Impact of Browning Reactions and Bran Pigments on Color of Parboiled Rice

ARTICLE *in* JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY · DECEMBER 2006

Impact Factor: 2.91 · DOI: 10.1021/jf062140j · Source: PubMed

Impact of Browning Reactions and Bran Pigments on Color of Parboiled Rice

LIEVE LAMBERTS,* KRISTOF BRIJS, RASTY MOHAMED, NEELKE VERHELST, AND JAN A. DELCOUR

Laboratory of Food Chemistry, Katholieke Universiteit Leuven, Kasteelpark Arenberg 20, B-3001 Leuven, Belgium

Rice color changes from white to amber during parboiling (soaking and steaming). Color parameters indicated that, during soaking, yellow bran pigments leached out in the water. The levels of the Maillard precursors (i.e., reducing sugars (RS) and free α-amino nitrogen (FAN)) depended on soaking temperature and time: leaching of RS was compensated by enzymic formation for long soaking times (>60 min), while proteolytic activity was too low to compensate for FAN leaching. Rice soaking under nitrogen, oxygen, or ambient conditions and determination of polyphenol oxidase activity allowed us to conclude that the effect of enzymic color changes on the soaked rice color was rather small. Color measurements of brown and milled mildly, intermediately, and severely parboiled rice samples showed that both brown and milled rice samples were darker and more red and yellow after parboiling and that the effect depended on the severity of parboiling conditions. Furthermore, steaming affected the rice color more and in a way opposite to that observed in soaking. The changes in RS and the loss of FAN during parboiling suggested that Maillard type reactions occur during brown rice steaming. Analyses of furosine levels confirmed Maillard browning of outer bran layers and endosperm during steaming. The level of this Maillard indicator increased with the severity of parboiling conditions in both brown and milled parboiled rice. Measurements of the levels of bran pigments indicated that bran pigments diffuse into the endosperm during parboiling and contribute to the parboiled rice color.

KEYWORDS: Rice; parboiling; color; Maillard reaction; furosine; pigment

INTRODUCTION

Parboiling is a hydrothermal treatment (soaking, heating, and drying) of paddy or brown rice that affects the final product quality. Cooked parboiled rice kernels are firmer and less sticky than their nonparboiled counterparts. The impact of parboiling on sensory properties is determined by the levels of its major components amylose and protein (*1*, *2*). Furthermore, parboiling changes the color of milled rice from white to amber. The degree of color change depends on time and temperature of soaking, heating, and drying (*3*−*6*). It has been hypothesized that the color changes during parboiling are caused by (i) diffusion of husk and bran pigments and (ii) nonenzymic browning of the Maillard type (*4*, *6*−*8*). Furthermore, it was recently suggested that (iii) enzymic color changes occur during brown rice soaking (*6*).

Pigments are not uniformly distributed in rice (*9*, *10*). Bran contains much higher levels of yellow and red pigment than endosperm. Therefore, migration of bran pigments in the soaking water and diffusion of bran pigments into the endosperm during soaking and/or heating may impact the brown and milled parboiled rice color.

Apart from bran pigments, Maillard reactions may contribute to parboiled rice color. Reducing sugars (RS) and free α-amino nitrogen (FAN) containing proteins and peptides are the precursors of Maillard products during brown rice heating. The decrease and/or increase of the levels of RS and FAN during parboiling support the hypothesis that Maillard reactions occur during the process (*6*, *8*). The effect of parboiling on the levels of Maillard precursors depends on the processing conditions used during soaking and heating.

Maillard reactions can be monitored by measuring the levels of some indicators in the processed samples. Some of these products (e.g., furosine [ϵ-*N*-(2-furoylmethyl)-L-lysine]) are related to early stages of the Maillard reaction. Furosine is formed during acid hydrolysis of the Amadori components fructosyl-lysine, lactulosyl-lysine, and maltulosyl-lysine. Furosine contents have been used to evaluate the extent of the Maillard reaction in milk products (*11*, *12*), cereals (*13*−*16*), pasta (*17*), and dairy products (*11*, *13*).

Finally, as was also hypothesized by Lamberts et al. (*6*), enzymic color changes may affect rice color. The impact of peroxidase and polyphenol oxidase activities on pasta color and on the discoloration of Chinese noodles has been described (*18*).

Color changes of parboiled rice have mostly been explained by Maillard browning and pigment diffusion. However, limited

research has been performed on the diffusion of bran pigments and enzymic activities and their effects on parboiled rice color. Furthermore, to the best of our knowledge, the hypothesis in the literature of Maillard browning during rice parboiling has not been supported by experimental data. Against this background, the present study was designed to increase insights in color changes during soaking and heating (by steaming) of brown rice. First, the color and the levels of RS and FAN of soaked and parboiled (soaked and steamed) rice samples were determined. Second, enzymic color changes during rice soaking were studied. Third, the furosine content of brown and milled parboiled samples was quantified to evaluate Maillard reactions during brown rice parboiling. Finally, the impact of bran pigments on the color of brown and milled parboiled rice was evaluated by measuring the pigment levels.

MATERIALS AND METHODS

Rice Soaking. Dehulled brown rice (*Oryza sativa* L.) from the long-grain variety Puntal (Spanish harvest 2003, 40.0 g) was soaked in excess water (200.0 mL) under different combinations of temperature (40 and 65 °C) and time (0−300 min). The soaking water was saturated with oxygen or nitrogen by bubbling these gases through the water at 40 °C. After saturation, brown and white rice samples were soaked for 30, 60, and 90 min. White rice was milled from brown rice (200.0 g) with a TM05C testing mill (Satake, Bredbury, UK). The degree of milling (DOM) (i.e. the weight percentage of rice outer layers removed by milling (*19*)) was 18%. The soaked rice kernels were freeze-dried and ground with a laboratory grinder to pass through a 250 μm sieve.

Rice Parboiling and Milling. Brown rice was soaked in excess water for 10 and 150 min at 68 and 65 °C, respectively. After draining, the soaked rice was steamed. To obtain mildly parboiled rice, the soaked (150 min, 65 °C) brown rice was steamed for 4 min at 110 °C. To obtain intermediately and severely parboiled rice samples, the soaked (10 min, 68 °C) brown rice was steamed for 9 min at 106 °C followed by 14 min at 115 °C or for 10 min at 106 °C followed by 15 min at 125 °C. The steamed rice samples were dried on trays for 48 h at room temperature. Brown rice samples were milled (50 s). DOM were ca. 14.2% (nonparboiled rice), 8.2% (mildly parboiled rice), 9.8% (intermediately parboiled rice), and 9.2% (severely parboiled rice). The brown and milled rice kernels were ground with a laboratory grinder to pass through a 250 μm sieve.

Chemicals. All chemicals used were of at least analytical grade and obtained from Sigma (Bornem, Belgium) unless indicated otherwise.

Moisture Content Determination. Moisture content (MC) determination of rice samples was according to the AACC method 44-15A (*20*) and was estimated from the mass loss of ca. 1.0 g of accurately weighed rice flour when heating for 90 min at 130 °C. Analyses were performed in duplicate. MC of soaked samples was calculated from the weight before and after soaking.

Leached Material After Rice Kernel Soaking. After soaking the rice kernels (cf. supra), the soaking water was freeze-dried, and the percentage of leached material was determined by weighing.

Color Measurements. The color of rice flour was measured using the CIE (Commission Internationale de l'Eclairage, 1976) L^*, a^*, and b^* color system, where L^* describes brightness, a^* is redness, and b^* is yellowness. In addition, the total color difference (ΔE) caused by parboiling was calculated

$$\Delta E = \sqrt{(L^*_{\text{sample}} - L^*_{\text{ref}})^2 + (a^*_{\text{sample}} - a^*_{\text{ref}})^2 + (b^*_{\text{sample}} - b^*_{\text{ref}})^2}$$

The flour of nonparboiled rice was used as a reference (called "ref"). Color measurements were performed in triplicate with a colorimeter (model Colorquest 45/0 LAV, CQ/ UNI-1600, HunterLab, Reston, VA) as described by Lamberts et al. (*6*).

Level of Reducing Sugars. The RS levels in rice flour were determined as described by Lamberts et al. (*6*) with glucose as a standard and expressed on dry matter basis. The level of leached RS was determined on the soaking water. Following centrifugation (30 min, 3000*g*), the supernatant (20 μL) was diluted with deionized water (980 μL), and the levels of RS were determined. Analyses were performed in triplicate. The coefficient of variation for the determination of RS was <7%.

Levels of Free α-Amino Nitrogen. Rice flour (300.0 mg) was extracted with sodium acetate buffer (5.0 mL, 200 mM, pH 5.0). Following centrifugation (10 min, 2000*g*), the level of FAN in the supernatant (20 μL) was determined by a trinitrobenzenesulfonic acid (TNBS) method with L-leucine as standard (*21*). The level of leached FAN was directly determined on soaking water (30 μL) after centrifugation (30 min, 3000*g*). Analyses were performed in triplicate. The coefficient of variation for the determination of FAN was <9%.

Polyphenol Oxidase Activity. The polyphenol oxidase (PPO) activity was determined based on the method of Park et al. (*22*). Brown rice flour (1.00 g) was defatted with hexane (6.0 mL). After shaking (10 min), the suspension was centrifuged (2500*g*, 10 min), and the supernatant was removed. This extraction was repeated, and the defatted pellet was dried with nitrogen. Sodium acetate buffer (5.0 mL, 50 mM, pH 5.0) was used to extract PPO from rice. After shaking at 4 °C (30 min), the suspension was centrifuged (3000*g*, 10 min). The supernatant (100 μL) containing PPO was added to a mixture of sodium phosphate buffer (2.6 mL, 50 mM, pH 6.5), L-dopamine (100 μL, 5 mM), l-ascorbic acid (100 μL, 2.1 mM), and ethylene diamine tetraacetic acid (100 μL, 0.065 mM) solutions and incubated for 30 min. Analyses were performed in triplicate, and the extinction of the mixture was measured at 265 nm (E_{265}) after incubation for 0, 10, 20, and 30 min. Sodium phosphate buffer (pH 6.5) was used as a control to correct for substrate autoxidation. Changes in extinction were measured, and from the linear decrease, the activity of each sample was calculated based on the following equation:

$$\text{units/g of sample} = \frac{\Delta E_{265}/\text{min sample} - \Delta E_{265}/\text{min control}}{0.001(\text{g of sample})}$$

One unit is defined as the change of 0.001 extinction (EU) per minute at E_{265} in a 3.0 mL reaction mixture containing L-dopamine and L-ascorbic acid at a given pH.

Level of Gelatinized Starch. Differential scanning calorimetry (DSC) analyses were performed in duplicate with a Q1000 DSC (TA Instruments, Newcastle, DE) as described by Lamberts et al. (*6*). Levels of gelatinized starch of parboiled rice were estimated from the enthalpies (ΔH) of starch gelatinization of the milled nonparboiled and parboiled rice flours.

Furosine Content. The level of furosine was measured according to Resmini et al. (*11*). Following hydrolysis of rice flour samples (300.0 mg) with 8.0 mL of HCl 8.0 M, suspensions were saturated with nitrogen (2 min) and heated (23 h, 110 °C). The filtrates (0.50 mL) were applied to a Maxi-Clean cartridge (C_{18}, 500 mg, Alltech, Belgium), prewetted with water (5.0 mL), and eluted with 3.0 mL of HCl 3.0 M. Duplicate sample hydrolysates were used. Furosine was quantified by RP-HPLC (Shimadzu, Kyoto, Japan) on a furosine-dedicated column (C_8, 250 mm × 4.6 mm, Metal-Free, Alltech, Belgium) according to Resmini et al. (*11*). The external furosine standard was obtained from Neosystem (Strasbourg, France). Analyses were performed in duplicate.

Level of Bran Pigments. Flour from brown and milled rice (0.20 and 0.50 g, respectively) was extracted with alkaline methanol [1:1 (v/v) 2% aqueous sodium carbonate/methanol] for 120 min by mechanical shaking (*23*). The level of bran pigments was determined from the extinction values at 420 nm. Analyses were performed in duplicate.

RESULTS AND DISCUSSION

Effect of Soaking Time and Temperature on Rice Color. **Table 1** shows the color parameters L^*, a^*, and b^* of the flour of brown rice soaked at different temperatures (40 and 65 °C) for different times (0−300 min). The nonsoaked rice flour was low in red pigments ($a^* = 0.9$), and soaking did not affect the redness. Soaking of brown rice kernels increased brightness (L^*)

Table 1. Moisture Content after Soaking, Amount of Leached Material, and Color Parameters *L** (Brightness), *a** (Redness), and *b** (Yellowness) of Brown Rice Soaked at Different Temperatures for Different Times

soaking temperature (°C)	soaking time (min)	moisture content after soaking (%)	leached material (%)	*L**	*a**	*b**
reference[a]		12		85.6	0.9	12.4
40	10	21	0.8	86.4	0.9	11.9
	30	25	1.0	86.9	0.9	11.6
	60	27	1.1	87.1	0.9	11.6
	120	29	1.5	87.7	0.8	10.8
	300	30	2.0	88.2	0.7	10.1
65	10	25	0.6	87.2	0.9	11.3
	30	29	1.5	87.9	0.8	10.6
	60	31	1.8	88.1	0.8	10.3
	120	31	2.2	88.4	0.8	9.9
	300	31	2.8	88.7	0.7	9.4

[a] Reference = nonsoaked rice.

and decreased yellowness (*b**). These color changes were also visually observable. The increase in brightness and decrease in yellowness as a function of soaking time were larger for flour of rice soaked at 65 °C than for that of rice soaked at 40 °C. The observed color changes can be explained by differences in the rate of water uptake and leaching of material at different soaking temperatures as shown in **Table 1**. For soaking times shorter than 120 min, the increased moisture content indicated that water diffusion was faster at higher soaking temperatures. It seems that a faster water transport corresponds to more leaching of material. For longer soaking times, maximal moisture contents were reached, while the level of leached material increased further. Furthermore, the decrease in yellowness (Δb^*) with increasing soaking time was linearly related with the level of leached material ($r = 0.99$ for both soaking temperatures), indicating that the level of leaching correlates with higher losses of yellow constituents. Additionally, less yellow soaked brown rice (*b**) corresponds to brighter (*L**) rice ($r = -0.97$ and -0.99 for rice soaked at 40 and 65 °C, respectively).

Effect of Soaking Time and Temperature on the Levels of Reducing Sugars. Figure 1 shows the RS levels of brown rice soaked for different times at 40 and 65 °C and of the corresponding soaking water. For both soaking temperatures and for short soaking times (≤30 min), the level of RS in the flour was lower than in the nonsoaked rice. Longer soaking times (>60 min) resulted in higher levels.

The data showed that the RS leaching increased with soaking time. For short soaking times (≤30 min), it markedly increased with temperature. It was further clear that RS were formed (e.g., by enzymic conversion of sucrose and raffinose) and leached in the soaking water.

Effect of Soaking Time and Temperature on the Levels of Free α-Amino Nitrogen. Figure 2 shows the results of FAN measurements. In contrast to RS levels, the FAN levels of brown rice did not increase after soaking. Analysis of the soaking water indicated that the level of leached FAN increased with soaking time. Furthermore, the level of total FAN (i.e., in brown rice and soaking water) increased for rice soaked at 40 °C, while it remained constant for rice soaked at 65 °C. The increase at 40 °C can be ascribed to enzymic formation during soaking. In contrast to RS (cf. supra), the released FAN leached out and did not increase the FAN content in soaked rice. The constant level of total FAN for rice soaked at 65 °C indicated that proteolytic enzymes were not active at this temperature and that

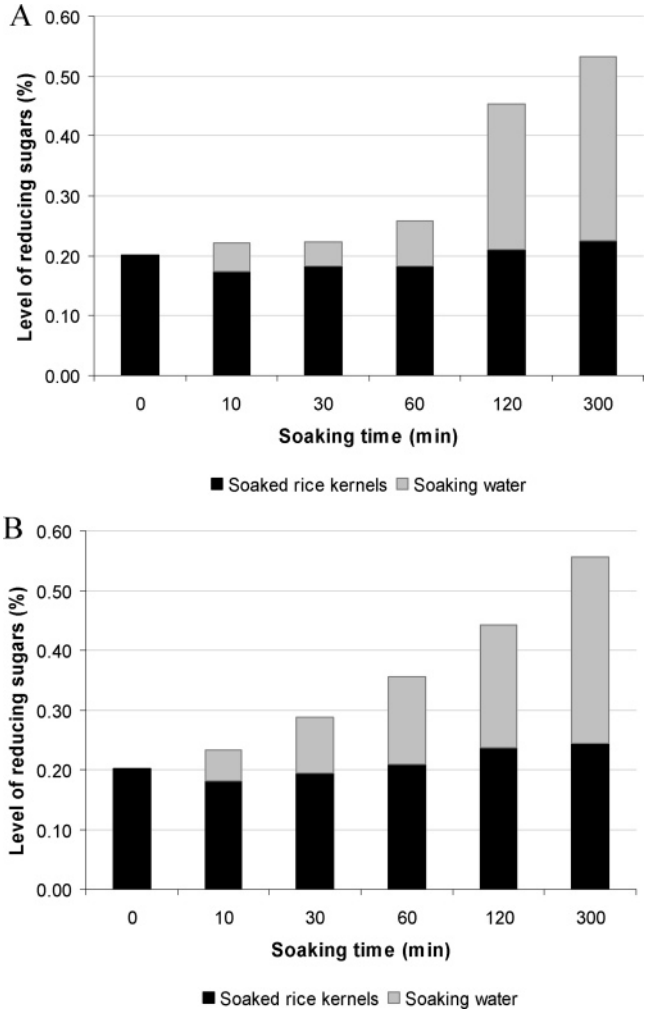

Figure 1. Levels of reducing sugars of brown rice soaked at 40 °C (**A**) and 65 °C (**B**) for different times.

enzymic release did not compensate for leaching of FAN. It was clear that proteolytic activity of rice was low, as indicated recently by Jones and Lookhart (*24*).

Effect of Soaking Atmosphere on Rice Color. Table 2 presents the color parameters *L** and *b** of the flour of brown and milled rice samples soaked for 30, 60, and 90 min at 40 °C under different atmospheres (nitrogen, oxygen, and ambient conditions). The redness (*a**) data are not shown since the level of red pigments of brown nonsoaked rice was low and the effects of soaking temperature and time were negligible (**Table 1**). Rice soaked under an oxygen atmosphere was darker and more yellow than that soaked under ambient conditions. In contrast, soaking under nitrogen increased brightness and lowered yellowness. The color changes are too small to be observable by the human eye. Probably, enzymic color changes occurred under soaking conditions, allowing oxidative processes (i.e., ambient conditions and oxygen atmosphere). Maximal PPO activity (ca. 160 units/g of rice) was measured at ca. 40 °C and pH 6.5 (results not shown).

Soaking of milled rice kernels only led to minor effects on color, suggesting that oxido-reductases responsible for enzymic color changes are more abundant in the outer rice layers (bran) than in the endosperm of brown rice as earlier observed by Lamberts et al. (*6*) and/or that the pigment (precursors) are (largely) removed by milling.

The data in **Tables 1** and **2** allow us to conclude that changes in brightness and yellowness are mainly attributed to outward

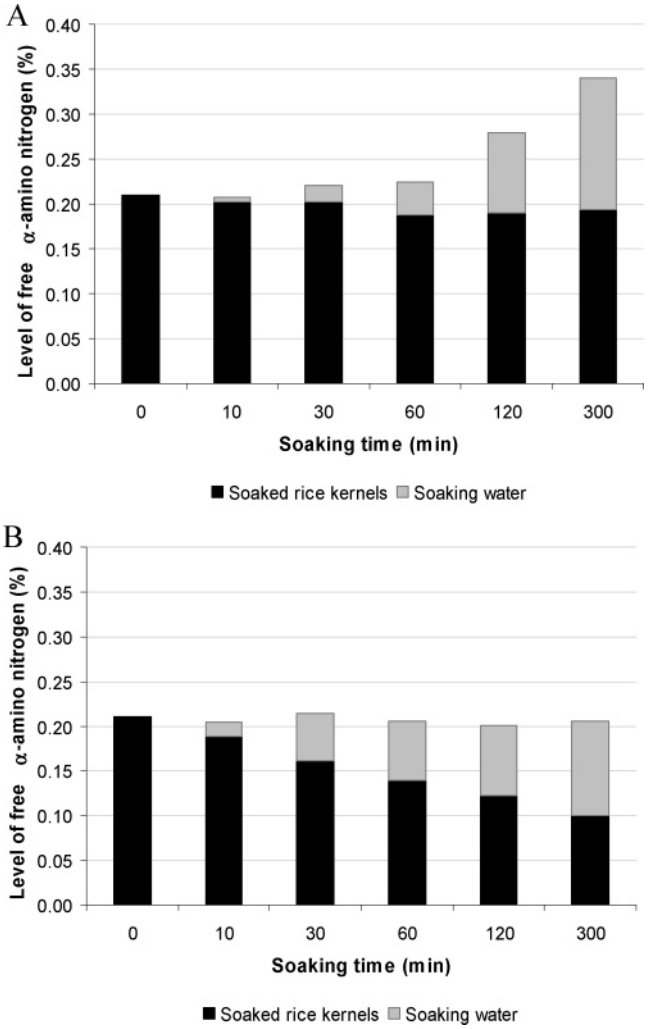

Figure 2. Levels of free α-amino nitrogen of brown rice soaked at 40 °C (**A**) and 65 °C (**B**) for different times.

Table 2. Color Parameters *L** (Brightness) and *b** (Yellowness) of Flour of Brown and Milled Rice Kernels Soaked at 40 °C for Different Times under Different Atmospheres

		brown rice		milled rice	
soaking time (min)	soaking atmosphere	*L**	*b**	*L**	*b**
30	nitrogen	87.3	10.7	95.4	3.3
	ambient[a]	87.4	11.0	95.4	3.3
	oxygen	87.1	11.3	95.0	3.4
60	nitrogen	88.4	9.8	95.4	3.0
	ambient	88.1	10.0	95.5	3.2
	oxygen	87.5	10.7	95.4	3.3
90	nitrogen	88.7	9.5	95.4	3.4
	ambient	88.3	9.9	95.3	3.2
	oxygen	87.7	10.5	95.6	3.2

[a] Ambient = rice soaking without bubbling gas through the water.

migration of bran pigments in the soaking water and, to a minor extent, to some enzymic color changes. Furthermore, determination of the levels of RS and FAN indicated that soaking conditions affected the levels of Maillard precursors. In the next section, the effect of parboiling (soaking and steaming) conditions on color characteristics of rice will be discussed.

Effect of Parboiling on the Levels of Gelatinized Starch. DSC analysis indicated that approximately 93 and 98% of the starch was gelatinized for mildly and intermediately parboiled rice, respectively. No residual endotherm was observed with severely parboiled rice samples.

Table 3. Color Parameters *L** (Brightness), *a** (Redness), *b** (Yellowness), Total Color Difference (Δ*E*), and Levels of Reducing Sugars and α-Amino Nitrogen of Flour of Brown and Milled Nonparboiled and Parboiled (pb) Rice

rice sample	*L**	*a**	*b**	Δ*E*	reducing sugars (%)	α-amino nitrogen (%)
			Brown Rice			
nonparboiled	85.6	0.9	12.4		0.20	0.21
mildly pb	78.9	2.4	16.5	8.0	0.22	0.06
intermediately pb	79.1	2.6	18.1	8.9	0.32	0.11
severely pb	77.1	3.1	19.7	11.4	0.33	0.12
			Milled Rice			
nonparboiled	92.4	−0.3	5.9		0.11	0.08
mildly pb	88.9	0.1	10.5	5.8	0.17	0.04
intermediately pb	88.3	0.5	12.2	7.5	0.24	0.09
severely pb	87.0	0.8	13.8	9.6	0.25	0.10

Effect of Parboiling and Milling on Rice Color. In contrast to what was observed following soaking, brightness (*L**) decreased and redness (*a**) and yellowness (*b**) increased as a result of parboiling (soaking and steaming). For both brown and milled rice samples, the decrease in brightness and increase in redness and yellowness were related to the severity of parboiling (**Table 3**). On the basis of the *L**, *a**, and *b** color parameters, the total color differences (Δ*E*) between flour of parboiled and nonparboiled rice were calculated. Δ*E* increased with increasing degree of parboiling. As expected, milling made the rice brighter and less red and yellow. The differences in color parameters between the milled rice samples were mainly the result of differences in parboiling conditions (soaking and steaming) rather than of differences in DOM as the latter varied only slightly (8−10% range).

Steaming affected rice color in the opposite direction and more drastically than soaking. It seems that leaching of bran pigments in the soaking water and oxidative color changes during brown rice soaking had a minor impact on the final color of parboiled rice and that color changes mainly occurred during brown rice steaming.

Effect of Parboiling and Milling on the Levels of Reducing Sugars. The RS contents of brown parboiled rice samples increased with the severity of parboiling conditions (**Table 3**). Mildly parboiled rice contained lower levels of RS (0.22%) than intermediately and severely parboiled rice samples (0.32 and 0.33%, respectively). Furthermore, the levels of RS decreased after milling, and the decrease was larger for nonparboiled than for parboiled rice.

Ali and Bhattacharya (*8*) found that the increased level of RS resulting from parboiling can in part be explained by sucrose conversion during soaking. In addition, degradation of starch occurs during steaming. The latter was investigated by Mahanta and Bhattacharya (*25*). To gain insight into the effect of parboiling (soaking and steaming) on the levels of RS, the differences in soaking conditions and hence sucrose (and raffinose) conversion had to be taken into account. From the effect of soaking conditions on the RS content of brown rice (**Figure 1B**), it was expected that the levels of RS would increase with soaking time. The observations that the RS content of mildly parboiled rice (soaked for 150 min) was lower than of intermediately and severely parboiled rice samples (soaked for 10 min) may indicate that thermal starch degradation increases with severity of steaming conditions. Furthermore, from this observation and from comparison of the RS contents

of brown mildly parboiled rice (0.22%) and of brown nonparboiled rice (0.20%), it seems that mild parboiling did not result in a significant increase in RS content. The small increase after parboiling may suggest that RS were not only formed during parboiling but were probably lost, for example, in Maillard-type reactions.

Milling decreased RS levels. The larger decrease in RS content of nonparboiled than of parboiled rice is partly explained by the difference in DOM (14 and 8−10% for nonparboiled and parboiled rice samples, respectively). RS are concentrated in the germ and bran layers, and their level decreases inward from bran layers to endosperm (*8*). Hence, more bran layer removal (nonparboiled rice) increased the loss of RS. Second, the smaller decrease in RS content after milling parboiled rice rather than after milling of nonparboiled rice can be ascribed to diffusion of RS from bran layers into the endosperm during steaming, as earlier described by Ali and Bhattacharya (*8*).

Effect of Parboiling and Milling on the Levels of Free α-Amino Nitrogen. Parboiling decreased the FAN content of brown rice (**Table 3**) to a level depending on the severity of parboiling conditions. Mildly parboiled rice showed the lowest FAN content (0.06%), while intermediately and severely parboiled rice contained similar levels of FAN (0.11 and 0.12%, respectively). Milling decreased FAN contents, and the decrease was larger for nonparboiled rice than for parboiled rice.

During soaking at higher temperatures (65 °C), FAN was lost by leaching (**Figure 2B**). Long soaking times (>60 min, i.e., mildly parboiled rice) resulted in a large reduction of FAN, while, for short soaking times (≤30 min, i.e., intermediately and severely parboiled rice), the decrease was limited. Comparison of the levels of FAN of nonparboiled, brown soaked, and brown parboiled rice samples (**Table 3**) indicated that the second step of the parboiling process (i.e., steaming) resulted in an additional loss of FAN. This additional loss of FAN increased with the severity of parboiling and suggests Maillard browning to increase with the degree of parboiling.

Milling decreased FAN levels. Milled mildly parboiled rice contained less FAN than its nonparboiled counterpart. Although FAN is concentrated in the outer bran layers and DOM of nonparboiled rice (14%) was higher than that of parboiled rice (8−10% range), milled nonparboiled rice did not contain the lowest FAN content. It seems that the large proportion (70%) of FAN lost by parboiling of brown rice exceeded that caused by the difference in bran layer removal during milling of nonparboiled and parboiled rice.

As suggested previously, the loss of RS and FAN during steaming can be ascribed to the reaction of FAN with RS in Maillard reactions. In the next section, we report on the occurrence of the Maillard indicator furosine.

Effect of Parboiling and Milling on Furosine Content. Table 4 shows the effect of parboiling and milling on the level of the early stage Maillard reaction product furosine. Nonparboiled rice contained only trace levels of furosine (5 ppm, dw rice basis). The furosine level of parboiled rice samples was significantly higher (76−134 ppm) and related to the severity of parboiling conditions. Milling of brown rice decreased the furosine content. This indicates that Maillard reactions mainly occur in the bran layers of brown rice. However, the furosine content of the milled parboiled rice samples also increased with severity of parboiling. This indicated that nonenzymic browning did not only occur at the brown rice surface but also in the starchy endosperm. Thus, the presence of furosine confirmed the hypothesis that nonenzymic browning reactions (partly) explain the color changes during brown rice parboiling (*4*, *6*−*8*).

Table 4. Levels of Furosine and Bran Pigments of Brown and Milled Nonparboiled and Parboiled (pb) Rice

rice sample	furosine (ppm)	bran pigments (E_{420}/g)
	Brown Rice	
nonparboiled	5	1.27
mildly pb	76	0.60
intermediately pb	126	0.86
severely pb	134	0.83
	Milled Rice	
nonparboiled	3	0.07
mildly pb	55	0.19
intermediately pb	87	0.33
severely pb	89	0.41

Effect of Parboiling and Milling on the Level of Bran Pigments. Extinction measurements at 420 nm (E_{420}) of brown and milled rice extracts indicated that parboiling decreases the levels of bran pigments of brown rice (**Table 4**). Brown mildly parboiled rice showed the lowest pigment concentration (E_{420} = 0.60). Brown intermediately and severely parboiled rice samples contained similar levels (E_{420} = 0.86 and 0.83, respectively). Milling decreased the level of pigments, and the pigment concentration of the milled rice samples increased with the degree of parboiling.

The decrease in bran pigment levels as a result of parboiling is due to the release of pigments in the soaking water. Brown rice soaked for 150 min at 65 °C (i.e., mildly parboiled rice) contained less bran pigments than the samples soaked for 10 min at 68 °C (i.e., intermediately and severely parboiled rice) since leaching is related to soaking time (**Table 1**). Therefore, differences in soaking time account for the lower extinction readings of mildly parboiled than of intermediately and severely parboiled rice samples.

The similar pigment contents of intermediately and severely parboiled rice samples were explained by their equal soaking times. Hence, pigments formed by Maillard reactions did not interfere with the bran pigment determination as suggested by Subba Rao and Bhattacharya (*23*).

Milling markedly decreased the level of bran pigments. The lower pigment content of milled nonparboiled rice than of the parboiled rice samples is due to its higher milling degree. Furthermore, as already mentioned, DOM of parboiled rice samples slightly differed, and this contributed (although to a limited extent) to the difference in bran pigment levels of milled rice samples (*10*). Therefore, the increase in pigment contents in milled parboiled rice with the degree of parboiling can mainly be ascribed to diffusion of bran pigments into the endosperm during brown rice steaming. The results equally induce that more severe steaming conditions go hand in hand with more pigment diffusion. Hence, besides leaching of bran pigments and enzymic color changes during soaking, and Maillard browning during steaming, diffusion of bran pigments into the endosperm during steaming also determined parboiled rice color.

In conclusion, bran pigments, oxidative, and Maillard reactions impact the color of parboiled rice. Soaking causes leaching of bran pigments and results in a brighter and less yellow brown rice. Furthermore, enzymic color changes are responsible for a small increase in darkness and yellowness during soaking under oxidative conditions. Parboiling (soaking and steaming) of brown rice increases darkness, redness, and yellowness of brown and milled rice. The color changes increase with severity of parboiling. The changes in levels of RS and FAN suggest the occurrence of Maillard reactions during steaming. The Maillard indicator furosine is present in both brown and milled parboiled

rice samples, indicating that Maillard reactions occur at the brown rice surface and in the starchy endosperm. Finally, besides leaching out of bran pigments during soaking, diffusion of bran pigments into the endosperm during steaming also determines parboiled rice color.

ABBREVIATIONS USED

CIE, Commission Internationale de l'Eclairage; DSC, differential scanning calorimetry; DOM, degree(s) of milling; EU, extinction units; FAN, free α-amino nitrogen; MC, moisture content; PPO, polyphenol oxidase; RS, reducing sugar(s).

ACKNOWLEDGMENT

Technical assistance by L. Van den Ende is gratefully appreciated.

LITERATURE CITED

(1) Ong, M. H.; Blanshard, J. M. V. Texture determinants of cooked, parboiled rice. I. Rice starch amylose and the fine structure of amylopectin. *J. Cereal Sci.* **1995**, *21*, 251−260.

(2) Derycke, V.; Veraverbeke, W. S.; Vandeputte, G. E.; De Man, W.; Hoseney, R. C.; Delcour, J. A. Impact of proteins on pasting and cooking properties of nonparboiled and parboiled rice. *Cereal Chem.* **2005**, *82*, 468−474.

(3) Jayanarayanan, E. K. Influence of processing conditions on the browning of parboiled rice. *Rice J.* **1965**, *68*, 16−17.

(4) Bhattacharya, K. R.; Subba Rao, P. V. Effect of processing conditions on quality of parboiled rice. *J. Agric. Food Chem.* **1966**, *14*, 476−479.

(5) Pillaiyar, P.; Mohandoss, R. Hardness and color in parboiled rice produced at low and high temperatures. *J. Food Sci. Technol.* **1981**, *18*, 7−9.

(6) Lamberts, L.; De Bie, E.; Derycke, V.; Veraverbeke, W. S.; De Man, W.; Delcour, J. A. Effect of processing conditions on color change of brown and milled parboiled rice. *Cereal Chem*. **2006**, *83*, 80−85.

(7) Subrahmanyan, V.; Sreenivasan, A.; Das Gupta, H. P. Studies on quality in rice. I. Effect of milling on the chemical composition and commercial qualities of raw and parboiled rice. *Ind. J. Agric. Sci.* **1938**, *8*, 459−486.

(8) Ali, S. Z.; Bhattacharya, K. R. Changes in sugars and amino acids during parboiling of rice. *J. Food Biochem.* **1980**, *4*, 169−179.

(9) Itani, T.; Tamaki, M.; Arai, E.; Horino, T. Distribution of amylose, nitrogen, and minerals in rice kernels with various characters. *J. Agric. Food Chem.* **2002**, *50*, 5326−5332.

(10) Lamberts, L.; De Bie, E.; Vandeputte, G. E.; Veraverbeke, W. S.; Derycke, V.; De Man, W.; Delcour, J. A. Effect of milling on color and nutritional properties of rice. *Food Chem*. **2007**, *100*, 1496−1503.

(11) Resmini, P.; Pellegrino, L.; Battelli, G. Accurate quantification of furosine in milk and dairy products by a direct HPLC method. *Ital. J. Food Sci.* **1990**, *3*, 173−183.

(12) Delgado, T.; Corzo, N.; Santa-Maria, G.; Jimeno, M. L.; Olano, A. Determination of furosine in milk samples by ion-pair reversed phase liquid chromatography. *Chromatographia* **1992**, *33*, 374−376.

(13) Acquistucci, R.; Panfili, G.; Marconi, E. Application of the microwave hydrolysis to furosine determination in cereal and dairy foods. *J. Agric. Food Chem.* **1996**, *44*, 3855−3857.

(14) Fernandez-Artigas, P.; Guerra-Hernandez, E.; Garcia-Villanova, B. Browning indicators in model systems and baby cereals. *J. Agric. Food Chem.* **1999**, *47*, 2872−2878.

(15) Guerra-Hernandez, E.; Corzo, N.; Garcia-Villanova, B. Maillard reaction evaluation by furosine determination during infant cereal processing. *J. Cereal Sci.* **1999**, *29*, 171−176.

(16) Ramirez-Jimenez, A.; Guerra-Hernandez, E.; Garcia-Villanova, B. Evolution of nonenzymic browning during storage of infant cereal. *Food Chem.* **2003**, *83*, 219−225.

(17) Garcia-Banos, J. L.; Corzo, N.; Sanz, M. L.; Olano, A. Maltulose and furosine as indicators of quality of pasta products. *Food Chem.* **2004**, *88*, 35−38.

(18) Feillet, P.; Autran, J.-C.; Icard-Vernière, C. Pasta brownness: an assessment. *J. Cereal Sci.* **2000**, *32*, 215−233.

(19) Wadsworth, J. I. Degree of milling. In *Rice: science and technology*; Marshall, W. E., Wadsworth, J. I., Eds.; Marcel Dekker, Inc.: New York, 1994; pp 139−176.

(20) American Association of Cereal Chemists AACC Method 44-15A. *Approved Methods of the AACC*, 10th ed.; AACC: St. Paul, MN, 2000.

(21) Brijs, K.; Bleukx, W.; Delcour, J. A. Proteolytic activities in dormant rye (*Secale cereale* L.) grain. *J. Agric. Food Chem.* **1999**, *47*, 3572−3578.

(22) Park, W. J.; Shelton, D. R.; Peterson, C. J.; Martin, T. J.; Kachman, S. D.; Wehling, R. L. Variation in polyphenol oxidase activity and quality characteristics among hard white wheat and hard red winter wheat samples. *Cereal Chem.* **1997**, *74*, 7−11.

(23) Subba Rao, P. V.; Bhattacharya, K. R. Effect of parboiling on thiamine content of rice. *J. Agric. Food Chem.* **1966**, *14*, 479−482.

(24) Jones, B. L.; Lookhart, G. L. Comparison of endoproteinases of various grains. *Cereal Chem.* **2005**, *82*, 125−130.

(25) Mahanta, C. L.; Bhattacharya, K. R. Thermal degradation of starch in parboiled rice. *Starch* **1989**, *41*, 91−94.

Received for review July 27, 2006. Revised manuscript received October 31, 2006. Accepted November 5, 2006.

JF062140J