LWT - Food Science and Technology 88 (2018) 64–70

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Different effects of extrusion on the phenolic profiles and antioxidant activity in milled fractions of brown rice

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ARTICLE INFO

Article history:
Received 19 July 2017
Received in revised form
24 August 2017
Accepted 28 September 2017
Available online 29 September 2017

Keywords:
Brown rice
Milled fraction
Extrusion
Phenolics
Antioxidant activity

ABSTRACT

Thermal treatment usually causes loss of phenolics while the mechanical effect of extrusion is helpful for releasing bound phenolics from food matrix. Due to the difference in textural property, effects of extrusion on phenolics in different rice fractions were assumed varied. Therefore, differences of the changes of phenolic profiles and antioxidant activities induced by extrusion process in milled fractions of brown rice were explored in this study. Extrusion increased the total phenolics, flavonoids, ferric reducing antioxidant power (FRAP) and oxygen radical absorbance capacity (ORAC) of rice bran by 7.3%, 4.9%, 10.7% and 5.9%, respectively, due to the increases of these parameters in free form. However, extrusion reduced free and bound phenolics, flavonoids, FRAP and ORAC values with a total reduction of 53.7%, 40.1%, 56.5% and 56.1%, respectively, in polished rice and 57.0%, 30.5%, 52.3% and 56.6%, respectively, in brown rice. Seven phenolic acids including ferulic, vanillic, *p*-coumaric, chlorogenic, gallic, caffeic and syringic acids were detected in rice fractions. Extrusion changed the individual phenolic contents differently among fractions but had no effects on their composition. These findings provide basis for screening resources of functional foods from different milled fractions of brown rice to meet growing demands of functional food market.

1. Introduction

Epidemiological studies have consistently evidenced the association between increased consumption of whole grain foods and reduced risk of major chronic abnormalities such as cardiovascular disease and type 2 diabetes (Zhu & Sang, 2017). Whole grains are cereal grains composed of germ, endosperm and bran. The starchy endosperm alone accounts for 75–80% of the grain, which is commonly consumed as polished grains. During production of polished grains, the germ is removed from grain kernels together with the bran fraction producing the byproduct of bran. However, the health benefits of whole grains over refined ones are mainly attributed to the presence of higher levels of various bioactive phytochemicals in the bran fraction (Okarter & Liu, 2010).

Brown rice (*Oryza sativa* L) is a representative of whole grains. It is a rich source of phytochemicals, including phenolic acids, flavonoids, proanthocyanidins, tocopherols, and γ-oryzanol. Phenolics in plant foods exist both in free form, extractable by a solvolytic solution, such as water, methanol, ethanol and acetone, and in bound form, conjugated with the structural components of cell wall such as cellulose, hemicelluloses, lignin, pectin, and rod-shaped structural proteins (Acosta-Estrada, Gutiérrez-Uribe, & Serna-Saldívar, 2014). The total content of phenolics in whole grains was reported to be equivalent to or even higher than that in many fresh fruits and vegetables (Adom & Liu, 2002).

Thermal treatment is an indispensable step for the consumption of rice in order to gelatinize the starch and ensure food safety. Despite the health benefits of phenolics, they are thermally sensitive and tend to be degraded during heating treatment. A negative effect of thermal processing on the phenolic content has been proved in polished and brown rice of different rice cultivars (pigmented and nonpigmented cultivars) in the previous study (Walter et al., 2013). Extrusion is a thermomechanical process in which the materials are exposed to high temperature, pressures and shear forces for a short period of time. Such a process can result in many structural and chemical transformations such as gelatinization of

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https://doi.org/10.1016/j.lwt.2017.09.042
0023-6438/

starch, denaturation of protein and formation of starch, lipids and proteins complexes in extruded materials (Alam, Kaur, Khaira, & Gupta, 2015). Furthermore, extrusion was reported to increase the content of soluble dietary fiber (DF) (Gajula, Alavi, Adhikari, & Herald, 2008) and improve the bioavailability and digestibility of nutrients in extrudates (Hole et al., 2013). Therefore, extrusion has been extensively used to produce cereal-based foods such as breakfast cereals and precooked grain flours.

Studies have shown the phenolic contents and antioxidant activity of various extruded food items included black rice (Ti et al., 2015), lentil (Morales et al., 2015) and common beans (Ai, Cichy, Harte, Kelly, & Ng, 2016). However, it has been found that the physiochemical properties of extrudates varied greatly when different levels of bran were enriched into the wheat flour (Robin et al., 2011). The effects of extrusion on the phenolic profiles in milled fractions might also differ due to their differences in the texture and the contents of starch and fiber. We have previously reported the changes of phenolic profiles and antioxidant activity in black rice before and after extrusion (Ti et al., 2015). Up till now, available information is limited on the changes of phenolic profiles and antioxidant activity in different fractions of non-pigmented rice after thermal treatment.

Therefore, the objectives of the present study were to (1) compare the changes of free and bound phenolic and flavonoid contents and their antioxidant activities in different milled fractions of brown rice due to extrusion; and (2) analyze the effects of extrusion on the composition and contents of individual phenolic compounds in free and bound form in milled fractions of brown rice.

2. Materials and methods

2.1. Chemicals and reagents

Trolox, trifluoroacetic acid (TFA), HPLC grade acetonitrile, 20,70-dichlorofluorescin diacetate (DCFH-DA), 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ), fluorescein disodium salt, gallic, chlorogenic, vanillic, caffeic, syringic, *p*-coumaric, and ferulic acids, and catechin hydrate were from Sigma Chemical Co. (St. Louis, MO, USA). $AlCl_3 \cdot 6H_2O$ of analytical grade were purchased from Fisher Scientific (Fair Lawn, NJ, USA). 2,20-Azobis (2-amidinopropane) dihydrochloride (ABAP) was purchased from Wako Chemicals USA Inc. (Richmond, VA, USA). Methanol, n-hexanes, ethyl acetate, HCl, acetic acid, Na_2CO_3 and NaOH were all analytical grade.

2.2. Grain samples and sample preparation

Indica brown rice was provided by the Rice Research Institute of Guangdong Academy of Agricultural Sciences. The brown rice was polished using a rice milling machine (Satake Co. Hiroshima, Japan) to obtain approximately 10% (w/w) rice bran and approximately 90% (w/w) polished rice. The bran, polished rice and brown rice samples were ground to powder completely through a 60-mesh sieve using a Cyclone Sample Mill (UDYCorporation, Fort Collins, CO, USA) and then stored at −20 °C until use.

2.3. Extrusion

A Werner and Pfleiderer Continua 37 co-rotating twin-screw extruder (Stuttgart, Germany) was used. The screw diameter, (L/D) ratio and die diameter were 37 mm, 27/1 and 6 mm, respectively. The extrusion process was performed under the same condition as that in our previous research (Ti et al., 2015). Extruded samples were milled to flour using a grinder (Sujata, India) to pass completely through a 60-mesh sieve. Ground extruded rice samples were kept at −20 °C until further analysis.

2.4. Extraction of free phenolics

Free phenolics in the raw and extruded powders were extracted using the method described previously (Liu et al., 2015). A total of 0.5 g of rice bran or 2 g of polished/brown rice were blended with 50 mL of chilled 80% (v/v) acetone. The mixture was homogenized using a T25 digital Ultra-Turrax homogeniser (IKA, Germany) at 10,000 rpm for 5 min in an ice bath and the homogenate was centrifuged at 2500 g for 10 min at 4 °C. The precipitate was then extracted again under the same conditions. The supernatants were pooled and concentrated under vacuum at 45 °C. The residue was reconstituted with methanol to 10 mL and stored at −80 °C until analysis.

2.5. Extraction of bound phenolics

The bound phenolics in different milled fractions of brown rice and their extrudates were extracted according to the methods of Sun, Chu, Wu, and Liu (2002). The residue after the free phenolic extraction was then hydrolyzed with 40 mL of 2 M NaOH for 1 h at room temperature with continuous shaking under nitrogen gas. After being neutralized to pH 2 with concentrated HCl, the mixture was extracted with hexane to remove lipids. The final solution was then extracted 5 times with ethyl acetate. Pooled ethyl acetate was evaporated at 45°C to dryness. Residue was reconstituted with distilled water to 10 mL and then stored at −80°C until analysis.

2.6. Determination of total phenolic content

The total phenolic content was determined using Folin-phenol reagent methods as described previously (Ti et al., 2015). The absorbance of reaction mixture was read at 760 nm using a Shimadzu UV-1800 spectrometer (Shimadzu Inc. Kyoto, Japan). Gallic acid was used as the standard, and the total phenolic content was expressed as milligrams of gallic acid equivalents (GAE) per 100 g of sample dry weight (DW).

2.7. Determination of total flavonoid content

The total flavonoids content of all the rice sample extracts were determined using a modified colorimetric method described earlier (Zhang et al., 2013). Diluted extract (250 μL) was mixed with 1.25 mL of distilled water in test tubes. A 75 μL of 5% $NaNO_2$ aqueous solution was subsequently added into the above mixture. After 6 min, 150 μL of 10% $AlCl_3 \cdot 6H_2O$ solution was added and allowed to stand for 5 min before 0.5 mL of 1 M NaOH solution was added in. The final volume was adjusted to 2.5 mL with distilled water and the absorbance was read immediately at 510 nm using a Shimadzu UV-1800 spectrometer. Catechin was used as the standard compound, and the total flavonoid contents were expressed as milligrams of (+)-catechin equivalents (CE) per 100 g DW.

2.8. HPLC analysis of individual phenolic acids

All the samples were analyzed by an Agilent 1200HPLC system (Waldbronn, Germany) (Liu et al., 2015). The mobile phase was 0.4% aqueous acetic acid (solution A) and acetonitrile (solution B). A gradient flow system of 0–40 min, 5–25% of solution B; 40–45 min, 25–35% of solution B; and 45–50 min, 35–50% of solution B was used with a flow rate of 1.0 mL/min. Samples were filtered with a 0.25 μm membrane filter (Millipore, Billerica, MA, USA) before injection. Injection volume was 20 μL and the column temperature was kept at 30 C. The 7 phenolic acids were detected at