Journal of Food Composition and Analysis 72 (2018) 83–92

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Individual Maillard reaction products as indicators of heat treatment of pasta — A survey of commercial products

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ARTICLE INFO

Keywords:
Maillard reaction
Pasta
Drying
Advanced glycation end product (AGE)
Amadori rearrangement product
Pyrraline
CML
Maltosine
Glucosyl isomaltol
Food analysis
Food composition

ABSTRACT

During pasta production, drying processes promote glycation reactions (non-enzymatic browning, Maillard reaction). Certain "traditionally produced" pasta products are often labelled with claims suggesting high quality due to a gentle heat treatment. The impact of heat treatment of food can be assessed by the measurement of Maillard reaction products (MRPs). In the present study, the MRPs *N*-ε-fructosyllysine, *N*-ε-maltulosyllysine, furosine, *N*-ε-carboxymethyllysine (CML), *N*-ε-carboxyethyllysine (CEL), pyrraline, formyline, maltosine, methylglyoxal-derived hydroimidazolone 1 (MG-H1), 3-deoxyglucosone, 3-deoxygalactosone, glucosyl isomaltol, and HMF were quantified in 31 pasta products. *N*-ε-Maltulosyllysine was found to be the predominating MRP (up to 2.4 g/100 g of protein). Between 4 and 28% of the essential amino acid lysine was found to be modified due to glycation reactions. Taking ten MRPs into account, a low-MRP and a high-MRP cluster could be distinguished by cluster analysis. Closer examination of the clusters revealed that the MRPs *N*-ε-maltulosyllysine, pyrraline, maltosine, HMF, and glucosyl isomaltol differ most strongly and should further be considered as potential heating markers. Lastly, a study on 5 pasta products with different shapes provided evidence that glycated amino acids are not degraded during cooking. Maltosine is formed additionally during cooking. The consumption of pasta contributes substantially to the daily intake of Amadori rearrangement products and CML.

1. Introduction

Pasta products are traditionally prepared from only two ingredients—water and durum wheat semolina. After mixing and working of semolina and water, the dough is extruded, giving the pasta products their final form. Beneath the characteristics of the raw materials, the heat treatment during pasta drying is of high importance for the quality of the final product. A certain heat impact can already occur during the extrusion process. Local heating may rise above 60 °C, but the processing time is very short in this step (Sicignano et al., 2015). Drying of the extruded intermediate goods to *ca.* 12.5% water content needs to be performed, in order to gain products that are microbiologically stable during storage at room temperature (Cavazza et al., 2013; Sicignano et al., 2015; Mercier et al., 2016). Drying times can be reduced through application of higher drying temperatures. Thus, different courses of heat treatment are applied during industrial pasta production, the more "traditional" low-temperature processes (below 60 °C), then high-temperature processes (60–80 °C, sometimes up to 100 °C) and very-high temperature cycles (80–100 °C and even higher) (Pagani et al., 1996; Giannetti et al., 2014; Sicignano et al., 2015). Multi-stage drying processes are often implemented, where different low- and high-temperature steps are combined: The drying temperature is changed during the drying process, and the relative humidity is regulated concomitantly (Zweifel et al., 2003; Cavazza et al., 2013; Mercier et al., 2016; Padalino et al., 2016). Beneath faster processing and reduced costs, it is a further advantage of higher drying temperatures, that the final products obtain better cooking performance (Zweifel et al., 2003; Padalino et al., 2016). On the other hand, thermal "damage", such as unwanted discoloration and negative sensory properties (*e.g.*, bread crust flavor), can occur in high-temperature heated pasta products (Pagani et al., 1996). Moreover, the digestibility of amino acids in these pasta products may be reduced (Stuknytė et al., 2014).

There is currently no legislative regulation concerning the differentiation between low- and high-temperature treatments. Therefore, manufacturers are relatively free in utilizing descriptions pointing to "low-temperature treatment", "long-time drying", or "gentle preparation", which is considered the traditional way of pasta drying.

Abbreviations: AGE, advanced glycation end product; ARP, Amadori rearrangement product; a_w, water activity; CEL, *N*-ε-carboxyethyllysine; CML, *N*-ε-carboxymethyllysine; HMF, 5-hydroxymethylfurfural; LOD, limit of detection; LOQ, limit of quantification; MG-H1, methylglyoxal-derived hydroimidazolone 1; MRM, multiple reaction monitoring; MRP, Maillard reaction product; NFPA, nonafluoropentanoic acid; RT, room temperature

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https://doi.org/10.1016/j.jfca.2018.06.009
Received 13 March 2018; Received in revised form 6 June 2018; Accepted 14 June 2018
Available online 18 June 2018
0889-1575/

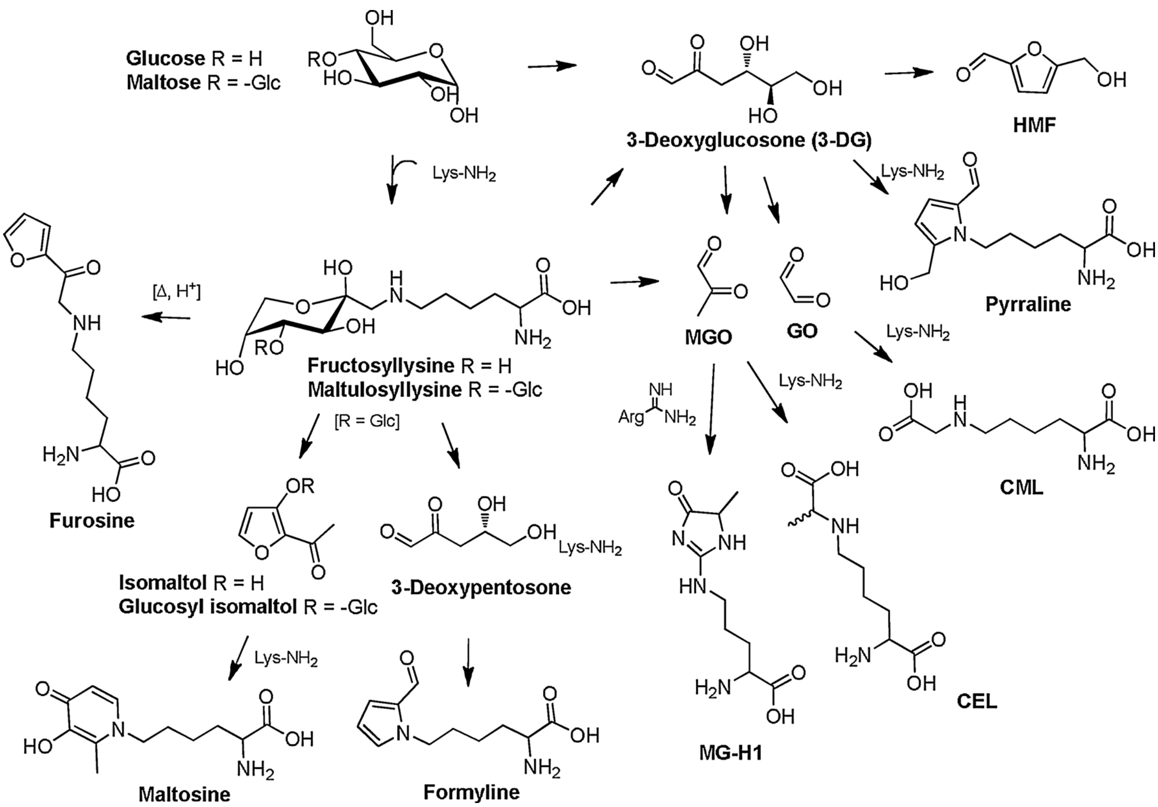

Fig. 1. Proposed pathways of sugar degradation and Maillard reaction in pasta products (Literature and abbreviations see text).

Consumers increasingly appear to demand gently dried pasta and be ready to pay higher prices for the respective products: On the German market, prices for 1 kg of spaghetti range from 2.38 € to 10.76 € for correspondingly labelled products and from 0.98 € to 3.18 € for products that are not labelled with such claims (Table S1).

Depending on the drying conditions and the relative humidity during drying, reactions between reducing sugars and amino and imino groups of free amino acids, peptides and proteins can take place, which are collectively called Maillard reaction, glycation or "non-enzymatic browning". The reaction can also take place during cooking (Hellwig and Henle, 2014). Due to α-amylase activity, an increase in the ratio between reducing sugars and reactive lysine residues is observed during the manufacturing process, which facilitates Maillard reactions during drying (Lintas and D'Appolonia, 1973; Resmini et al., 1993; Pagani et al., 1996; Testani et al., 2017). These reactions are furthermore supported by the reduction of the water activity during the drying process (final $a_w = 0.8$, Giannetti et al., 2014). In the first step of this reaction, Amadori rearrangement products (ARPs) are formed, which can collectively be quantified as furosine after acid hydrolysis (Fig. 1). Concentrations between 40 and 880 mg furosine per 100 g protein have been reported in pasta products, indicating that up to 60% of lysine residues can be modified in this fashion (Resmini and Pellegrino, 1994; Henle et al., 1995; Pagani et al., 1996; Acquistucci, 2000; Cavazza et al., 2013). The exact nature of the ARPs formed has not yet been assessed, but from the sugar composition of dried pasta products (Cavazza et al., 2013; Lintas and D'Appolonia, 1973), it can be expected that *N*-ε-fructosyllysine and *N*-ε-maltulosyllysine should predominate. The use of furosine for the assessment of heat treatment of pasta products has been suggested (García-Baños et al., 2004), but this is precluded by the low stability of ARPs during more intense heat treatment (Resmini and Pellegrino, 1994; Anese et al., 1999; Cavazza et al., 2013). In the second step of the Maillard reaction, ARPs decompose under formation of 1,2-dicarbonyl compounds, such as 3-deoxyglucosone (3-DG), methylglyoxal, and glyoxal. Up to 8.8 mg 3-DG per kg of cooked pasta has been determined, whereas methylglyoxal (MGO) was not detectable (Degen et al., 2012). Only traces of 5-hydroxymethylfurfural (HMF) were determined in pasta samples (Resmini et al., 1993), and it was not detectable in pasta products after cooking (Degen et al., 2012). The concentration of glucosyl isomaltol (up to 10 mg/kg), which is a degradation product of maltose, correlates well with the heat treatment of pasta (Resmini et al., 1993; Pagani et al., 1996).

In the late stage of the Maillard reaction, dicarbonyl compounds react with protein-bound amino acid residues, such as the ε-amino group of lysine or the guanidino group of arginine, to the so-called "advanced glycation end products (AGEs, Fig. 1)", whose formation in food is not reversible (Hellwig and Henle, 2014). Carboxyalkylation and pyrrole formation at the ε-amino group of lysine and hydroimidazolone formation at the guanidino group of arginine are the most prominent glycation events in the late Maillard reaction on proteins (Thornalley et al., 2003; Hellwig and Henle, 2014). Several AGEs, such as CML, CEL, pyrraline, formyline, maltosine, and MG-H1, have already been quantified in a limited number of cooked and uncooked pasta products (Resmini and Pellegrino, 1994; Hellwig and Henle, 2012; Hellwig et al., 2016a; Scheijen et al., 2016). Among these AGEs, only pyrraline has been suggested as a heating marker, whose concentrations increase especially at drying temperatures above 80 °C and pasta moisture contents below 15% (Resmini and Pellegrino, 1994).

Different drying cycles are applied for different pasta shapes, and these differences significantly influence the Maillard reaction, as was assessed using color indices, furosine, and maltulose formation (Cavazza et al., 2013). Thus, it was the aim of the present study to assess the suitability of a broader spectrum of MRPs as indicators of heat treatment of pasta products and to perform a survey on the concentrations of different MRPs in commercial spaghetti samples. Thereby, we wanted to gain insight into how modern drying conditions affect the concentrations of MRPs in pasta. Moreover, the stability of MRPs during cooking of pasta and the contribution of pasta consumption to the total daily intake of MRPs should be addressed.