Synthesis of *cis*-12,13-Epoxy-*cis*-9-octadecenol and 12(13)-Hydroxy-*cis*-9-octadecenol from Vernonia Oil Using Lithium Aluminum Hydride

Eisa B. Elhilo, Melissa A. Anderson, and Folahan O. Ayorinde*

Department of Chemistry, Howard University, Washington, DC 20059

ABSTRACT: Reduction of vernonia oil methyl esters (VOME) into epoxy fatty alcohol and diols was achieved with lithium aluminum hydride (LAH), under reflux and room temperature conditions, by using hexane and tetrahydrofuran (THF) as solvents . The reactions of VOME with LAH in hexane produced *cis*-12,13-epoxy-*cis*-9-octadecenol as a major product with an isolated yield of 73.62%, whereas the reactions with LAH in THF gave isomers of 12(13)-hydroxy-*cis*-9-octadecenol as the major products with an isolated yield of 95.1%. LAH was similarly reacted with vernonia oil (VO) to give the same products in lower yields. [1]H nuclear magnetic resonance (NMR), ^{13}C NMR, gas chromatography–mass spectrometry, and infrared were used to characterize these products.

This study demonstrates the ability to control the reactivity of the epoxy functionality in VO or VOME with the choice of polar or nonpolar solvents, and extends the range of oleochemicals that can be derived from vernonia oil.

Paper no. J9458 in *JAOCS 77*, 873–878 (August 2000).

KEY WORDS: ^{13}C NMR, *cis*-12,13-epoxy-*cis*-9-octadecenol, GC–MS, ^{1}H NMR, 12(13)-hydroxy-*cis*-9-octadecenol, IR, vernonia oil, vernonia oil methyl esters.

The most extensively used oleochemicals, after fatty acids, are fatty alcohols, and there are growing efforts aimed at developing new derivatives and applications for the alcohols (1). Current laboratory methodology for their synthesis involves direct reduction of fatty esters with lithium aluminum hydride (LAH) (2). LAH is among the most powerful complex metal hydride reducing agents, with the ability to reduce carbonyl functionality in aldehydes, ketones, and esters to corresponding alcohols, while leaving the carbon-carbon double bond or carbon-carbon triple linkages untouched (3–5). In the case of the reaction of LAH with esters (2), the reduction of the ester functionality proceeds by nucleophilic attack of the hydride ion on the carbonyl group, leading to the formation of intermediate alkoxide salts from which the alcohol is generated upon acidification. Micovic and coworkers (6) reported on the production of corresponding alcohols resulting from the LAH reduction of tripalmitin and triolein, olive oil, lard, and oil of chaulmoogra glycerides. In another study, Walborsky and Colombini (7) reported on the syntheses of alcohol mixtures by the LAH reduction of glycidic esters. Ernest and coworkers (8,9) have also demonstrated the ability of LAH to reduce epoxides to alcohols.

Therefore, we were interested in studying the reaction between LAH and vernonia oil (VO), which is a naturally epoxidized vegetable oil (10). The products from this reaction could constitute potential intermediates in the synthesis of oleochemicals from *Vernonia galamensis* seed oil, since it has been recognized as a potential oil seed crop (11,12). The initial interest was due to the unique fatty acid composition of its seed oil, which contains epoxidized triacylglycerols, of which trivernolin has been shown to be the major triacylglycerol (13,14).

Previous work in our laboratory indicated that the epoxy functionality in VO was reactive toward nucleophilic reagents only under acidic conditions (12), whereas aminolysis (15) of the oil gave epoxy-containing amides with no indication of epoxy opening. Also, the base-catalyzed methanolysis (14) of the oil resulted only in transesterification to give epoxidized methyl ester. Consequently, we were interested in studying the effect of a nucleophilic agent such as LAH on the epoxy functionality. Therefore, as part of an ongoing research effort we investigated the reaction of VO with LAH with a particular focus on the reactivity of its epoxy functionality under different reaction conditions of temperature and solvents. In this paper we report the effect of temperature and solvent on the reactions that involved LAH/VO and LAH/vernonia oil methyl esters (VOME) to give an epoxy alcohol and diols.

EXPERIMENTAL PROCEDURES

Reagents. The crude VO used in this study was obtained from International Exchange of Trade and Technology, Inc. (Culver, IN). Transesterification of VO with sodium methoxide yielded the VOME. Lithium aluminum hydride, hexane, tetrahydrofuran (THF), and methyl alcohol were purchased from Aldrich Chemicals Inc. (Milwaukee, WI).

Instrumentation. Reactions and products were monitored with a Hewlett-Packard 5890 series II gas chromatograph (Avondale, PA) coupled with a Hewlett-Packard 5989A mass

spectrometer. The interface oven and transfer line were maintained at 285°C, the ionizer temperature setting was at 150°C, using electron impact (EI) mode, with electron energy at 70 eV. High-resolution capillary gas chromatography was conducted with a Supelco fused-silica SPB-I (30 m, 0.32 mm inside diameter, 0.25 µm film) column (Bellefonte, PA), oven temperature was programmed from 50 to 300°C, and helium was used as the carrier gas with a head pressure of 10 psi. Characterization of alcohols by gas chromatography–mass spectrometry (GC–MS) was performed by dissolving a 10-mg sample of alcohol in 2 mL methylene chloride, from which 1 µL was injected on the column. The infrared (IR) spectra were obtained on a PerkinElmer model 1600-Infrared Spectrophotometer (Norwalk, CT). Solid samples were run with KBr, while liquid samples were run neat. The ^{13}C nuclear magnetic resonance (^{13}C NMR) and proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a GE-NMR QE-300 model spectrometer (Fremont, CA) with chloroform-*d* (CDCl$_3$) as solvent and source of internal standard.

Transesterification of VO to give VOME. VO (24.85 g, 0.08 mol) was transferred into a 500-mL round-bottomed flask. Hexane (125 mL) was added, followed by 12.5 mL sodium methoxide in methanol (25 wt%). The flask was fitted onto a rotary evaporator, and then allowed to rotate (approximately 240 revolutions/min) for about 80 min without heat or vacuum. The resulting mixture was transferred into a separatory funnel and 125 mL water was added. The flask was rinsed with approximately 20 mL water, and the rinse was added to the separatory funnel. The hexane layer was drawn off, and then stripped to give 24.51g (98.2% yield, based on methyl vernolate) of VOME. GC analysis indicated a mixture of methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl vernolate. MS diagnostic ions for methyl vernolate (*m/z*) were: 292 (M − H$_2$O) and 279 (M − OCH$_3$) and for ^{13}C NMR data (ppm), 173.49 (C=O), 132.03, 123.83 (CH=CH), 56.59, 55.98 (epoxy carbons), and 50.87 (OCH$_3$).

LAH reaction with VOME in hexane. To a 500-mL, three-neck, round-bottomed flask equipped with an air condenser, separatory funnel, and magnetic stirring bar, 60 mL hexane and 0.9 g (0.024 mol) LAH were added. Through the separatory funnel, 2.5 g (0.008 mol) of VOME was added with stirring. The separatory funnel was rinsed with 10 mL hexane and the rinse was added to the mixture in the flask. The reaction mixture was then stirred continuously for 2 h at room temperature, after which 5 mL water was slowly added. The mixture was further stirred for 15 min and then vacuum-filtered. The reaction flask was rinsed with 10 mL hexane and the rinse was added to the Buchner funnel. The filtrate was stripped with a rotary evaporator to give 2.14 g (94.30%) of a crude product that contained *cis*-12,13-epoxy-*cis*-9-octadecenol (epoxy alcohol) as a major product and hexadecanol, *cis*-9,12-octadecadienol, *cis*-9-octadecenol, and octadecanol as minor products. The crude product was analyzed by Fourier transform infrared (FTIR), which gave hydroxy absorption at 3298.3 cm^{-1} and absorptions at 820.6 and 846.0 cm^{-1} (epoxy group). The MS (EI) data of the epoxy alcohol

showed the molecular ion at *m/z* 282, and a diagnostic ion at *m/z* 264 (M − H$_2$O).

LAH reaction with VOME in THF. This reaction was performed under the same conditions as above, except that THF was used as solvent and the reaction was allowed to continue for 7 h. The resulting filtrate was stripped with a rotary evaporator to give 2.24 g (97.80%) of a crude product that contained isomers of (12)13-hydroxy-*cis*-9-octadecenol (diol) as major products and hexadecanol, *cis*-9,12-octadecadienol, *cis*-9-octadecenol, and octadecanol as minor products. The crude product was analyzed by FTIR to give hydroxy absorption at 3334.6 cm^{-1}. The MS (EI) data of the diols showed diagnostic ions at *m/z* 266 (M − H$_2$O) and *m/z* 248 (M − 2H$_2$O).

LAH reaction with VO under reflux conditions (in hexane or THF). To a 500-mL, three-neck, round-bottomed flask equipped with water condenser, separatory funnel, and magnetic stirring bar, 90 mL of solvent (hexane or THF) and 1.8 g (0.047 mol) LAH were added. Through the separatory funnel, 2.5 g (0.0027 mol) of VO was added with stirring. The separatory funnel was rinsed with 10 mL of the solvent, and the rinse was added to the mixture in the flask. The reaction mixture was then stirred continuously for 24 h under reflux, after which 5 mL water was slowly added. The mixture was further stirred for 15 min and then vacuum-filtered. The reaction flask was rinsed with 10 mL of the solvent and again the rinse was added to the Buchner funnel. The filtrate was stripped with a rotary evaporator to produce 1.75 g (76.75%) of a crude product (with hexane as solvent) that contained *cis*-12,13-epoxy-*cis*-9-octadecenol (epoxy alcohol) as a major product and hexadecanol, *cis*-9,12-octadecadienol, *cis*-9-octadecenol, and octadecanol as minor products. The crude product was analyzed by FTIR to give hydroxy absorption at 3433.8 cm^{-1} and absorptions at 820.6 and 840.0 cm^{-1} (epoxy group). The MS (EI) data of the epoxy alcohol showed the molecular ion at *m/z* 282, and diagnostic ion at *m/z* 264 (M − H$_2$O). The reaction in THF gave 2.00 g (86.96%) of the crude product, which contained isomers of (12)13-hydroxy-*cis*-9-octadecenol (diol) as major products and hexadecanol, *cis*-9,12-octadecadienol, *cis*-9-octadecenol, and octadecanol as minor products. Details of the isolation and further characterization of the epoxy alcohol and diols are provided below.

Isolation of cis-*12,13-epoxy-*cis*-9-octadecenol (epoxy alcohol).* The crude products from VOME/LAH, and VO/LAH reactions in hexane were dissolved separately in 50 mL hexane and the solution was cooled with ice/water (about 5°C) for 1 h. After crystallization, the solution was vacuum-filtered to obtain white crystals (epoxy alcohol) and a filtrate containing the remainder of the fatty alcohols. The white crystals were allowed to dry to give 1.4 g (76.92%) of pure epoxy alcohol from VOME/LAH, and 0.72 g (39.34%) of pure epoxy alcohol from VO/LAH. IR data (cm^{-1}): 3298.3 (OH), 820.6, 846.0 (epoxy group). MS data (*m/z*): 282 (M$^{+·}$) and 264 (M − H$_2$O). ^{1}H NMR data (ppm): 5.35–5.60 (C<u>H</u>=C<u>H</u>), 3.64 (O–C<u>H</u>$_2$), 2.90 (O–C–<u>H</u> of epoxide), 2.00–2.45 (C<u>H</u>$_2$–CH=CH–C<u>H</u>$_2$), 1.25–1.75 (C<u>H</u>$_2$)$_n$, and 0.90 (C<u>H</u>$_3$). ^{13}C NMR data (ppm): 132.481 and 123.697 (C=C), 56.461

and 57.107 (Cs of epoxide), 62.597 ($\underline{C}$–OH), 22.424–32.596 ($\underline{C}H_2)_n$, and 13.801 (CH_3).

Isolation of 12(13)-hydroxy-cis-9-octadecenol (diol). The crude products from VOME/LAH and VO/LAH reactions in THF were dissolved separately in 100 mL of $MeOH/H_2O$ (4:1, vol/vol ratio) and the solution was transferred to a separatory funnel and then extracted with 25 mL hexane (×4). The aqueous layer containing pure diol was separated, and the four hexane portions were combined. Then the combination of hexane portions was extracted twice with 25 mL of $MeOH/H_2O$ (4:1, vol/vol ratio). All the aqueous layers were combined, washed with 10 mL hexane, and then stripped with a rotary evaporator to give 1.74 g (95.1%) of pure diol isomers from VOME/LAH, and 1.5 g (81.5%) of pure diol isomers from VO/LAH. IR data (cm^{-1}): 3334.5 (OH). Both isomers showed similar MS data with the following diagnostic ions (*m/z*): 266 (M − H_2O) and 248 (M − $2H_2O$).^{1}H-NMR data (ppm): 5.35–5.60 ($\underline{C}H=\underline{C}H$), 3.60 (O–$\underline{C}H_2$), 2.65 (OH), 2.00– 2.193 ($\underline{C}H_2$ attached to CH=CH), 1.30–1.75 ($\underline{C}H_2)_n$, and 0.850 ($\underline{C}H_3$). ^{13}C NMR data (ppm): 132.739, 130.188, 129.154 and 125.118 (C=C) of the isomers, 71.349 (C attached to terminal OH), 62.403 and 62.113 (C_{12} and C_{13} attached to OH), 37.150–22.424 ($\underline{C}H_2)_n$, and 13.866 ($\underline{C}H_3$).

RESULTS AND DISCUSSION

Table 1 shows the reaction outcome of LAH reduction of VO and VOME under different reaction conditions. All the reaction completions were monitored by the disappearance of the ester carbonyl absorption in the IR spectra. The reduction of VO in hexane under reflux was incomplete, and hence it gave poor yield; however, all other reactions went to completion.

LAH reactions with VOME in hexane and in THF. The reactions of VOME/LAH in hexane were performed at room temperature and under reflux. Both sets of experiments yielded similar results except that the reaction under reflux was complete in 1 h, whereas the reaction at room temperature was complete in 2 h. These reactions resulted in the epoxy alcohol (*cis*-12,13-epoxy-*cis*-9-octadecenol) as a major product, and there was no evidence of epoxy ring opening. On the other hand, the reactions of VOME/LAH in THF at room temperature and under reflux gave the diol alcohols, 12(13)-hydroxy-*cis*-9-octadecenol as major products. How-

ever, in this case, there was a greater time differential, the reflux reaction was complete in 1 h, and the room temperature reaction was complete in 7 h. The greater time differential could be due to the possibility that ring opening of the epoxy functionality requires greater energy.

We propose that the difference in the outcome of these reactions could be due to the solubility of the intermediate alkoxide salt that is formed during the LAH reduction of the esters. Thus any subsequent reactions, such as epoxy ring opening, depend on the solubility of this intermediate salt. When THF (the more polar solvent) was used, there was ring opening due to the higher solubility of the intermediate lithium alkoxide. This conclusion was supported by the fact that all the reactions were monitored by IR spectroscopy, which indicated complete disappearance of the ester carbonyl prior to the reduction of the epoxy functionality when THF was used as the solvent.

The GC–MS of the VOME/LAH reaction in hexane at room temperature and under reflux indicated a chromatogram with a mixture of epoxy alcohol (*cis*-12,13-epoxy-*cis*-9-octadecenol), hexadecanol, *cis*-9,12-octadecadienol, *cis*-9-octadecenol, and octadecanol. The mass spectrum of the epoxy alcohol showed the normal alkene-type fragmentation due to the loss of water, with a molecular ion at *m/z* 282, and a fragment ion at *m/z* 264 (M − H_2O).

The GC-MS of the VOME/LAH reactions in THF at room temperature and reflux also indicated a chromatogram with a mixture of diol isomers 12(13)-hydroxy-*cis*-9-octadecenol, hexadecanol, *cis*-9,12-octadecadienol, *cis*-9-octadecenol, and octadecanol. The mass spectrum of each of the diols showed diagnostic ions at *m/z* 266 (M − H_2O) and *m/z* 248 (M − $2H_2O$).

LAH reactions with VO in hexane and in THF. The vernonia oil experiments provided a direct reduction of the triacylglycerols to the corresponding fatty alcohols without the intermediary methyl esters. The reactions were additionally monitored with GC–MS every 6 h using farnesol (3,7, and 11-trimethyl-2,6,10 dodecatrien 1-ol) as the internal reference. Reaction under reflux in hexane produced the epoxy alcohol (*cis*-12,13-epoxy-*cis*-9-octadecenol) as a major product, which was confirmed by GC–MS, while the reaction under reflux in THF produced the diol isomers [12(13)-hydroxy-*cis*-9-octadecenol] as major products, which was also confirmed by GC-MS. Attempts at performing these reactions at room

TABLE 1
Lithium Aluminum Hydride (LAH) Reduction of Vernonia Oil (VO) and Vernonia Oil Methyl Esters (VOME) to Give Epoxy Alcohol and Diols

Substrate used	Solvent used	Ester redn.[b] to alcohol	Epoxy ring opening	Reaction condition	Reaction time (h)	Yield of crude (%)	Isolated product[a] (%)
VOME	Hexane	Yes	No	RT[b]	2	94.30	76.92
VOME	Hexane	Yes	No	Reflux	1	90.75	73.62
VOME	THF[b]	Yes	Yes	RT	7	97.80	95.10
VOME	THF	Yes	Yes	Reflux	1	98.70	96.72
VO	Hexane	Yes	No	Reflux	24	76.75	39.34
VO	THF	Yes	Yes	Reflux	24	86.96	81.52

[a]Based on 80% vernolate in VOME.
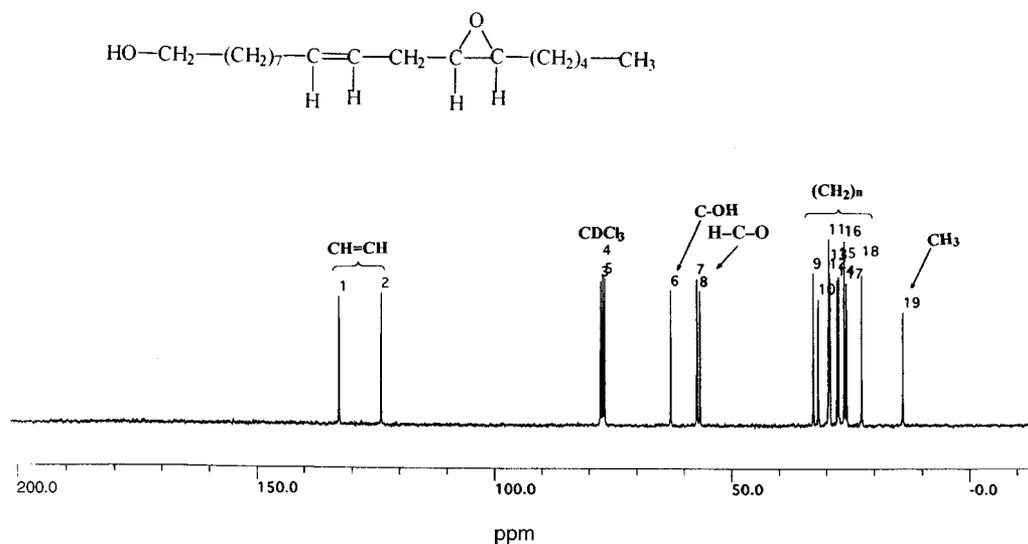[b]Redn., reduction; RT, room temperature; THF, tetrahydrofuran.

FIG. 1. [13]C nuclear magnetic resonance (NMR) spectrum of the epoxy alcohol. Chemical shifts (ppm): 132.481 and 123.697 ($\underline{C}$H=$\underline{C}$H), 56.461 and 57.107 (epoxy carbons, O–$\underline{C}$–H), 62.597 carbon attached to the hydroxyl group, 22.424–32.596 ($\underline{C}$H$_2$)$_n$, and 13.801 ($\underline{C}$H$_3$).

temperature were abandoned because of the prolonged reaction completion time.

NMR analysis. The ^{1}H NMR data from the epoxy alcohol indicated the presence of the olefinic protons (C$\underline{H}$=C$\underline{H}$) at 5.35 and 5.60, methylene protons (O–C$\underline{H}_2$) at 3.64, epoxy protons (O–C–$\underline{H}$) at 2.9, protons of methylene attached to olefinic group (–C$\underline{H}_2$–CH=C$\underline{H}$–C$\underline{H}_2$–) at 2.00–2.45, protons of other methylene groups (C$\underline{H}_2$)$_n$ at 1.25–1.76, and protons of methyl (C$\underline{H}_3$) groups at 0.90. ^{13}C NMR data (Fig. 1) showed the olefinic carbons of the epoxy alcohol ($\underline{C}$H=$\underline{C}$H) at 132.481 and 123.697, epoxide carbons (O–$\underline{C}$–H) at 56.461

and 57.107, carbon attached to the hydroxyl group ($\underline{C}$–OH) at 62.597, methylene carbons ($\underline{C}$H$_2$)$_n$ at 22.424–32.596, and methyl carbon ($\underline{C}$H$_3$) at 13.801. The ^{1}H NMR data from the diol mixture indicated the presence of the olefinic protons (C$\underline{H}$=C$\underline{H}$) at 5.35 and 5.60, methylene and methyne protons (C$\underline{H}_2$–OH and C$\underline{H}$–OH) at 3.60, protons of the methylene attached to olefinic group (–C$\underline{H}_2$–CH=CH–C$\underline{H}_2$–) at 2.01–2.62, protons of the hydroxyl groups (O$\underline{H}$) at 2.65, protons of other methylene groups (C$\underline{H}_2$)$_n$ 1.30–1.75, and protons of methyl (C$\underline{H}_3$) groups at 0.883. ^{13}C NMR data (Fig. 2) indicated the presence of olefinic carbons of the isomers ($\underline{C}$H=$\underline{C}$H) at
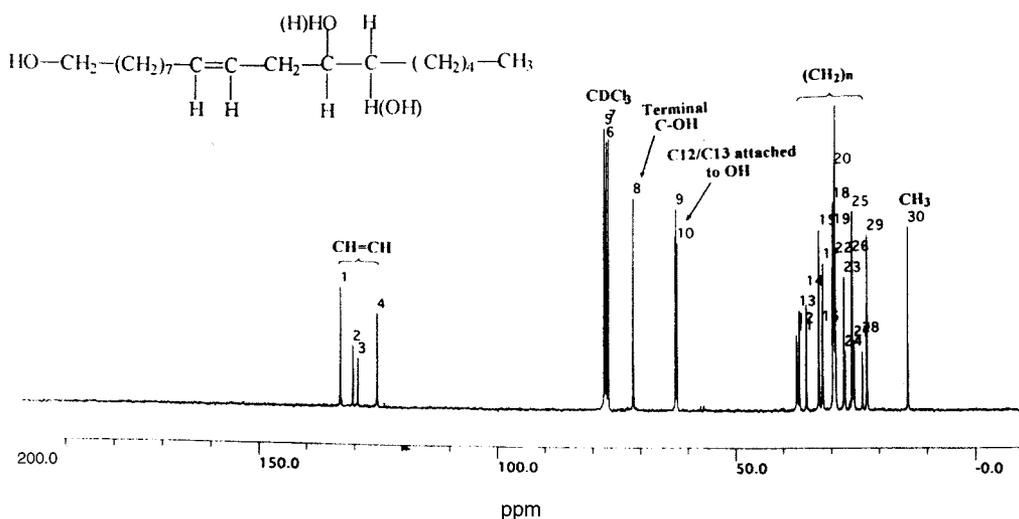

FIG. 2. ^{13}C NMR spectrum of diol isomers. Chemical shifts (ppm): 132.739, 130.188, 129.154, and 125.118 ($\underline{C}$H=CH), 71.349 carbon attached to the terminal hydroxyl group, 62.403 and 62.113 ($\underline{C}_{12}$ and $\underline{C}_{13}$), 37.150–22.424 ($\underline{C}$H$_2$)$_n$, and 13.866 ($\underline{C}$H$_3$). See Figure 1 for abbreviation.
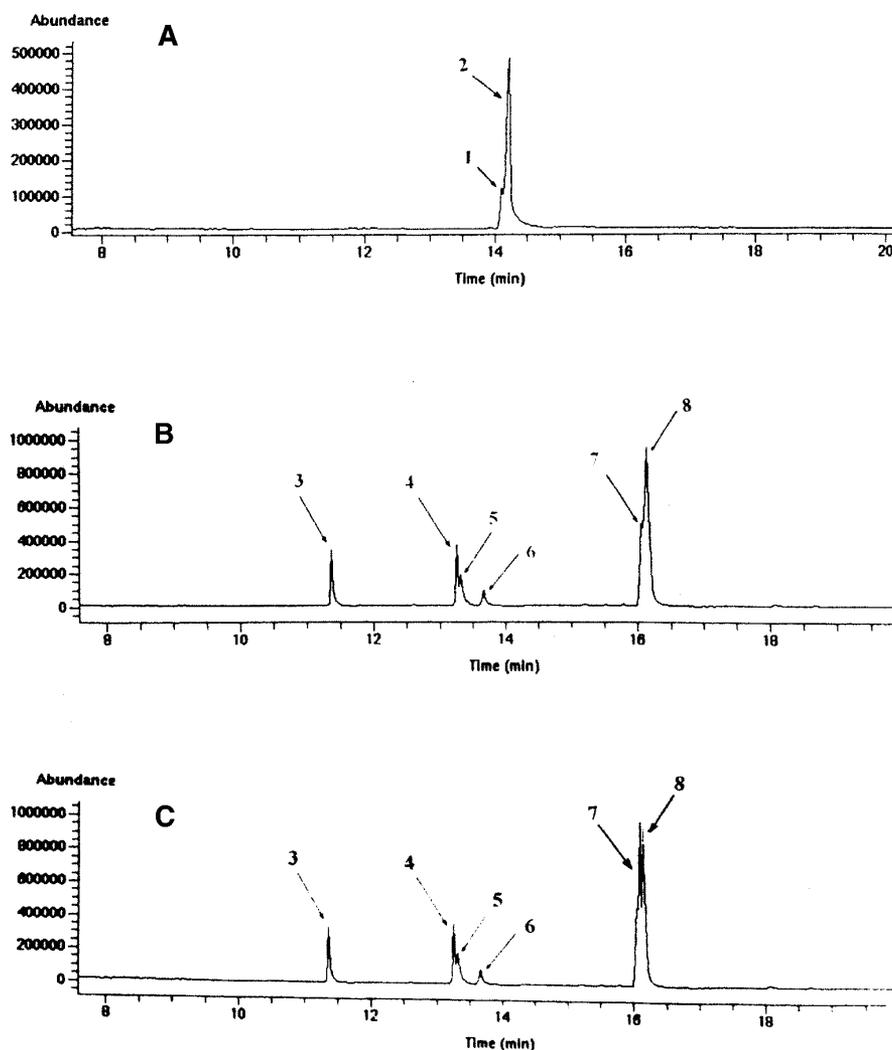
FIG. 3. (A) Gas chromatogram of the isolated diols from the vernonia oil methyl esters/lithium aluminum hydride (VOME/LAH) reaction in tetrahydrofuran (THF). Peak labeled as 1 is assigned to 12-hydroxy-*cis*-9-octadecenol, and peak labeled as 2 is assigned to 13-hydroxy-*cis*-9-octadecenol. (B) Gas chromatogram of the acetylated mixture from the VOME/LAH reaction in THF. Peaks labeled as 3, 4, 5, 6, 7, and 8 are due to the presence of the acetates of palmityl alcohol, linoleyl alcohol, oleyl alcohol, stearyl alcohol, and diols respectively. (C) Gas chromatogram of the spiked acetylated diols. Peak labeled as 7 is assigned to 12-hydroxy-*cis*-9-octadecenol (contribution from the acetylated diol from the reduction of castor oil methyl ester), and peak labeled as 8 is assigned to 13-hydroxy-*cis*-9-octadecenol.

132.739, 130.188, 129.154, and 125.118; carbon attached to the terminal hydroxyl group ($\underline{C}$–OH) at 71.349; carbons $\underline{C}_{12}$ and $\underline{C}_{13}$ attached to the internal hydroxyl groups of the isomers at 62.403 and 62.113; carbons of the methylene groups ($\underline{C}H_2)_n$ at 37.150–22.424; and carbons of methyl group ($\underline{C}H_3$) at 13.866. We should note that the complexity of the spectrum in Figure 2 is another confirmation that the product was a mixture of diol isomers. A total of 30 carbons is indicated (less than the expected 39), apparently due to the overlap of equivalent chemical shifts.

Acetylation of the diols. The GC of the isolated diols (Fig. 3A) showed two peaks, labeled as 1 and 2. In order to further confirm the occurrence of the diols, we acetylated this pro-

duct mixture. The chromatogram (Fig. 3B) of the acetylated mixture also showed two peaks, labeled as 7 and 8, both of which represent higher retention times relative to the diols. Other peaks in Figure 3B, labeled as 3, 4, 5, and 6 are due to the presence of acetates of palmityl alcohol, linoleyl alcohol, oleyl alcohol, and stearyl alcohol, respectively. The mass spectra of the acetylated diols (MW 368), showed no diagnostic ions that would enable unequivocal characterization. Both spectra exhibited the following major ions (*m/z*): at 308 (M – CH_3CO_2H), 248 (M – $2CH_3CO_2H$), and 265 (308 – CH_3CO). Furthermore, an acetylated diol (12-hydroxy-*cis*-9-octadecenol), which was obtained from the reaction of castor oil with LAH in THF, was spiked with the

acetylated diols of VOME/LAH reaction in THF. The GC of the spiked acetylated diols (Fig. 3C), showed an increase in peak 7, which implied that 13-hydroxy-*cis*-9-octadecenol was the major product of VOME/LAH reaction in THF. However, an accurate isomeric ratio has not been determined at this time.

ACKNOWLEDGMENT

REFERENCES

1. Tsushima, R., S.Tagata, Y.M. Yokota, and A. Fujiu, Surfactants from Natural Fats and Oils, *inform 4*:680–693 (1993).
2. Sykes, P., *A Guidebook to Mechanism in Organic Chemistry*, 6th edn., John Wiley & Sons, Inc., New York, 1986, p. 214.
3. Nystrom, R.F., and W.G. Brown, Reduction of Organic Compounds by Lithium Aluminum Hydride. I. Aldehydes, Ketones, Esters, Acid Chlorides, and Acid Anhydrides, *J. Am. Chem. Soc. 69*:1197–1199 (1947).
4. Nystrom, R.F., and W.G. Brown, Reduction of Organic Compounds by Lithium Aluminum Hydride. II. Carboxylic Acids, *Ibid. 69*:2548–2549 (1947).
5. Nystrom, R.F., and W.G. Brown, Reduction of Organic Compounds by Lithium Aluminum Hydride. III. Halides, Quinones, Miscellaneous Nitrogen Compounds, *Ibid. 70*:3738–3740 (1948).
6. Micovic, V.M., and M.Lj. Mikhailovic, Reduction of Glycerides by Lithium Aluminum Hydride, *Belgrade 14*:256–71 (1949).
7. Walborsky, H.M., and C. Colombini, Reduction of Glycidic Esters with Lithium Aluminum Hydride, *J. Org. Chem. 27*: 2387–2390 (1962).
8. Ernest, E.L., and D.W. Delmonte, The Mechanism of Halide Reductions with Lithium Aluminum Hydride. Vl. Reduction of Certain Bromohydrins and Epoxides, *J. Am. Chem. Soc. 80*:1744–1752 (1958).
9. Ernest, E.L., and M.N. Rerick, Reductions with Metal Hydride. VII. Reduction of Epoxides with Lithium Aluminum Hydride-Aluminum Chloride, *Ibid. 82*:1362–1367 (1960).
10. Ayorinde, F.O., B.D. Butler, and M.T. Clayton, *Vernonia galamensis*: A Rich Source of Epoxy Acids, *J. Am. Oil Chem. Soc. 67*:844–845 (1990).
11. Fernandez, A.M., C.J. Murphy, M.T. Decosta, J.A. Mason, and L.H. Sperling, in *Polymer Applications of Renewable Resource Materials*, edited by C.E. Carraher, Jr., and L.H. Sperling, Plenum Press, New York, 1983, pp. 273–288.
12. Ayorinde, F.O., G. Osman, R.L. Shepard, and F.T. Powers, Synthesis of Azelaic Acid and Suberic Acid from *Vernonia galamensis* Oil, *J. Am. Oil Chem. Soc. 65*:1774–1777 (1988).
13. Carlson, K.D., W.J. Schneider, S.P. Chang, and L.H. Princen, in *New Sources of Fats and Oils*, edited by E.H. Pryde, L.H. Princen, and K.D. Mukherjee, American Oil Chemists' Society, Champaign, 1981, pp. 297–318.
14. Ayorinde, F.O., J. Clifton, Jr., O.A. Afolabi, and R.L. Shepard, Rapid Transesterification and Mass Spectrometric Approach to Seed Oil Analysis, *J. Am. Oil Chem. Soc. 65*:942–947 (1988).
15. Kent, A., A. Bryant, C.P. Nwaonicha, H. Mahmoud, M.A. Anderson, and F.O. Ayorinde, Synthesis and Amidation of *Vernonia Galamensis* Seed Oil, *Ibid. 70*, 457–460 (1993).