Supplementary Material (ESI) for Green Chemistry

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Oxidation, Friction Reducing, and Low temperature Properties of Epoxy Fatty Acid Methyl Esters‡

Brajendra K. Sharma,[a,b] Kenneth M. Doll*,[a] and Sevim Z. Erhan

[a]USDA/NCAUR/ARS,** Food and Industrial Oil Research, 1815 N. University Street, Peoria IL 61604, USA

[b]Dept. of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA

* Phone: 309-681-6103; FAX: 309-681-6340; Email: dollkm@ncaur.usda.gov

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The syntheses of EMO, EMLO, and EMLEN

Epoxidations:

The reactions were carried out using a slightly modified synthesis of Bunker and Wool referenced in the main manuscript. The EMO synthesis is representative: 200.0 g (0.67 mol) of MO was placed in a 500 mL round bottom flask equipped with an overhead stirrer. 102 g (2.2 mol) of formic acid was slowly added forming a layered mixture. The reaction flask was cooled in an ice bath and 163 g of 30% hydrogen peroxide (1.44 mol) was added over about 5 min while monitoring the temperature of the solution. The peroxide was added slowly enough such that the temperature of the solution did not exceed 18.4 ^{o}C, but rapidly enough to keep the reaction solution from solidifying. Gas bubbles were evident as the hydrogen peroxide was added. The reaction was allowed to proceed at room temperature and aliquots were taken and analyzed by GC/FID. The GC/FID utilized was a Hewlett Packard (Loveland, CO) 5890 GC system equipped with a 6890 series injector and an FID detector. A J and W DB-1 column (15m x 320 um) was used with a helium flow rate of ~0.9 mL min^{-1}. The temperature program used started at 180 ^{o}C, held for two minutes, then increased to 280 ^{o}C at 5^{o} C min^{-1} and held for 5 min. The injection solution contained ~20 uL of sample dissolved in 1 mL of acetone or heptane. A 1 uL injection was used. Under these conditions, the starting material a shorter retention time compared to the products. For example, methyl oleate, methyl linoleate, and methyl linolenate are all detected between 7-8 min after injection. EMO however, retains for 9.9 min. This is a convenient method for monitoring of reaction time. The reaction typically took 8-12 hours, but was heavily dependent on the reaction mixing. The product was purified using a separatory funnel by dissolving the material in

200 mL of hexanes then discarding the aqueous / formic acid layer. The pH of the organic layer was measured with pH paper and was 6. Saturated sodium bicarbonate solution (200 mL) was shaken with the hexane layer and removed. This was repeated until the pH of the solution was >7 (3 times). The hexane layer was washed with saturated NaCl solution (400 mL x 3) and dried over ~28 g of anhydrous sodium sulfate, filtered through a fritted funnel and evaporated to dryness (60 ^{o}C; overnight). The product is a very slightly colored viscous liquid which slowly became cloudy when cooled below room temperature. The isolated yield was 221.1 g (97%) which was stored over molecular sieves. The product purification was also performed using Et_2O instead of hexanes, but solvent removal proved to be more difficult. The epoxidations of MLO (200 g) and MLEN (62.1) were performed in an analogous manner yielding 221.7 g (95%) and 61.0 g (85%) of epoxidized material, respectively.

The EMO ^{1}H NMR: (500 MHz, $CDCl_3$): δ 3.61 (s, 3, methoxy), δ 2.85 (t, 2, epoxide ring), δ 2.26 (t, 2, protons on carbon α to carboxy), δ 0.85 (t, 3, end of fatty chain), and un-resolvable signals from δ 1.3-2.3. ^{13}C NMR: (125 MHz, $CDCl_3$) δ 174 (carbonyl), δ 57 (epoxide), δ 51 (methoxy), δ 14 (end of fatty chain), and δ 20-35 (multiple signals).

The EMLO ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.66 (s, 3, methoxy), δ 3.12, 3.08, 2.98 (m, 4, epoxide ring), δ 2.30 (t, 2, protons on carbon α to carboxy), δ 0.91 (t, 3, end of fatty chain), and un-resolvable signals from δ 1.3-1.7 ppm. ^{13}C NMR: (125 MHz, $CDCl_3$) δ 174 (carbonyl), δ 54-57 (epoxide), δ 51 (methoxy), δ 14 (end of fatty chain), and δ 20-35 ppm (multiple signals).

The EMLEN ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.49 (s, 3, methoxy), δ 3.03, 2.96, 2.81 (m, 4, epoxide ring), δ 2.13 (t, 2, protons on carbon α to carboxy), δ 0.89 (t, 3, end of fatty chain), and un-resolvable signals from δ 1.2-1.7 ppm. ^{13}C NMR: (125 MHz, $CDCl_3$) δ 174 (carbonyl), δ 54-58 (epoxide), δ 51 (methoxy signals), δ 10 (end of fatty chain), and δ 18-34 ppm (multiple signals).