

Effects of Deuterium Oxide on Formation of Volatiles in Linoleic Acid Model Systems at Different Temperatures and Oxygen Limitation Conditions

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Received July 7, 2014; revised August 13, 2014; accepted August 13, 2014; published online February 28, 2015
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Abstract Effects of 30, 60, and 90°C treatments and oxygen limitation on formation of volatiles were determined for linoleic acid model systems containing deuterium oxide (D₂O) and deuterium free water. The presence of D₂O accelerated consumption of headspace oxygen, indicating that the rate of lipid oxidation increased in the presence of D₂O. The presence of deuterium in headspace volatiles was indirectly determined based on comparison of the amount of the fragmented mass to charge ratio (*m/z*) (molecular weight, Mw), which was 73.1/72.1 for *d*₁-pentane/pentane and 125.1/124.1 for *d*₁-2,4 octadienal/2,4 octadienal. The ratio of 73.1/72.1 (*m/z*) for pentane was significantly (*p*<0.05) higher for samples containing D₂O than for samples containing deuterium free water at 30, 60, and 90°C. Other volatiles did not follow the same pattern. 2,4-Octadienal in samples under unlimited oxygen conditions confirmed this trend, indicating that water was incorporated into volatiles during oxidation of linoleic acid under these conditions.

Keywords: deuterium oxide, lipid oxidation, elevated heating, oxygen limitation, headspace volatile

Introduction

Lipid oxidation is an important chemical reaction in lipid-rich foods, and lipid oxidation products lower nutritional values and cause deterioration of sensory attributes, which decrease consumer acceptability of foods (1–3). Many factors influence the rate of lipid oxidation, including the

degree of lipid unsaturation, types of oxygen molecules, and the presence of prooxidative and antioxidative minor components. Transition metals, the water content, pigments, sterols, and the amphiphilic substances phospholipids, free fatty acids (FFAs), monoacylglycerols (MAGs), and diacylglycerols (DAGs) also play important roles in the rate of lipid oxidation (1,4,5). Water is present in bulk oils in a range of approximately 200–800 ppm (4). Water can form an association with colloids containing amphiphilic compounds, and the lipid-water interface in the association with colloids is the predominant site of lipid oxidation (6–8).

Diverse roles of water in lipid oxidation have been evaluated using deuterium oxide (D₂O) in linoleic acid and corn oil systems (9,10). The presence of deuterium oxide accelerated the rate of lipid oxidation (10), and deuterium oxide seemed to participate in formation of volatiles during lipid oxidation. Previous experiments were conducted at 60°C. Therefore, it is necessary to investigate the involvement of water in formation of volatiles under different treatment temperatures. In addition, previous experiments were conducted under air-tight or oxygen limited conditions (9,10). It is possible that headspace volatiles react with each other to generate new volatile products, which may not directly originate from oxidation of linoleic acid. Therefore, it is necessary to confirm that headspace volatiles detected using solid phase microextraction (SPME) technology are produced solely from lipid oxidation. Data from samples generated under non-air-tight conditions may help to elucidate this issue since volatiles from lipid oxidation may be released into the air, which would lessen the chance of forming other volatiles due to interactions between substances.

The objective of this study was to determine the effects of treatment temperature, oxygen limitation, and deuterium oxide on the rate of lipid oxidation in linoleic acid model

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systems. The degree of lipid oxidation and the ratio of deuterium to hydrogen atoms in headspace volatiles were analyzed.

Materials and Methods

Materials Deuterium free water, D₂O, and linoleic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). SPME fibers (50/30 mm DVB/Carboxen/Polydimethylsiloxane (PDMS) StableFlex), GC vials, aluminum seals, and septa were purchased from Supelco, Inc. (Bellefonte, PA, USA). Other reagent grade chemicals were purchased from Daejung Chemical Co. (Seoul, Korea).

Sample preparation For study of the effects of elevated temperature, linoleic acid (0.1 g) was mixed with D₂O (0.9 g). Mixtures were stored in a drying oven (Hysc, Ltd., Seoul, Korea) at 30°C for 40 h, at 60°C for 11 h, and at 90°C for 3 h. Samples were prepared in triplicate.

For study of oxygen limitation, deuterium free water and D₂O were mixed in ratios of 2:0, 1:1, and 0:2 (w/w) and designated as D0, D1, and D2, respectively. Samples of D0, D1, and D2 contained 0, 50, and 100% D₂O. Linoleic acid (0.1 g) was mixed with 0.9 g of D0, D1, or D2. Mixed samples were placed in 10 mL bottles with and without air-tight seals, and the bottles were placed in a drying oven (Hysc Co., Ltd.) at 60°C for 4 h. Samples were prepared in triplicate. Samples with air-tight seals were used for oxygen limitation studies. Samples with limited and unlimited oxygen were named OL and OU, respectively. Therefore, OL_D0 designated a sample under limited oxygen conditions containing deuterium free water, while OU_D2 designated a sample under unlimited oxygen conditions containing D₂O.

Headspace oxygen analysis The headspace oxygen content in air-tight samples was determined based on injection of 20 mL of sample headspace gas into a gas chromatograph (GC) equipped with a thermal conductivity detector (Agilent Technologies, Palo Alto, CA, USA) and a stainless steel column (1.8 m×0.32 cm) packed with 60/80 Molecular Sieve 13X (Alltech Assoc., Inc. Deerfield, IL, USA) as the stationary phase. The helium gas flow rate was 20 mL/min, and the oven, injector, and thermal conductivity detector temperatures were 40, 120, and 180°C, respectively (11).

SPME fiber analysis of volatiles SPME fiber analysis conditions for volatile compounds were adapted from the method of Kim *et al.* (9). Samples without air-tight seals were removed from the drying oven and were made air-tight using septa and aluminum caps. Sample bottles with

caps were placed in the dark for 30 min at room temperature for equilibration of the volatile compounds in the headspace. Headspace volatiles were isolated and concentrated for 60 min using a 50/30 mm DVB/Carboxen/PDMS StableFlex solid phase at 30°C in a circulating water bath (RW-0525G; Lab Camp, Incheon, Korea).

Volatiles attached to the SPME solid phase were separated and identified using a Hewlett-Packard 6890 GC equipped with a 5971A mass selective detector (MS; Agilent Technology) and a DB-5ms column (30 m×0.25 mm i.d., 0.25 mm film thickness; Agilent, J & W, Folsom, CA, USA). The SPME solid phase was exposed to the injector for 2 min. Helium was the carrier gas at 1.0 mL/min, and the oven temperature was kept at 40°C for 3 min, then increased to 150°C at 4°C/min, and from 150 to 220°C at a rate of 15°C/min. All mass spectra were obtained at 70 eV and a 220°C ion source temperature. Compound identification was based on a combination of reference NIST Mass Spectra and comparisons with gas chromatographic retention times of standard compounds.

Detection of volatiles containing deuterium The presence of deuterium in lipid oxidation products was indirectly analyzed by comparison of the *m/z* value (mass to charge ratio, molecular weight, Mw) of each volatile. A peak of the *m/z* value (mass to charge ratio) representing molecular weight (Mw) representing a Mw value may not be the most abundant peak. If deuterium is incorporated into a molecule, the *m/z* value will increase by 1, compared with a deuterium free molecule. Molecular ions (M) were identified for each volatile among many *m/z* values from mass spectra. Comparison of peak responses for *m/z* values of M+1/M can show the presence of deuterium in a volatile. For example, for hexanal (M: 100.1) and pentane (M: 72.1), *m/z* values of 101.1 (*d*₁-hexanal)/100.1 (hexanal) and 73.1 (*d*₁-pentane)/72.1 (pentane), respectively, were determined from a GC/MS ion chromatogram in SIM mode (9,10).

Statistical analysis Data for changes in the headspace oxygen content and volatile contents were analyzed using the analysis of variance (ANOVA) and Duncan's multiple range test functions of the SPSS software program (SPSS, Inc., Chicago, IL, USA). A value of *p*<0.05 was considered significant.

Results and Discussion

Oxidative stability of linoleic acid-D₂O models after heat treatments The headspace oxygen contents of linoleic acid samples containing D₂O and deuterium free water at 30, 60, and 90°C in the dark are shown in Table

1. For an oxidation time of 31 h at 30°C, the headspace oxygen contents in samples containing D₂O and deuterium free water were 12.48 and 14.28%, respectively. At 60°C after 11 h, the headspace oxygen contents in samples containing D₂O and deuterium free water were 7.84 and 9.04%, respectively, whereas sample values at 90°C after 3 h were 8.63 and 9.45%, respectively. Thus, deuterium oxide significantly ($p < 0.05$) accelerated consumption of headspace oxygen at all tested temperatures, compared to deuterium free water samples.

The results of this study were in good agreement with a previous report of Kim *et al.* (10). Prooxidant properties of deuterium oxide have been studied in photosensitized systems (12). Deuterium oxide can extend the half-life of singlet oxygen, which in H₂O is 3–4 μs and in deuterium oxide is 65 μs (13). Deuterium oxide can change the oxygen solubility or activity of transition metals, which could be prooxidative factors for deuterium oxide in thermally oxidized linoleic acid.

Changes in total volatile contents in linoleic acid samples containing D₂O and deuterium free water at 30, 60, and 90°C in the dark are shown in Table 1. Depending on the incubation temperature, total volatile contents were different. Total volatile contents in linoleic acid samples containing D₂O were higher than in samples containing deuterium free water at 90°C after 3 h, while total volatile contents were lower at 30°C after 40 h. However, total volatile contents were not significantly different ($p > 0.05$), in agreement with a previous report (9).

Involvement of deuterium in headspace volatile contents with heat treatments Ratios of peak abundances of pentane, 2-propenal, hexanal, and *t*-2-heptenal in linoleic acid samples containing deuterium free water and D₂O at 30°C (A), 60°C (B), and 90°C (C) are shown in Fig. 1. Pentane, hexanal, and *t*-2-heptenal are typical volatiles produced during oxidation of linoleic acid, whereas 2-propenal can be produced from linolenic acid (14,15). Hexanal is a representative indicator for determination of the degree of lipid oxidation in bulk oil and oil-in-water emulsions containing linoleic acid rich oils (6,16,17).

Kim *et al.* (9,10) used a mass chromatogram in SIM mode of a volatile peak to determine the involvement of deuterium based on ratio comparisons of m/z (Mw+1) to m/z (Mw). For example, the Mw of pentane is 72.1, and the ratios of m/z (73.1) to m/z (72.1) were compared. An increase in the ratio of m/z (M+1) to m/z (Mw) provided indirect evidence for the presence of a deuterium atom in volatiles.

For pentane, m/z ratios of 73.1/72.1 were significantly ($p < 0.05$) higher in linoleic acid samples containing D₂O than in samples containing deuterium free water at 30, 60, and 90°C (Fig. 1), indicating that involvement of deuterium

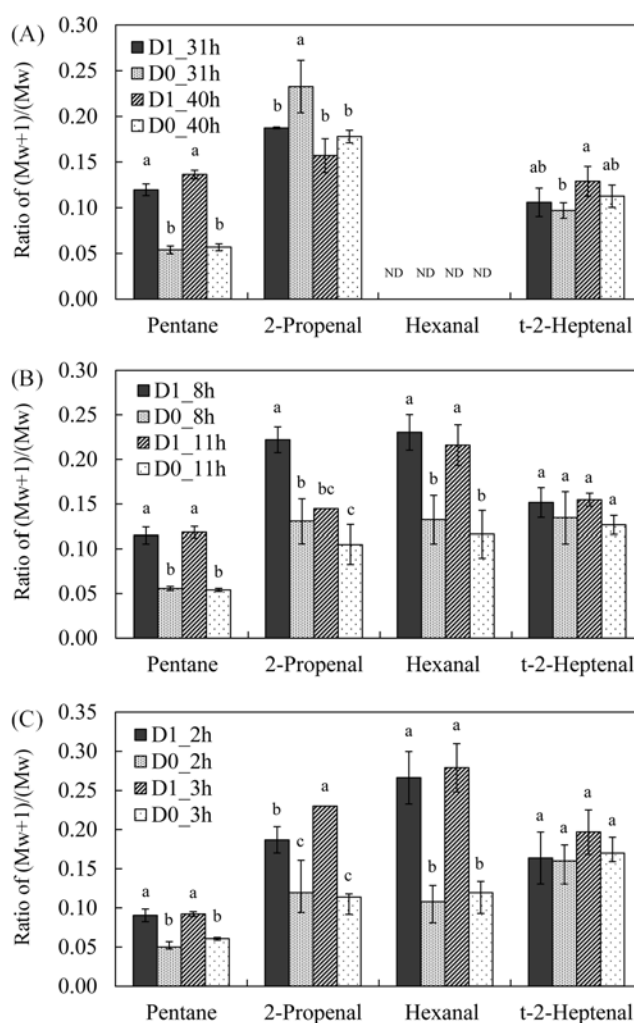


Fig. 1. Ratios of peak abundances of pentane, 2-propenal, hexanal, and *t*-2-heptenal in linoleic acid containing deuterium free water or D₂O at 30°C (A), 60°C (B), and 90°C (C). D0 and D1 are linoleic acid containing deuterium free water and deuterium oxide, respectively. Different letters on bars indicate significant differences at $p < 0.05$ among the same volatile. ND, not detected

in volatile production occurs regardless of temperature. Water can participate as an active substance in lipid oxidation at 30, 60, and 90°C. This trend was observed for 2-propenal, hexanal, and *t*-2-heptenal for linoleic acid samples containing either D₂O or deuterium free water. Previous reports have shown that the m/z (M+1)/(M) ratios of hexanal in samples containing D₂O were not significantly different at 60°C compared to those containing deuterium free water (9,10). However, in this study, hexanal in samples containing D₂O showed significantly ($p < 0.05$) higher m/z (Mw+1)/(Mw) ratios than samples containing deuterium free water (Fig. 1). More study is required on this aspect.

Peak responses for fragment ions from mass spectra of volatiles have been adapted to determine the degree of lipid oxidation (18) and to confirm the hydrogen exchange

Table 1. Headspace oxygen contents and total volatile contents in linoleic acid containing deuterium free water and D₂O at 30, 60, and 90°C

Temp. (°C)	Time (h)	Headspace oxygen content (%)		Total volatile (1×10 ⁷ pA)	
		D ₂ O	Deuterium free water	D ₂ O	Deuterium free water
30	31	12.48±0.38 ^{1) b2)}	14.28±0.47 ^a	17.19±5.00 ^a	13.17±1.41 ^a
	40	8.83±0.11 ^a	8.81±0.22 ^a	22.05±7.21 ^a	29.90±6.89 ^a
60	8	10.07±1.20 ^b	12.36±0.57 ^a	49.67±2.16 ^a	55.18±7.67 ^a
	11	7.85±0.50 ^b	9.07±0.06 ^a	51.18±14.63 ^a	47.46±7.59 ^a
90	2	12.12±0.49 ^a	13.50±0.94 ^a	56.70±10.57 ^a	57.37±9.95 ^a
	3	8.64±0.60 ^b	9.75±0.24 ^a	86.99±4.19 ^a	81.39±2.56 ^a

¹⁾Mean±standard deviation (SD) (*n*=3)

²⁾Different letters indicate significance in a row at *p*<0.05.

Table 2. Effects of oxygen-limitation on changes in selected major headspace volatiles from linoleic acid containing deuterium oxide and deuterium free water at 60°C in the dark after a 4 h treatment

Volatile compound	RT (min)	Identification	Peak areas (1×10 ⁶ pA)						
			0 h	Oxygen limitation (OL) ¹⁾			Oxygen un-limitation (OU)		
				OL_D0	OL_D1	OL_D2	OU_D0	OU_D1	OU_D2
2-Propenal	3.29	MS ²⁾	0.83 ±0.49 ³⁾	13.00 ±10.03 ^{b4)}	20.29 ±14.55 ^{ab}	28.30 ±14.75 ^a	22.70 ±1.84 ^{ab}	13.70 ±1.10 ^b	19.49 ±1.78 ^{ab}
Pentanal	5.21	MS, SC	10.61 ±0.00	11.51 ±10.48 ^a	18.28 ±15.25 ^a	25.17 ±17.48 ^a	14.18 ±1.03 ^a	13.05 ±2.38 ^a	16.28 ±2.94 ^a
Hexanal	7.38	MS, SC	ND	35.32 ±18.04 ^b	43.79 ±31.48 ^b	44.63 ±28.61 ^b	93.96 ±3.14 ^a	85.59 ±14.15 ^a	94.47 ±5.94 ^a
<i>t</i> -2-Heptenal	13.52	MS, SC	36.58 ±11.48	185.77 ±90.16 ^{ab}	222.26 ±126.00 ^{ab}	258.61 ±110.35 ^a	146.59 ±5.24 ^b	132.35 ±17.36 ^b	140.47 ±35.35 ^b
2-Octenal	16.03	MS, SC	4.75 ±1.73	136.28 ±85.87 ^{ab}	128.50 ±63.25 ^{ab}	160.72 ±60.32 ^a	119.14 ±10.11 ^{ab}	115.98 ±6.93 ^{ab}	66.66 ±15.59 ^b
2,4-Octadienal	18.60	MS	0.87 ±0.00	6.40 ±4.20 ^a	7.52 ±4.36 ^a	6.50 ±2.11 ^a	6.64 ±1.41 ^a	5.40 ±0.22 ^a	4.99 ±0.07 ^a
2,4-Decadienal	24.28	MS, SC	ND	7.10 ±4.50 ^{ab}	7.90 ±2.42 ^a	8.73 ±1.48 ^a	4.56 ±0.60 ^b	6.38 ±0.73 ^{ab}	7.51 ±0.59 ^a
Total peak areas (1×10 ⁸ pA)			2.61 ±1.31	7.39 ±3.92 ^{ab}	8.55 ±4.50 ^{ab}	8.64 ±5.78 ^{ab}	7.00 ±0.47 ^a	4.67 ±3.27 ^b	5.33 ±2.88 ^b

¹⁾OL and OU are samples under oxygen limitation and no oxygen limitation conditions, respectively. D0, D1, and D2 are linoleic acid with deuterium free water and deuterium oxide at ratios of 2:0, 1:1, and 0:2 (w/w), respectively.

²⁾MS, a peak was identified using a mass spectrum from an MS library; SC, a peak was identified by comparison of retention times with a standard compound.

³⁾Mean±SD (*n*=3); ND, not detected

⁴⁾Different letters indicate significance in a row at *p*<0.05.

reaction mechanism (19). Fenaille *et al.* (18) used the peak responses of *m/z* 56 from hexanal and *m/z* 58 from *d*₂-hexanal to determine the hexanal content for the degree of lipid oxidation in infant milk powder. In this study, temperatures of 30, 60, and 90°C significantly (*p*<0.05) increased (M+1)/(M) ratios for headspace volatiles, indicating that water is probably involved in formation of volatiles during lipid oxidation regardless of the treatment.

Effects of oxygen limitation on involvement of deuterium in headspace volatile production Samples in bottles with unlimited oxygen were not capped, so analysis of the depleted headspace oxygen content during lipid oxidation was not possible. The headspace oxygen

contents of 4 h treated samples of OL_D0, OL_D1, and OL_D2 were 16.56, 16.28, and 15.92%, respectively. Addition of deuterium oxide increased the consumption of headspace oxygen, in agreement with results from previous reports (9,10) and results of this study (Table 1).

Effects of oxygen limitation on changes in selected major headspace volatiles and total volatiles from linoleic acid containing deuterium oxide and deuterium free water at 60°C in the dark are shown in Table 2. Total volatile contents in OU_D0, OU_D1, and OU_D2 samples were 7.00, 4.67, and 5.33×10⁶ pA, respectively. Total volatile contents in OL_D0, OL_D1, and OL_D2 samples were 7.39, 8.55, and 8.64×10⁶ pA, respectively. *t*-2-Heptenal was the most abundant volatile, followed by 2-octenal and

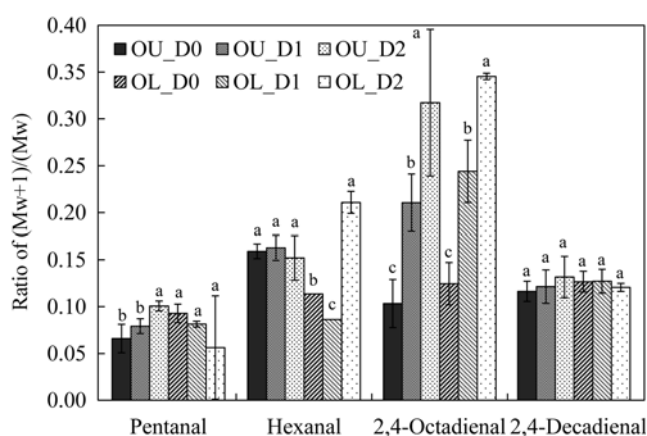


Fig. 2. Effects of oxygen-limitation on ratios of peak abundances of pentanal, hexanal, 2,4-octadienal, and 2,4-decadienal in linoleic acid containing deuterium oxide and deuterium free water at 60°C. OU and OL are samples under oxygen unlimited and oxygen limited conditions, respectively. D0, D1, and D2 are linoleic acid containing of deuterium free water and deuterium oxide at ratios of 2:0, 1:1, and 0:2 (w/w), respectively. Different letters on bars indicate significant differences at $p < 0.05$ for the same volatile.

hexanal in decreasing order. *t*-2-Heptenal was detected most abundantly in 93°C heated mixtures of fatty acids containing linoleic acid, and showed the highest standardized coefficient (-0.999) with changes in the linoleic acid content (20).

Effects of oxygen limitation on ratios of peak abundance values of pentanal, *t*-2-heptenal, 2,4-octadienal, and 2,4-decadienal from linoleic acid containing a mixture of deuterium oxide and deuterium free water at 60°C are shown in Fig. 2. As the concentration of deuterium oxide was increased from D0 to D2, the ratio of $(Mw+1)/(Mw)$ of some volatiles including pentanal and 2,4-octadienal in samples with unlimited oxygen increased significantly ($p < 0.05$), whereas the ratios for hexanal and 2,4-decadienal did not increase significantly ($p > 0.05$). Ratios of $(Mw+1)/(Mw)$ for 2,4-octadienal in OU_D0, OU_D1, and OU_D2 samples were 0.10, 0.21, and 0.31, respectively, whereas ratios in OL_D0, OL_D1, and OL_D2 samples were 0.12, 0.24, and 0.34, respectively. For 2,4-decadienal, a typical β -scission product of the C9 hydroperoxide of linoleic acid, $(Mw+1)/(Mw)$ ratios in samples with limited oxygen and unlimited oxygen were not significantly ($p > 0.05$) different. Pentane, a volatile used for study of different heating temperatures, was not detected in samples under unlimited oxygen conditions. Involvement of water in formation of volatiles differs depending on the degree of lipid oxidation and the type of headspace volatile.

Headspace volatiles contained deuterium and the deuterium atom probably originate from water in samples rather than from collisions of volatiles in the headspace. Air-tight conditions did not influence involvement of water in

formation of volatiles during lipid oxidation.

Deuterium oxide accelerated the rate of lipid oxidation at 30, 60, and 90°C, and headspace volatiles contained deuterium at all tested temperatures. Unlimited oxygen also produced headspace volatiles containing deuterium, confirming that volatiles containing deuterium originated from lipid oxidation and not from other sources. Further studies are needed to elucidate the sources of deuterium atoms in volatile formation during lipid oxidation.

Acknowledgments This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2013R1A2A2A01067293).

Disclosure The authors declare no conflict of interest.

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