Impact of Destroying the Structure of Model Gels on Volatile Release

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The release of a strawberry aroma from different composite gels taken as models of fruit preparations and from a sucrose solution was investigated. The composition of the model systems differed with regard to the gelling agent, either pectin or carrageenan, and to the rigidity of the gel. With the use of atmospheric pressure chemical ionization−mass spectrometry, the release profiles of the aroma compounds were determined under stirring. At the same time, purge and trap measurements were performed to determine the release profiles of the aroma compounds without stirring. The comparison of the patterns obtained using these two complementary methods made it possible to determine how the structure of the matrix, the mechanical treatment, and the properties of the aroma compound affect aroma release. A far greater proportion of the aroma compounds was retained in the fruit preparation systems than in the sucrose solution. The different release profiles could be interpreted in terms of the volatility of the aroma compounds and of their diffusion through the gels.

KEYWORDS: Aroma release; release rate; flavor profile; diffusion; structure; APCI-MS

INTRODUCTION

The flavor of a food product is a determinant factor in the acceptability of the product by the consumer. To be perceived, flavor must first be released from the food product so as to come into contact with the olfactory receptors. Flavor release from the product depends on intrinsic factors such as the physicochemical properties of the aroma compounds (e.g., hydrophobicity, volatility) or the type of food ingredients and on extrinsic factors such as the temperature, the dilution with air, or the shearing of the product.

Polysaccharides are widely used in the food industry as thickeners or as gelling agents. In fruit preparations, for example, cross-linked waxy corn starch is frequently combined with low-methoxy pectin, or, seldomly, with carrageenan to yield the properties required to design the texture of fruit yogurts. The matrixes obtained are described as composite gels, that is to say, biphasic systems with swollen starch granules embedded in a network containing the other polysaccharides in the continuous phase (*1*). In addition, the presence of polysaccharides has been reported to decrease flavor release and consequently to affect flavor perception (*2*). For example, Arvisenet et al. (*3*) studied the retention of aroma compounds in the presence of starch. A strong retention effect was found in a 7% cross-linked waxy corn starch suspension as compared with

water: 50% for isoamyl acetate, 60% for ethyl hexanoate, and 80% for linalool. In many studies dealing with gelled matrixes containing pectin or carrageenan, the retention of aroma compounds has also been reported (*4−11*). This effect has been ascribed to interactions between aroma compounds and the polysaccharide and/or to a decrease in the diffusion of aroma compounds in the gelled system due to the formation of the three-dimensional network. However, other studies showed little effect of the texture of the dessert on in vivo aroma release (*12*).

It is to be noted that the equilibrium conditions used by many authors to study the effect of hydrocolloids on flavor release are rarely found in real situations. Moreover, at equilibrium, only interactions are evidenced, since the structure effects are considered as minor (*13*, *14*). To better understand how the structure of the gels affects flavor release, dynamic conditions must be considered, especially the effect of destroying the gel structure or the effect of the air flow. Shearing relates to situations in which a product is either stirred in the container during the preparation procedure or destructured during consumption. The main effect of shearing is to increase the transferring surface between the product and the gas phase and hence to accelerate the transport of aroma compounds (*15*, *16*). Additionally, shearing may also break down interactions of weak energy. The dilution of the headspace with air, which occurs when a closed container is opened or when air is breathed during consumption, may also influence flavor release (*15−17*).

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**Table 1.** Composition of the Strawberry Aroma, *m/z* Value of Each Compound, and Method of Analysis

compound	composition (%, w/w)	*m/z* value	analysis
diacetyl	0.43	87	APCI-MS, purge and trap
ethyl acetate	1.79	89	purge and trap
butanoic acid	0.22	89	
hexanal	0.10	101	
(*Z*)-hex-3-enol	2.37	101	purge and trap
pentanoic acid	0.11	103	
ethyl butyrate	2.72	117	purge and trap
hexanoic acid	0.11	117	
maltol	3.25	127	APCI-MS
furaneol	1.85	129	
limonene	0.22	137	
ethyl hexanoate	2.24	145	APCI-MS, purge and trap
vanillin	1.57	153	APCI-MS
linalool	0.19	155	purge and trap
methyl cinnamate	0.22	163	
γ-decalactone	0.25	171	APCI-MS
ethyl octanoate	0.11	173	APCI-MS, purge and trap

The objective of this study was to investigate the impact of destroying the gel structure on the dynamic release of a blend aroma. This study was part of a larger one focused on the mechanisms involved in flavor release from composite gels. In the present work, fruit preparations taken as model matrixes were prepared with different amounts of polysaccharide to obtain gels of variable structures and rigidities. Matrixes were flavored with a strawberry aroma (17 volatile compounds). Two different in vitro techniques were used to follow aroma release, on-line analysis by atmospheric pressure chemical ionization−mass spectrometry (APCI-MS) and dynamic cumulative headspace analysis by trapping on an adsorbent polymer (purge and trap). APCI-MS was used to analyze flavor release from a mouth simulator. The model gels were destroyed under controlled conditions and followed by rheological measurements. This made it possible to simultaneously follow the evolution of the gel structure and the release of volatile compounds to understand the effect of destroying the gel structure. In addition, the aim of this study was to take into account the impact of the nature of the aroma compounds and to highlight the complexity of such an approach with a blend aroma.

MATERIALS AND METHODS

Composition of the Strawberry Aroma. The composition of the strawberry aroma is reported in **Table 1**. The aroma was prepared by dissolving each pure compound (Sigma Aldrich, purity ranging between 95 and 99%, food grade) in propylene glycol (Sigma Aldrich, purity 99.5%) at 25 °C under stirring. The aroma was stored at 4 °C for no more than 2 months. Before use, it was stirred at room temperature for 5 h and the concentration of each aroma compound was checked.

Composition and Sample Preparation. Commercial sucrose (Erstein, France), stabilized cross-linked waxy corn starch (Roquette Frères, France), amidated low-methoxy pectin (DE 33%, DA 18%) (Danisco, Denmark), a 50/50 mixture of a κ-carrageenan and a κ/ι hybrid carrageenan referred to as κ₂-carrageenan (Danisco, Denmark), calcium sulfate, potassium chloride, and a lactate buffer (pH 3.8) were used for this study. Four formulations were prepared as reported in **Table**
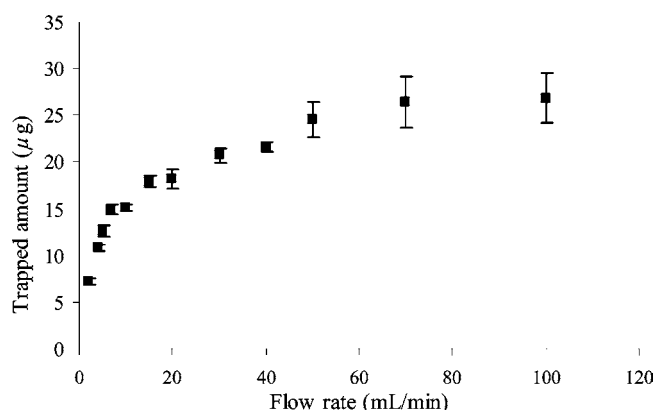
Figure 1. Release of ethyl hexanoate by purge and trap for 5 min as a function of the purge flow (matrix C2).

2. P was the model system of fruit preparation with pectin. C2 was designed to have textural properties close to P using carrageenan instead of pectin. C1 and C3 were obtained by varying the carrageenan content. S contained 35% sucrose and was prepared without polysaccharides.

Sucrose, starch, and then carrageenan or pectin were mixed together. The mixture was dispersed in a lactate buffer and stirred at room temperature for 20 min at 200 rpm to hydrate the ingredients. An LR 1000 reactor (IKA, Germany) provided the thermomechanical treatment required for starch swelling. The temperature was first raised from ambient to 85 °C in 10 min and maintained for 10 min at this temperature. The preparation was then cooled to 35 °C over 12 min. Throughout the temperature cycle, the preparation was stirred at 80 rpm.

Salts dissolved in the lactate buffer and the aromas were added to the preparation over 2 min at the beginning of the cooling step.

Purge and Trap/GC Analysis. (*a*) *Operating conditions for the Trapping of Volatile Compounds.* After preparation, a 5 g sample was poured into a 40 mL glass vial. The vial was hermetically sealed with a cap and stored for 24 h at 10 °C. For dynamic headspace analysis, the headspace above the sample was carried with purified nitrogen gas for 160 min. Thirty minutes before the experiment, the sample was placed in a water bath at 30 °C. Preliminary studies showed that this time made it possible to reach thermomechanical equilibrium. The sample was maintained at this temperature until the end of the experiment. The released volatile compounds were trapped in glass capillary tubes containing Tenax TA adsorbent (Perkin-Elmer).

In order to determine the appropriate gas flow, the amount of aroma compound released for 5 min was plotted for different gas flows ranging from 1 to 100 mL/min; it was estimated that this maximal value corresponded to the average rate of air flow reached during normal human breathing (*18*). Experiments were carried on in triplicate. The release curve of ethyl hexanoate is given as an example (**Figure 1**). The trapped amount of ethyl hexanoate increased sharply and almost linearly from 1 to 7 mL/min, and then the curve gradually leveled off until a constant level was reached beyond a flow rate of about 60 mL/min. For all the experiments of the present work, a gas flow of 70 mL/min was chosen, which corresponded to the part of the curve where the amount trapped did not depend on the gas flow.

(*b*) *GC Analysis.* Aroma compounds trapped on the Tenax adsorbent were desorbed using a thermal desorber (Turbo Matrix, Perkin-Elmer). The injector parameters were the following: precool the glass trap at −30 °C, preflush 1 min at 25 °C, desorption of the capillary glass tube at 250 °C for 5 min and then injection by quick heating of the glass

Table 2. Composition (%, w/w) of the Different Matrixes

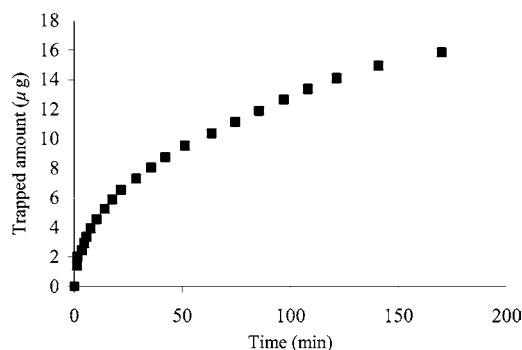| label	sucrose	starch	carrageenan	pectin	aroma	KCl	CaSO₄	buffer
S	35.0				0.40	0.16	0.03	64.41
C1	35.0	1.40	0.05		0.40	0.16	0.03	62.96
C2	35.0	1.40	0.33		0.40	0.16	0.03	62.68
C3	35.0	1.40	0.80		0.40	0.16	0.03	62.21
P	35.0	1.40		0.40	0.40	0.16	0.03	62.61

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Figure 2. Release of ethyl hexanoate by purge and trap as a function of time at 70 mL/min (matrix C2).

trap up to 300 °C. Through a heated transfer line (240 °C) compounds were directly analyzed using a DB-Wax column (30 m length, 0.32 mm i.d., and 0.5 μm film thickness), on a GC trace gas chromatograph (Thermoelectron) equipped with a flame ionization detector (250 °C). Helium was used for desorption and was then transferred toward the gas chromatograph as a carrier gas (90 kPa in the system). The oven temperature was maintained at 40 °C for 5 min and programmed to reach 240 °C at 5 °C/min; this temperature was then maintained for 10 min.

Before determining the quantity of aroma compounds released from the matrixes, a calibration procedure was performed: a known quantity of each aroma component dissolved in pentane was put into a glass tube and then each tube was analyzed by thermodesorption.

To study the release of aroma, a single sample of each matrix was used for the analysis. For each matrix, a total of 23 glass tubes used one after the other were used to trap the vapors released over time. The release curve was then plotted according to the amount of aroma trapped in the 23 successively filled tubes.

Three replicates of each matrix were analyzed. The release curve of ethyl hexanoate from the C2 matrix shown in **Figure 2** is given as an example. From each release curve, the following parameters were taken:

the initial release rate (k) from the initial linear part of the curve according to Roberts and Acree (*19*)

$$k = (\mathrm{d}[A]/\mathrm{d}t)_{\mathrm{trap}}/[A_0] \qquad (1)$$

where $[A]$ is the concentration in mg/L of aroma compound in the matrix, $[A_0]$ is the initial concentration (mg/L) of aroma compound in the matrix, and t is the time (min). The recovery (R), is calculated as follows

$$([A]_{160\mathrm{min}}/[A_0]) \times 100 \qquad (2)$$

where $[A]_{160\mathrm{min}}$ is the concentration (mg/L) of aroma compound recovered over 160 min.

Model Mouth/APCI-MS Analysis. (*a*) *Operating Conditions in the Model Mouth.* After preparation, 70 g of sample were placed in a mold and stored for 24 h at 10 °C. One hour before analysis, the sample was placed in a water bath at 30 °C to reach thermal equilibrium. The sample was then transferred with care from the mold in the model mouth, which was kept at 30 °C by water circulation through the double wall. This
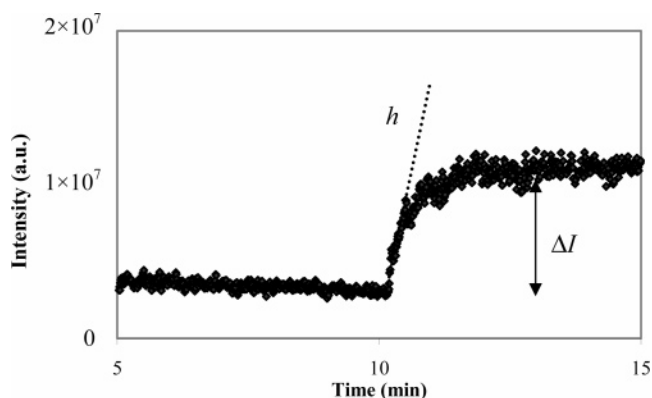

Figure 3. Release of ethyl hexanoate in the mouth simulator by APCI-MS: h is the release rate and ΔI is the magnitude of the increase of release when applying stirring (matrix C2).

model mouth, which was developed for semisolid foodstuffs, is described in Decourcelle (*20*). The headspace above the sample was directly analyzed on-line for 10 min without shearing, then for 10 min with shearing. Shearing was applied by means of a propeller with six 45° tilted blades rotating at a rate of 200 rpm estimated to correspond to a shear rate of 100 s^{-1}. This shear rate would correspond to shear conditions in the mouth for semisolid food products (*21, 22*).

(*b*) *APCI-MS Analysis.* The headspace above the sample was drawn from the model mouth at 70 mL/min and flowed through a heated capillary transfer line (150 °C, 0.53 mm i.d.) into an ion-trap mass spectrometer Esquire-LC (Bruker, France) equipped with a modified APCI source (*23*). Aroma compounds were ionized by a 5 kV positive ion corona pin discharge; data were collected for m/z values corresponding to the protonated molecular ion: m/z 87 (diacetyl), m/z 127 (maltol), m/z 145 (ethyl hexanoate), m/z 153 (vanillin), m/z 171 (γ-decalactone), and m/z 173 (ethyl octanoate) (**Table 1**).

Since the APCI-MS signal showed high variability, the intensity of the signal was measured using a 20 L Teflon bag inflated with nitrogen containing 250 mL of an aqueous solution of heptan-2-one (15 ppm) prior to each experiment. This made it possible to calculate a sensitivity index for each experiment. Data recorded for each sample were then divided by this index. Six replicates of each sample were analyzed. An example of the release curve of ethyl hexanoate from the C2 matrix is shown in **Figure 3**. The intensity of the signal is given in arbitrary units, the objective being to compare the effect of stirring alone. From each release curve, two parameters were taken: the release rate (h) taken at the beginning of the stirring at 10 min, which corresponds to the initial slope of the curve divided by the initial concentration of the considered aroma compound; and the magnitude (ΔI) defined as the difference between the average levels of release before (average from 5 to 10 min) and after stirring (average from 12 to 15 min).

(*c*) *Rheological Analysis.* In parallel, rheological parameters were determined by oscillatory measurements performed at 30 °C using an SR5 rheometer (Rheometric Scientific) in a cone-plate fixture (4 cm, 0.02 rad) equipped with a Peltier temperature controller. Measurements were performed in the dynamic regime at a constant strain amplitude of 1% from 100 to 1 rad/s. For each sample, the mechanical spectra

Table 3. Parameters from the Release Profiles by APCI-MS of Six Aroma Compounds from the Different Matrixes[a]

compound	h (× 10^{-5}, min^{-1})					ΔI (× 10^{-5}, a.u.)				
	S	C1	C2	C3	P	S	C1	C2	C3	P
ethyl hexanoate	223 a	84.3 c	98.5 c	155 b	114 bc	82.4 a	78.0 b	66.3 b	38.6 c	65.3 b
ethyl octanoate	10.8 a	3.72 c	5.20 bc	7.02 b	3.36 c	5.07 a	3.18 bc	3.87 b	2.75 c	3.29 bc
diacetyl						0.84 a	0.73 bc	0.78 b	0.68 a	0.74 bc
maltol										
vanillin	19.4 a	9.35 c	14.1 b	15.7 b	12.9 bc					
γ-decalactone	12.9 a	7.59 b	11.2 ab	11.8 ab	8.23 b	4.99 a	4.49 b	4.03 c	3.86 c	4.31 b

[a] Reported values are the average of six repetitions. For each parameter, different letters within the row mean that the results are significantly different between matrixes ($p < 0.05$).
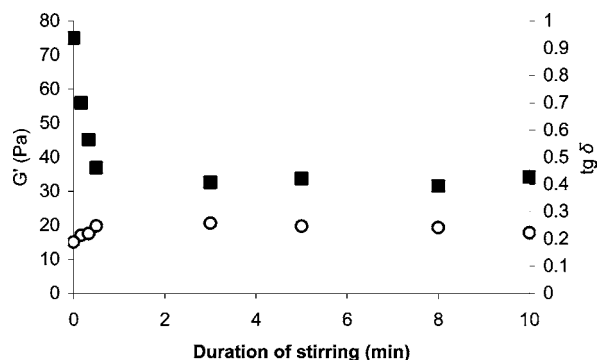
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Figure 4. Evolution of G' (■) and $tg \delta$ (○) variations as a function of the duration of stirring (matrix C2).

Table 4. G' Modulus (Pa) and $tg \delta$ (G''/G') before Shearing (initial) and after Shearing (for 10 min). Temperature: 30 °C; Frequency: 1 rad/s.

	G'		$tg \delta$	
matrix	initial	after shearing	initial	after shearing
C1	1.55	0.94	0.70	0.81
C2	75.0	34.2	0.19	0.22
C3	930	255	0.17	0.25
P	47.1	31.4	0.21	0.23

were immediately registered after a given shearing time in the model mouth: 0, 10, 20, 30, 180, 200, 480, or 600 s. A new sample was characterized at each shearing time.

Statistical Analysis. Analysis of varianceand least-significant-difference tests were used to assess significant differences between values in the different matrixes and for the different aroma compounds (*Statgraphics* software). The significance was established at $p < 0.05$.

RESULTS

APCI-MS and purge and trap are complementary methods that made it possible to detect different molecules of the strawberry aroma. On the one hand, the detection by purge and trap is based on the presence of the aroma compounds in the headspace of the product and their chromatographic behavior. On the other hand, the detection of a molecule R by APCI-MS is based on the identification of the protonated molecular ion, the mass of which corresponds to the addition of one proton [R + H]$^+$ (*24*). Thus, it requires the aroma compounds to have dissimilar masses so that they can be unambiguously identified. Among the 17 molecules of the strawberry aroma, 7 were measured by purge and trap (ethyl acetate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, (Z)-hex-3-enol, linalool, and diacetyl) while the APCI-MS device made it possible to detect 6 aroma compounds with different m/z values (ethyl hexanoate, ethyl octanoate, diacetyl, maltol, vanillin, and γ-decalactone) (**Table 1**). Thus, only 10 molecules among the 17 were detected with at least one method; 3 molecules were analyzed with both methods. Seven molecules were not analyzed because of a lack of volatility (organic acids) and consequential lack of sensibility for both methods. This underlined the complexity of studying a blend aroma.

In the first step, the release of ethyl hexanoate, a key aroma compound of the strawberry aroma, was reported using both methods. In the second step, the nine other compounds were considered, which allowed us to investigate the impact of the nature of the aroma compounds.

Release of Ethyl Hexanoate by APCI-MS. The release profile of ethyl hexanoate in the mouth simulator by APCI-MS for the C2 matrix is shown in **Figure 3**. During the first 10 min without stirring, the signal remained constant. At this moment, stirring was applied, and a sharp increase of the release of ethyl hexanoate was observed. To quantify this effect, two parameters were taken: the release rate (h) at the beginning of the stirring and the magnitude (ΔI). Similar patterns were found for the four gelled matrixes and for the 35% sucrose solution. The overall results are given in the first row in **Table 3**.

(*a*) *The Release Rate at the Beginning of the Stirring (h).* This parameter significantly varied depending on the matrix. Significant differences were found between the 35% sucrose

solution (S) and the four gels. As foreseen, the combination of starch and the hydrocolloid induced a decrease in the release rate. Between matrixes, significant differences were found between the C3 matrix and the C1 and C2 matrixes, while P was intermediate. An increase in the carrageenan concentration caused an increase in the release rate (h) whereas the P and C2 matrixes with similar textures did not exhibit any significant difference.

(*b*) *The Magnitude.* ΔI values for the five matrixes are also reported in **Table 3**. This parameter was significantly higher in the 35% sucrose solution than in the gelled matrixes. Among the four gels, ΔI was significantly lower for C3 than for the other three. As expected, the combination of starch with pectin or carrageenan reduced the amount of ethyl hexanoate released upon stirring. Moreover, the higher amount of carrageenan (C3) induced a higher retention effect than that found for C1, C2, and P.

(*c*) *Rheological Changes.* The variations in the storage modulus (G') and of the loss modulus (G'') as a function of frequency were recorded for the four gelled matrixes before stirring (0 min) and for different durations of stirring in the model mouth. Before stirring, the matrixes exhibited a solid-like behavior with $G' > G''$ and a slight frequency dependency. As illustrated by the values of G' and of the G''/G' ratio ($tg \delta$) before stirring at 1 rad/s given in **Table 4**, C1 could be regarded as a soft system and C3 as a rigid gel whereas C2 and P were intermediate, with close but not similar behaviors. The variations in G' and $tg \delta$ at 1 rad/s upon application of shear were recorded for different durations of stirring. The result for the C2 matrix is shown in **Figure 4**. During the first minute of shearing, a sharp decrease in G' was observed whereas $tg \delta$ increased slightly. Beyond this first minute, G' and $tg \delta$ remained almost constant. As a consequence, the stirring induced a rapid decrease in the rigidity of the gel as shown by the G' decrease while the structure of the matrix changed only slightly as seen from the $tg \delta$ values. The values of G' and $tg \delta$ at the end of the stirring period (10 min) for the different matrixes are also given in **Table 4**. After 10 min of stirring, the matrixes still exhibited a solid-like behavior ($tg \delta < 1$) with clear differences in their structures as estimated from G' values. From the variation of G' values between 0 and 10 min, it was possible to evaluate the destructuration caused by the stirring that occurred for these gelled matrixes during the first minute. The destructuration was higher for C3 (73%) than for C2 (54%), whereas C1 (39%) and P (33%) exhibited a similar level of destructuration.

Release of Ethyl Hexanoate by Purge and Trap. The release of ethyl hexanoate was determined using purge and trap in the different matrixes over a time period of 160 min. **Figure 2** illustrates the result obtained for the C2 matrix. The initial fast increase was followed by a region where the trapped amount slowed down. However, a plateau was not reached at the end of the experiment (160 min). This means that ethyl hexanoate
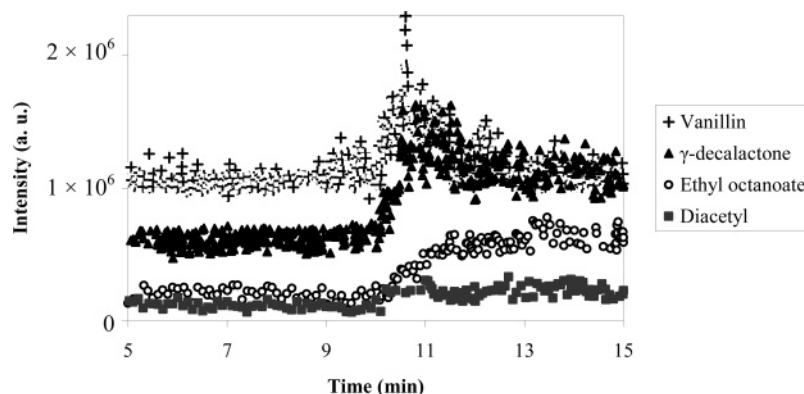
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Figure 5. Release of vanillin, γ-decalactone, ethyl octanoate, and diacetyl from the C2 matrix as measured by APCI-MS

Table 5. Initial Flavor Release (k) and Recovery (R) from the Release Profiles by Purge and Trap of the Different Aroma Compounds from the Different Matrixes[a]

compound	k ($\times 10^5$, min^{-1})					R (%)				
	S	C1	C2	C3	P	S	C1	C2	C3	P
ethyl hexanoate	1261 a	609 b	579 b	530 b	580 b	38.5 a	13.8 b	12.6 bc	11.3 c	12.3 bc
ethyl acetate	1052 a	843 b	788 bc	741 c	805 b	33.5 a	22.6 b	21.1 c	19.6 d	21.0 c
ethyl butyrate	1106 a	660 b	654 b	616 b	635 b	33.4 a	15.8 b	15.3 bc	14.2 c	14.4 bc
ethyl octanoate	3857 a	1045 b	831 bc	670 c	842 bc	79.7 a	12.3 b	10.6 bc	10.2 c	10.7 bc
(Z)-hex-3-enol	533 a	481 b	472 bc	433 c	467 bc	26.7 a	18.2 b	15.4 bc	15.1 bc	14.8 c
linalool	1861 a	1133 b	1056 bc	947 c	1087 bc	90.7 a	30.5 b	26.6 c	25.3 c	26.8 c
diacetyl	1103 a	978 b	980 b	762 c	915 b	75.0 a	33.1 b	32.9 b	26.2 d	29.5 c

[a] Values are the average of three repetitions. For each parameter, different letters within the row mean that the results are significantly different between matrixes ($p < 0.05$, except for value * $p < 0.1$).

was not totally recovered from the C2 matrix for this time-length. Similar profiles were obtained for the different matrixes. The characteristic parameters taken from the curves, that is to say, the initial release rate (k) and the percentage of aroma recovered (R) after 160 min, are given in **Table 5** (first row for ethyl hexanoate). The value of k was significantly higher in the 35% sucrose solution than in the four gelled preparations. The value of this parameter decreased as the carrageenan content increased. However, the differences were not significant [$F(4,-10) = 0.97$, $p = 0.45$], which is mainly due to the high coefficient of variance for the C3 and P matrixes.

The recovery (R) of ethyl hexanoate from the different matrixes after 160 min of purge and trap is given in **Table 5** (first row). Ethyl hexanoate was only partly recovered from the different matrixes, with values of 38.5% in the sucrose solution and 12.5% on average in the gelled model. This indicates that ethyl hexanoate was retained in the sucrose solution as well in the gelled models but to a lesser extent for the former system. A decrease in k was observed as the carrageenan content increased [$F(4,10) = 404$, $p < 0.05$] while R values of P and C2 were not significantly different.

Effect of the Nature of the Aroma Compounds. The strawberry aroma was formulated with 17 molecules. The release of 10 of them was measured by APCI-MS or by purge and trap. The objective was to know how the results obtained for the different aroma compounds differed from the ones obtained for ethyl hexanoate and to extent the initial balance of the strawberry note was changed in term of quantity.

(*a*) *Dynamic Release by APCI-MS.* It was possible to distinguish six aroma compounds unambiguously according to their *m/z* values: ethyl hexanoate, ethyl octanoate, maltol, vanillin, diacetyl, and γ-decalactone. Representative curves

in the case of the C2 matrix are shown in **Figure 5** for four of them: ethyl octanoate, diacetyl, vanillin, and γ-decalactone. The release profile of ethyl hexanoate has already been described (**Figure 3**). Regarding maltol, constant release was observed: stirring had no effect. For the aroma compounds presented in **Figure 5**, the release was accentuated as soon as the stirring was applied (at 10 min). However, the profiles were extremely different. Ethyl octanoate and diacetyl exhibited the same profile of release as ethyl hexanoate although the magnitude was lower particularly for diacetyl. Vanillin showed a sharp peak just after the application of stirring, but this was followed by a rapid return to the initial magnitude. In the case of γ-decalactone, a peak of release was also observed, followed by a rapid return; the final magnitude was, however, higher than the initial one.

As for ethyl hexanoate, the parameters h and ΔI were calculated when possible for the different matrixes (**Table 3**). For maltol, no significant effect was observed: h and ΔI were null. For diacetyl, the immediate increase made it impossible to determine h; for vanillin, after 2 min of stirring, no further effect of stirring was found. However, the release rate (h) could be measured.

Overall, the same conclusions as that for ethyl hexanoate could be drawn for the different matrixes. For all aroma compounds, the matrix had a significant effect on h and/or on ΔI. The parameters calculated in the sucrose solution were significantly higher than those in the gelled matrixes. Among them, h tended to increase with the carrageenan content; also, the P matrix exhibited a value close to that of the C1 matrix. On the other hand, ΔI tended to decrease as the carrageenan content increased. The P matrix showed values between those of C1 and C2.

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(*b*) *Dynamic Release by Purge and Trap.* Seven aroma compounds were detected in the headspace and analyzed by purge and trap. Contrary to the profiles found by APCI-MS, the release curves were similar for every compound. The characteristic parameters of the curves are given in **Table 5**. Overall, these values are in the same range as those reported using the same method (*7*).

Sucrose Solution. The values for *k* and *R* varied significantly according to the compound: *k* ranged from 533×10^{-5} min^{-1} for (*Z*)-hex-3-enol to 3857×10^{-5} min^{-1} for ethyl octanoate and *R* ranged from 26.7% for (*Z*)-hex-3-enol to 90.7% for linalool. For the homologous series of esters, *k* and *R* globally increased as the number of carbon atoms in the molecule increased. This can be related to the decreasing polar character of the compound when the carbonyl chain increases. Similar tendencies have been observed under equilibrium conditions (*11*). As generally seen in water (*19, 25*), higher release rates are observed for the hydrophobic compounds than for more hydrophilic ones.

Gelled Matrixes (**Table 5**). For all the compounds, *k* and *R* values were significantly lower in the gelled systems than in the sucrose solutions. Moreover, the values of these parameters globally decreased as the carrageenan content increased while the release from the P matrix was intermediate or similar to C1. The extent of the decrease varied depending on the hydrophobicity of the aroma compound for the ester series. In the C2 matrix, for example, *k* and *R* were reduced by 25 and 37%, respectively, for ethyl acetate (log *P* = 0.73), and by 78 and 86%, respectively, for ethyl octanoate (log *P* = 3.83), as compared with the sucrose solution. Likewise, in the P matrix, the retention effect of the more hydrophobic compounds was comparable to that of the C2 matrix: *k* and *R* were reduced by 23 and 38%, respectively, for ethyl acetate, and by 78 and 87%, respectively, for ethyl octanoate. If these results are verified for all the esters, it appears that other physiochemical characteristics should be considered for other compounds.

DISCUSSION

In the present study, flavor release was studied over a long time scale. The parameters calculated described the release either during the first seconds (*h, k*) or over a longer period (Δ*I, R*). The former parameters (*h* and *k*) reflect the rate of release and may be related to perception in the mouth while the latter (Δ*I* and *R*) correspond more to a steady state and may be related to the preparation, the storage, or the various shearing operations during processing.

If we consider first the results for ethyl hexanoate, we can propose some interpretations from the comparison of different matrixes. In purge and trap measurements, the gelled systems are not sheared. It is clear that the structure of these unsheared gelled matrixes plays a role in the release of ethyl hexanoate. For instance, in the case of the carrageenan-based composite systems, increasing the amount of carrageenan induced a decrease in the initial release rate as well as in recovery (**Table 5**). Under the experimental conditions used, the flow of aroma compound across the interface depends on the difference between the concentrations of aroma compound in the matrix and that in the gas phase and on the partition and diffusion coefficients of the aroma compound in the matrix (Fick's laws). Assuming that the partition and the diffusion coefficients remain constant and are independent of the concentration during the experiment, the driving force for the release of ethyl hexanoate is the difference between the concentrations. On this basis, we can interpret the curve presented in **Figure 1**. For the low flow

rates of the carrying gas (<7 mL/min), only part of the volatile compounds released in the gas phase is carried away. As a result, the difference in concentrations between the two phases is small. For higher flow rates (between 7 and 60 mL/min), more and more volatiles are carried away and the concentration difference increases up to a plateau, corresponding to the total purge of the gas phase. Beyond this flow rate (around 60 mL/min), a maximal concentration difference is reached and the release of aroma compounds no longer varies over time. Therefore, the dynamics of the system are essentially controlled by the partition of the aroma compound and its diffusion in the matrix. The partition coefficients of ethyl hexanoate have been previously determined under equilibrium by a static headspace method (*11*). It was shown that the partition coefficient does not differ between the gelled matrixes. This shows the absence of any interaction between ethyl hexanoate and the components of the composite gel. As a result, the differences among matrixes found in the present study are probably due to molecular diffusion rather than to partition phenomena. It is likely that the structure of the matrix influences flavor release by restricting the diffusion of aroma compounds. Increasing the rigidity of the gel may cause a decrease in molecular mobility through the formation of the network comprising swollen starch granules and carrageenan or pectin together, as has been postulated (*5, 7, 8, 26*).

APCI-MS experiments showed clearly that an increase in the release of ethyl hexanoate is triggered as soon as stirring is applied. From *h* values (initial slope), it is clear that this effect depends on the structure of the matrix. The more gelled the matrix, the faster the release and the lower the magnitude of Δ*I* (**Table 3**).

The period during which the increase in release was experienced (on the order of 1 min) can be related to the evolution of the structure while stirring. It is during the first minute of the stirring period that most of the destructuration of the matrix takes place (see **Figure 4**). Therefore, the breakdown of the structure brought about by applying the mechanical treatment for a few minutes and the increase in flavor release are concomitant phenomena. We also found that the higher the initial rigidity of the gel, the greater the degree of breakdown and the greater the amount of aroma compound released from the matrix. During this short period of time, a new structure is obtained and the level of destructuration of the gel can explain the increase in the release.

On the other hand, the magnitude of Δ*I* is measured after 2 min of stirring, that is, when the destructuration of the matrix has already occurred. From the rheological characteristics (**Table 4**), the matrixes still exhibited large differences in their properties. The differences in initial gel rigidity (before stirring) were not abolished by applying the mechanical treatment. Therefore, Δ*I* can be related to the difference in the rigidity of the matrixes. The more gelled the matrix, the higher the retention. All these results are consistent with the fact that the level of release is mainly determined by the rheology and the structure of the matrix before and after shearing.

The combination of the two different methods also allowed us to follow the release of different aroma compounds from the strawberry aroma and to investigate how their release was affected by the dynamic conditions and the structure of the product. While the profiles of the aroma compounds were found similar by purge and trap experiments, the APCI-MS profiles of release of the different aroma compounds under stirring varied widely (**Figure 5**). It is also noteworthy that the compounds detected by purge and trap were all retained in the matrix. As for ethyl hexanoate, retention in the gelled matrixes can be

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ascribed to a decrease in the diffusion of the aroma molecules. The characteristic parameters for the P and C2 matrixes indicate similar retention in both matrixes (**Tables 3** and **5**). In other words, the diffusion of aroma molecules is probably the same in matrixes containing pectin or carrageenan. This also suggests that it is the rheological property rather than the composition which determines the release from the matrixes. In contrast, the results with the S matrix (a sucrose solution) showed a higher release of aroma compounds as compared with the release from gels. That might be due to the higher diffusion coefficient that was found using NMR DOSY (*26*). This parameter was reduced by about 50% in the C3 matrix as compared with the 35% sucrose solution for ethyl butyrate.

Nevertheless, the extent of the retention effect in the gelled matrixes varies among volatile compounds according to their hydrophobicity. This may be due to the formation of weak interactions between aroma compounds and hydrophobic regions of the gel. In hydrophobic compounds such as esters, the affinity for the matrix increases with increasing chain length; this is also reported in other carrageenan matrixes (*7, 8*) and in pectin gels (*9, 27*).

With the use of APCI-MS, six aroma compounds were detected. These molecules exhibited different volatilities, which can be illustrated by the air/water partition coefficient (Canal Arle Database): ethyl octanoate ($K = 6.5 \times 10^{-2}$), ethyl hexanoate ($K = 3.4 \times 10^{-2}$), γ-decalactone ($K = 2.3 \times 10^{-2}$), diacetyl ($K = 5.6 \times 10^{-4}$), vanillin ($K = 9.9 \times 10^{-8}$), and maltol ($K = 3.6 \times 10^{-9}$). For all these compounds except for maltol, the least volatile one, stirring had an effect on release. However, for vanillin, which is also a low volatility compound, the release profile only showed a peak followed by a return to the initial intensity after the first minute of stirring ($\Delta I = 0$). To summarize, the release profile depends on the volatility of the aroma molecule. For $K > 10^{-4}$, stirring induced a significant increase in flavor release while almost no effect was found for $K \ll 10^{-4}$. These observations agree with the results reported by Roberts et al. (*16*) who showed that the release of highly volatile compounds was reduced in the presence of guar or carboxymethylcellulose in solution, whereas the less volatile compounds (maltol and vanillin) show less of an effect.

The various compounds were affected differently by stirring. Therefore, the proportions released vary from one aroma compound to another. In other words, the proportion retained in the product will differ from those in the initial strawberry aroma incorporated in the product. As expected, the higher losses took place mostly in the more volatile compounds. Any industrial process should take into account such variations and losses due to the stirring occurring during the preparation.

ABBREVIATIONS USED

APCI, atmospheric pressure chemical ionization; a.u., arbitrary unit; DOSY, diffusion-ordered spectroscopy; GC, gas chromatography, MS, mass spectrometry; NMR, nuclear magnetic resonance.

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