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Autoxidation of Unsaturated Fatty Acid Methyl Esters. II.

Nonconjugated Compounds

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Methyl linoleate and its *trans*, *trans* isomer, methyl linolenate, and a mixture of methyl eicosapentaenoate and methyl docosahexaenoate (50 : 50%) were autoxidized in the conditions free from natural antioxidants and metals. Their autoxidations gave the induction period of 49, 52, 18 and 11 h, and showed the oxidation rates of 3.61, 3.08, 5.24 and 9.41×10^{-5} mol/h, respectively, at the autoxidation level after the induction period (specified as the time required to gain 10 mg by weight). Relative autoxidation rates derived from the induction periods were almost similar to the ratio of the number of the active methylene group, but those from the oxidation rates were equal to the ratio of unsaturation degree. In comparison with the oxidation rate of methyl oleate, the abstraction of hydrogen from the active methylene groups by peroxyl radicals was superior by 1.54×10^{-5} mol/h in the rate to that from α-methylene groups. An Increase in the unsaturation degree of autoxidation substrates permitted the rapid and large formation of hydroperoxides, radicals, polymers, $\alpha,\beta,\gamma,\delta$-unsaturated carbonyls and etc. But in comparison at the same autoxidation level (weight gains) free from oxidative polymerization and decomposition, the amounts of these autoxidation products were similar each other. These data showed that the rate-determing step during induction period of autoxidation was the abstraction of hydrogen from the active methylene groups by oxygen molecules, and after the induction period was the diffusion of peroxyl radicals. The geometric isomeric effect that methyl linoleate was autoxidized easier than the *trans*, *trans* isomer was observed. This effect suggested the interaction of the oxygen molecule with the double boud of substrates in initiating the chain reaction.

1. Foreword

Many reports have been made on autoxidation of unsaturated fatty acid methyl esters with active methylene groups. According to these reports, autoxidation of unsaturated fatty acid methyl esters with active methylene groups proceeds through the release of hydrogen from active methylene groups and through the formation of conjugated diene hydroperoxides which accompanies it.1)-8) Furthermore, it has been pointed out that relative oxidation rates for methyl oleate, methyl linoleate and methyl linolenate at near room temperature are 1 : 10∼12 : 16∼25.9),10) These differences are thought to be based on differences in the dissociation energy of hydrogen from active methylene groups or α-methylene groups.11) Studies up to now, however, have not investigated dynamical data such as autoxidation rates and their relation with autoxidation mechanisms as seen from their products. Thus, differences in autoxidation mechanisms which form the base of dynamical data obtained from autoxidation of unsaturated fatty acid esters are still obscure. Moreover, the effect of geometric isomers of substrates on autoxidation rates and autoxidation products is unknown.

In this study, unsaturated fatty acid esters with active methylene groups free from natural antioxidants and metals were autoxidized. And their autoxidation mechanisms and the geometric isomeric effect of autoxi- p. 27
dation substrates were fully investigated from their autoxidation rates and products.

2. Experiment

2.1 Materials

Methyl *cis*-9, *cis*-12-octadecadienoate (methyl linoleate, *c*,*c*-MODD, GLC purity 99.9%) were prepared from safflower oil fatty acids followed by urea-adduct formation, methyl esterification, and column chromatography using silicic acid in n-hexane in order to remove trace amounts of peroxides and pigments. Preparation of methyl *trans*-9, *trans*-12-octadecadienoate (*t*,*t*-MODD, IR purity 100.0%): linoleic acid was treated with nitric acid and sodium nitrite,12) followed by column chromatography with silicic acid in n-hexane, low temperature recrystallization with acetone (mp 28.3~28.7°C; Reference value: 28~29°C 13),14)), and finally esterification. Methyl *cis*-9, *cis*-12, *cis*-15-octadecadienoate (methyl linoleate, MODT, GLC purity 99.5%) was prepared from linseed oil fatty acids followed by urea-adduct formation, esterification and column chromatography with silicic acid in n-hexane. Methyl eicosapentaenoate and methyl docosahexaenoate mixture (MEP + MDH, GLC purity 50.0 + 50.0%, isolated *trans*-double bond undetected by IR, see Figs. 2-5) was prepared from squid oil fatty acids followed by urea-adduct formation, esterification, distillation under reduced pressure (bp 179~181°C/0.7 mmHg) and column chromatography using silicic acid in n-hexane in order to remove peroxides and pigments.

The iron chloride (III)-2, 2'-bipyridine method15) and atomic absorption analysis confirmed that these autoxidation substrates were free from any natural antioxidants or metals.

2.2 Autoxidation

As described in previous reports,16)-23) autoxidation of samples (1.5000~1.5005 g) was carried out under conditions of 36.5 ± 0.5°C with oil thickness of 1.03 mm. Weight gains following autoxidation were determined by the gravimetric method.24)

2.3 Analysis

IR, UV, ESR and NMR spectra, peroxide values (POV), molecular weights (MW) and refraction indices of samples at each autoxidation level were measured. The details have been described in previous reports.16),21),23)

3. Results

Figure 1 shows time-course weight gains in autoxidizing samples. For weight gains during autoxidation, the time required for samples to attain 10 mg weight was considered the induction period. Table 1 shows rates of weight gains and maximum weight gains during and after induction periods where rapid changes in autoxidation levels were observed.

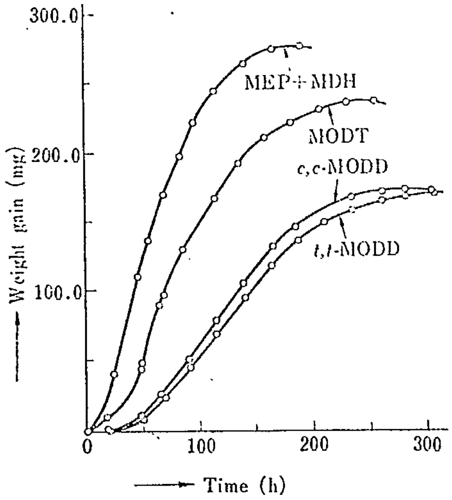

Fig.-1 Weight gain with time in autoxidizing *cis*-9, *cis*-12-methyl octadecadienoate (*c,c*-MODD), *trans*-9, *trans*-12- methyl octadecadienoate. (*t, t*-MODD), *cis*-9, *cis*-12, *cis*-15 · methyl octadecatrienoate (MODT), and methyl eicosapentaenoate + methyld – ocosaaxanoaie (MEP+MDH). Conditions : 36.5±0.5℃, oil thiohness, 1.03mm.

Table-1 Comparison of induction period, rate and maximum weight gain or maximum peroxide value, measured by weighing procedure or iodometric analysis.

	Weighing procedure			Iodometric analysis		
	Induction period[a] (h)	Rate (mg/h)	Max. weight gain (mg)	Induction period[a] (h)	Rate (meq·kg^{-1}·h^{-1})	Max. POV (×10^{3}meq/kg)
Methyl eicosapentaenoate + Methyl docosahexaenoate	11	3.05	278	10	123.5	6.13
Methyl linolenate	18	1.70	238	17	47.1	4.81
Methyl linoleate	49	1.17	174	44	20.3	4.23
Trans, trans isomer of methyl linoleate	52	1.00	168	46	19.8	4.21

a) time to gain 10 mg of weight gain or 0.38×10^3 meq/kg of peroxide value.

Results showed that autoxidation of unsaturated methyl esters with active methylene group produced short induction periods, large rates of weight gain and large maximum weight gains as unsaturation degree increased. Furthermore, in the autoxidation of methyl linoleate and its trans-trans isomer, the geometric isomeric effect where the cis-cis isomer was autoxidized easier than the trans-trans isomer was observed. p. 28

IR spectra at 0.10 mm cell of autoxidation samples of these unsaturated fatty acid methyl esters with active methylene group showed changes in the following absorption bands: (1) In hydroxyl group at 3600 cm^{-1} (increases), (2) in hydroperoxyl group at 3450 cm^{-1} (increases), (3) in α-methylene group at 3020 cm^{-1} (decreases), (4) in aldehyde group at 1725 cm^{-1} (increases), (5) in ketone group at 1715 cm^{-1} (increases), (6) in active methylene group at 1400 cm^{-1} (decreases) (the increase of absorption band at 1400~1100 cm^{-1} is due to polymerization), (7) in ring peroxides at 1100 cm^{-1} (increases), (8) in trans-trans conjugated diene at 988 cm^{-1} (increases), (9) in cis-trans conjugated diene at 982 and 948 cm^{-1} (increases), (10) in conjugated diene at 1650 and 1600 cm^{-1} (increases), (11) in the isolated trans double bond of 968 cm^{-1} (increases/decreases [respectively]), (12) in the isolated cis double bond of 913 cm^{-1} (decreases).

Amounts of hydroxyl groups formation at maximum oxidation levels were 0.52% for methyl linoleate and its trans-trans isomer, 1.59% for methyl linolenate, and 2.04% for a mixture of methyl eicosapentaenoate and methyl docosahexaenoate (mol/mol-sample).

Formation of aldehyde groups at 1725 cm^{-1} was large in proportion to unsaturation degree, and for methyl linoleate the formation was larger than its trans-trans isomer.

NMR spectra of autoxidation samples of methyl linoleate, its trans-trans isomer, methyl linolenate, and a mixture of methyl eicosapentaenoate and methyl docosahexaenoate showed the following [respective] changes in each proton: (1) 2.00, 1.93, 2.00 and 2.05 ppm α -methylene groups (doublet, decreases), (2) 2.70, 2.60, 2.80 and 2.83 ppm active methylene groups (singlet in trans-trans isomer, and triplet in the others, decreases), (3) 4.25, 4.25, 4.41 and 4.40 ppm methene with hydroperoxyl group (comparatively broad, increases), (4) 5.24, 5.30, 5.28 and 5.37 ppm vinylene groups (7 lines, decreases). Hydroperoxyl proton was for the most part unmeasurable due to formation of hydrogen bonds and the like. Fig. 2 shows changes in active methelene groups in autoxidation samples obtained by IR and NMR spectra.

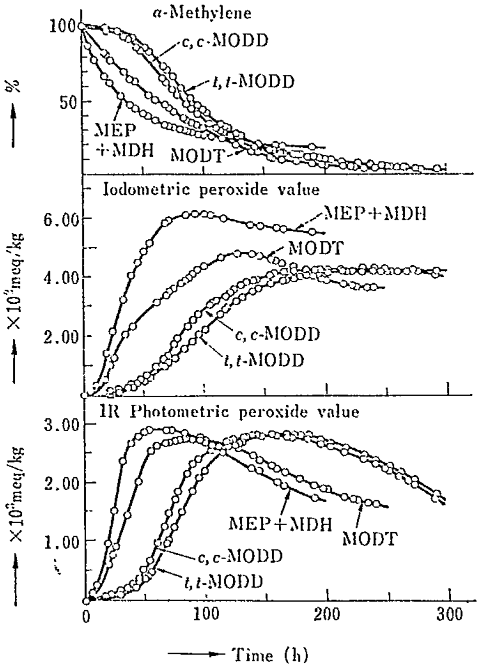

Fig.-2 Change in α-- methylene contents and peroxide values with time in autoxidizing substrates specified in Fig.-1.

Changes in α-methylene groups$^{2)}$ in autoxidation obtained by IR spectra were similar to those in active methylene proton signals of NMR spectra. Further, given that the *trans*-*trans* isomer of methyl linoleate did not show an IR absorption band at 3020 cm^{-1} because of its symmetric structure, it showed, rather, changes in active methylene proton signals of NMR spectra. Active methylene group disappeared quickly with the increase of unsaturation degree of autoxidation substrates. However, when plotted against weight gains instead of time, decreases of active methylene groups were roughly the same in all substrates up until about the 50 mg weight gain point.

Fig. 2 shows POV changes obtained by iodometric titration and IR spectra following autoxidation of samples. Changes in NMR proton signals based on methene group with hydroperoxyl group corresponded closely with these POV changes. POV changes were similar to oxidative weight gains (Fig. 1). In POV changes obtained by iodometric titration, the time required for samples to reach 0.38×10^3 meq/kg POV was considered the induction period. This, together with the formation rate of hydroperoxide and maximum hydroperoxide formation at oxidative levels after the induction period, is shown in Table 1.

Fig. 4 shows relations between oxidative weight gains and POV in autoxidation samples. A theoretical curve was obtained by assuming that oxygen absorbed by samples (weight gains) formed hydroperoxides quantitatively. POV based on iodometric titration corresponded to the theoretical curve until samples oxidized to the following weight gains: 83 mg for methyl linoleate and its *trans*-*trans* isomer, 68 mg for methyl linolenate and methyl eicosapentaenoate + methyl docosahexaenoate. On the other hand, POV obtained by IR spectra corresponded to the theoretical curve until oxidized to 63 and 56 mgs weight gains for these substrates, respectively. POV obtained by IR spectra displayed hydroperoxide components which can exist in a state of nonassociation. The absorption band at 3520 cm^{-1} which determined hydroperoxides, increased quantitatively until samples were oxidized to the following weight gains: 63 mg for methyl linoleate and its trans-trans isomer, 56 mg for methyl linolenate and methyl eicosapentaenoate + methyl docosahexaenoate. However, when samples were oxidized beyond the above-mentioned oxidation levels, an absorption band at 3450 cm^{-1} in addition to the one at 3520 cm^{-1} appeared. They increased with time and did not disappear even when samples were diluted to 1.00 g/l. Consequently, the absorption band at 3450 cm^{-1} is based on hydroperoxides which form an intramolecular hydrogen bond (contained in oxidative polymers). POV, based on hydroperoxides which form intramolecular hydrogen bonds, corresponded to the difference between each of the POVs obtained by iodometric titration and by IR spectra. p. 29

Fig. 3 shows changes in conjugated dienes calculated from UV and IR spectra following autoxidation of substrates.

The formation of conjugated dienes in all the substrates increased as autoxidation progressed, and attained maximum values. Conjugated dienes calculated from UV spectra were plotted against weight gains and are shown in Fig. 4.

The relation between conjugated dienes and oxidation weight gains coincided with the theoretical curve (amount of oxygen absorption, i.e. supposing that the weight gains are related quantitatively to conjugated diene formation) regardless of the kind of substrate until samples were

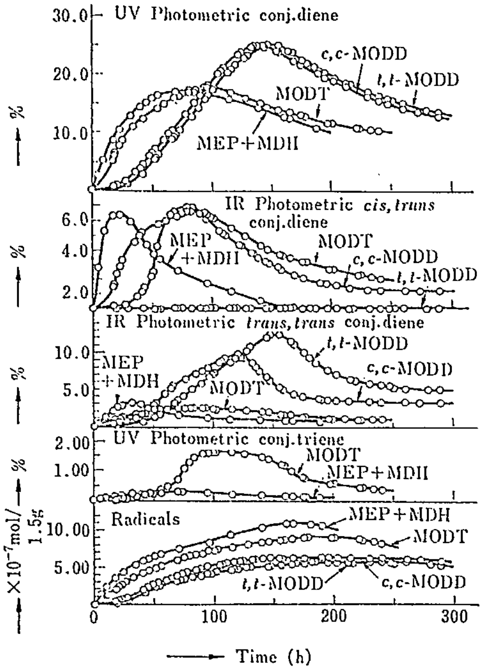

Fig.-3 Change in conjugated dienes, conjugated trienes, and radicals with time in autoxidizing substrates specified in Fig.-1.

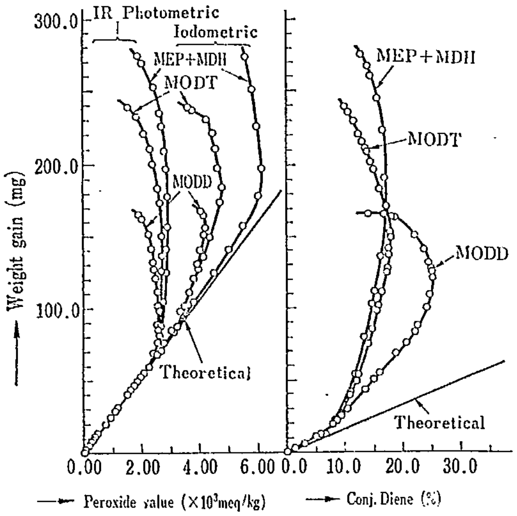

Fig.-4 Relations between oxidative weight gains and peroxide values or conjugated dienes in the autoxidation of substrates specified in Fig.-1.

oxidized to a weight gain of about 13 mg.

The fact that POV followed the theoretical curve to a higher oxidation level (weight gains) than conjugated dienes did prove therefore, that measured conjugated dienes originated in conjugated diene hydroperoxides. Maximum formation of conjugated dienes decreased following an increase of unsaturation degree of substrates. Analogous were methyl linoleate and its trans-trans isomer. Observed from IR spectra the formation of sis-trans conjugated dienes was faster in substrates having a high degree of unsaturation which were comparatively easily oxidized; yet, their maximum formations were roughly the same regardless of substrate. In the autoxidation of methyl linoleate trans-trans isomers, however, the formation of cis-trans conjugated dienes were not observed at all. Still, the maximum formation (products) of *trans-trans* conjugated dienes were in the following order: *trans-trans* isomer > methyl linoleate > methyl linolenate and methyl eicosapentaenoate + methyl docosahexaenoate. A comparison of changes in formations of *cis-trans* and *trans-trans* isomers accompanying autoxidation of substrates (Fig.3) showed that the formation of *cis-trans* conjugated dienes was at a low oxidation level prior to *trans-trans* conjugated diene formation. In addition to this result, the shift from 233 to 231 nm of the maximum absorption of conjugated dienes in UV spectra following the progression of oxidation of substrates, showed that *cis-trans* conjugated dienes appeared first, followed by a shift to *trans-trans* conjugated dienes. The autoxidation of samples above trienes paralleled the formation of conjugated dienes, yielding some conjugated trienes (268 nm) (Fig.3).

Fig. 3 illustrates changes in radical (g value. 2.0061) concentrations following autoxidation of substrates. Radical formation increased linearly after the induction period and deviated from the linear line near the maximum radical concentration. Radical formation was large in substrates with high unsaturation degrees, while the radical formation in both methyl linoleate and its *trans-trans* isomer was almost same. The rate of radical formation at post-induction period oxidative levels was roughly 5.70 x 10^{-9} mol/h regardless of substrate. In comparisons at equal autoxidation levels (weight gains) radicals presented roughly equal concentrations in all substrates until samples attained about 20 mg weight. p. 30

Fig. 5 shows data on isolated *trans* double bond and mean molecular weight calculated from IR spectra, $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyls (272 nm) calculated from UV spectra, and refractive indices at 20°C in autoxidizing samples.

Results indicated that when methyl linoleate and its trans-trans isomer, methyl linolenate and methyl eicosapentaenoate + methyl docosahexaenoate were oxidized to 70, 70, 52 and 44 mg weight gains, respectively, formation of polymers and unsaturated carbonyls increased gradually. Thus, the higher the degree of unsaturation the lower the autoxidation level (weight gains), producing polymers and unsaturated carbonyls.

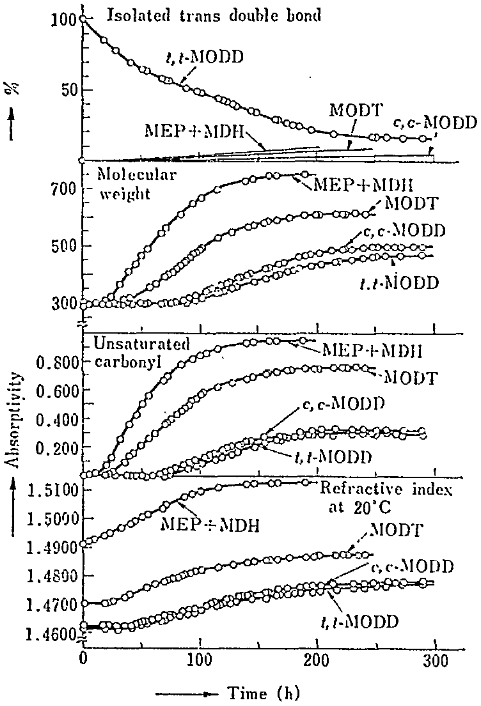

Fig.-5 Change in isolated *trans* double bond, molecular weight, α, β, γ, δ-unsaturated carbonyl, and refractive index with time in atoxidizing substrates speciiced in Fig-1.

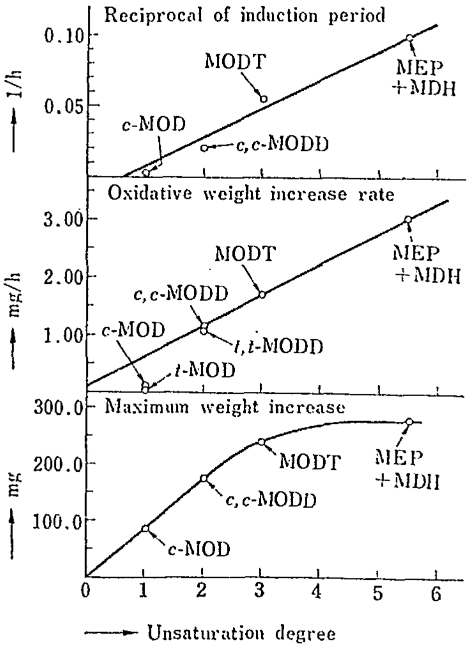

Fig.-6 Comparison of induction period, oxidative weight increase rate and maximum weight gain against the unsaturation degree of substrates specified in Fig-1, methyl *cis*-9-octadecenoate (*c*-MOD), and methyl *trans*-9-octadecenoate (*t*-MOD).

4. Discussion

The autoxidation mechanism of olefins has been generally reported as follows.25), 26)

$\mathrm{RH} + \mathrm{O_2} \longrightarrow \mathrm{R\cdot} + \mathrm{\cdot OOH}$ (1)
$\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{ROO\cdot}$ (2)
$\mathrm{ROO\cdot} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R\cdot}$ (3)
$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{\cdot OH}$ (4)
$\mathrm{RO\cdot} + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R\cdot}$ (5)
Various termination reaction induced by the coupling and disproportionation of free radicals (6)

The relation between POV and oxidative weight gains (Fig. 4) shows that up until methyl linoleate and its *trans*-*trans* isomer attained 83 mg weight gain and methyl linolenate and methyl eicosapentaenoate + methyl docosahexaenoate were oxidized to 68 mg, oxygen absorbed in these samples (weight gains) was used quantitatively in forming hydroperoxides. Accordingly, chain propagations based on equations (4) and (5) may be disregarded until samples reach the above-mentioned oxidation levels. Moreover, when considering the relation between POV and oxidative weight gains and the fact that the majority of the radicals in autoxidation under normal oxygen pressure (over 100 mmHg) are not alkyl radicals but rather peroxyl radicals,25) it is possible that the chemical species of the radicals (Fig. 3) measured in autoxidizing samples might be peroxyl radicals based on equations (1) and (2) up until samples autoxidized to the above-mentioned autoxidation levels. Consequently, the fact that changes in radical formation and rate of radical formation at the same autoxidation level were same shows that peroxyl radical concentrations in the autoxidation system and the formation rates of peroxyl radicals induced from equations (1) and (2) were roughly same regardless of substrates. Furthermore, weight gains (Fig. 1) following the autoxidation of samples, and changes in POV (Fig. 2) show that the autoxidation of substrates increased gradually and reached a maximum propagation rate after the induction period. p. 31

The rates of autoxidative weight gains and hydroperoxide formation (Table 1) after the induction period (when indicated in molar units) were almost the same, showing 9.42×10^{-5} mol/h for methyl eicosapentaenoate + methyl docosahexaenoate, 5.25×10^{-5} mol/h for methyl linolenate, 3.98×10^{-5} mol/h for methyl linoleate and 3.09×10^{-5} mol/h for its trans-trans isomer. The values demonstrate the full dynamics of equations (1) (2) and (3), and show the maximum chain propagation rates under conditions of this study.

Fig. 6 shows the relationship of induction periods, rates of weight gain and maximum weight gains determined during autoxidation of unsaturated fatty acid methyl esters with active methylene group to the unsaturation degree of substrates.

For comparison the results16) of methyl oleate and methyl elaidate have been provided. The ease of substrate autoxidation can be judged in comparison with induction periods and post-induction period oxidation rates. As shown in Fig. 6, plotting against the degree of unsaturation of the reciprocal of the induction period resulted in a linear relationship. Thus, the induction period decreased in proportion to unsaturation degree of oxidative substrates. From a comparison of induction periods relative oxidation rates of methyl oleate, methyl linoleate, methyl linolenate and methyl eicosapentaenoate + methyl docosahexaenoate were 1:8.0:21.7:39.0. The rate of oxidative weight gains following autoxidation of substrates (rates of hydroperoxide formation also showed similar relationships) followed a straight line in oxidation of substrates superior to dienes (as shown in Fig. 6) and showed an increase in oxidative rate in proportion to unsaturation degree. Monoen compounds deviated from this straight line, but the difference from the straight line shows the difference of oxidative rate due to abstraction of hydrogen from active methylene groups by peroxyl radicals and abstraction of hydrogen from α -methylene groups. This difference corresponded to 0.499 mg/h (1.55 x 10^{-5} mol/h). Relative oxidative rates of methyl oleate, methyl linoleate, methyl linolenate and methyl eicosapentaenoate + methyl docosahexaenoate were 1:11.0:16.0:28.8.

Results of analysis of autoxidation products showed that the autoxidation of non-conjugated substrates proceeds through abstraction of hydrogen from active methylene groups, formations of conjugated diene hydroperoxides, oxidative polymers, and decomposition products. At the oxidation level before the appearance of polymers and decomposition products, however, autoxidation products corresponded when compared at the same oxidation level (weight gains). This fact indicates that differences observed in autoxidation rates of these non-conjugated substrates did not result from differences of autoxidation products. Thus, it can be concluded that autoxidation rates of unsaturated fatty acid methyl esters with active methylene groups are dependent on the unsaturation degree of oxidative substrates or on the numbers of active methylene groups as is apparent in Fig. 6. If autoxidation rates of methyl linoleate, methyl linolenate, and methyl eicosapentaenoate + methyl docosahexaenoate are dependent on the unsaturation degree of substrates, the ratio of their rates becomes 2:3:5.5. If they are dependent on the number of active methylene groups in substrates, the ratio becomes 1:2:4.5. Relative oxidation rates seen from induction periods were close to the ratio of numbers of active methylene groups, and when seen from rates of weight gain they corresponded rather to the ratios of unsaturation degrees of substrates.

As shown by the induction periods and autoxidation rates (Table 1), a geometric isomeric effect was observed where methyl linoleate autoxidized easier than its trans-trans isomer. From the fact that no differences were observed in autoxidation products of methyl linoleate and its trans-trans isomer it is thought that this effect is attributable to differences in addition affinity of oxygen for double bonds which preceeded hydrogen abstraction from active methylene groups by oxygen molecules (as proposed in the oxidation mechanism of methyl oleate and methyl elaidate).[16] Still the geometric isomeric effect on autoxidation rates observed in methyl linoleate and its trans-trans isomer was not as great as observed in monoen compounds. This is explainable by the differences of hydrogen abstractions from α -methylene groups and active methylene groups by oxygen which has an addition affinity for double bonds. In addition, during autoxidation of unsaturated fatty acid methyl esters with active methylene groups cases which showed a relative oxidation rate according to the number of active methylene groups during induction period and to the degree of unsaturation of substrates in the post-induction period can be explained as follows. During the induction period hydrogen abstraction from active methylene groups by oxygen which has an affinity for double bond is the rate determining step. As the number of active methylene groups increases the oxidation rate increases. On the other hand, in post-induction period oxidation where peroxyl radicals are numerous the diffusion of peroxyl radicals becomes the rate determining step. Because of affinity of peroxyl radicals for double bonds, peroxyl radicals easily approached active methylene groups in proportion to the degree of unsaturation of the substrates. As shown in Fig. 6, the maximum oxidative weight gain increased following increases in the unsaturation degree of substrates. The theoretical weight increase, if 1 mol of substrate absorbs 1 mol of oxygen molecule, is 163 mg under the conditions of this experiment. In diene compounds oxygen was absorbed to roughly the theoretical weight, but with monoen compounds less than half that was absorbed, and with triene and above compounds more than the theoretical oxygen weight was absorbed. These results suggest that in oxidation of triene and above substrates more than 1 mol of oxygen molecules are absorbed for 1 mol of substrate, and that there are formations where there are two hydroperoxyl groups for 1 mol of substrate (e.g., the high formation amounts of hydroperoxyl in Fig. 2), or formations of dimers etc. where oxygen molecules function as bridges (high MW).

We believe that the data on autoxidation of unsaturated fatty acid methyl esters with active methylene groups obtained in this study will provide useful information in elucidating the autoxidation mechanisms of fats and oils, and will also be useful in the study of addition effects of antioxidants.

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