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Partition and Release of 21 Aroma Compounds during Storage of a Pectin Gel System

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The increasing popularity of low-fat products increases the need for a better understanding of how flavor release is affected by partial substitution of fat with hydrocolloids. Partitioning and release of aroma compounds from four pectin gels with different compositions were studied with static headspace and with a model mouth. Air/product partition coefficients determine the potential extent of aroma release, and mass transfer determines the rate at which aroma compounds are released to the vapor phase. This study showed that the gel network had large effects on the partition of aroma compounds between the gel and vapor phase. The specific properties of the aroma compounds were also of importance for the air/gel partition. Storage of the four gels showed that one of the weaker gels was influencing the concentration of aroma compounds in the headspace, probably caused by formation of a denser network over time.

KEYWORDS: Aroma; headspace concentration; pectin; gels; storage

INTRODUCTION

Over the past few years there has been a focus on foods containing an excess of energy, mainly in the form of fat, and modification of these products has been demanded. These food products are modified so that the fat is replaced with different kinds of hydrocolloids such as pectin. The ideal hydrocolloid should preferably not interfere with the flavor, aroma, or taste of the product and should be stable under normal storage conditions (*1*). One reason to use high-methoxyl pectins (HMP) for food manufacture is their healthy properties. Pectin belongs to the group called "roughage," which reduces the cholesterol content in the blood and affects fat metabolism (*2*). HMP are used, for example, in mayonnaise, tomato ketchup, cloudy juices, beverages, ice cream, and jellied sweets (*3*). Because replacing fat with a hydrocolloid not only changes the structure and texture of a food but also affects the flavor composition and perception, it is important to investigate how the flavor and structure parameters are related to each other.

The factors that affect flavor release from foods are phase partition and mass transport (*4*). Flavor release from product to vapor phase will take place only if the phase equilibrium is disturbed. At equilibrium the concentrations in these phases show the following relationship:

$$K_{gp} = C_g/C_p$$

where K_{gp} is a conventional gas-product partition coefficient and C_g and C_p are the concentrations of the flavor compound in air and product, respectively.

The partition coefficient can be influenced by many factors such as temperature and composition of the product phase. For example, sugar molecules influence the vapor pressure through their reducing effect on water activity. Binding of aroma compounds or formation of complexes also influences the partition of aroma molecules between the product and the vapor phase because only the free dissolved molecules exert a vapor pressure. (*4*). When food is eaten, there are the effects of mastication; addition of saliva also changes the partition of volatile aroma compounds between the food and the air phase (*5*).

Knowledge of the aroma and texture stability of foods throughout their shelf life is another important area, and therefore storage of the gels was investigated in this study. The first step in the gel-building process is that of initial intermolecular local contacts, involving hydrogen bonding between short chain segments. This process is the rate-determining process above 30 °C (*6*). The second step involves the aggregation of chains and enlargement of junction zones, governed by hydrophobic interactions, probably stabilized or strengthened by van der Waals forces and additionally by hydrogen bonds. This is the rate-determining step below 30 °C (*6*). As a result of the increasing junction zone density, a rapid increase of both the loss (G'') and storage (G') moduli has been shown by rheological oscillating measurements. After the rapid increase, the storage modulus keeps increasing slightly and continuously as a result of the slower formation and rearrangement of junction zones,

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Table 1. Gel Strength of the Four Gels Defined by the Value of the Highest Peak from Texture Analyzer Measurements (*F*)[a]

gel type	strongest gel (gel 1)	second strongest gel (gel 2)	second weakest gel (gel 3)	viscous solution (gel 4)
F value (g)	5600	3300	1300	<50
G′ (Pa)	1050	92	58	0.12
G″ (Pa)	83	34	50	2

[a] Values of *G′* and *G″* were measured in an earlier study (*10*).

reaching the pseudo-plateau region. After 4 days *G′* continues to increase, resulting from a continuous reorganization of the network (*7*).

How hydrocolloids affect the partition of aroma compounds and aroma release has been investigated by instrumental analysis before. Roberts et al. (*8*) found that highly volatile compounds are most affected by a change in viscosity. However, the sucrose, carboxymethyl cellulose (CMC), and guar gum used showed different aroma release patterns, indicating some kind of binding interactions with the aroma molecules. HMP was found to have a decreasing effect on some aroma compounds when the concentration was increased in a strawberry jam (*9*). This was confirmed by Hansson et al. (*10*), who showed that a stronger HMP gel gave a lower headspace concentration of aroma compounds due to entrapment in the gel structure.

In this study 21 aroma compounds with different properties were added to four pectin gels with different strengths and compositions. The aim was to study how the partition between the gas phase and gel and the mass transport of the compounds were affected by each gel. For these investigations both static headspace and a model mouth in combination with gas chromatography (GC) were used. The effect of storage on the structure of these gels and its effect on the release of aroma compounds and the aroma concentration in the gas phase at equilibrium were also investigated.

MATERIALS AND METHODS

Gel Preparation. The pectin gel system basically consisted of water, HMP, white syrup (34% sucrose, 24% glucose, 22% fructose, and 20% water) (Danisco Cultor, Arlöv, Sweden), citric acid, and 21 aroma compounds. The aroma compounds included alcohols (1-propanol, 1-butanol, 3-methyl-1-butanol, 2-pentanol, 1-hexanol, 2-nonanol, and *cis*-3-hexenol), ketones (2,3-butanedione, 2-butanone, 2-heptanone, 2-octanone, and 2-decanone), esters (ethyl acetate, ethyl hexanoate, propyl acetate, butyl acetate, and ethyl butyrate), aldehydes (hexanal, heptanal, and octanal), and a sulfur compound (dimethyl sulfide). The pectin used was Grindsted pectin CF 120 (Danisco Cultor), an extra-slow-setting, high-ester pectin standardized with sugars. As the first step in gel preparation white syrup was mixed with water and heated. Pectin was mixed with sodium citrate and added to the syrup solution, which was then heated until boiling. After 2 min of boiling, citric acid was added to the mixture. The aroma compounds were mixed with water at a concentration of 0.005% (v/w) and added to the mixture as the last preparation step, and after preparation, the samples were placed in a refrigerator. Four different gels with different gel strengths [defined by the force value (*F*) on the highest peak from the texture analyzer measurements (**Table 1**)] were mixed, each one prepared in three replicates (100 mL each). Gel 1 consisted of 90% white syrup, 1.5% pectin, and 3% citric acid; gel 2 of 79% white syrup, 1.85% pectin, and 1% citric acid; gel 3 of 85% white syrup, 2% pectin, and 1% citric acid; and gel 4 of 75% white syrup, 1.5% pectin, and 0.1% citric acid. The samples were balanced with water to 100%.

Static Headspace and Gas Chromatography—Flame Ionization Detection (GC-FID). For static headspace gas chromatography (SHGC), 2 g of the gel mixture was placed in a gastight vial (10 mL) that was sealed immediately. Two replicates were prepared from the same gel mixture, and they were incubated in an automated headspace unit (Combipal-CTC Analytics System; JVA Analytical Ltd., Dublin, Ireland) of the gas chromatograph (Varian CP-3800; JVA Analytical Ltd,) at 20 °C. The samples were equilibrated and agitated at 750 rpm for 10 min, and 2 mL of the gas phase containing the aroma compounds was injected on the GC by a splitless injection. The GC was equipped with a fused silica capillary column, a 1.0 μm thick film of BPX5 60 m × 0.32 mm i.d. (SGE, Kiln Farm, Milton Keynes, U.K.), and a flame ionization detector. An equilibration time of 10 min was found after equilibrating the samples for 5, 10, and 15 min, respectively. The temperature program used had an initial temperature of −30 °C maintained for 1 min, followed by increase at a rate of 100 °C min^{-1} to 40 °C. The temperature was maintained at 40 °C for 40 min and was subsequently increased at 2 °C min^{-1} to 90 °C, further at 4 °C min^{-1} to 130 °C, and finally at 8 °C min^{-1} to 250 °C. Concentrations of aroma compounds in the headspace at equilibrium above the four different gels were measured at four different time points [day 0 (gel preparing day), day 1, day 4, and day 7] and as three replicates.

Rheological Measurements. Gel strength was measured in the samples (three replicates of each sample) by a texture analyzer (model TA-XT2, Stable Micro Systems, Godalming, U.K.). One hundred grams of the gel mixture was poured into a glass, and this procedure was repeated four times corresponding to days 0, 1, 4, and 7 (48 samples in total). All samples were then placed in a refrigerator at 4 °C to let the gels settle. On day 0 the sample was placed in the refrigerator for 1.5 h before the measurements. The sample was then placed in a texture analyzer and penetrated by a probe until the surface was broken. The force (g) required to break the surface was registered. The probe used was 35-mm ∅, the test speed was 1 mm/s, and the penetration depth was 75% of the sample height (i.e., 18 mm). The samples were kept at room temperature before the measurements, and the temperature was measured in the samples afterward to state that room temperature was reached during the measurements.

Model Mouth and Gas Chromatography—Mass Spectrometry (GC-MS) Measurements. For isolation of the aroma compounds in the gels, 6 g of gel sample was placed in a sample flask (70 mL) of the model mouth system. The temperature was kept constant at 37 °C by water circulating around the flask. Artificial saliva (4 mL), consisting of distilled water, potassium phosphate dibasic trihydrate, sodium chloride, calcium chloride dehydrate, sodium nitrate, sodium bicarbonate, mucin, and α-amylase (*11*), was added to the sample. To trap the volatiles, a gas flow of purified nitrogen (100 mL min^{-1}) flushed the headspace above the gel/saliva mixture for 1 min while the volatile compounds were collected on Tenax within a tube. During collection, mastication was simulated by a plunger making up-and-down rotating movements (52 rpm). The aroma compounds were thermally desorbed from the Tenax (220 °C, 4 min) by a thermal desorption device (Tekmar purge and trap 3000 concentrator, JVA Analytical Ltd.), transferred via a heated line, and cryofocused at −120 °C using a Tekmar cryofocusing module (JVA Analytical Ltd.). The compounds were injected (235 °C, 2 min) onto a gas chromatograph (Varian Star 3400 CX, JVA Analytical Ltd.), where they were separated and finally quantified by a mass spectrometer (MS; Varian Saturn 3, JVA Analytical Ltd.). The GC column was a BPX5 capillary column of 60-m length, 0.32-mm i.d., and 1.0-μm film thickness. An initial oven temperature of 40 °C was used for 4 min, followed by an increase of 2 °C min^{-1} to 90 °C, then by 4 °C min^{-1} to 130 °C, and finally by 8 °C min^{-1} to 270 °C, with a final hold at 270 °C for 2 min. Three replicates of each gel were analyzed. The response of the detector was determined by injection of standard pentane solutions with known concentrations of the analyzed compounds, and the amounts released in the model mouth system were calculated by relating them to the standard solutions.

Aroma Release Calculations. For quantification of the aroma recovered, the amounts of aroma compounds released in the model mouth (w) were divided by the amount present in the sample flask of the model mouth before aroma collection (w).

Air/Gel Partition Coefficient Calculations. The air/gel partition coefficients of each aroma compound were determined by dividing the

Table 2. Differences in Air/Gel Partition Coefficients (× 1000) among the Four Different Gels[a]

compound	overall	gel 1	gel 2	gel 3	gel 4
dimethyl sulfide	ns	2.56a	4.21a	3.61a	6.12a
1-propanol	$p < 0.01$	2.20a	1.87b	1.75b	1.75b
1-butanol	$p < 0.01$	1.48a	1.21b	1.13b	1.14b
2-pentanol	$p < 0.01$	2.35a	2.03b	1.82c	1.86c
3-methyl-1-butanol	$p < 0.01$	1.86a	1.57b	1.49bc	1.42c
cis-3-hexenol	$p < 0.01$	2.62a	2.07b	1.92c	2.06b
1-hexanol	$p < 0.01$	1.87a	1.50b	4.49b	1.69b
2-nonanol	$p < 0.01$	1.23c	1.45b	1.55b	1.78a
hexanal	$p < 0.01$	2.26d	4.40b	3.64c	6.74a
heptanal	$p < 0.01$	1.30c	2.12b	2.62b	3.96a
octanal	$p < 0.01$		0.49b	1.77a	0.64a
2,3-butanedione	$p < 0.01$	2.58a	2.43b	2.14c	1.95d
2-butanone	ns	6.02a	6.85a	6.05a	5.86a
2-heptanone	$p < 0.01$	3.42c	4.86a	4.51b	6.23a
2-octanone	$p < 0.01$	2.14b	2.18a	3.72a	2.98a
2-decanone	$p < 0.01$	0.70c	0.87c	1.32a	1.07b
ethyl acetate	$p < 0.01$	7.72b	11.47a	9.36c	13.10a
propyl acetate	$p < 0.01$	6.41b	11.59a	8.20b	13.12a
ethyl butyrate	$p < 0.01$	4.65d	9.99b	6.77c	12.88a
butyl acetate	$p < 0.01$	4.63c	9.19b	6.17c	11.02a
ethyl hexanoate	$p < 0.01$	6.85b	12.75a	15.41a	18.24a

[a] Measurements were made by static headspace and GC-FID on day 1 of storage. Letters indicate significant differences ($p < 0.01$) among air/gel partition coefficients.

air phase concentrations (w/v) at equilibrium by the concentrations in the gel phase (w/v).

Statistical Analysis. To determine significant differences among the gels with regard to storage, analysis of variance (ANOVA) was used. If significant differences were found, Fisher's least significant difference tests (LSD) were performed (*12*). A significance level $p < 0.01$ was used throughout the study.

RESULTS AND DISCUSSION

Partition of Aroma Compounds between Various Types of Gels and Air. Static headspace measurements showed different partition coefficients of the aroma compounds between the air and the four gels, which could be related to the chain length, the functional group, and also the position of these functional groups of the aroma compounds. According to the results most of the aroma compounds showed significantly higher air/gel partitioning coefficients from weaker gels compared to that from a stronger gel (**Table 2**). This is in agreement with earlier studies (*10*, *13)* in which increased gel strength gave a lower concentration of aroma compounds in the headspace due to entrapment of aroma molecules in the network. However, the opposite trend is observed on alcohols, which showed an increased air/gel partition coefficient with increasing gel strength (**Table 2**). The air/gel partition of the aroma compounds was probably influenced by two mechanisms; one by addition of sucrose "salting out" or retention depending on the polarity of the aroma compound and one from the pectin that retained the molecules in the network either by sterical hindrance or by formation of nonpolar micelles. The alcohols had the lowest air/water partition coefficients among the aroma compounds analyzed (*14*) and were most likely localized in the water phase. Because gel 1 contained a low amount of water, the alcohols were salted out as seen in an earlier study (*15*), which contributed to a higher air/gel partition from this gel compared to the other gels. Furthermore, the decrease in concentrations of the alcohols between gels 1 and 4 could be related to the number of carbon atoms or polarity of these compounds (**Figure 1**). That is, the longer the carbon chain, the less polar alcohol, and the lower the air/gel partition coefficients of the alcohols

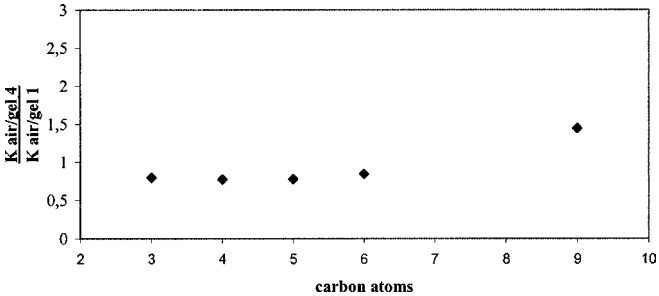

Figure 1. Relationship between carbon chain length of the alcohols and the ratio of air/gel partition coefficients between the viscous solution (gel 4) and the strongest gel (gel 1).

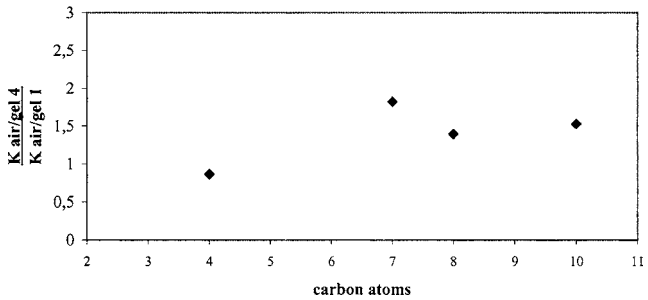

Figure 2. Relationship between carbon chain length of the ketones and the ratio of air/gel partition coefficients between the viscous solution (gel 4) and the strongest gel (gel 1).

above gel 1 compared to the viscous solution and the two weaker gels. The nonpolar alcohols were more easily retained in the gel with the dense network because it probably contained more nonpolar micelles. The same results were seen for gel 2, which gave a significantly lower concentration of long-chained alcohols in the headspace compared to gel 4.

The concentrations of aldehydes in the headspace decreased with increased density of the gel network. However, of the three aldehydes included in the study, only two showed large enough GC peaks to be evaluated. These two aldehydes showed a significantly lower concentration above gel 1 compared to the concentrations above the viscous solution and the weaker gels (**Table 2**). The values also indicated that a longer carbon chain could be related to a lower air/gel partition coefficient of the aldehydes from the three gels compared to that from the viscous solution, which was a behavior similar to that of the alcohols. There was, however, no such relationship between gels 2 and 3. Within each gel the air/gel partitioning for the aldehydes was also related to chain length: the longer the chain, the lower the air/gel partitioning coefficient, probably due to retention of a more nonpolar molecule in nonpolar cavities in the pectin gel network.

For the ketones there was no consistent relationship between gel strength or network density and concentrations of ketones in the headspace (**Table 2**). However, it was seen that the longer the carbon chain, the lower the concentration in the headspace above gel 1 compared to the other gels (**Figure 2**). It was also found that within each gel, the longer the carbon chain, the less polar the ketone and the lower the concentration in the headspace above all the gels compared to the ketones with fewer carbon atoms (**Figure 2**). This could be due to steric hindrance or retention in the nonpolar pectin gel as seen for the other aroma groups. It could also be an effect of interactions between HMP and ketones, in accordance with the results from Braudo et al. (*16*). These authors stated that 2-ketones bind to LMP via van der Waals interactions and that these interactions increase with an increase in alkyl chain length. However, 2,3-butanedione did

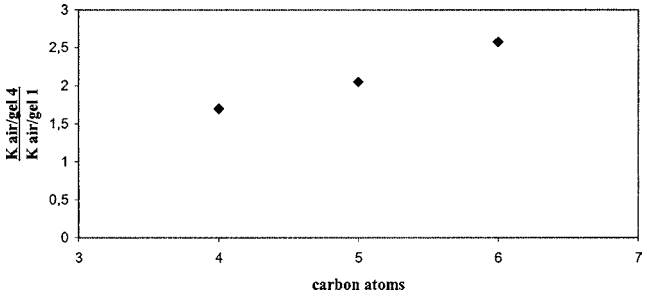

Figure 3. Relationship between carbon chain length of the esters and the ratio of air/gel partition coefficients between the viscous solution (gel 4) and the strongest gel (gel 1).

Table 3. Changes of Air/Gel Partition Coefficients (× 1000) over 7 Days of Storage of Gel 1[a]

compound	overall	day 0	day 1	day 4	day 7
dimethyl sulfide	ns	3.71a	2.56a	3.51a	2.44a
1-propanol	ns	2.30a	2.20a	2.32a	2.21a
1-butanol	ns	1.58a	1.48a	1.53a	1.47a
2-pentanol	ns	2.64a	2.35a	2.60a	2.49a
3-methyl-1-butanol	ns	1.98a	1.86a	1.95a	1.92a
1-hexanol	ns	1.98a	1.87a	2.03a	1.98a
cis-3-hexenol	ns	2.74a	2.62a	2.65a	2.58a
2-nonanol	ns	1.21a	1.23a	1.29a	1.25a
hexanal	ns	2.72a	2.26a	2.91a	2.78a
heptanal	ns	1.55a	1.30a	1.73a	1.64a
octanal	ns	0.16a			0.15a
2-heptanone	ns	4.32a	3.42a	4.60a	4.16a
2-octanone	$p < 0.01$	2.89a	2.14b	3.15a	2.86a
2-decanone	ns	0.75a	0.70a	0.90a	0.79a
propyl acetate	ns	8.66a	6.41a	8.41a	7.41a
ethyl butyrate	ns	6.26a	4.65a	6.41a	5.58a
butyl acetate	ns	6.13a	4.63a	6.25a	5.48a
ethyl hexanoate	ns	8.85a	6.85a	9.76a	8.79a

[a] Measurements were made by static headspace and GC-FID. Letters indicate significant differences ($p < 0.01$) among air/gel partition coefficients.

not follow this pattern, probably because of its molecular structure with two functional groups and its very polar nature.

The concentrations of the esters in the headspace were seen to decrease with increased gel strength as seen for the alcohols and aldehydes (**Table 2**). They were released to a great extent from the viscous solution that contained a large amount of water, followed by gel 2 with the second largest amount, then gel 3, and gel 1 with only a small amount of water. This was probably an effect of their low air/water partition coefficients. The esters showed the same relationship as the other compounds between chain length, polarity, and aroma concentration in the headspace (**Figure 3**). Above gel 1 the air/gel partition of the esters with long carbon chains was significantly lower compared to the other gels and the viscous solution (gel 4). Within each of the gels it was seen that aroma partition decreased with increasing carbon chain length. Ethyl hexanoate, however, showed the highest air/gel partition coefficients for all gels compared to the other compounds.

Differences in Aroma Headspace Concentrations Due to Storage. It was seen that the gels were not stabilized during day 0, and therefore the data used for evaluation were compared between days 1, 4, and 7. For gel 1 a significant decrease in aroma headspace concentration was seen between days 1 and 4 for 2-octanone (**Table 3**). No other compounds were affected. The aroma molecules were more easily retained in a denser network due to sterical hindrance or nonpolar cavities in the gel matrix, and this contributes to a lower aroma concentration in the headspace in general compared to the other gels. A possible increase in G' of this already strong network did not affect the aroma concentration in the headspace.

Table 4. Changes of Air/Gel Partition Coefficients (× 1000) over 7 Days of Storage of Gel 2[a]

compound	overall	day 0	day 1	day 4	day 8
dimethyl sulfide	$p < 0.01$	3.76ab	4.21a	2.84b	1.81c
1-propanol	$p < 0.01$	1.85a	1.87a	1.58b	1.56b
1-butanol	$p < 0.01$	1.11a	1.21a	0.95b	0.96b
2-pentanol	$p < 0.01$	1.91b	2.03a	1.59c	1.60c
3-methyl-1-butanol	$p < 0.01$	1.48b	1.57a	1.31c	1.31c
cis-3-hexenol	$p < 0.01$	2.07a	2.07a	1.83b	1.75b
1-hexanol	$p < 0.01$	1.44b	1.50a	1.39c	1.42c
2-nonanol	ns	1.45a	1.45a	1.3a	1.32a
hexanal	$p < 0.01$	3.80b	4.40a	3.10c	2.99c
heptanal	$p < 0.01$	2.13a	2.12b	1.83c	1.82c
octanal	ns	0.94a	0.49a	0.48a	0.45a
2,3-butanedione	$p < 0.01$	2.34a	2.43a	1.96b	1.93b
2-butanone	ns	6.31a	6.85a	5.45a	5.31a
2-heptanone	$p < 0.01$	4.84b	4.86a	4.27b	4.43b
2-octanone	ns	3.15a	2.18a	2.04a	2.15a
2-decanone	ns	0.87a	0.87a	0.83a	0.80a
ethyl acetate	$p < 0.01$	10.47a	11.47a	8.60b	8.33b
propyl acetate	$p < 0.01$	10.30a	11.59a	8.19b	8.14b
ethyl butyrate	$p < 0.01$	8.59ab	9.99a	6.66b	6.72b
butyl acetate	$p < 0.01$	8.03a	9.19a	6.32b	6.34b
ethyl hexanoate	ns	12.75a	12.75a	11.53a	11.95a

[a] Measurements were made by static headspace and GC-FID. Letters indicate significant differences ($p < 0.01$) among air/gel partition coefficients.

Table 5. Changes of Air/Gel Partition Coefficients (× 1000) over 7 Days of Storage of Gel 3[a]

compound	overall	day 0	day 1	day 4	day 7
dimethyl sulfide	ns	3.95a	3.61a	2.73a	2.08a
1-propanol	$p < 0.01$	2.10a	1.75b	1.75b	1.69b
1-butanol	$p < 0.01$	1.35a	1.13b	1.09b	1.07b
2-pentanol	$p < 0.01$	2.21a	1.82b	1.77b	1.73b
3-methyl-1-butanol	$p < 0.01$	1.71a	1.49b	1.47b	1.44b
cis-3-hexenol	$p < 0.01$	2.30a	1.92b	1.95c	1.97c
1-hexanol	ns	1.72a	4.49a	1.44a	1.55a
2-nonanol	ns	1.78a	1.55a	1.51a	1.58a
hexanal	ns	4.26a	3.64a	3.40a	3.15a
heptanal	ns	2.97a	2.62a	2.39a	2.24a
octanal	ns	2.06a	1.77a	1.69a	1.60a
2,3-butanedione	$p < 0.01$	2.55a	2.14b	2.10b	2.03c
2-butanone	ns	7.02a	6.05a	5.55a	5.08a
2-heptanone	ns	5.06a	4.51a	4.11a	3.94a
2-octanone	ns	3.84a	3.72a	2.38a	3.36a
2-decanone	ns	1.65a	1.32a	1.29a	1.38a
ethyl acetate	ns	10.54a	9.36a	8.12a	7.32a
propyl acetate	ns	9.29a	8.20a	7.07a	6.58a
ethyl butyrate	ns	7.67a	6.77a	5.85a	5.59a
butyl acetate	ns	7.02a	6.17a	5.41a	5.15a
ethyl hexanoate	ns	16.12a	15.41a	14.22a	14.96a

[a] Measurements were made by static headspace and GC-FID. Letters indicate significant differences ($p < 0.01$) among air/gel partition coefficients.

For gel 2 there was a significant decrease in the air/gel partitioning for 15 of the 21 aroma compounds between day 1 and days 4 and 7, respectively (**Table 4**). However, the air/gel partition of the six compounds that were not significantly reduced were also seen to decrease in concentration after 4 and 7 days, respectively. This could be explained by the fact that G' still increases after 4 days due to aggregation of pectin chains (*7*). Increase in G' could be an effect of an increase in the number of junction zones, leading to a denser network (*17*) or a strengthening of the network strands (*18*), and the aroma molecules were then more easily trapped in the pectin chain network. Although the texture analyzer measurements did not show any changes in gel strength due to storage, these

Table 6. Changes of Air/Gel Partition Coefficients (× 1000) over 7 Days of Storage of the Viscous Solution (Gel 4)[a]

compound	overall	day 0	day 1	day 4	day 7
dimethyl sulfide	ns	2.86a	6.12a	4.86a	3.35a
1-propanol	ns	1.69a	1.75a	1.80a	1.77a
1-butanol	$p < 0.01$	1.07b	1.14a	1.19a	1.19a
2-pentanol	ns	1.72a	1.86a	1.89a	1.91a
3-methyl-1-butanol	$p < 0.01$	1.32b	1.42a	1.41a	1.42a
cis-3-hexenol	ns	1.96a	2.06a	2.17a	2.23a
1-hexanol	ns	1.63a	1.69a	1.66a	1.74a
2-nonanol	$p < 0.01$	1.65b	1.78a	1.80a	1.81a
hexanal	$p < 0.01$	4.55b	6.74a	6.92a	6.63a
heptanal	$p < 0.01$	2.56b	3.96a	4.04a	3.88a
octanal	ns				
2,3-butanedione	ns	2.02a	1.95a	1.96a	1.98a
2-butanone	ns	4.87a	5.86a	5.86a	5.97a
2-heptanone	ns	4.13a	6.23a	6.23a	6.18a
2-octanone	ns	1.89a	2.98a	2.90a	2.95a
2-decanone	ns	1.20a	1.07a	1.06a	1.07a
ethyl acetate	$p < 0.01$	8.51b	13.10a	13.03a	12.58a
propyl acetate	$p < 0.01$	7.70b	13.12a	13.06a	12.18a
ethyl butyrate	$p < 0.01$	6.66b	12.88a	12.63a	11.30a
butyl acetate	$p < 0.01$	6.10b	11.02a	10.89a	9.99a
ethyl hexanoate	$p < 0.01$	11.03b	18.24a	17.62a	16.46a

[a] Measurements were made by static headspace and GC-FID. Letters indicate significant differences ($p < 0.01$) among air/gel partition coefficients.

Table 7. Differences in Aroma Release among Four Pectin Gels[a]

compound	overall	gel 1	gel 2	gel 3	gel 4
dimethyl sulfide	ns	0.90a	0.58a	0.00a	1.65a
1-propanol	$p < 0.01$	0.00b	0.49ab	0.77a	0.49b
1-butanol	$p < 0.05$	0.53a	0.56b	0.98a	0.56b
2-pentanol	$p < 0.01$	0.57b	0.76b	0.94a	0.60b
3-methyl-1-butanol	$p < 0.05$	0.55b	0.78b	1.29a	0.61b
cis-3-hexenol	ns	0.34a	0.35a	0.39a	0.30a
1-hexanol	ns	1.20a	1.74a	1.39a	1.20a
2-nonanol	ns	0.84a	2.43a		1.52a
hexanal	ns	1.68a	2.06a	2.13a	2.15a
heptanal	ns	0.26a	0.66a	0.29a	0.23a
octanal	ns	0.55a	0.65a	0.66a	0.43a
2,3-butanedione	ns	0.41b	0.39a	1.96a	0.39a
2-butanone	ns	0.70a	0.60a	0.29a	0.71a
2-heptanone	ns	1.81a	2.84a	2.17a	2.91a
2-octanone	ns	0.56a	0.69a	0.66a	0.57a
ethyl acetate	ns	1.23a	0.95a	0.52a	0.77a
propyl acetate	ns	2.60ab	2.64a	2.08a	1.83a
ethyl butyrate	ns	2.84b	3.37a	3.28a	2.31a
butyl acetate	ns	2.68a	3.14a	2.77a	1.92a
ethyl hexanoate	ns	0.15a	0.17a	0.19a	0.36a

[a] Measurements were made with a model mouth and GC-MS. Letters indicate significant differences ($p < 0.01$) among air/gel partition coefficients.

measurements show the results of only large deformations and there could still be an effect of G'. The trapping of the aroma molecules could be due to sterical hindrance or retention in nonpolar regions within the gel network.

For gel 3 no large differences in air/gel partition between day 1 and days 4 and 7, respectively, were seen for the aroma compounds (**Table 5**). 2,3-Butanedione showed a significantly decreased headspace concentration between days 1 and 7. G' probably continued to increase in this gel as well, and it was seen that the air/gel partition coefficients of most of the aroma compounds were decreased by storage, although not significantly. However, it is probable that the gels have different gelling properties and that in one gel the density of the network continued to increase during storage, whereas the others had an already stable structure.

For gel 4 there were no significant differences in aroma headspace concentration between day 1 and the other days

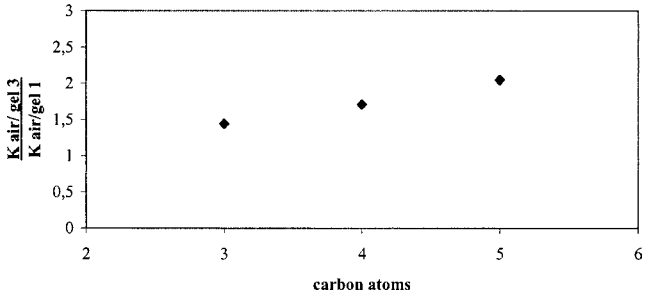

Figure 4. Relationship between carbon chain length of the alcohols and the ratio of release from gel 3 compared to gel 1.

Table 8. Changes in Aroma Release from Gel 2 during 7 Days of Storage[a]

compound	overall	day 0	day 1	day 4	day 7
dimethyl sulfide	ns	0.72a	0.58a	1.00a	1.21a
1-propanol	ns	0.46a	0.49a	0.45a	0.93a
1-butanol	ns	0.77a	0.56a	1.33a	2.46a
2-pentanol	$p < 0.05$	0.99b	0.76b	1.54a	1.14ab
3-methyl-1-butanol	ns	0.92a	0.78a	1.37a	2.24a
cis-3-hexenol	ns	0.34a	0.35a	0.77a	0.74a
1-hexanol	ns	1.82a	1.74a	2.61a	2.63a
2-nonanol	ns	1.49a	2.43a	2.13a	3.99a
hexanal	ns	1.87a	2.06a	2.92a	3.01a
heptanal	ns	0.28a	0.66a	0.77a	0.27a
octanal	ns	0.61a	0.65a	0.75a	0.89a
2,3-butanedione	ns	0.40a	0.39a	0.43a	0.96a
2-butanone	$p < 0.01$	0.94b	0.60b	1.60a	0.60b
2-heptanone	$p < 0.05$	2.18b	2.84b	4.24a	2.72b
2-octanone	ns	0.62a	0.69a	0.83a	1.87a
ethyl acetate	ns	1.21a	0.95a	2.05a	1.47a
propyl acetate	$p < 0.05$	2.65b	2.64b	3.91a	2.36b
ethyl butyrate	$p < 0.05$	3.25b	3.37b	4.57a	2.67b
butyl acetate	ns	2.91a	3.14a	4.31a	3.28a
ethyl hexanoate	ns	0.16a	0.17a	0.19a	0.19a

[a] Measurements were made with a model mouth and GC-MS. Letters indicate significant differences ($p < 0.01$) among air/gel partition coefficients.

(**Table 6**). Because the viscous solution did not contain any network, the viscosity was unchanged during storage.

Model Mouth—Dynamic Headspace/GC-MS. From the dynamic headspace measurements (model mouth) it was shown that the only significant ($p < 0.05$) differences between the gels in the headspace concentrations of the aroma compounds were seen for the alcohols (**Table 7**). This could be an indication that the viscosity or strength of the gel does not influence aroma release. Although it could be interpreted that the viscosity or strength of the gel does not influence aroma release, because the measurements in the model mouth were performed over 1 min, this could be long enough to break down the network in all of the gels, giving them equal viscosity or strength.

The alcohols showed a significantly higher release from gel 3 compared to gels 4 and 1. For 1-propanol and 2-pentanol there was also a significantly higher release from gel 3 compared to gel 2. Generally, it is assumed that mass transport across the product/saliva interface is rate-determining for flavor release (*4*). The higher concentration of alcohols above gel 3 could be explained by a faster transport between this gel and the saliva. Another explanation could be that this gel was more easily broken down during mastication, which would give a higher aroma release. A relationship between the length of the carbon chain of the alcohols and the release from gel 3 was also found (**Figure 4**). A longer carbon chain of the alcohol gave a higher release from gel 3 compared to gels 4 and 1. This could be explained by the fact that when the molecular weight of the

compound increases, its molecular size increases, leading to a slower diffusion rate (*19*).

No relationship was seen between the other gels and carbon chain length of the alcohols, and no other compounds showed a significant difference in aroma release between any of the gels.

Dynamic Headspace and Storage. The only results seen by storage during dynamic conditions as measured by the model mouth and GC-MS were significantly higher releases of 2-butanone, 2-pentanol, propyl acetate, ethyl butyrate, and 2-heptanone from gel 2 on day 4 compared to the other days (**Table 8**). This indicated that storage of the gels did not have any large effects on flavor release in the mouth when the concentrations of the aroma compounds were analyzed after being chewed in the model mouth for 1 min.

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