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Effects of photosensitisation and autoxidation on the changes of volatile compounds and headspace oxygen in elaidic *trans* fatty acid and oleic *cis* fatty acid

JaeMin Lee [a], Pahn-Shick Chang [b], JaeHwan Lee [a,*]

[a] Department of Food Science and Technology, Seoul National University of Technology, Seoul, Republic of Korea
[b] Department of Agricultural Biotechnology, Seoul National University, Seoul, Republic of Korea

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ABSTRACT

Headspace volatiles and oxygen in elaidic or oleic acids under methylene blue photosensitisation at 60 °C for 60 h were analysed by solid-phase microextraction (SPME)–gas chromatography (GC) with a mass selective detector (MS) and GC with a thermal conductivity detector (TCD), respectively. Headspace oxygen was significantly depleted in photosensitised samples compared to those in the dark ($p < 0.05$). Oleic acid absorbed more oxygen than elaidic acid for 60 h photosensitisation at 60 °C. Total volatiles from elaidic or oleic acids under photosensitisation increased significantly than those from samples in the dark for 60 h, respectively ($p < 0.05$). The increasing rates of oxidised volatiles in elaidic acid under photosensitisation were higher than those in oleic acid for 60 h. Peak areas of *t*-2-undecenal, 1-octanol and 1-heptanol were greatly increased in both elaidic and oleic acids under photosensitisation. Photosensitisation accelerated formation of volatiles in elaidic acid more than in oleic acid while oleic acid absorbed more oxygen than elaidic acid at 60 °C for 60 h.

1. Introduction

Recently, much attention has been focused on the *trans* fatty acids (*t*FAs) in processed foods prepared with partially hydrogenated vegetable oils. Clinical studies have shown that diet with high levels of *t*FAs is closely associated with the increases in the level of low density lipoprotein-cholesterol and total cholesterol, which are primary risk factors for the development of atherosclerosis and coronary heart disease, and decreases in the level of high density lipoprotein-cholesterol (Lemaitre, King, Mozaffarian, Sootodehnia, & Siscovick, 2006; Mitmesser & Carr, 2005). Also, high intakes of *t*FAs in diet are related with causing abnormal lipid metabolism, increases in tumour necrosis factor and activation of caspase 3 in HepG2 cells (Edward & Hunter, 2005; Horani, Haas, & Mooradian, 2006; Kondoh, Kawada, & Urade, 2007). Increasing health concerns on *t*FAs in diet have drawn regulations of labelling on the contents of *t*FAs in packaged foods in many countries including America, Denmark and Korea (Edward & Hunter, 2005).

One of the major naturally occurring *t*FAs found in dairy foods containing ruminant fats is vaccenic acid (18:1, *t*-11), while elaidic acid (18:1, *t*-9) is the most common *trans* isomer fatty acid in processed foods prepared with partially hydrogenated vegetable oil (Pfeuffer & Schrezenmeir, 2006). *trans* Double bond is thermodynamically more stable than *cis* double bond, and melting point of *trans* fatty acids is higher than the corresponding *cis* fatty acids (Sargis & Subbaiah, 2003; Zaima et al., 2005). Melting point of stearic (18:0) acid is 69.6 °C and introduction of *cis* and *trans* double bond at 9 position decreases the melting point to 15 and 46.6 °C, respectively. The oxidative stability of elaidic acid is better than the corresponding oleic acid in model systems (Kim, Won, & Song, 2002; Lemaitre et al., 2006; Sargis & Subbaiah, 2003).

Unsaturated fatty acids can be oxidised easily by diverse oxidation mechanisms. Light exposure and presence of photosensitisers such as riboflavin and chlorophyll can accelerate lipid oxidation through type I pathway of excited photosensitisers and singlet oxygen oxidation or type II pathway (Boff & Min, 2002; Foote, 1976). Effects of riboflavin photosensitisation on the formation of volatile compounds from fatty acid model systems have been reported (Yang, Lee, Lee, & Lee, 2007). Also, chlorophyll photosensitisation on lard model system has shown that photosensitisation caused more volatile formation than samples stored in the dark (Lee & Min, 2009). However, effects of photosensitised oxidation on the formations of volatiles from *t*FAs have not been reported in the literature.

Changes of volatile profiles can be used as indicators for determining the degree of oxidation in fats and oils. Analysis of the headspace volatiles using solid-phase microextraction (SPME) from unsaturated fatty acid model systems and edible vegetable

* Corresponding author. Address: Department of Food Science and Technology, Seoul National University of Technology, 172 Gongneung-2 dong, Nowon-gu, Seoul 139-743, Korea. Tel.: +82 2 970 6739; fax: +82 2 976 6460.
E-mail address: jhlee@snut.ac.kr (J. Lee).

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oils including soybean, linseed, sunflower and corn oils has been reported recently (Jelen, Obuchowska, Zawirska-Wojtasiak, & Wasowicz, 2000; Lee, Kim, Chang, & Lee, 2007). Lee et al. (2007) analysed volatile profiles from thermally oxidised mixtures of 60% linoleic acids using a SPME method and proposed that *t*-2-heptenal could be a reliable volatile marker to determine the degree of oxidation and antioxidant ability of free radical scavengers.

Although oxidative stability of *t*FAs under thermal oxidation is reported to be better than the corresponding *cis* fatty acids, effects of photosensitisation on *t*FAs are not fully understood yet.

The objectives of this study were to determine the effects of light irradiation and methylene blue photosensitiser on the formation of volatile compounds from *trans* and *cis* octadecenoic acid model systems and to compare the oxidative stability of *trans* and *cis* octadecenoic acids. Elaidic and oleic acids were chosen as representative *trans* and *cis* fatty acids, respectively.

2. Materials and methods

2.1. Materials

Elaidic acid (minimum 99%), oleic acid (minimum 99%), heptanal, octanal, nonanal, *t*-2-decenal and other chemical compounds were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Teflon-coated rubber septa, SPME-solid phase fibre (50/30 μm divinylbenzene/carboxen/polydimethylsiloxane – DVB/CAR/PDMS), glass liners, serum bottles, aluminium caps and a fibre assembly holder were purchased from Supelco, Inc. (Bellefonte, PA, USA). Methylene blue and other chemicals were purchased from Daejung chemical (Gyeonggi-do, Korea).

2.2. Sample preparation of elaidic and oleic acid model systems with methylene blue

Methylene blue was dissolved in chloroform and then mixed with 400 mg of elaidic or oleic acids to obtain 300 ppm (w/v). Solvent in the sample mixture was removed using nitrogen gas flow. Sample bottles were sealed air tight with Teflon-coated rubber septa and aluminium caps and placed in a circulating water bath at 60 °C. Light exposure on samples was conducted using six fluorescent lights with 1330 lux light intensity in a hand-made light box. Samples for dark condition were prepared wrapping the bottles with aluminium foil. Volatiles of samples were measured at 0, 12, 24, 36, 48 and 60 h. All samples were prepared in triplicate. Samples containing oleic acid with methylene blue in the dark, oleic acid with methylene blue under light, elaidic acid with methylene blue in the dark and elaidic acid with methylene blue under light were designated as OMD, OML, EMD and EML, respectively.

2.3. Headspace oxygen analysis

The oxygen contents of headspace gas in sample bottles were determined by gas chromatography (GC) equipped with a thermal conductivity detector (TCD) (Agilent Technology, Palo Alto, CA, USA) and a stainless steel column (3.0 m × 20 mm ID) packed with 60/80 Molecular Sieve 5A (Restek, Bellefonte, PA, USA). Injection volume was 25 μL using an air-tight syringe and the flow rate of helium gas was 20 mL/min. Temperatures of oven, injector and detector were 60, 180 and 180 °C, respectively.

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

Sample bottles taken from a light box were used for the analysis of headspace volatiles. Conditions of SPME for volatile analysis were adopted with the minor modification of Lee et al. (2007). Briefly, headspace volatiles in sample bottles were isolated by a DVB/CAR/PDMS solid phase fibre at 60 °C for 30 min in a water bath. The isolated volatile compounds were determined in a GC equipped with a mass selective detector (MS).

2.5. Gas chromatography condition for volatile compound analysis

An Agilent 6890 GC-5975B mass detector (Agilent Technology 5975, Palo alto, CA, USA) equipped with a HP-5 ms column (30 m × 0.25 mm ID, 0.25 μm film thickness) was used for the volatile analysis. Oven temperature started from 40 °C for 2 min, increased to 160 °C at 6 °C/min and to 220 °C at 10 °C/min, and stayed for 3 min. Helium was the carrier gas at 0.6 mL/min (10.3 kPa). The temperature of injector, ion source and MS quadrupole was 250, 230 and 150 °C, respectively. Volatiles from the SPME-solid phase fibre were desorbed for 2 min in a GC injector. All mass spectra were obtained at 70 eV. Identification of compounds was made by the combination of NIST Mass Spectra and gas chromatographic retention times of standard compounds. Volatile compounds were expressed in ion counts and the unit of slope of peak areas was ion counts/oxidation time (h).

2.6. Statistical analysis

The data were analysed statistically by ANOVA and Duncan's multiple range test using a commercially available software package SPSS software program (SPSS Inc., Chicago, IL). A p value <0.05 was considered significant.

3. Results and discussion

3.1. Headspace oxygen analysis

Monitoring the depletion of headspace oxygen is a reliable method to determine the degree of oxidation and the involvement of singlet oxygen in photosensitised model systems (Laguerre, Lecomte, & Villeneuve, 2007; Yang, Lee, & Min, 2002). The singlet oxygen quenching rate of compounds including α-tocopherol, riboflavin and β-carotene was determined using the depletion of

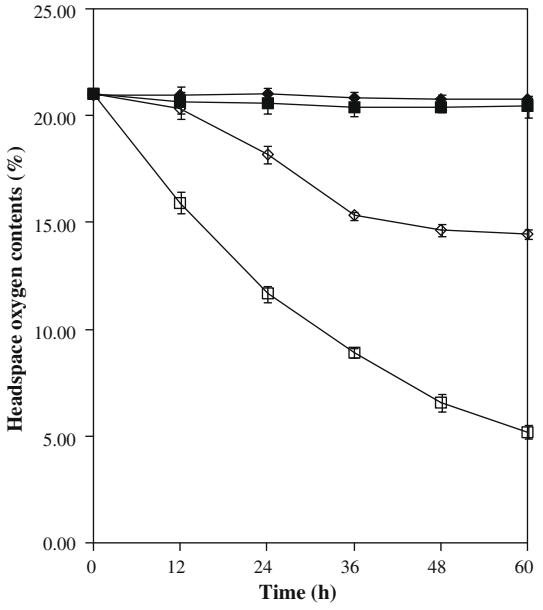

Fig. 1. Effects of photosensitisation on the headspace oxygen contents from OMD (■), OML (□), EMD (♦) and EML (◇) at 60 °C for 60 h.

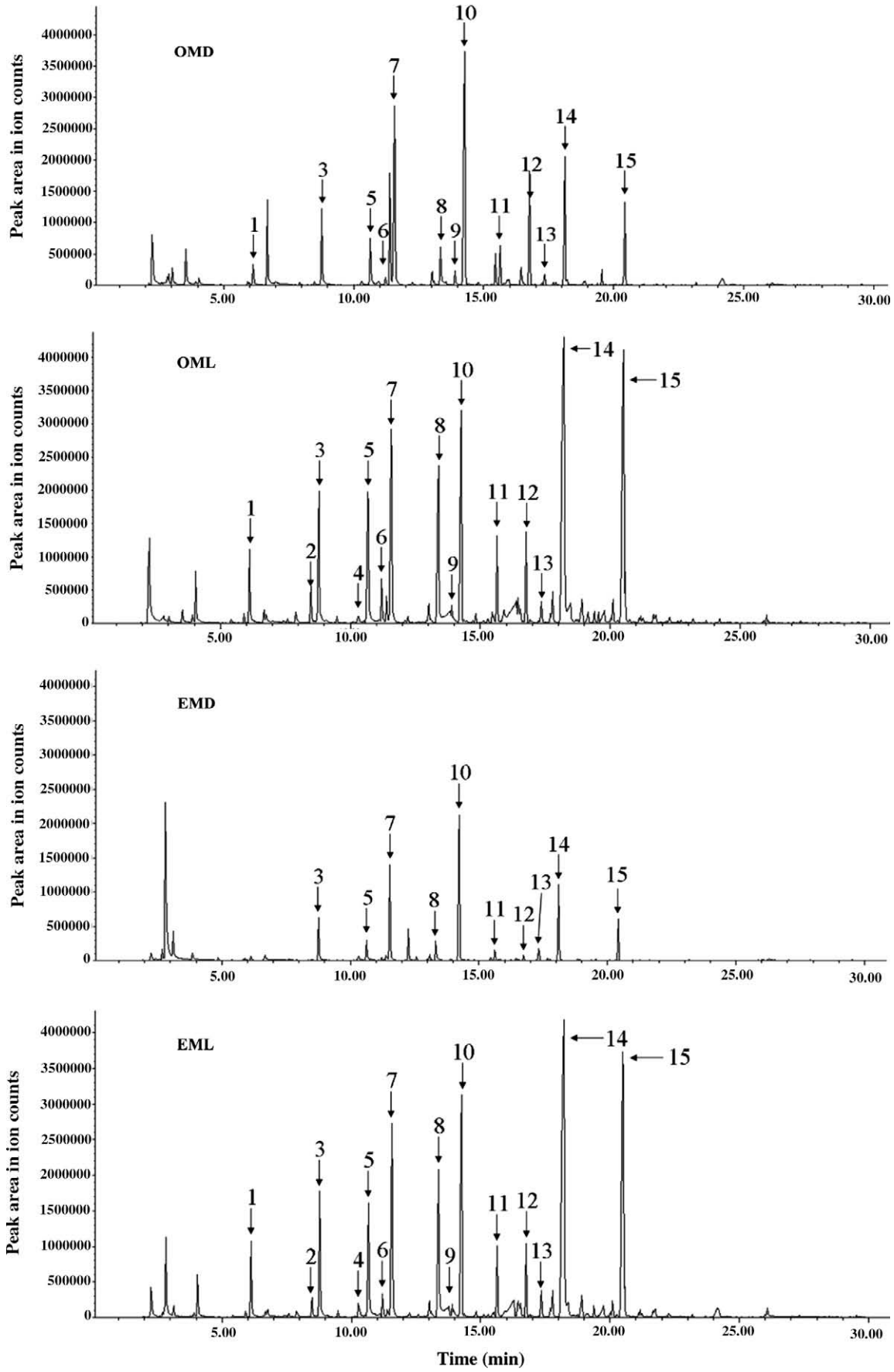

Fig. 2. GC chromatograms of headspace volatiles from oleic and elaidic acids with methylene blue under light or in the dark at 60 °C for 60 h.

headspace oxygen contents (Huang, Choe, & Min, 2004; Yang et al., 2002).

Changes of headspace oxygen in elaidic and oleic acids with methylene blue stored under light or in the dark are shown in Fig. 1. As oxidation time increased from 0 to 60 h, contents of headspace oxygen in OML and EML decreased significantly ($p < 0.05$) while those in OMD and EMD were not significantly different ($p > 0.05$). Contents of headspace oxygen in EML and OML decreased by 6.57% and 15.79%, respectively, for 60 h. Headspace oxygen contents in oleic acid under light decreased continuously for 60 h with a regression equation of $y = -0.264x + 19.54$ ($R^2 = 0.961$), where x is the oxidation time (h) and y is the oxygen percentage. In elaidic acid, headspace oxygen decreased with a regression equation of $y = -0.127x + 21.17$ ($R^2 = 0.882$) between 12 and 60 h. Oleic acid absorbed headspace oxygen about 2.0 times faster than elaidic acid during methylene blue photosensitisation for 60 h based on the comparison of slopes of each regression equation.

Methylene blue is a well-known type II photosensitiser generating singlet oxygen under light exposure. The generated singlet oxygen may react readily with oleic acid than elaidic acid at 60 °C under the current condition. However, there are some points to consider before determining the oxidative stability between *cis* and *trans* fatty acids. The initial state of samples could not be determined using a headspace oxygen depletion method. During the first 12-h light irradiation, headspace oxygen of OML and EML was decreased by about 4.98% and 0.56%, respectively. This significant difference in headspace oxygen may come from combination effects of autoxidation, singlet oxygen oxidation and/or difference in the initial oxidation state of lipid samples. This point was confirmed from the results of volatile analysis.

3.2. Analysis of volatile compounds from oleic and elaidic acid by SPME

Representative chromatograms of OMD, OML, EMD and EML for 60 h are shown in Fig. 2. Distribution and profiles of volatiles in elaidic and oleic acids under light were clearly different from those in the dark for 60 h (Fig. 2). More peaks were observed in the samples stored under light than samples in the dark, which may be due to the methylene blue photosensitisation. Some peaks including peak nos. 2 and 4 in oleic acid and peak nos. 1, 2, 4, 6 and 9 in elaidic acid were detected in photosensitised samples only in current experimental conditions (Fig. 2). Profiles of volatile peaks in EMD were not the same compared to those in OMD. However, most major oxidised volatiles detected in EML were also detected in OML.

Changes of total volatiles in OMD, OML, EMD and EML are shown in Fig. 3. Total volatile compounds from EML and EMD increased up to 14.35 and 3.69 ($\times 10^8$) for 60 h, respectively, in ion counts. Volatiles in OML and OMD for 60 h changed from 5.01 to 15.92 ($\times 10^8$) and from 5.87 to 9.01 ($\times 10^8$), respectively. Compared to volatiles of elaidic samples, oleic acid contained already substantial amount of volatiles at 0 h. Presence of volatiles is one of representative indicators for determining the degree of oxidation and antioxidant ability (Lee et al., 2007). Therefore, initial volatiles in oleic samples may contribute to the high oxygen depletion of OML for 60 h. Total peak areas of EML for 60 h were higher than those of EMD by 10.60 ($\times 10^8$) while those of OML were higher than OMD by 6.91 ($\times 10^8$). Methylene blue photosensitisation generated more volatiles in elaidic acid than in oleic acid at 60 °C for 60 h compared to those of corresponding fatty acid stored in the dark.

Methylene blue played important roles in accelerating the formations of volatiles from both elaidic and oleic acid model systems as a photosensitiser. Effects of photosensitisation and the involvement of singlet oxygen on the changes of volatiles have shown similar results in fatty acids and oils (Zhuang, Barth, & Hildebrand, 2002). Lee and Min (2009) reported that volatile compounds from lard under chlorophyll photosensitisation were greatly increased compared to those without chlorophylls or those stored in the dark.

Ratio of slopes of peak areas in OML/OMD and EML/EMD and difference of peak areas from OML–OMD and EML–EMD are shown in Fig. 4. The ratios of slopes in EML/EMD at every 12-h interval, that is, from 0 to 12, from 12 to 24, from 24 to 36, from 36 to 48 and from 48 to 60 h were 2.31, 3.41, 3.55, 3.73 and 3.88, respectively, while those in OML/OMD were 1.24, 1.50, 1.67, 1.82 and 1.77, respectively. The ratio of slopes in EML/EMD increased gradually for 60 h and is higher than those of OML/OMD, which implies that formation rate of volatiles in EML was faster than OML.

Difference of peak areas from OML–OMD and EML–EMD may show the effects of major mechanisms on the formation of volatiles during oxidation. Major oxidation mechanisms for OML and EML are photosensitisation and autoxidation, while those for OMD and EMD are autoxidation. Therefore, differences of total peak areas between samples stored under light and in the dark can be regarded as volatile from photosensitisation. For example, differences of volatile peak areas from EML to EMD at 12, 24, 36, 48 and 60 h were

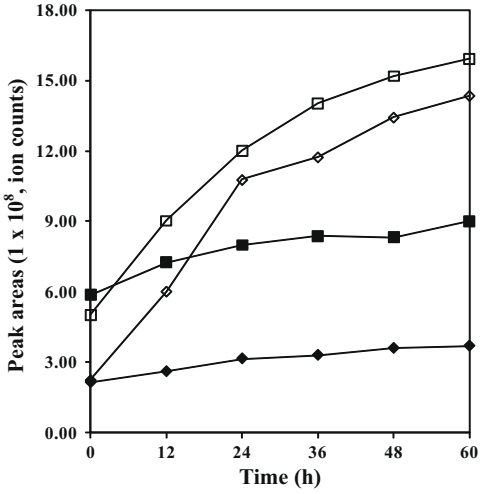

Fig. 3. Changes of total volatiles in OMD (■), OML (□), EMD (♦) and EML (◇) at 60 °C for 60 h.

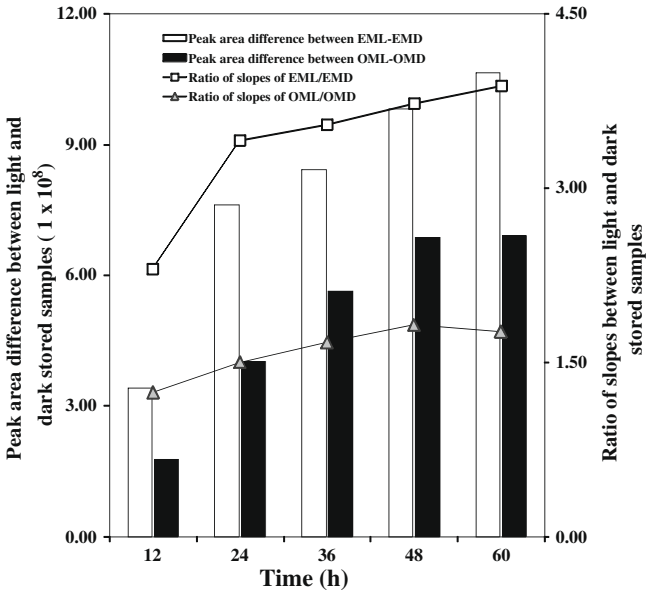

Fig. 4. Ratio of regression slope in OML/OMD and EML/EMD and peak area differences from OML–OMD and EML–EMD.

3.41, 7.61, 8.43, 9.82 and 10.65 ($\times 10^8$) in ion counts, respectively, while those from OML to OMD were 1.77, 4.01, 5.84, 6.86 and 6.91 ($\times 10^8$), respectively. Differences of volatiles from EML to EMD were higher than those of OML–OMD for 60 h photosensitisation (Fig. 4), which implies that elaidic acid generated more oxidised volatiles than oleic acid at 60 °C during photosensitisation.

Studies on the photosensitisation and lipid oxidation have been reported in *cis* fatty acid model systems and edible vegetable oils, and limited reports using *t*FAs are available. *trans* Fatty acids have been considered more resistant to the oxidation stress than *cis* fatty acids due to the structural similarity to saturated fatty acids and higher melting points. In this study, elaidic acid under methylene blue photosensitisation produced higher rate of volatile formations in ion counts than oleic acid. It may not be appropriate to compare directly the peak profiles of volatiles from elaidic and oleic acids in the same condition due to the difference of the melting points and of the initial oxidation state of elaidic and oleic acid samples. Also, 60 °C of temperature provides different effects of thermal oxidation on elaidic and oleic acids.

In this study, volatiles in EMD and OMD increased by 1.55 and 3.13 ($\times 10^8$) in ion counts, respectively, at 60 °C for 60 h. Oleic acid was more susceptive to autoxidation than elaidic acid based on the results of headspace oxygen depletion (Fig. 1). Even though total volatiles from elaidic acid were not larger than those from oleic acid, the increasing rate of volatiles from EML was higher than that from OML.

3.3. Possible formation pathways of oxidised volatiles from elaidic and oleic acids

Selected major volatiles in elaidic and oleic acids containing methylene blue stored under light or in the dark are listed in Table 1. Already some peaks were present in oleic acid samples at 0 h. As oxidation time increased, some new peaks including 1-decene, 1-octanol and 2-nonanone were formed in OMD. 1-Nonene and *t*-2-heptenal, which were not found in OMD, were detected in OML for 60 h. Major volatile compounds in OML at 24 h were in the order of *t*-2-decenal, *t*-2-undecenal, nonanal and octanal, while those in OMD were nonanal, octanal, decanal and *t*-2-decenal. *t*-2-Decenal showed the highest increase in peak areas in OML and then nonanal and octanal followed (Table 1).

In case of elaidic acid, one peak in EMD and four volatiles including octane, nonanal, decanal and *t*-2-decenal in EML were detected for 0 h (Table 1). Although both EMD and EML samples were prepared simultaneously, accidental exposure of light during volatile analysis by SPME may induce the formation of volatiles at 0 h sampling. As oxidation time increased to 12 h, six peaks such as nonanal, octanal, *t*-2-decenal, heptanal, *t*-2-undecenal and 1-heptanol were formed and detected in EMD while seven volatiles including octanal, 1-octanol, *t*-2-decenal, 1-heptanol, heptanal, *t*-2-undecenal and benzothiazole were formed and detected in EML samples. Some volatiles including 1-nonene, *t*-2-heptenal, 1-decene and 2-nonanone were detected in EML only, which

Table 1
Changes of major volatile compounds from OMD, OML, EMD and EML ($\times 10^6$ ion counts).

		OMD[a]	Oxidation time (h)					OML	Oxidation time (h)				
No.[b]	Volatile compound	0	12	24	36	48	60	0	12	24	36	48	60
1	Octane	17.9[c]	15.2	15.8	16.0	14.9	14.6	11.4	20.8	29.1	38.1	50.0	62.3
2	1-Nonene	ND[d]	ND	ND	ND	ND	ND	19.9	3.3	13.1	20.0	21.4	22.2
3	Heptanal	16.3	51.6	60.4	64.0	63.7	64.7	4.8	114.2	142.5	133.1	129.9	136.0
4	*t*-2-Heptenal	ND	ND	ND	ND	ND	ND	ND	4.2	4.8	4.8	4.8	4.8
5	1-Heptanol	3.7	16.7	22.3	25.6	26.5	28.1	4.7	81.1	138.8	168.2	175.5	178.2
6	1-Decene	ND	12.1	16.0	20.0	21.0	22.2	ND	3.0	13.3	21.3	23.8	25.0
7	Octanal	90.2	17.19	177.0	184.5	182.0	182.6	88.0	193.6	218.8	233.4	239.2	243.9
8	1-Octanol	ND	18.7	27.3	31.5	35.4	37.8	3.5	93.0	154.7	193.8	206.1	210.5
9	2-Nonanone	ND	4.0	9.0	10.2	11.8	12.7	ND	3.5	10.2	22.7	39.4	35
10	Nonanal	101.3	257.8	276.4	285.9	293.8	294.7	105.5	224.7	225.1	234.0	256.1	265.8
11	*t*-2-Nonenal	3.2	24.4	28.3	30.4	32.8	21.7	4.4	48.9	64.2	71.6	73.4	76.2
12	Decanal	37.1	82.2	81.4	78.5	82.4	80.5	37.1	48.8	48.3	62.1	72.3	76.8
13	Benzothiazole	ND	ND	ND	ND	4.9	6.1	ND	ND	5.3	13.6	16.3	18.7
14	*t*-2-Decenal	11.7	81.4	95.4	102.2	111.3	117.6	7.3	148.9	421.5	497.5	501.3	539.3
15	*t*-2-Undecenal	7.8	42.4	50.6	53.8	62.4	64.9	10.5	125.6	228.6	299.9	312.0	349.6
		EMD	Oxidation time (h)					EML	Oxidation time (h)				
No.	Volatile compound	0	12	24	36	48	60	0	12	24	36	48	60
1	Octane	ND	ND	ND	ND	ND	7.9	7.9	6.9	16.4	27.9	39.9	51.6
2	1-Nonene	ND	ND	ND	ND	ND	ND	ND	ND	7.9	12.6	16.2	18.9
3	Heptanal	ND	8.0	12.6	13.7	15.9	16.9	ND	37.0	106.3	142.9	150.4	153.9
4	*t*-2-Heptenal	ND	ND	ND	ND	ND	ND	ND	ND	1.2	19.1	19.4	18.6
5	1-Heptanol	ND	3.2	5.0	6.2	7.2	8.3	ND	21.5	76.8	123.4	145.3	164.1
6	1-Decene	ND	ND	ND	ND	ND	ND	ND	ND	3.8	13.1	18.7	22.3
7	Octanal	ND	17.1	25.8	33.4	38.9	42.5	ND	137.6	199.7	227.3	243.5	257.0
8	1-Octanol	ND	ND	4.7	6.4	8.0	9.5	ND	54.2	119.6	159.5	184.3	203.3
9	2-Nonanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.4	4.4	8.6
10	Nonanal	ND	45.7	63.8	74.1	84.1	88.9	9.4	156.7	218.9	254.4	269.9	290.1
11	*t*-2-Nonenal	ND	ND	ND	3.0	3.5	4.1	ND	16.5	32.3	41.8	49.9	56.4
12	Decanal	0.1	0.2	ND	ND	ND	ND	13.8	6.5	13.9	22.1	37.4	46.1
13	Benzothiazole	ND	ND	ND	3.9	5.5	6.0	ND	3.7	8.3	11.3	15.2	17.1
14	*t*-2-Decenal	ND	12.6	18.1	23.5	29.5	33.8	6.1	157.0	346.9	409.5	463.1	499.9
15	*t*-2-Undecenal	ND	5.7	8.6	11.4	12.5	15.5	ND	35.4	154.7	198.6	244.6	279.7

[a] OMD, OML, EMD and EML are oleic acid with methylene blue in the dark, oleic acid with methylene blue under light, elaidic acid with methylene blue in the dark and elaidic acid with methylene blue under light, respectively.
[b] No. indicates peaks in Fig. 2.
[c] Peak area of each volatile is average of triplicate in ion counts ($n = 3$).
[d] Not detected.

implies that formation of these volatiles was greatly influenced by the methylene blue photosensitisation (Table 1). *t*-2-Undecenal, nonanal, octanal and *t*-2-decenal were the most increased volatiles in EML for 60 h (Table 1). Peak areas of *t*-2-undecenal, 1-octanol and 1-heptanol were greatly increased in both elaidic and oleic acids under photosensitisation. Peak no. 13 was identified as benzothiazole, which came from degradation of nitrogen and sulphur-containing methylene blue.

The reaction mechanisms of singlet and triplet oxygen on unsaturated fatty acids are different (Boff & Min, 2002). Triplet oxygen, which is a di-radical, needs radical forms of unsaturated fatty acids to form hydroperoxides, while singlet oxygen can generate hydroperoxide through 'ene' reaction without initiation step of radical formation. Triplet oxygen can form hydroperoxides at 8, 9, 10 and 11 positions in oleic acid while singlet oxygen can form hydroperoxides at 9 or 10 positions in oleic acid (Min & Boff, 2002). Isomeric distribution of 8-, 9-, 10- and 11-hydroperoxides of *cis* octadecenoic acid from autoxidation was 26–28%, 22–25%, 22–24% and 26–28%, respectively, in relative percentage (Min & Boff, 2002).

Frankel, Neff, and Selk (1981) reported volatile profiles from thermally oxidised methyl oleate and photosensitised methyl oleate. Relative contents of octane, *t*-2-decenal and *t*-2-undecenal were higher in methyl oleate treated with photosensitisation than with autoxidation while those of octanal and decanal were higher in thermally oxidised oleate than photosensitised samples (Frankel et al., 1981). This trend agrees with the results of current study using oleic acid. Some difference of volatile distribution may come from different degrees of oxidation and/or analysis methods for volatiles. Major aldehydes from the cleavage of 8-, 9-, 10- and 11-hydroperoxides of 9-*cis* octadecenoic acid are *t*-2-undecenal, *t*-2-decenal, nonanal and octanal, respectively, and the relative contents of these volatiles are high in OMD in this study (Table 1). Frankel et al. (1981) reported that *t*-2-decenal was the highest volatile in photosensitised methyl oleate, which agrees with the results of this study. Yang et al. (2007) used 4000 ppm riboflavin as a photosensitiser and analysed volatiles from oleic acid at 35 °C for 39 h. The researchers reported that riboflavin–photosensitised oleic acid possessed relatively high concentrations of heptane, octane, heptanal, octanal, nonanal and *t*-2-nonenal and proposed the formation pathways of heptanal and *t*-2-nonenal from oleic acid using types I and II pathways of riboflavin.

Effects of photosensitisation were shown more clearly on elaidic acid than on oleic acid samples due to the absence of volatiles in elaidic acid at 0 h. Relative peak areas (%) of *t*-2-undecenal, *t*-2-decenal, nonanal and octanal in EML at 60 h were 11.67%, 19.25%, 8.75% and 8.29%, respectively, and those of EMD were 2.84%, 5.91%, 13.09% and 9.56%, respectively (Table 1). Peak areas of *t*-2-decenal (from 9-hydroperoxides) in EML were the highest and about 3.23 times at 12 h and 1.65 times at 60 h higher than *t*-2-undecenal (from 8-hydroperoxides). Unexpectedly, peak areas of nonanal (from 10-hydroperoxides) were not high enough compared to those of *t*-2-decenal. Although singlet oxygen oxidation was reported to generate 9- and 10-hydroperoxides from octadecenoic acids containing double bonds between 9 and 10 positions, high amounts of volatiles, which may be cleaved from 8- or 11-hydroperoxides, were also detected in elaidic acid under methylene blue photosensitisation. Frankel (1985) reported that thermal decomposition of 9- and 10-hydroperoxides into 8-, 9-, 10- and 11-hydroperoxides could occur at the 210 °C of injection port of GC. However, SPME method just isolates and concentrates the headspace volatiles and the possibility of thermal decomposition of hydroperoxides can be eliminated.

Octane (from 10-hydroperoxides), 1-decene (from 8-hydroperoxides) and 2-nonanone were detected in EML not in EMD, which could come from methylene blue photosensitisation. Formation pathways of some volatile compounds including *t*-2-nonenal, *t*-2-heptenal or heptanal in EMD and/or EML are not fully understood yet.

Distribution of headspace volatiles from oxidised elaidic acid was different from oxidised oleic acid under light or in the dark. Although photosensitisation or autoxidation mechanisms of lipid oxidation can explain major volatiles in elaidic or oleic acids, some light-induced volatile compounds could not be explained successfully using previous theories of photosensitisation. However, it is obvious that methylene blue photosensitisation caused the increases of volatile compounds from elaidic acids more than from oleic acid under current experimental conditions.

4. Conclusion

Oleic acid under methylene blue photosensitisation absorbed more headspace oxygen than elaidic acid at 60 °C for 60 h. However, elaidic acid produced more volatiles than oleic acid compared to the corresponding samples stored in the dark. As far as we have searched, effects of methylene blue photosensitisation on the volatile formations and profiles in elaidic acid model system have not been reported in the literature. Studies on the volatile profiles can be useful indicators explaining possible lipid oxidation mechanisms. Major volatiles in elaidic acid under photosensitisation were *t*-2-decenal, nonanal, *t*-2-undecenal and octanal while those in oleic acid were *t*-2-decenal, *t*-2-undecenal, nonanal and octanal. More studies need to confirm the oxidative stability of *trans* fatty acid under photosensitisation and formation mechanisms of volatiles.

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