Photo-oxidation of Lipids Impregnated on the Surface of Dried Seaweed (*Porphyra yezoensis* Ueda). Characterization of Volatiles

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ABSTRACT: Volatiles generated by the photo-oxidation of lipids applied to the surface of dried seaweed (*Porphyra yezoensis* Ueda) previously exposed to visible light were studied. The surface of dried seaweed was impregnated with eicosapentaenoic acid (EPA) ethyl ester or linoleic acid (LA) methyl ester. The sample was then divided into two parts, and each part was sealed in a 50-mL crimp-top vial with a PTFE silicone-lined cap. One vial was exposed to light from a 100-W tungsten bulb (6000 lux) in an oven at 45°C. The other vial was covered with aluminum foil to shield the seaweed from light and kept in the oven as a control. Volatile compounds in the headspace of the vials were collected by a solid-phase microextraction technique and analyzed by GC-FID and GC–MS. The numbers of peaks as well as the peak areas of volatiles in the light-exposed sample were much greater than those in the control in GC profiles obtained in the same oxidation period. The peak areas of volatiles changed with the prolongation of oxidation time, and the formation rates were different between volatiles. Approximately 28 volatiles were identified in the control kept in the dark as well as in the light-exposed sample impregnated with EPA ethyl ester. The relative amounts of propanal, 2-propenal, 1-penten-3-one, 1-penten-3-ol, 2-butenal, heptanoic acid, and 2-pentenal in the headspace of the light-exposed vials were significantly higher than those in the control, whereas the relative amounts of 3,5-octadien-2-one, ethyl butyrate, and 2,4-heptadienal in the control were significantly higher than those in the headspace of the light-exposed vial. Approximately 35 volatiles were identified from the dried seaweed impregnated with LA methyl ester. The relative amounts of hexanal, 2-heptenal, 2-octenal, octanoic acid methyl ester, and hexanoic acid in the headspace of the light-exposed vial were significantly higher than those in the control, and the relative amounts of 2-decenal, 2,4-nonadienal, and 2,4-decadienal in the control were significantly higher than those in the headspace of the light-exposed vial. We proposed the formation mechanisms of some volatiles to be the well-accepted homolytic–heterolytic cleavage of hydroperoxides that were generated by oxidation of the unsaturated lipids.

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KEY WORDS: Autoxidation, eicosapentaenoic acid ethyl ester, linoleic acid methyl ester, photosensitized oxidation, singlet oxygen, solid-phase microextraction, volatiles.

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Sun-drying, one traditional method of preserving seafood, is still a popular technique in developing countries, although industrialized countries have come to depend mainly on mechanical drying methods in recent years. Some consumers still prefer the characteristic aroma of sun-dried seafood to that of mechanically dried products. The major difference between sun-drying and mechanical-drying is that light is introduced to the products in processing. Many studies using unrealistic model systems (1–5) have proven that some colorants, such as methylene blue and chlorophyll, can act as photosensitizers. Photo-oxidation proceeds much faster than radical-generating oxidation, and the distribution of generated hydroperoxide isomers is different from those generated by autoxidation (6–10).

Another study from this laboratory (11) previously confirmed that the lipids in seaweed were oxidized by photosensitized oxidation when the seaweed was exposed to light. In this particular case, the chlorophyll in seaweed served as a photosensitizer. Since the distributions of isomeric hydroperoxides generated by photo-oxidation and autoxidation of lipids impregnated on the surface of the seaweed were different, these results strongly suggest that the distribution of volatiles formed by the decomposition of these hydroperoxides should be different. This probably means that sun-dried and mechanically dried seafood will differ in flavor.

In this study, edible seaweed rich in chlorophyll was used as a model food to examine the volatiles produced by the oxidation of seaweed lipids. Because the lipid content of the seaweed was very low, the volatiles produced by oxidation of the lipids inherent in the seaweed were quantitatively too low to be analyzed. Eicosapentaenoic acid (EPA) ethyl ester and linoleic acid (LA) methyl ester were therefore impregnated on the surface of the seaweed to enhance the FA composition.

Headspace solid-phase microextraction (HS-SPME) was used to collect volatiles obtained by the oxidation of lipids. Qualitative and quantitative analyses were carried out by GC and by GC–MS (3,4) to investigate the difference in flavor between sun-dried and mechanically dried seafood.

MATERIALS AND METHODS

Materials. Cis-9,*cis*-12-octadecadienoic acid methyl ester (LA methyl ester) of >99% purity was purchased from Sigma (St. Louis, MO). All-*cis*-5,8,11,14,17-EPA ethyl ester of >92% purity was recovered from Epadels® (Mochida Phar-

maceutical Co. Ltd., Tokyo, Japan) and purified with Sep-pak® silica cartridges (Waters Co., Milford, MA). All standard chemicals were of reagent grade and were obtained from Tokyo Chemical Industry (Tokyo, Japan), Sigma, or Wako (Tokyo, Japan). Mechanically dried seaweed products (*Porphyra yezoensis* Ueda) were purchased from a local retailer.

Photo-oxidation of lipids. A 200-mg portion of lipids was impregnated on the surface of 3 g of dried seaweed by dissolving the lipids in 200 mL of diethyl ether. The diethyl ether was stripped off at 30°C by a vacuum evaporator in the dark and further removed in a vacuum desiccator. The seaweed was then divided evenly into two parts, and each part was sealed into a 50-mL serum-type reaction vial (Supelco, Bellefonte, PA) using a cap with a PTFE silicone liner (Supelco). One vial was exposed to a 100-W tungsten light source (6000 lux) (2–4) in a 45°C oven. The other vial was covered with an aluminum foil shield as a control and kept in the same oven. Volatiles were collected by HS-SPME and subjected to GC and GC–MS analysis at appropriate intervals.

General SPME procedure. The SPME device equipped with a fused-silica fiber coated with 100 μm of polydimethylsiloxane was purchased from Supelco. To sample the volatiles, the SPME fiber was inserted into the headspace of a 50-mL vial containing 1.5 g of seaweed impregnated with lipids, and the fiber was equilibrated in the headspace of vial for 15 min at 50°C. Desorption of the volatiles from the fiber was carried out by holding the fiber in the injection port of the gas chromatograph or gas chromatograph–mass spectrometer for 15 min at 240°C.

GLC of volatiles. Volatile analysis was carried out on a Shimadzu model 12A gas chromatograph (Kyoto, Japan) equipped with a SUPELCOWAX-10™ fused-silica open tubular capillary column (0.25 mm i.d. × 30 m, 0.25 μm in film thickness; Supelco, Japan, Tokyo) and an FID. Helium was used as the carrier gas with a column inlet pressure of 3 kg/cm^2. The column temperature was programmed from 40 (holding for 2 min) to 240°C at a rate of 4°C/min. The injector and detector temperatures were 240°C.

GC–MS of volatiles. GC–MS analysis of volatiles was carried out on a Shimadzu model 17A gas chromatograph equipped with a SUPELCOWAX-10 fused-silica column (0.25 mm i.d. × 25 m, 0.25 μm in film thickness; Supelco). The outlet of the column was connected directly to a Shimadzu model QP 5000 mass spectrometer. The column temperature was programmed from 40 to 240°C at a rate of 4°C/min. The injection port temperature was 240°C. Helium was used as the carrier gas. The mass spectrometer was operated in electron ionization mode (70 eV). The scanning speed was set at 35–350 masses per second. The volatile compounds were identified by matching the mass spectra with those of reference compounds.

Determination of oxygen absorption in the headspace of the vial. A 0.1 mL portion of the headspace air in the vial was withdrawn with a gastight microsyringe and immediately injected into a Shimadzu model GC-3BT gas chromatograph equipped with a glass column (2.5 mm i.d. × 1.7 m) packed with molecular sieve 5A (80–100 mesh; Nihon Chromato Co. Ltd., Tokyo, Japan) and a thermal conductivity detector. Helium was used as the carrier gas at an inlet pressure of 1.2 kg/cm^2.

RESULTS

Changes in total peak areas of volatiles. Total peak areas of volatiles obtained by oxidation of the EPA ethyl ester increased with a prolongation of the oxidation period both in the light-exposed sample and in the control. Total peak areas of volatiles from the light-exposed sample increased much faster than those of the control in the same oxidation period; after 6 h of light exposure, the total peak areas of volatiles derived from the EPA ethyl ester increased sharply compared with the control. After 14 h of oxidation, a sharp increase occurred in the total peak areas of volatiles from the light-exposed sample, whereas the total peak areas of volatiles derived from the control sample increased steadily (Fig. 1).

A similar tendency was observed when the LA methyl ester was applied to the dried seaweed and exposed to light. The total peak areas of volatiles increased with prolongation

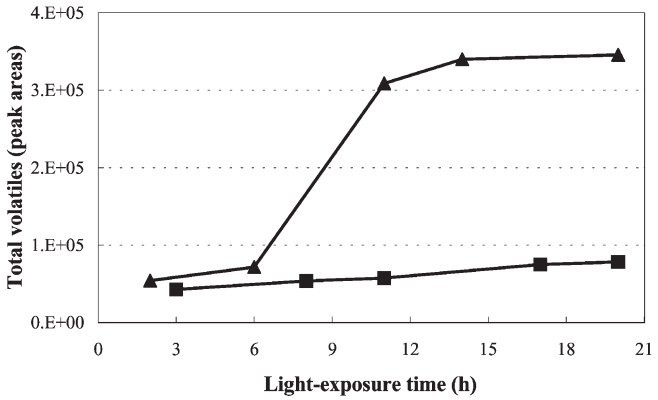

FIG. 1. Total peak areas of volatiles from oxidation of eicosapentaenoic acid ethyl ester applied to dried seaweed. (■) Control sample; (▲) light-exposed sample.

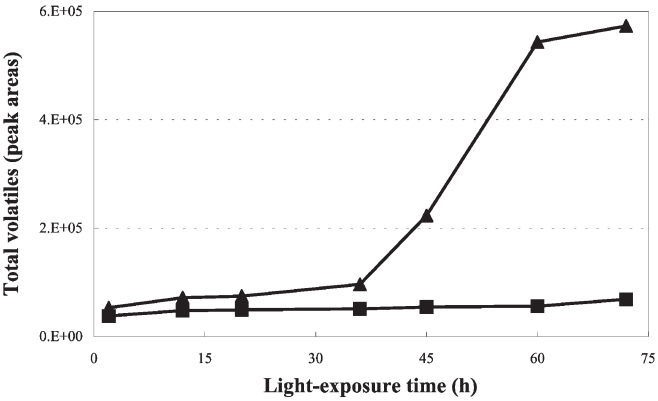

FIG. 2. Total peak areas of volatiles from oxidation of linoleic acid methyl ester applied to dried seaweed. (■) Control sample; (▲) light-exposed sample.

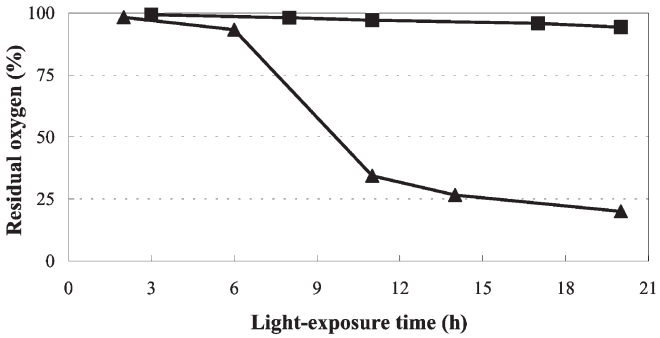

FIG. 3. Oxygen absorption attributable to oxidation of eicosapentaenoic acid ethyl ester applied to dried seaweed. (■) Control sample; (▲) light-exposed sample.

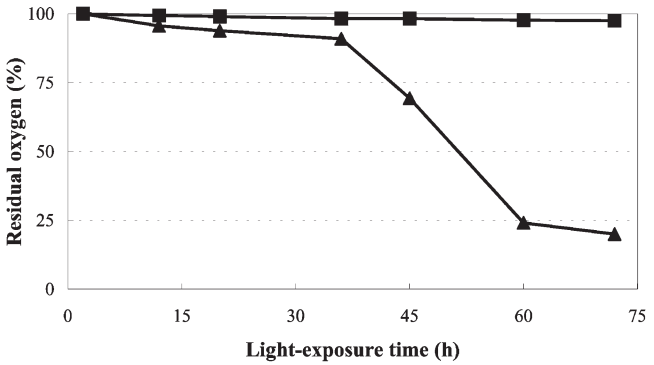

FIG. 4. Oxygen absorption attributable to oxidation of linoleic acid methyl ester applied to dried seaweed. (■) Control sample; (▲) light-exposed sample.

of the oxidation period in both the light-exposed sample and the control; however, the total peak areas of volatiles from the light-exposed sample increased much faster than those of the control in the same oxidation period. After 36 h of light exposure, the total peak areas of volatiles increased sharply and showed a significant difference from that of the control. After 60 h, the total peak areas of volatiles in the light-exposed sample decreased, whereas the total peak areas of volatiles in the control increased steadily (Fig. 2). These results strongly suggest that the photosensitized oxidation of lipids proceeded in the light-exposed seaweed with or without additional impregnation of the PUFA ester.

Oxygen uptake in the headspace of the vial. Oxygen was consumed much faster in the light-exposed sample compared with the control. After 6 h of light exposure, the residual oxygen in the light-exposed vial decreased sharply. After 14 h, the consumption rate of residual oxygen in the light-exposed

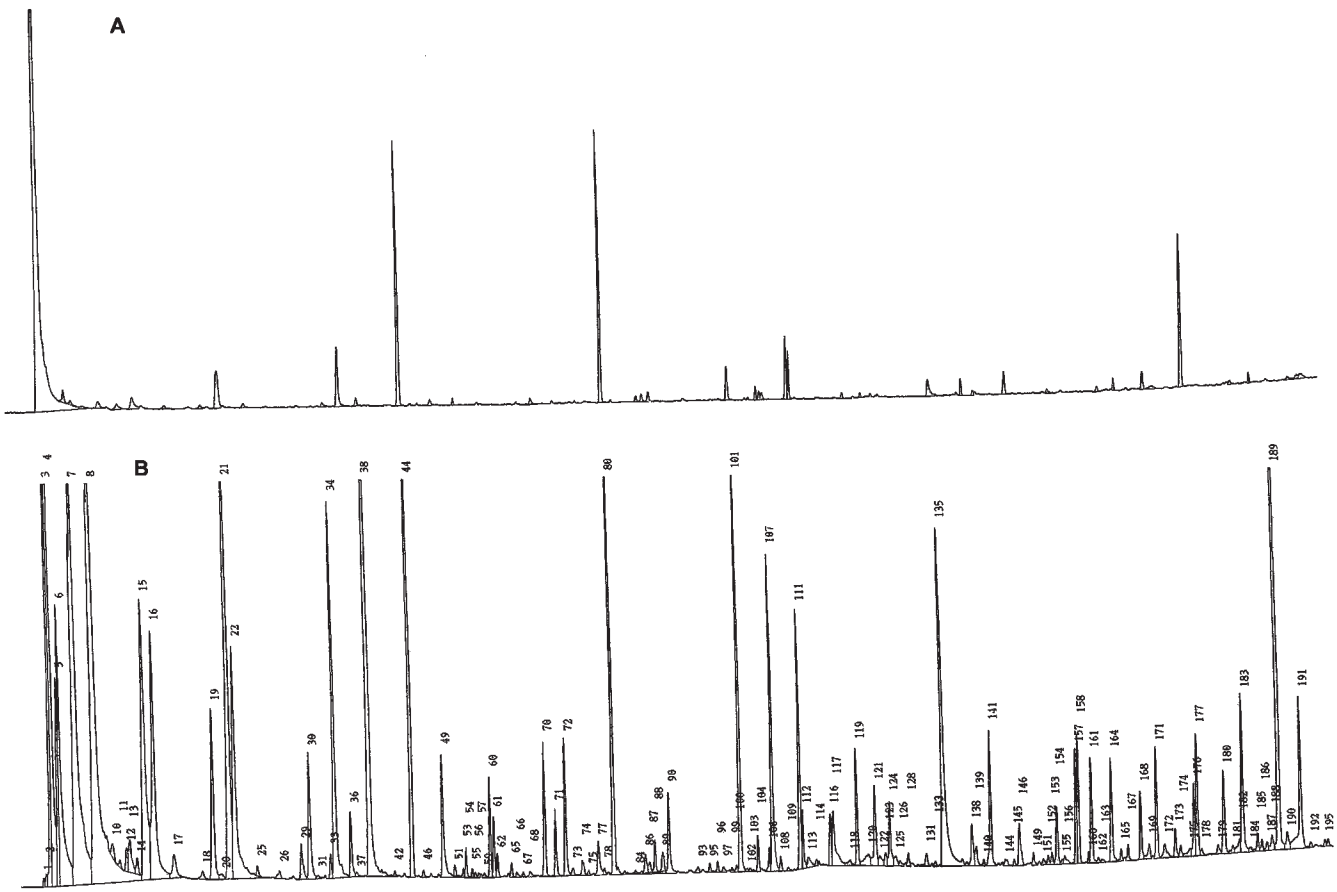

FIG. 5. Gas chromatograms of volatiles from eicosapentaenoic acid ethyl ester applied to dried seaweed at 11 h of oxidation. (A) Control sample; (B) light-exposed sample.

vial became slower, whereas that in the control continued to decrease (Fig. 3).

The results of oxygen absorption also correlated well with the change in the total peak areas of volatiles derived by oxidation of the LA methyl ester. Oxygen was consumed much faster in the light-exposed vial than in the control. After 36 h of light exposure, the rate of decrease in the residual oxygen of the light-exposed sample decreased sharply. After 60 h, the rate of oxygen uptake in the light-exposed sample became slower, whereas that in the control continued to decrease (Fig. 4). These results strongly suggest that the photosensitized oxidation of lipids proceeded rapidly in the light-exposed seaweed.

Volatiles from the oxidation of lipids. Typical gas chromatograms of volatiles derived by oxidation of the EPA ethyl ester in the light-exposed sample and in the control after the same oxidation period of 11 h were significantly different from each other. A number of additional peaks and larger peak areas were found in the light-exposed sample (Fig. 5). A similar result was observed in the oxidation of LA methyl ester impregnated on the dried seaweed and exposed to light. The gas chromatograms of volatiles from oxidation of the LA methyl ester in the light-exposed sample and in the control in the same oxidation period of 72 h were significantly different. A larger number of peaks were found in the light-exposed sample compared with those in the control (Fig. 6).

Volatiles derived by oxidation of the EPA ethyl ester. Approximately 28 volatiles were identified in both samples impregnated with EPA ethyl ester after 11 h of oxidation (Table 1). The relative concentrations of the same volatiles were different between the light-exposed sample and the control; the relative amounts of propanal, 2-propenal, 1-penten-3-one, 1-penten-3-ol, 2-butenal, heptanoic acid, and 2-pentenal in the light-exposed vials were significantly larger than those in the control, whereas the relative amounts of ethyl butyrate, 3,5-octadien-2-one, and 2,4-heptadienal in the control were significantly larger than those in the light-exposed sample (Fig. 7).

When the EPA ethyl ester was oxidized until the residual oxygen level had decreased to 20% (at 20 h for the light-exposed sample and at 73 h for the control), the volatile profiles of the light-exposed sample and those of the control sample differed on gas chromatograms. The relative amounts of volatiles identified also differed but were qualitatively very similar to those listed in Table 1 (data not shown).

Volatiles produced by oxidation of the LA methyl ester. Approximately 35 volatiles were identified in the control sample kept in the dark as well as in the light-exposed sample impregnated with the LA methyl ester after 72 h of oxidation

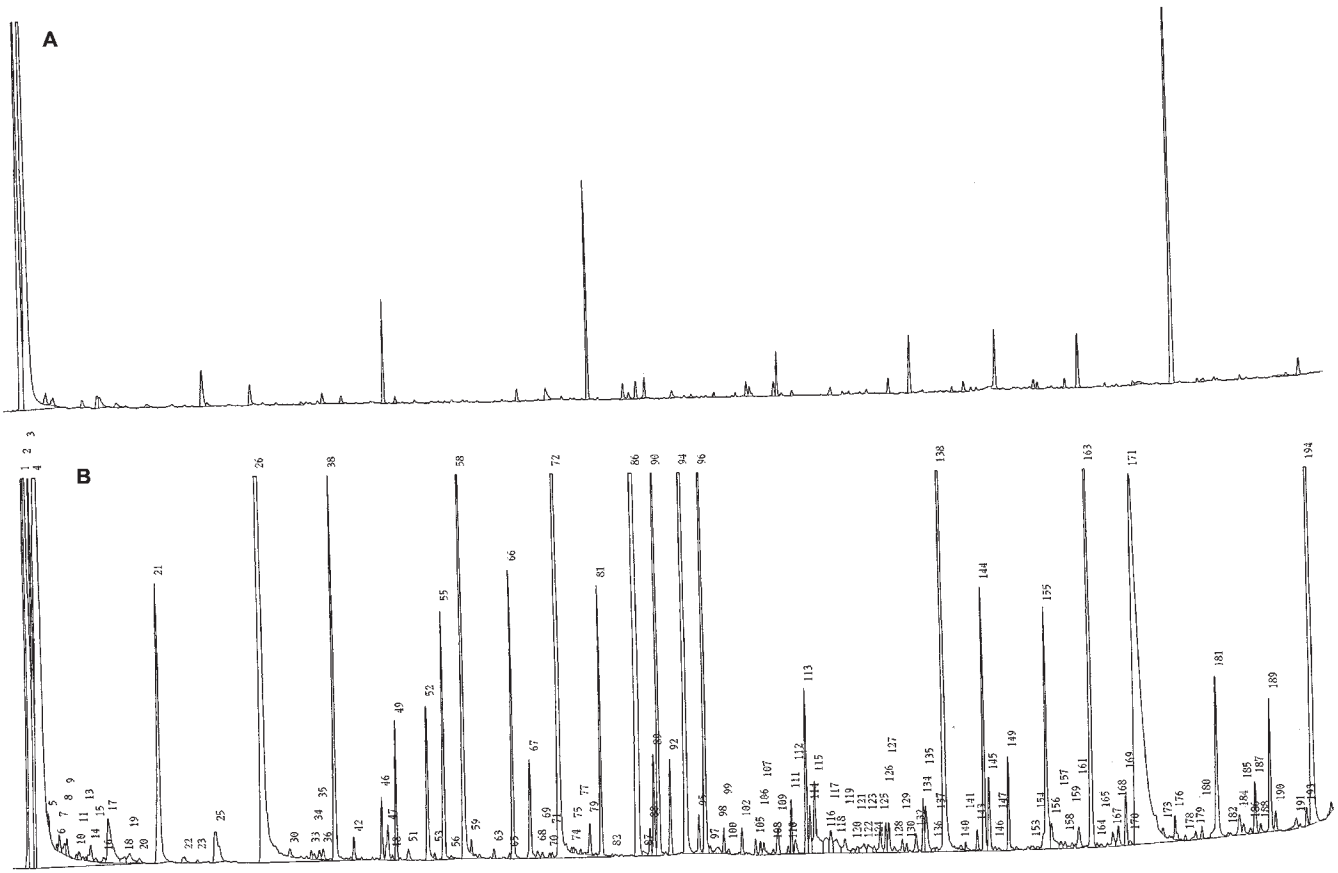

FIG. 6. Gas chromatograms of volatiles from linoleic acid methyl ester applied to dried seaweed at 72 h of oxidation. (A) Control sample; (B) light-exposed sample.

TABLE 1
Volatiles Identified from Eicosapentaenoic Acid Ethyl Ester Applied to Seaweed at 11 h of Oxidation (%)[a]

Peak no.[b]	Chemical name	Identification	Light-exposed sample	Control
7	Propanal	*	13.56	4.23
8	2-Propenal	*	9.96	1.52
15	2-Ethylfuran	*	6.54	3.14
16	3-Pentanone	*	4.32	7.61
19	1-Penten-3-one	*	2.12	0.00
21	Ethyl butyrate	*	7.27	20.93
22	2-Butenal	*	3.83	0.00
30	*cis*-2-Pentenal	*	1.35	0.47
34	*trans*-2-Pentenal	*	4.47	1.67
38	1-Penten-3-ol	*	13.78	2.37
49	*cis*-2-Hexenal	*	1.47	1.97
55	*trans*-2-Hexenal	*	0.31	1.52
60	*cis,trans*-1,5-Octadien-3-one	**	0.83	1.08
61	*trans,trans*-1,5-Octadien-3-one	**	0.17	0.47
70	2-Pentenyl furan	**	1.25	2.19
71	*cis*-2-Heptenal	*	0.61	0.31
72	*trans*-2-Heptenal	*	1.29	0.78
77	2-Penten-1-ol	*	0.47	0.70
90	*trans,trans*-2,4-Hexadienal	*	0.90	3.20
101	*cis,trans*-2,4-Heptadienal	*	3.84	9.86
107	*trans,trans*-2,4-Heptadienal	*	3.02	2.97
111	*cis,trans*-3,5-Octadien-2-one	**	2.21	15.94
116	*trans,trans*-3,5-Octadien-2-one	**	0.56	1.56
119	*cis,trans*-2,6-Nonadienal	*	0.96	1.92
121	*trans,trans*-2,6-Nonadienal	*	0.66	1.48
135	*cis,trans*-2,4-Nonadienal	*	5.28	7.98
141	*trans,trans*-2,4-Nonadienal	*	1.31	3.23
189	Heptanoic acid	*	7.69	0.78

[a]Weight of a compound per total weight of all compounds identified. *Identified by comparing MS and retention times with standard compounds. **Tentatively identified according to the MS fragmentations.
[b]Peak no. refers to the numbers in Figure 5B.

(Table 2). The relative amounts of hexanal, 2-heptenal, 2-octenal, octanoic acid methyl ester, and hexanoic acid in the light-exposed sample were significantly larger than those in the control, and the relative amounts of 2-decenal, 2,4-nonadienal, and 2,4-decadienal in the control were significantly larger than those in the light-exposed sample (Fig. 8).

When the LA methyl ester in the control was oxidized to a level of residual oxygen (20%) similar to that in the light-exposed sample (at 72 h for the light-exposed sample and at 7 d for the control), the volatile profiles of the samples on gas chromatograms were different. The relative amounts of volatiles identified also differed.

DISCUSSION

The data for oxygen consumption and distribution of volatiles clearly showed that lipids impregnated on the surface of the seaweed were oxidized in both the light-exposed sample and the control and that lipids were oxidized faster in the light-exposed samples. This was due not only to free radical oxidation but also to photosensitized oxidation. Photosensitized oxidation proceeded much faster than autoxidation in the light-exposed sample.

We showed that chlorophyll in the seaweed served as a photosensitizer and that the EPA ethyl ester impregnated on the surface of the seaweed underwent photosensitized oxidation when exposed to light (11). Dried seaweed kept in the dark contained eight hydroperoxide isomers of the EPA ethyl ester, namely, 5-hydroperoxy-*trans*-6,*cis*-8,*cis*-11,*cis*-14,*cis*-17-EPA ethyl ester, 8-hydroperoxy-*cis*-5,*trans*-9,*cis*-11,*cis*-14,*cis*-17-EPA ethyl ester, 9-hydroperoxy-*cis*-5,*trans*-7,*cis*-11,*cis*-14,*cis*-17-EPA ethyl ester, 11-hydroperoxy-*cis*-5,*cis*-8,*trans*-12,*cis*-14,*cis*-17-EPA ethyl ester, 12-hydroperoxy-

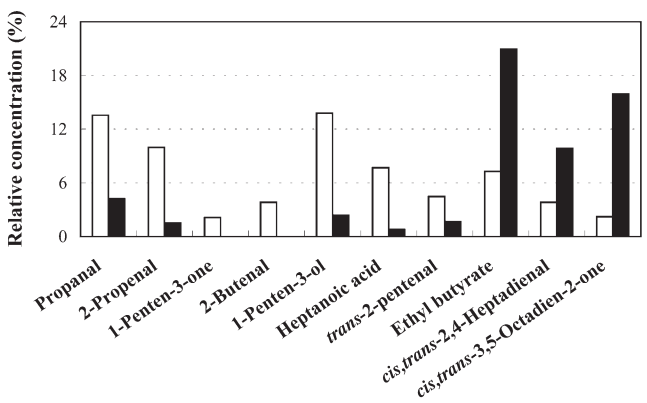

FIG. 7. Relative concentrations of volatiles from eicosapentaenoic acid ethyl ester applied to seaweed at 11 h of oxidation. (■) Control sample; (□) light-exposed sample.

TABLE 2
Volatiles Identified from Linoleic Acid Methyl Ester Applied to Seaweed at 72 h of Oxidation (%)[a]

Peak no.[b]	Chemical name	Identification	Light-exposed sample	Control
4	Pentane	*	1.71	2.80
6	Propanal	*	1.19	3.78
9	2-Propenal	*	2.10	3.24
17	Octadiene	*	3.78	5.04
21	Pentanal	*	2.36	1.57
26	Hexanal	*	15.70	6.14
38	2-Heptanone	*	2.04	3.47
46	Methyl hexanoate	*	0.29	0.17
47	Heptanal	*	0.22	0.42
55	2-Pentyl furan	*	0.97	0.18
59	1-Pentanol	*	0.05	0.28
66	Methyl heptanoate	*	1.08	0.18
67	Octanal	*	0.60	3.31
68	1-Octen-3-one	*	0.05	0.14
69	*cis*-2-Heptenal	*	0.17	0.28
72	*trans*-2-Heptenal	*	10.26	3.20
86	Methyl octanoate	*	18.50	7.35
90	*cis*-2-Octenal	*	2.66	0.29
94	*trans*-2-Octenal	*	9.81	2.75
96	1-Octen-3-ol	*	3.65	2.18
98	Methyl nonanoate	*	0.12	1.25
108	*cis*-3-Nonenal	**	0.27	0.14
110	*trans*-3-Nonenal	**	0.38	0.15
113	*cis*-2-Nonenal	*	0.68	0.14
115	*trans*-2-Nonenal	*	0.78	0.17
134	2-Decenal	*	0.29	13.58
138	*cis,trans*-2,4-Nonadienal	*	4.35	1.28
144	*trans,trans*-2,4-Nonadienal	*	1.21	14.71
149	Pentanoic acid	*	0.43	0.29
155	*cis,trans*-2,4-Decadienal	*	1.28	2.47
163	*trans,trans*-2,4-Decadienal	*	3.77	15.32
171	Hexanoic acid	*	7.53	2.70
189	Heptanoic acid	*	0.85	0.70

[a]Weight of a compound per total weight of all compounds identified. *Identified by comparing MS and retention times with standard compounds. **Tentatively identified according to the MS fragmentations.
[b]Peak no. refers to the numbers in Figure 6B.

cis-5,*cis*-8,*trans*-10,*cis*-14,*cis*-17-EPA ethyl ester, 14-hydroperoxy-*cis*-5,*cis*-8,*cis*-11,*trans*-15,*cis*-17-EPA ethyl ester, 15-hydroperoxy-*cis*-5,*cis*-8,*cis*-11,*trans*-13,*cis*-17-EPA ethyl ester, and 18-hydroperoxy-*cis*-5,*cis*-8,*cis*-11,*cis*-14,*trans*-16-EPA ethyl ester. For the dried seaweed exposed to light, the oxidized lipids contained not only the aforementioned eight isomers, but also 6-hydroperoxy-*trans*-4,*cis*-8,*cis*-11,*cis*-14,*cis*-17-EPA ethyl ester (6-*trans,cis*-20:5-OOH) and 17-hydroperoxy-*cis*-5,*cis*-8,*cis*-11,*cis*-14,*trans*-18-EPA ethyl ester (17-*cis,trans*-20:5-OOH). Based on the different hydroperoxide isomer distributions between the light-exposed sample and control, formation mechanisms applicable to some volatiles were proposed to explain the different distributions of the volatiles between the light-exposed samples and controls, as shown in Figure 9. Two characteristic hydroperoxide isomers of the EPA ethyl ester in the light-exposed sample, 6-*trans,cis*-20:5-OOH and 17-*cis,trans*-20:5-OOH, led to specific volatiles in the light-exposed sample. 17-*Cis,trans*-20:5-OOH could be the precursor of 2-butenal and propanal, which contributed to the specific or additional amounts of volatiles in the light-exposed samples. Theoretically, the characteristic hydroperoxide isomer 6-*trans,cis*-20:5-OOH should also contribute some specific or additional amounts of volatiles from

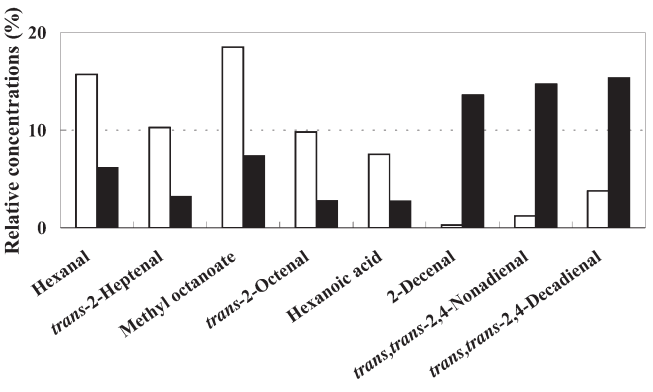

FIG. 8. Relative concentrations of volatiles from linoleic acid methyl ester applied to seaweed at 72 h of oxidation. (■) Control sample; (□) light-exposed sample.

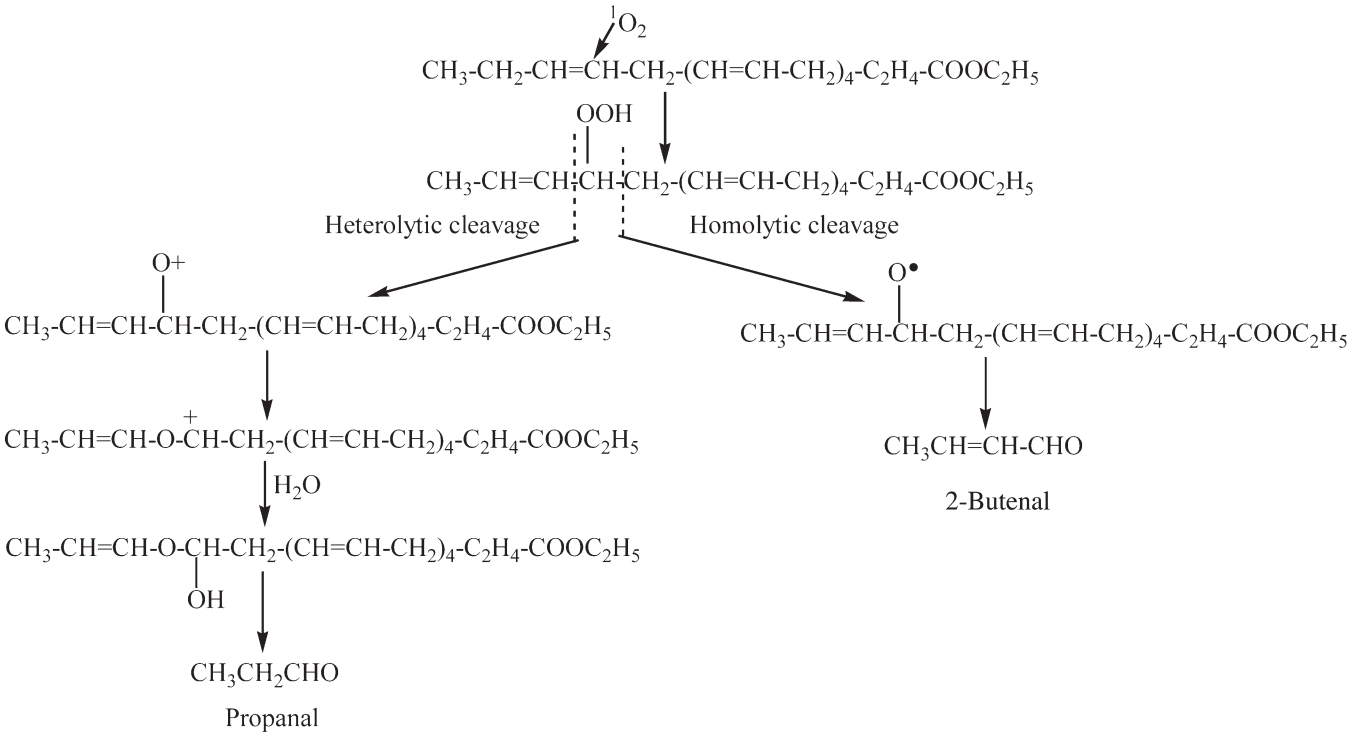

FIG. 9. Formation mechanisms of typical volatiles from photosensitized oxidation of eicosapentaenoic acid ethyl ester.

light-exposed samples, but we were unable to identify all of the volatiles, especially the semivolatiles that had relatively high M.W. or high b.p.

Chlorophyll in seaweed served as a photosensitizer, and the LA methyl ester impregnated on the surface of the seaweed underwent photosensitized oxidation when the seaweed was exposed to light (11). The dried seaweed kept in the dark contained four hydroperoxide isomers, namely, 13-hydroperoxy-*cis*-9,*trans*-11-octadecadienoate, 13-hydroperoxy-*trans*-9,*trans*-11 octadecadienoate, 9-hydroperoxy-*trans*-10,*cis*-12-octadecadienoate, and 9-hydroperoxy-*trans*-10,*trans*-12-octadecadienoate. For the dried seaweed exposed to light, the oxidized lipids contained not only these four isomers, but also 12-hydroperoxy-*cis*-9,*trans*-13-octadecadienoate (12-*cis,trans*-18:2-OOH) and 10-hydroperoxy-*trans*-8,*cis*-12-octadecadienoate (10-*trans,cis*-18:2-OOH). Based on the different distributions of hydroperoxide isomers between light-exposed samples and controls, formation mechanisms for some volatiles were proposed to explain the different distributions of volatiles between the light-exposed samples and controls (Fig. 10). The characteristic hydroperoxides of the LA methyl ester in the light-exposed sample, 12-*cis,trans*-18:2-OOH and 10-*trans,cis*-18:2-OOH, led to a difference in volatile distributions between the light-exposed sample and the control by serving as precursors of these volatiles. 12-*Cis,trans*-18:2-OOH could be the precursor of 2-heptenal and hexanal, and 10-*trans,cis*-18:2-OOH could be the precursor of 2-octenal and 3-nonenal. Although these particular precursors in the light-exposed sample did not produce specific volatiles when compared with the control, they did contribute to high concentrations of certain volatiles.

Much research has been done to clarify the relationship between the hydroperoxide isomers and resulting volatiles (1,7,12,13). Frankel *et al.* (7) and Chan *et al.* (13) thermally decomposed the pure hydroperoxides from autoxidized and methylene blue-photosensitized oxidation of oleic acid methyl ester, LA methyl ester, and linolenic acid methyl ester in the injector port of a gas chromatograph–mass spectrometer. They reported that although the hydroperoxides from autoxidized esters were isomerically different in position and concentration from those from photosensitized oxidation, the same major volatile products were formed but in different relative amounts, a finding similar to the results obtained from this study. However, more complete and comprehensive yields of low-M.W. volatiles were identified with the SPME-GC–MS system used in the present study.

Frankel *et al.* (7) and Chan *et al.* (13) have demonstrated that significant interconversion between hydroperoxides generated by autoxidized fatty esters and those from the corresponding photosensitized oxidation products changed by rearrangement, isomerization, and cyclization may be partly responsible for the same major volatiles between photosensitized oxidation and autoxidation. Moreover, hydroperoxides are very unstable and easily change to the secondary oxidation products, so the specific decomposition of hydroperoxides becomes elusive and complicated.

In complex food systems, the interaction of lipid hydroperoxides and secondary oxidation products with protein and

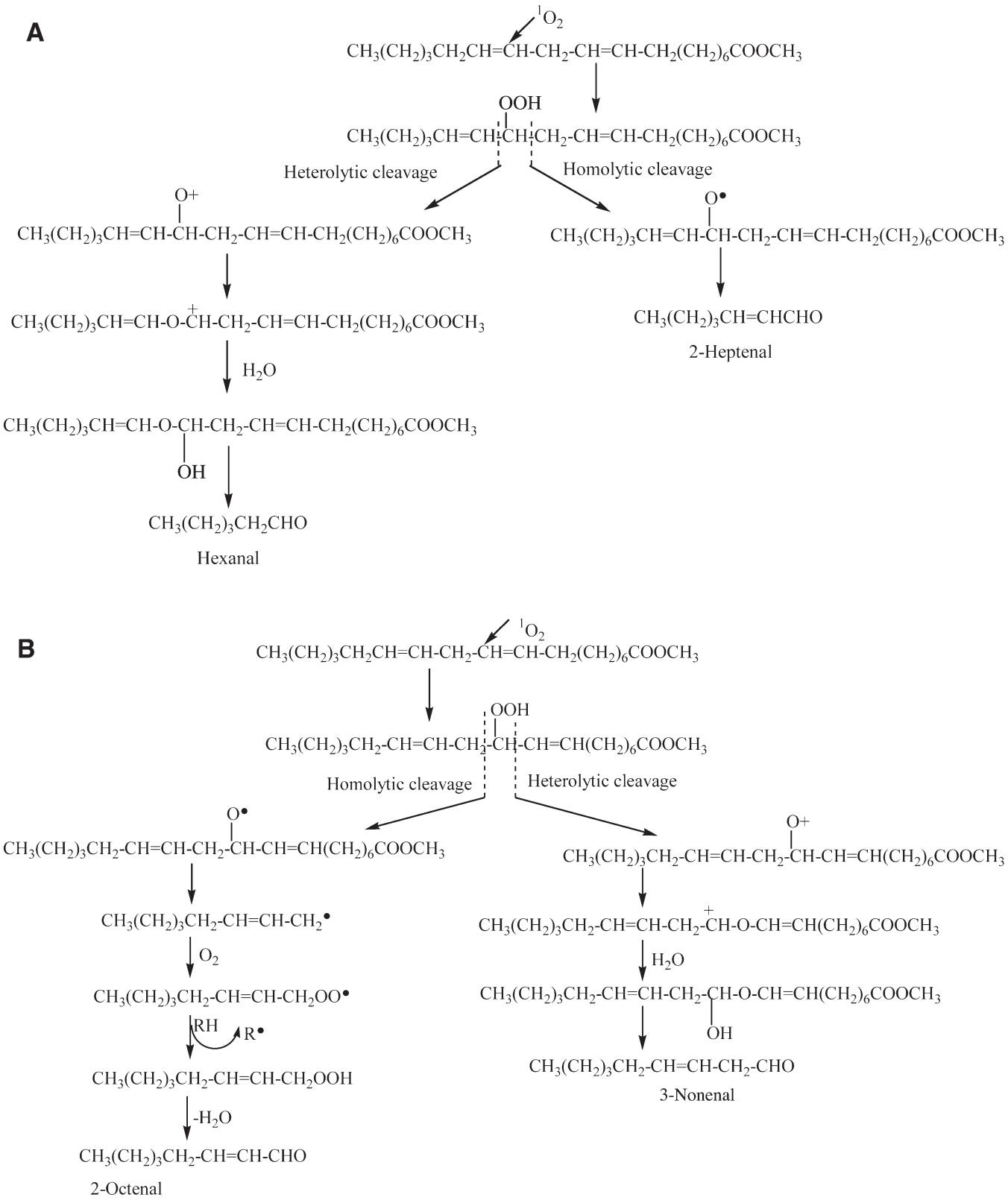

FIG. 10. Formation mechanisms of typical volatiles from photosensitized oxidation of linoleic acid methyl ester.

other components has a significant impact on oxidative and flavor stability and texture during processing and storage. Since the major volatiles from light-exposed samples were found to differ from the controls, the different relative concentrations of volatiles may contribute to differences in aroma and flavor between sun-dried and mechanically dried seafoods.

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