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NOVEL LINSEED OIL-BASED MONOMERS: SYNTHESIS AND CHARACTERIZATION

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This paper presents the study of the functionalization reactions of the linseed oil (LO) structure. The main purpose of this study was to obtain oil-based monomers that meet both "green chemistry" properties and reactive sites for the polymerization and also to possess a hydrophilic character. Functionalization of LO chains was achieved by a three step reaction involving sequentially: double bonds epoxidation, partial methacrylation of the epoxy rings and polyethyleneglycole (PEG) grafting by opening of the epoxides unreacted in the previous stage.

Keywords: linseed oil, hydrophile, epoxidation, methacrylate, PEG

1. Introduction

Lately, due to excessive use of fossil resources, the scientists and technologists made efforts to use alternative resources that may replace petro-based chemicals. Natural oils, obtained from plant seeds, may be an ideal alternative for chemical feedstock [1-3]. Oil-based products have many advantages compared with the compounds obtained from petroleum-based resources as biodegradability or low cost.

Vegetable oils are water insoluble products of plants and represent triesters of glycerol (or triglycerides) with saturated and unsaturated fatty acids. They can also be produced through reaction of glycerol with fatty acids [4]. Vegetable oil molecule includes an ester part (triglyceride) and a non-ester part represented by: phospholipids, sterols, vitamins and their precursors, antioxidants, pigments and impurities [5]. Triglyceride itself represents that part of the oil molecule which can be exploited in the industry, due to a great number of the double bonds on the fatty acid structure. The fatty acid composition of vegetable oils is the main factor influencing their properties, concerning both nutrition and exploitation as raw materials for oleo chemistry [6, 7].

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Linum usitatissimum, is a member of the family *Linaceae.* The unsaturated fatty acids content of linseed oil are in a range of 90% with high content of omega-3 and omega-6 fatty acids which makes it an excellent choice as edible oil (nutritional supplement), in surfactants and detergents, cosmetics and pharmaceutical industry. With iodine value of 175 - 204 g I2/100g, LO is part of drying oil category. LO is a polyfunctional monomer that can be converted to high-molecular-weight products through the introduction of more reactive functional groups. [8-10]

The objective of our research is the valorisation of LO to obtaining some ecological monomers with several eco-friendly applications. This purpose involves a few functionalization steps of the hydrophobic LO chains for grafting of the methacrylic moieties and get an increased hydrophilicity of this monomers through attaching polyethylene glycol (PEG) units on the polycarbonate chains. Epoxidation of fatty acids – a intermediary reaction stage – is a reaction of a carbon-carbon double bond with an active oxygen, usually from a peroxide or a peracid, converting the original C=C bond into a three-member epoxide (oxirane) ring [11-15]. These groups allow the attaching of the reactive methacrylate radicals and the hydrophilic PEG.

2. Materials and methods

2.1. Materials

Linseed oil (LO) extracted in a cold-pressing process was kindly supplied by Vandeputte Oleochemicals, Mouscron, Belgium. Polyethyleneglycol with MW ≈ 550 and 750 g/mol and methacrylic acid were purchased from Sigma-Aldrich. All other solvents and reagents were obtained from Sigma-Aldrich and used as received without any purification.

2.2. Instrumentation

Nuclear Magnetic Resonance Analysis

^{1}H nuclear magnetic resonance (^{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 1H nucleus, equipped with a direct detection four nuclei probe head and field gradients on z axis. The chemical shifts are reported in ppm, using the TMS as internal standard.

Gas Chromatography–Mass Spectroscopy Analysis (GC-MS)

Gas-chromatograms of the fatty acid methyl esters mixtures were recorded on an Agilent Technologies 6890 N instrument with flame ionization detector. Separation into components was made on a capillary column especially designed for the FAME analysis (Supelco SPTM 2560: 100 m length, 0.25 mm inner diameter, 0.2 μm film thickness). Fatty acids identification was made by comparing the retention time for each peak with a commercially available standard (mixture of 37 fatty acid methyl esters provided by Supelco^{TM}).

Fourier transforms infrared spectroscopy analysis (FTIR)

Fourier Transform Infrared (FTIR) spectra were registered on a Vertex 70 Brucker FTIR spectrometer equipped with an attenuated total reflectance (ATR) accessory in order to determine the chemical structure and also the curing degree of all the studied specimens. All FTIR measurements were performed in the ATR-FTIR cell on Ge crystal, at room temperature. The FTIR spectra were recorded using 32 scans in 600-4000 cm^{-1} wave number region.

2.3. Experimental

Oil characterization

Linseed oil (LO) was characterized through ^{1}H-NMR, GC-MS and FT-IR spectroscopy for determining their fatty acid profile.

Synthesis of epoxidized linseed oil (ELO)

The oil modification was performed in accordance with the literature [1, 16, 17]. The epoxidation reaction of LO was carried with H_2O_2 and glacial acetic acid. As diluent of the organic phase toluene was added and 50% H_2SO_4 was used as catalyst. The molar ratio of hydrogen peroxide (H_2O_2)/acetic acid/oil unsaturation (double bonds) was 10/2/1. 30% H_2O_2 was added drop wise into the reaction mixture formed by oil, toluene and acetic acid, kept at room temperature. When the entire amount of hydrogen peroxide was added into the reaction flask, the temperature was raised to 60 ºC, along with a constant stirring, and this procedure required 22 h to complete the reaction. The oily phase was separated and washed several times with water and then with saturated $NaHCO_3$ solution, until a neutral pH was attained. The solution was drying and the solvent was removed by evaporation under heat and vacuum. This protocol is applied both for partial and total epoxidized oil.

Synthesis of methacrylated epoxidized linseed oil (MELO)

Total epoxidized linseed oil was mixed with methacrylic acid (MA) in the present of triethylamine (TEA) or diazabicyclo octane (DABCO) as catalyst and hydroquinone (HQ) as free-radical inhibitor, according to some adjusted protocols from literature [16, 18, 19] for total or partial opening of the epoxy rings. Reaction mixture was heated at 75 ºC and kept with constant stirring 5 h. The reaction product was purified using 0.1N HCl to remove the catalyst. The methacrylated oil was then extracted in diethyl ether to remove free MA and then the final product was washed with water and saturated sodium bicarbonate solution. Finally the ether was removed. This protocol is applied both for 50% and 75% methacrylated oil.

Synthesis of PEG-ylated MELO

Polyethyleneglycol methyl ether (PEG) with molecular weight M≈550 or 750 g/mol was dissolved in THF and charged to a reaction flask and heated to 60 ºC. Boron trifluoride (0.05% on PEG) was added. MELO in THF with small amount of HQ was drop wise added over the PEG mixture and than the temperature was raised to 65 ºC for 30 minutes [20]. The product was filtered through a bed of sodium bicarbonate to remove catalyst residues. The solvent was evaporated under vacuum.

3. Results and discussions

Linseed oil characterization

The most important part of the oil, the triglyceride (ester part) represent ~95% of the oil molecule. A triglyceride contains one molecule of glycerol and three molecules of fatty acids. Fig. 1 shows a triglyceride structure with three different types of fatty acids (R_1, R_2 and R_3) and three carbon positions on the glycerol that may carry different fatty acids.

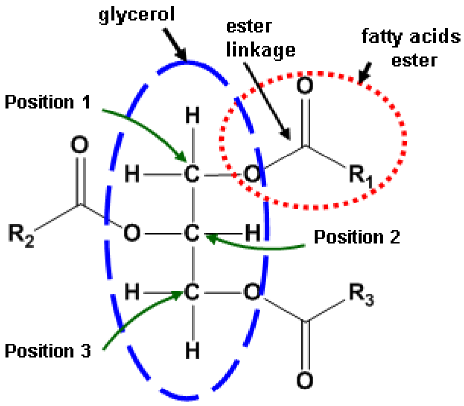


Fig 1. Structure of a triglyceride (with three positions that can carry different fatty acids: R_1, R_2, R_3)

In order to establish the LO fatty acids profile it was performed several analysis that can offer information about the structural composition of the oil.

^{1}H-NMR analysis of linseed oil

From the recorded spectral data, the fatty acids composition of the oil was calculated according to recently reported method [6]. Fig. 2 presents the ^{1}H-NMR spectrum of crude linseed oil and Table 1 lists the signals and peaks assignment of the crude LO. The fatty acid composition of LO is presented in Table 2.

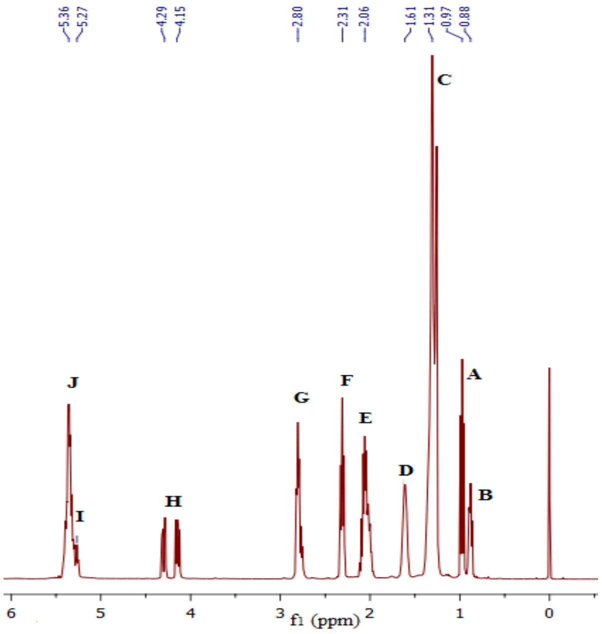


Fig. 2. ^{1}H-NMR spectrum of unmodified linseed oil

Table 1

^{1}H-NMR signals and peak assignment of linseed oil spectrum

Signal	δ (ppm)	Proton	Compound
A	0.97	$-CH_2=CH-CH_2-C\mathbf{H}_3$	linolenic acid
B	0.88	$-CH_2-CH_2-CH_2-C\mathbf{H}_3$	all acids except linolenic acid
C	1.31	$-(C\mathbf{H}_2)_n-$	all fatty acids
D	1.61	$-C\mathbf{H}_2-CH_2-COOR$	all fatty acids
E	2.06	$-C\mathbf{H}_2-CH=CH-$	all unsaturated fatty acids
F	2.31	$-C\mathbf{H}_2-COOR$	all fatty acids
G	2.80	$-CH=CH-C\mathbf{H}_2-CH=CH$	linolenic and linoleic fatty acid
H	4.15-4.29	$-C\mathbf{H}_2-O-COR$	glycerol (α-position)
I	5.27	$-C\mathbf{H}-O-COR$	glycerol (β-position)
J	5.36	$-C\mathbf{H}=C\mathbf{H}-$	all unsaturated fatty acids

Table 2

Linseed oil fatty acid composition by ^{1}H-NMR

Fatty acids	Amount (%)
linolenic acid 18:3	51
linoleic acid 18:2	19
mono-unsaturated 18:1 (oleic acid)	20
saturated acid 18:0	10

GC-MS analysis of linseed oil

In order to obtain the oil composition, a fatty acid methyl esters (FAME) mixture was prepared by oil transesterification, using NaOH-MeOH as catalyst [16]. The final concentration of mono-, di-, tri- and saturated fatty acids was determined using a commercially standard mixture of 37 fatty acids methyl esters (FAME). The same information regarding the fatty acid composition of the LO was obtained through GC-MS analysis.

Based on fatty acids composition determined by ^{1}H-NMR and GC-MS the average molecular weight and number of double bonds of the LO was calculated. Thereby, the average molecular weight of LO is M ≈ 869 g/mole; the ratio of double bond is ≈ 6.2 mol C=C /mol of LO.

FTIR analysis of linseed oil

To determine the chemical structure specific signals of the LO, FTIR spectrum were registered (Fig. 3).

ATR-FTIR signals: *FTIR (ATR, cm^{-1})*: 3010 ($\nu_{=CH-}$); 2925, 2856 (ν_{C-H} asim, sim), 1744 ($\nu_{C=O}$); 1655 ($\nu_{C=C}$ from unsaturated acids); 1456 (δ_{CH2}); 1368 (δ_{CH3}); 1235, 1162, 1100 (ν_{C-O}); 718 (ρ_{CH2}).

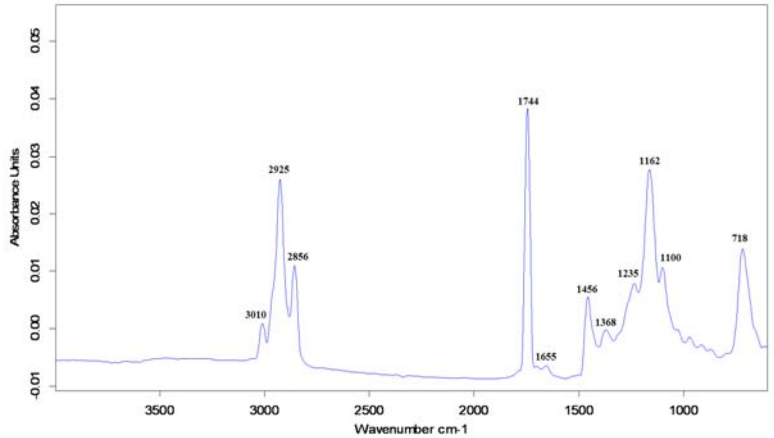
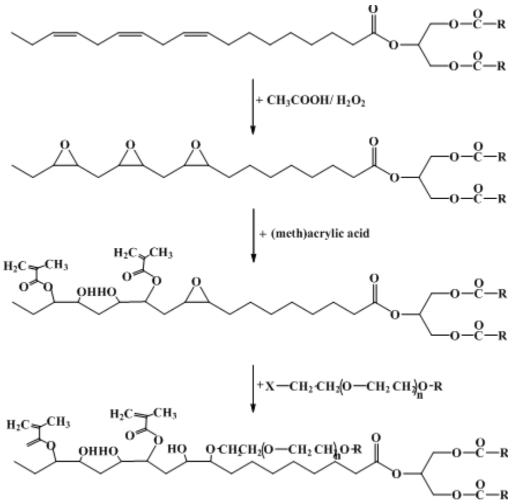


Fig. 3. FTIR spectrum of unmodified linseed oil

Synthesis of the MLO-PEG monomers

MLO-PEG compounds synthesis (Scheme 1) involves a three-step reaction where the first one represent the conversion of C=C double bond of the LO structure into epoxy rings, the second one represent the partial opening of the epoxide rings with methacrylic acid to produce MELO and the last step is representing by the opening of the unreacted epoxy groups and PEG units attaching thereby achieving MCO-PEG compounds.



Scheme 1. Synthesis route to produce novel MLO-PEG compound

Characterization of the obtained compounds

Epoxidized linseed oil (ELO)

The epoxidation of double bonds has been done in different proportions respectively 50, 75 and 100% from the total number of the double bond from the LO structure. Reaction yields: 88% for ELO_50%, 92% for ELO_75%, 94% for ELO 100%.

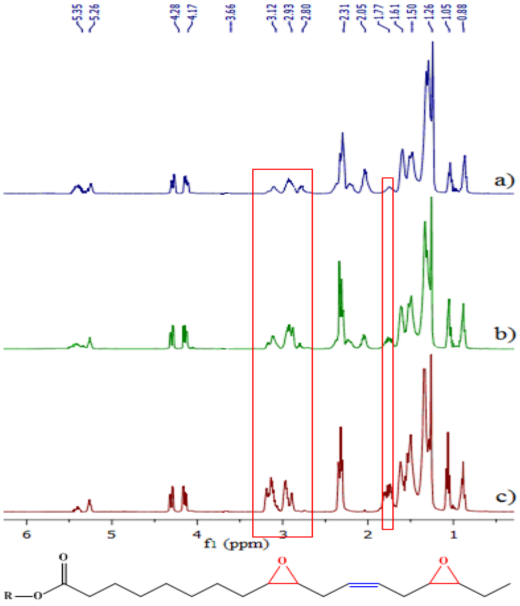


Fig. 4. ^{1}H-NMR spectra of epoxidized LO:
a) ELO_50%; b) ELO_75%; c) ELO_100%

The corresponding assignment of the signals for LO has been reported above (Fig. 2). Fig. 4 a), b) and c) correspond to ELO epoxidized at aproximatively 50%, 75%, 100%, respectively. The percentages were calculated from the integrals of double bonds and epoxy ring proton signals. The signals associated to the epoxy group are: 2.80-3.12 ppm representing internal and marginal -C**H** protons of the epoxy ring and 1.75 ppm which represents -C$\mathbf{H}_2$ protons between two epoxy rings. In the overlapped spectra it can be observed the increase of the intensity of the epoxy rings specific signals from ELO_50% to ELO_100% which demonstrate the increasing of the percentage of the epoxy groups attached to the oil chain. For ELO 50% and 75% can be observed a signal at 5.35 ppm corresponding to C=C double bond that still exists on the fatty acid chains while, for ELO 100%, the signal is very weak; this indicates that the epoxidation occurred at a rate close to 100%. Also, the 2.05 ppm signal intensity (-C$\mathbf{H}_2$-CH=CH-), decrease until extinction for ELO_100%.

ATR-FTIR signals: *FTIR (ATR, cm^{-1})*: 2926, 2857 ($\nu_{C\text{-}H}$ asim, sim), 1741 ($\nu_{C=O}$); 1640 ($\nu_{C=C}$ from unsaturated acids still present to the structure for ELO 50% and 75%); 1457, 1374 (δ_{CH} from CH_2 and CH_3); 1242, 1163, 1101 ($\nu_{C\text{-}O}$); 828 ($\nu_{C\text{-}O\text{-}C}$ from epoxi ring); 728 (ρ_{CH2}).

Methacrylated epoxidized linseed oil (MELO)

The methacrylation reaction had to be performed selectively, in order to affect only a desired amount of epoxy rings and to protect the remaining ones. Thus, in this reaction step, our goal was to obtain compounds with methacrylate moieties grafted and some unreacted epoxide groups on the LO structure.

Some protocols reported in the literature have been used [16-18], but adapted to our needs. Thus, in the methacrylation phase, a commonly catalyst – triethylamine (TEA) was used, but another less known catalyst – diazabicyclo octane (DABCO) has also been tested.

When TEA was the reaction catalyst, following reaction yields were obtained: 72% for MELO_50%, 89% for MELO_75%.

In parallel, the synthesis of the MELO compounds was performed with DABCO. It has been used in many organic synthesis as a good solid catalyst and has received considerable attention as an inexpensive, eco-friendly, high reactive, easy to handle and non-toxic base catalyst for various organic transformations, affording the corresponding products in excellent yields with high selectivity [19].

When the used catalyst was DABCO, the reaction yields obtained was: 69% for MELO_50%, 67% for MELO_75%. So, when TEA was used, we obtained better yields.

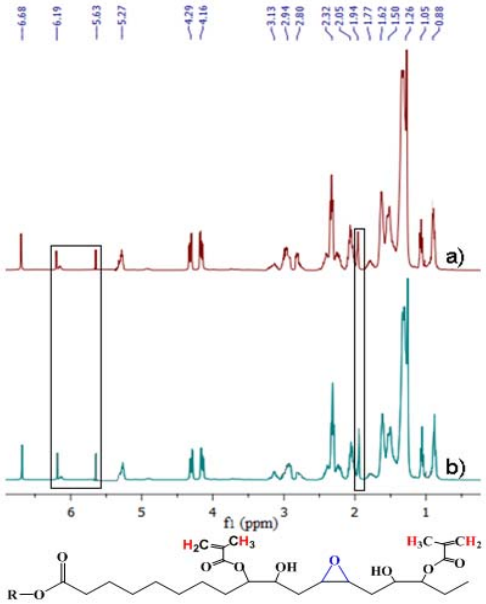


Fig. 5. ^{1}H-NMR spectra of methacrylated epoxidized LO:
a) MELO_50%; b) MELO_75%

^{1}H-NMR spectra were recorded for the methacrylated epoxidized LO (MELO) in different percentage, 50 and 75% respectively (Fig. 5). The percentages were calculated from the integrals of methacylate groups and epoxy ring proton signals. The representative signals for metacrylate groups were identified. The signals at 5.63 ppm and 6.19 ppm corresponding to C**H**$_2$ protons from methacrylate moieties and signal at 1.94 ppm corresponding to C**H**$_3$ protons from vinyl functionality of the methacrylated monomer. Signals from 2.80-3.13 ppm assigned to epoxy rings are present too and their intensity decrease in MELO_75% spectrum.

ATR-FTIR signals: *FTIR (ATR, cm^{-1}):* 2927, 2858 (ν_{C-H} asim, sim.); 1738 ($\nu_{C=O}$); 1634 ($\nu_{C=C}$ from methacrylic group); 1456, 1378 (δ_{CH} from CH_2 and CH_3); 1286, 1163, 1105 (ν_{C-O}); 1010, 946 (δ_{C-H} and $\delta_{=C-H}$); 820 (ν_{C-O-C} from epoxy ring); 731 (ρ_{CH2}).

There were not registered major differences between the recorded ^{1}H-NMR and FTIR signals when DABCO was used as reaction catalyst.

PEG-ilated methacrylated linseed oil (MLO-PEG)

MELO 50% and 75% was both reacted with PEG with different molecular weight (MW≈550 or 750 g/mol), following the same procedure, to produce hydrophilic compounds. Reaction yields: 96% for MLO_50%-PEG550, 97% for

MLO_75%-PEG550, 95% for MLO_50%-PEG750, 98% for MLO_75%-PEG750.

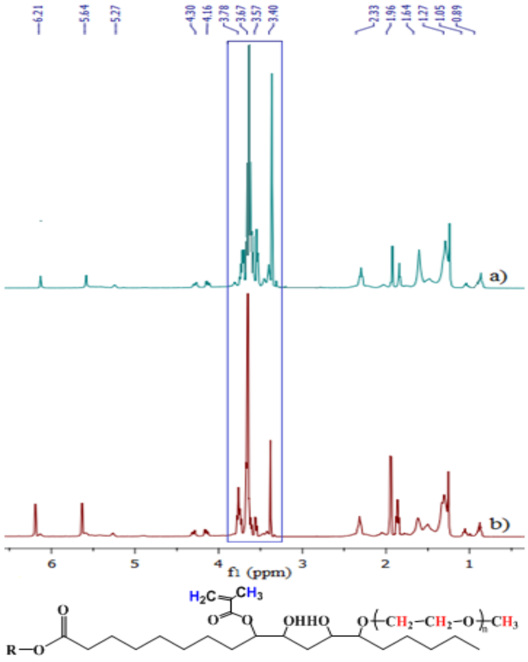


Fig. 6. ^{1}H-NMR spectra of MLO-PEG:
a) MLO_50%-PEG 550; b) MLO_75%-PEG 550

In Fig. 6 the overlapped ^{1}H-NMR spectra of MLO_50%-PEG550 (a) and MLO_75%-PEG550 (b) are presented. The percentages were calculated from the integrals of methacylate groups and PEG proton signals. The specific signals corresponding to the terminal CH_3 of the PEG chains appear around 3.40 ppm. 3.57-3.78 ppm represent the specific range of the CH_2 of the PEG units signals (repetitive groups). Oil and methacrylate groups specific signals have a low intensity due to the strong intensity of the specific PEG signals: CH_2 groups that are repeated several times (chain length).

ATR-FTIR signals: *FTIR (ATR, cm^{-1}):* 2923, 2864 ($\nu_{C\text{-}H}$ asim, sim.); 1741 ($\nu_{C=O}$); 1637 ($\nu_{C=C}$ from methacrylic group); 1457, 1354, (δ_{CH} from CH_2 and CH_3); 1293, 1246, 1105 ($\nu_{C\text{-}O}$); 946 ($\delta_{=C\text{-}H}$); 723 (ρ_{CH2}).

For hydrophilic compounds with PEG units with MW≈ 750 g/mol attached (MLO_50%-PEG750 and MLO_75%-PEG750), the same specific signals are recorded both in the case of ^{1}H-NMR and FTIR analysis.

4. Conclusions

Four linseed oil-based compounds have been synthesized and characterized in this study. They can be used as hydrophilic monomers in order to produce ecological materials with various applications. Thus, the use of the petroleum-based raw materials for chemical industry can be reduced and also vinylic and acrylic compounds currently used, can be replaced with some of these oil-based ecological monomers .

The properties of these monomers can be tuned by varying the type (molecular weight) of PEG units and the ratio between the polymerization functions-hydrophilic moieties.

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