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Maltulose and furosine as indicators of quality of pasta products

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Abstract

Maltulose, an isomer of maltose, is detected for the first time in dried pasta samples. Variable amounts of this compound were observed in dried macaroni, noodle, spaghetti and vermicelli; however, fresh pasta samples had no maltulose content. These results could indicate that maltulose is formed during drying processes of pasta elaboration. Variations of maltulose in dried pasta samples (between 0 and 36.9 mg/100 g dry matter) could be due to the different conditions (time and temperature) applied during the drying process. Furosine contents of these samples were also determined. High values of furosine and maltulose in samples may be attributable to very high temperature processes (VHT-ST), whereas low values of furosine and absence of maltulose may indicate that samples were submitted to long processes at low temperatures (LT-LT). Low values of maltulose and high contents of furosine may correspond to low temperature treatments, followed by short time high temperature processes (HT-ST).

Keywords: Pasta; Maltulose; Furosine; Quality indices

1. Introduction

Pasta is the most suitable food for satisfying nutritional requirements and safeguarding health at the same time (Costantini, 1985). Pasta is made up of a high content of carbohydrates (70.0 g/100 g of dried pasta), principally starch (63.0 g/100 g of dried pasta) and free carbohydrates. Proteins are also present in minor proportion (11.5 g/100 g of dried pasta) (Belizt & Grosch, 1992; Souci, Fatchmann, & Kraut, 1986).

Elaboration of pasta entails different steps: milling and dough formation, extruding and drying. The latter is a crucial operation for the quality of the pasta, since modifications of main components can take place. The traditional methods for drying pasta use low temperatures (29–40 °C) and long time of treatment (24–60 h) (LT-LT), but the use of low temperature treatments, followed by high temperatures (60–80 °C or 80–100 °C) and short times of treatment (5–12 h or 1–2 h) (HT-ST or VHT-ST) has been widely accepted (Dexter, Matsuo, & Morgan, 1981).

During the drying of pasta the Maillard reaction is favoured, due to the presence of carbohydrates and proteins, water activity (a_w) reached by the product and processing conditions (Anese, Nicoli, Massini, & Lerici, 1999; Resmini & Pellegrino, 1994). Resmini and Pellegrino (1992) proposed the determination of furosine (ε-2 furoylmethyl-lysine), a product obtained by the acid hydrolysis of the Amadori compound of lysine (ε-fructosyl-lysine), as a useful tool for optimising pasta processing with respect to the physiological nutritive quality of the product.

Pasta processing can also produce changes in carbohydrate content, thus during mixing, extruding and drying phases, starch can suffer damage, releasing free maltose. The changes of free carbohydrates (maltose, glucose and fructose) during drying of different pasta products have been extensively studied (Lintas & D'Appolonia, 1973; Resmini & Pellegrino, 1994; Sensidoni, Peresseni, Pollini, & Murani, 1996), however the formation of maltulose has not been reported. Maltulose has been quantified in several foods, such as bread (Wasterlung, Theander, & Aman, 1989), honey (Swallow & Low, 1990), and liquid enteral formulas (García-Baños, Olano, & Corzo, 2000), and the ratio maltose/maltulose has been proposed for the first time as an

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indicator to assess the heat treatment during manufacture and to monitor storage of enteral formulas (García-Baños, Olano, & Corzo, 2002).

The aim of this work was to determine the presence of maltulose in pasta products and its usefulness alone or in combination with furosine as an indicator of processing conditions during pasta manufacture.

2. Materials and methods

2.1. Standard

Maltulose was synthesised and purified according to the method described by Hicks, Symansky, and Pfeffer (1983). Furosine was acquired from Neosystem Laboratoire (Strasbourg, France) and trehalose was purchased from Merck (Darmstadt, F.R.).

2.2. Samples

Seven fresh pasta samples (two samples of spaghetti, one sample of macaroni and four samples of noodle) and 27 dried pasta samples (six samples of vermicelli, eleven samples of spaghetti, five samples of macaroni and five samples of noodle) from different manufacturers were purchased at local markets.

Samples were finely ground, using a domestic grinder (Moulinex 843 model). All samples were analysed before their deadline.

2.3. Analytical determinations

2.3.1. General

All analyses were carried out in duplicate.

Determination of total nitrogen content was carried out following AOAC Official Method No. 930.25 (AOAC, 1990a). Protein levels were calculated using 6.25 as conversion factor. Water content was determined, following the AOAC Method No. 926.07 (AOAC, 1990b).

2.3.2. Maltulose determination

Trimethyl silylated oxime derivatives of maltulose, prepared following the method of Li and Schumann (1981), were analyzed by GC, following the method of García-Baños et al. (2000) for quantifying carbohydrates in enteral formulas.

First, maltulose was extracted from pasta samples using 80% ethanol. 0.5 g of ground sample was mixed with 4.5 ml of deionized water and stirred for 20 min at room temperature. The mixture was diluted to 25 ml with ethanol and kept for 30 min. Samples were centrifuged at 5700*g* for 10 min. Fifteen milliliters of the extract was mixed with 1 ml of a solution of trehalose (0.02% w/v) as internal standard and evaporated under vacuum.

2.3.3. Furosine determination

Chromatographic determination of furosine in pasta samples was performed by ion-pair RP-HPLC, following the method of Resmini, Pellegrino, and Batelli (1990). Before analysis, samples (350 mg) of pasta were hydrolysed with 8 ml of 8 N HCl under inert conditions at 110 °C for 24 h in a screw-capped Pyrex vial with PTFE-faced septa.

The separation of furosine was performed in a C_8 column (250×4.6 mm i.d.) (Alltech furosine- dedicated) (Alltech Associates, Laarne, Belgium), thermostatted at 35 °C and with a linear binary gradient. A Dionex chromatograph (DX-300) and a variable wavelength detector at $\lambda = 280$ nm (LTD Analytical, SM 4000) were used. Acquisition and processing of data was achieved with HPChem Station (Hewlett-Packard) software. Quantitation was performed by the external standard method using a commercial standard of pure ε-2-furoylmethyl-lysine (furosine) (Neosystem Laboratories, Strasbourg, France).

3. Results and discussion

Maltulose was quantified by GC analysis, using trehalose as internal standard and its identity was confirmed by GC-MS (DeJoungh et al., 1969). Hundred percent of this compound was recovered after two consecutive steps of extraction. The precision of the method (extraction, derivatization and GC analysis) was evaluated. A relative standard deviation of 6.3% ($n = 6$) was obtained for samples containing 12.4 mg of maltulose/100 g dry matter.

Table 1 shows the minimum and maximum contents of water, furosine and maltulose of pasta samples. Whereas fresh samples had around 28% of water content, in dried samples these values were 12%.

As expected, low amounts of furosine were detected in fresh spaghetti, macaroni and vermicelli (Table 1). These results are in agreement with those obtained by Resmini and Pellegrino (1992) for fresh pasta, who indicated that the small amounts of furosine formed during these steps can be due to the low temperatures applied. Taking into account that all samples are from different brands, little variability was found between them (r.s.d. 9.8%). This fact is probably due to the homogeneity of milling of the semolina and dough formation processess in the industries.

Dried pasta samples showed high amounts of furosine, reaching values from 44.4 mg/100 g of protein up to 462 mg/100g of protein, these values being similar to those obtained by other authors (Acquistucci, 1996; Anese et al., 1999; Resmini & Pellegrino, 1992; Tirelli, 1998). The variations observed among samples could be attributed to the use of different conditions during the drying step.

Table 1
Minimum and maximum values of water content (%), furosine (mg/100 g protein) and maltulose (mg/100 g dry matter) in fresh and dried pasta samples

Samples	Water content (%)	Furosine (mg/100 g protein)	Maltulose (mg/100 g dry matter)
Fresh pasta			
Spaghetti ($n = 2$)	27.5–28.9	16.2–17.9	–[a]
Macaroni ($n = 1$)	21.3	18.8	–
Noodle ($n = 4$)	28.7–29.3	17.4–21.8	–
Dried pasta			
Vermicelli ($n = 6$)	10.7–12.6	98.6–265	5.2–17.4
Spaghetti ($n = 11$)	8.8–11.2	78.8–462	0.0–36.9
Macaroni ($n = 5$)	10.5–11.5	44.4–212	0.0–13.1
Noodle ($n = 5$)	11.2–12.4	58.6–329	0.0–27.9

[a] Not detected.

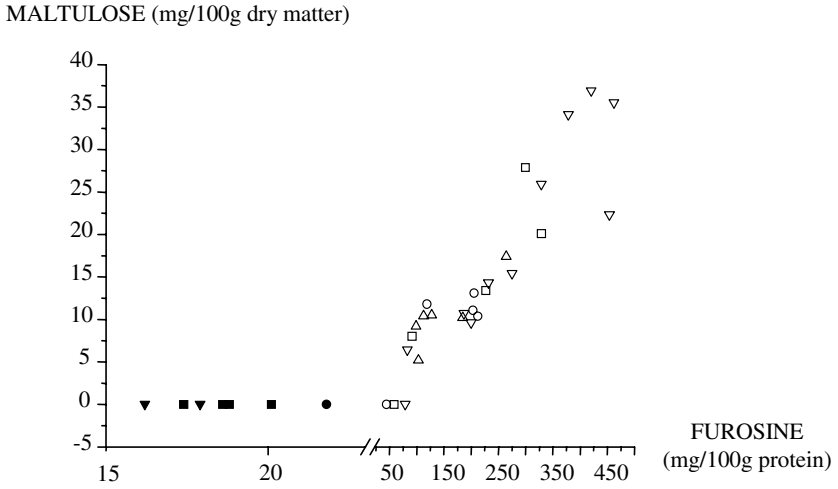

Fig. 1. Graphical representation of maltulose versus furosine contents of fresh (closed symbol) and dried (open symbol) pasta samples. ▼: Spaghetti; ▲: Vermicelli; ●: Macaroni; ■: Noodle.

Presence of maltulose was not detected in any fresh pasta samples, however, variable amounts of maltulose, ranging from 0 to 36.9 mg/100 g dry matter, were detected in dried pasta (Table 1). The presence of large amounts of maltulose in dried pasta and its absence in fresh pasta indicate that the formation of maltulose takes place only during the drying steps. Variations of maltulose contents found in dried pasta samples could be attributed to the different drying conditions (time and temperature) during their elaboration.

Fig. 1 shows a plot of individual values of furosine content versus maltulose content of all pasta samples studied. As has been previously indicated, fresh pasta showed low values of furosine and absence of maltulose. Most dried samples presented values of furosine between 100 and 200 mg/100 g of protein and maltulose between 5 and 15 mg/100 g of dry matter. However, a group of samples, mainly constituted by spaghetti, showed higher furosine and maltulose contents, probably due to the higher heat load applied during the drying process.

Three dried pasta samples (macaroni, spaghetti and noodle) showed the lowest values for furosine and no maltulose was detected. These data could indicate that these samples had been submitted to low temperatures and long time treatments.

Three vermicelli samples from the same manufacturer and of different thickness, fine, medium and thick, showed similar maltulose values (10.4, 10.5 and 10.2 mg/100 g dry matter, respectively), but different furosine levels (113, 128 and 185 mg/100 g protein, respectively). Taking into account that the isomerization reactions are favoured at high temperatures (López-Fandino & Olano, 1999), these samples could have been submitted to similar heat treatments (higher than 60 °C) during the first step of the drying process, which could allow the formation of maltulose and furosine. Differences in furosine values among samples may be due to the different times of processing at low temperatures applied during the second step of drying.

From these results, maltulose could be considered as a good index of the damage caused during elaboration of

pasta and it could be used, together with furosine, as a quality indicator of dried pasta. Samples without maltulose, and with low values of furosine, could have been submitted to processes of low temperature long time (LT-LT). High values of maltulose and furosine could indicate samples submitted to very high temperature short time processes (VHT-ST), while low values of maltulose and high contents of furosine could indicate samples submitted to low temperature treatments, followed by short time high temperature processes (HT-ST).

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