

Antioxidant Properties of Experimental Wholegrain Pastas Made With Different Cereals

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Abstract

Pasta represents an identifying ingredient of traditional healthy dishes, in particular in Mediterranean areas. Traditional pasta is made with durum wheat semolina only. However, pasta manufactured with different cereals has become available on the market and its consumption is rapidly increasing.

Five experimental dry pastas, manufactured with the same process by adding 60% wholegrain flours of different cereals (wheat, oat, rye, barley and rice) to the same durum wheat semolina, were supplied by Pavan s.p.a. (Galliera Veneta, PD, Italy).

For each product, aqueous-organic extracts and their residues were studied. Their antioxidant properties were evaluated by FRAP (Ferric Reducing Antioxidant Power) assay and Total Polyphenols Content (TPC) was determined by the Folin Ciocalteu method.

For cooked experimental wholegrain pastas made with different cereals, FRAP values ranged from 3.26 ± 0.08 $\mu\text{mol/g d.w.}$ to 19.52 ± 1.28 $\mu\text{mol/g d.w.}$ in aqueous-organic extracts and from 17.91 ± 2.83 $\mu\text{mol/g d.w.}$ to 87.83 ± 5.06 $\mu\text{mol/g d.w.}$ in residues. In both raw and cooked products the lowest FRAP values were found for semolina/60% whole rice pasta.

The barley pasta has interesting antioxidant properties and this result was matched by the TPC one.

Practical Application

The interest in more nutritious and potentially functional foods has prompted the cereal industry towards new formulations of wholegrain products. The functional properties of minor cereals have been poorly investigated. Our results show that wholegrain pastas made with different cereals are rich in antioxidants, in particular whole barley based pasta, providing a scientific basis for the development of grain based functional foods.

Then the study of free and bound bioactive compounds could be crucial to describe the potential of grains, with the aim of better understanding potential health benefits of wholegrain based food consumption.

Keywords: cereals, pasta, antioxidants, aqueous-organic extract, residue

1. Introduction

Pasta represents an identifying ingredient of traditional healthy dishes, in particular in Mediterranean areas (Krishnan & Prabhasankar, 2012).

A lot of scientific evidences have recognized the pasta's healthy place in the diet for its nutritional and beneficial properties (Augustin et al., 2001; Wolever et al., 2008).

Foods based on wholegrain cereals have a key role in health and well-being (Slavin, 2004; Okarter & Liu, 2010). Several researches suggest that eating wholegrain products as a part of a healthy diet could be useful to reduce the risk of several diseases (Venn & Mann, 2004; Lockheart et al., 2007; Munter, Hu, Spiegelman, Franz, & Dam, 2007; Venn & Green, 2007; Poutanen et al., 2008; Enright & Slavin, 2010; Harris & Kris-Etherton, 2010; Gil, Ortega, & Maldonado, 2011; Borneo & Leon, 2012).

Wholegrain cereals have a unique phytochemical composition: vitamins and minerals, unsaturated fatty acids,

tocotrienols, tocopherols, insoluble and soluble fiber, phytosterols, stanols, sphingolipids, phytates, lignans, and antioxidants like phenolics (Adom & Liu, 2002; Marquat, Slavin, & Fulcher, 2002; Jensen et al., 2004; Adom, Sorrells, & Liu, 2003; Adom, Sorrells, & Liu, 2005; Liu, 2007; Okarter, Liu, Sorrells, & Liu, 2010).

Cereals represent a potentially rich source of natural antioxidants (Manach, Scalbert, Morand, Remesy, & Jimenez, 2004). Polyphenols in cereals are present as easily extractable compounds (free) and as less extractable types (bound) (Bravo, Manas, & Saura-Calixto, 1993; Bravo, Albia, & Saura-Calixto, 1994). The content of antioxidants in cereals have been underestimated. Grains contain more antioxidants than previously thought due to a relatively high amount of bound components (Adom & Liu, 2002; Perez-Jimenez & Saura-Calixto, 2005). Chemical extraction is affected by several factors such as type of solvents, extraction time, and temperature as well as by the chemical compositions and physical characteristics of the sample. Previous investigations have studied and determined phenol content using ethanol, methanol and acetone to extract soluble phenols (Velioglu, Mazza, Gao, & Oomah, 1998; Zielinski & Kozłowska, 2000; Yu, Haley, Perret, & Harris, 2002a; Yu, Perret, Davy, Wilson, & Melby, 2002b; Adom, Sorrells, & Liu, 2003; Liyana-Pathirana & Shahidi, 2006). Several authors have used acidic methanol/water as extraction solvent to improve extraction (Iqbal, Bhangar, & Anwar, 2005; Awika, Rooney, & Waniska, 2005).

Recent investigations have used an alkaline hydrolysis, acid hydrolysis, or enzymatic digestion (Pérez-Jiménez & Saura-Calixto, 2005; Nagah & Seal, 2005; Moore et al., 2005).

In this work aqueous-organic extracts (extractable polyphenols) and potentially bioactive polyphenols that remain in the residues (non-extractable polyphenols) of experimental wholegrain pastas made with different cereals were investigated in the raw and in the cooked state.

2. Materials and Methods

2.1 Samples and Sample Preparation

Five experimental dry pastas, manufactured with the same process by adding 60% wholegrain flours of different cereals (wheat, oat, rye, barley and rice) to the same durum wheat semolina, were supplied by Pavan s.p.a. (Galliera Veneta, PD, Italy).

Preliminary tests were carried out by Pavan for determining the maximum percentage of non-semolina flour to use in the manufacturing of acceptable pasta as well as the best shape. All Pavan's pastas had the same shape (macaroni), average thickness (between 1.14 and 1.22 mm), optimum cooking time (between 8 and 9 min).

Raw pasta products were ground in a refrigerated mill (Janke and Kunkel, Ika Labortechnik, Germany) and the flours were sieved until a granulometry of 0.5 mm.

Wholegrain pastas were cooked following the manufacturer's directions in unsalted and distilled water, frozen, lyophilized and milled.

2.2 Chemicals and Reagents

All reagents and solvents used were of analytical or HPLC grade; all chemicals were purchased from Sigma-Aldrich Srl (Milan, Italy), Fluka Chemicals (Madrid, Spain), Carlo Erba (Milan, Italy). Double-distilled water (Millipore, Milan, Italy) was used throughout the study.

2.3 Sample Extraction

Extractable polyphenols (aqueous-organic extracts) and non-extractable polyphenols (residues) were extracted, isolated and studied as described by Durazzo et al. (2012). In particular in residues, among non-extractable polyphenols, hydrolysable polyphenols (comprising hydrolysable tannins, phenolic acids and hydroxycinnamic acids that are released from the food matrix by strong acidic hydrolysis) were determined. The antioxidant properties and the Total Polyphenol Content (TPC) were determined in both aqueous-organic extracts and their residues.

2.4 Determination of Total Polyphenol Content (TPC)

The Total Polyphenol Content (TPC) was determined using the Folin-Ciocalteu method previously described by Singleton, Orthofer, and Lamuela-Raventos, 1999. Briefly, the appropriate dilutions of extracts were oxidized with Folin-Ciocalteu reagent, and the reaction mixture was neutralized with sodium carbonate. The absorbance of the resulting blue color was measured at 760 nm against a blank after 2h of reaction at room temperature. Gallic acid was used as the standard.

2.5 Evaluation of Antioxidant Properties

Antioxidant properties have been determined by the FRAP (Ferric Reducing Antioxidant Power) assay. The

method was performed as described by Benzie and Strain (1996) and Pulido, Bravo, and Saura-Calixto, (2000) using a Tecan Sunrise® plate reader spectrophotometer. The method is based on the reduction of the yellow Fe^{3+} -TPTZ (2,4,6-tripyridyl-s-triazine) complex to the blue ferrous complex at low pH. The absorbance was recorded at 595 nm after 30 min incubation at 37 °C.

2.6 Statistical Analysis

The data presented are the means of three separate extractions and determinations. Results were expressed as mean \pm standard deviation (SD). Differences among groups using a significance level of $P < 0.05$ were performed by one-way analysis of variance (ANOVA) using the Statistica for Windows statistical package (release 4.5; StatSoft Inc., Vigonza PD, Italy). Significant differences between raw and cooked products have been evaluated by Student t test.

3. Results

Figures 1A-1B show TPC values (mg/100g d.w.) and FRAP values ($\mu\text{mol/g}$ d.w.) in aqueous-organic extracts and residues of raw, experimental, wholegrain pastas made with different cereals.

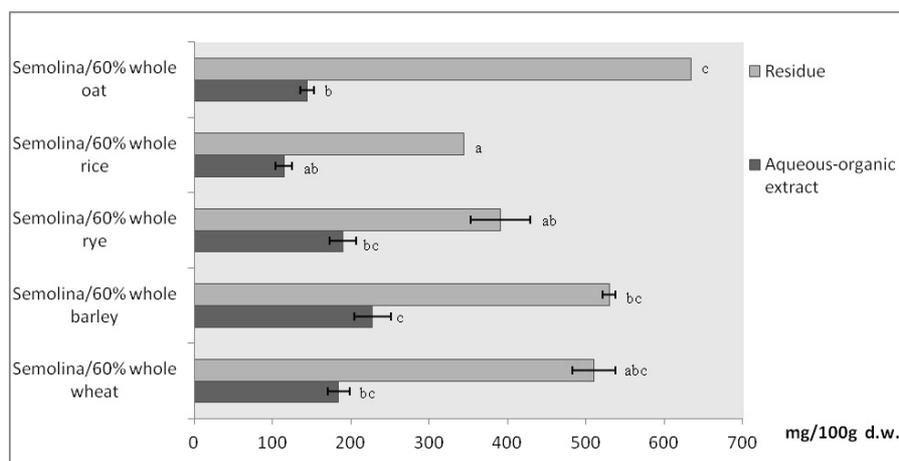


Figure 1A. TPC values in raw, experimental, wholegrain pastas made with different cereals *

*mean \pm S.D.; Anova, Tukey HSD Test; for each fraction, means followed by different letters are significantly different ($P < 0.05$).

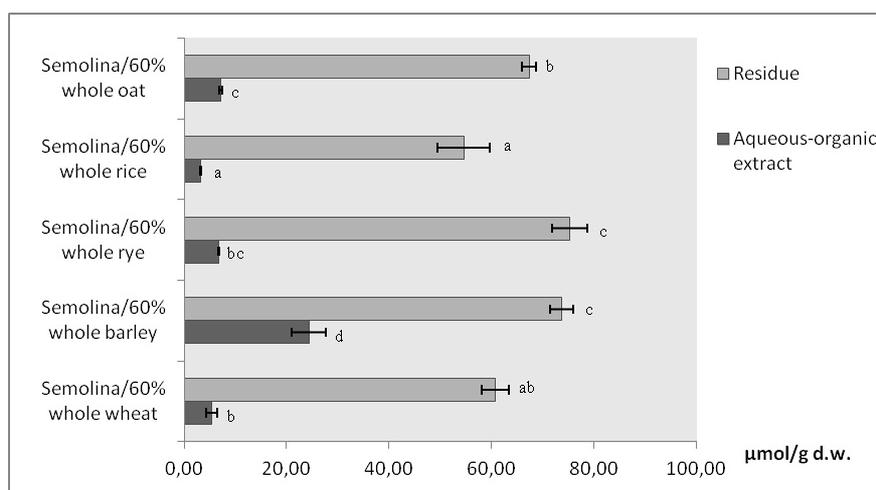


Figure 1B. FRAP values in raw, experimental, wholegrain pastas made with different cereals *

*mean \pm S.D.; Anova, Tukey HSD Test; for each fraction, means followed by different letters are significantly different ($P < 0.05$).

TPC (mg/100g d.w.) varies within the range 114.28-227.34 mg/100g d.w. in aqueous-organic extracts and within the range 343.55-634.30 mg/100g d.w. in residues (Figure 1A), whereas FRAP values ranged from 3.19 ± 0.09 $\mu\text{mol/g d.w.}$ to 24.4 ± 3.32 $\mu\text{mol/g d.w.}$ in aqueous-organic extracts and from 54.62 ± 5.14 $\mu\text{mol/g d.w.}$ to 75.35 ± 3.44 $\mu\text{mol/g d.w.}$ in residues (Figure 1B). The semolina/60% whole rice pasta had the lowest FRAP value for both aqueous-organic extract and residue, while the semolina/60% whole barley pasta reached the highest value for aqueous-organic extract and barley and rye based pastas for residue.

The barley pasta has interesting antioxidant properties and this result was matched by the TPC one. Several authors have demonstrated that pearled barley fractions are suitable for making functional pastas (Marconi, Graziano, & Cubadda, 2000; Verardo, Gomez-Caravaca, Messina, Marconi, & Caboni, 2011). Verardo, Gomez-Caravaca, Messina, Marconi, and Caboni (2011) have obtained spaghetti enriched in bioactive compounds using barley coarse fraction as an ingredient.

In addition it is interesting to underline that in all selected products the hydrolysable polyphenols represent a quantitatively important fraction of polyphenols: the hydrolysable polyphenols content is major than the extractable polyphenols one in all samples.

In particular in raw products the hydrolysable polyphenols contribution to antioxidant properties ranged from 75% in whole barley based pasta to 94% in whole rice based pasta, whereas in cooked pasta ranged from 81% to 92%.

In Figure 2A-2B TPC values (mg/100g d.w.) and Frap values ($\mu\text{mol/g d.w.}$) in aqueous-organic extracts and residues of cooked, experimental, wholegrain pastas made with different cereals were reported. Anese, Nicoli, Massimi, and Lericci (1999) have shown that temperature, time and moisture conditions of the drying process have a significant impact of antioxidant properties of pasta.

Slavin (2003) has observed that bioactive compounds produced during processing contribute to the antioxidant power of the grain products. Several researches have shown that non-enzymatic browning reactions such as the Maillard reaction could generate antioxidant molecules (Manzocco, Calligaris, Mastrocola, Nicoli, & Lericci, 2001; Amarowicz, 2009).

For cooked experimental wholegrain pastas made with different cereals, TPC varies within the range 128.84-226.38 mg/100g d.w. in aqueous-organic extracts and within the range 701.36-1041.10 mg/100g d.w. in residues (Figure 2A).

FRAP values ranged from 3.26 ± 0.08 $\mu\text{mol/g d.w.}$ to 19.52 ± 1.28 $\mu\text{mol/g d.w.}$ in aqueous-organic extracts and from 17.91 ± 2.83 $\mu\text{mol/g d.w.}$ to 87.83 ± 5.06 $\mu\text{mol/g d.w.}$ in residues (Figure 2B). In both raw and cooked products the lowest FRAP values were found for semolina/60% whole rice pasta. In addition, in rice based pasta, after cooking, a decrease of FRAP value has been reported in residue ($P < 0.001$), even if significant increases in TPC values have been reported in aqueous-organic extract ($P < 0.01$) and in residue ($P < 0.01$).

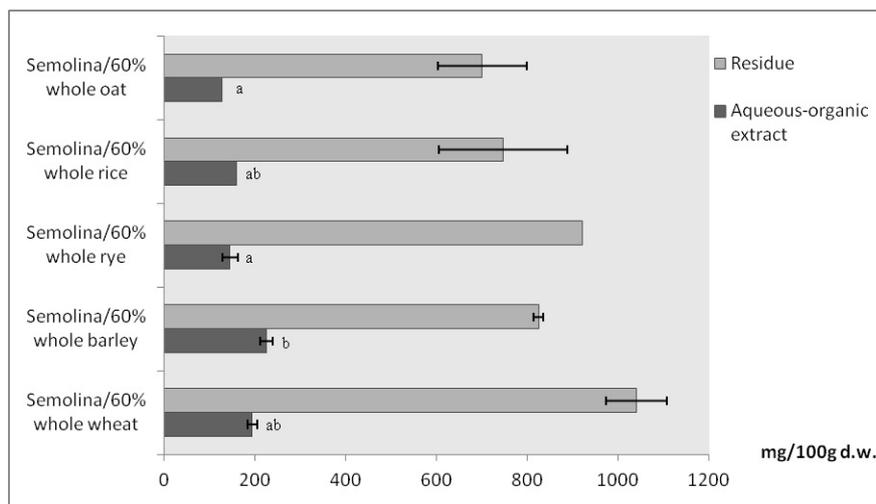


Figure 2A. TPC values in cooked, experimental, wholegrain pastas made with different cereals *

*mean \pm S.D.; Anova, Tukey HSD Test; for each fraction, means followed by different letters are significantly different ($P < 0.05$).

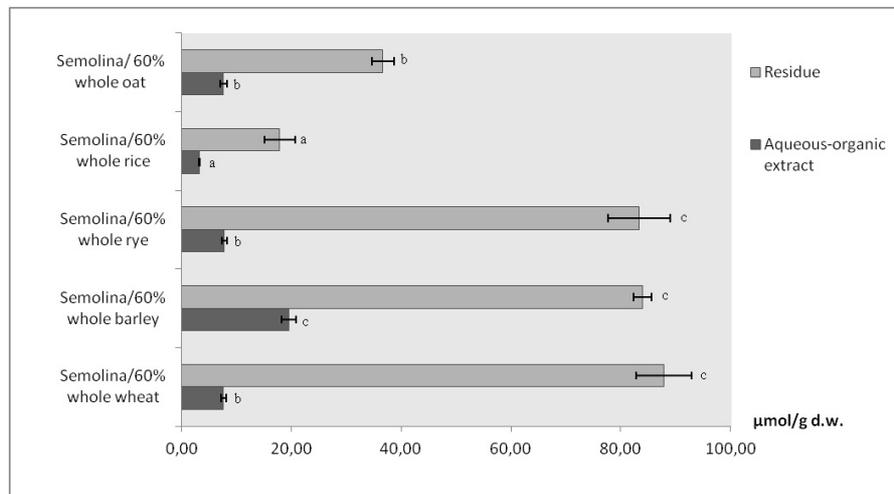


Figure 2B. FRAP values in cooked, experimental, wholegrain pastas made with different cereals *

*mean \pm S.D.; Anova, Tukey HSD Test; for each fraction, means followed by different letters are significantly different ($P < 0.05$)

Comparing raw and cooked products, a significant increase in FRAP values of aqueous-organic extract ($P < 0.05$) and residue ($P < 0.01$) as well as in TPC of residue ($P < 0.001$) has been reported for semolina/60% whole wheat pasta. Fares, Platani, Baiano, and Menga (2010) have shown that boiling water improve the extraction of bound phenolics from the food matrix in wheat pasta enriched with debranning fractions of wheat. On the contrary, Hirawan, Ser, Arntfield, and Beta (2010) have found that the total phenols content reduce by 40% in both regular and whole wheat brands after cooking.

From our results, after cooking, also for barley based pasta significant increases in FRAP value ($P < 0.01$) and in TPC ($P < 0.001$) were observed in residue.

For semolina/60% whole oat pasta a different trend was reported: significant decreases in FRAP value ($P < 0.001$) of residue and in TPC ($P < 0.05$) of aqueous-organic extract were observed.

Then cooked rye based pasta has higher FRAP value ($P < 0.05$) and lower TPC ($P < 0.05$) in aqueous-organic extract than raw product, whereas in residue after cooking an increase in TPC ($P < 0.001$) has been reported.

4. Conclusions

In this research our results have shown the antioxidant characteristics of wholegrain pastas made with different cereals, barley added pasta in particular. Our results confirm that the effect of cooking depends on the nature of food matrix. These results can provide a scientific basis for the development of wholegrain based functional foods.

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