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Changes in oxidation-derived off-flavor compounds of roasted sesame oil during accelerated storage in the dark

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ABSTRACT

Oil oxidation and off-flavor compounds were evaluated in roasted sesame oil during accelerated storage at 70 °C in the dark for 4 weeks. Oil oxidation was monitored by measuring contents of conjugated dienoic acid (CDA) and polar compounds as well as by analyzing fatty acid composition by gas chromatography (GC). Off-flavor compounds were evaluated with the headspace gas analysis using a solid phase microextraction (SPME) and GC. The roasted sesame oil showed little change in fatty acid composition during storage, and contents of CDA and polar compounds increased slowly. Among off-flavor compounds including pentane, hexane, hexanal, heptanal, 1-pentanol, acetic acid, and furfuryl alcohol, hexanal, heptanal, or 1-pentanol content increased with storage time and showed a high correlation with CDA values of the oil. Acetic acid and furfuryl alcohol did not show consistent trends throughout the 4 week storage. The results confirmed high oxidative stability of roasted sesame oil and suggested use of hexanal, heptanal, or 1-pentanol as an indicator off-flavor compound to monitor the autoxidation of roasted sesame oil.

1. Introduction

Sesame oil has attracted public attention due to its beneficial constituents to the health. It contains high amount of lignan compounds (1034 ppm) such as sesamol as well as tocopherols (44 ppm) having good antioxidant activities (Lee et al., 2008). Sesame oil also contains CoQ_{10}, which may work together with tocopherols in protecting the function of biological membranes and provide lipoproteins with increased resistance to oxidation (Pyo, 2010). High contents of essential linoleic and linolenic acids are another merit of sesame oil as a food source. Sesame oil is manufactured by solvent extraction from raw sesame seeds followed by the refining process, or by pressing roasted sesame seeds without refining. Roasted sesame oil has a characteristic flavor and is mainly used for a seasoning rather than for frying oil in Korea.

Off-flavor is a critical quality defect of roasted sesame oil, which determines the acceptability of consumers. Sesame oil industry has worked to solve the off-flavor problems for a long time. Oxidation is one of the reactions, which produce off-flavors in the oil. Although sesame oil is relatively resistant to the oxidation, serious problems can be arisen by the production of small amount of off-flavor compounds, especially those having low threshold values for detection. In addition to the production of off-flavors, the oil oxidation destroys essential fatty acids with production of *trans* acid and conjugated dienes. It also produces polar compounds such as oxidized polymers, some of which are detrimental to the health (Hamilton, 1994; Aruoma, 1998). Undesirable off-flavor compounds and nutritional loss from the oxidation of oil decrease the quality and values of oil.

The oxidation of oil is affected by external and internal factors such as temperature, light, fatty acid composition, antioxidants, and prooxidants (Choe and Min, 2006), and thus oxidative stability of oils during storage may depend on the oil source and manufacturing process. Roasted sesame oil contains free fatty acids (0.72%) while refined sesame, soybean, and corn oil do not have them (Chung and Choe, 2001; Kim and Choe, 2005). Roasting of sesame seeds at high temperature of 250 °C can produce free fatty acids by hydrolysis of mono-, di-, and triacylglycerols in the seeds and these free fatty acids can accelerate the oil oxidation (Choe and Min, 2006). Since there is no refining in manufacturing the roasted sesame oil, free fatty acids remain in the oil and can contribute to the increased production of off-flavor compounds from the increased oil oxidation. Roasted sesame oil also naturally contains useful antioxidants such as tocopherols and lignans, which can decrease off-flavor compounds formation. Co-presence of prooxidants and antioxidants in the roasted sesame oil at the significant amount should affect the off-flavor compounds profile resulted from its oxidation, and this information is a definite requisite for keeping good quality of roasted sesame oil during

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storage. This study was, therefore, performed to evaluate the oxidation-derived off-flavor compounds changes in roasted sesame oil during accelerated storage in the dark.

2. Materials and methods

2.1. Materials and chemicals

Roasted sesame oil was supplied from CJ Co. (Seoul, Korea). Silica gel 60, 14% BF_3–methanol, and methyl esters of standard fatty acid (palmitic, stearic, oleic, linoleic, and linolenic acid) were purchased from Sigma–Aldrich Co (St. Louis, MO, USA). Isooctane in UV grade was purchased from J.T. Baker, Inc. (Phillipsburg, NJ, USA). All other chemicals were of analytical grade.

2.2. Sample preparation and oxidation

Roasted sesame oil (7 g) was put into a 20 mL glass vial, which was then sealed with a Teflon-coated rubber septum and aluminum cap (Supelco Inc., Bellefonte, PA, USA). The vials were wrapped with aluminum foil to prevent light exposure and placed in an oven at 70 °C for 4 weeks to accelerate the oxidation. Samples were taken out every week for the analyses of fatty acid composition, oil oxidation, and off-flavor compounds contents. Samples were prepared in duplicate.

2.3. Determination of fatty acid composition of the oil

Fatty acid composition of the roasted sesame oil was analyzed by gas chromatography (GC) after esterification with 14% BF_3–methanol solution (Lee et al., 2004). The instrument was a Younglin M600D gas chromatograph (Younglin Co., Seoul, Korea) equipped with a Supelcowax™ capillary column (30 m × 0.53 mm, 0.5 μm thick: Supelco Inc.) and a flame ionization detector. Temperatures of the oven, injector, and detector were 200, 270, and 280 °C, respectively. Nitrogen flow rate was 5 mL/min, and the split ratio was 33:1. Each fatty acid in the GC chromatograms was identified by comparing retention times of standard fatty acid methyl esters and quantified by peak areas in electronic units (e.u.).

2.4. Analysis of the oil oxidation

Oxidation of the roasted sesame oil was evaluated by measuring contents of conjugated dienoic acid (CDA) and polar compounds by AOCS method Ti 1a-64 using spectrophotometry (AOCS, 1990) and by AOAC method 982.27 using gravimetry after passing through a glass column (2.1 cm × 45 cm) packed with silica gel 60 (AOAC, 1995), respectively.

2.5. Analysis of off-flavor compounds

Off-flavor compounds of the roasted sesame oil during accelerated storage in the dark were evaluated with the headspace gas analysis performed by solid phase microextraction (SPME) and GC by the method of Steenson et al. (2002) and Lee et al. (2003) after transferring them to the headspace of the vial from the oil. Off-flavor compounds in the headspace of the vial were extracted by SPME with 50/30 μm DVB/Carboxen/PDMS StableFlex fiber (Supelco Inc.). The fiber was inserted into the headspace of the vial for 30 min while the vial was incubated in a 60 °C water bath to facilitate transfer of the off-flavor compounds from the oil to the headspace. The extracted headspace off-flavor compounds were desorbed into the GC injection port, which was fitted with a splitless glass liner (0.75 mm internal diameter; Supelco Inc.) for 5 min at 250 °C. Desorbed off-flavor compounds were separated and detected using a Supelcowax™ capillary column (30 m × 0.53 mm × 0.5 μm thickness; Supelco Inc.) and a 270 °C flame ionization detector equipped to Younglin M600D GC (Younglin Co.). Nitrogen was used as a carrier gas. The GC oven temperature was programmed to hold at 40 °C for 4 min, increase to 80 °C at 8 °C/min, then increase to 220 °C at 7 °C/min, and finally hold at 220 °C for 2 min. Headspace off-flavor compounds were identified by the retention times of standard chemicals, and quantified by peak areas in electronic units (e.u.).

2.6. Statistical analysis

Duncan's multiple range test of the SAS System (version 8.2; SAS Inst. Inc., Cary, NC, USA) was performed to analyze the differences among samples. The significance level was 5%.

3. Results and discussion

3.1. Fatty acid composition changes in the roasted sesame oil during storage

Table 1 shows that the roasted sesame oil contained high amount of linoleic acid (41.5%), one of the essential fatty acids, which are used in the biosynthesis of arachidonic acid and thus some prostaglandins (Adam et al., 1986). In spite of health benefits, high amount of linoleic acid may exert adverse effects on the oxidative stability of the oil. In addition to linoleic acid, the roasted sesame oil contained palmitic (10.5%), stearic (6.0%), and oleic (42.0%) acids, with the content ratio of unsaturated fatty acids to saturated fatty acids (*U*/*S* ratio) of 5.05 before storage. It was well-reported that saturated fats increased the risk of heart diseases by increasing LDL cholesterol levels (Rivellese et al., 2003), and the American Heart Association recommended their consumption limit to less than 7% of daily calories (Lichtenstein et al., 2006). Therefore, the roasted sesame oil, which contained high amount of unsaturated fatty acids is, considered as a good oil source for health.

During storage at 70 °C in the dark for 4 weeks, the roasted sesame oil did not show a big change in the *U*/*S* ratio as well as fatty acid composition, even though there was a tendency of an increase in palmitic acid and decrease in oleic acid, resulting in a slight decrease in the *U*/*S* ratio. Decrease in *U*/*S* ratio with time resulting from the difference in oxidation rate between unsaturated fats and saturated ones has been well-reported previously (Lee et al., 2007). Unsaturated fats are more susceptible to the oxidation than saturated ones, primarily due to their low activation energy for the formation of lipid radicals (Przybylski et al., 1993). The activation energies for the autoxidation of trilinolein and trilinolenin were reported to be 34 ± 8 and 9 ± 2 kJ/mol (Zhu and Sevilla, 1990), respectively. Little change in fatty acid

Table 1
Fatty acid composition of the roasted sesame oil during storage at 70 °C in the dark.

Storage (week)	Fatty acid composition (relative %)				*U*/*S* ratio
	C16:0	C18:0	C18:1	C18:2	
0	10.5 ± 0.09	6.0 ± 0.08	42.0 ± 0.07	41.5 ± 0.12	$5.05 \pm 0.02^{a*}$
1	10.6 ± 0.14	6.1 ± 0.11	42.0 ± 0.15	41.4 ± 0.22	5.02 ± 0.04^{ab}
2	10.6 ± 0.03	6.1 ± 0.02	41.9 ± 0.05	41.5 ± 0.06	5.01 ± 0.01^{ab}
3	10.6 ± 0.17	6.1 ± 0.07	41.9 ± 0.07	41.4 ± 0.10	4.98 ± 0.05^{b}
4	10.6 ± 0.16	6.0 ± 0.00	41.9 ± 0.06	41.5 ± 0.11	5.00 ± 0.06^{ab}

* Different superscript means significant difference among samples at $\alpha = 0.05$.