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Furosine and flavour compounds in durum wheat pasta produced under different manufacturing conditions: Multivariate chemometric characterization

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ABSTRACT

The headspace solid-phase microextraction (HS-SPME) technique followed by GC/MS analysis was performed to evaluate the volatile fraction of durum wheat pasta produced under different process conditions (artisan manufacturing methods or industrial processes). At the same time, HPLC analysis was performed to quantify furosine in the same pasta samples. Furosine is commonly used as an index of nutritional damage occurring during pasta drying, although drastic thermal treatments may lead to its underestimation. Moreover, since furosine determination requires time/solvent-consuming methods, a more convenient approach could be the identification of volatile compounds formed during the drying step and detectable through simple and automated methods. Principal Component Analysis (PCA) was applied to experimental data in order to discriminate pasta samples according to their drying conditions. A limited number of volatile compounds including Maillard reaction and lipid-derived products (nonanal, hexanal, nonanoic acid, maltol and 2-furanmethanol) proved to be crucial in the differentiation of the samples. Therefore, these compounds could be used as pasta quality markers, alternatively to furosine, or as process markers to keep the drying treatment under control.

1. Introduction

According to the Italian law n. 580 of 1967 (amended by Presidential Decree 187/01), dried pasta is a simple product made exclusively with durum wheat semolina and water. Legislation does not consider any restriction regarding the production process, which includes different steps: milling, mixing, extrusion and drying. However, end product characteristics are not only related to raw materials, but also to manufacturing conditions. Indeed, throughout the transformation process several factors can affect both the cooking performance and the nutritional/organoleptic properties of the final product. As a matter of fact, dried pasta made from selected durum wheat following the artisan production methods (*artisanal* pasta) shows significant differences from pasta produced in industrial plants.

Typically, the artisan methods involve the use of coarsely milled semolina, while the industrial production entails finely milled semolina. The fine milling imposes mechanical stress acting on gluten and starch integrity, which positively affects dough formation and processing. Nevertheless, the increased availability of gluten proteins and free sugars favours the development of undesirable cross-reactions during the drying step. Moreover, the mixing and extruding steps, when performed by continuous industrial high-capacity extruders, can cause changes in pasta carbohydrates content, since starch further damaging leads to the release of free maltose and other sugars (Lintas & D'Appolonia, 1973; Resmini & Pellegrino, 1994; Sensidoni, Peressini, Pollini, & Munari, 1996). Mixing and extrusion conditions (e.g. the type of die) could influence several characteristics of the end product. For instance, pasta produced by modern extruders equipped with Teflon-coated dies shows a good breaking strength but a smooth and bright yellow colour surface due to a partial degradation of carotenoids (Hidalgo, Brandolini, & Pompei, 2010). On the other hand, artisan bronze-extruded pasta is more susceptible to breakage, but it is far appreciated by consumers due to its light yellow colour, rough and porous surface which better holds the sauces (Lucisano, Pagani, Mariotti, & Locatelli, 2008; Mercier, Marchais, Villeneuvea, & Foisy, 2011).

Drying process is undoubtedly a critical step for the final pasta characteristics since modification of its main components can take

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place. The artisan drying methods involve low temperatures (29–40 °C) and long time treatments (24–60 h) (LT-Lt), while high (75–100 °C) or very high (>100 °C) temperatures and short time treatments (5–12 h or 1–2 h) (HT-St and VHT-St, respectively) has been widely adopted in the industrial production (Dexter, Matsuo, & Morgan, 1981). The application of rapid and high-temperature treatments enables an improvement in pasta cooking properties, increase in plant productivity and reduction of microbial contamination (Aktan & Khan, 1992; Manser, 1990; Pavan, 1980), but the development of uncontrolled cross-reactions, such as the Maillard Reaction (MR), could be induced too (Resmini & Pellegrino, 1994). In the drying step, more than 50% of total water in pasta is removed and the moisture content reaches values of 12–13% equivalent to a water activity of 0.8, which is recognized as optimal condition for the development of MR (Labuza, 1980). During the early stage, the MR may affect the nutritional value of wheat protein reducing nutritionally-available lysine and methionine and inducing an excessive browning due to the loss of carotenoids and the formation of coloured compounds (Beleggia et al., 2011; Hidalgo et al., 2010). In the MR advanced stages, the formation of flavour compounds from free sugars can also occur (Lintas & D'Appolonia, 1973; Resmini & Pellegrino, 1994; Sensidoni et al., 1996) as well as significant changes in the flavour composition due to Strecker degradation (Hayashi, Ishii, & Shinoara, 1990) and thermal oxidation of lipids (Sayaslan, Chung, Seib, & Seitz, 2000).

The monitoring of volatile fraction, which contributes to flavour definition, could be relevant in order to characterize different pasta products. Several studies have showed that durum wheat semolina releases volatile compounds, which could differ depending on the wheat cultivar, affecting the aroma of the transformed product (Beleggia, Platani, Spano, Monteleone, & Cattivelli, 2009; Bredie, Mottram, & Guy, 2002; Parker, Hassell, Mottram, & Guy, 2000; Sjövall, Lapveteläinen, Johansson, & Kallio, 1997). Volatile composition is also influenced by process parameters such as temperature, air moisture and pH as MR evolution is related to temperature and water activity variation during the drying step (Bemis-Young, Huang, & Bernhard, 1993). Since pasta can be produced through different drying processes, the operating conditions should be set in order to improve the final aroma, retaining and enhancing the typical flavour of durum wheat. For instance, artisan methods entail the combined use of low temperature and high air moisture content during the thermal treatment in order to improve pasta sensorial properties. In this way, indeed, the internal humidity gradient is avoided and the water loss from pasta surface is slower, as well as the formation kinetics of flavoured compounds and other MR products (MRPs) (Migliori, Gabriele, de Cindio, & Pollini, 2005).

Over the years, many efforts have been spent to directly relate pasta nutritional/organoleptic properties to manufacturing conditions (Acquistucci, 2000; Didonè & Pollini, 1990; Migliori et al., 2005; Sensidoni, Peressini, & Pollini, 1999). Dried pasta quality is generally evaluated by merely technological parameters, such as colorimetric indices, or properties affecting the consumer preferences, such as cooking firmness. According to scientific approaches, furosine was used as an index of pasta nutritional value in relation to drying conditions (Anese, Nicoli, Massini, & Lerici, 1999; Cavazza et al., 2012; Garcıa-Baños, Corzo, Sanz, & Olano, 2004). Furosine is an Amadori compound formed between the ε-amino group of lysine and reducing sugars in the early stage of the MR. High values of furosine in pasta samples can be attributed to HT-St or VHT-St drying processes, while low values can be associated with LT-Lt treatments. However, furosine analysis involves a complex, time-consuming sample pre-treatment (hydrolysis and purification) followed by a solvent-consuming chromatographic determination with an expensive furosine-dedicated column (Resmini, Pellegrino, & Batelli, 1990). Moreover, the furosine content may be insufficient to discriminate differently processed pasta samples, since drastic heat treatments ($T > 100$ °C) can promote a dramatic progression of the MR. As a result, Amadori compounds undergo degradation which leads to furosine underestimation.

The study of the flavour may represent an interesting tool to characterize pasta samples in relation to the manufacturing conditions. In this work the furosine amount and the volatile fraction of different pasta samples were determined and the results were elaborated by multivariate statistical method in order to correlate the chemical information with the manufacturing conditions. Chemometric analysis of the data set was performed through Principal Component Analysis (PCA) which represents a useful exploratory tool to evaluate the ability of measured parameters to differentiate groups of samples through a data visualization technique. This work aimed to identify volatile compounds suitable to be used as quality/process markers of pasta, alternatively or in combination to furosine content. PCA enabled to synthesize information from the results obtained, avoiding redundancy and identifying a limited number of variables that could be used for pasta samples discrimination.

2. Materials and methods

2.1. Samples

The study was performed analysing short-shaped dried pasta samples made by *artisanal* and industrial processes. All samples were produced in Italy. *Artisanal* pasta samples were selected based on the information claimed on the label (e.g. *"produced from rough milled durum wheat semolina", "bronze die", "slow drying at low temperature"*). Eighteen different samples were purchased from shops selling local products. Twenty-three industrial pasta samples were purchased from supermarket (Large Scale Retail Trade) among the most common brands of mass-produced pasta. All samples were stored in their unopened packages (plastic) at room temperature until their use. The samples were selected having the same expiration year. Before analysis, samples were fine ground under liquid nitrogen to avoid heating during milling and thus loss of volatile compounds. The samples were analysed in duplicate.

2.2. Furosine determination

Chromatographic analysis of furosine in pasta samples was performed by a high performance liquid chromatography (HPLC) system entirely assembled with polyetheretherketone (PEEK) tubing (25 μL PEEK loop) and coupled to a diode array detector (DAD) (Waters) working at 280 nm according to the method of Resmini (Resmini et al., 1990). The separation of furosine was carried out in a C8 column (250 × 4.6 mm i.d.) by Supelco (Bellefonte, PA, USA), thermostated at 35 °C with a column heater (Tech-lab, K7). Acquisition and processing of data was achieved with Empower 2 software (Waters). Calibration curve for furosine quantitation was performed by the external standard method using a commercial standard of furosine dihydrochloride (72.4% of purity) supplied by Polypeptide Group (Strasbourg, France). Before chromatographic analysis, 350 mg of ground pasta were hydrolysed with 8 mL of chloridric acid (HCl) 8 N at 110 °C for 24 h in a screw-capped Pyrex vial with polytetrafluoroethylene (PTFE) faced septa, after purging with nitrogen for 2 min. Hydrolysed samples were filtered through a Durapore idrofile polyvinylidene difluoride (PVDF) membrane filter (0.22 μm) from Millipore (Bedford, France). The filtrate was purified on endcapped cartridge C18 using 3 mL of HCl 3 N after cartridge conditioning step. The Cromafix C18 cartridges were supplied by Macherey-Nagel (Düren, Germany).