**ABSTRACT:** The common milkweed (Asclepias syriaca L.) is a new industrial crop. Its seed oil (TAG) is highly polyunsaturated. In the search for novel applications for milkweed seed oil, the olefinic groups in the TAG were oxidized to polyhydroxy TAG via epoxidation and subsequent epoxy ring-opening reactions. These polyhydroxy TAG exhibit unique industrially desirable emulsoid properties in water. Esterification of the secondary polyhydroxy functionalities of the TAG derivatives of the oil with trans-4-hydroxy-3-methoxycinnamic acid (ferulic acid) has resulted in the development of novel cinnamate esters of milkweed oil. These cinnamates are also obtainable via direct ring-opening of the epoxy TAG intermediate with ferulic acid. Among the interesting characteristics of the ester derivatives is their UV radiation-absorbing property.

For a new industrial crop to achieve economic success, its components must have unusual properties that set it apart for new markets. Such markets are usually small-volume, value-added niches. The higher-value products give incentives to the farmer to undertake the initial capital investment necessary to cultivate the new crop. The situation for the common milkweed (Asclepias syriaca L.) would have presented a double impediment to commercialization because this species is viewed as a nuisance by most farmers who have encountered it in their crop fields or in the range. But in spite of its image, milkweed in recent years has again become a new industrial crop because of market demand for its floss (fiber) in hypoallergenic pillows and comforters. Interestingly, the floss is the same component of the seed that made milkweed a strategic material during World War II (1). But a one-product crop is hardly profitable. Fortunately for milkweed, the increasing demand for the fiber and the hulls has resulted in studies to explore possible uses for the seed components and the hulls. To generate new uses for the seed oil, which is 25–30% by weight of the seed, we have successfully converted the polyolefinic TAG of milkweed oil (Table 1) to the oxiranes and polyhydroxy TAG (2). In seeking further diversification of the nonfood industrial application for the oil, we have also explored conversion of the TAG intermediates (epoxy and polyhydroxy forms) into estolides. Estolides have been identified as naturally occurring in some seed oils especially those from species having a monohydroxy functional group in the acyl chain of the TAG (3–7). The synthesis of ricinoleic acid estolides had earlier been reported by Acharya (8). But it was the application of carbocation chemistry that enabled estolides to be prepared on a pilot scale from unsaturated carboxylic acids that have no hydroxyl functional groups (9). Mechanistically, unlike the traditional condensation reaction between an alcohol moiety of an acyl chain and a free carboxylic acid to form estolides, a larger-scale estolide reaction depends on the initial generation of an electrophile at one end of a C=C bond as a result of protonation of the double bond by a Brønsted acid catalyst. The resulting electrophile then accepts an electron pair from the carboxyl OH of a neighboring carboxylic acid moiety thus forming the estolide. Overall the reaction is an addition across a C=C bond by the –OH moiety of a carboxylic acid. These reactions have only been successful with monounsaturated carboxylic acids (10–12). Compton and coworkers (13) used lipase-catalyzed transesterification of soybean oil with ferulic acid ethyl ester to produce UV-absorbing glycerides. The present study reports the novel synthesis of a UV-absorbing estolide by condensation of milkweed polyhydroxy TAG with trans-4-hydroxy-3-methoxycinnamic acid (ferulic acid) to give the cinnamate ester of the intact TAG. This ester is also accessible by direct ring-opening of milkweed epoxi TAG with 4-hydroxy-3-methoxycinnamic acid in the presence of a Lewis acid catalyst.

**MATERIALS AND METHODS**

*Materials.* Crude, cold-pressed milkweed oil was obtained from Natural Fibers Corporation (Ogallala, NE). Activated acid clay (Bentonite) was obtained from Harshaw/Filtrol Clay Products Division, (Jackson, MS). Sample centrifugation was performed using a Beckman Coulter centrifuge, model J2-HS (Beckman Coulter, Inc., Fullerton, CA). Formic acid, 96% was

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**TABLE 1**

FA Composition of Milkweed (Asclepias syriaca) Oil

<table>
<thead>
<tr>
<th>Acid type</th>
<th>% Content</th>
<th>Acid type</th>
<th>% Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic</td>
<td>31.0 (Δ9, Δ11)</td>
<td>Palmitoleic</td>
<td>9.6 (Δ9, Δ11)</td>
</tr>
<tr>
<td>Linoleic</td>
<td>50.5</td>
<td>Palmitic</td>
<td>5.7</td>
</tr>
<tr>
<td>Linolenic</td>
<td>1.2</td>
<td>Stearic</td>
<td>2.5</td>
</tr>
</tbody>
</table>

*From Reference 2.
obtained from Fisher Scientific (Chicago, IL); hydrogen peroxide, 50% in water, and anhydrous ZnCl₂ powder were from Aldrich Chemical Company (St. Louis, MO). ¹H and ¹³C NMR spectra were obtained on a Bruker ARX-400 with a 5-mm dual proton/carbon probe (Bruker Spectrospin, Billerica, MA); the internal standard used was tetramethylsilane. Specific rotation [α]²⁰_D values were measured on a PerkinElmer Polarimeter model 341 (PerkinElmer, Norwalk, CT).

**Viscosity measurements.** Viscosity measurements were determined in a Temp-Trol viscosity bath (Precision Scientific, Chicago, IL) using Cannon-Fenske viscometers for transparent liquids (Cannon Instrument Company, State College, PA) in accordance with AOCS Official Method Tq 1a-64 (14). The size of the Cannon-Fenske viscometer used was number 400 (378E) or 300. The cleaned dry tube was loaded at room temperature with the sample oil and placed in its holder in the constant-temperature bath. The sample was allowed to equilibrate for 10 min at 40°C or 15 min at 100°C before the sample was suctioned into the lower bulb while the meniscus just overshot the mark above the lower bulb. The suction was removed and the meniscus was adjusted to the mark. The sample was allowed to flow at the same time the stop clock was started. The duration (in seconds) it took the meniscus to reach the mark below the bulb multiplied by the tube constant gave the viscosity of the fluid. The measurement was replicated for reproducibility.

**FTIR spectrometry.** Test samples of the reaction products were pressed between two NaCl discs (25 × 5 mm) to give thin transparent oil films for analysis by FTIR spectrometry. Spectra were measured on a Bomem Arid Zone FTIR spectrometer (Bomem MB-Series; Bomem, Québec, Canada) equipped with a deuterated triglycine sulfate detector. Absorbance spectra were acquired at 4 cm⁻¹ resolution and signal-averaged over 32 scans. Interferograms were Fourier-transformed using cosine apodization for optimal linear response. Spectra were baseline corrected and normalized to the methylene peak at 2927 cm⁻¹.

**Methods. (i) Synthesis of epoxy TAG.** Refined milkweed oil [186.8 g, 212.1 mmol, iodine value (IV) = 111.4] was placed in a 500-mL three-necked jacketed flask equipped with a mechanical stirrer and heated to 40.5°C. Formic acid (96%, 12.0 g, 25.0 mmol, ~0.3 equiv/mol of C=C) was added and the mixture stirred to homogeneity. Hydrogen peroxide (50%, 70.0 g, 57.4 mL, 4.75 equiv) was added slowly. At the end of the hydrogen peroxide addition, the temperature was raised to 70°C and vigorous stirring was continued for 7 h. The heat source was then removed; the reaction mixture was allowed to cool and was then transferred to a separatory funnel with ethyl acetate as diluent. The colorless sludge was stirred at 70°C overnight. The cream-colored product was then removed; the reaction mixture was allowed to cool to room temperature; stirring was stopped and the separated aqueous phase was removed. Deionized water (300 mL) was added followed by 6 M HCl (100 mL). The nearly colorless sludge was stirred at 70°C overnight. The cream-colored product was transferred into a separatory funnel using ethyl acetate as diluent. The aqueous layer was discarded and the separated aqueous phase was transferred into a separatory funnel using deionized water. The organic layer was then washed with deionized water. Ethanol (300 mL) was added followed by 6 M HCl (100 mL). The nearly colorless sludge was stirred at 70°C overnight. The cream-colored product was then removed and the reaction mixture was cooled to room temperature; stirring was stopped and the separated aqueous phase was removed. Deionized water (300 mL) was added followed by 6 M HCl (100 mL). The nearly colorless sludge was stirred at 70°C overnight. The cream-colored product was washed sequentially with saturated brine, then saturated NaHCO₃ until a pH of 7.5 in the wash water was achieved, followed with deionized water. Ethanol was added to facilitate separation of the phases. After removal of the aqueous layer, the product was concentrated in vacuo at 70°C to yield 711.6 g (92.1%) of the polyhydroxy TAG with an IV = 14 compared with an IV of 114 in the starting milkweed oil. The measured kinematic viscosities were: 2323.5 cSt at 40°C and 75.53 cSt at 100°C, that is, a viscosity index of 37.6 centistokes/°C. Specific rotation [α]²⁰_D = +0.37°, FTIR (film on NaCl) cm⁻¹: 3636–3168 D, 2927 vs, 2856 vs, 1743 vs, 1636 s, 1238 m, 1173 vs, 1097 s, 881 w, 725 w-m. ¹³C NMR (CDCl₃) δ: 173.2, 172.8 (–O=C–), 84.60 (HCO), 83.00 (COH), 82.50 (HCO), 82.00 (COH), 80.50 (COH), 74.40 (HCO), 73.82 (HCO), 73.20 (–HCO–), 68.82 (–OCH₂–), 29.28 (–CH₂–), 29.23 (–CH₂–), 29.15 (–CH₂–), 29.12 (–CH₂–), 28.92 (CH₂–), 28.88 (–CH₂–), 27.83 (–CH₂–), 27.77 (CH₂–), 27.75 (–CH₂–), 27.16 (–CH₂–), 26.88 (CH₂–), 26.55 (–CH₂–), 26.52 (–CH₂–), 26.08 (–CH₂–), 24.73 (–CH₂–), 22.51 (–CH₃), 13.93 (–CH₃). 

(ii) Synthesis of polyhydroxy TAG. In a 1-L jacketed flask, as in above setup, was placed reprocessed milkweed oil (648.0 g, 735.7 mmol). The oil was stirred vigorously at 40°C and formic acid (90.4%, 62.2 g, 1.22 mol) was added in one portion followed by a slow (dropwise) addition of H₂O₂ (50%, 203.0 g, 2.98 mol). At the end of peroxide addition, the temperature was increased to 70°C. After 15 h, the heat source was removed but stirring was continued, allowing the reaction mixture to cool to room temperature; stirring was stopped and the separated aqueous phase was removed. Deionized water (300 mL) was added followed by 6 M HCl (100 mL). The nearly colorless sludge was stirred at 70°C overnight. The cream-colored product was then removed and the reaction mixture was washed sequentially with saturated brine, then saturated NaHCO₃ until a pH of 7.5 in the wash water was achieved, followed with deionized water. Ethanol was added to facilitate separation of the phases. After removal of the aqueous layer, the product was concentrated in vacuo at 70°C to yield 711.6 g (92.1%) of the polyhydroxy TAG with an IV = 14 compared with an IV of 114 in the starting milkweed oil. The measured kinematic viscosities were: 2323.5 cSt at 40°C and 75.53 cSt at 100°C, that is, a viscosity index of 37.6 centistokes/°C. Specific rotation [α]²⁰_D = +0.37°, FTIR (film on KBr) cm⁻¹: 3636–3168 b, 2927 vs, 2856 vs, 1743 vs, 1463 s, 1378 m-s, 1240 m-s, 1173 vs, 1097 s, 881 w, 725 w-m. ¹³C NMR (CDCl₃) δ: 173.2, 172.8 (–O=C–), 84.60 (HCO), 83.00 (COH), 82.50 (HCO), 82.00 (COH), 80.50 (COH), 74.40 (HCO), 73.82 (HCO), 73.20 (–HCO–), 68.82 (–OCH₂–), 29.28 (–CH₂–), 29.23 (–CH₂–), 29.15 (–CH₂–), 29.12 (–CH₂–), 28.92 (CH₂–), 28.88 (–CH₂–), 27.83 (–CH₂–), 27.77 (CH₂–), 27.75 (–CH₂–), 27.16 (–CH₂–), 26.88 (CH₂–), 26.55 (–CH₂–), 26.52 (–CH₂–), 26.08 (–CH₂–), 24.73 (–CH₂–), 22.51 (–CH₃), 13.93 (–CH₃).