



# Derivatization of castor oil based estolide esters: Preparation of epoxides and cyclic carbonates

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## ABSTRACT

Estolides that are based on castor oil and oleic acid are versatile starting points for the production of industrial fluids with new properties. A variety of unsaturated estolides were derivatized by epoxidation with hydrogen peroxide. The epoxidized estolides were further modified using supercritical carbon dioxide and tetrabutylammonium bromide to chemically incorporate carbon dioxide into the material yielding a 5-membered cyclic carbonate structure. These new epoxides and cyclic carbonates exhibited higher pour points, oxidation onset temperatures, and viscosities, compared to the corresponding unsaturated precursors. One derivative had a dynamic viscosity of  $\sim 9000$  mPa s at 40 °C, demonstrating potential for use in industrial applications.

## 1. Introduction

Castor (*Ricinus communis* L.; Euphorbiaceae) oil is a useful industrial crop oil (Mutlu and Meier, 2010), which is different from many other triacylglycerol (TAG) structured crop oils since it contains approximately 90% ricinoleic acid (12(R)-hydroxy-octadec-cis-9-enoic acid; 12-OH 9c-18:1), a hydroxy-containing unsaturated fatty acid. The hydroxy moiety gives castor oil improved functionality and polarity that has historically been used advantageously in lubricants (Teeter et al., 1953) and polymer synthesis (Dietrich et al., 1999; Kluszczewski et al., 2012) and fuel additives (Moser et al., 2008).

There has been recent interest in a class of oligomeric esters based on vegetable oils and fatty acids that are termed estolides. Estolides are commonly prepared by reacting the carboxylic acid group of a fatty acid with a reactive site of another fatty acid to produce an ester linkage along the alkyl chain. The TAG structure of the oil can be preserved in the estolide or it can be transesterified into the corresponding alkyl esters. In some cases, strong acids, such as triflic acid (Mathers et al., 2008) are used. In other cases, such as when ricinoleic acid is used, any esterification catalyst will suffice (Nelson and Achatz, 2002). In an especially interesting work, ring opening of an epoxide compound was also shown to produce estolide structures (Pagès and Alfos, 2001). Although estolides have been prepared from many oils (Cermak and Isbell, 2001a; Cermak et al., 2015; Cermak and Isbell, 2001b; Cermak and Isbell, 2004; Cermak et al., 2011; Harry O Kuru et al., 2001; Isbell

et al., 2000), those that contain hydroxy groups along the alkyl chain (Scheme 1), such as castor oil, are especially amicable to estolide preparation (Awang et al., 2007; Cermak et al., 2006; Isbell and Cermak, 2002).

By controlling the synthetic conditions, estolides can also contain residual unsaturated sites that can subsequently be utilized to carry out further chemical modification. For example, the unsaturated sites of an estolide can be epoxidized (Forest and Bredsguard, 2012). Recently, it was shown that epoxy-containing estolides can be converted into their corresponding five-membered cyclic carbonates and subsequently ring-opened by alkyl amines (Doll et al., 2016). Potential uses of these compounds include lubrication, viscosity modification and polymer applications. However, this technology was not extended to the more industrially relevant castor oil estolides with their more facile estolide synthesis. Herein, the epoxidation and carbonation of castor oil based estolides are examined and, additionally, the previously unexplored idea of producing cyclic carbonate esters, whereby the TAG backbone remains intact, are also first reported.

## 2. Materials and methods

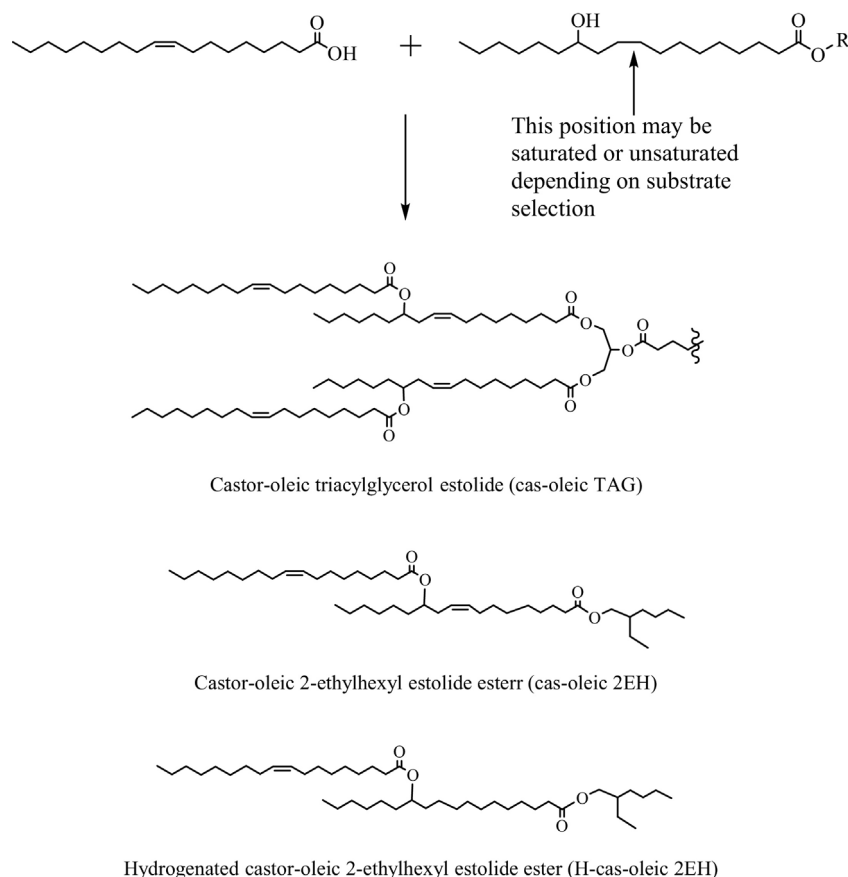
### 2.1. Materials and equipment

Hydrogen peroxide as a 30% aqueous solution (Sigma-Aldrich, St. Louis, MO, A.C.S. Reagent), formic acid (Sigma-Aldrich, St. Louis, MO,

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**Scheme 1.** The synthesis of estolides from oleic acid and castor oil alkyl esters or castor oil. R = the rest of the structure of a triacylglycerol in cas-oleic TAG, or 2-ethylhexyl in the estolide esters.

96%, A.C.S. reagent), toluene (Fisher, Fairlawn, NJ, 99.8%), hexanes (Sigma-Aldrich, St. Louis, MO, > 95%, HPLC grade), sodium chloride (Fisher, Fairlawn, NJ, A.C.S. Reagent), sodium sulfate (Fisher, Fairlawn, NJ, certified A.C.S.), glacial acetic acid (Fisher, Fairlawn, NJ, 99.9%), chlorobenzene (Sigma-Aldrich, St. Louis, MO, 99%), crystal violet (Sigma-Aldrich, St. Louis, MO, 95%), hydrobromic acid (Fluka, St. Louis, MO, 33% in acetic acid), potassium hydrogen phthalate (Mallinckrodt, St. Louis, MO, 99.5%), and tetrabutylammonium bromide (Sigma-Aldrich, St. Louis, MO, 99%) were used as received. Carbon dioxide (Airgas, Radnor, PA, 99.8%) was supplied in a pressurized tank with a dip tube. All estolides studied herein were synthesized according to literature methods (Cermak and Isbell, 2001a; Cermak and Isbell, 2001b; Isbell et al., 2000). Because of the hydroxy functionality in castor oil and its' alkyl esters, strong acid catalysis was not necessary for the estolide synthesis (Isbell and Cermak, 2002).

### 2.1.1. Spectroscopy and oxirane values

The Fourier transform infrared spectra (FTIR, Thermo Nicolet, Madison, WI, Nexus 470) were collected over 32 scans using a Smart Orbit accessory equipped with a diamond plate. A Bruker (Boston, MA) Avance 500 nuclear magnetic resonance (NMR) spectrometer, operating at 500 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$ , was used to collect spectra. Heteronuclear Single Quantum Correlation Spectroscopy (HSQC) and Heteronuclear Multi-Bond Correlation spectroscopy (HMBC) were performed in order to accurately assign signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Oxirane values of the relevant samples were determined following AOCS method Cd 9–57, which used hydrobromic acid in acetic acid as the titrant and has a standard deviation of  $\pm 0.2\%$  oxirane oxygen content.

### 2.1.2. Physical property and stability measurements

A TA Instruments-Waters L.L.C. (New Castle, DE) ARES controlled strain rheometer with 1 K FRTN1 transducer using TA Orchestrator software package 7.2.2.1 was used for viscosity measurements. Experiments were run with a constant shear rate of  $100\text{ s}^{-1}$  at varied temperatures, after confirming Newtonian behavior.

Pour points were measured by method ASTM D97-02 with a slight modification to reduce sample size. Using a slightly smaller vial inside of the cylindrical test jar, the sample size was reduced to  $\sim 9\text{ g}$ . The new method was validated by providing identical pour points to the full scale method using the olefinic estolide samples with a standard deviation of  $\pm 3\text{ }^\circ\text{C}$ .

### 2.1.3. Pressurized differential scanning calorimetry (PDSC)

Pressurized Differential Scanning Calorimetry (PDSC) experiments were carried out using a TA Instruments (New Castle, DE) Q-20 calorimeter. A 2 mg sample was used with a hermetically sealed aluminum pan containing a pinhole in the lid. The sample chamber was pressurized with air, 1379 kPa (200 PSI), equilibrated at  $50\text{ }^\circ\text{C}$ , and then heated using a scanning rate of  $10\text{ }^\circ\text{C min}^{-1}$  to a temperature of  $250\text{ }^\circ\text{C}$ . The onset temperature of oxidation was taken as the temperature obtained by fitting a straight line to the steepest point in rise of the exothermic peak. Samples were run in duplicate and had standard deviations  $< 2\text{ }^\circ\text{C}$ .

## 2.2. Epoxidation and carbonation reactions

The carbonated and epoxidized estolides were first synthesized through epoxidation with hydrogen peroxide and formic acid, followed by ring-opening with carbon dioxide using tetrabutylammonium bromide as catalyst (Scheme 2) following the method reported by Doll and

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