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Epoxy monomers obtained from castor oil using a toxicity-free catalytic system

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This article is dedicated to Dr. Georgiy Borisovich Shul'pin, our dear colleague and friend, on the occasion of his 70th birthday.

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ABSTRACT

In order to obtain monomers from vegetable source, the castor oil epoxidation process was investigated. The catalytic system used in this work, H_2O_2/alumina/ethyl acetate, can be considered as a green system, free of heavy metals and toxic solvents. These characteristics make the system appropriate for the purpose of this study since they increase the probabilities of obtaining a biomaterial with the desired specifications regarding toxicity. Reaction conditions of castor oil epoxidation were optimized using methyl ricinoleate as a model compound. In order to identify the operating region, it was developed an experimental design 2^3 with 17 assays (6 axial points and central point in triplicate) in which, methyl ricinoleate, hydrogen peroxide and catalyst initial quantities in the reaction mixture were the studied variables. The system showed great efficiency with 100% of selectivity in the methyl ricinoleate epoxide production. In optimized conditions, it showed conversion of 99% in 6 h. It was obtained a conversion of 94%, an epoxidation percentage of 84 and a selectivity of 89% toward the epoxides for the castor oil epoxidation. These results show the efficacy of the catalytic system used in this work. Epoxidized castor oil structure was confirmed by FTIR, Raman and ^{1}H NMR techniques.

1. Introduction

Vegetable oils are an excellent raw material since they are renewable resources. It can produce a large platform and allow a several structural modifications, are broadly available, have low cost of production and processing, ingrained biodegradability and environmental friendly aspects [1–4]. These characteristics make them attractive for a lot of applications, including polymers precursors, adhesives, coatings, lubricants, among others [3]. Particularly, the castor oil (CO) is special due to the presence of a hydroxyl group in its structure which offers distinct reactivity and a higher viscosity from the hydrogens bonds [5].

Although vegetable oils, in principle, can be directly polymerized, it is more interesting to functionalize them in order to obtain well defined monomers and polymers with improved characteristics [6]. Epoxidation is one of the most important functionalization reactions of the C–C double bonds [7]. Epoxidized vegetable oils are considered as promising and relatively inexpensive materials for industrial applications which share many of the characteristics of conventional epoxy thermosets [8].

In industry, the most used method for vegetable oils epoxidation involves the in situ formation of performic/peracetic acid (Prilezhaev reaction) [9,10], however, it has a low selectivity (oxirane ring opens) [10], it is a slow reaction [11], as well as it has a high environment impact since for each epoxide molecule produced, the same quantity of carboxylic acid is produced as by-product [12]. In order to address to this issue, different catalysts have been studied, including: transition metal complexes, ion exchange resins, venturello's catalyst, crown ethers and enzymes. However, these catalysts have not been achieved success on industrial scale [10].

It has been shown that alumina can be used for olefin epoxidation using hydrogen peroxide as a clean oxidant agent [11,13,14]. This catalytic system offers interesting advantages, among them the fact that alumina is a cheap heterogeneous catalyst; therefore, it is relatively easy to recover and it can be re-used several times [15]. Additionally, hydrogen peroxide is a low cost oxidant and produces water as by-product, which represents a large savings in chemical waste treatment, as well as an environmentally friendly option

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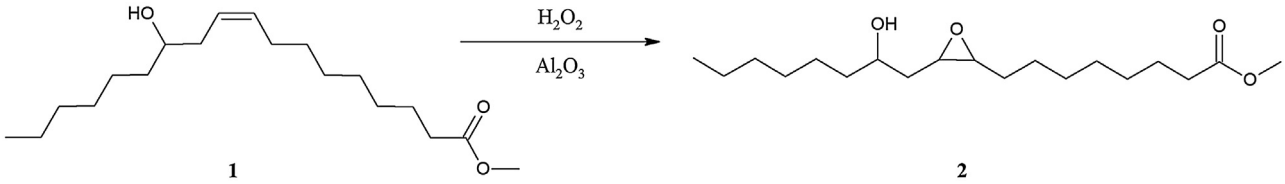

Fig. 1. Epoxidation of MR (1) with hydrogen peroxide catalyzed by alumina leading the formation of methyl ricinoleate epoxide (2).

[11]. These characteristics make the system appropriate for the purpose of this study since no heavy metals or toxic solvents are used, increasing therefore the probabilities of obtaining a biomaterial with the desired specifications regarding toxicity.

In order to obtain monomers from vegetable source, epoxidation of castor oil was investigated using the system developed and optimized by Bonon et al. [16]. The castor oil epoxidized is valuable for a lot of industrial applications that include its use as a natural-based plasticizer characterized by low toxicity and low migration, used principally on PVC formulations [8]; polyurethane foams production from polyols synthesis by the oxirane ring opening [3]; polyester derived from the reaction with polycarboxilic acids [17], among others.

Since ricinoleic acid comprises over 90% of the fatty acid of the castor oil [1], the methyl ricinoleate (MR) was used as model compound for optimizing the castor oil epoxidation conditions using alumina as catalyst and hydrogen peroxide as oxidant (Fig. 1) in an ethyl acetate medium. For the purpose to identify the optimal conditions to castor oil epoxidation, an experimental design 2^3 with 17 assays (6 axial points and central point in triplicate) was carried out. Methyl ricinoleate, hydrogen peroxide and alumina amounts were used as variables. This makes possible to identify the most suitable reaction condition to the castor oil epoxidation, as well evaluating the system performance, especially conversion and selectivity. Epoxidized castor oil (ECO) structure was analyzed using FTIR, Raman and ^{1}H NMR spectroscopy techniques.

2. Experimental

2.1. Reagents

High purity chromatograph grade γ-alumina, anhydrous hexadecane (99%), methyl ricinoleate (99%) and MnO_2 (85%) were obtained from Sigma-Aldrich, and they were used as received. Hydrogen peroxide was donated by Peróxidos do Brasil Ltda (70% aqueous) and ethyl acetate (99.5%) was obtained from Merck. Castor oil was obtained from Campestre Ind. e Com. de Óleos Vegetais Ltda.

2.2. Methyl ricinoleate epoxidation

The catalytic reactions were carried out in a two-necked round bottom flask heated in a glycerin thermostatic bath (80° C), and fitted with a reflux condenser. A mixture of methyl ricinoleate, H_2O_2, ethyl acetate and hexadecane (internal standard for gas chromatography) was heated under vigorous magnetic agitation until gentle reflux was achieved. Immediately before addition of the catalyst, a sample was taken from the reaction mixture for GC analysis (time 0 h). The catalytic reactions were started by adding Al_2O_3. The courses of the reactions were monitored by taking aliquots from the reaction mixtures at different reaction times. It was added MnO_2 in the collected samples to decompose H_2O_2 and stop the reaction. 1.5 mL of ethyl acetate was addicted to dilute the sample for GC analysis. Prior the injection, the Al_2O_3 and MnO_2 were removed by filtration using PTFE 0.45 μm porous membrane.

2.3. Product analysis

The samples were analyzed using an Agilent Technologies 6850 gas chromatograph equipped with a BP-25 SGE column (25m × 0.32mm × 25 μm film thickness) and a flame ionization detector (FID). Methyl ricinoleate conversion was determined by calibration curves with internal standard, obtained using standard solutions. The product was identified by GC–MS analysis in an Agilent 7890/5975C gas chromatograph equipped with a Stabil wax column (30m × 0.25mm × 0.25 μm).

2.4. Castor oil epoxidation

The castor oil epoxidation was carried out using the methyl ricinoleate procedure, without addition of the internal standard (hexadecane), since the purpose of this experiment is to obtain epoxidized castor oil. After 6 h of reaction, the alumina was removed by filtration, and the H_2O_2 was decomposed with MnO_2, followed by its removal by filtration. The product was concentrated in a rotary evaporator at 240 mbar and 40° C.

2.5. Fourier transform infra-red (FTIR) analysis

The FTIR spectra of CO and ECO were carried out in a Thermo Scientific spectrometer, model Nicolet 6700 (Madison/USA). The samples were analyzed in the transmittance mode using KBr disks, in a scanning range from 4000 to 400 cm^{-1}.

2.6. FT-Raman analysis

The FT-Raman spectra of CO and ECO were performed in a FT-Raman spectrometer from Thermo Scientific, model NXR (Madison/USA). The samples were analyzed in the transmittance mode using KBr disks without attenuator radiation (optical density 1.0), in a scanning range from 3700 to 200 cm^{-1}.

2.7. Nuclear magnetic resonance (^{1}H NMR)

The ^{1}H NMR spectra of CO and ECO were recorded by a Bruker Avance spectrometer operating at 250 MHz for ^{1}H using chloroform-*d3* as solvent.

2.8. Quantitative NMR analysis

The methodology reported by Miyake et al. [18] showed that iodine value (IV) can be calculated by average molecular weight (M) and absolute number of double bonds (ND) using the NMR spectrum. The integration values from resonance spectrum of castor oil (Fig. 6A) were used to calculate the average molecular weight (Eq. (1)) and the number of insaturations per mol (Eq. (2)) [18–20].

$$M = \left[\frac{15.034\,(K)}{3NF} + \frac{14.026\,(D+E+F+G+H+I+J)}{2NF} + \frac{17\,(OH)}{NF} + \frac{13\,(C)}{NF} + \frac{26.016\,(A-NF)}{2NF} + 173.1\right] \quad (1)$$