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VEGETABLE OILS FUNCTIONALIZATION WITH CARBOXYLIC ACIDS: A COMPARATIVE STUDY ON THEIR REACTIVITY

Laura MIU[1,2], Andrei-Iulian SLABU[2], Emilian GHIBU[1,2], Cristina-Elena STAVARACHE[2,3], Cristian Aurelian BOSCORNEA[1], Florina TEODORESCU[2*], Raluca STAN[1*]

Vegetable oils are valuable renewable raw materials due to their versatility and tunable fatty acid composition, which influences key properties such as color, stability, and functionality. This study explores the epoxidation and subsequent ring-opening reactions of three unsaturated oils (sunflower, safflower and sesame) using carboxylic acids to obtain sustainable materials. Initial functionalization with isovaleric acid indicated safflower oil as the most reactive, being selected for further modification with three dicarboxylic acids of varying chain lengths. Reactions under identical conditions yielded complete functionalized products, characterized by ^1H NMR, FT-IR, and TGA analyses to evaluate conversion and thermal stability.

Keywords: vegetable oils; epoxidation; carboxylic acids

1. Introduction

Vegetable oils are one of the most valuable bioresources known worldwide due to their availability, versatility and wide range of applications, the most produced types of oilseed being soybean, rapeseed, sunflower, peanuts, cottonseed and so on [1]. In Romanian agriculture, sunflower is the long-standing stock due to its rich oil content, primarily generating profit through the extraction of oil, which is then refined to produce edible oils. Although most vegetable oils are edible, the degree of unsaturation of the oils can determine their use for other purposes, for example, lubricants [2].

As well as sunflower oil (SUNO), safflower oil (SAFO) and sesame oil (SESO) are used primarily in food, but also in the cosmetic and pharmaceutical industry. They can be extracted by different methods (by cold or hot pressing,

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[1] Faculty of Chemical Engineering and Biotechnologies, National University of Science and Technology POLITEHNICA of Bucharest, Romania, e-mail: raluca.stan@upb.ro, corresponding author

[2] “C. D. Nenitzescu” Institute of Organic and Supramolecular Chemistry of The Romanian Academy, Bucharest, Romania, e-mail: florina.teodorescu@gmail.com, corresponding author

[3] Advanced Polymer Materials Group - APMG, Campus Research Institute, National University of Science and Technology POLITEHNICA of Bucharest, Romania.

organic solvent extraction, or nonconventional extraction such as ultrasound-assisted solvent extraction) [3], from seeds. The most important difference between these oils is represented by the fatty acid composition, which determines the functionalization temperature, oxidative stability, storage conditions and especially the final application [4]. From a nutritional point of view, fatty acid composition influences the colour, flavour, texture of oils and the absorption of fat-soluble vitamins (A, D, E, and K) in addition to many other benefits [5,6]. The fatty acid content of the oil also varies depending on other factors such as growth conditions and geographic area. As such, the sunflower oil has high oleic acid content (monounsaturated fatty acid), the safflower oil is a high linoleic oil (diunsaturated fatty acid), and sesame oil has almost equal amounts of linoleic and oleic acid [7].

Depending on their intended use, the vegetable oil's composition can be chemically modified in order to reach products with suitable properties, for example increased lubricity, reduced volatility, high viscosity index, good thermal and oxidative stability, lower cloud or pour point, increased flash and fire points, as well as being inexpensive, widely accessible, and highly biodegradable [8,9]. Fortunately, there are several ways to modify vegetable oil's structure, including: epoxidation and ring opening reactions, hydroformylation and hydrogenation, ozonolysis and hydrogenation, transamination, self-metathesis, and transesterification [10,11]. Out of all these functionalization pathways, epoxidation followed by ring-opening reaction is a commonly used versatile method, which can be performed in accordance with the principles of green chemistry through heterogeneous catalysis, increased conversion and minimized waste. On this topic, due to their nucleophilic properties, structural diversity, and high reactivity, the carboxylic acids qualify as suitable reagents for epoxide ring-opening reactions. From acylation of fatty epoxides with branched, medium and long-chain carboxylic acids, a various range of products can result: polymers [12], adhesives [13], bio-based materials [14] and many others [15]. Typically, short monocarboxylic acids lead mostly to polyols and later towards to polyurethanes [16], while long chain carboxylic acids are generally used for obtaining lubricants [17].

Considering all of the above, the aim of this work is to compare the epoxidation of SUNO, SAFO and SESO followed by each heterogenous ring-opening reaction using different carboxylic acid reagents. The chosen method is a well-researched technique in both literature [18-20] and previous work [21-23], and the carboxylic acids, isovaleric (IVA), succinic (SA), adipic (AA) and sebacic acids (SBA), were selected based on their structures, reactivity and possible applications.

2. Materials and Method

2.1 Materials

Using a procedure that has been previously documented in literature [21], the epoxidation of commercial oils, SAFO, SUNO and SESO was used to create epoxidized safflower oil (ESAFO), epoxidized sunflower oil (ESUNO) and epoxidized sesame oil (ESESO). The safflower and sesame oils were purchased from HerbalSana, Oradea, România, and sunflower oil was acquired from a local supplier. Sigma Aldrich supplied the carboxylic acids and the solvent used, toluene and limonene. MgAlLa LDH (layered double hydroxide) was used as catalyst and was offered by Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest.

2.2 Characterization

^{1}H NMR was used to examine the fatty acids composition of the oils and the resulting products after functionalization according to a literature method [24]. The samples (30 mg of each) were dissolved in 0.5 mL $CDCl_3$, and the spectra were recorded using a Gemini Varian 300 MHz instrument and the spectra were calibrated using the chloroform signal (7.26 ppm) and tetramethylsilane (TMS) as the internal standard. The solid materials were characterized by FTIR spectroscopy with a Bruker VERTEX 70 instrument, equipped with a Harrick MVP2 diamond ATR device. The thermal characterization of the obtained products was performed using a NETZSCH STA 449C Jupiter simultaneous TGA-DSC system at 10°C · min^{-1}, under He inert gas coupled with an Aeolos 2 mass spectrometer.

2.3 Oils epoxidation

Using a previously reported protocol [21,22], the double bond epoxidation reaction was carried out under the following conditions: molar ratio of 1:2:10 between double bonds, glacial acetic acid, and H_2O_2, in the presence of H_2SO_4 solution (50% vol.) as acid catalyst, and toluene as solvent. A three-neck flask fitted with a thermometer, condenser, and a drip funnel for hydrogen peroxide with a magnetic stirrer is used to conduct the reaction. For each oil epoxidation, 10 mmol of oil were mixed with the equivalent mass of glacial acetic acid and 2.5% wt. sulphuric acid and dissolved in toluene. Next, dropwise addition of the hydrogen peroxide was made at room temperature while stirring continuously. The literature [18] states that the temperature is raised to 60 °C once the reactants are added, and the reaction is kept there for at least 22 hours. SAFO, SUNO and SESO epoxidations were kept at this temperature for 24 hours. The organic phase and aqueous phase of each reaction mixture were separated, and the organic phase was repeatedly rinsed with distilled water and cleaned with saturated sodium bicarbonate solution. After that, the organic solvent was vacuum-evaporated, and ^{1}H NMR was used to identify and describe the obtained product.

2.4 Ring-Opening Reaction

The ring-opening reaction of each oil was carried out in heterogenous catalysis experimental conditions: 1 mmol of epoxidized vegetable oil, 1.2 mmol of the ring-opening reagent, heterogeneous catalyst (10 wt%), and 10–15 mL of solvent. Limonene was selected as the solvent, as it represents a green solvent with a high boiling point (176 °C). The catalyst selected is MgAlLa LDH, a basic brucite type catalyst which was used in previous studies [21,22]. The choice of catalyst and solvent adheres to principles of green chemistry, thereby making the method for the functionalization of vegetable oils a sustainable approach. The molar ratio of the reactants was set at 1:1.2 (epoxy groups:acid), with a slight excess of the ring-opening reagent added. The reagents used in this study were isovaleric acid and 3 different long chain dicarboxylic acid, specifically succinic acid, adipic acid and sebacic acid. The reaction mixture was heated to 170 °C and maintained under magnetic stirring for 24 hours. After this period, the reaction medium was filtered to remove the solid catalyst, and the resulting filtrate was subjected to vacuum evaporation in order to eliminate the solvent. The product obtained was dissolved in methylene chloride and washed with warm distilled water to remove traces of unreacted acid. Following solvent removal, a viscous reddish-brown liquid was obtained (throughout the article these products will be named using the association between the abbreviations of the specific oil and the ring-opening reagent, e. g. SUNO-IVA is the product of the epoxide ring-opening reaction of sunflower oil with isovaleric acid), which was characterized using spectroscopic (FT-IR and ^{1}H-NMR) and thermogravimetric methods (TGA-DSC).

3. Results and Discussion

The oils selected for this study were chosen for their distinct chemical properties, which can be better understood through their fatty acid composition. In order to identify the fatty acids composition and the unsaturation degree, the ^{1}H NMR analysis of the oils was performed. The signal from 2.76 ppm was attributed to the proton in the methylene group between two double bonds (a very intense signal observed in the safflower oil's spectrum) and the signal from 5.35 ppm was attributed to the protons involved in the double bonds (Fig. 1 A – signals marked with an arrow on the spectra). Based on this information, the fatty acid composition of the vegetable oils was calculated [24] (Table 1), getting for each triglyceride molecule an average unsaturation of 5 double bonds for SAFO, 2.8 double bonds for SUNO and 3.8 double bonds for SESO.

Table 1

Fatty acid composition of the vegetable oil used

Type of oil	Mass percentages, %				Average number of double bonds/triglyceride molecule	Average triglyceride mass, g/mol
	Tri-unsaturated acids	Di-unsaturated acids	Mono-unsaturated acids	Saturated acids		
SUNO	0.74	1.48	87.96	9.81	2.79	882.90
SAFO	0.67	76.46	11.49	11.8	4.99	878.44
SESO	0.99	40.78	43.34	14.89	3.84	880.77

It can be concluded that SAFO is a high linoleic oil, SUNO is a high oleic oil while SESO has an almost equal content of oleic and linoleic acid.

The first step of vegetable oil's functionalization was the epoxidation reaction performed as previously described (section 2.3). The epoxidized products were analyzed by ^{1}H NMR and, as can be seen in Fig. 1 B, the double bonds (5.35 ppm) disappear, being converted into epoxy rings (2.8–3.1 ppm) through total epoxidation.

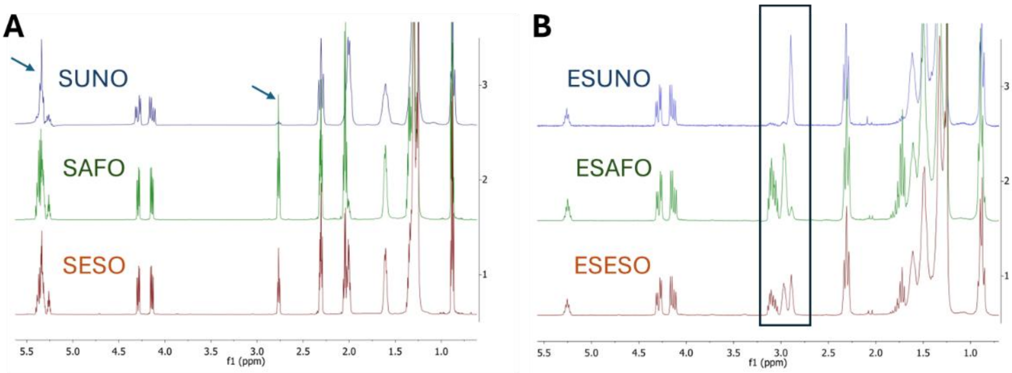


Fig 1. The stacked ^{1}H NMR spectra of A (SUNO, SAFO, SESO) and B (ESUNO, ESAFO, ESESO)

In order to study the influence of the vegetable oil structure on the ring opening reaction, the previously obtained epoxidized vegetable oils underwent a test reaction with a monocarboxylic acid, isovaleric acid. This reaction uses green solvent, limonene, and heterogenous catalysis to obtain products through the most sustainable methods. The obtained products were analyzed by ^{1}H NMR (Fig. 2), and the obtained spectra reveals the disappearance of signals corresponding to protons of the epoxide ring from 2.91 ppm (m, –CH protons at the terminal positions of the epoxy groups) and 3.1 ppm (m, –CH protons at the internal positions of the epoxy groups), along with the appearance of signals attributable to the epoxide ring-opening reagent (2.13 and 2.25 ppm). The reaction progress was also monitored by

FT-IR analysis of the final products, where the signal related to the ester group appearing at 1735 cm^{-1} can be observed while the signal related to the carboxylic acid groups, which should be found at 1700 cm^{-1}, is not present.

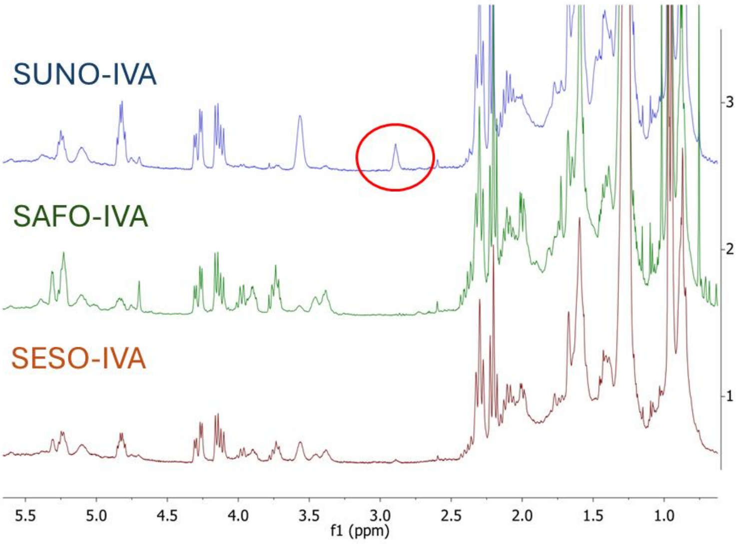


Fig. 2. The stacked ^{1}H NMR spectra of SUNO-IVA (blue), SAFO-IVA (green) and SESO-IVA (red)

The SUNO-IVA sample was the only vegetable oil that did not reach complete functionalization after 24 hours, probably due to its high oleic acid content, as indicated by the residual signal from 2.9 ppm (~90% epoxy conversion as can be seen in Fig. 2). From one perspective, oils with a high oleic content have an affinity to self-associate, generating a compact structure and adding more steric hindrance to the functionalization process [25]. This behavior has also been observed in some previous work [21], where sea buckthorn oil, also a high oleic oil, went under more severe reaction conditions in order to produce a fully functionalized product. From another perspective, internal fatty epoxides are less reactive than their terminal counterparts [15], requiring harsher reaction conditions, whereas terminal epoxides can be accessed and converted for further chemical modifications.

Based on this research facts, epoxidized safflower oil has been chosen for the comparative study on dicarboxylic acids reactivity through ring opening reaction. Therefore, the functionalization study with dicarboxylic acids was performed by reacting ESAFO with three linear aliphatic chain acids of different lengths (Fig. 3): SA (C4), AA (C6), and SBA (C10). The obtained products were noted further as SAFO-SA, SAFO-AA, and SAFO-SBA.

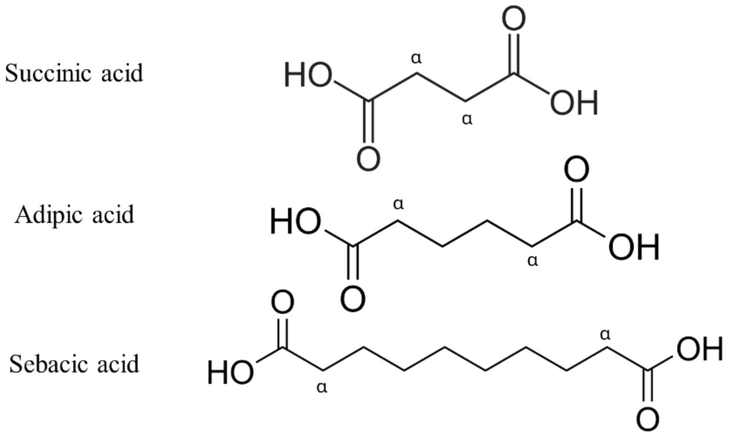


Fig. 3. The chemical structures of the dicarboxylic acids used as epoxide ring-opening agents

As can be seen in Fig. 4, comparison of the ^{1}H NMR spectra of ESAFO with those of SAFO-SA, SAFO-AA, and SAFO-SBA revealed the absence of characteristic epoxide proton signals (2.9–3.1 ppm) in the spectra of the functionalized products. Moreover, a key signal, namely the one corresponding to the methylene group (–CH_2–) in the structure of the functionalizing acids (α-position, Fig. 3), was clearly observed at 2.3–2.6 ppm in all three spectra of the functionalized products. These results confirm complete functionalization of the oils with the dicarboxylic acids mentioned above.

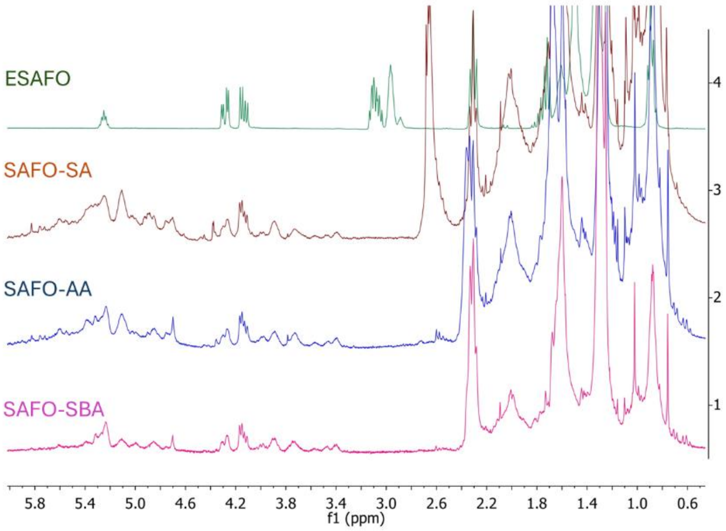


Fig. 4. The stacked ^{1}H NMR spectra of ESAFO, SAFO-SA, SAFO-AA and SAFO-SBA

Further, infrared spectroscopy was used as an additional analytical method for validating the results (Fig. 5). FT-IR spectra evidence the disappearance of epoxide vibrations band at 830 cm^{-1}, the intensification of ester bands at 1735-1740 cm^{-1}, the emergence of hydroxyl signals at 3500 cm^{-1} and the absence of the carboxylic group band (around 1650 cm^{-1}) [14]. As expected, these results also confirm the total functionalization of ESAFO with dicarboxylic acids.

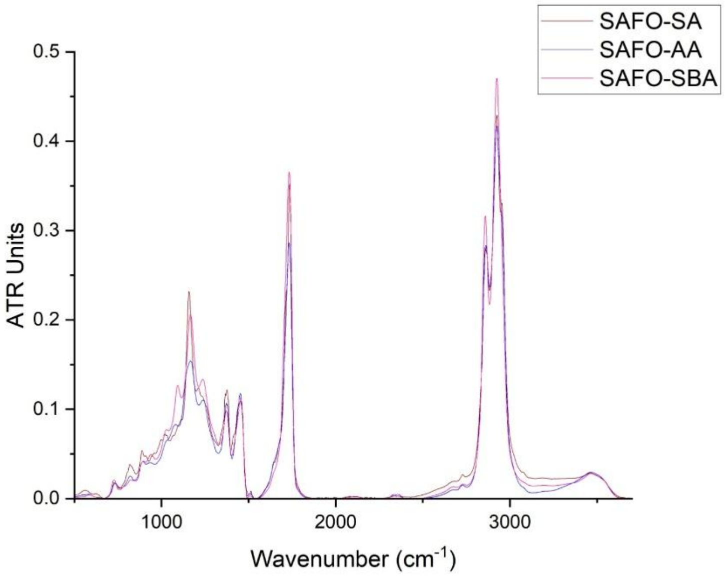
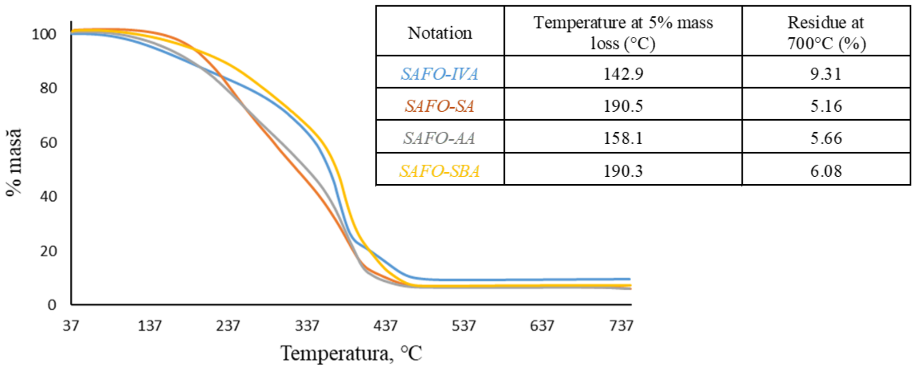


Fig. 5. The stacked FT-IR spectra of SAFO-SA, SAFO-AA and SAFO-SBA

With the purpose of understanding the thermal behavior of the final products, thermogravimetric analysis has been performed, revealing lower thermal stability for SAFO-IVA (5% mass loss at 142.9 °C, Fig. 6), whereas dicarboxylic acid derivatives displayed enhanced stability. This effect is attributed to the potential bridging of fatty acid chains via the two carboxyl groups. For the sebacic acid derivative (C10), the higher flexibility of the longer aliphatic chain likely promotes esterification with epoxide groups on the same fatty acid chain, rather than crosslinking between chains (Fig. 7). The final product morphology rather supports the absence of crosslinked structures. The working hypothesis is that the triglyceride's structural diversity and the reagent's chain flexibility can lead to the possible structures: interchain (Fig. 7 A) or intrachain (Fig. 7 B) products. However, more specific rheology analyses will be performed in the next stages of this research in order to identify the most suitable application domain for these products [26].



Notation	Temperature at 5% mass loss (°C)	Residue at 700°C (%)
SAFO-IVA	142.9	9.31
SAFO-SA	190.5	5.16
SAFO-AA	158.1	5.66
SAFO-SBA	190.3	6.08

Fig. 6. The TGA spectra of ESAFO's ring opening reaction products

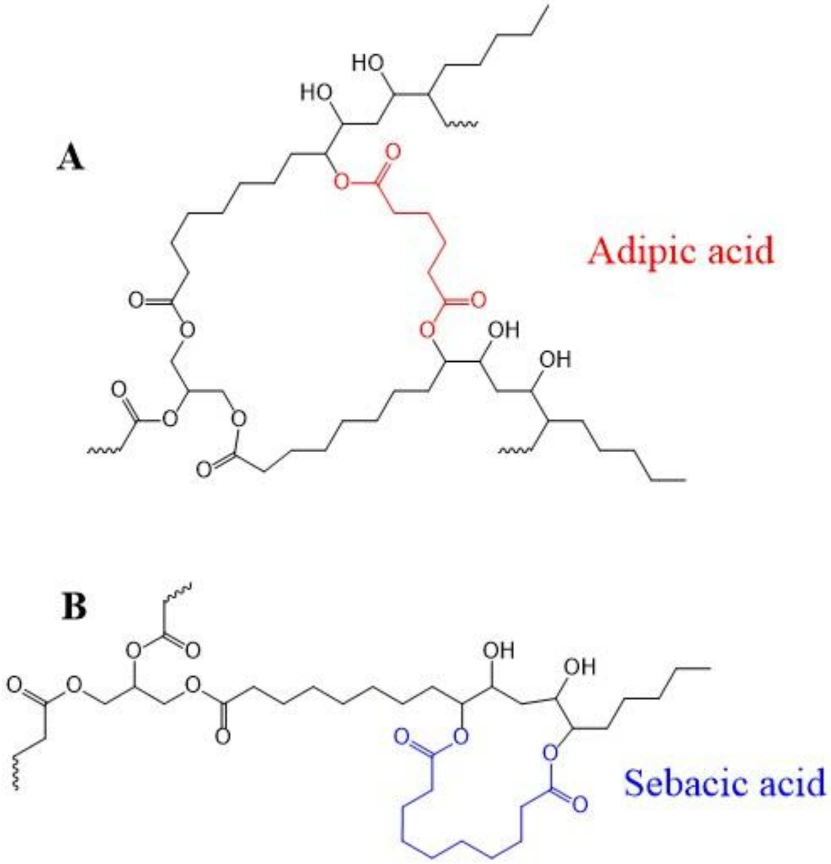


Fig. 7. Selected examples for ring opening reaction products.

4. Conclusions

Functionalized products were obtained using three vegetable oils with different degrees of unsaturation by reacting epoxidized oils, ESUNO, ESAFO and ESESO, with mono- and dicarboxylic acids, using a reusable catalyst, MgAlLa LDH. All the reactions that took place, including the ring-opening of the epoxy groups, led to final products which were analyzed and identified using spectroscopy techniques. In a preliminary experiment, the oils were functionalized with a short and branched monocarboxylic acid; based on the results, the oil that showed the highest reactivity (SAFO) was chosen for further studies involving dicarboxylic acids. In the subsequent experiments with dicarboxylic acids, the functionalization reactions achieved complete (100%) conversion, producing liquid materials with promising versatility for various applications (sustainable and environmentally friendly alternative to conventional petroleum-based materials, for example bio-based plasticizers, coatings, lubricants or resins). According to the TGA results, the functionalization with longer-chain diacids is probably to occur through grafting onto the same triglyceride branch rather than onto different fatty acid chains of oil, indicating that crosslinking of the oil does not take place.

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