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POLYOLS DERIVED FROM LINSEED OIL

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Epoxidized linseed oil (ELO) was used as a raw material to obtain polyols for possible polymer applications. Two types of polyols have been synthesized through oxirane ring opening with water under both acidic and alkaline media, on one hand, and with allylmagnesium bromide, on the other hand. The ring opening via Grignard derivatives allowed the simultaneous grafting of unsaturated allyl moieties onto the triglyceride backbone, thus leading to a polyunsaturated branched polyol. FT-IR and ^{1}H-NMR spectra confirmed the structure of the obtained products.

Keywords: epoxidized linseed oil, vegetable oils, polyol, NMR, FT-IR, Grignard.

1. Introduction

Vegetable oils are very attractive renewable resources both for the human diet (due to their sensory properties [1, 2] and high content of beneficial components such as polyunsaturated fatty acids (PUFA), oil soluble vitamins [3] phenolic acids and flavonoids [4]), but also as important renewable resource mainly in the energetic field (biodiesel) [5-7], as well as for different applications in the chemical [8], pharmaceutical [9-12] and cosmetic [13-15] industries.

Biobased materials obtained from renewable resources are receiving considerable interest for use in an increasing number of applications. Vegetable oils are very attractive as renewable raw materials because of their low price and their *a priory* possibility of biodegradation, thus leading to environmentally friendly compounds [16]. The chemical structure of triglicerides and especially the double bonds of PUFA allow the synthesis of a wide range of reactive compounds, such as polyols, halogen derivatives, epoxides [17] or amines [18-20].

Polyols from vegetable oils are compounds with interesting uses such as tensioactive agents or organogelators [21], corrosion inhibitors [19, 20], as well as valuable monomers for the synthesis of various types of macromolecular compounds (polyurethanes and coatings) [22]. Natural oils such as castor [23], soybean [22], camelina [24], palmkernel [25], jatropha [26], rapeseed [27, 28] have been used to synthetize polyols, which can be used as monomers in the

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preparation of polyurethane foams or as corrosion inhibitors for the coatings industry [20, 29, 30].

Polyols can be obtained from vegetable oils through different synthesis routes, such as Baeyer oxidation of the double bonds of PUFA [21], or alcoholysis of castor oil with glycerol [31]. An elegant and efficient access strategy to obtain polyols from vegetable oils is the ring opening of the remarkably reactive epoxidized oils with various nucleophilic agents, such as MeOH [23], phenol, cyclohexanol [22] diethyl phosphate [31], phtalic anhydride [16], or diethylene glycol [27]. Among vegetable oils, highly unsaturated oils such as linseed oil (LO) are the most interesting for different applications *via* their epoxidised derivatives [8].

The aim of this paper is the synthesis and structural characterization of two types of polyols obtained from epoxidized linseed oil (ELO) through oxirane ring opening reaction with water in acidic or alkaline conditions and with a Grignard compound (allyl magnesium iodide), leading to a novel polyunsaturated polyol. Both starting materials and obtained polyols were characterized through FT-IR and ^{1}H-NMR spectroscopic techniques.

2. Materials and methods

Materials: ELO was obtained from Chemont S.A., Mouscron, Belgium.

^{1}H-NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer, operating at 9.4 Tesla, corresponding to the resonance frequency of 400.13 MHz for the ^{1}H nucleus, equipped with a direct detection four nuclei probe head and field gradients on z axis. The NMR samples were prepared by dissolving 0.5 mL oil in 0.5 mL $CDCl_3$ and analyzed in 5 mm NMR tubes (Wilmad 507). The chemical shifts are reported in ppm, using TMS as internal standard. Typical parameters for ^{1}H-NMR spectra were: 30° pulse, 4s acquisition time, 6.4 kHz spectral window, 8 scans, 52 K data points. The FID was not processed prior to Fourier transformation.

FTIR spectra were recorded on a Bruker Vector 33 instrument, equipped with a Pike Miracle ATR device (ZnSe crystal), without solvent, acquiring 32 scans for background and 64 scans for sample acquisition, 2 cm^{-1} optical resolution. Spectra were recorded in the 590-5400 cm^{-1} range, collecting 2495 points with a DLaTGS detector.

Hydrolysis of ELO in alkaline medium

75 mL of a 5% NaOH aqueous solution was placed in a two neck round bottom flask fitted with reflux condenser, dropping funnel and efficient magnetic stirrer. A solution of 1.0 g ELO (6.6 mmoles) in 30 mL dioxane was added dropwise with stirring and the mixture was refluxed for 4h at 102^{o}C. The reaction mixture was allowed to cool to room temperature, neutralized with HCl solution

5%, and extracted three times with ethyl ether (3×25 mL). The combined extracts were washed three times with distilled water, dried on anhydrous $MgSO_4$ and filtered. The solvent was removed with a rotary evaporator and the product was obtained (0.68 g) as a viscous light yellow oil.

^{1}**H-RMN** ($CDCl_3$, 400 MHz), δ (ppm): 0.95 (t, 3H, CH_2-CH_2-C$\boldsymbol{H_3}$) ; 1.06 (t, 3H, -CH=CH-CH_2-C$\boldsymbol{H_3}$); 1.26-1.32 (m, -C$\boldsymbol{H_2}$-); 2.33 (t, 2H, -CO-C$\boldsymbol{H_2}$-) ; 3.5-3.7 (m, -$\boldsymbol{H}$C(OH)-CH(OH)-CH_2-HC(OH)-C$\boldsymbol{H}$(OH)-); 3.8-4.1 (m, -HC(OH)-C$\boldsymbol{H}$(OH)-CH_2-$\boldsymbol{H}$C(OH)-CH(OH)-).

IR (ATR, film, cm^{-1}) : 3420 (broad band, ν_{OH}) ; 2926 (ν_{CH2} *as*) ; 2855 (ν_{CH2} *sim*) ; 1714 ($\nu_{C=O}$) ; 1102 ($\nu_{C\text{-}OH\ sec.}$ *as*).

Hydrolysis of ELO in acidic medium

75 mL of a 5% HCl aqueous solution was placed in a two neck round bottom flask fitted with reflux condenser, dropping funnel and efficient magnetic stirrer. A solution of 1.0 g ELO (6.6. mmoles) in 30 mL dioxane was added dropwise with stirring and the mixture was refluxed for 4h at 102°C. The reaction mixture was allowed to cool to room temperature, neutralized with NaOH solution 5%, and extracted three times with ethyl ether (3×25 mL). The united extracts were washed three times with distilled water, dried on anhydrous $MgSO_4$ and filtered. The solvent was removed with a rotary evaporator and the product was obtained (0.82 g) as a viscous yellow oil.

^{1}**H-RMN** ($CDCl_3$, 400 MHz), δ (ppm): 0.95 (t, 3H, CH_2-CH_2-C$\boldsymbol{H_3}$) ; 1.06 (t, 3H, -CH=CH-CH_2-C$\boldsymbol{H_3}$); 1.26-1.32 (m, -C$\boldsymbol{H_2}$-); 2.33 (t, 2H, -CO-C$\boldsymbol{H_2}$-) ; 3.5-3.7 (m, -$\boldsymbol{H}$C(OH)-CH(OH)-CH_2-HC(OH)-C$\boldsymbol{H}$(OH)-); 3.8-4.1 (m, -HC(OH)-C$\boldsymbol{H}$(OH)-CH_2-$\boldsymbol{H}$C(OH)-CH(OH)-).

IR (ATR, film, cm^{-1}) : 3420 (broad band, ν_{OH}) ; 2926 (ν_{CH2} *as*) ; 2855 (ν_{CH2} *sim*) ; 1714 ($\nu_{C=O}$) ; 1102 ($\nu_{C\text{-}OH\ sec.}$ *as*).

Reaction of ELO with allylmagnesium iodide

0,6 g (25 mmoles) magnesium flakes (freshly activated at 140°C for 2 h) and 30 mL anhydrous ethyl ether were placed in a two neck round bottom flask fitted with reflux condenser, dropping funnel, Ar inlet and efficient magnetic stirrer. A solution of 3,36 g (20 mmoli) allyl iodide in 30 mL anhydrous ethyl ether is added dropwise with stirring under Ar atmosphere. If necessary, a small amount of CH_3I can be added to initiate the reaction. After complete addition of allyl iodide solution, the reaction mixture was refluxed for 3 h. The mixture was then allowed to cool to room temperature and a solution of 1,5 g (10 mmoles) ELO in ethyl ether was added dropwise, with efficient stirring. After complete addition of the ELO solution, the reaction mixture was refluxed again for 3 h, under Ar atmosphere. The Grignard intermediate was then decomposed with saturated ammonium chloride solution added dropwise. The reaction mixture is extracted with ethyl ether. After solvent evaporation, the product was obtained with 40% yield as a viscous yellow oil.

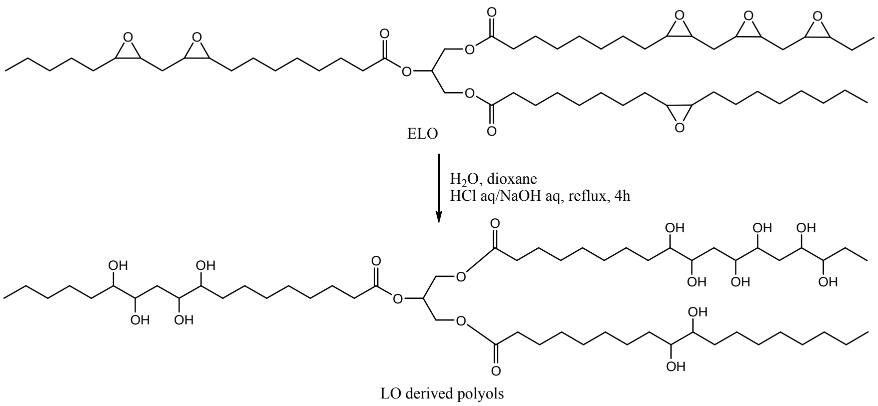
^{1}H-RMN ($CDCl_3$, 400 MHz), δ (ppm) : 0.88 (t, 3H, CH_2-CH_2-$C\boldsymbol{H_3}$) ; 1.07 (t, 3H, -CH=CH-CH_2-$C\boldsymbol{H_3}$**);** 1.26-1.32 (m, -$C\boldsymbol{H_2}$-) ; 1.60 (m, -HC(OH)-CH(CH_2-CH=CH_2)-$C\boldsymbol{H_2}$-HC(OH)-CH(CH_2-CH=CH_2)-) ; 2.31 (t, 2H, -CO-$C\boldsymbol{H_2}$-) ; 3.40 (m, -$\boldsymbol{H}$C(OH)-CH(CH_2-CH=CH_2)-CH_2-$\boldsymbol{H}$C(OH)-CH(CH_2-CH=CH_2)-) ; 4.20 (m, 4H, -$C\boldsymbol{H_2}$OCO-); 5.26 (t, 1H, -C$\boldsymbol{H}$OCO-).

IR (ATR, film, cm^{-1}): 3417 (broad band, ν_{OH}) ; 2925 (ν_{CH2} *as*) ; 2854 (ν_{CH2} *sim*); 1740 ($\nu_{C=O}$) ; 1101 ($\nu_{C\text{-}OH\ sec.}$ *as*) ; 823 ($\nu_{C\text{-}O\text{-}C\ epoxy}$) ; 724 ($\gamma_{C\text{-}H}$ *cis*).

3. Results and discussion

a. Hydrolisis of ELO

Epoxidized linseed oil (ELO) has been characterized through ^{1}H-NMR and FT-IR spectroscopy prior to hydrolysis. A functionalization degree of 2.1 moles epoxy groups per alkyl chain was assessed from ^{1}H-NMR spectra [32]. ELO has been hydrolyzed in order to obtain polyols with possible tensioactive or gelation properties.



Scheme 1: Hydrolysis of ELO

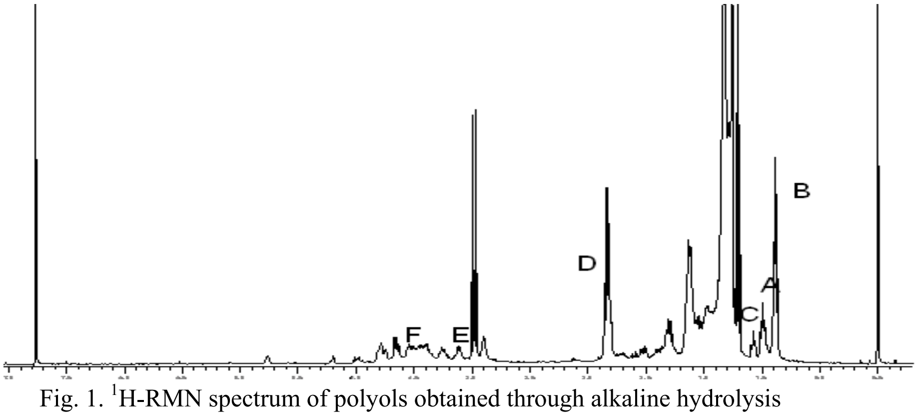


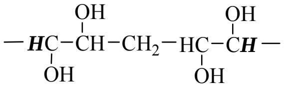
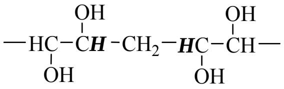
Fig. 1. ^{1}H-RMN spectrum of polyols obtained through alkaline hydrolysis

The hydrolysis reaction has been carried out under acidic (HCl) or alkaline (NaOH) medium, at 100 ^{0}C for 4h (Scheme 1). The reaction products have been analyzed through ^{1}H-NMR (Fig. 1) and FT-IR spectroscopy.

Spectral assignments of the characteristic signals are presented in *Table 1*.

Table 1

Chemical shifts and peak assignments for the ^{1}H-RMN spectrum of hydrolyzed ELO (acidic conditions)

Signal	δ (ppm)	Proton	Assignment
A	1.06	$-CH{=}CH-CH_2-C\boldsymbol{H_3}$	from hydrolyzed linolenic acid
B	0.95	$-CH_2-CH_2-CH_2-C\boldsymbol{H_3}$	from all fatty acids, excepting linolenic
C	1.08	$-CH{=}CH-CH_2-C\boldsymbol{H_3}$	from unhydrolyzed linolenic acid
D	2.33	$-CO-C\boldsymbol{H_2}-$	α position against carbonyl group
E	3.5-3.7	 $—\underset{OH}{\boldsymbol{H}C}-\overset{OH}{CH}-CH_2-\underset{OH}{HC}-\overset{OH}{C\boldsymbol{H}}—$	“marginal” polyol protons from oxirane ring
F	3.8-4.1	 $—\underset{OH}{HC}-\overset{OH}{C\boldsymbol{H}}-CH_2-\underset{OH}{\boldsymbol{H}C}-\overset{OH}{CH}—$	“internal”polyol protons from oxirane ring

In both cases the reaction conversion was determined from ^{1}H-NMR data (*Fig. 1*). For the quantitative analysis of the hydrolysis reaction, signal **D** (due to the two protons of the methylene group in α position relative to the carbonyl group) has a particular importance. It can be used to calculate the integral value per one proton in the spectrum, since it arises both in the reaction product and in the raw material (I_D / 2 = 4.45/2 = 2.22). It has been previously determined [32] that ELO has on average 2.1 oxirane groups per fatty acyl chain, each with two protons turning into hydroxyl groups. If the hydrolysis conversion would be 100%, the global integral of the germinal protons relative to OH groups in polyols would 2.1· 2· 2.22 = 9.32. In the spectrum, these protons give signals **E** and **F**, whose global integral is 1.69 + 5.53 = 7.22; the 7.22 / 9.32 = 0.77 ratio suggests a 77% conversion of ELO into polyol through hydrolysis in alkaline medium.

Similarly, a conversion degree of 46% was determined for the hydrolysis of ELO in acidic conditions.

The hydrolysis reaction of ELO was also analyzed through FT-IR spectroscopy applied both for the obtained polyols and the raw material. For better relevance, these spectra are shown overlapped in Fig. 2.

The disappearance of the band at 822 cm^{-1} (deformation vibration) – characteristic for oxirane rings – can be easily noticed, while the intensity of the large band at 3420 cm^{-1} ($\nu_{OH\ assoc.}$) increases in the hydrolysis product.

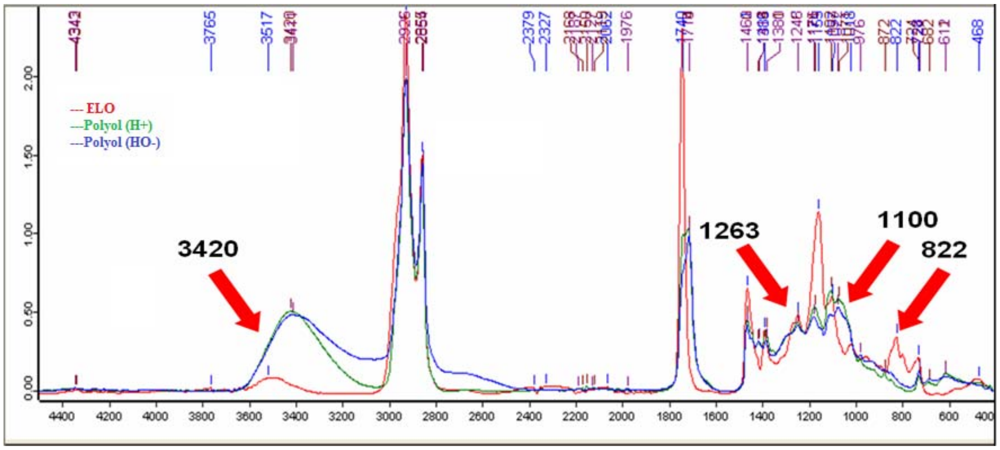
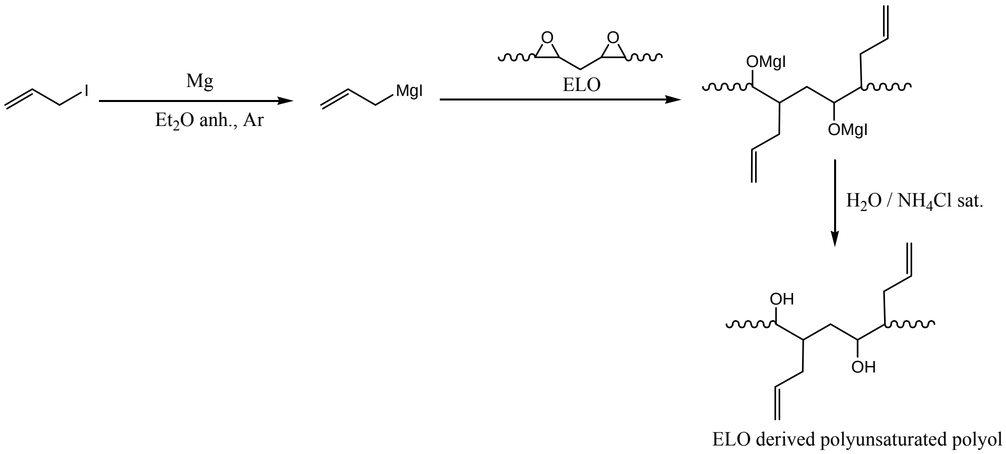


Fig. 2. Overlapped FT-IR spectra of ELO and hydrolysis products (H+ and HO^- media)

Another proof that the hydrolysis reaction of ELO has occurred is the disappearance in the FT-IR spectra of polyols of the “shoulder” at 1263 cm^{-1} (symmetrical elongation vibration) characteristic to oxirane rings. On the other hand, in the polyols spectra, it can be noticed the appearance of a band at 1100 cm^{-1}, assigned to C-O elongation vibration of secondary alcohols. These observations are in good agreement with literature data concerning spectral assignments for a large range of polyols [33].

b. Synthesis of a novel polyunsaturated polyol

An interesting polyol with possible applications in the polyurethane foams synthesis can be obtained from ELO by opening the oxirane rings with organomagnesium halides. Thus, the reaction of ELO with the Grignard compound obtained from allyl iodide and magnesium in anhydrous ethyl ether followed by hydrolysis of the intermediate leads to a novel polyol with grafted unsaturated hydrocarbon chains onto the fatty acyl chains, as shown in *Scheme 2*.



Scheme 2: Synthesis of ELO derived unsaturated polyol: i. reaction of ELO with allylmagnesium iodide; ii. Hydrolysis of the Grignard intermediate.

The obtained polyunsaturated polyol was characterized by FT-IR and ^{1}H-NMR spectroscopy. In the ^{1}H-RMN spectrum, the absence of signals in the 2.8 – 3.3 ppm spectral region (assigned to the protons of the oxirane rings) and the newly occurring deshielded signals corresponding to the unsaturated protons from the grafted allylic chains onto the tryglyceride backbones at 5.838 ppm (multiplet, $-CH_2-C\boldsymbol{H}=CH_2$), and 5.129 ppm ($-CH_2-CH=C\boldsymbol{H}_2$), respectively, as well as the multiplet signal at 3.395 ppm (assigned to the protons geminally situated with respect to the OH groups) confirm the structure of the reaction product (Fig. 3).

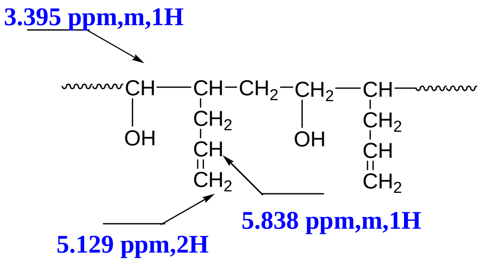


Fig. 3. Partial ^{1}H-RMN peak assignment of the polyunsaturated polyol

In the FT-IR spectrum of the reaction product the band from 822 cm^{-1} (C-O deformation vibration) – characteristic for the oxirane ring – is absent; instead, a significant intensity increase of the large band from 3416 cm^{-1} (assoc. OH) can be noticed. On the other hand, the band at 1100 cm^{-1} (C-O elongation vibration characteristic for secondary alcohols) and the weak band at 723 cm^{-1} (assigned to the C-H of the *cis* double bonds), corresponding to the allylic moieties grafted onto the aliphatic chains, confirm both the polyol and the polyunsaturated character of the reaction product.

4. Conclusion

Two types of polyols have been obtained from epoxidized linseed oil through the oxirane ring opening with two types of nucleophilic agents: water and allylmagnesium bromide. The ring opening *via* Grignard derivatives allowed the simultaneous grafting of unsaturated allyl moieties onto the triglyceride backbone thus leading to a polyunsaturated branched polyol. The structure of obtained products was confirmed by FT-IR and ^{1}H-NMR spectra.

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