, OH); 2.63–2.70 and 2.74–2.80 (m, 2H, H-1); 2.90–2.98 (m, 1H, H-2), 3.71–3.79 (m, 1H, $J_{2-3} = 2.9$ Hz, H-3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): *threo*: 14.0 (Me); 22.6, 25.2, 29.2, 29.5, 31.8 (C-5–C-11); 34.3 (C-4); 45.1 (C-1); 55.5 (C-2); 71.7 (C-3); *erythro*: 14.0 (Me); 22.6, 25.2, 29.2, 29.5, 31.8 (C-5–C-11); 33.5 (C-4); 43.4 (C-1); 54.6 (C-2); 68.5 (C-3).

trans-2,3-Epoxydodecane-1-ol. When submitted to alkaline conditions, the *erythro* isomer of 1,2-epoxydodecan-3-ol is transformed (Payne rearrangement). To an ethanol–ethanolate solution prepared with 700 ml of ethanol and sodium (184 mg, 8.0 mmol) was added the 1,2-epoxydodecan-3-ol (2.0 g, 1.0 mmol). After 24 h, a 1 N aqueous solution of hydrochloric acid was added until neutral pH and the solution was then concentrated. The residue was recovered with dichloromethane (200 ml) and washed with water (100 ml). The organic layer was dried on magnesium sulphate, filtered and concentrated under reduced pressure. The epoxides were isolated by silica gel flash chromatography (hexane/ethyl acetate 4/1) to give a 95/5 mixture of the *threo*/*erythro* isomers of 1,2-epoxydodecan-3-ol (Rf 0.29, oil, 0.55 g, 27%) and *trans*-2,3-epoxydodecane-1-ol (Rf 0.21, oil, 0.71 g, 35%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.86 (t, 3H, $J_{11-12} = 6.6$ Hz, Me); 1.16–1.57 (m, 16H, $(CH_2)_8$); 2.44 (s, 1H, OH); 2.85–2.95 (m, 1H, CHOH); 3.30–3.90 (m, 3H, CHOH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 14.7 (Me); 26.6, 30.0, 30.2, 32.2, 32.5 (C-4–C-11); 56.7 and 59.3 (C-2 and C-3); 62.4 (C-1).

2.2. Synthesis of O-(2,3-dihydroxydodecyl) sucrose in water

Experiment for product analysis. Sucrose (2.0 g, 5.8 mmol), 1,2-epoxydodecan-3-ol (0.6 g, 2.9 mmol), *N*-methylmorpholine (85 mg, 0.8 mmol) and 0.5 ml of water were poured in a sealed vial and heated at 110 °C for 8 h with a vigorous magnetic stirring (750 rpm). The crude mixture was purified directly by silica gel flash chromatography (dichloromethane/acetone/methanol/water: 56/20/20/4, Rf 0.29). The fraction of monoethers was lyophilised to give 342 mg of the mixture of regioisomers (22% yield). More apolar fractions were solubilised in methanol and dried under vacuum providing 160 mg (15% yield, Rf 0.50) of diethers and 107 mg (12% yield, Rf 0.58) of triethers as mixtures of regioisomers.

Experiment for kinetics monitoring. Sucrose (3.42 g, 10.0 mmol) and epoxide (hydroxylated: 1.0 g, not hydroxylated: 0.92 g, 5.0 mmol), *N*-methylmorpholine (142 mg, 1.4 mmol) and 0.68 ml of water were poured in a sealed vial and heated at 110 °C for 13 h. Samples of 50 mg were taken through the septum at regular intervals and analysed by HPLC.

Mono-O-(2,3-dihydroxydodecyl)sucrose, mixture of regioisomers. Elemental analysis: calc. ($C_{24}H_{46}O_{13} + 1.5$ equiv. H_2O): C: 50.6, H: 8.7, O: 40.7; found: C: 50.6, H: 8.6, O: 40.9. MS-HR (FAB+): *m/z* calc. ($[M+Na]^+$, $C_{24}H_{46}O_{13}Na$): 565.2836; found: 565.2833. ^{1}H NMR (D_2O, 300 MHz) δ (ppm): 0.86–0.97 (m, 3H, Me); 1.22–1.65 (m, 16H, $(CH_2)_8$); 3.36–4.41 (m, 17H, C*H*OH, CH_2OH); 5.38–5.62 (m, 1H, H-1).

Di-O-(2,3-dihydroxydodecyl)sucrose, mixture of regioisomers. White solid. MS-HR (FAB+): *m/z* calc. ($[M + Na]^+$, $C_{36}H_{70}O_{15}Na$): 765.4612; found: 765.4595. ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 0.94 (t, 6H, $J = 6.6$ Hz, 2Me); 1.28–1.65 (m, 32H,

2 (CH_2)$_8$); 3.23–4.38 (m, 21H, C*H*OH, C*H*$_2$OH); 5.38–5.75 (m, 1H, H-1).

Tri-O-(2,3-dihydroxydodecyl)sucrose, mixture of regioisomers. White solid. Elemental analysis: calc. ($C_{48}H_{94}O_{17}$ + 1.3 equiv. H_2O): C: 59.6, H: 10.1, O: 30.3; found: C: 59.4, H: 10.2, O: 29.9. MS-HR (FAB+): *m/z* calc. ([M + Na]$^+$, $C_{48}H_{94}O_{17}Na$): 965.6389; found: 965.6300. ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 0.94 (t, 9H, J = 6.6 Hz, 3Me); 1.25–1.78 (m, 48H, 3 (CH_2)$_8$); 3.23–4.35 (m, 25H, C*H*OH, C*H*$_2$OH); 5.38–5.70 (m, 1H, H-1).

2.3. Separation of the regioisomers of monoethers

Regioisomers could be further purified by preparative and semi-preparative HPLC, on NH_2-grafted columns from Touzard & Matignon: Nucleoprep NH_2 250 mm × 40 mm, solvent CH_3CN/H_2O 88/12, 80 ml/min and Nucleosil NH_2 250 mm × 20 mm, solvent CH_3CN/H_2O 88/12 and 86/14, 20 ml/min (pump Shimadzu LC-8A) with refractometric detection (Uniflows YRD-883). The concentrations of the solutions injected were about 50–100 mg/ml. Five major regioisomers (as mixtures of epimers on the dihydroxyalkyl chain) were obtained, in order of elution: at OH-2 (17.6 and 18.2 min), OH-3 (19.0 min), OH-6 (20.5 min), OH-1′ (22.8 min) and OH-6′ (24.9 min).

2-O-(2,3-Dihydroxydodecyl)sucrose: ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 0.83 (t, 3H, J = 6.2 Hz, Me); 1.16–1.49 (m, 16H, (CH_2)$_8$); 3.17 (dd, 1H, J_{2-3} = 9.6 Hz, H-2); 3.22–4.09 (m, 16H, C*H*OH, C*H*$_2$OH); 5.52 (d, 1H, J = 3.4 Hz, H-1). ^{13}C NMR (CD_3OD, 75 MHz) δ (ppm): 13.5 (Me); 22.8, 26.1, 29.5, 29.8, 29.8, 29.9, 32.1, 33.1 ((CH_2)$_8$); 61.3 (C-6); 62.2 (C-6′); 63.1 (C-1′); 70.4 (C-4); 71.8 (CHOH); 73.1 (CHOH); 73.1 (C-3); 73.4 (C-5); 73.7 (OCH_2); 74.3 (C-4′); 77.7 (C-3′); 81.3 (C-2); 82.6 (C-5′); 90.3 (C-1); 104.6 (C-2′). 3-O-(2,3-*Dihydroxydodecyl)sucrose*: ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 0.74 (t, 3H, J = 6.2 Hz, Me); 1.07–1.44 (m, 16H, (CH_2)$_8$); 3.10 (dd, 1H, J_{2-3} = 9.8 Hz, H-2); 3.14–4.00 (m, 16H, C*H*OH, C*H*$_2$OH); 5.44 and 5.47 (2 d, 1H, J = 3.6 Hz, H-1). ^{13}C NMR (CD_3OD, 75 MHz) δ (ppm): 13.5 (Me); 22.8, 26.1, 29.5, 29.8, 29.8, 29.9, 32.1, 33.1 ((CH_2)$_8$); 61.2 (C-6); 62.2 (C-6′); 63.1 (C-1′); 70.5 (C-4); 71.8 (CHOH); 72.1 (C-2); 72.8 (CHOH); 73.1 (C-5); 73.4 (OCH_2); 74.4 (C-4′); 77.8 (C-3′); 81.0 (C-3); 82.6 (C-5′); 90.5 (C-1); 104.6 (C-2′). 6-O-(2,3-*Dihydroxydodecyl)sucrose*: ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 0.83 (t, 3H, J = 6.6 Hz, Me); 1.16–1.52 (m, 16H, (CH_2)$_8$); 3.20–4.06 (m, 17H, C*H*OH, C*H*$_2$OH); 5.31 (d, 1H, J = 3.6 Hz, H-1). ^{13}C NMR (CD_3OD, 75 MHz) δ (ppm): 13.5 (Me); 22.8, 26.1, 29.5, 29.8, 29.8, 29.9, 32.1, 33.1 ((CH_2)$_8$); 62.4 (C-6′); 63.1 (C-1′); 70.7 (C-4); 70.9 (d, C-6); 71.9 (d, CHOH); 72.1 (C-2); 72.4 (CHOH); 72.8 (d, C-5); 73.4 (OCH_2); 73.5 (C-3); 74.5 (C-4′); 78.2 (C-3′); 82.6 (C-5′); 92.4 (C-1); 104.2 (d, C-2′). 1′-O-(2,3-*Dihydroxydodecyl)sucrose*: ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 0.82 (t, 3H, J = 6.6 Hz, Me); 1.15–1.49 (m, 16H, (CH_2)$_8$); 3.20–4.10 (m, 17H, C*H*OH, C*H*$_2$OH); 5.31 (d, 1H, J = 3.4 Hz, H-1). ^{13}C NMR (CD_3OD, 75 MHz) δ (ppm): 13.5 (Me); 22.8, 26.1, 29.5, 29.8, 29.8, 29.9, 32.1, 33.1 ((CH_2)$_8$); 61.2 (C-6); 62.3 (C-6′); 70.4 (C-4); 71.6 (C-1′); 71.8 (CHOH); 72.3 (C-2); 72.7 (CHOH); 73.3 (C-5); 73.6 (OCH_2); 73.7 (C-3); 74.3 (C-4′); 78.2 (C-3′); 82.4 (C-5′); 93.0 (C-1); 103.9 (C-2′). 6′-O-(2,3-*Dihydroxydodecyl)sucrose*: ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 0.92 (t, 3H, J = 6.6 Hz, Me); 1.26–1.58 (m, 16H, (CH_2)$_8$); 3.30–4.13 (m, 17H, C*H*OH, C*H*$_2$OH); 5.40 (d, 1H, J = 3.6 Hz, H-1). ^{13}C NMR (CD_3OD, 75 MHz) δ (ppm): 13.5 (Me); 22.8, 26.1, 29.5, 29.8, 29.8, 29.9, 32.1, 33.1 ((CH_2)$_8$); 61.5 (C-6); 62.8 (C-1′); 70.6 (C-4); 71.8 (d, CHOH); 72.3 (C-2); 72.7 (d, C-6′); 72.8 (d, CHOH); 73.0 (OCH_2); 73.2 (C-5); 73.8 (C-3); 75.7 (d, C-4′); 77.9 (C-3′); 81.0 (C-5′); 92.5 (C-1); 104.4 (C-2′).

2.4. Synthesis of O-(2,3-dihydroxydodecyl) sucrose in DMSO

Sucrose (3.4 g, 10.0 mmol), epoxide (α-hydroxylated: 1.0 g, not hydroxylated: 0.92 g, 5.0 mmol), grounded potassium hydroxide (165 mg, 2.5 mmol) were poured in DMSO. The total volume of the solution was 10 ml. The mixture was heated for 5 h at 110 °C. Samples of about 50 μl were taken at regular intervals and analysed by HPLC.

2.5. Analysis

The regiosiomer distributions of the monoethers were analysed on a HPLC column Touzard & Matignon Spherisorb NH_2 250 mm × 4.6 mm, at 30 °C,

coupled to a pump Shimadzu LC-10AS and a refractometer Water 410. The solvent was CH_3CN/H_2O 9/1 at 0.8 ml/min.

The analyses of the reaction mixtures were made on a HPLC column Touzard & Matignon Nucleosil C8 250 mm × 4.6 mm, with a solvent methanol/water 78/22 at 0.8 ml/min. This system allowed the quantification of monoethers (5.4 min), 1,2,3-dodecanetriol (7.3 min) and epoxides (1,2-epoxydodecan-3-ol: *threo* 8.2 min, *erythro* 8.4 min, *trans*-2,3-epoxydodecan-1-ol 8.3 min). For the reaction with 1,2-epoxydodecane, the solvent was methanol/water 82/18: monoethers 5.3 min, 1,2-dodecanediol 6.9 min, 1,2-epoxydodecane 10.5 min.

2.6. Analysis of oligomers

LSIMS of a crude reaction mixture performed in water with *N*-methylmorpholine, NBA + LiCl: 286 (ammonium), 393 (5, dimer of epoxide), 470 (55, ammonium dimer), 533 (7, monoether), 717 (10, diether), 901 (20, triether), 1086 (3, tetraether). The ammonium species result from the addition of the amine on the epoxide and give high intensities, due to their positive charge.

Analysis of oligomers obtained from a reaction without sucrose: water (5.00 g), epoxydodecane (5.39 g, 29.2 mmol) and *N*-methylmorpholine (0.853 g, 8.4 mmol) are poured together in a sealed vial and heated at 110 °C for 10 h. Analysis by HPLC (C8, MeOH–H_2O 82/18) gave a yield of 23% for dodecanediol. The rest of the products are oligomers, analysed by TLC, MS and ^{1}H NMR. TLC: ethyl acetate/hexane 3/7: dodecanediol, Rf = 0.1; dimer, Rf = 0.3; trimer, Rf = 0.5, tetramer, Rf = 0.8. FAB+ mass spectroscopy of the fractions (NBA): dimer, Rf = 0.3: 369 (M-18 + 1), 387 (M + 1), 409 (M + 23); trimer, Rf = 0.5: 369, 571 (M + 1), 593 (M + 23); tetramer Rf = 0.8: 369, 755 (M-18 + 1). LSIMS of the crude reaction mixture (NBA + LiCl): 393 (dimer), 470 (25, ammonium dimer), 577 (65, trimer), 654 (15, ammonium trimer), 761 (3, tetramer). ^{1}H NMR: dimer, white solid, mixture of stereoisomers: 3.7 (m, 1H), 3.55 (dt, 1H), 3.35 (m, 1H), 2.6 (s, 1H), 1.6–1.1 (m, 18H), 0.9 (t, 3H). Trimer, white solid, mixture of stereoisomers: 3.6–3.9 (m, 1H), 3.4–3.6 (m, 1H), 3.2–3.4 (m, 1H), 1.1–1.7 (m, 18H), 0.9 (t, 3H).

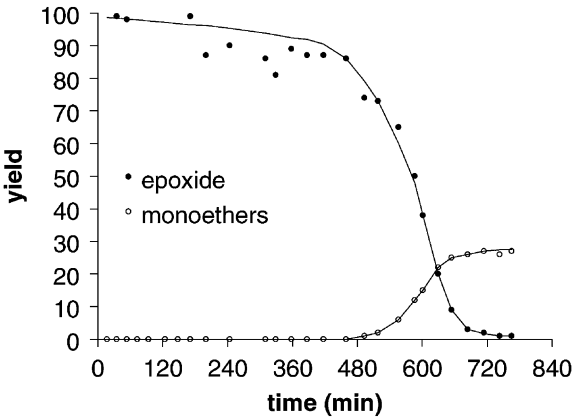

Fig. 2. Kinetics of the reaction in water with 1,2-epoxydodecane.

3. Results and discussion

The reaction of sucrose with 1,2-epoxydodecane (Fig. 2) and 1,2-epoxydodecan-3-ol (Fig. 3) in water in presence of *N*-methylmorpholine as the base was studied in terms of kinetics and distribution of the products (Table 1). The formation of the monoethers follows a sigmoidal kinetics for both reactions, indicating the occurrence of an interfacial reaction, fastened when the interfacial area increases with the production of more and more surface-active compounds. In the case of the consumption of 1,2-epoxydodecane, the sigmoidal shape (Fig. 2) has been ascribed to both the consumption of the epoxide in the oil phase via homogeneous reactions, giving polysubstituted

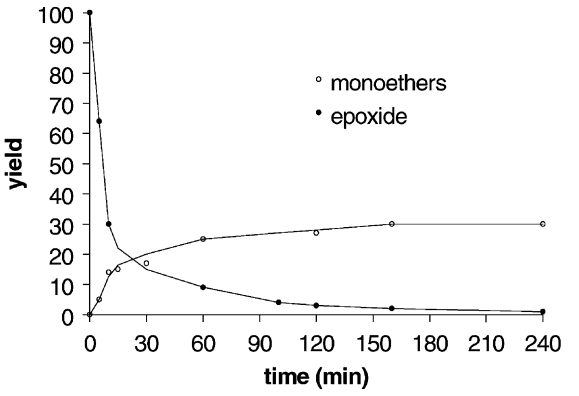

Fig. 3. Kinetics of the reaction in water with 1,2-epoxydodecan-3-ol.

Table 1
Yields of the reaction of sucrose on the fatty epoxides in water calculated with respect to the starting epoxide

	Monoethers (%)	Diethers (%)	Monoethers/ diethers ratio	Estimated global yield of sucrose ethers	Diol or triol (%)	Reaction time (h)
1,2-Epoxydodecane	26	18	1.44	52[a]	11	15
1,2-Epoxydodecan-3-ol	22	15	1.47	49[b]	12	4
1,2-Epoxydodecane, catalysis by CTAB[c] [7]	35	20	1.75	68[a]	8	4

[a] Estimated by difference from the sucrose consumption measured by HPLC.
[b] Estimated from chromatographic separation.
[c] Cetyltrimethylammonium bromide.

sucrose ethers or oligomers of the epoxide and the increase of the surface area by emulsification [7].

The direct quantification of monoethers, diethers, dodecanediol and the quantification of sucrose ethers of higher substitution degree from the sucrose consumption led to an incomplete epoxide balance. Other by-products are formed during the reaction, resulting from the oligomerisation of the epoxide or the addition of the amine on the epoxide and its further oligomerisation. The oligomers have been observed by TLC and mass spectroscopy of crude reaction mixtures. More precise analyses have been made by reacting 1,2-epoxydodecane with water in the same conditions, but without sucrose. In this case, higher contents of oligomers from dimers to tetramers are obtained, up to 75% of the mixture and have been isolated. In the case of the reaction with sucrose, these products are formed in smaller quantities, but account for the rest of the epoxide balance. These reactions also compete with the formation of sucrose ethers and occur in a homogeneous way in the oil phase.

With 1,2-epoxydodecan-3-ol (Fig. 3), no induction time could have been detected. The epoxide is consumed from the very beginning and sucrose monoethers are formed without delay. The global reaction time is far shorter. This result can be explained in three different ways. First, the α-hydroxy epoxide, although still rather hydrophobic, is however slightly more soluble in water and should have an increased interfacial concentration compared to the non-hydroxylated epoxide. Secondly, the presence of the hydroxyl group assists the opening of the epoxide through intramolecular bonding and then increases the reaction rate. This aspect was estimated by comparing the reactivity of both epoxides in a fully homogeneous reaction (see below). Finally in the case of the hydroxylated epoxide, all the necessary partners of the oligomerisation reaction are present in the oil phase (base, epoxide and a free reactive hydroxyl group). This would facilitate the process providing oligomers from the very beginning of the reaction without any induction time, whereas in the case of 1,2-epoxydodecane, this reaction could not occur as long as a small amount of dodecanediol was produced through an interfacial, thus slow reaction.

The fact that 1,2-epoxydodecan-3-ol is in equilibrium with 2,3-epoxydodecan-1-ol through a Payne rearrangement [8–11] (Fig. 4) did not affect the analyses and the results. In alkaline solution, the *erythro*-1,2-epoxydodecan-3-ol followed a rearrangement to give the *trans*-2,3-epoxydodecan-1-ol. The *threo* isomer did not rearrange since no *cis*-2,3-epoxydodecan-1-ol has been observed. Similar results have been described in the literature [9,11]. The two epoxides, internal and terminal, are in equilibrium but from the analysis of the monosucrose ethers, only the terminal epoxide reacted with sucrose on the primary carbon and thus the equilibrium is shifted. When the internal epoxide is used as starting material, the same sucrose monoethers are formed. On HPLC analyses, both epoxides are eluted in the same peak and then the kinetic curve corresponds to the mixture, the main epoxide being the internal epoxide after about 10 min of reaction. We made the approximation that the two epoxides had the same refractometric response.

The yields and the distributions of the final products, in terms of DS, provide some information on the nature of the interfacial catalysis, since monoethers come from an interfacial reaction, while diethers and oligomers of the epoxide come from homogeneous reactions in the oily phase. The yields of monoethers are similar with both epoxides (Table 1) thus showing

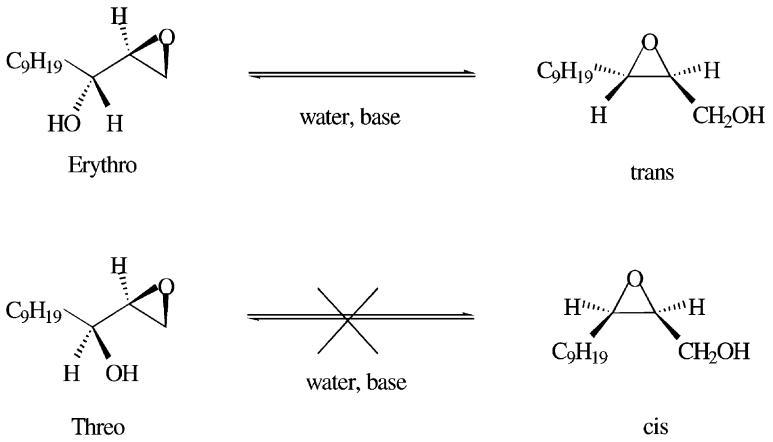

Fig. 4. Payne rearrangement of 1,2-epoxydodecan-3-ol.

that with the hydroxylated epoxide the formation of sucrose ethers remained competitive towards the oligomerisation, despite its ability to react in the oily phase from the very beginning of the reaction. The monoethers/diethers ratio is also a meaningful element which tell us about the relative reactivity of the epoxide in the oily phase versus the interface. In a preceding paper [7], we showed that it was possible to direct the reaction towards the formation of low DS sucrose ethers by the addition of a cationic surfactant, cetyltrimethylammonium bromide (CTAB) to the reaction medium. The latter increases the interfacial area and accelerates the formation of monoethers to the detriment of homogeneous reactions. In the case of the reaction with 1,2-epoxydodecan-3-ol, this ratio remained similar (Table 1) showing that the rate enhancement cannot be only ascribed to an increase of the interfacial area.

In order to assess the relative reactivity of the epoxides in homogeneous conditions, the comparison of the kinetics has been made in DMSO (Fig. 5). The 1,2-epoxydodecan-3-ol showed a slightly enhanced reactivity. The ratio of the initial rates for the reaction with 1,2-epoxydodecan-3-ol versus 1,2-epoxydodecane is 3.2 for the formation of monoethers and 2.7 for the epoxide consumption. The activation can be ascribed to a stereoelectronic effect of the α-hydroxyl group for the opening of the epoxide function, through an intramolecular hydrogen bonding (Fig. 6).

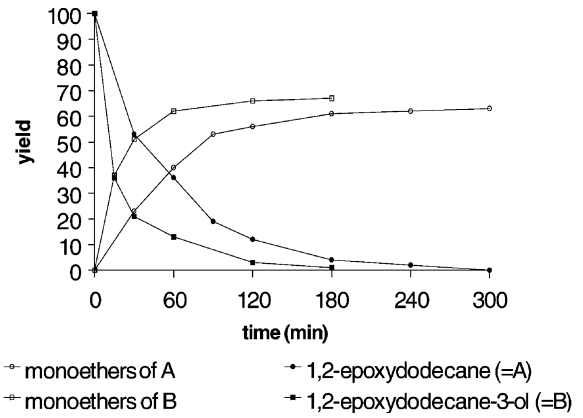

Fig. 5. Kinetics of the reaction in DMSO.

From the point of view of regiochemistry, the reaction of sucrose with 1,2-epoxydodecan-3-ol in water gave the following distribution of the regioisomers 2 (∼20%) >1′ (∼20%) > 6, 6′ (∼10% each) >3 (∼5%). The presence of four epimers for each isomer did not allow the complete identification and quantification

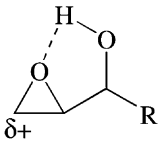

Fig. 6. Intramolecular assistance of the epoxide opening.

of all isomers. However, the distribution of the major products which could be purified by preparative chromatography is similar to that obtained with 1,2-epoxydodecane and confirmed the greater reactivity of the OH-1′ and OH-2 in water.

4. Conclusions

New amphiphilic α,β-dihydroxyalkyl sucrose ethers have been prepared in water. The addition of a hydroxyl group on the chain of the fatty epoxide dramatically increases the rate of its reaction with sucrose in aqueous medium. The activation is ascribed to the increased reactivity of the 1,2-epoxydodecan-3-ol provided by the hydroxyl group in the a position to the initiation of the reaction from the very beginning by the rapid formation of surface-active compounds and to an increased interfacial concentration of the epoxide. No further modification of the interface was observed as seen by the unchanged distribution of the products. On the other hand, the regioisomeric distribution of the monosubstituted sucrose ethers could confirm our earlier findings on the relative reactivity of sucrose in water with a pre-eminent reactivity at OH-2 and OH-1′.

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