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Characterization of total antioxidant capacity and (poly)phenolic compounds of differently pigmented rice varieties and their changes during domestic cooking

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(+)-Catechin (PubChem CID: 9064)
Ferulic acid (PubChem CID: 445858)
p-Coumaric acid (PubChem CID: 637542)
Protocatechuic acid (PubChem CID: 72)
Quercetin 3-*O*-glucoside (PubChem CID: 11557027)
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ABSTRACT

In the recent years, the pigmented rice varieties are becoming more popular due to their antioxidant properties and phenolic content. In this study, we characterized the antioxidant capacity (TAC) and the phenolic profile in white, red and black rice varieties, and evaluated the effect of two cooking methods (i.e. "risotto" and boiling) on these compounds. Before the cooking, all the varieties contained several phenolic acids, whereas anthocyanins and flavonols were peculiar of black rice and flavan-3-ols of red rice. Among the rice varieties, the black had the highest TAC value. The content of (poly)phenolic compounds and TAC decreased after cooking in all three varieties, but to a lesser extent after the risotto method. As a consequence, the risotto cooking, which allows a complete absorption of water, would be a good cooking method to retain (poly)phenolic compounds and TAC in pigmented and non-pigmented whole-meal rice.

1. Introduction

Rice (*Oryza sativa* L.) is one the most important staple food in the world. The most common varieties belong to the white genotype, even if there is an increasing interest for the pigmented varieties, due to their antioxidant properties and phenolic content in the outer layer of the caryopsis (Finocchiaro, Ferrari, & Gianinetti, 2010). The major classes of phenolic compounds present in rice are phenolic acids, flavonols, anthocyanins and procyanidins. Non-pigmented varieties generally contain only phenolic acids, whereas pigmented ones are qualitatively and quantitatively more rich in polyphenolic structures. In particular, red rice is characterized by the presence of procyanidins, whereas in black rice anthocyanins or both anthocyanins and procyanidins can be present, depending on the variety (Finocchiaro et al., 2010). In the vast majority of the studies present in the literature, these bioactive molecules have been quantified spectrophotometrically as total phenolics and total flavonoids (Massaretto, Madureira Alves, Mussi de Mira, Karaoglanovic Carmona, & Lanfer Marquez, 2011; Min, Gu, McClung, Begman, & Chen, 2012; Walter et al., 2013), whereas the profile of single phenolic acids and flavonoids was less evaluated (Guo & Beta, 2013; Pereira-Caro, Cros, Yokota, & Crozier, 2013; Zhou, Robards, Helliwell, & Blanchard, 2004).

Considering the effect of cooking, previous studies have reported that thermal treatments generally cause a decrement of antioxidant capacity and phenolic content in cereals (Finocchiaro et al., 2007; Massaretto et al., 2011; N'Dri et al., 2013; Towo, Svanberg, & Ndossi, 2003; Walter et al., 2013). In the case of rice, a decrease of antioxidants in white and red varieties after cooking

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was reported, with a higher reduction in red rice and in the samples cooked by boiling (Finocchiaro et al., 2007). A similar result was observed by Massaretto et al. (2011), who reported a 50% reduction of phenolic content in pigmented rice, whereas no significant effect was observed in white varieties. A thermal degradation of anthocyanins was observed in black rice cooked with three different methods (Hiemori, Koh, & Mitchell, 2009) and in whole-meals containing blue-wheat bran (Abdel Aal & Hucl, 2003). A detrimental effect of thermal treatment was also noted on flavonoids of buckwheat groats (Dietrych-Szostak & Oleszek, 1999). Similarly, in buckwheat spaghetti, nearly 40% of total phenolics (composed mainly by flavonoids) was lost, with 12% recovered in cooking water (Verardo et al., 2011). Conversely, contrasting results have been reported for phenolic acids, with different hypothesized effects of cooking on this class of compounds: (i) a partial release from the bound form with the consequent increase of the soluble one, (ii) a decrease of the soluble fraction due to thermal degradation and (iii) an increase of the bound form caused by interactions of phenolic acids with macromolecules of the food matrix (N'Dri et al., 2013).

As there are only few studies on the fate of single phytochemicals in differently pigmented rice varieties after the thermal treatments, the aim of this work was to characterize the phenolic profile and the total antioxidant capacity (TAC) in white, red and black rice varieties, selected because of their different (poly)phenolic composition, and to evaluate the effect of cooking on these compounds.

2. Materials and methods

2.1. Materials

Three commercial varieties of whole-meal commercial rice were analyzed: a white variety (Ribe), a red variety (Ermes) and a black variety (Venere). The grains were purchased at a local market in Parma (Italy).

2.2. Chemicals

Ferulic, vanillic, sinapic, *p*-coumaric, *m*-coumaric and protocatechuic acids, catechin, procyanidin A2, quercetin 3-*O*-glucoside and 2,4,6-tripyridyl-s-triazine were purchased from Sigma–Aldrich (Steinheim, Germany). Cyanidin 3-*O*-glucoside and cyanidin 3-*O*-rutinoside were purchased from Extrasynthase (Genay Cedex, France). All chemical used in the study were of analytical grade. Ultrapure water from a MilliQ system (Millipore, Bedford, MA, USA) was used throughout the experiments.

2.3. Cooking procedure

Two different domestic cooking techniques were applied: boiling and risotto. Both applied cooking procedures were designed to achieve the complete starch gelatinization. Briefly, 110–120 mg of rice was weighed into a 10 mL glass tube. The tube was placed in a water bath at 100 °C, added with a previously determined amount of boiling water and covered. The ratio water/cereal was 3.6/1 (w/w) for risotto and 20/1 (w/w) for boiling. In the case of risotto, the initial volume of water was determined to guarantee that at the end of cooking all the water was absorbed by the rice. During cooking the samples were manually stirred every 10 min. The cooking time was 40 min for all studied varieties and for each cooking procedures. The cooked cereals were then cooled in an ice bath for 5 min. For each variety, cooking experiments were performed in triplicate.

2.4. Extraction procedure

The antioxidant compounds of samples, i.e. raw and cooked rice varieties, were extracted following the previously described procedures (N'Dri et al., 2013; Zaupa et al., 2014) with some modifications. Raw grains were ground to fine flour using a coffee grinder (model AR100, Moulinex, Ecully Cedex, France), whereas cooked grains were ground by Ultraturrax (model T25, Ika, Werke, Staufen im Breisgau, Germany) directly in the tube in which the rice was cooked. To obtain the soluble extract, each sample was first extracted with 3 mL of water/formic acid (99/1, v/v) under agitation for 15 min at room temperature. The extraction was successively repeated with 2 mL of water/formic acid (99/1, v/v). Each extraction step was followed by centrifugation at $9200\times g$ for 10 min and the clear supernatants were combined. The extraction was repeated twice with ethanol/water/formic acid (98/2/1, v/v/v), and the supernatants were combined. The sum of aqueous and ethanolic fractions represents the free soluble fraction. The extraction residue was further used to extract the bound phenolic compounds. For this purpose, the residue underwent an alkaline hydrolysis by means of 1.5 mL of 2 mol/L sodium hydroxide at room temperature for 1 h. The pH of the mixture was then adjusted to 3 by adding 1.35 mL of 3 mol/L citric acid. The samples were extracted twice with 5 mL of ethyl acetate and the supernatants were combined. The ethanol and ethyl acetate extracts were evaporated to dryness under a gentle steam of nitrogen at room temperature and the residue was dissolved in aqueous methanol (50/50, v/v) acidified with formic acid (0.1%, v/v). Soluble and bound extracts were kept at −20 °C in the dark prior to analysis.

2.5. LC–MS^n analyses

Phenolic acids, flavonols, anthocyanins and flavan-3-ols in the three rice varieties were analyzed using an Accela UHPLC 1250 equipped with a linear ion-trap mass spectrometer (LTQ XL, Thermo Fisher Scientific Inc., San Jose, CA, USA) fitted with a heated-electrospray ionization probe (H-ESI-II; Thermo Fisher Scientific Inc.). The separation was performed using a Blue Orchid-175–1.8 μm C18A (50 × 2 mm) column (Knauer, Berlin, Germany).

2.5.1. Anthocyanins

The anthocyanin analysis was carried out in positive ionization mode, using the LC–MS conditions reported by Romain et al. (2014). The analyses were carried out in Full MS^2 mode, monitoring the specific ions that were subsequently fragmented using a collision induced dissociation (CID) of 15 (arbitrary units).

The quantification of cyanidin 3-glucoside and cyanidin 3-rutinoside was performed through a calibration curve with the respective commercial standard. Peonidin 3-glucoside was quantified as cyanidin 3-glucoside equivalents, while cyanidin diglucoside and peonidin 3-rutinoside were expressed as cyanidin 3-rutinoside equivalents.

2.5.2. Phenolic acids, flavonols and flavan-3-ols

Phenolic acids, flavonols and flavan-3-ol analysis was carried out in negative ionization mode, using the following conditions. The MS worked with a capillary temperature set to 275 °C, while the source heater temperature was 200 °C. The sheath gas flow was 40 unit, while auxiliary and sweep gases were equal to 5 units, respectively. The source voltage was 4 kV, while capillary voltage and tube lens were set to −42 and −117.71 V, respectively. For chromatography, the mobile phase, pumped at a flow rate of 0.3, was kept for 13 min in a linear gradient from 5 to 45% acetonitrile in 0.1% aqueous formic acid. The column was then cleaned with 80% acetonitrile and then re-equilibrated to initial conditions.