

# Oxidative Stability and Volatile Formations in Linoleic Acid-D<sub>2</sub>O Models in the Presence of Deuteron or Electron Donors

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**Abstract** Effects of deuteron (D<sup>+</sup>) and electron donors on the oxidative stability in linoleic acid–water model systems were evaluated by analyzing headspace oxygen content and headspace volatiles. Acetic acid-*d* and tetrakis(dimethylamino)ethylene (TDAE) were selected as a deuteron and an electron donor, respectively. Samples containing acetic acid-*d* had significantly lower headspace oxygen content than controls while those containing TDAE had significantly higher headspace oxygen content ( $p < 0.05$ ). Combination of acetic acid-*d* and TDAE accelerated the consumption of headspace oxygen. Volatiles including *t*-2-heptenal, 2-octenal, or 2,4-octadienal had higher mass to charge ratio ( $m/z$ ) of (molecular weight +1)/molecular weight in samples with deuterium oxide than in samples with deuterium free water. However, no significant difference was observed in the  $m/z$  ratio of (molecular weight +1)/molecular weight of those volatiles among samples with or without deuteron or electron donors. Also, lipid hydroperoxides with deuterium, were not found in samples containing deuterium oxide and acetic acid-*d*. Therefore, added acetic acid-*d* may not be involved on the formation of lipid hydroperoxides and volatiles directly.

**Keywords** Deuteron donor · Electron donor · Deuterium oxide · Lipid oxidation · Volatile formation

## Introduction

Lipid oxidation is a chemical reaction among unsaturated lipid and oxygen molecules. Besides unsaturated fatty acids and oxygen molecules, other compounds including prooxidative metal ions, antioxidative compounds, moisture content, and amphiphilic minor compounds including free fatty acid (FFA), monoacylglycerols (MAG), diacylglycerols (DAG), and phospholipid (PL) may play important roles in the rates of lipid oxidation [1–4]. Moisture can form association colloids with minor amphiphilic compounds and the interfaces of oil–water in association colloids has been proposed as key places for lipid oxidation [1, 4, 5]. During the lipid oxidation process, the moisture content in the lipids can change and the moisture can be transferred from the atmosphere to the oil [6, 7]. The antioxidant properties of chemical compounds are affected by the presence of moisture in the lipid. Kim *et al.* [8, 9] reported that antioxidant activities of  $\alpha$ -tocopherol and ascorbic acid were greatly affected by the content of moisture in bulk oils. Also, aglycone quercetin and glycoside rutin showed various oxidative stability in vegetable oils depending on the moisture content and stripping process of the bulk oils [10].

Recently, the possibility of moisture as a substrate during the lipid oxidation has been reported by using analytical techniques for headspace volatiles in linoleic acid-deuterium oxide (D<sub>2</sub>O) model system [11, 12]. Headspace volatiles like pentane had more deuterium (D<sup>-</sup>) in linoleic acid with D<sub>2</sub>O than those in deuterium free water (H<sub>2</sub>O), which implies that moisture can participate in the formation of volatiles during lipid oxidation [11]. This phenomenon can be observed in linoleic acid–water model systems without air-tightness or different treatment temperature condition [12].

From previous studies, volatile compounds had higher ratios of D<sup>-</sup> when tested in lipid-D<sub>2</sub>O model compared to

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those of  $D\cdot$  in lipid- $H_2O$  model from lipid oxidation. To produce  $D\cdot$  from  $D_2O$ , high energy should be applied to dissociate covalent bonding between deuterium and oxygen. However, previous studies used 30–90 °C, which may not provide enough energy to dissociate  $D_2O$  into  $D\cdot$ . Because  $D_2O$  can generate deuteron ( $D^+$ ) due to the pD like ordinary water,  $D^+$  is likely to participate in the formation of volatiles from linoleic acid oxidation instead of  $D\cdot$ . To evaluate this hypothesis, acetic acid-*d* and tetrakis(dimethylamino)ethylene (TDAE) were selected as a deuteron donor or electron donor, respectively. Acetic acid-*d* is an organic compound with the chemical formula  $CH_3COOD$  and deuteron ( $D^+$ ) can be separated from the carboxyl group ( $-COOD$ ) of acetic acid-*d*. TDAE is known as a very electron-rich and strong organic electron donor with an ionizing potential close to zinc (6.12 eV) [13]. Addition of deuteron or electron donors may influence the formation of certain oxidation products, which can be indirect evidence for the involvement of deuteron or electron donors on the steps of lipid oxidation.

The objectives of this study were to determine the effects of deuteron or electron donors on the oxidative stability in linoleic acid- $D_2O$  or -deuterium free water systems and to compare the increase in  $D\cdot$  in headspace volatiles from oxidized model systems in the presence of acetic acid-*d*. Also, the presence of deuterium in lipid hydroperoxides (LOOD) was tested.

## Materials and Methods

### Materials

Deuterium free water ( $H_2O$ ),  $D_2O$ , linoleic acid, acetic acid-*d*, and TDAE were purchased from Sigma-Aldrich (St. Louis, MO). Fiber of solid phase microextraction (SPME) [50/30 mm DVB/Carboxen/Polydimethylsiloxane (PDMS) StableFlex] was purchased from Supelco, Inc. (Bellefonte, PA). Vials, magnetic seals, and septa were purchased from Agilent technologies, Inc. (Santa Clara, CA). Other reagent grade chemicals were purchased from Daejung Chemical Co. (Seoul, Korea).

### Sample Preparation

Acetic acid-*d* or TDAE were dissolved in  $D_2O$  or  $H_2O$  at the concentration of 416 or 1 mM, respectively. Preliminary study was conducted to find the concentration of acetic acid-*d* or TDAE to make detectable changes in the oxidative stability. The 0.2 g of linoleic acid was mixed with 0.6 g water containing acetic acid-*d* or TDAE in a 10-mL bottle. The sample bottles were sealed air-tight with rubber septa and aluminum caps and stored at 60 °C in a drying oven (HYSC, Seoul, Korea) for 6 h. Samples

without adding acetic acid-*d* nor TDAE were prepared as controls. Controls in  $H_2O$  or  $D_2O$  were named as D0 or D1, respectively. Samples were prepared in triplicate and analyzed at 2, 4, and 6 h.

For the combination effects of mixtures of a deuteron donor and an electron donor, 0.6 g water containing both 416 mM acetic acid-*d* and 1 mM TDAE was mixed with 0.2 g of linoleic acid in 10-mL bottles, which were sealed air-tight with rubber septa and aluminum caps. Sample bottles were treated at 60 °C in the drying oven (HYSC, Seoul, Korea) for 7 h. Samples were prepared in triplicate. Samples containing TDAE, acetic acid-*d*, and a combination of acetic acid-*d* and TDAE were designated as TD, AD, and ADTD, respectively. Samples in  $H_2O$  or  $D_2O$  were differentiated adding 0 or 1 after their names like TD0 or TD1, respectively in the case of samples with TDAE.

### Headspace Oxygen Analysis

A Hewlett-Packard 7890 gas chromatograph (GC) (Agilent Technologies, Inc., Santa Clara, CA) equipped with a 60/80 packed column (3.0 m  $\times$  2 mm ID, Restek Ltd.) and a thermal conductivity detector (TCD) from Agilent Technologies (Palo Alto, CA) was used to determine headspace oxygen content in air-tight sample bottles according to methods of Kim *et al.* [14]. The 30  $\mu$ L headspace gas was transferred from a sample bottle using an air-tight syringe to a GC-TCD. The flow rate of helium gas was 200 mL/min. Temperatures of the oven, the injector, and the detector in GC were 60, 180, and 180 °C, respectively.

### Identification of Lipid Hydroperoxides

Lipid hydroperoxides in samples of D1, D0, ADD1, and ADD0 were analyzed using a 5600 Q-TOF LC/MS/MS system (AB Sciex, Foster City, CA) using a Ultimate 3000 RSLC HPLC system (Dionex), including a degasser, an autosampler, diode array detector, and a binary pump. Stationary phase was a Hypersil GOLD column (2.1  $\times$  50 mm, 1.9  $\mu$ m, Thermo scientific) with a mobile phase A (0.1% formic acid in water) and a mobile phase B (0.1% formic acid in acetonitrile). The flow rate was 0.25 mL/min. The linear gradient was as follows. The injection volume was 5  $\mu$ L. Mass spectra were acquired under negative or positive electrospray ionization (ESI) with an ion spray voltage of  $\pm$ 4500 V. The source temperature was 500 °C. The curtain gas, ion source gas 1, and ion source gas 2 were 35, 65, and 55 psi, respectively. Scan was conducted from 50 to 1500 (mass/charge). Mass spectra of peaks for hydroperoxides were analyzed to detect LOOD from LOOH by comparing the  $m/z$  (mass to charge ratio).

## Analysis of Headspace Volatiles by Solid Phase Microextraction (SPME)

Analysis conditions of SPME for volatile compounds were adapted from the methods of Kim *et al.* [9]. For equilibration of the volatile compounds in the headspace, sample vials were placed in a water bath (RW-0525G; Lab Camp, Incheon, Korea) at 30 °C for 30 min, and then moved into an agitator of multipurpose sampler. Headspace volatiles were isolated and extracted for 30 min using a 50/30 mm DVB/Carboxen/PDMS StableFlex solid phase at 30 °C.

Volatiles attached in the solid phase of SPME were separated and identified using a Hewlett-Packard 6890 GC apparatus equipped with a 5971A mass selective detector (MS) (Agilent Technology) and a DB-5 ms column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent J & W, Folsom, CA). Solid phase of SPME was exposed in an injector for 3 min. Helium was carrier gas at 1.0 mL/min and the oven temperature was held at 40 °C for 3 min and increased from 40 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 220 °C ion source temperature with electron impact ionization mode. The temperature of the quadrupole was 150 °C. The identification of compounds was made by a combination of NIST Mass Spectra version and gas chromatographic retention times of standard compounds.

## Detection of Volatiles Containing Deuterium

The presence of D· in volatiles was analyzed by comparing  $m/z$  (mass to charge ratio) of each volatile [11, 12]. A peak representing molecular weight may not be the most abundant peak. If a D· is incorporated in a molecule,  $m/z$  will increase by 1 compared to those in a deuterium free molecule. Comparison of  $m/z$  (molecular weight +1)/molecular weight can show the presence of D· in each volatile. For example, in case of *t*-2-heptenal (molecular weight of 112.17) and 2-octenal (molecular weight of 126.20), the  $m/z$  of 113.17 from  $d_1$ -*t*-2-heptenal/112.17 from *t*-2-heptenal, and 127.20 from  $d_1$ -2-octenal/126.20 from 2-octenal, respectively were determined at each sampling time from the GC/MS ion chromatogram. The retention time of *t*-2-heptenal, 2-octenal, 2,4-octadienal, and 2,4-decadienal were 13.52, 16.03, 18.60, and 23.24 min, respectively.

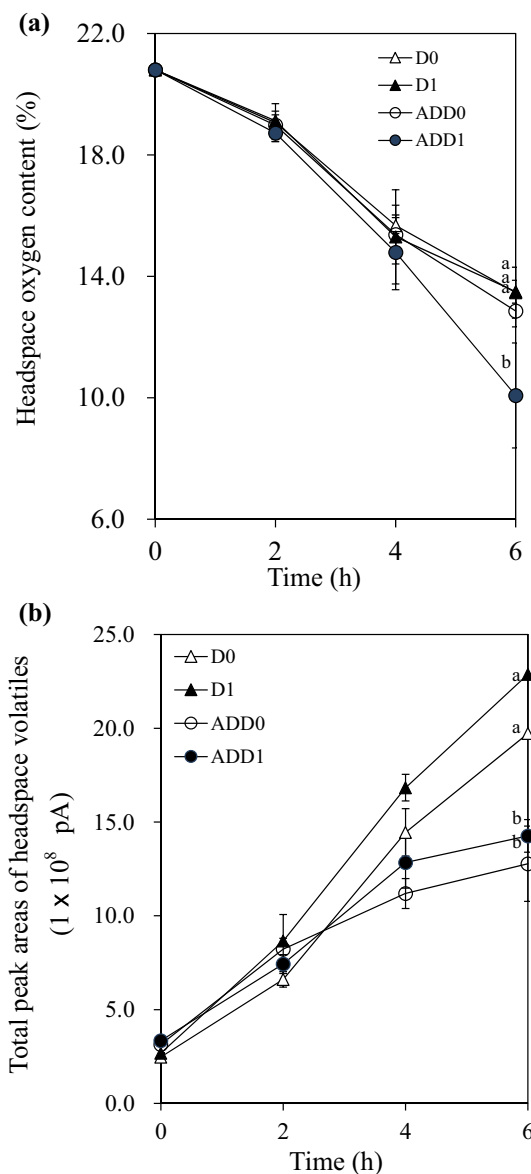
## Statistical Analysis

Data of the headspace oxygen content, total volatile contents, and the  $m/z$  of (molecular weight +1)/molecular weight of headspace volatiles were analyzed statistically by ANOVA and Duncan's multiple range test using SPSS software program version 19 (SPSS Inc., Chicago, IL). A  $p$  value <0.05 was considered significant.

## Results and Discussion

### Effects of Deuteron Donor Acetic Acid-*d*

Changes of headspace oxygen content (a) and total peak areas of headspace volatiles (b) in a linoleic acid-deuterium free water model system containing acetic acid-*d* at 60 °C for 6 h are shown in Fig. 1. Preliminary study on



**Fig. 1** Changes of headspace oxygen content (a) and total peak areas of headspace volatiles (b) in linoleic acid-deuterium free water model system containing acetic acid-*d* at 60 °C for 6 h. Samples containing acetic acid-*d* in deuterium oxide or deuterium oxide free water were designated as ADD1 and ADD0, respectively while samples in deuterium oxide or deuterium oxide free water were designated as D1 and D0, respectively. Different lower case letters indicate significant differences at 0.05

the determination of acetic acid concentration showed that 416.32 mM acetic acid was needed to show its' effects on the oxidative stability in the adapted model systems (data not shown). As oxidation time increased, headspace oxygen content in all the samples decreased gradually. After 6 h of treatment, ADD1 showed significantly low headspace oxygen content compared to other samples, which implies that acetic acid-*d*, a deuterium donor, acted as a prooxidant (Fig. 1a). Oxidative stability of edible oils is greatly influenced by the pH of the solution [15]. Oils with a non-buffered solution of pH 4 had low oxidative stability whereas oils with a buffered solution of pH 4 did not show any differences in their oxidative stability compared to oils with a pH of 7 [15]. Because non-buffered solution of acetic acid was added to the oil system, results of the current study agree with the previous report [15].

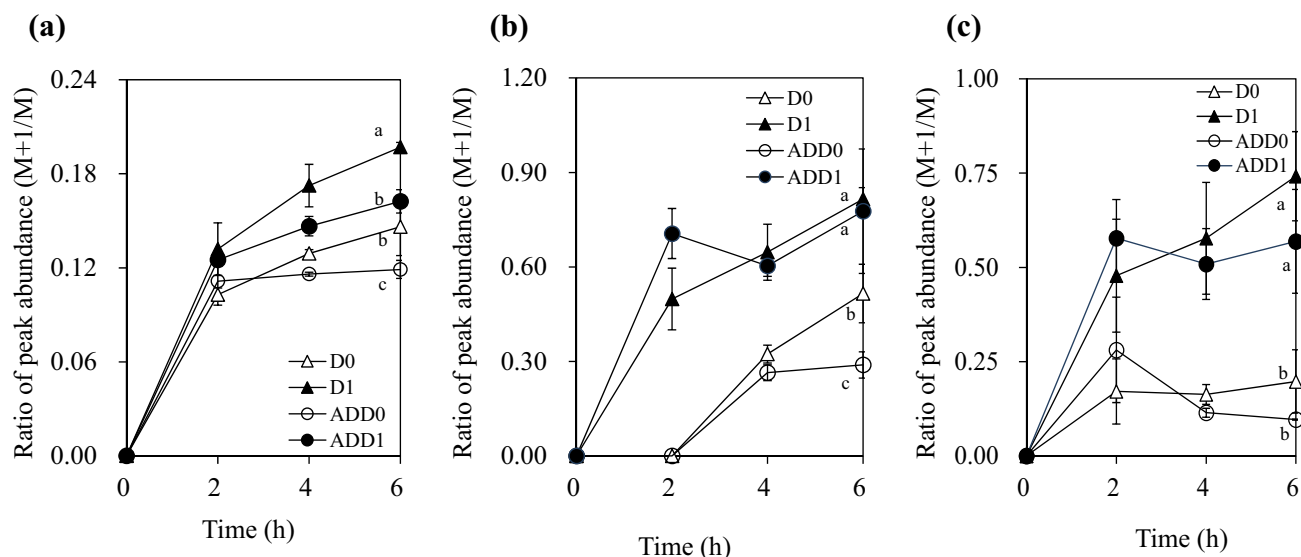
The total peak area of headspace volatile compounds was calculated excluding the peak area of acetic acid due to the high strength of acetic acid. Peak areas from D0 to D1 were significantly higher than ADD0 and ADD1 ( $p < 0.05$ ) (Fig. 1b). Samples with deuterium oxide (D1 or ADD1) generated more total peak areas of volatiles than corresponding samples (D0 and ADD0), although no significant difference was observed ( $p > 0.05$ ). Although addition of acetic acid-*d* accelerated the consumption of oxygen molecules based on Fig. 1a, some volatiles may be co-eluted with the large peak of acetic acid-*d* and results of total peak areas might not show prooxidative properties of acetic acid-*d*. Usually, presence of D<sub>2</sub>O significantly accelerated the consumption of headspace oxygen and generate more volatiles in samples compared to deuterium free H<sub>2</sub>O [11, 12]. However,

prooxidative properties of D<sub>2</sub>O were not observed in current experimental conditions.

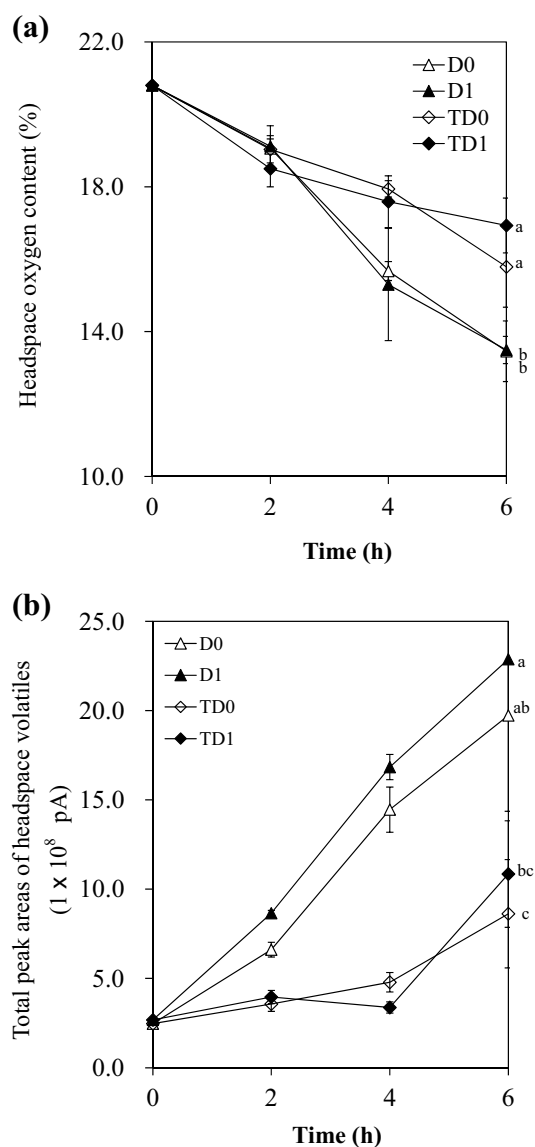
The mass to charge ratio ( $m/z$ ) of (molecular weight +1)/molecular weight of *t*-2-heptenal (a), 2-octenal (b), and 2,4-octadienal (c) in linoleic acid-deuterium free water model system containing acetic acid-*d* at 60 °C for 6 h are shown in Fig. 2. *t*-2-Heptenal, 2-octenal, and 2,4-octadienal were reported as oxidation products of linoleic acid or trilinolein [16, 17]. For 2-octenal, the  $m/z$  ratios of 127.20/126.20 were significantly higher in linoleic acid samples containing D<sub>2</sub>O than in samples containing deuterium free water regardless of the addition of acetic acid-*d* ( $p < 0.05$ ). This trend was observed for *t*-2-heptenal, and 2, 4-octadienal for linoleic acid samples containing either D<sub>2</sub>O or deuterium free water (Fig. 2). However, addition of acetic acid-*d* (ADD0) did not cause any significant changes in the  $m/z$  of (molecular weight +1)/molecular weight of *t*-2-heptenal, 2-octenal, and 2,4-octadienal in samples with deuterium free water (D0) (Fig. 2), which implies deuterium (D<sup>+</sup>) dissociated from acetic acid-*d* may not be major factors for the formation of volatiles during linoleic acid oxidation. The  $m/z$  of (molecular weight +1)/molecular weight of 2-octenal and 2,4-octadienal in ADD1 were not significantly different from those in D1 although *t*-2-heptenal had different result.

### Effects of Electron Donor TDAE

Changes of headspace oxygen content (a) and total peak areas of headspace volatiles (b) in linoleic acid-deuterium free water model system containing TDAE at 60 °C for 6 h are shown in Fig. 3. As oxidation time increased to 6 h, samples containing TDAE had significantly high



**Fig. 2** Ratios of peak abundance of *t*-2-heptenal (a), 2-octenal (b), and 2,4-octadienal (c) in linoleic acid-deuterium free water model system containing acetic acid-*d* at 60 °C for 6 h. Abbreviations were listed in Fig. 1. Different lower case letters indicate significant differences at 0.05



**Fig. 3** Changes of headspace oxygen content (a) and total peak areas of headspace volatiles (b) in linoleic acid-deuterium free water model system containing TDAE at 60 °C for 6 h. Samples containing TDAE in deuterium oxide or deuterium oxide free water were designated as TD1 and TD0, respectively. Samples in deuterium oxide or deuterium oxide free water were designated as D1 and D0, respectively. Different lower case letters indicate significant differences at 0.05

headspace oxygen content compared to other control samples ( $p < 0.05$ ), which implies that TDAE acted as an antioxidant (Fig. 3a). There was no significant difference in headspace oxygen content between TD0 and TD1 or D0 and D1, which implies that deuterium oxide did not give detectable changes in the headspace oxygen consumption under current experiment conditions ( $p > 0.05$ ).

Total peak areas from D0 to D1 were significantly higher than TD0 and TD1 since 2 h treatment ( $p < 0.05$ ). D1 and TD1 had more total peak areas of volatiles than D0 and TD0,

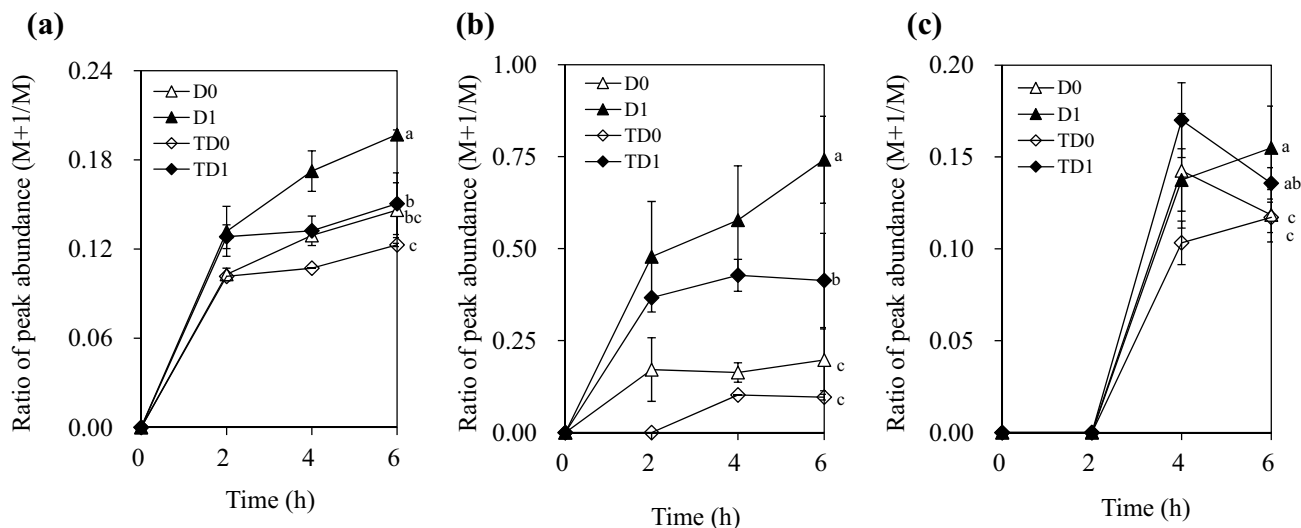
respectively, although there was no significant difference in the peak areas between D1 and D0 and between TD1 and TD0 at 6 h ( $p > 0.05$ ) (Fig. 3b).

The mass to charge ratio ( $m/z$ ) of (molecular weight +1)/molecular weight of *t*-2-heptenal (a), 2,4-octadienal (b), and 2,4-decadienal (c) in linoleic acid-deuterium free water model system containing TDAE at 60 °C for 6 h are shown in Fig. 4. 2,4-Decadienal is one of representative oxidation volatiles from linoleic acid or trilinolein [16, 17]. The  $m/z$  of (molecular weight +1)/molecular weight of 2,4-octadienal was significantly higher in linoleic acid samples containing  $D_2O$  than in samples containing deuterium free water regardless of the addition of TDAE ( $p < 0.05$ ). This trend was observed for *t*-2-heptenal, and 2, 4- decadienal for linoleic acid samples (Fig. 4), which agrees with the results of Fig. 2. TD1 with added TDAE did not increase the  $m/z$  of (molecular weight +1)/molecular weight of selected volatiles compared to D1 (Fig. 4), which implies electrons may not enhance the incorporation of deuterium in volatiles. On the contrary, the  $m/z$  of (molecular weight +1)/molecular weight of *t*-2-heptenal and 2-octenal in TD1 were significantly lower than those in D1 ( $p < 0.05$ ). Electrons may interfere the incorporation of deuterium during the volatile generation.

### Combination Effects of Deuteron Donor Acetic Acid-*d* and Electron Donor TDAE

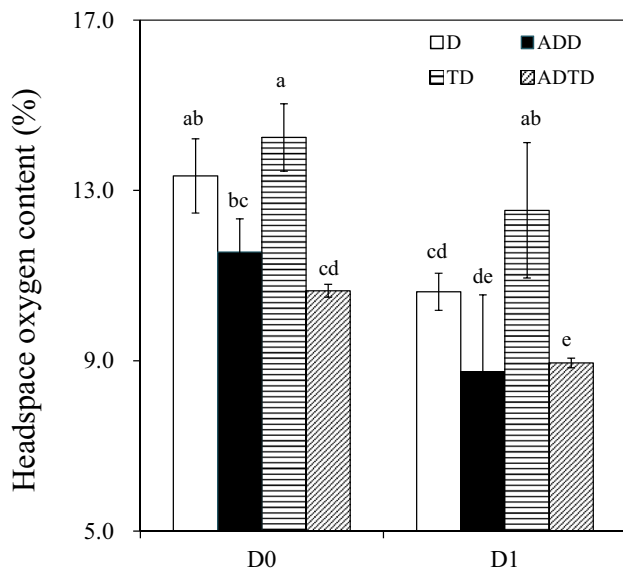
Changes of headspace oxygen content in linoleic acid-deuterium free water model system containing TDAE and acetic acid-*d* at 60 °C after 7 h of treatment are shown in Fig. 5. Generally, headspace oxygen content in deuterium oxide was lower than those in deuterium free water. Addition of acetic acid-*d* induced the consumption of headspace oxygen (ADD) and samples containing TDAE had higher headspace oxygen content than control samples (Fig. 5), which agrees with the results of deuteron or electron donor addition (Figs. 1, 3). In the case of combination of acetic acid-*d* and electron donor (ADTD), headspace oxygen content was significantly lower than controls or samples with TDAE ( $p < 0.05$ ). However, no significant difference was observed between ADTD and ADD samples ( $p > 0.05$ ), which implies prooxidative properties of acetic acid-*d* may overwhelm the antioxidant properties of TDAE. The presence of electron donor did not affect the consumption of headspace oxygen when acetic acid was present. If TDAE had stronger factor than acetic acid, combination of TDAE and acetic acid should have antioxidant properties.

The  $m/z$  of (molecular weight +1)/molecular weight of selected volatiles in linoleic acid-deuterium free water model system containing TDAE and acetic acid-*d* at 60 °C after 7 h treatment are shown in Fig. 6. Generally, samples with deuterium oxide produced more  $m/z$  of (molecular weight +1)/



**Fig. 4** Ratios of peak abundance of *t*-2-heptenal (a), 2,4-octadienal (b), and 2,4-decadienal (c) in linoleic acid-deuterium free water model system containing TDAE at 60 °C for 6 h. Abbreviations were listed in Fig. 3. Different lower case letters indicate significantly differences at 0.05

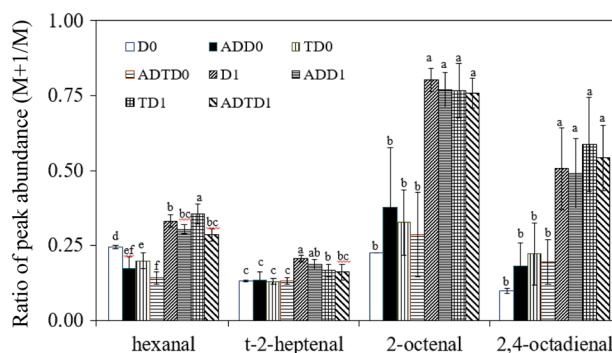
molecular weight of volatiles than samples with deuterium free water. The  $m/z$  of (molecular weight +1)/molecular weight of 2-octenal and 2,4-octadienal in D1, ADD1, TD1, and ADTD1 were significantly higher than those in D0, ADD0, TD0, and ADTD0, respectively ( $p < 0.05$ ) although there were no significant difference among them ( $p > 0.05$ ).



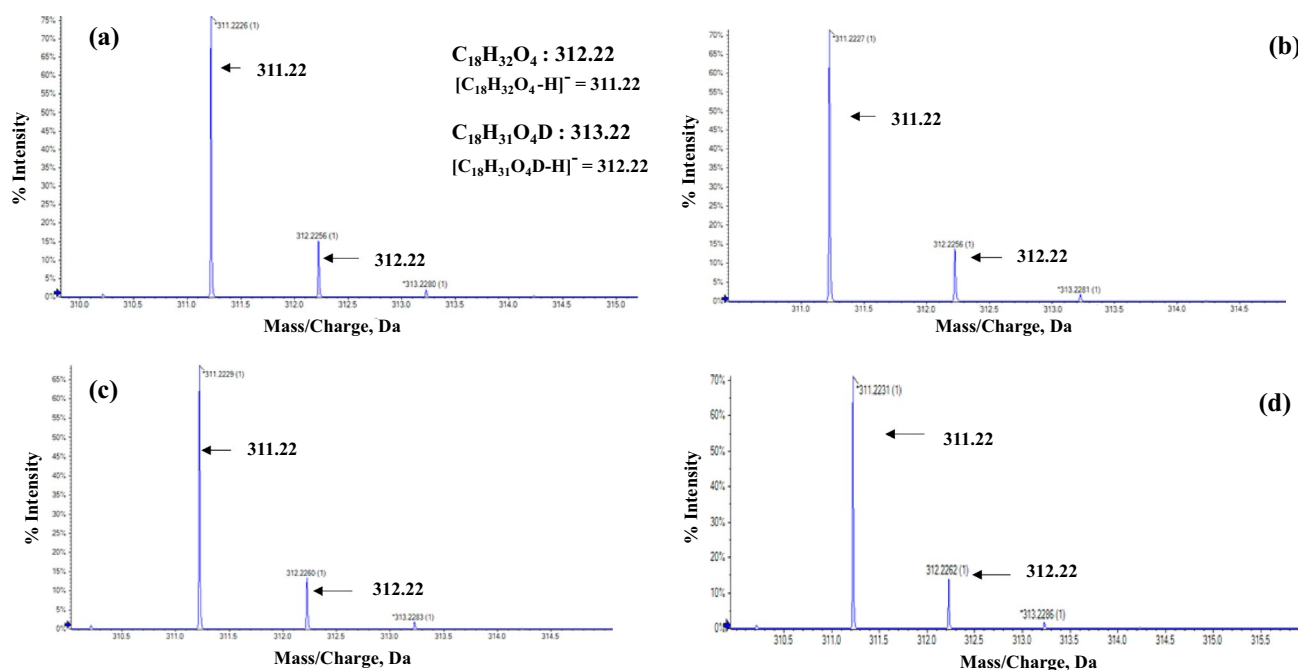
**Fig. 5** Changes of headspace oxygen content in linoleic acid-deuterium free water model system containing TDAE and acetic acid-*d* at 60 °C after 7 h treatment. ADTD, TD, and ADD were samples containing combination of TDAE and acetic acid-*d*, TDAE, and acetic acid-*d* in deuterium oxide, respectively. Samples in deuterium oxide or deuterium oxide free water were designated as D1 and D0, respectively. 'D' indicate samples without addition of TDAE nor acetic acid-*d*. Different lower case letters indicate significantly differences at 0.05

#### Detection of LOOD by LC/MS/MS

Mass spectra of lipid hydroperoxides from linoleic acid-deuterium oxide model (D1) (a), linoleic acid-deuterium free water model (D0) (b), linoleic acid-deuterium oxide model with acetic acid-*d* (ADD1) (c), and linoleic acid-deuterium free water model containing acetic acid-*d*



**Fig. 6** Ratios of peak abundance of selected volatiles in linoleic acid-deuterium free water model system containing TDAE and acetic acid-*d* at 60 °C after 7 h treatment. Samples containing acetic acid-*d* in deuterium oxide or deuterium oxide free water were designated as ADD1 and ADD0, respectively while samples in deuterium oxide or deuterium oxide free water were designated as D1 and D0, respectively. Samples containing TDAE in deuterium oxide or deuterium oxide free water were designated as TD1 and TD0, respectively. ADTD1 and ADTD0 are samples containing combination of TDAE and acetic acid in deuterium oxide or deuterium oxide free water, respectively. Different lower case letters indicate significantly differences at 0.05



**Fig. 7** LC/MS/MS chromatograms of lipid hydroperoxides from linoleic acid-deuterium oxide model or D1 (a), linoleic acid-deuterium free water model or D0 (b), linoleic acid-deuterium oxide model with

acetic acid-*d* or ADD1 (c), and linoleic acid-deuterium free water model containing acetic acid-*d* or ADD0 (d) at 60 °C after 6 h storage

(ADD0) (d) at 60 °C after 7 h of storage are shown in Fig. 7. Four peaks of lipid hydroperoxides were eluted in LC/MS/MS chromatogram (data not shown) and mass spectra were the average of all the peaks of lipid hydroperoxides. Molecular weight of hydroperoxides from linoleic acid is 312.22 and that of lipid hydroperoxides containing deuterium should be 313.22. Because negative mode was used for collecting ions, mass to charge of hydroperoxides from linoleic acid without and with deuterium should be 311.22 and 312.22, respectively (Fig. 7). All the mass spectra from D1, D0, ADD1 and ADD0 showed peaks of 311.22 and 312.22 clearly, which came from lipid hydroperoxides (Fig. 7). Peak intensity of 312.22 mass to charge in D1 was similar to that in D0 (Fig. 7a, b) and that in ADD1 and ADD0 were also similar each other (Fig. 7c, d). Therefore, the addition of acetic acid-*d* (ADD1) or deuterium oxide (D1) did not detectably increase the concentration of deuterium containing lipid hydroperoxides.

Lipid hydroperoxides from unsaturated double bonds can be formed using oxygen molecules and unsaturated double bonds. Also, addition of hydrogen donating antioxidants including  $\alpha$ -tocopherol or quercetin could decrease the formation of lipid hydroperoxides [18]. If deuterium from acetic acid-*d* participates the formation of a lipid hydroperoxides peak of LOOH should increase. It seems that there is no step of inserting protons or deuterium from

moisture into the formation of lipid hydroperoxide. Therefore, volatiles possessing deuterium may be generated during decomposition of lipid hydroperoxides.

Antioxidant properties of electron-donating compounds or reducing compounds have been documented in the literature. Hydrogen atom transfer (HAT) mechanisms or an electron transfer (ET) mechanism are typical theories to explain antioxidant properties of phenolic compounds. Bond dissociation enthalpy (BDE) and ionization potential (IP) could be good indicators for HAT or ET mechanisms of phenolic compounds, respectively [19–21]. Chemical compounds like curcumin with high IP should donate electrons to lipid radicals like peroxy radicals ( $LOO\cdot$ ) and then lipid radicals will be anionic non-radicals ( $LOO^-$ ), which will receive protons ( $H^+$ ) and become lipid hydroperoxides (LOOH) [19, 22]. Since TDAE is a potent electron donating compound, the lipid radicals would be non-radical forms of lipids without sacrificing unsaturated fatty acids, which can explain the strong antioxidant properties of TDAE. Therefore, TDAE may be involved in the steps of formation of LOOH by protecting LH as a primary antioxidant. The added deuterium ( $D^+$ ) did not affect LOOH formation as shown in Fig. 7. Samples of ADD1 produced a lower content of deuterated volatiles compared to those of D1, which implies deuterium ( $D^+$ ) from acetic acid-*d* may not participate efficiently for the formation of volatiles. Deuterium from  $D_2O$  may be involved

in the  $\beta$ -scission steps of lipid hydroperoxides and may participate in the formation of volatiles, which needs further reseraches to confirm this specualtion.

## Conclusion

Effects of deuterion and electron donors on the oxidative stability were evaluated in linoleic acid–water system. Acetic acid-*d*, a deuterion ( $D^+$ ) donor, accelerated the lipid oxidation rate while TDAE delayed the oxidation process. Oxidative stability in samples containing both acetic acid-*d* and TDAE in deuterium oxide was lower than that in deuterium free water. Under current experimental conditions, the addition of deuterion ( $D^+$ ) from acetic acid-*d* may not be involved in the formation of volatiles from linoleic acid oxidation. Lipid hydroperoxides containing deuterium (LOOD) were not detected in sample with deuterion ( $D^+$ ), which suggests that moisture could be involved in the lipid oxidation during the decomposition stage of lipid hydroperoxides rather than formation of lipid hydroperoxides. Providing a strong electron donor can be a practical strategy for controlling the rates of lipid oxidation.

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