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Investigating the influence of selected texture-improved pretreatment techniques on storage stability of wholegrain brown rice: Involvement of processing-induced mineral changes with lipid degradation

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ABSTRACT

This work aimed at investigating the effects of emerging texture-improved processing techniques including high hydrostatic pressure (HHP; 150–450 MPa/10 min), high-intensity ultrasonication (HIU; 17.83 $W\cdot cm^{-2}$/30 min) and germination (37 °C/36 h) pretreatments on lipid hydrolysis and oxidation development of wholegrain brown rice (WBR) during storage, in an attempt to ascertain a possible link between lipid degradation and the underlying mechanisms. The results showed that HHP and HIU treatments enhanced lipid hydrolysis and oxidation as indicated by the formation of free fatty acids (FFA) and thiobarbituric acid reactive substances (TBARS) respectively, whereas an opposite pattern was observed for germination. Storage process rather than after immediate treatments observed an increase in lipid oxidation of HHP and HIU-processed samples, which was related to processing-induced liberation of minerals. Quantitative and qualitative characterization via inductively coupled plasma-optical emission spectrometry (ICP-OES) and micro X-ray fluorescence (μ-XRF) analysis confirmed the shifts of mineral distribution in WBR grains in response to different pretreatments. The WBR-derived lipase was activated by Ca^{2+}, and μ-XRF mapping indicated calcium enrichment in pericarp/aleurone layer and its mobilization to embryo during germination process where magnesium and manganese were significantly reduced. Multivariate analysis revealed a close relationship between increased lipid degradation and minerals including magnesium and manganese. This is the first time for reporting the effects of selected texture-improved techniques on lipid stability of WBR grains across storage process as well as validating the involvement of processing-induced mineral release in lipid degradation.

1. Introduction

Consistent evidences from experimental and epidemiological studies have indicated a close link between wholegrain brown rice (WBR) products intake and a reduction of chronic diseases, such as diabetes, hyperlipidemia, hypertension, and cancer (Heiniö et al., 2016; Wu, Yang, Touré, Jin, & Xu, 2013). However, sensory characteristics of WBR play an extremely important role in determining consumer acceptance, and related quality attributes still limit its widespread consumption. To promote WBR acceptability, the enhancement of sensory characteristics has been achieved by several newly-employed processing techniques in recent years, including high hydrostatic pressure (HHP) (Boluda-Aguilar, Taboada-Rodríguez, López-Gómez, Marín-Iniesta, & Barbosa-Cánovas, 2013; Yu, Ge, Zhu, Zhan, & Zhang, 2015), germination (Han, Arijaje, Jinn, Mauromoustakos, & Wang, 2016), and ultrasonication (Cui, Pan, Yue, Atungulu, & Berrios, 2010; Park & Han, 2016), which mainly highlighted the improvement of palatability and cooking properties after treatments. Particularly, our recent results suggested potential application of high-intensity ultrasonication (HIU) in obtaining a softer texture and shortened cooking time as well as improving antioxidants utilization (Tao, Xia, & Li, 2017). In addition, it has been further proved by our another latest work that both germination and HHP treatments significantly enhanced the bioaccessibility of micronutrients occurring in WBR, especially antioxidants, gama-aminobutyric acid and minerals (Xia, Wang, Xu, Mei, & Li, 2017). However, better quality control of WBR grains with these emerging techniques requires a complete evaluation of the processing effects during entire process, extending from immediate effects after treatments to storage process. So far, there is no information reported concerning the effects of the above-mentioned processing methods on storage characteristics of WBR grains to our best knowledge.

WBR grains possess only a small proportion of lipid which ranges

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from 1 to 4%, depending on the rice varieties and degree of milling (DOM) (Ha et al., 2006; Zhou, Blanchard, Helliwell, & Robards, 2003). Nevertheless, this fraction plays an extremely important role in determining final flavor formation and storage attributes of WBR products because of lipid hydrolysis and oxidative deterioration. During storage, the decomposition of lipid in WBR grains into free fatty acids (FFA) is readily catalyzed by endogenous lipase, leading to the perception of soapy taste, reduced pH and increased acidity and in turn a shortened shelf life of WBR products. Further, FFA formed by the lipase-induced hydrolysis are more susceptible to oxidation than bound lipid (Pingret, Fabiano-Tixier, & Chemat, 2013), resulting in that lipid hydrolysis and oxidation are largely influenced by lipase. Hence, several latest efforts have deactivated lipolytic activities of lipase and achieved a significant reduction in the rate of FFA formation during storage, such as the application of microwave irradiation (Zhong et al., 2013), pulsed electric field (Qian, Gu, Jiang, & Chen, 2014), gamma irradiation (Chen, Jiang, et al., 2015), infrared radiation (Ding et al., 2015) and low-pressure plasma (Chen, Hung, Lin, & Liou, 2015). These investigations have verified that the processing-derived changes in lipase activity depend on the type of processing techniques, operational conditions and the susceptibility of lipase from different sources. In terms of HHP and ultrasonication, the two methods show the capabilities to enhance or inhibit enzymatic activities dependent upon numerous extrinsic and intrinsic factors (Knorr, Heinz, & Buckow, 2006; O'Donnell, Tiwari, Bourke, & Cullen, 2010), while germination as biological process involves in the transformation of enzyme molecules. However, surprisingly little literature has reported the effects of these texture-improved techniques on lipid hydrolysis and oxidation as well as on the lipase activities.

It is well-recognized that lipid oxidation follows a chain reaction composed of initiation, propagation and termination processes during which the oxidation rate is affected by many factors such as the composition of fatty acids, enzymes, minerals and oxygen types (Pingret et al., 2013). Particularly, the metals with two valence states, including iron (Fe), copper (Cu) and manganese (Mn) as well as magnesium (Mg), can serve as active catalyst by decreasing activation energy of the initiation step through one-electron transfers (Schaich & Pryor, 1980). Processing technique may mediate lipid oxidation by influencing the interaction between metals and ions-containing molecules and thus leading to mineral release. Correspondingly, it has been inferred that the release of transition metal ions from complexes could be the major mechanism underlying the enhanced lipid oxidation in HHP-treated meats, as evidenced by the significant decrease in oxidation after chelation of free minerals using different chelators including ethylenediamine tetraacetic acid (EDTA), EDTA-disodium salt (Na_2EDTA) and citric acids (Beltran, Pla, Yuste, & Mor-Mur, 2004; Cheah & Ledward, 1997; Ma, Ledward, Zamri, Frazier, & Zhou, 2007). However, the qualitative and quantitative changes in mineral distribution induced by HHP treatment, together with HIU and germination treatments, as well as their potential correlation with lipid degradation within the prolonged storage process, have not been investigated.

Therefore, the purpose of this study was to examine lipid hydrolysis and oxidation development of WBR grains treated by HHP, HIU and germination, which was performed using an accelerated storage testing. Additionally, the effects of selected texture-improved pretreatment on spatial distribution and variation in contents of mineral elements of interest were characterized, to reveal a possible link between processing-induced mineral shifts and lipid degradation.

2. Materials and methods

2.1. Samples, reagents and standards

Rice grains used in this investigation were Sanqiuding QTXD (SQD; *Oryza sativa* subsp. *japonica*), which were dehulled by industry and widely consumed in China (Xia, Mei, Yu, & Li, 2017). The samples were sealed in polythene bags and stored at − 20 °C after it was obtained in a local supermarket.

Standard solutions of sodium hydroxide (0.5 M), isooctane and methyl heptadecanoate were purchased from Aladdin Chemistry Co., Ltd. A standard stock solution of methyl heptadecanoate (500 mg/L) was prepared by dissolving 500 mg of the compound in isooctane (100 mL), and 10-fold dilution was made prior to use. Ethanol, sodium methoxide, and the salts to be used in enzyme activity determination including copper sulphate ($CuSO_4·5H_2O$), ferrous sulphate ($FeSO_4·7H_2O$), magnesium sulphate ($MgSO_4$), calcium sulphate ($CaSO_4$) and manganese sulphate ($MnSO_4$) were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals used were analytical or chromatographic grade.

2.2. Sample treatments and experimental design

The procedures of HHP processing were performed based on our previously published literature (Xia, Mei, et al., 2017). WBR grains (200 g) together with 100 mL ultrapure water (18.25 MΩ) were packed in a high-density polyethylene bag, which were pressurized in a hydrostatic pressurization unit (HHP-750; BaoTou KeFa Co., Ltd., China) under the pressures of 150, 350 and 450 MPa for 10 min at ambient temperature (20 ± 1 °C). These samples were marked as HHP1, HHP2 and HHP3, respectively.

To obtain pre-germinated WBR grains (GER), germination process was carried out in a climatic cabinet (RGX-260B, Hualian Med., China), as described previously (Xia, Mei, et al., 2017). After sterilization by sodium hypochlorite (0.2%), the grains (300 g) were immersed in water (1000 mL) at darkness and followed by the incubation at 37 °C for 36 h, obtaining grains with an approximate germinal length of 1.0 mm. During the process, deionized water used for germination was changed every 4 h.

WBR samples were subjected to ultrasonic irradiation from an ultrasonication generator (THC-2B, Tianhua Co., Jining, China) with a fixed frequency (28 kHz), of which the highest ultrasonic power is 400 W and its intensity is 17.83 $W·cm^{-2}$ (Zhang, Yang, & Zhao, 2015). WBR samples were mixed with ultrapure water (1/3, w/v) and then sonicated at ultrasonic intensity of 100% power for 30 min. After the sonication was finished, the water was drained and the grains were collected for further use.

After different treatments were finished, all samples were immediately dried in a hot air oven (YHG-9030A, Shanghai Yaoshi Instrument Co., Ltd., China) at 45 °C for 4 h, to obtain proximate moisture contents of 12%. Subsequently, the dried grains were stored in an incubator at 30 °C to accelerate the detection of processing effects. Storage process continued for 20 days, during which samples were withdrawn on certain days for physicochemical analysis. For the purpose of comparison, grains without processing treatments were soaked in ultrapure water at room temperature for 30 min, and then dried using same procedures as the treated samples.

2.3. Determination of total contents of FFA

FFA was determined according to the method describe by Zhong et al. (2013) with little modification. Prior to the mixture of ethanol (20 mL, 95%) and grains (1 g), the samples were ground with a disintegrator (GX-02, Gaoxiang, China) and passed through an 80-mesh screen. Then, the mixture was vortexed for 15 s and shaking for 30 min, and then filtered by Whatman filter paper. The filtrate was titrated with sodium hydroxide (0.01 M, Aladdin, China) until the color of the solution was changed to light pink, using phenolphthalein as the indicator. The volume of sodium hydroxide (V_m) consumed was recorded. Results were expressed as meq mg FFA per 100 g sample, using oleic acid as equivalent. FFA values were calculated by Eq. (1):

$$y = (V_m - V_0) \times 282 \times N \times 100/W \quad (1)$$