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Effect of milling on colour and nutritional properties of rice

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Abstract

Brown rice (long-grain variety Puntal) was abrasively milled (0–100 s) to various degrees of milling (DOM, 0–25%). The non-linear relationship between milling time and DOM indicated a variability in hardness within the different rice fractions. The hardness of the bran layers increased from outer to inner bran layers, while the different endosperm fractions were of comparable hardness. The colour parameters L^*, a^* and b^* and extinction measurements of water-saturated butanol extracts of flour, from rice with different DOM, indicated that bran contained much more yellow and red pigment than endosperm. The levels of yellow and red pigment decreased from the surface of the brown rice to the middle endosperm (DOM = 15%). Once bran (DOM = 9%) and outer endosperm (additional DOM = 6%) were removed, the yellowness and redness of the middle endosperm of the raw rice remained constant, indicating that the pigments were uniformly distributed in the middle endosperm. Cooking of rice containing residual bran layers (DOM < 9%) increased rice brightness (L^*) and decreased its redness (a^*) and yellowness (b^*), as expected from a dilution effect resulting from the uptake of water, as well as from leaching of pigments in the cooking water and diffusion of bran pigments to the endosperm. Cooking of rices with DOM > 9% resulted in products of constant brightness and redness but with yellowness which decreased as a function of DOM. Proteins, minerals and starch were not uniformly distributed in the brown rice kernel. The endosperm (DOM > 9%), contained most of the rice kernel proteins (84.2%), and proteins were mostly concentrated in the outer endosperm (9% < DOM < 15%). Bran (0% < DOM < 9%) contained most of the minerals (61.0%), and starch (84.6%) was concentrated in the core endosperm fraction (DOM 25%).

Keywords: Brown rice; Milled rice; Degree of milling; Colour; Proteins; Minerals; Starch

1. Introduction

Mature rice is harvested as a covered grain, designated as paddy rice. The hull, the outer covering, corresponds to 18–20% of the weight of paddy rice. It is removed from the brown rice by dehulling. White rice can be obtained by milling brown rice to remove the germ (2–3% of brown rice weight) and the bran layers (5–8% of brown rice weight) from the underlying starchy endosperm. Different markets require different degrees of bran removal. The colour of rice is an important sensory parameter. Generally, the whiter the milled rice, the more value it has in the market place (Wadsworth, 1994). In milled rice, storage conditions (Wang, Wang, Shepard, Wang, & Patindol, 2002) and degree of milling (DOM) (Chen & Siebenmorgen, 1997; Lyon et al., 1999; Stermer, 1968) can affect the colour. Only the surface of brown rice contains pigments (Champagne, Wood, Juliano, & Bechtel, 2004; Itani, Tamaki, Arai, & Horino, 2002). Park, Kim, and Kim (2001) reported taste panel results showing that the colour of cooked rice (8.0% < DOM < 14%) decreases with increasing degree of milling. Furthermore, analysis of successive abrasive brown rice milling fractions has shown that nutrients are not uniformly distributed in brown rice (Itani et al., 2002;

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Kennedy, Schelstraete, & Del Rosario, 1974; Resurreccion, Juliano, & Tanaka, 1979). In the cited studies, the contents of rice constituents were analysed in milling fractions obtained after multistep milling of brown rice. Approximately 80% of the kernel proteins were located in the starchy endosperm (DOM > 12%; Resurreccion et al., 1979), while minerals were more abundant in the outer bran layers. The starch content was highest in the endosperm, whereas the protein and mineral contents decreased from the outer bran layers to the endosperm (Itani et al., 2002; Resurreccion et al., 1979).

The purpose of the present study was to add existing knowledge on the effect of milling on the colour and the composition of long-grain rice. To that end, the colour and the contents of proteins, minerals and total and damaged starch of rice with different DOM (0–25%, 14 fractions) were determined. Furthermore, the colour of cooked rice was measured, to investigate the effect of cooking on the colour parameters of rice with different DOM.

2. Materials and methods

2.1. Rice samples, milling, grinding and cooking

Dehulled brown rice from the long-grain variety Puntal (Spanish harvest 2002) was obtained from Masterfoods (Olen, Belgium). Samples (200.0 g, moisture content 12.0%, 1000-kernel weight 19.4 g) were abrasively milled (0–100 s) with a TM05C testing mill (Satake, Bredbury, UK) to obtain rice with different DOM (0–25%). The DOM, i.e., the weight percentage of rice layers removed by milling, was calculated from the weight of rice before and after milling (Wadsworth, 1994). Broken kernels were removed using a test rice grader. The rice kernels with different DOM were used for analyses. Milling fractions obtained after 0–9%, 9–15% and 15–25% rice fraction removal were designated as bran, outer and middle endosperm, respectively. Rice with a DOM of ca. 25% contained only core endosperm. The rice kernels of variable DOM were ground with a laboratory grinder and passed through a 250 μm sieve.

Rice (20.0 g) was cooked (10 min, 100 °C) in deionised water (150 ml), in duplicate. After draining (1.5 min), the rice was cooled to ambient temperature (20 min) and used for colour determinations.

2.2. Analyses

A Hunterlab Colorquest™ 45/0 LAV colorimeter model CQ/UNI-1600 (HunterLab, Reston, VA, USA) was used for all colour determinations. Prior to colour measurements, the instrument was calibrated with a white and black calibration tile. The colorimeter was set to an illuminant condition D_{65} (medium daylight) and a 10° (field of view) standard observer. Colour measurements were made at least in five fold on samples placed in a clear petri dish. Each sample was covered with a white plate. The colour was measured in CIE 1976 L^*, a^*, b^* colour space. L^* is a measure of the brightness from black (0) to white (100). Parameter a^* describes red-green colour with positive a^*-values indicating redness and negative a^*-values indicating greenness. Parameter b^* describes yellow-blue colour with positive b^*-values indicating yellowness and negative b^*-values indicating blueness (Good, 2002).

Pigment extraction from the flour of rice with different DOM was based on AACC Method 14–50 (AACC, 2000). Water-saturated butanol (6.0 ml) was added to rice flour (1.75 g), to extract carotenoids. After shaking (2.5 h), the suspensions were filtered and the filtrates were scanned from 335 nm to 535 nm. These wavescans showed two peak maxima at ca. 360 and ca. 420 nm. Yongsmith, Kitprechavanich, Chitradon, Chaisrisook, and Budda (2000) showed that the extinctions at 370 nm (in our experiment at ca. 360 nm) and 420 nm are a measure of yellow and orange pigment concentrations, respectively.

Protein content was determined in duplicate using an adaptation of the AOAC Official Method (AOAC, 1995) to an automated Dumas protein analysis system (EAS vario Max N/CN, Elt, Gouda, The Netherlands). A conversion factor of 5.95 was used to calculate protein from nitrogen contents (Juliano, 1985). Mineral content was determined in duplicate according to AACC Method 08-01 (AACC, 2000). Total starch was determined in triplicate according to the Megazyme procedure (AACC Method 76-13). Starch damage was determined in triplicate according to the Megazyme procedure (AACC Method 76-31). The results of all chemical analyses are expressed on a dry matter basis.

2.3. Statistical analyses

For statistical analyses, t-test (PROC ANOVA) was used (significance level $P < 0.05$). Pearson's correlation coefficient values were determined (significance level $P < 0.05$). Statistical analyses were conducted using the Statistical Analysis System software 8.1 (SAS Institute, Cary, NC, USA).

3. Results and discussion

3.1. Relation between milling time and degree of milling (DOM)

Brown rice was abrasively milled (0–100 s) to obtain rice with various DOM (0–25%). Fig. 1 shows DOM as a function of milling time. An increase in milling time did not result in a linear increase in DOM. There was a change in the rate constant (slope) during the milling process. The slope decreased with milling time from 0 to 15 (DOM of ca. 9%). Milling times of at least 15 s (DOM > 9%) resulted in a constant (lower) slope and a linear relationship between DOM and milling time ($r = 0.99$). The transition at a DOM of ca. 9% was probably related to a significant difference in hardness between bran and endo-

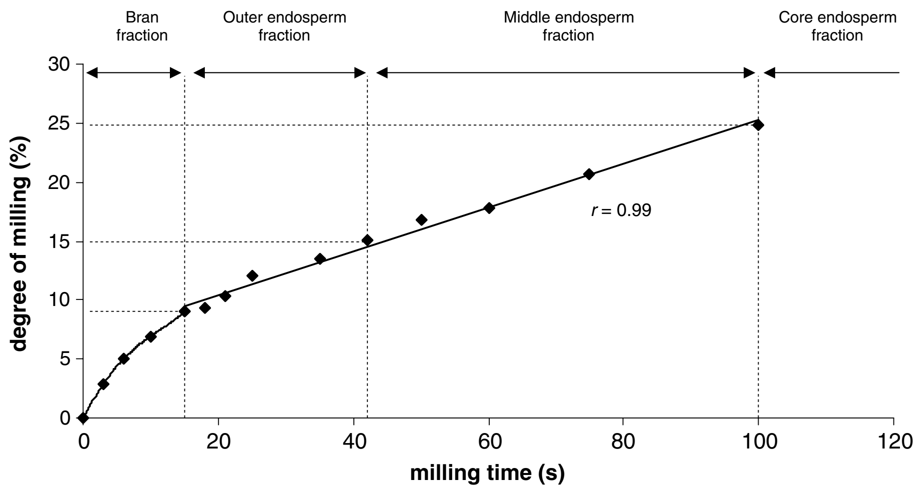

Fig. 1. Effect of milling time on the degree of milling of rice.

sperm. The hardness of the bran decreased from outer to inner layers, whereas the hardness of the different endosperm fractions was similar. In line with Wadsworth (1994), the fraction corresponding to 9% rice layer removal (milling time 15 s) was designated as the bran fraction. Fractions removed after milling times exceeding 15 s are described as endosperm. Resurreccion et al. (1979) further divided the starchy endosperm into different fractions. The fractions corresponding to 9–15% and 15–25% removal were designated as outer and middle endosperm, respectively (as shown in Fig. 1).

3.2. Distribution of colour pigments in raw and cooked rice

3.2.1. Colour parameters (L^*, a^* and b^*) of raw rice as a function of DOM

Fig. 2 shows the colour parameters of the kernels and flours from rice with different DOM. Brightness (L^*) of the raw rice kernels and the rice flours increased until a DOM of ca. 15% (bran and outer endosperm removed) (Fig. 2A). Further milling did not affect the rice brightness. For the raw rice kernels and rice flours, redness (a^*) and yellowness (b^*) decreased until a DOM of ca. 15% was reached (Fig. 2B and C). This indicated that the levels of red and yellow pigments decreased from the surface of the brown rice to the middle endosperm. It also demonstrated that bran and outer endosperm contain more red and yellow pigments than the middle and core endosperm. It seems that the pigments are uniformly distributed in the middle and core endosperm. Furthermore, these endosperm fractions contained very low levels of red pigments since a^* is approximately 0. The differences between the colour parameters of the flour from rice with different DOM were smaller than the differences between the colour parameters of the rice kernels themselves. This may be explained by a dilution effect. Grinding of rice kernels results in a mix of a small dark, coloured fraction (bran and outer endosperm) and a large light, less pigmented fraction (middle and core endosperm).

3.2.2. The level of yellow and orange colour pigments of raw rice as a function of DOM

For all flours of the rice with different DOM, the extinction values at the peak maxima were determined (Fig. 3). As expected, the levels of yellow-orange pigments decreased from the outer bran layers to the middle endosperm. The extinction values of rice after bran and outer endosperm removal remained constant, indicating that the yellow-orange pigments are uniformly distributed in the middle and core endosperm. This had already been concluded from the colour measurements, i.e., L^*, a^* and b^*-values as a function of DOM of rice kernels and the corresponding flours and indicates that both the colour parameter b^* and the sum of the extinction values at 360 and 420 nm are good indicators for the level of yellow-orange pigments in rice. Fig. 4 shows a linear relationship between these two parameters ($r = 0.96$).

3.2.3. Colour parameters (L^*, a^* and b^*) of cooked rice as a function of DOM

As the colour of cooked rice is an important sensory characteristic, the effect of cooking on the colour of rice with different DOM was studied. Fig. 2 shows the colour parameters L^*, a^* and b^* of the cooked rice. The brightness (L^*) of cooked kernels increased until a DOM of 9% (bran removed) was reached. These trends were similar to those observed for the raw rice kernels. Secondly, after bran removal (DOM > 9%), the brightness and redness (a^*) of the cooked rice kernels did not change, while the yellowness (b^*) further decreased with increasing DOM. This indicated that, in contrast to what was observed for raw rice, the brightness and redness of the cooked kernels in the outer endosperm fraction (9%<DOM<15%) do not decrease with increasing DOM. However, as in the case of raw rice, the yellowness of the cooked rice in the outer endosperm fraction decreased as a function of DOM. These differences in colour between raw and cooked rices could be explained by a difference in moisture content between cooked rice kernels with different DOM and by

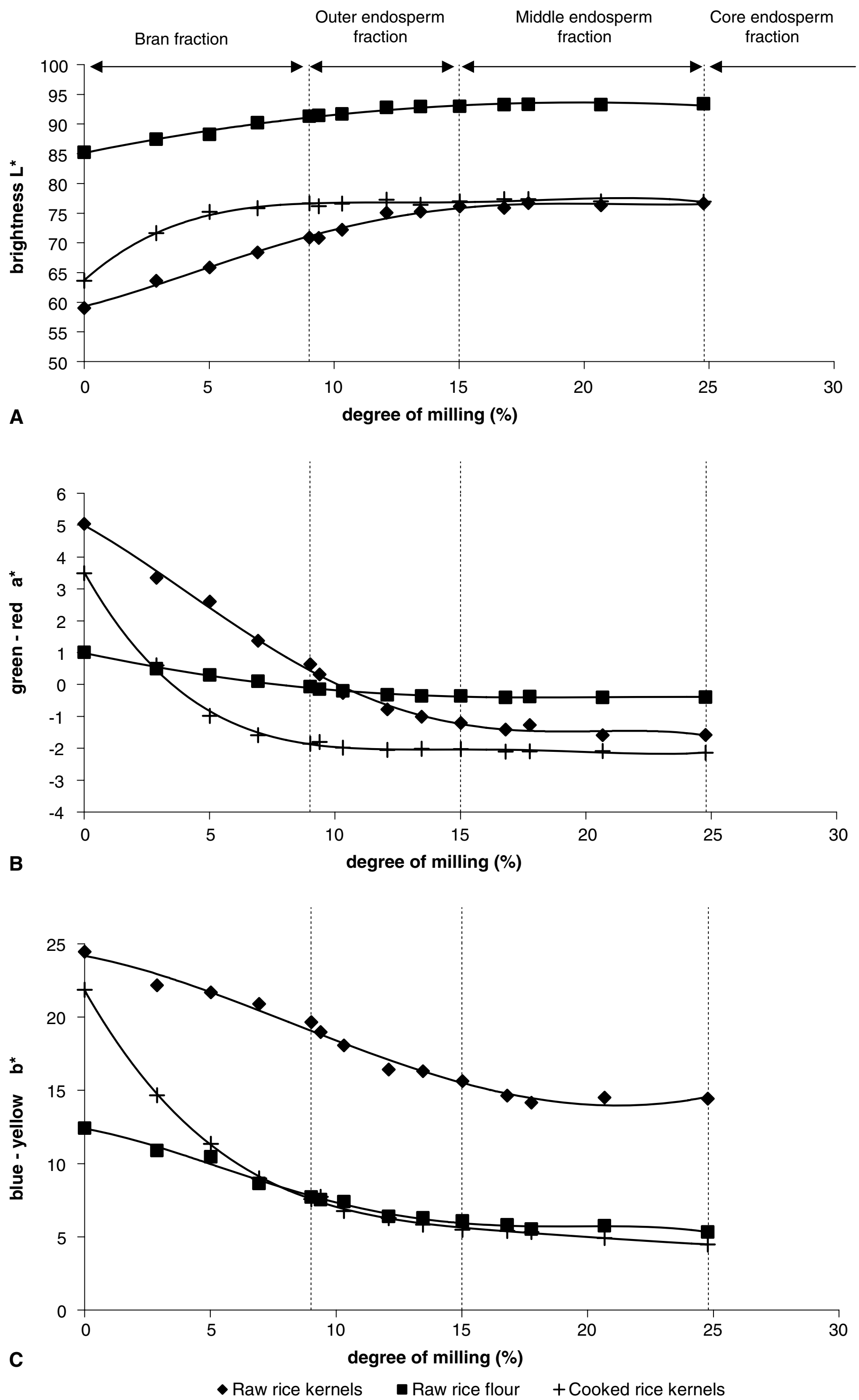

Fig. 2. Colour parameters L^* (brightness), a^* (redness) and b^* (yellowness) of rice (raw kernels, corresponding flours and cooked kernels), as a function of degree of milling.

diffusion of pigments during cooking of rice. For rice kernels, an increasing DOM is correlated with more water uptake during cooking (Park et al., 2001; Tran, Suzuki, Okadome, Homma, & Ohtsubo, 2004). This increase in water uptake with increasing DOM resulted in lower pigment concentrations in the cooked rice kernels with increasing DOM. The dilution effect also explained the lower yellowness and redness of the cooked rice kernels, when compared to those of the raw kernels. However, in contrast to raw rice, the decrease in pigment concentration with increasing DOM was not correlated with a decrease in redness in the outer endosperm fraction. This indicated that phenomena other than differences in moisture content are important in the colour of cooked rice. Probably, leaching

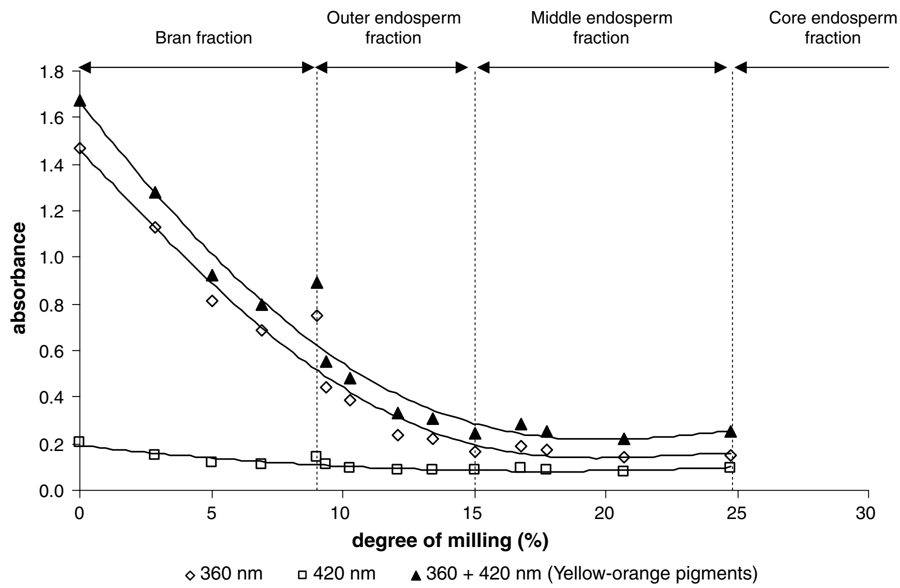

Fig. 3. Extinction values of peak maxima (360 and 420 nm) of the wavescans of water-saturated butanol extracts of rice as a function of degree of milling.

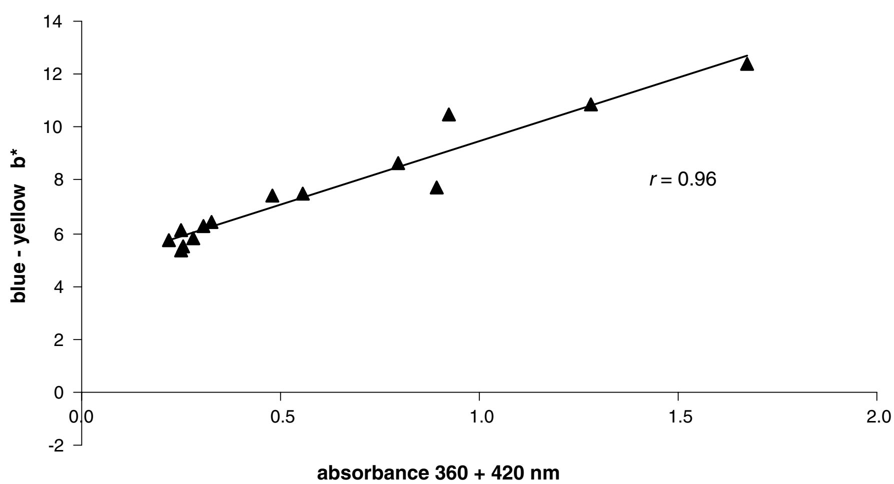

Fig. 4. Correlation between the colour parameter b^* (yellowness) and the sum of the extinction values at 360 and 420 nm of water-saturated butanol extracts of rice with different degree of milling.

of pigments in the cooking water and diffusion of pigments from the rice surface towards the endosperm during cooking may also contribute to the colour of cooked rice. It seems that the effect of difference in water uptake on the pigment concentration was partly compensated by a decrease in leaching and/or diffusion of pigments with increasing DOM during rice cooking, as the redness of the cooked rices with residual outer endosperm ($9\% < \text{DOM} < 15\%$) remained constant. Also, after bran and outer endosperm removal (DOM > 15%), the brightness and redness of the cooked rice kernels remained constant, while the yellowness slightly decreased with increasing DOM. The latter is in contrast with the observations for raw rice kernels, which showed a constant yellowness in the middle endosperm. Furthermore, the colour trends of the middle endosperm ($15\% < \text{DOM} < 25\%$) of the cooked rice kernels are similar to those of the outer endosperm.

3.3. Distribution of proteins, minerals and total and damaged starch in brown rice

3.3.1. Protein content as a function of DOM

Fig. 5 shows the protein contents as a function of DOM. The protein content (9.2%) of brown rice (DOM = 0%) decreased as a function of DOM, indicating that the protein concentration in bran layers decreased from the rice surface to the endosperm. Also, the fact that the protein content decreased further after bran removal (DOM > 9%) suggests that proteins were not homogeneously distributed in the endosperm. The protein concentration decreased from the outer to the core endosperm.

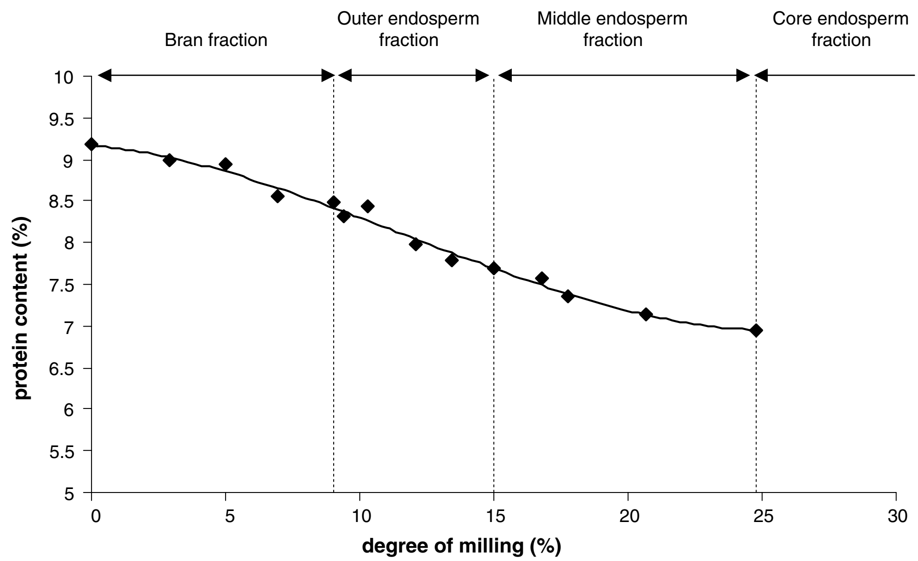

Fig. 5. Protein content of rice, as a function of degree of milling.

This corresponds with earlier work (Itani et al., 2002; Resurreccion et al., 1979). Based on the protein levels in the rice samples with different DOM, and taking into account the weight percentage of rice removed during milling, the relative amounts of proteins in the bran and the different endosperm fractions were calculated (Table 1). The bran, the outer, middle and core endosperm contained 15.8%, 12.8%, 14.4% and 57.0% of the total proteins. These values are comparable to earlier data (Resurreccion et al., 1979), and show that the outer endosperm contains the highest

Table 1
Distribution of proteins, minerals and starch in the different rice fractions

Nutrient	Percentage of nutrient in each fraction				Percentage content in brown rice (DOM)
	Bran (DOM[a] 0–9)	Endosperm			
		Outer (DOM 9–15)	Middle (DOM 15–25)	Core (DOM 25–100)	
Protein	15.8	12.8	14.4	57.0	9.2
Mineral	61.0	23.7	3.7	11.6	1.6
Total starch	6.4	2.8	6.2	84.6	76.4

[a] Degree of milling.

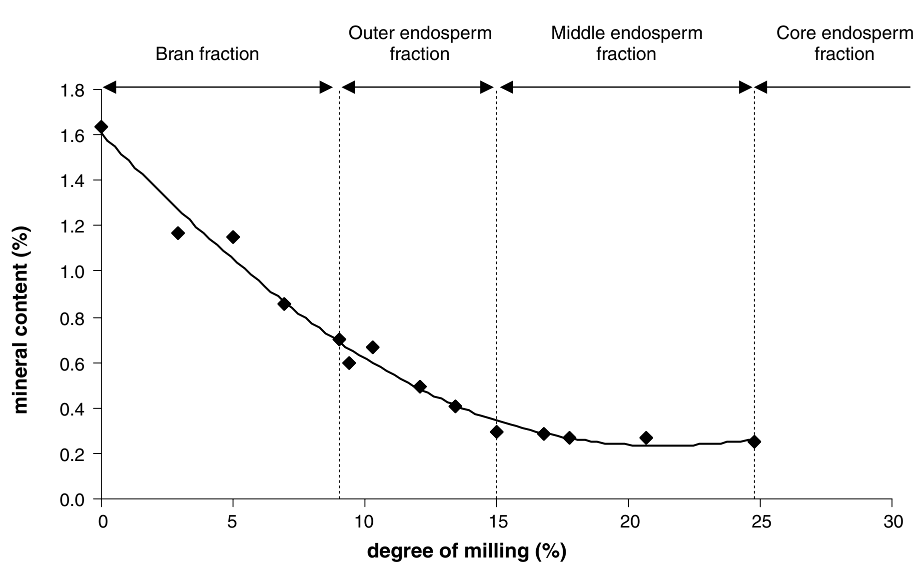

Fig. 6. Mineral content of rice, as a function of degree of milling.

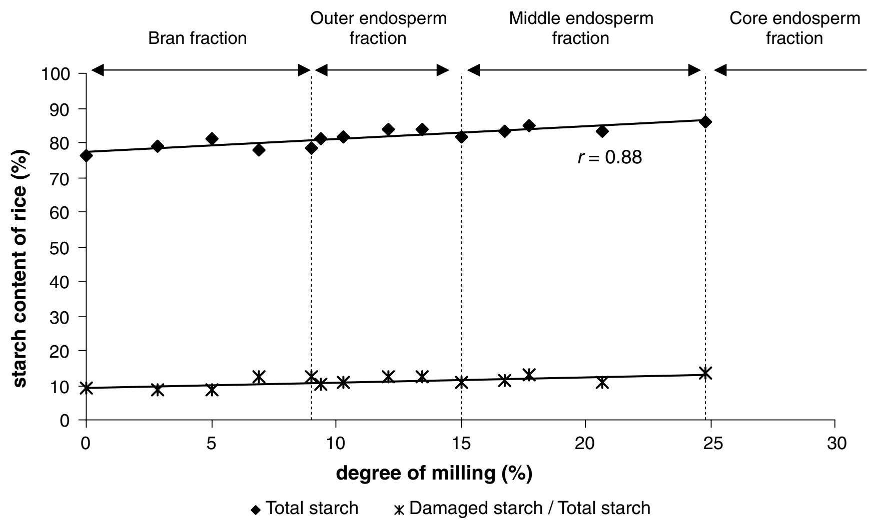

Fig. 7. Total and damaged starch contents of rice, as a function of degree of milling.

protein concentration. Probably the polish fraction, which is known as a high protein fraction in rice (Resurreccion et al., 1979), is a part of the outer endosperm fraction.

3.3.2. Mineral content as a function of DOM

Fig. 6 shows the mineral content as a function of DOM. Its average level in brown rice (DOM = 0%) was 1.6%, and mineral concentrations decreased from the outer bran layers towards the middle endosperm. Once the bran and outer endosperm were removed (DOM > 15%), the level of minerals remained constant, indicating that the minerals are rather uniformly distributed in the middle and core endosperm. These observations are in agreement with results of Itani et al. (2002) and Resurreccion et al. (1979). The relative amounts of minerals in the bran and endosperm fractions indicate that most of the minerals are present in the bran (61.0%). About one fourth (23.7%) of the total mineral content is present in the outer endosperm, 3.7% in the middle endosperm and 11.6% in the core endosperm (Table 1).

3.3.3. Total starch and damaged starch contents as a function of DOM

Fig. 7 shows the total and damaged starch contents as a function of DOM. The total starch in brown rice (DOM = 0%) was 76.4% (Table 1). The linear relation between total starch and DOM ($r = 0.88$) indicated that the level of total starch increased with increasing removal of rice fractions. As expected, the core endosperm (DOM = 25%) contained the highest level of total starch (84.6%). The level of damaged starch slightly increased with increasing DOM. Flour from brown rice (DOM = 0%) contained ca. 9% damaged starch, while flour from rice with a DOM of 25% had about 14% damaged starch, indicating that the milling and grinding processes induced starch damage.

4. Conclusions

The analyses of the colour indicated that the level of pigments decreased from the surface to the endosperm and that yellow and red pigments were concentrated in bran and outer endosperm. Colour pigments were uniformly distributed in the middle and core endosperm. Colour measurements of cooked rice indicated that: (i) water uptake during cooking, (ii) leaching of pigments in the cooking water (excess water was used in the cooking experiment) and (iii) diffusion of pigments from the rice surface to the inner layers are responsible for differences in colour between raw and cooked rices. To gain more insight into the different rice pigments, identification of the rice pigments present in the different rice layers is needed.

The study of the effect of milling on the nutritional properties confirmed that the level of proteins and minerals decreased from the surface to the endosperm of brown rice and that the level of total starch increased from the surface to the endosperm.

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References

AACC International. (2000a). *Approved methods of the American Association of Cereal Chemists* (10th ed.). Method 14-50. St. Paul, MN: The Association.

AACC International. (2000b). *Approved methods of the American Association of Cereal Chemists* (10th ed.) . Method 08-01. St. Paul, MN: The Association.

AACC International. (2000c). *Approved methods of the American Association of Cereal Chemists* (10th ed.). Method 76-13. St. Paul, MN: The Association.

AACC International. (2000d). *Approved methods of the American Association of Cereal Chemists* (10th ed.). Method 76-31. St. Paul, MN: The Association.

AOAC. (1995). *Official methods of analysis of the Association of Official Analytical Chemists* (16th ed.). Method 990.03. Washington, DC: The Association.

Champagne, E. T., Wood, D. F., Juliano, B. O., & Bechtel, D. B. (2004). *Rice: Chemistry and technology* (3rd ed., pp. 77–107). USA: The American Association of Cereal Chemists, Inc.

Chen, H., & Siebenmorgen, T. J. (1997). Effect of rice kernel thickness on degree of milling and associated optical measurements. *Cereal Chemistry, 74*, 821–825.

Good, H. (2002). Measurement of color in cereal products. *Cereal Foods World, 4*, 5–6.

Itani, T., Tamaki, M., Arai, E., & Horino, T. (2002). Distribution of amylose, nitrogen, and minerals in rice kernels with various characters. *Journal of Agricultural and Food Chemistry, 50*, 5326–5332.

Juliano, B. O. (1985). *Rice: Chemistry and technology* (2nd ed., pp. 59–174). USA: The American Association of Cereal Chemists, Inc.

Kennedy, B. M., Schelstraete, M., & Del Rosario, A. R. (1974). Chemical, physical, and nutritional properties of high-protein flours and residual kernel from the overmilling of uncoated milled rice. 1. Milling procedure and protein, fat, ash, amylose and starch content. *Cereal Chemistry, 51*, 435–448.

Lyon, B. G., Champagne, E. T., Vinyard, B. T., Windham, W. R., Barton, F. E., Webb, B. D., et al. (1999). Effects of degree of milling, drying condition and final moisture content on sensory texture of cooked rice. *Cereal Chemistry, 76*, 56–62.

Park, J. K., Kim, S. S., & Kim, K. O. (2001). Effect of milling ratio on sensory properties of cooked rice and on physicochemical properties of milled and cooked rice. *Cereal Chemistry, 78*, 151–156.

Resurreccion, A. P., Juliano, B. O., & Tanaka, Y. (1979). Nutrient content and distribution in milling fractions of rice grain. *Journal of the Science of Food and Agriculture, 30*, 475–481.

Stermer, R. A. (1968). An instrument for objective measurements of degree of milling and color of milled rice. *Cereal Chemistry, 45*, 358–364.

Tran, T. U., Suzuki, K., Okadome, H., Homma, S., & Ohtsubo, K. (2004). Analysis of the tastes of brown rice and milled rice with different milling yields using a taste sensing system. *Food Chemistry, 88*, 557–566.

Wadsworth, J. I. (1994). *Rice: Science and technology* (1st ed., pp. 139–176). New York: Marcel Dekker, Inc.

Wang, Y., Wang, L., Shepard, D., Wang, F., & Patindol, J. (2002). Properties and structures of flours and starches from whole, broken, and yellowed rice kernels in a model study. *Cereal Chemistry, 79*, 383–386.

Yongsmith, B., Kitprechavanich, V., Chitradon, L., Chaisrisook, C., & Budda, N. (2000). Color mutants of *Monascus* sp. KB9 and their comparative glucoamylases on rice solid culture. *Journal of Molecular Catalysis B, 10*, 263–272.