

## TWO NEW METHODS FOR PRODUCING EPOXIDIZED OILS FOR INDUSTRIAL USES

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### Abstract

Epoxidized vegetable oils are produced in excess of 200 million lbs per year in the US. These epoxidized oils are used mainly as stabilizers-plasticisers for PVC. Currently epoxidation is conducted on an industrial scale using hydrogen peroxide with ether acetic or formic acid (1). This procedure is not selective, and it causes corrosion problems that are related to the acidity of the generated percarboxylic acids. Additionally, the product epoxides must be separated from the acids to limit oxirane ring-opening that nevertheless causes oxirane values to be 15-20% lower than theoretical. We have investigated two new ways to introduce epoxide functionality into fats and oils. In the first method dimethyldioxirane (DMDO) is generated and used in a biphasic system with a phase transfer catalyst (2). The second method uses the enzyme lipoxygenase to generate a hydroperoxide derivative. This is rearranged by a titanium catalyst to generate an epoxy alcohol derivative. The advantage of the former procedure over currently used epoxidation methodology is that epoxidation is nearly quantitative, and removal of reactants is simplified. The advantage of the second procedure is that an epoxy alcohol is obtained that has the potential to expand industrial uses of fats and oils.

### Introduction

Figure 1 shows the plasticizer production from plant oils and petrochemical feedstocks in the US in 1991. Although the plant oil based plasticizers are only a fraction of total plasticizer production, they still amount to 200 million pounds per year. If better methods of preparing plant oil based plasticizer could be found, the cost of these materials would be reduced, and their market share could be increased considerably. This would allow the US to decrease its dependence on imported petroleum.

We have developed two new procedures for epoxidizing plant oils. The first procedure uses a non-acidic epoxidation reagent under phase transfer conditions (3); the second procedure uses a combination of enzymatic and chemical catalysis to produce hydroxy epoxy derivatives of oils that have the potential of expanding the usage of fats and oils as plasticizers.

### Methods

**Chemical catalysis of epoxide formation under phase transfer conditions (Figure 2).** A typical reaction procedure with sunflower oil is shown as follows. The oil (2.03 g, 10.7 mmol

alkene) was dissolved in 20 mL 2-butanone (methyl ethyl ketone, MEK) that was stirred vigorously with a mixture of  $\text{NaHCO}_3$  (6.56 g, 78 mmol) and 0.5 g 18-crown-6, the phase transfer catalyst (PTC). A solution of Oxone™ (Aldrich Chemical Company, Milwaukee, WI), potassium monoperoxysulfate, (13.2 g, 21.5 mmol) in 75 mL distilled water was added over a 10 min period with the flask wrapped in foil to protect against light. After 2 h the reaction mixture was diluted with 100 mL water and extracted with 3 x 30 mL portions of diethyl ether. The combined organic extract was washed with 50 mL water and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent in vacuo, the epoxidized oil was subjected to transmethylation by treating it (0.10 g) with 0.05 g sodium methoxide in 10 mL methanol with stirring at RT for 1 h. The mixture was diluted with 20 mL water and extracted with 2 x 20 mL ether. After washing and drying over anhydrous  $\text{Na}_2\text{SO}_4$ , the ether was removed, and the product was subjected to GLC analysis.

**Epoxy hydroxy formation using sequential application of enzymatic and chemical catalysis (Figure 3).** *Methyl 13(S)-hydroperoxy-9(Z),11(E)-octadecadienoate (Me-HPODE) formation.* Linoleic acid (80 mg) was placed in a 125 mL Erlenmeyer flask along with 80 mL 0.2 M borate buffer, pH 9.0. The flask was packed in ice, and stoppered with a rubber septum. The contents were stirred gently for one-half hour while oxygen was slowly bubbled into the buffer using a metal syringe needle. Four 50  $\mu\text{L}$  aliquots of a lipoxygenase solution (32 mg/mL) in borate buffer were added at 30 min time intervals. The pH of the reaction media was lowered to 3 with 1 M HCl, and HPODE was extracted with 2 x 50 mL diethyl ether. The diethyl ether was dried over potassium sulfate, and the diethyl ether was removed under a stream of nitrogen. HPODE was dissolved in 5 mL  $\text{CH}_2\text{Cl}_2$  and treated with diazomethane to give the methyl ester.

*Titanium treatment.* Me-HPODE (27 mg, 83  $\mu\text{mol}$ ) dissolved in 4.7 mL  $\text{CH}_2\text{Cl}_2$  was treated with 63  $\mu\text{L}$  (212  $\mu\text{mol}$ )  $\text{Ti}(\text{O}-i\text{-Pr})_4$  for 1 h at 5°C. The reaction was quenched by the addition of 0.3 mL  $\text{H}_2\text{O}$ , and the reaction mixture was allowed to stand for 30 min at room temperature. The solid matter was removed by filtration through Celite. After washing the Celite with 10 mL of diethyl ether, the filtrate and wash were combined and the solvent was removed under a stream of dry nitrogen. The residue was dissolved in 6 mL  $\text{CH}_2\text{Cl}_2$ .

*Vanadium treatment.* Me-HPODE (95 mg, 291  $\mu\text{mol}$ ) dissolved in 14 mL  $\text{CH}_2\text{Cl}_2$  was treated with 26  $\mu\text{L}$  (1.5  $\mu\text{mol}$ )  $\text{VO}(\text{acac})_2$  for 1 h at 5°C. The reaction mixture was diluted with 50 mL diethyl ether and washed with water (3 x 30 mL). After drying over potassium sulfate, the solvent was removed under a stream of nitrogen.

## Results and Discussion

**Chemical catalysis of epoxide formation under phase transfer conditions.** A biphasic procedure in which a water-insoluble ketone is employed as both dioxirane reagent and organic solvent in conjunction with a phase transfer catalyst was investigated for its ability to introduce the epoxide functionality into fats and oils (3). Comparison of several ketones suggested that 2-butanone (ethylmethylketone, MEK) functioned best in this regard. Moreover, MEK is relatively insoluble in water and thus provides a phase for more intimate contact of the oxidant ethylmethyldioxirane (EMDO) with the triglycerides. In addition, the stability of EMDO with

respect to autodecomposition by radical fragmentation would be very similar to that of dimethyldioxirane and better than that of more highly substituted dioxiranes. The reactions involved in this sequence are summarized in Figure 2.

The results of an initial epoxidation of a number of fats and oils are shown in Table 1. The list of triglycerides is organized by type; namely, Group 1: low  $\alpha$ -linolenic acid residues ( $\leq 1\%$ ); Group 2: medium to high  $\alpha$ -linolenic acid content (7 to 54%) and Group 3: oils that contain less frequently encountered unsaturated fatty acids. Gas liquid chromatography was used to establish completeness of the epoxidation through loss of unsaturated fatty acids. This analysis, of course, would not permit an indication of possible polymerization due to ring cleavage. Oxirane determination (4) also is inexact because the addition of HBr to an epoxide ring can cause reaction of a neighboring epoxide ring to form a tetrahydrofuran (5). Thereby two epoxide rings are cleaved, but only a single HBr residue is consumed; ie, the stoichiometry of the standard method characteristically underestimates the oxirane content of epoxidized polyunsaturated materials. Our effort, therefore, was geared to obtaining oxirane numbers that would be better than or comparable to those of commercial samples of epoxidized soybean oil.

The low  $\alpha$ -linolenic oils and fats in Table 1 were converted to epoxidized products, and the GLC chromatograms of the corresponding methyl esters indicated little or no residual unsaturation. Corn oil, for example, was converted to an oxidized product that after transmethylation consisted of the epoxide of *cis*-9-octadecenoic acid and the diastereomeric diepoxides of *cis*, *cis*-9,12-octadecadienoic acids (5). In contrast, complete epoxidation of soya and canola oils, both of which contain significant amounts of linolenic acid (7-10%), proved difficult. Epoxidation of the soya oil with meta-chloroperbenzoic acid in methylene chloride did provide material that was free of unsaturation and that titrated near the theoretical oxirane value (89%). A commercial sample of epoxidized soybean oil likewise gave an oxirane value that was 90% of theoretical. A higher ratio of Oxone™ to oil (4:1) did not increase the epoxide content, and so we examined the epoxidations of methyl linoleate and linolenate. Using a ratio of 2.5:1 of Oxone™ to alkene (methyl linoleate) the product distribution was 29% monoepoxides, 61% diepoxides and 11% unreacted alkene; the total crude product titrated for 74% of theoretical oxirane. Rationalizing the low conversion as a slower epoxidation of the monoepoxidized material in competition with radical autodecomposition (6), the oxidant was added in two portions with an hour separating the additions. When conducted in this manner, the reaction mixture contained <2% unreacted alkene (GLC) and 83% of the theoretical oxirane content (titration). Similarly, methyl linolenate epoxidation was improved from 68% unreacted alkene to >99% triepoxides (GLC) and 87% of theoretical oxirane. Accordingly, both soybean and canola oil were epoxidized using the two-step addition of Oxone™ (total 2:1). Both epoxidized oils contained only minor amounts of residual unsaturated fatty acids and had 84% of the theoretical oxirane value. The efficiency of the two step epoxidation procedure was demonstrated further in the epoxidation of flax seed oil (54% linolenic acid). The product consists almost exclusively of the monoepoxide from oleic acid, the two diastereomeric diepoxides from linoleic acid and the four diastereomeric epoxides from linolenic acid and the unreactive saturated acids, palmitic and stearic. An example of the complete epoxidation of other oils in Table 1 is that of castor oil, where the ricinoleic acid was oxidized to the diastereomeric epoxides of (R)-12-hydroxy-*cis*-9-octadecenoic acid. As noted previously, biphasic oxidation favors epoxidation of the double

bond over oxidation of the alcohol to the ketone (7). On the other hand, biphasic oxidation of tung oil, whose major fatty acyl component is  $\alpha$ -eleostearic acid a conjugated polyunsaturated fatty acid, gave a product with the lowest oxirane value. Furthermore, GLC showed little unreacted unsaturated acyl groups and only small amounts of epoxide products indicating that tung oil triglycerides were polymerized rather than epoxidized.

Additional reaction parameters were evaluated to determine their importance to the epoxidation rate and the degree of conversion of the oils. Not surprisingly, the heterogeneous reaction mixture responded to those parameters normally associated with interfacial contact. Although an increase in the PTC, 18-crown-6, increased the rate of reaction, use of a Florence flask with vigorous magnetic stirring produced the same high conversions in about 1 h without additional PTC. The epoxidation of methyl oleate was conducted with varying amounts of Oxone™ under otherwise standardized conditions (nature of reaction vessel, agitation, amounts of solvents, PTC, NaHCO<sub>3</sub>, and rate of addition of the oxidant) and conversion to epoxidized ester was monitored by GLC. Approximately 75% of the oxidizing power of the Oxone™ was used during the first 30 min of reaction time counting the 10 min interval employed for the addition. Reactions would be essentially complete, therefore, in 1-2 h. This also indicated that more effective use could be made of the oxidant were it added in portions rather than at one time as noted above. Also, the amount of NaHCO<sub>3</sub> required for effective reaction depends upon maintaining a sufficiently high pH to sustain nucleophilic oxygen (persulfate anion). Reactions employing decreasing amounts of bicarbonate indicated consistent success with a 2.5:1 molar ratio of NaHCO<sub>3</sub> to Oxone™.

Other PTC's that served well included tetrabutylammonium chloride and bisulfate, and Aliquat™ 336. These were added in the same weight amounts as was the 18-crown-6 in the epoxidation of olive oil. Results from these reactions were not significantly different from those given in Table 1. The use of ammonium salts in place of crown ethers has notable advantages, since the salts are generally less expensive, are less toxic, and are recoverable from the reactions. Biphasic reactions of dioxiranes were conducted using organic solvents other than the ketone from which the dioxirane was prepared. In Table 2 is shown the degree of conversion achieved for the oxidation of soybean oil with several cosolvents. In each case the 2-butanone was present in 10-fold molar excess to the ester. In none of these cases was the conversion greater than when 2-butanone was employed as the solvent.

In summary, we studied the epoxidation of unsaturated fats and oils using Curci's biphasic method (3) employing 2-butanone as solvent and ethylmethyldioxirane as oxidant. The best conversions of polyunsaturate-containing oils were obtained with two-step addition of oxidant (Oxone™) with a molar ratio of oxidant to oil of 2.5:1. Moreover, epoxidation reactions also were successful when quaternary ammonium salts were used as phase transfer catalyst.

**Epoxy hydroxy formation using sequential application of enzymatic and chemical catalysis.** Me-HPODE was incubated with Ti(O-*i*-Pr)<sub>4</sub> for 1 h at 5°C. Analysis of the products by normal phase HPLC revealed a simple profile (Figure. 4). The peaks corresponding to minor products A were collected together. Their mass spectra were consistent with these being a mixture of methyl linoleate and conjugated methyl linoleate.

Product B comprised approximately 30% of the total product. Product B was identified as

methyl 13-hydroxy-9,11-octadecadienoate by comparison of its mass spectra to that of an authentic standard purchased from Oxford Biomedical Research (Oxford, MI).

Major product C accounted for approximately 67% of the total product. Its mass spectrum showed an ion at  $m/z$  288 (M-[18+31]). After formation of the  $(\text{CH}_3)_3\text{Si}$  derivative, its mass spectrum showed ions at  $m/z$  383 (M-15), 367 (M-31), 327 (M-71), 270 (M-128; rearrangement with expulsion of  $\cdot\text{CO}-\text{CH}(\text{O}\cdot)-\text{CH}_2)_4-\text{CH}_3$ ) (8) and 173 ( $(\text{CH}_3)_3\text{SiO}^+=\text{CH}-(\text{CH}_2)_4-\text{CH}_3$ ). The UV/VIS spectrum showed end absorbance below 210 nm. Thus the data show that compound C is a monounsaturated 18 carbon epoxy alcohol methyl ester containing the hydroxyl group at C-13.

The neat infrared spectrum of product C showed a broad band centered at  $3425\text{ cm}^{-1}$  (hydrogen bonded hydroxyl),  $1739\text{ cm}^{-1}$  (ester carbonyl), and  $890\text{ cm}^{-1}$  (*trans* epoxide). No absorption band appeared in the region  $900-1000\text{ cm}^{-1}$ , excluding the presence of *trans* double bond(s) (9).

The decoupled  $^{13}\text{C}$  NMR (100 MHz) spectrum of product C obtained in  $\text{C}_6\text{D}_6$  showed important signals at  $\delta$  51.6 ( $\text{OCH}_3$ ), 52.9 (C-12), 63.7 (C-11), 71.6 (C-13), and 174.2 ( $\text{C}(\text{O})\text{OCH}_3$ ). The solvent signal partially obscured those from the double bond carbons. Thus the  $^{13}\text{C}$  NMR spectrum was also obtained in  $\text{C}_4\text{D}_8\text{O}_2$  to give the signals for the double bond:  $\delta$  129.4 (C-10) and 137.5 (C-9). Since there are only two signals for the epoxide carbons, two signals for the double bond carbons, and one signal for the alcoholic carbon, product E is predominantly one structural isomer.

The  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz) spectrum of product C showed important signals at  $\delta$  2.97 (dd,  $J = 2.2, 4.6\text{ Hz}$ , 1H, H-12), 3.60 (br s, 1H, H-13), 3.88 (dd,  $J = 2.3, 8.7\text{ Hz}$ , 1H, H-11), 5.39 (dd,  $J = 9.0, 11.0\text{ Hz}$ , 1H, H-10), 5.80 (dt,  $J = 7.5, 11.2, 1\text{ Hz}$ , H-9). The coupling constant  $J_{9,10}$  was 11-11.2 Hz, demonstrating that the double bond is in the *cis* configuration:  $J = 5-14\text{ Hz}$  for *cis* protons and 12-18 Hz for *trans* protons (9). The coupling constant  $J_{11,12}$  was 2.2-2.3 Hz, demonstrating that the configuration of the epoxide group is *trans*:  $J = 4.3$  for *cis* and 2.1-2.4 for *trans* (10). The coupling constant  $J_{12,13}$  is 4.6 Hz, indicating that the relationship between the adjacent protons of the alcohol and the epoxide is *threo*:  $J = 5$  for *threo* and 3.25 for *erythro* (11). An analogous coupling constant reported for the *threo* derivative of an alcoholic epoxide derived from the action of the fungus, *Saprolegnia parasitica*, upon arachidonic acid was 4.5 Hz (12). In support of the *threo* assignment H-13 resonates at 3.60 ppm:  $3.8 \pm 1\text{ ppm}$  for *erythro* and  $3.5 \pm 1\text{ ppm}$  for *threo* (13).

From all of the data it is concluded that the stereochemical structure of product C is methyl 11(*R*),12(*R*)-epoxy-13(*S*)-hydroxy-9(*Z*)-octadecenoate (Figure 5).

Minor product D is formed from C when the epoxide is hydrolyzed. This was inadvertently shown when the reaction was conducted with a wet sample of Me-HPODE: Product D was the major product formed. The mass spectrum of the  $(\text{CH}_3)_3\text{Si}$  derivative of D and its UV/VIS spectrum demonstrated that product D is a 18 carbon trihydroxy methyl ester with a single double bond.

Larger amounts of product were subjected to HPLC analysis, and minor peaks were collected in order to determine if the *erythro* or other structural epoxy alcohol isomers were being formed. No other isomers were detected. One minor product identified was methyl 13-keto-9,11-octadecadienoate (14).

As an additional check on the findings, Me-HPODE was subjected to the action of  $\text{VO}(\text{acac})_2$ ,

since prior work had shown that both the *erythro* and *threo* epoxy alcohol isomers were formed by the action of this catalyst (15). HPLC and GC-MS analysis of the products derived from the action of VO(acac)<sub>2</sub> showed that two products had mass spectra identical to that of epoxy alcohol C. The *threo* epoxy alcohol eluted at 17.6 min, and the *erythro* isomer (vide ante) eluted at 14.6 min. The *erythro* and *threo* isomers comprised approximately 70% of the product, and the ratio of *erythro* to *threo* was 1.0:1.1. A minor product had a mass spectrum identical to that of alcohol B.

The results of the study with VO(acac)<sub>2</sub> showed that the *erythro* isomer of the epoxy alcohol and the alcohol B elute very closely during HPLC analysis. If the *erythro* isomer of the epoxy alcohol had been produced by Ti(O-*i*-Pr)<sub>4</sub> catalysis, then this isomer would have been collected along with alcohol B when sample was obtained for NMR analysis. Examination of the <sup>13</sup>C NMR of alcohol B in the region where epoxide carbons resonate revealed no discernible signals. From consideration of the signal to noise ratio, an estimate for the upper limit of the yield of the *erythro* isomer by Ti(O-*i*-Pr)<sub>4</sub> is 3%. Thus the results demonstrate that Ti(O-*i*-Pr)<sub>4</sub> is more *threo* selective than VO(acac)<sub>2</sub>. There have been few studies on the direct action of Ti(O-*i*-Pr)<sub>4</sub> on unsaturated hydroperoxides. However, the transfer of oxygen from saturated hydroperoxide to α,β-unsaturated alcohol has been intensively studied (16). These studies also showed that Ti(O-*i*-Pr)<sub>4</sub> is more *threo* selective than VO(acac)<sub>2</sub> (17).

Recent work has focused on the commercial development of plant species that contain unique fatty acid compositions (18). Two such species are *Lesquerella* and *Vernonia* which produce lesquerolic acid (14-hydroxy-*cis*-11-eicosenoic acid) and vernolic acid (12,13-epoxy-*cis*-9-octadecenoic acid), respectively. The alcohol epoxy material produced by the Ti(O-*i*-Pr)<sub>4</sub> rearrangement of Me-HPODE can be considered to be a hybrid of these two acids, and it has valuable properties that will make it uniquely useful for industrial use.

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**TABLE 1**  
**Epoxidation of Fats and Oils with Ethylmethyldioxirane<sup>a</sup>**

	Conversion <sup>b</sup>	Oxirane % <sup>c</sup>	Unsaturated Fatty Acyl Content(%)		
			Mono <sup>d</sup>	Di <sup>e</sup>	Tri <sup>f</sup>
<b>Group 1</b>					
Coconut	100	92	6	2	trace
Tallow	100	90	44	3	1
Corn	100	84	25	61	1
Olive	100	96	79	8	1
Safflower	100	88	13	78	trace
Sunflower	100	84	20	69	0
<b>Group 2</b>					
Soya	73	62	24	54	7
	99 <sup>g</sup>	89			
Canola	75	68	58	25	10
	99 <sup>g</sup>	90			
Rapeseed	96 <sup>g</sup>	88	60 <sup>h</sup>	12	7
Flaxseed	78	71	21	16	54
	99 <sup>g</sup>	92			

Group 3	Conversion <sup>b</sup>	Oxirane % <sup>c</sup>	Unsaturated Fatty Acyl Content(%)		
			Mono <sup>d</sup>	Di <sup>e</sup>	Tri <sup>f</sup>
Castor	100	97	94 <sup>i</sup>	4	0
Coriander	100	81	80 <sup>j</sup>	15	trace
Meadowfoam	100	91	71, <sup>k</sup>	20 <sup>l</sup>	0
Tung	97	38	7	.5	82 <sup>m</sup>

<sup>a</sup>These reactions used 2.0:1 Oxone™ to alkene equivalents.

<sup>b</sup>% Conversion of unsaturated fatty acids in the starting fat or oil to epoxides as determined by GLC of methyl esters.

<sup>c</sup>Determined by HBr/acetic acid titration (7).

<sup>d</sup>Oleic acid.

<sup>e</sup>Linoleic acid.

<sup>f</sup> $\alpha$ -Linolenic acid.

<sup>g</sup>Two-step addition of Oxone™.

<sup>h</sup>cis-13-Docosenoic acid (47%).

<sup>i</sup>12-Hydroxy-cis-9-octadecenoic acid (87%).

<sup>j</sup>cis-6-Octadecenoic acid (70%).

<sup>k</sup>cis-5-Eicosenoic acid (61%) + cis-13-docosenoic acid (10%).

<sup>l</sup>cis, cis-5,13-Docosadienoic acid (20%).

<sup>m</sup>cis, trans, trans-9,11,13-Octadecatrienoic acid (82%).

**TABLE 2****Phase Transfer Catalyzed Epoxidations of Soy Oil with Co-solvents<sup>a</sup>**

<b>Solvent</b>	<b>Conversion %<sup>b</sup></b>
2-butanone	73
chloroform	35
1,2-dichloroethane	44
methylene chloride	65

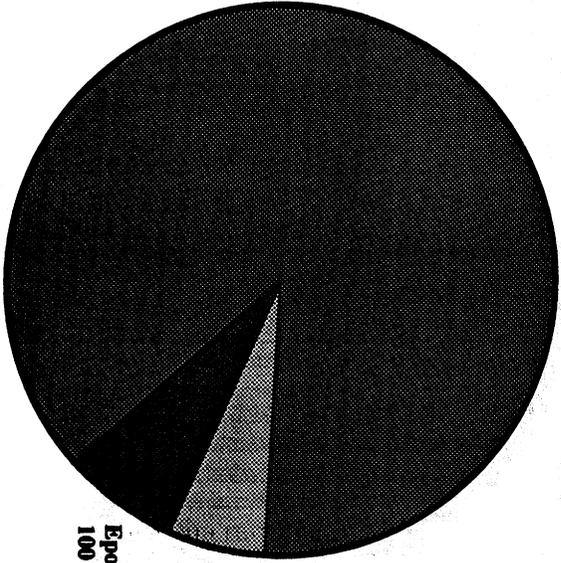
<sup>a</sup>Reactions were conducted with one-step addition of Oxone<sup>TM</sup> (see Materials and Methods) substituting the indicated solvent for 2-butanone and using 10 equivalents of the ketone to generate the dioxirane.

<sup>b</sup>Determined by GLC of methyl esters.

### Figure Legends

- Figure 1. Plasticizer production from plant oils and petrochemical feedstocks in the US.
- Figure 2. Generation of ethylmethyldioxirane (EMDO) and its use in methylethylketone (MEK) to convert unsaturated fats to epoxy derivatives.
- Figure 3. Generation of Methyl 13(*S*)-hydroperoxy-9(*Z*),11(*E*)-octadecadienoate (Me-HPODE) from oxygen using the enzyme lipoxygenase (LOX), and its conversion to alcohol epoxide using  $\text{Ti}(\text{O-}i\text{-Pr})_4$ .
- Figure 4. Normal phase HPLC analysis of the products obtained by the treatment of methyl 13(*S*)-hydroperoxy-9(*Z*),11(*E*)-octadecadienoate with  $\text{Ti}(\text{O-}i\text{-Pr})_4$ . Structural analyses, as discussed in the text, resulted in the following elucidations: A, methyl linoleate and its conjugated isomer; B, methyl 13(*S*)-hydroxy-9(*Z*),11(*E*)-octadecadienoate; C, methyl 11(*R*),12(*R*)-epoxy-13(*S*)-hydroxy-9(*Z*)-octadecenoate; D, trihydroxy hydrolysis product of C.
- Figure 5. Absolute configuration of alcohol epoxide arising from the rearrangement of Me-HPODE with  $\text{Ti}(\text{O-}i\text{-Pr})_4$ .

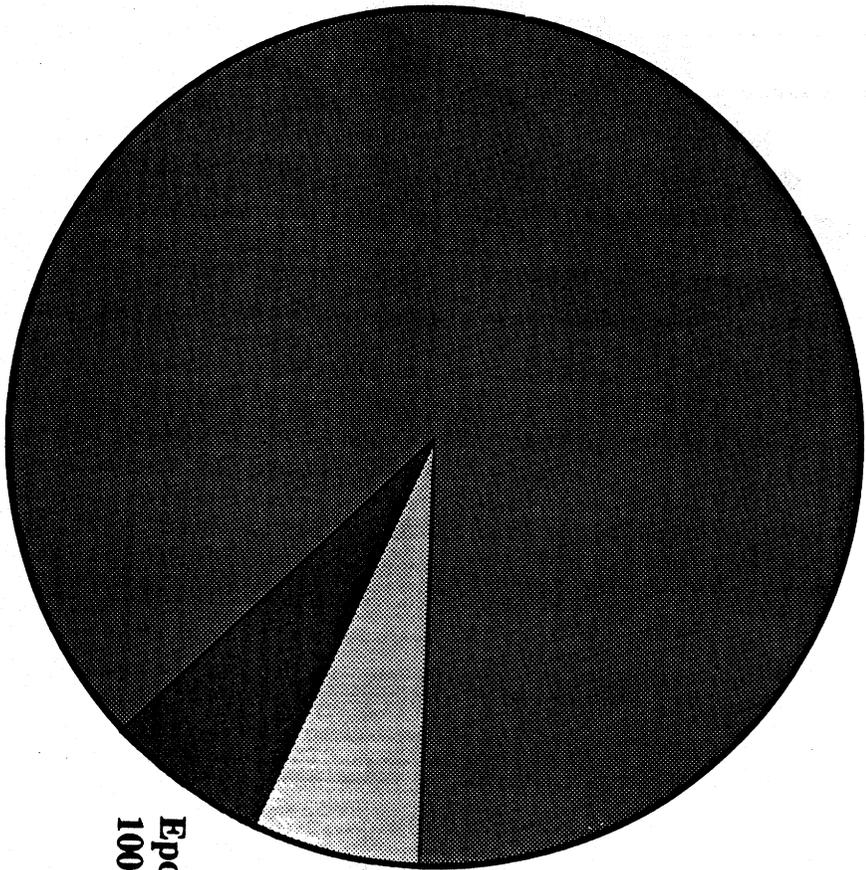
**Petrochemical Plasticizers  
1324 MM lb.**



**Other Plant-Based  
Plasticizers, 100 MM lb.**

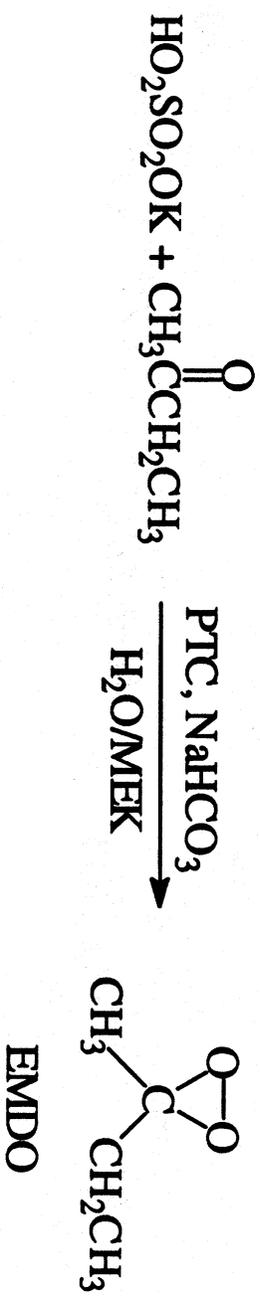
**Epoxidized Soybean Oil  
100 MM lb.**

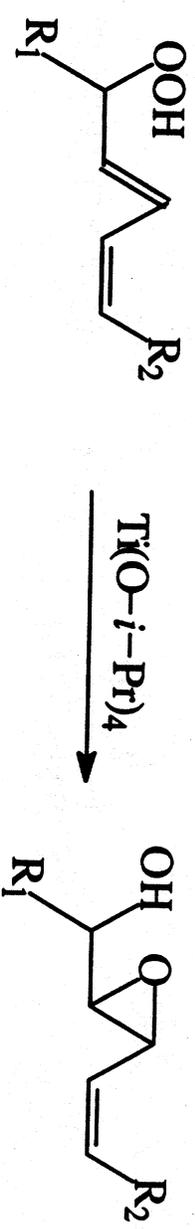
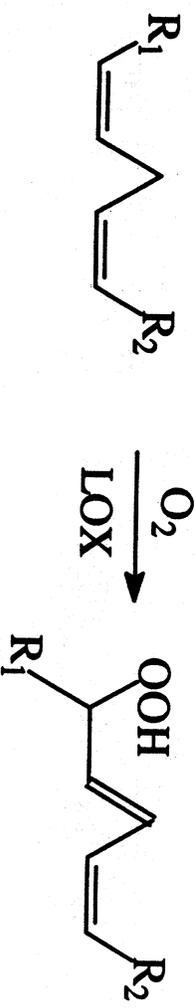
**Petrochemical Plasticizers  
1324 MM lb.**

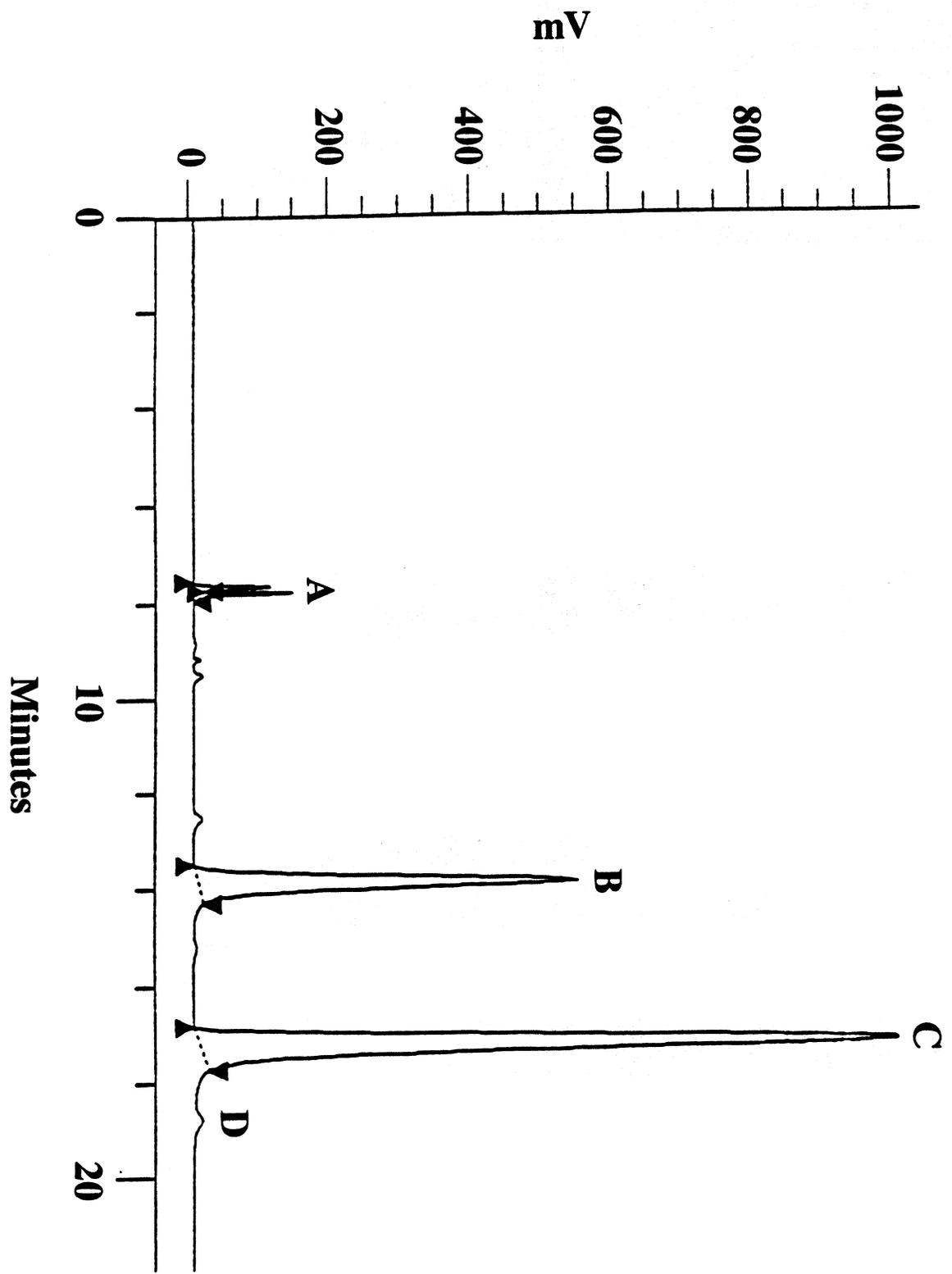


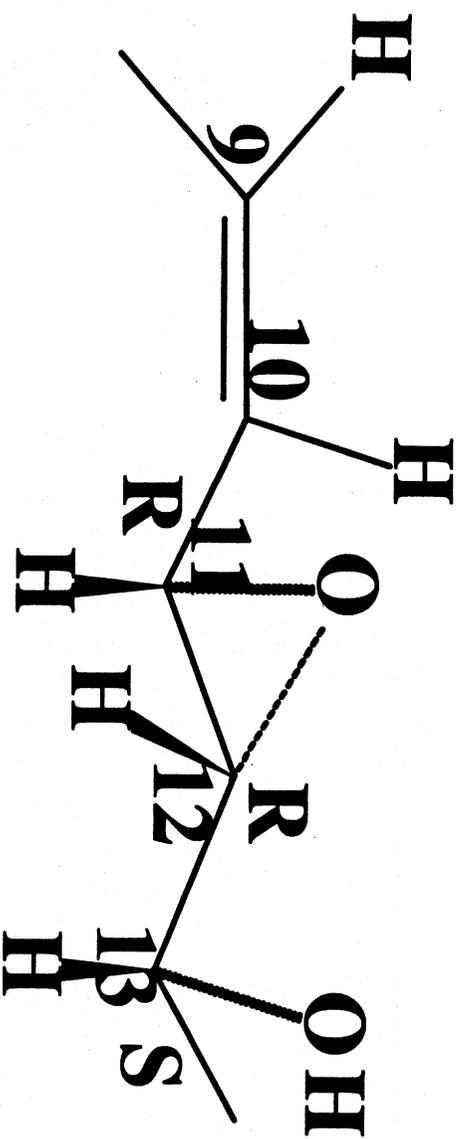
**Other Plant-Based  
Plasticizers, 100 MM lb.**

**Epoxidized Soybean Oil  
100 MM lb.**









Proton	Chemical Shift	Appearance of Spectrum	Coupling Constants
H-9	5.80 ppm	dt	7.5, 11.2 Hz
H-10	5.39 ppm	dd	9.0, 11.0 Hz
H-11	3.88 ppm	dd	2.3, 8.7 Hz
H-12	2.97 ppm	dd	2.2, 4.6 Hz
H-13	3.60 ppm	br s	

## Soapstock composition and its impact on the quality of cottonseed meal

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Except for a few small plants that use expellers, most cottonseed oil mills in the United States have converted to expanders to prepare kernels for oil extraction. These mills also incorporate miscella refining to increase productivity and to improve oil quality.

Soapstock is the main co-product of the refining process. Because of the limited markets for this material, most soapstock is blended with the defatted meal (marc) prior to solvent recovery and toasting.

If high quality seed is milled, the quantity of soapstock produced during refining is relatively small and the effect of added it to the extracted marc is minimal and predictable. Seed quality, though, is affected by weather condition before and during harvest. Wet weather activates lipases, which hydrolyze triglycerides to form free fatty acids (FFAs). The FFA content of high quality seed is typically less than 1%. In contrast, the FFA content of low quality seed can be above 10%. In addition to the degradation of oil that results because of lipase activity, the high FFAs increase the production of soapstock and the loss of neutral oil in soapstock. Addition of this added soapstock can reduce the percentage of meal protein below commercial specifications, which can only be compensated for by a reduction in the percentage of added hulls or high protein additives.

The composition of soapstock generated from several oil mills during the 1994-1995 processing season was studied. Soapstock from these mills averaged 41-45% moisture and residual solvent. On a dry basis, the material contained 47-52% sodium soap, 10-37% neutral oil, 4.2-10.5% gossypol, and 11.3-14.3% ash.

To ensure the composition of cottonseed meal, mills should account for the meal variation associated with the addition of soapstock. A discussion of the effects of adding soapstock to meal is presented, and general guidelines are given to regulate meal quality during times when poor quality seed must be processed.