Journal of Functional Foods 17 (2015) 214–226

Available online at www.sciencedirect.com

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

Improved bioaccessibility of phenolics and antioxidant activity of glutinous rice and its fermented Chinese rice wine by simultaneous extrusion and enzymatic hydrolysis

Enbo Xu [a,b], *Zhengzong Wu* [a,b], *Jie Long* [a,b], *Fang Wang* [a,b], *Xueming Xu* [a,b], *Zhengyu Jin* [a,b,*], *Aiquan Jiao* [a,b,**]

[a] *The State Key Lab of Food Science and Technology, School of Food Science and Technology, Jiangnan University, Wuxi 214122, China*

[b] *Synergetic Innovation Center of Food Safety and Nutrition, Jiangnan University, Wuxi 214122, China*

ARTICLE INFO

Article history:
Received 12 March 2015
Received in revised form 23 May 2015
Accepted 25 May 2015
Available online

Keywords:
Extrusion
Enzymatic hydrolysis
Phenolics
Antioxidant activity
Rice properties
Chinese rice wine

ABSTRACT

The effect of simultaneous extrusion and enzymatic hydrolysis on the phenolics and antioxidant activities of glutinous rice and further fermented Chinese rice wine was investigated. Great modification on rice properties (water absorption/solubility index) related to higher total phenolic content (TPC) retention (87.73%) was determined in enzymatically extruded rice compared to traditionally cooked or extruded rice (37.61–50.85% TPC retention). A total of ten phenolic acids (in free/bound forms) with great loss rates were identified in different treated rice, except the enzymatically extruded rice showing effective inhibition of phenolics loss (only 2.66, 2.04, 22.49, 1.89 and 6.37% loss for total gallic, chlorogenic, vanillic, syringic, and ferulic acids, respectively). After fermentation, the level of *p*-hydroxybenzoic and *p*-coumaric acids increased predominantly, while chlorogenic acid dramatically decreased to an extremely low level, indicating a changed chemical proportion of phenolics in Chinese rice wine. Compared with raw rice, enzymatically extruded rice achieved a higher antioxidant activity (DPPH, ABTS, reducing capacity and FRAP), probably due to the synergy of phenolic retention and Maillard-derived products formation. Moreover, this advantage of simultaneous extrusion and enzymatic hydrolysis could be further exhibited in Chinese rice wine products via fermentation processing.

1. Introduction

Rice (*Oryza sativa L.*) is consumed as a staple diet in many Asian countries, and could be used as the fermenting material of Chinese rice wine, especially the sort of glutinous rice for its abundant amylopectin, protein and bioactive compounds (Thammapat, Meeso, & Siriamornpun, 2015; Zhang, Shao, Bao, & Beta, 2015). Higher total phenolics, reducing capacity and hydroxyl radical scavenging activity have been detected in

* *Corresponding author.* State Key Laboratory of Food Science and Technology, School of Food Science and Technology, Jiangnan University 1800 Lihu Road, Wuxi, Jiangsu 214122, China. Tel.: +86 510 85913299; fax: +86 510 85913299.
E-mail address: jinlab2008@yahoo.com (Z. Jin).

** *Corresponding author.* State Key Laboratory of Food Science and Technology, School of Food Science and Technology, Jiangnan University 1800 Lihu Road, Wuxi, Jiangsu 214122, China. Tel.: +86 510 85320225; fax: +86 510 85320225.
E-mail address: jiaoaq@jiangnan.edu.cn (A. Jiao).

http://dx.doi.org/10.1016/j.jff.2015.05.032

glutinous rice compared to Thailand basmati rice, Shanghai Wuyu rice, long basmati rice and northeast China rice as previously reported (Rao, Yang, Gao, Song, & Weiming, 2014). Chinese rice wine, manufactured from these high-starchy cereals via “wheat Qu” and yeast, contains many bioactives identified as phenolics, amino acids and oligosaccharides (Que, Mao, & Pan, 2006). Que et al. (2006) also demonstrated that Chinese rice wine labelled as Nuomi (i.e., glutinous rice) had the highest content of phenolic compounds and antioxidant activity than other wines labelled as Guyuelongshan, Hongqu, Shousheng and Foshou.

Fermented products, like Chinese rice wine, have been associated with health-promoting effects for the abundant presence of phenolics (especially phenolic acids) liberated from raw material, with respect to the antioxidant activity for the prevention of deleterious processes including cancer, diabetes, ageing, atherosclerosis, cardiovascular diseases and neurological disorders (de Sá et al., 2014; Que et al., 2006; Wang, He, & Chen, 2014). However, the traditional pretreatment of this beverage appears to be adverse to the retention of phenolic acids, flavonoids, and other bioactives for the process of long-time soaking (5–10 days) and steam cooking (20–30 min) (Thammapat et al., 2015; Xu et al., 2015). Therefore, many novel pretreatments, such as the liquefaction technology and the extrusion, instead of steam cooking have been applied to make better utilisation and higher available nutritional value of raw material for Chinese rice wine fermentation (Xu, Jiao, Li, Wu, & Xu, 2013).

Extrusion, considered as a high-temperature-short-time processing involving mixing, heating, kneading and shaping process units, has been applied in Chinese rice wine production to achieve higher ethanol yield and fermentation efficiency with lower energy input (Chiu, Peng, Tsai, & Lui, 2012; Xu et al., 2015). Besides, Brennan, Brennan, Derbyshire, and Tiwari (2011) reported that extrusion could enhance the digestibility and bioavailability of phenolics compared to conventional cooking. However, some phenolic compounds may undergo decarboxylation or polymerisation at undesirable levels during extrusion, probably attributed to their sensitivity towards operating conditions such as temperature and moisture content. Many attempts had been made on the loss of phenolics and other antioxidants in raw materials during conventional extrusion (Chiu et al., 2012; Ozer, Herken, Guzel, Ainsworth, & Ibanoglu, 2006; Sharma, Gujral, & Singh, 2012), but with little information available on avoiding this disadvantage effectively.

In our previous studies, Chinese rice wine fermented from enzymatically extruded rice had milder operating conditions for starch gelatinisation, protein denaturation and lipid medication compared to other traditionally cooked or extruded rice, achieving great modification on the physicochemical properties (Xu et al., 2015). This rheological change of enzymatic extrudate tends to avoid the inactivation of α-amylase itself (van der Veen, van Iersel, van der Goot, & Boom, 2004), which may be possible for indirectly attaining better liberation and retention rate of phenolics in the extrudate theoretically. Thus the study was aimed at: 1) evaluating the effect of simultaneous extrusion and enzymatic hydrolysis on the phenolics and antioxidant activities; 2) determining the changes of some individual phenolic acids in enzymatically extruded rice and its fermented wine; and 3) investigating if there is a relationship between some modified physicochemical properties and antioxidant capacities.

2. Materials and methods

2.1. Materials and chemicals

Glutinous rice (TYPE: 535 nuo) was obtained from CPFCO Co., Ltd. (Wuxi, China), milled through a 0.6 mm sieve and stored at 4 °C for further analysis. The proximate composition of glutinous rice was starch 88.29 ± 0.41% (dry basis, db), protein 8.73 ± 0.27% (db) and lipid 0.92 ± 0.13% (db).

The thermostable α-amylase (Termamyl 120 L with an optimum pH of 6–8, a density of 1.2 g/ml, and an activity of 120 KNU/g, 1KNU = Kilo Novo α-amylase Unit defined as the amount of enzyme which hydrolyses 5.26 g of starch per h) from *Bacillus licheniformis* was presented by Novozyme (Beijing, China), which was used in the enzymatic extrusion for rice. Yeast was purchased from Angel Yeast Co., Ltd. (Shanghai, China). Wheat Qu was acquired from Nverhong Shaoxing Wine Co., Ltd. (Zhejiang, China). Gallic acid, *p*-hydroxybenzoic acid, chlorogenic acid, vanillic acid, caffeic acid, syringic acid, 3,4-dihydroxybenzoic acid, *p*-coumaric acid, sinapic acid and ferulic acid were purchased from Aladdin Industrial Inc. (Shanghai, China). 1,1-Diphenyl-2-picrylhydrazyl (DPPH), 2,2-azino-bis-(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), 2,4,6-tripyridyl-S-triazine (TPTZ), and 2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were purchased from Sigma-Aldrich (Shanghai, China). The Folin–Ciocalteu reagent, sodium acetate and sodium carbonate were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol and ethanol obtained from Aladdin Industrial Inc. were of HPLC grade. All other chemicals and reagents were of analytical grade.

2.2. Sample treatments

Four treatments were conducted in this study, and the details of rice pretreatment were illustrated: the traditional steam (TS) cooking was designed as control group, according to the traditional method for industrial Chinese rice wine brewing. The head rice for TS was soaked with abundant water (15 °C, 60 h) and cooked with superheated steam for 30 min. Then the traditional extrusion *No.1* (TE1) with severe operating conditions was designed as another reference, which had been studied as a novel pretreatment of Chinese rice wine over recent decades. Besides, the traditional extrusion *No.2* (TE2) with the same mild conditions of enzymatic extrusion (EE) was designed mainly to investigate if the α-amylase addition would indirectly influence the total phenolic content (TPC) retention of extrudate as well as its antioxidant activity during extrusion. For extruded samples, raw rice flour was mixed thoroughly with water (20, 36 and 36%, db) and thermostable α-amylase (0, 0 and 0.1%, db of starch), respectively, for TE1, TE2 and EE samples. Thereafter, mixture was sealed in plastic bags and stored for 12 h at 4 °C to equilibrate the enzyme and water prior to extrusion.

Three extrudates were prepared using a laboratory scale twin screw extruder (TYPE: TSE 24 MC, Thermo Scientific, Waltham,