Release of Strawberry Aroma Compounds by Different Starch-Aroma Systems

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Abstract: In the food industry, the addition of flavours is used to reinforce the aroma profile of different goods. However, interactions between starch and aroma compounds can occur, and this can impact upon aroma release and perception. In the present study, we have investigated the influence of starch type on aroma release from starch-aroma systems. The food model system used was composed of an aqueous starch dispersion (1 g dry starch/100 g dispersion) and 10 aroma compounds (ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl pentanoate, methyl hexanoate, ethyl hexanoate, methyl ethyl propanoate, hexyl acetate, 3-hexenol, and phenyl methyl acetate). Different commercially available starches were used: Amilogels P, K, PDP, G, MVK, HP, OK and HPW, and carrageenan (Amilogel CAR) and guar gum (Amilogel GG). Aroma release from these starch-aroma systems into the gas phase above food (headspace) were monitored by GC-MS analysis with a solid-phase micro-extraction technique. The smell of the starch-aroma system was also evaluated sensorially by a trained panel. The release of aroma compounds from the different starch-aroma systems was statistically significant ($P < 0.0001$) for all of the aroma compounds, with the exception of ethyl pentanoate. A correlation between the concentration of individual aroma compounds in the headspace and the sensory evaluation (smell) was seen. Starch-aroma systems comprising corn starch (Amilogel G), physically modified starches that are soluble in cold water (Amilogels K, PDP), and hydroxypropyl distarch phosphate (Amilogels HP) had sensorially superior smells compared to the other types of starches tested. At the same time, the headspace GC-MS analyses showed ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate and ethyl pentanoate to be at the highest concentrations, which are all typical aroma compounds of strawberry fruit, and which also have low perception thresholds. Dextrin-roasted starch, guar gum and carrageenan provided the lowest sensory scores, although in contrast, they more strongly retained these aroma compounds.

Keywords: strawberry; aroma compounds; starch; GC-MS; sensory evaluation

INTRODUCTION

Aroma compounds in food matrices are of great importance in food acceptability to consumers. Starch is a food constituent that is applied frequently as a thickener, stabiliser and carrier. It usually interacts with aroma compounds (Arvisenet *et al.* 2002a, b; Lubbers *et al.* 2007). Both amylose and amylopectin are known to form inclusion complexes with low molecular weight organic compounds (Jouquand *et al.* 2006), where the partition of volatile compounds in gas/liquid systems takes place (Jouquand *et al.* 2004). Interactions between food components and aroma compounds are responsible for the release/retention of aroma molecules from food matrices into the gas phase above the food (headspace). The perception of aroma volatiles is directly related to their concentrations in the headspace. Factors affecting the availability of aroma compounds in the headspace include: rheological properties (Seuvre et *et al.* 2006; Tietz *et al.* 2008), and the presence of and reactions/interactions among proteins, lipids, carbohydrates and salts (Pozo-Bayon *et al.* 2008). All of these factors can have great impact on the release/retention of aroma compounds by starch-based matrices (Guichard 2002).

The nature and treatment of starch, its physicochemical characteristics and its physical state are known to also have significant impact on aroma release (Goubet *et al*. 1998; Boutboul *et al*. 2002). Strawberry aroma compounds include numerous esters, alcohols, aldehydes and acids that have different retention effects in starch-aroma systems (Savary *et al*. 2006).

The aim of the present study was to investigate the influence of the nature of starch on the retention of some strawberry aroma compounds. The release of each aroma compound into the headspace was followed according to the nature of the starch, and the smells of each starch-aroma systems were evaluated sensorially to determine possible correlations with the individual aroma compounds in the headspace.

MATERIALS AND METHODS

Different commercially available starches were used (Helios Domžale, Slovenia): Amilogel P (E 1422 acetylated distarch adipate), Amilogel K (a physically modified starch, soluble in cold water), Amilogel PDP (a physically modified starch, soluble in cold water), Amilogel G (corn starch), Amilogel MVK (E 1422 acetylated distarch adipate), Amilogel HP (E 1442 hydroxypropyl distarch phosphate), Amilogel OK (E 1404 oxidised starch), Amilogel HPW (E 1442 hydroxypropyl distarch phosphate), carrageenan (E 407) and guar gum (E 412). A model food system was used, composed of aqueous starch dispersions (1 g dry starch/100 g dispersion) with the addition of 0.05% of the commercial strawberry flavour mixture.

Preparation of the starch-aroma system. Aqueos solutions of each starch type (1 g/100 g) were heated to 75°C for 1 h. The starches soluble in cold water were not heat treated. After cooling, 0.05% of commercial strawberry flavour mixtures were added. Ten g of gelatinised starches were provided with the strawberry flavour mixtures in 20-ml glass vials that were closed with crimp caps. After an equilibration period of 72 h at 4°C, headspace analyses of the aroma volatiles were carried out.

The concentrations of ten aroma volatiles (ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl pentanoate, methyl hexanoate, ethyl hexanoate, methyl ethyl propanoate, hexyl acetate, 3-hexenol, and phenyl methyl acetate) in the headspaces of these commercial strawberry flavour mixtures were investigated using GC-MS.

Gas chromatography–mass spectrometry. Analyses were carried out using a gas chromatograph (6890N, Agilent Technologies, USA) equipped with an autosampler (MPS2, Multipurpose Sampler, Gerstel, Germany) and mass ion-selective detector Hewlett-Packard 5971A (Palo Alto, CA, USA). The gas chromatograph was fitted with a 60 m × 0.32 mm × 0.5 µm ZB-WAX capillary column (Phenomenex, USA). He 6.0 was used as carrier gas with a flow rate of 1.2 ml/min, at 40°C. The aroma volatiles were sampled for 30 min at 30°C using a solid-phase micro-extraction (SPME) fibre, with a carbowax/ polydimethylsiloxane coating (CW/PDMS, StableFlex, 85 µm thickness). For thermal desorption, the SPME fibre remained in the injector (270°C) for 5 min. The oven temperature programme was set at 40°C for 5 min, ramped from 40°C to 230°C at a rate of 4°C/min, and kept for 5 min at 230°C. The mass selective detector was operated at 70 eV with electron impact ionisation. The transfer line was set to a temperature of 280°C. Mass spectra were acquired in full-scan mode (30–300 m/z). The peaks were identified by comparison of experimental spectra with those of the National Institute for Standards and Technology database (NIST, USA).

Sensory evaluation test. Sensory evaluation of smell (1, non-typical, to 8, typical) was carried out by ten trained panellists.

Statistical methods. The data were evaluated using variance analysis with the Duncan test ($P < 0.05$), with the SAS/SAT Software programme.

RESULTS AND DISCUSSION

The type of starch had significant influences on the retention of all of the aroma compounds,

Table 1. Influence of starch type on concentrations of the strawberry aroma volatiles

	Ethyl butanoate	Ethyl 2-methyl butanoate	Ethyl 3-methyl butanoate	Ethyl pentanoate	Methyl hexanoate	Ethyl hexanoate	Ethyl propanoate	Hexyl acetate	*cis*-3-Hexenol	Phenyl methyl acetate
P value	< 0.0001	< 0.0001	< 0.0001	0.1227	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001

except for ethyl pentanoate (Table 1). Among all of the compounds, ethyl hexanoate was the most abundant in the headspace, while the concentration of methyl hexanoate was the lowest. Seuvre *et al.* (2006) also showed ethyl hexanoate to be the component most released from starch systems. As reported by Seuvre *et al.* (2006), *cis*-3-hexenol was the component most strongly retained by starch systems. Our results confirm the above-mentioned statement that the headspace concentrations of ethyl hexanoate were higher than those of *cis*-3-hexenol.

In general, Amilogel G (corn starch) was the best retainer for the majority of the compounds. This was in part confirmed by Arvisenet *et al.* (2002a), who demonstrated that corn starch retains ethyl hexanoate better than corn waxy starch. Savary *et al.* (2007) showed that the distribution of aroma compounds depended mainly on the composition of the system, and that the nature of the aroma molecule did not have a great impact.

Our study focused on correlations between the chemical analyses of individual aroma compounds in the headspace and the sensory perception of smell. The results of the sensory evaluation are presented in Table 2. The best score for smell was found in the Amilogel G starch (corn starch), followed by Amilogel HP (hydroxypropyl distarch phosphate) and Amilogel K (a physically modified starch, soluble in cold water). We detected the highest concentrations of ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate and ethyl pentanoate in these starch-aroma systems. These aroma volatiles are typical aroma compounds of strawberry fruit (Schieberle & Hofmann 1997; Martuscelli *et al.* 2008). They all have a fruity character and a low perception treshold (Schieberle & Hofmann 1997). On the other hand, the starch-aroma systems with the lowest smell scores had higher headspace concentrations of the not-so-typical strawberry aroma compounds, including ethyl hexanoate, ethyl propanoate, hexyl acetate, 3-hexenol and phenyl methyl acetate. 3-hexenol is known to have an odour characteristic that resembles green leaves or green banana (Azodanlou *et al.* 2003). Higher correlations between headspace concentrations and sensory scores for smell were found for the typical strawberry aroma compounds (Table 3). The not-so-typical compounds showed lower or negative coefficients.

Table 2. Sensory evaluation of smell of starch-aroma systems

Starch	LSM ± SE (scale 1–8)
Amilogel P	3.9 ± 0.5^{cde}
Amilogel K	5.5 ± 0.5^{bc}
Amilogel PDP	5.3 ± 0.5^{bc}
Amilogel G	7.2 ± 0.5^{a}
Amilogel GG	3.5 ± 5de
Amilogel CAR	3.4 ± 0.5^{e}
Heliodex KR	0.1 ± 0.5^{f}
Amilogel MVK	5.3 ± 0.5^{bc}
Amilogel HP	6.6 ± 0.5^{ab}
Amilogel OK	5.1 ± 0.5^{bcd}
Amilogel HPW	4.7 ± 0.5^{cde}
P-value	< 0.0001

Values followed by a different letter are significantly different in the Duncan (0.05) test.

Table 3. Correlation coefficients between the concentrations of the individual aroma compounds and the sensory scores

	Pearson correlation coefficient (*r*)
Ethyl butanoate	0.24
Ethyl 2-methylbutanoate	0.39
Ethyl 3-methylbutanoate	0.29
Ethyl pentanoate	0.58
Methyl hexanoate	0.03
Ethyl hexanoate	0.01
Ethyl propanoate	–0.01
Hexyl acetate	–0.64
3-Hexenol	0.12
Phenyl methyl acetate	–0.13

CONCLUSIONS

In the present study, the type of starch had a significant influence on retention of the aroma compounds in these starch-aroma systems. The typical strawberry aroma does not depend on a single compound, but is rather the result of a complex multicomponent relationship among the many aromatic constituents. Starches are used as thickeners and form viscous products that can interact with the aroma compounds. These interactions depend mainly on the nature of the starch and its modifications, on the molecular weight and polarity of the aroma compounds, and on competition between the aroma compounds. The present study focused on correlations between the headspace concentrations of the individual aroma compounds and sensory perception of the smell. Starch-aroma systems that received high scores for smell had higher headspace concentrations of the typical strawberry aroma compounds, and *vice versa*, lower smell scores meant that the typical aroma compounds were more strongly retained by the starch matrices. Although starch is used in many products, mainly as a thickener or stabiliser, we have shown here that it can have pronounced effects on the release/retention of individual aroma compounds, and consequently on the overall sensory impression of a product.

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