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Effects of riboflavin-photosensitization on the formation of volatiles in linoleic acid model systems with sodium azide or D_2O

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Abstract

Effects of riboflavin-photosensitization on volatile formations were studied in linoleic acid model systems with sodium azide or D_2O. Linoleic acid with riboflavin solution were stored under light or in the dark and volatiles were analyzed by a combination of solid phase microextraction (SPME), gas chromatography (GC), and mass spectrometry (MS). Riboflavin-photosensitization produced 27.9% more total volatiles than samples stored in the dark for 16 h. Addition of sodium azide decreased the total volatiles by 28.4% compared to samples without sodium azide. Linoleic acid in D_2O had higher increases in total volatiles than samples in H_2O system. Decrease of total volatiles in samples with sodium azide and increase of total volatiles in D_2O sample indirectly showed the presence of singlet oxygen in riboflavin-photosensitization. Hexanal, 2-heptenal, 1-octen-3-ol, 2-octenal, and 2,4-decadienal were greatly influenced by the addition of sodium azide and in D_2O, which indicates that formation of these volatiles was related to singlet oxygen oxidation. Especially, 2-heptenal showed the highest peak area among volatiles under riboflavin-photosensitized linoleic acid for 16 h.

Keywords: Riboflavin; Linoleic acid; Volatile compounds; Singlet oxygen; Sodium azide; D_2O

1. Introduction

Severe light exposure can accelerate the deterioration of sensory quality of foods and decrease their consumer acceptance. Discoloration in meat and cheese, and off-flavor formation in beer, vegetable oils, and milk are common quality defects caused by light exposure in foods and beverages (Boff & Min, 2002; Skibsted, 2000). Lipids with unsaturated double bonds are one of the most sensitive substrates to light-induced oxidation during food processing and storage. Lipids, especially unsaturated fatty acids, undergo oxidation with singlet or triplet oxygen and form hydroperoxides. The decomposition of hydroperoxides in unsaturated fatty acids produces aldehydes, alcohols, ketones, and hydrocarbons, which are responsible for the rancid off-odor in oxidized foods (Choe & Min, 2002; Min, 1998). Unsaturated fatty acids can be oxidized easily due to the low one-electron reduction potential compared with saturated fatty acids (Decker, 1998).

Oxygen in nature occurs as triplet and singlet state. Two types of singlet oxygen, $^1\Delta$ and $^1\Sigma$ types, are found and the energy states of $^1\Delta$ and $^1\Sigma$ type singlet oxygen are higher than that of triplet oxygen by 22.4 and 35 kcal/mol, respectively. $^1\Delta$ type of singlet oxygen is more important than $^1\Sigma$ type due to its relatively long half-life (Foote, 1976). Decay rate of singlet oxygen depends on the types of solvents in the systems. For example, decay rates of singlet oxygen in water, ethanol, and chloroform are 3.10×10^5, 6.7×10^4, and 4.0×10^3 (s^{-1}), respectively. Photosensitized production of singlet oxygen is much researched and provides a simple and controllable method for singlet oxygen studies (Kochevar & Redmond, 2000). Colored pigments including rose bengal, methylene blue, riboflavin, chlorophylls, and myoglobin are well-known photosensitizers (Edwards & Silva, 2001; Kochevar & Redmond, 2000). Photosensitizers can act in two pathways: one is type I pathway, in which

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photosensitizers abstract electron or hydrogen from substrates to generate radicals, and the other is type II pathway, generating singlet oxygen from triplet oxygen (Bradley & Min, 1992; Boscá, Miranda, Morera, & Samadi, 2000; Foote, 1976). Riboflavin, water soluble vitamin B_2, has been reported to play important roles in the formation of light-induced off-flavor in dairy products such as milk and cheese (Kim, Lee, & Min, 2003; Lee, 2002). Riboflavin may follow both type I and type II mechanisms, which are competitive depending on the solubility and concentration of triplet oxygen (Edwards & Silva, 2001). The reduction potential of triplet riboflavin is about 1.7 V at pH 7, which is high enough to abstract electron or hydrogen atom from food compounds including polyunsaturated fatty acids, ascorbic acid, and tocopherol (Lu et al., 1999).

Besides photosensitization, singlet oxygen can be produced by several chemical methods such as the reaction of sodium hypochlorite with H_2O_2 and the decomposition of hydroperoxides through tetroxide intermediates (Frankel, 1985; Miyamoto, Martinez, Medeiros, & Di Mascio, 2003).

Reaction of singlet oxygen with food components can induce the deterioration of food quality and nutritional loss and it is important to analyze singlet oxygen reaction products. One useful indicator for singlet oxygen reaction products in foods is the amount and profiles of volatile compounds from singlet oxygen oxidation with unsaturated fatty acids. Lee (2002) determined volatile compounds in riboflavin-photosensitized milk with synthetic antioxidants and/or sodium azide and indirectly proved the presence of singlet oxygen. Jung, Yoon, Lee, and Min (1998) reported that singlet oxygen is responsible for the formation of dimethyl disulfide in milk stored under the sun or fluorescent light.

Linoleic acid is a C18:2 fatty acid with two double bonds at C9 and C12 and is one of the major unsaturated fatty acid in vegetable oils. The content of linoleic acid in soybean, corn, and sunflower oils is about 51, 61, and 67%, respectively. The isomeric structures of hydroperoxides and decomposition volatile compounds from linoleic acid or methyl linoleate by autoxidation and photosensitized oxidation have been studied extensively (Frankel, 1985; Frankel, Neff, & Selk, 1983). However, the effects of riboflavin-photosensitization on the formation of volatile compounds in linoleic acid system have not been reported in the literature.

The objective of this work was to study the effects of light, riboflavin, and singlet oxygen on the formation of volatile compounds from linoleic acid model systems using sodium azide or D_2O.

2. Materials and methods

2.1. Materials

Riboflavin, linoleic acid (minimum 99%), sodium azide, D_2O, hexanal, heptanal, 1-octen-3-ol, and other compounds were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Teflon-coated rubber septa, aluminum caps, serum bottles, glass liners, the fiber assembly holder, and 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) were purchased from Supelco, Inc. (Bellefonte, PA, USA).

2.2. Sample preparation for linoleic acid model systems with riboflavin

Riboflavin was dissolved with magnetic stirring in deionized water to obtain 400 ppm (w/v). Sodium azide is a well-known selective physical quencher for singlet oxygen. D_2O prolongs the half-life of singlet oxygen more than H_2O in solution. Sodium azide was dissolved in riboflavin solution to obtain a 400 ppm (w/v) concentration. For the preparation of D_2O model system, deionized water was replaced with D_2O and riboflavin was dissolved in D_2O to make a concentration of 400 ppm (w/v). One gram of linoleic acid was mixed with two grams of solutions (at the ratio of 2–1, w/w) and placed in 10-mL serum bottles and sealed air-tight with Teflon-coated rubber septa and aluminum caps. The model system does not produce an emulsion and is composed of riboflavin solution in the bottom and linoleic acid on the top. No emulsifier was added in order to avoid the effects of emulsifiers on volatile formation and oxidation of linoleic acid.

Sample bottles were kept at 30 °C in a hand-made light box for 16 h. Five fluorescence lamps with 1,330 Lux light intensity (Tenmars Electronics Co., Taipei, Taiwan) were used as light source. Sample bottles in the dark were used as control groups and dark condition was ensured by wrapping sample bottles in aluminum foil. Samples with riboflavin only under light (RO), samples with riboflavin and sodium azide under light (RS), samples stored in the dark (CON), samples with riboflavin in D_2O under light (RDL), and samples with riboflavin in D_2O in the dark (RDD) were prepared in duplicate. The entire experiment was repeated twice.

2.3. Analysis of volatile compounds by solid phase microextraction (SPME)

Sample bottles taken from the light box were placed in the dark for 2 h at room temperature to equilibrate the volatile compounds in the headspace of bottles. Conditions of solid phase microextraction (SPME) for volatile compound analysis were adopted by modification of the method of Lee (2002). The volatile compounds of samples were isolated using a 65 μm PDMS/DVB solid phase at 30 °C for 30 min in a water bath. The isolated volatile compounds were determined using a gas chromatograph (GC) equipped with a flame ionization detector (Shimadzu GC-17A, Kyoto, Japan).

2.4. Gas chromatography condition

A Shimzdu G17A gas chromatograph, equipped with a 0.75 mm ID glass injection liner, a flame ionization detector, and a 30 m × 0.32 mm ID, 0.25 μm film, DB-5 (Agilent

J&W, Folsom, CA, USA) column was used. The oven temperature was held at 40 °C for 2 min and increased from 40 to 160 °C at 6 °C/min and from 160 to 220 °C at a rate of 10 °C/min and held for 3 min. The temperatures of injector and detector were 250 and 300 °C, respectively. The flow rate of nitrogen carrier gas was 1.0 mL/min. Splitless mode was used and the isolated volatile compounds in solid phase of SPME were desorbed at 250 °C for 2 min in a GC injector.

2.5. Identification of volatile compounds

A Hewlett-Packard 5890 GC-5971A mass selective detector (MS) (Agilent Technology, Palo Alto, CA, USA) equipped with a Hewlett-Packard 59822 B ionization gauge controller was used. All mass spectra were obtained at 70 eV and 220 °C ion source temperature. The identification of compounds was made by a combination of NIST Mass Spectra and gas chromatographic retention times of standard compounds. Volatile compounds without standard compounds were identified tentatively only using GC-MS spectra. Helium carrier gas at 1.0 mL/min and a 30 m × 0.25 mm i.d., 0.25 μm film thickness, DB-5ms (Agilent J&W, Folsom, CA, USA) column were used. The oven conditions for GC-MS were the same as the gas chromatographic analysis conditions described previously.

2.6. Statistical analysis

Results were statistically analyzed using commercially available software package, SPSS software program (SPSS Inc., Chicago, IL, USA) and Microsoft Excel program. A p value <0.05 was considered significant.

3. Results and discussion

3.1. Analysis of volatile compounds from linoleic acid by SPME

A representative GC chromatogram of volatile compounds in riboflavin-photosensitized linoleic acid is shown in Fig. 1. SPME is a rapid, solvent-free, and simple method for volatile analysis and has been widely employed in testing many types of food. However, studies on volatiles by SPME from lipid sources such as vegetable oils or free fatty acids are relatively limited in the literature. Steenson, Lee, and Min (2002) measured volatile compounds from soybean and corn oils using a SPME-GC method and reported that SPME can be a useful volatile isolating and concentrating method from vegetable oils. Lee (2002) determined volatile compounds from lard and linoleic acid with the addition of chlorophylls using SPME solid phase of PDMS/DVB. Although the distribution profiles of volatiles in fat and oils by SPME method are influenced by many factors including characteristics of SPME solid phase and volatility of compounds, SPME can be used successfully to analyze volatile compounds and differentiate the

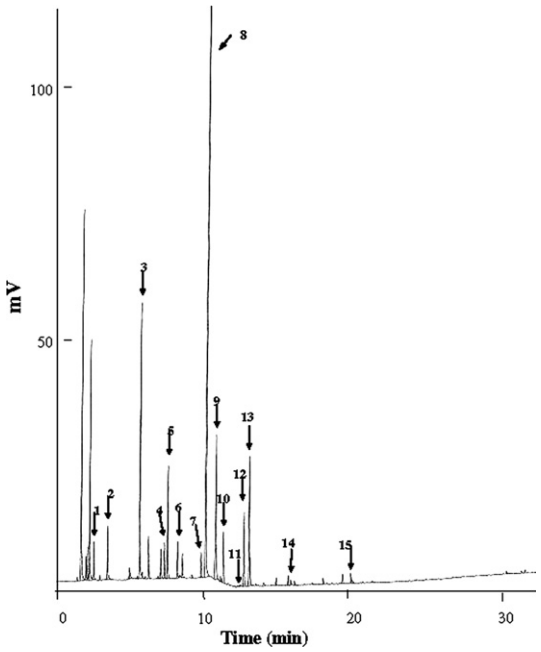

Fig. 1. GC chromatogram of riboflavin-photosensitized linoleic acid model systems stored under light by SPME. Peaks with numbered arrow are listed in Table 1.

oxidized vegetable oils (Jelen, Obuchowska, Zawirska-Wojtasiak, & Wasowicz, 2000; Kalua, Bedgood, & Prenzler, 2006).

3.2. Effects of sodium azide and D_2O on total volatiles from linoleic acid model system with riboflavin

Relative total volatile compounds in linoleic acid with riboflavin stored under light or in the dark for 16 h are shown in Fig. 2. Total volatiles from RO and RDL increased significantly for 16 h light exposure compared to those in CON and RDD, respectively ($p < 0.05$). Total volatile compounds in RO increased by 27.9% compared to those in CON. Riboflavin is a well-known water-soluble photosensitizer and the increase of total volatile compounds in the sample under light was expected. Riboflavin dispersed in oil did not act as a photosensitizer (Yang, Chang, & Lee, 2005), which is a noticeable difference from chlorophyll, a well-known lipid-soluble photosensitizer. Addition of sodium azide decreased the formation of volatile compounds. Total volatile compounds in RS were significantly lower than those in RO ($p < 0.05$) and were not significantly different from those in CON for 16 h ($p > 0.05$). The reaction rates of triplet and singlet oxygen with linoleic acid are 8.9×10^1 and $1.3 \times 10^5\ M^{-1}\ s^{-1}$, respectively (Rawls & VanSanten, 1970). Singlet oxygen oxidation in linoleic acid occurs about 1460 times faster than triplet oxygen oxidation or autoxidation. As a selective physical quencher for singlet oxygen, sodium azide can protect vitamin C from photo-decomposition (Jung, Kim, & Kim, 1995) and prevent dimethyl disulfide formation in milk (Lee, 2002) from the destructive reaction of

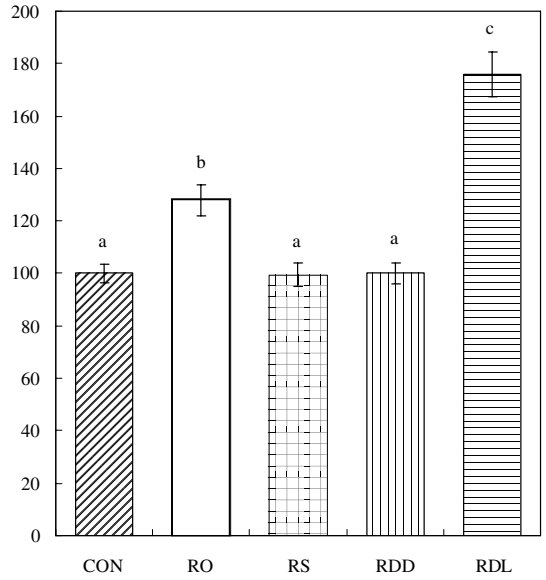

Fig. 2. Relative total peak area in riboflavin-photosensitized linoleic acid model systems. CON: control sample stored in the dark, RO: samples with riboflavin only under light, RS: samples with riboflavin and sodium azide under light, RDD: samples with riboflavin in D_2O in the dark, RDL: samples with riboflavin in D_2O under light. Different letters on the bar graph were significant at 0.05.

singlet oxygen. Decreased volatile compound formation is an indirect evidence for the involvement of singlet oxygen during riboflavin-photosensitization.

Riboflavin in D_2O system also acts as a photosensitizer and total volatiles from D_2O system under light were more than those stored in the dark. Total volatile compounds in RDL for 16 h were 175% of those in RDD (Fig. 2). The increase of total volatiles in RDL was higher than that in RO by 45.7%, which indicates that D_2O accelerates the formation of volatile compounds compared with H_2O systems under light. D_2O can stabilize singlet oxygen and the half-life of singlet oxygen in D_2O is about 65 μs while that in H_2O is about 3–4 μs (Nardello & Aubry, 2000). Therefore, singlet oxygen has more chances to react with linoleic acid in D_2O system and may generate more volatile compounds than that in H_2O model systems due to the 16.5–33 time prolonged stability. Model systems using D_2O for the detection of singlet oxygen have not been used to examine the volatile formations from unsaturated fatty acids. The presence of singlet oxygen can be indirectly proven using singlet oxygen quenching effects of sodium azide or singlet oxygen stabilizing effects of D_2O.

3.3. Volatile compounds formations in linoleic acids in model system

Major volatile compounds identified from linoleic acid model systems with riboflavin stored for 16 h are shown in Table 1. Peak area (PA) of hexanal, 2-heptenal, 1-octen-3-ol, and 2-octenal, which were detected in 0 h sample, increased in all RO, RS, and CON samples for 16 h. Hexanal is regarded as a representative volatile from oxidized lipid and has been used as an oxidation marker in foods (Jensen, Danielsen, Bertelsen, Skibsted, & Andersen, 2005; Sanches-Silva, Rodrıguez-Bernaldo, López-Hernández, & Paseiro-Losada, 2004). PA of hexanal in CON, RO, and RS increased by 134, 203, and 187%, respectively, compared to that in 0 h sample. This difference of hexanal among samples could be due to the autoxidation and type I and type II mechanisms of riboflavin. Autoxidation or free radical chain reaction, was a major oxidation pathway in CON samples. For RS samples, autoxidation and type I pathway played important roles and for RO samples, autoxidation, type I, and type II mechanisms were responsible for the formation of volatiles. Therefore, about 34% (=134–100%, CON-0 h sample), 53% (=187–134%, RS–CON), and 16% (=203–187%, RS–RO) of hexanal could be generated through autoxidation, type I mechanism, and singlet oxygen, respectively. Type I mechanisms of riboflavin occurred more than type II mechanisms based on the PA of hexanal. Riboflavin can follow both type I and type II mechanisms with competitive manner and type I of riboflavin was preferred due to the low solubility of oxygen in water and easy oxidation–reduction property of riboflavin (Gutierrez, Criado, Bertolotti, & Garcia, 2001; McGinnis, Adams, & Middlebrooks, 1999).

PAs of 2-heptenal and 1-octen-3-ol in RO increased greatly compared with those of CON while in RS, the increases of PAs were reduced. Therefore, formations of 2-heptenal and 1-octen-3-ol are dependent on singlet oxygen oxidation. Frankel (1985) reported that 2-heptenal and 1-octen-3-ol are specifically detected volatiles in photosensitized oxidation of methyl linoleate while autoxidation generated trace amounts of these compounds. Interestingly, PAs of 2-heptenal and 1-octen-3-ol in RS was lower than those of CON, which shows that presence of sodium azide slow down the oxidation of linoleic acid during autoxidation. Not all volatiles showed this trend and volatiles including hexanal, 2-octenal, and 2,4-decadienal in RS were higher than those in CON. It has been reported that singlet oxygen can be generated chemically from peroxyl radicals through the formation of a tetroxide intermediate (Miyamoto et al., 2003; Miyamoto, Martinez, Martins, Medeiros, & Di Mascio, 2003). Miyamoto et al. (2003) observed the formation of singlet oxygen from the reaction of linoleic acid hydroperoxides using dimol and monomol light emission method. Radiative transition of singlet oxygen to ground state triplet oxygen can be monitored through dimol light emission in the red spectral region (Eq. (1)) or monomol light emission at near-infrared spectral region (Eq. (2)).

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + hv \ (\lambda = 634 \text{ and } 703 \text{ nm}) \quad (1)$$

$$O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + hv \ (\lambda = 1270 \text{ nm}) \quad (2)$$

Singlet oxygen generation during autoxidation may provide a possible explanation on the changes of oxidative volatiles but further studies are needed.

Table 1
Major volatile compounds detected in riboflavin-photosensitized linoleic acid model system stored for 16 h in electronic counts ($\times 10^5$)

No.[a]	Volatile compound	R.T.[b] (min)	0 h[c] H_2O	CON[c]	RO[c]	RS[c]	0 h[c] D_2O	RDD[c]	RDL[c]
1	Pentane[MS d]	2.7	1.31	0.88	0.67	0.72	1.05	1.11	0.88
2	Pentanal[e]	3.9	0.01	0.13	0.18	0.17	0.01	0.78	0.32
3	Hexanal	6.1	0.55	0.73	1.11	1.03	0.46	0.59	1.25
4	Unidentified	7.5	n.d[f]	0.06	0.14	0.12	n.d	0.08	0.24
5	2-Hexenal[MS]	8.0	0.77	0.74	0.56	0.69	0.73	0.76	0.85
6	Heptanal	8.8	n.d	0.01	0.01	n.d	n.d	n.d	0.03
7	Unidentified	10.2	n.d	0.09	0.10	0.05	n.d	0.08	0.19
8	2-Heptenal	10.5	0.08	2.75	3.14	2.56	0.11	2.47	5.85
9	1-Octen-3-ol[MS]	11.2	0.02	0.53	0.69	0.46	0.03	0.39	1.30
10	2-Pentylfuran	11.6	n.d	0.01	0.02	0.08	n.d	0.01	0.05
11	3-Octen-2-one[MS]	12.8	n.d	n.d	0.01	n.d	n.d	n.d	0.01
12	Unidentified	13.1	n.d	0.11	0.23	0.06	n.d	0.08	0.27
13	*trans*-2-Octenal	13.5	0.03	0.19	0.42	0.24	0.03	0.14	0.43
14	Octanoic acid	16.5	n.d	n.d	0.02	0.01	n.d	n.d	0.02
15	2,4-Decadienal	20.4	n.d	0.02	0.05	0.03	n.d	0.01	0.08

[a] Numbers of peaks were shown in Fig. 1.
[b] Retention time.
[c] 0 h H_2O: linoleic acid in H_2O model system at 0 h, CON: linoleic acid stored in the dark, RO: linoleic acid with riboflavin only under light, RS: linoleic acid with riboflavin and sodium azide under light, 0 h D_2O: 1inoleic acid in D_2O model system at 0 h, RDL: linoleic acid with riboflavin in D_2O under light, RDD: linoleic acid with riboflavin in D_2O in the dark.
[d] Volatiles were tentatively identified with mass spectrometry only.
[e] Volatiles were identified with a combination of mass spectrometry and retention time of standard compounds.
[f] Not detected.

Some volatiles including 2,4-decadienal and unidentified compounds which were not detected in 0 h samples, were found in RO, RS, and CON for 16 h. 2,4-Decadienal is a typical volatile compound formed from linoleic acid oxidation. PA of 2,4-decadienal in RO and RS increased to 257 and 143%, respectively, compared with that in CON. Both triplet and singlet oxygen can generate hexanal and 2,4-decadienal from linoleic acid. Singlet oxygen can form hydroperoxides at C9, C10, C12, or C13 positions in linoleic acid while triplet oxygen can form hydroperoxides at C9 or C13 positions in linoleic acid (Frankel, 1985). Hexanal and 2,4-decadienal can be generated from C13 and C9 hydroperoxides of linoleic acid, respectively, and representative volatiles from linoleic acid oxidation (Frankel, 1985). However, PA of hexanal was higher than that of 2,4-decadienal, which might be associated with the differences of volatility, selectivity of solid phase of SPME, or further decomposition of 2,4-decadienal to other volatiles.

Effects of riboflavin in D_2O system on the volatile formations for 16 h are shown in Table 1. Volatiles such as heptanal, 2-pentylfuran, and 2,4-heptadienal were not detected in 0 h sample in D_2O system, which agrees with H_2O systems and these volatiles in RDL had higher peak areas than RDD showing that singlet oxygen plays an important role in the formation of these volatiles. PA of 2-heptenal was largest among volatiles under riboflavin-photosensitized linoleic acid in both H_2O and D_2O samples.

Comparison of relative peak areas of hexanal, 2-heptenal, 1-octen-3-ol, and 2-octenal are shown in Fig. 3. PAs of hexanal, 2-heptenal, 1-octen-3-ol, and 2-octenal in RDL increased by 111, 136, 231, and 207%, respectively, compared to those of RDD while those in RO increased by 52, 13, 29, and 121%, respectively, compared to those of CON. These volatiles in D_2O system increased significantly higher than in H_2O system ($p < 0.05$). This difference between RDL and RO on the increase ratio of volatiles originated from prolonged shelf-life of singlet oxygen in D_2O system. PAs of these volatiles in RS were lower than those of RO (Fig. 3), which also indicates that singlet

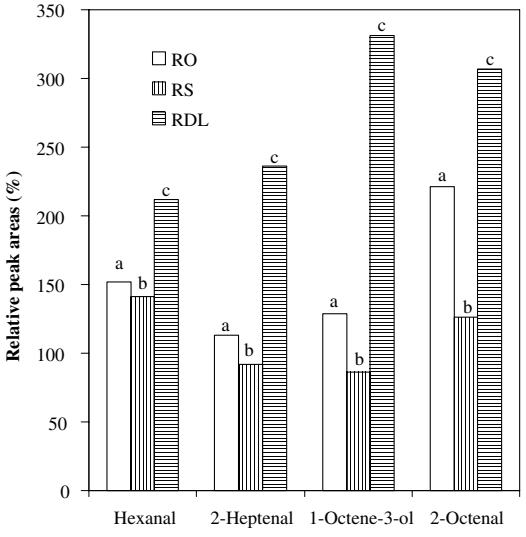

Fig. 3. Relative peak areas of hexanal, 2-heptenal, 1-octene-3-ol, and 2-octenal among RO, RS and RDL. RO: samples with riboflavin only under light, RS: samples with riboflavin and sodium azide under light, RDL: samples with riboflavin in D_2O under light. Relative peak area of selected compounds in RO and RS were compared tothose in CON and that of RDL was compared to that of RDD, respectively. Different letters on the bar graph were significant among RO, RS, and RDL at 0.05.

oxygen is directly associated with the formation of these volatiles from linoleic acid.

Frankel (1985) has reported the oxidation volatile profiles from hydroperoxides of methyl oleate, methyl linoleate, and methyl linolenate through autoxidation or photosensitization. Many volatiles were detected in both samples under either autoxidation or photosensitization with different relative percentages. Addition of sodium azide and/or D_2O model system may help to show the presence of singlet oxygen during photosensitization. Preliminary studies showed that the effects of photosensitization in more oxidized linoleic acid were less obvious than in less oxidized linoleic acid on the volatile formations (data not shown). Although SPME method has some limitations on detecting all volatiles from samples, the distribution of volatile profiles in this study clearly shows the involvement of singlet oxygen in riboflavin-photosensitized linoleic acid.

4. Conclusions

Effects of riboflavin-photosensitization on the formation of volatiles from linoleic acid were studied using sodium azide or D_2O model systems. By a combination of sodium azide or D_2O model systems, volatile compounds due to singlet oxygen oxidation could be identified. Addition of sodium azide decreased volatile formation due to singlet oxygen. Total volatile compounds in D_2O model system were significantly higher than those in the H_2O systems. Some volatiles including hexanal, 2-heptenal, 1-octen-3-ol, 2-octenal, and 2,4-decadienal were greatly influenced by the addition of sodium azide or in D_2O system. Especially, peak area of 2-heptenal was the highest among volatiles under riboflavin-photosensitized linoleic acid for 16 h. Both riboflavin and linoleic acid are important food components and light exposure on foods containing both compounds may undergo fast volatile formations in a relatively short time. The results of this study may help understanding the volatile formation and off-flavors in foods containing unsaturated fatty acids and riboflavin stored under light.

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