

action of perbenzoic acid and vinyl oleate at 30°, it may be concluded that the epoxidation by an aromatic peracid proceeds at about 4.5 times the rate by an aliphatic peracid.

Summary

A polarographic technique which uses a non-aqueous electrolytic solution consisting of 0.25 M ammonium acetate in glacial acetic acid is a suitable medium for the investigation of the kinetics of fatty acid ester epoxidations. From the polarographic data the specific reaction rate constants for the perlauric acid epoxidation of vinyl laurate, methyl oleate, and vinyl oleate in benzene at 25°C. were found to be 12, 232, and 270 x 10⁻³ l./mole⁻¹ min⁻¹.

The Arrhenius equation for the epoxidations of methyl oleate and vinyl oleate by perlauric acid can be expressed as $k = 5.53 \times 10^7 e^{-\frac{11,500}{RT}}$ and $k = 8.61 \times 10^6 e^{-\frac{10,300}{RT}}$.

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Reactions of Conjugated Fatty Acids. V. Preparation and Properties of Diels-Alder Adducts and Their Esters from Trans,Trans-Conjugated Fatty Acids Derived from Soybean Oil¹

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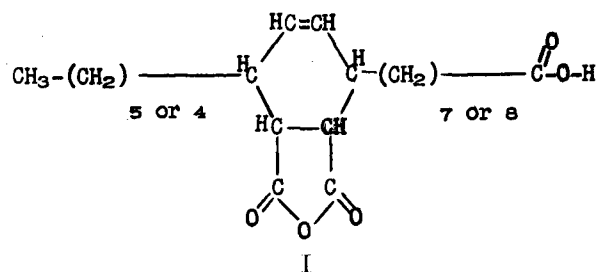
IN A PREVIOUS PUBLICATION (10) we have described the preparation of Diels-Alder addition products of *trans,trans*-9,11-octadecadienoic acid and a variety of dienophiles to produce the normal cyclic adducts. The acrylic acid and maleic anhydride adducts were very readily prepared. If this reaction could be extended to include linoleic acid derived from soybean fatty acids, the products would be good sources for di- and tri-basic acids. These polyacids could find use as intermediates for various types of plasticizers, polyesters, and polyamides. This paper describes the preparation of adducts from elaidinized conjugated soybean fatty acids and acrylic acid and maleic anhydride, esterification of the adducts, and epoxidation of the esters. Preliminary information on the properties of these esters and epoxidized esters as plasticizers is presented.

Addition of a dienophile to a dienoic system is dependent upon the steric and electronic configurations of both diene and dienophile. A conjugated diene can exist in three forms, *cis,trans*, *trans,trans*, and *cis,cis*. The addition of a dienophile to form a normal Diels-Alder adduct is facilitated if the dienoic system is in the *trans,trans* form. The adduct of a dienophile and *trans,trans*-9,11-octadecadienoic acid was shown to have a cyclohexenyl structure (10). Addition of maleic anhydride to the *cis,trans* form of the conjugated fatty acid requires high temperatures. No reaction is observed with acrylic acid. At elevated temperatures, maleic anhydride will react with oleic acid (8) and non-conjugated linoleic acid (9), but substituted succinic anhydride derivatives are formed.

In order to prepare the cyclic adduct from the soybean fatty acids, it is therefore necessary to convert the contained linoleic acid to the *trans,trans*-conjugated form. Alkali conjugation of soybean fatty acids, as reported by Riemenschneider (6), results in

the formation of *cis,trans* isomers of linoleic acid. Subsequent elaidinization is required to obtain the desired *trans,trans* isomers. There are many methods of elaidinization, but iodine was chosen because it minimizes side reactions and undesired double-bond migrations. It was possible to convert the *cis,trans*-conjugated acids to the *trans,trans* form to the extent of 60–70%.

The maleic anhydride adduct (I) was prepared.



It is a mixture of products from *trans,trans*-9,11- and *trans,trans*-10,12-octadecadienoic acids. The melting range of the product varied between 50°–60°. Multiple recrystallization raised the melting point of one fraction to 90°–98°. Intermediate melting points represent melting points of mixtures of the isomers involved. The infrared spectrum of the mixture was identical to the spectrum of the adduct prepared from pure *trans,trans*-9,11-octadecadienoic acid. Shifting the six-membered ring one carbon atom down the chain from the 9,11 to the 10,12 position of the fatty acid moiety was apparently not sufficient to alter the spectrum. Theoretical neutralization and saponification equivalents were not obtainable from the maleic anhydride adduct or any of its esters that were prepared. Both adduct and esters were refluxed for as long as 5 hrs. in 1 N alkali without success. A similar observation was made by Morrell (5) with adducts of α - and β -eleostearic acid and maleic anhydride. Bo-

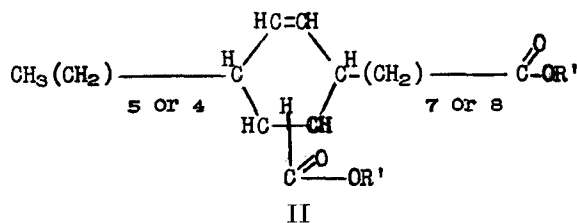
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TABLE I
 Esters and Epoxidized Esters of Adducts of Maleic Anhydride and Acrylic Acid with *Trans,Trans*-Conjugated Soybean Fatty Acids

Compound	Formula	Carbon		Hydrogen		n_D^{20}	Boiling point	Acid value	Sp. Gr. 25°/4°	Viscosity, centistokes		
		Calcd.	Found	Calcd.	Found					25°C.	0°C.	-25°C.
Maleic Anhydride Derivatives												
Maleic anhydride adduct.....	C ₂₂ H ₃₄ O ₅	69.81	69.90	9.06	9.08	M.P. 55°-90°
Epoxy adduct.....	C ₂₂ H ₃₄ O ₆	66.98	67.15	8.68	8.70	M.P. 148°-149°
Trimethyl ester.....	C ₂₆ H ₄₂ O ₆	68.46	68.36	9.60	9.31	1.4718	223°/0.4	0.4	1.0278	149.00	1177.0	30,360
Epoxy trimethyl ester.....	C ₂₆ H ₄₂ O ₇	66.05	66.11	9.31	9.30	1.4698	0.1	1.0615	293.70	2302.0	102,600
Triethyl ester.....	C ₂₈ H ₄₈ O ₆	69.96	69.74	10.07	9.82	1.4679	218°-223°/0.2	0.4	1.0006	90.93	476.4	6,242
Epoxy triethyl ester.....	C ₂₈ H ₄₈ O ₇	67.70	67.65	9.74	9.64	1.4649	0.8	1.0277	132.50	810.2	13,173
Tripropyl ester.....	C ₃₁ H ₅₄ O ₆	71.22	71.01	10.41	10.37	1.4662	245°-252°/0.3	0.0	0.9828	95.83	503.4	6,000
Epoxy tripropyl ester.....	C ₃₁ H ₅₄ O ₇	69.11	69.19	10.10	10.17	1.4648	0.0	1.0099	154.00	897.0	13,100
Dihydro-tripropyl ester.....	C ₃₁ H ₅₆ O ₆	70.95	70.94	10.40	10.52	1.4621	1.2	0.9801	47.56	622.2	6,800
Tributyl ester.....	C ₃₄ H ₆₀ O ₆	72.29	72.16	10.70	10.58	1.4661	248°/0.13	0.0	0.9706	85.49	431.8	4,417
Epoxy tributyl ester.....	C ₃₄ H ₆₀ O ₇	70.30	69.97	10.41	10.38	1.4648	0.3	0.9879	128.60	682.5	8,063
Triallyl ester.....	C ₃₁ H ₄₈ O ₆	72.06	71.81	9.36	9.42	1.4801	238°-245°/0.26	0.8	1.0073	66.18	307.4	2,937
Acrylic Acid Derivatives												
Dimethyl ester of adduct.....	C ₂₃ H ₄₀ O ₄	72.59	72.67	10.60	10.54	1.4681	186°-200°/0.2	0.4	0.9692	44.57	198.0	1,952
Epoxy dimethyl ester.....	C ₂₃ H ₄₀ O ₅	69.66	69.96	10.17	10.24	1.4671	0.6	1.0084	80.84	453.3	6,510
Diethyl ester.....	C ₂₅ H ₄₄ O ₄	73.48	73.32	10.85	10.53	1.4641	200°-207°/2-3	0.1	0.9529	41.13	147.0	1,168
Epoxy diethyl ester.....	C ₂₅ H ₄₄ O ₅	70.12	70.59	10.45	10.32	1.4636	0.2	0.9907	59.24	302.5	2,761
Dipropyl ester.....	C ₂₇ H ₄₈ O ₄	74.26	74.46	11.08	11.01	1.4639	204°-208°/0.3	0.6	0.9434	42.42	170.4	1,183
Epoxy dipropyl ester.....	C ₂₇ H ₄₈ O ₅	71.64	71.64	10.69	10.61	1.4625	0.3	0.9775	68.12	314.5	3,012
Dibutyl ester.....	C ₂₉ H ₅₂ O ₄	74.95	75.14	11.28	11.26	1.4634	220°-222°/0.27	0.4	0.9369	42.83	186.0	1,258
Epoxy dibutyl ester.....	C ₂₉ H ₅₂ O ₅	72.45	72.43	10.90	10.92	1.4632	0.2	0.9691	69.39	304.5	2,556
Diallyl ester.....	C ₂₇ H ₄₄ O ₄	74.95	75.04	10.25	9.95	1.4735	193°-198°/0.13	0.2	0.9612	32.47	127.7	829

eseken (1) reported theoretical saponification equivalents for the *trans,trans*-9,11-octadecadienoic acid adduct and its monoethyl ester; however we were unable to reproduce Boeseken's results. There is no apparent reason why the octadecadienoic acid adduct should be difficult to saponify or neutralize, especially when it can be readily esterified. Saponification or neutralization of the acrylic acid adduct and its esters presented no difficulties.

The acrylic acid adduct was prepared; and the crude reaction mixture was esterified and distilled, yielding the adduct ester (II). Saponification of the



ester produced the free acid adduct having an infrared spectrum and refractive index identical to those of the acid adduct prepared from *trans,trans*-9,11-octadecadienoic acid.

Both adducts were esterified in the normal manner with the desired alcohol and an acid catalyst. Bronze powder (4) was used as a polymerization inhibitor for the preparation of the triallyl ester. These compounds are readily reduced to form polysubstituted cyclohexanes.

Oxirane compounds are desirable as stabilizers for polyvinyl chloride resins because of the scavenging effect of the oxirane ring for hydrogen chloride. Epoxidation of the various esterified adducts was accomplished by using perbenzoic acid. The method of Swern (2), using peracetic, caused considerable hydrolysis of the oxirane moiety. When plasticized films were subjected to a heating period of 45 min. at 160°C. (3), the films plasticized with an epoxy ester remained colorless, or nearly so, while the non-epoxy esters turned yellow to brown. The epoxidized maleic anhydride adduct when heated to temperatures above its melting point polymerized to a tough resin.

The specific gravity and viscosity of the compounds

prepared were determined and are shown in Table I. The following generalities may be drawn:

Specific gravity: epoxy esters > esters; triesters > diesters; and low m.w. alcohol esters > high m.w. alcohol esters.

Viscosity: epoxy esters > esters; triesters > diesters.

All of the esters prepared, except the allyl esters, appear to be primary plasticizers for polyvinyl chloride. Plasticization of cellulose acetate was poor. At compatible concentrations the films were horny.

Experimental

Alkali Conjugation of Fatty Acids and Their Triglycerides. To a solution of 18 kg. of ethylene glycol and 2.7 kg. of sodium hydroxide were added 18 kg. of fatty acid or triglyceride. The resulting solution was heated and stirred in a kettle to 200°C. under an inert atmosphere at 3 to 5 p.s.i. for 1.5 hrs. Upon completion of the heating period 1 pint of water was added, and the contents were cooled to 140°. The reaction mixture was then acidified with a solution of 3.6 kg. of sulfuric acid in 10 gal. of water, and the free fatty acids were isolated in the usual manner. The acids obtained contained 49.2% diene and 2.1% triene conjugation when prepared from soybean oil. Infrared spectra showed that the diene conjugation present was in the *cis,trans* configuration.

Elaidinization. To a solution of 9.0 g. of iodine in 14 liters of pentane-hexane were added 14 kg. of alkali-conjugated fatty acids. This solution was placed in direct sunlight for 3 hrs. and then concentrated to 3 to 4 liters. The concentrate was washed twice with a solution that contained 9.0 g. of potassium iodide and 9.0 g. of sodium thiosulfate and had been made acid to litmus paper with acetic acid. The fatty acid solution was washed with water to remove traces of acetic acid and dried, and the solvent was removed. There was obtained 13.8 kg. of elaidinized fatty acids, in which 60% of the diene conjugation had been converted to the *trans,trans* configuration as determined by infrared spectroscopy.

Maleic Anhydride Adduct of Soybean Fatty Acids. In a 3-neck flask fitted with a reflux condenser, stirrer; and a gas-inlet tube were placed 600 g. (2.14 mole; 29.3% *trans,trans* conjugation) of fatty acid, 1.41 g. (1.41 mole) of maleic anhydride, and 3.5 liters of *n*-heptane. The solution was stirred and refluxed for 4 hrs. under an inert atmosphere. The

reaction mixture was kept at 0° overnight, and the solids that separated were removed by filtration. This solid material was dissolved in ether, and unreacted maleic anhydride was removed by washing with water. The ethereal solution was dried and evaporated to yield 430 g. of crude adduct. Recrystallization from a solution of 1,400 cc. of *n*-heptane and 600 cc. of ether yielded 212 g. (89.6% based on *trans,trans* conjugation) of maleic anhydride adduct of sufficient purity for esterification. Further recrystallization yielded a sample of analytical purity.

Anal. Calcd. for $C_{22}H_{34}O_5$: C, 69.81; H, 9.06
Found: C, 69.9; H, 9.08

The infrared spectrum of the adduct is identical to the adduct of *trans,trans*-9,11-octadecadienoic acid and maleic anhydride.

Acrylic Acid Adduct of Soybean Fatty Acids. A solution of 1,385 g. (4.95 mole; 29.3% *trans,trans* conjugation) of fatty acids and 132 g. (1.83 mole) of glacial acrylic acid was heated to 206° under an inert atmosphere for 2 hrs. The reaction mixture was cooled, and the excess acrylic acid was removed by heating under vacuum. The residue was used as described below for esterification without further purification. Adduct esters so prepared can be obtained in 90% yield based on *trans,trans* conjugation.

A sample of the pure dimethyl esters of this adduct was saponified with 1 *N* potassium hydroxide in ethylene glycol. The free diacid had an infrared spectrum and refractive index identical to those of the adduct of *trans,trans*-9,11-octadecadienoic and acrylic acid.

Esterification. The adducts were esterified in the usual manner, using 2% of sulfuric acid or anhydrous hydrogen chloride as a catalyst. *p*-Toluenesulfonic acid was used as catalyst and bronze powder (4) as a polymerization inhibitor in esterification with allyl alcohol. The esters were purified by distillation and by passing an ethereal solution through an alumina-charcoal column. Analyses and physical constants of the esters are shown in Table I.

Epoxidation of Esterified Adducts. The esterified adduct was added to a cold solution of perbenzoic acid (7) in chloroform. A 10% excess of peracid was used; the volume of chloroform was dependent on the peracid concentration. The resulting solution was allowed to stand at room temperature until the reaction was complete, as determined by titration of the unreacted perbenzoic acid. Ether was added to the chloroform solution until the density was less than that of water. Benzoic acid was removed by washing with 10% sodium hydroxide. The organic layer was washed until neutral and dried, solvent was removed, and the last traces of solvent were removed in high vacuum at 100°. Each epoxy compound was purified by passing an ethereal solution through an alumina-charcoal column, removing solvent, and heating the residue to 100° under vacuum to remove last traces of solvent. Analyses and physical properties of the epoxy compounds are given in Table I. Epoxidation with peracetic acid produced a 50-50 mixture of oxirane compound and the hydroxy acetoxy derivative.

Hydrogenation of the Tripropyl Ester of the Maleic Anhydride Adduct. The ester was reduced at 40 p.s.i. in acetic acid, using Adams' catalyst. The catalyst was removed, and the acetic acid solution was poured into water and extracted with ether. The

TABLE II
Compatibilities of Esters and Epoxy Esters with Polyvinyl Chloride and Cellulose Acetate

Compound	Polyvinyl chloride		Cellulose acetate	
	25% Plastizer	50% Plastizer	25% Plastizer	50% Plastizer
Maleic Anhydride Derivatives				
Trimethyl ester.....	+	+	+	+
Epoxy trimethyl ester.....	+	+	+	+
Triethyl ester.....	+	+	+	+
Epoxy triethyl ester.....	+	+	+	+
Tripropyl ester.....	+	+	+	+
Epoxy tripropyl ester.....	+	+	+	+
Dihydro-tripropyl ester.....	+	+	+	+
Tributyl ester.....	+	+	+	+
Epoxy tributyl ester.....	+	+	+	+
Triallyl ester.....	-	-	+	-
Acrylic Acid Derivatives				
Dimethyl ester.....	+	+	+	-
Epoxy dimethyl ester.....	+	+	+	-
Diethyl ester.....	+	+	+	-
Epoxy diethyl ester.....	+	+	+	-
Dipropyl ester.....	+	+	+	-
Epoxy dipropyl ester.....	+	+	+	-
Dibutyl ester.....	+	+	+	-
Epoxy dibutyl ester.....	+	+	+	-
Diallyl ester.....	-	-	+	-

ethereal solution was washed with saturated sodium bicarbonate and dried, and the solvent was removed. Analyses and physical properties of the product are given in Table I.

Preparation of Films for Compatibility Tests. The various esters were added to solutions of polyvinyl chloride in tetrahydrofuran or cellulose acetate in acetone. The mixtures were spread on glass with a doctor blade set at 0.040 in. The compatibilities were checked at 2-week and 2-month intervals. The results are shown in Table II.

Summary

Soybean fatty acids were conjugated with alkali, and the contained, conjugated dienoic acids were isomerized with iodine to the *trans,trans* configuration. Adducts were prepared from these *trans,trans*-conjugated acids by condensation with maleic anhydride and acrylic acid. The adducts were isolated, purified, and converted to esters by using a variety of alcohols, including methyl, ethyl, *n*-propyl, *n*-butyl, and allyl alcohols. Esters made from saturated alcohols were converted into the corresponding epoxy derivatives.

All of the esters (except allyl) and all of the epoxy esters were compatible with an equal weight of polyvinyl chloride and appeared to be primary plasticizers for this plastic. The epoxy esters were effective in inhibiting heat deterioration of polyvinyl chloride.

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