A Facile Synthesis of Aminohydroxy Triglycerides from New Crop Oils

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ABSTRACT: Vegetable oils as the main source of plant lipids are currently generating much interest as renewable industrial feedstocks for nonfood industrial applications both as biobased lubricants and biodiesel fuels. But of particular interest for us is use of new crop oils in novel industrial applications. These oils, in general, are glyceryl esters with olefinic bonds, which are readily functionalizable. Aminated lipids are important intermediates in many applications including pharmaceutical formulations because they have a modifying effect on cell membranes. We have exploited the nucleophilic property of the carbon–carbon double bonds in two seed oils to generate the oxirane derivatives of the lipids. Ring opening of the epoxy intermediates with amines under anhydrous $ZnCl_2$ catalysis is facile, and the reaction proceeds smoothly at moderate temperatures to give the aminohydroxy TG of milkweed and salicornia oils.

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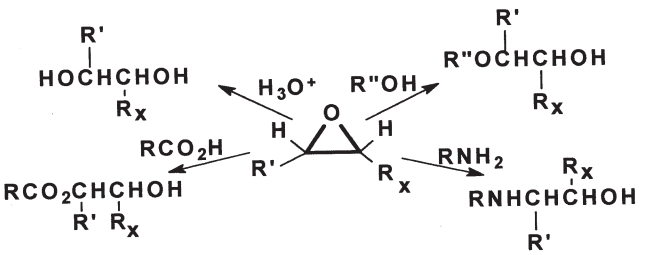
KEY WORDS: Aminated lipids, aminohydroxy triglycerides, epoxidation, *in situ*-generated peroxy acid, milkweed oil, salicornia oil.

The increasing importance of vegetable oils as industrial feedstocks stems from their renewability as well as their environmental friendliness at the end of their useful lifetime. Although most seed oils are glycerol esters with no more functionality on the carbon–carbon chains than olefinic groups in the structure, the level of unsaturation is important for specific applications. The nucleophilic character of these double bonds makes them amenable to functionalization with appropriate electrophiles to furnish new derivatives of lipids. The functionalization platform we chose for this study was the oxirane TG. The reactivity of an oxirane group in a lipid provides abbreviated pathways to several functional derivatives of a modified vegetable oil that would not be readily accessible otherwise (Scheme 1). Of the routes to oxirane, the least hazardous and most cost-effective procedure is the *in situ* peroxy acid pathway. The advantage of this route is that it bypasses the hazards of isolation of the peroxy acid in a preparatory step as well as the handling involved in procuring a peroxy acid reagent. In the *in situ* method, the peracid is generated within the reaction environment and is consumed by the reacting substrate (1–4). Although earlier efforts at creating amine derivatives from lipid epoxides were achieved in low yields at high temperatures and pressures in over 12 h (3), the use of a Lewis acid catalyst, $ZnCl_2$, allowed smooth reaction at 70–80°C under atmospheric pressure conditions with or without solvents in 3–4 h at approximately a 1:1 reactant ratio (5–7). In a recent report, $ZnCl_2$ catalysis was also exploited to synthesize amine-functionalized soybean oil (8). These amine derivatives when completely developed would find markets not only as lubricant additives but also as cell membrane modifiers in pharmaceutical applications (9,10). In this paper we present a facile reaction in which the epoxy TG of milkweed (*Asclepias syriaca* L.) and salicornia (*Salicornia bigelovii* Torr.) oils are converted to the corresponding aminohydroxy TG derivatives of these new crop oils.



SCHEME 1

EXPERIMENTAL PROCEDURES

Materials. Milkweed (*A. syriaca* L.) oil was obtained from Natural Fibers Corporation (Ogallala, NE) and salicornia (*Salicornia bigelevii*) oil was obtained from Seaphire (Phoenix, AZ). Hydrogen peroxide 50%, methylamine hydrochloride, dibutylamine, and ammonia were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO), whereas formic acid 99% and anhydrous $ZnCl_2$ were from Fisher Scientific (Chicago, IL).

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 (11). The size of the Cannon–Fenske viscometer used was number 500. 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 until the meniscus just overshot the mark above the lower bulb. The suction was removed and the meniscus ad-

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justed to the mark. The sample was allowed to flow at the same time the stop clock was started. The time (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. 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, adjusted for mass differences, and normalized to the methylene peak at 2927 cm^{-1}. FTIR spectra of starting oils and their reaction products are shown in Figures 1 and 2.

Spectral band deconvolution and integration. Band deconvolutions and integrations were performed with a routine provided in GRAMS/AI software (Galactic Industries, Salem, NH). The area of the epoxy (oxirane) absorbance band, which existed in the derivatized oils as two overlapping peaks centered at 846 and 824 cm^{-1}, was measured above a baseline drawn between the two minima between 880 and 790 cm^{-1}. Deconvolution was used to correct the epoxy band of one sample spectrum, which showed an interfering peak of unknown origin at 835 cm^{-1}. Figures 1 and 2 are examples showing the difference between the integrated band areas of the starting epoxy salicornia and milkweed oils and the oils after reaction with dibutylamine.

Methods. (i) Synthesis of salicornia epoxy TG. A dry 1000-mL three-necked, round-bottomed jacketed flask equipped with an overhead stirrer was heated to 40°C. Salicornia oil (475.5 g, 583.65 mmol, iodine value = 132.8) and 99% formic acid (49.56 g, 40.6 mL) were added to the reaction vessel, and the mixture was stirred to homogeneity. Hydrogen peroxide (50%, 274.87 g, 4.0416 mol, 232.9 mL) was added slowly to the stirring mixture. At the end of peroxide addition, the reaction temperature was raised to 70°C while vigorous stirring was continued for 7 h. The heat source was removed, and the reaction mixture was allowed to cool to room temperature. It was then diluted with ethyl acetate (300 mL) and transferred into a separatory funnel. The resulting aqueous layer was removed, and the organic phase washed sequentially with brine (2 × 400 mL) followed with saturated Na_2CO_3 solution (50 mL) in additional saturated NaCl solution. This ensures cleaner separation of phases. The organic layer was then dried over Na_2SO_4 and concentrated under reduced pressure to give a colorless slightly viscous liquid (548.9 g). An overnight drying of the product at the pump yielded 512.9 g (98.9%) of the polyepoxy TG. A transparent film of the product on NaCl discs showed the following FTIR spectral bands, ν cm^{-1}: 2994 *m* (**H–C**O stretch epoxide), 2969 *s* (CH_3 asym), 2940 *vs* (CH_2 asym stretch), 2881 *s* (CH_3 sym stretch), 2866 *vs* (CH_2 sym stretch), from the (2927 *vs* and 2856 cm^{-1} *s*) bands, 1756 *vs* (C=O), 1463 *m-s* (–CH_2– deform), 1377 *m* (CH_3 deform), 1241 *m-s* (O–C=O), 1161 *s* (–C–CH–O–), 1104, 1048 (CH_2O stretch), [844, 825] *m* (**C–O–C** epoxide stretch), 726 *m*. In contrast, the native oil gave IR bands at 3019 *w-m* (**H–C**=C), 2969 *s* (CH_3 asym stretch), 2940 *vs* (CH_2 asym), 2878 *s* (CH_3 sym), 2861 *s-vs* (CH_2 sym) from the (2927 and 2855 region), 1746 *vs* (C=O), 1654 *w* (C=C puckering), 1462 *m* (CH_2 deformation), 1376 *w-m* (CH_3 deform), 1237 *m-s* (**O–C=O–C**–), 1163 *s* (–CH–O–C–), 1100 *m-s*, 914 *w*, and 723 *m* (CH_2 wag) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 5.26 *bs* (1H), 4.31 *d* (*J* = 11 Hz, 1H), 4.13 *m* (4H), 3.09 *d* (*J* = 23 Hz, 4H), 2.93 *d* (*J* = 38.2 Hz, 4H), 2.32

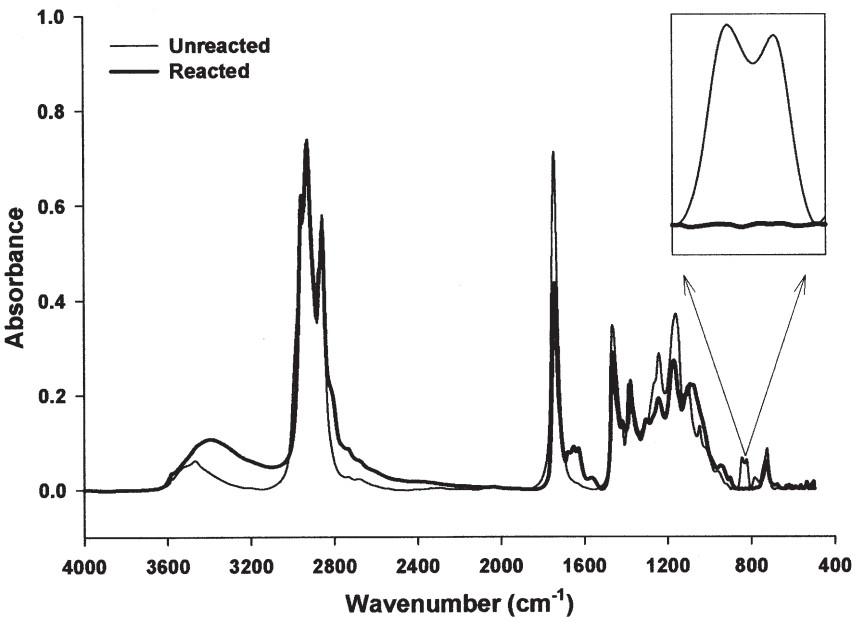


FIG 1. Reaction of epoxy salicornia oil with dibutylamine.

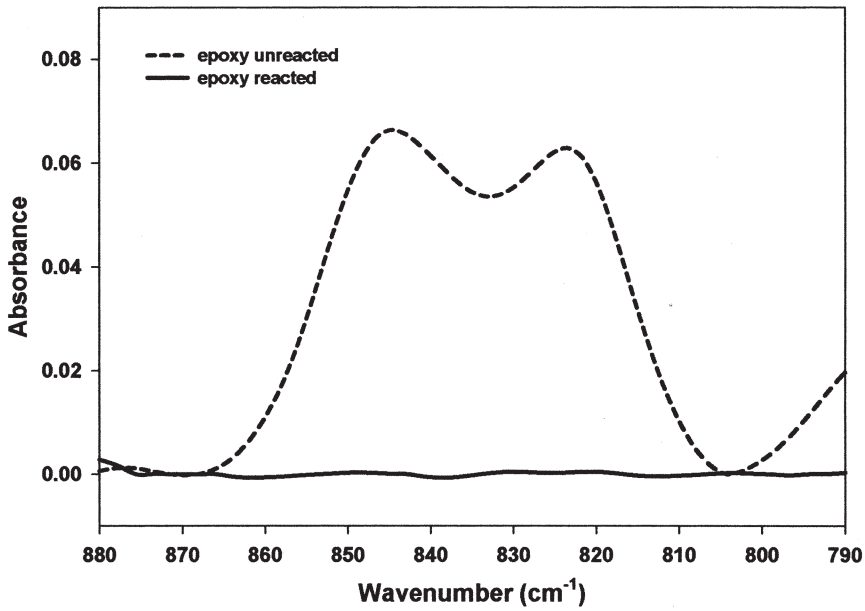


FIG 2. Difference between epoxy bands before and after reaction of epoxy milkweed oil with dibutylamine.

s (6H), 2.04 *d* (*J* = 3.6 Hz, 2H), 1.8–1.2 *m* (69H), 0.90 *bs* (9H). ^{13}C NMR ($CDCl_3$) δ: 173.14 (C=O ester), 172.74 (C=O ester), 68.90 (–**C**HO–C=O– glyceryl), [62.08, 60.34 (**C**H_2O, glyceryl)], [57.17, 57.11, 56.98, 56.91, 56.70, 56.62, 54.31, 54.15] epoxy methines, 34.12 (–**C**H_2–CHOCH–), 33.95 (–**C**H_2–CHOCH–), 31.65 (–**C**H_2–CO_2–), 29.67(–O_2C–**C**H_2–CH_2–), 29.64 (–O_2C–CH_2–CH_2–**C**H_2–), 29.52 (–O_2C**C**H_2–CH_2–CH_2**C**H_2–), 29.33, 29.29, 29.25, 29.16, 28.97, 27.89, 27.87, 27.82, 27.80, 27.21, 26.92, 26.59, 26.55, 26.44, 26.23, 26.12, 24.79 (–O_2C**C**H_2–**C**H_2–), 24.76, 22.55 (–CH_2–CH_3), 14.18 (CH_3–), 13.96 (CH_3–) ppm.

(ii) Synthesis of milkweed oil epoxy TG. In an analogous procedure (4), milkweed oil (186.8 g, 212 mmol; iodine value 111.4) was reacted with formic acid (99%, 12.00 g), and 50% hydrogen peroxide (70.00 g, 1.029 mol) for 7 h at 70°C to yield 188.0 g (95%) of the polyoxirane derivative of milkweed oil. The IR spectrum of this intermediate gave bands at 2994 *w* (HCO of the epoxide), 2969 *s* (CH_3 asym stretch), 2940 *vs* (CH_2 asym), 2876 *s* (CH_3 sym), 2866 *v* (CH_2 sym stretch) cm^{-1} from (2927 and 2856 cm^{-1}), 1754 (C=O), 1470 (–CH_2– deform), 1383 (CH_3 deform), 1186, 1125 (–CH–O–C– and –CH_2O– overlap), 844–824 (–C–O–C– stretch of oxirane), and 725 cm^{-1}; whereas the unmodified oil had bands at 3019 (H–C=C), 2969 (CH_3 asym), 2943 (CH_2 asym), 2878 (CH_3 sym), 2866 (CH_2 sym stretch), 1746 (C=O), 1654 (C=C breathing mode), 1461 (CH_2 deform), 1375 (CH_3 deform), 1238 (OC=O), 1164, 1099 (CHO and CH_2O overlapping stretch), and 723 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.29 *dd* (*J* = 4.3, 11.9 Hz, 2H), 4.14 *dd* (*J* = 5.9, 11.9 Hz, 2H), 3.1 *m* (2H), 2.96 *m* (2H), 2.89 *m* (2H), 2.3 *m* (6H), 1.75–1.25 *m* (72H), 0.87 *m* (9H); ^{13}C NMR ($CDCl_3$) δ: 173.1 (C=O), 172.7 (C=O), 68.87 (–**C**HOC=O), 62.02 (–**C**H_2O–), [57.10, 57.05, 56.91, 56.85, 56.63, 56.55, 54.25, 54.09] epoxy methine carbons, 34.06 (–HC–O–CH–**C**H_2–CH–O–CH–), 33.90 (–**C**H_2–CO_2–), 31.79 (–CHOCH–**C**H_2), 31.61 (–**C**H_2–CH_2–CH–O–CH–), 29.63 (–O_2C–**C**$H_2$$CH_2$–), 29.47 (–$O_2$C–$CH_2$$CH_2$**C**$H_2$–), 29.28, 29.23, 29.15 (–O_2C$CH_2$$CH_2$$CH_2$**C**$H_2$–), 29.12, 28.88, 27.83, 27.77, 27.75, 27.16, 26.84, 26.55, 26.52, 26.10 (**C**H_2–CH_2CH_3), 24.73 (–O_2C–CH_2–**C**H_2), 22.51 (**C**H_2–CH_3), 13.93 (–CH_3) ppm.

Synthesis of α-methylaminohydroxy TG from salicornia oil epoxide. In a dry three-necked round-bottomed flask (250 mL) were placed 19.9 g (21 mmol) of salicornia epoxide, methylamine hydrochloride (7.23 g, 107 mmol), $ZnCl_2$ (0.5 g, 3.7 mmol), and dry acetonitrile (80.0 mL). The reaction mixture was refluxed for 36 h then allowed to cool to room temperature and poured into a saturated sodium hydrogen carbonate solution (500 mL). The mixture was stirred, then extracted with ethyl acetate (4 × 150 mL). The extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a light-red viscous oil; yield 17.0 g (~71.5%); kinematic viscosity was 2,220 cSt at 40°C, 90.27 cSt at 100°C. FTIR cm^{-1}: 3435 *bs* (OH/NH), 2927 *vs* (CH_3, CH_2 asym stretch), 2858 *s* (CH_3, CH_2 sym), 1743 *vs* (C=O), 1671 *w-m* (N–C=O amide I), 1553 *w* (–C=ON amide II), 1461 *m* (–CH_2– deform), 1377 *m* (–CH_3 umbrella effect), 1242 *m* (–OCO_2–), [1163 *m-s*, 1101 *m*] (–C–CH–O stretch), 1048 *m* (–CH_2O– stretch), 844 *w* (residual epoxy –C–O–C– stretch), 726 *w*. ^{1}H NMR ($CDCl_3$) δ: 5.22 *bs* (NH 1H), 4.27 *t* (*J* = 7.3 Hz, 2H), 4.11 *m* (4H), 4.0–3.31 *m* (4H), 3.28–2.60 *m* (6H), 2.28 *bs* (CH_3N, 9H), 1.8–1.10 *m* (87H), 0.85 *t* (9H); ^{13}C NMR ($CDCl_3$) δ: 173.18 (C=O), 172.89 (C=O), 73.77 (–**C**HOH–), 72.68 (–**C**HOH–), 71.80 (–**C**HOH–), 70.43 (–**C**HOH–), 68.89 (–**C**HOC=O–), 68.70, 62.06 (–**C**H_2O), 57.22 (unreacted epoxide), 57.00 (unreacted oxirane), 56.95, 56.72 (–CHN–), 56.64 (–**C**H_2–$NHCH_3$–), 54.33 (–**C**HNH–CH_3), 54.18 (–**C**HNH–), 34.57

(–CHO–**C**H_2–CHN–), 34.10 (–**C**H–O–C=O), 34.00 (–O_2-C**C**H_2–), 33.94, 31.87 (–**C**$H_2$$CH_2$$CH_3$), 31.81 (–**C**$H_2$$CH_2$$CH_3$), 31.62, 31.25 (–**C**$H_2$–$CH_2$–$CH_2$$CH_3$), 29.64 (–$O_2$C**C**$H_2$–**C**$H_2$–), 29.61 (–**C**$H_2$), 29.57, 29.48 (–**C**$H_2$–), 29.43 (–**C**$H_2$–), 29.31 (–$CH_2$–), 29.25 (–$CH_2$–), 29.22 (–$CH_2$–), 29.17 (–$CH_2$–), 29.14 ($CH_2$), 29.12, 29.06 ($CH_2$), 29.01 (–**C**$H_2$$CH_2$–), 28.90 (–**C**$H_2$), 28.90 (–**C**$H_2$–), 27.96 (–$CH_2$–), 27.85, 27.82, 27.77, 27.75, 27.14, 26.87, 26.55, 26.40, 26.09, 24.81 (–O_2C–CH_2**C**H_2–), 24.76, 22.64 (CH_2), 22.62 (CH_2), 22.53 (CH_2), 22.46 (–**C**$H_2$$CH_3$), 14.08 (–$CH_3$), 13.95 (–$CH_3$) ppm.

Synthesis of α-dibutylaminohydroxy TG from salicornia oil oxiranes. To a dry three-necked round-bottomed flask equipped with a heating mantle and a magnetic stirrer and fitted with a reflux condenser were added salicornia oxirane (106.0 g, 110.3 mmol), dibutylamine (99.5%, 103.23 g, 798.7 mmol), and anhydrous $ZnCl_2$ (1.00 g, 7.4 mmol). The reaction mixture was vigorously stirred and heated to gentle reflux. Reaction progress was monitored by TLC on precoated silica gel G60 (5 × 20 cm plates) using hexanes/EtOAc/AcOH 10:5:2 as solvent. The developed plate was visualized by spraying with H_2SO_4/methanol (1:3) and heating to 110°C. After 4 h, reaction was judged complete when product showed an R_f = 0.24 relative to R_f values of 0.37, 0.43, and 0.57 for the starting oxirane. The system was allowed to cool to room temperature, and the solution was transferred into a separatory funnel by decantation with 200 mL of EtOAc and washed with saturated sodium chloride solution (3 × 150 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 51°C. The viscous product was further dried overnight using a vacuum pump at 51°C to remove any residual dibutylamine. The yield was 142.6 g (81.4%); kinematic viscosity was 1,288 cSt at 40°C and 59.90 cSt at 100°C. FTIR cm^{-1}: 3401 *b* (OH), 2954 *vs* (H_3C– asym stretch), 2929 *vs* (–CH_2 asym stretch), 2857 *s* (CH_3, CH_2 sym stretch), 1743 *s* (C=O), 1671 *w* (–CON amide I), 1551 *w* (amide II), 1463 *m-s*, 1377 *m*, 1244 *m*, 1168 *m-s*, 1080 *m-s*, 727 *w*. ^{1}H NMR ($CDCl_3$) δ: 4.27 (*m,* 2H), 4.11 (*m,* 2H), 3.8–3.1 (*m,* 5H), 2.51 (*t, J* = 7.7 Hz, 3H), 2.50–2.30 (*m,* 22H), [1.61–1.25 overlapping multiplets (126H)], 0.90 overlapping (*t,* 39H); ^{13}C NMR ($CDCl_3$) δ (ppm): 173.80 (–**C**=ON– very small), 173.21 (–C=O–), 172.80 (C=O), 81.78 (–H**C**OH–CHN=), 81.71 (–**C**HO–CH–N=), 81.35 (–H**C**OH–CHN=), 80.26 (–H**C**OH–CHN=), 75.25 (–H**C**O–CHN=), 74.37 (–HCOH–**C**HN=), 70.55 (CHOH**C**HN=), 69.77 (–HCO–**C**HN=), 68.87 (–**C**HO–C=O), 67.95 (–H**C**–N=), 66.27 (–H**C**–N=), 66.17 (–H**C**–N=), 65.06 (–**C**H_2O–), 63.72 (–H_2**C**–N=), 63.22 (–HC–N=), 62.06 (–CH_2O–), 61.49 (–H**C**–N=), 51.42 (–**C**H_2–N=), 51.11 (–**C**H_2–N=), 48.79 (–**C**H_2–N=), 34.01 (–**C**H_2–CO_2–) , 31.76 (–**C**H_2–CH_2–N=), 30.41 (–**C**H_2—HCOH–), 30.09 (–**C**H_2–CH_2–CH_2–CH_3), 29.67, 29.33, 29.24, 29.09 (–O_2CCH_2–**C**H_2–), 28.36, 27.02, 26.38, 24.83 (–**C**$H_2$$CH_3$), 22.64, 22.48 (–$CH_2$$CH_3$), 20.68 (–**C**$H_2$$CH_3$), 20.54 (–**C**$H_2$$CH_3$), 20.51 ($CH_2$$CH_3$), 20.35 (–$CH_2$–$CH_3$), 14.04 (–$CH_3$), 13.82 (–$CH_3$) ppm.

Synthesis of α-dibutylaminohydroxy TG from milkweed oil epoxides. Into a dry two-necked round-bottomed flask fitted with a reflux condenser, magnetic stirrer, and heating mantle were added epoxy TG of milkweed oil (36.2 g, 38.97 mmol), dibutylamine (99.5%, 50.36 g, 65.7 mmol), and anhydrous $ZnCl_2$ (1.00 g, 7.4mmol). The reaction mixture was stirred and heated to gentle reflux for 4 h when TLC indicated complete conversion, that is, no starting oxirane was left. TLC in hexanes/EtOAc/AcOH (10:5:2) gave R_f values of 0.37, 0.43, and 0.57 for the starting oxirane whereas the product had an R_f of 0.24. The heat source was then removed, and the contents of the flask were allowed to cool to room temperature and the crude product was diluted with ethyl acetate (200 mL) and decanted into a separatory funnel. The solution was washed with saturated NaCl (3 × 150 mL) and the organic phase dried over $MgSO_4$. The filtered solution was concentrated at 51°C under reduced pressure and further vacuum-dried with a pump overnight at the same temperature to yield 46.4 g (88.4%). This product had kinematic viscosities of 1,620 cSt at 40°C and 70.31 cSt at 100°C. FTIR cm^{-1}: 3394 *bs*, 2967 *s*, 2939 *vs*, 2878 *s*, 2863 *s*, 1753 *s*, 1687 *w*, 1555 *vw*, 1474 *m-s*, 1385 *m*, 1250 *m*, 1190 *m-s*, 1093 *bm*, 726 *w*. ^{1}H NMR ($CDCl_3$) δ (ppm): 5.23 *bs* (OH, 1H), 4.23 *m* (*CH_2OH*, 2H), 4.15 *m* (*CH_2OH*, 4H), 3.8–3.2 (*m*, 7H), 2.40 (*m,* 23H), 1.61–1.25 (*m,* 124H), 0.92 (*m,* 39H); ^{13}C NMR ($CDCl_3$) δ: 173.83 (amide C=O), 173.25 (C=O ester), 172.81 (C=O ester), 81.75 (–H**C**OH–CHNBu_2, 81.69 (–**C**HOH–CHNBu_2), 81.39 (–CHOH–CHNBu_2–), 81.36 (–**C**HOH–CHNBu_2), 80.21 (–**C**HOH–CHNBu_2), 75.27 (–**C**HO–CHNBu_2), 75.21 (–**C**HCHNBu_2), 74.39 (–**C**HNBu_2), 70.60 (H**C**O), 69.79 (–CHNBu_2), 68.87 (–**C**HO–C=O–), 68.09 (–**C**HNBu_2), 66.31 (–**C**HNBu_2), 66.20 (–**C**HNBu_2), 65.07 (–CH_2O–), 63.75 (–**C**HNBu_2–), 63.25 (–**C**HNBu_2), 62.07 (–CH_2O–), 51.42 (–**C**H_2–NBu_2–), 51.11 (–**C**H_2 NBu_2), 47.18 (–**C**H_2–N), 41.87 (–**C**H_2–N–CH–), 34.51 (–CH_2–C=O), 34.02 (**C**$H_2$$CH_2$N), 31.91 (–**C**$H_2$$CH_2$N–), 31.84 (–**C**$H_2$$CH_2$N–), 31.66 (–**C**$H_2$$CH_2$N–), 30.73 (–**C**$H_2$$CH_2$N–), 30.22 ($CH_2$-**C**$H_2$$CH_2$N–), 30.15 (–$CH_2$**C**$H_2$$CH_2$N–), 30.09 (–$CH_2$**C**$H_2$-$CH_2$N–), 29.95 (–$O_2CCH_2$$CH_2$–**C**$H_2$–), 29.90 ($O_2CCH_2$-$CH_2$**C**$H_2$), 29.68 (–$CH_2$$CH_2$**C**$H_2$), 29.42 ($CH_2$), 29.37 (–$CH_2$–), 29.34 (–$CH_2$–), 29.29 ($CH_2$), 29.25 ($CH_2$), 29.17 ($CH_2$), 29.09 ($CH_2$), 28.96 ($CH_2$), 28.31 ($CH_2$), 27.00 ($CH_2$), 26.38 ($CH_2$), 26.33 ($CH_2$), 24.82, 22.64, 20.69 (–**C**$H_2$$CH_3$), 20.54, 20.51, 20.12 (–**C**H_2–CH_3), 14.04 (–CH_3) ppm.

RESULTS AND DISCUSSION

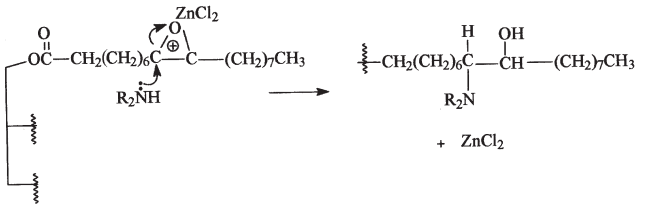
The epoxidation of the highly unsaturated *S. bigelovii* Torr and *A. syriaca* L. oils, with FA profiles shown in Table 1, were readily achieved in excellent yields under neat reaction conditions. The main FTIR spectral features observed in the oxirane products were the –**H–**COC–H– at 2994 cm^{-1} and the –C–O–C– doublet at 844 and 824 cm^{-1}, along with the corresponding disappearances of the alkene **H**–**C=**C stretch at 3019 cm^{-1} and the –**C=C**– puckering mode at 1654 cm^{-1} of the starting oils. An initial attempt to generate the amine derivative from the oxirane at room temperature with anhydrous ammonia under pressure for 7 d without a catalyst was unsuccessful. A more successful procedure was the use of methylamine hydrochloride with anhydrous $ZnCl_2$ in dry acetonitrile under reflux. Even under these reaction

TABLE 1
FA Composition (%) of the Vegetable Oils Used

FA composition, %	*Salicornia bigelovii*	*Asclepias syriaca*
C14:0	0.1	
C16:0	8.98	5.7
C16:1	0.14	9.6
C18:0	2.85	2.5
C18:1	16.3	31.0
C18:2	66.69	50.5
C18:3	1.81	1.2
C20:0	0.51	
C20:1	0.28	
C20:2	0.06	
C22:0	0.31	
?	1.41	
C24	0.15	

TABLE 2
Oxirane + Amine Reaction Efficiency Estimates from FTIR Spectra.

Sample no.	Epoxy oil	Amine	Reacted %
1	Salicornia	Methyl	70.1
2	Salicornia	Methyl	12.2
3	Salicornia	Dibutyl	100
4	Milkweed	Dibutyl	99.6
5	Salicornia	Dibutyl	99.4



SCHEME 2

conditions, the epoxy ring opening was incomplete with this amine. The slow ring opening was mainly attributable to the low solubility of the amine hydrochloride salt in the solvent. An attempt to improve the amine availability to the oxirane by the addition of small amounts of solid sodium hydrogen carbonate to the reaction mixture simply exacerbated the competing amidation reaction rather than improving the aminolysis of the oxirane as seen in entry 2 of Table 2. The use of neat dibutylamine in place of methylamine hydrochloride greatly accelerated the addition of the amine to generate the α-dibutylaminohydroxy TG in 3–4 h with only trace amounts of amide by-products. The FTIR spectra of the products confirmed that $ZnCl_2$ catalyzed the reaction of methylamine or dibutylamine with the epoxy TG of salicornia and milkweed oils. As shown in Figures 1 and 2, the product spectra typically showed decreases in the oxirane bands (846 to 824 cm^{-1}) compared with the unreacted epoxy oil. These product spectra also showed broad new bands (centered at 3250 cm^{-1}), attributed to the hydrogen-bonded hydroxyl group generated by the aminolytic ring cleavage of the oxirane (Scheme 2). Besides confirming the reaction, one other objective of FTIR analysis was to measure the efficiency of the reaction by estimating the fraction of unreacted epoxy groups remaining in the product oil. From the spectral peak integrations in Figures 1 and 2, one can see that the areas of the epoxy bands in the spectra of typical reaction products were greatly reduced and the reactions were nearly complete. For example, in Table 2, the salicornia and milkweed products, entries 3 and 4, lost 100 and 99.6%, respectively, of their original epoxy groups. In other words, these two

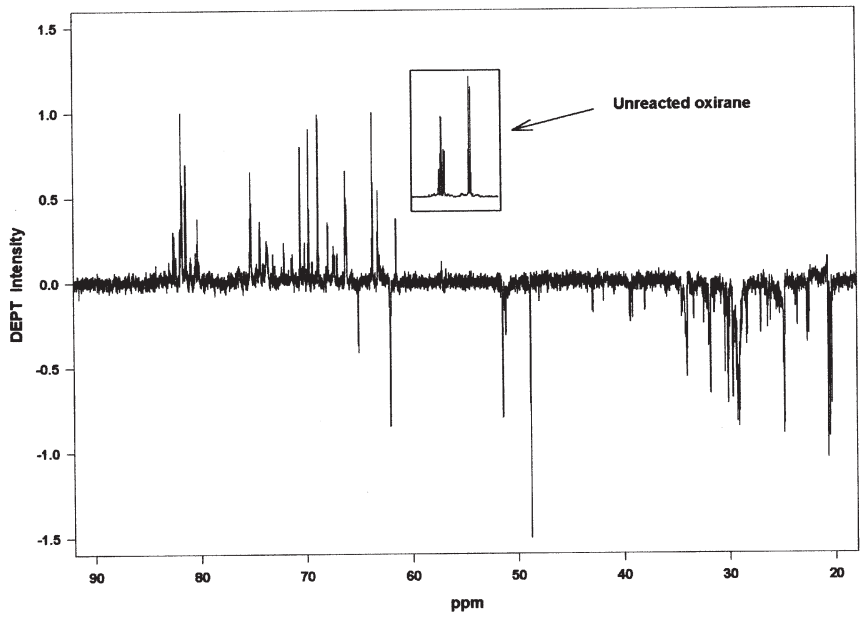


FIG. 3. ^{13}C NMR distortionless enhancement proton transfer (DEPT) experiment spectrum of dibutylaminohydroxy TG of milkweed/salicornia oils.

epoxy reactions with dibutylamine were virtually complete. Furthermore, the spectra of typical reaction products also showed decreased ester carbonyl absorbance at 1743 cm^{-1}, which may indicate some hydrolytic side reaction of the amine on the ester function of the TG. This is not unexpected in a neat reaction environment with a basic substrate even with a 1:1 reactant ratio. And the evidence of such transamidation is substantiated by the 1670 and 1540 cm^{-1} bands, even though these absorbances are small. The ^{13}C NMR does confirm an amide carbonyl at 173.8 ppm. A possible contribution to the observed attenuation of the ester carbonyl absorbance of the aminohydroxy TG besides amidation could also be due to large changes in molecular mass of these products compared with the oxiranes. Presuming a pentaoxirane TG starting material, the product of a complete reaction acquires an additional 646 mass units/mol resulting from addition of dibutylamine groupings to ring-open all five epoxy moieties. This increase is only in the alkyl component of the derivatives with no corresponding increase in the ester carbonyl component. The ^{13}C NMR distortionless enhancement proton transfer experiment (DEPT) (Fig. 3) shows some five nitrogen-bearing (67.95 to 61.49 ppm) methine carbons as well as six oxygen-bearing (81.78 to 69.77 ppm) methine carbons. The chemical shifts observed for the methine carbons attached to nitrogen atoms are farther downfield as a result of steric crowding from the dibutylamine substituents. The DEPT also shows the chemical shifts corresponding to the two hydroxymethyl carbons (65.06 and 62.07 ppm) and the lone methine carbon (68.87 ppm) for the glyceryl segment of the aminohydroxy ester. This spectrum also shows the complete absence of oxirane methine carbons in the dibutylamine products. The insert in Figure 3 is the spectral region bearing the oxirane methine carbons; this spectral region is transparent in the aminohydroxy product. Instead, resonances indicative of the presence of nitrogen-attached methylene carbons (51.42 to 41.87 ppm) appear adjacent to the methine region, but at a higher field. The remaining high-field spectral region displays the remaining methylenes from 34.51 to 20.12 ppm and the terminal methyl carbons at 14.04 and 13.82 ppm.

It is surprising that naturally occurring aminoTG are rare in seed oils in spite of the abundance of nitrogen compounds in the environment. Nevertheless, a reactive TG platform such as the oxiranes under conducive reaction conditions would give the corresponding aminohydroxy TG with the appropriate amines. This report shows that aminohydroxy TG are readily available in good to excellent yields at moderate temperatures and at atmospheric pressure from the epoxy TG of salicornia and milkweed seed oils. Keys to the success of the reaction at a 1:1 reactant ratio are use of a one-phase reaction system, without solvent, and a moderate-cost, classic Lewis acid catalyst, anhydrous $ZnCl_2$.

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