Preparation and Characterization of Methyl 11-Amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate and Methyl 8-Amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate

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ABSTRACT: Allylic amination of methyl oleate with bis(*N*-*p*-toluenesulfonyl) sulfodiimide results in a mixture of methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate and methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate in 58% yield. These novel products were isolated and characterized by nuclear magnetic resonance, infrared spectroscopy, mass spectrometry, and melting point. The reaction was analyzed by high-performance liquid chromatography and thin-layer chromatography.
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KEY WORDS: Allylic amination, methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate, methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate, bis(*N*-*p*-toluenesulfonyl) sulfodiimide, methyl oleate.

About 13 billion pounds of soybean oil are produced annually in the United States. While much of this oil is used in food and feed and about 300 million pounds are used for industrial products, there is a need to develop additional value-added products. To meet these needs, our laboratory applies synthetic organic chemistry techniques to functionalize soybean oil or its fatty acids to produce unique fatty acid materials with varying physical properties. Because reactive sites within a triacylglycerol molecule are limited to unsaturation and carboxylate moieties, limited chemical modifications can be effected to functionalize the triacylglycerol. Although modifications of the glycerol backbone are possible, frequently it is desirable to maintain the chemical/physical properties of that moiety. Thus, we directed our attention to the unsaturated carbon–carbon bond(s) of the acyl group in soybean oil. For this study, we desired to maintain the olefin functionality within the oil but utilize its unique chemistry to modify the physical properties of the carbon chain. Extensive work has been done in the area of allylic halogenation and oxidation of fats and oils (1–3), but formation of allylic amines has received limited attention. It was reported that bis(*N*-*p*-toluenesulfonyl) sulfodiimide (1) may react with alkenes to form *N*-(allylic alkenyl) sulfinamidines (4,5). Allylic amination has been investigated (6–10), but these reactions have not been applied to fats and oils.

This article reports a one-step synthesis from methyl oleate to allylic methyl 8- and 11-aminotosylate-9-*trans*-octadecenoates in good yield. This methodology should be applicable to develop fats with an amine functionality in an allylic position. The work discussed below details the formation of allylic amines. The clear advantage of this method is that it furnishes allylic amines in a one-step process (4) and retains the ester functionality. To facilitate understanding and observation of the reaction process and mechanism, methyl oleate served as a model substrate. Characterization was done by using nuclear magnetic resonance (NMR), infrared (IR), and mass spectrometry (MS). Analysis of the reaction was performed by high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC). Olefinic and amine substitution positions were further identified by gas chromatography (GC) and GC–MS analysis of ozonolysis products (11–14) from methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate.

EXPERIMENTAL PROCEDURES

Materials. Methyl oleate (>99%) was purchased from Nu-Chek-Prep (Elysian, MN). Thionyl chloride (99+%) was obtained from Aldrich Chemical Co. (Milwaukee, WI). *p*-Toluenesulfonamide was purchased from Lancaster Synthesis Inc. (Windham, NH). Solvents for chromatography and extraction were of HPLC quality and were used without further purification. The following reaction solvents were dried (by the methods described) and handled under a nitrogen atmosphere: benzene (EM Science, Gibbstown, NJ) was distilled from $CaCl_2$ (Fisher Scientific, Fair Lawn, NJ), pyridine (Mallinckrodt Specialty Chemicals Co., Paris, KY) was distilled from NaOH (Fisher Scientific), dichloromethane (EM Science) was distilled from $CaSO_4$ (W.A. Hammond Drierite Co., Xenia, OH), and carbon tetrachloride (J.T. Baker Chemical Co., Phillipsburg, NJ) was passed through a column of

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neutral alumina (Alupharm Chemicals, New Orleans, LA) and stored over 4 Å molecular sieves (Aldrich Chemical Co.).

Synthesis of N-*sulfinyl*-p-*toluenesulfonamide* (15): A 250-mL single-necked round-bottom (SNRB) flask and a reflux condenser were oven-dried (130°C), then allowed to cool in a desiccator. The flask and condenser were assembled, and a $CaCl_2$ drying tube was attached atop the condenser. The flask was charged with 31.25 g *p*-toluenesulfonamide and 125 mL benzene as solvent. Thionyl chloride (25 g) was added to the reaction mixture. The reaction solution was refluxed for 5 d. After being allowed to cool, the yellowish solution was filtered to remove precipitates. The solvent was removed *in vacuo,* and the residue was Kugelrohr-distilled (160°C at 20 torr) to obtain 7.7 g of the *N*-sulfinyl-*p*-toluenesulfonamide.

*Synthesis of bis(*N-p-*toluenesulfonyl) sulfodiimide* (5). The following operations were performed in a glove bag with a nitrogen atmosphere. *N*-Sulfinyl-*p*-toluenesulfonamide (7.7 g) was placed in a dried 25-mL SNRB flask, and then 10 mL benzene and 1 mL pyridine were added. The reaction mixture was stirred overnight, at which point a precipitate had formed. The solid was collected under vacuum filtration and washed with dry carbon tetrachloride. The material was dried under high vacuum to afford 6.5 g bis(*N-p*-toluenesulfonyl) sulfodiimide. It was found that for best results the sulfodiimide should be used immediately.

Allylic amination of methyl oleate. Continued use of the glove bag and a nitrogen atmosphere is crucial for a successful reaction. The bis(*N-p*-toluenesulfonyl) sulfodiimide (6.5 g) and 26 mL dry dichloromethane were added to a dried 100-mL SNRB flask. Methyl oleate (3.9 g) was added, and the reactants were stirred for 3 d. Then, the reaction was quenched with sodium carbonate (6 g) in 45 mL methanol/water (2:1, vol/vol), and the resulting solution was stirred overnight. The mixture was then extracted with diethyl ether/ethyl acetate (1:1, vol/vol). The organic layer was sequentially washed with water, 4% vol/vol NaOH:brine (1:1), then brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The products were purified by flash column chromatography with a solvent system of hexane/ethyl acetate (80:20 vol/vol) to obtain 3.57 g of product. Methyl 11-amino-(*N-p*-toluenesulfonyl)-9-*E*-octadecenoate/m.p. 47.5–48.5°C, eluted off the column first. The methyl 8-amino-(*N-p*-toluenesulfonyl)-9-*E*-octadecenoate, m.p. 42.5–43.5°C, eluted second.

Ozonolysis of the allylic aminotosylate ester. Ozonolysis was performed as described by Isbell *et al*. (16). Tosylate ester (3 mg) was dissolved in hexane (4 mL), and the solution was cooled to −78°C (dry ice/acetone bath). Ozone was passed through the solution until a faint blue color appeared. Triphenylphosphine was added in excess to reduce the ozonide. The resulting aldehyde and aldehyde-ester mixture was passed through a glass wool plug, then directly injected into the GC and GC–MS for analysis under GC conditions previously described.

Purification. Isolation of products and analytical samples were obtained by flash column chromatography with silica gel (200–400 mesh, 60Å) purchased from Aldrich Chemical Company, Inc. Samples were eluted with hexane/ethyl acetate (90:10, vol/vol), and fractions were collected in 10-mL test tubes. The fractions were analyzed by TLC on silica gel 60 F_{254} (25 μm thick on 20 × 20 cm plates) from EM Science and by HPLC. R_f values (TLC) of 0.38 and 0.36 were obtained for methyl 11-amino-(*N-p*-toluenesulfonyl)-9-*E*-octadecenoate and methyl 8-amino-(*N-p*-toluenesulfonyl)-9-*E*-octadecenoate, respectively, when using a hexane/ethyl acetate (70:30, vol/vol) solvent system. The isomeric products of both compounds were resolved by HPLC. A center portion of each was collected, freed of solvent, and then used for characterization.

Instrumentation. HPLC analysis was performed on a Hewlett-Packard 1050 HPLC system (Naperville, IL), equipped with an autosampler/injector and connected in series with a variable wavelength detector and a Varex evaporative light-scattering detector (Burtonsville, MA). A normal-phase econosphere silica column (25 cm × 4.6 mm i.d., 5 μm) from Alltech Associates, Inc. (Deerfield, IL) was used, and all samples were eluted with hexane/ethyl acetate (90:10). Baseline separation of the two isomers was attained, with retention times of 15.3 and 19.1 min, respectively.

NMR data were obtained from a Bruker ARX 400 (Billerica, MA), operating at 400 MHz for proton and 100.61 MHz for carbon. The instrument used a 5-mm dual, proton/carbon, probe, and samples were dissolved in $CDCl_3$.

The NMR data set for methyl 11-amino-(*N-p*-toluenesulfonyl)-9-*E*-octadecenoate is as follows: ^{1}H NMR (400 MHz) δ 7.70 (*d*, *J* = 8.2 Hz, 2H), 7.24 (*d*, *J* = 8.0 Hz, 2 H), 5.28 (*dt*, *J* = 15.3, 6.7 Hz, 1 H), 5.01 (*dd*, *J* = 15.3, 7.4 Hz, 1 H), 4.54 (*d*, *J* = 7.8 Hz, 1 H), 3.69–3.64 (*m*, 1 H), 3.65 (*s*, 3H), 2.39 (*s*, 3H), 2.28 (*t*, *J* = 7.5 Hz, 2 H), 1.79–1.76 (*m*, 2 H), 1.60–1.57 (*m*, 2 H), 1.41–1.16 (*m*, 20 H) and 0.84 ppm (*t*, *J* = 7.0 Hz, 3 H). ^{13}C NMR (100.61 MHz) δ 174.3, 142.9, 138.6, 132.6, 129.4, 129.3, 127.2, 56.1, 51.4, 36.0, 34.0, 31.9, 31.7, 29.1, 29.0, 28.2, 28.7, 25.3, 24.8, 22.6, 21.4, and 14.0 ppm.

The NMR data set for methyl 8-amino-(*N-p*-toluenesulfonyl)-9-*E*-octadecenoate is as follows: ^{1}H NMR (400 MHz) δ 7.70 (*d*, *J* = 8.2 Hz, 2 H), 7.24 (*d*, *J* = 8.1 Hz, 2 H), 5.26 (*dt*, *J* = 15.3, 6.7 Hz, 1 H), 5.00 (*dd*, *J* = 15.3, 7.4 Hz, 1 H), 4.54 (*d*, *J* = 7.8 Hz, 1 H), 3.67–3.63 (*m*, 1 H), 3.64 (*s*, 3 H), 2.39 (*s*, 3 H), 2.25 (*t*, *J* = 7.5 Hz, 2 H), 1.78–1.75 (*m*, 2 H), 1.56–1.53 (*m*, 2 H), 1.42–1.11 (*m*, 20 H) and 0.86 ppm (*t*, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100.61 MHz) δ 174.2, 142.9, 138.3, 132.8, 129.3, 129.1, 127.2, 56.1, 51.4, 36.0, 34.0, 32.0, 31.8, 29.4, 29.2, 29.1, 28.9, 28.8, 28.7, 25.2, 24.7, 22.6, 21.4, and 14.1 ppm.

IR spectra were obtained as CCl_4 solutions by using a Perkin-Elmer 1750 Infrared Fourier Transform Spectrometer (Norwalk, CT). The IR data for both isomers were the same: (NaCl) 3276.8 (*m*), 2929.6 (*s*), 2857.3 (*s*), 1738.0 (*s*), 1600.6 (*w*), 1499.3 (*w*),1463.1 (*m*), 1434.2 (*m*), τ 1325.7 (*m*), 1253.4 (*w*), 1202.8 (*m*), 1159.4 (*s*), 1094.3 (*m*), 1047.3 (*w*), 967.7 (*w*), 815.9 (*w*), 707.4 (*w*), 664.0 (*m*), 577.2 (*w*), and 555.5 cm^{-1} (*w*).

Electron ionization (EI) MS data for methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate were accumulated by direct inlet probe on a Finnigan MAT TSQ 700 (San Jose, CA). The probe chamber was ramped from 30 to 230°C at 6°C/min, and 1 scan/s was collected. Masses and relative abundances were as follows: *m/z* 434.3 (3.1; M – 31, – OMe), 366.2 (100), 334.2 (21.2), 294.2 (12.5), 211.2 (18.0), 155.0 (60.0), 137.2 (11.4), 91.1 (65.5), and 55.2 (12.2).

Electrospray ionization MS data for methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate were obtained on a Finnigan MAT SSQ710C Mass Spectrometer with the sample dissolved in hexane/isopropyl alcohol (50:50, vol/vol) with ethanolamine (MW = 61) used to produce an ionic adduct. The single peak at *m/z* 527.5 (M + 62) represents the adduct of methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate and the protonated ethanolamine.

EI–MS data for methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate were accumulated by a 70-VSE mass spectrometer at the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. The probe chamber was at 245°C. Mass data collected and relative abundances were as follows: 466.4 (15.1; M + 1), 323.2 (25), 322.2 (100), 310.3 (11.3), 295.3 (42.2), 155.0 (13.9), 91.1 (28.6).

Ozonolysis fragments were analyzed by using a Hewlett-Packard 5890 Series II GC, equipped with a flame-ionization detector and an autosampler/injector (Palo Alto, CA). Analysis was conducted on an SP 2330 column, 30 m × 0.25 mm i.d. (Supelco, Bellefonte, PA) with the following conditions: column flow rate 1.48 mL/min under a helium head pressure of 25 psi; split ratio 40:1; ramp program from 50 to 250°C at 5°C/min and held at 250°C for 5 min. Injector and detector temperatures were set at 250°C.

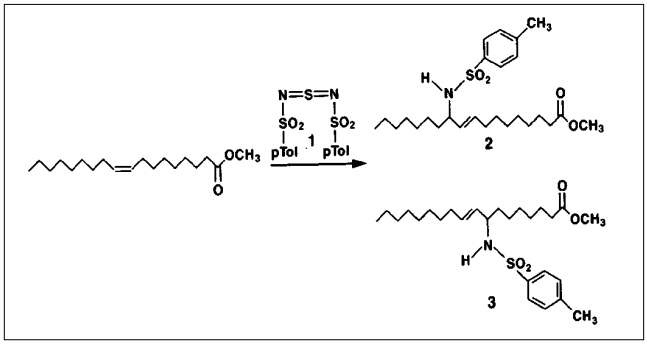
GC–MS data of the ozonolytic reaction mixture were obtained with a Hewlett-Packard 5890A GC, equipped with a 15 m × 0.25 mm i.d. DB-1 column (J & W Scientific, Folsom, CA) and a Hewlett-Packard 5970 mass selective detector. GC conditions: helium head pressure 5 psi; split 50:1; injector and transfer line temperature at 250°C; ramp program 170 to 270°C at 3°C/min. MS conditions: mass range 50 to 550 amu; electron multiplier 200 volts relative. Mass data collected and relative abundances for nonan-9-al-1-ate methyl ester were as follows: *m/z* 155.2 (10)(M + peak), 143.1 (17), 111.1 (29), 87.1 (72), 83.1 (39), 74.1 (100), 69.1 (19), 67.1 (13), 59.1 (29), 57.1 (15), 55.1 (90).

RESULTS AND DISCUSSION

Synthesis. It was our goal to prepare allylic amines of fatty acyl esters, including triacylglycerols, and thus increase their reactivity for possible exploitation in prospective polymerization reactions. To survey the allylic amination process, a model system was studied with methyl oleate as the substrate. This reaction provided a mixture of two novel compounds with possible elevated reactivity. Specifically, bis(*N*-*p*-toluenesulfonyl) sulfodiimide (1.4 equivalent) was reacted with methyl oleate (1 equivalent) to form a 1:1 ratio of methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate to methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate in 58% yield (Scheme 1). This technique provided a one-step process to an allylic amine compound.

The bis(*N*-*p*-toluenesulfonyl) sulfodiimide was made in the laboratory with the procedure developed by Hori *et al*. (15). Preparation of the reagent requires a moisture-free environment. Rapid use of the reagent also appeared to be a factor in the success and performance of the allylic amination.

Characterization. The proton NMR spectra of the products clearly showed the appropriate signals to identify these compounds. Because of the close similarity of the NMR spectra of 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate (Fig. 1) and methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate (Fig. 2), the following discussion will be limited to the NMR spectrum of methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate. The aromatic proton signals of the *p*-toluene group appeared as a doublet of doublets at 7.70 and



SCHEME 1

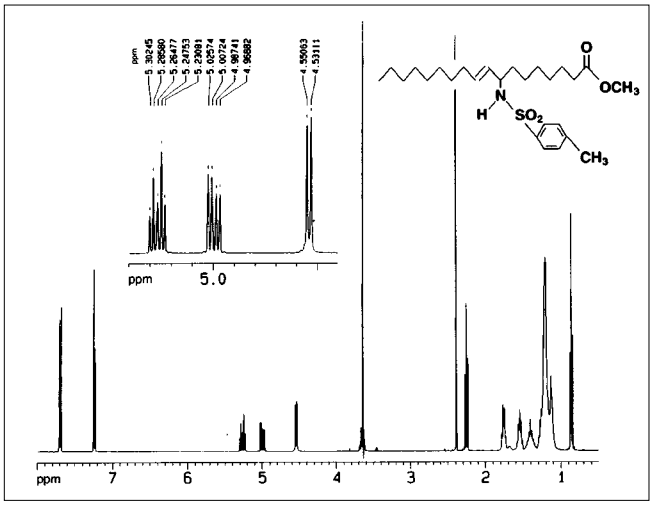


FIG. 1. ^{1}H nuclear magnetic resonance of methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate (2).

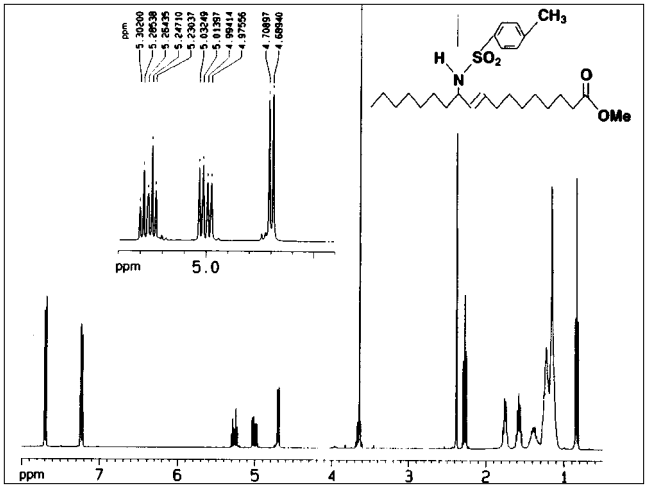


FIG. 2. ^{1}H nuclear magnetic resonance of methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate (3).

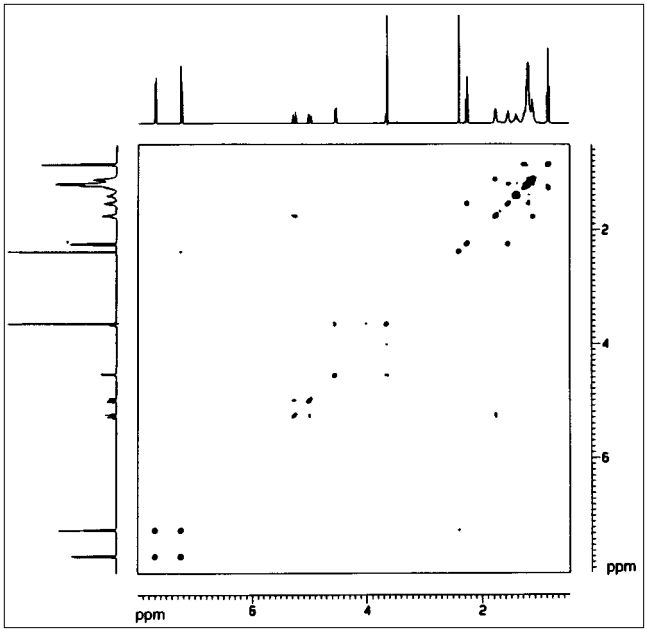


FIG. 3. COSY spectrum of methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate (3).

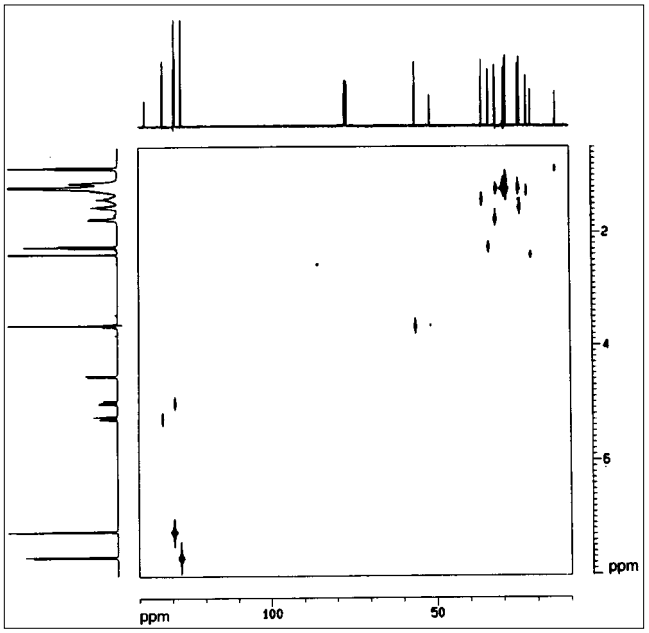


FIG 4. HETCOR spectrum of methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecanoate (3).

7.24 ppm. The COSY data show that not only there is interaction between the aromatic protons but also with the toluene methyl substituent at 2.39 ppm (Fig. 3).

At 5.26 ppm, there was a doublet of triplets, which integrates to one proton. The peaks in that spectral region indicate an olefinic proton, and the peak pattern would suggest the olefin proton farthest from the nitrogen substituent. The coupling constants were 15.3 and 6.7 Hz. The 15.3 Hz denotes a *trans* olefin configuration. The other olefin proton signal appears at 5.00 ppm as a doublet of doublets with coupling constants of 15.3 and 7.4 Hz and integrates to one proton. This agrees with the literature report that the carbon–carbon double bond in allylic amination products is solely *E* in configuration (17).

The nitrogen proton peak at 4.54 ppm is a doublet with a coupling constant of 7.8 Hz. Assignment was confirmed by peak distortion by the addition of deuterium oxide to the NMR sample, and the two-dimensional proton/carbon plot indicated that there was no carbon signal related to this proton (Fig. 4).

There are multiple signals near 3.6 ppm with an integration of four protons. The singlet at 3.65 ppm is characteristic of an ester methoxyl group. The multiplet at 3.67–3.63 ppm is in the appropriate region for a proton attached to a carbon bearing a heteroatom.

Additional structural connectivity information can be obtained from the COSY data (Fig. 3) where the peak at 5.26 ppm shows correlation with the peak at 5.00 ppm and the multiplet at 1.78–1.75 ppm. In addition, the signal at 5.00 ppm has correlation with the signal at 5.26 ppm and a multiplet at 3.67–3.65 ppm. The 4.54 ppm peak (which is the proton signal from the amine) also has a correlation with the 3.67–3.65 ppm multiplet. This information is consistent with the structural configuration shown in Figure 5. The arrows indicate the COSY interactions between protons.

Further examination of the proton spectrum in Figure 2 shows that at 2.39 ppm there is another three-proton signal, which represents the toluene methyl group. The remaining proton spectrum is typical of long-chain fatty acid methyl esters, and the proton integration corresponds to the expected number of hydrogens.

The carbon spectrum shows a carbonyl peak at 174.2 ppm and peaks at 142.9 and 138.3 ppm, which represent the quaternary carbons of the aromatic ring. The peaks at 132.8 and

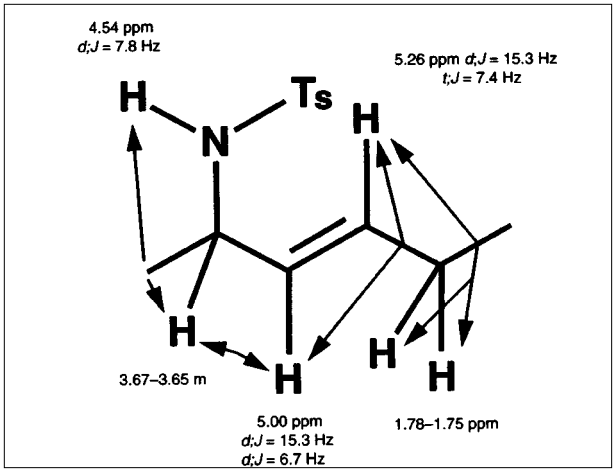


FIG. 5. Structural assignment.

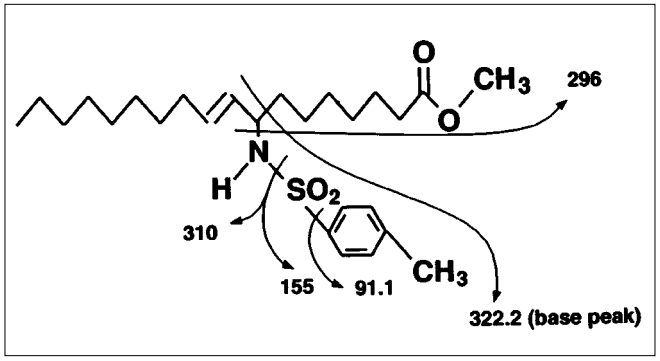


FIG. 6. Fragmentation pattern for methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate (2).

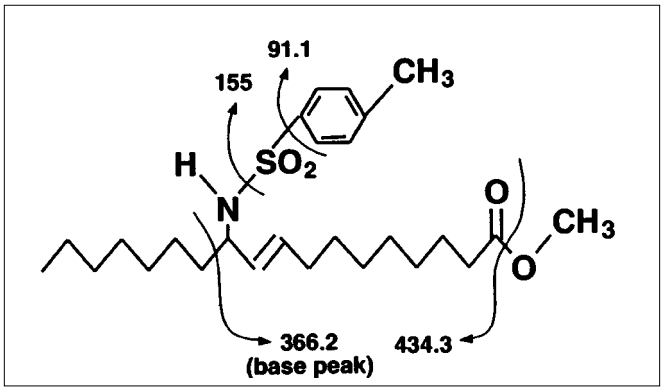


FIG. 7. Fragmentation pattern for methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate (3).

129.1 ppm are of equal intensity and are in the region typical for alkenes. The hydrogen–carbon two-dimensional correlation plot gives further proof of the alkene structure with the 132.8 ppm signal of the carbon spectra corresponding to the 5.26 ppm signal of the proton spectra; and the 129.1 ppm peak of the carbon spectra corresponding to the 5.00 ppm peak of the proton spectra (Fig. 4). The aromatic 129.3 and 127.2 ppm carbon peaks coincide with the 7.70 and 7.24 ppm proton peaks. The 56.1 and 51.4 ppm signals represent carbon attached to the nitrogen and the methoxy carbon, respectively. The additional 13 peaks found upfield constitute the remainder of carbons in the compound.

IR analysis provides additional proof of structure with the N-H stretching at 3276.8 cm^{-1}, carbonyl at 1738.0 cm^{-1}, sulfoxide stretching at 1325.7 cm^{-1} and 1159.4 cm^{-1}, and S-N stretching at 664.0 cm^{-1}. Confirmation of the *trans* double bond appears at 967 cm^{-1}.

Electrospray ionization mass-spectral data for methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate were obtained in the form of a single signal with a mass of *m/z* 527.5 (M + 62), corresponding to the ionic adduct of methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate with ethanolamine that was used as the ion source. Fragmentation data obtained from the electron ionization of methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate are shown in Figure 6. The *m/z* 434.3 signal is the loss of 31 amu (methoxy group) from the expected parent molecule, a typical loss with fatty methyl ester fragmentation (18). The mass peak of *m/z* 155, resulting from N-S cleavage, is common with compounds that contain *p*-toluenesulfonyl moieties (19). The base peak of *m/z* 366.2 is the loss of 99 amu, representing the loss of C_7H_{15} by cleavage between C_{11} and C_{12}. The base peak provides evidence that the *p*-toluenesulfonamide function is located on carbon-11. Fragmentation of fatty acids with amino groups is known to occur adjacent to the amino group (20).

Mass-spectral data for methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate showed a parent peak at *m/z* 466.4 (M + 1). Spectra with additional fragmentation were obtained from the electron ionization of the sample (Fig. 7). Major fragment pathways are indicated by arrows. The base peak at *m/z* 322.2 is the loss of 143.2 amu, representing the loss of $C_9H_{15}O_2$ from the methyl ester end of the molecule, and provides confirming evidence that the *p*-toluenesulfonamide function is located on carbon-8. Fragment ions *m/z* 310 and 296 probably represent loss of the *p*-toluenesulfone and *p*-toluenesulfonamide functional groups, respectively. Ions of *m/z* 155 and 91 are common to both regioisomers and represent the *p*-toluenesulfonyl and *p*-toluene moieties, respectively.

Ozonolysis products from methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate and methyl oleate were analyzed by GC and GC–MS. There were two distinct chromatographic peaks detected for methyl oleate oxidation. GC and GC–MS identified the peaks as nonanal and methyl 9-aldehydo-nonanoate. Only methyl 9-aldehydo-nonanoate was identified from ozonolysis of 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate. This indicated that the double bond 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate was indeed in the 9,10 carbon position. The expected substituted amino-nonanal peak was not observed. Thus, the mass spectra fragmentation data and the ozonolysis products from 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate indicate

that the *p*-toluenesulfonamide group is on carbon-11. Compound 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate was not examined by ozonolysis.

The chromatographic and spectral data confirm that the compounds made by reacting bis(*N*-*p*-toluenesulfonyl) sulfodiimide and methyl oleate resulted in the formation of methyl 11-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate and methyl 8-amino-(*N*-*p*-toluenesulfonyl)-9-*E*-octadecenoate.

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REFERENCES

1. Knothe, G., D. Weisleder, M.O. Bagby, and R.E. Peterson, Hydroxy Fatty Acids Through Hydroxylation of Oleic Acid with Selenium Dioxide/*tert*-butylhydroperoxide, *J. Am. Oil Chem. Soc. 70*:401–404 (1993).
2. Turk, A., M. Lebanon, and P.D. Boone, Oxidized Olefin Liquids, U.S. Patent 2,469,059 (1949).
3. Naudet, M., and E. Ucciani, Allylic Halogenation and Oxidation of Unsaturated Esters, in *Topics in Lipid Chemistry*, edited by F.D. Gunstone, John Wiley & Sons, New York, 1971, Vol. 2, pp. 99–158.
4. Kresze, G., and H. Münsterer, Bis(methoxycarbonyl) Sulfur Diimide, a Convenient Reagent for the Allylic Amination of Alkanes, *J. Org. Chem. 48*:3561–3564 (1983).
5. Singer, S.P., and K.B. Sharpless, Synthesis of *dl*-Gabaculine Utilizing Direct Allylic Amination as the Key Step, *Ibid. 43*:1448–1455 (1978).
6. Hayashi, T., A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, and K. Yanagi, Asymmetric Synthesis Catalyzed by Chiral Ferrocenylphosphine-Transition-Metal Complexes. 8. Palladium-Catalyzed Asymmetric Allylic Amination, *J. Am. Chem. Soc. 111*:6301–6311 (1989).
7. Sharpless, K.B., T. Hori, L.K. Truesdale, and C.O. Dietrich, Allylic Amination of Olefins and Acetylenes by Imido Selenium Compounds, *Ibid. 53*:269–271 (1976).
8. Brimble, M.A., and C.H. Heathcock, Allylic Amination by the Lewis-Acid-Mediated Ene Reaction of Diethyl Azodicarboxylate with Alkenes, *J. Org. Chem. 58:*5261–5263 (1993).
9. Johannsen, M., and K.A. Jørgensen, Iron-Catalyzed Allylic Amination, *Ibid. 59*:214–216 (1994).
10. Shea, R.G., J.N. Fitzner, J.E. Fankhauser, A. Spaltenstein, P.A. Carpino, R.M. Peevey, D.V. Pratt, B.J. Tenge, and P.B. Hopkins, Allylic Aelenides in Organic Synthesis: New Methods for the Synthesis of Allylic Amines, *Ibid. 51*:5243–5251 (1986).
11. Lorenz, O., and C.R. Parks, Ozonides from Asymmetrical Olefins. Reaction with Triphenylphosphine, *Ibid. 30*:1976–1981 (1965).
12. Benton, F.L., A.A. Kiess, and H.J. Harwood, Ozonolysis as a Method for Establishing the Positions of Olefinic Linkages, *J. Am. Oil Chem. Soc. 36*:457–460 (1959).
13. Privett, O.S., and E.C. Nickell, Studies on the Otonitation of Methyl Oleate, *Ibid. 41*:72–77 (1964).
14. Isbell, T.A., and R. Kleiman, Characterization of Estolides Produced from the Acid-Catalyzed Condensation of Oleic Acid, *Ibid. 71*:379–383 (1994).
15. Hori, T., S.P. Singer, and K.B. Sharpless, Allylic Deuteration and Titration of Olefins with *N*-Sulfinylsulfonamides, *J. Org. Chem. 43*:1456–1459 (1978).
16. Isbell, T.A., R. Kleiman, and S.M. Erhan, Characterization of Monomers Produced from Thermal High-Pressure Conversion of Meadowfoam and Oleic Acids into Estolides, *J. Am. Oil Chem. Soc. 69*:1177–1183 (1992).
17. Bussas, R., and G. Kresze, En-reaktionen mis Schwefeldiimidenstruktur der En-Kumponente und Reaktivitat bei der Umsetzundy mit Ditosylschwefeldiimid, *Liebigs Ann. Chem.*: 629–649 (1980).
18. Alexander, L.R., and J.B. Justice, Fatty Acid Composition of Human Erythrocyte Membranes by Capillary Gas Chromatography–Mass Spectrometry, *J. Chromatogr. 342*:1–12 (1985).
19. Glaspy, P.E., R.A. Hancock, and B.S. Thyagarajan, Mass Spectral Rearrangements of 3-Arylsulphonyl-2-arylthiopropenes and *N*-(4′-arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)anilines, *Org. Mass Spectrom. 20*:281–287 (1985).
20. Sun, K.K., and R.T. Holman, Mass Spectrometry of Lipid Molecules, *J. Am. Oil Chem. Soc. 45*:810–817 (1968).

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