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Original Research Article

Effects of milling on proximate composition, folic acid, fatty acids and technological properties of rice

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ABSTRACT

In an effort to meet consumer demands, the rice industries have intensified the milling process to produce whiter rice, using degrees of milling between 8% and 14%. However, this technique reduces the nutritional value of rice. This work is the first study to evaluate effects of milling on the folic acid content and fatty acid composition of rice. Moreover, the present work also evaluates the proximate composition, amylose content and technological properties of rice as a function of the degree of milling. The results showed a 72.23%, 41.60% and 65.23% decrease in the content of folic acid, ash and fat, respectively, even when only 8% degree of milling was used. The lightness of the rice increased as a function of the degree of milling. The fatty acid content decreased with the fat reduction while the fatty acid profile did not change with an increase in the degree of milling. The grain cooking time, hardness and adhesiveness, as well as the protein, fibre and amylose contents varied between brown and milled rice but did not differ among the rice samples milled to different degrees (8–14%).

1. Introduction

Rice is the staple food for more than half of the world's population, mainly in developing countries. More than 90% of rice is produced and consumed in South and Southeast Asia, and it is an important food crop for Africa, Latin America and the Middle East (Khush, 1997; Sellapan et al., 2009). As a result of its high consumption and because rice is an important source of vitamins, minerals, fibre and bioactive compounds, it represents an appropriate vehicle for nutrient delivery to these populations.

Several factors affect the nutritional value of rice, such as genotype, environmental conditions during growth, crop management, storage and post-harvest processes, especially the milling process. Rice is commonly milled by removing the hull and the bran layer of the rough rice kernel, or paddy, to produce white rice (Perdon et al., 2001). According to Sellapan et al. (2009), the milling of rice grains is an essential process carried out by all rice manufacturers and commercial farmers to remove the oil rich aleurone layer that would otherwise make the rice grain rancid during long storage periods. Moreover, the majority of consumers prefer well-milled white rice with little or no bran remaining on the endosperm (Mohapatra and Bal, 2007; Roy et al., 2008).

The proteins, fats, vitamins and minerals are concentrated in the germ and the outer layer of the starchy endosperm (Itani et al., 2002; Juliano and Bechtel, 1985); therefore, milling the rice may result in a reduction of these nutrients. Recent studies have shown a decrease in the selenium content (Liu et al., 2009), phytic acid content and Zn distribution (Liang et al., 2008) in rice as a function of the degree of milling.

Folic acid has been gaining more attention globally (Kam et al., 2012); the significant roles of this vitamin include its potential ability to prevent abnormalities in early embryonic brain development and malformations of the embryonic brain or spinal cord (neural tube defects) (Czeizel and Dudas, 1992) and its

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involvement in nucleic acid synthesis and protein metabolism (Choi and Manson, 2002). Low folate status is also associated with an elevation in plasma homocysteine levels, which is a risk factor for cardiovascular diseases (Wald et al., 2002).

The World Health Organization (WHO/FAO, 1998) recommends the highest folic acid intakes for pregnant women (600 $\mu g\ day^{-1}$), followed by lactating women (500 $\mu g\ day^{-1}$), adults and adolescents (400 $\mu g\ day^{-1}$), children between 7 and 9 years old (300 $\mu g\ day^{-1}$), children between 4 and 6 years old (200 $\mu g\ day^{-1}$), children between 1 and 3 years old (150 $\mu g\ day^{-1}$) and infants up to 12 months (80 $\mu g\ day^{-1}$).

Several studies have been conducted on the cooking, colour and sensory quality of rice grains subjected to different degrees of milling (Lamberts et al., 2007; Mohapatra and Bal, 2006, 2007; Roy et al., 2008; Tran et al., 2004; Yadav and Jindal, 2008); however, no studies have been performed to assess the presence of folic acid and fatty acids in rice as a function of the degree of milling. Therefore, the objective of this study was to evaluate the presence of folic acid and free fatty acids as well as the proximate composition and technological properties of rice milled to different degrees.

2. Materials and methods

2.1. Materials

One variety of rice (long grain with high amylose content, *Oryza sativa* L.) was cultivated under an irrigation system in Pelotas, State of Rio Grande do Sul, Brazil. The rice grains were harvested when the moisture content was approximately 20%, were transported to the *Laboratório de Pós-Colheita, Industrialização e Qualidade de Grãos* of the *Universidade Federal de Pelotas* and were submitted to the cleaning and the drying processes until a 13% moisture content was achieved. All chemicals used in this study were of analytical grade or better.

2.2. Sample preparation

The rice grains (100 g) were dehusked and polished using a Zaccaria rice machine (Type PAZ-1-DTA, Zaccaria, Brazil). Brown rice samples, after cleaning and grading, were polished until four different degrees of milling were achieved: 8, 10, 12 and 14%. The degree of milling was determined using the following equation: DOM = [1 − (weight of the milled rice/weight of the brown rice)] × 100. Samples that resulted in DOMs of 8, 10, 12 and 14% after the milling process were analysed.

Experiments were conducted in triplicate, and the average values were used for analysis. Broken grains were removed using the laboratory grader of the same Zaccaria rice machine (Type PAZ-1-DTA, Zaccaria, Brazil). The brown rice grains and the grains polished to the four different degrees of milling (8, 10, 12 and 14%) were ground to a 70 mesh size powder using a laboratory mill (Perten 3100, Perten Instruments, Sweden).

2.3. The proximate composition and amylose content

The moisture content of the samples was determined by weighing the grains before and after the drying process in an oven at 105 ± 3 °C with natural air circulation for 24 h. The fat content was determined in accordance with the AACC method 30-20 (AACC, 1995). The nitrogen content was determined using the AACC method 46-13 (AACC, 1995), and the protein content was obtained using a conversion factor of nitrogen to protein of 5.95. The ash content was determined by the method 08-01 of AACC (AACC, 1995). The fibre content was determined as described by Angelucci et al. (1987). The amylose content was determined according to the method described by Juliano (1971). These tests were carried out in triplicate, and the moisture content was expressed as a percentage (%).

2.4. Lightness

The colour parameter of lightness was measured with a Zaccaria milling meter (MBZ-1, Zaccaria, Brazil). The results were expressed using the scale provided by the meter (GBZ).

2.5. Folic acid

The folic acid quantification was performed according to the method described by Crepaldi (2006), with modifications. Approximately 1.0 g of rice flour was extracted with 3.0 mL KOH 0.1 mol l^{-1} and 3.0 mL of acetonitrile (LabSynth, Brazil) for 10 min in an ultrasonic bath. Afterwards, 500 μL of tricloroacetic acid (25 g l^{-1}) were added and the volume was brought to 10 mL with phosphate buffer solution at a pH of 6.5. Next, the extract was purified prior to analysis using high performance liquid chromatography (HPLC); the first purification step utilised common filter paper, and the second step was accomplished with a 0.45 μm syringe filter (FHLP 1300 PVDF, Millipore).

Analyses were performed using an HPLC system equipped with a single pump (model LC-10ATVP, Shimadzu, Japan), a solvent delivery module (FCV-10ALVP, Shimadzu, Japan), a degassing pump (DGU-14A, Shimadzu, Japan), a system controller (SCL-10ATVP, Shimadzu, Japan), a block heater oven (CTO-10ASVP, Shimadzu, Japan) and an auto sampler (SIL-10AF, Shimadzu, Japan). The HPLC separation of all compounds was performed on the chromatographic octadecyl column Shim-Pak CLC-ODS (3.9 cm × 150 mm × 4 μm). A UV/VIS detector was used for detection (UV/VIS SPD-10AXL, Shimadzu, Japan).

The folic acid quantification was based on an external standard using an analytical calibration curve constructed with 10 concentration levels (0.025, 0.050, 0.100, 0.150, 0.200, 0.300, 0.400, 0.500, 0.600 and 0.700 $\mu g\ mL^{-1}$), where each point was represented by the average of three values. The standard solutions of folic acid were dissolved in a phosphate buffer at a pH of 6.5 (Na_2HPO_4 0.25 mol l^{-1}/KH_2PO_4 0.37 mol l^{-1}) and filtered with a 0.45 μm syringe filter (FHLP 1300 PVDF, Millipore); 10 μL of the solution was injected into the HPLC analyser. The relationship between the folic acid concentration and the absorbance was used to calculate the linear calibration curve (R^2 = 0.9914) using the equation $y = 34.868x$, where "y" represents the peak area and "x" represents the concentration in $\mu g\ mL^{-1}$.

The gradient elution was performed at a flow rate of 0.8 mL min^{-1}, initially using a 95% aqueous mobile phase (prepared by mixing 20 mL acetic acid and 700 μL KOH 50% and then adjusting the volume to 1000 mL with Milli-Q water) and a 5% organic mobile phase consisting of acetonitrile. The mobile phase proportion was changed for up to 15 min until a ratio of 80% aqueous mobile phase to 20% organic mobile phase was achieved. The initial chromatographic conditions were gradually increased until 18 min, at which point the ratio was maintained for 30 min to rebalance the chromatographic column. The detection was accomplished at a 290 nm wavelength, and the data were analysed using Class-VP software.

2.6. Fatty acids

A gas chromatograph (GC-14B, Shimadzu, Kyoto, Japan) with a flame ionisation detector (FID) and a fused silica capillary column measuring 30 m × 0.25 mm × 0.25 μm DB-225 (50% cyanopropyl methyl and 50% methyl phenyl silicone, J&W Scientific, Folsom, CA, USA) was used. The injector and detector were both maintained at