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Characteristics of Structured Lipid Prepared by Lipase-Catalyzed Acidolysis of Roasted Sesame Oil and Caprylic Acid in a Bench-Scale Continuous Packed Bed Reactor

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Structured lipid (SL) was prepared from roasted sesame oil and caprylic acid (CA) by *Rhizomucor miehei* lipase-catalyzed acidolysis in a bench-scale continuous packed bed reactor. Total incorporation and acyl migration of CA in the SL were 42.5 and 3.1 mol %, respectively, and the half-life of the lipase was 19.2 days. The SL displayed different physical and chemical properties, less saturated dark brown color, lower viscosity, lower melting and crystallization temperature ranges, higher melting and crystallization enthalpies, higher smoke point, higher saponification value, and lower iodine value, in comparison to those of unmodified sesame oil. The oxidative stability of purified SL was lower than that of sesame oil. There were no differences in the contents of unsaponifiables including tocopherols and phytosterols. However, total sesame lignans content was decreased in SL due to the loss of sesamol when compared to sesame oil. Most of the 70 volatiles present in roasted sesame oil were removed from SL during short-path distillation of SL. These results indicate that the characteristics of SL are different from those of original sesame oil in several aspects except for the contents of tocopherols and phytosterols.

KEYWORDS: Acidolysis; caprylic acid; continuous packed bed reactor; Lipozyme RM IM; roasted sesame oil; sesame lignans; short-path distillation; structured lipids

INTRODUCTION

Structured lipids (SLs) are restructured fats or oils in which the composition and positional distribution of fatty acids (FAs) are modified from the native state by chemical or enzymatic methods (*1*). In the synthesis of SLs, the enzymatic methods have several advantages over chemical methods, such as selectivity and little or no formation of undesirable byproducts (*1*). However, despite these benefits, the application of the enzymatic methods for the industrial production of SLs has been slow. The main disadvantage of the enzymatic methods in industrial scale application is the high cost of the lipase as compared to chemical methods. To overcome this problem, the use of immobilized lipase is preferred because it would allow the recovery and reutilization of the enzyme.

Continuous packed bed reactors are the most commonly used reactors for immobilized lipase in industrial scale applications because of their ease of construction and operation, resulting in relatively low cost and labor. The potential for reutilization of immobilized lipase is much higher in the continuous packed bed reactors as compared to stirred batch reactors because rupture of the supporting materials for immobilized lipase can be avoided in the former. Because such rupture is known to facilitate acyl migration, which is one of the most significant problems in the synthesis of SLs, such undesirable side reactions can also be reduced in the continuous packed bed reactors (*2*, *3*). Moreover, because the ratio between substrate and enzyme is much lower in a continuous packed bed reactor than is the case with a stirred batch reactor during enzymatic reactions, the lower substrate/enzyme ratio results in shorter reaction time and higher reaction rate, thereby reducing acyl migration (*4*). In these respects, continuous packed bed reactors would be the most desirable and feasible reactor type for the industrial scale production of SLs.

In the present work, we produced SLs from roasted sesame oil in a continuous packed bed reactor. Sesame oil used in this study is an edible oil obtained from the seed of sesame (*Sesamum indicum* L.), which is one of the world's oldest oilseed crops and has been cultivated mainly in Asia and Africa for centuries (*5*, *6*). Two different types of sesame oil are commercially produced: one is refined, bleached, and deodorized (RBD) unroasted sesame oil (also called sesame salad oil) and the other is unrefined roasted sesame oil. Unlike RBD oil, unroasted sesame oil prepared from sesame seeds cooked with steam, roasted sesame oil is produced by expelling sesame seeds roasted at ≈180−200 °C followed by filtration without a further

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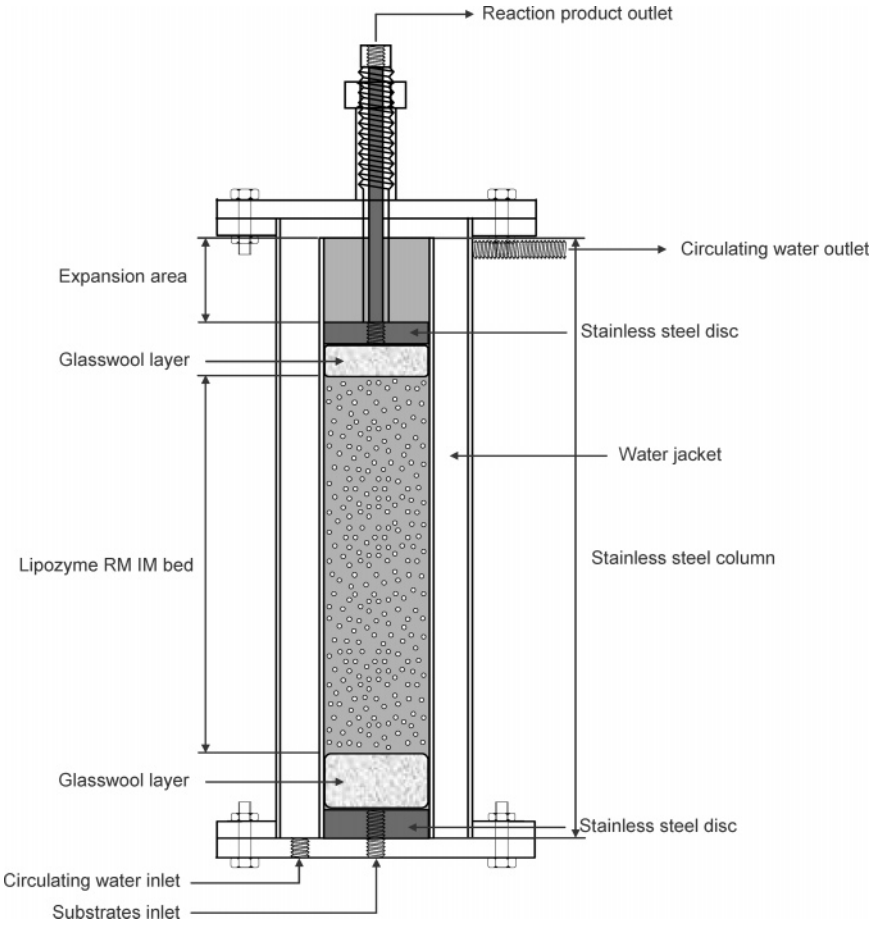

Figure 1. Cross section of the bench-scale continuous packed bed reactor used in this study.

refining process. Roasting of sesame seeds gives a dark brown color to the oil and develops a characteristic roasted flavor in the oil mainly due to thermochemical reactions, such as Maillard reactions (*6*, *7*). Roasted sesame oil is indispensable in Eastern Asian dishes because of such a characteristic roasted flavor especially preferred by Eastern Asians, such as the Korean, Chinese, and Japanese.

Roasted sesame oil consists mainly of neutral triacylglycerols (TAGs) containing ≈80% unsaturated FAs (USFAs), such as oleic and linoleic acids, with a relatively larger quantity of free FAs (FFAs) (1−3%) than other RBD vegetable oils because of the absence of refining processes (*6*). Compared to other vegetable oils, sesame oil also contains a relatively large amount of unsaponifiable matter (1−3%) that includes phytosterols, tocopherols, and unique compounds called sesame lignans including sesamol, sesamin, and sesamolin (*6*). Roasted sesame oil is known to have superior resistance to oxidation despite its relatively high concentration of FFAs as compared to other vegetable oils (*6*). The remarkable oxidative stability of sesame oil is reported to be due to the presence of sesame lignans as well as tocopherols (*5*, *6*). Sesame lignans are also demonstrated to display several interesting physiological effects, such as antioxidant, anticarcinogen, and hypocholesterolemic activities in animal models (*5*).

So far, numerous studies on SL synthesis from diverse kinds of vegetable oils have placed too much importance on RBD oils, whereas there were few studies on crude oils, such as roasted sesame oil (*8*−*13*). Because roasted sesame oil possesses several special attributes as compared to other vegetable oils, such as distinctive flavor, superior oxidative stability, and the existence of unique and beneficial minor components (sesame lignans, phytosterols), it might be meaningful to use the roasted sesame oil as the source oil for SL synthesis to evaluate the characteristics of the resultant SL.

The objectives of our study were to compare the characteristics of roasted sesame oil based MLM-type SL with those of original roasted sesame oil and to investigate the effect of SL synthesis processes on the attributes and minor components. In this study, we produced the SL by lipase-catalyzed acidolysis of roasted sesame oil with caprylic acid (CA) in a bench-scale continuous packed bed reactor. First, we evaluated the levels of incorporation and acyl migration of CA in the SL and the stability of the *sn*-1,3 specific lipase from *Rhizomucor miehei* under the acidolysis reaction conditions used in our work. Then, we investigated several physical and chemical properties, the oxidative stability of the SL, and the compositions of several components present in the SL, such as FAs, minor components (phytosterols, tocopherols, sesame lignans), and volatile compounds.

MATERIALS AND METHODS

Materials. Unrefined roasted sesame oil was purchased from Spectrum Organic Product, Inc. (Petaluma, CA). CA (C8:0, purity > 98%) was obtained from Aldrich Chemical Co. (Milwaukee, WI). Lipozyme RM IM, a *sn*-1,3-specific immobilized lipase from *R. miehei*, was provided by Novozymes North America Inc. (Franklinton, NC). Tocopherols, sesamol, and sesamin were from Sigma-Aldrich Co. (St. Louis, MO). Plant sterol mixture and 5β-cholestan-3β-ol were products of Matreya Inc. (Pleasant Gap, PA). All other reagents were of analytical or HPLC grade.

Continuous Packed Bed Reactor Setup. Figure 1 depicts the cross section of the continuous packed bed reactor used in this study. The

reactor has a jacketed stainless steel column (50 cm × 4.7 mm i.d.). The column was packed with 250 g of Lipozyme RM IM, and the upper and lower ends of the column were layered with glass wool at a thickness of 3 and 7 cm, respectively. The column temperature was maintained at a constant level by a circulating water bath. The substrate mixture was fed upward through the column using an FMI Lab pump (model QV, Fluid Metering Inc., Oyster Bay, NY) for the time period to elute 1 bed volume (≈700 mL) to condition the enzyme bed before collection of the reaction products for analysis.

Acidolysis Reaction. The SL synthesis was performed by acidolysis reaction between sesame oil and CA in the continuous packed bed reactor. The reaction was carried out under the following conditions: substrate flow rate, 1.15 mL/min; column temperature, 45 °C; substrate molar ratio 1:6 (sesame oil/CA).

Evaluation of Lipase Stability. The stability of Lipozyme RM IM during acidolysis reaction in the continuous packed bed reactor was evaluated by estimating the half-life of the lipase. Five milliliters of reaction products eluted from the outlet of the reactor was sampled at 2 L intervals from 0 to 8 L of total elution volumes after collection of products started. The sampled reaction products at each elution volume were used to measure the total incorporation of CA, and the half-life of the lipase was calculated from the change in the total incorporation over the reaction time.

Short-Path Distillation. Short-path distillation was used to purify the synthesized SL with a KDL-4 unit (UIC Inc., Joliet, IL) under the following conditions: holding temperature, 25 °C; heating oil temperature, 185 °C; cooling water temperature, 15 °C; and vacuum pressure, <50 mbar. The SL was passed through the unit five times to reduce the free FA (FFA) content to the same level as that of original sesame oil.

Methylation and GC Analysis. Fifty milligrams of oil sample was methylated in 3 mL of 6% HCl solution (in methanol) at 75 °C for 2 h. The FA methyl esters (FAMEs) were extracted and analyzed by gas chromatography (GC). An Agilent Technologies 6890N gas chromatograph (Agilent Technologies Inc., Palo Alto, CA), equipped with a flame ionization detector (FID) and a fused silica capillary column (AT-225, 30 m × 0.25 mm i.d., Alltech Associates, Inc., Deerfield, IL), was used. The carrier gas was helium and the total gas flow rate was 23 mL/min. The injector and detector temperatures were maintained at 250 and 260 °C, respectively. The column was initially held at 40 °C for 3 min and programmed to increase to 130 °C at the rate of 10 °C/min. After a 3 min hold at 130 °C, the column was then programmed to increase to 215 °C at the rate of 20 °C/min. The FAMEs were identified and their relative contents were calculated as mole percent with heptadecanoic acid (C17:0) as an internal standard.

Pancreatic Lipase-Catalyzed *sn*-2 Positional Analysis. Fifty milligrams of oil sample was used to analyze the FAs, which were esterified at the *sn*-2 position according to the pancreatic lipase hydrolysis procedure described by Luddy et al. (*14*).

Color and Viscosity Analysis. The color of oil samples was determined by measuring CIE L^* (lightness), a^* (redness), and b^* (yellowness) values and C (chroma) and $h°$ (hue angle) with a Minolta chroma meter (model CR-300, Minolta Co. Ltd., Osaka, Japan). Viscosity of oil sample was measured at 10 °C intervals from 5 to 35 °C using a Brookfield Digital Viscometer (model DV-E, Brookfield Engineering Laboratories Inc., Middleboro, MA).

Melting and Crystallization Profile Analysis. The melting and crystallization profiles of oil sample were determined using Perkin-Elmer differential scanning calorimeter (DSC) (model DSC 7, Perkin-Elmer Co., Norwalk, CT) according to AOCS recommended procedure Cj 1-94 (*15*) with a slight modification of the temperature program. Normal standardization was performed with indium (mp 156.60 °C, ΔH = 28.45 J/g) as a reference standard. Dry ice was used as the coolant. A sample of 6−8 mg was hermetically sealed in a 30 μL capacity aluminum pan (Perkin-Elmer Co., Norwalk, CT), with an empty sealed pan used as a reference. Oil sample was rapidly heated from room temperature to 80 °C and held at this temperature for 10 min to destroy any previous crystalline structure, before being cooled to −60 °C at a rate of 5 °C/min to obtain the crystallization profiles. After a 10 min hold at −60 °C, samples were heated to 80 °C at a rate of 5 °C/min to generate melting profiles. However, the crystallization profiles of the SLs, which could not be obtained by the operating conditions above, were generated as follows: SL was rapidly heated from room temperature to 80 °C and held at that temperature for 10 min and then cooled to −60 °C at a rate of 1 °C/min. The profiles were analyzed by the software provided with the DSC (Pyris software, Perkin-Elmer, Shelton, CT).

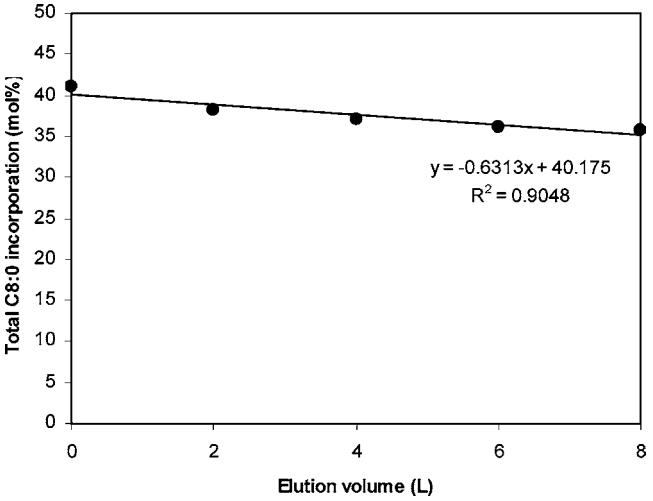

Figure 2. Changes in activity of Lipozyme RM IM over elution volume of reaction products during acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

Chemical Properties Analysis. FFAs content, unsaponifiable matter content, smoke point, saponification value, and iodine value of oil sample were determined according to AOCS official methods (*15*), respectively.

Tocopherol Analysis. Tocopherols of the oil sample were analyzed by normal phase HPLC following the method described by Ye et al. (*16*).

Phytosterol Analysis. Phytosterols of oil sample were analyzed by GC according to the method described by Jekel et al. (*17*) with a slight modification as described below. Oil sample (1.0 g) was weighed into a screw-capped tube and added to 1 mL of internal standard solution (100 μg/mL of 5α-cholestan-3β-ol in toluene). After flushing with nitrogen, the sample was saponified with 0.5 mL of saturated KOH in water at 80 °C for 30 min in the presence of 8 mL of 3% pyrogallol in ethanol. After cooling to room temperature, the sample was added to 20 mL of hexane and 12 mL of water. The tube was shaken for 5 min to extract the unsaponifiables. As layers separated, an aliquot of 10 mL was taken from the top layer and then dried under nitrogen. The dried unsaponifiables were added to 1 mL of hexane, and 1 μL of this solution was injected into the GC. A Hewlett-Packard 5890 series II gas chromatograph (Agilent Technologies Inc., Palo Alto, CA), equipped with a FID and a fused silica capillary column (SAC-5, 30 m × 0.25 mm i.d., Supelco Inc., Bellefonte, PA), was used. The carrier gas was nitrogen, and the total gas flow rate was 20 mL/min. The injector and detector temperatures were maintained at 270 and 300 °C, respectively. The column was initially held at 155 °C for 3 min and programmed to increase to 275 °C at the rate of 20 °C/min. The phytosterols of the oil sample were identified by comparison with the GC chromatogram of a plant sterol mixture, and their contents were calculated as milligrams per 100 g with 5β-cholestan-3β-ol as an internal standard.

Sesame Lignan Analysis. Sesamol, sesamin, and sesamolin in oil samples were analyzed by HPLC following the method of Han et al. (*18*). The oil sample (0.2 mL) was injected into a Waters Sep-pak C18 cartridge (Waters Co., Milford, MA) activated with methanol and eluted with 5 mL of methanol. The eluate (20 μL) was injected into a Hewlett-Packard 1100 series HPLC equipped with a Beckman Ultrasphere C18 ODS column (25 cm × 4.6 mm i.d.; Beckman Coulter Inc., Fullerton, CA) and a UV detector at 288 nm. The isocratic mobile phase was a mixture of methanol and water (70:30, v/v) at a flow rate of 0.8 mL/min. The concentration of each lignan compound in the oil was determined from the calibration curve of standard sesamol and sesamin.

Table 1. Fatty Acid Composition of Total, *sn*-2, and *sn*-1,3 Positions of TAG of Sesame Oil and SL (Mole Percent)[a]

	total		*sn*-2		*sn*-1,3[b]	
fatty acid	sesame oil	SL[c]	sesame oil	SL	sesame oil	SL
C8:0		42.5 ± 0.1		3.1 ± 0.1		62.3 ± 0.2
C12:0	tr[d]				tr	
C14:0	tr				tr	
C16:0	10.0 ± 0.0	2.7 ± 0.0	1.1 ± 0.0	1.2 ± 0.0	14.4 ± 0.0	3.5 ± 0.0
C16:1	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
C18:0	3.6 ± 0.0	1.2 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	5.3 ± 0.0	1.6 ± 0.0
C18:1n-9	37.0 ± 0.0	21.8 ± 0.1	40.2 ± 0.6	39.1 ± 0.1	35.4 ± 0.3	13.1 ± 0.1
C18:2n-6	48.4 ± 0.0	31.1 ± 0.0	57.3 ± 0.7	55.2 ± 0.0	44.0 ± 0.3	19.0 ± 0.0
C18:3n-3	0.9 ± 0.0	0.6 ± 0.0	1.0 ± 0.0	1.0 ± 0.0	0.8 ± 0.0	0.4 ± 0.0
SFA[e]	13.6 ± 0.0	46.5 ± 0.1	1.5 ± 0.1	4.6 ± 0.1	19.7 ± 0.0	67.4 ± 0.2
USFA[f]	86.4 ± 0.0	53.5 ± 0.1	98.5 ± 0.1	95.4 ± 0.1	80.3 ± 0.0	32.6 ± 0.2

[a] Mean ± SD, $n = 2$. [b] *sn*-1,3 (mol %) = [3 × total (mol %) − *sn*-2 (mol %)]/2. [c] Structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor. [d] Trace, <0.05 mol %. [e] Saturated FA. [f] Unsaturated FA.

Oil Stability Index (OSI) Analysis. The induction period of oxidation of oil sample was determined according to AOCS official method Cd 12b-92 (*15*) by using an oxidative stability instrument (Omnion Inc., Rockland, MA).

Weight Gain. Oil sample (2 ± 0.01 g) was weighed into glass vials and then incubated in a dry oven kept at 60 ± 2 °C. The weight gain of the oil sample was monitored at 5 day intervals for 40 days.

Volatile Compound Analysis. Thirty grams of oil sample was weighed into a 250 mL Erlenmeyer flask, and the top of the flask was sealed with a silicon stopper. The flask containing the sample was placed in a water bath maintained at 40 °C for 1 h. A stainless steel sorbent tube packed with 100 g of 60/80 mesh Tenax TA (Alltech Associates Inc., Deerfield, IL) was connected to the top of the flask through a silicon tube to absorb the volatile compounds, which were generated from the sample, in the headspace of flask. Purified air was passed into the flask through a column packed with activated charcoal during the extraction of volatile compounds from the sample. Extracted volatile compounds were desorbed at 250 °C for 5 min using an automated short-path thermal desorption/cryofocusing system (model TD-5, Scientific Instrument Services Inc., Ringoes, NJ) that sits directly on the injector area of the GC-MS. An Agilent Technologies 6890N gas chromatograph (Agilent Technologies Inc., Palo Alto, CA), equipped with a fused silica capillary column (HP-5ms, 30 m × 0.25 mm i.d., Agilent Technologies Inc.) and an Agilent Technologies 5973 mass selective detector, was used to analyze the volatile compounds. Helium gas was used as the carrier gas at a flow rate of 1 mL/min. The injection system was split 1:5. The column was initially held at 35 °C for 1 min, increased to 120 °C at the rate of 1.5 °C/min, held at 120 °C for 1 min, and then increased to 280 °C at the rate of 20 °C/min. The injector temperature was maintained at 225 °C. The volatile compounds were identified by comparing the mass spectral data with the reference in mass spectral libraries NIST 02 and Wiley 7.

Statistical Analysis. Statistical analysis was conducted with the SAS software package (*19*). One-way analysis of variance (ANOVA) was performed to determine the differences in sesame oil before and after acidolysis to produce SL. When F values for the ANOVA were significant, differences in means were determined using Duncan's multiple-range test as a procedure of mean separation ($P < 0.05$).

RESULTS AND DISCUSSION

Lipase Stability. Figure 2 shows the changes in total incorporation of CA into the TAG of sesame oil over the elution volume of reaction products during the acidolysis reactions and the regression equation on the relationship between them. Total incorporation of CA in the SL was shown to decrease linearly ($R^2 = 0.9048$) as the elution volume increased, indicating that the activity of lipase decreased as the reaction time increased. The half-life of the lipase was estimated from the regression equation in **Figure 2**, as a stability indicator of the lipase under the reaction conditions used in this study. The half-life of an enzyme is defined as the time it takes for the activity to reduce to half of the initial activity. Therefore, the total incorporation of caprylic acid at the time when the elution volume is zero was designated the initial activity (i.e., 40.2 mol %). As a result, total incorporation was expected to decrease to 20.1 mol % after 31.8 L of reaction products would have eluted. Because the flow rate of substrates fed to the reactor was 1.15 mL/min, the half-life of ≈19.2 days could be obtained for this lipase under the SL synthesis conditions used in this study.

FA Composition. FA compositions of sesame oil and SL are given in **Table 1**. Total incorporation of CA into TAG of sesame oil was 42.5 mol %. The level of acyl migration (CA found at the *sn*-2 position) in the SL was 3.1 mol %. Acyl migration is a major side eeaction occurring during lipase-catalyzed acidolysis and is well-known to be affected by several factors: reaction temperature, reaction time, reactor type, and reaction system (*20*, *21*). Kim and Akoh (*22*) showed that relatively lower temperature and higher substrate molar ratio (FA/target oil) were required to reduce the acyl migration as well as to minimize the decrease in total incorporation. From the standpoint of reactor type and reaction systems, a continuous packed bed reactor and solvent-free systems are preferred to a batch-type reactor and solvent systems (e.g., hexane) for the prevention of acyl migration (*20*, *23*, *24*). In these respects, we have used a higher substrate molar ratio (sesame oil/CA) of 1:6 and a lower reaction temperature of 45 °C as the reaction conditions for our current work as compared to the reaction conditions (e.g., 1:5 and 65 °C) of our previous works (*25*−*27*) to synthesize SLs by acidolysis of several vegetable oils with caprylic acid. When compared with SLs prepared in the previous studies mentioned above, the SL synthesized in the current study showed a relatively lower level of acyl migration. Because of this suppression of acyl migration, two major unsaturated FAs (oleic acid and linoleic acid) at the *sn*-2 position of original sesame oil remained almost intact at that position in the SL (**Table 1**). The FA profile at *sn*-1,3 positions was also obtained by calculation using the following equation: *sn*-1,3 (mol %) = [3 × total (mol %) − *sn*-2 (mol %)]/2. The result showed that the incorporation of CA into *sn*-1,3 positions, as we intended, by using Lipozyme RM IM (a *sn*-1,3-specific lipase), reached 62.3 mol % (**Table 1**).

Therefore, the results above indicate that we successfully produced MLM-type SL, in which *sn*-1,3 positions predominantly consist of CA, medium-chain FAs (MCFAs), and the *sn*-2 position is mostly composed of long-chain FAs (LCFAs) originally present in sesame oil.

Physical Properties. The color of SL was compared with

Table 2. CIE *L*a*b** Color of Sesame Oil and SL[a]

parameter	sesame oil	SL[b]
*L**	24.27 ± 0.08A	24.31 ± 0.04A
*a**	0.54 ± 0.03A	0.28 ± 0.02B
*b**	1.90 ± 0.06A	1.79 ± 0.04A
C	1.97 ± 0.07A	1.81 ± 0.04B
h°	74.27 ± 0.68B	81.30 ± 0.85A

[a] Mean ± SD, $n = 3$; means with the same letter in the same row are not significantly different ($P < 0.05$). [b] Structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

Table 3. Viscosity of Sesame Oil and SL (Millipascal Seconds)[a]

temperature (°C)	sesame oil	SL[b]
5	110.4 ± 0.1A	105.6 ± 0.1B
15	76.0 ± 0.2A	73.6 ± 0.2B
25	54.5 ± 0.1A	53.0 ± 0.2B
35	40.1 ± 0.1A	36.5 ± 0.2B

[a] Mean ± SD, $n = 3$; means with the same letter in the same row are not significantly different ($P < 0.05$). [b] Structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

that of original sesame oil by measuring CIE color values (**Table 2**). Both oils have low *L** (lightness) value and positive *a** (redness) and *b** (yellowness) values with a *h*° (hue angle) value of >45°, meaning that they have dark reddish yellow (i.e., dark brown) colors. However, the *a** value of SL was significantly ($P < 0.05$) smaller than that of sesame oil, resulting in a significant ($P < 0.05$) decrease in the *C* (chroma) value of SL. This result suggests that some reddish pigments might have been removed from sesame oil during SL synthesis or purification steps. We surmise that the short-path distillation step to reduce the FFAs content of SL also removed some Maillard reaction compounds, which were generated during the roasting step of sesame seeds and responsible for the red color of sesame oil.

The viscosities of sesame oil and SL at different temperatures are shown in **Table 3**. As the temperature increased, the viscosities of both oils decreased, respectively. SL was significantly ($P < 0.05$) less viscous than sesame oil over the range of temperature investigated. The lower viscosity of SL is due to the decrease in the molecular weight of SL arising from the replacement of some of the original LCFAs in sesame oil with CA (MCFA).

Melting and crystallization behaviors of sesame oil and SL were evaluated by DSC thermal profiles (**Figure 3**). Edible oil is a complex molecular system comprising predominantly diverse TAG species with a few diacylglycerols (DAGs), monoacylglycerols (MAGs), and FFAs. Therefore, the melting and crystallization of oils containing mixed FAs do not occur at a particular temperature, but over a wide temperature range. **Figure 3A** shows the DSC melting curve of sesame oil and SL. Sesame oil had four melting peaks overlapping each other, whereas SL showed only two melting peaks. The smaller number of melting peaks of SL is shown to be due to the decrease in the diversity of TAG species of SL arising from the replacement of several kinds of LCFA in sesame oil with a considerable amount of CA (42.5 mol % from **Table 1**). This substitution is also shown to induce the formation of one distinct big melting peak 2 in SL, unlike sesame oil, which shows no large difference in the peak sizes. The melting ranges of sesame oil and SL were also compared to each other. First, each melting peak was labeled 1, 2, 3, and 4 (for sesame oil) and 1 and 2 (for SL), in the order of low to high temperatures, respectively, as shown in **Figure 3A**. Then, the melting onset temperature

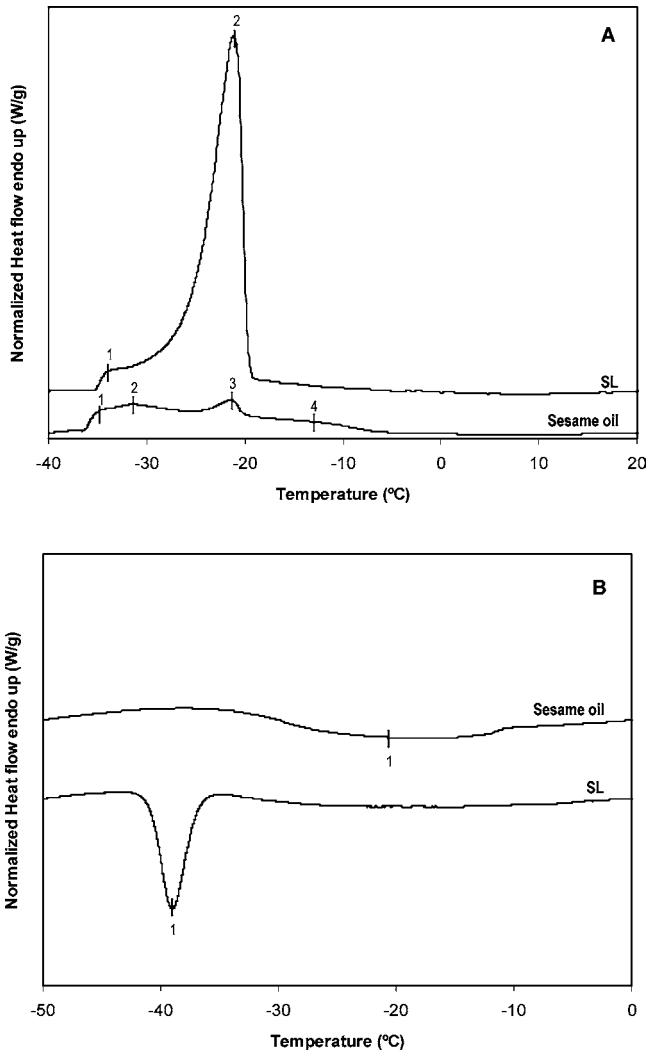

Figure 3. DSC melting (**A**) and crystallization (**B**) profiles of sesame oil and SL. SL indicates the structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

(T_o) of peak 1 and the melting completion temperature (T_c) of peak 4 were considered as the temperatures at which the melting starts and ends, respectively, for sesame oil. In a similar manner, T_o of peak 1 and T_c of peak 2 were considered as the temperatures of melting starting and ending, respectively, for SL. **Table 4** shows that both sesame oil and SL started to melt at almost the same temperature (≈−35 °C), but the melting of SL was completed at significantly ($P < 0.05$) lower temperature than that of sesame oil. **Table 4** also shows that SL exhibited ≈3 times higher overall melting enthalpy (ΔH) than sesame oil, indicating that more energy was necessary to drive the melting of SL. We concluded that the higher ΔH value of SL is related to the higher saturation degree of SL than that of sesame oil. This is because the most abundant FA in SL is CA (SFA), having a linear structure unlike the sesame oil, which is predominantly composed of USFA having bent structure. TAG molecules were packed closer in SL than in sesame oil. This compact arrangement of TAG molecules in SL means a larger amount of energy was required for SL melting. The DSC crystallization curves of sesame oil and SL are presented in **Figure 3B**. Both oils showed only one crystallization peak. Therefore, the crystallization T_o and T_c of each peak 1 could be considered as the temperature at which the crystallization starts and ends, respectively, for sesame oil and SL, respectively. **Table 4** shows that SL was crystallized (or solidified) at

Table 4. Comparison of DSC Melting and Crystallization Properties of Sesame Oil and SL[a]

property	sesame oil	SL[b]
melting		
T_o[c] (°C)	−35.2 ± 1.8A	−34.9 ± 0.4A
T_c[d] (°C)	−5.4 ± 0.3A	−18.6 ± 0.5B
ΔH[e] (J/g)	21.4 ± 2.1B	66.1 ± 1.1A
crystallization		
T_o[f] (°C)	−10.7 ± 0.1A	−36.7 ± 0.4B
T_c[g] (°C)	−30.6 ± 2.1A	−40.5 ± 0.5B
ΔH[h] (J/g)	−10.2 ± 1.9A	−49.1 ± 1.1B

[a] Mean ± SD, $n = 3$; means with the same letter in the same row are not significantly different ($P < 0.05$). [b] Structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor. [c] Melting onset temperature; melting onset temperature of peak 1 was used for sesame oil and melting onset temperature of peak 1 was used for SL as shown in **Figure 3A**. [d] Melting completion temperature; melting completion temperature of peak 4 was used for sesame oil and melting completion temperature of peak 2 was used for SL as shown in **Figure 3A**. [e] Melting enthalpy; overall melting enthalpies of peaks 1–4 were used for sesame oil and overall melting enthalpy those of peaks 1 and 2 were used for SL as shown in **Figure 3A**. [f] Crystallization onset temperature. [g] Crystallization completion temperature. [h] Crystallization enthalpy.

Table 5. Chemical Properties of Sesame Oil and SL[a]

property	sesame oil	SL[b]
free fatty acid (%, oleic acid)	0.7 ± 0.0A	0.7 ± 0.0A
unsaponifiable matter (%)	1.2 ± 0.3A	1.1 ± 0.1A
smoke point (°C)	167.3 ± 1.2B	176.3 ± 4.0A
saponification value	193.7 ± 2.5B	236.5 ± 0.1A
iodine value	118.0 ± 2.1A	93.2 ± 0.9B

[a] Mean ± SD, $n = 2$ (for smoke point, $n = 3$); means with the same letter in the same row are not significantly different ($P < 0.05$). [b] Structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

significantly ($P < 0.05$) lower temperature than sesame oil. Both **Figure 3B** and **Table 4** also show that the solidifying process of SL occurred at a narrower temperature range as compared to that of sesame oil, which occurred at a much wider temperature range. This narrower temperature range of SL crystallization is also shown to be related to the smaller diversity in TAG species of SL as mentioned above.

Chemical Properties. Several important chemical characteristics of sesame oil and SL are listed in **Table 5**. Original sesame oil contained 0.7% FFA (**Table 5**). Roasted sesame oil is known to contain a relatively large amount of FFAs as compared to other RBD vegetable oils because the refining steps were absent (*6*). In the acidolysis reaction to produce SL, the purification step to remove the FFAs is indispensable because a large amount of FFAs remains in the SL after the reaction. In our current work, the FFA content of SL was reduced to 0.7%, which was the same level as that of the original sesame oil, using a short-path distillation technique.

Table 5 also shows that no significant ($P < 0.05$) difference was found in unsaponifiable matter content between sesame oil and SL. This result indicates that the short-path distillation step removed few unsaponifiable matters from SL. The unsaponifiable matter of sesame oil is known to consist mostly of tocopherols, phytosterols, and sesame lignans (*6*). The effect of the short-path distillation step on each unsaponifiable component above is discussed later in this paper.

The smoke points of sesame oil and SL are compared in **Table 5**. SL had a significantly ($P < 0.05$) higher smoke point (≈176 °C) compared to that of the original sesame oil (≈167 °C). RBD oils usually have higher smoke points than unrefined oils because pigments and unsaponifiable matters are removed during the refining process (*7*). The short-path distillation step in the current study is a kind of physical refining. Therefore, the higher smoke point of SL might be due to the removal of some unsaponifiable matters during the short-path distillation of SL. However, we noted that the unsaponifiable matter content of SL was not significantly ($P < 0.05$) different from that of the original sesame oil as mentioned. On the other hand, it is known that in order for an edible oil to be used as a frying oil, its smoke point should be >170 °C (*7*, *28*). Therefore, on the basis of smoke point values, this result indicates that the SL may be used as a frying oil unlike roasted sesame oil. Because the SL contained a considerable amount of CA, which has a pungent odor and an unpleasant rancid taste, the sensory aspects of SL would also need to be evaluated before its use as a frying oil.

Table 6. Tocopherol, Phytosterol, and Sesame Lignan Contents of Sesame Oil and SL (Milligrams per 100 g)[a]

component	sesame oil	SL[b]
tocopherol		
α	93.7 ± 2.5A	93.0 ± 3.5A
β		
γ	15.8 ± 0.0A	15.3 ± 0.0B
δ	0.6 ± 0.0A	0.5 ± 0.0B
total	110.1 ± 2.5A	108.8 ± 3.5A
phytosterol		
brassicasterol	9.4 ± 0.5A	9.6 ± 0.2A
campesterol	65.6 ± 5.4A	74.6 ± 5.8A
stigmasterol	25.1 ± 2.2A	28.2 ± 2.4A
β-sitosterol	260.5 ± 18.6A	293.1 ± 25.7A
Δ^5-avenasterol	20.3 ± 1.6A	24.8 ± 1.3A
Δ^7-stigmasterol	5.0 ± 0.2A	5.2 ± 0.6A
Δ^7-avenasterol	9.3 ± 1.1A	8.6 ± 0.2A
total	395.2 ± 27.3A	440.0 ± 34.3A
sesame lignan		
sesamol	18.7 ± 0.8A	2.6 ± 0.1B
sesamin	75.6 ± 4.3A	75.9 ± 5.1A
sesamolin	22.1 ± 1.3A	21.7 ± 1.3A
total	118.7 ± 4.1A	100.1 ± 6.2B

[a] Mean ± SD, $n = 3$ (for tocopherol, $n = 2$); Means with the same letter in the same row are not significantly different ($P < 0.05$). [b] Structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

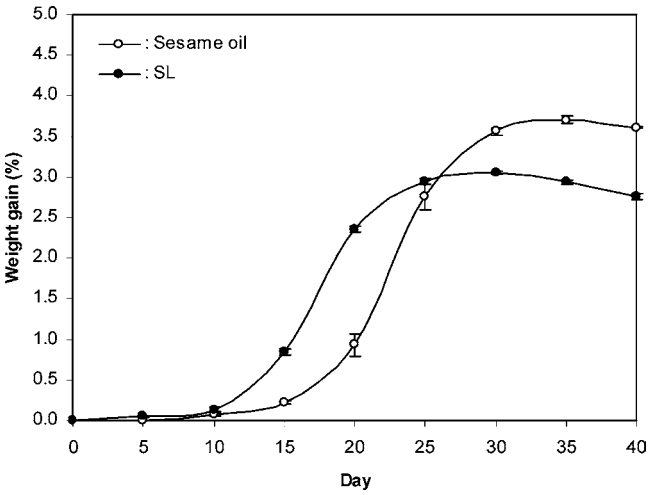

Figure 4. Oxidative stability of sesame oil and SL (weight gain method). SL indicates the structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

Table 7. Oil Stability Index of Sesame Oil and SL[a]

	oil stability index (h, at 120 °C)
sesame oil	3.2 ± 0.1A
SL[b]	2.4 ± 0.0B

[a] Mean ± SD, $n = 3$; means with the same letter in the same column are not significantly different ($P < 0.05$). [b] Structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

Saponification value (SV) was measured as an indication of the average molecular weight of oil sample (**Table 5**). According to the official standards of sesame oil adopted by the Codex Alimentarius Comission, sesame oil should have a SV of 187−195 SV (*29*). The SV of the sesame oil used in this study was 193.7 and within the Codex range, whereas, as expected, the SL showed a SV of 236.5, significantly ($P < 0.05$) higher than that of sesame oil, meaning that the molecular weight of SL is lower than that of sesame oil.

Iodine value (IV) was measured as an indication of the unsaturation degree of oil sample (**Table 5**). Sesame oil IV of 118.0 was within the Codex range of 104−120 (*29*), whereas the SL showed a significantly ($P < 0.05$) lower IV (93.2), meaning that the SL was more saturated than the sesame oil.

Minor Components. Sesame oil contains a relatively large amount of unsaponifiable matter, mostly tocopherols, phytosterols, and sesame lignans as mentioned before (*6*). In this section we examine the change in the content of each minor component between sesame oil and SL and discuss the effect of the short-path distillation step, which was our purification process for SL, on the minor components content during the production of SL.

Table 6 shows the tocopherol contents of sesame oil and SL. α-Tocopherol was the most abundant in both oils, followed by γ- and δ-tocopherols in that order. β-Tocopherol and tocotrienol isomers were not detected in either oil. No significant differences ($P < 0.05$) were found in the total content of tocopherols between sesame oil and SL. There were significant ($P < 0.05$) differences in the contents of γ- and δ-tocopherols; these differences arose from the very high precision (i.e., standard deviation was 0) of our analysis technique and were shown to be negligible in absolute terms. This result indicates that the tocopherol content was not changed during the short-path distillation step for SL purification. Tocopherols are known to be retained throughout the refining process of edible oils, although there is slight loss during the deodorization step (*30*). Therefore, our result indicates that short-path distillation also has no effect on the tocopherol content of oil, similar to the commercial refining process. On the other hand, the total tocopherol content of roasted sesame oil is known to be generally in the range of 40−70 mg/100 g (*5*, *6*). In addition, it was reported that the tocopherols found in sesame oil are predominantly γ-tocopherol (96−98%) and α-tocopherol (2−3%) with trace amounts of β- and δ-tocopherols (*5*, *6*). However, our oil samples showed a higher total tocopherol content (≈110

Table 8. Volatile Compounds of Sesame Oil

- pyrazines
  - 2-methylpyrazine
  - 2-isopropylpyrazine
  - 2-ethyl-5(or 6)-methylpyrazine
  - trimethylpyrazine
  - 2-propylpyrazine
  - acetylpyrazine
  - 2-isopropenylpyrazine
  - 3-ethyl-2,5-dimethylpyrazine
  - 2-acetyl-5-methylpyrazine
  - 2-acetyl-6-methylpyrazine
  - 5*H*-5-methyl-6,7-dihydrocyclopentapyrazine
- furans
  - 2-furfural
  - 5-methyl-2-furfural[a]
  - methyl 2-furoate
  - 2-pentylfuran
  - 2-furylmethyl acetate
- nitrogen-containing compounds
  - 2-methylpyridine
  - 2-ethylpyridine
  - 4,6-dimethylpyrimidine
  - trimethyloxazole
  - *N*,*N*-dimethylethanamide
  - 3,4-dimethylpyridine
  - 2,3(or 4)-dimethylpyridine
  - 3-ethylpyridine
  - 2-hexylpyridine
  - indole
- aldehydes and ketones
  - hexanal[a]
  - 2-hexenal[a]
  - heptanal[a]
  - 2-heptenal
  - benzaldehyde[a]
  - 2-octenal[a]
  - nonanal[a]
  - 2-nonenal[a]
  - 2,4-decadienal
  - 2-heptanone
- aldehydes and ketones (continued)
  - 2-octanone[a]
  - acetophenone
  - 2-nonanone
- alcohols
  - pentanol
  - 2(or 3)-furanmethanol
  - hexanol[a]
  - 1-octen-3-ol[a]
  - 2-ethyl-1-hexanol[a]
  - 3,5-octadien-2-ol
- acids
  - octanoic acid[a]
- hydrocarbons
  - undecane[a]
  - ethylbenzene
  - xylene
  - styrene
  - 1,3-dimethylbenzene
  - propylbenzene
  - 1,2,3(or 4)-trimethylbenzene
  - limonene
  - 3-ethyl-2-methyl-1,3-hexadiene
  - 3,7-dimethyl-1,3,6-octatriene
  - butylbenzene
  - pentylbenzene
  - dodecane
  - tridecane
  - tetradecane
- phenols
  - 2-methoxyphenol[a]
  - 2-methoxy-4-vinylphenol
- sulfur-containing compounds
  - 4(or 5)-methylthiazole
  - 4-methylthiazole
  - 2,4(or 5)-dimethylthiazole
  - 5-ethylthiazole
  - 4,5-dimethylthiazole
  - 2-acetyl-4-methylthiazole
  - benzothiazole[a]

[a] Volatile compound also found in structured lipid.

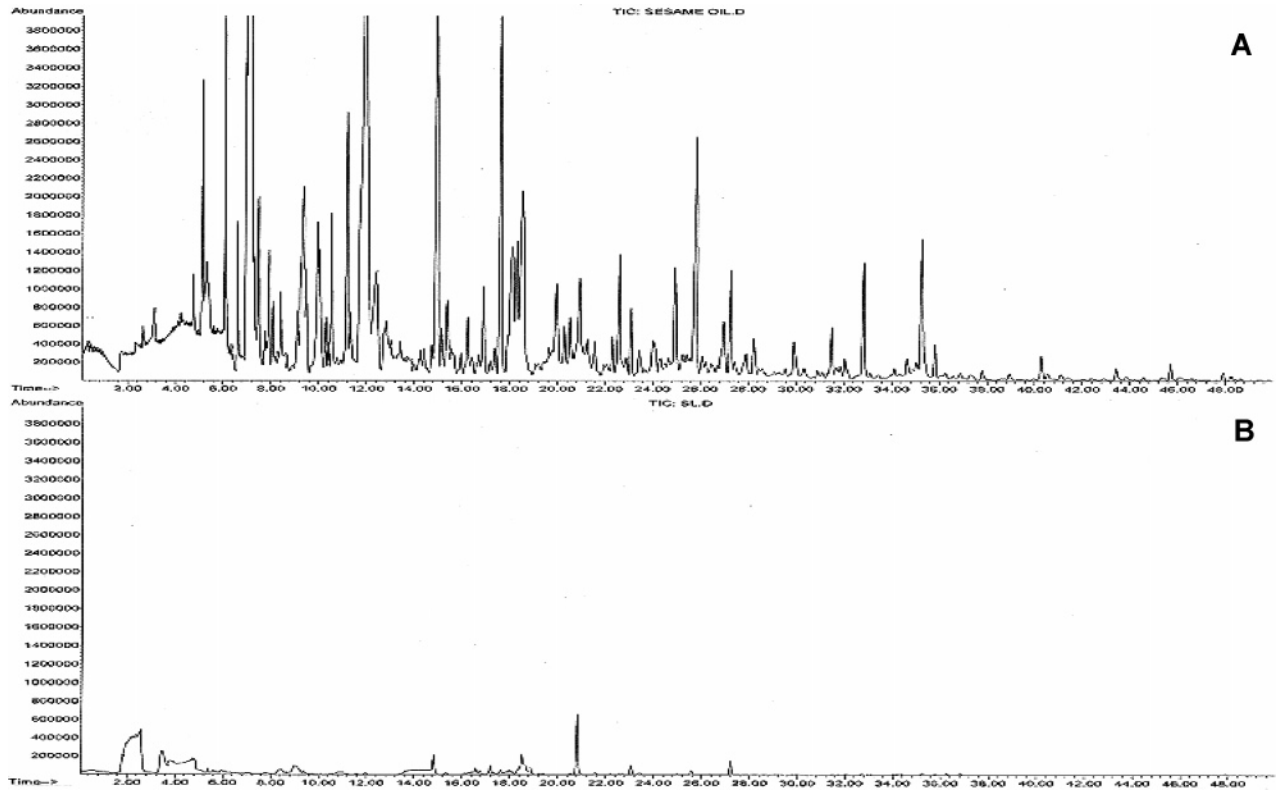

Figure 5. Total ion chromatograms of volatile compounds of sesame oil (**A**) and SL (**B**). SL indicates the structured lipid prepared by acidolysis of sesame oil with caprylic acid in a bench-scale continuous packed bed reactor.

mg/100 g) and the content of α-tocopherol was much higher than that of γ-tocopherol as compared to other studies above (**Table 6**). We assumed that the reason was that extra α-tocopherol may have been added as an antioxidant to the sesame oil by the manufacturer during packaging.

Table 6 lists the phytosterol contents of sesame oil and SL. β-Sitosterol was the most abundant in both oils, followed by campesterol and stigmasterol. There were no significant differences ($P < 0.05$) in the content of the phytosterol analogues as well as the total phytosterol content of sesame oil and SL. This result indicates that the phytosterol content was also not affected by the short-path distillation process as for tocopherol.

Table 6 also shows the contents of representative sesame lignan compounds, such as sesamol, sesamin, and sesamolin, of sesame oil and SL. Sesamin was found most abundantly in both oils, followed by sesamolin and sesamol. There were no significant differences ($P < 0.05$) in the content of sesamin and sesamolin between sesame oil and SL. However, SL showed a significantly ($P < 0.05$) lower content of sesamol than sesame oil. This result indicates that sesamin and sesamolin were not removed during the short-path distillation step, whereas sesamol was lost under the conditions of the short-path distillation process used in our study. Such loss of sesamol can be explained by the fact that sesamol is a relatively lower molecular weight compound (MW 138.1) than sesamin (MW 354.4) and sesamolin (MW 370.3). Namiki (*5*) also mentioned that negligible amounts of sesamol were found in the RBD sesame oil because the commercial deodorizing process tends to remove most of the sesamol in sesame oil. On the other hand, our roasted sesame oil sample was shown to contain relatively smaller amounts of sesame lignans as compared to other roasted sesame oils used in another published work (*7*). For example, the roasted sesame oil used in our study contained only 22.1 mg of sesamolin in 100 g of oil, whereas Kim and Choe (*7*) reported that the concentration of sesamolin in their oil sample was ≈200 mg/100 g of oil. The sesamin content of our oil sample was also lower than that of their oil sample (75.6 vs 466.0 mg/100 g). Such smaller sesame lignan contents of our oil samples may be related to their relatively decreased oxidative stability, as discussed below, compared to the superior oxidative stability of roasted sesame oil reported in other published works (*5*, *6*).

Oxidative Stability. Roasted sesame oil has been known to be very stable to oxidative deterioration compared to other vegetable oils due to the existence of well-known antioxidants, such as sesame lignans and tocopherols, as well as potential and unidentified antioxidants, such as brown color pigments generated by the Maillard reaction during the roasting step of sesame seeds (*5*).

The induction period of oxidation in SL, which was measured according to the traditional weight gain method (**Figure 4**) and the oil stability index (OSI) (**Table 7**), was shorter than that of sesame oil. **Figure 4** also shows that SL displayed a smaller weight gain than sesame oil after ≈25 days despite the shorter induction period. This could be related to the fact that SL was more saturated than sesame oil as indicated in **Tables 1** and **5**. These results indicate that the oxidative stability of SL was lower than that of sesame oil. We believe that such lower oxidative stability of SL, when compared to the original sesame oil, arose from two possibilities: First, the loss of sesamol during the short-path distillation process, as mentioned above, might decrease the oxidative stability of SL even though some researchers questioned the antioxidative activity of sesamol and reported that other kinds of sesame lignan compounds, such as sesamolinol and sesaminol, were more efficient antioxidants than sesamol in sesame oil (*5*). Second, we may have removed some reddish pigments that may have antioxidative activity during the short-path distillation process as seen from the results of color measurement (**Table 2**). On the other hand, our roasted sesame oil had a shorter OSI induction period of 3.2 h at 120 °C than the 6.0 h of the Codex standard at the same temperature

(*29*) (**Table 7**). This result is also due to the lower levels of sesame lignans content in our oil sample compared to those in other researchers' oil samples (*7*).

Volatile Compounds. Roasted sesame oil is used widely in Eastern Asian countries as an important flavoring agent due to its characteristic roasted flavor (*6*, *7*). The characteristic roasted flavor of the oil is mainly developed by thermochemical reactions, such as Maillard reactions, during the roasting step of the sesame seed at 180−200 °C, before it is expelled from the seed (*5*). So far, ≈220 kinds of volatile compounds have been identified in the oil. These compounds include pyrazines, furans, other nitrogen-containing compounds, carbonyl compounds (aldehydes and ketones), alcohols, lactones, esters, acids, hydrocarbons, and sulfur-containing compounds. Among these compounds, some pyrazines, which are generated by Maillard reactions, and some furan compounds are believed to contribute to the representative roasted flavors of sesame oil (*5*, *31*). Apparently, no single key compound responsible for the characteristic roasted flavor has been found yet (*5*).

Table 8 lists 70 volatile compounds identified from our sesame oil: 11 pyrazines, 5 furans, 10 other nitrogen-containing compounds, 13 aldehydes and ketones, 6 alcohols, 1 acid, 15 hydrocarbons, 2 phenols, and 7 sulfur-containing compounds. Most of these compounds including pyrazines and furans were not found in SL except for a few compounds, such as aldehydes, ketones, and alcohols, which are probably not critical contributors to the characteristic flavor of sesame oil (**Table 8**). Moreover, **Figure 5** shows that the content of volatile compounds in SL was negligible compared to that of sesame oil. These results indicate that, as expected, most volatile compounds were removed from SL during the short-path distillation step, resulting in the loss of characteristic sesame oil flavor in SL. Therefore, we suggest that SL would not be able to substitute for original sesame oil in dishes that require the characteristic flavor of sesame oil. However, the flavorless character of SL might make it easy to be used as an ingredient for incorporation into other food products.

In conclusion, the characteristics of roasted sesame oil based SL, which was produced in a bench-scale continuous packed bed reactor, were different from those of the original sesame oil in many aspects, such as physical and chemical properties, the composition of several components (FAs, sesame lignans, volatile compounds), and oxidative stability except for the contents of some components (tocopherols, phytosterols).

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