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Effect of processing on phenolic acids composition and radical scavenging capacity of barley pasta

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ABSTRACT

Phenolic acids, total phenolics content and DPPH radical scavenging capacity in raw ingredients, fresh and dried spaghetti, and in uncooked and cooked spaghetti were evaluated and compared with semolina spaghetti as a reference. Ferulic acid was the major phenolic acid found in the free and bound phenolic extracts in all the investigated pasta samples. The addition of barley flour into pasta at incorporation levels of 30, 50 and 100% increased phenolic acids and total phenolics content. Pasta processing did not significantly affect the total phenolics content and free radical scavenging capacity, but a significant reduction in total phenolic acids measured by HPLC was found. Drying process differently affected individual phenolic compounds in the free and bound fractions, and thus, the total phenolic acids content. Free vanillic, caffeic and *p*-coumaric acids did not significantly change, while *p*-hydroxybenzoic and ferulic acids of the free extracts showed higher values compared to the corresponding fresh pasta. Cooking did not greatly affect total phenolic acids, more leading to conserving free and bound phenolic compounds.

1. Introduction

Whole grains, including barley, are rich in a wide range of compounds with known health benefits.

Demand for functional foods that offer therapeutic and disease prevention is globally increasing. In this regard, barley represents an opportunity because it is an excellent source of healthy dietary fiber, particularly β-glucan, and other bioactive constituents such as tocols, B complex vitamins, minerals and phenolic compounds (De Paula, 2014; Gray, Abdel-Aal, Seetharaman, & Kakuda, 2009; Madhujith & Shahidi, 2009; Messia, Candigliota, De Arcangelis, & Marconi, 2017). Phenolic compounds are naturally occurring phytonutrients that possess one or more aromatic rings with one or more hydroxyl groups. In barley, there are several classes of compounds that have a phenolic structure, such as benzoic and cinnamic acid derivatives, proanthocyanidins, quinones, flavonols, chalcones, flavones, flavanones and amino phenolic compounds (Adom & Liu, 2002; Hernanz et al., 2001).

Currently interest in phenolic acids and other secondary metabolites is rising because of their potential protective roles in human health. They are known for their ability to inhibit oxidation of methyl linoleate (Kahkonen et al., 1999), to scavenge free radicals (Abdel-Aal, Choo, Dhillon, & Rabalski, 2012), to inhibit oxidation of human LDL cholesterol (Abdel-Aal & Gamel, 2008) and to impede singlet oxygen or chelate pro-oxidant metals (Larson, 1988). Phenolic acids are the main phenolic compounds in cereal grains, such as barley and wheat (Abdel-Aal et al., 2012; Adom & Liu, 2002). They are present in free and bound form primarily in the outer layers of the cereal kernels. Ferulic acid and its dehydrodimer derivatives are the major phenolic compounds in cereals present mainly in bound form, which is ester linked to the cell wall in the outer layers of the grain kernels (Hernanz et al., 2001; Manach, Scalbert, Morand, Rémésy, & Jiménez, 2004). Polyphenols, including phenolic acids, could play significant roles in human nutrition and health due to their anti-inflammatory antioxidant, and anti-carcinogenic effects (Kahkonen et al., 1999; Sies, Schewe, Heiss, & Kelm, 2005).

Content and bioavailability of phenolic acids could be altered during processing. Processing of cereals may positively or negatively affect the content of phenolic compounds which possibly impacts their bioactive properties and health benefits (Duodu, 2011). In particular, the literature seems to show that pasta production and cooking may increase or decrease phenolic acids content and its antioxidant activity (Fares, Platani, Baiano, & Menga, 2010; Verardo, Gòmez-Caravaca, Messia, Marconi, & Caboni, 2011). Processing may affect the levels of free and bound phenolic acids in pasta along with their bioavailability

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and subsequent physiological effects. In this regard, to achieve the maximum benefits from a food it is critical to understand its composition of nutrient and bioactive components as well as the effects of food formula, food processing and cooking on the composition and bioavailability of these beneficial components.

Based on these remarks, this study was designed to investigate effects of formulation, pasta making (e.g. extrusion and drying), and cooking on individual phenolic acids in fresh, dried and cooked barley spaghetti.

2. Material and methods

2.1. Materials

The two-rowed, hulless, waxy barley cultivar (CDC Fibar) characterized by high beta-glucan content (9.87% d.b.) was obtained from the University of Saskatchewan (Saskatoon, Saskatchewan, Canada). Commercial durum wheat semolina, xanthan gum (El Peto Products), annatto food colour (Calico), sea salt (Life stream) were bought from a local store in Guelph (ON, Canada).

CDC Fibar grain was ground using a cyclone Sample Mill (UDY Corp., Fort Collins, CO, USA) equipped with a 0.5 mm screen. The barley flour and semolina were refrigerated until pasta preparation.

2.2. Pasta preparation

The recipes for making pasta (spaghetti) were chosen to meet the health claim requirements for β-glucan accordingly to the FDA (0.75 g of β-glucan per serving) (FDA (Food and Drug Administration), 2015) and the European Food Safety Authority (EFSA) (≥ 1 g of β-glucan per quantified portion) (EFSA (European Food Safety Authority), 2011) and to meet the needs of the North American market (De Paula, Abdel-Aal, Messia, Rabalski, & Marconi, 2017).

Barley flour (CDC Fibar) (β-glucan content = 9.9% d.b.) was blended with different amounts of semolina. Four formulations were tested: 1) 100% barley flour; 2) 50% barley flour + 50% durum wheat semolina; 3) 30% barley flour + 70% durum wheat semolina; 4) 100% durum wheat semolina (pasta control), subsequently referred to as 100% barley flour, 50% barley flour, 30% barley flour and 100% semolina. Moisture content was adjusted during processing on the basis of appropriate water absorption and extrusion behavior of barley blends (De Paula et al., 2017). Salt, xanthan gum and annatto solution were added to flours, as reported in a previous paper to improve flavor, texture and colour of pasta (Aldughpassi, Abdel-Aal, & Wolever, 2012). The dry ingredients were mixed in a pasta maker (PastaMatic MX700, Simac-Vetrella, Italy) for 3 min. After that, water was added and all ingredients were mixed for 6 min, then the dough was extruded.

The optimum cooking time of pasta (the time necessary to obtain complete gelatinization of starch shown by the disappearance of the white central core of the spaghetti strand) was determined according the AACCI Method 66-50.01 (AACCI, 2010).

After the extrusion, half of each batch was freeze-dried (i.e. fresh pasta), half was dried at 80 °C in an air oven (Baking Center Duke, Model E101-EV, Duke Manufacturing, St. Louis, MO, USA) for 4 h (e.g. dried pasta). Part of fresh and dried pasta was cooked (e.g. fresh cooked, and dried cooked). Cooked pasta was freeze-dried for chemical assays (Virtis Genesis 25 EL Laboratory - Pilot Freeze Dryer, VirTis, Stone Ridge, NY, USA). All samples were ground using cyclone Sample Mill equipped with a 0.5 mm screen and refrigerated for future analysis.

2.3. Extraction of free and bound phenolic acids

The free phenolic acids were extracted from 0.5 g of the whole grain flour twice on an IKA shaker VXB (IKA Works, Wilmington, NC, USA) with 80% methanol. The extraction was carried out under nitrogen for 30 min. The tube contents were centrifuged at 10,000 × *g* for 20 min. The extracts were pooled together and evaporated under vacuum at 40 °C using a rotary evaporator to remove methanol and concentrated to approximately 2 mL; then, they were diluted to 4 mL with water and acidified to pH 2 with 2 M HCl. The free acidified extract was centrifuged at 10,000 × *g* for 15 min and transferred into a clean separatory funnel. The free acidic supernatant was extracted three times with 10 mL of ethyl ether and ethyl acetate in a 1:1 ratio (*v*/v) on an IKA shaker for 10 min each and then centrifuged. The organic phase was collected, passed through anhydrous sodium sulfate, and dried under a stream of nitrogen. The residue was re-dissolved in 1.5 mL of Nanopure water. Prior to HPLC analysis, the free phenolic extracts were filtered through a 0.45 μm Acrodisc syringe filter (PN4484, Pall, Port Washington, NY, USA).

The residual pellet obtained after extraction of free phenolic acids was immediately processed for the analysis of bound phenolic acids. First the pellet was washed with 15 mL of hexane, and then it was centrifuged at 10,000 × *g* for 10 min. The supernatant was discarded. Five milliliters of 2 M NaOH was added to the pellet, and then the contents were purged with nitrogen and mixed on an IKA stirring plate for 1 hr at 70 °C. After hot extraction, the mixture was cooled, acidified to pH 2 with 2 M HCl, and centrifuged at 10,000 × *g* for 15 min. The acidic supernatant was transferred into a clean separatory funnel. The pellet was washed with 10 mL of nanopure water and then centrifuged at 10,000 × *g* for 15 min. The water supernatant was combined with the acidic supernatant, and the mixture was extracted three times with 10 mL of ethyl ether and ethyl acetate in a 1:1 ratio (*v*/v) on an IKA shaker for 10 min each and then centrifuged. The organic phase was collected, passed through anhydrous sodium sulfate, and dried under a stream of nitrogen. The residue was re-dissolved in 5 mL of nanopure water and then filtered through a 0.45 μm Acrodisc syringe filter (PN4484, Pall) and stored in a freezer prior to HPLC analysis.

2.4. Analysis of free and bound phenolic acids by HPLC

Phenolic acids in barley extracts were separated and quantified by HPLC equipped with a quaternary pump, temperature-controlled injector, temperature-controlled column thermostat, degasser, photodiode array detector (DAD), and ChemStation Rev.B.02.01-SR2 data acquisition system with the capability of conducting isoabsorbance plot and 3D graphic analyses (Agilent Technologies Canada, Mississauga, ON, Canada). A 25 cm × 4.6 mm i.d., 5 μm Supelcosil column LC-18 (58,298, Supelco, Bellefonte, PA, USA) was employed for the separation of phenolic compounds. A mixture of 12 authentic phenolic acid standards including gallic, protocatechuic, *p*-hydroxybenzoic, gentisic, 3-hydroxybenzoic, vanillic, caffeic, syringic, *p*-coumaric, ferulic, sinapinic, and *o*-coumaric acids was used for calibration, identification, and quantification. For separation of phenolic acids, a gradient system was applied starting with 100% of 6% formic acid and 0% of acidified acetonitrile. The gradient was gradually changed over 35 min to 82% of 6% formic acid and 18% acidified acetonitrile and then held for next 5 min. After that, 2 min was allowed to return to the starting conditions. The total run time was 42 min. Separated phenolic acids were monitored at five different wavelengths (260, 275, 300, 380, and 330 nm) to enhance accuracy of phenolic acid quantification. In other words, protocatechuic, *p*-hydroxybenzoic, and vanillic acids were quantified at 260 nm; syringic acid at 275 nm; *p*-coumaric acid at 300 nm; and caffeic, ferulic, and sinapinic acids at 380 nm. The identity of phenolic acids was confirmed by the isoabsorbance plot analysis. The chromatogram was obtained at 275 nm, at which all 12 phenolic acids showed reasonable response except for gentisic acid. Gentisic acid appeared clearly at 330 nm, but other phenolic acids had low responses. In the current study, each phenolic acid was quantified at its maximum absorption wave-length to enhance the method's accuracy (Abdel-Aal et al., 2012).