



Phytochemical profiles and antioxidant activity of processed brown rice products



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ABSTRACT

The phytochemical profiles and antioxidant activity of free, soluble-conjugated, and bound fractions of brown rice and its processed products (textured rice, cooked rice and rice noodle) were studied. Nineteen phenolic acids were identified. *Trans*-ferulic acid was the most abundant monomeric phenolic acid with *trans*-*trans*-8-*O*-4' diferulic acid being most abundant diferulic acid. Processing increased the content of free phenolic acids, but decreased the content of soluble-conjugated phenolic acids. The content of bound phenolic acids was increased by improved extrusion cooking technology and cooking, but not affected by rice noodle extrusion. The total phenolic contents and antioxidant activities of free and soluble-conjugated fractions were decreased after processing, whereas those of bound fraction were increased by improved extrusion cooking technology and cooking, but not affected by rice noodle extrusion. Results indicated that whole foods designed for reducing chronic disease risk need to consider the effects of processing on phytochemical profiles and antioxidant activity of whole grains.

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1. Introduction

Epidemiological studies suggest that increased consumption of whole grains and whole grain products has been associated with

reduced risk of chronic diseases, including cardiovascular disease, type II diabetes, obesity and cancer (Jiang, Li, & Liu, 2016; Okarter & Liu, 2010; Xi & Liu, 2016). The phytochemicals in whole grains are proposed to be partly responsible for the health benefits of whole grains and whole grain products consumption (Liu, 2007; Okarter & Liu, 2010). Rice (*Oryza sativa* L.) is the most important grain crop in Asia, and its processed products, such as cooked rice, rice noodle and textured rice, are staple foods in most populations. Whole grain rice is a rich source of phytochemicals with antioxidant activity (AOA), including phenolic acids (PAs), flavonoids, anthocyanins, proanthocyanidins, tocopherols, tocotrienols and γ -oryzanol (Okarter & Liu, 2010). PAs are the most common

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phenolic compounds found in rice (Liu, 2007). Phenolics exist as free, soluble-conjugated, and bound forms, with bound form being predominant (Adom & Liu, 2002). The bound phenolics are linked to cell wall structural components, such as cellulose, lignin and proteins (Acosta-Estrada, Gutierrez-Urbe, & Serna-Saldivar, 2014; Liu, 2007). Some monomeric and dimeric phenolics have been detected and structurally identified in whole grains (Guo & Beta, 2013; Qiu, Liu, & Beta, 2010). High concentrations of these phenolics are present in the germ and bran layers (Adom, Sorrells, & Liu, 2005). However, these bioactive phenolics are removed by polishing or milling. Whole grain rice with abundant phytochemicals exhibit several unique bioactivities, such as antioxidant (Adom & Liu, 2002), antimicrobial (Zhang, Ali, & Khan, 2014), antiviral (Ray et al., 2013), anti-inflammatory (Niu et al., 2013), anticancer and immunomodulatory activities (Hudson, Dinh, Kokubun, Simmonds, & Gescher, 2000; Verschoyle et al., 2007), thus promoting overall human health.

Since whole grains are thermally processed before consuming, it is important to understand the effect of processing on bioactive phenolics. A few researchers have done this work. In case of total phenolic contents (TPCs) and AOAs of free fractions, most studies found decreases after processing (Massaretto, Madureira Alves, Mussi de Mira, Carmona, & Lanfer Marquez, 2011; N'Dri et al., 2013; Scagliioni, de Souza, Schmidt, & Badiale-Furlong, 2014; Walter et al., 2013; Zaupa, Calani, Del Rio, Brighenti, & Pellegrini, 2015). Dewanto, Wu, and Liu (2002) reported increases in sweet corns, whereas de la Parra, Saldivar, & Liu (2007) observed both decreases and increases in corns. When it came to TPCs and AOAs of bound fractions, a few studies found decrements after processing (de la Parra et al., 2007; Dewanto et al., 2002; N'Dri et al., 2013; Scagliioni et al., 2014). Massaretto et al. (2011) observed increments, whereas Zaupa et al. (2015) reported decrements, increments, and no significant effects in different grain varieties. These processing effects depended on the processing methods applied, the type, and variety of whole grains analyzed. There is no related report on the effect of processing on the TPCs and AOAs of soluble-conjugated fractions in these studies. Processing may cause depolymerisation of oligomers and high polymers into dimers and trimers, concomitant polymerisation reactions, and formation of strong complexes of the soluble phenolics with macromolecules in a food matrix, which may reduce their solubility (Massaretto et al., 2011), thus influencing health benefits of rice. Acosta-Estrada et al. (2014) reviewed that different forms (free, soluble-conjugated, and bound) of phytochemicals are released and absorbed at different sites of the human gastrointestinal tract, thus exhibiting different health benefits. To conclude, however, limited data are available to understand the effect of processing on the phytochemical profiles and AOA in free, soluble-conjugated and bound fractions of brown rice (BR).

The objectives of the present study were (1) to identify phenolic compounds in free, soluble-conjugated and bound fractions of BR; (2) to determine the effects of three processing methods of the staple foods, i.e. improved extrusion cooking technology (IECT), cooking, and rice noodle extrusion (RNE), on TPC and AOA; and (3) to determine the effect of processing on phenolic profiles of BR.

2. Materials and methods

2.1. Materials

Chlorogenic acid (CHA), *p*-hydroxybenzoic acid (*p*-HA), vanillic acid (VA), *trans*-caffeic acid (*trans*-CFA), syringic acid (SYA), *trans*-*p*-coumaric acid (*trans*-*p*-COA), *trans*-ferulic acid (*trans*-FA), *trans*-sinapic acid (*trans*-SIA), gallic acid, Folin-Ciocalteu reagent, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), 6-hydrox-

y-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), 2,4,6-tri (2-pyridyl)-s-triazine (TPTZ), ascorbic acid, and 2',7'-dichlorofluorescein-diacetate (DCFH-DA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetone, ethyl acetate, methanol, hexane, potassium hydroxide (KOH), potassium phosphate monobasic, potassium phosphate dibasic, sodium carbonate, sodium hydroxide (NaOH), potassium persulfate, hydrochloric acid (HCl), EDTA disodium salt (Na₂EDTA), ferric chloride, ferrous sulfate, high performance liquid chromatography (HPLC) grade acetonitrile and acetic acid were purchased from Xilong Chemical Co., Ltd. (Guangdong, China). 2,2'-Azobis (2-amidinopropane) dihydrochloride (ABAP) was purchased from Wako Chemicals (Richmond, VA, USA). Mass spectrometry (MS) grade acetonitrile and formic acid were purchased from Merck (Darmstadt, Germany).

2.2. Brown rice sample and sample preparation

A BR (*Oryza sativa* L.) cultivar (Sonjing 16) was used in this study. It was grown in Wuchang (Heilongjiang Province, China) during the 2014 growing season, and harvested in October. After dehulled, BR was stored in sealed polyethylene containers at -20°C until use. For chemical determination, BR was ground by a DFY-200 mill (Linda Machinery, Zhejiang, China) and sieved (100 mesh) to a uniform size, then stored in sealed polyethylene containers at -20°C .

Cooked rice. BR grains were cooked using 400 ml of tap water to 200 g of rice. BR was cooked for 30 min in an electric pressure cooker (Medea MY-12SS509A, Guangdong, China). After cooling, cooked rice was dried overnight in an oven at 45°C , then ground to a fine powder by a DFY-200 mill and sieved (100 mesh) to uniform size. The cooking treatment was performed in triplicate. Samples were stored in sealed polyethylene containers at -20°C .

Texturized rice. Texturized rice was made using a single-screw extruder based on the method reported previously (Liu et al., 2011). BR grains were soaked in excess tap water for 2 h, drained and then ground to a fine powder to pass through a 0.25 mm mesh screen in a hammer mill (Hongxing Machinery Limited Liability Company, Jiangxi, China). The moisture content of the rice flour was measured by a halogen moisture analyzer HR83 (Mettler-Toledo International Inc., Greifensee, Switzerland). In order to obtain a total feed moisture content of 40%, 8 kg of the BR flour was blended with 2226 ml tap water in a mixer (Jinan Saixin Machinery Ltd., Shandong, China) for 20 min at a high speed (365 rpm) to ensure homogeneity of the feeding material before IECT. The temperature profiles in the feed, mix, screw conveyor, shearing compression metering, and die head zones were kept constant at 50, 65, 85, 120, and 95°C , respectively. The feed and screw speeds were 30 and 37.5 rpm, respectively. The rotary cut frequency was set as 35.5 Hz. After cooling, texturized rice was dried overnight in an oven at 45°C , then ground to a fine powder by a DFY-200 mill and sieved (100 mesh) to uniform size. The IECT was performed in triplicate. Samples were stored in sealed polyethylene containers at -20°C until analysis.

Rice noodle. Rice noodle was made by a traditional rice noodle machine. Briefly, 8 kg of BR grains were soaked in excess tap water overnight. The soaked rice grains and proper water were passed through an instant rice noodle machine (Shengdi Machinery Factory, Zhejiang, China). The BR grains were extruded and milled at high speed (800 rpm) in the noodle machine, resulting in heat generation and flour steaming rapidly. Then the gelatinized BR flour was passed through a 72-hole die to produce uniform strips. Long strips obtained from the cutting rolls of the rice noodle machine were dried at room temperature for 24 h. The rice noodles were ground to a fine powder by a DFY-200 mill and sieved (100 mesh) to uniform size. The RNE treatment was performed in triplicate. Samples were stored in sealed polyethylene containers at -20°C .

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