Catalytic hydrolysis of epoxyfatty esters with solid sulfonic acids

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ABSTRACT

Four sulfonic resins are able to promote the hydrolysis of several epoxyfatty esters becoming a very interesting strategy to obtain polyols from epoxyfatty derivatives. The choice of the aqueous solvent and temperature is critical to improve the accessibility of reagents to the acidic catalytic sites. *Tert*-butanol/water mixture as solvent at 80 °C allows to obtain good results with all resins. The recovery of the heterogeneous catalyst during at least 11 reaction cycles avoids the drawbacks of the homogeneous ones including corrosion problems. In addition, this procedure can be applied to several epoxyfatty esters with different chain size, stereochemistry of the epoxide or with additional functionalities, obtaining good yields of structurally different polyols.

1. Introduction

Although fats represent only 5% of the biomass, they are probably the most important processed renewable raw material in the chemical industry [1–3]. Whereas most of the industrial transformations of fatty acid derivatives take place on the carboxylic group, the interest in the reactivity of the unsaturated hydrocarbon chains is growing [4–8] due to the wide range of possible applications of the modified fatty acid derivatives, such as biolubricants [9,10], biosurfactants [11] or biopolymers [12,13].

The introduction of a vicinal diol group in the hydrocarbon chain of unsaturated fatty acids or esters can be a key step for the preparation of biolubricants [14], polysulfate biosurfactants [15], hyperbranched polymers [16] or in the cleavage of unsaturated fatty acids to give shorter carboxylic acids and diacids [17,18]. For this reason, the direct or indirect (via epoxide) dihydroxylation of unsaturated fatty esters or acids has been widely studied [19]. The direct dihydroxylation implies harmful catalysts, such as OsO_4 [15], and hence the indirect synthesis has been more commonly used. The indirect dihydroxylation requires a first step of epoxidation and a second step of hydrolysis. In some cases, these two steps have been carried out in one pot, mainly thanks to the acidity of the epoxidation catalyst (H_2WO_4) and the inherent presence of water in the oxidant (H_2O_2 30 wt%) [17]. The hydrolysis of the epoxyfatty derivatives has been described using strong mineral acids, such as phosphoric acid [16] or perchloric acid [14]. Nevertheless, these methods with homogeneous acidic catalysts show different drawbacks, such as the impossible recovery of the catalyst and the corrosion problems. However, heterogeneous catalysts have been very seldom applied

to the hydrolysis of epoxyfatty derivatives, and usually associated to the one-pot two-step epoxidation-hydrolysis (Prilezhaev epoxidation) [20], with sulfonic polystyrene resins as the most commonly used catalysts.

Moreover, the development of heterogeneous catalysts for the hydrolysis or alcoholysis of non-fatty epoxides remains a topic of general interest, trying to solve some of the limitations of the existing procedures. Heterogeneous catalysts, such as high silica zeolites [21], stannosilicates [22,23], Fe-incorporated molecular sieves [24], Co(salen) based porous solids [25–27], metal-organic frameworks [28], or sulfonic solids [29–31], have been recently described for the hydrolysis of different types of epoxides.

In the context of our ongoing project about catalytic transformation of fatty esters, we have tried a divergent synthetic pathway to functionalized derivatives from epoxyfatty esters (Scheme 1), including the Meinwald rearrangement to ketofatty esters [32] and the hydrogenolysis to hydroxyfatty esters [33]. In this paper, we present our results in the hydrolysis of epoxyfatty esters to produce dihydroxyfatty esters using heterogeneous catalysts.

2. Experimental

2.1. Materials

Epoxyfatty esters were prepared following our previously described procedure [32] from the corresponding fatty ester: methyl oleate (96%, Alfa Aesar), methyl elaidate (>98%, TCI), methyl erucate (>98%, TCI), methyl ricinoleate (>75%, TCI) and methyl linoleate (>95%). Triflic acid (99%) was purchased from Fluorochem and the resins (Aquivion

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PW97S, Aquivion P98, Nafion NR50 and Dowex 50Wx2) from Merck. Tetrahydrofuran (>99.6%), *tert*-butanol (>99.5%), ethyl acetate (>99.5%) and Oxone® (2 KHSO$_5$ · KHSO$_4$ · K$_2$SO$_4$) were purchased from Fisher Scientific. The chemicals used in the experiments did not require further purification and were used as received, with the exception of methyl ricinoleate, which was purified by column chromatography using a mixture hexane:ethyl acetate (9:1 v/v) as eluent..

2.2. Instruments

Gas chromatography was performed using Agilent 7890A and 6890 N chromatographs, both equipped with FID detectors, and ZB-5HT Inferno capillary columns (30 m × 0.25 mm × 0.25 µm). Helium was used as carrier gas at 17 psi in column head. Injector temperature: 280 °C. Detector temperature: 250 °C. Oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C (0 min) and 5 °C min^{-1} to 250 °C (15 min).

Nuclear magnetic resonance (NMR) spectroscopy was carried out with a Bruker Avance 400 and the chemical shifts were expressed in ppm. Deuterated chloroform (CDCl$_3$) was used as both solvent and reference (7.26 ppm).

2.3. Preparation of the acidic form of Aquivion P98 resin

To a 50 mL round bottom flask, 5.0 g of Aquivion P98-SO$_2$F (5.1 mmol –SO$_2$F), 30 mL of a 2.0 M aqueous solution KOH and 5 mL of DMSO were added and the mixture was stirred at 120 °C for 72 h. The solid was filtered off and washed with distilled water until neutral pH. Then, the wet solid and 30 mL of 2.0 M aqueous solution H$_2$SO$_4$ were added to a 50 mL round bottom flask and the mixture was stirred at 120 °C for 24 h. The solid was again filtered off and washed with distilled water until neutral pH.

The acid sites of the solid sulfonic acid were determined by indirect volumetric determination. 1.0 g of solid sulfonic acid previously dried was packed in a chromatographic column. Then, the acid sites were exchanged with 2.0 M aqueous solution NaCl. The resulting HCl solution was titrated with 1.0 mM aqueous solution NaOH and phenolphthalein as indicator. The functionality of Aquivion P98-H^+ is 0.98 mmol H^+/g (96% of active sites exchanged).

2.4. General procedure

163.3 mg of Aquivion P98 in its acidic form (0.16 mmol), dried at 120 °C under vacuum for 20 h, were added to a solution of the corresponding epoxyfatty ester (1.6 mmol) in 10 mL *t*BuOH/H$_2$O (3:1 v:v). The mixture was stirred at 80 °C and the reaction was monitored by GC-FID until full conversion. Then, the catalyst was filtered off and the solvent was removed by evaporation under reduced pressure. Finally, the diol was purified by recrystallization from cyclohexane and characterized by NMR.

After completion of the reaction, the filtered catalyst was washed with dichloromethane and dried under vacuum at 120 °C overnight. The solid was reused in a new hydrolysis reaction following the same procedure.

## 2.5. Tandem hydrolysis-cleavage of methyl-9,10-epoxystearate

163.3 mg of Aquivion P98 in its acidic form (0.16 mmol), dried at 120 °C under vacuum for 20 h, were added to a solution of methyl 9,10-epoxystearate (500 mg, 1.6 mmol) in 10 mL *t*BuOH/H$_2$O (3:1 v:v). The mixture was stirred at 80 °C for 16 h. Then, the catalyst was filtered off and 38.4 mg of KBr (0.32 mmol, 20 mol%) and 1967 mg of Oxone® (6.4 mmol) were added to the solution. The mixture was stirred at room temperature for 24 h. The reaction crude was diluted with distilled water (25 mL) and the products were extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (20 mL), dried with anhydrous MgSO$_4$, and filtered. By GC-FID, a 97% of conversion was obtained. The mixture of nonanoic (pelargonic) acid and azelaic acid monomethyl ester (1:1 molar ratio) was obtained with a 95% of isolated yield.

3. Results and discussion

3.1. Hydrolysis of simple fatty epoxides

The optimization of the reaction conditions was performed with methyl *cis*-9,10-epoxystearate. In all cases the hydrolysis generates the methyl *syn*-9,10-dihydroxystearate, as confirmed by NMR [34]. The homogeneous reaction was tried with triflic (trifluoromethanesulfonic) acid under the conditions described for HClO$_4$ [35], using a catalytic amount of acid. Total conversion and selectivity to *syn*-9,10-dihydroxystearate were obtained in 24 h with 20 mol% of triflic acid at room temperature in THF/water (3:2) as solvent, and then the same conditions were tried with a variety of heterogeneous analogous of triflic acid (Table 1).

When the reaction was tested with Dowex 50 *W* × 2, an arenesulfonic resin that had been used in the one-pot epoxidation-hydrolysis [36,37], the reaction was slow and the ketostearates **2** were also detected (Table 1, entry 1), as a result of the competitive Meinwald rearrangement of the epoxide, also catalysed by sulfonic solids [32]. A similar result was obtained with the perfluorinated resin Nafion NR50 (entry 2), in spite of being a stronger acid, more similar to triflic acid. However, another analogous solid, Aquivion PW79S (entry 3), showed a much improved performance. The difference between these two structurally similar solids (Fig. 1) may be ascribed to the textural properties (lower particle size and shorter side chains) that may affect the diffusion of the reagent in the intraparticle space of the catalyst, with a much better accessibility to the sites in the case of Aquivion PW79S. With this catalyst is possible to improve the reaction rate by increasing the temperature to 50 °C (entry 4), but with somehow lower selectivity to diol, 80 vs 88%. In an attempt to increase selectivity, the reaction was carried
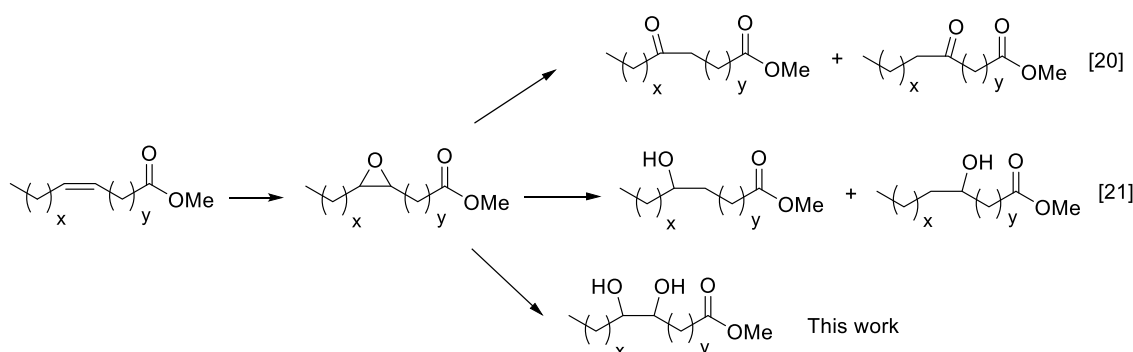
Scheme 1. Divergent synthetic pathway through the epoxyfatty esters.

Table 1
Results of the hydrolysis of methyl *cis*-9,10-epoxystearate with different sulfonic acids.[a]

Entry	Acid	T (°C)	t (h)	Conv. (%)[b]	Selectivity (%)[b]		
					1	2	3
Solvent: THF/H₂O (3:2 v/v)[c]							
1	Dowex 50 *W* × 2	r.t.	24	33	85	15	0
			120	76	87	13	0
2	Nafion NR50	r.t.	24	23	65	35	0
			72	60	83	17	0
3	Aquivion PW79S	r.t.	24	77	87	13	0
			96	>99	88	12	0
4	Aquivion PW79S	50	24	>99	80	20	0
5	Aquivion PW79S	0	24	35	46	54	0
			48	53	60	40	0
6	Aquivion P98	50	24	46	85	15	0
			120	>99	88	12	0
Solvent: *t*BuOH/H₂O (3:1 v/v)[d]							
7	Dowex 50 *W* × 2	80	6	>99	84	12	4
8	Nafion NR50	80	6	>99	88	7	5
9	Aquivion P98	80	6	>99	87	7	6

[a] Scale: 1.6 mmol of epoxide; 0.32 mmol of sulfonic groups (20 mol%, see ESI).
[b] Determined by GC by comparison of the integrated areas of reagent and products.
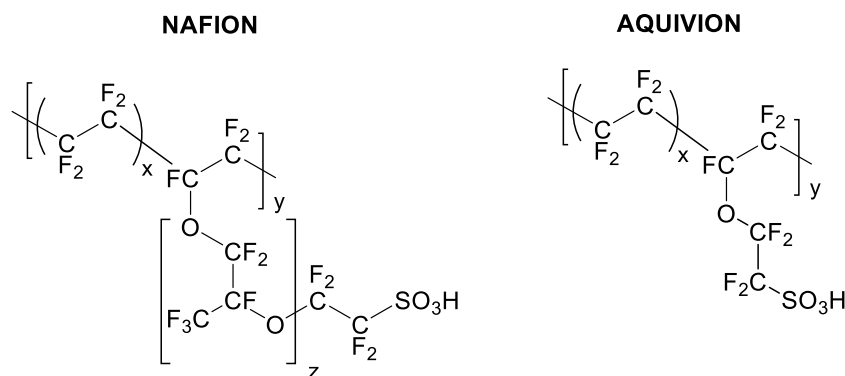[c] 25 mL.
[d] 10 mL.

Fig. 1. Chemical structures of Nafion and Aquivion.

out at 0 °C (entry 5). However, the reaction was not only slower but also much less selective.

One of the objectives of this work was the development of a method for epoxide hydrolysis with a recoverable and reusable catalysts. In this regard, Aquivion PW79S, which is sold in powder form, was not suitable. A gel-like structure was formed in the reaction medium, probably due to the very small particle size, and it was impossible to filter. Thus, we envisaged the use of another Aquivion catalyst with a different particle size, namely Aquivion P98 in the form of pellets. The commercially available form bears fluorosulfonyl groups (-SO₂F) that were converted in the acidic form (-SO₃H) by an experimental procedure developed from a very brief description in literature, which includes successive treatments with KOH and H₂SO₄ [38]. The effect of textural properties is clear in the case of Aquivion P98 (entry 6), which is less active than the analogous PW79S, in agreement with accessibility issues due to its larger particle size. Some important effects of the textural properties have been also reported in the case of arenesulfonic resins for

the one-pot epoxidation-hydrolysis process, related in one case to the cross-linking degree (divinylbenzene percentage) [36] or changes in the resin morphology due to the drying process [37].

The diffusion problems can be overcome by changes in solvent and temperature. An alternative solvent mixture also used in literature to carry out acid hydrolysis of methyl *cis*-9,10-epoxystearate is *tert*-butanol/water (3:1) [16,39]. Thus, the three solids with this kind of problem were tested in *tert*-butanol/water mixture as solvent and at 80 °C (entries 7–9). In all the cases a minor amount (4–6% selectivity) of an additional by-product, identified as 9(10)-*tert*-butoxy-10(9)-hydroxystearate (**3**), was detected as result of the competitive *tert*-butanolysis of the epoxide. With the three catalysts, the reaction was faster (total conversion after 6 h), with high selectivity to diol (84–88%). Thus, under these reaction conditions, the acid strength does not show a significant influence in the result, as demonstrated by the similar performance of arenesulfonic (weaker) and perfluoroalkanesulfonic (stronger) groups. In the three cases, the solvent system including *tert*-butanol

showed a swelling capacity of the resins, which can be the reason for a better accessibility of the catalytic sites and hence a higher catalytic performance. Fig. 2 shows the obvious differences in size of Aquivion after stirring in both solvent mixtures. Swelling is higher in *tert*-butanol/water than in THF/water, which can be the reason for a better accessibility of the catalytic sites and hence a higher catalytic performance in *tert*-butanol/water. *Tert*-butanol is also more environmentally friendly than THF, according for example to the GSK's [40], Sanofi's [41] or CHEM21 [42] classifications of organic solvents.

The reaction conditions, temperature and catalyst amount, were optimized with Aquivion P98, considering 24 h as the maximum reaction time (Table 2). At 80 °C, the amount of catalyst can be reduced from 20 mol% to 10 (entry 3) and even 7.5 mol% (entry 5), keeping the high selectivity to diol (87–90%) with total conversion within the time limit, whereas with 5 mol% (entry 6) the conversion is not complete. The reaction rate significantly drops when the temperature is reduced to 50 °C (entries 2 and 4).

3.2. Reuse of Aquivion P98

One of the main interest in using heterogeneous catalysts for this kind of reaction is the possibility of recovering and recycling of the catalyst. As commented above, Aquivion P98 can be more easily filtered than P79S.

As can be seen in Fig. 3, the catalyst was used in 11 consecutive reactions without any loss of activity (total conversion after 16 h) and only minor variations in selectivity (87–90% of diol). Thus, the total productivity obtained with Aquivion P98 was 96.8 mol of diol per mol of sulfonic groups, with a catalyst still active.

3.3. Hydrolysis of other epoxyfatty esters

The optimized conditions for Aquivion P98 were tested in the hydrolysis of other fatty epoxides (Scheme 2). The first example was methyl *trans*-9,10-epoxystearate (epoxide from elaidate) to test the effect of the stereochemistry of the epoxide. The result was similar after 16 h, with total conversion and 92% yield of *anti*-9,10-diol, whose stereochemistry was confirmed by the chemical shift in ^{1}H NMR [34]. The effect of the chain length was tested with methyl *cis*-13,14-epoxydocosanoate (epoxide from erucate). Again the result was similar after 16 h, with total conversion and 90% yield of *syn*-13,14-diol. In both cases small amounts of ketones (2–4%) and tert-butoxy-hydroxy derivatives (6%) were also obtained.

The hydrolysis reaction of fatty epoxides with additional functionalities was tested first with methyl *cis*-9,10-epoxy-12(*R*)-hydroxystearate (epoxide from ricinoleate) was carried out under the same conditions (Scheme 3). The total conversion after 16 h led to the expected 9,10,12-triol as the main product with 75% yield (determined by GC-FID), presumably as a mixture of diastereomers (9*S*,10*S*,12*R* and 9*R*,10*R*,12*R*) although it was not possible to separate them and determine the diastereomeric ratio. It should be noted that this result significantly improves that described previously using H_3PO_4 (25% vs 75% yield) [16]. On the other hand, as it happened in the case of
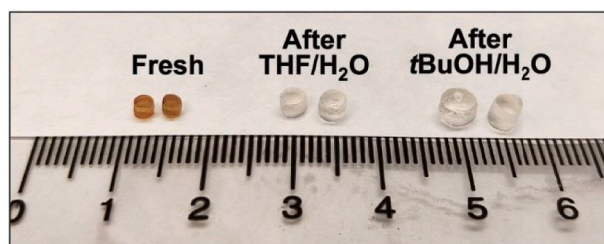
Table 2

Optimization of the hydrolysis of methyl *cis*-9,10-epoxystearate with Aquivion P98.[a]

Entry	mol%	T (°C)	t (h)	Conv. (%)[b]	Selectivity (%)[b]		
					1	2	3
1	20	80	6	>99	87	7	6
2	20	50	24	97	87	7	6
3	10	80	16	>99	90	7	3
4	10	50	24	81	85	9	6
5	7.5	80	24	>99	88	7	5
6	5	80	24	96	88	7	5

[a] Scale: 1.6 mmol of epoxide in 10 mL of *t*BuOH/H$_2$O (3:1 v/v).
[b] Determined by GC by comparison of the integrated areas of reagent and products.

Meinwald rearrangement [32] and hydrogenolysis [33], the side reaction was the acid-catalysed cyclization by attack of 12-hydroxyl to position 9 of the epoxide, leading to 3-hydroxytetrahydrofuran and the corresponding furan after aromatization (Scheme 3).

On the contrary, the hydrolysis of methyl *cis,cis*-9,10:12,13-diepoxystearates (diepoxides of linoleate) does not produce any polyol but only cyclization products (Scheme 4). The first hydrolysis leads to an epoxy-diol very prone to this side reaction. In the case of hydrolysis of the 9,10-epoxide, hydroxyl in 10 attacks position 13 of the other epoxide, leading to 9,12-dihydroxy-10,13-tetrahydrofuran. In the case of hydrolysis of the 12,13-epoxide, hydroxyl in 12 attack position 9 of the other epoxide, leading to 10,13-dihydroxy-9,12-tetrahydrofuran. In this case only a minor fraction (3%) of tetrahydrofurans was able to aromatize to furans. Although in this case, tetraols are not detected, the presence of two hydroxyl groups in the 97% of the molecules obtained would allow to evaluate their use in the same type of applications as the other diols here described. The dihydroxy tetrahydrofurans could provide different properties to the final material since these hydroxyl groups are incorporated in conformationally more constrained structures.

3.4. Hydrolysis-cleavage tandem process

The objective of our project was the development of a divergent synthetic strategy from epoxyfatty esters, leading to different transformations by using heterogeneous catalysis. In previous works we explored the sequential epoxidation-Meinwald rearrangement to obtain ketofatty esters [32], and the sequential epoxidation-hydrogenolysis to obtain hydroxyfatty esters [33]. More recently, we have described the simple and transition metal free oxidative cleavage of dihydroxyfatty esters [43], and the possibility of a sequential hydrolysis-cleavage process has been also explored taking advantage of the use of the same solvent in both individual processes.

This strategy was tested with methyl *cis*-9,10-epoxystearate in one-pot by adding simultaneously Aquivion P98 as catalyst for the hydrolysis step and Oxone® and KBr as reagent and catalyst, respectively, for the cleavage step. After 24 h at 80 °C (the optimal temperature for hydrolysis), the epoxide conversion was complete, but 57% of methyl 9,10-dihydroxystearate was still present in the reaction mixture. One possible explanation would be the unproductive decomposition of Oxone® at that temperature.

Therefore, the tandem process was carried out in a sequential manner (Scheme 5). The hydrolysis was carried out at 80 °C, the reaction mixture was cooled at room temperature, the Aquivion P98 catalyst was filtered off, the oxidant (Oxone®) and catalyst (KBr) for the cleavage step were added to the mixture, and the second step was carried out at room temperature. Under those conditions 97% yield of cleavage products (nonanoic acid and azelaic acid monomethyl ester, 1:1 molar ratio) was obtained, with only 2% of methyl 9(10)-ketostearate from the Meinwald rearrangement of the starting epoxide. The by-product of epoxide ring opening with *tert*-butanol, methyl 9(10)-*tert*-butoxy-10(9)-
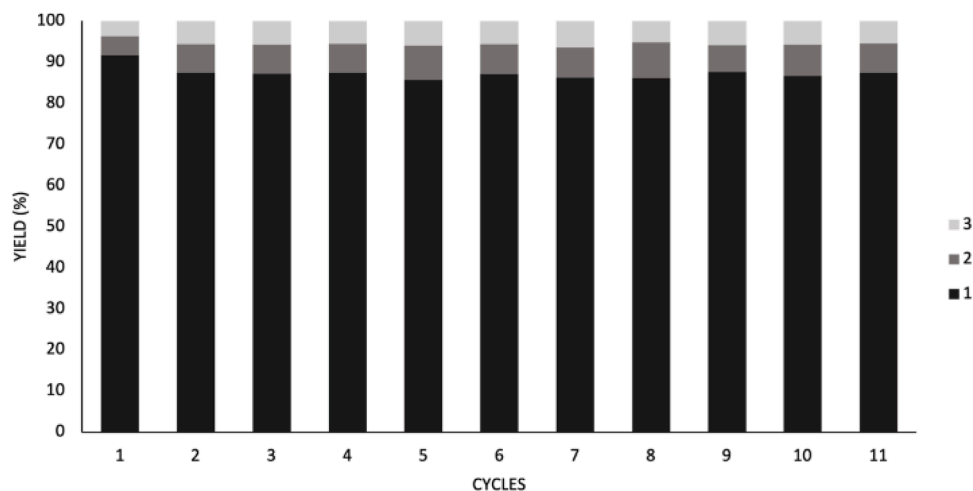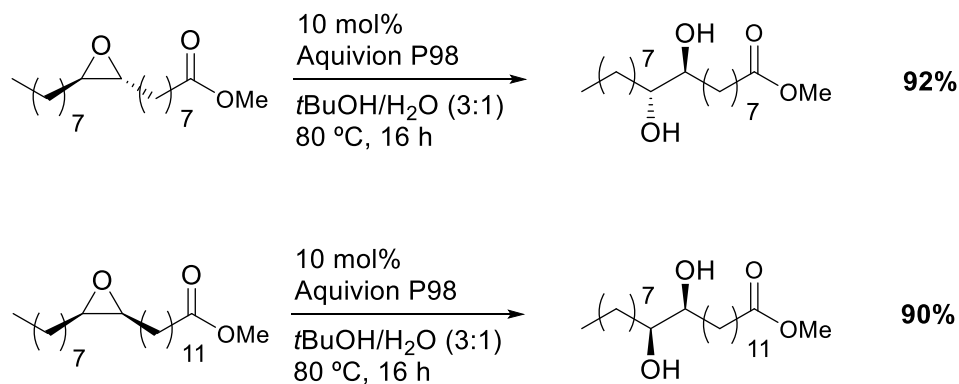

Fig. 2. Swelling of Aquivion P98 in THF/water at 50 °C (medium) and *tert*-butanol/water at 80 °C (right).

Fig. 3. Reuse of Aquivion P98 in the hydrolysis of methyl *cis*-9,10-epoxystearate to methyl 9,10-dihydroxystearate (1), and by-products ketostearates (2) and *tert*-butoxy-hydroxystearates (3). Reaction conditions: 1.6 mmol epoxide, 10 mL *t*BuOH/H$_2$O (3:1 v/v), 10 mol% catalyst, 80 °C, 16 h.

Scheme 2. Hydrolysis of simple fatty epoxides.
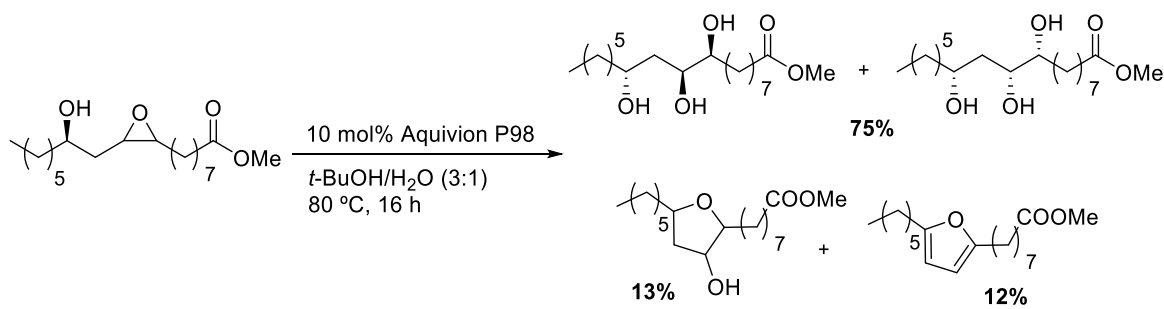
Scheme 3. Hydrolysis of methyl *cis*-9,10-epoxy-12(*R*)-hydroxystearate.
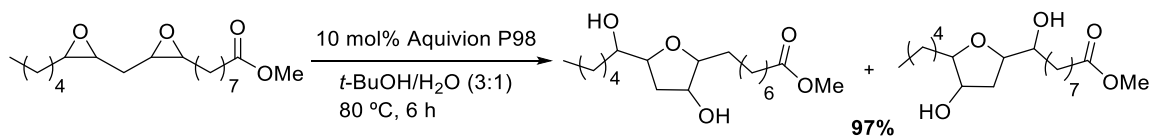

Scheme 4. Hydrolysis of methyl *cis,cis*-9,10:12,13-diepoxystearates.

hydroxystearate (**3**) was not detected, probably due to its cleavage under the oxidation conditions, showing that purification is not required in this case.

4. Conclusions

The use of sulfonic resins as recoverable heterogeneous catalysts has allowed the development of an efficient strategy to carry out the acid hydrolysis of methyl epoxyfatty esters. Textural properties of the resins
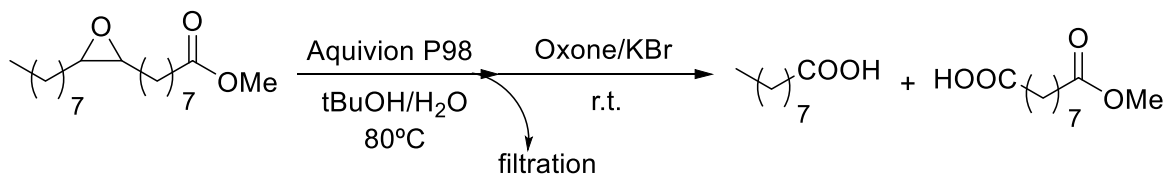
Scheme 5. Tandem hydrolysis-cleavage of methyl 9,10-epoxystearate.

directly affect the diffusion of the reagents in the intraparticle space, and the right choice of solvent and temperature help to improve their accessibility and therefore to obtain the best results in reasonable times. All the sulfonic resins reach the same good results in the hydrolysis of methyl *syn*-9,10-dihydroxystearate using a *tert*-butanol/water mixture at 80 °C, showing that under these conditions, an adequate swelling of all the resins is produced, making the hydrolysis results independent of their textural properties.

From the point of view of the recycling of the catalyst, the particle size is fundamental to avoid solid losses during its filtration. In this respect, Aquivion P98, in form of pellets, allows its recovery and reuse for at least 11 reaction cycles without deactivation.

The hydrolysis of the elaidate epoxide and the erucate epoxide allows to evaluate the effect of the epoxide stereochemistry and the fatty chain length in the optimal reaction conditions, achieving similar results (>90% yield) to those obtained with the oleate epoxide. The hydrolysis of the epoxide from ricinoleate, which incorporate a hydroxyl group in the fatty chain, leads to 9, 10, 12-triols with a non-negligible 75% yield and 25% yield of cyclic by-products. Same kind of by-products are also obtained in the hydrolysis of the diepoxides of linoleate as a result of the intramolecular reaction of the epoxy-diols formed as intermediates from a partial hydrolysis of the diepoxide.

The use of the same solvent system allows carrying out the tandem hydrolysis-cleavage process, leading to an almost quantitative synthesis of the cleavage products, with only filtration of the heterogeneous catalyst of the first reaction and no further intermediate purification.

Electronic supplementary information (ESI)

Supplementary material related to this work is available, in the online version, at doi:… This material includes data of the functionalization of the sulfonic resins, chromatograms of the reactions and NMR characterization of the products.

CRediT authorship contribution statement

Vicente Dorado: Investigation, Methodology, Data curation, Writing – review & editing. **Clara I. Herrerías:** Conceptualization, Methodology, Writing – review & editing. **José M. Fraile:** Conceptualization, Writing – original draft, Supervision, Visualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2023.113282.

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