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New perspectives of European oleochemistry
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Dossier

From crops to products for crops: preserving the ecosystem through the use of bio-based molecules

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Abstract – In a context of dwindling oil reserves and environmental pressures, the chemical industry needs to innovate by developing new processes for producing bioproducts from raw plant materials. Unsaturated fatty acids from vegetable oils constitute a highly promising renewable resource that can be used to diversify productions, decreasing reliance on petroleum. A starting material rich in oleic acid has been obtained through the selection of high-oleic sunflower varieties and enzymatic hydrolysis of the oil they produce. The double bonds of this unsaturated raw material have been cleaved in green oxidizing conditions involving a biphasic lipophilic-aqueous system including hydrogen peroxide as an oxidant and a peroxo-tungsten complex $Q_3\{PO_2[WO(O_2)_2]_4\}$ as a phase-transfer catalyst (PTC) and co-oxidant. This PTC efficiently transferred oxygen to the substrate in the lipophilic phase. A mono-acid (pelargonic acid) and a di-acid (azelaic acid), with shorter, unusual hydrocarbon chains not present in the natural state, were synthesized and purified through an intensive process. Pelargonic acid was then formulated as an environmentally friendly biocontrol agent for weeds. We extended this green process of oxidative scission to other fatty acids and derivatives, to obtain other short-chain acids with diverse potential applications. This production chain (crops, reaction and purification processes, products, applications) is based on a sustainable development strategy.

Keywords: Oxidative scission / oleic acid / green process / ecodesign / biocontrol

Résumé – De la plante aux bioproduits destinés au biocontrôle : préserver l'écosystème par l'utilisation de molécules biosourcées. Dans un contexte de diminution des réserves fossiles et de pressions réglementaires et environnementales, l'industrie chimique tend à innover en développant de nouveaux procédés pour la production de bioproduits d'origine végétale. Les acides gras insaturés d'une huile végétale constitue une ressource renouvelable prometteuse qui peut être utilisée pour diversifier les productions et réduire la dépendance vis-à-vis du pétrole. Dans cet article, une matière première riche en acide oléique a été obtenue par l'hydrolyse enzymatique de l'huile de tournesol hautement oléique, obtenue par sélection variétale. Les doubles liaisons de cette matière première insaturée ont été clivées dans des conditions oxydantes impliquant un système biphasique aqueux-lipophile, avec le peroxyde d'hydrogène comme oxydant et le complexe peroxo-tungtène $Q_3\{PO_2[WO(O_2)_2]_4\}$ comme catalyseur de transfert de phase (CTP) et co-oxydant. Ce CTP a permis d'assurer un transfert efficace vers le substrat en phase lipophile. Un mono-acide (acide pélargonique) et un di-acide (acide azélaïque) à chaînes impaires plus courtes, peu présentes à l'état naturel, ont été ainsi synthétisés et purifiés grâce à un procédé intensifié. L'acide pélargonique a été formulé en tant qu'agent de biocontrôle écocompatible. Ce procédé vert de scission oxydante a été appliqué à d'autres acides gras et à leurs dérivés pour obtenir de nouveaux acides à chaînes courtes ayant différentes applications potentielles. Cette filière de production (culture, procédés de transformation et de purification, produits et leurs application) est basée sur une stratégie de développement durable.

Mots clés : Scission oxydante / acide oléique / procédé vert / écoconception / biocontrôle

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1 Introduction

Unlike petrochemical feedstocks, oilseeds from cultivated plants can provide oxygen-containing molecules (*e.g.* triglycerides) without damage to the ecosystem or human health. Sunflower was imported from America by Spanish settlers in the 16th century, and a tradition of sunflower cultivation has become established in southern Europe. Sunflower (*Helianthus annuus*) is an annual plant cultivated principally for its oil-rich seeds. In addition to their high oil content (about 44% of the whole seed), these seeds also contain usefully large amounts of protein (18%) and cellulose (about 15%) (Borredon *et al.*, 2011).

Conventional sunflower oil contains high levels of unsaturated fatty acids essential for humans: 50–73% linoleic acid (C18:2), also known as omega-6, and 13–36% monounsaturated oleic acid (*cis*-9-octadecenoic acid or C18:1), also known as omega-9 (Codex). These two fatty acids account for more than 85% of the composition of the oil. Sunflower oil also contains a remarkably large amount of alpha-tocopherol or vitamin E (50 to 60 mg per 100 g oil), which has antioxidant properties (Ayerdi-Gotor *et al.*, 2016).

In recent years, plant breeders have modified the unsaturated fatty acid contents of oilseed crops, to develop new industrial markets for both food and other products. This diversification has included the development of high-oleic sunflower, which has a number of industrial applications, through chemical transformations into bio-based products.

ARTERRIS (France) has developed a number of sunflower varieties with a "high oleic" acid content (87–88%), OLEIS with a "very high" oleic acid content (90–92%) and LINOLEIS which is enriched in linoleic acid (72%). The oils from these varieties are innovative high added-value products reducing the reliance of the processing industry on imported oils. Note that other works aim to develop new sources of high oleic oils in the seed and fruit oils such as very high-oleic rapeseed varieties called "canola" with about 84% of C18:1 and a low level of polyunsaturated fatty acids (6%) (Baudoin *et al.*, 2014; Murphy *et al.*, 2014). In the field of biotechnology, oleic oils are also prepared from yeast (Tsakraklides *et al.*, 2016). This research allows to diversify the starting substrates to supply the same production chains in functional compounds.

We describe here one example of the development of a non-food application for high-oleic sunflower oil (Fig. 1), revealing the potential of unsaturated fatty acids in commercial oils for the generation of other platform molecules as valuable intermediates for the preparation of end-products.

2 Characterization and pretreatment of the oils used as raw materials

2.1 Oil analysis

A sunflower oil can be characterized by its fatty-acid profile, by gas chromatography, as described below. We analyzed and quantified the triglycerides present in the samples 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 µm) was purchased from Varian (USA). The carrier gas was helium (Air Liquide, France), at a pressure of 15 psi at the head of the column. The injector and detector temperatures were 250 °C. Oven temperature was held at 185 °C for 40 min, then ramped up to 250 °C at a rate of 15 °C.min^{-1} and set at 250 °C for 10 min (55 min in total).

Triglycerides and free fatty acids were converted to fatty acid methyl esters (FAMEs) with TMSH (trimethylsulfonium hydroxide). We dissolved about 20 mg of sunflower oil in 1 ml of MTBE (methyl tert-butyl ether). We added 100 µl of this solution to 50 µl of 0.5 mol.l^{-1} TMSH in methanol.

Table 1 shows the fatty-acid composition of three sunflower oils. The triglyceride composition of sunflower oil can be determined as described by Perrin and Prévot (1986). Trilinoleate dominates the triglyceride composition of conventional sunflower oil (Multon *et al.*, 1997). Finally, for the vegetable oils, the acid value (AV) is used to quantify free-fatty acid content (AFNOR, 2009), and the iodine value (IV) indicates the degree of unsaturation (AFNOR 2013). For a typical high-oleic sunflower oil, the acid value is below 2 mg KOH/g oil and the iodine value is between 80 and 90 g of iodine per 100 g of oil (Dufaure *et al.*, 1999).

2.2 Enzymatic hydrolysis of high-oleic sunflower oil

High-oleic sunflower oil (supplied by ARTERRIS) is a source of oleic acid, a raw material for production processes that is rich in unsaturated compounds. The double bonds of these compounds can be used as reaction centers for the production of high-value compounds.

This vegetable oil (22.5 kg) was hydrolyzed (Fig. 2) with the *Candida cylindracea* lipase in distilled water (20.1 kg), at 40 °C for 5 h, with stirring, (Valentin *et al.*, 2013). The fatty-acid composition of the hydrolysate was determined by gas chromatography, to check that there were no residual triglycerides present. Glycerol is used as a building block (Mouloungui, 2004), leaving the fatty acids available for the oxidative scission process.

2.3 Oxidative cleavage of monounsaturated acids

Oleic acid, a monounsaturated fatty acid obtained from high-oleic sunflower oil, is a useful platform molecule for the chemical industry (Turnwald *et al.*, 1998). It can be used for processes involving C=C transformations, such as epoxidation, hydroxylation and oxidative cleavage. Oxidative scission is a particularly attractive process, as it generates C9 products, such as aldehydes (Pouilloux *et al.*, 2014) and acids (Godard *et al.*, 2011; Köckritz *et al.*, 2010). These short-chain aldehydes and acids are particularly useful platform molecules for the preparation of numerous bio-based products. For example, C9 aldehyde (methyl azelaaldehydate) can be converted into a monomer for the polymer industry, by hydrogenation or reductive amination. C9 di-acid (azelaic acid or nonanedioic acid) can be transformed into different esters for the preparation of polymers (nylon 6:9), plasticizers, biodegradable lubricants (Emery Oleochemicals GmbH), adhesives, solvents,

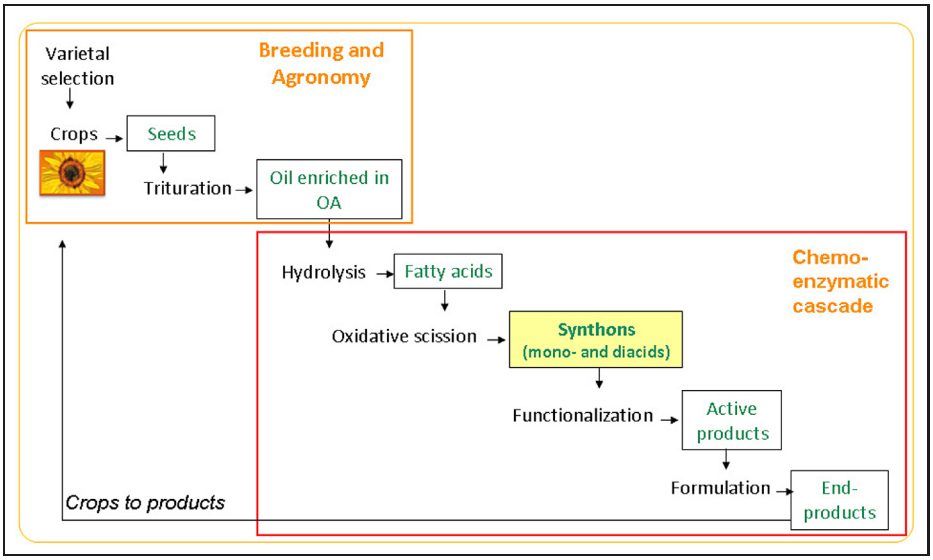

Fig. 1. Sequence of steps in the production chain developed in the OLEOVISION project.

Table 1. Characterization of three sunflower oils.

Fatty acid profiles	Conventional sunflower oil (SO)	Oleic acid-rich sunflower oil (OSO)	High-oleic sunflower oil (HOSO)	Very high-oleic sunflower oil (VHOSO)
Palmitic acid C16:0	6.3	4.0	3.5	3.3
Stearic acid C18:0	3.6	2.8	3.0	1.5
Oleic acid C18:1 (n-9)	30.2	82.9	87.6	90.4
Vaccenic acid C18:1(n-7)	0.0	0.0	0.0	1.0
Linoleic acid C18:2(n-6)	58.7	8.9	4.8	2.5
Arachidic acid (C20:0)	0.3	0.2	0.2	0.2
Eicosenoic acid C20:1 (n-9)	0.3	0.3	0.1	0.3
Behenic acid C22:0	0.7	0.8	0.8	0.7

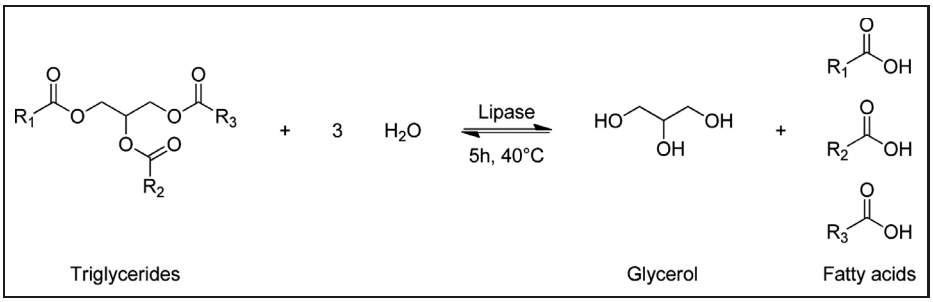

Fig. 2. Hydrolysis of triglycerides.

corrosion inhibitors, and anti-acne agents for cosmetics (Telos *et al.*, 1999; Sefton, 2001). The mono-acid (pelargonic acid or nonanoic acid) is an intermediate in the production of lubricants, plasticizers (Emery Oleochemicals GmbH), perfumes, herbicides, fungicides, and resins (Noureddini *et al.*, 1996). Pelargonic acid is a fatty acid naturally present in the leaves of certain plants and in animal fats. It was first extracted from the leaves of *Pelargonium roseum*, from which it takes its name.

We focused on the oxidative cleavage of unsaturated fatty acids to yield unusual short-chain monocarboxylic and dicarboxylic acids that are rare in nature and are currently produced from fossil resources for industrial applications (Fig. 3).

2.4 Progress in methods for oxidizing unsaturated fatty acids

Several routes of oxidation have been described for oleic acid and its methyl ester. Depending on the operating conditions used, different pathways have been reported, for which reaction intermediates can be observed or isolated (Fig. 4): the

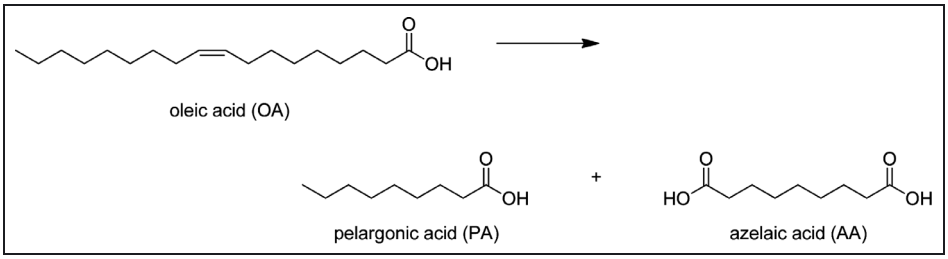

Fig. 3. Oxidative cleavage of oleic acid.

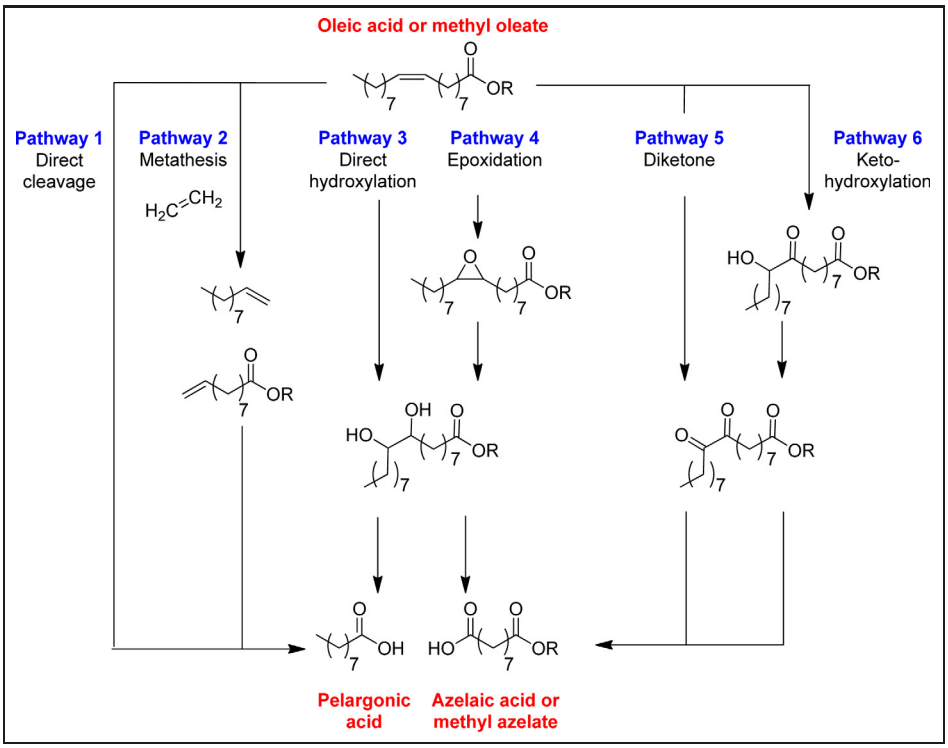

Fig. 4. Oxidative cleavage of oleic acid or methyl oleate.

direct cleavage of the C=C bond in a one-step reaction (pathway 1) or multi-step procedures, *via* the formation of a diol intermediate (obtained either directly (pathway 3, Bieser *et al.*, 2012; Lemaire *et al.*, 2013), or from an epoxide intermediate (pathway 4, Lemaire *et al.*, 2016), *via* a diketone intermediate (obtained either directly (pathway 5, Knothe *et al.*, 2002; Rup *et al.*, 2009) or from an intermediate ketol (pathway 6, Kulik *et al.*, 2014; Turnwald *et al.*, 1998), or *via* a terminal unsaturated fatty acid obtained by metathesis with ethylene (pathway 2, Corma *et al.*, 2007).

The first oxidation systems for cleaving the double bond of oleic acid (or its derivatives) were discovered in the late 19th century and were massively developed in the middle of the 20th century. These systems were based on chromic acid, nitric acid, potassium permanganate, periodates ($NaIO_4$), potassium peroxymonosulfate (Oxone®), peracids (performic acid), or hypochlorites (NaOCl) (Tab. 2). However, most of these conventional oxidants are hazardous and not environment-friendly, as they generate unwanted by-products and the yields of the desired compounds are low. Another oxidant, ozone, was chosen for the synthesis of methyl azelaaldehydate from methyl oleate (Pouilloux *et al.*, 2014) and the large-scale production of AA and PA from oleic acid. These reactions are very selective and yields are high, but they are expensive and have environmental drawbacks (energy consumption, toxicity, explosion hazard) (Zaldman *et al.*, 1998). Hydrogen peroxide has been identified as an interesting alternative to ozone. Indeed, this agent is highly reactive (high percentage of "active" oxygen), benign, cheap and, unlike most oxidation systems, it does not generate waste or polluting effluents.

In this study, we aimed to develop an oxidative cleavage process that was effective, selective, readily applicable at an industrial scale and fulfilling the principles of sustainable chemistry. These criteria led us to focus on an oxidation system based on hydrogen peroxide and a phase-transfer catalyst to transfer the oxidant from the aqueous to the organic phase. Under these conditions, the oxidation reaction takes place in an organized reaction medium favoring the transfer of mass and energy between the aqueous and organic phases. The use of such a system therefore eliminates the need to use an organic solvent, consistent with the requirements of green chemistry.

Table 2. Major oxidants and associated catalysts.

Oxidant	Oxidative catalytic agent	References
O_3	–	Rebrovik *et al.*, 1995
HNO_3	MnO_2 or NH_4VO_3	Ellingboe *et al.*, 1940; Price, 1944
H_2CrO_4	–	Johnson *et al.*, 1989
$KMnO_4$	–	Abboud *et al.*, 2011
$NaIO_4$	$KMnO_4$	Lemieux *et al.*, 1955
$NaIO_4$	RuO_4 or $RuCl_3$	Miyamoto *et al.*, 2009, Baümer *et al.*, 2003
NaOCl	RuO_4	Foglia *et al.*, 1977
Oxone®	OsO_4	Whitehead *et al.*, 2006
Performic acid	$K_2OsO_2(OH)_4$	Kocritz *et al.*, 2009
O_2	MCM-41 (in SC-CO_2)	Dapurkar *et al.*, 2009
H_2O_2	$H_3PW_{12}O_{40}$/PTC	Fujitani *et al.*, 1998, Noyori *et al.* 2003, Godard *et al.*, 2013a
H_2O_2	Alkylated polyethylene-imine/$\{PO_4[WO(O_2)_2]_4\}^{3-}$	Haimov *et al.*, 2004

2.5 Study of a process for the oxidative scission of oleic acid using tungsten peroxo-complexes

We hypothesized that the target process with the H_2O_2/phase transfer catalyst oxidative system would be cheaper and safer than ozonolysis (the only operational industrial process), while maintaining a high reaction yield and selectivity.

The oxidative scission of oleic acid (OA prepared from HOSO hydrolysis) with the $H_2O_2/Q_3\{PO_4[WO(O_2)_2]_4\}$ system was optimized by reducing the number of reaction steps, determining the most favorable operating conditions for oxidative scission and developing a more effective and environmentally friendly way of treating the reaction medium to separate and purify azelaic acid (AA) and pelargonic acid (PA).

The reactions were monitored by gas chromatography, as follows. The samples were analyzed and quantified 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 µm) was purchased from Varian (USA). The carrier gas was helium (Air Liquide, France), at a pressure of 15 psi at the head of the column. The injector and detector temperatures were 250 °C. Oven temperature was held at 100 °C for 5 min, then ramped up to 180 °C at a rate of 5 °C.min^{-1}. It was then maintained at 180 °C for 10 min, increased to 250 °C at a rate of 10 °C.min^{-1}, and maintained at this temperature for 5 min (43 min in total). All samples (10 mg ml^{-1} dissolved in MTBE, 50 µl) were converted to FAME by reaction with TMSH (50 µl). Pentadecanoic acid was added as an internal standard (2 mg ml^{-1}). With this analytical procedure, we were able to calculate the conversion of OA, the yields of PA and AA and of some of the intermediate products, such as aldehydes (nonanal and 9-oxo-nonanoic acid) and epoxides (9,10-epoxyoctadecanoic acid).

Hydrogen peroxide was an effective oxidant in this system, as oleic acid underwent oxidative cleavage with a catalytic amount of a peroxo-tungsten complex in the presence of hydrogen peroxide, without the need for an organic solvent. The catalytic cycle responsible for the oxidative cleavage of an alkene in the presence of tungstophosphoric acid and hydrogen peroxide is described in Figure 5. In the reaction medium containing hydrogen peroxide and OA, the PTC was transformed *in situ* into a peroxo complex $Q_3\{PO_4[WO(O_2)_2]_4\}$. Due to its lipophilic nature, the pyridinium ion can efficiently transfer the peroxo anion, which becomes the co-oxidant. This anion is converted into an oxo-complex in the oxidation reaction but has the advantage of being regenerated in the aqueous phase by reaction with hydrogen peroxide. The addition of this phase-transfer catalyst turned out to be essential to ensure the compatibility of the biphasic "oleic acid (reagent)/hydrogen peroxide (oxidant)" system. It mediated the transfer of oxygen from the aqueous phase to the organic phase, and increased the area of contact between the two phases, through the formation of an oil-in-water emulsion. The partial solubility of the fatty acids in water also contributed to the quality of the emulsion.

Kinetic studies at different temperatures showed the successive formation of synthesis intermediates (epoxide, diol, aldehyde), thus confirming the oxidative cleavage mechanism: OA oxidation to the epoxide form, followed by ring opening and the oxidative cleavage. By studying several operating parameters, we were able to define conditions favorable for the oxidative scission of oleic acid (Tab. 3). The best yields of AA and PA (81.5% and 86.1%, respectively), were obtained for heating at 85 °C for 5 h, with the AO/H_2O_2/$[C_5H_5N(n\text{-}C_{16}H_{33})]_3\{PO_4[WO(O_2)_2]_4\}$ system, corresponding to a molar ratio of 50/250/1, coupled with *in situ* catalyst preparation (Godard *et al.*, 2013b). It means that hexadecylpyridinium chloride was used for the preparation of the peroxo-tungten complex. Preparation of the catalyst *in situ* limits the loss of material and overcomes the need for preliminary preparation and purification stages. This is a key advantage in terms of the potential industrialization of the process. Furthermore, the two-phase (fatty acid/water) medium facilitates post-reaction treatment, because the oxidizing agent is removed by decantation. A final low-temperature treatment makes it possible to recover and recycle the catalyst.

The method used to purify the two acids (PA and AA) took into account their physical-chemical properties (Tab. 4). The monoacid (PA) and the diacid (AA) were purified by extraction of the aqueous phase with ethyl acetate. The organic phases were pooled and dried with anhydrous sodium sulfate. PA was obtained by vacuum distillation, with a purity of 92%. The distillation residue was recovered and dissolved in water for the crystallization of AA, which was obtained with a purity of 94%. Figure 6 shows the sequence of steps in the oxidative cleavage of oleic acid. The diagram indicates how material

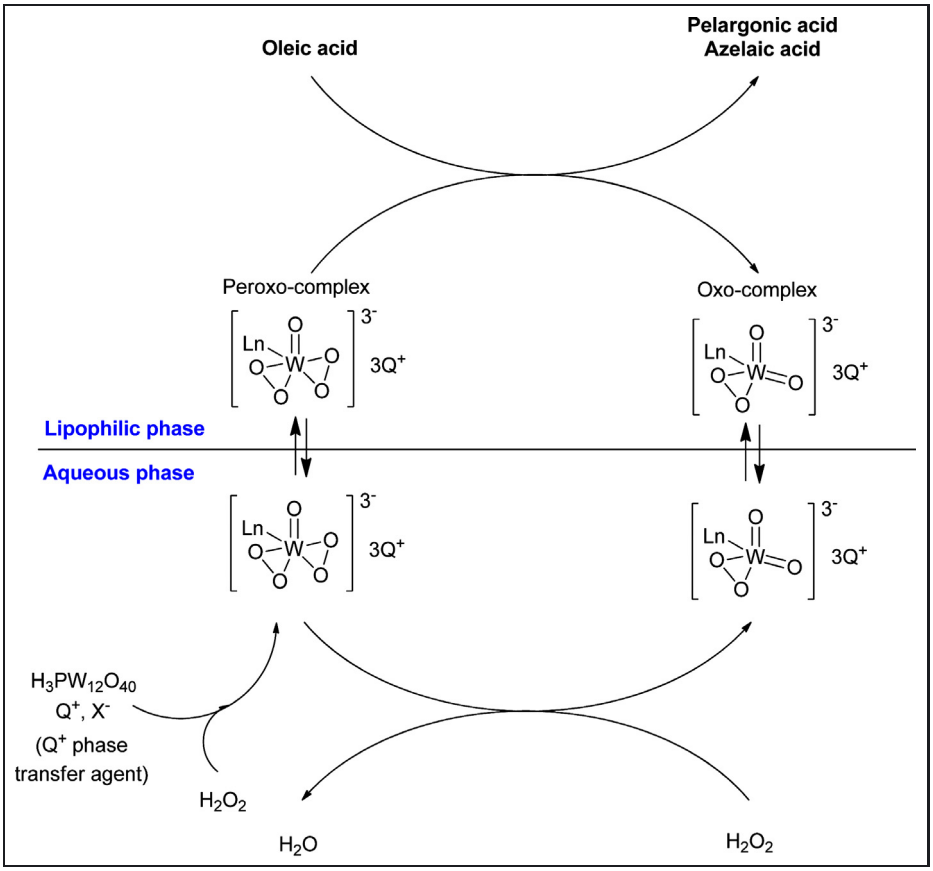

Fig. 5. Catalytic cycle for the oxidative cleavage of oleic acid.

Table 3. Activity of catalytic peroxo-complexes on the oxidative scission (Godard *et al.*, 2013a, b).

Catalyst system	X^-	χ_{OA} (%)	Y_{AA} (%)	Y_{AP} (%)
		38.1	1.8	2.2
$[MeN(n\text{-}C_8H_{17})_3]_3\{PO_4[WO(O_2)_2]_4\}$	Cl^-	100	75.7	80.7
$[n\text{-}Bu_4N]_3\{PO_4[WO(O_2)_2]_4\}$	Cl^-	100	77.6	80.9
$[(n\text{-}C_8H_{17})_4N]_3\{PO_4[WO(O_2)_2]_4\}$	Cl^-	100	73.2	76.5
$[C_5H_5N(n\text{-}C_{16}H_{33})]_3\{PO_4[WO(O_2)_2]_4\}$	Cl^-	100	81.5	86.1

Conditions: $AO/H_2O_2/Q_3\{PO_4[WO(O_2)_2]_4\}$ (1/5/0,02), 85 °C, 5 h, 400 rpm. Standard deviation (3 analyses) between 0.1 to 3.9%.

Table 4. Physical-chemical characteristics of azelaic acid and pelargonic acid.

	Appearance	Density (20 °C) (g/mL)	Melting point (°C)	Boiling point (°C)	Solubility in water (g/l)	pKa (25 °C)
Azelaic acid (AA)	white solid	1.443	109–111	286 $^{100\ mm\ Hg}$	2.14	4.550 and 5.498
Pelargonic acid (PA)	clear yellow oily liquid	0.905	12.4	254.5	0.30	4.95

flows are organized to intensify the global process and minimize waste.

Finally, this process has the advantage of being applicable to other fatty acids with several double bonds and/or hydroxyl groups on the chain, unsaturated fatty acid esters and epoxides (Fig. 7). This process is not stereospecific, and is suitable for compounds containing *cis* or *trans* double bonds.

For linoleic acid (technical grade, 62%), scission of the two double bonds was achieved with double the amount of hydrogen peroxide and catalyst; two diacids (malonic acid and AA with a yield of 49.8%) and a monoacid, hexanoic acid (with a yield of 60.7%) were obtained. As malonic acid is soluble in water, it was not quantified. From ricinoleic acid, 3-hydroxynonanoic acid and AA were produced, with yields of 83.2% and 60.8%, respectively. Finally, the oxidative scission

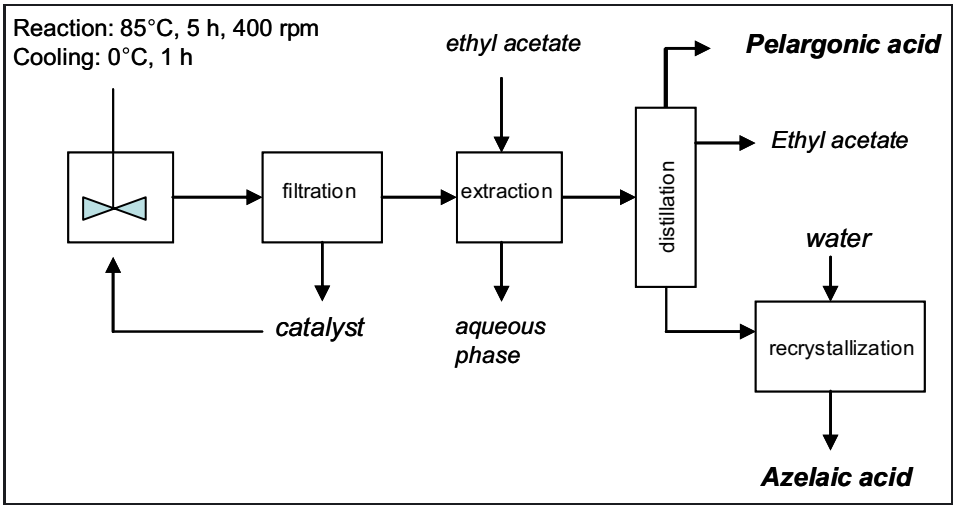

Fig. 6. Patented process for the oxidative scission of oleic acid (Godard *et al.*, 2013a).

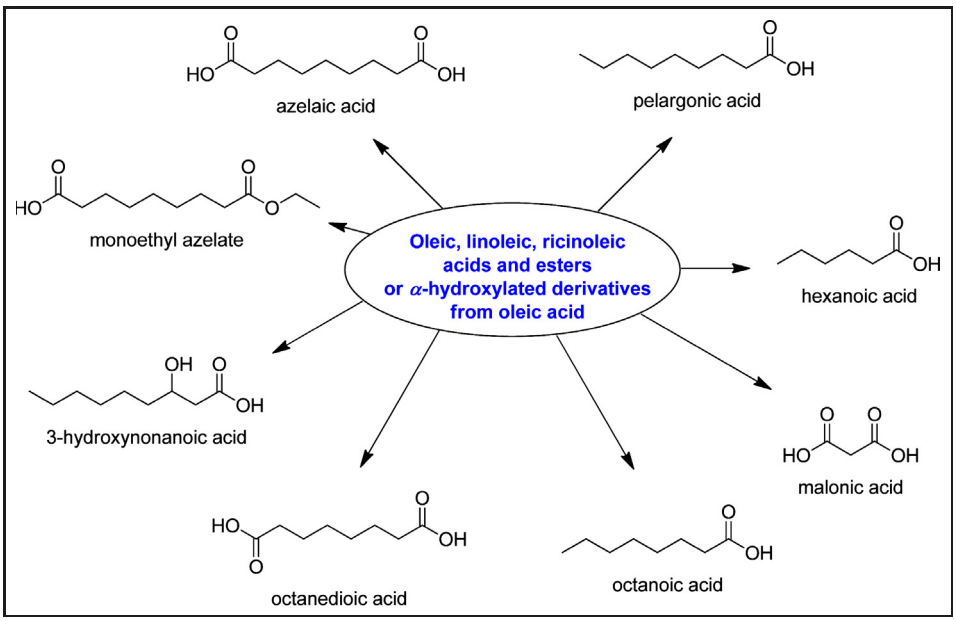

Fig. 7. Panel of bio-based acids and diacids synthesized through homogeneous catalysis.

conditions were also applied to other substrates prepared by the hydroxylation of OA ((E)-9-hydroxyoctadec-10-enoic and (E)-10-hydroxyoctadec-8-enoic acids), leading to the production of octanoic acid and octanedioic acid, each with a yield of 70%.

We tested a process with a supported catalyst system in a solvent-free medium, as a means of simplifying catalyst recycling. The polyoxotungstate $PW_{12}O_{40}^{3-}$ anion and the peroxopolyoxotungstate $\{PO_4[WO(O_2)_2]_4\}^{3-}$ anion (active species of the catalyst) were supported on three types of anion exchange resin; Amberlite IRA 900, Lewatit K 7367 and Merrifield resin modified *via* a nucleophilic substitution by 1,3-(8-hydroxydioctyl)-2-methylimidazole as a spacer group (Poli *et al.*, 2011).

Oxidative scission of oleic acid in the solvent-free and biphasic medium was observed only with the modified Merrifield resin, with a yield above 30%. These resins are amphiphilic and contain a spacer, facilitating access to the cationic sites of the resin. The results of these preliminary experiments are encouraging, by showing the possibility to work with supported catalysis systems, more suitable for scaled-up processes. The two other resins tested (Lewatit K7367 and Amberlite IRA 900) were found to be efficient catalysts for another type of functionalization of the double bond of oleic acid (acetalisation, Fig. 8) in the presence of a reactant/solvent as described by Godard (2014).

In summary, the oxidative scission process was intensified by phase transfer catalysis. This technology made it possible for all the chemical reactions to take place in the same reactor, by favoring contact between chemical species at the lipophilic/hydrophilic interface.

The whole cycle is thus monitored, from the crop to the purification of functional products (AA and PA).

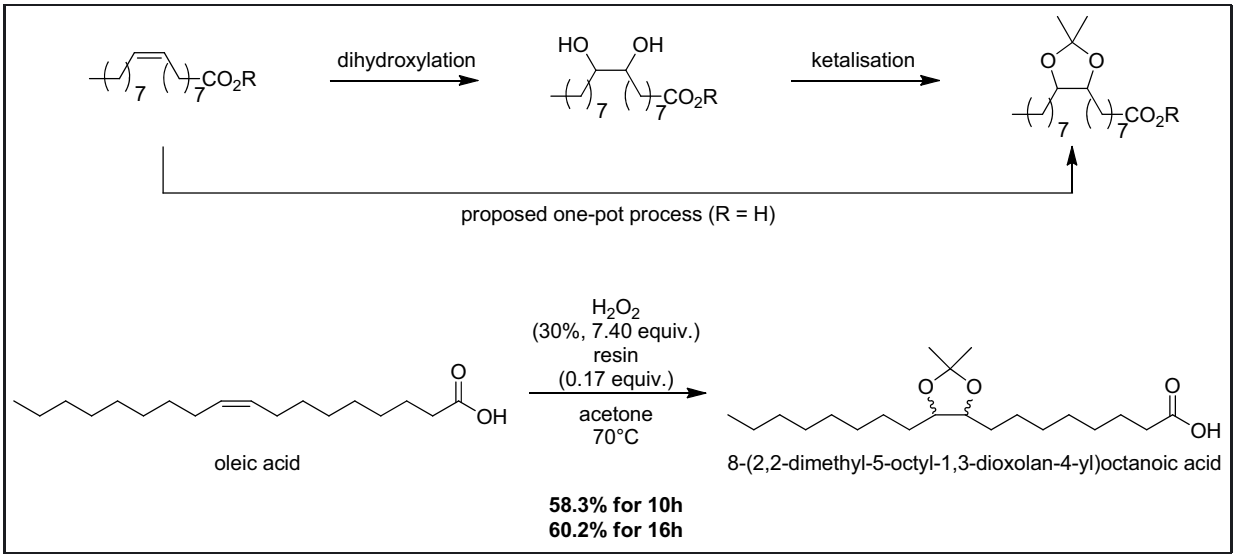

Fig. 8. Synthesis of an acetal from oleic acid (Godard *et al.*, 2014).

3 Assessment of the ecocompatibility of the process

Process efficiency has long been evaluated on the basis of chemical yield, regardless of the by-products formed and the waste generated. The concept of green chemistry was developed in the early 1990s (Anastas, 1998), to address current environmental concerns. Green chemistry aims to develop products and chemical processes reducing or eliminating the use and synthesis of toxic substances. Green indicators (green metrics) were created to quantify the environmental impact of chemical transformations. They are used to check the expected environmental gain from the syntheses of renewable bioproducts. We thus calculated green indicators to determine how environmentally friendly the process developed was, relative to other oxidative scission processes for oleic acid. The indicators used were atom economy (AE), as defined by Trost (1995), and the environmental factor (E-factor) introduced by Sheldon (1997, 2007). The limiting reactant is oleic acid, and the co-reactants are the oxidizing agent and the catalytic co-oxidant. PA and AA were considered to be two valuable products. The process developed includes *in situ* catalyst formation, followed by cold treatment for recovery of the catalyst by filtration, the mono- and di-fatty acids being extracted with ethyl acetate (Fig. 9).

The objective was to compare the environmental impacts of the process developed here with three other previously reported methods including Emery ozonolysis process. The method developed by Pai (2005) involves the oxidation of oleic acid with the same oxidizing system $H_2O_2/Q_3\{PO_4[WO(O_2)_2]_4\}$ as in our process, but with a catalyst formed *ex situ*, with a treatment performed at room temperature and an extraction of fatty acids with dichloromethane.The second process, developed by Abboud (2011), uses a conventional oxidizing agent, potassium permanganate, and sodium oleate (NaOA) as the substrate. At the end of the reaction, sulfuric acid is added to generate the acids, which are extracted at room temperature with ethyl acetate. As for ozonolysis process currently applied to the oxidative scission of oleic acid, according to the patent of Brown (1957), it requires a thorough control of various parameters (Walker, 2014). A part of the PA is used to fluidize the mixture oleic acid /ozone in the contact area. The patent states that in the reactor at 100 °C, 500 g of OA subjected to a countercurrent stream of O_3/O_2, leads to 200 g of PA and 260 g of AA. In the final medium, 20% of by-products (alcohols, aldehydes, other acids) are found. The corresponding weight (115 g) will be the only waste considered for the calculation of the E-factor.

Atom economy (AE) reflects the incorporation of the reagents into the final product. It is calculated from the molar mass of the reactants and products. An atom economy of 100% indicates that the reaction is waste-free, with no loss of carbon.

In our process and in that developed by Pai, the equation for the reaction and the AE are as follows:

$$OA + 3H_2O_2 \rightarrow AA + PA + 2H_2O_2,$$

$$AE = \frac{M_{AA} + M_{PA}}{M_{AA} + 3M_{H_2O_2}} \times 100.$$

In the case of oxidation with potassium permanganate, the reaction equation can be written as follows:

$$3NaOA + 8KMnO_4 + 4H_2O + 2H_2SO_4$$
$$\rightarrow 3AA + 3PA + 8KMnO_2 + 8KOH + Na_2SO_4 + NaHSO_2.$$

None of the products generated other than azelaic acid and pelargonic acid can be recovered. The unrecoverable products are considered to be waste. Carbon economy can therefore be calculated as follows:

$$AE = \frac{3M_{AA} + 3M_{PA}}{3M_{NaAO} + 8M_{KMnO_4} + 4M_{H_2O} + 2M_{H_2SO_4}} \times 100.$$

In the case of ozonolysis, we consider the reaction equation below, with a slight excess of oxidant consumed for the formation of both products and by-products.

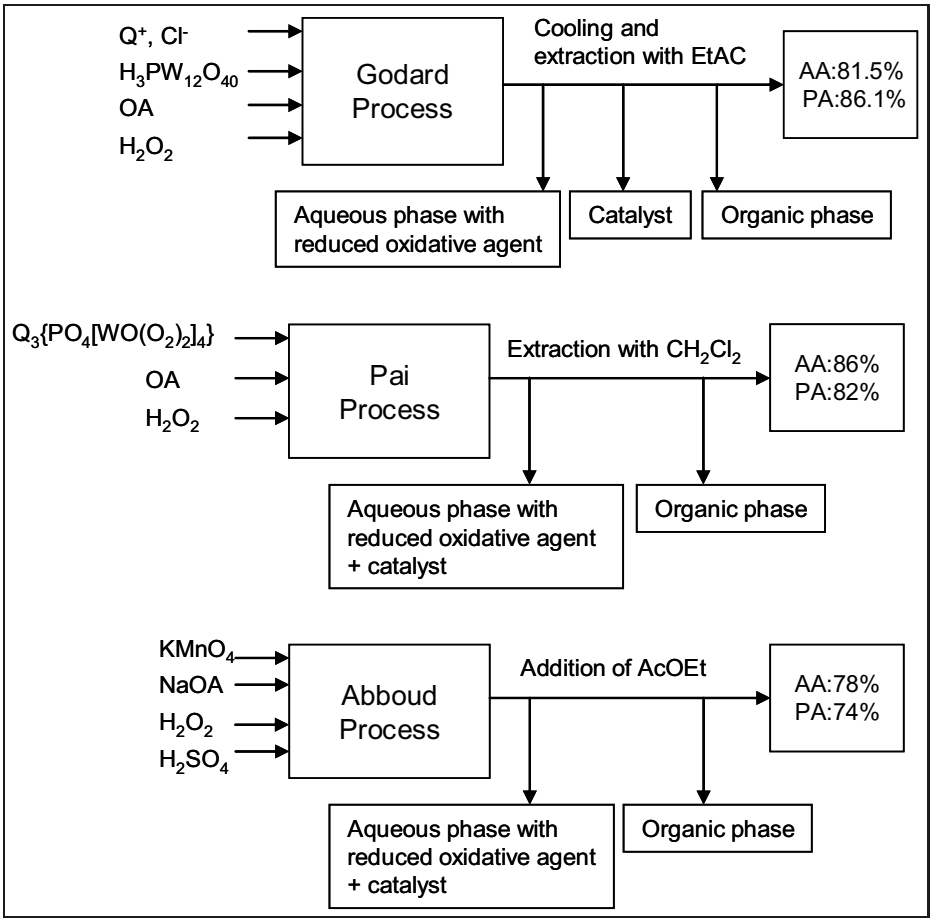

Fig. 9. Processes developed by Godard *et al.* (2013a), Pai (2005), and Abboud (2011).

$$OA + O_3/O_2 \rightarrow AP + AA + \text{mixture of by-products}$$

$$AE = \frac{M_{PA} + M_{AA}}{M_{OA} + M_{O_3} + M_{O_2}} \times 100.$$

The environmental factor or E-factor is used to assess the environmental impact of a chemical process, by comparing the amount of waste generated with the amount of product formed, as follows:

$$E_{\text{factor}} = \frac{\sum_i (m_{\text{waste}})_i}{m_{\text{product}}}$$

m_{waste}: mass of waste i (kg), m_{product}: mass of product (kg).

Lower environmental factor values indicate lower levels of waste. The calculation is based on the balance of masses at the reactor outlet. Are regnonized as wastes, synthetic intermediates (epoxide, aldehyde, diol), extraction solvents, catalysts, unreacted OA and the products resulting from the reduction of the oxidizing agent. The extraction solvents (ethyl acetate or dichloromethane) are recycled once, for a second reaction, which halves the mass of waste. For our process, the catalyst can be recycled once, through the cold treatment. The aqueous phase is also recycled, so only half the hydrogen peroxide (5 eq., corresponding to the oxidant) is introduced to start the second oxidation. Finally, the weights of the products (AA and AP) are calculated according to the new yield obtained with catalyst recycling. For the other two processes, no recycling of the oxidant and/or catalyst was envisaged by the authors.

Table 5. Comparison of green indicators.

Process	AE (%)	E_{factor}
Godard	90.1	13.0
Pai	90.1	16.3
Abboud	42.5	49.9
Emery Process	83.7	0.25

Table 5 shows that our process and that of Pai which involve the same oxidizing system ($H_2O_2/Q_3\{PO_4[WO(O_2)_2]_4\}$), have identical atom economy values. These oxidative scission conditions resulted in high atom economy values, slightly better than the conventional oxidizing system (ozonolysis). Indeed the formation of by-products corresponding to a lower selectivity of this process explains the decrease of AE. For the scenario including a single recycling, the E-factor of our process was lower than that of the Pai process. The method developed by Abboud generates larger amounts of waste, mainly due to the choice of oxidizing agent (potassium permanganate) and substrate (sodium oleate). Pai's method also generates larger amounts of aqueous phase, due to greater hydrogen peroxide consumption, for both oxidation and catalyst synthesis. Ozonolysis process has the advantage

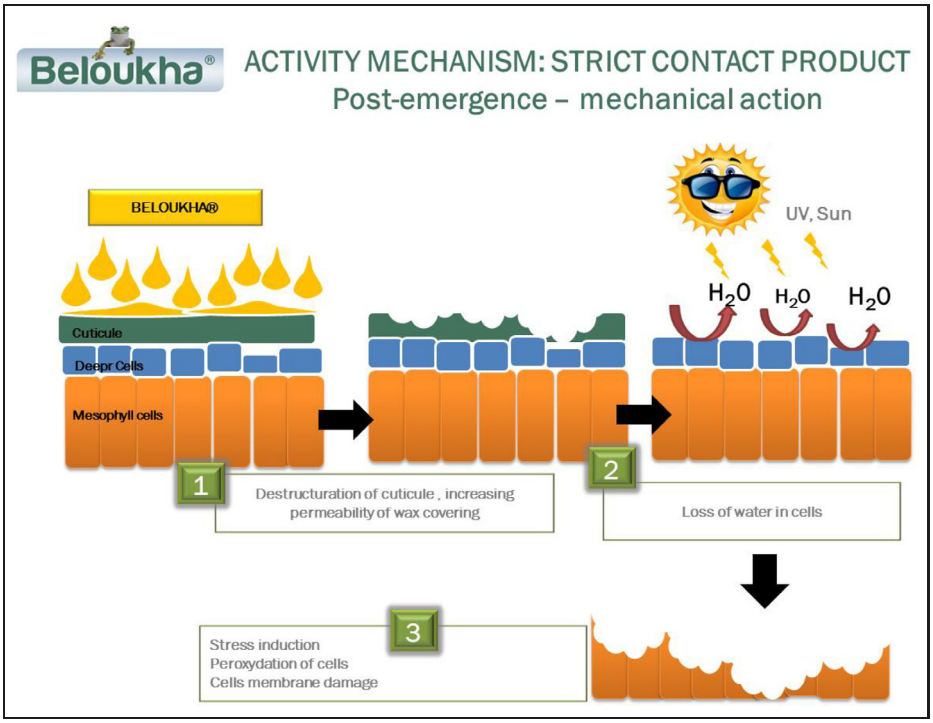

Fig. 10. Action of Beloukha®, a herbicide based on pelargonic acid (biocontrol product) – (Authors: Caroline N'Guyen-Chaumes and Alain Chemin).

to minimize the generation of waste, due to a quasi-total conversion of OA. Other criteria such as energy consumption, cost of equipment and safety were not assessed, but they generally motivate the substitution approach of ozonolysis process by numerous authors.

In conclusion, the values obtained for the green metrics considered indicated that the method developed here is more ecofriendly than the previously described processes in batch reactors. These results allow the choice of these conditions for further study.

4 Focus on a biocontrol application for environment preservation

Weed management is becoming increasingly difficult, with the withdrawal of many active ingredients and increasing concern about environmental issues.

Six years of development by Jade (a French company), GEP (good experimental practice) and more than 300 trials in Europe and in French overseas territories were required to achieve Beloukha®, the first bio-based weed control product authorized for use in European agriculture. This non-selective herbicide has haulm-killing and desiccant effects. Its active ingredient is pelargonic acid (PA). After application on the plant, the active substance disorganizes cuticle structure, and cells located deeper in the plant tissues begin to lose water (dehydration). This effect is strengthened by UV irradiation, resulting in the rapid desiccation of leaves (Fig. 10). Beloukha® is, thus, a rapidly acting broad-spectrum,, non-persistent, non-systemic, strict contact herbicide.

5 Conclusion

This paper illustrates the steps of eco-conception in the design of processes for generating functional products, such as PA and AA. The starting material was first enriched in OA by plant breeding and varietal selection. This material was then hydrolyzed and subjected to a green catalytic process for the production of two molecules of interest. Hydrogen peroxide was the oxidant chosen for this process, because it is effective, nontoxic, widely available and cheaper than other conventional oxidants. A peroxo-tungsten complex formed *in situ* was able to transfer oxygen from the aqueous phase to the lipophilic phase. The formation of an oil/water emulsion (stabilized by the fatty acids) then increased the area of contact between the two phases. This process presents only one step (after the hydrolysis of oil) and includes an efficient post-reaction treatment for catalyst recycling. It has also been successfully used for the oxidative cleavage of unsaturated compounds (linoleic acid) and other fatty acid derivatives (ethyl oleate, ricinoleic acid, epoxide derived from OA and α-hydroxy compounds).

The benign nature of the reagents, the recyclable catalyst, the solvent-free medium, the mild operating conditions and the green indicators obtained, all suggest that this process is safe and likely to have a smaller impact on the environment than reference methods in a batch reactor. Moreover, the formulation based on PA developed by Jade is used as a bio-based herbicide, with fewer deleterious effects on human health and the environment than many previous synthetic herbicides.

The oxidative scission process for OA studied here provides an example of the use of renewable starting materials, with the integration of a series of unit operations and a green chemistry approach, leading to the generation of high-value

environmentally friendly products. The unit operation sequence has been implemented by students in the framework of their laboratory work, since it is the basis of practical studies for the international Master of Science and Technology in "Green Chemistry and Processes for Biomass" (Green CAP, ENSIACET - INP Toulouse).

This novel technique for the oxidative cleavage of unsaturated fatty acids may also have social and economic implications, by making it possible to introduce short production chains to obtain bio-based molecules from local sunflower crops growing in Mediterranean areas. The ultimate aim is to set up a new industry based on agronomy and renewable carbon chemistry, which will be rich and innovative, with multiple avenues of valorization, to strengthen economic activity in the areas concerned.

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