# Products Formed by Photosensitized Oxidation of Unsaturated Fatty Acid Esters

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## ABSTRACT AND SUMMARY

Photosensitized oxidation of unsaturated fatty acid methyl ester was carried out using methylene blue as a sensitizer. Oxidation products, monohydroperoxides, were identified as trimethylsilyl derivatives. Methyl oleate gave the 9- and 10-isomers; methyl linoleate, the 9-, 10-, 12-, and 13-isomers; and methyl linolenate, the 9-, 10-, 12-, 13-, 15-, and 16-isomers, respectively. The double bond to which the hydroperoxide group attached was shifted to the adjacent position in each isomer. Thus, both conjugated and nonconjugated isomers were present in methyl linoleate monohydroperoxides and methyl linolenate monohydroperoxides. By the inhibition experiment, it was ascertained that the above reaction proceeded via singlet oxygen. The relative rates of methyl oleate, methyl linoleate, and methyl linolenate were 1.0:1.7:2.3, respectively. These results obtained from the methyl esters were applied to the photosensitized oxidation of triglycerides purified from vegetable oils, and the reaction mechanism on triglycerides was proposed.

## INTRODUCTION

The oxidative deterioration of vegetable oils has long been known to be caused by the free radical mechanism (1,2). In the oxidation process it is assumed that hydroperoxide groups attach to the carbon atom of unsaturated fatty compounds, and subsequently the breakdown of hydroperoxides gives a chain reaction of autoxidation (2). However, the free radical mechanism would be insufficient to explain the initiation process of autoxidation. On the other hand, earlier workers (3) mentioned that visible light accelerated autoxidation of oils, although the effect of visible light was not elucidated clearly. A role of photosensitized oxidation at the initiation reaction of fat oxidation was suggested by Rawls et al. (4) who demonstrated the participation of singlet oxygen in the photosensitized oxidation of methyl linoleate. A trace amount of pigments in vegetable oil was considered to be a sensitizer for the photosensitized oxidation (5). Recently, Sattar et al. (6) suggested that the stability of oils in the presence of light depends on the content of β-carotene, which is well known as a quencher of singlet oxygen (7). It has been generally accepted that fatty acids react with singlet oxygen to produce hydroperoxides. The photosensitized oxidation mechanism was proposed as follows (4):

$$^1\text{Sens} \rightarrow {}^1\text{Sens}^* \rightarrow {}^3\text{Sens}^*$$

$$^3\text{Sens}^* + {}^3\text{O}_2 \rightarrow {}^1\text{Sens} + {}^1\text{O}_2^*$$

$$^1\text{O}_2^* + \text{A} \rightarrow \text{AO}_2$$

The sensitizer of the triplet state excited the oxygen of the ground state by triplet-triplet annihilation, and singlet oxygen was generated (8). The structures of hydroperoxides in chlorophyll-sensitized photooxidation of unsaturated fatty acids were reported to be different from those produced by autoxidation, although no structure was clarified (9,10).

In this work, photosensitized oxidation of methyl oleate, methyl linoleate, and methyl linolenate was examined using methylene blue as a sensitizer. The structures of produced hydroperoxides were determined by gas chromatography-mass spectrometry (GC-MS) and infrared (IR). In addition, the kinetic data were given in order to compare the reactivities of these three methyl esters toward singlet oxygen. The results obtained from fatty acid esters were applied to triglycerides, which were purified from vegetable oil, and the photosensitized oxidation mechanism of triglyceride is discussed.

## EXPERIMENTAL PROCEDURE

### Materials

Methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate were obtained from Nakarai Chem. Co. Ltd., (location, Japan) 99% grade, which were shown by GLC to be free from isomers. The sources of triglycerides were safflower oil supplied by Nihon Koyu Co. Ltd. (location, Japan) and soybean oil and olive oil which were purchased from Nakarai Chem. Co. Ltd. All triglycerides were purified by treatment with active charcoal (11), followed by column chromatography using Florisil (100/200 mesh) (12). Solvents and other reagents were of commercial grade and used without further purification.

### Photooxidation

Photosensitized oxidation was carried out in ethanol solution containing $0.11 \times 10^{-3}$M methylene blue. The solution in a reaction vessel (5 ml) was placed in a water bath (20 ± 0.1 C) and shaken with an amplitude and frequency adjusted to give rapid equilibration between air and solution. Light source was a 30 W tungsten projection lamp (intensity at the sample, 0.43 mW/cm$^2$). The rates of oxidation were determined from the concentration of produced hydroperoxides, which were measured by an iodometric method based on that of Wills (13). To 1 ml of acetic acid-chloroform (3:2, v/v), 0.1 ml of reaction mixture was added, after which 0.1 ml of saturated KI solution was added. The mixture was left in the dark for 30 min. The 3 ml of 0.5% cadmium acetate was added, and the mixture was shaken and centrifuged. The absorbance at 350 nm was then measured in the aqueous layer. Hydroperoxide concentrations were calibrated using a standard solution of benzoyl peroxide in ethanol. In the inhibition experiment of methyl linoleate oxidation by β-carotene, butyl hydroxytoluene, and tetramethylethylene, the amount of conjugated diene was determined from the absorbance at 232 nm after appropriate dilution.

### Fatty Acid Composition of Triglycerides

Fatty acid composition of purified triglyceride was determined by GLC after methanolysis using sodium methoxide in methanol solution (14). GLC was carried out with a Shimadzu gas chromatography GC-5A, equipped with a 2.5 m x 3 mm glass column packed with 15% DEGS on 60/80 mesh Neopack AS. The flow rate of nitrogen gas was 60 ml/min and the column oven temperature was 187 C.

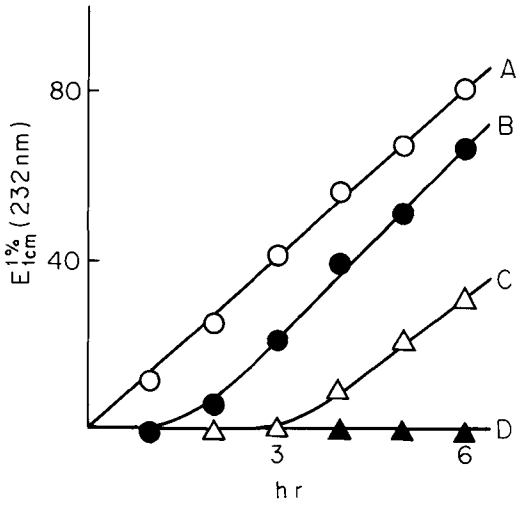


FIG. 1. Inhibition of photosensitized oxidation of methyl linoleate (0.069 M) by tetramethylethlene (A = 0 M, B = 0.085 M, C = 0.109 M, D = 0.338 M).

### Structural Analysis of Hydroperoxides

The reaction mixture irradiated for 6 hr was reduced by $NaBH_4$ and/or hydrogenated by a stream of hydrogen gas according to the method described in the preceding paper (15). The mixture was silylated after reduction or hydrogenation. GC-MS analysis was carried out with a LKB-9000S gas chromatograph-mass spectrometer, equipped with a glass column (2.0 m x 3 mm) packed with 3% SE-52 and 60/80 mesh Chromosorb W, programmed temperature from 220-260 C (3 C/min). Operational conditions were as follows: an ion source temperature of 290 C, a separator temperature of 270 C, an ionizing electron energy of 70 eV, a trap current of 60 $\mu$A and an accelerator voltage of 3.5 kV.

Methyl linoleate monohydroperoxide for IR analysis was purified by column chromatography using silica gel as follows. Silica Gel G (Merck 60/200 mesh) activated at 110 C for 2 hr was throughly mixed with hexane and was packed into a column (2.0 x 25 cm). The photosensitized solution was charged on the column and eluted with the solution of ethyl ether in hexane of 5, 50, and 100% successively, and finally methanol. Methyl linoleate monohydroperoxides fraction eluted with 50% ethyl ether in hexane was collected and concentrated in vacuo. IR spectra were taken in a sodium chloride cell with a Hitachi Model 285 spectrophotometer.

## RESULTS

### Inhibition of Methyl Linoleate Photosensitized Oxidation

$\beta$-Carotene and butyl hydroxytoluene were used for the inhibition experiment. The former is well known to be an efficient quencher for singlet oxygen (7), and the latter, an antioxidant for autoxidation (16). Photooxidation was inhibited 80% when $0.46 \times 10^{-3}$ M $\beta$-carotene was added to the reaction containing $84.9 \times 10^{-3}$M methyl linoleate. But the same molar ratio of butyl hydroxytoluene scarcely inhibited the oxidation for 6 hr irradiation. On the other hand, methyl linoleate photooxidation was also inhibited in the presence of tetramethylethylene, which is known to react strongly with singlet oxygen (8,17). A lag appeared in the production of hydroperoxides as shown in Figure 1.

### Structures of Monohydroperoxides from Photosensitized Oxidation

The result of column chromatography indicated that

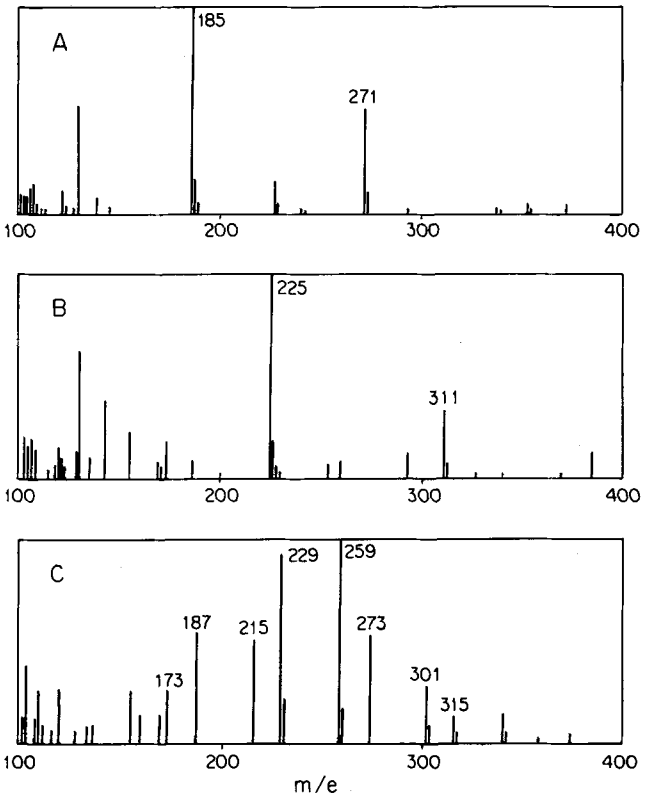


FIG. 2. Mass spectra of trimethylsilyl derivatives of methyl linoleate monohydroperoxides after reduction A, B and hydrogenation C.

only nonoxidized methyl linoleate and monohydroperoxides were present and that secondary oxidation products were not detected in the reaction mixture of methyl linoleate after 6 hr irradiation. IR spectrum of purified monohydroperoxides showed the absorption at the vicinity of 950 and 985 $cm^{-1}$ due to conjugated diene and 970 $cm^{-1}$ due to isolated *trans* double bond. However, the absorption of 970 $cm^{-1}$ was scarcely observed in the spectrum of that from autoxidized methyl linoleate (these data are not shown here). The gas chromatogram of the silylated reaction mixture gave the peaks of nonoxidized methyl linoleate and monohydroperoxides within 10 min. Trimethylsilyl (TMS) derivatives of monohydroperoxides had only one broad peak after hydrogenation, whose mass spectrum are shown in Figure 2-C. A series of large peaks based on the $\alpha$-cleavage of the TMS group were assigned to C-9 (259,229), C-10 (273,215), C-12 (301,187), and C-13 (315,173) positional isomer, respectively. Monohydroperoxides were separated into two peaks, A and B, in the gas chromatogram of reduced derivatives in which the double bonds were kept intact. It has been known that the $\alpha$-cleavage of the TMS group occurred preferentially on the side of the carbon atom which forms no double bond and that no significant cleavage is observed between the TMS group and allylic double bond (18). Accordingly, in the mass spectrum of Figure 2-A, the fragment ion peak at m/e 185 was from the cleavage of C-12 isomer between C 11 and C 12. A peak at m/e 271 was also due to the cleavage of C-10 isomer between C 10 and C 11. Mass spectrum of peak B, shown in Figure 3-B, was also determined as the mixture of C-9 and C-13 isomer containing a conjugated diene structure. This spectrum was similar to that of the hydroperoxides from autoxidation in the preceding paper (15).

The monohydroperoxide from methyl oleate showed only one peak in the gas chromatogram after reduction and hydrogenation. In the mass spectrum of hydrogenated derivatives (Figure 3-B), two pairs of ions were observed at

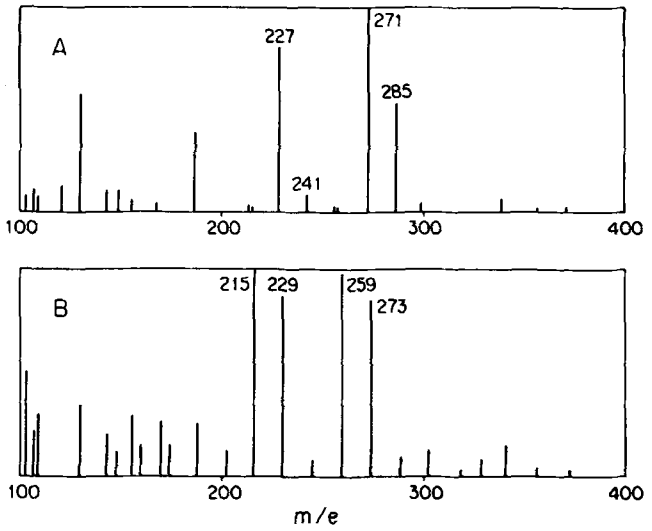


FIG. 3. Mass spectra of trimethylsilyl derivatives of methyl oleate monohydroperoxides after reduction A and hydrogenation B.

259, 229 and 215, 273, which were assigned to the α-cleavage of the TMS groups at C-9 and C-10 positions, respectively. These fragment ions have almost the same intensity as shown in Figure 3-B. TMS fragment ions after reduction in Figure 3-A showed the two pairs of ions, 227, 285 and 271, 241 due to C-9 and C-10 isomers, respectively. Location of the double bond was considered to be C 10-11 in the C-9 isomer and C 8-9 in the C-10 isomer. The C-8 and C-11 isomers with a double bond at C 9-10 have the possibilities of producing the fragment ions at m/e 241 and 285 in the mass spectrum of reduced derivatives. But these isomers were confirmed to be absent in methyl oleate monohydroperoxides, because the mass spectrum of hydrogenated derivatives had no fragment ions based on the α-cleavage of these isomers, such as m/e 245, 243, 287, and 201.

In the gas chromatogram of methyl linolenate (Figure 4), TMS derivatives of monohydroperoxides after hydrogenation were separated to three peaks, (A,B,C), whose mass spectra are shown in Figure 4-A, B, and C. The fragment pattern in Figure 4-A was similar to that of methyl linoleate shown in Figure 2-C. This spectrum was attributed to the mixture of C-9, C-10, C-12, and C-13 positional isomers of TMS group. The peak B and peak C were also identified to be C-15 and C-16 isomers from the mass spectra shown in Figure 4-B and C. Reduced derivatives were separated to two peaks in the gas chromatogram (not shown here). Large ions appeared at m/e 143, 183, 223, 271, and 311 in the mass spectra. These ions were assigned to the α-cleavage of TMS groups at C 15, C 12, C9, C 10, and C 13, respectively. Absence of the peak due to the C-16 isomer would be explained by the secondary cleavage or by the difficulty of the cleavage of this position.

The structure and ratio of the monohydroperoxide isomers were summarized in Table I. The hydroperoxide groups of all isomers were attached to the carbon atoms which originally existed at both sides of a double bond, which shifted to the adjacent position.

### Reactivity of Unsaturated Fatty Acid Methyl Ester

Photosensitized oxidation of methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate was carried out for 6 hr under the same condition with various concentrations of ester. The amounts of produced hydroperoxides increased almost linearly with the irradiation time in methyl oleate, methyl linoleate, and methyl linolenate. But

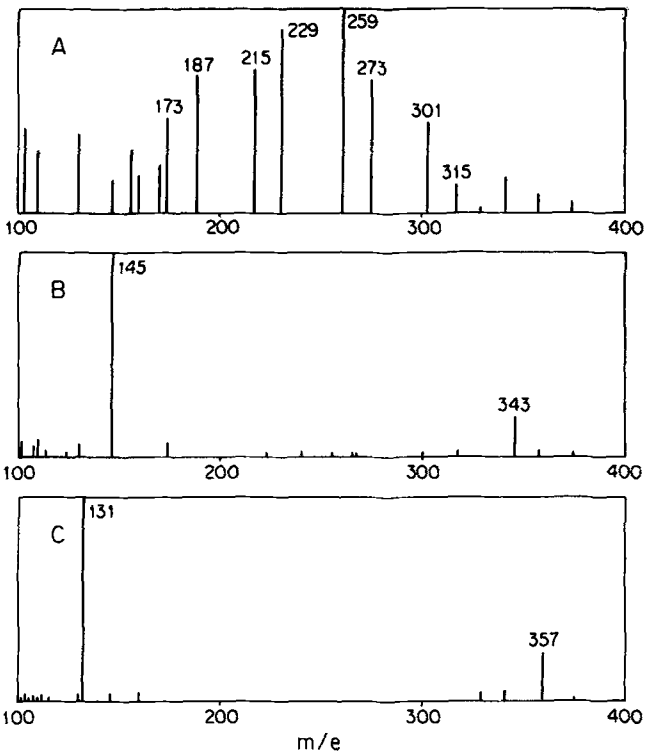


FIG. 4. Mass spectra of silylated products from photosensitized oxidation of methyl linolenate ($ML_n$) after hydrogenation.

no hydroperoxide was produced entirely in methyl stearate which contained no double bond. Oxidation of methyl oleate, methyl linoleate, and methyl linolenate did not occur in the absence of methylene blue. Therefore, the participation of autoxidation in this system seems to be negligible.

The kinetics of photosensitized oxidation was proposed by Foote et al. (19,20) as follows:

$$^1O_2 \xrightarrow{k_1} {}^3O_2 \qquad \text{(I)}$$

$$^1O_2 + A \xrightarrow{k_2} AO_2 \qquad 1 \qquad \text{(II)}$$

TABLE I

Structures of Monohydroperoxide Isomers from Methylene Blue-Sensitized Photooxidation

| Unsaturated fatty ester | Position of hydroperoxide | Position of double bond | Percent yield |
|---|---|---|---|
| Methyl oleate | 9 | 10-11 | 50[a] |
| | 10 | 8-9 | 50[a] |
| Methyl linoleate | 9 | 10-11,12-13 | 53[b] |
| | 13 | 9-10,11-12 | |
| | 10 | 8-9,12-13 | 47[b] |
| | 12 | 9-10,13-14 | |
| Methyl linolenate | 9 | 10-11,12-13,15-16 | 74[c] |
| | 10 | 8-9,12-13,15-16 | |
| | 12 | 9-10,13-14,15-16 | |
| | 13 | 9-10,11-12,15-16 | |
| | 15 | 9-10,12-13,16-17 | 8[c] |
| | 16 | 9-10,12-13,14-15 | 18[c] |

[a]Determined by the intensities of the fragment ions in the mass spectrum (Figure 3-B).

[b]Determined by the peak area of the reduced derivatives A and B in the gas chromatogram.

[c]Determined by the peak area of the hydrogenated derivatives A, B and C in the gas chromatogram. These peak areas were measured by gas liquid chromatography (GLC) with flame ionitation detector (FID).

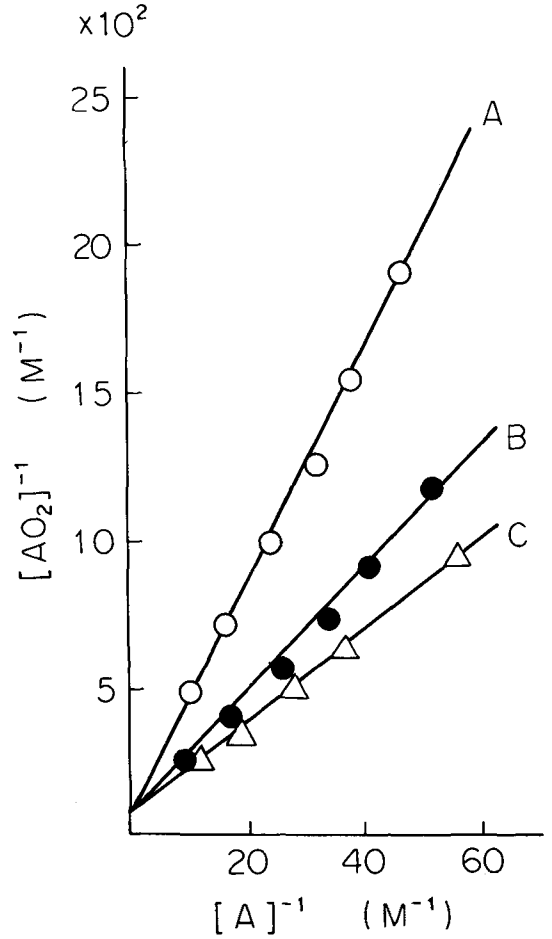


FIG. 5. Determination of β-value for unsaturated fatty acid methyl esters (A = methyl oleate, B = methyl linoleate, C = methyl linolenate).

Singlet oxygen undergoes reaction with an acceptor (II) or is deactivated to ground state oxygen (I) in which $k_1$ and $k_2$ are the rate constant of these reactions. Steady state treatment gives the concentration of the produced hydroperoxide $[AO_2]$ (20);

$$[AO_2] = I_{abs} \cdot \psi_{isc} \{k_2[A]/(K_2[A] + K_1)\} \quad \text{(III)}$$

The term $\psi_{isc}$ is the intersystem crossing yield for the sensitizer and $I_{abs}$ is the number of mole quanta per liter absorbed during the irradiation time. Reciprocal of $[AO_2]$ is;

$$[AO_2]^{-1} = (I_{abs} \cdot \psi_{isc})^{-1} \{1 + (k_1/k_2)[A]^{-1}\} \quad \text{(IV)}$$

The equation (IV) was applied to the data of photosensitized oxidation of methyl oleate, methyl linoleate, and methyl linolenate. Reciprocals of the mean concentration of the unsaturated ester during reaction and those of produced hydroperoxides were plotted in Figure 5. In this figure, $[AO_2]$ represents the average hydroperoxide concentration per 1 hr irradiation. The linear relationship was given between $[A]^{-1}$ and $[AO_2]^{-1}$ in each isomer. Therefore, the photooxidation in this system seems to satisfy the equation (IV). The intercept represents the reciprocal of $I_{abs} \cdot \psi_{isc}$. The value of $I_{abs} \cdot \psi_{isc}$ was determined to be ca. 0.015M. A parameter called β-value, $k_1/k_2$, was calculated from the ratio of the slop to the intercept. The ratio of $k_2$ was obtained from the assumption that $k_1$ was identical in these methyl esters. These results are shown in Table II.

### Photosensitized Oxidation of Triglycerides

The sources of triglycerides were safflower, soybean, and olive oil. The fatty acid composition of the purified triglycerides was given in Table III. After 6 hr irradiation of all triglycerides, 16:0 and 18:0 did not decrease but 18:1, 18:2, and 18:3 decreased 10-13%, 15%, and 30%, respectively. The concentration of produced hydroperoxides per 1 hr was shown as $[AO_2]$ in Table IV. Molar concentrations of the three triglycerides were obtained from their average molecular weights, and the equivalent molar concentration of each unsaturated fatty acid moiety, $[A_n]$, was calculated from the initial fatty acid composition. It was postulated that the rate parameter of the fatty acid moiety of triglyceride was the same as that of the corresponding methyl ester. Accordingly, the hydroperoxide concentration of each moiety, $[A_nO_2]$, was calculated from the β-value in Table II. $\Sigma[A_nO_2]$, were total concentration of $[A_nO_2]$ obtained from the following equation (V):

$$\Sigma[A_nO_2] = [A_1O_2] + [A_2O_2] + [A_3O_2] \quad \text{(V)}$$

($A_1$; 18:1, $A_2$; 18:2, $A_3$ 18:3)

The calculated value, $\Sigma[A_nO_2]$, was roughly in accord with the observed value, $[AO_2]$, in the three triglycerides.

TABLE II

Relative Reactivities of Unsaturated Fatty Acid Methyl Esters

| | Oleate | | Linoleate | | Linolenate |
|---|---|---|---|---|---|
| β-value[M] $(k_1/k_2)$ | 0.63 | | 0.36 | | 0.27 |
| $k_2$ ratio | 1.0 | : | 1.7 | : | 2.3 |

TABLE III

Fatty Acid Composition of Triglycerides

| Triglyceride | 16:0 | 18:0 | 18:1 | 18:2 | 18:3 |
|---|---|---|---|---|---|
| Safflower | 8.1 | 1.5 | 15.8 | 74.6 | – |
| Soybean | 17.0 | 2.2 | 23.2 | 53.3 | 4.2 |
| Olive | 11.0 | 1.8 | 84.4 | 2.8 | – |

TABLE IV

Photosensitized Oxidation of Triglycerides

| Triglyceride | [A] mM | $[AO_2]$ mM[a] | $\Sigma[A_nO_2]$ mM[b] |
|---|---|---|---|
| Safflower | 25.9 | 3.05 | 2.83 |
| Soybean | 26.7 | 2.61 | 2.55 |
| Olive | 30.0 | 1.89 | 1.75 |

[a]Determined by the iodometric method described in Experimental Procedure.

[b]Calculated from the equation (IV) of each fatty ester.

## DISCUSSION

Two mechanisms have been proposed for photosensitized oxidation of olefins. In Shenk's mechanism (21), the excited state of the sensitizer reacts with oxygen to give a diradical adduct (.Sense-O-O.). Kautsky et al. (22) have proposed that the metastable $^1\Delta_g$ state of oxygen is reactive intermediate. Kopecky et al. (23) have suggested that this singlet oxygen participates in the methylene blue-sensitized photooxidation of olefins. It is well known that β-carotene inhibits the production of hydroperoxide by quenching the singlet oxygen (7). No inhibition by butyl hydroxytoluene indicates that photooxidation in this system is not caused by the free radical mechanism. On the other hand, tetramethylethylene has a high reactivity with

singlet oxygen (8,17) and hence acts as a singlet oxygen capture as shown in Figure 1. Therefore, it is evident that the photosensitized oxidation in this system proceeds via singlet oxygen.

Isomeric hydroperoxides are produced from the photosensitized oxidation of unsaturated fatty acid methyl ester (Table I). Cobern et al. (9) showed that these isomers were also formed by chlorophyll-sensitized photooxidation. It has been demonstrated by autoxidation experiment that oleate gives the 8-, 9-, 10-, and 11-isomers; linoleate, the 9- and 13-isomers; and linolenate, the 9-, 12-, 13-, and 16-isomers (2,24). The distribution of hydroperoxide isomers of photosensitized oxidation is different from that of autoxidation. The position of the hydroperoxide group in photosensitized oxidation is the carbon atom located at both sides of the double bond. Therefore, the number of isomers produced is two times that of the double bonds in each fatty acid methyl ester. The double bond shifts to the adjacent position, and hence both conjugated and nonconjugated isomers are formed. The IR data of methyl linoleate hydroperoxides suggest that the shifted double bond has a *trans* configuration. The singlet oxygen oxidation mechanism of the unsaturated ester is assumed to be a concerted "ene-type" reaction via a six-membered transition state (17,25). The singlet oxygen enters *cis* to the hydrogen to be transferred (25). A mechanism involving perepoxide intermediate also accounts for the formation of these nonconjugated isomers (26). The amounts of the two isomers, 9- and 10-isomers, are almost the same in the photosensitized oxidation of methyl oleate. However, a slight predominance of the conjugated isomers occurred in methyl linoleate- and methyl linolenate-photosensitized oxidation, although the yields of all isomers were not determined. Preferential formation of the conjugated isomer has been reported in the singlet oxygen oxidation of the compounds containing a 1,4-diene system (5).

Gunstone et al. (27) found that the rates of autoxidation of methyl oleate, methyl linoleate, and methyl linolenate are 1:12:25, respectively. But the relative reactivities of these esters with singlet oxygen are 1.0:1.7:2.3, respectively, as shown in Table II. Consequently, it seems a characteristic of photosensitized oxidation that a remarkable difference of reactivity is not present among mono-, di-, and tri-enoid fatty acids. Preliminary data show that triglyceride reacts with singlet oxygen in a manner similar to that of the corresponding methyl ester. Each fatty acid moiety of triglyceride seems to react with singlet oxygen independently as follows:

$$A_1 + {}^1O_2^* \xrightarrow{k_{21}} A_1O_2$$
$$A_2 + {}^1O_2^* \xrightarrow{k_{22}} A_2O_2$$
$$A_3 + {}^1O_2^* \xrightarrow{k_{23}} A_3O_2$$
$${}^1O_2^* \xrightarrow{k_1} {}^3O_2$$

The symbols, $A_1$, $A_2$, and $A_3$ represent each fatty acid moiety of triglyceride, respectively. The yield of hydroperoxides from photosensitized oxidation of triglyceride is assumed to be obtained as given below:

$$[AO_2] = [A_1O_2] + [A_2O_2] + [A_3O_2]$$
$$= I_{abs} \cdot \psi_{isc} \{ k_{21}[A_1]/(k_{21}[A_1] + k_1) + k_{22}[A_2]/(k_{22}[A_2] + k_1) + k_{23}[A_3]/(k_{23}[A_3] + k_1) \} \quad \text{(VI)}$$

Table IV shows that the observed value, $[AO_2]$, is somewhat higher than the calculated value obtained from the ratio of the fatty acid moiety, $[A_nO_2]$. This tendency might be explained by the slight difference of the $\beta$-value between the fatty acid moiety and the corresponding methyl ester. From these data, it is concluded that the photosensitized oxidation mechanism of triglyceride is similar to that of the unsaturated fatty acid methyl ester.

The autoxidation experiment with these triglycerides (Terao and Matsushita, unpublished data) has shown that the triglyceride of olive oil which contains predominantly oleic acid as unsaturated fatty acid was not oxidized for 30 day incubation, although that of safflower or soybean oil is subjected to autoxidation. Furthermore, the oleic acid moiety of the latter two triglycerides scarcely disappeared in autoxidation, but the linoleic acid and linolenic acid moieties undergo degradation. On the other hand, in photosensitized oxidation of triglyceride, the oleic acid moiety was also remarkably oxidized to produce hydroperoxides as similar to linoleic acid and linolenic acid moieties. Chlorophyll- like pigment is assumed to be a sensitizer in vegetable oil, though some other sensitizer also has been suggested (5). It has been considered that a part of the chlorophyll-sensitized oxidation arose from the proton abstruction by the activated carbonyl group of chlorophyll (4). But singlet oxygen oxidation seems to account for the most part of the photosensitized oxidation of vegetable oils.

These studies have shown that the unsaturated fatty acid moiety of triglyceride is subjected to the reaction with singlet oxygen which is generated by an excited sensitizer. It has also suggested that the difference of reactivity among mono-, di-, and tri-unsaturated fatty acid is much less than that of autoxidation.

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