

tion of the linoleate had been carried to about 0.25 mole O_2 per mole of linoleate, which is relatively high, and some of the zones in the chromatogram may represent secondary oxidation products. It appears from the displacement diagram that some of the products exhibit low ultraviolet absorption and are thus not the primary products of oxidation, which appear to be conjugated.¹² It should also be pointed out that the enzyme preparation used was soybean extract, and it could conceivably contain enzymes capable of promoting secondary reactions. However, it may be concluded from this experiment that displacement chromatography is a very useful tool for the separation and isolation of the product of oxidation of linoleate, being able to separate a large number of closely related substances.

Discussion

To the authors' knowledge, the isolation of what appears to be 11-hydroxylinoleate from reduced peroxides, represents the first chemical evidence for the existence of the non-conjugated peroxide of linoleic acid among its oxidation products. Bergström¹³ concluded from his studies on autooxidation of methyl linoleate that the non-conjugated peroxide did not occur. He chromatographed on alumina the hydroxy stearates obtained by hydrogenation of the peroxides. The 9- and 13-hydroxystearates were isolated and identified, but no 11-

(12) S. Bergström and R. T. Holman, *Nature*, **161**, 55 (1948).

(13) S. Bergström, *Arkiv Kemi Mineral. Geol.*, **A21**, 14 (1945).

hydroxy stearate could be demonstrated. This was not taken as proof that the non-conjugated isomer did not exist, because isomerization could have taken place during the hydrogenation. However, in the present investigation, the appearance of the non-conjugated substance in some preparations and not in others, when all were treated in identical ways, speaks strongly for the absence of the non-conjugated peroxide among the products of autooxidation. The non-conjugated product has been conclusively demonstrated only in chlorophyll-photooxidation which is believed to proceed by a mechanism different from that in autooxidation, and which is not a chain reaction.⁸ It is possible also that zone 1 of the lipoxidase preparation could be this substance.

The preliminary experiments described here demonstrate the applicability of displacement analysis to problems involving the products of oxidation of fats or fatty acids. A segregation of *cis-trans* and *trans-trans* conjugated dienes has been shown in all cases, although the separation of these is not as sharp as between these and other products of oxidation. In general, the separation of substances has been verified by the infrared spectra of the fractions wherever this means of identification has been applied.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Fatty Acid Esters of 3-Butene-1,2-diol. II.¹ The Copolymerization of Erythryl Dilinoleate with Styrene²

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Erythryl dilinoleate was polymerized with styrene by heating under nitrogen at 80° in the presence of benzoyl or *p*-chlorobenzoyl peroxide to give low yields of linear, soluble polymers containing from 2.8 to 28 mole % of erythryl dilinoleate units. Limiting viscosity numbers varied from 7.6 to 12.6. The ester did not homopolymerize to high polymers. Saponification of two of the polymers and analysis of the main chain indicated that approximately nine-tenths of the linkages by which the ester was attached to styrene involved the erythryl rather than the linoleic unsaturation. Polymers containing more than 12 mole % of the ester were cross-linked by heat treatment.

A number of recent papers⁴⁻⁸ have been concerned with the polymerization of allyl and substituted allyl esters of fatty acids. However, limited attention¹ has been given to esters of polyhydric alcohols containing the allyl structure. The present investigation of the linoleic acid diester of erythryl (3-butene-1,2-diol) is undertaken to determine whether the compound is homopolymerizable or

copolymerizable with styrene and to study the linkages found in such polymerization.

The nature of unsaturation and polyfunctionality in erythryl dilinoleate, $CH_2=CHCH(OCOC_{17}H_{31})CH_2(OCOC_{17}H_{31})$, offered rather unusual possibilities for polymerization. Polymerization through the allylic unsaturation, with or without styrene, would yield a linear chain with linoleic acid residues as branches. Such a structure should be convertible to a three-dimensional cross-linked polymer, by reaction of the linoleic unsaturation. Furthermore, it was of interest to know the extent to which the linoleic unsaturation could enter into linear copolymerization.

The linoleic acid was obtained from safflower seed oil⁹ as the ethyl ester. Conversion to eryth-

(1) Paper I, E. Dyer, T. G. Custer and W. C. Meisenhelder, *THIS JOURNAL*, **71**, 2728 (1949).

(2) Based upon the Ph.D. dissertation of George A. Weisgerber, University of Delaware, 1951.

(3) Armstrong Cork Company Research Fellow, 1948-1951.

(4) P. D. Bartlett and R. Altschul, *THIS JOURNAL*, **67**, 812, 816 (1945).

(5) (a) D. Swern, G. N. Billen and H. B. Knight, *ibid.*, **69**, 2439 (1947); (b) D. Swern and E. F. Jordan, *ibid.*, **70**, 2334 (1948); (c) D. Swern, *ibid.*, **71**, 2377 (1949).

(6) S. A. Harrison and D. H. Wheeler, *ibid.*, **73**, 839 (1951).

(7) E. Dyer and W. C. Meisenhelder, *ibid.*, **73**, 1434 (1951).

(8) N. G. Gaylord and F. R. Birch, *ibid.*, **74**, 337 (1952).

(9) Of the total fatty acids in the oil, 76.7% was normal linoleic acid, as shown by ultraviolet spectrophotometric analysis. Thanks are due to the Chemurgy Project, University of Nebraska, for generously supplying the safflower seed oil.

ryl dilinoleate was carried out by way of the acid chloride. Erythryl dilinoleate and also the ethyl linoleate intermediate were treated with activated alumina for the simultaneous removal of free fatty acids and peroxidized components. This step was important because of the ease of peroxidation of these esters and the effect of peroxides on polymerizations.

Erythryl dilinoleate failed to polymerize to any great extent when heated in bulk at 80° for 44 hours under nitrogen, using 4% benzoyl peroxide. Since the product of this treatment was completely soluble in petroleum ether and in absolute ethanol, high polymers were absent. An addition reaction leading to a low polymer such as a dimer was suggested by the reduction in iodine value (shown in Table II) and the slight increase in viscosity of the recovered ester. Failure to polymerize to a molecule larger than a dimer has been noted with similar compounds: 2-chloroallyl linoleate⁷ and erythryl dipalmitate.¹ Polymerization has been found to occur, however, with erythryl diacetate.¹

Mixtures of erythryl dilinoleate and styrene in various proportions gave copolymers in yields of 5.8 to 20.5% when heated in bulk at 80° with benzoyl peroxide or *p*-chlorobenzoyl peroxide as initiators. These products contained 14 to 70 weight % (2.8 to 28 mole %) of erythryl dilinoleate, as determined by saponification numbers. In Table I are shown the yields, composition and properties of the ethanol-insoluble copolymers.

The data show that for a given initiator concentration, a higher proportion of styrene in the monomer charge gave a higher yield of precipitated copolymer with a markedly higher content of styrene and slightly higher limiting viscosity. Comparison of the results of two different initiator concentrations for mixtures having identical monomer charges indicated that more initiator gave a slightly better yield of copolymer, with a considerably higher ester content and a higher limiting viscosity.

Irrespective of monomer charge or initiator concentration the yields of ethanol-insoluble copolymers were quite low and a large amount of ester as well as of styrene was uncombined. This suggests that the ester behaved as a polymerization retarder or transfer agent. Such an effect has been previously observed with linoleic soaps,¹⁰ vinyl and allyl oleates and linoleates⁶ and allyl acetate.⁴

Isolation of the non-volatile material in the ethanol filtrates from the precipitated copolymer indicated that some styrene was present here in combined form, presumably as soluble copolymers of very low molecular weight. For example, in the case of runs A and B, where a relatively large proportion of the ester was found in the precipitated polymer, the weight balance indicated that 37 and 20%, respectively, of the original styrene remained in the residues obtained on evaporating the ethanol filtrates under reduced pressure. This result could be accounted for by a marked chain transfer action of the erythryl dilinoleate.

Two of the ethanol-insoluble polymers (A and B) were saponified and the resultant backbone polymer isolated. The acid values of the backbone

polymers provided a basis for estimating the relative reactivity of the two types of ester unsaturation—erythryl (type I) and fatty acid (type II). For example, polymer B, having a 7:1 ratio of styrene to ester units, would yield a backbone of zero acid value if all the ester molecules were joined to the chain at the erythryl group (type I); or it would yield a backbone of acid value 86.7 if only the linoleic double bonds entered into the polymerization (type II). The experimental acid value of 15.2 showed that 88 mole % of the ester was combined through the erythryl unsaturation. Similar data on saponified polymer B indicated that 94 mole % of the ester in the original polymer was linked to styrene through type II bonds.

Since about nine-tenths of the ester in polymers A and B was combined through the erythryl unsaturation, most of the linoleic groups were lost on saponification and the backbone polymers consisted largely of polystyrene with a few butane-diol units. Hence approximate figures for the viscosity average molecular weights of the backbone polymers could be obtained by use of constants for polystyrene. From the limiting viscosity numbers of saponified polymers A and B approximate molecular weights of 2300 and 2500, respectively, were obtained with Pepper's equation.¹¹ These values are of the same order of magnitude as the figures 3500 and 3700, which are the minimum molecular weights for the backbone polymers, calculated from their acid numbers, data on the composition of the original polymers, and the assumption that the unsaponified molecule contained one type II structure in which each linoleic radical terminated a chain. (For example, the figure of 3700 for backbone polymer B is derived from an original polymer having 7.39 units of type I and 1 unit of type II. Each unit of type I or type II contained 1 erythryl dilinoleate and 7 styrene groups.)

The foregoing data indicate that the mode of combination of styrene with the erythryl dilinoleate is probably through both a limited amount of copolymerization involving erythryl unsaturation and also through chain termination (or transfer) involving linoleic unsaturation. Evidence for a certain amount of copolymerization is the presence of more than one or two erythryl dilinoleate groups per chain. Evidence for the chain termination or transfer is the low molecular weight of the products and the fact that the composition of the polymers isolated at approximately the same conversions varies with the quantity of initiator used. The low yields indicate that termination by the ester is more prominent than chain transfer.

It is difficult to explain the considerable loss in unsaturation that occurred during the polymerization. This loss (shown in Table II) was sufficient to suggest dimerization of pendant linoleic radicals. However, the temperature of the polymerization (80°) was far below that usually necessary to cause diene addition.¹² Other factors that could cause a loss of double bonds would be addition of the benzoate radical to the Δ -9 or Δ -12 double bonds of the linoleate group⁶ or the presence of admixed homo-

(11) D. C. Pepper, *J. Polymer Sci.*, **7**, 349 (1951).

(12) J. S. Brod, W. G. France and W. L. Evans, *Ind. Eng. Chem.*, **31**, 114 (1939).

(10) J. W. Wilson and R. S. Pfau, *Ind. Eng. Chem.*, **40**, 530 (1948).

polymer of the ester. The former reaction, limited by the weight of benzoyl peroxide present, could not have occurred to an extent great enough to cause the observed lowering of unsaturation. The presence of admixed ester homopolymer in the copolymer fractions was thought unlikely because of the repeated precipitation of the major polymer from chloroform with ethanol.

The polymers having an ester content as high as 46% by weight were readily cross-linked by heating at 78 or 137° in the absence of air. The resulting products had greatly reduced solubility and fusibility. It is suggested that the conversion proceeded through the residual unsaturation in the styrene-ester copolymer.

Experimental

Linoleic Acid.—Linoleic acid was separated from safflower acids by the bromination-debromination method,¹³ followed by distillation of ethyl linoleate at 122–124.5° (0.02–0.03 mm.). Peroxide impurities were removed by passage of a 10% solution of the ethyl linoleate in petroleum ether (b.p. 30–60°) through a column (300 mm. length, 10 mm. i.d.) containing 30 g. of activated alumina (Eimer and Amend, 80–200 mesh), using gravity flow. Repeated passage of the solution was generally necessary. Partial elution with fresh solvent improved the yield of ester without removal of adsorbed peroxides. The solvent was removed in the absence of air and the product shown by analysis to be peroxide free.

The ethyl linoleate obtained had the following analysis: iodine no., 163.7 (calcd. 164.6); peroxide no., 0; acid no., 0; conjugated dienoate,¹⁴ 2.34%; conj. trienoate, 0.08%; conj. tetraenoate, 0%; non-conj. dienoate, 96.2%; non-conj. trienoate and tetraenoate, 0%; oleate (by difference), 1.4%.

The ethyl ester was saponified at room temperature^{15a} and the linoleic acid obtained¹⁵ was used immediately in the preparation of erythryl dilinoleate.

Erythryl Dilinoleate.—Erythrol, 3-butene-1,2-diol, was prepared by hydrolysis of butadiene monoxide¹⁶ according to the method of Pariselle.¹⁷ The alcohol, after two distillations (b.p. 75° at 2 mm.) had an iodine value of 288.0 (calcd. 288.0).

Linoleyl chloride was prepared from linoleic acid in 80% yield by using a 150–200% excess of oxalyl chloride in benzene.¹⁸ *Anal.* Calcd. for C₁₈H₃₁OCl: Cl, 11.86. Found: Cl, 11.94.

A solution of 73.5 g. of linoleyl chloride in 550 ml. of petroleum ether (b.p. 30–60°) was cooled in an ice-bath and 23 ml. of pyridine (15% molar excess) was added dropwise with stirring, followed by 10 g. of erythrol, allowing a 10% molar excess of the linoleyl chloride. The mixture was refluxed for four hours, cooled, filtered to remove pyridinium salts and repeatedly washed with water until neutral to litmus. Alkaline washings were avoided. The solution which was dried over anhydrous sodium sulfate, contained 70.4 g. of a mixture of erythryl dilinoleate and unreacted linoleic acid. By acid number determination this was found to represent a yield of 78% of pure ester.

Purification of the crude product to remove both the free acid and any peroxidic components was accomplished by adsorption of these materials on activated alumina from a petroleum ether solution. Yields for this step were low

(about 30–50%) and dependent upon the extent of treatment required. Removal of the solvent under reduced pressure and an inert gas gave the final product, 22 g., a clear colorless liquid having a very faint slightly fatty odor and a viscosity comparable to liquid petrolatum. The ester was not solidified on cooling to –76°. Erythryl dilinoleate was not distillable up to 275° (0.25 mm.), at which temperature it was decomposed and partially polymerized. Although the ester, a new compound, could not be further purified by distillation or crystallization, the following constants are reported. *Anal.* Calcd. for C₄₀H₆₈O₄: C, 78.38; H, 11.18; acid no., 0; peroxide no., 0; iodine no., 207.1; saponification no., 183.0; molecular refraction, 187.9. Found: C, 77.59; H, 11.02; acid no., 0; peroxide no., 0; iodine no., 199.3; saponification no., 184.0; molecular refraction, 188.3; *d*₄²⁵, 0.9126; *n*_D²⁵, 1.4728.

Polymerization.—Bulk mixtures of erythryl dilinoleate, styrene (washed with alkali and freshly distilled) and benzoyl peroxide or *p*-chlorobenzoyl peroxide¹⁹ (recrystallized from chloroform-methanol) were heated for 44–48 hours at 80 ± 0.3° in a sealed tube under an atmosphere of purified nitrogen (less than 0.001% O₂). The various mixtures are indicated in Table I.

Isolation of Polymers.—Since monomeric erythryl dilinoleate was observed to be quite readily saponifiable by alkaline solutions, washing with such solutions to remove excess catalyst or catalyst fragments from the polymerization mixture was avoided.

In the case of tubes A–C, Table I, the polymerization mixtures were precipitated with ethanol, the monomeric ester remaining in solution. Reprecipitation from chloroform with ethanol was done a total of twelve times, and after each precipitation the supernatant liquid was tested for the presence of peroxides,²⁰ until a negative peroxide test was obtained. Polymers were dried to constant weight under vacuum at room temperature.

In the case of tubes E–H, Table I, the polymerization mixtures were precipitated with ethanol, the polymers were then dissolved in 40 ml. of benzene and twice treated with ferrous ion to destroy the peroxide catalyst, as follows: to the benzene solution was added 6 ml. of a freshly prepared solution of 7% ammonium thiocyanate and 10% ferrous ammonium sulfate dissolved in 2 *N* hydrochloric acid, followed by 75 ml. of acetone which solubilized the two phases. The ruby color of ferric thiocyanate developed. After a five-minute period addition of 300 ml. of 0.1 *N* hydrochloric acid gave phase separation, and the benzene layer was washed with 0.1 *N* hydrochloric acid and then water until washings were neutral. The polymer was precipitated by addition of the benzene to 80% ethanol, then reprecipitated two more times from chloroform with ethanol. Polymers were dried to constant weight under vacuum at room temperature.

The linear copolymers were gummy to flaky in appearance depending upon the amount of styrene copolymerized. They were soluble in such solvents as benzene, chloroform and acetone, and they were fusible as noted in Table I.

The liquors from the precipitation of polymers A–C and E–H were treated to recover monomeric erythryl dilinoleate and low molecular weight polymers and to remove monomeric styrene, thereby obtaining a material balance useful in determining the consumption and disposition of the two monomers in the various states—insoluble polymer, soluble low molecular weight polymer or unreacted monomer.

In the case of the control tests, tubes D and I, polystyrene was precipitated four times with chloroform-methanol and dried to constant weight.

Polymer Analysis.—Saponification number was determined as follows: 0.2–0.5 g. of polymer was dissolved in 4 ml. of dioxane (previously distilled over potassium hydroxide), exactly 10 ml. of 0.5 *N* potassium hydroxide in 1:1 diethylene glycol:dioxane²¹ was added and the mixture refluxed for two hours under nitrogen. Then 20 ml. of dioxane and 50 ml. of water were added and the mixture titrated potentiometrically with 0.1 *N* hydrochloric acid, obtaining a differential plot. A blank determination was made.

(19) Sample of *p*-chlorobenzoyl peroxide generously supplied by the Lucidol Division of Novadel-Agene Corporation.

(20) By a modification of the method of F. E. McKenna, E. C. Lingafelter and H. V. Tartar, *THIS JOURNAL*, **71**, 2263 (1949).

(21) C. E. Redemann and H. J. Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

(13) (a) J. W. McCutcheon, *Org. Syntheses*, **22**, 75 (1942); (b) J. S. Frankel and J. B. Brown, *THIS JOURNAL*, **65**, 415 (1943).

(14) By spectrophotometric analysis according to the method of B. A. Brice, M. L. Swain, B. B. Schaeffer and W. C. Ault, *Oil and Soap*, **22**, 219 (1945).

(15) The acid prepared above was supplemented with a portion of linoleic acid from the Hormel Foundation, Austin, Minn. Iodine value 180.6 (calcd. 181.0), conj. dienoic acid, 1.43%; conj. trienoic acid, 0.24%; conj. tetraenoic acid, 0%.

(16) Obtained through the courtesy of Columbia Chemicals Division, Pittsburgh Plate Glass Co.

(17) H. Pariselle, *Ann. chim. phys.*, **24**, 315 (1911).

(18) (a) S. T. Bauer, *Oil and Soap*, **23**, 1 (1946); (b) T. R. Wood, F. L. Jackson, A. P. Baldwin and H. E. Longenecker, *THIS JOURNAL*, **66**, 289 (1944).

TABLE I
COPOLYMERIZATION OF ERYTHRYL DILINOLEATE AND STYRENE AT 80°

Run no.	A	B	C	D	E	G	G	H	I
Ester:styrene in charge, moles	1:1	1:2	1:0	0:1	1:1	1:2	1:2.5	1:3	0:1
Initiator, ^a % ^b	4	4	4	4	1	1	1	1	1
Yield ^b of polymer, %	8.2	19.3	0	96	5.8	12.0	16.8	20.5	94
Sapon. no. of polym.	128	84.7	88.7	39.0	29.8	26.4
Ester:styrene in polymers, moles	1:2.5	1:7	1:6.3	1:22	1:30	1:35
Wt. % ester in polymers	70	46	48	21	16	14
Total ester used found in pptd. polym., %	7	12	0	3.3	3.4	3.9	4.4
Total styrene found in pptd. polym., %	17	41	...	96	21	37	47	52	94
Melting range ^c of polymer, °C.	112 ^{d,e}	79-123	...	122-160	62-105	83-115	85-124	90-136	136-162
Soly. ^f of polymer, %	31 ^d	100	...	100	72	100	100	100	100
[η] ^g of sol. polym.	12.6	...	19.0	7.6	9.6	10.4	10.6	41.3

^a Benzoyl peroxide A-D, *p*-chlorobenzoyl peroxide E-I; A-D heated 44 hr., E-I, 48 hr. ^b Based on total monomers. ^c From first sintering point to free flow in a 1-mm. capillary melting point tube. ^d After partial cross-linking; see Experimental. ^e Not completely fusible below 250°. ^f Tested with 100 ml. solvent per 0.4-g. sample for 48 hours at room temperature; A-D in acetone, E-I in benzene. ^g Limiting viscosity numbers in benzene at 25°.

The compositions of the copolymers were calculated from the saponification numbers. No corrections were made for the possible effect of benzoate end groups on the saponification numbers. However, the magnitude of the probable error from this cause is shown by the fact that if polymer B, of estimated molecular weight 11,000, had one benzoate radical per chain, the number of styrene units for each erythryl dilinoleate unit would be 7.5 instead of 7.0 as reported.

The solubility of linear or cross-linked polymers was determined in acetone or benzene according to the method of Marvel, Inskeep and Deanin.²² Limiting viscosity numbers²³ were determined in benzene at 25° with an Ostwald viscometer.

Backbone Structure.—About 0.6 g. of polymer B was dissolved in 10 ml. of 0.5 *N* potassium hydroxide in 1:1 diethylene glycol:dioxane and refluxed 6 hours. The saponified polymer, representing the main chain or backbone was precipitated by adding methanol. The backbone polymer was redissolved in dioxane and acidified with hydrochloric acid to convert potassium soaps to carboxylic acid, and then reprecipitated four more times from dioxane into 90% methanol. A negative chloride test was obtained on the precipitate. The resultant flocculent polymer was dried to constant weight. The polymer melted at 105-128°. The acid number was measured by titration of a solution of the polymer in 95% acetone with 0.05 *N* alcoholic potassium hydroxide to the phenolphthalein end-point. The limiting viscosity number was determined in benzene at 25° and an approximate viscosity average molecular weight was calculated using the Pepper constants.¹¹

Found for saponified polymer B: acid no., 15.2; [η], 7.6; approx. mol. wt., 2500. Found for saponified polymer A (prepared similarly): acid no., 16.6; [η], 7.2; approx. mol. wt., 2300.

Heat Convertibility of Polymers.—The gummy polymer originally isolated from mixture A was soluble in chloroform, benzene and acetone. It readily became partially cross-linked and hardened upon heating at about 70° under carbon dioxide. The resultant product was brittle, essentially infusible and had reduced solubility, as shown in Table I. The ease of cross-linking was attributed to the high content of erythryl dilinoleate in the copolymer. Likewise, polymer E contained a certain amount of three-dimensional structure.

(22) C. S. Marvel, G. E. Inskeep and R. Deanin, *Ind. Eng. Chem.*, **39**, 1488 (1947).

(23) Report on Nomenclature of the International Union of Pure and Applied Chemistry, *J. Polymer Sci.*, **8**, 270 (1952).

Experiments to evaluate the potential cross-linking properties of the linear copolymers were done as follows: 0.3 g. of copolymer was weighed into a small glass cup and placed in the chamber of a drying pistol which was flushed with nitrogen and evacuated. The material was heated for 24 hours at 78 or 137°. The solubility of the product was tested by allowing a 0.4-g. sample to stand with 100 ml. of solvent at 25° for 48 hours. When samples of polymers A and B were heated at 78°, A became completely infusible and had a solubility of 25.2%, while B then melted at 135° and was 94.5% soluble in acetone. After heating at 137°, B became largely infusible and had a solubility of 63.0% in acetone. Polymers E, F, G and H, after heating at 137°, had the following solubilities in benzene: 18.8, 87.7, 92.7 and 97.9%.

TABLE II

Isolated polymer	I. V. found ^a	I.V. calculated ^b for:	
		No loss of unsat.	Loss of 2 double bonds ^c
Run A	53.0	111.5	55.7
Run B	37.7	72.6	36.3
Recovered unpolm. ester ^d			
Run A	131.3	199.3	119.6
Run B	123.2	199.3	119.6
Run C	123.2	199.3	119.6

^a Wijs method, 1 hour, using 400-600% excess of ICl for polymers, 140-200% excess for the ester. ^b Values for polymers are calculated from the experimental I.V. of ester monomer and the ester content of polymer and allow for loss of one double bond by polymerization. ^c Per erythryl linoleate unit. ^d Separated from polymerization mixture by solubility in ethanol.

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