

Effects of hot-air fluidized-bed drying on cooking quality, antioxidant activity and bioactive compounds in germinated brown rice

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ABSTRACT

Germinated brown rice (GBR) is a nutrition-added product that gains much interest from consumers in Thailand. Drying GBR helps prolonging product shelf-life for the commercial production. However, it could bring about loss in some quality aspects. Therefore, this work investigated the effects of drying on physical quality, cooking quality, antioxidant activity and bioactive compounds of germinated paddy using fluidized-bed dryer. The germinated paddy rice (*Phitsanulok 2* variety) with the initial moisture content of 48.5% (dry basis) was dried using a fluidized-bed dryer at the temperature of 110-150°C to obtain the moisture content of 19-21%. Experimental results showed that the head rice yield and the cooking time increased but the solid loss and the volume expansion decreased with increasing drying temperatures. The water uptake and the volume expansion were drying temperature independence. The amylose-lipid complex in GBR, determined by X-ray diffractometry, was discovered when drying in the hot-air temperature of 110°C and 130°C but not the temperature of 150°C. The total phenolic content, the ferric reducing antioxidant power and the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity of GBR were close to those of the reference GBR. Moreover, the drying temperature did not influence the γ -aminobutyric acid and the gamma-oryzanol content of the GBR. The study indicated the advantage of hot-air fluidized-bed drying in preserving antioxidative capacities and nutritional values of GBR.

Keywords: drying; GABA; germinated paddy; x-ray diffraction

1. INTRODUCTION

Staple food in many Asian countries is rice. It is normally crumbled and polished into white rice for preparing food, though unpolished rice contains many nutritional and bioactive compounds. Nevertheless, germinated brown rice (GBR), a full source of many bioactive compounds along with dietary fiber, antioxidants, and other health beneficial compounds, especially the γ -aminobutyric acid (GABA) (Patil and Khan, 2011), also attracted much attention from Thai

consumers. The GABA has many physiological functions, for example, neurotransmissions and hypotension inductive effects, tranquilizing effects and diuretic effects (Jakobs et al., 1993). It was also reported that GBR extracts containing GABA restrained cancer cell propagations (Oh and Oh, 2004). Furthermore, brown rice is also an ordinary source of γ -oryzanol, which is a fusion of at least 10 lipophilic phytosteryl ferrulates that also exhibits several bioactivities (Lerma-Garcia et al., 2009).

The traditional process of GBR production consists of soaking and drying brown rice. The current conventional hot-air drying method resulted in cracks or fissures in the kernels and therefore lowering the head rice yield (Srisang et al., 2011). To increase head rice yield, it has to use the high suitable drying techniques and situations. Though there are a large amount of dryers that could be used to dry paddy, the fluidization perhaps is the most suitable one because it can grant fine mixing and high mass transferring rates (Soponronnarit and Prachayawarakorn, 1994; Jaiboon et al., 2009). Also, microorganisms on the paddy could be reduced to the safe level (Srisang et al., 2011). The drying medium utilized for carrying the evaporated water and fluidizing particles could be hot-air (Taechapiroj et al., 2006). Taechapiroj et al. (2003) examined the possibility of paddy drying using fluidized-bed. They discovered that the head rice yield depended on the final moisture content. The reduction of head rice yield influenced rice quality which decreased because of the broken rice, therefore bringing about the low commercial value and quality.

Limited number of literature on drying the GBR with a fluidized-bed technique were found. Therefore, the purpose of this research was to produce the GBR from germinated paddy by using hot-air fluidized-bed drying technique. The paddy of *Phitsanulok 2* was chosen for studying because it is not a major rice cultivar in Thailand and low in price. Therefore, processing this rice into GBR will help to add its commercial value. The GBR quality was determined in terms of physical properties, cooking qualities, antioxidant activities and bioactive compounds.

2. MATERIALS AND METHODS

2.1 Materials

The paddy (*Phitsanulok 2*) was harvested in September, 2017 from the Rice Research Institute, Phitsanulok province, Thailand. The paddy rice was cleaned, dried and stored in plastic bags at 4°C, for three

months before the germination study 2,4,6-tripiridyl-s-triazine (TBTZ), 2,2-Diphenyl-1-picrylhydrazyl (DPPH), Folin-Ciocalteu's reagent, 2-hydroxy-naphthaldehyde (HN) and γ -aminobutyric acid were procured from Sigma-Aldrich (MO, USA). γ -oryzanol (97.0% purity) was obtained from Wako Pure Chemical (Osaka, Japan).

2.2 Sample preparation

The paddy was steeped in water at the temperature of 30°C for 50 h by changing water every 6 h to obtain germinated paddy with the small bud size of 0.5-1.5 mm at rice germ. Primary moisture content of the germinated paddy was defined by an oven drying at 103°C for 72 h which was 48% dry basis (db.) (AACC, 1995). A batch of 1.4 kg germinated brown rice was dried in a laboratory-made fluidized-bed dryer (Figure 1).

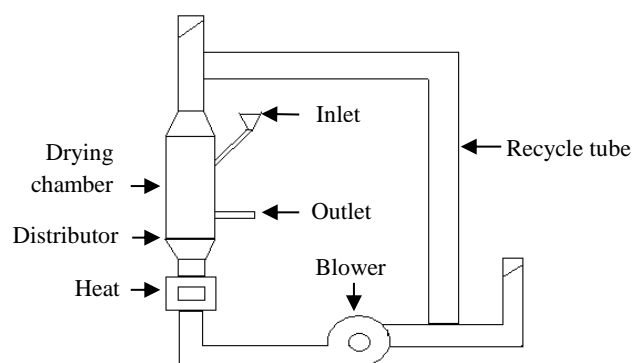


Figure 1 Schematic representation of a fluidized-bed dryer.

The dryer composed of a cylindrical shaped chamber, a backward curve blade centrifugal fan driven by a 1.5 kW motor and a 9 kW electrical heater. A drying temperature was managed by a PID controller with an accuracy of $\pm 1^\circ\text{C}$. The drying was carried out at 110, 130 and 150°C using a superficial air velocity of 2.5 m/s. Samples were taken from a fluidized-bed dryer every 2 min for 10 min. The desired moisture content of the paddy after fluidized-bed drying was 19-21% db. After fluidized-bed drying, the GBR was

ventilated with ambient air until its final moisture content was in a range of 14-16% db. Finally, samples were kept in the seal plastic bags at 4-6°C for 14 d before quality evaluation. Reference GBR was prepared by the ambient air drying of germinated paddy (shade drying) for 24 h. All preparation and analysis of samples were performed in triplicate.

2.3 Determination of head rice yield

The head rice yield was calculated from the mass of GBR remaining as head rice after milling divided by the mass of paddy specimen. The head rice yield of GBR was then calculated by:

$$\begin{aligned} \text{Head rice yield (\%)} \\ = (\text{Head brown rice mass/paddy mass}) \times 100 \quad (1) \end{aligned}$$

2.4 Determination of fissured kernel

The GBR samples containing 200 grains were examined visually by placing over a light bulb and examine the kernel that appeared fracture.

2.5 Determination of rice starch crystallinity

The degree of crystallinity and the type of crystalline structure of GBR were determined by using X-ray diffractometry (XRD). Measurements were carried out in the transmission mode using discovery diffractometry (MiniFlexII, Rigaku, Japan) under the subsequent conditions of 30 kV and 15 mA with Cu-anode source (Cu K α -radiation of wavelength $\lambda=1.54$ Å). The diffraction of X-ray was found out at every 0.01° of diffraction angle and the range of diffraction angle began from 3° to 40°. The degree of crystallinity of samples can be calculated by dividing crystalline area (A_c) with total area (crystalline area (A_c)+ amorphous area (A_a)), using Topas3 program (Coelho Software, Brisbane, Australia) as the following was calculation:

$$X_c = \frac{A_c}{A_c + A_a} \times 100\% \quad (2)$$

2.6 Determination of cooking quality

The GBR (2 g) was soaked in 20 mL of distilled water and cooked in hot water ($98 \pm 1^\circ\text{C}$) until reaching the cooking time (25-32 min for each sample) and the water uptake, the solid loss and the volume expansion were evaluated according to Soponronnarit et al. (2008) as the following was calculation:

$$\text{Water uptake (\%)} = \frac{W_c - W_{uc}}{W_{uc}} \times 100 \quad (3)$$

where W_{uc} and W_c are the weight of 20 uncooked and cooked kernels, respectively.

$$\begin{aligned} \text{Solids loss (\%)} = \\ \frac{\text{Increase weight of Erlenmeyer flask}}{\text{Weight of rice sample}} \times 100 \quad (4) \end{aligned}$$

$$\text{Volume expansion} = \frac{V_c - V_{uc}}{V_{uc}} \times 100 \quad (5)$$

where V_{uc} and V_c are the height uncooked and height cooked kernels, respectively.

2.7 Determination of total phenolic content and antioxidant activity

The extraction was carried out in accordance with Tian et al. (2005). Briefly, 2 g of GBR powder was mixed with 25 mL of 70% (v/v) ethanol in an Erlenmeyer flask, stirred for 20 min, centrifuged at $4,000 \times g$ for 10 min before the liquid was gathered. The dregs was re-extracted under the identical condition, and the liquid from two extractions were consolidated. The mixture of supernatants was filtered through Whatman No.5 filter paper. The solvent was consequently displaced under vacuum at 40°C.

The Folin-ciocalteu was utilized to determine the total phenolic content (TPC) (Skerget et al., 2005). The ferric reducing antioxidant power (FRAP) assay was accomplished in accordance with the way expressed by Benzie and Strain, (1996). The DPPH' radical scavenging ability of each separate was assessed in accordance with the scheme of Maisuthisakul et al. (2007).

2.8 Determination of GABA content

The GABA extraction was functioned according to Komatsuzaki et al. (2007). The GBR powder was extracted in the same manner as mentioned in 2.7. The content of GABA was determined by using HPLC method described by Khuhawar and Rajper, (2003). The HPLC system (Shimadzu, Kyoto, Japan) consisted of LC-20AD pump and SPD-20A DAD detector. The chromatographic separation was achieved on Inertsil ODS-3 column (4.6 mm × 250 mm, 5 μm, GL Sciences, Japan). The mobile phase was a mixture of methanol: water (40:60 v/v) with 0.1% v/v trifluoroacetic acid at a flow rate of 1.5 mL/min and the GABA was monitored at 330 nm. The calibration curve was built with the external standard.

2.9 Determination of gamma-oryzanol content

The gamma-oryzanol extraction was functioned in accordance with Pascual et al. (2013). The GBR powder (2 g) was extracted with 20 mL of acetone, vortex mixed for 2 min and then centrifuged at 4500 × g for 10 min before the liquid was collected. The dregs was re-extracted with 10 mL of acetone under the identical conditions. Collected liquid fractions were concentrated under vacuum at 45°C, then re-dissolved in 5 mL of acetone. The extracts filtered through a 0.45-μm membrane filter.

The gamma-oryzanol content was determined by the same HPLC system mentioned above in accordance with the way expressed by Khuwjitjaru et al. (2009). The mobile phase was a blend of methanol: acetonitrile: acetic acid (25:72:3 v/v) with the flow rate of 1.8 mL/min and the gamma-oryzanol was monitored at 330 nm. The gamma-oryzanol standard was separated into four peaks between 15 to 25 min. Determination of total gamma-oryzanol was based on the total of those four highest areas.

2.10 Statistical analysis

One-way analysis of variance (One-way ANOVA) with Bonferroni correction test was utilized to evaluate

the difference between means. The data values were revealed as mean ± standard deviation ($n = 3$).

3. RESULTS AND DISCUSSION

3.1 Drying characteristics

Figure 2 presents the drying characteristics of paddy undergoing fluidization at various temperatures. As anticipated, the higher drying temperature made the moisture extraction rate improved. The drying rate extended with increased drying temperature. An increase in drying rate was owing to the dissimilarity between the grain temperature and the drying temperature, which was associated with heat transfer rate and water evaporation. The well-known Page model was used to explain the drying kinetics data, written as:

$$MR = \frac{M_t - M_{eq}}{M_0 - M_{eq}} = \exp(-kt^n) \quad (6)$$

The moisture ratio (MR) was used in this fitting model where M_0 is the primary moisture content, M_{eq} is the equilibrium moisture content, which could be assumed to be closed to zero at the high temperature above 100°C, M_t is the moisture content at time t , k and n are the constant of model shown in Table 1. The model parameters were estimated of nonlinear regression using Microsoft Excel solver. As seen in Figure 2, the Page model could well explain the drying characteristics of the germinated paddy in fluidized-bed dryer. The required drying time, determined at the paddy moisture content of 21% db. using the fitted model (Tirawanichakul et al., 2014), was 10.3, 8.3 and 6.9 min for 110, 130 and 150°C, respectively.

3.2 Head rice yield

The effect of moisture content and drying temperature after fluidization on head rice yield is presented in Figure 3. When the drying temperature increased, the head rice yield increased accordingly and higher than that of the reference GBR (53.5%), owing

to the gelatinized starch (Poomsa-ad et al., 2002). The swelling of starch granules caused them closer and fastened the creation of a strong internal structure of molecules. However, considering the drying temperature, moisture inside the kernel below 21% db. resulted in a lower head rice yield because of the moisture difference

between surface and core of paddy, resulting in internal stress of the paddy leading to cracking, fissuring and lowering head rice yield. From this result, we chose samples with the highest head rice yield for each drying temperature for further analyses.

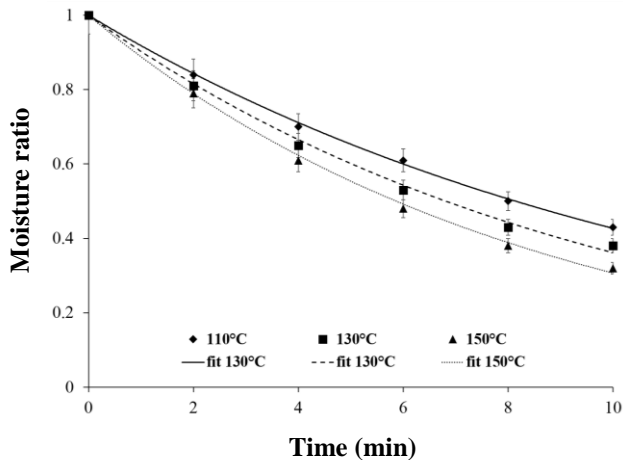


Figure 2 Drying curves of GBR dried by fluidization. Lines were drawn from the fitted model using Eq. (2).

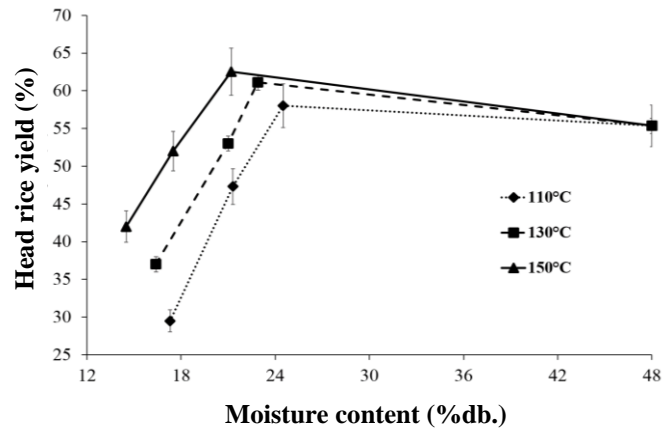


Figure 3 Effects of moisture content and drying temperature after fluidization on head rice yield (head rice yield of reference GBR = 52.86%).

Table 1 Parameters of Page model for predicting of drying characteristics

Treatment	Model constants	R ²	RMSE
110°C	$k = 0.1123, n = 0.8523$	0.9970	0.0133
130°C	$k = 0.1501, n = 0.8241$	0.9989	0.0056
150°C	$k = 0.1514, n = 0.8847$	0.9939	0.0168

R² = Coefficient of determination, RMSE = The root-mean-square error

3.3 Fissure of GBR

The fissured kernels of GBR affected by fluidization are presented in Table 2. After the germination, the fissured kernel of the reference GBR was significantly different from that of brown rice. To explain, the paddy soaking brought about high stress grain kernels which caused increased fissured grain kernels. (Yamaguchi et al., 1984; Srisang et al., 2011). The fissured percentage of kernels was decreased from

3.16 to 1.33-2.17%, which was significantly different from that of reference GBR. The low fissured grain kernels when compared to the reference GBR is owing to the consequence of gelatinization existing in the grain kernel. In gelatinization step, when the highly moist GBR was boiled up and the temperature of grain gets to 65 and 70°C, its starch cells will bulge with loss of crystalline (Atwell et al., 1998). This caused the denatured protein, which will then infiltrate into void

spaces in the amid of the starch granules, appearing in diminution of fissures within GBR grain. (Raghavendra Rao and Juliano, 1970), thus decreasing number of cracked kernels.

Table 2 Percentages of fissured kernels of *Phitsanulok 2* after processing

Treatment	Fissured grain (%)
Brown rice	2.33 ± 0.29 ^b
Reference GBR	3.16 ± 0.61 ^a
110°C	2.17 ± 0.14 ^b
130°C	1.67 ± 0.04 ^c
150°C	1.33 ± 0.29 ^d

Different superscripts mean that the values are significantly different ($p < 0.05$).

3.4 XRD pattern

The patterns of XRD in brown rice, reference GBR and GBR dried with fluidization are shown in Figure 4. All samples showed peaks at $2\theta = 15^\circ, 17^\circ, 18^\circ, 20^\circ$ and 23° . Table 3 shows the crystallinity of 19.54° and 19.08° for brown rice and reference GBR which were not significant, same as GBR dried with fluidization, which was not significant. On the other hand, the crystalline region could not be ascertained for the GBR dried at 150°C , which indicated that amylose-lipid complexes were destroyed. Prasad et al. (2012) found that the physical damage of native amylopectin lead to the degradation of the starch. This structure of V-type crystal indicated the complexes of amylose-lipid which are produced during the starch gelatinization (Hibi et al., 1990).

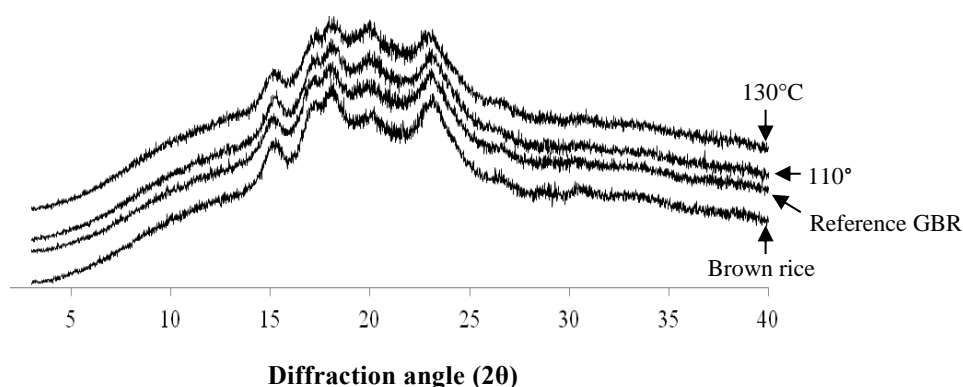


Figure 4 X-ray diffraction patterns of GBR dried by fluidized-bed dryer.

Table 3 Degree of crystallinity of GBR after processing

Treatment	Degree of crystallinity of	Degree of crystallinity of	Total degree of crystallinity (%) ^{ns}
	A type (%)	V type (%) ^{ns}	
Brown rice	19.54 ± 0.41 ^a	ND	19.54 ± 0.41
Reference GBR	14.68 ± 0.09 ^b	4.40 ± 0.04	19.08 ± 0.13
110°C	14.45 ± 0.06 ^b	4.59 ± 0.34	19.04 ± 0.40
130°C	14.46 ± 0.30 ^b	4.56 ± 0.08	19.02 ± 0.38
150°C	ND	ND	ND

Different superscripts in the same column mean that the values are significantly different ($p < 0.05$).

ND = not detected, ^{ns} = not significant

3.5 Cooking qualities: water uptake, solid loss and volume expansion

The cooking attributes in terms of cooking time, water uptake, solid loss and volume expansion are shown in Table 4. The results showed that the cooking time of fluidized-bed drying rice was significantly longer than that of reference GBR and brown rice. Considering the consequence of drying temperature, it was discovered that the cooking time increased with increasing drying temperature, due to a decrease in water absorption as a result of the loss of hexagonal starch structure (Pushpamma and Reddy, 1979).

The percentage of water uptake of brown rice was significantly different from that of GBR ($p < 0.05$). It could be due to amylose reduction during germination of brown rice (Wu et al., 2013), resulting in a decrease in water uptake (Juliano, 1985; Singhal et al., 1997). However, comparing amongst GBR samples, the water uptake was insignificantly changed with the drying

temperature as presented in Table 4. The gelatinization in rice might help to decrease cracks inside grain kernels. Thus, the water sucked in the kernels was limited (Swasdisevi et al., 2010). Considering the outcome of drying temperature, it was discovered that the water uptake expanded with the increased drying temperature. These were in accordance with decreasing solid loss of GBR as drying temperature increased. The ratio of volume expansion of GBR dried at various temperatures did not change with increased drying temperature. The volume expansion of fluidized-bed dried rice was certainly lower than that of reference GBR and brown rice. This could be described by the fact that the cell walls of GBR were more strengthened, due to starch gelatinization, and could preserve the hexagonal shape, providing higher water adsorption (Soponronnarit et al., 2008; Jaiboon et al., 2009; Jaiboon et al., 2011

Table 4 Cooking time, water uptake, solid loss and volume expansion of GBR after processing

Treatment	Cooking time (min)	Water uptake (%)	Solid loss (%)	Volume expansion (%) ^{ns}
Brown rice	25	207.17 ± 13.90 ^a	2.50 ± 0.10 ^a	440.00 ± 52.92
Reference GBR	25	175.17 ± 5.06 ^b	2.17 ± 0.18 ^b	446.67 ± 46.19
110°C	29	176.33 ± 4.04 ^b	2.00 ± 0.20 ^b	433.33 ± 11.55
130°C	30	177.83 ± 6.75 ^b	1.83 ± 0.29 ^{bc}	430.33 ± 11.55
150°C	32	181.83 ± 5.86 ^b	1.67 ± 0.29 ^c	426.67 ± 23.09

Different superscripts in the same column mean that the values are significantly different ($p < 0.05$).

^{ns} = not significant

3.6 Total phenolic content (TPC)

Among several phenolic compounds identified in brown rice or rice bran, gamma-oryzanol and ferric acid are the most (Zhou et al., 2004). The TPC of brown rice and GBR determined by Folin-ciocalteu method was in the range of 1.35-1.47 mg GAE/g extract (Table 5). These values were slightly higher than those reported by Butsat and Siriamornpun, (2010) for the

cultivar '*Khao Dawk Mali 105*' and by Moongnarm and Saetung, (2010) for the cultivar *RD-6*. which were in the range of 0.6-1.3 and 0.7-1.1 mg GAE/g dry weight, respectively. The results showed that germination and drying process did not influence the phenolic content of the GBR while Moongnarm and Saetung, (2010) indicated that the germination process increased the TPC value significantly.

3.7 DPPH[•] radical scavenging activity

The free-radical scavenging activity of the extracts of rice after processing was assessed using the DPPH assay (Table 5). The inhibition (%) of DPPH radical for brown rice, reference GBR and fluidized-bed dried GBR were varied from 79.11% to 81.23%. The results showed that germination and drying process did not affect the DPPH radical scavenging activity, which was in accordance with the TPC value. This can be explained by the fact that gamma-oryzanol and ferulic acids, which are the most plentiful phenolic compounds in bran also possess DPPH radical scavenging activity (Tian et al., 2004).

3.8 Ferric reducing antioxidant power (FRAP)

The antioxidant power of all extracts of rice expressed in FRAP value is shown in Table 5. The FRAP value of GBR was also not necessarily different from that of brown rice and reference GBR. The explanation was similar to the result of DPPH assay mentioned above. GBR had a high FRAP value of 26.86-26.92 $\mu\text{mol FeSO}_4/\text{g}$ dry weight. Butsat and Siriamornpun, (2010) reported that the FRAP value was the range of 6.3-12.4 $\mu\text{mol FeSO}_4/\text{g}$ in brown 'Khao Dawk Mali 105' rice.

Table 5 TPC, %inhibition DPPH[•] radical and FRAP value of GBR after processing

Treatment	TPC (mg GAE/g extract) ^{ns}	% inhibition DPPH [•] ^{ns}	FRAP ($\mu\text{mol FeSO}_4/\text{g}$ extract) ^{ns}
Brown rice	1.47 \pm 0.03	81.23 \pm 0.53	26.91 \pm 3.62
Reference GBR	1.36 \pm 0.12	79.42 \pm 3.66	26.90 \pm 3.61
110°C	1.35 \pm 0.02	80.68 \pm 1.73	26.86 \pm 1.72
130°C	1.36 \pm 0.01	80.90 \pm 1.98	26.92 \pm 3.91
150°C	1.36 \pm 0.02	79.11 \pm 0.78	26.99 \pm 3.79

Different superscripts in the same column mean that the values are significantly different ($p < 0.05$).

^{ns} = not significant

3.9 GABA content

GABA is a very special component found predominately in GBR. Table 6 shows the GABA content of brown rice and GBR after drying, using the HPLC analysis. The GABA content increased from 8.75 mg/100 g dry weight for the brown rice to 20.81 mg/100 g dry weight for the reference GBR. The increase of GABA content was due to the change of germ in grain during the germination process (Komatsuzaki et al., 2007). After drying, GABA content was not essentially influenced by drying temperature because drying was in a short time (drying temperature of 110, 130 and 150°C for drying time of 9 min, 8 min and 6 min, respectively). The stability data of GABA due to the thermal treatment

was scarcely reported, however Ito et al. (2006) reported that GABA in 3% NaCl solution remained almost 100% after heating at 100°C for 240 h. This outcome was in accordance with that informed by Srisang et al. (2011).

3.10 Gamma-oryzanol content

Gamma-Oryzanol usually presents at high amount in rice bran (Moure et al., 2001). The gamma-oryzanol content in each sample of rice is shown in Table 6. For all extracts of the GBR, the amount of gamma-oryzanol was in the range of 28.3 to 28.9 mg/100 g dry weight. The gamma-oryzanol content of GBR was not influenced by drying temperature, as reported by Khuwijitjaru et al. (2009) that gamma-oryzanol was quite stable in thermal treatment even at high temperature.

Table 6 The GABA and gamma-oryzanol contents of GBR after processing

Treatment	GABA (mg/100 g dry weight)	Gamma-oryzanol (mg/100 g dry weight) ^{ns}
Brown rice	8.8 ± 2.3 ^b	28.9 ± 0.3
Reference GBR	20.8 ± 2.0 ^a	28.3 ± 5.3
110°C	20.6 ± 4.4 ^a	28.4 ± 3.1
130°C	20.9 ± 2.9 ^a	28.5 ± 1.3
150°C	20.7 ± 4.1 ^a	28.8 ± 2.9

Different superscripts in the same column mean that the values are significantly different ($p < 0.05$).

^{ns} = not significant

4. CONCLUSION

From the study of hot-air fluidized-bed drying of to produce GBR, it was discovered that the drying of the germinated paddy at high temperature reached to an augmentation of the head rice yield. After processing, volume expansion and water uptake of GBR were not associated with the drying temperature while its solid loss decreased and cooking time increased. During drying, the amylase-lipid complexes, defined by XRD, was discovered in the hot-air temperature at 110, 130°C but was not found in the hot-air temperature of 150°C. The GABA content of GBR was higher than that of brown rice. It was not influenced by drying temperature. Antioxidant activity and gamma-oryzanol content of GBR remained unchanged as compared to those of brown rice. Thus, hot-air fluidized-bed drying was an efficient process for preparation of GBR with preserved antioxidative capacity and nutritional value.

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