JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

# Free Radical Addition of Butanethiol to Vegetable Oil Double Bonds

GRIGOR B. BANTCHEV,* JAMES A. KENAR, GIRMA BIRESAW, AND MOON GYU HAN

Cereal Products and Food Science Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604

Butanethiol was used in ultraviolet-initiated thiol−ene reaction with canola and corn oils to produce sulfide-modified vegetable oils (SMVO). The crude SMVO product was successfully purified by solvent extraction, vacuum evaporation, and silica gel chromatography. The SMVO products were characterized by nuclear magnetic resonance and Fourier transform infrared spectroscopy. Further product characterization and analysis was conducted using GC and GC-MS on the fatty acid methyl esters obtained by the transesterification of the SMVO products. Investigation of the effect of reaction conditions showed that high yield and high conversion of double bonds into thiol were favored at low reaction temperatures and high butanethiol/vegetable oil ratios. Canola and corn oils gave similar double-bond conversions and yields of the desired SMVO product even though they have big differences in the relative numbers of single and multiple double bonds in their structures. Under best reaction conditions, up to 97% of double-bond conversion and 61% isolated yields of the purified SMVO products were attained.

**KEYWORDS: Canola oil; corn oil; Fourier transform infrared spectroscopy; free radical addition; gas chromatography; mass spectroscopy; nuclear magnetic resonance; photochemistry; sulfides; thiol ethers**

## INTRODUCTION

The first lubricants used in metalworking processes were oils and fats from vegetable and animal sources (*1*). Later, these were displaced by cheaper petroleum-based lubricant products. Today, with the rising cost of petroleum and increased demand, in conjunction with environmental concerns, there is a renewed interest in the utilization of vegetable oils as biobased lubricants (*2*). Because vegetable oils are derived from renewable resources, they are generally considered to be nontoxic and biodegradable. This, in conjunction with their low volatility and good boundary lubrication characteristics, makes vegetable oils good candidates for lubricant applications (*2*). For vegetable oils to regain market share, they must perform as well as or better than current petroleum-based lubricants at a competitive price.

Despite their many positive attributes, the widespread use of vegetable oil-based lubricants in unmodified form is hindered by their poor thermal and oxidative stabilities and poor low-temperature properties. Their poor thermal and oxidative stabilities arise mainly from the presence of allylic and bisallylic methylene hydrogens along the triglyceride alkyl chains. These allylic and bisallylic methylene hydrogens have bond dissociation energies of approximately 88 and 76 kcal/mol, respectively, which are significantly lower than the bond dissociation energy of the hydrogens away from double bonds (105 kcal/mol) (*3*). These lower dissociation energies make the allylic and bisallylic methylene hydrogens much more susceptible to attack by free radicals. Abstraction of these labile hydrogen atoms from triglyceride molecules generates lipid radicals that subsequently enter into a myriad of oxidative and degradative reactions, thereby diminishing the physiochemical attributes and performance of vegetable oils during storage and/or lubricant application (*4*).

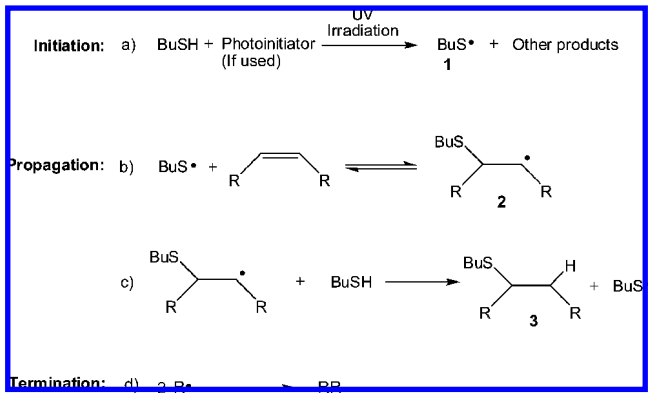
On the other hand, vegetable oils that contain high quantities of saturated fatty acids can form wax crystals at low temperatures. Thus, upon long exposure to cold temperatures (−10 to 0 °C), most vegetable oils become cloudy, form precipitates, or solidify, leading to poor flow properties and low-temperature performance. Because of these problems, much effort is focused on chemical or enzymatic modification of vegetable oils to improve their performance in various applications such as lubrication (*5*, *6*).

In many petroleum- and vegetable oil-based lubricant formulations, sulfur-containing compounds are commonly introduced as additives to improve wear and friction properties by maintaining boundary lubricating properties through physical and chemical adsorption to metal (*7*). For example, sulfurized vegetable oils obtained by reaction between elemental sulfur

* Author to whom correspondence should be addressed (telephone (309) 681-6239; fax (309) 681-6685; e-mail Grigor.Bantchev@ars.usda.gov.

10.1021/jf802774g 
Published on Web 01/23/2009

**Scheme 1.** General Radical Reaction Steps for the Thiol−Ene Reaction




and vegetable oils have been found to provide good extreme-pressure and antiwear properties (*8*−*11*). However, the sulfurization process must be carefully controlled and the total sulfur content maintained below 10%. Higher sulfur content causes excessive cross-linking and gives highly viscous or rubbery products. In addition, excess sulfur can leach out of the formulation and stain substrate surfaces (*9*).

Recently, Sharma and co-workers (*5*) have simultaneously introduced sulfide and hydroxyl groups into soybean oil by nucleophilic ring opening of epoxidized soybean oil. In their work, different alkanethiol nucleophiles were used in an effort to produce a variety of sulfur-containing oils for lubricant applications. They report that the sulfide groups improved lubrication in the boundary regime. Interestingly, the free hydroxyl groups produced during the reaction were found to increase the viscosity of the oil. We think that the hydroxy group can also present a solubility problem when formulated in some nonpolar base oils.

In this context, thiol−ene chemistry represents a direct and efficient method of introducing the sulfide groups into vegetable oils without additionally introducing unnecessary functionality such as hydroxyl groups. The thiol−ene reaction has been well studied for many types of double bonds (*12*−*14*). The reaction occurs via free radical addition to double bonds and, importantly, can be performed in air without the complication of competing side reactions with oxygen. As shown in **Scheme 1**, the initial product formed upon exposure of the labile alkanethiol sulfur−hydrogen bond (RS−H, ∼88 kcal/mol) to free radical initiators or UV irradiation is the alkylthiyl radical, **1**.

The alkylthiyl radical, **1**, adds to the unsaturated substrate to form a carbon-atom-centered radical, **2**. Radical **2** subsequently removes a hydrogen atom from another alkylthiol molecule to give the sulfide product **3** and a new alkylthiyl radical, thereby propagating the radical chain (*12*). This is the rate-determining step and is dependent upon the thiol structure. Termination reactions between two alkylthiyl radicals, **1**, or two radical **2** give the corresponding disulfide product and oligomeric products, respectively. For a more complete set of the radical reactions in the system, see the Supporting Information.

Although the addition of $H_2S$ or alkanethiols to fatty acids and their esters has been explored extensively (*15*−*18*), literature reports concerning the application of the thiol−ene reaction to polyunsaturated vegetable oils are relatively few (*19, 20*). Recently, Swedish researchers (*20*−*23*) reported an interesting series of studies on the addition of various trimercapto thiols to methyl oleate, methyl linoleate, and linseed oil to synthesize thin polymeric films on solid surfaces. In this paper, we report the synthesis and characterization of sulfide-containing corn and canola oils. They were obtained by photolytic ($\lambda$ < 325 nm) free radical addition of alkanethiols to the unsaturated sites. Details on the reaction and products characterization using Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), gas chromatography (GC), gel permeation chromatography (GPC), and gas chromatography−mass spectroscopy (GC-MS) are provided.

## MATERIALS AND METHODS

**Materials.** 1-Butanethiol (99%), KOH (85+ % pellets), methanol (Chromasolv, >99.9%), hexane (Chromasolv, >98.5%), and ethyl acetate (Chromasolv, >99.8%) were from Sigma Aldrich (St. Louis, MO) and used as received. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (99%), was from Acros Organics (Fair Lawn, NJ) and used as supplied. Corn and canola oils were purchased from the local supermarket and used as supplied. The vegetable oils were transesterified as described below, and GC analysis of the resulting fatty acid methyl esters (FAME) mixtures was used to determine the major fatty acid components. **Table 1** provides this information and compares it with literature data (*24*). The number of double bonds per 100 g of vegetable oil was calculated from the molar content of major fatty acid chains in the oil multiplied by the number of double bonds in the fatty acid chain.

**Synthetic and Purification Procedures.** *Synthetic Procedure.* Photolysis was accomplished using the unfiltered radiation from a 450 W Hanovia mercury lamp (55.7 W or 7.7 × $10^{19}$ photons/s, at $\lambda$ < 325 nm) (Ace Glass Inc., Vineland, NJ). (More detailed specifications of the lamp are listed in the Supporting Information.) The lamp was placed in a water-cooled (18 °C) immersion jacket, and the samples to be irradiated were placed in 100 mL quartz test tubes. The quartz tubes (27 mm i.d., 190 mm height) contained 100 mL of the corn oil−butanethiol mixture and were loosely stoppered with rubber stoppers. The samples were in contact with air and were not purged to remove the oxygen. In some experiments, 2,2-dimethoxy-2-phenylacetophenone (0.002 mol to 1 mol of double bonds in the oil) was added to photoinitiate the reaction. The samples in the test tubes were not mixed during the reaction. The samples and immersion jacket were wrapped together in aluminum foil, submerged in a cooling bath, and irradiated for up to 32 h. The light intensity was 0.076 W/mL or 1.1 × $10^{17}$ photons/(s mL) at $\lambda$ < 325 nm. The high-temperature reaction was carried out without the cooling bath, and for ambient temperature a cold water bath was used. The temperature was measured with an alcohol thermometer placed next to the samples.

For some experiments an Ace Glass low-temperature immersion well 7858 and photochemical reaction vessel 7841 wrapped in aluminum foil were used. The lamp was placed in the well, which was inserted in the center of the cylindrical reaction vessel. The well consisted of an inner cooling jacket and outer vacuum chamber. The thickness of the layer of reacting mixture that was illuminated by the lamp was estimated to be 8 mm, whereas the volume not directly illuminated by the lamp was around 50% of total. The total reaction mixture was 500 mL. In this case the mixture was stirred with a magnetic stirrer. The reactor was placed in a water or dry ice/acetone cooling bath. The temperature was monitored with a thermometer in the mixture. In the case of the acetone/dry ice bath, the temperature reported was the temperature of the acetone/dry ice mixture (−78 °C), because it was out of the range of the thermometer.

A summary of the reported experiments is given in **Table 2**.

The progress of the reaction was monitored by analyzing the reaction mixture periodically. To do this, aliquots were removed at regular intervals and placed in vials protected from light. Excess alkanethiol was removed by four successive washings of the sample with an equal volume of methanol, followed by vacuum evaporation (0.005 atm) of residual material at 90 °C for 3 h to yield a crude sulfide-modified vegetable oil (SMVO) product. The degree of conversion of double bonds in the resulting crude SMVO was determined by monitoring the vinyl protons with $^1$H NMR (see below). Additionally, samples of the crude SMVO were transesterified into sulfide-modified fatty acid methyl esters (SMFAME), and the resulting SMFAME were analyzed with GC and GC-MS. The crude SMVO was further purified by flash

**Table 1.** Major Fatty Acid Composition of Corn and Canola Oils

| | fatty acid composition,[a,b] % | | | | | |
|---|---|---|---|---|---|---|
| oil | C16:0 | C18:0 | C18:1 | C18:2 | C18:3 + C20:1 | double bonds/100 g of oil, mol[c] |
| corn | 10.8 (10.4) | 1.9 (2.0) | 28.4 (26.3) | 56.0 (59.0) | 1.1 (0.3 + 0.3) | 0.50 |
| canola | 4.4 (4.1) | 2.4 (1.8) | 60.7 (60.9) | 19.0 (21.0) | 8.7 (8.8 + 1.0) | 0.45 |

[a] Fatty acid composition determined by GC analyses of FAMEs in this work (standard deviation ~ 0.1%) [b] Values in parentheses are from ref *24*. [c] Moles of double bonds = (moles of oleic acid) + (2 × moles of linoleic acid) + (3 × moles of linolenic acid) in 100 g of vegetable oil.

**Table 2.** Summary of the Experiments (Experiments 4−8 Are Shown in **Figure 4** with Data for Additional Times)

| | | | | | conversion,[b] %, after | |
|---|---|---|---|---|---|---|
| no.[a] | butanethiol/double bonds/ initiator molar ratio | *T*, °C | container | oil | 2 h | 8 h |
| 1A | 1.5:1:0.002 | 90 | test tube | corn | –[d] | 18 |
| 2B | 1.5:1:0 | 18 | test tube | corn | –[d] | 31 |
| 3C | 1.5:1:0.002 | 18 | test tube | corn | –[d] | 33 |
| 4C | 1:1:0.002 | 18 | test tube | corn | –[d] | 22 |
| 5C | 2:1:0.002 | 18 | test tube | corn | –[d] | 38 |
| 6C | 3:1:0.002 | 18 | test tube | corn | –[d] | 55 |
| 7C | 6:1:0.002 | 18 | test tube | corn | –[d] | 88 |
| 8D | 6:1:0 | 18 | test tube | corn | 75 | 89 |
| 9D | 6:1:0.002 | 18 | test tube | corn | 71 | 89 |
| 10E | 6:1:0 | 18 | test tube | corn | –[d] | 88 |
| 11E | 6:1:0 | 18 | test tube | canola | –[d] | 93 |
| 12F | 6:1:0 | 20 | reactor | corn | –[d] | 86 |
| 13G | 6:1:0 | –78[c] | reactor | corn | 97 | 97 |

[a] Samples with the same letter were irradiated simultaneously. [b] The columns "2 h %" and "8 h %" show estimated percent of the reacted double bonds, determined by NMR after 2 and 8 h of irradiation, correspondingly, respectively. [c] Temperature of the dry ice/acetone bath. The actual temperature was not measured. [d] –, not determined.

chromatography, as described below, to yield purified SMVO. The resulting purified SMVO was analyzed by NMR, FT-IR, GPC, GC, and GC-MS.

*Flash Chromatography Separation.* The crude SMVO was purified by flash chromatography. Purification was accomplished using a Buchi (Flawil, Switzerland) flash chromatography system consisting of a pump manager C-615 with two pump modules C-605, a UV detector C-635, and a fraction collector C-660. The sample was passed through a plastic column (40 mm × 150 mm) containing 80 g of silica gel (Sorbent Technologies, Atlanta, GA). The silica gel had a particle size between 20 and 45 $\mu$m and a surface area of 500 $m^2$/g. Eight milliliters of the crude product was diluted with eight mL of hexane and injected onto the column. Column flow was 30 mL/min. The material was eluted with 100% hexane (8 min) followed by a gradient mixture of hexane/ethyl acetate ranging from 100:0 to 80:20 over 30 min, followed by a gradient mixture of 80:20 to 50:50 over 10 min. The desired product started eluting at 92:8 hexane/ethyl acetate, and we stopped collecting the main fraction, containing predominantly the desired product, at 87:13 hexane/ethyl acetate. The last eluting fractions were collected separately and were found to be enriched in oligomeric products.

**Product Identification and Quantification.** *NMR Analysis.* NMR spectra of the samples were obtained in $CDCl_3$ on a Bruker Avance 500 NMR spectrometer (Billerica, MA) operating at 500 MHz for $^1$H and 125 MHz for $^{13}$C and using a 5 mm BBI probe. Chemical shifts are reported in parts per million from tetramethylsilane calculated from the lock signal. Distortion enhancement by polarization transfer, correlation spectroscopy, heteronuclear multiple quantum correlation, and heteronuclear multiple bond correlation experiments were conducted to help with the assignments of the spectral peaks. Integrals for signals in the $^1$H NMR spectra were normalized relative to the signal between 3.96 and 4.50 ppm corresponding to the four glycerol methylene hydrogen atoms of the triglyceride oils. The degree of unsaturation in the vegetable oils and products was determined utilizing the integral areas for the vinyl proton signals observed between 5.05 and 5.55 ppm (one hydrogen atom was subtracted from this area to account for the glycerol methine hydrogen atom at 5.27 ppm).

*FT-IR Analysis.* Neat samples were placed between two KBr disks (25 mm × 2.5 mm). Their FT-IR spectra were collected using a Varian 3100 FTIR (Randolph, MA) spectrometer. Thirty-two repeat scans were averaged over a range of 600−4000 $cm^{-1}$ at a spectral resolution of 4 $cm^{-1}$.

*Transesterification Procedure.* Samples of vegetable oils and reaction mixtures were converted into their corresponding methyl esters according to the following procedure. A sample of oil (20 mg) was mixed with 0.5 M KOH (1.0 mL) in methanol and heated in a sealed vial at 100 °C for 90 min. The mixture was then cooled, and 1.0 M $H_2SO_4$ (2.0 mL) in methanol was added. The vial was sealed again and heated at 100 °C for 20 min. $H_2O$ (2 mL) and hexane (2 mL) were added to the cooled sample, the vial contents were stirred thoroughly, and the water phase was removed. A small amount of $Na_2SO_4$ was added, and the hexane phase was transferred into a GC vial. All samples were prepared in triplicate and the results averaged.

*GC Analysis.* The methyl esters were analyzed on a Hewlett-Packard 6890 series gas chromatograph (Palo Alto, CA) equipped with a 30 m × 0.25 mm × 0.2 $\mu$m film thickness SP-2380 capillary column from Supelco (Bellefonte, PA). The oven temperature program was as follows: 190 °C for 12 min, ramped at 10 °C/min to 220 °C, ramped at 5 °C/min to 265 °C, and held at 265 °C for 16 min. Injector and flame ionization detector (FID) temperatures were 280 °C; GC head pressure was 10 psi (69 kPa). The relative ratios of the fatty acids were determined from the integration of peak areas. Methyl palmitate was used as an internal standard. Peaks with areas of <1% of the area of methyl palmitate were neglected. The identities of the starting fatty acids were confirmed by comparing retention times with authentic samples and mass spectrometry. The sulfide products were identified by mass spectrometry as described below.

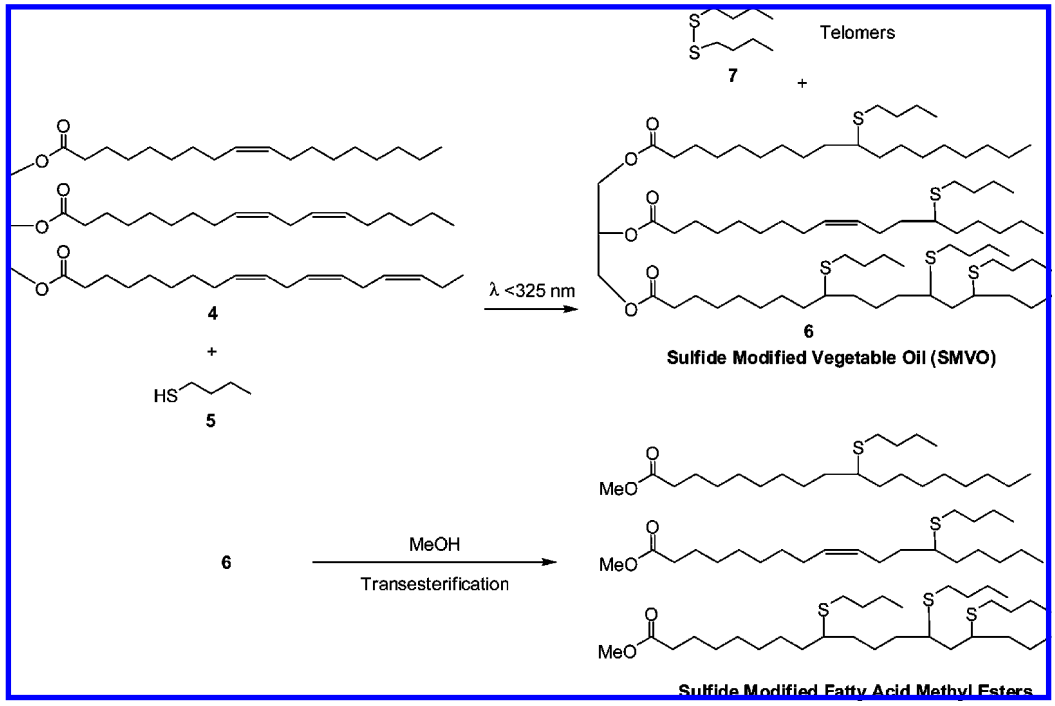
*GC-MS.* Mass spectra of the methyl esters were collected using a Hewlett-Packard 5890A GC with a 30 m × 0.25 mm i.d. × 0.2 $\mu$m film thickness SP-2380 capillary column (Supelco) and a Hewlett-Packard 5970 mass selective detector. GC conditions were as follows: helium head pressure, 15 psi (103 kPa) at 170 °C; split ratio, 1:1; injector temperature, 280 °C; transfer line temperature, 280 °C. The oven temperature program was identical to that used for GC as described above. Mass spectroscopy (MS) in electron impact (EI) mode was used. MS conditions were as follows: mass range, 50−550 amu; electron multiplier, 200 V relative.

*GPC.* Molecular weights of polymeric products obtained during the reaction were determined using GPC from Shimadzu Scientific Instruments (Columbia, MD). The instrument consisted of an autoinjector (SIL-10AD VP), column oven (TO-10AS VP), liquid chromatograph pump (LC-10AT VP), and system controller (SCL-10A VP). The size exclusion column was a 7.6 mm × 300 mm Asahipak GF-510 HQ column (Shodex, New York). Samples were run at 25 °C with acetone eluent at a flow rate of 0.3 mL/min. An Optilab DSP Interferometric Refractometer (Wyatt Technology, Santa Barbara, CA) and DAWN EOS Enhanced Optical System light scattering (Wyatt Technology) were used to detect and record sample responses.

## RESULTS AND DISCUSSION

As depicted in **Scheme 2**, the UV initiated ($\lambda$ < 325 nm) thiol−ene reaction between corn or canola oil **4** and butanethiol **5** (6 mol of BuSH per mole of double bonds contained in the oil) gave the desired butanethiol addition product **6** as the major product. Other products of this reaction were butyl disulfide, **7**, unreacted vegetable oil, and unidentified oligomeric products, possibly formed by the addition of the carbon-centered radical **2** to other double bonds of the vegetable oils. Gas was evolving during the reaction that we think was hydrogen. Despite no

**Scheme 2.** Thiol−Ene Reaction between Vegetable Oil and Butanethiol To Give Vegetable Oil Containing Sulfide Groups (Subsequent Transesterification with MeOH Gives Sulfide-Modified Vegetable Oil Fatty Acid Methyl Esters)




precautions being taken to remove the oxygen, the reaction was not inhibited by its presence. For most radical reactions, oxygen reacts with the radicals, generating relatively stable peroxide radicals and effectively stopping the process. For the thiol−ene reactions, the thiol hydrogen can be extracted by the peroxide radical, so the reactions are not inhibited (*13*).

Methanol washing of the reaction mixture removed the majority of the butanethiol. Residual butanethiol was removed by applying a vacuum (0.005 atm) at 90 °C for 3 h. Silica gel chromatography of the resulting crude material using 100% hexane separated a substantial amount of butyl disulfide as the front fraction. Further silica gel chromatography using an ethyl acetate gradient of 8−13% in hexane gave the purified SMVO, **6**. It had an amber color and was obtained in approximately 61% of the theoretically expected amount from either corn or canola oil. GPC analysis of this material showed that it contained approximately 2% oligomeric materials, assuming that the different compounds in the mixture have the same refractive index. The fractions collected using more than 13% of ethyl acetate in the eluent were rejected. These fractions were dark colored, and GPC analyses showed that they contained between 35 and 45% of higher molecular weight oligomeric materials. On the basis of these results, we estimate that approximately 10% of the crude SMVO was oligomeric product.

Examination of the $^1$H NMR spectra, **Figure 1A**, for the purified SMVO from corn oil clearly showed the disappearance of the vinylic and allylic hydrogen signals at 5.35 and 2.00 ppm, respectively. (For complete description of the NMR and IR data, see the Supporting Information.)

In addition to the disappearance of the vinyl and allylic proton signals, new peaks corresponding to hydrogen atoms α (2.56 and 2.48 ppm), $\beta$ (1.54 ppm), and $\gamma$ (1.42 ppm) to the sulfur atoms were also clearly visible in the SMVO from corn oil. $^{13}$C NMR of purified SMVO from corn oil confirmed that the expected reaction products were formed (**Figure 1B**). The peaks between 120 and 135 ppm corresponding to double-bond carbon atoms were undetectable. New peaks at 45.9 and 30.0 ppm, at 35.0 and 32.0 ppm, and at 26.8 and 22.1 ppm for carbons α, $\beta$, and $\gamma$ to the sulfur atom were detected.

Ferreri and co-workers (*25*) have reported that the thiyl radical can abstract allylic hydrogen atoms from fatty acid residues, leading to formation of fatty acids with conjugated double bonds. The formation of conjugated double bonds was confirmed in their work from the characteristic chemical shifts in the $^1$H NMR spectra between 6.15 and 6.35 ppm. We did not observe any signals in this region of the $^1$H NMR spectra (**Figure 1A**) for either corn or canola oils. This is indicative that, for our experimental condition, this side reaction did not occur.

The extent of double-bond conversion into sulfide groups was estimated by $^1$H NMR spectra in the 5.05−5.55 ppm range for the crude SMVOs. Comparison of the integral values showed that approximately 89% of the double bonds in the starting corn oil underwent the thiol−ene reaction. Similar observations, concerning the disappearance of vinyl hydrogen signals and the appearance of sulfide-related hydrogens, were observed for canola oil under similar conditions. $^1$H NMR analysis showed that approximately 93% of the double bonds present in canola oil underwent the thiol−ene reaction and converted into the corresponding sulfides.

FT-IR spectra of the purified SMVOs provided an indirect support for the formation of sulfide groups during the reaction. Peaks corresponding to vegetable oil double bonds at 3009 cm$^{-1}$, (H−C= stretching) and 1652 cm$^{-1}$ (cis-stretching C=C) disappeared, confirming the addition of butanethiol to the double bonds. The peak corresponding to cis-bending vibration of H−C=C− at 724 cm$^{-1}$ decreased. This peak did not disappear completely, because it overlapped with the peak of $CH_2$ rocking vibrations. Also noted in the FT-IR spectra of the purified SMVOs was a peak at 968 cm$^{-1}$ corresponding to the presence of trans-double bonds. The presence of trans-double bonds in the product is not surprising even though vegetable oils naturally possess only cis-double bonds. It is well-known that alkylthiyl radical additions to double bonds occur reversibly and have been used to isomerize (stereomutate) cis-double bonds into their

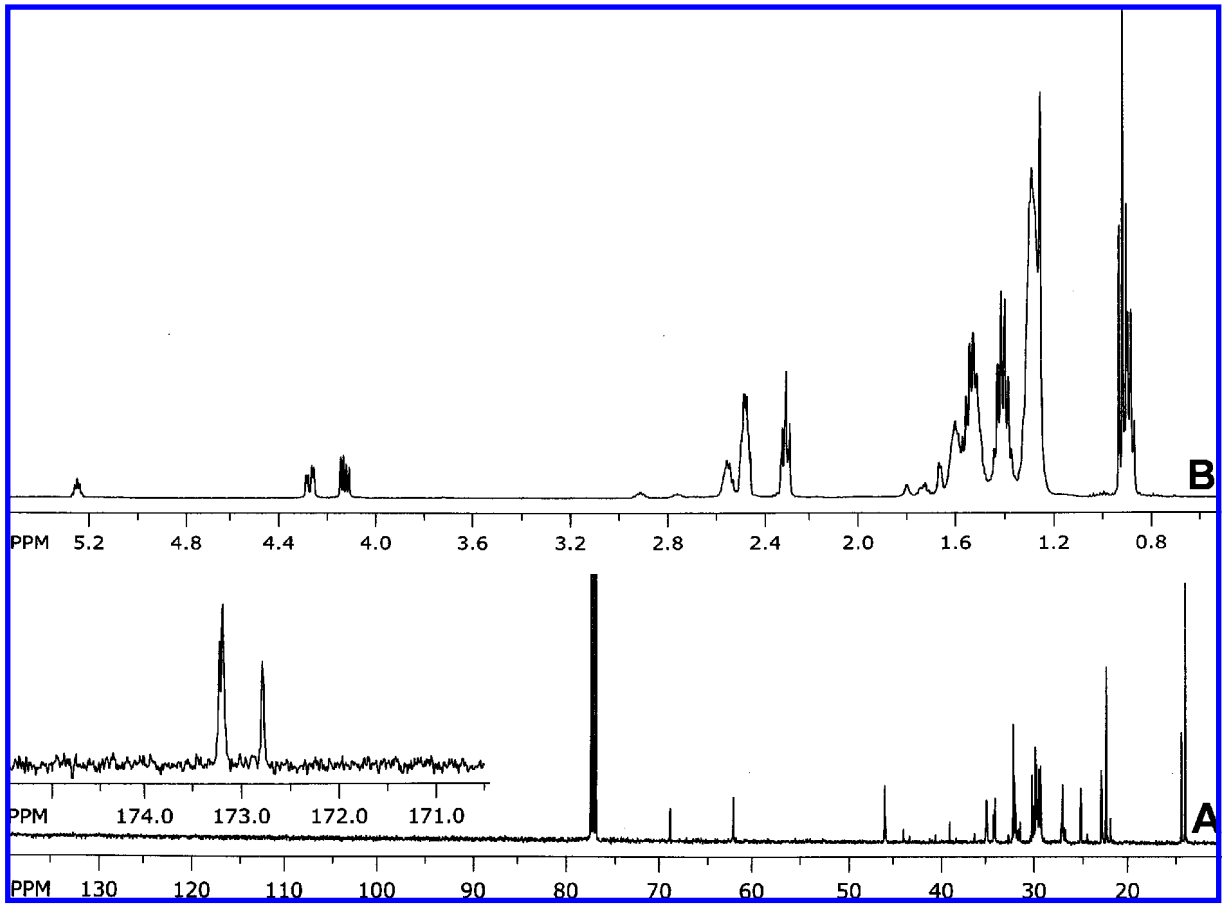



**Figure 1.** (**A**) $^{1}$H NMR of sulfide-modified corn oil (97% double bond conversion at 6:1 butanethiol/corn oil. Irradiated for 2 h at −78 °C. (**B**) $^{13}$C NMR of the same sulfide-modified corn oil.

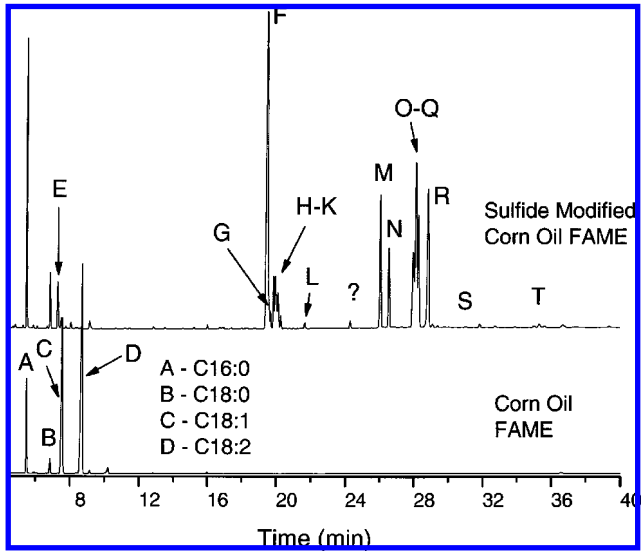



**Figure 2.** Typical GC chromatogram of the fatty acid methyl esters of corn oil before and after the thiol−ene reaction. Assignments of peaks F−T are given in **Table 2**.

corresponding trans-configuration (*26*). The formation of C−S bonds in the product could not be detected by FT-IR because the expected peak at 600−700 cm$^{-1}$ had too low of an intensity.

Further analysis of SMVOs was done by converting them into their corresponding sulfur-modified fatty acid methyl esters (SMFAME) and analyzing them directly by GC and GC-MS. **Figure 2** shows a typical GC chromatogram of the FAMEs from corn oil and from the transesterified crude product of the thiol−ene reaction of corn oil.

Comparison of the GC chromatograms of the oil FAMEs, before and after the reaction, supports the NMR and FT-IR results that the unsaturated oleate and linoleate double bonds in the triglyceride molecules have been converted to sulfides. Identification of GC chromatogram peaks of the SMFAMEs was made possible using GC-MS analyses. **Table 3** gives the important mass fragments obtained from EI mass spectra of these SMFAMEs. The entries in **Table 3** correspond to the letters assigned to the peaks in **Figure 2**.

**Figure 3** shows a typical EI mass spectrum for methyl 9(10)-butylthiooctadecanoate regioisomers (monoadduct of oleic acid, peak F in **Figure 2**) obtained from transesterification of SMVO from corn oil. The observed fragment ions are demonstrative of the SMFAME.

The molecular ion at *m*/*z* 386 is clearly seen, as is an ion at 355 ([M − 31]$^{+}$) representing the loss of a methoxyl group and confirming that the molecule is indeed a methyl ester. The molecular ion in some of the other sulfide-modified methyl esters was not always this prominent. Loss of the $C_4H_9$ moiety gave *m*/*z* 329 in 43% relative abundance, whereas an ion of *m*/*z* 297 was observable from cleavage of $SC_4H_9$. The location of the sulfur moiety along the fatty acid chain was readily apparent from the prominent fragment ions observed at *m*/*z* 259 and 229 for the methyl 9-butylthiooctadecanoate regioisomer and *m*/*z* 273 and 215 for the methyl 10-butylthiooctadecanoate regioisomer. Similar interpretation for the mass spectra obtained for the other SMFAMEs derived from the sulfide-modified corn oil allowed their identification and determination of the locations of the sulfur atom(s).

**Table 3.** Electron Impact (EI) Mass Spectral Data for Sulfide-Modified Fatty Acid Methyl Esters Obtained from Sulfide-Modified Corn Oil Prepared in the Present Work

| entry[a] | EI-MS |
|---|---|
| methyl 9(10)-butylthiooctadecanoate (F) | 386 ($[M]^+$, 21%), 355 ($[M - OCH_3]^+$, 6%), 329 ($[M - C_4H_9]^+$, 43%), 297 ($[M - SC_4H_9]^+$, 26%), 259 ($[M - C_9H_{19}]^+$, 61%), 273 ($[M - C_8H_{17}]^+$, 58%), 229 ($[C_{14}H_{29}S]^+$, 91%), 215 ($[C_{15}H_{31}S]^+$, 100%). |
| Mmethyl 12-butylthiooctadecanoate (G) | 386 ($[M]^+$, 17%), 355 ($[M - OCH_3]^+$, 5%), 329 ($[M - C_4H_9]^+$, 12%), 297 ($[M - SC_4H_9]^+$, 31%), 301 ($[M - C_6H_{13}]^+$, 91%), 269 (60%), 187 ($[C_{11}H_{23}S]^+$, 100%) |
| methyl butylthiooctadecenoate (H) (mixture of 4 linoleic monoadducts) | 384 ($[M]^+$, 0.2%), 353 ($[M\text{-}OCH_3]^+$, 1%), 327 ($[M\text{-}C_4H_9]^+$, 25%), 295 ($[M\text{-}SC_4H_9]^+$, 2%), 273 ($[C_{15}H_{29}O_2S]^+$, 21%), 259 ($[C_{14}H_{27}O_2S]^+$, 11%), 241 (15%), 187 $[C_{11}H_{23}S]^+$, 100%), 173 ($[C_{10}H_{21}S]^+$, 29%) |
| methyl butylthiooctadecenoate (I) (mixture of linoleic monoadducts) | 384 ($[M]^+$, 0.4%), 353 ($[M - OCH_3]^+$, 1%), 327 ($[M - C_4H_9]^+$, 58%), 295 ($[M - SC_4H_9]^+$, 4%), 273 ($[C_{15}H_{29}O_2S]^+$, 82%), 259 ($[C_{14}H_{27}O_2S]^+$, 63%), 241 (57%), 227 (20%), 187 ($[C_{11}H_{23}S]^+$, 54%), 173 ($[C_{10}H_{21}S]^+$, 32%), 55 (100%) |
| methyl 12-butylthio 9-octadecenoate (J) | 384 ($[M]^+$, 0.1%), 353 ($[M - OCH_3]^+$, 0.2%), 327 ($[M - C_4H_9]^+$, 17%), 295 ($[M - SC_4H_9]^+$, 1%), 273 ($[C_{15}H_{29}O_2S]^+$, 5%), 187 ($[C_{11}H_{23}S]^+$, 100%), 173 ($[C_{10}H_{21}S]^+$, 5%) |
| methyl 10-butylthio 12-octadecenoate (K) | 384 ($[M]^+$, 0.1%), 353 ($[M - OCH_3]^+$, 0.2%), 327 ($[M - C_4H_9]^+$, 14%), 295 ($[M - SC_4H_9]^+$, 1%), 273 ($[C_{15}H_{29}O_2S]^+$, 100%), 241 (68%), 213 ($[C_{13}H_{25}S]^+$, 2%) |
| methyl 11(12)-butylthioeicosanoate (L) | 414 ($[M]^+$, 14%), 357 ($[M - C_4H_9]^+$, 38%), 325 ($[M - SC_4H_9]^+$, 30%), 301 ($[C_{17}H_{33}O_2S]^+$, 18%), 287 ($[C_{16}H_{31}O_2S]^+$, 45%), 269 (18%), 229 ($[C_{14}H_{29}S]^+$, 100%), 215 ($[C_{13}H_{27}S]^+$, 69%) |
| methyl 10,12-bis(butylthio)octadecanoate (M) | 474 ($[M]^+$, 6%), 443 ($[M - OCH_3]^+$, 2%), 417 ($[M - C_4H_9]^+$, 100%), 385 ($[M - SC_4H_9]^+$, 2%), 327 ($[C_{19}H_{35}O_2S]^+$, 7%), 295 ($[C_{18}H_{31}OS]^+$, 8%), 273 ($[C_{15}H_{29}O_2S]^+$, 6%), 241 (5%), 187 ($[C_{11}H_{23}S]^+$, 11%) |
| methyl 10,12-bis(butylthio)octadecanoate (N) | 474 ($[M]^+$, 7%), 443 ($[M - OCH_3]^+$, 2%), 417 ($[M - C_4H_9]^+$, 100%), 385 ($[M - SC_4H_9]^+$, 2%), 327 ($[C_{19}H_{35}O_2S]^+$, 8%), 295 ($[C_{18}H_{31}OS]^+$, 9%), 273 ($[C_{15}H_{29}O_2S]^+$, 6%), 187 ($[C_{11}H_{23}S]^+$, 14%) |
| methyl 9,12-bis(butylthio)octadecanoate (O) | 474 ($[M]^+$, missing), 443 ($[M - OCH_3]^+$, 2%), 385 ($[M - SC_4H_9]^+$, 22%), 327 ($[C_{19}H_{35}O_2S]^+$, 53%), 259 ($[C_{14}H_{27}O_2S]^+$, 100%), 227 (187 ($[C_{11}H_{23}S]^+$, 93%) |
| methyl 9(10),12(13)-bis(butylthio)octadecanoate (P) | 474 ($[M]^+$, 10%), 443 ($[M - OCH_3]^+$, 12%), 417 ($[M - C_4H_9]^+$, 32%), 385 ($[M - SC_4H_9]^+$, 38%), 327 ($[C_{19}H_{35}O_2S]^+$, 100%), 295 ($[C_{18}H_{31}OS]^+$, 16%), 273 ($[C_{15}H_{29}O_2S]^+$, 42%), 263 (15%), 259 ($[C_{14}H_{27}O_2S]^+$, 56%), 241 (13%), 227 (16%), 187 ($[C_{11}H_{23}S]^+$, 58%), 173 ($[C_{10}H_{21}S]^+$, 96%) |
| methyl 10,13-bis(butylthio)octadecanoate (Q) | 474 ($[M]^+$, 2%), 443 ($[M\text{-}OCH_3]^+$, 5%), 417 ($[M\text{-}C_4H_9]^+$, 2%), 385 ($[M\text{-}SC_4H_9]^+$, 17%), 295 ($[C_{18}H_{31}OS]^+$, 7%), 273 ($[C_{15}H_{29}O_2S]^+$, 51%), 241 (18%), 173 ($[C_{10}H_{21}S]^+$, 100%). |
| methyl 9,13-bis(butylthio)octadecanoate (R) | 474 ($[M]^+$, missing), 443 ($[M - OCH_3]^+$, 2%), 385 ($[M - SC_4H_9]^+$, 39%), 259 ($[C_{14}H_{27}O_2S]^+$, 71%), 227 (13%), 173 ($[C_{10}H_{21}S]^+$, 86%) |
| methyl 9(10),13(15)(16)-bis(butylthio)octadecanoate (S) | 474 ($[M]^+$, 3%), 417 ($[M - C_4H_9]^+$, 3%), 385 ($[M - SC_4H_9]^+$, 29%), 327 ($[C_{19}H_{35}O_2S]^+$, 78%), 273 ($[C_{15}H_{29}O_2S]^+$, 23%), 259 ($[C_{14}H_{27}O_2S]^+$, 30%), 207 (38%), 173 ($[C_{10}H_{21}S]^+$, 96%), 145 ($[C_8H_{17}S]^+$, 47%), 131 ($[C_7H_{15}S]^+$, 82%), 55 (100%) |
| methyl 10,12(13),15-tri(butylthio)octadecanoate (T) | 562 ($[M]^+$, out of range), 505 ($[M - C_4H_9]^+$, 100%), 473 ($[M - SC_4H_9]^+$, 7%), 415 (30%), 383 (58%), 273 ($[C_{15}H_{29}O_2S]^+$, 14%), 145 ($[C_8H_{17}S]^+$, 51%) |

[a] Letters correspond to **Figure 2**.

On the basis of the GC-MS data, the GC chromatogram for SMVO from corn oil (**Figure 2**) can be dissected into four major regions corresponding to the various sulfide-containing reaction products: (1) the region between 4 and 10 min corresponded to unreacted or isomerized FAMEs from corn oil; (2) the region between 19 and 24 min related with regioisomers of monobutyl sulfide adducts to the oleic double bond and monobutyl sulfide adducts to one of linoleic double bonds; (3) the region between 25 and 30 min corresponded to dibutyl sulfide adducts to linoleate; and finally (4) the region between 30 and 36 min corresponded to di- and triadducts of linolenate. Similar results were observed in the GC chromatograms for SMVO from canola oil, except that the peak from the oleic monoadducts had a higher intensity and the compounds in the 30−36 min region were more pronounced due to the higher content of linolenate in canola oil (8.7%) relative to corn oil (1.1%). Separation of these SMFAME into individual compounds was not performed as we were more interested in the SMVO than the individual sulfide-modified methyl esters. SMFAME can be readily obtained by performing the reaction starting with pure methyl oleate, linoleate, or linolenate.

The intensities of the GC peaks were used to determine the degree of reaction of the individual fatty acids with butanethiol. The peaks for methyl palmitate remained unchanged because palmitic acid contains no double bonds to participate in the reaction (**Figure 2**). The methyl oleate peak was significantly reduced, whereas the methyl linoleate peak disappeared. Also, a peak corresponding to methyl elaidate (*trans*-C18:1) appeared in the GC chromatogram of the SMFAME (peak E, **Figure 2**). The latter confirms the oleic acid stereomutation observed by FT-IR.

Interestingly, the methyl stearate peak derived from the starting oils increased approximately 0.4% during the course of the reaction relative to methyl palmitate (see the Supporting Information). Although the observed increase in methyl stearate was small, it was consistently observed in our reactions, and we believe it may have resulted from the addition of a hydrogen radical (formed during the initiation

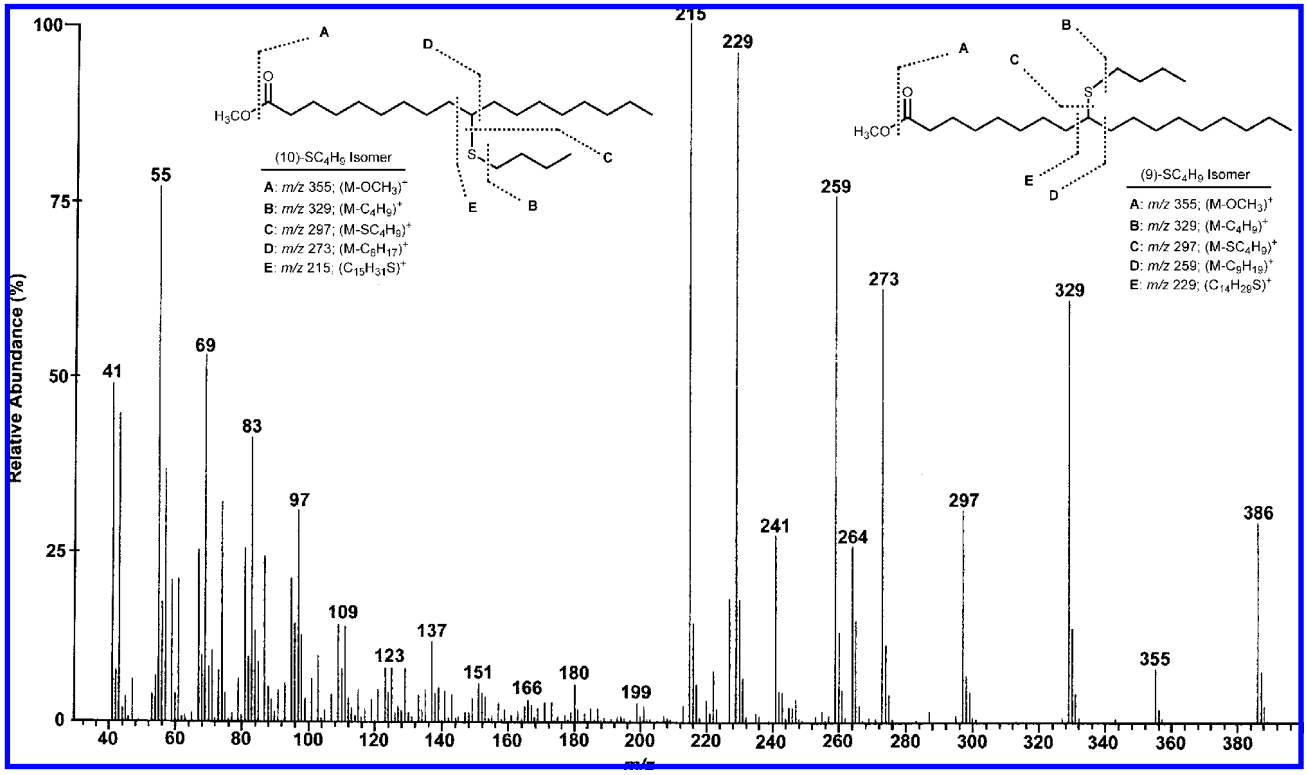



**Figure 3.** Electron impact mass spectrum of methyl 9(10)-butylthiooctadecanoate regioisomers (monoadduct of oleic acid, peak F in **Figure 2**) obtained from transesterification of sulfide-modified corn oil.

step) to the double bond of oleate to form the corresponding carbon-centered radical. This radical could subsequently abstract a hydrogen atom from a butanethiol molecule to give the stearate chain and a thiyl radical. Because the levels of C16:1 in corn and canola oils are very low, the methyl palmitate peak was not affected by the reduction side reaction. A reduction of the double bonds in the linoleate would lead to the formation of the methyl 12-butylthiooctadecanoate (entry G from **Table 3**) in the GC-MS data. This compound can be formed by reduction of the double bond on the 9-position and an addition of thiol molecule to the 12-position. The numerical evaluation of the increase of the stearate can be interpreted as 1.9 ± 1.3% of the reacted double bonds being reduced. See the Supporting Information for further details. Although it seems unlikely, we cannot dismiss the possibility of selective partitioning of methyl stearate and methyl palmitate during the ester preparation used to analyze product mixtures. Further work on this point needs to be performed.

We have run quantitative $^1$H NMR and GC analyses of a series of SMVO with different degrees of conversion. GC provided qualitative support of the NMR and FT-IR data. It also was in a good quantitative agreement with $^1$H NMR data about the degree of reaction of the double bonds. The disappearance of both oleic and linoleic fatty acids was in agreement with the $^1$H NMR data for overall reaction of double bonds. (See the Supporting Information.) This observation reinforced the validity of using the $^1$H NMR method to monitor the progress of the reaction. In addition, it implies that the double bonds in the two acids had the same reactivity toward the thiyl radical. We did not calibrate the FID for the sulfur-containing products. Because of this, we could not extract precise information for the reactivity of the second double bond in linoleic acid, after the first double bond had reacted. We suspect that the addition of a side chain reduced, to some degree, the reactivity of the second double bond. This conclusion is based on the observation that, under identical conditions, the linoleic-rich corn oil showed the slightly lower overall degree of conversion (89%) relative to oleic-rich canola oil (93%).

**Examination of Reaction Variables.** To better understand how the reaction parameters influenced SMVO formation, experiments were carried out in which the following reaction conditions were varied: temperature, oil/butanethiol ratio, prescence of photoinitiator, and type of oil. The effect of these parameters on conversion of double bonds and product yield was quantified by NMR and GC. Because the two methods gave close results (see Supporting Information, Figure A4), we report only the $^1$H NMR data.

*Effect of Temperature and Photoinitiator.* A 1.5:1 (molar ratio) butanethiol/corn oil solution containing 0.2 mol % of photoinitiator was photolyzed at 90 °C for 8 h (entry 1, **Table 2**). NMR analysis showed that 18% of the double bonds from the starting vegetable oil were consumed after an 8 h reaction time. It also showed the formation of approximately 5.8 wt % of a solid material, which we assume to be polymeric byproduct formed during the reaction. Because this solid material did not represent the desired SMVO product, it was not subjected to further in-depth characterization. In another experiment, the same initial molar ratio of reactants and photoinitiator were photolyzed at 18 °C over 8 h (entry 3, **Table 2**). Thirty-three percent of the vegetable oil double bonds were consumed, and the amount of solid material formed was reduced to approximately 1.5 wt %.

At 6:1 butanethiol/corn oil double-bond ratio, further improvement of the conversion of double bonds into sulfides was realized when the solution was irradiated at even lower temperature. Thus, a 2 h irradiation of the solution with 6:1 butanethiol/corn oil double-bond ratio in the dry ice/acetone bath resulted in a 97% double-bond conversion (entry 13, **Table 2**). In addition, no solid polymer formation was observed, although GPC analyses showed a 2% oligomeric product formation. This result is much better than the other experiment in the reactor,

entry 12, where only 86% conversion was achieved at ambient temperature for 8 h. For irradiation times of 2 h, comparison can be made with entry 8, where a similar mixture at ambient temperature gave only 75% conversion.

The improved reaction of vegetable oil double bonds and higher yield of SMVO at lower temperatures can be attributed to the facile and reversible nature of alkylthiyl addition to double bonds (*12*, *26*). At higher temperatures, the dissociation of the thiyl double bond adduct radical, **2**, was entropically favored. This shifted the equilibrium toward reactants (**Scheme 1**, reaction c) before radical **2** can be trapped through butanethiol hydrogen abstraction, thus reducing the overall conversion. Our results are consistent with literature reports that show carbon-centered radical generated from addition of thiyl radicals to be slower to dissociate at lower temperatures (*27*).

When the reaction was performed at similar conditions, but with or without the photoinitiator, the reactions proceeded in a similar fashion (entry 2 vs entry 3 and entry 9 vs entry 8 from **Table 2**). These findings were not surprising because the sulfur hydrogen bond in alkylthiols is labile (RS−H, ∼88 kcal/mol) and can easily undergo cleavage upon irradiation with the appropriate wavelengths, making the photoinitiator unnecessary. On the basis of this observation, the rest of the experiments were performed without the use of the photoinitiator.

*Effect of Thiol to Double-Bond Ratio.* The effect of the starting molar ratio of butanethiol to the double bonds in corn oil was also examined. Reaction solutions containing 1:1:0.002, 2:1:0.002, 3:1:0.002, and 6:1:0.002 butanethiol/double bond/initiator molar ratios were irradiated over a period of 32 h at 18 ± 3 °C (entries 3−8, **Table 2**). Aliquots were taken every 8 h and analyzed by $^1$H NMR for the amount of double bonds reacted. The rate of double-bond disappearance was highly dependent on the concentration of butanethiol present in the initial reaction mixture. As can be seen in **Figure 4**, larger butanethiol concentrations relative to the starting vegetable oil double bond resulted in faster double bond consumption. They also gave greater overall conversion into the desired SMVO product.

The reaction with the 6:1 butanethiol/corn oil double-bond ratio was completed after 8 h of reaction time and showed a total double-bond conversion of 89%. This is a 3-fold increase in the formation of SMVO over 1:1 butanethiol/corn oil double-bond ratio. GPC analyses of the 6:1 product mixture showed 9% oligomer formation. Lower butanethiol/double-bond ratios required longer reaction times to maximize the conversion of double bonds into sulfide groups. The 1:1 butanethiol/corn oil double-bond ratio showed slight improvement after 32 h of reaction time, whereas the 2:1 and 3:1 ratios showed maximal improvement after 8−16 h time intervals. Presumably, at higher butanethiol concentrations, the slow chain transfer step between the thiyl−double bond adduct radical **2** and a butanethiol occurred more frequently. This effectively trapped radical **2** and gave the desired SMVO and a thiyl radical that went on to propagate the reaction. In addition to lower double-bond conversions, the lower 1:1, 2:1, and 3:1 butanethiol/corn oil double-bond ratios also caused more solid polymeric products. This was visually observable on the walls of the test tubes after 8, 16, and 32 h of reaction time, respectively.

We believe that further improvement of the conversion can be achieved if higher butanethiol/double-bond ratios are used. In addition, higher ratios most probably will decrease the side products and accelerate the reaction. Further investigation of this possibility is needed.

*Effect of Oil Type.* Corn and canola oil were chosen because of the drastic difference in the relative compositions of single

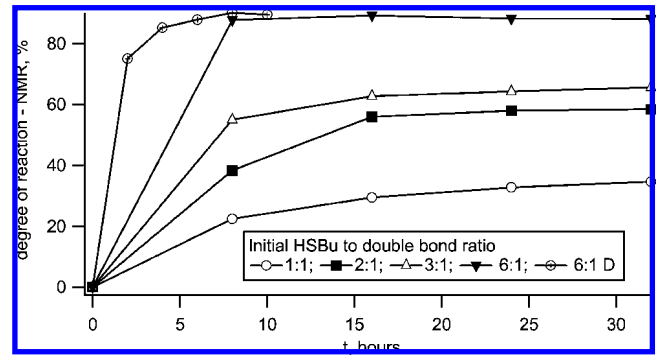



**Figure 4.** Rate of disappearance of corn oil double bonds by $^1$H NMR for different initial butanethiol/corn oil double-bond ratios. Reaction conditions: 0.2 mol % initiator relative to corn oil double bonds, 18 ± 3 °C, and irradiation 1.1 × $10^{17}$ photons/(s mL) at $\lambda$ < 325 nm.

and multiple double bonds in their structures. As can be seen in **Table 1**, corn oil contains predominantly the diunsaturated linoleic (56% C18:2), whereas canola contains predominantly the monounsaturated oleic (61% C18:1) in its structure. In addition, corn oil and canola oil contain 1.1 and 8.7%, respectively, of the triunstaurated linolenic acid (C18:3). It was of interest to find out if differences in the composition of unsaturation sites have an effect on percent conversion to thio or overall SMVO yield. As mentioned earlier, the two oils gave close overall SMVO yields, as well as degrees of conversion of the double bonds (entries 10 and 11, **Table 2**). On the basis of the comparison of the conversion of the two fatty acids we can conclude that the reactivities of the double bonds in oleate and linoleate were the same (see Supporting Information Figure A4 for more details). The reactivity of the double bond in the monoadduct of linoleic acid apparently was slightly lower, because the overall conversion of linoleic-rich corn oil was slightly less than the conversion of the oleic-rich canola oil.

## ACKNOWLEDGMENT

We thank Armand Loffredo for laboratory support, Dr. Karl Vermillion for collection of NMR spectra and help with their interpretation, and Dr. Steven Cermak for the GC-MS instrument and help with its use.

**Supporting Information Available:** Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

## LITERATURE CITED

(1) Byers, J. P. *Metalworking Fluids*; Dekker: New York, 1994; pp 1−23.
(2) Willing, A. Lubricants based on renewable resources—an environmentally compatible alternative to mineral oil products. *Chemosphere* **2001**, *43*, 89–98.
(3) Pratt, D. A.; Mills, J. H.; Porter, N. A. Theoretical calculations of carbon-oxygen bond dissociation enthalpies of peroxyl radicals formed in the autoxidation of lipids. *J. Am. Chem. Soc.* **2003**, *125*, 5801–5810.
(4) Adhvaryu, A.; Erhan, S. Z.; Liu, Z. S.; Perez, J. M. Oxidation kinetic studies of unmodified and genetically modified vegetable oils using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. *Thermochim. Acta* **2000**, *364* (1−2), 87–97.
(5) Sharma, B. K.; Adhvaryu, A.; Erhan, S. Z. Synthesis of hydroxyl thio-ether derivatives of vegetable oils. *J. Agric. Food Chem.* **2006**, *54*, 9866–9872.

(6) Cermak, S. C.; Skender, A. L.; Deppe, A. B.; Isbell, T. A. Synthesis and physical properties of tallow-oleic estolide 2-ethylhexyl esters. *J. Am. Oil Chem. Soc.* **2007**, *84*, 449–456.
(7) Brophy, J. E.; Zisman, W. A. Surface chemical phenomena in lubrication. *Ann. N.Y. Acad. Sci.* **1951**, *53*, 836–861.
(8) Erikson, F. L.; Anderson, R. E.; Landis, P. S. Vegetable oil derivatives as lubricant additives U.S. Patent 4,134,845, 1990.
(9) Kammann, K. P., Jr.; Phillips, A. I. Sulfurized vegetable oil products as lubricant additives. *J. Am. Oil Chem. Soc.* **1985**, *62*, 917–923.
(10) Rossrucker, T.; Fessenbecker, A. Sulfur carriers In *Lubricant Additives: Chemistry and Applications*; Rudnick, L. R. , Ed.; CRC Press: Boca Raton, FL, 2003; pp 259−292.
(11) McDonald, R. A. Zinc dithiophosphates In *Lubricant Additives: Chemistry and Applications*; Rudnick, L. R., Ed.; CRC Press: Boca Raton, FL, 2003; pp 29−44.
(12) Walling, C.; Helmreich, W. Reactivity and reversibility in the reaction of thiyl radicals with olefins. *J. Am. Chem. Soc.* **1959**, *81*, 1144–1148.
(13) Hoyle, C. E.; Lee, T. Y.; Roper, T. Thiol-enes: chemistry of the past with promise for the future. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5301–5338.
(14) Stacey, F. W.; Harris, J. F., Jr. Formation of carbon-hetero atom bonds by free radical chain additions to carbon−carbon multiple bonds In *Organic Reactions*; Cope, A. C., Ed.; Wiley: New York, 1963; Chapter 4.
(15) Kircher, H. W. The elaidinization of methyl oleate with mercaptans. *J. Am. Oil Chem. Soc.* **1964**, *41*, 351–354.
(16) Schwab, A. W.; Gast, L. E.; Cowan, J. C. Free radical addition of hydrogen sulfide and thiols to linseed oil and methyl oleate. *J. Am. Oil Chem. Soc.* **1968**, *45*, 461–464.
(17) Gadd, P. G.; Gillespie, H. M.; Heywood, F. W.; McKenna, E. G. Lubricating oil compositions Eur. Patent 0713867,1996.
(18) Schwab, A. W.; Gast, L. E. Free radical addition of hydrogen sulfide to conjugated and nonconjugated methyl esters and to vegetable oils. *J. Am. Oil Chem. Soc.* **1970**, *47*, 371–373.
(19) Refvik, M. D.; Hasenberg, D. M.; Hankinson, M. S.; Matson, M. S.; Solaas, D. M.; Herron, S. J.; Byers, J. D. Thiol ester compositions and processes for making and using same U.S. Patent Appl. 20050197391, 2005.
(20) Bexell, U.; Berger, R.; Olsson, M.; Grehk, T. M.; Sundell, P.-E.; Johansson, M. Bonding of vegetable oils to mercapto silane treated metal surfaces: surface engineering on the nano scale. *Thin Solid Films* **2006**, *2*, 838–841.
(21) Samuelsson, J.; Jonsson, M.; Brinck, T.; Johansson, M. Thiol-ene coupling reaction of fatty acid monomers. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6346–6352.
(22) Bexell, U.; Olsson, M.; Sundell, P.-E.; Johansson, M.; Carlsson, P.; Hellsing, M. A ToF-SIMS study of linseed oil bonded to mercapto silane treated aluminum. *Appl. Surf. Sci.* **2004**, *231*−*232*, 362–365.
(23) Bexell, U.; Olsson, M.; Johansson, M.; Samuelsson, J.; Sundell, P.-E. A tribological study of a novel pre-treatment with linseed oil bonded to mercaptosilane treated aluminium. *Surf. Coat. Technol.* **2003**, *166*, 141–152.
(24) Lawate, S. S.; Lal, K.; Huang, C. Vegetable oils—structure and performance In *Tribology Data Handbook*, 1st ed.; Booser, E. R., Ed.; CRC Press: New York, 1997; pp 103−116.
(25) Ferreri, C.; Costantino, C.; Perrotta, L.; Landi, L.; Mulazzani, G. C.; Chatgilialoglu, C. Cis−trans isomerization of polyunsaturated fatty acid residues in phospholipids catalyzed by thiyl radicals. *J. Am. Chem. Soc.* **2001**, *123*, 4459–4468.
(26) Knothe, G.; Kenar, J. A.; Gunstone, F. D. In *The Lipid Handbook with CD ROM*, 3rd ed.; Gunstone, F. D., Harwood, J. L., Dijkstra, A. J., Eds.; CRC Press: Boca Raton, FL, 2007; pp 555−557.
(27) Goering, H. L.; Relyea, D. I., III. The radical addition of hydrogen sulfide, thiophenol and thioacetic acid to 1-chlorocyclohexene. *J. Am. Chem. Soc.* **1956**, *78*, 348–353.

**Received for review September 8, 2008. Revised manuscript received November 26, 2008. Accepted November 29, 2008. Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may be suitable.**

JF802774G