JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

J. Agric. Food Chem. **2008,** *56,* 5611–5616 **5611**

Azide Derivatives of Soybean Oil and Fatty Esters

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An environmentally friendly water-based pathway to form the azide derivatives of soybean oil and fatty esters is reported. This entails first the formation of epoxides and then the azidization of the epoxides. The azidization reaction is carried out at high yields in water with only a small amount of an ionic liquid as a catalyst. The distribution of azide and alcohol functionalities on the fatty acid moiety is approximately random. This reaction has been applied to methyl oleate, methyl linoleate, soybean oil, and methyl soyate. The resulting structures have been studied by NMR.

KEYWORDS: Soybean oil; azide; NMR; ionic liquid; epoxides

INTRODUCTION

Recently there have been a lot of research activities on azides. The azide functionality is useful as an intermediate in organic synthesis (e.g., Tamiflu) (*1*). It is also a good synthon for click reactions (*2–4*). In addition, azide is known to be thermally and photochemically labile. It can be readily converted to other functional groups, for example, to amines via reduction (*5–8*).

The azide is often produced via the chloroalkyl group using the sodium azide reaction (*9, 10*). An alternative is to lithiate the substrate and react it with a suitable azide under anhydrous conditions to replace most of the lithium with the azide (*11, 12*). Although many organic and polymeric substrates have been azidized, as far as we know, the azidization of fatty acids, esters, and vegetable oils has not been previously reported.

Vegetable oils and fatty acids are abundant natural materials. There is much interest in the literature in the reactions of these materials to produce cost-effective derivatives (*13*). Some examples are epoxidized oil (*14, 15*), soybean oil methyl ester (methyl soyate) (*16, 17*), maleated products (*18, 19*), derivatives of vegetable oils and fatty esters with diethyl azidodicarboxylate (*20, 21*), soybean oil polymers (*22–24*), and others (*25, 26*).

A goal of our work is to develop alternative methods for the introduction of nitrogen-containing derivatives to vegetable oil and fatty acids. Earlier we have explored some selected derivatives of soybean oil and fatty esters (*20, 21, 27, 28*). Many of these derivatives have interesting structures and properties. In this work, we report the azidization of soybean oil and fatty esters using an environmentally friendly synthetic pathway.

MATERIALS AND METHODS

Materials. Epoxidized soybean oil (Atofina, VIKOFLEX 7170, 4.2 oxirane moieties per triglyceride), methyl oleate (Sigma-Aldrich, St. Louis, MO, tech 70%; Nu Check Prep, Elsyian, MN, >99%), methyl linoleate (Nu Check Prep, >99%), methyl epoxy soyate (Arkema, Philadelphia, PA, 5.6% oxirane content), hydrogen peroxide (Sigma-Aldrich, ACS reagent, 30% solution), formic acid (Sigma-Aldrich, 96%, ACS reagent), hexanes (Sigma-Aldrich, >95%, HPLC grade), NaCl (Fisher, Fair Lawn, NJ, ACS reagent), and $NaHCO_3$ (Fisher, ACS reagent) were all used as received. All other materials were acquired from Sigma-Aldrich.

Epoxidation Reaction. The epoxidation of the unsaturated methyl esters of soybean oil has been performed as described elsewhere (*29–33*) The epoxidation of methyl oleate, methyl linoleate, and methyl linolenate resulted in fully epoxidized methyl oleate (EMO; methyl-9,10-oxirane octadecanoate), epoxidized methyl linoleate (EMLO; methyl-9,10:12,13-dioxirane octadecanoate), and epoxidized methyl linolenate (EMLEN; methyl- 9,10:12,13:15,16-trioxirane octadecanoate), respectively.

An epoxidation reaction was performed using hydrogen peroxide and formic acid catalyst. The reaction was followed directly by GC, to ensure complete conversion yet limit the productions of various polyhydroxy compounds. Purification was achieved using a separatory funnel. Extraction of the material with hexanes was also possible in the EMO and EMLO syntheses, which improved yields to 97 and 95%, respectively. The yield in the EMLEN case was 85%. Details on these syntheses are available elsewhere (*29–32*).

Azidization Reaction. To a 50 mL round-bottom flask containing 10 mL of water were added 10 g (44 mmol) of ionic liquid (IL) 1-methyl imidazolium tetrafluoroborate (*34*) and 5 g of epoxidized soybean oil (5.6 mmol) or 4.7 g of epoxy methyl linoleate (15 mmol). Sodium azide (1.9 g, 30 mmol) in water (5 mL) was added to the reaction mixture, and it was stirred using a stirring bar and heated at

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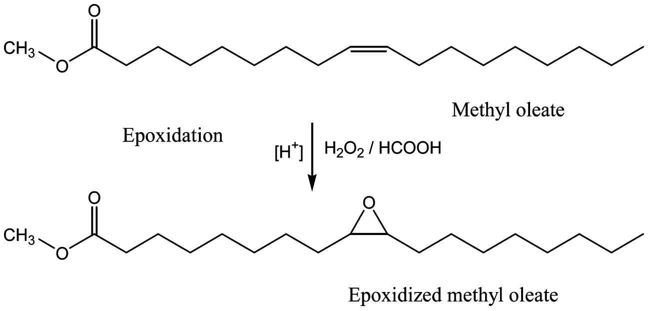
10.1021/jf800123t CCC: $40.75

Scheme 1. Epoxidation of Methyl Oleate To Form Epoxidized Methyl Oleate



65 °C for a few hours to a few days. The pH of the aqueous layer was 6.5. The mixture was cooled to room temperature and transferred to a 125 mL separatory funnel. It was then extracted with 30 mL of ethyl acetate twice. The ethyl acetate extracts were combined, washed successively with water and saturated sodium chloride solution, dried with magnesium sulfate, filtered, and evaporated in a rotatory evaporator to give the product as an oil in a very quantitative yield.

NMR Spectroscopy. All ^1H and ^{13}C NMR spectra were recorded quantitatively with a Bruker ARX-500 spectrometer (Bruker, Rheinstetten, Germany) at a frequency of 500 MHz (^1H) and 125 MHz (^{13}C) and a 5 mm dual probe. The sample solutions were prepared in deuterochloroform ($CDCl_3$, 99.8% D, Cambridge Isotope Laboratories, Inc., Andover, MA). Standard operating conditions were used.

RESULTS AND DISCUSSION

To incorporate the azide functionality to the fatty acid moiety, we need a suitable reaction sequence. A facile route is to convert the olefin on the fatty acid moiety into the 1,2-epoxide and then convert the epoxide to the azide. The first reaction (olefins to epoxides) is well-known; in fact, epoxidized soybean oil is commercially available. In this work, we carry out this reaction via formic acid and hydrogen peroxide. The example of methyl oleate is shown in **Scheme 1**.

The next step is to react the epoxide with sodium azide to form azidohydrin (β-azido alcohol). Whereas such a reaction is known to occur under different experimental conditions (*35–37*), we prefer to use mainly water as an environmentally friendlier medium. Unfortunately, the reaction barely proceeds in pure water. Taking a cue from Yadav et al. (*38*), we discovered that a small amount of an ionic liquid (IL) can catalyze this reaction in water.

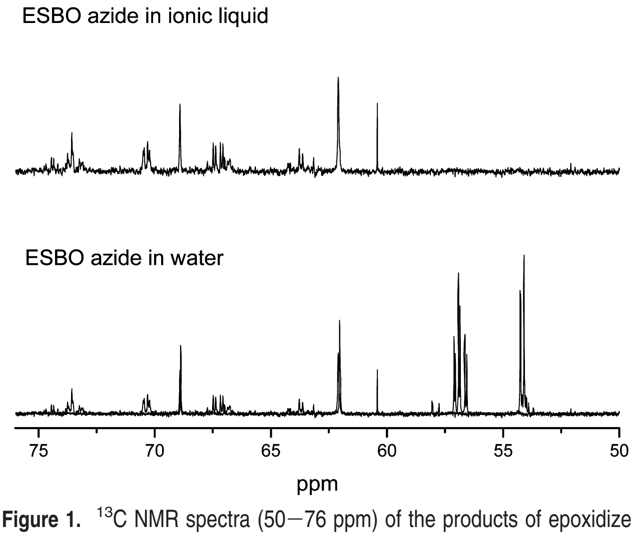


Figure 1. ^{13}C NMR spectra (50−76 ppm) of the products of epoxidized SBO and sodium azide in water and in ionic liquid.

Table 1. Reaction of Epoxidized Methyl Oleate with NaN_3[a]

sample	temperature (°C)	reaction time (days)	unreacted methyl oleate (%)	epoxide derivative (%)	azidohydrin derivative (%)
1	65	2	14	54	32
2	65	5	14	25	63
3	65	12	14	0	85

[a] Quantitation of unreacted methyl oleate and its epoxide and azidohydrin derivatives comes from ^{13}C NMR.

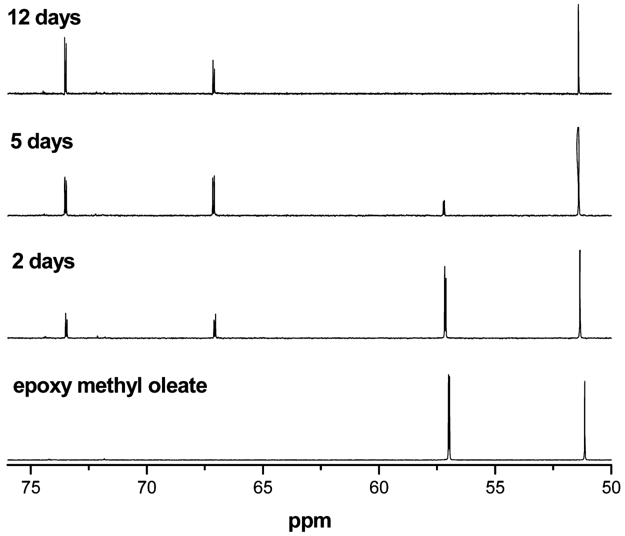


Figure 2. ^{13}C NMR spectra (50−76 ppm) of unreacted epoxidized methyl oleate (lower trace) and samples of its reaction with sodium azide (as shown in **Table 1**).

Table 2. Reaction of Epoxidized Methyl Linoleate with NaN_3[a]

sample	temperature (°C)	reaction time (days)	unreacted methyl linoleate (%)	epoxide derivative (%)	azidohydrin derivative (%)
4	65	1	2	78	20
5	65	3	2	18	80
6	65	6	2	0	98
7	65	15	2	0	98

[a] Quantitation of unreacted methyl linoleate and its epoxide and azidohydrin derivatives comes from ^{13}C NMR.

As an example, two reactions are carried out, one with water only and one with water and ionic liquid. The ^{13}C NMR spectrum of the reaction of epoxidized soybean oil and sodium azide in water and an ionic liquid is given in **Figure 1**, upper trace (2.1 g of 1-methylimidazolium tetrafluoroborate; ESBO 1.0 g, 1.1 mmol; NaN_3 0.653 g, 10 mmol; 2 mL of DI water; at 65 °C for 3 days). In this case, the ionic liquid is 1-methylimidazolium tetrafluoroborate. It is clear from the spectrum that all of the epoxides (which resonate at 54 and 57 ppm) have been reacted. In contrast, the ^{13}C NMR spectrum of the corresponding reaction of epoxidized soybean oil and sodium azide in water in the absence of an ionic liquid is given in **Figure 1**, lower trace (ESBO 1.038 g, 1.1 mmol; NaN_3 0.781 g, 12 mmol; 4 mL of DI water; at 65 °C for 3 days). The epoxide signals are mostly intact.

The reaction was carried out at lower temperature also, but the reaction was slower and took longer to complete. At 75 °C, no rate increase benefit was observed in the reaction; therefore, a reaction temperature of 65 °C was used in this study. To better

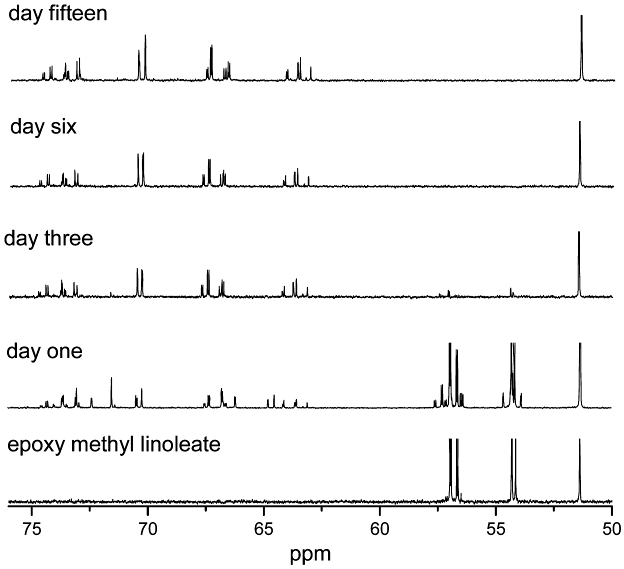


Figure 3. ^{13}C NMR spectra (50−76 ppm) of unreacted epoxidized methyl linoleate (lower trace) and samples of its reaction with sodium azide (as shown in **Table 2**).

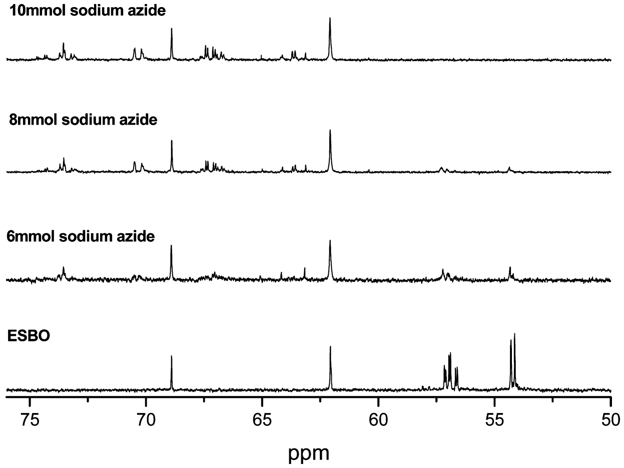


Figure 4. ^{13}C NMR spectra (50−76 ppm) of unreacted epoxidized SBO (lower trace) and samples of its reaction with sodium azide (as shown in **Table 3**).

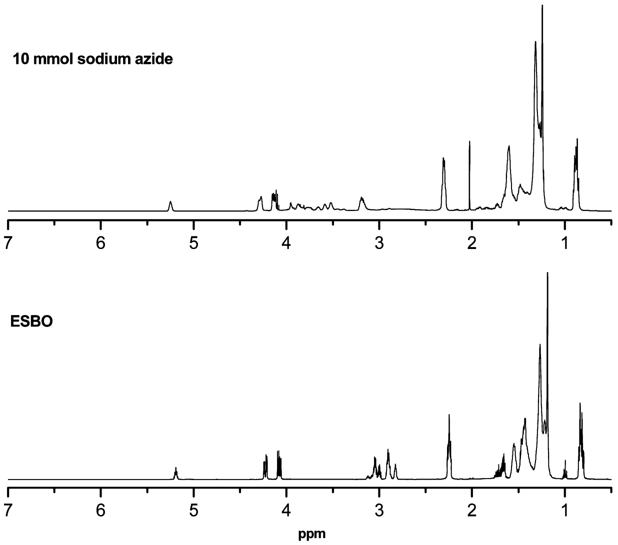


Figure 5. ^{1}H NMR spectra of unreacted and reacted epoxidized soybean oil.

Table 3. Reaction of Epoxidized Soybean Oil (1.1 mmol) with NaN_3[a]

sample	temperature (°C)	reaction time (days)	NaN_3 (mmol)	unreacted olefins (%)	epoxide derivative (%)	azidohydrin derivative (%)
8	65	1	6	2	48	50
9	65	2	8	2	10	88
10	65	2	10	2	0	98

[a] Quantitation of unreacted olefins and their epoxide and azidohydrin derivatives comes from ^{13}C NMR.

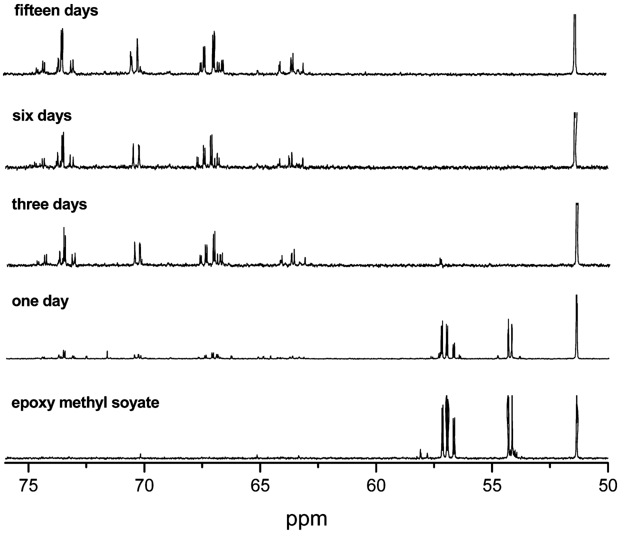


Figure 6. ^{13}C NMR spectra (50−76 ppm) of unreacted epoxidized methyl soyate (lower trace) and samples of its reaction with sodium azide (as shown in **Table 4**).

understand the reaction mechanism and to fully interpret the NMR spectra, we first studied the same reaction with methyl oleate and methyl linoleate.

Reaction with Methyl Oleate. Because the oleate moiety has only one olefin, this represents a simple case of azidization reaction (**Scheme 2**). Several examples of reactions involving epoxidized methyl oleate and sodium azide in the presence of water and an ionic liquid are shown in **Table 1**.

The reaction is complete in 12 days under the reaction conditions described. The ^{13}C NMR spectra are straightforward (**Figure 2**). The epoxide peaks are found at 57.18 and 57.23 ppm. In the product, the carbinol peak is found at 73.47 and 73.53 ppm, and the carbon bearing the azide resonates at 67.09 and 67.16 ppm. Two peaks are observed for the oleate olefinic carbons at ca. 129.4 ppm; this is known in the literature and has been explained via electric field effect (*39, 40*) or σ-inductive model (*41–43*)

Reaction with Methyl Linoleate. The linoleic acid moiety has two olefins, which add one additional degree of complexity. A reaction was carried out between epoxidized methyl linoleate and sodium azide at 65 °C at pH 6.5 in the presence of water and the ionic liquid 1-methylimidazolium tetrafluoroborate. A small aliquot was pulled from the reaction vessel at different times and analyzed by ^{13}C NMR. The samples are summarized in **Table 2**.

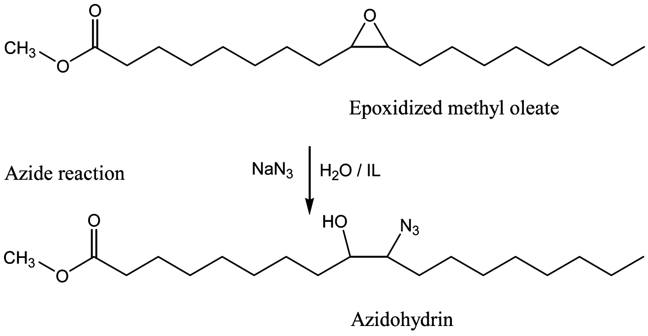
The reaction is complete in 6 days under similar reaction conditions. The ^{13}C NMR spectra are, however, much more complex (**Figure 3**). The spectrum of the starting epoxide is already complex: there are two clusters of peaks found at around 54.3 and 56.8 ppm, with a total of eight resolvable resonances. Gunstone (*44*) has previously made tentative assignments and shown that these are due to two diastereomers, where one is

Table 4. Reaction of Epoxidized Methyl Soyate with NaN_3[a]

sample	temperature (°C)	reaction time (days)	unreacted olefins (%)	epoxide derivative (%)	azidohydrin derivative (%)
11	65	1	<1	80	20
12	65	3	<1	10	90
13	65	6	<1	0	100
14	65	15	<1	0	100

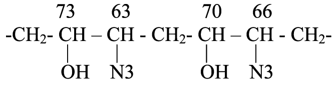
[a] Quantitation of olefins and their epoxide and azidohydrin derivatives comes from ^{13}C NMR.

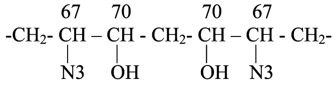
Scheme 2. Reaction of Epoxidized Methyl Oleate To Form the Corresponding Azidohydrin

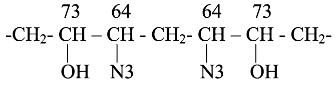


produced in larger amounts than the other. With azide reaction, many more peaks start to show up in the region of 63−75 ppm (**Figure 3**, day 1). When the reaction is complete, about 30−40 resolvable peaks can be found (**Figures 3**, days 6 and 15).

Because of the large number of peaks and diastereoisomerism, a detailed peak-by-peak assignment is not possible. However, we are able to carry out a group assignment. If we observe the peaks in the 63−75 ppm region, the peaks fall roughly into four groups: group 1 at 72.8−75.0 ppm, group 2 at 70.0−72.8 ppm, group 3 at 66.0−68.0 ppm, and group 4 at 62.0−65.0 ppm. If we look at possible azidohydrin structures that can result from azidization of epoxide, three structures are possible:


$$-CH_2-\overset{73}{\underset{OH}{CH}}-\overset{63}{\underset{N3}{CH}}-CH_2-\overset{70}{\underset{OH}{CH}}-\overset{66}{\underset{N3}{CH}}-CH_2-$$
structure I


$$-CH_2-\overset{67}{\underset{N3}{CH}}-\overset{70}{\underset{OH}{CH}}-CH_2-\overset{70}{\underset{OH}{CH}}-\overset{67}{\underset{N3}{CH}}-CH_2-$$
structure II


$$-CH_2-\overset{73}{\underset{OH}{CH}}-\overset{64}{\underset{N3}{CH}}-CH_2-\overset{64}{\underset{N3}{CH}}-\overset{73}{\underset{OH}{CH}}-CH_2-$$
structure III

We can use the empirical additive shift rules (*45*) and carry out an approximate calculation of the expected ^{13}C chemical shifts for the three structures. For OH in the tertiary structure, $\alpha = 48.0$, $\beta = 10.1$, $\gamma = -3.2$, $\delta = 0.8$. For the azide, we use two amines in sequence; approximately $\alpha = 38.8$, $\beta = 7.8$, $\gamma = -2.7$, $\delta = 0.3$. The 1,2-disubstitution correction factor used is −13.0 ppm. The calculated shifts are shown above under each structure. Thus, in the ^{13}C NMR spectrum, the four groups of peaks can be assigned to these three structures: group 1 (72.8−75.0 ppm), one carbon from structure I and two carbons from structure III; group 2 (70.0−72.8 ppm), one carbon from structure I and two carbons from structure II; group 3 (66.0−68.0 ppm), one carbon from structure I and two carbons from structure II; group 4 (62.0−65.0 ppm), one carbon from structure I and two carbons from structure III.

Of course, this group assignment ignores the fine structures observed within each group. These are due to diastereomerism arising from each structure. [The situation is analogous to polymer NMR, where stereoisomers and regioisomers are found (*46, 47*).] Additional (minor) splitting can occur due to electric field effect, just as in the case of methyl oleate. From quantitative integration, the spectral areas for groups 1−4 are roughly equal. Thus, there is no regiospecificity; the azidohydrin formation is random. The epoxide ring has approximately the same environment on both sides; thus, the effect of regioselectivity on product distribution was not observed. The epoxides in linoleate appeared to react equally at 65 °C.

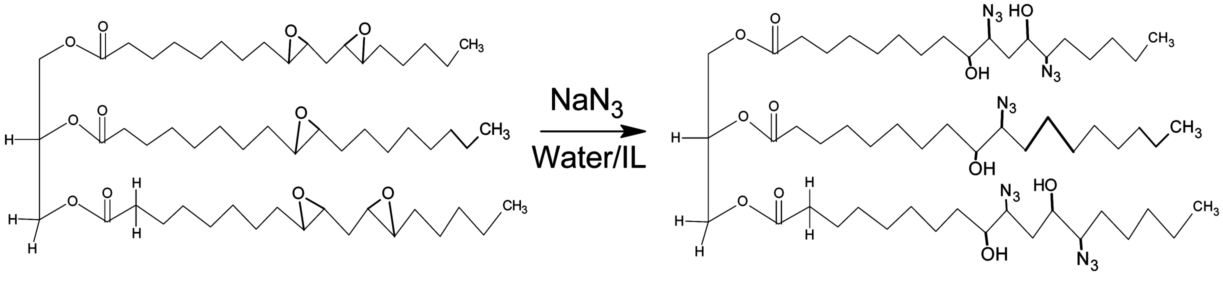
It may be noted that in addition to the main peaks in the NMR spectra, there are many small peaks as well. These are due to side reactions, particularly cyclic products.

Reaction with Soybean Oil (SBO). With a better knowledge of the NMR spectra of epoxidized methyl linoleate/sodium azide reaction, we are ready to tackle the epoxidized soybean oil/sodium azide reaction. SBO contains mostly triacylglycerols with a mixture of fatty acids moieties (typically 51% linoleic acid, 25% oleic acid, 10% palmitic acid, 7% linolenic acid, and 5% stearic acid). Palmitic and stearic acids will not undergo epoxidation reaction. The only added complication comes from linolenic acid moiety. The structures from epoxidized linolenic/sodium azide are expected to be more complex because of the many more diastereomers possible. However, because linolenic acid is present at only 7%, we can ignore it as a first approximation. Thus, we can treat the ^{13}C NMR spectrum of ESBO/sodium azide approximately as the sum of the epoxidized (oleic + linoleic)/sodium azide spectra.

Some examples of ESBO/sodium azide reaction are shown in **Table 3**. As before, the reactions were conducted at 65 °C. The amount of sodium azide was varied and was found to have a noticeable effect on the rate of reaction.

Two peaks stand out that are different from linoleate and oleate (at 62.0 and 68.9 ppm). These are due to the glycerol moiety, which is absent in the fatty esters. Other than these glycerol peaks, the ^{13}C NMR spectra in the 60−75 ppm region

Scheme 3. Reaction of Epoxidized Soybean Oil with Sodium Azide To Form Azide Derivative[a]



[a] The placement of azide and alcohol along the fatty acid moieties is approximately random.

can be organized into four groups, as in the linoleate case. In addition, the oleate carbons contribute to the scheme. The oleate carbinol is found in the peaks in group 1, and the oleate carbon directly bonded to azide is found among the peaks in group 3. The peaks (53 and 57 ppm) show a steady progression as epoxide decreases from 100 to 0% (**Figure 4**). Relative to the spectra of methyl linoleate, the ESBO/sodium azide spectra show peaks that are somewhat broadened and slightly less resolved. This is due to the overlap of peaks due to linolenate reactions.

^{1}H NMR data of the above reactions have also been obtained. The results basically corroborate the ^{13}C NMR findings. Examples of the ^{1}H NMR spectra of epoxidized soybean oil and soybean oil azidohydrin are given in **Figure 5**. After azide reaction, the epoxide peaks at ca. 3.0 ppm disappear, and the azidohydrin peaks appear as a complex pattern at around 3.4−4.0 ppm.

Thus, SBO can be converted to the azide derivative through the sequence of two reactions (epoxidation and azidization). From the ^{13}C NMR data, the reaction is essentially quantitative. The placement of azide and alcohol along the fatty acid moiety is approximately random. The reaction is shown in **Scheme 3**.

Reaction with Methyl Soyate. A popular derivative of soybean oil is methyl soyate (methyl ester of soybean oil). This is being used as a "biodiesel" for fuel applications and as a useful industrial solvent for grease removal. It is of interest to see if the azidization reactions can be applied to this material.

Epoxidation of methyl soyate is straightforward. The ^{13}C NMR spectrum shows that the reaction is essentially quantitative, with no residual olefin left (spectra not shown). The epoxide region (53−58 ppm) (**Figure 6**, lower trace) is rather similar to that of soybean oil.

The sodium azide reaction was carried out with epoxidized methyl soyate at 65 °C in the presence of water and the ionic liquid. A small aliquot was pulled from the reaction vessel at different times and analyzed by ^{13}C NMR. The samples are summarized in **Table 4**.

In this case, the azidization is complete in 6 days under similar reaction conditions. Interestingly, the ^{13}C NMR spectra are also similar, except for the absence of the glycerol peaks at 62.0 and 68.9 ppm. Again, the assignments can be based on four groups of reacted linoleate peaks and the reacted oleate peaks in groups 1 and 3.

In this work we have devised a water-based reaction for the azidization of epoxides in fatty esters and soybean oil. Only a small amount of an ionic liquid is needed to achieve high yields. The placement of azide and alcohol functionalities is approximately random. This reaction has been applied not only to methyl oleate, methyl linoleate, and soybean oil but also to methyl soyate (biodiesel). The structures have been confirmed by detailed NMR studies.

ACKNOWLEDGMENT

We thank Janet Berfield for expert technical assistance.

LITERATURE CITED

(1) Yarnell, A. Complexity of Tamiflu manufacturing may hamper on-demand production. *Chem. Eng. News* **2005**, *83* (35), 22.

(2) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click chemistry: diverse chemical function from a few good reactions. *Angew. Chem. Int. Ed.* **2001**, *40* (11), 2005–2021.

(3) Evans, R. A. The rise of azide-alkyne 1,3-dipolar 'click' cycloaddition and its application to polymer science and surface modification. *Aust. J. Chem.* **2007**, *60* (6), 384–395.

(4) Van Steenis, D. J. V. C.; David, O. R. P.; Van Strijdonck, G. P. F.; Van Maarseveen, J. H.; Reek, J. N. H. Click-chemistry as an efficient synthetic tool for the preparation of novel conjugated polymers. *Chem. Commun.* **2005**, (34), 4333–4335.

(5) Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G. Radical reduction of aromatic azides to amines with triethylsilane. *J. Org. Chem.* **2006**, *71*, 5822–5825.

(6) Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G. Radical reduction of aromatic azides to amines with tributylgermanium hydride. *J. Org. Chem.* **2006**, *71*, 434–437.

(7) Nyffeler, P. T.; Liang, C. H.; Koeller, K. M.; Wong, C. H. The chemistry of amine−azide interconversion: catalytic diazotransfer and regioselective azide reduction. *J. Am. Chem. Soc.* **2002**, *124*, 10773–10778.

(8) Lin, W.; Zhang, X.; He, Z.; Jin, Y.; Gong, L.; Mi, A. Reduction of azides to amines or amides with zinc and ammonium chloride as reducing agent. *Synth. Commun.* **2002**, *32* (21), 3279–3284.

(9) Kalir, A.; Balderman, D. 2-Phenyl-2-adamantanamine hydrochloride. *Organic Syntheses*; Wiley: New York, 1990; Collect Vol. VII, p 433.

(10) Nishikubo, T.; Iizawa, T.; Imagawa, I.; Kobayashi, K. Study of photopolymers. XVI. Novel syntheses of the polymers with azidonitrobenzoyl groups and their photochemical and thermochemical reactions. *J. Polym. Sci.: Polym. Chem. Ed.* **1981**, *19* (11), 2705–2719.

(11) Shey, J.; Holtman, K. M.; Wong, R. Y.; Gregorski, K. S.; Klamczynski, A. P.; Orts, W. J.; Glenn, G. M.; Imam, S. H. The azidation of starch. *Carbohydr. Polym.* **2006**, *65* (4), 529–534.

(12) Guiver, M. D.; Robertson, G. P. Process for producing azide-substituted aromatic polymers and the products thereof. U.S. Patent 5,475065, 1995.

(13) Biermann, U.; Friedt, W.; Lang, S.; Luhs, W.; Machmuller, G.; Metzger, J. O.; Rusch Gen. Klaas, M.; Schafer, H. J.; Schneider, M. P. New syntheses with oils and fats as renewable raw materials for the chemical industry. *Angew. Chem. Int. Ed.* **2000**, *3913*, 2207–2224.

(14) Petrovic, Z. S.; Zlatanic, A.; Lava, C. C.; Sinadinovic-Fiser, S. Epoxidation of soybean oil in toluene with peroxoacetic and peroxoformic acids−kinetics and side reactions. *Eur. J. Lipid Sci. Technol.* **2002**, *104* (5), 293–299.

(15) Kuo, M. C.; Chou, T. C. Kinetics and mechanism of the catalyzed epoxidation of oleic acid with oxygen in the presence of benzaldehyde. *Ind. Eng. Chem. Res.* **1987**, *26*, 277–284.

(16) Knothe, G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process. Technol.* **2005**, *86* (10), 1059–1070.

(17) Srivastava, A.; Prasad, R. Triglycerides-based diesel fuels. *Renewable Sustainable Energy Rev.* **2000**, *4* (2), 111–133.

(18) Warth, H.; Mulhaupt, R.; Hoffmann, B.; Lawson, S. Polyester networks based upon epoxidized and maleinated natural oils. *Angew. Makromol. Chem.* **1997**, *249*, 79–92.

(19) Tran, P.; Seybold, K.; Graiver, D.; Narayan, R. Free radical maleation of soybean oil via a single-step process. *JAOCS, J. Am. Oil Chem. Soc.* **2005**, *82* (3), 189–194.

(20) Biswas, A.; Sharma, B. K.; Willet, J. L.; Vermillion, K.; Erhan, S. Z.; Cheng, H. N. Novel modified soybean oil containing hydrazino-ester: synthesis and characterization. *Green Chem.* **2007**, *9* (1), 85–89.

(21) Biswas, A.; Sharma, B. K.; Willet, J. L.; Erhan, S. Z.; Cheng, H. N. Room-temperature self-curing ene reactions involving soybean oil. *Green Chem.* **2008**, doi 10.1039/b712385j.

(22) Li, F.; Hanson, M. V.; Larock, R. C. Soybean oil−divinylbenzene thermosetting polymers: synthesis, structure, properties and their relationships. *Polymer* **2001**, *42* (4), 1567–1579.

(23) Sharma, V.; Kundu, P. P. Addition polymers from natural oils−a review. *Prog. Polym. Sci. (Oxford)* **2006**, *31* (11), 983–1008.

(24) Khot, S. N.; Lascala, J. J.; Can, E.; Morye, S. S.; Williams, G. I.; Palmese, G. R.; Kusefoglu, S. H.; Wool, R. P. Development and application of triglyceride-based polymers and composites. *J. Appl. Polym. Sci.* **2001**, *82* (3), 703–723.

(25) Baber, T. M.; Graiver, D.; Lira, C. T.; Narayan, R. Application of catalytic ozone chemistry for improving biodiesel product performance. *Biomacromolecules* **2005**, *6* (3), 1334–1344.

(26) Benecke, H. P.; Vijayendran, B. R.; Elhard, J. D. U.S. Patent 6797753, 2004.

(27) Biswas, A.; Adhvaryu, A.; Gordon, S. H.; Erhan, S. Z.; Willett, J. L. Synthesis of diethylamine-functionalized soybean oil. *J. Agric. Food Chem.* **2005**, *53*, 9485–9490.

(28) Biswas, A.; Shogren, R. L.; Willet, J. L.; Erhan, S. Z.; Cheng, H. N. Modified soybean oil containing hydrazino-ester: derivatives from enzymatic reactions. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2006**, *47* (2), 259.

(29) Doll, K. M.; Erhan, S. Z. Synthesis of carbonated fatty methyl esters using supercritical carbon dioxide. *J. Agric. Food Chem.* **2005**, *53*, 9608–9614.

(30) Kurth, T. L.; Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Adsorption behavior of epoxidized fatty esters via boundary lubrication coefficient of friction measurements. *Chem. Eng. Commun.* **2007**, *194* (8), 1065–1077.

(31) Doll, K. M.; Erhan, S. Z. Synthesis and performance of surfactants based on epoxidized methyl oleate and glycerol. *J. Surfactants Detergents* **2006**, *9* (4), 377–383.

(32) Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Oxidation, friction reducing, and low temperature properties of epoxy fatty acid methyl esters. *Green Chem.* **2007**, *9*, 469–474.

(33) Bunker, S. P.; Wool, R. P. Synthesis and characterization of monomers and polymers for adhesives from methyl oleate. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (4), 451–458.

(34) Zhu, H. P.; Yang, F.; Tang, J.; He, M. Y. Brønsted acidic ionic liquid 1-methylimidazolium tetrafluoroborate: a green catalyst and recyclable medium for esterification. *Green Chem.* **2003**, *5* (1), 38–39.

(35) HudlickyT. Synthesis of sphingosines. U.S. Patent 5,488,167, 1996.

(36) Tamami, B.; Mahdavi, H. Synthesis of thiocyanohydrins from epoxides using quaternized amino functionalized cross-linked polyacrylamide as a new solid-liquid phase-transfer catalyst. *Tetrahedron Lett.* **2002**, *43* (35), 6225–6228.

(37) Sabitha, G.; Babu, R. S.; Reddy, M. S. K.; Yadav, J. S. Ring opening of epoxides and aziridines with sodium azide using Oxone® in aqueous acetonitrile: a highly regioselective azidolysis reaction 1. *Synthesis* **2002**, (15), 2254–2258.

(38) Yadav, J. S.; Reddy, B. V. S.; Jyothirmai, B.; Murty, M. S. R. Ionic liquids/H_2O systems for the reaction of epoxides with NaN_3: a new protocol for the synthesis of 2-azidoalcohols. *Tetrahedron Lett.* **2005**, *46* (38), 6559–6562.

(39) Batchelor, J. G.; Prestegard, J. H.; Cushley, R. J.; Lipsky, S. R. Electric field effects in the13C nuclear magnetic resonance spectra of unsaturated fatty acids. A potential tool for conformational analysisa. *J. Am. Chem. Soc.* **1973**, *95*, 6358–6364.

(40) Batchelor, J. G.; Cushley, R. J.; Prestegard, J. H. Carbon-13 fourier transform nuclear magnetic resonance. VIII. Role of steric and electric field effects in fatty acid spectra. *J. Org. Chem.* **1974**, *39*, 1698–1705.

(41) Bianchi, G.; Howarth, O. W.; Samuel, C. J.; Vlahov, G. Inductive interaction through up to fourteen saturated C−C bonds. *J. Chem. Soc., Chem. Commun.* **1994**, *5*, 627–628.

(42) Bianchi, G.; Howarth, O. W.; Samuel, A, C. J.; Vlahov, G. Long-range ?-inductive interactions through saturated C−C bonds in polymethylene chains. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1427–1432.

(43) Howarth, O. W.; Samuel, C. J.; Vlahov, G. The ?-inductive effects of C═C and C?C bonds: predictability of NMR shifts at sp2 carbon in non-conjugated polyenoic acids, esters and glycerides. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2307–2310.

(44) Gunstone, F. D. Study of natural epoxy oils and epoxidized vegetable oils by 13C nuclear magnetic resonance spectroscopy. *JAOCS, J. Am. Oil Chem. Soc.* **1993**, *70* (11), 1139–1144.

(45) Cheng, H. N.; Bennett, M. A. Trends in shift rules in carbon-13 nuclear magnetic resonance spectroscopy and computer-aided shift prediction. *Anal. Chim. Acta* **1991**, *242* (1), 43–56.

(46) Cheng, H. N. Structural studies of polymers by solution NMR *RAPRA Rev. Rep.* **2001**, *11* (5)(RAPRA Report 125).

(47) Cheng, H. N. Polymerization and statistical models. In *Encyclopedia of NMR*;Wiley: New York, 1995; pp 3713−3721.

Received for review January 14, 2008. Revised manuscript received March 24, 2008. Accepted April 16, 2008. 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 also be suitable.

JF800123T