Analysis of Fat Acid Oxidation Products by Countercurrent Distribution Methods. IV. Methyl Linoleate[1]

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THE literature dealing with the autoxidation of linoleates has recently been summarized by Lundberg, Chipault, and Hendrickson (10). General agreement exists that linoleate oxidizes by a free radical mechanism yielding monohydroperoxides, a high proportion of which contain diene conjugation. Little agreement however was found concerning the amount or existence of unconjugated diene monoperoxides and the formation of cyclic and polymeric peroxides. On the basis of their preliminary studies, those authors suggest that unconjugated peroxides form, that some diperoxides result possibly from the 1,4 addition of oxygen to conjugated monoperoxide, and that appreciable amounts of oxygenated products do occur which are not reduced by potassium iodide. Their analytical work was carried out upon concentrates of oxygenated products obtained by "fractionation procedures which were found preferentially to isolate the more-highly oxidized products of oxidation." Since countercurrent distribution methods afford a precise, efficient, and yet mild method of fractionation for fat oxidation products and account for all the material, both oxidized and unoxidized, this technique, supplemented by chemical analysis, infrared, and ultraviolet spectroscopy, was employed in order to confirm and to extend observations of previous workers.

Experimental Procedure

The oxidation of methyl linoleate was performed with pure oxygen at atmospheric pressure. It was carried to levels of 0.11, 0.62, and 1.12 moles oxygen absorbed per mole ester at room temperature and to 0.1 mole level at 0°C. Samples of 2.5 to 5 grams were subsequently subjected to countercurrent distribution between 80% ethanol and pentane-hexane. Techniques of controlled oxidation in manometric apparatus, of countercurrent distribution, and of analysis for conjugation, hydroxyl groups, peroxide values, hydrogen numbers, and molecular weights have been described previously (4). Infrared spectra from 2-15μ have been obtained by use of a Perkin-Elmer Model 21 infrared spectrophotometer.[4]

The results of infrared studies presented herein demonstrate that the linoleate hydroperoxides possess a high proportion of cis-trans conjugated bonds. It is therefore more appropriate to apply absorption coefficients for cis 9-trans 11 linoleate (a_{232}-82.5) and trans 10, cis 12 linoleate (a_{232}-97.7) (7) to the hydroperoxides than that for the trans-trans linoleate (109.5) (8). Assuming equal amounts of the 10-12 and 9-11 unsaturated isomeric hydroperoxides form, a coefficient of 81.3 is calculated for methyl cis-trans linoleate hydroperoxides. This coefficient is used for the calculations of this paper.

The methyl linoleate used in these experiments was obtained from the Hormel Foundation and was isolated by bromination, debromination, and distillation procedures. It had an iodine value of 172.4 and 0.17% of diene conjugated esters.

Results

The autoxidation of methyl linoleate was followed by measuring the rate of oxygen absorption manometrically. Approximately 95 hours were required at room temperature for the introduction of 0.11 mole of oxygen per mole ester and 198 hours for 1.12 moles. At 0°C., 20 days were required for the introduction of 0.1 mole. If the previously and widely accepted absorption coefficient for diene-conjugated linoleate (a-115 for the free acid, 109.5 for the methyl ester, and 98.79 for the methyl ester hydroperoxide) is used, results given in the literature (3) are confirmed, namely, 1 mole of peroxide and approximately ⅔ mole conjugated ester are calculated to be formed per mole oxygen absorbed for low mole levels (see figures for 0.1 mole level in parentheses in Table I). However by applying the absorption coefficient of 81.3 described above, a much higher yield of conjugated ester per mole oxygen absorbed was calculated.

At higher levels of oxidation (0.63 and 1.12 moles oxygen per mole ester) the yield of peroxide and

[1]Presented in part at the spring meeting of the American Oil Chemists' Society, May 1-3, 1951, in New Orleans, La.
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[3]One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946.

[4]The mention of products does not imply endorsement or recommendation by the Department of Agriculture over other products of a similar nature not mentioned.

TABLE I

Analyses of Oxidized Methyl Linoleate and of Fractions After Countercurrent Distribution

	Oxidation level (moles O_2 absorbed per mole ester)				Fractions after distribution					
					0.11 moles O_2/mole		0.62 moles O_2/mole		1.12 moles O_2/mole	
	Starting material	0.11	0.62	1.12	Tubes 9-10	Tube 26	Tube 1	Tube 7	Tubes 1-3	Tubes 8-14
Component[1]	.....	.....	.....	.....	II	I	III	II	III	II
Peroxide value	68	801	3,280	4,225	.....	5	2,800	4,630	3,115	4,265
Hydrogen number	.....	128	127	147	98	140	136	126	166	137
Hydroxyl (%)	.....	.....	.....	5.25	.....	.....	.....	.....	5.9	4.2
Moles peroxide/mole ester	.01	.12	.52	.69	.....	.0007	0.457	0.756	0.51	0.70
Moles H_2 absorbed/mole ester	2.16	2.30	2.48	2.24	2.99	2.10	2.40	2.58	1.97	2.38
Moles hydroxyl/mole ester	.....	.....	.....	1.0	.....	.....	.....	.....	1.1	0.81
Moles conjugation/mole ester	0.04 (0.03)[2]	0.086 (0.07)	0.29 (0.24)	0.33 (0.27)	0.90 (0.74)	.....	0.17 (0.14)	0.79 (0.65)	0.22 (0.18)	0.86 (0.71)
Mole weight	.....	.....	.....	.....	.....	.....	307	331	.....	.....

[1]Component I is unoxidized methyl linoleate, Component II is the monohydroperoxide, and Component III is the polar secondary oxidation product.
[2]Figures in parentheses are calculated with a previously accepted constant corresponding to a_{234}=115 for the free acid (7).

conjugation was reduced. In the table it may be seen that methyl linoleate oxidized to the 0.11 mole level was found to have 0.11 mole peroxide oxygen per mole ester; it may also be seen that for 1.12 moles oxygen absorbed, only 0.69 mole peroxide was found. Similarly the yield of conjugated esters, in terms of moles conjugation per moles oxygen absorbed, was found to be 0.73 (0.086/0.11) at the 0.11 mole oxidation level but only 0.29 (0.33/1.12) at the 1.12 mole oxidation level.

Hydrogenation data on the autoxidized methyl linoleate are also given in Table I. The experimental ratio of moles hydrogen absorbed per mole ester for the methyl linoleate was 2.16. If hydroperoxides were the exclusive reaction product with oxygen, the increase in moles hydrogen absorbed should be equal to the moles oxygen absorbed. At high levels of oxidation, the peroxide, conjugation, and hydrogenation data show deviations in behavior from that predicted by simple theory involving hydroperoxide formation and accompanying shift of double bonds. While the accuracy of the hydrogen ratio determinations is not great, it is apparent that the additional hydrogen required to reduce the peroxidic groups falls off drastically with increasing oxidation level.

The weight-distribution curve resulting from the countercurrent distribution of methyl linoleate oxidized at room temperature to the 0.11 mole level is given in Figure 1. Component I with maximum in

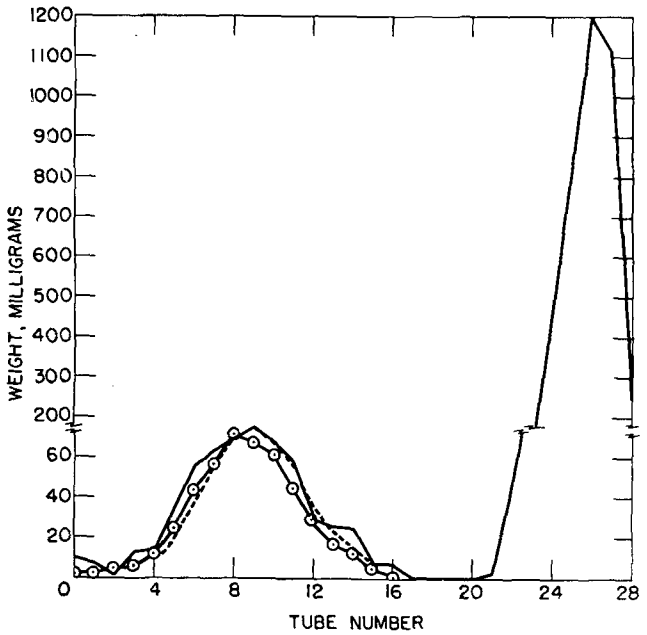


FIG. 1. Weight-distribution curve (solid line) following countercurrent fractionation of autoxidized methyl linoleate (0.11 mole oxygen absorbed per mole ester). Circles indicate weight of diene-conjugated esters. The broken line is the theoretical curve.

tube No. 26 was unoxidized methyl linoleate (see table), and Component II with maximum in tube No. 9 was the monohydroperoxide of methyl linoleate. More will be given later concerning Component III which was present in tubes 0, 1, and 2, but in small amounts at this oxidation level.

Summation of the weights in tubes 19 to 28 for the unoxidized ester and for tubes 0 to 18 for oxi-

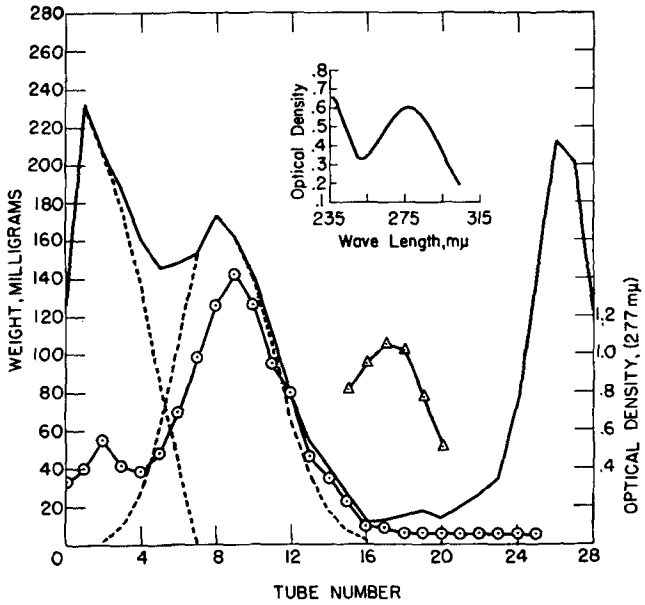


FIG. 2. Weight-distribution curve (solid line) following countercurrent fractionation of autoxidized methyl linoleate (1.12 moles oxygen absorbed per mole ester). Circles indicate weight of diene-conjugated esters; triangles indicate the optical density measured at 277 mμ. The broken line is the theoretical curve while the dashed line is the difference curve. The insert is the absorption spectrum of tube No. 17 diluted three times.

dized ester shows that 11% of the weight falls in the monohydroperoxide portion of the curve. This agrees with the moles of oxygen initially absorbed by the methyl linoleate (0.11 mole O_2/mole ester) and the moles peroxide formed (0.12 mole peroxide O_2/mole ester).

Summation of the weights of conjugated ester in tubes 3 to 16 divided by the total weight in the same tubes indicates a ratio of 0.83 (0.68 calculated with $a=98.79$). This is comparable with the figure of 0.79 given earlier on the unfractionated oxidation mixture for the ratio of moles conjugation formed to moles O_2 absorbed.

The theoretical ratio of hydrogen absorbed per mole ester of unoxidized methyl linoleate is, of course, 2.0 whereas 2.16 is the experimental value (Table I). For the unfractionated oxidation mixture the theoretical ratio is 2.11 (experimental 2.3) and for pure monohydroperoxide the theoretical ratio is 3.0 (experimental 2.99). Unfortunately the small amount of material in tubes 9 and 10 did not permit a peroxide determination on these tubes. However peroxide values in tubes 6 and 11 were determined and were 4,210 and 4,005, respectively. These values are far below the theoretical value of 6,125 expected for the monohydroperoxide. However, as noted later, indications are that hydroperoxides decompose when formed under conditions of room temperature autoxidation probably to give hydroxy esters which are inseparable from the hydroperoxide by the present countercurrent distribution procedure.

Countercurrent distribution data for methyl linoleate oxidized to the 1.12 mole level is represented in Figure 2 and provides an explanation for the deviation in peroxide, conjugation, and hydrogenation data observed in the autoxidation. Components I, II, and III were again present, the chief difference between Figures 1 and 2 being the predominance of Component III at the higher oxidation level. The relative propor-

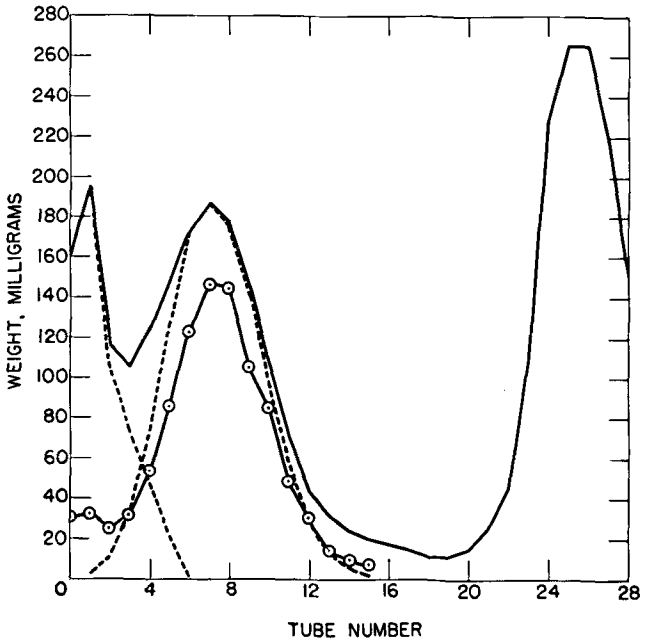


FIG. 3. Weight-distribution curve (solid line) following countercurrent fractionation of autoxidized methyl linoleate (0.62 mole oxygen absorbed per mole ester—light catalyzed). Circles indicate weight of diene-conjugated esters. The broken line is the theoretical curve while the dashed line is the difference curve.

tions of the three components may be estimated in this mixture by the calculation of the theoretical curve for the monoperoxide and by estimation of Component III as the difference between the total weight per tube and the calculated or theoretical weight of monoperoxide per tube in tubes 0 to 9. By this procedure it was determined that unoxidized ester comprised 32.6%, the monohydroperoxide 38.3%, and Component III, 29.1%. With the use of these figures it is possible to calculate the average ratio (R) of moles oxygen to moles ester in Component III, assuming Component II to be monohydroperoxide with one mole oxygen per mole ester.

$$1.12\times100\%=32.6\%\times0+38.3\%\times1+29.1\%\times R$$

The molar ratio for Component III is calculated thus to be 2.45.

The average ratio of moles conjugation to moles ester for Component II may be calculated, as described above, by dividing the summation of conjugated esters (tubes 5 to 16) by the summation of the total weight for the same tubes. In this manner the conjugation ratio is determined as 0.77 (0.63 with α=98.8). This high ratio of conjugation stands in sharp contrast to the ratio of 0.22 found in Component III (tubes 1-3 in the table). It is the low conjugation of this major oxidation product which accounts for the deviation from the theoretical yield observed at the high oxidation levels.

Analyses performed upon the combined tubes Nos. 1, 2, and 3 and upon Nos. 8 to 14 from the countercurrent distribution raise interesting questions to be discussed later. It is apparent that the more oxygenated fraction, Component III, has a lower peroxide content than Component II; yet it has a higher hydroxyl content after reduction (hydrogen on Pd catalyst) than Component II. The hydrogen absorption of Component III is not only lower than the monoperoxide, but it actually drops below the 2.1 moles value of the original methyl linoleate. The molecular

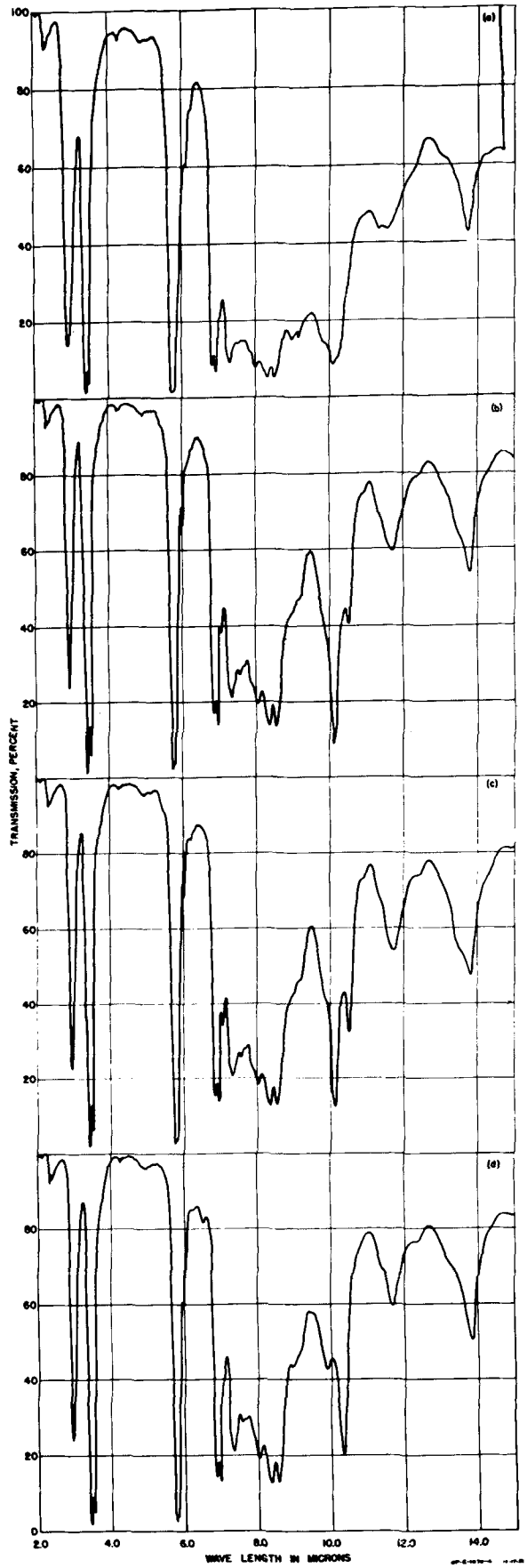


FIG. 4. Infrared absorption spectra of (a) the secondary oxidation product (Component III) of methyl linoleate, tube 2-room temperature autoxidation; (b) methyl linoleate hydroperoxide, tube 9-room temperature autoxidation; (c) methyl linoleate hydroperoxide, tubes 5-14, inclusive, 0°C. autoxidation; (d) methyl oleate hydroperoxide refractionated by countercurrent distribution.

weight of these fractions establishes them as being primarily monomeric.

Ultraviolet absorption spectra of the monoperoxide tubes have not been given since they have merely the peak at Ca. 234 mμ and the well-known structure characteristic of diene conjugation. In tubes 15 to 20 however an absorbing substance was found whose optical density at 2,770 Å is plotted against tube number in Figure 2. It is apparent that this product is a minor component percentage-wise, there being no clear evidence of its presence in the weight-distribution curve. The ultraviolet absorption spectrum of tube No. 17, which is given in the insert of Figure 2, is similar to that recorded for ketoelaidic acid (6).

Experimental data for the 0.62 mole level of oxidation are presented in Figure 3 and in Table I. They are given at this point since the over-all result is intermediate between the 0.11 and the 1.12 mole levels. In this instance light from a glass-inclosed mercury lamp was used to catalyze the reaction; however no significant deviations in composition of the autoxidation mixture were noted between this experiment and a repeat experiment conducted in the absence of u.v. catalysis. Infrared spectra were measured on samples from a repeat run for the secondary oxidation product (tube 2-p.v. 6,510) and for the hydroperoxide (tube 9-p.v., 5,450). These transmission curves are presented in Figures 4a and 4b, respectively.

By autoxidizing methyl linoleate at 0°C. to a level of 0.1 mole oxygen per mole ester the hydroperoxide was isolated in relatively high purity by countercurrent distribution. In this instance tubes 5-14 were combined in order to give sufficient material for peroxide determination and infrared analysis. The peroxide value was found to be 5,720, corresponding to 93% purity. Its absorption coefficient at 234 mμ was found to be 75.0 corresponding to 92.3% conjugation of cis-trans bonds, its refractive index, ($N^{D}_{30°C.}$), was 1.4811. In Figure 4c is given the infrared absorption.

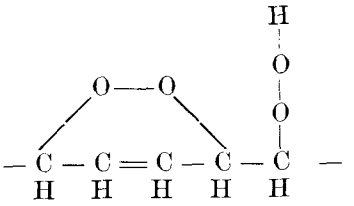
For comparative purposes an infrared curve for methyl oleate hydroperoxide is included. An 84.4% concentrate (p.v.=5,178) was furnished us by Daniel Swern of the Eastern Regional Research Laboratory. This material was subjected to a 24-transfer countercurrent distribution in an attempt to increase its purity. Combined tubes 8-14 provided the sample whose spectrum is shown in Figure 4d. While the peroxide value was not significantly improved by this fractionation (p.v. 5,355), many of the infrared absorption spectrum bands were markedly sharpened.

Discussion

Countercurrent distribution methods have permitted previous observations on the autoxidation of methyl linoleate to be confirmed and extended. Not only has the theoretical yield of moles peroxide group formed per mole oxygen absorbed been confirmed at low levels of oxidation (11), but the theoretical yield of monohydroperoxide has been isolated. This linoleate peroxide absorbed the theoretical three moles of hydrogen per mole ester: it also was found in agreement with the literature to contain approximately ⅔ diene-conjugated esters if the previously accepted absorption coefficient of 115 is employed. However use of a more appropriate absorption coefficient raised the calculated conjugation to higher than 90%. On this basis, it would appear that non-conjugated esters are formed to only a minor extent during autoxidation.

Oxidation to high levels [0.3 mole oxygen per mole ester and above, see also (1)] results in the secondary oxidation of the monohydroperoxides and forms what is designated here as Component III.

Component III is more polar than the monohydroperoxide as judged by the partition coefficient. The addition of oxygen to the monoperoxide appears to yield no increase in number of peroxide groups but does cause loss of diene conjugation and a decrease in moles of hydrogen absorbed per mole ester. After reduction with hydrogen on a palladium catalyst and with hydriodic acid approximately one hydroxyl is present per mole ester. These experimental facts are consistent with the structure postulated by Lundberg *et al.* (10) and Bergström *et al.* (2),



if the oxygen-ring structure is stable under conditions of peroxide determination and hydrogenation.

The infrared spectrum of this component (Fig. 4a) adds little more to our information except by its contrast with the hydroperoxide spectrum.

The intensity of the trans band is very greatly decreased. The band is much broader than in the hydroperoxide spectra. Although the apparent peak remains near 10.12μ, the background on which the trans absorption is superimposed is so steep that the apparent peak represents only the short wavelength limit of the broad true peak, which indicates the appearance of an appreciable proportion of unconjugated trans material. These observations are consistent with the destruction of diene-conjugated bonds measured in the ultraviolet.

A new peak has come in at 11.35μ, where the hydroperoxides show only a weak shoulder. A striking feature of the spectrum is the low intensity of the CH_2 rocking band at 13.75μ as compared with the corresponding band in the spectra of other long-chain fatty acids and their derivatives. While the infrared spectrum is not inconsistent with the postulated structure, only loss of trans conjugation can be cited in support.

The hydroperoxide fractions, isolated from mixtures autoxidized to various levels and at different temperatures, are not identical. The ratio of moles hydrogen absorbed per mole ester decreases (2.99, 2.58, 2.38) in the peroxides isolated from mixtures oxidized to higher levels; yet little influence of this change is observed in its conjugation ratio. Decomposition of hydroperoxides to hydroxyl groups during room temperature autoxidation might account for these observations since hydroxy linoleate would not be separated from linoleate hydroperoxide under these conditions of countercurrent distribution (15).

Analysis of the infrared spectra of the hydroperoxides leads to further information concerning their structural configurations. Spectra of oleate hydroperoxide and of the two linoleate hydroperoxides resemble each other very closely except in the spectral region 10 to 10.6μ. All three hydroperoxide samples showed a band at about 11.7μ, which supports the assignment of this band to the hydroperoxide group

by Shreve (14). The peak optical density of this band changes in the same direction as the purity of sample as determined by peroxide values.

An unexpected feature of all the spectra is a splitting of the carbonyl absorption to give peaks at 5.74 and 5.80μ. The splitting is not an artifact since it appears in each tracing we have made.

The spectral region 10 to 10.6μ has been assigned bands arising from trans configurations of unconjugated (13) and conjugated (6) double bonds.

The trans band of the methyl oleate hydroperoxide (Figure 4d) is at 10.33μ and shows very nearly the same optical density as a sample of methyl elaidate run in the same cell. Apparently the hydroperoxide group has no effect on the position of the trans band. In order to determine whether the intensity has been affected, it would be necessary to have an independent estimate of the total amount of trans material present in the sample. A more suitable designation for the sample would apparently be methyl trans-octadecenoate hydroperoxide.

A comparison of the curves, obtained from the samples of methyl linoleate hydroperoxide with the absorptions found by Wheeler (7) for conjugated cis-trans and trans-trans linoleic esters, shows a very high proportion of conjugation must occur in the hydroperoxides. There is no evidence of an unconjugated trans band in the spectrum of either sample. The two samples showed significant differences in the 10 to 10.6μ region which cannot be accounted for by the difference in peroxide values. Although both show a pair of bands at 10.12 and 10.52μ, the relative intensities of the two bands are quite different in the two samples. The peak optical density of the 10.12μ band is 3.3 times that for the 10.52μ band in the spectrum of the sample prepared from the room temperature autoxidation mixture. This ratio is 2.1 for the hydroperoxide sample prepared from the 0°C. autoxidation mixture and 1.3 for Wheeler's purified cis-trans ester. This indicates that both samples are principally composed of cis-trans and trans-trans conjugated hydroperoxides and that the room temperature autoxidation sample has an appreciably higher proportion of the trans-trans isomer than does the 0°C. autoxidation sample. If the 10.12μ band of the cis-trans isomer is assumed to have an extinction coefficient of half that for the 10.12μ band of the trans-trans isomer, and approximately equal to that of the 10.33μ band of an isolated trans bond, and if the thickness of the cell is assumed to be the same for these two samples and a sample of methyl elaidate whose spectrum we have obtained (the same spacer was used for all three samples), the room-temperature peroxide is about 60% trans-trans and the low-temperature peroxide is about 30% trans-trans.

From the evidence presented it would appear that the mechanism of oxidation of methyl linoleate not only involves migration of a double bond but that this movement results in a cis bond being converted to a trans configuration. This observation is in accord with the study made by Knight *et al.* (9) of methyl oleate autoxidation and further appears to conform to rules set up by Nichols *et al.* (12) for the alkali conjugation of linoleate. There is a strong tendency for conjugated forms of peroxides to predominate over the statistically predicted amount of unconjugated forms. The latter are anticipated to be present to the extent of ⅓ according to the theory of Bolland and Koch (3). In support of the predominance of conjugated forms may be cited the isolation by Bergström of 9 and 13 hydroxy-stearate from hydrogenated autoxidation mixtures of linoleate but the apparent absence of 11-hydroxystearate (1). The infrared data herein cited gave no support to the presence of unconjugated trans bonds. The mechanism by which the room-temperature, high-level autoxidation hydroperoxides gain increased trans-trans configuration is at present only a matter of speculation.

Summary

Methyl linoleate oxidized at room temperature to levels of 0.11, 0.62, and 1.12 moles oxygen per mole ester has been fractionated in the Craig countercurrent extraction apparatus. The weight-distribution curves are composed of three peaks corresponding to three components: a) unoxidized methyl linoleate, b) methyl linoleate monohydroperoxide, and c) secondary oxidation products.

At the 0.11 mole oxidation level Component III was virtually absent and the theoretical yield (11%) of oxidized esters appeared in Component II as the monohydroperoxide. Upon hydrogenation Component II absorbed 3 moles of hydrogen per mole to give monohydroxystearate. Approximately two-thirds of the monohydroperoxide molecules contained dienoic conjugation based on the previously accepted absorption coefficient of 115. Use of a recently published constant, assumed to hold for cis-trans linoleate, raises the calculated conjugation to higher than 90%.

At the 0.62 and 1.12 mole level of oxidation the proportion of Component III increased. Its presence destroyed the stoichiometric relationship found at the 0.11 mole level between moles oxygen absorbed, moles monohydroperoxide isolated, and dienoic conjugation.

Component III isolated from the 1.12 mole level oxidation mixture was calculated to have over 2 moles oxygen per mole ester, yet its peroxide value was lower than that for the monoperoxide. It possessed only 17-22% dienoic conjugation and a greatly reduced number of conjugated trans bonds and absorbed only 2 moles hydrogen per mole ester to yield approximately 1.0 mole hydroxyl per mole ester. Molecular weight determinations showed it to be primarily monomeric.

Infrared analysis of hydroperoxides isolated from methyl linoleate autoxidations conducted at 0°C. and room temperature leads to the conclusions that conjugated cis-trans hydroperoxides are formed predominately at 0°C. and conjugated trans-trans peroxides at room temperature. The lack of evidence for an unconjugated trans band in the infrared spectrum and the high dienoic conjugation observed in the ultraviolet indicate that unconjugated monohydroperoxides are formed to only a minor extent.

Acknowledgment

The authors are grateful to J. C. Cowan for his interest and encouragement, to C. H. Van Etten for the hydroxyl determinations, and to Daniel Swern of the Eastern Regional Research Laboratory for the methyl oleate hydroperoxide.

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[Received March 12, 1952]

Dilatometric Investigations of Fats. VII. Melting Dilation and Polymorphism of an Alpha and Beta Tung Oil[1,2]

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DESPITE the large volume of consumption and the multiplicity of application of tung oil there is little reliable information available with respect to its thermal properties. The specific heats of tung oils of unknown history have been reported by two groups of investigators (3, 4), and Ward, *et al.* (7), recently reported data for the heat capacity of domestic tung oil *(Aleurites fordii)*. No data have heretofore been reported for the change in volume which accompanies heating of tung oil or with respect to the polymorphism exhibited by this oil.

Data are reported here for the changes in volume occurring during heating and cooling of a specific tung oil, the expansibilities of the alpha and beta forms of the oil in the solid and liquid states, the melting dilation and absolute specific volume of each oil at various temperatures over their ranges of melting, and the interplanar spacings, calculated from x-ray diffraction patterns, for the three crystalline forms of beta tung oil.

Experimental

Oils. The tung oil used in the present investigation was a fresh commercial product, expressed from the nuts of *Aleurites fordii*. A portion of alpha (liquid) tung oil was isomerized to the beta (solid) isomer by adding 0.5% powdered potassium iodide, stirring for 4 hours, and filtering. The oil treated in this manner isomerized and solidified overnight. Spectrophotometric analysis of the original and isomerized oil by the method of O'Connor, *et al.* (5), showed that the alpha oil contained glycerides equivalent to 82.0% alpha, no beta, and 80.6% total eleostearic acid. The beta (isomeized) oil contained glycerides equivalent to 14.9% alpha, 58.0% beta, and 74.0% total eleostearic acid.

Polymorphism. Three polymorphic forms of beta tung oil (7) were observed.

Form I, which had the highest melting point (52.8° C.), was obtained in the present investigation when the beta oil was either melted and allowed to cool for several hours, or when it was solidified and tempered.

Form III was obtained by rapidly cooling the melted beta oil by immersing it in a mixture of acetone and dry ice.

TABLE I

Interplanar Spacings of Isomerized (Beta) Tung Oil

Form I		Form II		Form III	
"d" Spacing	Intensity[a]	"d" Spacing	Intensity[a]	"d" Spacing	Intensity[a]
4.54	F (broad)	4.55	M	4.49	F
4.14	VS	4.19	VS	4.02	VS (broad)
3.81	S	3.92	VS	2.28	F
3.58	M	2.30	F		
3.44	M				
3.23	M				
2.87	M				
2.53	M				
2.27	F				

[a] VS = very strong; S = strong; M = medium; F = faint.

Form II was obtained when Form III was melted at 28°C. and allowed to resolidify at the same temperature. The resolidified material (Form II) was observed to melt when placed in a bath held at 44.4°C. or to be transformed without melting to the highest melting modification (Form I) if tempered at about 42-43°C. for a short time.

The transformation of beta tung oil from the lowest melting (Form III) to the highest melting Form I proceeded in the direction of thermodynamic stability and was not reversible in the solid state.

Polymorphism in alpha tung oil was not detected although considerable supercooling was evident to below —38°C., which is the practical limit of the dilatometric method employed.

X-ray diffraction patterns corresponding to Forms I, II, and III were obtained by photographing beta tung oils contained in capillary tubes. The freshly prepared Form III was aligned on the camera mount contained in a large cooler maintained at 0°C., and the mounted sample placed in an insulated box cooled to 0°C. with dry ice. This precaution was necessary to avoid exceeding the transition temperature of Form III during the time it was exposed to the radiation. Forms I and II were photographed satisfactorily at room temperature.

The diffraction photographs were obtained with a General Electric Diffraction X-ray Unit, Model XRD, using CuK_α radiation with a nickel filter (0.0007-inch thick) and a plate distance of approximately 6 centimeters. The "*d*" spacings of Forms I, II, and III were calculated from the photographs. The spacings and their intensities are recorded in Table I.

[1] Report of study made under the Research and Marketing Act of 1946.
[2] Presented at the 43rd Annual Meeting of the American Oil Chemists' Society, Houston, Tex., Apr. 28-30, 1952.
[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.