# Synthesis of 13(14)-Hydroxy-*cis*-10-nonadecenyl Amine Hydrochloride

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**ABSTRACT:** Compatibility between a hydrophilic nanoclay reinforcement and organophilic polymer matrix resin is achieved by ion exchange reaction substitution of intra gallery mono- or divalent cation with foreign aliphatic long-chain cation. The exchange of long-chain cation increases the organophilicity of the clay layers and provides sufficient layer separation for polymer chains to impregnate into the formation of a nanocomposite. This study demonstrates the synthesis of hydroxy functional long-chain amine hydrochloride from *Vernonia galamensis* oil (VO). *Vernonia galamensis* oil, containing a naturally epoxidized long-chain TG, was transesterified under basic conditions to yield VO methyl esters (VOMe). The VOMe were reduced using lithium aluminum hydride (LAH) in hexane to obtain *cis*-12,13-epoxy-*cis*-9-octadecenol (vernanol) as the primary product. Vernanol was then converted to vernanyl mesylate, followed by reaction with potassium cyanide to obtain *cis*-13,14-epoxy-*cis*-10-nonadecenitrile ($C_{19}$ nitrile). The $C_{19}$ nitrile was reduced with LAH in diethyl ether medium and later reacted with hydrochloric acid to obtain the title product. $^1H$ and $^{13}C$ NMR, FTIR, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) techniques were used to characterize the intermediates and the title product.

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**KEY WORDS:** $C_{19}$ nitrile, hydroxyl-functionalized amine hydrochloride, intercalant, LAH reduction of epoxy group, LAH reduction of nitrile, long-chain primary amine hydrochloride, nanocomposites, nanomer, surfactant, vernanyl mesylate, vernonia oil.

Vegetable oils are generally TG of long-chain FA. Some of these long-chain FA contain functional groups such as double bonds, hydroxyl, and the like. For example, the castor oil derivative ricinoleic acid contains a hydroxyl group and an olefinic bond, whereas the vernonia oil (VO) derivative vernolic acid contains an epoxy group and an olefinic bond. These double bonds provide potential reactive sites for polymerization and cross-linking. This aspect has been widely exploited to make a polymer that is completely derived from natural materials as well as to form interpenetrating polymer networks between TG oil polymers, vinylic polymers, and a semi-interpenetrating network phase-separated material (1,2). Several articles also have highlighted the potential usefulness of VO in plastic formulations, adhesives, plasticizers, stabilizers, surfactants, and as a diluent for coatings (3–5). Furthermore, VO is a more ecologically attractive feedstock than petroleum-based chemical feedstock for certain applications, because the seed (*vernonia galamensis*) from which VO is derived can be cultivated in arid climates.

Besides recovering functionalized oil from oilseed crops, there is growing interest in synthesizing new derivatives and intermediates from functionalized oil. At present, laboratory methodology exists for derivatizing VO to vernolic acid (6), vernamide (7), and vernanol (8). In particular, the reactivity study between VO and lithium aluminum hydride (LAH) gives useful information about the reactivity of epoxy functionality in VO as it relates to solvent medium, temperature, and time (8). Elhilo *et al*. (8), showed that the epoxy group in VO methyl esters (VOMe) can be retained to give vernanol during LAH reduction. The present paper exploits this chemistry to synthesize a functionalized long-chain primary ammonium chloride from VOMe. Long-chain amine salts ($C_{19}$ amines) with functional group(s) along the backbone chain can be a useful clay intercalant in promoting compatibility between the nanoclay platelets and polymer matrix in nanocomposite (9–11). This article reports the synthesis of a long-chain amine that has multiple functionality for possible use in nanocomposites.

## EXPERIMENTAL PROCEDURES

*Reagents.* Crude VO was procured from International Exchange of Trade and Technology Inc. (Culver, IN). LAH, hexane, sodium methoxide in methanol, methane sulfonyl chloride, dichloromethane, triethylamine, potassium cyanide, and diethyl ether were purchased from Fisher Scientific (Atlanta, GA). Triethylamine was further purified by distillation, and the remaining chemicals were used without further purification.

*Instrumentation.* An FTIR spectrophotometer (Nicolet-Magna IR 560; Thermo Nicolet, Madison, WI) was used to obtain IR spectra. Liquid samples were run neat (NaCl plate), and solid samples were run using the KBr pellet method. Synthetic conversions were monitored with a Hewlett-Packard 5890 series II gas chromatograph (GC) coupled to a Hewlett-Packard 5989A mass spectrometer (Avondale, PA). The interface oven and transfer line were set at 285°C and the injection port at 150°C, using EI mode, with electron energy at 70 eV. High-resolution capillary GC was conducted with a Supelco fused-silica SPB-1 (30 m, 0.32 mm inside diameter, 0.25 μm film thickness; Bellefonte, PA) as the column, oven temperature programmed at 40°C for 3 min, 20°C/min to 300°C, and 300°C

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for 1 min, injector temperature at 240°C, and detector temperature at 285°C; helium was used as the carrier gas with a head pressure of 10 psi. By dissolving an aliquot of sample in dichloromethane and injecting 1 µL of sample at the port, GC–MS measurements were performed. $^1H$ and $^{13}C$ NMR data were obtained with a General Electric 300 MHz NMR spectrometer (GE NMR Instruments, Fremont, CA). Deuterated chloroform was used as solvent and source of internal reference in performing NMR experiments for all samples except the final product, $C_{19}$ salt. Deuterated dimethyl sulfoxide (DMSO-$d_6$) was used as solvent in performing NMR experiments for the final product, $C_{19}$ salt.

*Matrix-assisted laser desorption ionization/time-of-flight mass spectrometry (MALDI-TOFMS) characterization.* We used *meso*-tetrakis (pentafluorophenyl) porphyrin (F20TPP) (Mid-Century Chemicals, Chicago, IL) as the matrix for MALDI-TOFMS characterization. Ninety microliters of matrix solution (prepared by dissolving 10 mg of porphyrin in 1 mL of CHCl$_3$) was added to 10 µL of analyte solution (1% solution in CHCl$_3$) and vortexed for 15 s (13). One microliter of (analyte + matrix) solution was deposited on the sample plate. The solvent was allowed to evaporate from the sample plate, leaving behind matrix and analyte. The sample plate was loaded into the MALDI ion source. MALDI-TOFMS experiments were performed using a PerkinElmer Biosystems Voyager-DE STR workstation (Foster City, CA). Positive ion MALDI spectra were acquired using both delayed-extraction and reflector modes with accelerating voltage at 20,000 V, grid voltage at 75%, nitrogen laser (337 nm) with the attenuator setting at 2300 or 2500, and the low mass gate set at *m/z* 300. Minima of 20 experiments were performed to confirm reproducibility of the MALDI-TOFMS spectra. MALDI-TOFMS experiments were performed with a two-stage acceleration ion source. A signal-to-noise ratio of greater than five was treated as sufficient signal for peak assignment.

*Methodology. (i) Transesterification of VO to VOMe followed by conversion to vernanol.* We followed the procedure outlined by Elhilo *et al.* (8) to convert VO into VOMe and then to vernanol. Crude vernanol was purified by repeating the crystallization at 5°C in *n*-hexane medium. The yield from recrystallization was about 5.6 g (56%). Using GC, we characterized vernanol before and after crystallization. Details on purity of vernanol can be found in the Results and Discussion section.

*(ii) Conversion of vernanol to vernanyl mesylate.* In a dry three-necked 100-mL round-bottomed flask equipped with magnetic stirring bar and a nitrogen inlet, a mixture of vernanol, 4.4 g (0.016 mol), and triethylamine, 2.36 g (0.023 mol), in CH$_2$Cl$_2$ (25 mL) was prepared and cooled to 0°C. Methane sulfonyl chloride, 2.68 g (0.023 mol), in CH$_2$Cl$_2$ (5 mL) was gradually added to the cooled mixture over 30 min by syringe. The reaction mixture was then stirred for an additional 30 min at 0°C, transferred to a separatory funnel, washed with cold water (100 mL), 5% HCl (100 mL), 20% NaHCO$_3$ (100 mL), and saturated aqueous NaCl (100 mL) solution. The resulting CH$_2$Cl$_2$ extract was dried over MgSO$_4$, filtered, and concentrated by rotary evaporator to give 5 g (90%) of a yellowish liquid. $^1H$ NMR of product: δ, 0.86 (*t*, *J* = 7 Hz, 3H), 1.04–1.34 (*m*, 16H), 1.44 (*m*, 2H), 1.69 (*m*, 2H), 1.99 (*m*, 2H), 2.08–2.37 (*m*, 2H), 2.9 (*m*, 2H), 2.95 (*s*, 3H), 4.2 (*t*, *J* = 7 Hz, 2H), 5.36–5.47 (*m*, 2H); $^{13}C$ NMR: δ, 12.9, 21.9, 25.13, 25.16 (2C), 27.2–28.4 (7C), 31.46, 36.63, 56.1 (2C), 69.6, 123.6, 132.1; IR (NaCl) (cm$^{-1}$) 3022, 2960, 2924, 2852, 1655, 1460, 1352, 1184, 974, 943, 820–845 (broad epoxy group), 523; MS *m/z* 360 (M$^+$), 359 (M – 1), 341, 121, 109, 95, 79, 67, 55.

*(iii) Conversion of vernanyl mesylate to $C_{19}$ nitrile.* To a solution of 1.625 g (0.025 mol) of potassium cyanide in water (18.5 mL), 4.5 g (0.013 mol) of vernanyl mesylate was added. The solution was refluxed for 6 h and allowed to cool to room temperature. The product was extracted with diethyl ether (150 mL), dried over MgSO$_4$, filtered, and concentrated in a rotary evaporator to give 3.1 g (85%) of liquid. $^1H$ NMR: δ, 0.86 (*t*, *J* = 7 Hz, 3H), 0.99–1.37 (*m*, 16H), 1.47 (*m*, 2H), 1.57 (*m*, 2H), 2.0 (*m*, 2H), 2.08–2.3 (*m*, 2H), 2.28 (*t*, *J* = 7 Hz, 2H), 2.9 (*m*, 2H), 5.38–5.46 (*m*, 2H); $^{13}C$ NMR 12.4, 15.8, 21.4, 24.9 (2C), 25.6, 26.7, 27.0–27.9 (6C), 31.1, 55.4 (2C), 118.4, 123.1, 131.3; IR (NaCl) (cm$^{-1}$) 3534, 3017, 2960, 2935, 2853, 2238, 1485, 1352, 846, 821, 528; MS *m/z* 291 (M$^+$), 292 (M + 1), 162, 148, 134, 95, 81, 67, 55.

*(iv) Reduction of $C_{19}$ nitrile with LAH in diethyl ether medium.* In a 200-mL flask, a mixture of 1.21 g (0.032 mol) of LAH in 100 mL of diethyl ether was allowed to stir for 1 h at room temperature. Then 3.1 g (0.011 mol) of $C_{19}$ nitrile was gradually added to the mixture in the flask, and the reaction mixture was allowed to stir overnight. The reaction was terminated by addition of water (5 mL) in small increments to hydrolyze the complex product and unreacted LAH. The supernatant ether layer was filtered and collected. An equivalent amount of concentrated HCl (0.88 mL) was added to the filtrate and stirred for 1 h. The diethyl ether was stripped from the mixture to recover 3.25 g (92%) of a white solid of 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride. The m.p. of this final product was a broad range of 72 to 85°C, presumably as a result of the mixture of two positional isomers. $^1H$ NMR: δ, 0.85 (*t*, *J* = 7 Hz, 3H), 1.05–1.41 (22H), 1.52 (*m*, 2H), 1.96 (*m*, 2H), 2.01 (*m*, 2H), 2.7 (*m*, 2H), 3.37 (*m*, 1H), 4.31 and 4.42 (*s*, 1H), 5.29 and 5.35 (*m*, 2H), 8.14 (*s*, 3H); $^{13}C$ NMR: δ, 13.4, 21.6, 22.5, 24.7, 25.0, 25.7, 28.06–28.2 (6), 31.1, 35.0, 36.3, 38.3, 69.0, 69.6, 126.4, 129.1, 129.13, 129.6; IR of 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride: (KBr pellet) (cm$^{-1}$) 3360, 3210, 3017, 2960, 2925, 2848, 1583, 1521, 1470, 1132, 1070, 718. MALDI characterization of the title product is presented in the Results and Discussion section. The overall yield from purified vernanol to the title product, 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride was about 70%.

## RESULTS AND DISCUSSION

The synthetic route to convert VO into VOMe and the subsequent reduction of methyl esters to the corresponding alcohol and purification of vernanol are available (8). The steps adopted to synthesize the title product from vernanol are summarized in Figure 1. Because we were interested in synthesizing a
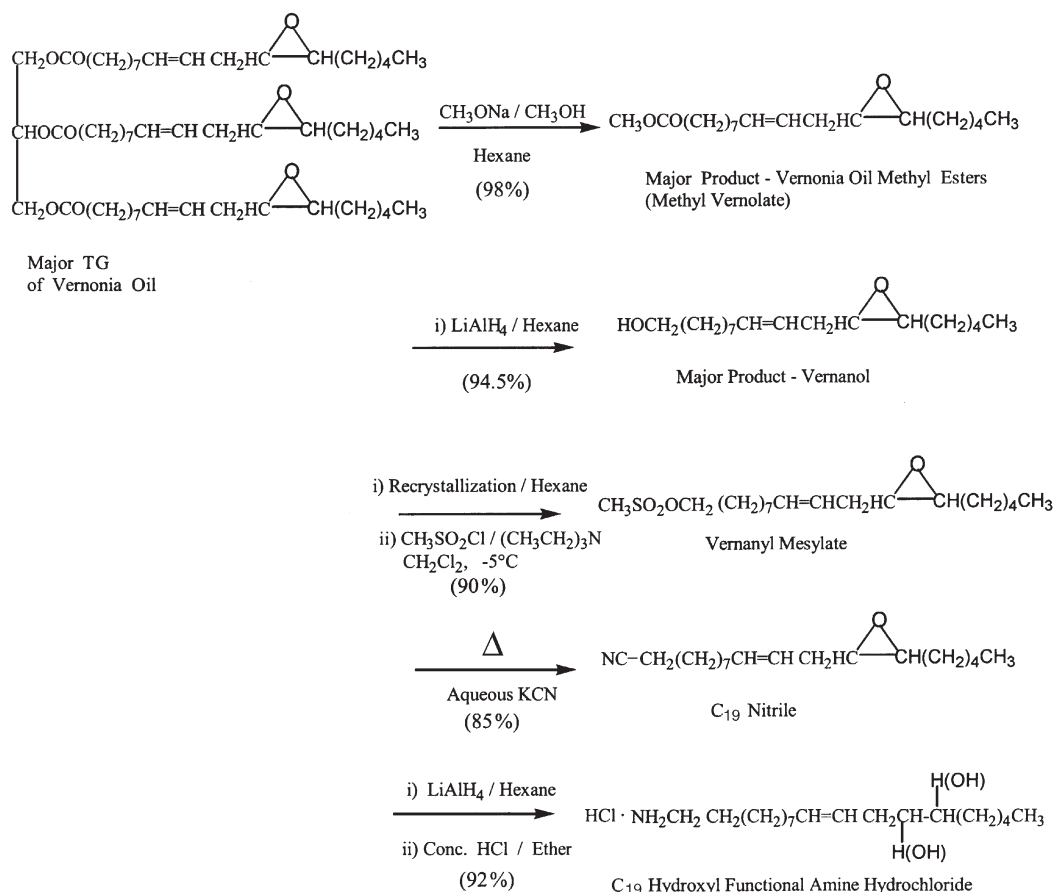
**FIG. 1.** General overall reaction scheme for the synthetic conversion from vernonia oil through 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride. For simplicity, until the vernanol formation step, only the prominent chemical ingredient of the reactants/products mixture is shown in the reaction scheme.

surfactant molecule with an ammonium cation functionality only at the terminal position, our synthetic strategy required the retention of the epoxy group during transesterification of VO and LAH reduction of VOMe. The opening of an epoxy group in VOMe during reduction could lead to an unwanted diamine product. Similarly, if an alternative feedstock were considered (e.g. the major fatty alcohol derivative of castor oil contains two alcohol groups) instead of vernanol, this could also lead to unwanted diamine formation in the proposed synthetic strategy.

Using GC, we recrystallized vernanol to test its purity. The gas chromatogram of vernanol before purification showed multiple peaks representing fatty alcohols, i.e., vernanol, linoleyl alcohol, palmityl alcohol, oleyl alcohol, and stearyl alcohol. Upon crystallization, GC showed a peak for vernanol and the absence of peaks representing other compounds. The mass spectrum of purified vernanol showed a molecular ion peak at *m/z* 282 and a fragment peak at *m/z* 264 (M$^+$ − 18). The remaining fragmentation pattern is that of a normal alkane type. The $^1$H NMR and $^{13}$C NMR spectra (data not included) for purified vernanol were in agreement with reported literature values for vernanol (8). The $^1$H NMR spectrum showed a signal for the epoxy group corresponding to a chemical shift of 3.0 ppm, the olefinic hydrogens at 5.5 ppm, the alcohol hydrogen at 1.6

ppm, and an α methylene group at 3.6 ppm. We also assigned the various signals in the $^{13}$C NMR spectrum for the olefinic, epoxy, and α methylene groups in vernanol. The absence of a secondary alcohol signal in the region of 60–75 ppm suggests that the recrystallized vernanol is free of 12(13)-hydroxy-*cis*-9-octadecenol, i.e., a product of epoxy ring opening.

The purified vernanol was then subjected to mesylation so that the introduction of the mesylate group at the terminal position can assist in subsequent nucleophilic substitution of the CN$^-$ group at the terminal end of this intermediate product. The $^{13}$C NMR spectrum of vernanyl mesylate showed a signal at 69.6 ppm, which corresponds to a carbon α to the mesylate group, thereby indicating the presence of the mesylate group at the terminal hydroxyl group of vernanol. Other significant signals include a signal corresponding to a chemical shift of 56.1 ppm due to the epoxy group in the intermediate product. The absence of other signals in the region of 60–75 ppm confirmed the retention of the epoxy group. FTIR of the product showed absorption peaks at 821 and 840 cm$^{-1}$ (epoxy group) and strong absorption peaks at 1350 and 1175 cm$^{-1}$ for the mesylate group in vernanyl mesylate.

The $^{13}$C NMR spectrum of the C$_{19}$ nitrile product showed the disappearance of the signal at 69.6 ppm and the appearance of a
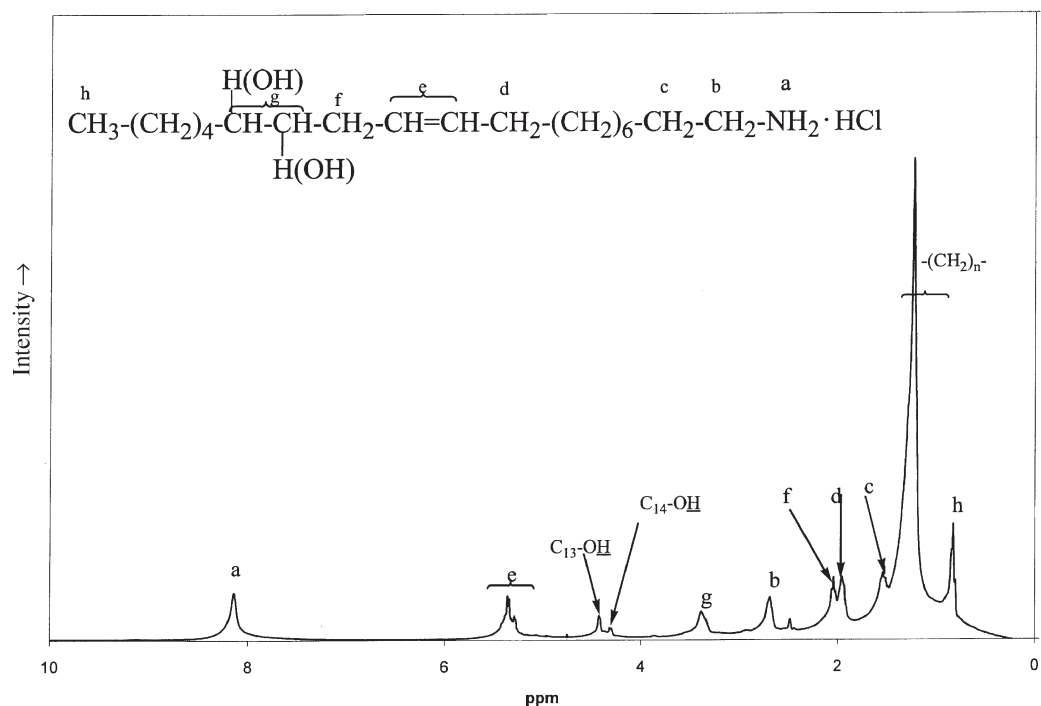
**FIG. 2.** ^{1}H NMR spectrum of 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride. Chemical shifts (ppm): 8.14 amine hydrochloride proton ($-N\underline{H}_2 \cdot HCl$); 5.29 and 5.35 ($C\underline{H}=C\underline{H}$); 4.3 and 4.4 ($-O-\underline{H}$), 3.37 alkyne protons ($C\underline{H}-O-H$); 2.7 ($C\underline{H}_2-NH_2 \cdot HCl$); 1.96 and 2.01 ($C\underline{H}_2-CH=CH-C\underline{H}_2$), 1.05–1.41 ($C\underline{H}_2)_n$; and 0.85 ($C\underline{H}_3$). Deuterated DMSO solvent signal appears at 2.49 ppm.
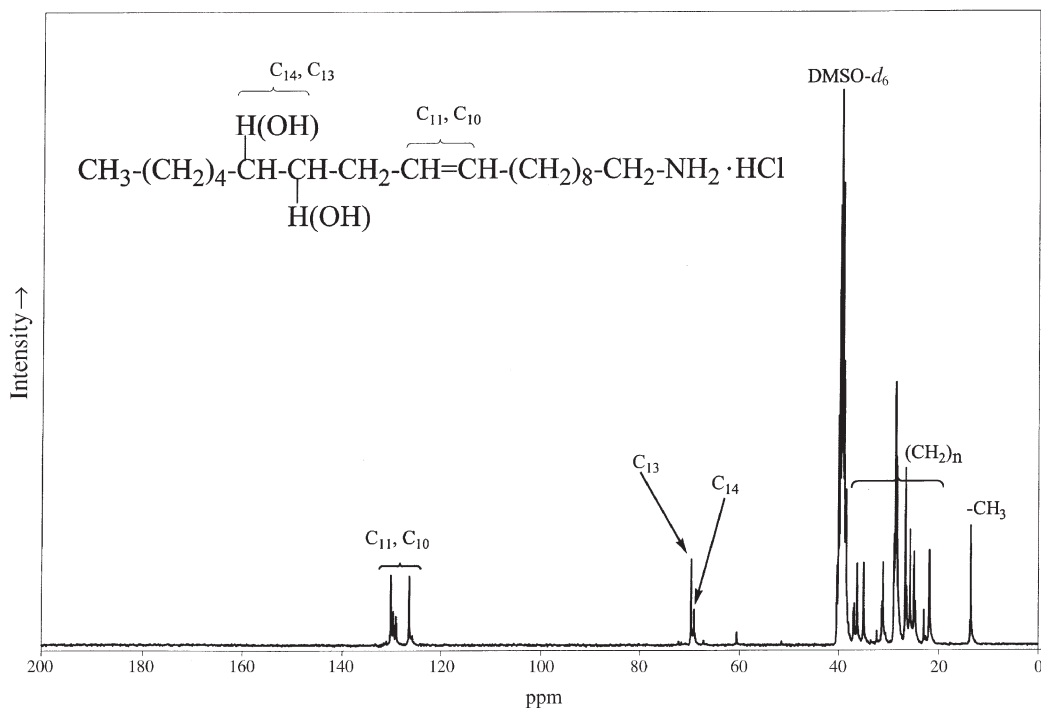


**FIG. 3.** ^{13}C NMR spectrum of 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride. Chemical shifts (ppm): 126.4, 129.1, 129.13, and 129.6 ($\underline{C}H=\underline{C}H$), 69.0 and 69.6 ($\underline{C}_{13}$ and $\underline{C}_{14}$), 21.6–38.3 ($\underline{C}H_2)_n$, and 13.37 ($\underline{C}H_3$).
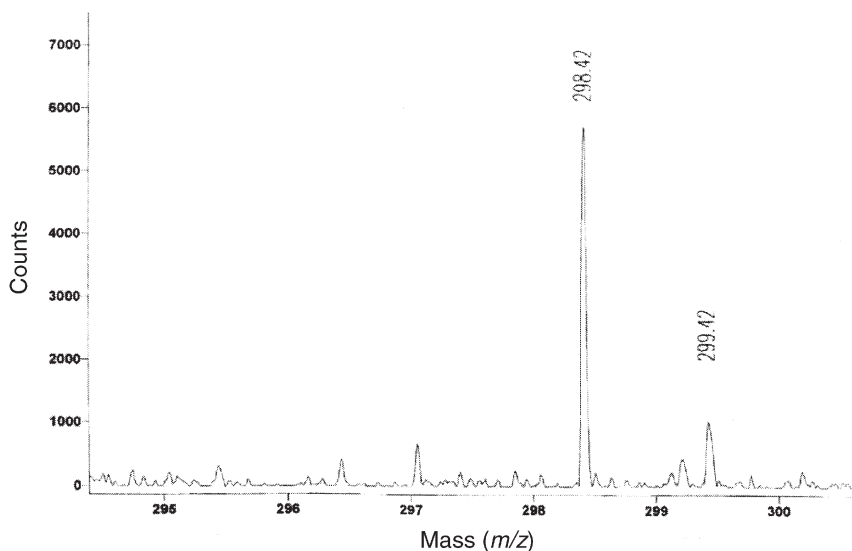
**FIG. 4.** Matrix-assisted laser desorption/ionization time-of-flight mass spectra for 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride. The peak corresponding to the *m/z* 298.4 value is assigned to the primary ammonium cation part of this product (M⁺); the peak corresponding to the *m/z* 299.4 value is assigned to the (M + 1) isomer of this cation.

signed characteristic of the nitrile group at 118.4 ppm, which is indicative of the conversion of vernanyl mesylate to $C_{19}$ nitrile. The interesting feature is that $^{13}C$ NMR shows a prominent signal at 55.4 ppm, which corresponds to epoxy group carbon atoms, i.e., major retention of the epoxy group and only a small amount of epoxy ring opening at this stage of conversion. The less intense signal at 62 ppm was assigned to the secondary alcohol functionality in the nitrile intermediate product, i.e., an indication of minor epoxy ring opening. The assignment for secondary alcohol in $C_{19}$ nitrile was further supported by FTIR data, which indicated the diminishing intensity (absorbance) of the epoxy group and the appearance of a less intense peak at 3500 cm⁻¹ for the hydrogen-bonded hydroxyl group. Furthermore, a peak at 2245 cm⁻¹ was observed for the nitrile functional group. MS fragmentation data for the $C_{19}$ nitrile showed a molecular ion peak at *m/z* 291.

In the subsequent step, the nitrile intermediate product was converted to 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride. Figures 2 and 3 show the $^{1}H$ and $^{13}C$ NMR spectra, respectively, of 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride. The signal at a chemical shift of 8.14 ppm in the $^{1}H$ NMR spectrum is characteristic of the primary amine hydrochloride in the final product. The $^{13}C$ NMR spectrum of the final product shows characteristic signals for secondary alcohol groups at 69.0 and 69.6 ppm, which suggests that the epoxy ring has opened during LAH reduction of the nitrile intermediate product. Unlike vernanol, where only two signals were observed in the 130 ppm region, the final product showed four signals. Observation of two additional signals in the 130 ppm region can be accounted for by the different chemical environments generated by the presence of hydroxyl groups at either the $C_{13}$ or $C_{14}$ position. In other words, the olefinic carbons appear as four signals in the 130 ppm region (8). In the C-13 hydroxyl positional isomer, the double bond (C-10–C-11) is in

close proximity (β) to the hydroxyl carbon, whereas in the C-14 hydroxyl positional isomer, the double bond is further away (γ) from the hydroxyl carbon. Therefore, we assign the more scattered and high intense pair of olefinic carbon signals that appear at 126.4 and 129.6 ppm to the olefinic group of the C-13 positional isomer, whereas the less scattered and less intense pair of signals that appear at 129.1 and 129.13 ppm are assigned to the olefinic group of the C-14 isomer. Based on similar reasoning, we assign the hydroxyl proton signals in $^{1}H$ NMR that appear at 4.42 and 4.31 ppm to the C-13 and C-14 isomers, respectively.

Based on $^{1}H$ NMR and $^{13}C$ NMR data, the final product was found to be a mixture of 13-hydroxy-*cis*-10-nonadecenyl amine hydrochloride and 14-hydroxy-*cis*-10-nonadecenyl amine hydrochloride. Appearance of internal hydroxyl carbon signals in the 69.0 and 69.6 ppm region confirms there are two different (C-13/C-14 hydroxyl) isomers of this product. The ratio of the two isomers was determined by integration of the hydroxyl proton signals from the $^{1}H$ NMR result and found to represent 70% C-13 hydroxyl positional isomer plus 30% C-14 hydroxyl positional isomer. Since both isomers can be useful for the nanocomposite application, we did not attempt to isolate the two positional isomers.

The MALDI-TOF mass spectra for 13(14)-hydroxy-*cis*-10-nonadecenyl amine hydrochloride appear in Figure 4. The diagnostic ions observed in the MALDI-TOFMS spectral data of the primary ammonium ion are M⁺ and M + 1⁺ peaks at *m/z* 298.4 and 299.4 amu, respectively. This spectrum shows the cation form of the amine salt $[RNH_3]^+$, consistent with the reported results of studies on FA from vegetable oils in which the mode of ionization was by cationization (13).

We also performed the LAH reduction of $C_{19}$ nitrile in hexane medium to yield *cis*-13,14-epoxy-*cis*-10-nonadecenyl amine hydrochloride. Because of the limited solubility of the

intermediate lithium alkylate salt of the $C_{19}$ nitrile complex in hexane, we expected limited ring opening of the epoxy group and a high yield of *cis*-13,14-epoxy-*cis*-10-nonadecenyl amine hydrochloride. Instead, the reaction yielded only a small fraction of *cis*-13,14-epoxy-*cis*-10-nonadecenyl amine hydrochloride. The reason is that *cis*-13,14-epoxy-*cis*-10-nonadecenyl amine hydrochloride is highly unstable and amine hydrochloride has been known to react with epoxy in the $C_{19}$ ammonium salt to form branched molecules through intermolecular reaction (14). Therefore, attempts at synthesizing the epoxy functionalized ammonium salt were discontinued.

In summary, a methodology to synthesize the title product from VO, a renewable raw material, was reported. The present study represents the first report of a hydroxyl functional and long-chain primary amine hydrochloride surfactant for potential nanoclay polymer hybrid composites application. The hydroxyl group in the backbone chain of the amine salt can assist in condensation/addition polymerization with an appropriate monomer or in bonding between the clay and polymer matrix, and the double bond in the backbone chain of the amine salt can serve as a potential reactive site for olefinic polymerization and cross-linking with the polymer matrix.

## ACKNOWLEDGMENTS

## REFERENCES

1. Barrett, L.W., O.L. Shaffer, and L.H. Sperling, Polymer Networks Composed of Polyethylene Terephthalate and Vernonia Oil, *J. Appl. Polym. Sci. 48*:953–958 (1993).
2. Kim, S.C., D. Klempner, K.C. Frisch, N. Radigan, and H.L. Frisch, Polyurethane Interpenetrating Polymer Networks 1. Synthesis and Morphology of Polyurethane/Polymethyl Methacrylate Interpenetrating Polymer Networks, *Macromolecules 9*:258–263 (1976).
3. Cuadrado, T.R., and R.J.J. Williams, Castor Oil as a Flexibilizer for Anionically Polymerized Epoxy Resin, *Polym. Comm. 30*:239–240 (1989).
4. Dirlikov, S.K., I. Frischinger, M.S. Islam, and J. Graham, Vernonia Oil—A New Reactive Monomer, *Polym. Mat. Sci. Eng. 62*:217–219 (1990).
5. Carlson, K.D., and S.P. Chang, Chemical Epoxidation of a Natural Unsaturated Epoxy Seed Oil from *Vernonia galamensis* and a Look at Epoxy Oil Markets, *J. Am. Oil Chem. Soc. 62*:934–939 (1985).
6. Smith, C.R., K.F. Kock, and I.A. Wolff, Isolation of Vernolic Acid from *Vernonia anthelmintica* Oil, *Ibid. 36*:219–220 (1959).
7. Bryant, K.A.A., C.P. Nwaonicha, M. Hassan, M.A. Anderson, and F.O. Ayorinde, Synthesis and Isolation of Epoxy Secondary Amides *via* Direct Amidation of *Vernonia galamensis* Seed Oil, *Ibid. 70*:457–460 (1993).
8. Elhilo, E.B., M.A. Anderson, and F.O. Ayorinde, Synthesis of *cis*-12,13-Epox-*cis*-9-octadecenol and 12(13)-Hydroxy-*cis*-9-octadecenol from Vernonia Oil Using Lithium Aluminum Hydride, *Ibid. 77*:873–878 (2000).
9. Ishida, H., S. Campbell, and J. Blackwell, General Approach to Nanocomposite Preparation, *Chem. Mater. 12*:1260–1267 (2000).
10. Messersmith, P.B., and E.P. Giannelis, Synthesis and Characterization of Layered Silicate-Epoxy Nanocomposite, *Ibid. 6*:1719–1725 (1994).
11. Brown, J.M, D. Curliss, and R.A. Vaia, Thermoset Layered Silicate Nanocomposites. Quaternary Ammonium Montmorillonite with Primary Diamine Cured Epoxies, *Ibid. 12*:3376–3384 (2000).
12. Usuki, A., Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamingato, Synthesis of Nylon 6–Clay Hybrid, *J. Mater. Res. 8*:1179–1184 (1993).
13. Ayorinde, F.O., K. Garvin, and K. Saeed, Determination of Fatty Acid Composition of Saponified Vegetable Oils Using Matrix Assisted Laser Desorption Ionization/Time of Flight Mass Spectrometry, *Rapid Commun. Mass Spectrometry 14*:608–615 (2000).
14. Pinnavaia, T.J., T. Lan, Z. Wang, S.H. Shi, and P.D. Kaviratna, Clay-Reinforced Epoxy Nanocomposites Synthesis, Properties and Mechanical Properties and Mechanism of Formation, *Polym. Mat. Sci. Eng. 73*:250–261 (1995).