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ORIGINAL PAPER

Changes in structure and aroma release from starch–aroma systems upon α-amylase addition

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Abstract The influence of starch hydrolysis by α-amylase addition on structural properties and aroma release from starch–aroma systems was studied. A food model system composed of aqueous tapioca starch dispersion (4 g dry starch/100 g dispersion) and one aroma compound (menthone) was investigated. Structure breakdown and related changes in starch fraction (amylose) were measured by rheology and iodine-binding. Menthone release from the aroma-starch system in the headspace was followed by proton transfer reaction-mass spectrometry (PTR-MS) upon starch hydrolysis. A slightly higher viscosity was found for the starch–menthone system compared to the starch system without menthone upon α-amylase addition. One could hypothesise that menthone acts as a kind of nucleation agent for inducing structure build-up of starch segments, hindering starch degradation. An extensive aroma release from aroma–starch systems upon α-amylase addition was expected, but, instead, just a slight volatile increase was found after a starch hydrolysis time of 60 min. It is suggested that aroma release is the result of several superimposed effects ranging from viscosity effects to interactions between aroma compounds and starch degradation products.

Keywords Starch · Amylose · Aroma · Amylose inclusion complexes · α-Amylase · Starch degradation · Aroma release · Proton transfer reaction mass spectrometry (PTR-MS)

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Introduction

Starch is a natural polymer and a major component of plant origin-based foods. As a food ingredient, starch is applied as a thickener, stabiliser and carrier [1]. Pure starch should be tasteless and odourless. Nevertheless, specific odours have been ascribed to starch of different origin [2–4]. Besides endogenous volatile compounds, the interaction of starch with added aroma is of relevance for aroma retention and release. In general, binding interactions of carbohydrates and aroma compounds are governed by adsorption, hydrogen binding, complexation and encapsulation [5, 6]. A rather specific binding mechanism is the formation of helical starch inclusion complexes with a variety of aroma compounds. In particular, the linear amylose fraction has the ability to form inclusion complexes with a number of ligands such as iodine, monoacyl lipids and aroma compounds like terpenes and aldehydes [7–9]. The helication of starch in the presence of complexing aroma compounds influences the structure of starch at different length scales as manifested by spherulitic crystallisation, starch gelation or bulk phase separation [10–12]. Also, the release of aroma compounds from starch systems is thought to be related to the ability of the molecules to interact with starch. Starch may be more or less degraded by α-amylases, but it is not clear to which extent the modification of starch

at the molecular level influences the binding and the release of aroma compounds. On one side, the application of α-amylases during processing of starch systems to tailor the structural properties of starch is of interest. On the other hand, the effect of salivary α-amylases on the release of aroma compounds is important with respect to aroma perception during food consumption. Extensive starch degradation could lead to an increase in volatile release due to a higher solute concentration, which is also termed 'salting out'. The opposite effect is named 'salting in' where small sugars may interfere with the diffusion of volatile compounds and thus slow down their release [13]. On the other hand, studies on starch–lipid complexes and partly crystalline starch–aroma spherulites showed a reduced susceptibility of starch to α-amylase and a slow attack [10, 14]. The effect of an artificial saliva on aroma release was studied on model mouth systems by static headspace and by a dynamic approach (proton transfer reaction-mass spectrometry) [15, 16]. The model mouth simulated the conditions in the mouth and the aroma concentration in the headspace was measured. Interactions between artificial saliva components and volatiles were investigated with respect to volatile partition. Some effects on partition were observed to be influenced by proteins (mucin), salts and sugars [17].

The aim of this investigation was to observe the impact of α-amylase on structural changes and aroma release of a simple food model system composed of water, starch and an aroma compound. Rather low amylase activities were selected not only to simulate the addition of an α-amylase as a processing aid to tailor starch properties, but also to simulate the conditions in the mouth to a certain extent. Breakdown of starch structure was characterised by rheology and amperometric iodine titration. Aroma release into the headspace was followed by proton transfer reaction-mass spectrometry (PTR-MS), as it allows measuring very low aroma concentrations in the vapour phase due to the high sensitivity [18, 19]. Besides the release of added aroma compounds, changes in the profile of endogenous starch volatiles were of interest in this study.

Materials and methods

Native tapioca starch (C*Creamtex 70001) was obtained from Cerestar (Wädenswil, Switzerland). Menthone (purity > 97%) was supplied by Fluka (Buchs, Switzerland). Chemical purity was checked by gas chromatography–mass spectrometry (GC–MS). Hog pancreas α-amylase with an activity of 46.5 U/mg was obtained from Fluka (Buchs, Switzerland). Distilled water was used for all experiments.

Preparation of aqueous starch dispersions with aroma

Starch dispersions were prepared by heating aqueous starch suspensions with stirring. The starch suspension at a concentration of 4.3 g dry starch/100 g dispersion was heated in an Erlenmeyer flask in a water bath that was mounted on a hot plate stirrer (IKA Labortechnik). The temperature in the starch suspension was monitored and heating to 95 °C was accomplished at a rate of approximately 3 ± 0.5 °C/min. The starch dispersions were heated for 45 min at 95 °C, followed by cooling to 30 °C. The amount of evaporated water was assessed gravimetrically and replaced. The starch dispersion (28 g) was mixed with 2 ml aqueous aroma solution in a 300 ml Erlenmeyer flask and hermetically covered with an headspace cap. Mixing of the system was accomplished by shaking for 10 s. The final sample weight was 30 g and the starch concentration in the system was 4 g dry starch/100 g dispersion. The menthone concentration was 0.13 mg/100 g sample. An aqueous aroma solution with same aroma concentration served as references. Samples were kept at 25 °C for 24 h before further analysis.

Starch amylolysis

Hog pancreas α-amylase with an activity of 46 g 5 U/mg was dissolved in distilled water at 25 °C and hermetically stored (1 U corresponds to the amount of enzyme that releases μmol maltose/min at pH 6.9 and 25 °C). The enzyme solutions were freshly prepared every day. The enzyme solution was added to the starch dispersion so that a final enzyme concentration of approximately 46 U/g dry starch in the sample was achieved. For the aroma release experiments the enzyme was directly injected into the sample through a septum by a syringe.

Influence of α-amylase on viscosity

The shear viscosity of starch dispersions with and without menthone (0.13 mg/100 g dispersion) was followed upon α-amylolysis with a shear rate-controlled rheometer (TA Instruments AR 2000, Surrey, UK) using a conical cylinder geometry (rotor radius: 14 mm, stator radius: 15 mm, gap 5,920 μm). Measurements were carried out at a constant shear rate of 5 s^{-1} at 25 °C for 60 min. First, the starch dispersion was placed in the rheometer geometry, followed by the addition of α-amylase solution by a syringe. Thereafter, the measurement was immediately started. A starch dispersion without aroma served as reference and 1.2 ml of distilled water instead of α-amylase solution was added. For every measurement, freshly prepared α-amylase solutions were used. All measurements were performed at least in triplicate.

Measurement of the iodine-binding capacity (IBC)

Changes in the starch (amylose) fraction upon α-amylolysis were followed by measuring the iodine-binding capacity using a DL-58 titrator (Mettler Toledo, Schwerzenbach, Switzerland). The voltage of the polarization was set to 140 mV and the attenuation of the polarizer to 5 mA. Starch samples with and without menthone (0.13 mg/100 g dispersion) were measured at different α-amylase (46 U/g dry starch) hydrolysis times (0, 10, and 60 min). Three repetitions were performed. A 40-g of sample containing 100 mg dry starch (S_{tot}), 1 ml 1 mol/L HCl and deionized water was titrated with a 0.005 mol/l iodine solution (Titrisol, Merck). The titration rate was 1 ml/min and samples were constantly stirred during titration. Titration curves were recorded by an analytical software (Labplus). The amount of bound iodine (I_b) was evaluated graphically as described by Hollo [20]. The iodine-binding capacity was calculated as follows:

$$\text{IBC} = \frac{I_b}{S_{tot}} \quad [\text{mg iodine}/100\ \text{mg dry starch}].$$

Headspace analysis using proton transfer reaction-mass spectrometry (PTR-MS)

The volatile organic compounds (VOC's) in the headspace of liquid samples were measured using PTR-MS (Ionicon, Innsbruck, Austria). The flasks were directly connected to the PTR-MS without any aroma loss and the headspace above the sample was purged with ambient air with an inlet flow of 180–190 ml/min. The Flasks were ventilated by a ventilation system to avoid a vacuum in the sample. In this study, headspace gas was continuously introduced into the drift tube at 15 sccm gas through a heated transfer-line (130 °C) into the reaction chamber (110 °C). As just a small amount of purging gas was needed for analysis, residual gas was released through the exhausted line in the ambient air. In the drift tube, a controlled ion density of H_3O^+, and buffer gas is present. Volatile organic compounds (VOC's) with proton affinities larger than water are ionised in the drift tube by proton transfers from H_3O^+ and primary and product ions are then detected by mass spectrometry. The ion source produces nearly exclusively H_3O^+ ions (>98%) that are extracted and transferred into the drift tube [21]. The inlet system was heated with an infrared light positioned over the inlet part to avoid memory effects. Measurements were performed with a constant drift voltage of 600 V. Transmission of the ions through the quadrupole was considered according to the specification of the instrument. Results were background corrected. Detailed description of the PTR-MS systems can be found in the following references [19, 22, 23].

Volatile profile of starch dispersions before and during starch hydrolysis

On one side, the endogenous starch volatile compounds were measured by PTR-MS before and after α-amylase treatment. The headspace of tapioca starch dispersion was analysed before α-amylase addition and after an incubation time of 10 min from mass 20 to 200 by PTR-MS. Totally, five consecutive cycles per starch dispersion were measured and the same number of cycles was taken with boiled water, which served as reference. The final spectra were calculated by subtracting the reference spectrum (water) from the sample spectrum. The spectra are presented as averages of three replicates. All masses that decreased in the background after sample connection to the PTR-MS were ignored as they belonged to the ambient air.

Aroma release from starch systems upon α-amylase hydrolysis

On the other hand, the release of added menthone from starch dispersion upon α-amylase hydrolysis was followed by PTR-MS. Fragmentation masses of menthone (*m/z* 155; *m/z* 137; *m/z* 95 and *m/z* 81) were analysed in the multiple ion mode (MID) using a dwell time of 0.2 s per mass [24]. Mass *m/z* 95 was chosen as representative for menthone. The resulting headspace intensities ($I_{average}$) were calculated as an average intensity of 20 cycles, corresponding to 20 s (Fig. 1). PTR-MS measurement was started approximately 20 s before enzyme injection as indicated in Fig. 2.

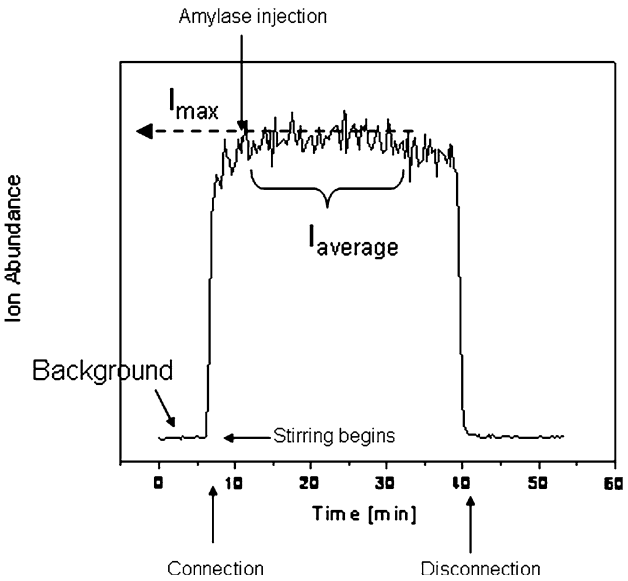

Fig. 1 Schematical presentation of a headspace determination by means of a PTR-MS measurement showing a maximum intensity (I_{max}). The evaluated region of headspace calculation is indicated by $I_{average}$

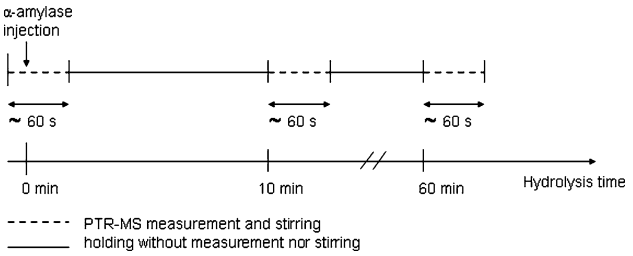

Fig. 2 Experimental set-up for following aroma release from starch dispersions upon α-amylase hydrolysis

Then the α-amylase was injected under stirring and measurement was continued for another approximately 40 s. Thereafter, the sample was disconnected from the PTR-MS, hermetically closed and kept without stirring. The headspace of the same sample was again measured after 10 and 60 min hydrolysis time. During the measurement, the sample was stirred with a magnetic stirrer (Ika Labortechnik, Staufen, Germany).

Results and discussion

Effect of α-amylase on viscosity

The changes in viscosity of the starch dispersions upon α-amylase addition were followed by rheological measurements at 25 °C. Viscosity was measured at a shear rate of 5 s^{-1} which also contributed to an homogeneous distribution of α-amylase in the sample. The influence of α-amylase (46 U mg/g dry starch) on the viscosity as a function of time was observed for starch dispersions with and without menthone and is shown in Fig. 3. A viscosity-time curve of the starch dispersion without enzyme addition is included as reference. The reference curve showed no changes in viscosity over a time period of 60 min. Upon α-amylase addition a rapid decrease in viscosity was observed within the first 10 min of the measurements. The endo mechanism of the α-amylase contributes to the rapid viscosity decrease. Similar results were found using porcine pancreas α-amylase or human saliva in other studies [25, 26]. The influence of menthone on the viscosity changes as induced by α-amylase was very small compared to the starch system without menthone. The viscosity of systems with menthone tended to be slightly higher in the final hydrolysis phase. One hypothesis is that structure degradation is hindered by the build-up of supramolecular structures with the association of helicated amylose segments [10]. In this sense, menthone could also be considered as a kind of nucleation agent for inducing structure build-up of starch segments.

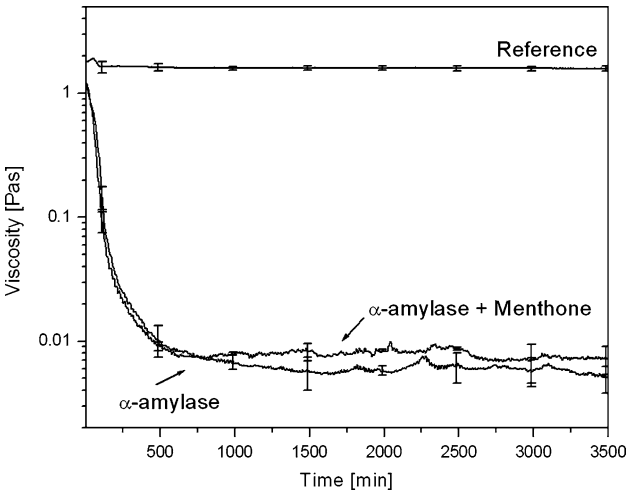

Fig. 3 Influence of α-amylase (46 U/mg dry starch) on the viscosity of tapioca starch dispersion (4 g dry starch/100 g dispersion) without menthone (reference) and with 0.13 mg menthone/100 g dispersion during a hydrolysis time of 60 min 24 h after sample preparation. The average viscosity curve of three replicates is presented and the standard deviation is included for selected time points

Effect of α-amylase on the iodine-binding capacity

Starch degradation was examined by following the iodine-binding capacity (IBC). Starch dispersions with and without menthone were hydrolysed by α-amylase (46 U/g dry starch) during 60 min. The iodine-binding capacity was measured directly after α-amylase addition, after 10 and 60 min hydrolysis time and the results are shown in Fig. 4.

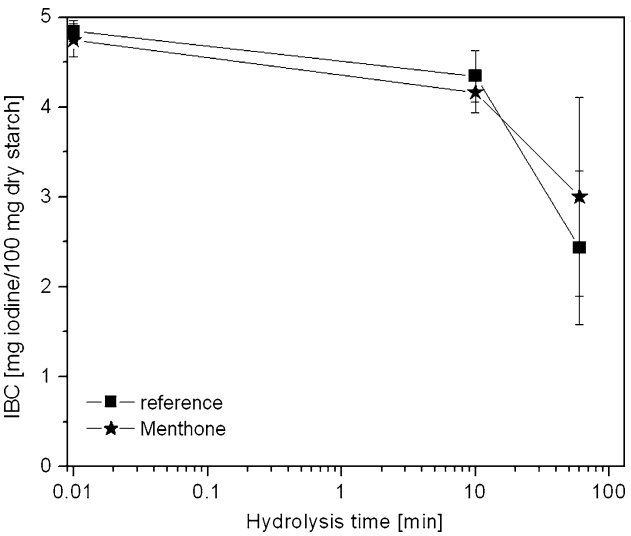

Fig. 4 Influence of α-amylase (46 U/mg dry starch) on IBC of tapioca starch dispersion (4 g dry starch/100 g dispersion) without menthone (reference) and with menthone (0.13 mg/100 g dispersion) during a hydrolysis time of 60 min. 24 h after sample preparation. The mean of four replicates and standard deviation is presented ($n = 4$)

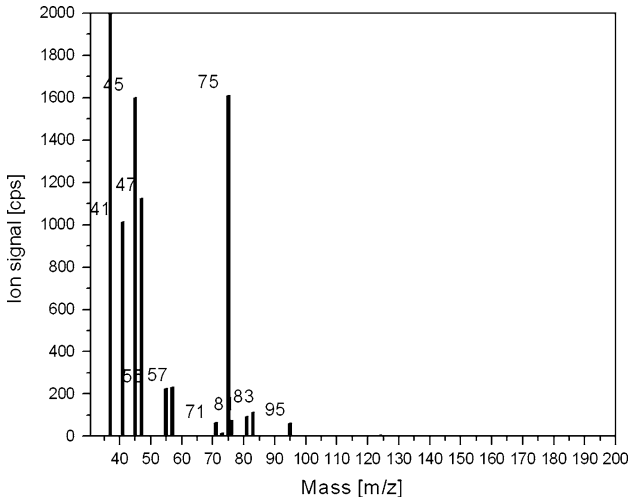

Fig. 5 Spectra of the headspace of tapioca starch dispersion (4.3 g dry starch/100 g dispersion) after headspace subtraction of boiled water. Calculated average of three replicates ($n = 3$) is given

The IBC is based on the ability of iodine to form inclusion complexes with amylose. Pure amylose has an IBC of around 19 mg iodine/100 mg dry starch [27]. For tapioca starch an IBC of 4.3 mg iodine/100 mg dry starch was found, which corresponds to an amylose content of approximately 23%. The measured IBC directly after α-amylase addition was around 4.7 mg iodine/100 mg dry starch for systems with menthone (0.13 mg/100 g dispersion) and without menthone (reference). The addition of α-amylase led to a decrease of the IBC to 2.4 and 3 mg iodine/100 mg dry starch, respectively, after 60 min hydrolysis time.

In the first 10 min, the random cleavage of starch by the endo acting α-amylase causes a strong decrease in viscosity, but the IBC remains almost unchanged since the size of the degradation products is still large enough to form helical inclusion complexes with iodine. Further enzymatic degradation leads in a decrease of the IBC due to the degradation of starch into small segments (degree of polymerisation < 200) that are no longer able to form inclusion complexes with iodine. The applied α-amylase activity and a hydrolysis time of 60 min did not allow a complete hydrolysis of starch, which is confirmed by the fact that the degradation products were still able to bind iodine. The starch dispersion containing menthone (0.13 mg/100 g dispersion) showed a similar degradation pattern, but the samples with menthone tended to show higher viscosity values than the reference. This may be due to the build-up of partly crystalline amylose structures which are known to present a reduced susceptibility towards α-amylase [10, 14].

Changes in endogenous starch volatiles upon α-amylase addition

The headspace of the starch dispersion (4 g dry starch/100 g dispersion) was measured on-line by PTR-MS to determine the mass spectra resulting from endogenous starch volatiles. Spectra were recorded directly after α-amylase injection and after a hydrolysis time of 10 min (Fig. 6). A tapioca starch dispersion without α-amylase addition served as reference (Fig. 5). The mass spectra indicate that quite a high number of volatiles were present in both headspaces, but the spectra differed in mass intensities and composition. To elucidate the changes in headspace composition due to the enzymatic impact, the whole spectrum at 10 min hydrolysis time was subtracted from the spectrum at 0 min hydrolysis time. Figure 7 presents the difference between the two spectra shown in Fig. 6. Negative intensities correspond to masses that

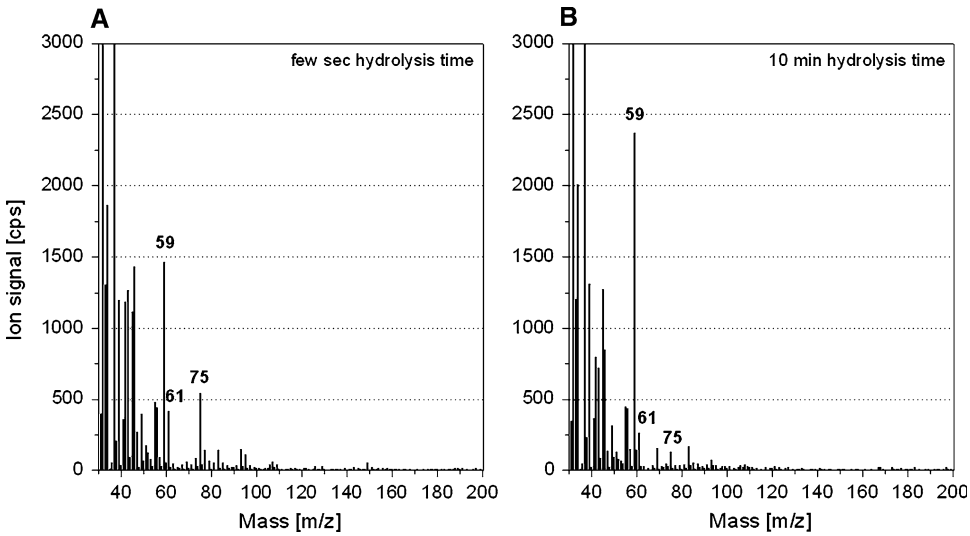

Fig. 6 Spectra of the volatile fraction of starch dispersion directly few seconds after α-amylase addition and after an hydrolysis time of 10 min. Stirring was done during on-line observation

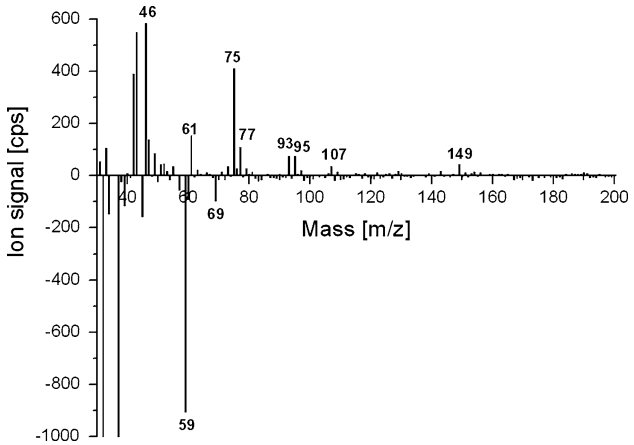

Fig. 7 Calculated spectra of starch dispersion after subtraction spectra of 10 min hydrolysis time from spectra obtained directly after α-amylase addition (0 min hydrolysis time)

resulted due to starch hydrolysis or belonged to the enzyme, and positive intensities reflect masses that presented higher intensities in the initial starch system or masses that were not influenced by starch hydrolysis. Most of the masses (75, 77, 93, 95) exhibited positive intensities, only a few had negative intensities such as mass 59 and 69. This observation means that α-amylase has an influence on the endogenous starch volatiles. Overall, it can be concluded that volatiles released from the starch itself exist in the headspace of tapioca starch dispersion independent of enzymatic treatment. The detected masses might correspond to volatile compounds that contribute to the characteristic odour of tapioca starch and they were also found in chemically modified tapioca starch (results not shown). PTR-MS technique does not allow the direct identification of the volatiles. Sayaslan et al. [2, 4] concluded that aldehydes like hexanal, benzaldehyde, nonanal and decanal, and alcohols like 2-propanol, esters, ketones and terpenes are in the headspace of commercial starches using computer matching by spectral database. Our preliminary evaluation of the fragmentation patterns supports the conclusions presented in literature (results not shown)

Release of added aroma compounds from starch dispersion upon α-amylase hydrolysis

Starch dispersions (4 g dry starch/100 g dispersion) containing menthone (0.13 mg/100 g dispersion) were prepared and treated with hog pancreas α-amylase (46 U/g dry starch). Low menthone concentrations were chosen due to instrumental limitations. Starch–aroma systems were aged for 24 h at 25 °C prior to enzymatic treatment. The effect of α-amylase on menthone (*m*/*z* 95) release from the starch systems was followed on-line by PTR-MS. Aroma release was not followed continuously over the whole hydrolysis time of 60 min, but aroma intensity in the headspace was measured directly after enzyme injection, after 10 and 60 min hydrolysis time. Samples were continuously stirred during the measurements. Results are presented in counts per seconds (cps) and in relative intensities (%) in Table 1 and as release curves in Fig. 8. As expected, the headspace intensities were lower for the starch system compared to the reference (water). A trend towards higher headspace intensities ($I_{average}$) was found for menthone in tapioca starch systems after 60 min hydrolysis times. Constant headspace intensities were found in control experiments using starch dispersions without α-amylase addition (results not shown). A pronounced influence of the enzyme on the release of menthone (*m*/*z* 95) by the starch system directly after injection was not observed. Based on the fact that menthone has the ability to form starch inclusion complexes [24], a pronounced aroma release upon starch degradation by α-amylase could have been expected. Instead, a slight increase in headspace intensity of menthone in the starch system after prolonged hydrolysis times (60 min) was found, which can be related to several superimposed effects that influenced aroma release.

The breakdown of the starch matrix results in a viscosity decrease (Fig. 3) and the mass transfer of volatile compounds to the surface increases with decreasing viscosity, which would contribute to an increase in volatile release [28]. An additional effect may be due to the increase of the

Table 1 Influence of α-amylase on the headspace intensities of menthone (0.13 mg/100 g dispersion) released from water (reference) and starch dispersion directly after α-amylase injection, after 10 and 60 min hydrolysis time

	Water		Starch dispersion	
	Absolute (cps)	Relative (%)	Absolute (cps)	Relative (%)
$I_{average}$ (0 min)	785 (±78)	100	592 (±62.0)	100
$I_{average}$ (10 min)	748 (±74)	95	538 (±48.0)	91
$I_{average}$ (60 min)	740 (±59)	94	647 (±41)	109

Mass 95 is representative of menthone. Release curves were recorded with stirring of the samples

$I_{average}$ calculated average over 20 cycles

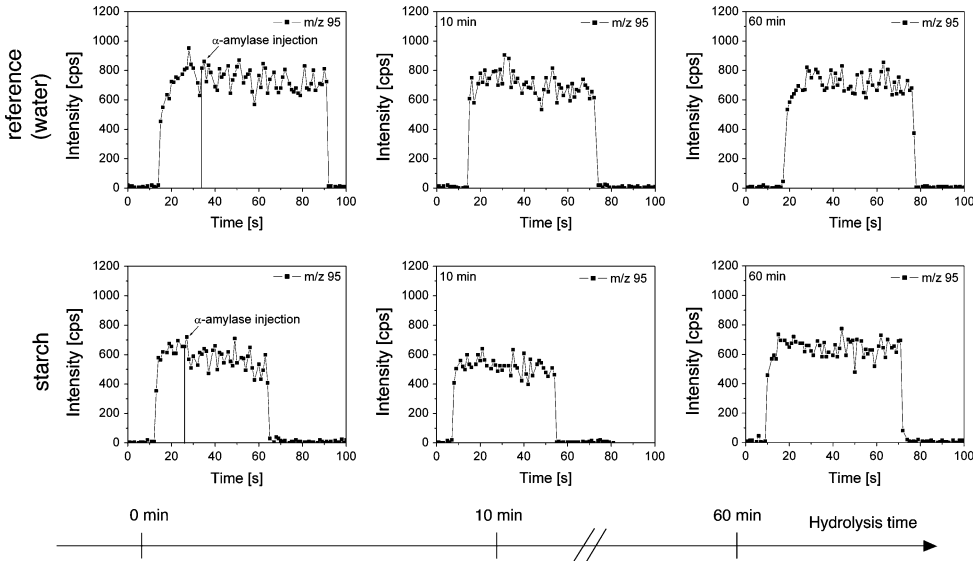

Fig. 8 Headspace intensity of menthone released from water (reference) and from tapioca starch dispersion (4 g dry starch/100 g dispersion) directly after α-amylase injection, after 10 min and 60 min of hydrolysis time. Mass *m/z* 95 was taken as representative for menthone

solute content in the liquid phase as a consequence of starch degradation. It is conceivable that upon extensive starch hydrolysis, the starch degradation products such as maltodextrins, maltose and glucose promote aroma release, which is also known as 'salting out' phenomenon [13]. On the other hand, aroma release could be reduced due to non-specific binding of aroma compounds to the starch degradation products. For instance, maltodextrins are known to bind aroma compounds by unspecific binding involving hydrogen bonds between the hydroxypropyl group of starch and the aroma compounds [5, 6, 16]. It is also conceivable that a partial degradation of starch favours the helication of starch and the inclusion of aroma compounds as guest molecules. Heinemann et al. [10] showed that partial enzymatic degradation of starch contributes to a perfectioning of spherocrystalline structures based on starch–aroma complexes. Finally, the enzyme protein itself can also affect aroma release, for instance, by adsorbing at the liquid–gas interface. Several studies have shown that protein–aroma interactions occurred leading to a decrease in aroma release [15, 29, 30]. Furthermore, it is likely that the extent of aroma release in starch systems varies depending on the extent of starch degradation (hydrolysis time), the enzyme activity and the aroma concentration applied.

Conclusion

Molecularly dispersed starch in the presence of menthone can be hydrolysed by α-amylase. Based on the iodine-binding capacity results, starch degradation at low α-amylase activity is not extensive after 60 min hydrolysis time, since the degradation products bind an appreciable amount of iodine. Nevertheless, the endo-acting α-amylase contributes to a strong viscosity decrease. Based on the small differences in the iodine-binding capacity, it is hypothesised that a simultaneous structure build-up and breakdown takes place during starch degradation. In this sense, menthone could be considered as a kind of nucleation agent for inducing structure build-up of starch segments. Although a pronounced aroma release upon starch degradation by α-amylase was expected, only a moderate increase in headspace intensity of menthone after 60 min hydrolysis time was found. Aroma release from aroma–starch systems upon α-amylase addition is influenced by several superimposed effects ranging from viscosity effects to interaction between aroma compounds and starch degradation products. It is likely that the impact of starch degradation will influence single aroma compounds in different ways that an overall release schema cannot be created.

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