

# Production of polyols and mono-ols from 10 North-American vegetable oils by ozonolysis and hydrogenation: A characterization study



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## ABSTRACT

Ozonolysis and hydrogenation reaction was performed on ten North-American vegetable oils. From these oils, canola oil and sunflower oil were chemically refined. Camelina, juvenile canola, three types of flax and three types of mustard were cold pressed and their oils were processed without further treatment. The production of polyols from unrefined vegetable oils by the ozonolysis–hydrogenation process is reported for the first time. The resulting polyols and mono-ols were characterized by GC-FID, DSC, GPC, HPLC, and their acid and hydroxyl numbers, viscosity and molecular weight distribution were determined. Results showed that the physical properties of the refined vegetable oils were different from the unrefined vegetable oils as they displayed higher hydroxyl values. However, the physical properties of the polyols from the unrefined starting materials are expected to be sufficient to be utilized as monomers for the production of polymeric materials.

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## 1. Introduction

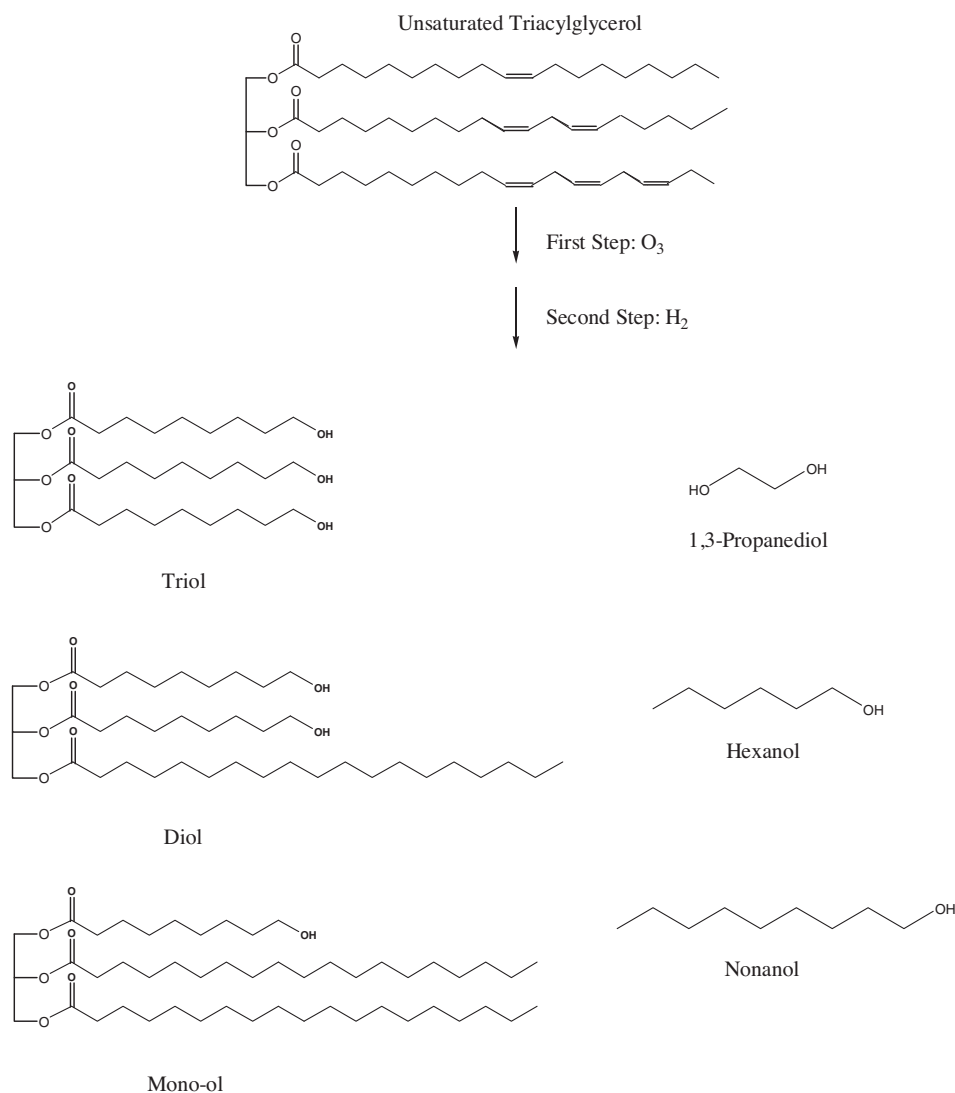
The production of polyol (poly-alcohols) monomers from vegetable oils has been an area of focus in polymer chemistry, particularly for the production of polyurethanes, to reduce the dependence on petroleum-based hydrocarbons. The epoxidation (Guo et al., 2000; Kiatsimkul et al., 2008; Kong et al., 2012) and ozonolysis–hydrogenation (Petrovic et al., 2005; Narine et al., 2007a) reactions are efficient and well-known chemical routes to introduce hydroxyl groups on triacylglycerols (TAGs). There are major structural differences found in the resulting monomers depending on the chemical route favored. Through epoxidation, the hydroxyl groups are located in a secondary position while through ozonolysis–hydrogenation, the hydroxyl groups are in a primary position. Furthermore, the co-products of the latter reaction are of commercial interest. These are short-chain mono-alcohols (mono-ols) or di-alcohols (diols) (Fig. 1). Mono-ols, such as hexanol, are used by the perfume industry (Kandra and Wagner, 1998) whereas diols, such as 1,3-propanediol, are used as chain extenders (Miao et al., 2013; Rashmi et al., 2013). The main drawbacks of the ozonolysis–hydrogenation reaction are the formation of acid at

the ozonolysis stage and the high cost of the reaction. Recently, Omonov et al. (2011) focused their efforts to optimize the ozonolysis step by selecting conditions in order to reduce the amount of carboxylic acid formed in the aldehyde pool. It is important to note that the concentration of acid in the resulting polyols is not above the limit to prevent the formation of polyurethanes (Petrovic et al., 2005; Kong et al., 2007; Narine et al., 2007b,c).

This publication is focused on the production of polyols, diol and mono-ols from unrefined vegetable oils in order to reduce the cost and increase the environmental friendliness of the ozonolysis–hydrogenation process. The unrefined vegetable oils selected were mustard oils (brown, yellow and oriental), flax oils (Nulin 50, CDC Bethune and Linola 2090), camelina oil and immature canola oil. The flaxes are of particular interest since they were genetically modified and therefore contained a unique fatty acid profile. Mustard oils were selected due to their high content in erucic acid which renders them indigestible for humans (Al-Jasass and Al-Jasser, 2012). Camelina oil was selected since it is used as industrial oil (Zubr, 1997) and immature canola was selected since it does not meet the allowable chlorophyll limit for food consumption (Daun and Symons, 2000; Daun, 2003). Because unrefined vegetable oils were not physically or chemically treated, they contained molecules other than TAGs such as sterols and tocopherols. Therefore, the study of the influence of the non-TAG content on the resulting polyols, mono-ols and diols was an objective of this study.

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**Fig. 1.** Scheme of ozonolysis–hydrogenation reaction of vegetable oils.

The polyols and light alcohol content of these oils were compared to canola oil and sunflower oil which acted as standards since these oils were chemically refined.

## 2. Materials and methods

### 2.1. Chemicals and materials

Refined sunflower oil was supplied by Bunge oil (Alberta), canola oil was supplied by Cargill Canada (Alberta), seeds of flax (Nulin 50, CDC Bethune and Linola 2090) were supplied by Viterra Inc. Vegreville (Alberta), and seeds from brown, oriental, and yellow mustard were supplied by Viterra Specialty Crops (Alberta), cold pressed immature canola oil and seeds of camelina were supplied by local farmers (Alberta).

Ethyl acetate (ACS reagent  $\geq 99.5\%$ ) was purchased from Sigma–Aldrich and used as solvent for ozonolysis reaction. Sponge Nickel (A-7063) promoted with 1% molybdenum (slurry in water) was obtained from Alfa Aesar and used as the hydrogenation catalyst. Celite was obtained from Fisher Scientific USA.

The following reagents were used as calibrating standards for GC-FID. Propanal ( $\geq 98\%$ ), propanoic acid ( $\geq 98\%$ ), hexanal ( $\geq 98\%$ ), nonanal ( $\geq 98\%$ ), methyl nonanoate ( $\geq 98\%$ ), ethyl nonanoate ( $\geq 98\%$ )

and heptanoic acid ( $\geq 99\%$ ) were purchased from Sigma–Aldrich. Propanol (99%), hexanol (99%), heptanol (99%), nonanol (97%), hexanoic acid (99%), nonanoic acid (97%) were purchased from Acros. 1,3-Propanediol ( $\geq 99\%$ ) was supplied by DuPont Tate & Lyle Zemea. p-Anisaldehyde ( $\geq 98\%$ ) was purchased from Sigma–Aldrich and used as an internal standard for the GC-FID measurements.

### 2.2. Cold press

A Komet screw oil expeller was used to crush the seeds of the different varieties of flax and mustard in order to extract the vegetable oil. The processing rate ranged from 4 to 6 kg/h.

### 2.3. Centrifugation

Cold press mustard, camelina, flax and juvenile canola oils were centrifuged with a Beckman Coulter Avanti J26XPI centrifuge with a JLA 8.1000 rotor. The speed used was 6500 rpm (which equals  $10,543 \times g$ ) for 30 min at room temperature.

### 2.4. Vegetable oil characterization

The analysis of fatty acid methyl esters (FAMES) was carried out using a Perkin Elmer Clarus 500 gas chromatograph

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