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Physicochemical properties and metabolomic profile of gluten-free spaghetti prepared with unripe plantain flours

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ABSTRACT

Alternative ingredients such as unripe plantain (whole and pulp), maize and chickpea flour were used to prepare extruded dry gluten-free spaghetti with functional characteristics. The chemical composition, cooking quality and metabolomic profile in different processing steps (dough formation, uncooked and cooked) were analysed. Two formulations were prepared using unripe plantain pulp and whole unripe plantain fruit (pulp and peel). The two spaghetti samples showed a similar chemical composition, but the whole flour product had a higher dietary fibre content. No difference in cooked weight and cooking loss of the spaghetti samples was found, and the optimal cooking time was slightly lower for spaghetti with whole flour. The spaghetti sample with whole flour showed higher hardness than spaghetti with pulp flour but was similar to commercial spaghetti. The water absorption of spaghetti with whole flour was lower than spaghetti with pulp flour, but this did not affect the diameter of the cooked spaghetti. The metabolomic profile for both spaghetti was similar; a decrease in the area of metabolites present in the spaghetti was observed with uncooking and cooking, but an important number of metabolites was maintained after cooking. It is possible to develop gluten-free pasta with quality characteristics using whole unripe plantain flour.

1. Introduction

Currently, the agro-food chain emerging from agricultural by-products and underused products represents an alternative to problems associated with the final disposal and efficient use of food crops (Pingali, Alinovi, & Sutton, 2005). In this sense, the development of new foods with an impact on human health (functional foods) is of interest for the food industry due to the increase in diseases associated with food consumption, such as obesity, diabetes mellitus, celiac disease, heart disease, cancer and malnutrition. One group of functional foods is foods with a high content of non-digestible carbohydrates (dietary fibre) (Wolever, 2003). Pasta is among the most consumed foods worldwide, and spaghetti is the pasta type most consumed in Mexico. Spaghetti is produced by mixing wheat semolina and water. The compactness of spaghetti structure is mainly due to the gluten network produced during spaghetti processing, which gives the quality characteristics of this product (Bello-Pérez, Flores-Silva, Camelo-Méndez, Paredes-López, & Figueroa-Cárdenas, 2015). The main problem in gluten-free spaghetti is the poor protein network due to the absence of gluten. Thus, the use of protein-rich and starch-rich flours such as chickpea (*Cicer arietinum*) and maize (*Zea mays*) can be used in combination with hydrocolloids (e.g., hydroxypropylmethylcellulose) to increase the viscoelastic properties of the dough (Mancebo, San Miguel, Martínez, & Gómez, 2015). Another negative characteristic of gluten-free spaghetti is its low nutritional quality; however, the addition of ingredients with nutraceutical potential is feasible in the production of a paste with acceptable nutritional properties. Unripe plantains contain a high content of non-digestible polysaccharides (dietary fibre) as well as starch that is resistant to enzymatic hydrolysis (Juarez-Garcia, Agama-Acevedo, Sayago-Ayerdi, Rodriguez-Ambriz, & Bello-Perez, 2006; Aurore, Parfait, & Fahrasmane, 2009). Therefore, unripe plantain flour can be used as a source of antioxidants and metabolites of interest for the development of gluten-free spaghetti. The potential use of unripe plantain flour from pulp to starch isolation or ingredients in extruded products is feasible (Hoyos-Leyva, Bello-Pérez, Agama-Acevedo, & Alvarez-Ramirez, 2015). The use of unripe plantain flour

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from the fruit pulp (UPF) in a blend with semolina was reported; the resistant starch (RS) content in the spaghetti with the highest substitution level reached 12.4 g/100 g, but dietary fibre was not determined; instead, the indigestible fraction (29.6 g/100 g) was reported (Ovando-Martinez, Sayago-Ayerdi, Agama-Acevedo, Goñi, & Bello-Perez, 2009). UPF was used for blending with chickpea and maize flours; cooked gluten-free spaghetti with the highest substitution level of UPF (25–30 g/100 g) presented a RS content between 3.5 and 4.1 g/100 g, with a medium predicted glycemic index (Flores-Silva, Berrios, Pan, Osorio-Díaz, & Bello-Pérez, 2014). Dietary fibre content was not determined. Cooked spaghetti made of pure UPF showed a RS content of 5.6 g/100 g, with a slowly digestible starch content of 6.4 g/100 g, but dietary fibre content was not reported (Bello-Pérez et al., 2015). The peel of unripe plantains can be used to produce flour with better functional and nutritional characteristics than flour from the pulp. Additionally, the peel represents approximately 35 g/100 g of the fruit weight (wet basis) (Agama-Acevedo, Sañudo-Barajas, Vélez De La Rocha, González-Aguilar, & Bello-Peréz, 2016), and the whole fruit can be used to produce flour with lower waste and higher yield compared to unripe plantain flour made solely from the pulp. Chickpea flour is an option for making extruded products, since it is a good source of protein, carbohydrates, vitamins, phytochemicals and dietary fibre (Frohlich, Boux, & Malcolmson, 2014). Corn flour offers a significant content of starch and dietary fibre (Flores-Silva et al., 2014). A mixture of unripe plantain flour (with peel) with corn and chickpea flour may help to increase the content of non-digestible carbohydrates (Bello-Pérez et al., 2015). Some studies have examined the principal aspects of flours incorporation into pasta (Goni & Valentin-Gamazo, 2003; Sabanis, Makri, & Doxastakis, 2006), but the quality of pasta produced from blends of flours (maize, chickpea and unripe whole plantain flour) has not been thoroughly investigated. The aim of this study was to investigate extruded gluten-free spaghetti with a mixture of maize, chickpea and whole unripe plantain flours and to evaluate the chemical, texture, quality characteristics and metabolomics profile.

2. Materials and methods

2.1. Reagents

All reagents used are commercially available from Sigma Aldrich (Sigma Chemicals Co., St Louis, MO, USA), Fermont (Productos Químicos Monterrey, Monterrey, Mexico) and JT Baker (Avantor Performance Materials, Center Valley, PA, USA).

2.2. Raw materials

Whole unripe plantain (*M. paradisiaca* L.), chickpea (*C. arietinum* L.), and pigmented maize (*Z. mays* L.) flours were used to develop the spaghetti. Unripe plantains were purchased from a local market in Cuautla, Morelos, Mexico, and the flour was obtained using the pulp (without peel) and the complete fruit (with peel) (Ovando-Martinez et al., 2009), the material was dried (40 °C for 4 h) and milled (sifted through a no. 50) to obtain flours. Chickpeas were obtained from an experimental field at UAS (Sinaloa Autonomous University) Culiacan, Sinaloa, Mexico. Pigmented maize was obtained from the experimental field of INIFAP Texcoco, Edo. Mexico, Mexico. Raw material (maize and chickpea) were selected, pooled (approximately 3–5 kg), dried and milled to obtain flours. To obtain the flour, whole grains were milled (A10 analytical mill, Tekmar Co., Cincinnati, OH, USA) and sifted through a no. 50 sieve and stored in airtight, opaque containers at 4 °C.

2.3. Spaghetti formulation and processing

Two formulations (two batches of each one) with a blend of unripe plantain, chickpea, and maize flours were prepared to evaluate the gluten-free spaghetti (Table 2). The water content was 32 g/100 g in both formulations. One formulation was made with the pulp of unripe plantain flour (PF), named F1, and the second formulation was made with whole unripe plantain flour (PFP), named F2. A single screw-extruder Beutelspacher was used at a constant screw speed of 75 rpm. At the first zone of the barrel, the temperature was 50 °C. The temperatures at the blend zone and at the end zone were 114 and 100 °C, respectively. Spaghetti sample was dried at 45 °C for 4 h in an oven (Biotecnica del Bajio, Celaya, Guanajuato, Mexico); these conditions were determined based on the final moisture content (14 g/100 g). The spaghetti samples were stored in sealed plastic containers until further analysis. The commercial product used in this study was gluten-free spaghetti made of maize and rice flours (Barilla®).

2.4. Chemical composition

The moisture content was determined by drying 2 ± 0.01 g of spaghetti sample for 1 h at 130 °C according to AACC 44-15 method (AACC, 2000). Ash was assessed according to the AACC method 08-01 (AACC, 2000). Fat was determined by weight difference after sample extraction with petroleum ether (Fisher Scientific, Fair Lawn, NJ, USA) in an accelerated solvent extractor (ASE 200, Dionex Corp., Sunnyvale, CA, USA). Protein content (equivalents/L x 6.25) was determined according 46-13 AACC method. All analyses were performed in triplicate, and the results were reported on a dry weight basis. Total dietary fibre (TDF) was assessed according to 32-05 method (AACC, 2000). Total starch (TS) was measured according to AACC method 76.13 (AACC, 2000).

2.5. Cooking quality and texture of cooked spaghetti samples

The cooking quality of the spaghetti was assessed according to AACC 66–50 method (AACC, 2000). The optimal cooking time was determined with 8 g of spaghetti sample cooked in boiling water (100 mL) until the white colour in the pasta's central core disappeared, as evaluated after squeezing the spaghetti sample between two glass slides. The cooked weight of spaghetti sample was determined as the final weight of 10 g of spaghetti sample cooked for the optimal cooking time in 300 mL of boiling water. Cooking loss was determined after the remaining cooking water collected from each sample was evaporated overnight at 110 °C, and the residue was weighed and reported as a percentage. Texture analysis of cooked spaghetti samples was performed: hardness, adhesiveness, elasticity and chewiness. For all the measurements, the texture analyser (Brookfield CT3, Middleboro, MA) was used. The machine was equipped with a 25 kg load cell. The spaghetti samples were prepared and kept until measured according to the approved AACC method (66.50 pasta cooking quality-firmness; AACC, 2000). Water absorption of the spaghetti samples was achieved with the method previously reported using 5 cm long pieces and cooked in 300 mL boiling distilled water for 8 min (Flores-Silva, Rodriguez-Ambriz, & Bello-Pérez, 2015).

2.6. Metabolomic profile

To identify the major metabolites in the spaghetti samples, we used the LC-MS/MS method described below. In brief, 250 mg of samples, namely flour mixtures and uncooked and cooked spaghetti sample (lyophilized, milled and sieved), were treated with methanol extraction using 1 mL of methanol (HCl 0.1 mol/L). The samples were vigorously shaken for 60 min under cooling conditions (4–10 °C). The methanolic extracts were centrifuged 5 min at 14,000 rpm under cooling conditions (4–10 °C) and the supernatants were collected in new tubes. The samples were analysed in a micrOTOF-Q (Bruker®) in ESI positive ionization mode. Capillary and collision cell RF were set to 4500 V and 150 Vpp, respectively. The dry heater temperature was 180 °C, and the dry gas