on oils, but reduced their iodine value, apparently by promoting oxidation, and by reacting at the double bond. Iodine value decreased with reaction time when the catalyst was used in the presence of chloroform, and high and erratic results were obtained in the presence of sulfur. Comparative iodine values with an iodine-chlorine reagent also tended to increase with prolonged reaction, but were only slightly affected by the presence of sulfur or chloroform.

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The Isolation and Characterization of the Polymers Formed During the Autoxidation of Ethyl Linoleate[1]

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THE oxidative polymerization of ethyl linoleate could involve the formation of polymers through carbon to oxygen or carbon to carbon linkages. Triebs (1) and Farmer (2) favored the former viewpoint, but each proposed a different kind of carbon to oxygen bond. Triebs proposed that two moles of fatty ester were combined through a 2,5-dihydroxy-dioxane ring while Farmer suggested that they were joined through a polymeric peroxide of high stability. On the other hand, Powers (3) and Powers, Overhold, and Elm (4) suggested that carbon to carbon linked polymers were produced as a result of a peroxide catalyzed reaction and that the link was formed through a vinyl or a Diels Alder type reaction.

Whether polymers are formed through carbon to oxygen or carbon to carbon linkages has been difficult to ascertain as polymers are not easily isolated in pure form. Most of the mechanisms suggested to date (5) have been based on unfractionated oxidation mixtures and on interpretations of the changes in the physical or chemical properties which accompany the polymerization step. In order to overcome these objections Swern *et al.* (6) attempted to separate oxidized methyl oleate by subjecting it to molecular distillation. However Kass (7) has pointed out that the thermal effect may have altered the nature of the components. Similarly, chromatography is not applicable for this type of separation as Privett, Lundberg, and Nickell (8) have shown that chemical changes in the autoxidation products may take place on the chromatograph column.

In the present work the oxidized products of pure ethyl linoleate were separated into various fractions by solvent extraction at room temperature. The more polar polymer fractions were then characterized and the molecular structure which corresponded most closely to these analytical results was determined. This structure was then substantiated by characterization of the depolymerized products of the polymer fractions.

TABLE 1

Analysis of the Solvent Extracted Fractions

Fractions	Solvents		Weight of Extract (grams)	Density 25°C.	Refractive Index $n_D^{25°}$	Molecular Weight
	% Skelly Solve F	% Diethyl Ether				
1	100	0	47.60	0.0948	1.4651	406
2	98	2	19.91	1.004	1.4671	494
3	96	4	16.48	1.011	1.4679	472
4	94	6	15.15	1.021	1.4691	516
5	92	8	17.31	1.026	1.4706	536
6	90	10	13.50	1.030	1.4711	543
7	88	12	12.14	1.038	1.4725	586
8	84	16	12.72	1.043	1.4739	646
9	80	20	14.80	1.051	1.4759	808
10	76	24	16.40	1.061	1.4778	865
11	68	32	9.99	1.065	1.4788	1046
12	60	40	12.84	1.068	1.4810	1070
13	50	50	7.14	1.077	1.4821	1130

Experimental

Preparation of Material. The ethyl linoleate was prepared from corn oil according to a modification of Rollet's method (9). The ethyl ester had a Wijs iodine number of 164.1 (theoretical 164.6), a peroxide value of zero and a specific absorption coefficient of 0.2 at 2320 Å.

Oxidation Procedure. Two different batches of ethyl linoleate of approximately 250 g. each were weighed into a 50 x 460 mm. glass tube, the tube suspended in a constant temperature bath kept at 30 ± 0.5°C., and the ester aereated with dry air for 350 hours. The air was introduced through a fritted glass disk sealed into the bottom of the tube.

Solvent Extraction. The oxidized product was separated into 13 fractions with a solvent pair made up of redistilled Skellysolve F and anhydrous diethyl ether. The amount of solvent used in each solvent

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[2] Portion of a thesis presented by S. S. Chang as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Food Technology.

pair was twice the volume of the sample (Table 1). The following extraction procedure was used in order that the solvent and solute could be covered with nitrogen atmosphere at all times, a relatively large volume of solvent (800 ml.) and solute could be handled, and the extraction could be carried out in an all-glass apparatus free from stopcock grease and other possible contamination. In this extraction procedure the solvent and sample were introduced into a 1-liter three-necked flask fitted with a mechanical stirrer and the mixture agitated vigorously for 30 minutes. After both layers had cleared, which took from 30 minutes to 3 hours, the solvent layer was removed to another round bottom flask with the aid of an inverted fritted glass disc and the controlled suction of a water pump. The fine fritted glass disc prevented the disturbance of the liquids and allowed a good clear separation of the two layers. The epiphase was freed from solvent under vacuum at room temperature and the hypophase which remained in the three-necked flask was kept under an atmosphere of nitrogen. The next solvent pair was added to the hypophase and the extraction procedure repeated. The very viscous polymer fractions obtained by this procedure were almost colorless liquids.

Depolymerization Procedures. 1. With Hydrochloric Acid. Fourteen grams of combined fractions 11 and 12 and 84 ml. of a 2.5 N. hydrochloric acid in 80% aqueous ethyl alcohol were introduced into a three-necked round bottom flask and stirred vigorously. The flask was connected to a reflux condenser, fitted with a thermometer, and the mixture heated to 80°C. by means of an oil bath. After two hours the reaction mixture was cooled under tap water and diluted with an equal volume of distilled water. The mixture was extracted three times with an equal volume of redistilled Skellysolve F, the combined extracts washed with distilled water until free of acid, dried over anhydrous sodium sulfate, decolorized with activated carbon, and freed from solvent under vacuum at room temperature. The molecular weight, refractive index, iodine number, peroxide number, and a proximate analysis of a representative sample of the residue was determined. The remaining residue was dissolved in 1,400 ml. of Skellysolve F, cooled to —70°C., and the brownish precipitate which settled out removed by filtration. The filtrate was successively reduced under vacuum at room temperature to a volume of 280, 140, 50, and 35 ml., cooled to —70°C. after each reduction in volume, and freed of precipitate by filtration. No precipitate formed at —70°C. at a volume of 35 ml. The total weight of the combined precipitate was 3.2 g. The 35 ml. of filtrate were freed from solvent under vacuum, taken up in 10 ml. of dioxane and 40 ml. of water, 9 ml. of concentrated hydrochloric acid added, and the mixture was heated to 100°C. for one half hour to break up any ketal groups which may have been formed during the depolymerization process. The hydrolyzed mixture was cooled, diluted with water, extracted with Skellysolve F, washed free of hydrochloric acid with water, dried, and freed from solvent under vacuum; 7.3 g. of hydrolyzed material was obtained.

2. With hydrobromic acid. Two grams of the combined fractions 11 and 12 were mixed with 20 ml. of 3 N. hydrobromic acid in 67% aqueous ethyl alcohol and the mixture stirred vigorously for 24 hours at room temperature. An equal volume of water was added and the mixture extracted three times with Skellysolve F. The combined extracts were washed free of acid, dried over anhydrous sodium sulfate, and the solvent removed under vacuum. The product weighed 1.3 grams.

3. With hydroiodic acid. Two grams of the combined fractions 11 and 12 were mixed with 20 ml. of 1.2 N. hydroiodic acid in aqueous 80% ethyl alcohol and the mixture stirred vigorously for 24 hours. An equal volume of water was added and the mixture extracted three times with Skellysolve F. The combined extracts were shaken with dilute sodium bisulfite solution until completely decolorized, washed free of acid with water, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum; 1.4 grams of residue were obtained.

4. With hydrochloric acid after catalytic hydrogenation. Two grams of the combined fractions 11 and 12 were dissolved in 20 ml. of anhydrous ethyl alcohol and the solution hydrogenated in a Parr shaker type hydrogenator at 30 p.s.i. gauge for two hours. One per cent of platinum oxide prepared according to the method of Adams *et al.* (10) was used as catalyst. The hydrogenated product which had no peroxide and iodine number was depolymerized with hydrochloric acid; 1.6 grams of depolymerized product were obtained.

Analytical Procedures. Molecular weights were determined by the cryoscopic method (11) with either cyclohexane or benzene as solvents. The molecular weights determined at three to five different concentrations were plotted against molal concentrations. The straight line thus obtained was extrapolated, and the molecular weight at infinite dilution was taken as the true molecular weight.

The infrared absorption spectra of the polymer fractions were determined with the use of a Perkin-Elmer Infrared spectrophotometer. The samples were pressed between two sodium chloride plates as smears. Ultra-violet absorption spectra readings were determined with the aid of a Beckman spectrophotometer and with absolute ethanol as a solvent. Alkaline isomerization of the samples was carried out by the method of Potter and Kummerow (12).

When the hydroxyl value of the oxidized fractions was determined according to standard procedures (13), low values were obtained. These results were in agreement with the observation of Roberts and Schuette (14), who pointed out that the acetylated oxidation products of fatty esters are unstable and that they may hydrolyze when the excess acetic anhydride is treated with potassium hydroxide. Furthermore the pyridine used in the standard procedures may cause condensation reactions as indicated by the dark color which forms in its presence. The following procedure was therefore used to overcome these objections. A 0.2 to 0.3 gram sample and 1 ml. of acetic anhydride were sealed in a glass tube and heated to 170°C. for one hour. The contents of the tube were transferred quantitatively to a 50 ml. round-bottom flask with absolute ethyl alcohol, the flask was connected to a dry ice trap and evacuated to 200 microns for eight hours. The residue was hydrolyzed by refluxing with 10 ml. of 1 N. potassium hydroxide in ethyl alcohol for one hour, and the excess potassium hydroxide titrated with 0.25 N. hydrochloric acid, using phenolphthalein as an indicator. The saponification value of the sample was determined under ex-

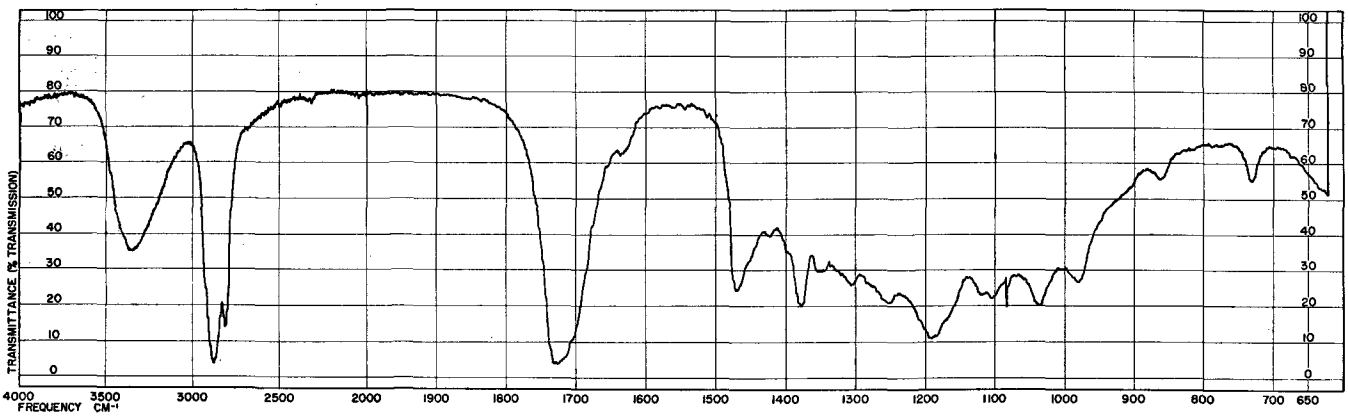


FIG. 1. The absorption spectrum of Fraction 9 in the Infrared Region.

actly the same conditions. The moles of hydroxyl group per mole of ester were then calculated from these data. The possible presence of halogens was tested for by the sodium fusion method according to the procedure given by McElvain (15). Carbonyl groups were determined by the method of Bryant and Smith (16), with the aid of hydroxylamine hydrochloride. Peroxide numbers were determined by the method of Fugger, Cannon, Zilch, and Dutton (17), and iodine numbers were determined by the Wijs method after the sample had been reduced by potassium iodide and acetic acid. Ethoxyl groups were measured according to the procedure of Samsel and McHard (18). Epoxy numbers were determined by the method of Swern *et al.* (19).

Results and Discussion

The present data indicated that it was possible to separate autoxidized ethyl linoleate into fractions of increasing molecular weight and polarity by solvent extraction with Skellysolve F and diethyl ether at room temperature. As the concentration of diethyl ether in Skellysolve F was increased from 0 to 50%, the density, refractive index, and molecular weight of the various fractions gradually increased (Table I).

The molecular weights of fractions 9 and 13 corresponded closely to those of a dimer and trimer, respectively, if one assumes a dimer to be composed of two moles of ethyl linoleate plus 4 moles of oxygen and a trimer, three moles of ethyl linoleate plus 6 moles of oxygen. Ultimate analysis of the polymer fractions (Table II) indicated that this assumption was valid.

Fractions 9 and 13 had almost identical absorption spectrum in the infrared region (Figures 1 and 2). The ketonic carbonyl group which was shown to be present by chemical analysis could not be distinguished from the ester carbonyl with the Model 21 Perkin-Elmer Infrared Spectrophotometer. However, with a Perkin-Elmer Model 112 Infrared Spectrophotometer with double pass optics, a weak shoulder was found at 1,715 cm^{-1} in addition to strong absorption at 1,735 cm^{-1}. These observations agreed with those of Dugan *et al.* (20).

TABLE II

Analysis of Fractions 9 and 13

	Fraction Number	
	9	13
Molecular Weight	808	1130
Density at 25°C	1.051	1.077
Specific refraction $r_D^{25°}$	0.2699	0.2648
Iodine Number (Wijs on reduced sample)	68.51	64.23
Peroxide Number (Millimoles per Kg.)	801.2	735.8
Epoxide Group (Moles per mole)	0.0	0.0
Peroxide Group* (Moles per mole)	0.586	0.822
Hydroxyl Group* (Moles per mole)	1.394	2.346
Carbonyl Group except Ester Carbonyl[a] (Moles per mole)	3.016	4.074
Ultimate Analysis C percentage	65.15	63.98
H percenetage	9.54	9.39
O percentage	25.31	26.63

[a] Calculations are made on the basis that each mole of dimer is made up of two moles of ethyl linoleate with four moles of oxygen and each trimer is made up of three moles of ethyl linoleate with six moles of oxygen.

Fractions 9 and 13 also had almost identical absorption spectrum in the ultraviolet region (Figure 3). The absorption maximum which developed at

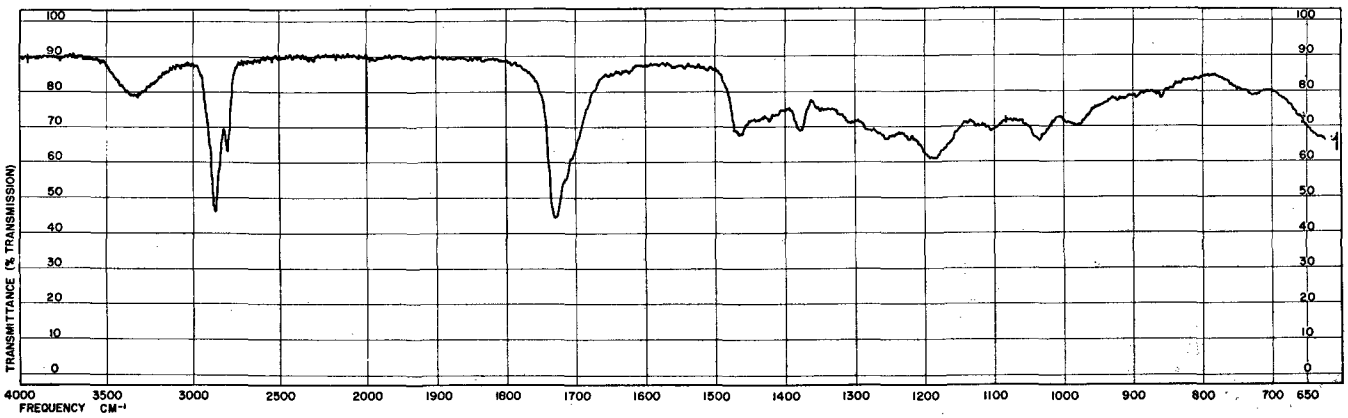


FIG. 2. The absorption spectrum of fraction 13 in the Infrared Region.

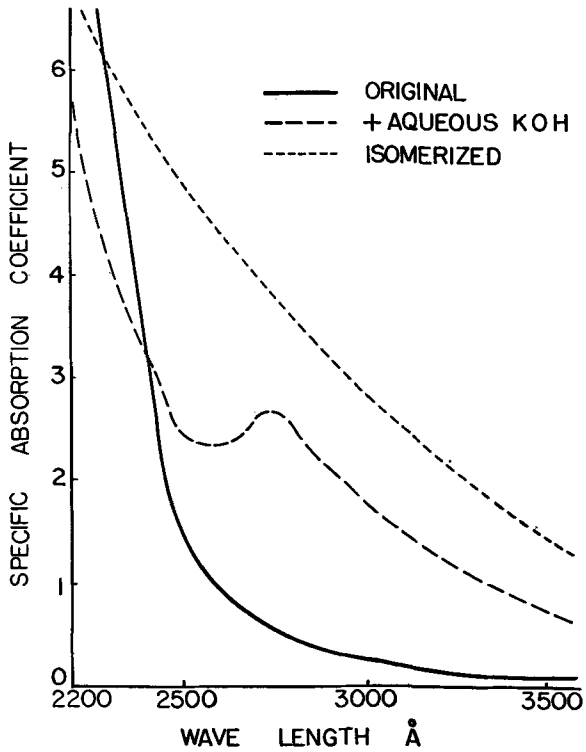
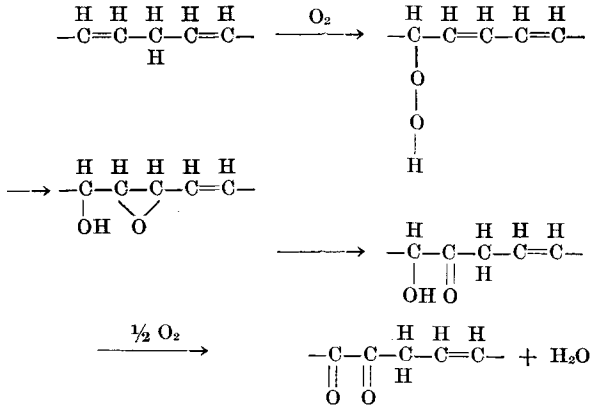


FIG. 3. The absorption spectrum of fraction 13 in the ultraviolet region.

2750 Å. when a sample of the polymer fraction 13 was diluted with 50% alcoholic solution of potassium hydroxide was probably due to a conjugated system of three double bonds formed through enolization of an alpha diketone in conjugation with a double bond.

The alpha diketone could be formed during autoxidation of unsaturated fatty esters as postulated by Morrel and Philips (21):



That an alpha diketone was present was further supported by the development of a strong reddish-brown color when the polymer fraction was treated with alcoholic potassium hydroxide. This coloration, according to O'Daniel and Parsons (22), was due to the quinoid compounds which are formed by aldol condensation of the alpha diketones in a manner analogous to the formation of para-xyloquinone from diacetyl. The absorption spectra in the ultraviolet region also indicated that neither the dimer nor trimer fraction contained a 1,4 system of conjugated double bonds. Furthermore a 1,4 conjugated system did not develop on isomerization with alkali (Figure 3).

The iodine values of fractions 9 and 13 (Table II) indicated that on polymerization from dimers to trimers only a slight decrease occurred in the amount of double bonds per mole of polymerized ethyl linoleate. This observation would not suggest that a Diels-Alder type of reaction had taken place. The iodine value of a trimer formed by such a reaction would have to decrease considerably.

The peroxide value reached a maximum in the third and sixth fraction, or 775 and 882, at a molecular weight of 472 and 543, respectively (Figure 4). These

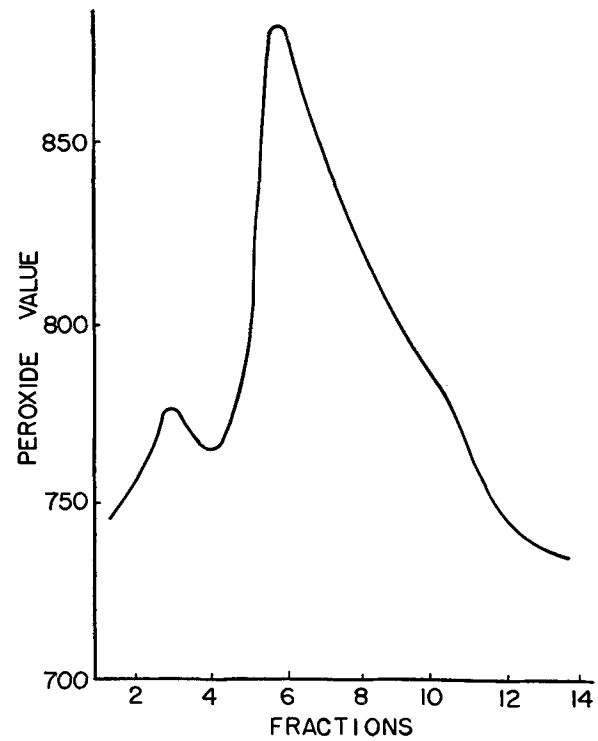


FIG. 4. Peroxide numbers of the solvent extracted fractions.

data seemed to indicate that during autoxidation some of the peroxide oxygen remained as peroxide and some decomposed or rearranged to form different functional groups (Table II). Fraction 13 had a slightly lower peroxide value and higher hydroxyl value than fraction 9, indicating that the scission of peroxides was still progressing slowly during polymerization.

On the basis of an ultimate analysis and molecular weight determinations, both fractions 9 and 13 corresponded most nearly to n $C_{20}H_{36}O_6$ (Table II). If n is equal to two a dimer made up of two moles of ethyl linoleate with four moles of oxygen and if n is equal to three, a trimer made up of three moles of ethyl linoleate with six moles of oxygen should have been present. However the total amount of oxygen identified as functional groups did not add up to the same amount of oxygen as determined by ultimate analysis. In fraction 9 a total of only 9.58 and in fraction 13 a total of only 14.06 atoms of oxygen could be identified whereas ultimate analysis indicated 12 and 18 atoms, respectively, were present.

This discrepancy could have been due to the presence of additional functional groups which did not respond to any of the various analytical procedures or to the presence of oxygen in the polymeric linkages. The latter was probably true as the physical and chemical constants determined on fractions 9 and 13 agreed very well with the mechanism as suggested by Bolland and Gee (23), who postulated that the oxidative polymers are joined through polymeric peroxides of high stability.

The possibility that the oxidative polymers were joined through carbon to oxygen type polymeric peroxide linkages was also shown by the result obtained on depolymerization of the more polar polymer fractions. The polymers could be depolymerized successfully with reagents which are commonly used to cleave linkages of the carbon to oxygen type.

Hydroiodic, hydrobromic, as well as hydrochloric acid depolymerized the Skellysolve F insoluble polymers with a molecular weight of 1,067 and a refractive index of 1.4795 to Skellysolve F soluble products with a molecular weight of 352 to 341 and a refractive index of 1.4650 to 1.4630 respectively (Table III).

TABLE III

Comparison of the Properties of the Oxidative Polymers of Ethyl Linoleate Before and After Depolymerization

	Before Depolymerization	After Depolymerization		
		By HCl	By HBr	By HI
Average Molecular Weight	1067	341.3	301.1	352.4
Refractive Index $n^{25°C.}_{D}$	1.4795	1.4630	1.4576	1.4650
Solubility in Skellysolve F	Insoluble	Miscible	Miscible	Miscible
Ultimate Analysis C%	64.72	67.26	66.44	66.90
H%	9.39	9.88	9.51	9.63
O%	25.89	22.86	24.05	23.47
Halogen %	0.00	0.00	0.00	0.00
Iodine Number (Wijs)	66.21	65.83	50.18	96.90
Peroxide Number	758.9	0.00	201.7	0.00

The depolymerized product contained no halogen and was lower in oxygen content than the polymers. The iodine number of the product depolymerized by hydrochloric acid was about the same as that of the polymers, but the product depolymerized by hydrobromic acid was lower and that depolymerized by hydroiodic acid was higher in iodine number than the original polymers. The product depolymerized by hydrochloric and hydroiodic acid contained no peroxide oxygen while the product depolymerized by hydrobromic acid had a lower peroxide number than the original polymers.

To insure that cleavage of the polymers by the hydrochloric acid treatment was essentially at the polymeric linkages, the polymers were hydrogenated catalytically in order to reduce the peroxide groups and to saturate the carbon to carbon double bonds. The Skellysolve F insoluble hydrogenated product which had an average molecular weight of 1,003 and no iodine or peroxide number could be similarly depolymerized with hydrochloric acid to an average molecular weight of 339.

That the oxidative polymers were joined through carbon to oxygen linkages was further substantiated by characterization of the depolymerized product. The brownish precipitate obtained from the Skellysolve F solution of the depolymerized product was not an entity. However the fraction which remained in solution after low temperature crystallizations consisted essentially of diketo-mono-hydroxy derivatives of ethyl oleate. The chemical constants determined on this fraction agreed closely with those calculated from theoretical values (Table IV). This seemed to indicate that the main reaction of the hydrochloric acid treatment involved a depolymerization through the carbon to oxygen polymeric linkage and not a cleavage of the carbon to carbon chain of the original fatty ester.

TABLE IV

Comparison of Calculated and Observed Values of the Fraction of the Depolymerized Product which Remained in Skellysolve F Solution

	Observed	Calculated for Diketo-mono-hydroxyl-derivatives of ethyl oleate
Molecular Weight	342.0	358.3
Ultimate Analysis C%	67.07	66.97
H%	10.20	10.69
O%	22.73	22.32
Ethoxyl group (%)	13.47	12.57
Carbonyl group (Moles per mole)	1.83	2.00
Hydroxyl group (%)	4.25	4.74
Iodine Number (Wijs)	69.98	70.82

Summary

Ethyl linoleate autoxidized at 30°C. for 350 hours was separated into fractions of increasing polarity and molecular weight by extraction with solvent pairs of Skellysolve F and diethyl ether. The analytical results obtained on characterization of the more polar polymer fractions indicated that the oxidative polymers of ethyl linoleate were linked through carbon to oxygen bonds rather than carbon to carbon bonds. This postulation was substantiated by a successful depolymerization of the polymers and the catalytically hydrogenated polymers with hydrochloric, hydrobromic, or hydroiodic acid in aqueous ethyl alcohol. Characterization of the depolymerized product also indicated that the oxidative polymers were joined through carbon to oxygen bonds.

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