

# Chemical Epoxidation of a Natural Unsaturated Epoxy Seed Oil from *Vernonia galamensis* and a Look at Epoxy Oil Markets

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## ABSTRACT

Since 1963, production of all epoxy esters has ranged from 60 to 150 million lb annually, a steady 7% of the 1 to 2 billion lb of annual plasticizer production. Growth rates in production averaged 4.3% for all plasticizers, 3.8% for all epoxy esters and 5.0% for epoxidized soybean oil (ESBO). ESBO accounted for 70-76% of total epoxy ester production (1963-1982). The natural liquid epoxy oil from *Vernonia galamensis* seed, with oxirane value (4.1%) and viscosity (100 cps) similar to some commercial epoxy fatty esters but with molecular weight similar to epoxidized vegetable oils, combines some of the properties of both commercial types. Chemical epoxidation of *Vernonia* oil raises the oxirane content to 8.2, intermediate between ESBO and epoxidized linseed oil (ELSO), while consuming less of the costly epoxidizing reagents. Epoxidation proceeds in stepwise fashion through partially epoxidized products, which are converted to final product. Since the major fatty components of *Vernonia* oil are *cis*-12,13-epoxy-9-octadecenoic (75%) and linoleic (13%) acids, further epoxidation produces fatty acids that are specifically epoxidized at the 9,10- and 12,13-positions, and the major product has 6 epoxy units per triglyceride molecule. The resulting mixture of products has compositional and physical properties distinctly different from commercial samples of ESBO and ELSO.

## INTRODUCTION

### Trends in Production of Epoxidized Esters

Referred to collectively as epoxidized esters, three basic groups of epoxidized products are made from vegetable oils: (a) epoxidized triglyceride oils, (b) mixed epoxy fatty esters (e.g., linseedates, tallates) and (c) specific epoxy fatty esters (e.g., oleates, stearates). Their importance as plasticizers and additives in flexible polyvinyl chloride (PVC) resins stems from excellent heat and light stability imparted to the finished products by the oxirane groups (1). Since 1963, production of all such epoxidized esters has ranged from 60 to 150 million lb annually, averaging 7% of the 1 to 2 billion lb of annual plasticizer production (Fig. 1) (2). Epoxidized soybean oil (ESBO) accounted for 70-76% of the total epoxidized ester production (1963-1982). Miscellaneous epoxy esters and epoxidized linseed oil (ELSO) made up the remainder. Growth rates in production during this period averaged 4.3% for all plasticizers, 3.8% for epoxidized esters and 5.0% for ESBO. Production of the plasticizer industry standard, dioctylphthalate (DOP), has declined in recent years from peak levels of the 1970's. The volatility of the industry, however, is illustrated in Figure 2, which shows the mean annual growth rates for all plasticizers, DOP and all epoxy esters (1966-1982). Exceptional growth periods were followed by marked recessionary periods, the most notable adjustments occurring around the oil embargo period in the mid-1970's. The steep price increases associated with this extraordinary event are shown for the epoxidized esters in Figure 3. Prices for all epoxidized esters averaged 26¢/lb prior to 1974, doubled during 1974-1975 and stabilized at ca. 50¢/lb thereafter (1975-1982). ELSO appears to have settled at a level 50% higher at 76¢/lb (1974-1982). Peak production of ESBO (130 million lb) occurred as a result of especially rapid production growth rates in 1972 (21%) and 1973 (38%). Production since 1974 has stabilized near 85 million lb at an average

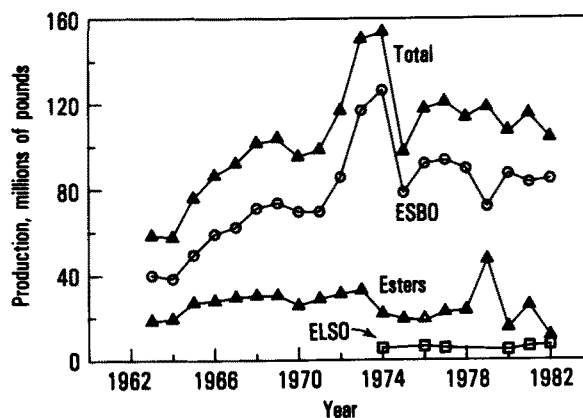


FIG. 1. Production of epoxidized vegetable oils and their esters from 1963 to 1982. ELSO = epoxidized linseed oil; ESBO = epoxidized soybean oil; Esters = misc. epoxidized tallates, oleates and stearates. (Source: U.S. Int. Trade Commission, Ref. 2.)

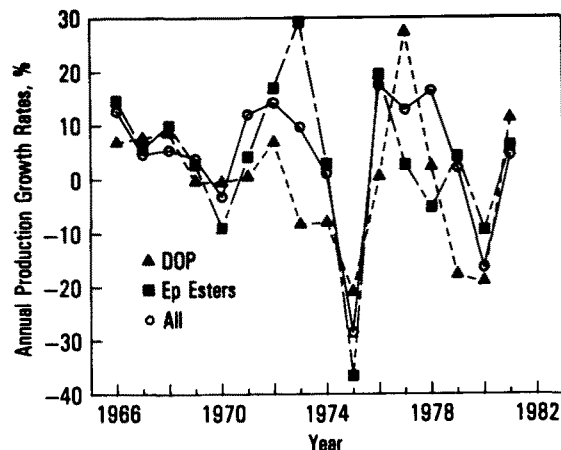


FIG. 2. Annual growth rates in production of selected plasticizers. DOP = dioctyl phthalates; ALL = all plasticizers; Ep Esters = all epoxidized oils and their esters. (Source: U.S. Int. Trade Commission, Ref. 2.)

price of 48¢/lb (1974-1982). According to the U.S. International Trade Commission's annual tabulations of production and sales of synthetic organic chemicals (2), at least 20 companies have reported production of epoxidized esters over the years, with 7-11 mainstays in any given year. Only two or three companies have produced epoxidized esters continuously since 1963. Most recent data show five producers of ELSO, nine of ESBO and four of other epoxidized esters. Following the events of 1974-1975, the average number of producers of high-priced ELSO doubled (from 2 to 4), the average number of producers of miscellaneous epoxidized esters (tallates, oleates, stearates) decreased (from 8 to 4) and the number of ESBO producers remained the same at seven or eight.

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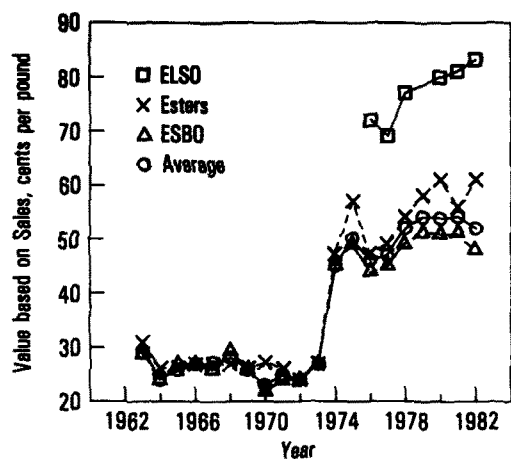


FIG. 3. Price trends of epoxidized vegetable oils and their esters. ELSO = epoxidized linseed oil; ESBO = epoxidized soybean oil; Esters = epoxidized tallates, oleates, stearates; Average = Average for all epoxidized vegetable oil and esters. (Source: U.S. Int. Trade Commission, Ref. 2.)

### Potential of a Natural Epoxy Seed Oil

The higher oxirane oxygen contents (7-9%), molecular weights (ca. 1,000) and viscosities (300-1,500 cps) of commercially epoxidized triglycerides (ESBO, ELSO), combined with similar or lower values for the simple commercial epoxy esters (4-9% oxirane, MW ca. 300-400, viscosity of 30-100 cps), provide useful ranges of properties for specific applications where heat- and light-stabilization, plasticizing action, resin compatibility, chemical purity, viscosity, volatility or low-temperature flexibility may be important considerations. The natural, liquid epoxy oil from *Vernonia galamensis* (Cass.) Less. seed has properties, such as oxirane content (4.1%), viscosity (110 cps) and molecular weight (917), that relate to both commercial types. *V. galamensis* seed yields 40-42% oil containing 72-78% vernolic (*cis*-12,13-epoxy-*cis*-9-octadecenoic) acid, making the native African plant an excellent source of naturally epoxidized triglyceride oil (3). Furthermore, vernolic (76%), oleic (4%) and linoleic (13%) acid levels in *V. galamensis* oil (VO) represent additional epoxidizable unsaturation (110% monoene equivalent), so that fully epoxidized VO could have an oxirane value near 10%. The usefulness of such oils as plasticizer-stabilizers in PVC resins has been reported (1,4-6). Composition of VO and its epoxidized product (EVO) are reported here, and some comparisons are made between EVO and its commercial cousins, ESBO and ELSO, relative to chemical compositions and potential markets.

## EXPERIMENTAL PROCEDURES

### Materials

*Vernonia galamensis* oil (oxirane oxygen = 4.1%) and methyl vernolate were available from previous work (2). *m*-Chloroperbenzoic acid (PBA) was obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin). Epoxidized soybean (Epoxol 7-4) and epoxidized linseed (Epoxol 9-5) oils were available from other work (Swift Specialty Chemicals, Chicago, Illinois), as were epoxidized *Limnanthes alba* and *Lithospermum tenuiflorum* oils.

### Transesterifications

Methyl esters were prepared from 10 mg to 1.0 g of the oils by transesterification with 1 to 10 ml of 0.28 M sodium methoxide in methanol. The mixtures were gently refluxed

(5-15 min) until all oil was dissolved and a clear solution obtained. The esters were then extracted with hexane or diethyl ether after addition of saturated NaCl solution. The procedure leaves epoxy groups intact.

### Epoxidation

*V. galamensis* oil (20 g in 200 ml benzene) was epoxidized with PBA (18.5 g in 300 ml benzene, 10% excess) in the presence of NaHCO<sub>3</sub> (15 g) as described by Chang (7), except that the PBA in benzene was added in quarters, each portion over ca. 20-min intervals, and aliquots of reaction mixture were removed just prior to each addition. Progress of epoxidation was then retrospectively examined by oxirane oxygen determinations and by TLC evaluations of these aliquots. The reaction mixture remained at 25 C overnight prior to workup (7). Yield of epoxidized vernonia oil was 19.1 g (90%, oxirane value = 8.2%). GC analysis as methyl esters showed the product to consist of 2.8% palmitate, 2.7% stearate, 3.0% 9,10-epoxy stearate, 0.5% minor components and 91.0% of methyl *cis*-9,10-*cis*-12,13-diepoxy stearates (anti and syn) in the ratio of 68:32. The pair of diastereomers was expected from previous research (6,8-11).

Pure methyl vernolate (1.0 g in 10 ml benzene) was similarly epoxidized with PBA (0.67 g in 15 ml benzene) in the presence of 0.25 g NaHCO<sub>3</sub> by adding all of the PBA solution over a 15-min period to the stirred methyl vernolate solution. After 4 hr of stirring at 25 C, the reaction mixture was stored overnight at -5 C and worked up according to Chang (7). The product was stored in benzene at -5 C. GC analysis showed 3% residual methyl vernolate and 97% of the methyl 9,10-12,13-diepoxy stearate diastereomers in the anti:syn ratio of 68:32, identical by GC to the major ester products from EVO.

### Analyses

Oxirane oxygen was determined by HBr titration in acetic acid at 25 C (AOCS Method Cd 9-57). Oil viscosities were determined at 25 C with a Brookfield Model LVT Synchro-Lectric Viscometer (Brookfield Engineering Laboratories, Stoughton, Massachusetts). Thin-layer chromatographic analyses (TLC) were performed on commercial precoated plates (0.25 mm silica gel 60 F-254, E. Merck, Cincinnati, Ohio). Development solvent was hexane/diethyl ether (70:30 or 60:40, v/v), at times with 1 part of acetic acid added. Visualization was by charring at 130 C after spraying the plate with sulfuric-chromic acid solution. Epoxy groups in oil or ester samples were revealed on TLC plates (without fluorescent indicators) by the picric acid technique (12-13). Separation of triglyceride components of VO and methyl esters of VO into normal- and epoxy-types has been described (3), and isolation of triglyceride fractions of EVO (1 g) was achieved similarly. Progress of these fractionations was monitored by TLC. Methyl esters were analyzed using a Spectra-Physics SP-7100 gas chromatograph equipped with a fused-silica capillary column (1.8 m × 0.32 mm, SE-30 liquid phase, He carrier set at 50 ml/min at 5 kPa, temp. program of 1-min hold, then 100 to 200 C at 10 C/min, injector and detector at 350 C, hydrogen FID). The same system and column were used for analysis of VO triglycerides, except the temp. program was 160 to 350 C at 30 C/min and He flow was set at 250 ml/min at 5 kPa. Helium flow through the capillary column was 2-4 ml/min under our conditions. Esters were identified by comparing GC elution times with known ester mixtures. Melting points were taken as the endothermic melting transition, T<sub>m</sub>, determined by differential scanning calorimetry (DSC, Perkin-Elmer DSC-2) at a scan rate of 10 K/min.

## RESULTS AND DISCUSSION

### Composition of the *Vernonia* Oil

By quantitative column chromatography as previously described (3), four triglyceride families were isolated from *V. galamensis* oil in the following relative amounts: 48.2% trivernolin (TVTG), 37.2% divernoloyl triglycerides (DVTG), 9.4% monovernoloyl triglycerides (MVTG) and 5.3% normal (unepoxidized) triglycerides (NTG) (85% recovery). In the current work, GC analysis of the oil found a somewhat different ratio of 59.2% TVTG, 28.1% DVTG, 9.5% MVTG and 3.3% NTG. GC analyses of methyl ester mixtures prepared from these previously isolated vernolic acid-containing fractions (3) gave methyl vernolate:normal ester ratios consistent with identities ascribed to these different fractions in Table I; e.g., MVTG and DVTG gave ester mixtures with ca. 1/3 and 2/3 methyl vernolate, respectively, and the TVTG fraction gave >95% methyl vernolate. Chromatographic separation of the whole-oil methyl esters previously gave a normal esters:methyl vernolate gravimetric ratio of 24:76 (3), and this was confirmed in this work by GC analysis of the oil methyl esters (Table II). Typical GC curves for the oil triglycerides and the methyl esters are shown in Figure 4. Triglyceride identities shown on the GC curve are not confirmed, but are consistent with available evidence.

### Epoxidation of *Vernonia* Oil

Progress of the epoxidation of *Vernonia* oil was examined by TLC analysis of aliquots removed after addition of each quarter of PBA. Figure 5 shows the transformation (lanes 1-4) of the four triglyceride groups of *Vernonia* oil to three new triglyceride groups in the epoxidized *Vernonia* oil (lanes 4-6). When the concentration of epoxidizing agent is limiting (Fig. 5, lanes 1 and 2, 1/4 and 1/2 PBA added), *Vernonia* oil is transformed sequentially via intermediates assumed to be unsaturated tetraepoxy (UTETG) and pentaepoxy (UPETG) triglycerides, most likely derived from trivernolin (TVTG) as follows: TVTG → UTETG's → UPETG's. For example, Maerker et al. (10) observed that monoepoxidation of methyl linoleate is essentially complete before significant amounts of the diepoxides appear. With additional PBA (Fig. 5, lanes 3-4), the intermediates and other oil components are converted to fully epoxidized products. Isolated by column chromatography and characterized by GC as their methyl esters, the final product triglycerides were found to be tetra- (TETG), penta- (PETG) and hexaepoxy (HETG) triglycerides in approximately 17%, 4% and 79%, respectively (Table I). The TETG fraction consisted of triglycerides with two diepoxy stearyl (DESt) groups, the third group being evenly divided between palmitic (16:0) and stearic (18:0) acid. PETG's had two DESt and one monoepoxy stearyl (MEST) groups, while HETG's had three DESt groups. No unsaturated esters (18:1, 18:2) were detected in any of the product esters (Tables I and II), showing that epoxidation was complete. The predominance of HETG in the EVO and the amount of DESt (91%) in the methyl esters is accounted for by the high combined level of vernolic and linoleic acids in *V. galamensis* oil (Table II).

Epoxidation of pure methyl vernolate provided an authentic mixture of diastereomeric methyl *cis*-9,10-*cis*-12,13-diepoxystearates (DESt) for comparison with the EVO esters. The identical ratios of diastereomers (anti:syn = 68:32), whether from epoxidation of methyl vernolate or from EVO, indicates that neighboring acyl groups in the triglycerides do not significantly influence the stereoselectivity of the epoxidation process. However, the asymmetric centers of an existing epoxy group, e.g., in natural vernolate

or in epoxyoleate groups from linoleate, stereoselectively direct the approach of epoxidizing agent to the double bond during formation of the second epoxy group within the same chain (9-11). The predominant isomer, eluting first by GC, is likely the sterically preferred anti diastereomer (10,11,14). When the diastereomers are derived from epoxidation of methyl vernolate, the lesser isomer has low optical activity, presumably due to the syn relationship of the epoxy groups and a resulting pseudoplane of symmetry in this diastereomer (10).

### Comparison of EVO with Other Epoxidized Oils

Table II shows that the oxirane content of EVO (8.2%) was exactly double that of VO (4.1%) and was intermediate between those of ESBO and ELSO. Melting points of both VO (10.8 C) and EVO (32.3 C) are higher than those of ESBO (-10.2 C) and ELSO (-8.2 C). The higher mp of EVO undoubtedly relates to its chemical "purity" relative to ESBO and ELSO. Both the latter have relatively complex TLC patterns compared to EVO (e.g., see Fig. 5). This is further illustrated by comparing the GC curves for the methyl esters prepared from the three epoxidized oils (Fig. 6). ELSO contains roughly equal amounts of saturated esters (16:0 and 18:0), monoepoxy stearate (MEST, methyl *cis*-9,10-epoxy stearate), diepoxy stearates (DESt) and triepoxystearates (TESt, 4 GC peaks, diastereomers from epoxidation of linolenate) (Table II). On the other hand, ESBO contains less than 2% TESt, but 50% DESt and similar amounts of saturated esters and MEST. EVO contains 91% DESt and only small amounts (ca. 3%) of MEST, 16:0 and 18:0. Obviously, EVO would be a rich source of DESt's in relatively pure form. The ratio of the DESt diastereomers (anti:syn = 68:32) is the same regardless of oil source and, as we saw above, epoxidation of methyl vernolate gave this same ratio of diastereomers. Since there are 2 GC peaks representing enantiomeric pairs of 4 diastereomers when vernolate or linoleate are epoxidized, one expects and finds 4 GC peaks in ELSO representing 4 enantiomeric pairs of diastereomers when linolenate in linseed oil is epoxidized (Fig. 6). Our GC system did not resolve the peaks adequately for quantitation of the 4 TESt peaks, but the expected ratio would be 46:22:22:10 (anti:anti:anti:syn:syn:anti:syn:syn) if approach of peracid oxygen to the third double bond (linolenate) is controlled with the same stereo-selectivity as is the approach to the second double bond (vernolate or linoleate).

The measured oxirane content of EVO was only 82% of the theoretical value based on the calculated iodine value (IV) of VO. When oxirane contents of a series of oils, including ESBO and ELSO, were plotted against original IV values, a smooth curve was obtained that increasingly diverged from the theoretical at higher oxirane and IV's (Fig. 7). The divergent oxirane values ranged from 89% of theory for an epoxidized high-monoene oil (*Limnanthes alba*, ELAO) to only 73% for an epoxidized high-tetraene oil (*Litherspermum tenuiflorum*, ELO) where fatty acid chains could have up to four epoxy groups. Since we observed no residual unsaturated esters (18:1, 18:2, 18:3) from EVO, ESBO or ELSO, the divergence is not attributable to incomplete reaction of the double bonds during epoxidation. Therefore, we presume that the low oxirane values are related to the method of oxirane determination (8,10,14). For example, polyepoxy moieties in the more highly epoxidized materials could undergo ring opening reactions that do not consume equimolar amounts of HBr during the titration. Such reactions could be acid-catalyzed opening of epoxy groups, leading to a variety of intra- and interchain reaction products of the triglycerides. For isomeric epoxy esters, incomplete reaction of HBr with one

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TABLE I

Composition of Triglyceride Fractions Isolated from *V. galamensis* Oil (VO) and Epoxidized *Vernonia* Oil (EVO)

Analyzed as	VO triglycerides <sup>a</sup>			EVO triglycerides <sup>b</sup>		
	MVTG	DVTG	TVTG	TETG	PETG	HETG
Triglycerides				— Not Analyzed —		
By GC, %	9.5	28.1	59.2	17	4	79
By col. chrom., %	9.4	37.2	48.2			
Methyl esters, GC, %						
16:0	6.3	4.6	—	16.3	1.3	trace
18:0	13.7	7.7	—	16.4	1.6	trace
18:1 + 18:2	44.3	22.3	—	—	—	—
Me Vernolate	31.0	65.0	95.3	—	—	—
MEST <sup>c</sup>	—	—	—	1.0	27.0	trace
DESt <sup>c</sup>	—	—	—	59.9	61.2	95.6
Other <sup>d</sup>	4.8	0.4	4.7	6.5	9.0	4.4

<sup>a</sup>Monovernoloyl (MVTG), divernoloyl (DVTG) and trivernoloyl (TVTG), triglycerides, respectively. Normal unepoxidized triglycerides represent 3-5% of the oil triglycerides.

<sup>b</sup>Triglycerides having 4 (TETG), 5 (PETG) or 6 (HETG) epoxy groups per molecule as *cis*-9,10-epoxystearoyl and *cis*-9,10-*cis*-12,13-diepoxyestearoyl moieties.

<sup>c</sup>Monoepoxystearate (MEST, *cis*-9,10-epoxystearate) and diepoxyestearate (DESt, *cis*-9,10-*cis*-12,13-diepoxyestearate).

<sup>d</sup>Unidentified components.

TABLE II

Fatty Acid Distributions, Oxirane Values, Melting Points and Viscosities of Several Epoxy Oils<sup>a</sup>

Analysis	VO	EVO	ESBO	ELSO
Methyl esters (GC), %				
16:0	3.1	2.7	17.0	12.2
18:0	3.2	2.7	5.6	5.5
18:1 + 18:2	16.5	—	—	—
Me Vernolate	76.8	—	—	—
MEST <sup>b</sup>	—	3.0	26.1	29.2
DESt <sup>b</sup>	—	91.2	49.5	24.6
TEST <sup>b</sup>	—	—	1.3	28.5
Other	0.4	0.4	0.5	0.5
DESt ratio, anti (68%) <sup>c</sup> syn (32%) <sup>c</sup>	—	62.6 28.6	33.4 16.1	16.7 7.9
Oxirane, %	4.1	8.2	7.0	8.9
M.p., C <sup>d</sup>	10.8	32.3	-10.2	-8.2
Viscosity, cps (25 C)	112	(solid)	445	1,470

<sup>a</sup>*V. galamensis* (VO), epoxidized *V. galamensis* (EVO), epoxidized soybean (ESBO) and epoxidized linseed (ELSO) oils.

<sup>b</sup>Monoepoxy (MEST, *cis*-9,10-epoxy), diepoxy (DESt, *cis*-9,10-*cis*-12,13-diepoxy) and triepoxy (TEST, 4 isomers) stearates.

<sup>c</sup>Presumed relationship of epoxy groups in the two diastereomers.

<sup>d</sup>Endothermic melting transition by differential scanning calorimetry (DSC).

stereoisomer (liquid form) was said to lead to low oxirane values (8,10,14).

### Potential of VO and EVO

The potential of *V. galamensis* as a seed source of oil with inherent usefulness because of its oxirane content has been considered recently from both botanical and chemical viewpoints (3; Perdue, Carlson and Gilbert, in preparation). Use of *Vernonia* oil for coatings (3) and in the preparation of a variety of polymeric materials from hard resins to elastomers (15-17) has been shown to be feasible. The latter application involves the interesting concept of generating novel polymers by sequential or simultaneous polymeriza-

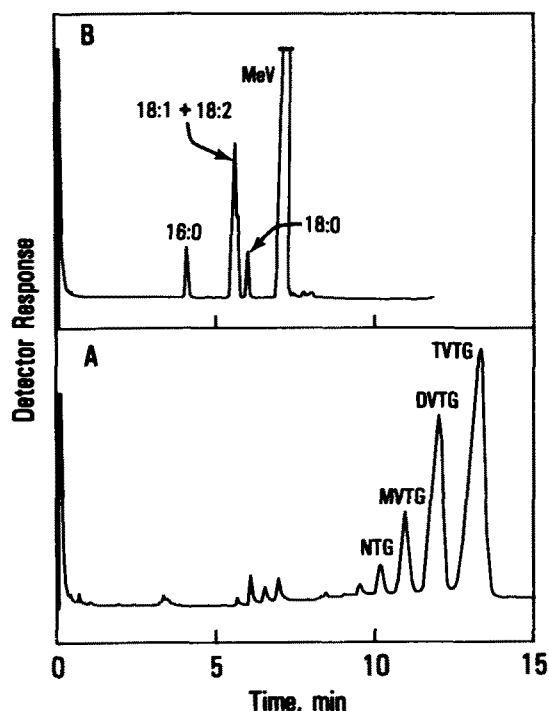


FIG. 4. GC of *V. galamensis* oil (A) and its methyl esters (B). SE-30 capillary column, 160-350 C at 30 C/min (A) and 100-200 C at 10 C/min (B). MeV = methyl vernolate; NTG = normal triglycerides; MVTG, DVTG and TVTG = mono-, di- and trivernoloyl triglycerides, respectively.

tion of natural and petrochemical monomers to give interpenetrating polymer networks (IPN's). IPN's have the potential for tailor-made properties for specific product applications. It is conceivable that *Vernonia* oil could function as a diluent, pour point depressant or viscosity improver in admixture with other epoxy oils in some applications. Separation of vernolic acid from VO in the form of trivernolin (18) or alkyl esters (6,11) may be commercially feasible. Epoxidation of either form yields high purity, high oxirane products (HETG and DESt) that have been shown

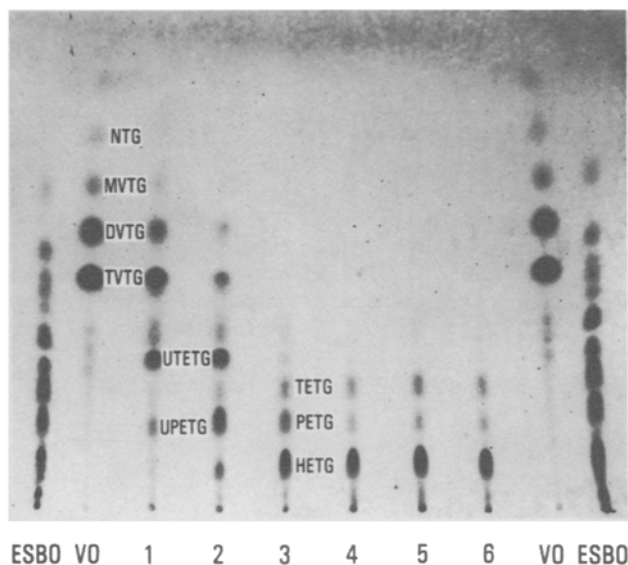


FIG. 5. Epoxidation of *V. galamensis* oil with *m*-Cl-perbenzoic acid (PBA) followed by TLC of aliquots removed during reaction. ESBO = epoxidized soybean oil; VO = starting *V. galamensis* oil; Lanes 1, 2, 3, 4 = 1/4, 1/2, 3/4 and all PBA added, respectively; Lane 5 = all PBA + 1 hr; Lane 6 = after 18 hr at 25 C. Identified spots by decreasing Rf are: normal (NTG), monovernoloyl (MVTG), divernoloyl (DVTG), trivernoloyl (TVTG), tetraepoxy (TETG), pentaepoxy (PETG) and hexaepoxy (HETG) triglycerides. Hexane/ether/acetone (50:50:1).

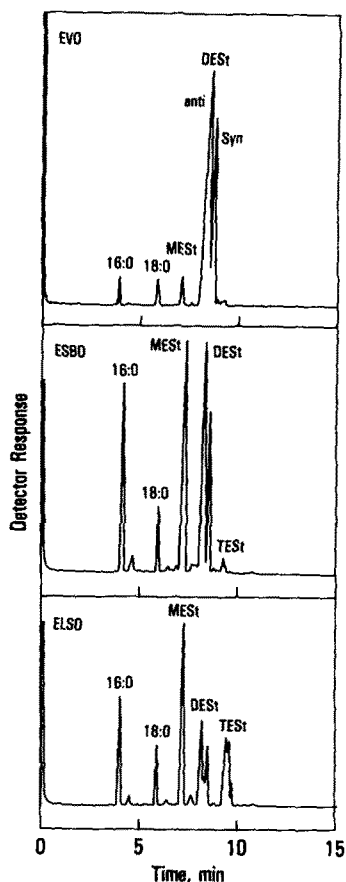


FIG. 6. GC of methyl esters of epoxidized *V. galamensis* (EVO), soybean (ESBO) and linseed (ELSO) oils. MESi, DESi and TEST are mono-, di- and triepoxystearates, respectively. Syn and anti refer to stereochemical relationship of epoxy groups to each other. SE-30 capillary column, 100-200 C at 10 C/min.

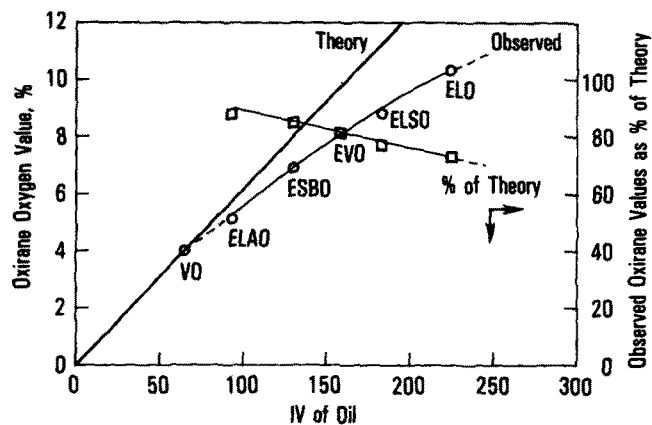


FIG. 7. Oxirane values as a function of initial iodine values (IV) for several epoxy oils: *V. galamensis* (VO) and epoxidized *V. galamensis* (EVO), *Limnanthes alba* (ELAO), soybean (ESBO), linseed (ELSO) and *Litbospermum tenuiflorum* (ELO) oils.

to function well as plasticizer-stabilizers in PVC resins (1, 11). Alternatively, the DESi's may be obtained directly from EVO in 90% purity by simple transesterification. EVO should function well as plasticizer-stabilizer for PVC (1).

Epoxidation of *Vernonia* oil requires only ca. half the costly reagent of an oil such as soybean or linseed oil, which would balance an expected higher vernonia oil production cost, especially relative to soybean oil. Of course, whether or not *V. galamensis* oil can be produced in significant quantities at competitive oil prices remains to be tested.

#### Future Trends for Epoxidized Esters

As discussed earlier, demand for epoxidized esters has been tied closely to their value as plasticizers-stabilizers in the PVC resin markets, and ESBO has been the mainstay over the past 20 yr, its price being closely tied to soybean oil prices. Availability of linseed oil and cost of ELSO have limited the latter's use to specialized applications where especially high oxirane content is critical. Where low-temperature applications are important, the simple epoxidized esters will continue to find favor. Esters of EVO could find application here by analogy because of their high oxirane content and inherent purity. On the other hand, EVO might find high-temperature applications where its higher mp and its oxirane value would be advantageous.

Recent patent literature shows that epoxidized vegetable oils and esters can be important components of refrigeration lubricating oils (19) and of internally plasticized phenolic resins (20) used to prepare laminates for critical-use insulating materials in the electronics industry. It is in new or potential markets such as these where growth for epoxidized esters could come. No significant swings in production levels and pricing of the existing mix of commercial epoxidized esters is anticipated unless new products and markets are developed.

Certainly the compositions of EVO and its esters are unique compared with the commercial oils and esters and, therefore, may find some specialized product applications.

#### ACKNOWLEDGMENTS

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