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New Environmentally Friendly Oxidative Scission of Oleic Acid into Azelaic Acid and Pelargonic Acid

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Abstract Oleic acid (OA) is a renewable monounsaturated fatty acid obtained from high oleic sunflower oil. This work was focused on the oxidative scission of OA, which yields a mono-acid (pelargonic acid, PA) and a di-acid (azelaic acid, AA) through an emulsifying system. The conventional method for producing AA and PA consists of the ozonolysis of oleic acid, a process which presents numerous drawbacks. Therefore, we proposed to study a new alternative process using a green oxidant and a solvent-free system. OA was oxidized in a batch reactor with a biphasic organic-aqueous system consisting of hydrogen peroxide (H₂O₂, 30 %) as an oxidant and a peroxo-tungsten complex $Q_3\{PO_4[WO(O_2)_2]_4\}$ as a phase-transfer catalyst/co-oxidant. Several phase-transfer catalysts were prepared in situ from tungstophosphoric acid, H₂O₂ and different quaternary ammonium salts (Q⁺, Cl⁻). The catalyst $[C_5H_5N(n-C_{16}H_{33})]_3\{PO_4[WO(O_2)_2]_4\}$ was found to give the best results and was chosen for the optimization of the other parameters of the process. This optimization led to a complete conversion of OA into AA and PA with high yields (>80 %) using the system OA/H₂O₂/[C₅H₅N(n- $C_{16}H_{33}$]₃{PO₄[WO(O₂)₂]₄} (1/5/0.02 molar ratio) at 85 °C for 5 h. In addition, a new treatment was developed in order to recover the catalyst.

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A. Godard · P. De Caro · S. Thiebaud-Roux · E. Vedrenne · Z. Mouloungui INRA, UMR 1010 CAI, 31030 Toulouse, France **Keywords** Hydrogen peroxide · Oleic acid · Oxidative cleavage · Peroxo-tungsten complex · Phase-transfer catalysis · Solvent-free reaction · Tungstophosphoric acid

Abbreviations

AA	Azelaic acid
EO	Ethyl oleate
FAME	Fatty acids methyl esters
LA	Linoleic acid
OA	Oleic acid
PA	Pelargonic acid
RA	Ricinoleic acid
RT	Room temperature
TBME	tert-Butyl methyl ether
TMSH	Trimethylsulfonium hydroxide
TPA	Tungstophosphoric acid

Introduction

Monounsaturated fatty acids are renewable starting materials that are particularly attractive for the chemical industry because of their low price and worldwide availability. Among them, oleic acid or *cis*-9-octadecenoic acid (OA) is a C18:1 monounsaturated fatty acid, which can be obtained from high oleic sunflower oil. This renewable resource is commonly grown in the south of France and in other Mediterranean countries. OA thus represents an interesting building block for the chemical industry [1].

The most common C=C transformations of OA are epoxidation, hydroxylation and oxidative cleavage. The oxidative scission is particularly attractive as it provides a C9 mono-acid (pelargonic acid or nonanoic acid, PA) and a C9 di-acid (azelaic acid or nonanedioic acid, AA). These saturated acids exhibit short and odd hydrocarbon chains that are present in very low amounts in natural resources. Their rarity is all the more problematic since these acids are very interesting starting materials for the preparation of numerous bio-based products [1, 2]. AA is, for example, converted into different esters for the preparation of polymers (Nylon 6:9), plasticizers, adhesives, solvents, biode-gradable lubricants, corrosion inhibitors, and anti-acneic agent for cosmetics [1, 3, 4]. PA is an intermediate in the production of lubricants, plasticizers, perfumes, herbicides, fungicides, resins [1, 5].

Several oxidant systems have been developed to cleave the double bond of OA or methyl oleate using chromic acid, nitric acid, potassium permanganate, osmium tetroxide, peracids, periodates, or hypochlorites [6]. However, most of these conventional oxidants are not eco–friendly and the desired compounds are obtained in low yields. Another oxidant, ozone, was chosen for the large-scale production of AA and PA from OA. This reaction is very selective and gives high yields, but it also presents numerous economical and environmental drawbacks (energy and oxidant consumption, toxicity, explosion hazard) [7].

In this context, the aim of this work was to propose a new alternative process using a greener and safer oxidant system, such as hydrogen peroxide, as it produces only water as a waste product [8]. We thus decided to develop new conditions combining its use with a phase-transfer catalyst, which would enhance the contact between the organic substrate and the hydrophilic oxidant. Several phase-transfer catalysts were prepared in situ from tungstophosphoric acid, hydrogen peroxide and different quaternary ammonium salts (Q^+ , Cl^-). The resulting catalysts are peroxotungsten complexes Q_3 {PO₄[WO(O₂)₂]₄} that are thought to act as co-oxidants [1]. The peroxo anion is the active ionic species able to transfer oxygen to the organic phase thanks to its association with a lipophilic cation.

To our knowledge, a triphasic system $OA/H_2O_2/Q_3\{PO_4[WO(O_2)_2]_4\}$, without any organic solvent, had already been used to epoxidize the double bond of OA [6, 9] but less to perform its cleavage [1, 10, 11, 17]. This system was a strategic choice in order to develop a green process, as no organic solvent is used for the reaction itself and only benign wastes are obtained (if the workup solvent is recycled). Furthermore, others novelties of this work are the use of a couple of ammonium quaternary salts ([*n*-Bu₄N]⁺, X⁻; [(*n*-C₈H₁₇)₄N]⁺, X⁻) which have never been tested for the cleavage of OA with the selected system, and the development of a more efficient workup in order to improve the yields and recycle the catalyst.

The influence of various parameters was investigated, and the reaction conditions were optimized to obtain a complete conversion and high yields.

Experimental Procedures

Materials and Reagents

High oleic sunflower oil was purchased from Iterg (Pessac, France). Aqueous hydrogen peroxide (aqueous solution, 30 %), tungstophosphoric acid (H₃PW₁₂O₄₀·nH₂O, TPA, reagent grade), linoleic acid (LA, w/w 62.0 %), formic acid (97–98 %), Aliquat[®] 336, cetylpyridinium chloride monohydrate, tetrabutylammonium chloride (≥97 %), tetrabutylammonium bromide (99 %), potassium iodide (99 %), ethyl acetate (technical grade) and tert-butyl methyl ether (TBME, reagent grade) were purchased from Sigma Aldrich Co. Ammonium heptamolybdate tetrahydrate and sulfuric acid solution (4 N) were provided from VWR. Candida cylindracea lipase, trimethylsulfonium hydroxide (TMSH) and sodium thiosulfate solution (0, 1 N) were respectively purchased from Lyven, Macherey-Nagel and Fluka.

Hydrolysis of High Oleic Sunflower Oil

High oleic sunflower oil (22.5 kg) was hydrolyzed using *Candida cylindracea* lipase in distilled water (20.1 kg) under stirring at 40 °C for 5 h [12]. The fatty acid composition of the hydrolysate was determined by GLC (w/w): 87.6 % oleic acid, 4.7 % linoleic acid, 3.5 % palmitic acid, 3.1 % stearic acid, 0.2 % capric acid and 0.9 % of others fatty acids. It was used as the source of oleic acid for all experiments.

Synthesis of Peroxo-Tungsten Catalytic Complexes

TPA was pre-treated with hydrogen peroxide to form the peroxo-tungsten catalytic complex. Two methods were tested.

Method a: Catalytic complexes were synthesized prior to the reaction according to a known procedure [10].

Method b: An in-situ protocol was developed for our study. A solution ammonium quaternary salt (3.6 mmol) in water (2 mL) was added dropwise to OA in a three-necked flask. A pre-stirred solution (30 min at room temperature, RT) of a 30 % aqueous solution of H_2O_2 (34 mL, 325.0 mmol) and $H_3PW_{12}O_{40}\cdot nH_2O$ (TPA, 4 g, 1.2 mmol) in water (5 mL) was then added dropwise.

The following peroxo-tungsten catalytic complexes A, B, C, D were formed in situ:

- A: $[n-Bu_4N]_3\{PO_4[WO(O_2)_2]_4\}$
- B: $[C_5H_5N(n-C_{16}H_{33})]_3\{PO_4[WO(O_2)_2]_4\}$
- C: $[MeN(n-C_8H_{17})_3]_3{PO_4[WO(O_2)_2]_4}$
- D: $[(n-C_8H_{17})_4N]_3\{PO_4[WO(O_2)_2]_4\}$

Oxidative Cleavage of Oleic Acid

Typically, a 250-mL, three-necked, round-bottom flask was charged with 21 g (65.0 mmol) of OA and the catalyst A, B, C or D (1.2 mmol). This reactor was equipped with a condenser, a mechanical stirrer and a thermocouple. The reaction medium was heated at 60 °C and a 30 % aqueous solution of H₂O₂ (325.0 mmol) was added dropwise over 5 min. The reaction mixture was then heated at 85 °C while stirring (400 rpm). After 5 h, this mixture was allowed to cool down to room temperature. The pH was adjusted to 1 with an aqueous hydrochloric acid solution (4 N). A green ethyl acetate solvent (which can be biosourced) (100 mL) was then added and the reaction mixture was cooled to the desired temperature (T < 4 °C or RT). For catalysts A and B, the white precipitate was filtered and washed with ethyl acetate (50 mL). The organic and aqueous layers were separated in a 500-mL separating funnel. The aqueous phase was extracted twice with ethyl acetate (100 mL). The combined organic layers were dried with anhydrous sodium sulfate (Na₂SO₄) and evaporated under reduced pressure. Fatty acids were obtained and analyzed without a further purification of the crude material.

Epoxidation of Oleic Acid

The epoxide (9,10-epoxyoctadecanoic acid) was prepared from OA (71.0 mmol) in freshly made performic acid, according to a known protocol [13]. The reaction proceeded at RT for 3 h (400 rpm). The 9,10-epoxyoctadecanoic acid was obtained as a colorless and powdery solid in 72 % yield (purity of 65 %, 51.0 mmol).

Analytical Techniques

The collected samples were analyzed and quantified by gas chromatography on a Varian instrument coupled to a flame ionization detector (FID). The silica capillary column (CP for FAME fused silica WCOT, 50 m, 0.25 mm, 0.25 μ m) was purchased from Varian (USA). The carrier gas was helium (Air Liquide, France) at a pressure of 1.03 bar at the head of the column. Injector and detector temperatures were 250 °C. The temperature in the oven was held at 100 °C for 5 min, then ramped to 180 °C at 5 °C min⁻¹ for 10 min and finally increased to 250 °C at 10 °C min⁻¹ for 5 min (held 43 min).

All samples (10 mg mL⁻¹ dissolved in TBME, 50 µL) were converted to FAME with TMSH (50 µL). Pentadecanoic acid was added as the internal standard (2 mg mL⁻¹).

This analytical procedure allowed us to calculate the conversion of OA (χ_{OA}), the yields of azelaic acid (Y_{AA}),

pelargonic acid (Y_{PA}) and of some intermediate products, such as aldehydes (nonanal and 9-oxo-nonanoic acid) and epoxide (9,10-epoxyoctadecanoic acid).

The structures of the resulting compounds were identified by FT-IR spectroscopy (PerkinElmer), ammonia chemical ionization mass spectrometry (MS), ¹H and ¹³C NMR (Bruker).

Titration of Hydrogen Peroxide

The hydrogen peroxide amount was titrated with an iodometric method. The aqueous solution containing hydrogen peroxide (1 mL) was diluted with 100 mL of distilled water, 30 mL of sulfuric acid (4 N), 35 mL of potassium iodide (100 g L⁻¹), 1 mL ammonium molybdate (5 g L⁻¹). The diiodine (I₂) formed was titrated with a sodium thiosulfate solution (0.1 N).

Results and Discussion

Effects of the Type of Catalyst/Co-oxidant

In order to gain more insight into the oxidative cleavage of OA using the Q_3 {PO₄[WO(O₂)₂]₄}/H₂O₂ system, the influence of the nature of the catalyst was first studied.

A blank experiment, without any catalyst, gave a mediocre conversion of OA and low AA and PA yields (Table 1). GLC analysis confirmed the presence of known intermediate products [10] such as the aldehydes or the diol and the epoxide formed on the double bond of OA:OA was partially oxidized but not to the desired products, showing that a catalyst is needed for this oxidative reaction.

A substrate/oxidant/catalyst molar ratio of 1/5/0.02 was then chosen for the other experiments. The peroxo-tungsten complex Q₃{PO₄[WO(O₂)₂]₄} was formed using a quaternary ammonium salt (Q⁺, X⁻), TPA and H₂O₂, following the protocol described in the experimental procedures (method b). Four quaternary ammonium cations Q⁺ were tested in order to form various peroxo-tungsten complexes with hydrogen peroxide: n-Bu₄N⁺ (a), C₅H₅N(n-C₁₆H₃₃)⁺ (b), MeN(n-C₈H₁₇)⁺₃ (c), (n-C₈H₁₇)₄N⁺ (d).

The addition of catalyst $Q_3\{PO_4[WO(O_2)_2]_4\}$ led to the complete conversion of OA, for all the tested catalysts. This demonstrated that the catalyst is required to transfer the oxygen of the hydrogen peroxide to the substrate. In fact, the peroxo anion is the active ionic species able to transfer oxygen to the organic phase thanks to its association with a lipophilic cation. Then, in the aqueous phase, the catalyst (thus under the oxo form) was reoxidized by H_2O_2 into the peroxo form [1].

Furthermore, among those experiments, catalyst B gave the best yields. This can be explained by the formation of an

Catalyst	Catalyst preparation method	\mathbf{X}^{-}	χ _{OA} (%)	$Y_{\rm AA}~(\%)$	$Y_{\rm PA}~(\%)$
_	b	_	38.1	1.8	2.2
А	b	Cl ⁻	100.0	77.6	80.9
А	a	Cl^{-}	100.0	52.0	57.1
А	b	Br^-	100.0	71.8	76.2
В	b	Cl^{-}	100.0	81.5	86.1
В	a	Cl^{-}	100.0	70.2	75.1
В	a*	Cl^{-}	100.0	68.0	73.3
С	b	Cl^{-}	100.0	75.7	80.7
D	b	Cl ⁻	100.0	73.2	76.5

Table 1 Activity of different catalytic peroxo complexes, obtained from Q^+ , X^- and TPA, on the oxidative cleavage of OA

* H₂O₂ (420 mmol, 6.5 equiv.)



observable emulsion during the reaction. The total interface area is more important with this catalyst, as it allows the interfacial tension to be lowered. Moreover, the emulsion is stabilized by the presence of fatty acids as described as surfactants [5]. The medium thus emulsified, favors the contact at the interface between the reactants in the organic phase and the oxidant in the aqueous phase. The quaternary ammonium cation of catalyst B, which is very accessible because of the planar geometry of the pyridinium scaffold, efficiently transfers the peroxo anion to the organic phase [14].

The influence of the counter-ions was then investigated by the substitution of the chlorine atom by bromine for catalyst A. AA and PA yields were lower (4–6 %) using the bromide-based catalyst. Indeed, the higher reducing power of the bromide salts compared to the chloride can generate the partial decomposition of the peroxo-tungsten complex according to the following reaction: $W_2O_5 + 2Br^- + 2H^+ \rightarrow Br_2 + 2WO_2 + H_2O$ [10].

Effects of the Catalyst Preparation

Peroxo-tungsten complexes can be either synthesized prior to the reaction [10] (method a) or in situ with a solvent for the epoxidation [15]. In this study, the peroxo-tungsten complex was formed in situ but without any organic solvent, which, to our knowledge, has never been described for such a cleavage reaction (method b). Different protocols (methods a, a*, b) were compared using catalysts A and B (Table 1). In all cases, a large excess of H_2O_2 was used as it has already been described that a catalytic or thermal decomposition of H_2O_2 occurs [1].

Compared to methods a and a*, yields of AA and PA were considerably increased with the in-situ formation of the peroxo-tungsten complex (method b). Several experiments were run to understand those results. First, the amount of H₂O₂ needed for the preparation of the catalyst using method a was determined by the H₂O₂ titration left in the aqueous filtrate: 120 mmol for 1.2 mmol of prepared catalyst. With method b, a total amount of 650 mmol (325 + 325 mmol) of H₂O₂ is added to the reaction mixture. The oxidant left at the end of the reaction was determined by titration and was 110 mmol. As 120 mmol should be needed to form the catalyst (as in method a), it means that 420 mmol (6.5 equiv.) was consumed during the intrinsic oxidation (oxidant consumption: 80 %). Method a* which uses the same amount of H2O2 that method b did not improve yields of AA and PA. Therefore, the efficiency of the in situ method comes from the method of preparation of the catalyst.

Effects of the Reaction Temperature

The influence of the reaction temperature was then studied for the three peroxo catalysts A, B and C (Table 2).

For catalysts A and B, the reaction was found to be optimal between 85 and 90 °C, whereas, for the catalyst C, it was between 90 and 95 °C. At a lower temperature (65 °C), there was still some starting OA, even after 5 h of reaction and a significant amount of intermediate products was found: epoxide (1.9 %), diol (<2 %) and aldehydes (14 %) along with a minor amount of non-quantified compounds. Raising the temperature above 90–95 °C

 Table 2
 Effect of the reaction temperature on the oxidative cleavage of OA with A, B and C

Catalyst	Temperature (°C)	χ _{OA} (%)	$Y_{\rm AA}~(\%)$	$Y_{\rm PA}~(\%)$
A	75	100.0	59.2	66.5
А	85	100.0	77.6	80.9
А	95	99.5	65.8	73.3
В	65	96.6	40.8	44.2
В	75	100.0	66.8	71.1
В	85	100.0	81.5	86.1
В	95	100.0	77.6	80.2
В	105	99.3	60.9	60.5
С	75	100.0	69.2	74.8
С	85	100.0	75.7	80.7
С	95	99.8	78.5	82.0
С	105	100.0	71.5	76.1
С	115	100.0	72.8	77.2

Reaction conditions: OA (65.0 mmol), H_2O_2 (325.0 mmol, 30 %), catalyst (1.2 mmol), 5 h, 400 rpm

generated a decrease in the desired products yields. This behavior is likely due to either the degradation of hydrogen peroxide at high temperature or the oligomerization of the expected acids. MS analysis confirmed the second hypothesis, as compounds exhibiting high molecular weights were detected in the crude reaction mixture (m/z = 332, 376, 587 and 761). The oligomerization was already observed but the masses obtained did not correspond to identified oligomers in the literature [16].

An optimal temperature of 85 $^{\circ}$ C was thus chosen for the rest of the study, associated with the catalyst B which gave the best results.

Effects of the Catalyst Load

To pursue the investigation of the process, we then studied the effect of the amount of catalyst on the yields. Experiments using a catalyst concentration over a range of 1-4 mol% were carried out at 85 °C with an OA/H₂O₂ molar ratio of 1/5.

Table 3 shows that a catalyst concentration of 2 mol% gave the best results. Noteworthy, at higher concentrations,

 Table 3
 Effects of the catalyst load on the oxidative cleavage of OA with the catalyst B

Catalyst load (mol%)	χοa (%)	$\begin{array}{c} Y_{\mathrm{AA}} \\ (\%) \end{array}$	Y _{PA} (%)	Aldehyde (%)	Epoxide (%)
1	100.0	69.3	68.3	1.6	0.8
2	100.0	81.5	86.1	1.6	1.6
4	100.0	70.9	62.3	0.0	1.1

Reaction conditions: OA (65.0 mmol), H_2O_2 (325.0 mmol, 30 %), 85 °C, 5 h, 400 rpm



Fig. 1 Effects of the agitation speed on the oxidative cleavage of OA with the catalyst B. Y_{AA} (filled rectangles), Y_{PA} (filled triangles)

the yields of AA, PA and intermediate products decreased. For example, there was no aldehyde left using 4 mol% of catalyst. Besides, the presence of oligomers was detected with MS analyzes (m/z = 332, 689 and 861).

Effects of the Mechanical Stirring Speed

The effect of the stirring speed on the oxidative cleavage at $OA/H_2O_2/[C_5H_5N(n-C_{16}H_{33})]_3\{PO_4[WO(O_2)_2]_4\}$ (1/5/0.02, by mol) was studied by varying the number of revolutions per minutes (rpm) of the mechanical agitation (Fig. 1).

The optimal speed agitation appeared to be around 400 rpm. Above this speed, a decrease in the acid yields was observed. This could be explained by the introduction of air bubbles in the media, which tends to decrease the contact of the substrate/oxidant. The observation of the increase of reaction volume with the agitation illustrated this hypothesis. An agitation speed of 400 rpm was kept for the rest of the study, as a stable emulsion, favoring the active species transfer at the interface during the reaction, was obtained along with a quite fast decantation afterwards.

Kinetic Investigation

A kinetic investigation was then performed to complete this study, using the optimized conditions. Samples of the reaction media were taken at various times and analyzed by GL C. The evolution in time of desired products (AA, PA) and intermediate products (epoxide, diol, aldehydes) was studied (Fig. 2). The sample, taken 10 min after the end of the H_2O_2 addition, showed that OA was almost totally consumed, confirming that the peroxo anion is efficiently transferred. Intermediates (epoxide, diol, aldehydes) were rapidly formed but disappeared slightly slower with time, which could explain the little shoulder on the AA and PA formation curves (between 20 and 60 min). Noteworthy, the maximum amounts of diol and aldehydes were obtained after the



Fig. 2 Relative areas evolution with time using OA (65.0 mmol), H_2O_2 (325.0 mmol, 30 %), catalyst B (1.2 mmol), 85 °C, 400 rpm. A_{AA}/A_{total} (filled rectangles), A_{PA}/A_{total} (filled triangles), $A_{epoxide}/A_{total}$ (open diamonds), A_{diol}/A_{total} (filled circles), $A_{nonanal}/A_{total}$ (-), $A_{9-oxo-nonanoic}$ acid/ A_{total} (+). The end of the H_2O_2 addition was considered as time 0

maximum amount of epoxide, which thus appears to be the first intermediate of the intrinsic oxidation reaction.

In the literature, different pathways have been described for the oxidative scission of oleic acid or of the methyl ester (comprising one to four steps) [2, 11]. In our case, this study clarified the mechanism: OA was oxidized to the epoxide form, followed by the ring opening and the oxidative cleavage. Thus, the species presented in the organic phase were OA, epoxide, diol, aldehydes, AA and PA.

Influence of the Treatment

In the previous papers reporting the use of catalysts A, B and C, the extraction solvents used appeared to be harmful (dichloromethane [10, 17] or diethyl ether [1, 9, 18]). In contrast, ethyl acetate, which has already been used with an other oxidant system [19], is safer and was thus chosen for the optimization of the treatment after the oxidative cleavage reaction. Two protocols with ethyl acetate were tested: one at room temperature and the other one at a temperature below 4 °C by cooling the reaction mixture in an ice bath (Table 4).

The extractions performed at low temperature gave better results, with an increase in the yields of 5–7 %. Indeed, it is well-known that the acids formed are partially soluble in water, especially the di-acid (AA) (2.4 g L⁻¹ at 20 °C) [20]. Cooling the crude reaction mixture allowed their solubility in water to decrease and finally to get a better extraction of the organic molecules from the aqueous phase.

In addition, solubility tests of freshly prepared catalysts A and B were carried out and proved that at low temperatures (below 4 °C); catalysts A and B were almost insoluble either in water or in ethyl acetate. After a low temperature treatment, a filtration yields a recovery of

 Table 4
 Effects of catalyst preparation and temperature treatment on the oxidative cleavage of OA

Catalyst	Catalyst preparation method	Treatment temperature	Y_{AA} (%)	Y _{PA} (%)
A	b	RT	72.9	73.9
А	b	Ice bath	77.6	80.9
В	b	RT	71.8	70.9
В	b	Ice bath	81.5	86.1
С	b	RT	71.3	77.2
С	b	Ice bath	75.7	80.7

Reaction conditions: OA (65.0 mmol), H_2O_2 (325.0 mmol, 30 %), catalyst (1.2 mmol), 85 °C, 5 h, 400 rpm

35 % mol of B. In order to have an efficient recycling for the catalyst B, both the solid catalyst and the entire aqueous phase needed to be reused to obtained good yields (74.1 % of AA and 68.9 % of PA). The catalyst B has probably evolved but it is still active under its new form in the aqueous phase. This result is very interesting in terms of sustainable chemistry (limitation of effluent wastes) and for cost reduction (recovery).

Generalization of the Oxidative Scission to Other Substrates

Finally, the oxidative scission conditions were applied to four other substrates (Table 5; Fig. 3).

The first substrate, 9,10-epoxyoctadecanoic acid, is an epoxide. AA and PA were obtained in excellent yields (respectively 87.3 and 86.5 %) using our optimized conditions. To our knowledge, this is the first example of an epoxide cleavage using this oxidative system. These results

 Table 5 Oxidative cleavage of fatty substrates

Catalyst	Substrate	Conversion (%)	Mono-acid (%)	Di-acid (%)
B^{a}	LA	100.0	47.7	41.0 ^c
B ^b	LA	100.0	60.7	49.8 ^c
\mathbf{B}^{d}	Epoxide	98.9	87.3	86.5
B ^e	RA	99.9	60.8	83.2
\mathbf{B}^{a}	EO	99.9	62.3	68.6

Reaction conditions

 a Substrate (60 mmol), H2O2 (350 mmol, 5.8 equiv., 30 %), catalyst (1.2 mmol, 2 mol%)

 $^{\rm b}$ LA (22 mmol), H_2O_2 (220 mmol, 10.0 equiv., 30 %), catalyst (0.9 mmol, 4 mol%)

 $^{\rm c}$ The di-acid is exclusively AA as malonic acid is soluble in water (solubility at 20 $^{\circ}{\rm C}{\rm :}$ 73 g $L^{-1})$

 d Epoxide (51 mmol), H_2O_2 (255 mmol, 5 equiv., 30 %), catalyst (1.2 mmol, 2 mol%)

e RA (14 mmol), H2O2 (163 mmol, 30 %), catalyst (2 mol%)



showed that the epoxide derivative is one of the intermediates of the oxidative cleavage of double bonds.

Our second choice was linoleic acid (*cis*-9, *cis*-12 octadecadienoic acid, LA). Indeed, this acid bears two double bonds which can be cleaved leading to two diacids, azelaic and malonic acid and a monoacid, hexanoic acid. Good yields were obtained, thanks to the use of a double amount of hydrogen peroxide and catalyst, to cleave both of the double bonds of LA.

The following substrate was ricinoleic acid ((9Z,12R)-12-hydroxyoctadec-9-enoic acid, RA). This fatty acid, obtained from the castor oil, contains a hydroxyl on the hydrocarbon chain. It is interesting to note that the hydroxyl was mainly conserved: 3-hydroxynonanoic acid and azelaic acid were obtained in good yields (respectively 83.2 and 60.8 %) [21].

The last substrate was not an acid but a fatty acid ester: ethyl oleate (EO). The cleavage was successfully achieved with 62.3 % of mono-methyl azelate and 68.9 % of PA The process could be extended to other fatty acid esters derivatives.

Conclusion

This study revealed that the oxidative cleavage of OA was successfully achieved using a catalytic amount of

peroxo-tungsten complex Q_3 {PO₄[WO(O₂)₂]₄}, in the presence of hydrogen peroxide as an oxidant and without any organic solvent. The emulsifying system promoted the OA reactivity in a biphasic medium through the transfer of the active peroxo-tungsten complex. The surfactant power of fatty acids contributed to the stability of the emulsion. The study of the mechanism showed the successive formation of intermediate products (epoxides, diol, aldehydes).

It was proved that the catalytic activity of Q_3 {PO₄ $[WO(O_2)_2]_4$ depends on the type and the lipophily of the associated quaternary ammonium salt Q⁺, X⁻. The study of several parameters allowed us to provide optimized conditions for the oxidative scission. Thus, high AA and PA yields were obtained at 85 °C for 5 h with an OA/ $H_2O_2/[C_5H_5N(n-C_{16}H_{33})]_3\{PO_4[WO(O_2)_2]_4\}$ molar ratio of 1/5/0.02 associated with an in-situ protocol for the preparation of the catalyst. This in-situ protocol allows us to limit the loss of matter and the catalyst can be efficiently recovered thanks to a treatment at low temperature. Finally, this new process was generalized for the use of other starting acids, demonstrating that these conditions can be used to cleave several double bonds and even epoxides. This clean process could be easily extended to other fatty acids derivatives in order to obtain new short carbon chains for bio-based products.

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