Synthesis of Triglyceride Estolides from Lesquerella and Castor Oils

Terry A. Isbell* and Steven C. Cermak

New Crops Processing and Technology Research Unit, National Center for Agricultural Utilization Research, ARS, USDA, Peoria, Illinois 61604

ABSTRACT: Triglyceride (TG) estolides were synthesized from the hydroxy moieties of lesquerella and castor oils with oleic acid. Complete esterification of the hydroxy oils was possible when a slight excess of oleic acid was employed (1 to 1.5 mole equivalents). The estolides could be formed in the absence of catalyst at 175 to 250°C under vacuum or a nitrogen atmosphere. The optimal reaction conditions were found to be under vacuum at 200°C for 12 h for lesquerella and 24 h for castor oil. The lesquerella esterification reaction was completed in half the time of that for castor and with lower equivalents of oleic acid due to the difunctional hydroxy nature of lesquerella TG compared to the trifunctional nature of castor TG. Interesterification or dehydration of the resulting estolides to conjugated FA was not a significant side reaction, with only a slight amount of dehydration occurring at the highest temperature studied, 250°C. Use of a mineral- or Lewis-acid catalyst increased the rate of TG-estolide formation at 75°C but resulted in the formation of a dark oil, and the reaction did not go to completion in 24 h. Estolide numbers (i.e., degree of estolide formation) for the reaction and characterization of the products were made by ^{1}H NMR and ^{13}C NMR. The decrease in the hydroxy methine signal at 3.55 ppm was used to quantify the degree of esterification by comparing this integral to the integral of the alpha methylene protons on the glycerine at 4.28 and 4.13 ppm.

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KEY WORDS: Castor, estolide, lesquerella, ^{13}C NMR, ^{1}H NMR, oleic acid, synthesis.

Lesquerella fendleri is a winter annual seed oil crop native to the desert southwestern United States and is currently undergoing an intensive research effort for its successful introduction into agriculture. Lesquerella produces a small seed that has 25–30% oil that contains 55–64% hydroxy FA (1–3). The hydroxy FA of lesquerella (3) are lesquerolic (55–60%, 14-hydroxy-*cis*-11-eicosenoic acid) and auricolic (2–4%, 14-hydroxy-*cis*-11-*cis*-17-eicosenoic acid). The distribution of TG is 10% nonhydroxy acyl, 15% monohydroxyacyl, and 73% dihydroxyacyl, which indicates that lesquerella oil is essentially a difunctional TG in terms of hydroxy functionalities (3). Furthermore, the hydroxy moieties are principally located at the 1- and 3- (TG) positions (4).

The hydroxy functionality provides a site for additional esterification on the TG structure. The hydroxy TG has been converted to estolides that have been used as dehydrating oils and thickeners for lubricants (5,6). Free lesquerolic acid estolides were also reported using a lipase catalyst and oleic acid (7); however, there are no detailed reports on the synthesis of TG estolides from lesquerella oil. A patent by Lawate (5) principally describes the synthesis in xylene of castor and lesquerella TG estolides using heptanoic acid to esterify the hydroxyl functionality using a *p*-toluenesulfonic acid catalyst. A reaction temperature of 150°C was employed to allow the water of esterification to be removed azeotropically. Characterization of the estolide product was not reported. More detailed reports can be found on the synthesis of TG-estolides from castor oil and oleic acid in kinetic studies by Erciyes *et al.* (8). Modak and Kane (9) described the effects of temperature and catalysts on the rate of estolide formation and their decomposition utilizing acid value to follow the time course of the reaction. The reactions were performed at 200–250°C with or without catalyst, and conditions were found that the best catalyst (tin chloride) gave a 200-fold increase in the rate constant at 200°C. Partial decomposition occurred when the reaction was run at 250°C using a *p*-toluenesulfonic acid catalyst as evidenced by an increase in the dienoic content. Modak and Kane's work (9) on FFA esterifications found that higher temperatures (>225°C) promoted the formation of dehydrated castor FA from the decomposition of estolide.

Since a detailed study on the effect of FA concentration and temperature on TG-estolide formation has not been reported, we performed a series of experiments to explore the extent of estolide formation for lesquerella and castor estolides. It is anticipated that estolides will be studied for their potential as functional fluids by comparing their physical properties.

EXPERIMENTAL PROCEDURES

Materials. Lesquerella oil was obtained by vacuum filtration of crude cold-pressed *L. fendleri* seed, pressed in our laboratory. This oil was used without further refining. Castor oil, concentrated sulfuric acid, hexanes, ethyl acetate, and methanol were obtained from Fisher Scientific Co. (Fair Lawn, NJ). Boron trifluoride–methanol complex and FAME standards were obtained from Alltech Associates (Deerfield, IL).

Instrumentation. GC was performed with a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA), equipped with an FID and an autosampler/injector. Analyses were conducted on SP 2380 30 m × 0.25 mm i.d. (Supelco,

*To whom correspondence should be addressed at NCAUR-ARS-USDA, NCP, 1815 North University St., Peoria, IL 61604.
E-mail: isbellta@ncaur.usda.gov

Bellefonte, PA) and BP1 30 m × 0.22 mm i.d. (Scientific Glass Engineering, Austin, TX) columns. Saturated C_8–C_{30} FAME provided standards for calculating equivalent chain length (ECL) values, which were used to make FAME assignments.

SP 2380 analyses were conducted as follows: column flow 3.3 mL/min with helium head pressure of 20 psi; split ratio 22:1; programmed temperature ramp: 150 to 180°C at 7°C/min, 180 to 265°C at 15°C/min; injector and detector temperatures set at 250°C.

BP1 analyses were conducted as follows: column flow 2.2 mL/min with helium head pressure of 25 psi; split ratio 39.2:1; programmed temperature ramp 100 to 175°C at 15°C/min, 175 to 265°C at 5°C/min, 265 to 275°C at 10°C/min; injector and detector temperatures set at 250°C.

HPLC. Reverse-phased HPLC (C8) analyses were performed on a Spectra-Physics 8800 system with ternary pump (San Jose, CA) and Spectra System AS3000 autosampler/injector from Thermo Separation Products (Fremont, CA) coupled to an ELSD from Alltech Associates. A Dynamax (250 mm × 4.6 mm, 60 Å, 8 µm) C8 column purchased from Rainin Instrument Co., a division of Varian (Walnut Creek, CA), was used to separate the mixtures. Components were eluted from the column using the following gradient program: 0–2 min hold: acetonitrile/acetone 60:40; gradient to 100% acetone up to 20 min; held at 100% acetone up to 25 min; reverse gradient to 60:40 acetonitrile/acetone at 30 min; the latter composition held to 35 min. A flow rate of 1 mL/min was used. The ELSD drift tube was set at 55°C with 20 psi N_2 fed to the nebulizer to give a flow rate of 2.0 standard liters per minute (SLPM).

NMR. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ARX-400 (Karlsruhe, Germany) with a 5-mm dual proton/carbon probe (400 MHz ^{1}H/100.61 MHz ^{13}C) using $CDCl_3$ as a solvent in all experiments.

^{1}H NMR of lesquerella-oleic estolide: δ 5.47–5.23 (*m*, 12.7H, –C*H*=C*H*– and (–O–CH$_2$)$_2$–C*H*–O–), 4.87 (*p*, *J* = 6.2 Hz, 1.8H, –(CH$_2$)$_2$–C*H*–(O–CO–R), 4.28 (*dd, J* = 4.3 and 11.9 Hz, 2H, (–O–C*H*$_2$–)$_2$–CH–O–), 4.13 (*dd, J* = 6.0 and 11.9 Hz, 2H, (–O–C*H*$_2$–)$_2$–CH–O–), 2.78 (*m*, 2H, –(CH=CH)$_2$–C*H*$_2$–), 2.35–2.22 (*m*, 13.7H, –*CH*$_2$–CO$_2$R), 2.10–1.92 (*m*, 16.2H, –C*H*$_2$–CH=CH–) 1.70–1.45 (*m*, 14.5H, –C*H*$_2$–), 1.38–1.14 (*m*, 94H, –C*H*$_2$–), and 0.87 ppm (*t, J* = 7.0 Hz, 15H, –C*H*$_3$). ^{13}C NMR δ 173.6 (*s*, –*C*=O), 173.3 (*s*, –*C*=O), 172.7 (*s*, –*C*=O), 132.6 (*d*, –*C*=*C*–CH$_2$CH–O–), 130.1 (*d*, –*C*=*C*–), 130.0 (*d*, –*C*=*C*–), 129.8 (*d*, –*C*=*C*–), 129.7 (*d*, –*C*=*C*–), 124.3 (*d*, –*C*=*C*–CH$_2$CH–O–), 73.7 (*d*, –*C*H–O–CO$_2$R), 68.9 (*d*, (–OCH$_2$)$_2$–*C*H–O–), 62.1 (*t*, (–O*C*H$_2$–O–)$_2$–CH–O–), 34.7 (*t*, –*C*H$_2$–), 34.2 (*t*, –*C*H$_2$–), 34.0 (*t*, –*C*H$_2$–), 33.7 (*t*, –*C*H$_2$–), 32.1 (*t*, –*C*H$_2$–), 32.0 (*t*, –*C*H$_2$–), 31.8 (*t*, –*C*H$_2$–), 29.8 (*t*, –*C*H$_2$–), 29.8 (*t*, –*C*H$_2$–), 29.7 (*t*, –*C*H$_2$–), 29.6 (*t*, –*C*H$_2$–), 29.5 (*t*, –*C*H$_2$–), 29.4 (*t*, –*C*H$_2$–), 29.4 (*t*, – *C*H$_2$–), 29.3 (*t*, –*C*H$_2$–), 29.2 (*t*, –*C*H$_2$–), 29.2 (*t*, –*C*H$_2$–), 29.1 (*t*, –*C*H$_2$–), 29.1 (*t*, –*C*H$_2$–), 27.4 (*t*, –*C*H$_2$–), 27.3 (*t*, –*C*H$_2$–), 27.2 (*t*, –*C*H$_2$–), 25.4 (*t*, –*C*H$_2$–), 25.2 (*t*, –*C*H$_2$–), 24.9 (*t*, – *C*H$_2$–), 22.7 (*t*, –*C*H$_2$–), 22.6 (*t*, –*C*H$_2$–), 14.2 (*q*, –*C*H$_3$), and 14.1 ppm (*q*, –*C*H$_3$).

^{1}H NMR of castor-oleic estolide: δ 5.50–5.23 (*m*, 7H, –C*H*=C*H*– and (–O–CH$_2$)$_2$–C*H*–O–), 4.87 (*p, J* = 6.3 Hz, 2.6H, –(CH$_2$)$_2$–C*H*–(O–CO–R), 4.28 (*dd*, *J* = 4.3 and 11.9 Hz, 2H, (–O–C*H*$_2$–)$_2$–CH–O–), 4.13 (*dd*, *J* = 6.0 and 11.9 Hz, 2H, (–O–C*H*$_2$–)$_2$–CH–O–), 2.35–2.22 (*m*, 17H, –*CH*$_2$–CO$_2$–R), 2.05–1.95 (*m*, 6H, –C*H*$_2$–CH=CH–), 1.70–1.15 (*m*, 124H, –C*H*$_2$–), and 0.87 ppm (*t*, *J* = 7.1 Hz, 17H, –C*H*$_3$). ^{13}C NMR δ 174.0 (*s*, –*C*=O), 173.7 (*s*, –*C*=O), 173.2 (*s*, –*C*=O), 133.0 (*d*, –C=*C*–CH$_2$CH–O–), 124.9 (*d*, –*C*=C–CH$_2$CH–O–), 74.1 (*d*, –*C*H–O–), 69.4 (*d*, (–O–CH$_2$)$_2$–*C*H–O–) 62.6 (*t*, (–O–*C*H$_2$)$_2$–CH–O–), 35.2 (*t*, –*C*H$_2$–) 35.2 (*t*, –*C*H$_2$–), 34.7 (*t*, –*C*H$_2$–), 34.5 (*t*, –*C*H$_2$–), 34.2 (*t*, –*C*H$_2$–), 32.5 (*t*, –*C*H$_2$–), 32.4 (*t*, –*C*H$_2$–), 32.3 (*t*, –*C*H$_2$–), 30.2 (*t*, –*C*H$_2$–), 30.2, (*t*, –*C*H$_2$–), 30.1 (*t*, –*C*H$_2$–), 30.1 (*t*, – *C*H$_2$–), 30.0 (*t*, –*C*H$_2$–), 29.9 (*t*, –*C*H$_2$–), 29.8 (*t*, –*C*H$_2$–), 29.7 (*t*, –*C*H$_2$–), 29.7 (*t*, –*C*H$_2$–), 29.6 (*t*, –*C*H$_2$–), 29.6 (*t*, –*C*H$_2$–), 27.9 (*t*, –*C*H$_2$–), 25.8 (*t*, –*C*H$_2$–), 25.6 (*t*, –*C*H$_2$–), 25.4 (*t*, –*C*H$_2$–), 25.3 (*t*, –*C*H$_2$–), 23.2 (*t*, –*C*H$_2$–), 23.1 (*t*, –*C*H$_2$–), 14.6 (*q*, –*C*H$_3$), and 14.6 ppm (*q*, – *C*H$_3$).

Preparation of methyl esters for GC. Estolides, oils, and FAME were prepared by treating a 10-mg sample with 0.5 mL of 0.5 M KOH/MeOH in a sealed vial for 1 h at 100°C in a heating block. After cooling to room temperature, 1.5 mL of 1 M H_2SO_4/MeOH was added, and then the vial was resealed and heated to 100°C in a heating block for 10 min. The mixture was transferred to a 2-dram vial and 1 mL of water was added. The solution was extracted with 1 mL of hexane, 2 mL of 50:50 hexane/ethyl acetate, and 1 mL of hexane sequentially. The combined extracts were dried over sodium sulfate and than injected onto the GC for FAMEs analysis.

Synthesis of TG-estolides. TG (200 g, 0.205 mol for lesquerella oil or 0.215 mol for castor oil) was placed in a three-necked round-bottomed flask. The appropriate mass of oleic acid was added according to the mole equivalents listed in Tables 2 and 3 for each reaction entry A through AC. The flask was fitted with a temperature probe, vacuum/nitrogen adapter, and a stopper. All reactions were mixed continuously by a magnetic stir bar. For reactions performed under vacuum, the flask

TABLE 1
Chemical Composition of Lesquerella Oil, Castor Oil, and Oleic Acid

FAME[a]	Lesquerella oil (mass %)	Castor oil (mass %)	Oleic acid (mass %)
16:0	1.1	1.0	0.4
16:1	0.7	—	—
18:0	1.8	—	2.5
18:1	15.4	3.7	90.4
18:2	6.9	4.4	5.3
18:3	12.2	—	0.7
20:0	0.2	—	—
20:1	1.0	—	—
20:2	0.2	—	—
18:1 Hydroxy	0.6	89.0	—
20:1 Hydroxy	55.4	1.1	—
20:2 Hydroxy	3.8	—	—

[a]FAME assignments were made by ECL values determined by GC on a polar SP 2380 (Supelco, Bellefonte, PA) and a nonpolar BP-1 (Scientific Glass Engineering, Austin, TX) column.

TABLE 2
Chemical Properties of Estolides from Oleic Acid and Lesquerella Oil

Entry	FA equiv.[a]	Atmosphere	Temp. (°C)	Time (h)	Conversion (%) to estolide	EN[b] crude (NMR)	EN[b] residue (NMR)	20:2 (mol%)[c]	Monomer hydroxy (mol%)[c]
A	1	Vacuum	200	24	56.1	1.06	1.08	0.0	0.0
B	2	Vacuum	200	24	100.0	1.89	1.89	1.0	0.0
C	3	Vacuum	200	24	100.0	1.89	1.89	0.0	0.0
D	4	Vacuum	200	24	100.0	1.89	1.89	0.0	0.0
E	2	Nitrogen	200	24	76.7	1.45	1.62	0.0	2.4
F	2	Vacuum	50	24	0.0	0.00	0.25	0.0	0.0
G	2	Vacuum	100	24	5.3	0.10	0.40	0.0	0.0
H	2	Vacuum	150	24	82.0	1.55	1.57	0.0	1.2
I	2	Vacuum	175	24	97.3	1.84	1.83	0.0	2.3
J	2	Vacuum	250	24	100.0	1.89	1.89	3.5	0.0
K	2	Vacuum	200	3	84.1	1.59	1.59	0.0	2.2
L	2	Vacuum	200	6	89.4	1.69	1.63	0.0	2.3
M	2	Vacuum	200	12	100.0	1.89	1.89	0.0	1.0

[a]Mole equivalents of oleic acid based on the moles of lesquerella.
[b]Estolide number (EN) values were determined by the H_{14} integration.
[c]Mole percentage determined by GC on distilled monomer fraction.

was evacuated by house vacuum (~10 torr). For reactions under a nitrogen blanket, a positive nitrogen blanket was maintained by use of a continuous flow of nitrogen through a mineral oil bubbler. The reactions were warmed to the desired set points listed in Tables 2 and 3 using a heating mantle controlled by a J-Kem Gemini-2 (St. Louis, MO) temperature controller utilizing a temperature probe immersed below the liquid level in the flask. Solutions with lesquerella oil transformed from a light red color to pale yellow as the temperature surpassed 175°C. For solutions with castor oil, the material went from colorless to pale yellow over the course of the experiment. When the reaction time had been reached, the solution was allowed to cool to room temperature under vacuum or nitrogen, and an aliquot of the crude product was removed for analysis by NMR. The remaining material was subjected to vacuum distillation either by kügelrohr or short-path molecular distillation to remove residual oleic acid. The isolated estolide was then analyzed by NMR and GC analysis.

Kügelrohr distillation of TG-estolides. The crude reaction mixture was placed in a 2-L distillation flask that was connected to a kügelrohr distillation unit (Aldrich Chemical Co., Milwaukee, WI) fitted with a 500-mL receiving flask. The material was distilled at 150–170°C under 0.2–0.4 torr. A colorless distillate of oleic acid was obtained with a yellow residue of TG-estolide. Distillations typically required 3 h to remove the residual oleic acid completely, and the extended time at this temperature promoted the formation of additional estolide.

TABLE 3
Chemical Properties of Estolides from Oleic Acid and Castor Oil

Entry	FA equiv.[a]	Catalyst	Catalyst equiv.	Atmosphere	Temp. (°C)	Time (h)	Conversion to estolide (%)	EN[b] crude (NMR)	EN[b] residue (NMR)	18:2 (mol%)[c]	Monomer hydroxy (mol%)[c]
N	1	None	0.00	Vacuum	200	24	36.7	0.98	1.47	3.2	0.9
O	2	None	0.00	Vacuum	200	24	59.2	1.58	1.73	3.8	0.0
P	3	None	0.00	Vacuum	200	24	92.1	2.46	2.51	6.0	3.2
Q	4	None	0.00	Vacuum	200	24	100.0	2.67	2.67	3.6	0.3
R	4	None	0.00	Nitrogen	200	24	83.9	2.24	2.55	4.2	0.0
S	4	None	0.00	Vacuum	50	24	0.0	0.00	0.88	4.6	0.2
T	4	None	0.00	Vacuum	100	24	10.1	0.27	1.04	4.6	0.4
U	4	None	0.00	Vacuum	150	24	53.9	1.44	1.57	4.1	0.7
V	4	None	0.00	Vacuum	175	24	88.8	2.37	2.67	2.9	4.5
W	4	None	0.00	Vacuum	250	24	100.0	2.67	2.67	3.2	0.4
X	4	None	0.00	Vacuum	200	3	56.5	1.51	1.66	3.9	1.0
Y	4	None	0.00	Vacuum	200	9	87.6	2.34	2.35	3.9	0.6
Z	4	None	0.00	Vacuum	200	12	90.6	2.42	2.43	3.8	0.0
AA	4	BF_3	0.01	Vacuum	50	24	3.0	0.08	0.56	4.0	1.5
AB	4	H_2SO_4	0.05	Vacuum	50	24	9.7	0.26	0.90	4.0	0.0
AC	4	H_2SO_4	0.05	Vacuum	75	24	64.8	1.73	2.03	3.5	0.0

[a]Mole equivalents of oleic acid based on the moles of castor.
[b]Estolide number (EN) values were determined by the H_{12} integration.
[c]Mole percentage determined by GC.

Short-path molecular distillation of TG-estolides. Molecular distillations were performed in a Meyers Lab 3 still (Meyers Vacuum, Kittanning, PA). Crude estolides were placed in the feed reservoir and degassed under vacuum, 0.02–0.07 torr. The material was then passed at 1–2 drops/s onto a heated rotor that was maintained at 150°C. The condenser temperature was set at 20°C. The distillation yielded oleic acid as a colorless distillate and TG-estolides as a yellow residue. Only slight increases in estolide numbers were observed over the short time that the oil was on the heated rotor.

RESULTS AND DISCUSSION

Table 1 lists the FA composition for both of the hydroxy oils and oleic acid. Lesquerella and castor oil consist mostly of 1,3-dihydroxyacyl and trihydroxyacyl TG, respectively. These hydroxyl functionalities served as a site for esterification with oleic acid to give TG-estolides (Scheme 1). Esterification can proceed by condensation of the hydroxyl functionality of the TG with the carboxylic acid function of oleic acid. Loss of water yields the corresponding monoestolide which we label as a TG-estolide with an estolide number (EN) of 1. Complete esterification of lesquerella would result in an EN = 1.89 based on 59.2% hydroxy acids in lesquerella oil. Similarly, castor would produce a TG-estolide with an EN = 2.69 based on 90.1% hydroxy acids in castor oil.

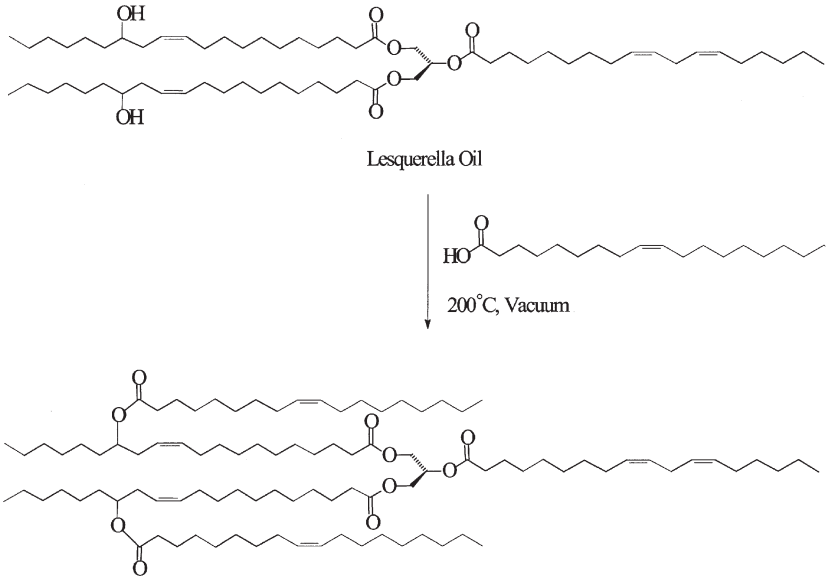
Other mechanistic paths could compete for the formation of estolides as depicted in Scheme 2. Upon formation of estolide, deacylation could occur under the reaction conditions to produce conjugated dienes. Lakshminarayana *et. al.* (10) report that conjugated dienes (18:2) are the major decomposition products of castor estolide. Therefore, the 20:2 and 18:2 contents can be followed by GC to determine the extent of dehydration occurring during the course of lesquerella and castor oil estolide synthesis. A second alternative path outlined in Scheme 2 is ester interchange, which may provide a deleterious path whereby hydroxy functionalities are lost from the TG. The free hydroxy FA would promote the formation of homo- or oleic-oligomeric estolides of the hydroxy FA.

The structures of TG-estolides were characterized by ^{1}H NMR and ^{13}C NMR spectra (Fig. 1). The key spectral features are the appearance of the estolide methine signal of the protons and the carbon signal at position 14. The estolide methine proton has a resonance at 4.87 ppm. This signal arises at the expense of the hydroxy methine resonance at 3.55 ppm from position 14 of lesquerella oil during the course of the esterification. The estolide methine carbon appears at 73.7 ppm in the ^{13}C NMR and coincides with the disappearance of the hydroxy carbon at 71.4 ppm in lesquerella oil. The other key spectral feature for the TG-estolide is the appearance of the oleate-olefin carbons at 130.0 and 129.8 ppm, previously absent in the lesquerella oil spectrum. Estolide numbers were calculated from the ^{1}H NMR of the crude estolide using the ratio of the integration of the hydroxy methine proton (3.55 ppm) after setting the integration of the glycerine's α-methylene protons (4.28 and 4.13 ppm) to a value of 4. The following equations provide the EN number:

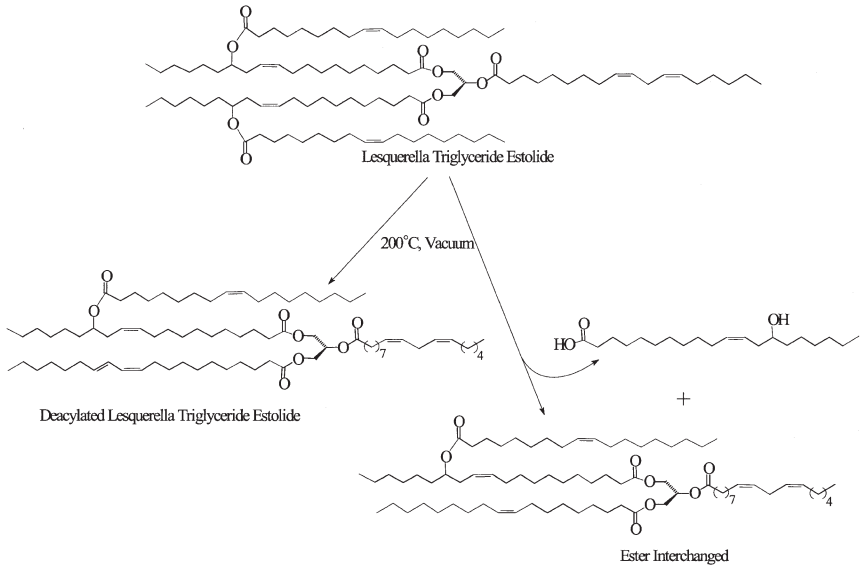
$$\text{lesquerella estolide EN} = 1.89 - H_{14} \quad [1]$$

$$\text{castor EN} = 2.67 - H_{12} \quad [2]$$

The 1.89 and 2.67 constants are the maximum estolide number possible for lesquerella and castor oil estolides based on the amount of hydroxy moieties present in the oils. With



SCHEME 1



SCHEME 2

these two equations, EN values were assigned to both the crude and the final reaction mixtures listed in Tables 2 and 3.

Table 2 lists the results of the synthesis of lesquerella-oleic estolides under various reaction conditions. Entries A–D demonstrate the difunctional nature of lesquerella oil where two mole equivalents of oleic acid, per mole of lesquerella oil provided a sufficient excess of oleic acid to completely esterify the hydroxyl functionalities. A larger excess of oleic acid, as in entries C and D, may provide shorter reaction times, but the reaction rates at these concentrations were not explored.

The atmospheric conditions within the flask play a crucial role on the rate of reaction as evidenced by entry B vs. E. In entry E, the reaction was performed under a nitrogen blanket and failed to provide the same level of water removal as the reaction performed under vacuum as seen by the lower EN value of 1.45 for entry E compared to 1.89 for entry B. In the case where vacuum is applied to the reaction, water of reaction is continuously removed, driving the esterification reaction to completion. However, in reactions where a nitrogen blanket is used, the water of reaction remains in equilibrium with the solution (some water condensed on the glassware and in the vapor phase above the reaction as well as in solution). Because of the presence of this water, equilibrium conditions exist and complete esterification is not possible.

Entries F–J demonstrate the dependence on the rate of reaction on the reaction temperature. At low temperatures (entries F and G), when the temperature is less than 100°C, essentially no reaction occurred. The reaction is sluggish at 150°C where an EN = 1.55 is obtained in 24 h. Beyond 175°C, the reaction goes to completion in 24 h. The work of Modak and Kane (9) concerning castor FA oligomerization agrees well with these observations; they found the reaction to be sluggish below 187°C. However, at 250°C, dehydration of the TG-estolide occurs as evidenced by the increased formation of 20:2 in the glyceride product shown in entry J. Similarly, Modak and Kane (9) found that castor FA at a temperature of 225°C initially produced an estolide, which began to decompose over time to produce conjugated FA (10).

Entries K–M of Table 2 demonstrate that the reaction reaches completion after 12 h with an EN = 1.89. Minimal dehydration of the estolide occurred at 200°C when the reaction time was 24 h.

Distillation of the crude estolides to remove excess oleic acid gave TG-estolides with slightly increased EN values due to the continuation of the esterification reaction under the distillation conditions. Short-path molecular distillation with a Meyers Lab 3 still produced a much smaller increase in residue EN values (entries A–M and W–Z) compared to kügelrohr (entries N, T, S, AA, and AB). The molecular still has a considerably shorter residence time (seconds) on the heated surface than the kügelrohr, which holds the entire sample at distillation temperature for several hours.

The ester interchange reaction appears to be of little consequence, as evidenced by the small amounts of hydroxy FA found in the monomer fraction. Traces of the monomer fraction revealed by reversed-phase HPLC indicated that those fractions containing hydroxy FA were not contaminated by small amounts of estolide from the distillation, further supporting that ester interchange had occurred.

Table 3 presents a similar set of experiments on the formation of TG-estolide from castor oil with oleic acid. Entries N–Q demonstrate the dependence of estolide formation on the concentration of oleic acid. Castor oil TG molecules typically possess three hydroxy moieties, with 89% of the oil being ricinoleic acid. Because of the trifunctional nature of castor, four equivalents of oleic acid were necessary to provide a sufficient excess of oleic acid to yield TG-estolide in a 200°C reaction over a 24-h period (entry Q). Acylation of three

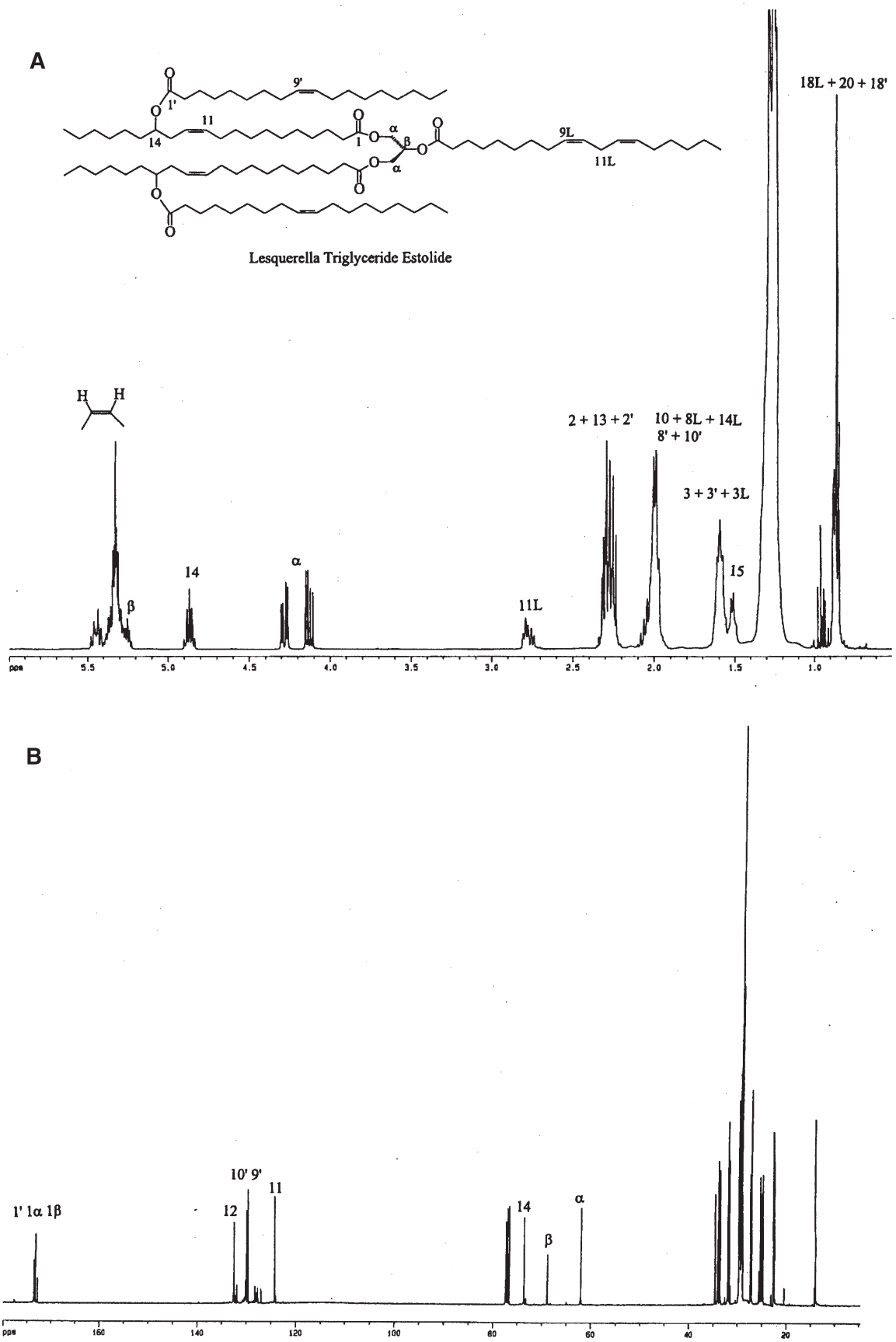


FIG. 1. (A) ^{1}H NMR (400 MHz) and (B) ^{13}C NMR (100.61 MHz) spectra of crude lesquerella-oleic estolide. Sample run in $CDCl_3$.

hydroxy groups (castor) appears to be more difficult than two (lesquerella) because the reaction time for complete ester formation is considerably longer than for lesquerella where complete ester formation required 12 h (entry M, Table 2 vs. entry Z, Table 3). In addition, the castor reaction has a larger excess of oleic acid, 1.48 mole equivalents compared to 1.04 mole equivalents in the lesquerella reaction. Steric hindrance probably plays a significant role in the reduced rate of reaction for castor oil trifunctionalization.

Castor oil TG-estolide formation shows the same temperature dependence (entries S–W) as lesquerella oil with the exception that dehydration of the TG-estolide does not appear to be occurring in the 250°C reaction for castor as seen by the apparent absence of an increase in the 18:2 concentration.

Interesterification appears not to be significant for castor with only small percentages of hydroxy FA in the monomer fraction. Reversed-phase HPLC indicated estolides were not present in the distillate fraction, further supporting that interesterification did occur to a small extent.

The synthesis of TG-estolide at lower temperature was attempted with two acid catalysts. Boron trifluoride failed to yield significant amounts of estolide at 50°C. Sulfuric acid at 0.05 equivalents gave 65% conversion to TG-estolide at 75°C in 24 h (entry AC). This quantity of sulfuric acid, however, promoted a darkening of the reaction mixture. Higher reaction temperatures were not explored because sulfuric acid catalysts (8) did not appear to provide significant rate improvements over uncatalyzed reactions to justify their use.

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