JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

# Delayed Volatile Compound Release Properties of Self-Assembly Structures in Emulsions

VAN-ANH PHAN, YONG-CHENG LIAO, NICOLAS ANTILLE, LAURENT SAGALOWICZ, FABIEN ROBERT, AND NICOLAS GODINOT*

Nestlé Research Center, Vers-chez-les-Blanc, 1000 Lausanne 26, Switzerland

Temporal release and retention of aroma compounds from structured emulsions (where unsaturated monoglycerides are added to the oil) and conventional oil-in-water emulsions were studied using *in vitro* dynamic headspace analysis by proton-transfer reaction mass spectrometry and static headspace analysis by gas chromatography–mass spectrometry. Under dynamic conditions, the structured emulsion exhibited delayed release compared to the oil-in-water emulsion containing the same lipid content of 5%. The time to maximum concentration $T_{max}$ of amphiphilic and lipophilic aroma compounds increased by a factor of 1.2 (for 3*E*-hexenal) to 1.9 (for octanal). The aroma release profile of the 5% lipid structured emulsion was close to that obtained for the oil-in-water emulsion containing 10% lipid. Under static conditions, the 5% lipid structured emulsion retained more of the most lipophilic aroma compounds than its counterpart 5% oil-in-water nonstructured emulsion. The present study provides potential solutions for modulating aroma release profiles of reduced-fat foods by self-assembly structures.

**KEYWORDS: Delayed aroma release; self-assembly structures; structured emulsion; lipid content; low fat; proton-transfer reaction mass spectrometry**

## INTRODUCTION

Fat is well-known to play an important role in flavor perception of fat-containing foods (*1–3*). In the early 1990s, Bennett (*4*) showed that perceived aroma intensity of nonfat products is strong initially but then dissipates quickly, whereas the perceived aroma intensity of fatty products gradually builds up and persists for a longer time. An increase in the headspace concentration of lipophilic aroma compounds when lowering fat content in the matrix has been shown by instrumental analysis for *in vitro* (*5–17*) and *in vivo* (*5, 14, 17–19*) conditions. Some contradictory results were found on the effect of fat reduction when studying the temporal aspects of *in vitro* and *in vivo* aroma release; while some authors found quicker release (*15, 16, 18, 19*) and low persistence (*5, 8, 18*) for lipophilic aroma compounds, the data obtained by Miettinen et al. (*10, 17*) only partly supported these findings. Although not reported in one case for ethyl 2-methylbutyrate (*20*), most sensory studies revealed an increase in perceived aroma intensity induced by lipophilic compounds perceived orthonasally (*9, 10, 14*) or retronasally (*14, 15, 17–19, 21*) with reduced fat content. These sensory results are consistent with instrumental results. The influence of fat content on the behavior of lipophilic aroma compounds is well-explained by the fact that fat acts as solvent for these compounds (*22*). Hence, if fat is reduced, lipophilic aroma compounds become more concentrated in the fat phase and consequently partition more into the water phase or into the air phase within or surrounding the matrix. Concerning hydrophilic aroma compounds, most of the instrumental measurements did not detect any significant effect of fat content on release either *in vitro* (*10, 11, 14, 17*) or *in vivo* (*14, 18, 19*). The absence of effect on hydrophilic aroma compounds was verified perceptually in several cases (*9, 10, 21*). However, a decrease in the perceived intensity was reported in ice cream for some hydrophilic aroma compounds having low thresholds, for example, maltol (*20*) and vanillin (*15, 23, 24*). Altogether, the changes mentioned above because of the reduction of fat are anticipated to disturb the original aroma balance of traditional full-fat products (*12*).

Commercial emulsifiers, such as monoglycerides, can form self-assembly structures when mixed with water or oil under given physicochemical conditions, such as L2 phase, cubic phases, or hexagonal phases (*25*). The applications of the self-assembly structures in the pharmaceutical industry were reviewed as delivery systems for active high molecular-weight compounds, such as proteins, enzymes, hormones, or drugs thank to their controlled release properties (*25*). In the food industry, Miller et al. (*26*) presented the potential application of self-assembly structures for use in low-fat and fat-free products. Researchers have also studied self-assembly structures for controlling the release of volatile aroma compounds, which are relatively low molecular-weight compounds. A cubic phase composed of 80% unsaturated monoglyceride and 20% water

* To whom correspondence should be addressed. Telephone: +41-21-785-8057. Fax: +41-21-785-8554. E-mail: nicolas.godinot@rdls.nestle.com.

10.1021/jf072520k CCC: $40.75 
Published on Web 01/16/2008

**Table 1.** Composition and Final Concentration by Weight of Each Constituent in Simple Emulsion 10%, Simple Emulsion 5%, and Structured Emulsion 5%

| ingredients | simple emulsion 10% (g/100 g) | simple emulsion 5% (g/100 g) | structured emulsion 5% (g/100 g) |
|---|---|---|---|
| Dimodan MO90 | 0.00 | 0.00 | 0.25 |
| MCT oil | 10.00 | 5.00 | 4.75 |
| sodium caseinate | 14.40 | 7.60 | 7.60 |
| MilliQ water | 75.60 | 87.40 | 87.40 |

displays weaker capability to retain aroma compounds in comparison to a water-in-oil emulsion containing 80% triglycerides (*27*), which was explained by the extremely large interfacial oil–water area of the cubic phase. However, a L2 phase containing 90% lipids (30% unsaturated monoglyceride, 60% triglyceride, and 10% water) was shown to better retain some aroma compounds, such as butanol, octanol, nonanal, than a water-in-oil emulsion having the same hydration value (Table 2 of ref *28*). The author explained this observation by the higher interfacial area of the microstructure of L2 phase that could play a role in the retention of aroma compounds having a certain amphiphilic structure.

These two studies (*27, 28*) examined only the bulk systems of self-assembly structures, with a water content of less than 30%. Such systems with a high lipid content do not have a wide application in real food products. Therefore, the objective of the present study was to investigate controlled release of aroma compounds from the dispersed phase of self-assembly structures in an emulsified water solution, closer to popular food products in terms of lipid content. It is hypothesized that this dispersion containing a low amount of monoglycerides, would also influence the aroma retention properties of L2 phase and would delay the release of lipophilic aroma compounds compared to a conventional oil-in-water emulsion with the same lipid content. If this hypothesis is validated, then using such dispersions could contribute to control aroma release in reduced-fat foods.

## MATERIALS AND METHODS

**Chemicals.** The following nine aroma compounds were purchased from Aldrich-Sigma, Co. (Steinheim, Germany) with purities higher than 92%: 2,3-butanedione, acetaldehyde, 2*E*-hexenal, 3*Z*-hexen-1-ol, benzaldehyde, ethyl butanoate, 3-methyl, pyrazine, 3-isobutyl, 2-methoxy, octanal, linalool. Medium-chain triglycerides (MCT) (Delios, Cognis, Germany), unsaturated monoglyceride (Dimodan MO90, Danisco A/S, Braband, Denmark) having the fatty acid composition of 3.5% C16, 3.4% C18, 79.3% C18:1, and 11.6% C18:2, sodium caseinate (Emmi, Dagmersellen, Switzerland), and MilliQ water (Millipore S.A., Molsheim, France) were used to prepare emulsions.

**Preparation of Samples.** *Emulsions.* Oil-in-water emulsions containing 5 or 10% of MCT oil were made by dispersing MCT oil in sodium caseinate solutions in MilliQ water using a Polytron (Kinematica AG, Switzerland, 6 min, 10 000 rpm) and homogenizing the obtained dispersions (Rannie homogenizer Kindler, Switzerland, 10 min, 400 bar). These oil-in-water emulsions were denoted as simple emulsion 5% and simple emulsion 10%. Emulsions containing 5% of a lipid mixture (Dimodan MO90: MCT oil in the ratio 1:20 by weight) were prepared with the same protocol as above, except that the lipid mixture and the sodium caseinate solution were heated separately up to 60 °C in a water bath prior to the Polytron treatment. This emulsion was denoted as structured emulsion 5%. The final concentrations of all of the constituents of the emulsions are shown in **Table 1**. The structured emulsion 5% had the same appearance as the simple emulsion 5%. Preliminary experiments reported that the median diameter of lipid droplets was 0.35 $\mu$m for simple emulsion 10%, 0.39 $\mu$m for simple emulsion 5%, and 0.33 $\mu$m for structured emulsion 5% (Mastersizer S, Malvern Instruments, U.K.). The average of triplicate measurements of viscosity at room temperature was 0.35 mPa s for simple emulsion 5% and 0.40 mPa s for structured emulsion 5% (Rheometer RS150, Haake, Germany, controlled shear stress mode, double gap concentric cylinder geometry DG41).

**Table 2.** Final Concentration of Aroma Compounds Used in *in Vitro* Dynamic Aroma Release Analysis (PTR−MS) and Static Headspace Analysis (GC−MS)[a]

| | | final concentration in emulsion | | | |
|---|---|---|---|---|---|
| | | for PTR−MS | | for GC−MS | |
| aroma compounds | log $P$[b] | ppmV | $\mu$M | ppmV | $\mu$M |
| 2,3-butandione | −1.3 | 20 | 217 | 20 | 217 |
| acetaldehyde | −0.1 | 10 | 176 | *c* | *c* |
| 2*E*-hexenal | 1.5 | 20 | 169 | 60 | 507 |
| 3*Z*-hexen-1-ol | 1.6 | 20 | 166 | 60 | 498 |
| benzaldehyde | 1.6 | 20 | 193 | 20 | 193 |
| ethyl butanoate, 3-methyl | 2.1 | 20 | 130 | 6 | 39 |
| pyrazine, 3-isobutyl, 2-methoxy | 2.6 | 100 | 590 | 100 | 590 |
| octanal | 3.0 | 100 | 588 | 50 | 294 |
| linalool | 3.2 | 100 | 542 | 100 | 542 |

[a] Two mixtures of pure aroma compounds were prepared separately and stored at −29 °C for use throughout the experiment period. A volume of 42.5 and 42.8 $\mu$L, for PTR−MS analysis and for GC−MS analysis, respectively, was dissolved in 100 mL of emulsion to obtain the final concentration, expressed here in part per million volume (ppmV, equal to $\mu$L/L) and micromole per liter ($\mu$M). [b] Octanol−water partition coefficient, SciFinder database, calculated and truncated. [c] Aroma compound not used in the measurements.

*Aroma Incorporation.* The concentrations of aroma compounds in emulsions used in either *in vitro* dynamic aroma release analysis by PTR−MS or static headspace analysis by GC−MS were chosen independently based on preliminary experiments on each instrument. Two mixtures of pure aroma compounds were prepared separately and stored at −29 °C for use throughout the experiment period. A volume of 42.5 and 42.8 $\mu$L, for PTR−MS analysis and for GC−MS analysis, respectively, was dissolved in 100 mL of emulsion to obtain final concentrations of aroma as listed in **Table 2**. Aroma compounds were sampled with capillary pistons (Gilson's Microman, U.K.).

***In Vitro* Dynamic Aroma Release Monitored by PTR−MS.** The proton-transfer reaction mass spectrometry PTR−MS (Ionicon Analytik) was used in the oven/PTR−MS system (*29*), which allowed online aroma analysis under dynamic conditions. A sample of 100 mL was first heated to 36 °C for 10 min and poured into a double-jacketed glass cell (250 mL total volume), which was held at 36 °C with a circulating water bath during the measurement. The cell was then quickly and tightly reconnected to its lid with a clamp and magnetically stirred at 135 rpm. The double-jacketed glass cell was fixed inside a temperature-controlled oven at 60 °C to avoid cold points and water condensation. The headspace cell was continuously purged at 200 sccm (standard cubic centimeters per minute) with nitrogen (purity 99.995%). The sampling gas from the cell outlet was diluted with 1960 sccm of nitrogen prior to introduction into the PTR−MS.

In preliminary experiments, the fragmentation of aroma compounds induced by PTR−MS was determined individually to be able to choose a specific atomic mass $m/z$ for each compound and their concentration in the aroma mixture to avoid overlapping and to calculate the fragmentation factor for data analysis. In this preliminary experiment, the release of single aroma compound from a 5 ppmV solution in MilliQ water was monitored in SCAN mode where all atomic masses from $m/z$ 20−160 were scanned with 0.2 s dwell time per mass.

In the main measurements, the mixture of nine aroma compounds used for PTR−MS analysis (**Table 2**) was incorporated into simple emulsion 10%, simple emulsion 5%, and structured emulsion 5%. The samples were stored at 5 °C for 24 h before aroma analysis. The release of aroma compounds from the three aroma-containing emulsions was monitored in MID mode where chosen specific atomic masses based on the scan data were followed, i.e., $m/z$ 45 for acetaldehyde, $m/z$ 83 for 3*Z*-hexen-1-ol, $m/z$ 87 for 2,3-butanedione, $m/z$ 99 for 2*E*-hexenal, $m/z$ 107 for benzaldehyde, $m/z$ 111 for octanal, $m/z$ 131 for ethyl butanoate, 3-methyl, $m/z$ 137 linalool, $m/z$ 167 for pyrazine, 3-isobutyl,

2-methoxy, as well as the primary ion $H_3O^+$ by *m/z* 21 and water (cluster) by *m/z* 37. The measurement lasted 10 min for each sample. The cell was then removed, washed with soap, rinsed with methanol and hexane, and dried before being reconnected into the system. Six replicates for each sample were performed: two batches of emulsion preparation with three incorporations of the aroma mixture for each batch.

**Static Headspace Analysis by GC−MS.** The mixture of eight aroma compounds used for GC−MS analysis (**Table 2**) was incorporated into simple emulsion 5% and structured emulsion 5%. A volume of 8 mL of aroma-containing emulsion was put in 15 mL GC vials. They were kept at room temperature for 24 h before static headspace measurement. Four replicates were performed for each aroma-containing emulsion, which were based on one emulsion preparation batch.

All samples were analyzed using a HP 5890 series gas chromatograph coupled to a Grestel MPS2 automatic sampler and an Agilent model 5972N series mass spectrometer operating in EI model at 70 eV, a DB-Wax fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness, J&W Scientific, Folsom, CA). The oven temperature was held for 3 min at 20 °C, programmed to 100 at 6 °C/min, then programmed to 240 at 10 °C/min, and finally, held for 15 min. The sample was incubated for 30 min at 50 °C with agitation at 300 rpm. Injector parameters were temperature, 50 °C; injection volume, 1 mL; split ratio, 1:4. The flow rate of the helium carrier gas was 1 mL/min. MS detection started after 3.5 min to avoid the solvent peak.

**Statistical Analysis.** The following parameters were extracted from the release curves obtained by *in vitro* dynamic aroma release analysis: the maximum concentration ($C_{max}$), the time to maximum concentration ($T_{max}$), and the area under the curve between 0 and 600 s (AUC). One-way analysis of variance (ANOVA) was applied to test differences in mean values between simple emulsion 10%, simple emulsion 5%, and structured emulsion 5%. This analysis was performed separately for each of the three parameters $C_{max}$, $T_{max}$, and AUC, and for each of the nine aroma compounds. The Fisher's least significant difference (LSD) was selected as multiple comparison procedure and allowed to determine if the difference between each pair of samples was significant. A 95% confidence level was applied to all tests.

Static headspace data was represented by the area of the peak detected by GC−MS for each aroma compound above simple emulsion 5% and structured emulsion 5%. Student's *t* test (paired) was used to assess the significance of the differences in the chromatographic peak areas between the two model emulsions for each of the eight aroma compounds.

## RESULTS

***In Vitro* Dynamic Aroma Release Monitored by PTR−MS.** **Figure 1a** shows the area under the curve between 0 and 600 s (AUC) for each of the nine aroma compounds over the three emulsions. This value represents the total amount of a given aroma compound released during the first 600 s. For amphiphilic and lipophilic aroma compounds, the AUC values of the simple emulsion 10% are significantly lower than those measured for both emulsions at 5% lipid. The two hydrophilic compounds were released to a greater extent from simple emulsion 10% than from the two other emulsions. When structured emulsion 5% was compared to simple emulsion 5%, there was no difference in AUC values for any of the compounds, except for 2*E*-hexenal, an amphiphilic compound, whose release was significant higher from structured emulsion 5%.

Maximum concentrations ($C_{max}$) of the nine aroma compounds released into the headspace of the three emulsions are given in **Figure 1b**. The measured $C_{max}$ was significantly higher for amphiphilic and lipophilic aroma compounds and significantly lower for hydrophilic compounds over the simple emulsion 5% than over the simple emulsion 10%. **Figure 1b** also indicates that $C_{max}$ of lipophilic aroma compounds in the headspace above the structured emulsion 5% was significantly lower than that above the simple emulsion 5% and no difference with that of the simple emulsion 10% was found, except that $C_{max}$ of linalool was still significantly higher for the structured emulsion 5% than for the simple emulsion 10%. No difference in $C_{max}$ of hydrophilic and amphiphilic aroma compounds was demonstrated between structured emulsion 5% and simple emulsion 5%.

The time to maximum concentration ($T_{max}$) of the nine aroma compounds for the three emulsions is presented in **Figure 1c**. Significant reduction of $T_{max}$ was found for amphiphilic and lipophilic compounds released from simple emulsion 5% compared to simple emulsion 10%. Besides, the structured emulsion 5% exhibited significantly higher $T_{max}$ compared to simple emulsion 5% and no difference in $T_{max}$ with simple emulsion 10% for these compounds. The increase factor was 1.2 for 2*E*-hexenal, 1.5 for 3*Z*-hexen-1-ol, 1.3 for benzaldehyde, 1.6 for ethyl butanoate, 3-methyl, 1.7 for pyrazine, 3-isobutyl, 2-methoxy, 1.9 for octanal, and 1.7 for linalool. $T_{max}$ values were not significantly different among the three emulsions for the two hydrophilic compounds, 2,3-butanedione and acetaldehyde.

**Static Headspace Analysis by GC−MS.** The chromatographic peak area for each of the eight aroma compounds in the headspace of simple emulsion 5% and structured emulsion 5% is shown in **Figure 2**. Two of four lipophilic aroma compounds, pyrazine, 3-isobutyl, 2-methoxy and linalool, have significantly lower peak areas for structured emulsion 5% compared to simple emulsion 5%. Octanal followed the same trend at the limit of significant difference. No differences in peak areas of the other compounds between were found the two model emulsions.

## DISCUSSION

The results of the *in vitro* dynamic aroma release analysis showed that when the lipid content is reduced from 10 to 5% in simple emulsions, the total amount of aroma released (AUC) as well as the maximum concentration ($C_{max}$) in the headspace of total amphiphilic and lipophilic aroma compounds increased significantly, which is in agreement with the literature. Whereas previous instrumental analysis did not detect the influence of fat reduction on the release of hydrophilic aroma compounds, our measurements showed significantly lower AUC and $C_{max}$ for 2,3-butanedione and acetaldehyde. This diminution detected by PTR−MS could be partly due to the decrease in the concentration of these compounds in the water phase of the emulsion while replacing the reduced amount of oil by water as hypothesized by Shamil et al. (*30*). In contrast, Schirle-Keller et al. (*12*) found an increase of 40% in vapor pressure for diacetyl when oil content was reduced from 10 to 2%. These conflicting observations can be the result of varying experimental systems with different hydrodynamic conditions, leading to different limiting steps of mass transfer during release experiments. Furthermore, the reduction of lipid content from 10 to 5% in simple emulsions also led to an earlier release of all amphiphilic and lipophilic aroma compounds by inducing a significantly shorter time to maximum concentration ($T_{max}$). These results are in agreement with the study of Brausse et al. (*18*), who also found significantly smaller $T_{max}$ for anethole and terpinolene released from yogurts containing 0.2% fat than from 10% fat yogurts by nosespace analysis. However, the observations given in the literature on the temporal aspects of aroma release are quite varied. For example, the rate of release of lipophilic aroma compounds was shown to increase because of the reduction of oil content in oil-in-water emulsions using dynamic aroma release analysis (*16*). The same conclusion was

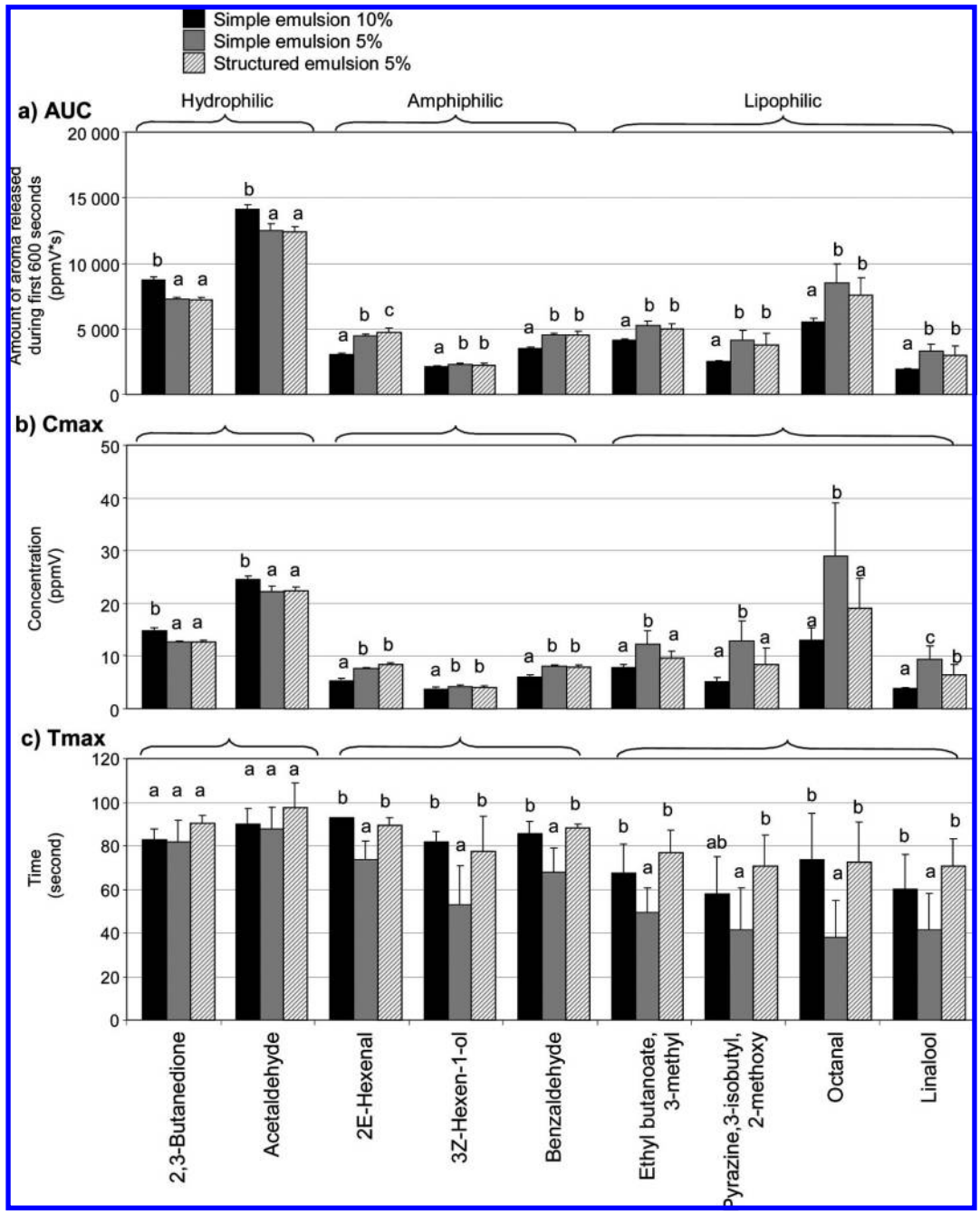


**Figure 1.** Area under the curve AUC (**a**), maximum concentration $C_{max}$ (**b**), and time needed to reach maximum concentration $T_{max}$ (**c**) of the nine aroma compounds released into the headspace of simple emulsion 10% (black bars), simple emulsion 5% (gray bars), and structured emulsion 5% (hatched bars) under *in vitro* dynamic condition during 10 min, monitored by PTR−MS. The aroma compounds are sorted along their log *P*. For each compound, two bars identified with different letters (**a**, **b**, and **c**) represent values that are significantly different ($p < 0.05$). Error bars represent standard deviations.

drawn by Malone et al. (*19*) for the rate of release of ethyl hexanoate and heptan-2-one in *in vivo* nosespace measurements. Nevertheless, the latter authors found no difference in $T_{max}$ for these compounds when changing oil content in the emulsions. Miettinen et al. (*17*) did not find changes in $T_{max}$ for linalool. Despites some disagreement, our results support the general observation on aroma imbalance when reducing fat in foods (*4, 12, 22*).

The structured emulsion 5% did not show significant differences in the total amount of aroma released into the headspace (AUC) compared with simple emulsion 5% for any of the studied aroma compounds, except for 2*E*-hexenal. However, structured emulsion 5% lowered the maximum concentration of all four lipophilic aroma compounds and delayed the release of amphiphilic and lipophilic compounds by increasing their $T_{max}$ compared to simple emulsion 5%. These values exhibited no significant differences to those of simple emulsion 10%. The findings on $T_{max}$ can be represented in another way by plotting the lipophilicity of aroma compounds, expressed as log *P* over $T_{max}$ for the three model emulsions (**Figure 3**). The concentration of aroma compounds in the headspace reached a maximum between 60 and 100 s for the simple emulsion 10%, while the span was between 40 and 100 s for the simple emulsion 5% because of earlier release of the more lipophilic compounds. Structured emulsion 5% delayed release of these compounds

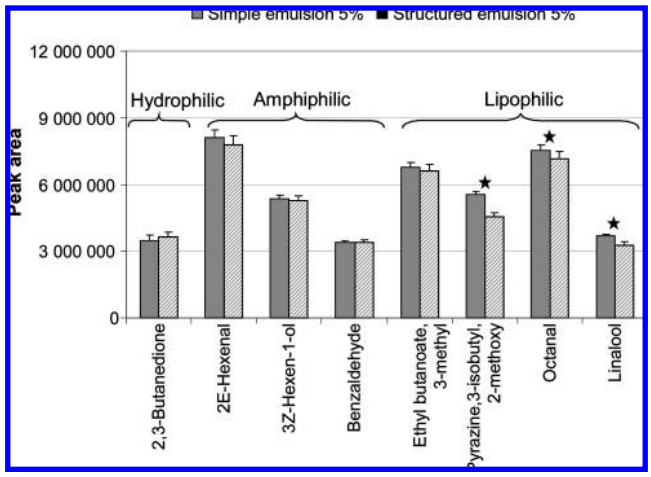


**Figure 2.** Peak area of eight aroma compounds obtained from the static headspace analysis by GC−MS above simple emulsion 5% (gray bars) and structured emulsion 5% (hatched bars). The aroma compounds are sorted along their log *P*. For each compound, two bars identified with a star represent values that are significantly different ($p < 0.05$). Error bars represent standard deviations.

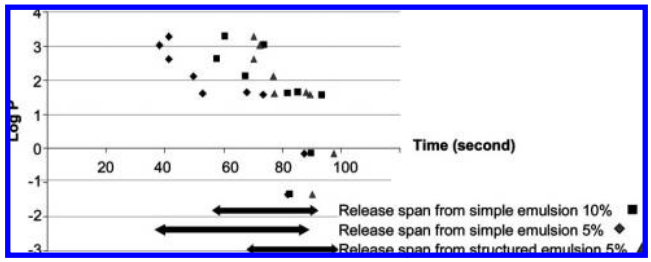


**Figure 3.** Delayed release effect of structured emulsion on amphiphilic and lipophilic aroma compounds. Nine aroma compounds released from each of the three model emulsions, simple emulsion 10%, simple emulsion 5%, and structured emulsion 5%, are presented by nine spots spread along their $T_{max}$ value on the *x* axis and log *P* on the *y* axis.

by producing a $T_{max}$ span between 65 and 100 s, which is in the same range as that found for simple emulsion 10%.

It is observed that the structured emulsion did not influence the release of hydrophilic molecules compared to the simple emulsions. This is to be expected because small hydrophilic constituents are mainly located in the water matrix and their release is not influenced by oil droplets.

To understand the cause of the difference in $C_{max}$ and $T_{max}$ for lipophilic aroma compounds between structured emulsion 5% and simple emulsion 5%, static headspace analysis was performed. The results showed lower chromatographic peak areas for three of four lipophilic aroma compounds above the structured emulsion 5%, reflecting a stronger retention of these compounds. This suggests a binding effect, which affects the distribution of these aroma compounds between the emulsion and its headspace at the equilibrium and also their oil-to-water and/or oil-to-air transfer under dynamic conditions. Still, the effect of the structured emulsion on $T_{max}$ was found under dynamic conditions not only for the four lipophilic aroma compounds but also for all amphiphilic compounds. This suggests a diffusion effect of the amphiphilic and perhaps lipophilic aroma compounds, which can influence their oil-to-water and/or oil-to-air transfer under dynamic conditions.

Vauthey et al. (*27*) did not find any significant difference in the retention of aroma compounds by pure triglyceride and pure unsaturated monoglyceride. However, when the unsaturated monoglyceride was mixed with the triglyceride in the ratio of 60:40, this lipid mixture (bulk L2 phase) displayed a better retention compared to the pure triglyceride for six of nine aroma compounds including all of the lipophilic aroma compounds (Table 3 of ref *28*). In this work, some aroma compounds were also shown to be more retained by L2 phase than by a water-in-oil emulsion with equivalent hydration value of 10% (Table 2 of ref *28*). These findings show that the distribution of aroma compounds between the matrix and its headspace at the equilibrium depends upon not only its affinity for the pure constituents of the matrix themselves but also its specific interactions with the structure of the matrix. In this case, when the monoglyceride was mixed with the triglyceride, the polar head groups of the monoglyceride molecules self-assemble thermodynamically while forming hydrophilic domains inside the lipid mixture (*31*). This structurization is anticipated to modify the interaction of the volatile aroma compounds with the matrix depending upon their physicochemical properties, hence their oil-to-water or oil-to-air partition coefficient and in consequence, their vapor pressure in the headspace. The present study revealed a more important retention of the most lipophilic aroma compounds by the structured emulsion, a dispersion of L2 phase in an emulsified water solution, than by the simple oil-in-water emulsion containing the same lipid content of 5%. This result again confirms the interaction between some aroma compounds and structured lipids even in the presence of a small amount of monoglyceride (5% in lipid mixture and 0.25% in final emulsion). Landy et al. (*28*) explained the better retention of L2 phase toward certain aroma compounds by their amphiphilic structures. However, in our study, the lipophilicity of the aroma compounds appears to be an important criterion for this binding-effect enhancement in dispersed systems. Besides, preliminary experiments reported no difference in viscosity and distribution of oil droplet size between structured emulsion 5% and simple emulsion 5%. Therefore, we can exclude the influence of these parameters on the diffusion of aroma compounds. The difference in temperature used in dynamic analysis (36 °C) and in static analysis (50 °C) makes it difficult to use retention data to explain the findings of an increased $T_{max}$ for the amphiphilic and lipophilic aroma compounds in the structured emulsion. However, the increase could be due to the specific interactions of aroma compounds with the self-assembly structure, created by the monoglycerides. The self-assembly structure generates different domains, with different physical−chemical properties. Those domains can solubilize amphiphilic and lipophilic molecules of various physical characteristics. These specific interactions could be enhanced by dynamic processes compared to static state.

This work presents potential applications of structured emulsions in low- or reduced-fat food products, which may help to improve their aroma or maintain the aroma balance of traditional full-fat counterparts. Logically, the link between instrumental measurements and sensory analysis can be foreseen.

## ABBREVIATIONS USED

PTR−MS, proton-transfer reaction mass spectrometry; GC−MS, gas chromatography–mass spectrometry; AUC, area under the curve; $C_{max}$, maximum concentration; $T_{max}$, time to maximum concentration; MCT, medium-chain triglycerides.

## ACKNOWLEDGMENT

We gratefully acknowledge the expert technical help of Santo Ali and Philippe Pollien in the use of PTR−MS and Elizabeth Prior for the English proofreading.

## LITERATURE CITED


(1) de Roos, K. B. How lipids influence food flavor. *Food Technol.* **1997**, *51*, 60–62.

(2) Drewnowski, A. Why do we like fat? *J. Am. Diet Assoc.* **1997**, *97* (Suppl.), S58–S62.

(3) Forss, D. A. Role of lipids in flavors. *J. Agric. Food Chem.* **1969**, *17*, 681–685.

(4) Bennett, C. J. Formulating low-fat foods with good taste. *Cereal Foods World* **1992**, *37*, 429–432.

(5) Brauss, M. S.; Balders, B.; Linforth, R. S. T.; Avison, S.; Taylor, A. J. Fat content, baking time, hydration and temperature affect flavour release from biscuits in model-mouth and real systems. *Flavour Fragrance J.* **1999**, *14*, 351–357.

(6) Carey, M. E.; Asquith, T.; Linforth, R. S. T.; Taylor, A. J. Modeling the partition of volatile aroma compounds from a cloud emulsion. *J. Agric. Food Chem.* **2002**, *50*, 1985–1999.

(7) Doyen, K.; Carey, M.; Linforth, R. S. T.; Marin, M.; Taylor, A. J. Volatile release from an emulsion: Headspace and in-mouth studies. *J. Agric. Food Chem.* **2001**, *49*, 804–810.

(8) Giroux, H. J.; Perreault, V.; Britten, M. Characterization of hydrophobic flavor release profile in oil-in-water emulsions. *J. Food Sci.* **2007**, *72*, 125–129.

(9) Miettinen, S. M.; Tuorila, H.; Piironen, V.; Vehkalahti, K.; Hyvonen, L. Effect of emulsion characteristics on the release of aroma as detected by sensory evaluation, static headspace gas chromatography, and electronic nose. *J. Agric. Food Chem.* **2002**, *50*, 4232–4239.

(10) Miettinen, S. M.; Hyvonen, L.; Tuorila, H. Timing of intensity perception of a polar vs nonpolar aroma compound in the presence of added vegetable fat in milk. *J. Agric. Food Chem.* **2003**, *51*, 5437–5443.

(11) Roberts, D. D.; Pollien, P.; Watzke, B. Experimental and modeling studies showing the effect of lipid type and level on flavor release from milk-based liquid emulsions. *J. Agric. Food Chem.* **2003**, *51*, 189–195.

(12) Schirle-Keller, J. P.; Reineccius, G. A.; Hatchwell, L. C. Flavor interactions with fat replacers: Effect of oil level. *J. Food Sci.* **1994**, *59*, 813–815.

(13) Seuvre, A. M.; Diaz, M. A.; Voilley, A. Influence of the food matrix structure on the retention of aroma compounds. *J. Agric. Food Chem.* **2000**, *48*, 4296–4300.

(14) Weel, K. G.; Boelrijk, A. E.; Burger, J. J.; Jacobs, M. A.; Gruppen, H.; Voragen, A. G.; Smit, G. Effect of emulsion properties on release of esters under static headspace, in vivo, and artificial throat conditions in relation to sensory intensity. *J. Agric. Food Chem.* **2004**, *52*, 6572–6577.

(15) Chung, S. J.; Heymann, H.; Grün, I. U. Temporal release of flavor compounds from low-fat and high-fat ice cream while eating. *J. Food Sci.* **2003**, *68*, 2150–2156.

(16) Haahr, A. M.; Bredie, W. L. P.; Stahnke, L. H.; Jensen, B.; Refsgaard, H. H. F. Flavour release of aldehydes and diacetyl in oil/water systems. *Food Chem.* **2000**, *71*, 355–362.

(17) Miettinen, S. M.; Hyvonen, L.; Linforth, R. S.; Taylor, A. J.; Tuorila, H. Temporal aroma delivery from milk systems containing 0–5% added fat, observed by free choice profiling, time intensity, and atmospheric pressure chemical ionization−mass spectrometry techniques. *J. Agric. Food Chem.* **2004**, *52*, 8111–8118.

(18) Brauss, M. S.; Linforth, R. S. T.; Cayeux, I.; Harvey, B.; Taylor, A. J. Altering the fat content affects flavor release in a model yogurt system. *J. Agric. Food Chem.* **1999**, *47*, 2055–2059.

(19) Malone, M. E.; Appelqvist, I. A.; Goff, T. C.; Homan, J. E.; Wilkins, J. P. G. A novel approach to the selective control of lipophilic flavor release in low fat foods. In *Flavor Release*; Roberts, D. D., Taylor, A., Eds.; American Chemical Society: Washington, D.C., 2000.

(20) Wendin, K.; Solheim, R.; Allmere, T.; Johansson, L. Flavour and texture in sourmilk affected by thickeners and fat content. *Food Qual. Prefer.* **1997**, *8*, 281–291.

(21) Mialon, V. S.; Ebeler, S. E. Time−intensity measurement of matrix effects on retronasal aroma perception. *J. Sens. Stud.* **1997**, *12*, 303–316.

(22) Hatchwell, L. C. Implications of fat on flavor. In *Flavour−Food Interactions*; McGorrin, R. J., Leland, J. V., Eds.; American Chemical Society: Washington, D.C., 1996.

(23) Graf, E.; de Roos, K. B. Performance of vanilla flavor in low-fat ice cream. In *Flavor−Food Interactions*; McGorrin, R. J., Leland, J. V., Eds.; American Chemical Society: Washington, D.C., 1996.

(24) Roland, A. M.; Phillips, L. G.; Boor, K. J. Effects of fat content on the sensory properties, melting, color, and hardness of ice cream. *J. Dairy Sci.* **1999**, *82*, 32–38.

(25) Sagalowicz, L.; Leser, M.; Watzkem, H. J.; Michel, M. Monoglyceride self-assembly structures as delivery vehicles. *Trends Food Sci. Technol.* **2006**, *17*, 204–214.

(26) Miller, M.; Akashe, A.; Das, D. Mesophase-stabilized emulsions and dispersions for use in low-fat and fat-free food products. U.S. Patent 6,068,876, 2000.

(27) Vauthey, S.; Visani, P.; Frossard, Ph.; Garti, N.; Leser, M.; Watzke, H. J. Release of volatiles from cubic phases:monitoring by gas sensors. *J. Dispersion Sci.Technol.* **2000**, *21*, 263–278.

(28) Landy, P.; Pollien, P.; Rytz, A.; Leser, M.; Sagalowicz, L.; Blank, I.; Stahnke, L. H. Model studies on the release of aroma compounds from structured and nonstructured oil systems using proton transfer reaction−mass spectrometry. *J. Agric. Food Chem.* **2007**, *55*, 1915–1922.

(29) Pollien, P.; Lindinger, C.; Yeretzian, C.; Blank, I. Proton transfer reaction mass spectrometry, a tool for on-line monitoring of acrylamide formation in the headspace of Maillard reaction systems and processed food. *Anal. Chem.* **2003**, *75*, 5488–5494.

(30) Shamil, S.; Wyeth, L. J.; Kilcast, D. Flavour release and perception in reduced-fat foods. *Food Qual. Prefer.* **1992**, *3*, 51–60.

(31) Yaghmur, A.; De Campo, L.; Sagalowicz, L.; Glatter, O.; Michel, M.; Watzke, H. Oil-in-water emulsion for delivery. WO Patent 110,370, 2005.


**Received for review August 21, 2007. Revised manuscript received November 28, 2007. Accepted December 1, 2007.**

JF072520K