Epoxidation of Natural Triglycerides with Ethylmethyldioxirane[1]

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ABSTRACT: Phase-transfer catalyzed biphasic epoxidation of a series of fats and oils with ethylmethyldioxirane in 2-butanone was conducted. The series of glycerides studied varied from monounsaturated (olive) to highly polyunsaturated (flaxseed) oils. Best conversions for polyunsaturate-containing oils were obtained with a molar ratio of 2.5:1 (oxidant/oil) with two-step addition of oxidant. Conversion to epoxides was monitored by gas–liquid chromatography, and oxirane content was determined by titration. The effect of phase-transfer catalyst or solvent used for the epoxidation reaction also was investigated.
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KEY WORDS: Biphasic epoxidation, epoxides, oils and fats, oxirane, phase-transfer catalyzed.

The conversion of soybean oil to epoxidized materials is conducted on a large scale with hydrogen peroxide and either acetic or formic acid (1). This procedure causes some concerns about safety and engenders corrosion problems that are related to the acidity of the percarboxylic acids used. Additionally, the product epoxides must be separated from the acids to limit oxirane ring-opening that would lower the oxirane values. More generally, peracid epoxidation of triglycerides that contain linoleoyl and linolenoyl acyl residues produces di- and triepoxides that have greater chemical sensitivity to acidic reagents. A newer epoxidation procedure for alkenes incorporates a phase-transfer catalyst (PTC) that is a solubilized tungsten catalyst, namely, trioctylmethylammonium tetra(diperoxotungsto) phosphate, with hydrogen peroxide (2). Use of this technique for epoxidation of soybean oil, however, gave products with low oxirane values (<80% of theory). Moreover, a technique for residue analysis (3) showed that this reaction left residual tungsten and phosphorus in the product that would limit its use.

Recently, the application of Curci *et al.*'s (4) two-phase technique (4) for epoxidizing alkenes with a dioxirane was reported, noting that the reaction of tallow and olive oil appeared to be complete (5). Here we report the results of a more comprehensive survey of the epoxidation of fats and oils and provide additional observations bearing on the efficacy of the dioxirane epoxidation reaction.

MATERIALS AND METHODS

Materials. All reagents were purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received. The sources of the triglycerides are as follows: coconut oil, Stokely Van-Camp, Inc. (Harrison, NJ); corn, canola, and sunflower oils, Wesson Co. (Fullerton, CA); castor oil, Thrift Drug, Inc. (Pittsburgh, PA); coriander and meadowfoam oils were obtained from Dr. Robert Kleiman of NCAUR, ARS, USDA (Peoria, IL); olive oil, Sigma Chemical Co. (St. Louis, MO); rapeseed oil, Calgene Chemical Co. (Skokie, IL); safflower oil, Pet Inc. (St. Louis, MO); soybean oil (Pioneer Hybrid International, Inc., Des Moines, IA); tallow, Miniat Inc. (Chicago, IL); tung oil was obtained from Dr. Edith Conkerton of SRRC, ARS, USDA (New Orleans, LA).

Analysis. Gas–liquid chromatography (GLC) of methyl esters of epoxidized triglycerides was performed with a Chrompack-Packard Model 438A instrument (Avondale, PA) with helium carrier gas in a 50:1 split ratio and a flame-ionization detector. An SPB-1 column (0.25 mm i.d. × 30 m) from Supelco (Bellefonte, PA) was used with the following program: 200°C (17 min), 5°C/min to 250°C, 250°C (10 min). Methyl esters of the triglycerides were analyzed by GLC on an SP-2340 column (0.25 mm i.d. × 60 m) from Supelco with the following oven program: 140°C, 0.5°C/min to 150°C, then 2°C/min to 200°C, 200°C (20 min) to obtain a value of equivalents of alkene/per gram of triglyceride. This information, coupled with GLC data from the methyl esters of the epoxidized triglycerides, allowed determination of the degree of conversion. Analysis for oxirane content was by titration of the epoxidized oil with standard HBr/acetic acid to a methylene blue endpoint (6). Chromatographic identification of the epoxidized products was made by direct comparison with the epoxidation products obtained from *m*-chloroperbenzoic acid treatment of methyl oleate, linoleate, and linolenate. A recently published analysis of epoxidized soybean oil indicated chromatographic detail that was indistinguishable from that produced in this study (7); the oxidation products are now so familiar that no additional justification of structure was sought.

Biphasic oxidation of triglycerides. The following procedure constitutes the "standard" one-step addition reaction and

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[1] In our previous report we referred to the oxidant as methylethyldioxirane to indicate its source by common name, methylethylketone. The IUPAC name alphabetizes the alkyl groups.

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is exemplified with sunflower oil. The oil (2.03 g, 10.7 mmol of alkene) was dissolved in 20 mL of 2-butanone that was stirred vigorously with a mixture of NaHCO$_3$ (6.56 g, 78 mmol) and 0.5 g of 18-crown-6, the PTC catalyst. A solution of Oxone™ (Aldrich, Milwaukee, WI), potassium monoperoxysulfate (13.2 g, 21.5 mmol) in 75 mL of 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 of water and extracted with 3 × 30 mL portions of diethyl ether. The combined organic extract was washed with water (50 mL) and then dried (anhydrous Na$_2$SO$_4$), and the solvent was removed *in vacuo*. The crude reaction product, an oil, was then stored at 0–5°C for subsequent oxirane and GLC analysis.

For the two-step epoxidation procedure, the Oxone™ (molar ratio of 2:1; oxidant:alkene) in 75 mL of water was added in two equal portions, 1 h apart. Reaction products were isolated as in the one-step procedure.

Transmethylation of epoxidized oils. The epoxidized triglyceride (0.10 g) and 0.05 g sodium methoxide in 10 mL methanol were stirred at room temperature for 1 h. The mixture was diluted with 20 mL of water and extracted with ether (2 × 20 mL). The combined ether layer was washed twice with 10 mL portions of water, dried (Na$_2$SO$_4$) and concentrated. Materials were stored at 0–5°C for GLC analysis.

RESULTS AND DISCUSSION

Dioxiranes have been prepared by reaction of ketones with aqueous slurries of sodium bicarbonate and Oxone™, monopotassium peroxysulfate, as solutions in the parent ketones (8). These solutions have been employed to conduct oxidations of diverse classes of organic compounds. For an industrially useful process, however, a single step, in which the dioxirane is generated and used directly, seemed preferable. Curci's biphasic procedure (4), in which a water-insoluble ketone is employed as both dioxirane reagent and organic solvent in conjunction with a PTC, appeared attractive. 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 ***I*** with the triglycerides. In addition, the stability of ***I*** with respect to autodecomposition by radical fragmentation would be similar to that of dimethyldioxirane and better than that of more highly substituted dioxiranes. The reactions involved in this sequence are summarized in Equations 1 and 2 (Scheme 1).

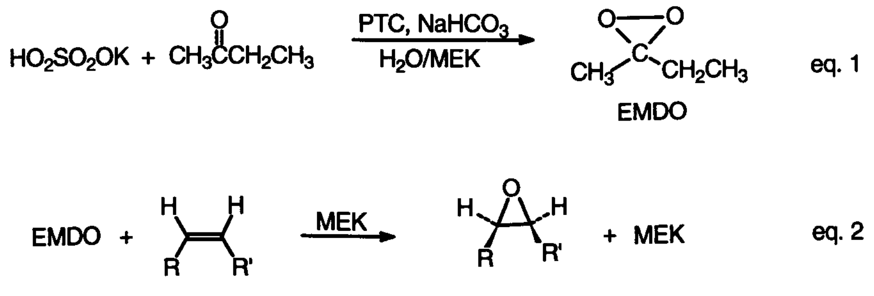
The results of initial epoxidations of a number of fats and oils are shown in Table 1. The reaction details are provided in the experimental section; the data shown are the average of at least two trials. The list of triglycerides is organized by type, namely, Group 1, low α-linolenic acid residues ($\leq$1%); Group 2, medium to high α-linolenic acid content (7–54%); and Group 3, oils that contain less frequently encountered unsaturated fatty acids. Details of the analyses are also provided in the Experimental section. GLC 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 (6) also is inexact because the addition of HBr to an epoxide ring can cause reaction of a neighboring epoxide ring to form a tetrahydrofuran (9). In this way, two epoxide rings are cleaved, but only a single HBr residue is consumed, i.e., 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.

TABLE 1
Epoxidation of Fats and Oils with Ethylmethyldioxirane[a]

		Unsaturated fatty acyl content (%)			
	Conversion[b]	Oxirane %[c]	Mono[d]	Di[e]	Tri[f]
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
Soy	73	62	24	54	7
	99[g]	89			
Canola	75	68	58	25	10
	99[g]	90			
Rapeseed	96[g]	88	60[h]	12	7
Flaxseed	78	71	21	16	54
	99[g]	92			
Castor	200	97	94[i]	4	0
Coriander	100	81	80[j]	15	trace
Meadowfoam	100	91	71[k]	20[l]	0
Tung	97	38	7	5	82[m]

[a] These reactions used 2.0:1 Oxone™ (Aldrich, Milwaukee, WI) to alkene equivalents.
[b] Percentage conversion of unsaturated fatty acids in the starting fat or oil to epoxides as determined by gas–liquid chromatography of methyl esters.
[c] Determined by HBr/acetic acid titration (Ref. 7).
[d] Oleic acid.
[e] Linoleic acid.
[f] α-Linolenic acid.
[g] Two-step addition of Oxone™.
[h] *cis*-13-Docosenoic acid (47%).
[i] 12-Hydroxy-*cis*-9-octadecenoic acid (87%).
[j] *cis*-6-Octadecenoic acid (70%).
[k] *cis*-5-Eicosenoic acid (61%) + *cis*-13-docosenoic acid (10%).
[l] *cis, cis*-5,13-Docosadienoic acid (20%).
[m] *cis, trans, trans*-9,11,13-Octadecatrienoic acid (82%).

The low α-linolenic oils and fats in Table 1 were converted to epoxidized products, and the chromatograms (GLC) 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 (9) of *cis, cis*-9,12-octadecadienoic acids (Fig. 1A). In contrast, complete epoxidation of soy and canola oils, both of which contain significant amounts of linolenic acid (7–10%), proved difficult. Epoxidation of the soy oil with *meta*-chloroperbenzoic acid in methylene chloride did provide



SCHEME 1

material that was free of unsaturation (GLC) and that titrated near the theoretical oxirane value (89%). A commercial sample of epoxidized soybean oil similarly gave an oxirane value that was 90% of theoretical. A higher ratio of Oxone™ to oil (4:1) did not increase the epoxide content; thus, we examined the epoxidations of methyl linoleate and linolenate. With a ratio of 2.5:1 of Oxone™ to alkene (methyl linoleate), the GLC product distribution was 29% monoepoxides, 61% diepoxides, and 11% unreacted alkene; the total crude product titrated to 74% of theoretical oxirane. Rationalizing the low conversion as a slower epoxidation of the monoepoxidized material in competition with radical autodecomposition (10), the oxidant was added in two portions with 1 h 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 oils were epoxidized by 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 (Fig. 1B and C, respectively). The efficiency of the two-step epoxidation procedure was demonstrated further in the epoxidation of flaxseed oil (54% linolenic acid). As shown in Figure 1D, 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 (Fig. 2). As noted previously, biphasic oxidation favors epoxidation of the double bond over oxidation of the alcohol to the ketone (5). On the other hand, biphasic oxidation of tung oil, whose major fatty acyl component is α-eleaostearic 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.

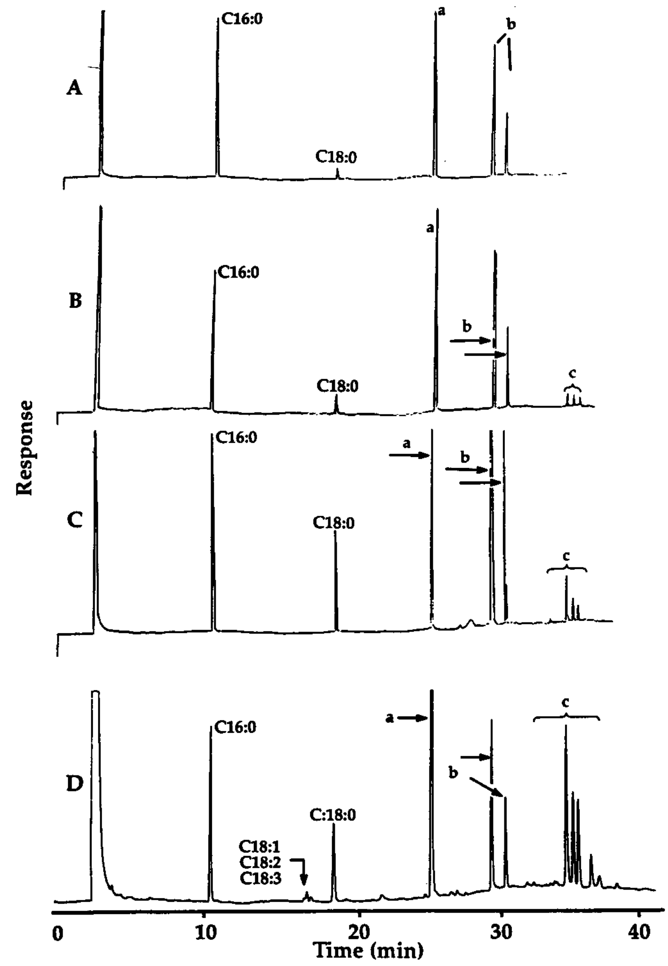


FIG. 1. Gas-liquid chromatography of methyl esters of epoxidized oils. A: Epoxidized corn oil; 16:0, methyl palmitate; 18:0, methyl stearate; a, methyl *cis*-9,10- epoxystearate; b, diastereomers of methyl *cis,cis*-9,10-12,13-diepoxystearate. B: Epoxidized soy oil; c, diastereomers of methyl *cis, cis, cis*,-9,10-12,13-15,16-triepoxystearate. C: epoxidized canola oil. D: epoxidized flaxseed oil; 18:1, methyl oleate; 18:2, methyl linoleate; 18:3, methyl linolenate.

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, $NaHCO_3$, and rate of addition of the oxidant), and con-

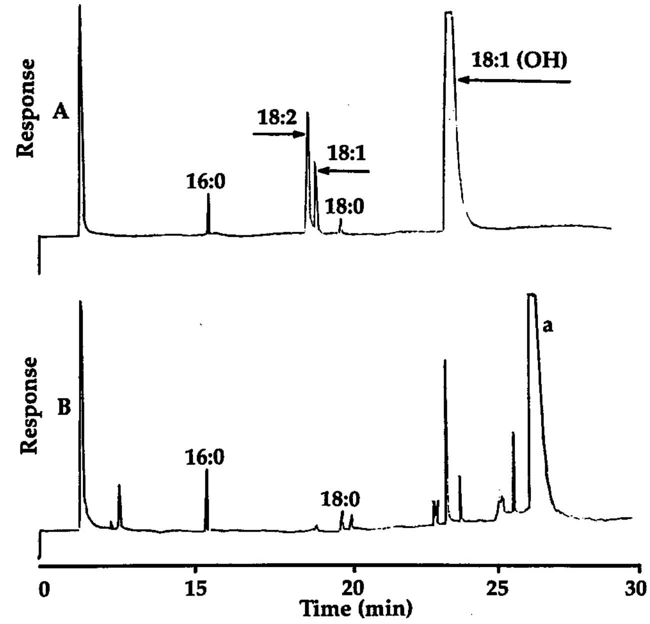


FIG. 2. Gas–liquid chromatography of methyl esters of castor oil (A) and epoxidized castor oil (B): 16:0, methyl palmitate; 18:0, methyl stearate; 18:1, methyl oleate; 18:2, methyl linoleate; 18:1 (OH), methyl ricinoleate; a, methyl-12-hydroxy-*cis*-9,10-epoxystearate.

version 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 if it were added in portions rather than at one time, as noted above. Also, the amount of $NaHCO_3$ 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 $NaHCO_3$ to Oxone™.

Other PTC 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 because the salts are generally less expensive, less toxic, and can be recovered from the reactions. Biphasic reactions of dioxiranes were conducted in organic solvents other than the ketone in which the dioxirane was prepared. Table 2 shows the degree of conversion achieved for the oxidation of soybean oil with several co-solvents. 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.

TABLE 2
Phase-Transfer Catalyzed Epoxidations of Soy Oil with Co-Solvents[a]

Solvent	Conversion %[b]
2-Butanone	73
Chloroform	35
1,2-Dichloroethane	44
Methylene chloride	65

[a]Reactions were conducted with one-step addition of Oxone™ (see Materials and Methods for details and Table 1 for company source) substituting the indicated solvent for 2-butanone and using 10 equivalents of the ketone to generate the dioxirane.

[b]Determined by gas–liquid chromatography of methyl esters

In summary, we have studied the epoxidation of unsaturated fats and oils by Curci *et al.*'s (4) biphasic method with 2-butanone as solvent (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 PTC.

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