Influence of Heat Treatment on the Formation of Amadori Compounds in Carrots

A. WELLNER*, Ch. HÜTTL and T. HENLE

Institute of Food Chemistry, Technische Universität Dresden, D-01062 Dresden, Germany
**E-mail: anne.wellner@chemie.tu-dresden.de*

Abstract: The formation of Amadori products (APs) during heat treatment of carrot juice and dehydration of carrots was studied. APs were measured as the corresponding *N*-furoylmethyl amino acids (FMAAs) after acid hydrolysis using RP-HPLC. Commercial samples of juices contained up to 108 mg furosine/100 g protein, 18 mg FM-Ala/100g protein, 13 mg FM-Val/100 g protein and 32 mg FM-GABA/100 g protein. The concentrations in dehydrated carrots were extensively higher with up to 1553 mg furosine/100 g protein, 1144 mg FM-Ala/100 g protein, 88 mg FM-Val/100 g protein and 908 mg FM-GABA/100 g protein. Heat treatment of fresh carrot juice caused only a marginal increase of Amadori compounds. Samples contained at most 16 mg furosine/100 g protein and 19 mg FM-GABA, respectively, while FM-Ala and FM-Val were not detectabele at all. In contrast, drying of carrots led to a significant increase of FMAAs. The dehydrated samples contained up to 989 mg furosine/100 g protein, 1201 mg FM-Ala/100 g protein and 969 mg FM-GABA/100 g protein, while FM-Val was not detectable.

Keywords: carrot; heat treatment; furosine; *N*-furoylmethyl amino acids

INTRODUCTION

During the early stage of the Maillard reaction, Amadori compounds (1-amino-1-deoxy-2-ketoses) are formed by reaction of aldoses with free amino groups of amino acids and proteins. They are the first stable intermediates and act as precursors for numerous substances responsible for flavour and browning in foods. Furthermore, Amadori compounds may influence the nutritional value of proteins by blockage of essential and semi-essential amino acids (mainly lysine and arginine). Because Amadori compounds are formed before appearance of sensory changes, they are used as indicators for early recognition of quality changes caused by the Maillard reaction (Henle 2005). During acid hydrolysis, protein-bound Amadori products of lysine are degraded to ε-*N*-(2-furoylmethyl)-lysine (furosine), while N-terminal Amadori compounds are converted into α-*N*-(2-furoylmethyl)-amino acids (α-FMAAs). So far, there are only few papers dealing with Amadori compounds or FMAAs in processed fruits and vegetables, and mainly dehydrated fruits (Sanz *et al*. 2001), tomato products (Sanz *et al*. 2000) and dehydrated orange juice (Del Castillo *et al*. 1999) were analysed. In air-dried carrots, numerous Amadori compounds were detected and quantified (Reutter & Eichner 1989). The aim of the present study was to investigate the formation of Amadori compounds during heat treatment of carrot juice and dehydration of carrots, and to compare these results with values obtained for commercially available products.

MATERIALS AND METHODS

Five samples of commercial carrot products (three juices, two dried carrots) were from local retail stores. Furosine was from NeoMPS (Strasbourg, France). Furoylmethyl alanine (FM-Ala) and valine (FM-Val) were synthesised according to Penndorf *et al*. (2007). Furoylmethyl γ-aminobutyric acid (FM-GABA) was synthesised according to Sanz *et al*. (2000). Fresh carrot juice was heated in closed tubes at different temperatures (90, 100, 120°C) for 10 and 20 minutes. Heated juices were

freeze-dried before subsequent analysis. Fresh carrots were sliced and dried at 70, 80 and 90°C in an oven. Samples were taken after 30 min, 1, 2, 3, and 5 hours. Analysis of FM-Ala, FM-GABA, furosine and FM-Val was performed after by acid hydrolysis by RP-HPLC/DAD according to the methods described by Penndorf *et al.* (2007).

RESULTS AND DISCUSSION

In all commercial carrot products, furosine, FM-Ala, FM-Val and FM-GABA were detectable after acid hydrolysis. The concentrations in the juices ranged from 60 to 108 mg furosine/100 g protein, 7 to 18 mg FM-Ala/100 g protein, 9 to 13 mg FM-Val/100 g protein and 16 to 32 mg FM-GABA/100 g protein. The contents of FMAAs in dried carrots were considerably higher with 1541 to 1553 mg furosine/100 g protein, 690 to 1144 mg FM-Ala/100 g protein, 61 to 88 mg FM-Val/100 g protein and 697 to 908 mg FM-GABA/100 g protein. While the concentration of furosine primarily describes the modification of protein-bound lysine, FM-Ala and FM-Val give information mainly about free Amadori products and secondarily about modified N-terminal amino acids in proteins and peptides. In contrast, the non-proteinogenic amino acid GABA, which is formed by decarboxylation of glutamic acid, only occurs as free amino acid.

For investigation of the formation of Amadori compounds during heat treatment, fresh carrot juice was heated at different temperatures. All heated samples contained furosine and FM-GABA after acid hydrolysis, whereas FM-Val and FM-Ala were not detectable. Figure 1 shows the formation of FMAAs during heat treatment. Even in the non-heated sample, small amounts of furosine and FM-GABA were detectable, probably due to their formation during freeze-drying. After heating the juice for 20 min, a small increase was observed, but there were no significant differences by varying the heating temperature. The contents ranged from 12 to 16 mg furosine/100 g protein and 13 to 19 mg FM-GABA/100 g protein respectively. While the concentrations of furosine are considerably lower than in the analysed commercial samples, the contents of FM-GABA are comparable.

Furthermore, the formation of Amadori compounds during dehydration of carrots was investigated at different temperatures. In the dried samples, furosine, FM-GABA and FM-Ala were detectable after acid hydrolysis, while FM-Val could not be identified. As shown in Figure 2, the formation of FMAAs started earlier with increasing temperature. Furosine reached a similar level after 5 h (between 904 and 989 mg/100 g protein) independent of the temperature. In contrast, the concentrations of FM-GABA and FM-Ala after 5 h increased with rising temperature and ranged from 275 to 969 mg FM-GABA/100 g protein and 226 to 1201 mg FM-Ala/100 g protein, respectively. Compared to the commercially available dehydrated carrots, the samples dried at 90°C for 5 h contained lower amounts of furosine whereas the concentrations of FM-GABA and FM-Ala were similar.

The observed differences in FMAA contents between commercial products and samples from heating experiments probably are caused by the carrot varieties, as these can differ in the composition of amino acids and reducing sugars. For all heating experiments, the same carrot variety was used, but it is unknown which varieties were processed for the analysed commercial carrot products.

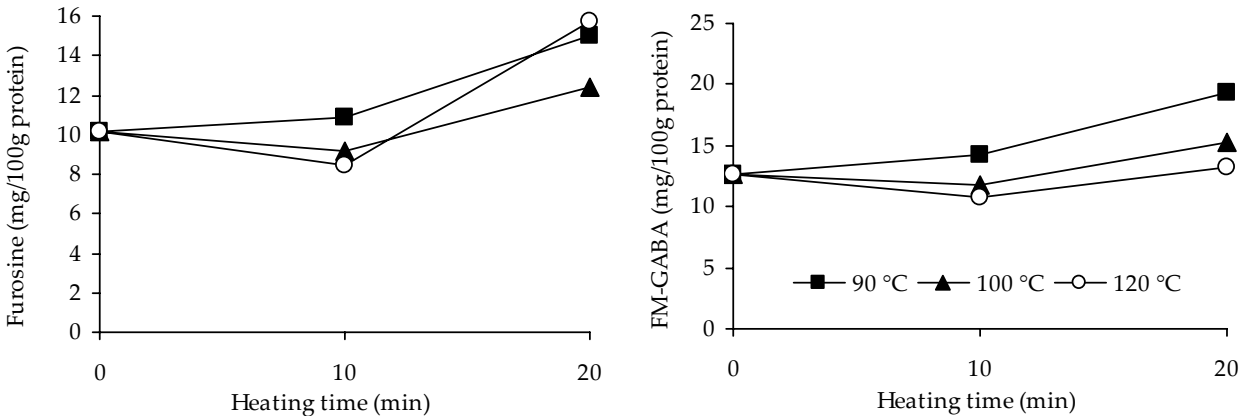

Figure 1. Formation of furosine and FM-GABA during heat treatment of carrot juice

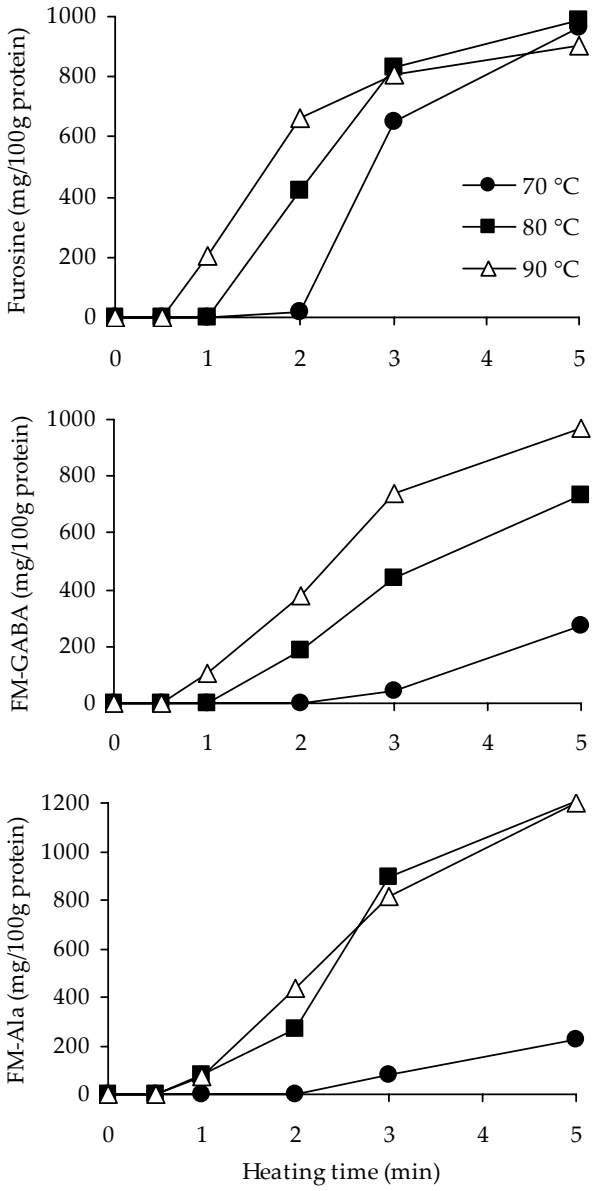

Figure 2. Formation of furosine, FM-GABA and FM-Ala during dehydration of carrots

In conclusion, heat treatment of fresh carrot juice leads only to a marginal increase of Amadori compounds. An extensive increase of Amadori compounds, however, was observed during dehydration of carrots, and the temperature had an obvious influence on the content and the rate of formation.

References

Del Castillo M.D., Corzo N., Olano A. (1999): Early stages of Maillard reaction in dehydrated orange juice. Journal of Agricultural and Food Chemistry, **47**: 4388–4390.

Henle T. (2005): Protein-bound advanced glycation endproducts (AGEs) as bioactive amino acid derivatives in foods. Amino Acids, **29**: 313–322.

Penndorf I., Biedermann D., Maurer S. V., Henle T. (2007): Studies on N-terminal glycation of peptides in hypoallergenic infant formulas: quantification of α-*N*-(2-furoylmethyl) amino acids. Journal of Agricultural and Food Chemistry, **55**: 723–727.

Reutter M., Eichner K. (1989): Separation and determination of Amadori compounds by high-pressure liquid chromatography and postcolumn reaction. Zeitschrift für Lebensmittel-Untersuchung und -Forschung, **188**: 28–35.

Sanz M.L., Del Castillo M.D., Corzo N., Olano A. (2001): Formation of amadori compounds in dehydrated fruits. Journal of Agricultural and Food Chemistry, **49**: 5228–5231.

Sanz M.L., Del Castillo M.D., Corzo N., Olano A. (2000): Presence of 2- furoylmethyl derivatives in hydrolysates of processed tomato products. Journal of Agricultural and Food Chemistry, **48**: 468–471.