Available online at www.sciencedirect.com
ScienceDirect
Food Chemistry 108 (2008) 1192–1199
Food Chemistry
www.elsevier.com/locate/foodchem

Interaction between starch and aroma compounds as measured by proton transfer reaction mass spectrometry (PTR-MS)

M. Tietz [a], A. Buettner [b,1], B. Conde-Petit [a,*]

[a] ETH Zurich, Institute of Food Science and Nutrition, CH-8092 Zurich, Switzerland
[b] Deutsche Forschungsanstalt für Lebensmittelchemie, Lichtenbergstr. 4, D-85748 Garching, Germany

Received 15 January 2007; received in revised form 16 July 2007; accepted 6 August 2007

Abstract

The interaction between starch and the complexing aroma compounds hexanal and menthone was investigated by headspace analysis using proton transfer reaction mass spectrometry (PTR-MS). Starch systems with non-modified and modified tapioca starch were prepared containing single aroma compounds (hexanal, menthone) or a blend of the two aroma compounds at low aroma concentrations (6×10^{-3} mg/100 g). The headspace intensity of starch–aroma systems was slightly reduced due to starch–aroma interactions compared to aroma water-systems. The combination of hexanal and menthone did not lead to competitive aroma release effects, but hexanal retention increased by increasing the equilibration time from 48 to 96 h. Non-modified and chemically modified starch showed similar aroma release behaviour. It is concluded that the formation of starch–aroma complexes influences aroma release, but that at low aroma concentration the dissociation of the complex is not hindered by the aggregation of amylose–aroma complexes.

Keywords: Starch; Amylose; Modified starch; Aroma; Amylose inclusion complexes; Flavour release; Headspace measurement; Proton transfer reaction mass spectrometry; PTR-MS

1. Introduction

Retention and release of aroma compounds from food matrices is largely governed by the physico-chemical properties of the aroma compound and by more or less specific interactions between aroma compounds and food components (Goubet, Le Quere, & Voilley, 1998; van Ruth & Roozen, 2002). The formation of helical inclusion complexes is an example of specific binding of aroma compounds to starch (Conde-Petit, Escher, & Nuessli, 2006; Escher, Nuessli, & CondePetit, 2000; Rutschmann, Heiniger, Pliska, & Solms, 1989). In particular the linear amylose fraction has the ability to form inclusion complexes with iodine, lipids and aroma compounds like alcohols, aldehydes, terpenes, lactones, etc. (Biliaderis, Page, Slade, & Sirett, 1985; Heinemann, Escher, & Conde-Petit, 2003; Kuge & Takeo, 1968; Le Bail, Rondeau, & Buleon, 2005), and ligand binding theories have been applied to describe this interaction (Rutschmann et al., 1989). In general the binding strength is higher for long linear molecules compared to bulky molecules like terpenes, but the opposite is true for the binding capacity (Rutschmann & Solms, 1990a; Wulff, Avgenaki, & Guzmann, 2005). For amorphous complexes it can be assumed that the guest molecule is included in the helical cavity (Conde-Petit et al., 2006; Wulff et al., 2005). Extensive amylose complexation as induced by high ligand concentration may promote the crystallisation of complexes, which leads in some cases to an exclusion of the guest molecule from the helix to be bound between the helices in the crystal (Biais, Le Bail, Robert, Pontoire, & Buleon, 2006; Rondeau-Mouro, Le Bail, & Buleon, 2004). In real food systems more than

* Corresponding author. Tel.: +41 44 632 37 31; fax: +41 44 632 11 23.
E-mail address: beatrice.conde@ilw.agrl.ethz.ch (B. Conde-Petit).
[1] Present address: Fraunhofer Institute Process Engineering and Packaging, Product and Analysis, Giggenhauser Str. 35, D-85354 Freising, Germany.

0308-8146/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2007.08.012

one type of complexing aroma compound may be present, and in this case mixed complexes, where more than one type of aroma are co-included into the helix, may be formed (Arvisenet, Le Bail, Voilley, & Cayot, 2002, 2002; Rutschmann & Solms, 1990a; Rutschmann & Solms, 1990c; Wulff et al., 2005).

The properties of starch–aroma complexes have been studied mainly by X-ray diffraction, differential scanning calorimetry, NMR, iodine titration, rheology and by determing the amount of included guest molecule (Biais et al., 2006; Brisson, Chanzy, & Winter, 1991; Rondeau-Mouro et al., 2004). However, most of these methods are not suitable for detecting starch–aroma complexes at low degrees of amylose complexation, which is the reason why generally rather high aroma concentrations are applied. On the other hand, the measurement of aroma release from starch matrices is a possibility to assess starch–aroma interactions. Aroma release from starch systems can be followed by static headspace and the exponential dilution method (Arvisenet, Le Bail, et al., 2002, Arvisenet, Voilley, & Cayot, 2002; Jouquand, Ducruet, & Le Bail, 2006; Langourieux & Crouzet, 1994). New real-time dynamic headspace techniques were developed in recent years such as the atmospheric pressure chemical ionisation (APCI) mass spectrometry technique (Marin, Baek, & Taylor, 1999; Taylor, Linforth, Harvey, & Blake, 2000) and proton transfer reaction mass spectrometry (PTR-MS) (Lindinger, Hansel, & Jordan, 1998; van Ruth, Floris, & Fayoux, 2006). The PTR-MS technique allows monitoring of very low aroma concentrations due to the relatively high sensitivity, and observation of real-time flavour release from real food or model systems. Aroma release from starch matrices is relevant in connection with food processing, flavour encapsulation and flavour perception upon food consumption (de Roos, 2006; Kant, Linforth, & Taylor, 2003).

The aim of the present study was to investigate the interaction between starch and complexing aroma compounds at low aroma concentrations by following the release of specific aroma constituents. Aroma intensities in the headspace were measured by proton transfer reaction mass spectrometry (PTR-MS). Two aroma compounds, namely hexanal and menthone, were selected for the experiments. Hexanal and menthone are well described complexing agents for starch, menthone presenting a higher affinity for starch than hexanal (Wulff et al., 2005). Low aroma concentrations were applied to simulate relevant aroma concentrations in food. Besides single aroma compounds, the combined addition of hexanal and menthone to starch dispersions was investigated to study possible competitive starch–aroma interactions. The investigated starch systems were aqueous starch dispersions with a starch concentration of 4 g/100 g being considered representative as models for liquid foods such as soups, sauces and custards. Besides non-modified tapioca starch, chemically modified starch was included in the study, since the latter is frequently applied in food.

2. Materials and methods

Non-modified tapioca starch (C*Creamtex 70001) and hydroxypropyldistarch phosphate (C*Creamtex 75720) were obtained from Cerestar (Wädenswil, Switzerland). Menthone (purity > 97%) was supplied by Fluka (Buchs, Switzerland). Hexanal was kindly supplied by Givaudan SA (Dübendorf, Switzerland). Chemical purity was checked by gas chromatography–mass spectrometry (GC–MS). Distilled water was used for all experiments.

2.1. Preparation of starch based food models

Starch dispersions based on non-modified and modified tapioca starch were prepared by heating aqueous starch suspensions under 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 approx. 3 ± 0.5 °C/min. Non-modified and modified tapioca starch were heated for 45 and 30 min at 95 °C, respectively. Thereafter the starch dispersion was cooled to 30 °C. The amount of evaporated water was assessed gravimetrically and replaced. The starch dispersions were used immediately after preparation.

2.2. Starch based models with one aroma compound

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 aroma concentrations ranged between 1.3×10^{-4} and 13.3 mg/100 g sample after preparation. Samples were equilibrated at 25 °C for 24 h.

2.3. Starch based models with two aroma compounds

Starch aroma systems with two aroma compounds were prepared with constant concentrations of menthone and varying hexanal concentrations. The aroma compounds were added to the starch dispersion as 1 ml aqueous aroma solution. Menthone was added at a concentration of 0.06 mg/100 g. Hexanal concentrations in the samples ranged from 6×10^{-3} to 6×10^{-1} mg/100 g dispersion in 10-fold concentration steps. The samples were equilibrated at room temperature (25 °C) for 48 h and 96 h.

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

The release of hexanal and menthone in the headspace of starch dispersions was measured using PTR-MS (Ioni-

con, Innsbruck, Austria). The flasks (300 mL) 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. Flasks were ventilated by a ventilation inlet system to avoid a vacuum in the sample. The headspace was continuously sampled into the PTR-MS at 15 sccm gas through a heated transfer-line (130 °C) into the reaction chamber (110 °C). The inlet system was heated with an infrared light positioned over the inlet part. Measurement were performed with a constant drift voltage of 600 V. Detailed description of the PTR-MS systems can be found in following references (Hansel et al., 1995; Lindinger, Pollien, Ali, Blank, & Märk, 2005; Lindinger et al., 1998).

In separate experiments, fragmentation patterns of hexanal and menthone were recorded. Mass intensities were recalculated as described elsewhere (Buhr, van Ruth, & Delahunty, 2002). Masses related to hexanal were *m/z* 101 (4%), *m/z* 83 (47%) and *m/z* 55 (100%). Mass 55 is a product of a fragment ion of hexanal and the water cluster $H_3O^+(H_2O)_2$, coming from the generation of primary H_3O^+ and headspace humidity. Therefore, it is preferable to select *m/z* 83 as the molecular ion for the detection of hexanal. Menthone fragmentation mainly yielded masses *m/z* 155 (11%), *m/z* 137 (26%), *m/z* 95 (31%) and *m/z* 81 (100%). Mass *m/z* 95 was chosen as representative for menthone. All fragmentation masses were measured in the multiple ion mode (MID) using a dwell time of 0.1 s per mass. Measurements were always started with the sample with the lowest concentration of the respective volatile constituent followed by the next higher concentrated sample. This measuring procedure was chosen in order not to overload the instrument, which may result in changed fragmentation patterns. Intensities of MID measurements of aroma-starch dispersions were corrected by substraction of headspace intensities obtained for boiled water that served as a blank. The release of volatiles was recorded in counts per second (cps). Results of MID measurements are presented as a calculated average of 30 cycles of each mass at the constant plateau which corresponds approximately to a time of 24 s (Fig. 1). For the experiments with two aroma compounds, aroma intensities were adjusted to an assumed theoretical intensity of 10^7 H_30^+ of the primary ion.

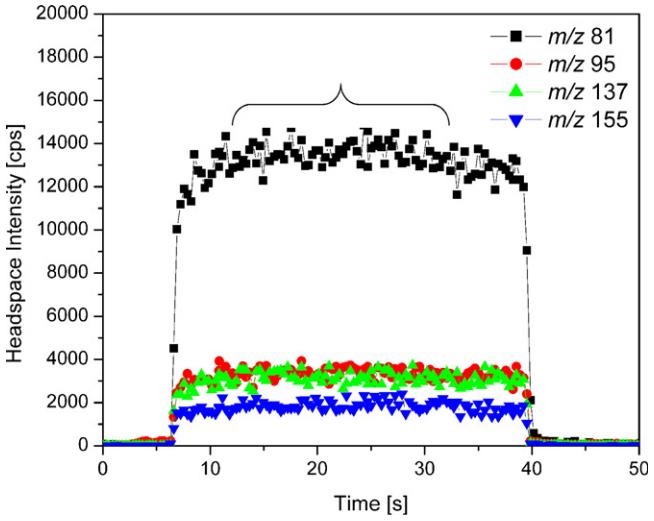

Fig. 1. PTR-MS measurement of menthone released from aqueous solution (1.33 mg aroma/100 g). Region used for evaluation indicated in the figure. Fragmentation pattern of menthone: *m/z* 81, *m/z* 95, *m/z* 137, *m/z* 155.

3. Results and discussion

3.1. General remarks on the PTR-MS measurements

The PTR-MS measurements were carried out on systems with a rather large headspace to liquid volume ratio (270:30) and large liquid–gas interface area (approx. 55 cm^2). The headspace was diluted using an air flow rate of 180–190 ml/min, which corresponds to a headspace replacement of around 0.7 per minute. The samples were measured for less than 60 s, and the sharp increase of headspace intensity was followed by a plateau as shown in Fig. 1. The constant headspace intensity reflects the pseudo steady state release of volatiles during the initial phase of the measurement at low headspace dilution. Headspace intensities were evaluated approx. 24 s in the initial plateau region where the registered intensities are primarily determined by the equilibrium headspace concentration of volatiles and to a lesser extent by the release of volatiles from the solution (Fig. 1). In this sense, the measured intensities correspond to the first orthonasal impression upon 'sniffing' at the headspace of a food system. Continuity of the PTR-MS measurements was investigated regarding the raw ion counts of the analytes. Typically, the coefficient of variation for repetitions carried out under identical experimental conditions on the same day was around 2%. On the other hand, large variations were detected when comparing measurements carried out on different days (CV = 48%, $n = 22$ days). This effect is related to the non constant H_3O^+ signal dependent on the cleanness of the ion source and the secondary electron multiplier (SEV). Accordingly it is possible to compensate day-to-day fluctuations, by adjusting the H_3O^+ signal to a defined signal (10^7 cps) and by standardising other instrumental parameters like p-drift, O_2 ratio and inlet flow. Nevertheless, only those series of measurements carried out under the same experimental conditions (measurements of the same day) were compared in the present study. Apart from that, comparison over different measuring days was limited to relative aroma release values.

Although PTR-MS is described as a quantitative method, there are still some aspects to be regarded for the quantification of volatiles (Lindinger et al., 2005). Headspace data is given by the instrument's software in intensity (cps) or in concentration (ppb). The latter assums standard conditions of the instrument, constant

reaction times and reaction rates for all volatile organic compounds. However, for further calibration procedures it would be required to take into account fragmentation patterns under certain ionisation conditions and other instrumental parameters such as temperature of the inlet system (Buhr, Buettner, & Schieberle, in press). However relative determinations were the main focus of the present work so that data as expressed on an ion count basis.

Aroma release from water was measured over a broad aroma concentration range to assess the response linearity by PTR-MS. Fig. 2 presents the obtained intensities in counts per second (cps) in relation to the aroma concentrations of fragmentation masses relating to hexanal (*m/z* 55, *m/z* 83, *m/z* 101). A linear relation between headspace intensities and aroma concentration was found between 1.3×10^{-3} and 1.3 mg/100 g for all fragmentation masses of hexanal in an aqueous system. The detection limit for the present system was determined to be at 1.3×10^{-3} mg aroma/100 g sample since headspace intensities below this aroma concentration were constant and the response disappeared in the background noise, that is due to environmental contamination with diverse volatile organic compounds (VOCs). Likewise, the same detection limit and a linear relationship between headspace intensity and menthone concentration in water was found between 1.3×10^{-3} and 1.3 mg/100 g. For both aroma compounds there was no shift in the fragmentation pattern at different aroma concentrations and the intensity ratios of the fragmentation masses remained constant over the whole aroma concentration range. With the described experimental approach it was possible to measure headspace intensities of starch–aroma systems at very low aroma concentrations (6×10^{-3}–1.3 mg/100 g), similar to concentrations which are relevant in real food systems. The aroma concentrations applied in the experiments were in the range of the linear detection region.

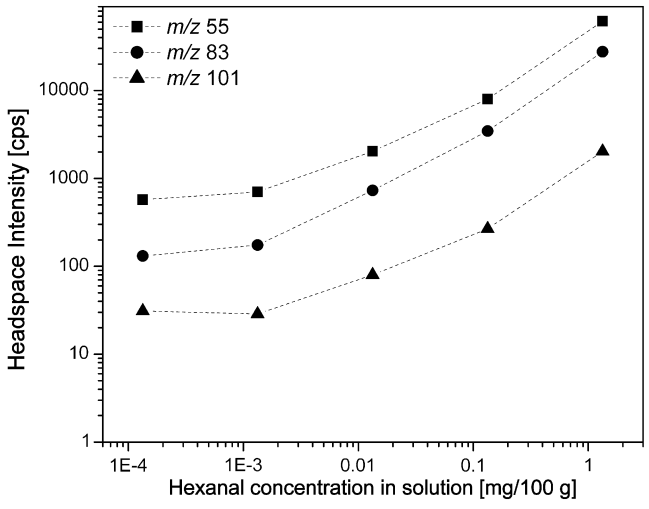

Fig. 2. Headspace intensities of hexanal released from aqueous solution. Measured fragmentation masses for hexanal: *m/z* 55, *m/z* 83, *m/z* 101.

3.2. Hexanal and menthone release from starch dispersions

Headspace intensities of aqueous starch dispersions with hexanal and menthone were measured by PTR-MS and compared to aroma-water systems after a time period of 24 h to obtain equilibrium between gas and liquid phase. Masses *m/z* 83 and *m/z* 95 were chosen as representative masses for hexanal and menthone, respectively, as they could be exclusively assigned to hexanal and menthone. Table 1 shows the relative release of aroma from starch dispersion compared to water (100%). Both aroma compounds showed a small but significant ($p < 0.05$) reduced release from aqueous starch systems compared to water. Overall, the release of aroma in the starch systems was rather high which is explained by the rather low binding strength of starch–aroma complexes and the low aroma concentrations applied in this investigation. For instance, the highest menthone concentration (1.33 mg/100 g) was far lower than the available binding sites as determined for aqueous potato starch dispersions by (Rutschmann et al., 1989) (Binding capacity $B_{max} = 43.94$ mmol menthone/mol glucose which corresponds to 166 mg aroma/100 g starch dispersion at 4% starch concentration). At low aroma concentration the binding to starch is completely reversible which in the present study might have contributed to increase flavour release. In contrast, at high aroma concentration the formation of partly crystalline amylose–aroma aggregates impairs the dissociation of the complex (Conde-Petit et al., 2006). This could explain the higher aroma retention values in starch systems found in other studies (Heinemann, Zinsli, Renggli, Escher, & CondePetit, 2003; Jouquand et al., 2006), where the high aroma concentrations favoured the formation of supramolecular amylose–aroma assemblies.

Regarding the two starch types, it is noteworthy that the differences in headspace intensities of non-modified and chemically modified starch systems were very small for hexanal and for menthone. The intensities tended to be higher for modified starch, although the opposite could have been expected. Different authors (Kim, Eliasson, & Larsson, 1992; Wulff, Steinert, & Holler, 1998) found that the complexing ability of starch decreases with the degree of starch substitution. However, a low level of hydroxypropylation did not impair complex formation (Wulff et al., 1998).

3.3. Flavour release from ternary systems

Previous work on starch–aroma inclusion complexes showed that the binding capacity of starch and the binding strength is influenced by the presence of other complexing compounds like lipids or aroma compounds (Rutschmann & Solms, 1990a, 1990c; Wulff et al., 2005; Wulff et al., 1998). In the present study the competitive interaction between two complexing aroma compounds in starch systems was investigated by following aroma release using PTR-MS after equilibration times of 48 and 96 h. Menthone was added at a constant concentration and the concen-

Table 1
Headspace intensities of hexanal (1.33 mg/100 g) and menthone (1.33 mg/100 g) released from aqeuous starch dispersions compared to aroma-water systems

	Hexanal (*m/z* 83) intensity Relative intensities (%)	Menthone (*m/z* 95) intensity Relative intensities (%)
Water	100	100
Non-modified starch	95 ± 0.6	84 ± 1.0
Modified starch	87 ± 6.8	80 ± 0.5

Headspace intensities are given as relative release intensities (%). Relative hexanal intensities are an average of four repetitions ($n = 4$). Relative menthone intensities are an average of three repetitions ($n = 3$). Standard variation is given in ±SD.

tration of hexanal varied, and experiments were performed using non-modified and modified starch. Fig. 3 presents hexanal and menthone intensities in the headspace of dispersions after a storage time of 48 h. The headspace intensities in counts per second (cps) are plotted versus the hexanal concentration. The main fragmentation masses of hexanal (*m/z* 55; *m/z* 83; *m/z* 101) and of menthone (*m/z* 81; *m/z* 95; *m/z* 137; *m/z* 155) are presented. Increasing hexanal concentration from 6×10^{-3} to 6×10^{-1} mg/100 g increased hexanal intensity in the headspace, while the menthone intensity remained constant for all hexanal concentrations. The constant release of menthone was found for both the non-modified and the modified starch. However, in particular at low hexanal concentrations, the headspace intensity of hexanal was higher for non-modified starch compared to modified starch. Fig. 4 presents a comparison of hexanal and menthone intensities for both starch systems after equilibration times of 48 and 96 h. Hexanal intensity represented by *m/z* 83 was clearly lower after 96 h compared to 48 h. Most probably, the hexanal intensities for the lowest hexanal concentration in the sample equilibrated for 96 h fell below the detection limit as consequence of binding to starch. On the other hand, menthone intensities remained constant for all hexanal concentrations and were not affected by equilibration time. Regarding the type of starch, no differences were found in terms of hexanal and menthone release in the samples after a long equilibration time (96 h).

The fact that no changes in the menthone headspace intensities were found suggests that hexanal does not compete with menthone for binding sites and, therefore, does not promote the release of menthone. Based on previous studies, a competitive interaction between two aroma compounds and starch could have been expected. For instance Rutschmann and Solms (1990a) found that the complexation of decanal and menthone decreases the overall binding stability of the complexes. Likewise Wulff et al. (2005) showed that mixed amylose complexes with inclusion of hexanal and guaiacol can be formed, but that the combination leads to pronounced lower amounts of included guest molecules in the amylose helices compared to systems with only one type of aroma. In the present investigation no competitive interaction between complexing flavour compounds and starch was found. This is most probably due to the fact that very low aroma concentrations were used compared to previous studies. The applied aroma concentrations correspond to concentrations which can be found in food, but were around hundred times lower than the maximum binding capacity of starch (Rutschmann & Solms, 1990a). The changes in hexanal intensity as a function of time most likely reflect the low complexation rate of this ligand at the applied conditions. On the other hand, the binding of menthone to starch is a comparatively fast process since equilibrium was reached after 48 h as manifested by the constant intensities. Previous studies on

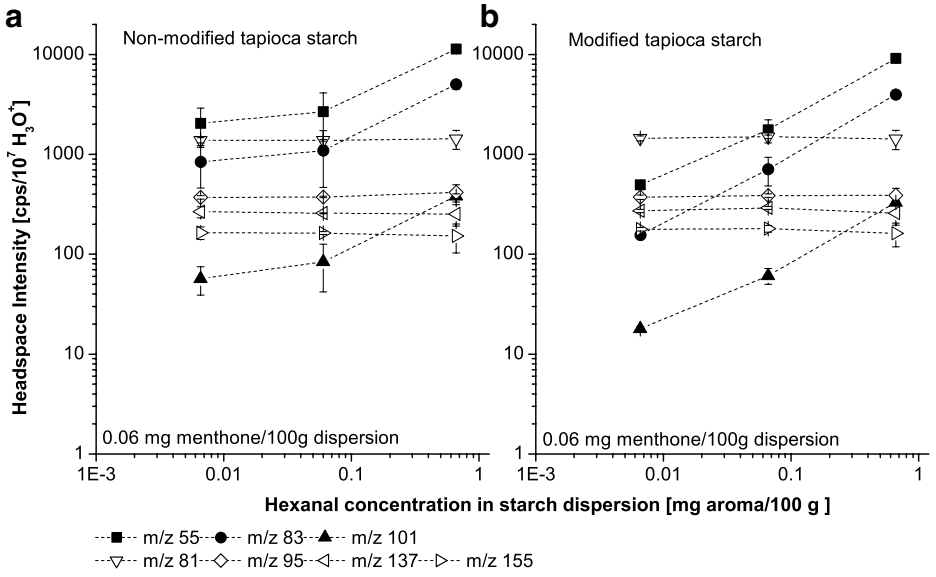

Fig. 3. Headspace intensities of hexanal and menthone released from non-modified (a) and modified (b) starch dispersion after an equilibration time of 48 h. Hexanal: *m/z* 55, *m/z* 83, *m/z* 101; menthone: *m/z* 81, *m/z* 95, *m/z* 137, *m/z* 155. Mean of two repetitions.

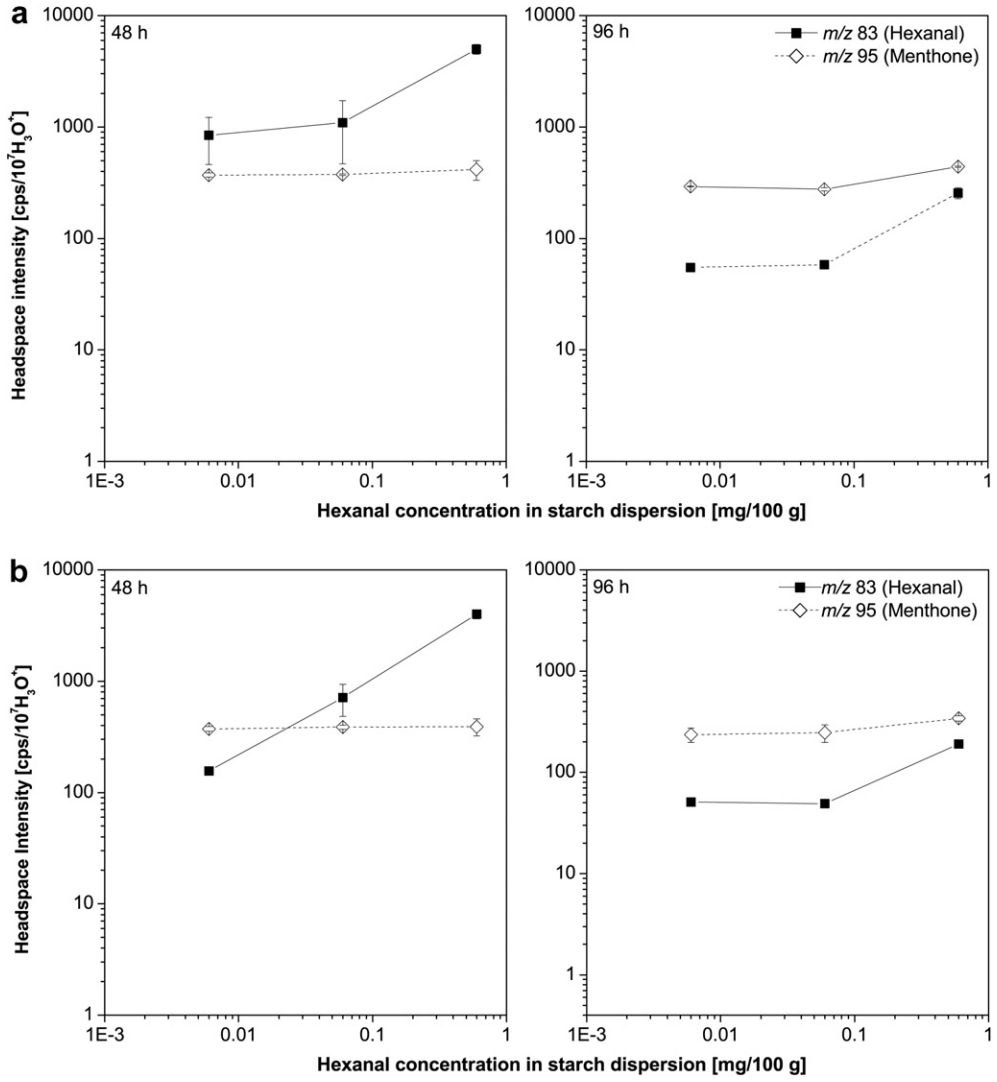

Fig. 4. Headspace intensities of hexanal and menthone released from non-modified (a) and modified (b) starch dispersion after an equilibration time of 48 h and 96 h. *m/z* 83 is representative for hexanal and *m/z* 95 for menthone. Mean of two repetitions.

starch–aroma complexation also came to the conclusion that equilibrium is reached only after two to four days (Heinemann, Escher, et al., 2003; Nuessli, Conde-Petit, Trommsdorff, & Escher, 1995). The nature of the interaction cannot be unambigously established by headspace analysis. The interaction between starch and aroma by inclusion complexation does not exclude non-specified interactions, for instance the adsorption of aroma molecules to the starch surface although the latter become more important at high aroma concentration (Rutschmann & Solms, 1990b). Interestingly, no important difference was found between non-modified and modified starch. As already mentioned, this might be due to the moderate modification degree of starch, where the influence on complex formation is not pronounced (Eliasson, Finstad, & Ljunger, 1988; Kim et al., 1992; Wulff et al., 1998). The fact that in the present study the chemical modification did not influence the binding of aroma to starch may again be due to the low aroma concentrations, which did not require extensive helication of the linear starch segments.

4. Conclusion

The characterisation of aroma release from aqueous starch dispersions into the headspace is a valuable tool for understanding the interactions between starch and complexing aroma compounds. Headspace measurements by PTR-MS are particularly valuable for investigation systems at very low aroma concentrations (6×10^{-3} mg/100 g). At these conditions, the retention of complexing aroma compounds like hexanal or menthone are low reflecting the low binding strength and the reversibility of the interaction. In addition, the combination of hexanal and menthone at low concentration does not lead to competitive release effects, most probably due to the fact that the number of binding sites is far larger than the ligand (aroma) concentra-

tion. Nevertheless, the results also show that aroma compounds which form low stability complexes like hexanal present very low binding rates, and equilibrium is not reached within two days. Finally, the chemical modification of starch does not influence binding of low levels of aroma compounds. In conclusion it is hypothesised that the limited helication of starch due to low aroma concentration leads to the formation of soluble complexes, where competitive effects are negligible and where the complexes are not driven out of solution by helix–helix aggregation (crystallisation). Overall, the reversibility of the interaction contributes to much higher flavour release compared to systems where the starch–aroma complexes are crystalline.

Acknowledgements

The PTR measurements were carried out at *Deutsche Forschungsanstalt für Lebensmittelchemie* (D-Garching) and we wish to thank Prof. P. Schieberle for his support of our scientific work. We also thank Dr. Katja Buhr (TU Garching), Dr. Jeannette Nuessli and Prof. Felix Escher (both ETH Zurich) for fruitful discussions. This study was financially supported by the *Swiss Secretariat for Education and Research*, by the COST Action 921 (STSM grant for Melanie Tietz) and by the *Deutsche Forschungsanstalt für Lebensmittelchemie* and the HWP II-program for excellent junior researchers (Andrea Buettner).

References

Arvisenet, G., Le Bail, P., Voilley, A., & Cayot, N. (2002). Influence of physicochemical interactions between amylose and aroma compounds on the retention of aroma in food-like matrices. *Journal of Agricultural and Food Chemistry, 50*(24), 7088–7093.

Arvisenet, G., Voilley, A., & Cayot, N. (2002). Retention of aroma compounds in starch matrices: Competitions between aroma compounds toward amylose and amylopectin. *Journal of Agricultural and Food Chemistry, 50*(25), 7345–7349.

Biais, B., Le Bail, P., Robert, P., Pontoire, B., & Buleon, A. (2006). Structural and stoichiometric studies of complexes between aroma compounds and amylose. Polymorphic transitions and quantification in amorphous and crystalline areas. *Carbohydrate Polymers, 66*(3), 306–315.

Biliaderis, C. G., Page, C. M., Slade, L., & Sirett, R. R. (1985). Thermal behavior of amylose–lipid complexes. *Carbohydrate Polymers, 5*, 367–389.

Brisson, J., Chanzy, H., & Winter, W. T. (1991). The crystal and molecular-structure of V_h amylose by electron-diffraction analysis. *International Journal of Biological Macromolecules, 13*(1), 31–39.

Buhr, K., Buettner, A., & Schieberle, P. (in press). Troubleshooting proton transfer reaction-mass spectrometry. In: *Proceedings of the eighth wartburg symposium on flavor chemistry & biology, Eigenverlag Deutsche Forschungsanstalt für Lebensmittelchemie, Garching, Deutschland.*

Buhr, K., van Ruth, S., & Delahunty, C. (2002). Analysis of volatile flavour compounds by proton transfer reaction-mass spectrometry: Fragmentation patterns and discrimination between isobaric and isomeric compounds. *International Journal of Mass Spectrometry, 221*(1), 1–7.

Conde-Petit, B., Escher, F., & Nuessli, J. (2006). Structural features of starch-flavor complexation in food model systems. *Trends in Food Science & Technology, 17*(5), 227–235.

de Roos, K. B. (2006). Understanding and controlling the behaviour of aroma compounds in thermally processed foods. *Trends in Food Science & Technology, 17*(5), 236–243.

Eliasson, A. C., Finstad, H., & Ljunger, G. (1988). A study of starch-lipid interactions for some native and modified maize starches. *Starch-Starke, 40*(3), 95–100.

Escher, F., Nuessli, J., & CondePetit, B. (2000). Interactions of flavor compounds with starch in food processing. In D. D. Roberts & A. J. Taylor (Eds.), *Flavor release* (pp. 230–245). Washington, DC: American Chemical Society.

Goubet, I., Le Quere, J. L., & Voilley, A. J. (1998). Retention of aroma compounds by carbohydrates: Influence of their physicochemical characteristics and of their physical state. A review. *Journal of Agricultural and Food Chemistry, 46*(5), 1981–1990.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., & Lindinger, W. (1995). Proton-transfer reaction mass-spectrometry-online trace gas-analysis at the ppb level. *International Journal of Mass Spectrometry, 150*, 609–619.

Heinemann, C., Escher, F., & Conde-Petit, B. (2003). Structural features of starch–lactone inclusion complexes in aqueous potato starch dispersions: The role of amylose and amylopectin. *Carbohydrate Polymers, 51*(2), 159–168.

Heinemann, C., Zinsli, M., Renggli, A., Escher, F., & CondePetit, B. (2003). Starch-flavour inclusion complexation in aqueous systems. In J. L. Le Quere & P. X. Etievant (Eds.), *Flavour research at the dawn on the twenty-first century* (pp. 33–38). Paris: Editions Tec & Doc.

Jouquand, C., Ducruet, V., & Le Bail, P. (2006). Formation of amylose complexes with C6-aroma compounds in starch dispersions and its impact on retention. *Food Chemistry, 96*(3), 461–470.

Kant, A., Linforth, R. S. T., & Taylor, A. J. (2003). Flavour retention and release from starch solutions. In J. L. Le Quere & P. X. Etievant (Eds.), *Flavour research at the dawn of the twenty-first century* (pp. 103–106). Editions Tec & Doc: Paris.

Kim, H. R., Eliasson, A. C., & Larsson, K. (1992). Dynamic rheological studies on an interaction between lipid and various native and hydroxypropyl potato starches. *Carbohydrate Polymers, 19*(3), 211–218.

Kuge, T., & Takeo, K. (1968). Complexes of starchy materials with organic compounds.2. Complex formation in aqueous solution and fractionation of starch by L-Menthone. *Agricultural and Biological Chemistry, 32*(10), 1232–1238.

Langourieux, S., & Crouzet, J. (1994). Study of aroma compounds polysaccharides interactions by dynamic exponential dilution. *Food Science and Technology-Lebensmittel-Wissenschaft & Technologie, 27*(6), 544–549.

Le Bail, P., Rondeau, C., & Buleon, A. (2005). Structural investigation of amylose complexes with small ligands: Helical conformation, crystalline structure and thermostability. *International Journal of Biological Macromolecules, 35*(1–2), 1–7.

Lindinger, W., Hansel, A., & Jordan, A. (1998). On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) – Medical applications, food control and environmental research. *International Journal of Mass Spectrometry, 173*(3), 191–241.

Lindinger, C., Pollien, P., Ali, S., Blank, I., & Märk, T. (2005). Direct inter-comparison of datasets obtained by different PTR-MS: A novel approach to optimize and adapt the fragmentation pattern using a standardization procedure. In: *Proceedings of the second international conference on proton transfer reaction mass spectrometry and its application* (pp. 89–95). Innsbruck University: Innsbruck, Austria.

Marin, M., Baek, I., & Taylor, A. J. (1999). Volatile release from aqueous solutions under dynamic headspace dilution conditions. *Journal of Agricultural and Food Chemistry, 47*(11), 4750–4755.

Nuessli, J., Conde-Petit, B., Trommsdorff, U. R., & Escher, F. (1995). Influence of starch flavour interactions on rheological properties of low concentration starch systems. *Carbohydrate Polymers, 28*(2), 167–170.

Rondeau-Mouro, C., Le Bail, P., & Buleon, A. (2004). Structural investigation of amylose complexes with small ligands: Inter- or intra-helical associations? *International Journal of Biological Macromolecules, 34*(5), 309–315.

Rutschmann, M. A., Heiniger, J., Pliska, V., & Solms, J. (1989). Formation of inclusion complexes of starch with different organic-compounds. 1. Method of evaluation of binding profiles with menthone as an example. *Lebensmittel-Wissenschaft & Technologie, 22*(5), 240–244.

Rutschmann, M. A., & Solms, J. (1990a). Formation of inclusion complexes of starch in ternary model systems with decanal, menthone, and 1-naphthol. *Food Science and Technology-Lebensmittel-Wissenschaft & Technologie, 23*(5), 457–464.

Rutschmann, M. A., & Solms, J. (1990b). Formation of inclusion complexes of starch with different organic-compounds. 2. Study of ligand-binding in binary model systems with decanal, 1-naphthol, monostearate and monopalmitate. *Lebensmittel-Wissenschaft & Technologie, 23*(1), 70–79.

Rutschmann, M. A., & Solms, J. (1990c). The formation of ternary inclusion complexes of starch with menthone and monostearate – A possible food model system. *Food Science and Technology-Lebensmittel-Wissenschaft & Technologie, 23*(5), 451–456.

Taylor, A. J., Linforth, R. S. T., Harvey, B. A., & Blake, A. (2000). Atmospheric pressure chemical ionisation mass spectrometry for in vivo analysis of volatile flavour release. *Food Chemistry, 71*(3), 327–338.

van Ruth, S. M., Floris, V., & Fayoux, S. (2006). Characterisation of the volatile profiles of infant formulas by proton transfer reaction-mass spectrometry and gas chromatography-mass spectrometry. *Food Chemistry, 98*(2), 343–350.

van Ruth, S., Roozen, J. P. (2002). Delivery of flavours from food matrices. In *T.A.J. Food flavour technoly* (pp. 167–181). Nottingham Sheffield Academic Press.

Wulff, G., Avgenaki, G., & Guzmann, M. S. P. (2005). Molecular encapsulation of flavours as helical inclusion complexes of amylose. *Journal of Cereal Science, 41*(3), 239–249.

Wulff, G., Steinert, A., & Holler, O. (1998). Modification of amylose and investigation of its inclusion behavior. *Carbohydrate Research, 307*(1–2), 19–31.