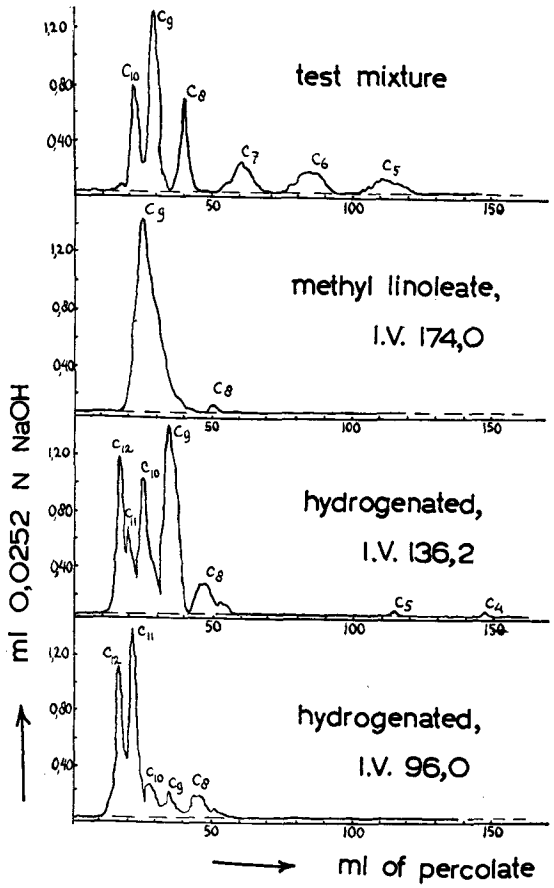

FIG. 2. Chromatographic analysis of dicarboxylic acids, obtained from partly hydrogenated methyl linoleate.

determination of saturated fatty acids in hydrogenation products of methyl esters of oleic and linoleic acid (12).

Summary

The displacement of the double bond of several unsaturated fatty acid methyl esters during hydrogenation with a nickel-kieselguhr catalyst at 180°C. was investigated. The analysis of the dicarboxylic acids (obtained by oxidation of the reaction products with $KMnO_4$ in acetic acid solution) by means of partition chromatography enabled a reliable semiquantitative determination of the position isomers formed.

During hydrogenation of methyl esters of oleic, elaidic, petroselinic, and linoleic acid formation of large amounts of position isomers was proved to occur. Migration of the double bonds in both directions took place but was in all cases strongly pronounced in a direction opposite the ester group. The place and configuration (cis or trans) of the double bonds in the starting material apparently were of little importance in this respect. It follows that hydrogenation of fatty acid esters leads to products which are far more complicated, as is generally known. This is especially of importance with respect to the application of hydrogenated fatty oils in the food industries.

Acknowledgment

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Structure of Hydroperoxides Obtained from Autoxidized Methyl Linoleate[1,2]

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THE course and mechanism of the autoxidation of linoleate esters have been extensively studied (3, 4, 5, 15, 16). It appears well established that the principal products formed initially under mild conditions of oxidation are monomeric monohydroperoxides, a high proportion of which contain conjugated diene systems (4, 5, 15). The geometric configurations in the double bond systems of the autoxidation products have not hitherto been established.

Previous estimates of the amount of conjugated peroxide (3, 4, 5, 15, 16) have been based on the molecular extinction coefficient for trans, trans linoleic acid (32,200 at 230-234 mμ, mole/liter, 1 cm.). The peroxides were estimated to be 70 to 75% conjugated. The remaining peroxide was assumed to be nonconjugated. However a linoleate peroxide formed at 0° with lipoxidase catalyst was reported with 97.5% conjugation on this basis (2).

The trans, trans isomers were the only pure conjugated linoleates then known. More recent work has shown that the cis, trans conjugated linoleates have lower molecular extinction coefficients, 27,400 (11) or 28,700 (17). Obviously a knowledge of the geometric

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isomers of the conjugated hydroperoxides is necessary for accurate estimates of the amount of conjugation present. Recent infrared studies on cis, trans and trans, trans linoleates show that these two isomers can be distinguished and estimated in mixtures (11).

These facts gave impetus to the present study, the objects of which were a) to obtain evidence concerning the geometric configuration of the double bonds in peroxides formed in the early stages of the autoxidation of methyl linoleate, and b) to reevaluate the proportions of conjugated and unconjugated hydroperoxides on the basis of infrared and ultraviolet spectral data.

It was found that methyl linoleate, oxidized at 0 to 2°C. to a relatively low level of oxidation (12% of theoretical for pure monohydroperoxide), yielded hydroperoxides which were at least 90% cis, trans conjugated hydroperoxide octadecadienoate and therefore contained not more than 10% of nonconjugated material. Methyl linoleate autoxidized at 24°C. however yielded hydroperoxides which contained a considerable proportion of trans, trans conjugated material.

Experimental

Preparation of octadecadienoate hydroperoxides. The methyl linoleate used in this investigation was obtained from the Hormel Foundation and was prepared by debromination of pure tetrabromstearic acid. Its iodine value was 173.0 (theoretical 172.4), and it contained less than 0.1% conjugated material. Samples of methyl linoleate prepared in an identical manner were previously found by Brown (6) to contain no less than 90% of the cis, cis isomer. The balance presumably consisted primarily of the cis, trans and trans, cis isomers of methyl 9,12 octadecadienoate.

The 117.1 grams of methyl linoleate were oxidized in the dark at 0 to 2°C. in a loosely stoppered Erlenmeyer flask. After a peroxide value of 761 me/kg., measured as described elsewhere (16), had been attained, the oxidized fraction was completely and quantitatively separated from unoxidized linoleate by partition between Skellysolve F and aqueous ethanol (19).

The weight of the recovered oxidized fraction was 13.63 grams. This compares favorably with a theoretical yield of 13.75 g. of monohydroperoxides based on the peroxide value of the autoxidized linoleate. The peroxide value of the separated oxidized fraction was 6,100 m.e./kg., again in good agreement with the theoretical value of 6,125 for pure octadecadienoate hydroperoxides. Apparently under the conditions employed in this oxidation only relatively small amounts of secondary products were produced.

For comparison 50 grams of methyl linoleate were oxidized in the dark at 24°C. in a loosely stoppered Erlenmeyer flask. After 20 days' storage at this temperature the peroxide value was 325 m.e./kg. The oxidized fraction was completely and quantitatively separated from the unoxidized linoleate as before (19). Analyses of the oxidized fraction disclosed significant differences between this peroxide concentrate (II) and the one obtained at 0°C. (I). Most significant was the fact that the peroxide value was only 5,600 m.e./kg., compared with 6,100 for concentrate I. Concentrate II also contained a relatively high percentage of free acid (6.5% as linoleic acid), indicating that secondary reactions had occurred to an appreciable extent. Nevertheless on the basis of the specific absorption coefficient at 234 mμ, it appears that most of the oxidation products in the concentrate were conjugated peroxides.

Analysis of octadecadienoate peroxides. It was previously shown (14, 15) that some analyses of the oxidation products of linoleate are reliable only if the peroxides are first reduced to their corresponding hydroxyl derivatives. In the present case reduction was accomplished quantitatively and with no apparent side reactions with the aid of stannous chloride. On the basis of auxiliary experiments this reducing agent appeared to be generally preferable to sodium sulfite, sodium bisulfite, or acidulated potassium iodide. Stannous chloride is appreciably soluble in ethyl alcohol and diethyl ether; thus reduction may be conducted homogeneously in either of these solvents. The reaction was found to proceed well even at temperatures as low as —40°C.

The general procedure followed in this investigation was to react the peroxides concentrate with 2 to 5 times the stoichiometrically required amount of a 0.5% alcoholic solution of anhydrous stannous chloride at room temperature. Under these conditions the reaction was 99% complete in about 2½ hours. During the reduction oxygen-free nitrogen was bubbled through the solution to prevent any further oxidation. The results of various standard analyses of the peroxides produced at 0 to 2° and their reduction products are given in Table I.

TABLE I

Chemical Analysis of Unreduced and Reduced Linoleate Peroxide Concentrate (I) (Oxidation conducted at 0 to 2°C.)

Analysis	Peroxide concentrate	$SnCl_2$ reduced concentrate
Peroxide value (m.e./kg.)[a]	6,100	50
Mol. extinction (232 mμ)	24,960	25,100
(276 mμ)	268	311
Epoxy oxygen (mol/mol) (12)	0.022	0.012
Carbonyl oxygen (mol/mol) (9)	.....	.03
Hydroxyl (mol/mol) (24)	.....	1.0
Acid value	nil	nil
Alpha glycolic (mol/mol) (18)	.....	0.037
Iodine value (Woburn) (23)	.....	174.7
Iodine value (hydrogenation)	.....	163.0[b]

[a] The theoretical peroxide value of pure methyl linoleate hydroperoxide is 6125 m.e./kg. A polarographic analysis made by Mr. Constantine Ricciuti showed the methyl linoleate hydroperoxide to be 100.5% monohydroperoxide.

[b] The theoretical iodine value for methyl monohydroxy octadecadienoate is 163.2.

The iodine values indicate that very little if any of the unsaturation was destroyed during autoxidation. It is also apparent from the close correspondence between the peroxide and hydroxyl values that the product consisted almost entirely of hydroperoxides. The values for epoxy, carbonyl, and alpha glycolic content do not necessarily represent quantitative amounts of these materials inasmuch as the reagents used in these tests lack specificity when used on this type of material. Recently King (13) found that alpha carbonyl compounds such as those formed in autoxidation of methyl oleate (8) reacted with hydrogen chloride as used for the determination of epoxy groups. The values for alpha glycolic content are also not believed to be reliable on this material as values of almost the same order are given by such compounds as methyl linoleate, linolenate, and ricinoleate.

From the data in Table I it is concluded that the fraction of oxidized material obtained from the autoxidized linoleate consisted almost entirely of the corresponding methyl hydroxy-octadecadienoates.

Because only a limited amount of material was available, no chemical analyses other than the peroxide value (P.V. 5,600) and acid value (6.49% as linoleic acid) were conducted on the peroxide concentrate (II) obtained from the methyl linoleate autoxidized at 24°C. The specific absorption coefficient of the concentrate at 234 and 276 mμ was 69.9 and 1.1, respectively. The spectral coefficient was determined at 276 mμ as well as 234 mμ because it was the maximum point in a broad band in this region of the spectrum.

Infrared absorption analyses. The analyses were made with a Beckman IR-2 instrument equipped with special slit drives (22) for use with both rock salt and LiF prism. Ten per cent solutions of the materials in either carbon disulfide or tetrachlorethylene were used, depending on the wavelength region under examination.

In Figure 1 the infrared spectrum of peroxide concentrate no. 1 (Table I) in the region of 8.5 to 11 μ is compared with that of a highly purified sample of a conjugated cis, trans methyl octadecadienoate isolated by Jackson and co-workers (11) from alkali isomerized linoleate. Since the molecular extinction coefficient for cis, trans conjugated octadecadienoate has not been determined at 10.55 and 10.18 μ, a quantitative comparison of the two compounds cannot be made. However Figure 1, as well as the others, are reproductions of tracings made by the infrared instrument, and since the curves were made under identical conditions, a direct comparison of curves is possible. The absorption curve for the pure cis, trans conjugated linoleate (curve A, Figure 1) was placed in the same figure as that for the peroxide concentrate (curve B, Figure 1) in order to show the relative congruency of the doublet absorption bands at 10.55 and 10.18 μ.

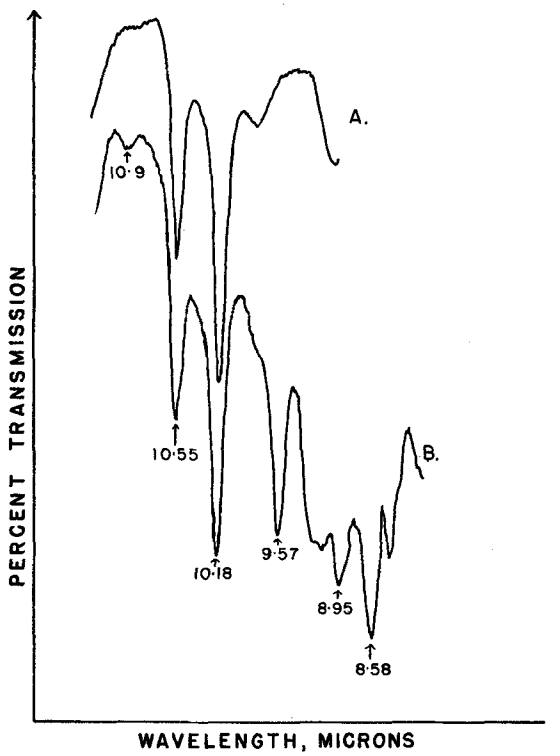


FIG. 1. Infrared absorption spectra. A. Conjugated cis, trans methyl octadecadienoate. B. Isolated peroxide concentrate from methyl linoleate autoxidized at 0 to 2°C. (in CS_2).

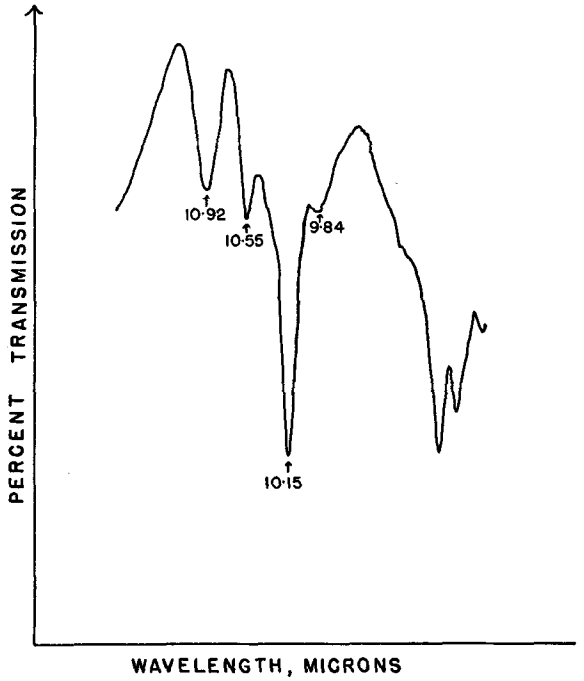


FIG. 2. Infrared absorption spectra. Isolated peroxide concentrate from methyl linoleate autoxidized at 24°C. (in CS_2).

For comparison the infrared absorption band of the peroxide concentrate (II) obtained from the sample of methyl linoleate autoxidized at room temperature is shown in Figure 2. It is evident that concen-

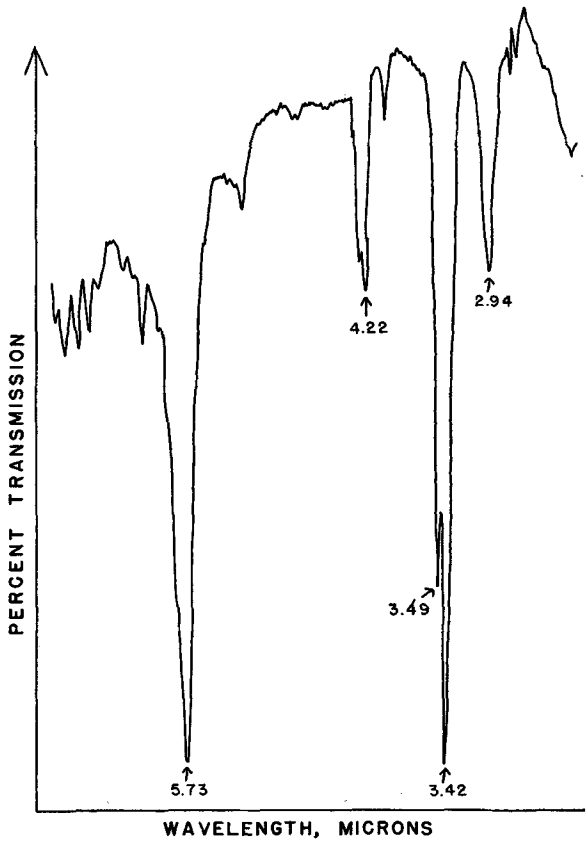


FIG. 3. Infrared absorption spectra. Linoleate peroxide concentrate from sample oxidized at 0 to 2°C. (in C_2Cl_4).

trate II contained much less cis, trans conjugated diene than I. On the other hand, an appreciable amount of trans, trans conjugated diene was formed, as shown by the intensity of the band at 10.15 μ.

Figure 3 shows the absorption of peroxide concentrate I in the region of 7 to 2 μ obtained with the rocksalt prism. The peroxide band was observed at 2.94 μ, as previously noted by others (1, 7). No absorption band at 3.30 μ, such as reported by others (1, 20) to be due to alpha methylene groups, was detectable in this spectrogram, but it showed as a very weak band with the LiF prism (Figure 4). Adams

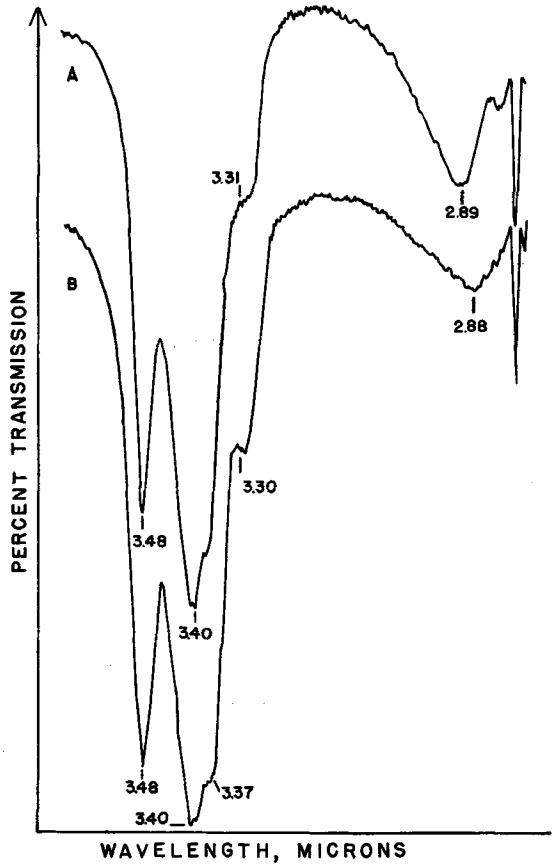
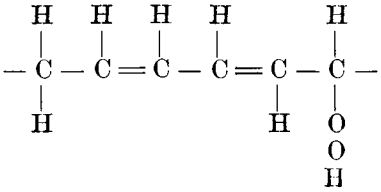


FIG. 4. Infrared absorption spectra. Linoleate peroxide concentrate from sample oxidized at 0 to 2°C. (Lithium fluoride prism) (in C_2Cl_4). A. Before reduction. B. After reduction.

and Auxier (1) observed that the intensity of this band diminished simultaneously with oxidation of dipentaerythritol linoleate. They attributed the decrease in this band to the loss of methylenic groups adjacent to a double bond. In support of this assignment they showed that the intensity of this band was very small in oleate, greater in linoleate, and still greater in linolenate.

We have confirmed the increasing intensity of the band at 3.31 μ in the series normal oleate, linoleate, linolenate (LiF prism). Conjugated cis, trans linoleate also showed a band at 3.30 μ of the same intensity as the 3.31 band of oleate. Adams and Auxier assign this band to alpha methylene groups whereas Sinclair *et al.* (19a) assign it to C — H of C = C. This band was much weaker in the conjugated peroxide concentrate I than in oleate or in cis, trans conjugated linoleate. The doublet at 10.18 and 10.55 μ in the conjugated peroxide indicates that its = C — H bonds are intact. The expected structure of the peroxide:



would have only one alpha methylene, compared to two for oleate or conjugated linoleate, three for linoleate, and four for linolenate. These facts agree best with the assignment of 3.31 μ band to the alpha methylene group.

Figure 4 also shows the spectrum from 2.9 to 3.5 μ for the peroxide concentrate (A) and for its reduced form (B). The spectra were obtained with the LiF prism. The two curves differ in that the band for OH group occurs at a slightly lower wavelength and is less intense than that of the — OOH group. Honn and coworkers (10) observed a similar effect.

Absorption of peroxide concentrate I in the carbonyl region (5.5 to 6.0 μ) is shown in Figure 5, using

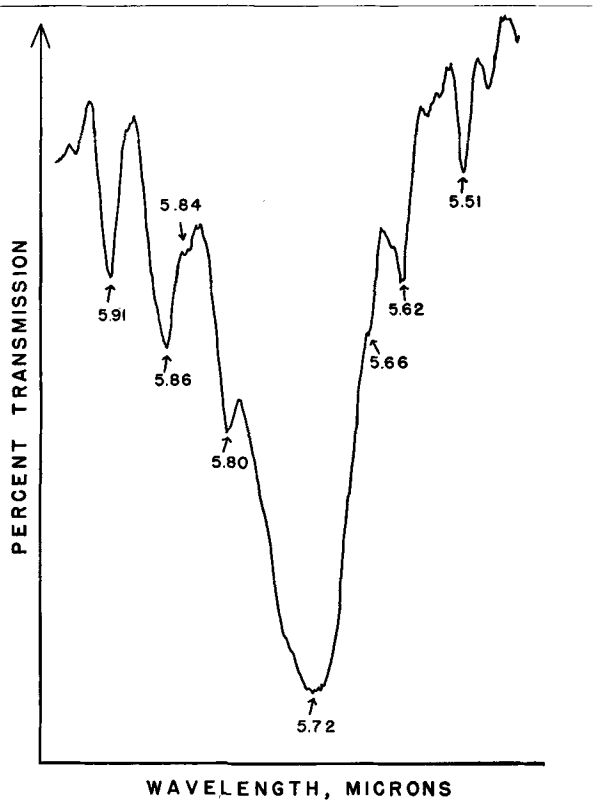


FIG. 5. Infrared absorption spectra. Linoleate peroxide concentrate from sample oxidized at 0 to 2°C. (Lithium fluoride prism) (in C_2Cl_4).

the lithium fluoride prism. The strong ester carbonyl band at 5.72 is evident. The remainder of the bands are not assigned here.

Discussion

It is seen in Figure 1 that strong absorption bands appear in the infrared curves for the conjugated methyl octadecadienoate at 10.55 and 10.18 μ. These

bands constitute a doublet which has been shown to be associated with the conjugated cis, trans diene configuration (11). The same bands appear in the curves for the linoleate hydroperoxide concentrate.

Another observation of considerable importance, as will be apparent from the ensuing discussion, is that at each of the two wavelengths the intensity of the absorption for the pure cis, trans, conjugated octadecadienoate and the peroxide concentrate obtained by oxidation at 0°C. is virtually the same.

Conjugated trans, trans octadecadienoates show a single absorption band at 10.12 μ (11). Absorption at 10.12 μ due to a small amount of conjugated trans, trans diene in the linoleate hydroperoxide obtained at 0°C. may be obscured by the intense absorption at 10.18 μ due to the conjugated cis, trans diene. The presence of any appreciable amount of trans, trans conjugated diene would cause the maximum to shift from 10.18 μ toward 10.12 μ.

Since there is no evidence of a band at 10.12 μ and because the ratios of the intensities of the bands at 10.55 and 10.18 are the same in both curves of Figure 1, it was concluded that the hydroperoxides in this sample contained little if any (less than 10%) conjugated trans, trans diene.

Ultraviolet data further confirm the presence of a high proportion of conjugated diene hydroperoxides. The preceding discussion indicates that conjugated peroxides in concentrate I are in the cis, trans form. Therefore the extinction coefficient for cis, trans conjugated linoleate should be used in calculating the amount of conjugation in the peroxide concentrate I. Using the value reported by Jackson *et al.* (11), peroxide concentrate I is 87% conjugated. Using the value of Nichols *et al.* (17), it is 91.3% conjugated.

These calculations are based on two assumptions: a) that only cis, trans conjugated material was present and b) that the molecular extinction of the conjugated hydroperoxide is the same as that of unoxidized conjugated linoleate. Analogous cis, cis conjugated compounds have not yet been isolated, and their infrared and ultraviolet properties are unknown. It is conceivable that cis, cis conjugated dienes would have absorption bands which would require a complete reinterpretation of these data, and until they have been characterized, their presence in these peroxide concentrates cannot be excluded. The peroxide value and the hydrogenation iodine value are theoretical for diene hydroperoxide so that the balance of the material (about 10%) is most likely a nonconjugated hydroperoxide.

The composition of peroxide concentrate II is significantly different from that of concentrate I. The lower peroxide value of II indicates some nonperoxide oxidation products. Its infrared band at 10.55 is weaker, and the band at 10.15 is stronger as well as displaced from the 10.18 position characteristic of conjugated cis, trans dienes.

Trans, trans conjugated dienes show a very strong band at 10.12 μ but no band at 10.55 μ. Mixtures of cis, trans and trans, trans conjugated dienes have a band at 10.55 μ whose intensity is a direct measure of the amount of cis, trans isomer. In such mixtures the 10.12, 10.18 bands merge to a band of intermediate wavelength (11). Figure 2 indicates that the conjugated portion of concentrate II is a mixture of cis, trans and trans, trans conjugated dienes. The formation of conjugated trans, trans peroxides in concentrate II probably results from a shift in configuration of the cis, trans isomer first formed. The shift is possibly catalyzed by peroxide at the higher temperature.

The 10.9 μ band shown by concentrate II is many times more intense than that shown by concentrate I. The structure responsible for this band is not known to us.

Bergstrom and Holman (2) reported a molecular extinction of 31,400 for the peroxide of linoleate formed at 0° with pure lipoxidase catalyst. Tappel *et al.* (21) reported average values of 28,400 in initial stages of the oxidation at low temperatures, using a crude lipoxidase. These values are 13-24% higher than our values for the cis, trans peroxide formed in the absence of catalyst. Lipoxidase peroxides are being prepared in this laboratory in order to study their structure by ultraviolet and infrared spectroscopy.

Summary

A sample of debromination methyl linoleate has been autoxidized to a peroxide value of 671 m.e./kg. at approximately 0°C. in the dark. An essentially pure concentrate of methyl octadecadienoate monohydroperoxide was quantitatively separated; infrared and ultraviolet spectral studies were made on the peroxide concentrate and on the corresponding hydroxyl derivative obtained by reducing the peroxides with stannous chloride.

The infrared data showed no conjugated peroxides having geometric configurations other than cis, trans; the same data also showed that the peroxide concentrate contained at least 90% conjugated cis,trans forms. Calculations based on ultraviolet spectrophotometric methods also indicated that the peroxides were at least 90% conjugated. The remaining 10% of the sample is most likely nonconjugated diene hydroperoxide. Since analogous cis, cis conjugated dienes have not been isolated and their infrared and ultraviolet properties are unknown, their presence here in small amounts is possible. Ultraviolet and infrared spectra of the reduced compounds conform closely to those of the peroxides except for reduction in the intensity of the OH bond at 2.88 μ.

The infrared absorption spectra of the C—H structure and carbonyl groups of an essentially pure conjugated cis, trans methyl octadecadienoate monohydroperoxide were recorded, using a LiF prism.

The infrared absorption spectra of the C-H strucfraction isolated from methyl linoleate autoxidized in the dark at 24°C. indicated that appreciable amounts of conjugated trans, trans hydroperoxides were present, in addition to those of the cis, trans type. It is possible that the conjugated cis, trans isomers were formed originally but were labile at the higher temperature and in the presence of catalysts (*e.g.*, peroxides) were transformed to the thermodynamically more stable conjugated trans, trans isomer.

Acknowledgment

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Low-Temperature Solvent Fractionation of Animal Fats. Part I. Evaluation of Anhydrous Solvents for Crystallization of White Grease

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THE work reported in this paper is one phase of a broad program directed toward finding new outlets for surplus fats and oils by improving products already available or by preparing new products of greater utility. This phase of the program relates specifically to the fractionation of inedible white grease to produce liquid fractions similar to lard oil, having specific pour points and iodine values and evaluation of methods for such production.

Lard oil has been produced ordinarily from inedible hog fat, known as white grease or yellow grease. It is the more unsaturated, liquid portion of these greases and is more valuable than the raw material because it remains liquid at temperatures normally encountered in its use.

The method used in production of lard oil for many years is the graining and pressing method, in which the grease is cooled slowly for a relatively long period, 3 to 6 days, at about 50°F. It is then placed in bags and pressed to express the lard oil. The slow chilling is necessary to produce a crystal of the type from which the liquid portion will be readily released on pressing. It has been reported (4) that by this method from 50 to 65% of the white grease is expressed as lard oil of 40°F. pour point. The pour point is defined as the temperature, in degrees Fahrenheit, at which the oil will just flow; it is controlled by the temperature to which the grease is chilled and the temperature and care exercised in the pressing. The solid fraction, or stearines, constituting the remainder of the grease, has a higher melting point than the white grease and a lower iodine value but apparently commands no premium over the raw material. The economic success of the process therefore depends on the efficiency with which the yield of the liquid fraction, lard oil, can be held at a high level and the control of its quality. It is apparent that the graining and pressing process has certain disadvantages. Among these are the high labor costs involved in the handling and pressing operations, the high degree of skill required to produce a lard oil of uniform quality from batch to batch, and inability of the process to be run continuously.

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

Background

The general method of dissolving fats, oils, or fatty acids in various solvents, of cooling these solutions to temperatures at which the higher melting point components become solids, and of separating the solid and liquid phases of the slurries thus formed by filtering has been described by various investigators.

In the laboratory separation of fatty acids and their derivatives Swern (7) and coworkers report on a method employing crystallization from acetone and discuss its applicability to commercial production. Kistler *et al.* (3) describe "The Commercial Solvent Separation of Fatty Acids," by the Emersol Process, which operates on the principle of controlled crystallization of solid fatty acids from a polar solvent and removal of solid acids by filtration. Methanol of 90% concentration is used. Fractionation of lard and tallow by crystallization from anhydrous acetone on a laboratory scale is described by Riemenschneider *et al.* (6). Processes have been developed for the fractionation of glycerides by crystallization from various solvents. Among these are propane (4), acetone (2), isopropyl acetate, methyl ethyl ketone, ethyl acetate, ethyl ether, and methyl isobutyl ketone (5).

The need for the solvent evaluation work reported in this paper became apparent in the course of the operation of a low-temperature crystallization pilot plant designed for fractionation of fatty acids, fats, and greases. The process currently under study is the production of oils of improved qualities from commercial greases by controlled crystallization from solvent solutions. Design and cost data are to be developed for the production of the various products made in these operations.

Preliminary work in the pilot plant unit was done with acetone as the solvent, and early tests indicated