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Model Studies on Volatile Release from Different Semisolid Fat Blends Correlated with Changes in Sensory Perception

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ABSTRACT: The effect of dispersed aqueous droplets in water-in-oil (W/O)-emulsion semisolid fats on aroma release and sensory perception was investigated on margarine models where model aroma substances were added. Aroma release from W/O-emulsion fat blends and bulk fat blends with added monoglycerides combining different fatty acids of various short-chain free fatty acids, methylketones, esters, and lactones were measured using headspace solid phase microextraction−gas chromatography/mass spectrometry (SPME−GC/MS), and their perception profiles were evaluated by sensory analysis. The presence of aqueous phase in a fat blend significantly reduced the headspace concentrations of butanoic acid and hexanoic acid, and also decreased the perceived intensity of total aroma and cheesy aroma. The aroma release of methylketones, esters, and lactones from the W/O-emulsion fat blends increased with increasing carbon chain length of the volatile molecules. The intensity of aroma perception in a W/O-emulsion fat blend depended on the melting point of the fatty acids (oleic, palmitic, stearic, and behenic) of the monoglyceride used as an emulsifier. Thus, aroma release from a W/O-emulsion semisolid fat blend was influenced by interactions between aroma volatiles and the dispersed aqueous droplets and by their viscoelastic properties.

KEYWORDS: emulsion, aroma, flavor release, sensory analysis, SPME−GC/MS, storage modulus

INTRODUCTION

The acceptability of a food item depends on its sensory qualities and, in particular, its flavor.[1,2] Important to the perception of aroma is the presence of aromatic compounds, which are organic molecules whose vapor pressures are sufficiently high for the molecules to be partially present in the gas phase. The concentration of free volatile substances in the gas phase depends on several factors, including physicochemical properties of matrix, concentration, and interactions with other food constituents.

The composition of the food matrix is known to affect the sensory perception of flavor. The behavior of aromatic compounds in complex multiphase media is of great interest for many researchers, because the nature of volatile compounds and the composition and structure of food products play important roles on the aroma release.[3,4]

Fat is an important aroma carrier and flavor-release modulator, and reportedly influences qualitative, quantitative, and temporal perceptions of flavor.[5,6] Thus, the fat content affects the perceived intensity of flavor and can also affect the quality of the aroma of an emulsion as well as the duration of perception.[7]

The release of volatile compounds is influenced by the interactions at the interface between the lipid and aqueous phases in a two-phase system.[8,9] In foods, hydrophilic aromas are concentrated in the aqueous phase, which greatly reduces their partitioning into the air and lipid phases. However, characterization of the affinity of a volatile compound for the different phases (vapor, aqueous, and lipid) in bulk solutions of a lipid food product is not sufficient to explain the perception of aroma during eating, especially for the time profiling, which measures the rate of aroma release from food products.[10] This is the reason why studies of the physicochemical interactions between the volatile and other constituents of the matrix have been so thoroughly reviewed. Various techniques have been developed to allow further study of the release of volatiles from food, especially during eating.[11−14]

Margarine and fat spread are water-in-oil (W/O) emulsions consisting of semisolid fats, water, emulsifiers, and other ingredients.[15] Semisolid fats include high-melting fats that form crystal network structures and improve the physical properties of these products. Table spreads are multiphase colloidal systems consisting of an aqueous phase dispersed as droplets within a continuous oil phase and a fat crystal network. The fat crystal network prevents destabilized water droplets from coalescing with crystallized emulsifiers adsorbed at the oil−water interface.[16,17] The crystals interact with each other to form a three-dimensional network that lends the spread a hard, solid character. These rheological behaviors have been determined by the evaluation of storage moduli, solid fat content, optical anisotropy, and additional parameters.[18,19]

Emulsifiers such as monoglycerides, lecithin, sucrose, and sorbitan fatty acid esters are often added to fat products to increase the stability of the dispersed phase and to control the fat crystal properties and morphology. Monoglycerides are widely used in the margarine manufacturing industry to increase the stability of the W/O emulsion. The key to preparing a stable emulsion is to form small aqueous droplets in a continuous lipid phase with an adequate emulsifier and viscosity to prevent coalescence of the aqueous droplets. Many studies have reported aroma release from the O/W emulsions and the interactions between aromatic compounds and emulsions. However, little is yet known about the behavior of aromatic compounds in the W/O emulsion systems, particularly those with crystals in the semisolid fat matrix.

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Table 1. Formulation of Fat Blend Samples

%	bulk fat blends	W/O emulsion fat blends
fully hydrogenated rapeseed oil	2.840 (2.0[a])	2.0
palm oil	28.410 (20.0[a])	20.0
soybean oil	68.190 (48.0[a])	48.0
monoglyceride[b]	0.500	0.500
β-carotene	0.001	0.001
water	0.000	29.400
total[c]	100	100

[a] Ratio in total oil phase. [b] Oleate, palmitate, stearate, behenate. [c] 0.1% flavor mix was added to fat blends.

Table 2. Fatty Acid Composition of the Total Fats

fatty acid	%
C12:0	0.1
C14:0	0.3
C16:0	19.5
C18:0	5.3
C18:1 cis	26.7
C18:2 cis	38.9
C18:2 trans	0.2
C18:3 cis	4.7
C18:3 trans	0.7
C20:0	0.6
C20:1 cis	0.2
C22:0	1.6
Others	1.2
Total	100.0

Despite previous studies on palm oil-based blend, information is critically lacking in understanding the aroma release from palm oil-based blend. Our objective in this study is to investigate the influence of dispersed aqueous droplets in the W/O-emulsion palm oil-based blends and the effect of monoglyceride fatty acids on the aroma release. To this end, we first prepared model W/O emulsions and bulk semisolid fats with added monoglycerides and model aromas; we then performed sensory evaluations, headspace solid phase microextraction−gas chromatography/mass spectrometry (SPME−GC/MS) determinations of aroma volatiles, and viscoelastic analyses. Our results provide important information for the selection of emulsifiers and aroma formulations as they affect the acceptability of margarines and shortenings containing palm oil-based fat, in particular low-trans fatty acid types.

MATERIALS AND METHODS

Preparation of Fat Blends. Bulk fat blends (100% fat) and W/O-emulsion fat blends (70% fat) were prepared using the major ingredients listed in Table 1. Palm oil-based fat blend was prepared from soybean oil, palm oil, and fully hydrogenated rapeseed oil; trans fatty acid content of this fat blend was <1.0%. The main saturated fatty acids in the fat blends were palmitic acid (C16:0) and stearic acid (C18:0), listed in Table 2. A constant amount (0.5 wt %) of monoglyceride (either oleate, palmitate, stearate, or behenate) was added. The distilled monoglycerides were supplied by Riken Vitamin Co (Tokyo, Japan). The fatty acid composition of the monoglycerides is listed in Table 3. The melting points of the acids were as follows: oleic acid 14.0 °C, palmitic acid 63.1 °C, stearic acid 69.6 °C, and behenic acid 81.5 °C. The W/O-emulsion fat blends

Table 3. Fatty Acid Composition of Monoglycerides Used in This Study

%	oleic acid MG	palmitic acid MG	stearic acid MG	behenic acid MG
C12:0	0.0	0.3	0.0	0.6
C14:0	0.0	1.1	0.1	0.0
C16:0	3.8	43.6	10.8	4.6
C18:0	3.1	53.8	86.3	9.9
C18:1c	85.3	0.0	0.1	0.0
C18:1t	0.3	0.4	0.8	0.2
C18:2c	5.4	0.0	0.1	0.2
C20:0	0.3	0.5	0.7	4.1
C22:0	0.9	0.1	0.7	79.1
others	0.9	0.2	0.4	1.3
total	100.0	100.0	100.0	100.0

were prepared according to the procedure of Hui.[15] The palm oil-based fat blends were melted and mixed at 60 °C, emulsifiers were added with gentle agitation, and the aqueous phase was added to the fat phase with agitation at 50 rpm for 10 min to form a W/O emulsion with mixer (OFT, Nichiraku-Kikai Co, Saitama, Japan). Model aroma mix was added, and the emulsion was rapidly cooled from 60 to 10 °C by means of a heat exchanger (Schröder GmbH & Co, Germany) to form a semisolid fat. Model aroma mix was obtained from commercial source (Soda Aromatic Co., Ltd., Tokyo, Japan). Bulk fat blends were prepared by a procedure similar to W/O-emulsion fat blends except without addition of water phase. All reference aroma compounds and standard compounds were purchased from Wako Pure Chemicals Industries, Ltd. (Tokyo, Japan).

Fatty Acid analysis. The fatty acid compositions of the fat blends and monoglycerides were determined according to AOCS official Ce 1c-89.[20] A GLC using HP5890 (Agilent Technologies, Inc., Palo Alto, CA, USA) with SP-2560 column (Supelco, Inc., Bellefonte, PA, USA) and equipped with a FID operated at 300 °C was employed. The injector port temperature was held at 250 °C, and analyses performed by ramping from 180 to 200 at 2 °C/min after an initial holding time of 45 min at 180 °C.

Headspace Solid-Phase Microextraction (SPME). Headspace volatiles of fat blends were evaluated by SPME−GC/MS. All fat blends (1 g) were loaded in 20 mL vials with steel flat tops containing silicone faced in PTFE (Supelco, Bellefonte, PA, USA). 50 mg of internal standard solution (1-pentanol at 10 ppm in MCT, Sigma-Aldrich, Milwaukee, WI, USA) was added to each vial to control for analysis variability with sample. Sample vials were placed in a constant-temperature bath at 37 °C for 10 min to establish equilibrium between the headspace and the sample.[21] A SPME device equipped with a fiber assembly coated with a Stableflex 50/30 μm DVB-Carboxen-PDMS fiber film (Supelco, Bellefonte, PA, USA) was used to sample the volatiles. The SPME fiber was inserted into the sample container through the septum, and then exposed to the headspace for 60 min. These analyses were run in duplicate.

Gas Chromatographic (GC) Analysis. Volatile headspace compounds from the samples were thermally desorbed in the injection port (250 °C), in splitless mode, of a GC (6890N, Agilent Technologies, Santa Clara, CA, USA) coupled to a mass spectrometer (MS; 5973, Agilent Technologies, Santa Clara, CA). Volatile compounds were separated on a GC column (length 50 m, i.d. 0.32 mm, thickness 0.52 μm; DB-5, Agilent J&W). The column temperature was held at 37 °C for 8 min during injection, increased at a rate of 4 °C/min to 190 °C, then increased at a rate of 40 °C/min to 280 °C and held for 8 min. Carrier gas (helium) flow rate was 2.4 mL/min. Electron impact mass spectrometric data from m/z 30 to 300 were collected with an ionization voltage of 70 eV. Relative abundance of compounds in headspace was calculated using the calculated recovery of the internal standard concentration to determine relative concentrations of

each compound. Volatile compounds were identified using the NIST 2005 library of spectra and retention indices. Retention indices were calculated using an alkane series (GL Science Inc., Tokyo, Japan).

Sensory Evaluation. Sensory evaluations were performed with a trained panel of four females and two males (age 30−45 years), selected for their capacity to recognize, memorize, and discriminate aroma and to describe their perceptions when testing the semisolid fat blends. They had been trained in sensory vocabulary and methodology, and had extensive experience with a variety of foods. Seven sensory attributes were evaluated: total aroma intensity, top aroma, last aroma, buttery aroma, fruity aroma, sweet aroma, and cheesy aroma. Panelists were trained to evaluate the intensity of each attribute, compared to the standard sample, on a 10 cm continuous 10-point scale ranging from "weaker in intensity" at the left to "no difference" at the center to "stronger in intensity" at the right. In this evaluation, top aroma indicated time to first perception of aroma, and panelists were instructed on the scale ranging from "shorter time" at the right to "longer time" at the left. The last aroma indicated time for overall perception of aroma until the extinction time, and panelists were instructed on the scale ranging from "longer time" at the right to "shorter time" at the left. Samples were presented in a random sequence, and water was used for cleaning the palate between the samples. Panelists were not told what parameters of each sample were being changed. The standard sample was a bulk fat blend with added oleic acid monoglyceride.

Solid Fat Content. Solid fat content (SFC) was determined using an NMR analyzer (mq20, Bruker Optik GmbH, Ettlingen, Germany). Samples were obtained by inserting plastic cylinders into the sample at random locations by hand. The filled cores were removed and deposited directly into NMR tubes (length 18 cm, i.d. 0.8 cm). SFC values were measured at 5 and 37 °C. All measurements were performed in triplicate.

Droplet Size Distributions. The droplet distributions of the W/O-emulsion fat blends were evaluated using scanning electron microscopy (SEM). Samples were observed using a cryo-SEM (S-4300, Hitachi High Technologies Corp., Tokyo, Japan) with an accelerating voltage of 2 kV and a magnification of ×3000. Numerous images were acquired, and the images of a typical field of each sample were captured. Image analysis software (A-zou Kun, Asahi Kasei Engineering Co., Tokyo, Japan) was used to calculate the droplet diameter of four representative images for each sample.

Dynamic Compression Experiments. Dynamic compression experiments were performed according to the method of Rohn et al.[18] to determine the influence of temperature on the textural properties. The storage modulus G' obtained from constant-frequency dynamic compression experiments was selected as a rheological parameter because solid-like behavior has been shown to be well described by the storage modulus.[22] A rheometer (ARES, TA Instruments, New Castle, DE, USA) was used to perform dynamic compression experiments between parallel plates. The specimens were placed between the plates and slightly compressed to achieve contact over the entire surface. The gap between the plates was adjusted to 2.0 mm. The lower plate was thermostated by means of a rheometer circulator (FS18, Julabo Labortechnik GMBH, Seelbach, Germany). Small strain frequency (1.0 rad/s) and strain (0.5%), which have a linear viscoelastic region, were applied at a rate of 1 °C/min at temperatures in the range 5−50 °C. All tests were run in duplicate.

Statistical Analyses. Data were analyzed by two-way ANOVA tests, followed by Ryan-Einot-Garbriel-Welsch tests. Statistical analyses were performed using PASW statistic 18 (SPSS Japan Inc., Tokyo, Japan) with $P < 0.05$ considered statistically significant.

RESULTS AND DISCUSSION

Differences between Bulk Fat and W/O Emulsion System. Table 4 shows volatile compounds measured by SPME−GC/MS of a bulk fat sample with added oleic acid monoglyceride. The concentrations of the following were determined: two short-chain fatty acids (butanoic acid and hexanoic acid), 2,3-butanedione, five methylketones (2-butanone, 2-pentanone, 2-heptanone, 2-nonanone, and 2-undecanone), five fatty acid esters (ethyl acetate, ethyl butanoate, methyl hexanoate, ethyl hexanoate, and methyl octanoate), and five lactones (γ-hexalactone, γ-octalactone, γ-decalactone, δ-octalactone, and δ-decalactone).

Table 4. Identities of Volatile Compounds Isolated by SPME from the Headspace of Samples

peak no.	compound	RI[a]
1	2,3-butanedione	590
2	2-butanone	597
3	ethyl acetate	611
4	2-pentanone	684
5	butanoic acid	797
6	ethyl butanoate	802
7	2-heptanone	890
8	methyl hexanoate	924
9	hexanoic acid	975
10	ethyl hexanoate	998
11	γ-hexalactone	1053
12	2-nonanone	1091
13	methyl octanoate	1123
14	γ-octalactone	1259
15	δ-octalactone	1286
16	2-undecanone	1293
17	γ-decalactone	1471
18	δ-decalactone	1499

[a] Retention indices (RI) were calculated from GC/MS data.

Figure 1 shows the concentrations of volatile compounds in the headspace over the bulk fat blends and the W/O emulsion-fat blends, both with added oleic or palmitic acid monoglyceride. The bulk fat blend and the W/O blend showed large difference in the aroma over the headspace; in the bulk fat both butanoic acid and hexanoic acid were released independent of monoglycerides. On the contrary almost no acids were in the headspace over the W/O-emulsion fat blend (Figure 1A). In contrast, the concentrations of 2-heptanone (Figure 1B) and methyl hexanoate (Figure 1C) were lower in the headspace over the bulk fat blend than in the W/O-emulsion fat blend. Different volatile-release characteristics, depending on the fat blend, were observed for aroma compounds used in this study. This result suggests that free fatty acids such as butanoic acid are retained at the interface between the fat and dispersed aqueous droplets.

Effect of Carbon Chain Length of Flavor Compound. Figure 2 shows the ratio of concentrations into the headspace of volatile 2,3-butanedione, methylketones, esters, and lactones from the W/O-emulsion fat blend and the bulk fat blend. The volatile compounds are listed in the figure from left to right in the order of the carbon chain length for each species of compound. In the headspace, the ratio of concentrations of volatile compounds for the W/O-emulsion fat blend (70% fat compound) to that for the bulk fat blend (100% fat compound)—designated the "70%/100% fat ratio"—is >1.0, indicating that aroma release is higher for the W/O-emulsion fat blend than for the bulk fat blend. Among the volatile methylketones, the ratio for 2-butanone was <1.0, while that for 2-undecanone was >1.0. Thus, for volatile methylketones, esters, and lactones, the ratio increased with increasing carbon chain length. This is consistent with the

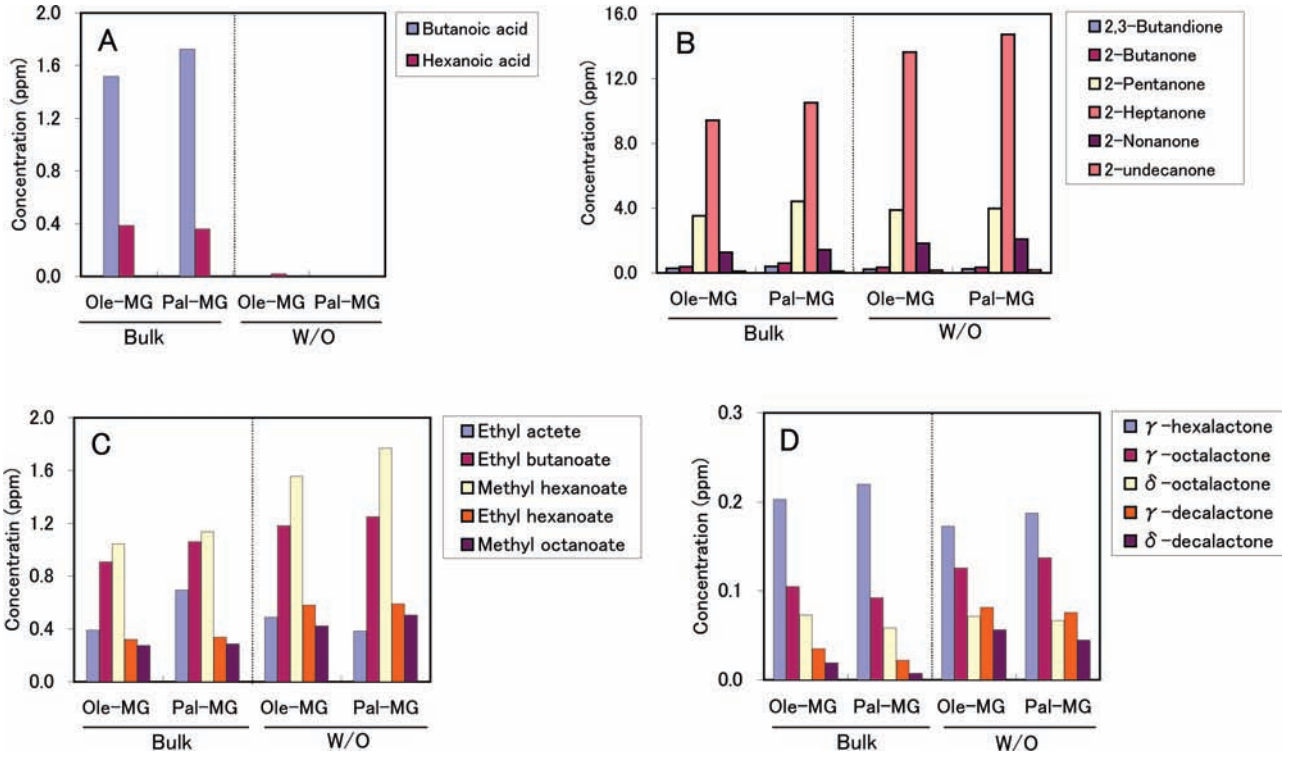

Figure 1. Effect of the aqueous phase on the headspace concentrations of the selected aroma volatiles. Expressed as peak areas relative to that of the internal standard: Ole-MG Bulk, bulk fat blend with added monoglyceride oleic acid; Pal-MG Bulk, bulk fat blend with added monoglyceride palmitic acid; Ole-MG W/O, W/O-emulsion fat blend with added monoglyceride oleic acid; Ole-MG Bulk, W/O-emulsion fat blend with added monoglyceride palmitic acid.

known theoretical relationship that the lipophilic characteristics of volatile compounds increase with increasing carbon chain length. These results show that, in the presence of dispersed aqueous droplets, the concentration of volatile compounds in the headspace increases with increasing lipophilic properties.

The polarity of compounds influences their behavior in a complex fat−water−air system. Lipophilic compounds preferentially leave a W/O emulsion in the presence of an aqueous phase, and thus become more available for release into the headspace. Dependence on the carbon chain length is stronger for the fat blend with the added palmitic acid monoglyceride than for the fat blend with the added oleic acid monoglyceride. The concentration of γ-decalactone and δ-decalactone is higher for the 70%/100% fat ratio with the added palmitic acid monoglyceride than for the ratio with the added oleic acid monoglyceride. These results showed that lactones with longer carbon chains released into headspace more easily when the interfacial structure of an aqueous phase composed of saturated fatty acid monoglycerides in comparison with unsaturated fatty acid monoglycerides.

Sensory Evaluation. The perception of flavor characteristics greatly depends on the nature of the food matrix. Figure 3 shows the effect of aqueous droplets in a W/O emulsion with added monoglycerides on sensory perceptions. Short-chain fatty acids, methylketones, esters, and lactones are known to possess the following notes, respectively: buttery and cheesy, cheesy, fruity, and sweet. Panelists were asked to rate, for each sample, the relative intensity of each sensory attribute as compared with its value for a bulk fat blend with added oleic acid monoglyceride. The intensities of two sensory attributes—total (A) and cheesy aroma (G)—were stronger for the bulk fat blend than for the W/O-emulsion fat blend. The intensity of one attribute—top aroma (B)—was stronger for the bulk fat blend with the added oleic acid monoglyceride than with the added palmitic acid monoglyceride. The intensities of two attributes—fruity aroma (E) and sweet aroma (F)—were rated equally strong. The intensities of all the attributes were rated equal for the W/O-emulsion fat blends with the added oleic acid and palmitic acid monoglyceride. Short-chain free fatty acids, including butanoic acid, which have a cheese or rancid odor, are known to contribute keynotes to dairy products such as butter and cheese. The headspace volatile-compound concentration of butanoic acid for the W/O-emulsion fat blend was lower than that of bulk fat blend as shown in Figure 1. Our results suggested that the intensities of the cheesy attributes for the W/O-emulsion fat blends were low due to interaction between the butanoic acid and the dispersed aqueous droplets, and the release of butanoic acid from this fat blend was decreased to affect sensory perception.

Effect of Interfacial Surface. SFC levels for samples at 5 and 37 °C are listed in Table 5. Levels were the same for bulk fats and W/O-emulsion fats, and for the added palmitic acid monoglyceride and the oleic acid monoglyceride at 37 °C. Roberts et al. (2003) reported that higher SFC increased flavor release from the semisolid fats.[13] However, the aroma-release properties observed in this study are not due to the SFC.

To evaluate the effect of dispersed aqueous droplets, the aroma release from the W/O-emulsion fat blends whose aqueous phase had been removed was determined using headspace SPME−GC/MS. To prepare the samples, the W/O-emulsion fat blends with the added oleic acid monoglyceride were melted at 70 °C, and separated into upper lipid phase and lower aqueous phase. Figure 4

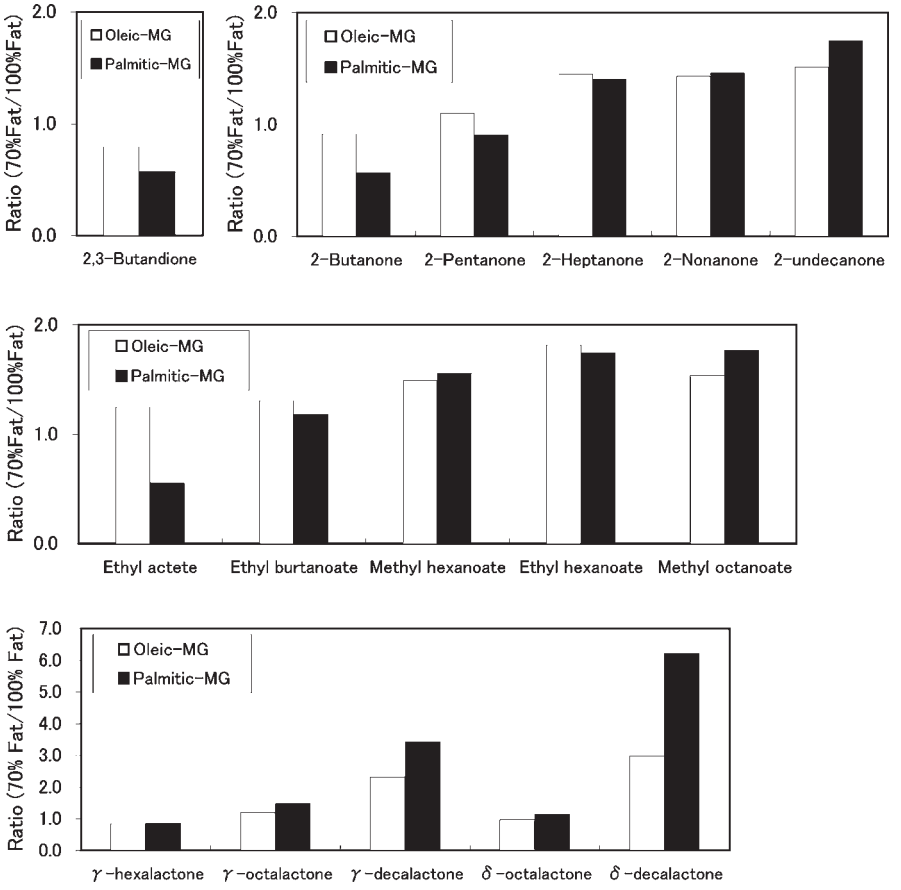

Figure 2. Headspace concentrations of aroma compounds from the W/O-emulsion fat blend and from the bulk fat blend.

shows the ratio of headspace concentration of butanoic acid and hexanoic acid. In the headspace, the ratio of concentrations of volatile compounds for the extracted lipid phase from W/O-emulsion fat blend (extracted phase) to that for W/O-emulsion fat blend (emulsion)—designated the "extracted phase/emulsion ratio"—is > 1.0, indicating that aroma release is higher for the extracted lipid phase than for the W/O-emulsion fat blend. For butanoic acid and hexanoic acid, the flavor release increased with removal of aqueous phase of W/O-emulsion fat blend. The presence of dispersed aqueous droplets in a fat blend significantly reduced the headspace concentrations of butanoic acid and hexanoic acid, and also decreased the perceived intensity of total aroma and cheesy aroma. The aroma release of methylketones, esters, and lactones from the W/O-emulsion fat blends increased with increasing carbon chain length of the volatile molecules. In emulsions, volatile compounds distribute themselves among the aqueous phase, the oil phase, and the interface between the two phases. Thus, aroma release from a W/O-emulsion semisolid fat blend was influenced by interactions between flavor volatiles and the dispersed aqueous droplets.

Charles et al. (2000) have discussed the effect of oil-droplet size on the flavor release in the O/W-emulsion systems.[4] The droplet size distribution in the W/O-emulsion fat blends with the added oleic acid monoglyceride and palmitic acid monoglyceride was determined. The average sizes of the droplet diameter of the W/O emulsion fat blends were calculated from the electron microscope images. The average droplet sizes obtained for the samples with oleic acid and palmitic acid monoglyceride were 1.24 and 1.45 μm, respectively. Both blends showed similar droplet diameter (maximum size 1.0−1.5 μm) (Figure 5). Our results of differences for aroma release were obtained from these W/O emulsions showing similar dispersed aqueous droplet size.

Dependence of Fatty Acid of Monoglycerides. The effect of the fatty acid composition of the monoglyceride on the flavor release was compared for the W/O-emulsion fat blends with the added oleic acid, palmitic acid, stearic acid, and behenic acid. Sensory evaluations and headspace SPME−GC/MS measurements were also performed.

Figure 6 shows that the intensities of two sensory attributes—last aroma (A) and sweet aroma (B)—are significantly higher for the added oleic acid monoglyceride than for the added stearic acid monoglyceride and behenic acid monoglyceride. The intensity of aroma perception decreased as the melting point of the monoglyceride fatty acid increased. The intensities of the five sensory attributes—total aroma intensity, top aroma, buttery aroma, fruity aroma, and cheesy aroma—showed no differences among fatty acid of monoglycerides. For the W/O-emulation fat blends, no differences were observed in the headspace volatile-compound concentrations, SFC values, and droplet sizes (data not shown). The intensities of the two sensory attributes—last aroma release (A) and sweet aroma (B)—were affected by the monoglyceride fatty acid composition. Among flavor compounds determined in this study, lactones are related to sweet attribution. This result suggested that the decreased intensity of the attribute sweet aroma was influenced by lactone behavior.

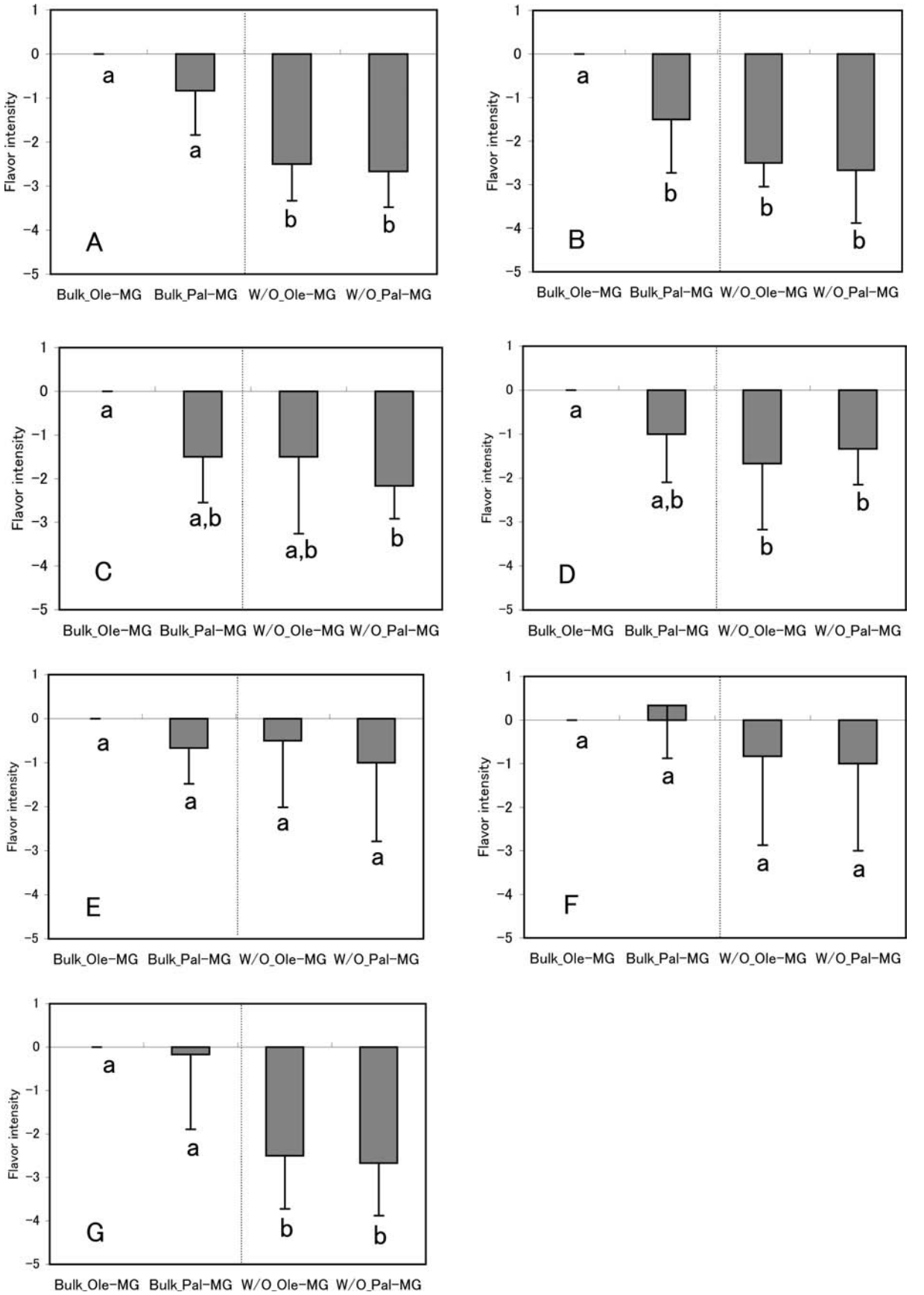

Figure 3. Effect of the aqueous phase on the perception of various sensory attributes: A, total aroma intensity; B, top aroma; C, last aroma; D, buttery aroma; E, fruity aroma; F, sweet aroma; G, cheesy aroma. Different letters indicate significant differences ($P < 0.05$).

Table 5. SFC of Fat Blends at 5 and 37 °C

%	5 °C	37 °C
bulk fat added oleic acid MG	17.42 ± 0.07	1.94 ± 0.35
bulk fat added palmitic acid MG	18.14 ± 0.12	2.01 ± 0.20
W/O fat added oleic acid MG	13.78 ± 0.20	1.74 ± 0.27
W/O fat added palmitic acid MG	13.70 ± 0.13	2.05 ± 0.10

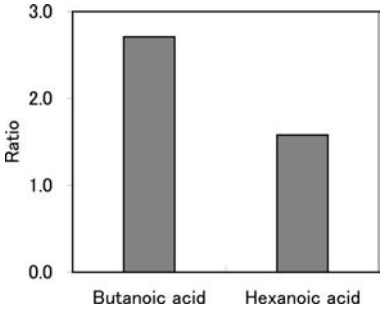

Figure 4. Effect of removing the aqueous phase from a W/O-emulsion fat blend on the headspace volatile concentration of butanoic acid and hexanoic acid. In the headspace, the ratio of concentrations of volatile compounds for the extracted lipid phase from W/O-emulsion fat blend (extracted phase) to that for W/O-emulsion fat blend (emulsion).

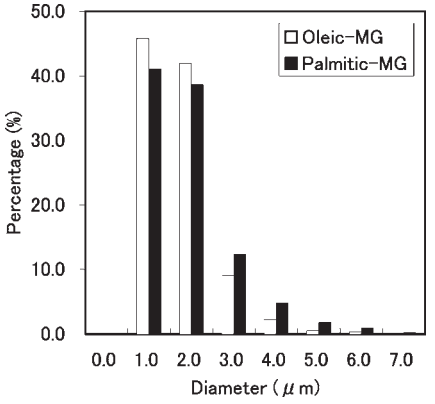

Figure 5. Droplet distribution for W/O-emulsion fat blends: oleic-MG, with added oleic acid monoglyceride; palmitic-MG, with added palmitic acid monoglyceride.

Viscoelastic Properties of Samples. Margarine and shortening are known to behave as elastoplastic substances in the temperature range over which they are normally consumed. The effect of dispersed aqueous droplets and the fatty acid composition of the monoglyceride on the viscoelastic properties of the samples is thus of interest.

Figure 7 shows the plots of storage modulus G' as a function of temperature for various fat blends. In the range 5−50 °C, with heating at a rate of 1 °C/min, G' generally decreases with increasing temperature for all blends. In the range 5−20 °C, G' was essentially the same for all of the blends. In the range 30−40 °C, which includes the temperature of the human mouth, G' is 10 times lower for the bulk fat blends than for the W/O-emulsion fat blends. These results suggested that G' related to viscosity of fat blend was due to the existence of interfacial surface which influenced flavor release. The differences of cheesy note among samples obtained in this study were influenced by the interfacial surface of W/O emulsions.

Further, G' increased as the melting point of the monoglyceride fatty acid increased. The rheological behaviors of plastic fats are known to be governed by the interactions between fat crystals in an aggregated three-dimensional, solid−liquid fat, fat−water droplet matrix, and these behaviors affect properties such as consistency and mouth feel.[18,19] The differences in the sensory perception described above for the two attributes last aroma and sweet note among the W/O-emulsion fat blends with added monoglycerides (Figure 6) suggest a relationship with the fat crystal network structure. The network structure is characterized by the presence of dispersed aqueous droplets that relate to the three-dimensional crystal network providing a solid character to spreads.[17] Therefore, the differences in G' are presumably due to differences in the crystal network structure, due in part to destruction or coalescence of emulsions. The G' at 37 °C of W/O-emulsion fat blend with added behenic acid monoglyceride was higher than that of W/O-emulsion fat blend with added oleic acid monoglyceride. This result indicated that the crystal network of W/O-emulsion fat blend with added behenic acid monoglyceride was stronger, and the structural fat melts slower, than that with added oleic acid monoglyceride at body temperature. Lee (1986) studied the T-I flavor properties of butter-like products prepared with either stearin palm oil or olein palm oil.[23] The response curves clearly demonstrate several facets of the influence of the physical properties of lipids on the perceived flavor. They showed that the structure collapses more slowly with the slowly melting stearin fat, thus allowing slower release of

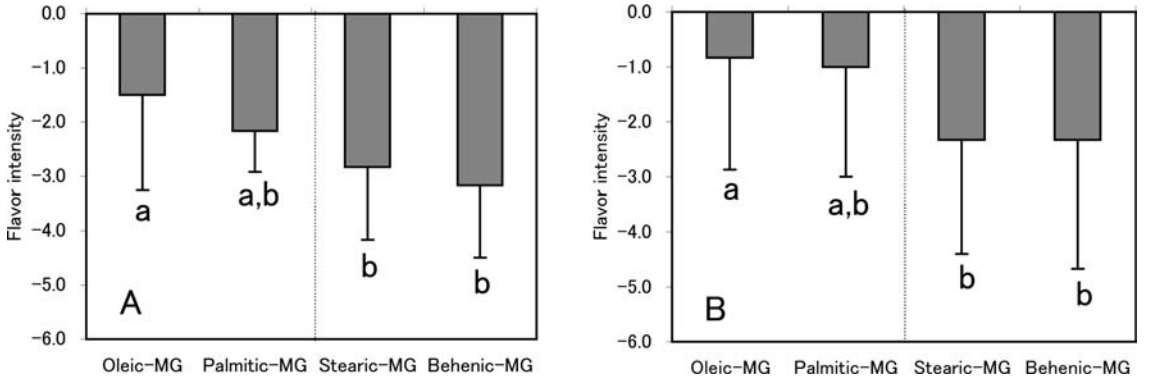

Figure 6. Effect of the fatty acid composition on the perception of various sensory attributes: A, last aroma; B, sweet aroma. Different letters indicate significant differences ($P < 0.05$).

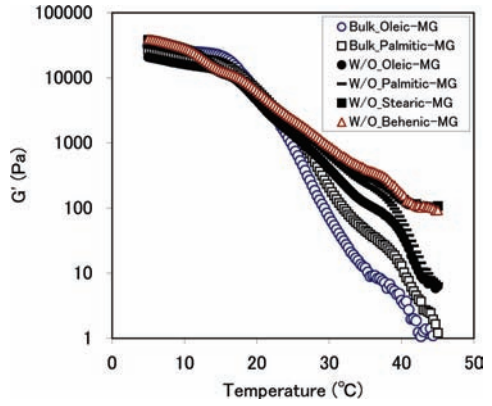

Figure 7. G' as a function of temperature for a W/O-emulsion fat blend and a bulk fat blend.

flavor to the mouth headspace. Decreasing interfacial surface area, due to the progression of coalescence, seems to result in decreasing the release of lipophilic aroma volatiles such as long-chain lactones. The lower sensory attributes of last aroma release and sweet aroma of W/O-emulsion fat blend with added behenic acid monoglyceride in this study were suggested to be influenced by these different physical behaviors. The storage modulus G' of the W/O-emulsion fat blend at 37 °C depended on the melting point of the fatty acids of the monoglyceride used as an emulsifier, and affected the intensity of aroma perception. The perception of aroma for a W/O-emulsion semisolid fat was affected by the interactions between the dispersed aqueous droplets, aroma compounds, and by the viscosity of the fat blends.

When foods are eaten, many changes take place—such as hydration/dilution with saliva and increase in the surface area—that affect the release of volatiles, and therefore, the profile of volatiles that are sensed in the nose. Lee (1986) outlined an instrumental technique for studying aroma release using model mouth systems.[3] Van Ruth et al. (1995) used a device to add artificial saliva to low-moisture foods and mimic the mechanical effects of eating using a plunger with a screw action to simulate breakdown in the mouth.[12] Semisolid fats show temperature dependence of SFC. Therefore, the hardness of semisolid fat was decreased with increasing the temperature in oral conditions. Measuring the temperature dependence of G' has advantage to obtain the information of changes of physical properties of semisolid fat products.

Our results suggested that aroma release from a W/O-emulsion semisolid fat depends on the affinity of the aroma volatiles to the aqueous phase and can also depended on the structure of the emulsion. Almost all margarines commercially available contain monoglyceride emulsifiers to stabilize the W/O emulsions. Selecting emulsifiers prevents undesirable crystallization behavior such as the growth of granular crystals that impair the softness and spreadability of the margarine containing palm oil-based blend, and allows better understanding of the influence of emulsifier structure on polymorph behavior under the formulations in manufacture. We investigated the effect of monoglyceride fatty acids on aroma perception. Our results provide important information for the selection of emulsifiers and flavor formulations as they affect the acceptability of margarines, in particular low-trans fatty acid types, and of shortening.

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