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Molecular rearrangements in extrusion processes for the production of amaranth-enriched, gluten-free rice pasta

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A B S T R A C T

Gluten-free pasta represents a challenge for food technologists and nutritionists since gluten-free materials used in conventional formulations have poor functional and nutritional properties. A novel extrusion-cooking process was set up to improve the textural characteristics of rice-based pasta, and to enrich it with amaranth. Mineral and fiber content, and protein digestibility were improved by amaranth enrichment. Extrusion-cooking of a 75/25 mixture of rice flour and amaranth prior to pasta-making gave the best results as for the textural characteristics of the final product. The firmness of cooked pasta increased due to the extrusion-cooking process, that also decreased protein solubility in the amaranth-enriched pasta. The content in accessible thiols also decreased in amaranth-enriched pastas, indicating that amaranth proteins may be involved in forming disulphide bonds during the pasta-making process. Our results suggest that starch in rice flour interacts best with amaranth proteins when starch gelatinization occurs simultaneously to protein denaturation in the extrusion-cooking process.

1. Introduction

Gluten-free (GF) foodstuffs – typically based on rice and maize – have a comparatively low content of poor-quality proteins, and are low in fiber, calcium, and iron. GF products also have a high fat and caloric content, to compensate for decreased sensorial acceptability (Thompson, 2009). Macronutrients content in amaranth flour is similar to wheat, and 2–3 times higher than other GF sources (Calderón de la Barca, Rojas-Martínez, Islas-Rubio, & Cabrera-Chávez, 2010). Proteins from amaranth have better amino acid nutritional balance than other vegetable proteins, including cereals, and the fiber and mineral content in amaranth is much higher than in other GF grains (Pedersen, Knudsen, & Eggum, 1990). Amaranth flour has already been used to enrich cereal-based foods, including GF pasta. However, noodles produced from amaranth alone had decreased firmness and increased cooking losses with respect to reference materials (Schoenlechner, Drausinger, Ottenschlaeger, Jurackova, & Berghofer, 2011).

When rice flour is used as the only ingredient for pasta production, it requires additives or particular processing techniques to modify in a suitable way the properties of macromolecular components (starch and proteins) relevant to the structure of the final product. Either gelatinization of the rice flour or steaming of the pasta may improve the textural properties of the final product (Lai, 2001; Pagani, 1986), and a process was developed for rice-based pasta, in which extrusion-cooking of the starting flour was followed by conventional pasta-making processes (Marti, Seetharaman, & Pagani, 2010). Extrusion-cooking causes starch gelatinization followed by retrogradation, forming a rigid starch network and improving the cooking quality of the product. Amaranth proteins in amaranth-enriched rice-based pasta could rearrange their organization or their interaction with other components of the systems at various stages in the process, and the ensuing interactions among proteins or between proteins and other pasta components may improve the textural properties of the product.

The goal of this work was to prepare high-quality amaranth-supplemented rice pasta using extrusion-cooking of each or both

Abbreviations: GF, Gluten-free; RF, Rice flour; AF, Amaranth flour; P1, Pasta sample 1; P2, Pasta sample 2; P3, Pasta sample 3; P4, Pasta sample 4; P5, Pasta sample 5; DTT, Dithiothreitol; DTNB, 5,5′-dithiobis-(2-nitrobenzoate); OCT, Optimum cooking time; BU, Brabender units.

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the starting materials, followed by conventional pasta-making. The effects of supplementation with amaranth and of processing conditions on the pasta properties were assessed, along with the nature of the intermolecular interactions ensuing from the various combinations of ingredients and processes. Information provided from a number of diverse approaches was combined to define a molecular-based rationale for the properties of the final product.

2. Materials and methods

2.1. Flours and pasta samples

Parboiled milled rice (*Oryza sativa*, cultivar Indica; amylose, 25 g/100 g total starch; Riso Viazzo s.r.l., Crova, Italy) was milled into flour (RF; total starch: 80.9 g; damaged starch: 5.9 g; protein: 10.7 g; lipid: 0.4 g; ash: 0.9 g; fiber: 4.2 g, in 100 g dry matter). Amaranth seeds (*Amaranthus hypochondriacus*) were a mixture of organically grown commercial and non-commercial varieties (Cooperativa Quali, Tehuacan, Mexico), milled just prior to use into amaranth flour (AF; total starch: 61.1 g; damaged starch: 7.0 g; protein: 19.1 g; lipid: 9.7 g; ash: 3.0 g; fiber: 18.6 g, in 100 g dry matter). On the basis of previous unpublished trials, 25 parts of AF were mixed with 75 parts of RF to prepare amaranth-enriched pasta. This mixture of flours contained: 73.7 g total starch; 6 g damaged starch; 12.9 g protein; 2.9 g lipids; 1.3 g ash; 5.3 g fiber, in 100 g dry matter.

As summarized in Table 1, pasta samples P1 and P4 were made by room-temperature extrusion from RF and AF in the absence of other treatments. In other cases, flours or flour mixtures were treated prior to pasta-making in a Progel two-zone extrusion-cooker (2 min, extruder zone temperature 120 °C; single screw; Braibanti, Milano, Italy). The process was applied to RF (samples P2 and P5), or to a 75/25 mixture of RF and AF (P3). Pasta was prepared using RF only (untreated, P4; extrusion-cooked, P5), or a mixture of 25/75 combination AF/RF (both untreated, P1; extrusion-cooked RF and untreated AF, P2). Sample P3 was prepared from pellets obtained from extrusion-cooking of a 75/25 mixture of RF and AF. Water content in dough prior to forming was always 400 g kg^{-1}. Pasta was formed into macaroni shape (7 mm outer diameter) in a laboratory-scale extruder (20 kg h^{-1}; MAC 30, Italpast, Parma, Italy; extrusion temperature 25 °C), and dried at low-temperature (50 °C max, 14 h).

2.2. Pasta quality indexes

Cooking losses were evaluated by determining the solids lost into cooking water (grams of matter lost for 100 g of dry pasta; D'Egidio, Mariani, Nardi, Novaro, & Cubadda, 1990), at a pasta:water ratio = 1:10 with no salt addition. Olive oil (10 mL L^{-1}) was added to limit leaching. After cooking, pasta was drained, water was brought back to the initial volume, and an aliquot was dried to constant weight at 105 °C. Weight increase of pasta due to water absorption during cooking was evaluated gravimetrically. For the purpose of recording leaching kinetics, pasta was also cooked longer than the optimum cooking time (OCT) (D'Egidio et al., 1990).

Texture measurements at OCT for each sample were carried out in a Texture Analyzer TA-HD (Stable Micro Systems, Surrey, UK). The maximum force assessed from the force–time diagram was used as an indicator of firmness.

Table 1
Flours, flour mixtures, and treatments of flours and flour mixtures used for pasta-making.

Pasta sample	Flour content (g/100 g)		Flour treatment	
	Rice	Amaranth	Rice	Amaranth
P1	75	25	None	None
P2	75	25	Extrusion-cooked	None
P3	75	25	Extrusion-cooked[a]	Extrusion-cooked[a]
P4	100	0	None	–
P5	100	0	Extrusion-cooked	–

[a] A 75/25 (rice flour, RF/amaranth flour, AF) mixture was subjected to extrusion-cooking, and the resulting material used for pasta-making.

Table 2
Proximate analysis (on a dry matter basis) and protein digestibility of the various pasta samples.

	Pasta sample				
	P1	P2	P3	P4	P5
Ash (g kg^{-1})	12.8[a]	12.6[a]	12.9[a]	9.0[b]	9.6[b]
Protein (g kg^{-1})	128.8[a]	129.3[a]	126.5[a]	107.3[b]	100.1[b]
Total carbohydrates (g kg^{-1})	829.0[a]	827.7[a]	830.9[a]	879.8[b]	886.8[b]
Fat (g kg^{-1})	29.3[a]	30.1[a]	29.7[a]	3.9[b]	3.5[b]
Total fiber (g kg^{-1})	54.8[a]	59.7[a]	58.9[a]	31.9[b]	30.5[b]
Zn (g kg^{-1})	0.071[a]	0.073[a]	0.072[a]	0.007[b]	0.007[b]
Fe (g kg^{-1})	0.075[a]	0.076[a]	0.075[a]	0.016[b]	0.017[b]
Ca (g kg^{-1})	0.296[a]	0.299[a]	0.288[a]	0.036[b]	0.034[b]
Protein digestibility score	83.99[a]	84.74[a]	82.86[b]	80.38[c]	79.97[c]

Different superscripts in a given row indicate statistically significant differences ($P < 0.05$). All data are from triplicate determinations on two sets of samples.

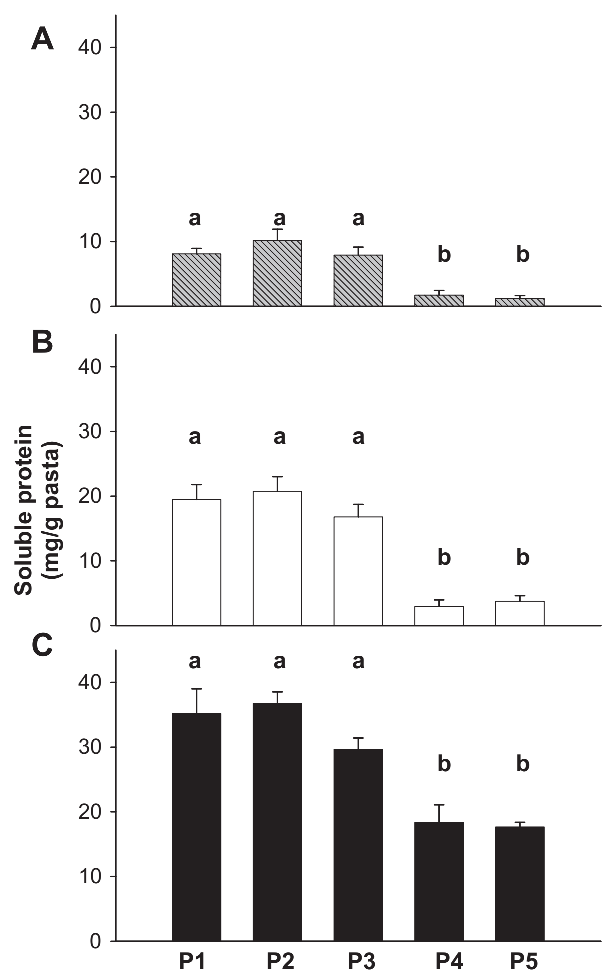

Fig. 1. Solubility of proteins from pasta samples in phosphate/saline buffer in the absence (A) or in the presence of urea (B) and of urea/DTT (C). Standard deviation is given for each sample ($n = 3$). Different letters within each panel indicate statistically significant differences ($P < 0.05$).