

# Distribution of Amylose, Nitrogen, and Minerals in Rice Kernels with Various Characters

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The distribution of chemical constituents is known not to be even within a rice kernel. To improve the eating quality of rice or to give it some special traits by adjusting the milling intensity, we investigated the distribution of amylose, nitrogen (N), and specific minerals (P, K, Mg, Ca, and Mn) in rice kernels of 11 cultivars with various characteristics cultivated under similar conditions. The distributions of these constituents were determined using flour samples prepared consecutively by abrasive milling from the outer to the inner portions of hulled rice. In all the cultivars tested, N and the minerals were found to be more abundant in the outer than in the inner portion, but amylose was rich in the inner portion. P, Mg, K, and Mn were extremely rich in the outer portion, while N and Ca were only relatively rich there. Koshihikari, which is the most popular cultivar in Japan because of its excellent eating quality, showed the highest Mg/K ratio in the outermost portion of polished rice. The color of flour samples became pure white going from outside portions toward the center of the kernel, even if the sample was from red rice or purple-black rice because only the surface of hulled rice contains pigments. These findings suggest that the outer portion contains various compounds other than starch and the inner portion contains relatively pure starch. Rice palatability and other characteristics can be improved through controlling the degree of milling using the biased distribution of chemical constituents within a rice kernel.

KEYWORDS: Amylose; aromatic rice; distribution; minerals; nitrogen; purple-black rice; red rice

# INTRODUCTION

The average production of rice per year in the world during 1997–1999 amounted to 585 million metric tons, nearly all used for human consumption (1, 2). The production of wheat and corn amounted to 596 and 600 million metric tons respectively, but 20% of the wheat and 65% of the corn went to animal feed. Thus, rice is the world's number one human food crop. In addition, cultivated rice has as large a divergence in grain characteristics as in morphological and ecological characteristics (3).

Recently in Japan and also in other countries, rice consumers have been requesting a wide range of added values for this staple food. These food characteristics include, for example, food texture (stickiness, hardness, etc.), food nutrients and constituents (protein, amylose, allergens, etc.), and aroma, color, size, and shape of the kernels. Since rice, however, originally has had a diverse variation in kernel characteristics, rice breeders have tried to incorporate these kernel characteristics of rice and have developed some novel cultivars promising to satisfy consumers' demands (4, 5). In addition, several rice cultivars with red, purple-black, and other colored kernels have attracted much attention, not only from rice consumers, but also from rice growers and processors in many districts in Japan. This interest has resulted in the emergence of many kinds of secondary products (colored noodles, cakes, alcoholic beverages, etc.) from these rice kernels and ultimately in the promotion of regional social activities (for example, rice festivals within a particular region or with other regions) (6, 7).

It is obviously essential to have good eating quality in the rice cultivars with new kernel characteristics. Many studies have indicated that the amylose and nitrogen (N) content in rice kernels were the principal chemical constituents affecting eating quality (8, 9). Most of these studies, however, examined the content of these constituents using one of a whole grain of hulled (brown) rice kernel or milled rice kernel. Rice, like other cereals, does not show a homogeneous structure in its hulled rice kernel. Instead, the rice kernel is differentiated into zones, from its outer (surface) to inner (central) portions. That is, the distribution of chemical constituents differs from the outer to the inner portions of the rice kernel. The influences of the milling intensity to rice quality have been attracting our attention for a long time (10-24).

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Table 1. Profiles and Characteristics of the Hulled Rice of the 11 Cultivars Us	sed
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cultivars	days to heading	characteristics and origin <sup>a</sup>	length/width ratio	1000 grain weight (g)	thickness <sup>b</sup> (mm)					
		Nonalutinous								
Koshihikari	95	common, improved	1.72	22.2	1.8					
Akitakomachi	92	common, improved	1.75	22.5	1.8					
Nakateshinsenbon	107	common, improved	1.87	21.1	1.8					
Miyakaori	92	aromatic, improved	1.74	21.3	1.8					
Hieri	110	aromatic, partly improved	1.49	25.2	1.9					
Sari Queen	114	aromatic, long-grain, improved	2.76	15.8	1.5					
Akamai	121	red rice, indigenous in Okayama Pref.	1.85	21.1	1.7					
Hoshiyutaka	119	high amylose, long-grain, improved	2.34	17.9	1.5					
Glutinous										
Tanchomochi	103	common, improved	1.77	22.2	1.8					
Akamochi	119	red rice, indigenous in Nagasaki Pref.	1.79	18.5	1.7					
Kuromai	104	purple-black rice, partly improved in China	2.59	19.0	1.5					

<sup>a</sup> The 10 cultivars except Kuromai origining in Japan. <sup>b</sup> Determined by passing through sieves of different slit sizes.

In the present study, we examined the special distribution of amylose, N, and some minerals within a hulled rice kernel, from the outer to inner portions, and their variations in new rice cultivars. Hulled rice kernels are generally milled with a definite degree of intensity, depending on the intended purpose (20). In this context, the information from the present study should be useful because the chemical compositions in milled rice kernels can be regulated by adjusting the milling intensity, as well as by breeding and/or cultivation practices. Particularly in rice cultivars with colored kernels, it is important to observe whether the colored portion differs markedly relative to the kernel surface. We thus examined the distribution of color characteristics in the hulled rice kernels from cultivars with colored kernels.

## MATERIALS AND METHODS

Plant Materials. We used eight nonglutinous rice cultivars and three glutinous rice cultivars in this study. Table 1 shows their agronomic profiles and other characteristics. Koshihikari, Akitakomachi, and Nakateshinsenbon are the leading Japanese rice cultivars with good eating quality. Miyakaori and Hieri are japonica-type aromatic rice cultivars. Sari Queen is also an aromatic rice cultivar but is an indicatype bred from a cross between Nipponbare (japonica-type) and Basmati 365 (indica-type from Punjab). Akamai, Akamochi, and Kuromai have genetically controlled red or purple-black hulled rice. The former two red rice cultivars have tannin pigments and are not as a weedy type as the red rice in the USA or Brazil (25), but indigenous cultivars. Akamai has been cultivated at a Shinto Shrine in Japan for over 1000 years for religious purposes (7). The last cultivar, Kuromai, has anthocyanin as the predominant pigment. Kuromai is an indica-type and originated in China (7). Hoshiyutaka was bred as a long-grained and high-amylose type for fried rice, rice curry, or paella. Tanchomochi is a common glutinous cultivar.

In 1992, these eleven cultivars were seeded in seed boxes on April 28 and transplanted at a density of three plants per hill to the rice fields of Hiroshima Prefectural University, Shobara, Hiroshima, Japan, on May 29. Inter-row spacing was 30 cm, and inter-plant spacing was 15 cm in the paddy field. All fertilizers were applied as basal dressing at the ratio of N:P:K =  $5:8:8 \text{ g m}^{-2}$ . The harvested and dried hulled rice was passed through sieves of different sizes (**Table 1**) to remove immature kernels, and damaged kernels were removed with tweezers.

**Flour Preparation.** Two hundred grams of hulled rice were milled abrasively by a testing mill (TM5, SATAKE Co. Ltd., Japan) with different milling times. A fraction of flour was collected by milling from 100% (w/w) down to 91% of the hulled rice kernels and was designated as F0 in this study. This F0 fraction roughly corresponded to the bran layer of hulled rice. Similarly, fractions of flour were consecutively collected from 91% to 86% (F1), 86% to 81% (F2), 81% to 76% (F3), 76% to 71% (F4), and 71% to 66% (F5), that is, from the

outer to inner portions of hulled rice kernels. The residual central portion of the hulled rice (F6) and also 200 g of hulled rice as a whole kernel were pulverized completely with a Retsch ultracentrifugal mill (Mitamura Riken Kogyo co., Japan). The F0 fraction sometimes contained a small amount of broken rice.

**Method of Constituents Analyses.** For amylose analyses, rice flour was diluted in 1 N KOH for a night at cool temperature, and its amyloseiodine was analyzed by automated colormetric procedure (Auto-analyzer 2, Method No. 185-72A, Technicon Co. Ltd., USA). For N and P content, rice flour was digested with sulfuric acid and potassium sulfate by the Kjeldahl method and analyzed by the sodium salicylate method and the molybdated antimony method, respectively, using the same procedure (Auto-analyzer 2, Method No.334-74A/A). For K, Mg, Ca, and Mn content, extracts from fractions dissolved in 0.34N HCl were analyzed by Polarized-Zeeman Atomic Absorption Spectrophotometry (Z8000, HITACHI Co. Ltd., Japan) (26). For Ca, the lanthanum chloride solution was added to control interferences with P.

**Color Measurements.** The seven fractions from six cultivars were tightly bagged in plastic bags (0.04 mm thick), and the Hunter  $L^*$ ,  $a^*$ , and  $b^*$  values of reflected color were measured using a colorimeter (CR-200, Minolta Co. Ltd., Japan) with eight repetitions. The hue angle  $H^*$  was determined as arc tan ( $b^*/a^*$ ). The negative values of the hue angle were transferred to the first and second quadrants to obtain yellow tones (27).

#### **RESULTS AND DISCUSSION**

Cultivar Differences in the Constituents of Whole Hulled **Rice.** Table 2 shows the content of amylose, N, and minerals and the Mg/K ratio in whole hulled rice kernels and in each fraction. The 11 cultivars showed wide variations in their amylose, N and mineral content. Three cultivars with good eating quality, Koshihikari, Akitakomachi, and Nakateshinsenbon, showed intermediate amylose content, 17.0-18.4% (w/ w), while Hoshiyutaka showed the highest amylose content, 27.9%. The Mn content showed the widest variation, from 2.45 (Sari Queen) to 5.08 mg/100 g (Hoshiyutaka), among the five minerals. Kuromai showed the highest content of N and all the minerals except Mn. Generally, it is apparent that most minerals are rich in colored rice cultivars. People have used purple-black rice or red rice in medicinal diets from ancient times in China and Nepal (7). Chinese rice breeders have noticed that purpleblack rice has high levels of minerals and anthocyanin that may be good for one's health. Yang et al. (28) analyzed Fe, Mn, Cu, and Zn in polished rice grains of 285 cultivars from China and elsewhere, and red rice cultivars were reported to be richer in Zn than white rice cultivars. The variations in minerals that we have shown in the present study suggest that new types of rice rich in minerals may be bred for a healthy diet, such as protein-rich rice.

Table 2. Amylose, N, and Mineral Content and the Mg/K Ratio of Whole Hulled Rice and Different Portions of Hulled Rice<sup>a</sup>

				content	db	-					alativa (	0/) to b.	بالمط الم		
cultivar portion	amylose (%)	N (%)	P (ma/100 a)	Mg (ma/100 a)	K (ma/100 a)	Ca (mg/100 g)	Mn (ma/100 a)	Mg/K ratio	aml	N	P	%) to ni Ma	Illea rice	e Ca	Mn
portion	(/0)	(70)	(ing/100 g)	(119,100 9)	(119/100 9)	Koshihikari	(iiig/100 g)	1010	unn.		•	mg		00	
HR <sup>a</sup>	18.0	1.543	361.5	151.0	267.9	10.61	2.79	1.81	100	100	100	100	100	100	100
F0	2.4	3.025	2519.3	1192.1	1946.1	18.05	17.69	1.97	13	196	697	789	726	170	634
F1 F2	8.2 11.9	3.339	1598.8	/41.6	1143.8	14.93	8.66 1 19	2.09	45 66	216	442 176	491 192	427	141	310
F3	14.4	2.638	242.1	90.2	168.2	8.18	1.97	1.72	80	171	67	60	63	77	71
F4	16.0	2.066	164.0	43.1	100.1	6.47	1.33	1.39	89	134	45	29	37	61	48
F5	17.4	1.758	115.0	23.6	70.5	5.60	1.00	1.08	97	114	32	16	26	53	36
F6	20.4	0.989	60.7	6.2	42.7	4.54	0.73	0.47	113	64	17	4	16	43	26
סוו	17.0	1 207	2E2 (	120 (	202.4	Akitakomach	i 2.00	1 5 2	100	100	100	100	100	100	100
F0	2.9	2.761	2346.4	1073.0	293.0	9.92 16.97	2.90	1.52	100	215	664	774	699	171	601
F1	8.0	2.844	1528.1	673.0	1206.7	16.08	9.47	1.79	47	221	432	486	411	162	318
F2	11.5	2.692	810.0	334.8	630.3	16.20	5.81	1.71	68	209	229	242	215	163	195
F3 F4	14.5 16.4	2.193	320.2 152.2	116.9	247.4 101.0	9.42	2.52	1.52	85 96	170 131	/13 /13	84 25	84 37	95 63	85 11
F5	17.5	1.326	92.8	16.4	69.3	5.45	0.97	0.76	103	103	26	12	24	55	33
F6	19.1	0.824	57.1	4.6	49.1	4.41	0.72	0.30	112	64	16	3	17	44	24
						Nakateshinsent	oon								
HR	18.4	1.442	346.9	134.2	290.5	11.66	2.94	1.49	100	100	100	100	100	100	100
F0 F1	2.6	2.985	2345.0	1050.6	2066.3	18.31	18.97	1.64	14	207	6/6 425	/83	/11 /17	15/	645 207
F2	12.6	2.973	666.3	266.9	525.8	16.82	4.19	1.63	68	206	192	199	181	144	143
F3	15.5	2.490	233.8	80.4	177.9	9.10	1.94	1.45	84	173	67	60	61	78	66
F4	17.7	1.906	142.1	31.3	90.7	6.75	1.23	1.11	96	132	41	23	31	58	42
F5 F6	18.5	1.690	113.3 59.7	20.7 4.4	/0.5 44 1	6.38 4.68	1.11	0.94	101 114	66	33 17	15	24 15	55 40	38 26
10	20.7	0.750	57.7	7.7	11.1	Miyakaori	0.70	0.52	114	00	17	5	15	-10	20
HR	16.2	1.875	409.3	144.6	276.2	10.94	2.78	1.68	100	100	100	100	100	100	100
F0	2.4	3.244	2284.1	1020.0	1950.6	19.54	16.98	1.68	15	173	558	705	706	179	611
F1	6.4	3.419	1843.1	807.9	1427.0	15.34	9.35	1.82	39	182	450	559	517	140	336
FZ F3	10.0	3.430 3.044	385.7	450.6 161.2	774.7 286.2	17.82	5.41 2.51	1.87	61 82	183	255 94	312 111	280 104	103	195
F4	15.2	2.529	165.1	41.5	89.6	6.98	1.16	1.49	94	135	40	29	32	64	42
F5	16.8	1.933	105.2	23.2	56.8	6.32	0.93	1.31	104	103	26	16	21	58	33
F6	18.8	1.321	67.0	8.5	32.2	5.05	0.79	0.85	116	70	16	6	12	46	28
ЦD	20.5	1 /21	250.7	122.2	201 <i>I</i>	Hieri	2 7 2	1 5 1	100	100	100	100	100	100	100
F0	20.5	2.743	2326.1	1025.8	201.4	17.99	16.29	1.65	100	100	648	775	711	166	599
F1	9.6	3.176	1374.8	546.1	1073.0	21.20	7.89	1.64	47	222	383	413	381	195	290
F2	14.5	2.881	660.6	252.8	509.6	17.02	4.23	1.60	71	201	184	191	181	157	156
F3 F4	17.9	2.379	305.3 212 7	112.2 59.3	222.7 132.6	10.53	2.33	1.62 1.44	87 94	166 143	85 59	85 45	/9 47	97 72	86 61
F5	20.3	1.754	153.8	34.0	88.2	6.61	1.31	1.24	99	123	43	26	31	61	48
F6	23.1	0.939	65.7	5.9	37.5	4.82	0.83	0.51	113	66	18	4	13	44	31
						Sari Queen									
HR	18.8	1.660	377.9	138.0	267.9	13.35	2.45	1.66	100	100	100	100	100	100	100
FU F1	3.2 6.7	2.713	2301.6	983.1 716.9	1841.0 1311.2	23.24	14.74	1.72	36	103	609 421	712 519	087 489	1/4	602 358
F2	9.5	2.882	1224.3	480.9	864.0	23.90	5.66	1.79	50	174	324	348	323	179	231
F3	15.5	2.722	686.0	275.9	495.1	17.25	3.36	1.79	82	164	182	200	185	129	137
F4 F5	17.8	2.285	244.7 1717	79.4 29.0	152.8	10.10	1.57	1.67	95 103	138	65 37	58 21	57 25	/6 6/	64 15
F6	21.6	1.216	69.4	6.7	32.5	6.28	0.71	0.66	115	73	18	5	12	47	29
						Akamai									
HR	21.9	1.747	372.7	138.8	273.5	14.48	4.64	1.63	100	100	100	100	100	100	100
F0	2.7	2.696	1989.4	859.6	1665.2	21.68	26.06	1.66	12	154	534	619	609	150	562
F1 F2	7.0 12.4	3.208 3.194	1//5.9 1173 0	/4/.2 485.4	1376.4	22.38 21.85	15.75 8.91	1.75 1.83	32 57	184 183	476 315	538 350	503 312	155 151	339 192
F3	16.8	3.218	511.9	192.8	342.4	15.61	4.45	1.81	77	184	137	139	125	108	96
F4	19.7	2.856	259.5	72.7	137.8	10.57	2.73	1.70	90	163	70	52	50	73	59
F5 F6	21.8	2.358	163.9	34.7	/3./	8.58 6.15	1.98 1.10	1.51	99 114	135	44 19	25	2/	59 12	43
10	23.0	1.244	07.0	0.5	ZJ.7	U.IJ	1.17	0.07	114	/ 1	10	J	7	42	20
HR	27.9	1,294	345.7	119.9	283.5	13.52	5.08	1,36	100	100	100	100	100	100	100
F0	4.3	2.704	2261.7	921.3	1974.2	23.28	29.74	1.50	16	209	654	768	696	172	585
F1	13.7	2.670	1331.4	533.7	1127.0	26.20	15.27	1.52	49	206	385	445	398	194	301
F∠ F3	20.3 26.1	2.351 1.988	709.2 320.4	207.4 90.1	008.4 221 1	25.07 13 22	10.21 4.52	1.41 1 31	/3 94	182 154	223 92	223 75	215 78	182 98	201 80
F4	28.4	1.647	173.5	35.3	109.6	9.17	2.79	1.04	102	127	50	29	39	68	55
F5	29.8	1.383	117.1	16.3	70.0	7.60	1.98	0.75	107	107	34	14	25	56	39
F6	31.1	0.897	64.6	2.7	40.7	5.45	1.30	0.21	111	69	19	2	14	40	26

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	content db																	
cultivar	amylose	Ν	Р	Mg	К	Са	Mn	Mg/K	relative (%) to hulled rice					;				
portion	(%)	(%)	(mg/100 g)	ratio	aml.	Ν	Р	Mg	Κ	Са	Mn							
						Tanchomoch	i											
HR	0.7	1.592	372.6	140.8	303.6	12.29	3.50	1.49	100	100	100	100	100	100	100			
F0	0.7	2.943	2422.7	1014.6	2014.6	20.20	21.76	1.62	97	185	650	721	664	164	622			
F1	1.1	3.279	1747.9	689.9	1377.5	15.18	11.08	1.61	156	206	469	490	454	124	317			
F2	0.7	3.192	1098.0	421.9	874.2	18.61	7.73	1.55	101	201	295	300	288	151	221			
F3	0.7	2.799	423.2	142.4	299.0	12.67	3.15	1.53	94	176	114	101	98	103	90			
F4	0.7	2.710	415.3	125.6	272.9	11.76	2.91	1.48	93	170	111	89	90	96	83			
F5	0.6	2.110	133.7	38.8	99.6	8.00	1.54	1.25	91	133	36	28	33	65	44			
F6	0.7	1.047	28.2	5.0	37.3	5.11	0.77	0.43	106	66	8	4	12	42	22			
						Akamochi												
HR	0.8	1.746	394.2	141.4	337.8	15.62	4.30	1.35	100	100	100	100	100	100	100			
F0	0.6	3.016	2184.7	894.4	1911.2	24.59	22.18	1.51	78	173	554	633	566	157	516			
F1	0.7	3.348	1528.8	587.6	1220.2	26.98	11.35	1.55	81	192	388	416	361	173	264			
F2	0.7	3.100	848.7	312.4	670.8	27.01	6.82	1.50	84	178	215	221	199	173	159			
F3	0.7	2.852	388.1	111.2	276.5	14.74	3.56	1.29	85	163	98	79	82	94	83			
F4	0.7	2.408	178.9	41.3	137.7	9.88	2.29	0.96	85	138	45	29	41	63	53			
F5	0.7	2.016	101.5	17.2	89.1	8.30	1.78	0.62	91	115	26	12	26	53	41			
F6	0.8	1.217	41.3	2.3	53.0	5.74	1.17	0.14	103	70	10	2	16	37	27			
						Kuromai												
HR	0.8	2.038	449.8	171.8	352.8	16.47	3.89	1.57	100	100	100	100	100	100	100			
F0	0.7	3.169	2092.3	893.3	1712.4	25.07	20.63	1.68	91	155	465	520	485	152	530			
F1	1.0	3.404	1852.2	731.5	1396.6	21.50	11.23	1.68	130	167	412	426	396	131	289			
F2	0.7	3.311	1249.2	502.2	938.8	22.45	6.43	1.72	90	162	278	292	266	136	165			
F3	0.7	3.160	795.2	303.5	582.7	17.32	3.58	1.68	86	155	177	177	165	105	92			
F4	0.7	2.993	489.1	173.1	336.9	12.19	2.20	1.65	81	147	109	101	95	74	57			
F5	0.7	2.669	243.4	79.1	167.5	8.38	1.35	1.52	84	131	54	46	47	51	35			
F6	0.7	1.518	42.9	8.2	51.1	4.61	0.71	0.52	91	74	10	5	14	28	18			

<sup>a</sup> HR: hulled rice. Ratio of milling: F0, 91–100% (bran); F1, 86–91%; F2, 81–86%; F3, 76–81%; F4, 71–76%; F5, 66–71%; F6, 0–66% (inner portion). F0 contained a small amount of broken rice. Mg/K ratios are shown in chemical equivalence.

**Distribution of Constituents among Different Fractions of a Hulled Rice Kernel.** The relative values (fraction/whole grain) of amylose, N, and minerals in each of the 7 fractions are shown in **Table 2** and the average relative values among 11 cultivars are shown in **Figure 1**.

For all the eight nonglutinous cultivars, amylose was rich in the fractions of the inner kernel parts. For all the 11 cultivars, the content of N and all minerals was highest in the fractions of the outermost part and lowest at the center of the kernels. This finding suggests that the starch content is highest in the inner parts because the ratio of amylose content to starch content (= amylose + amylopectin) is assumed to be homogeneous within a rice kernel (14). When the cut face of a rice grain was stained with iodine, two layers could be distinguished in a kernel (**Figure 2**): the inner layer turned purple with iodine, and the outer layer was difficult to stain. This finding indicates that the outer layer contains compounds other than starch in agreement with Son et al. (19).

In contrast with the distribution of amylose, the content of N and all minerals decreased from the outermost fraction to the central fraction of a kernel in all cultivars. This trend was previously reported (*10*, *22*). In the case of P, Mg, K, and Mn content, extremely biased distributions were observed within hulled rice. The mineral content began to decline immediately from F0 (bran) and showed very low values at F6 (the central part). For example, the Mg content in the F0 (bran) of Koshihikari was about 1192.1 mg/100 g, but in F6 it was only 6.2 mg/100 g. The N and Ca content for F1 and F2, however, were equal to or higher than that for F0 (bran). The Ca content showed a less biased distribution than Mg. The different pattern of declining content in N and Ca may indicate that N and Ca are essential for the inner cells to grow. Yanatori (*15*), however, reported that K and Ca translocation finished at the early

ripening stage in rice in a study on the accumulation pattern of N and minerals in grains from the early ripening to harvesting stages.

The Mg/K ratio showed a wide divergence among cultivars and fractions (Figure 3). Horino et al. (29) investigated the chemical constituents among many species and cultivars of cereals (rice, wheat, barley, sorghum, and so on), buckwheat, and pulses. In rice, Horino and Okamoto (26) demonstrated that the content of N, K, Ca (all negatively), and Mg (positively) in the hulled or white rice grain correlated closely with the sensory test score for the overall quality (palatability) of cooked rice. Koshihikari, which is the most popular cultivar in Japan because of its excellent eating quality, showed the highest Mg/K ratio in the outermost layer of polished rice (the 91-86% fraction). Akitakomachi and Nakateshinsenbon, which are also evaluated as good eating quality rice cultivars, showed the second highest Mg/K ratio in the area where one makes direct contact with one's tongue to taste, namely, the outermost layer of polished rice. It is important to clarify both the genetic differences in constituents of hulled rice and the distribution pattern within the grain, and also the effects of weather conditions and fertilizer application.

Given the difference in the content of the constituents, hulled rice can be said to be composed of many layers. Hulled rice is technically the fruit of the rice plant, but is in its entirety a seed covered with a thin pericarp. The testa that covers the seed is very thin, too, inside of which the endosperm and embryo exists (30). Wadsworth (20) demonstrated that other substances not examined in the present study, such as fat, thiamine, riboflavin, and niacin, also decreased progressively from the outside parts toward the center of hulled rice.

**Color of Flours. Figure 4** shows the reflected color of flour from different portions of the hulled rice of six cultivars. From



**Figure 1.** Average relative values (%, fraction/whole grain) for 11 cultivars for amylose, N, and mineral content in each of the 7 fractions of hulled rice. The findings for amylose were excluded for the three glutinous cultivars. The horizontal axis shows the fractions of hulled rice kernels collected from the surface to the inner portion: 91–100% (F0, bran), 86–91% (F1, the outermost portion of polished rice), 66–86% (F2–5, middle portions), and 0–66% (F6, inner portion). The vertical bars show the standard deviations.

the fraction of the outermost part to the center,  $L^*$  values (brightness) and hue angle ( $0^\circ$  = reddish-purple,  $90^\circ$  = yellow,  $180^\circ$  = bluish-green,  $270^\circ$  = blue) increased for all the six cultivars measured. a\* values (positive means red and negative means green) and b\* values (positive means yellow and negative means blue) decreased for five cultivars except Kuromai. In the case of Kuromai,  $a^*$  was highest in F1, and  $b^*$  increased slightly from the outer to inner portions. Three noncolored rice cultivars (Koshihikari, Akitakomachi, and Hoshiyutaka), of both short and long kernel types, showed nearly similar readings for all the color characteristics. Kuromai, the red rice group (Akamai and Akamochi), and the noncolored rice group could be divided clearly. As for the  $a^*$  value, Akamai showed the highest level, and the values decreased from the outermost portion to the center for almost all the cultivars. Kuromai showed the highest  $a^*$  value at the F1 layer. As for the  $b^*$  value, the white rice group showed the highest and Kuromai showed the smallest value in all the layers. The hue angle showed an escalating change toward the



Figure 2. Mg/K ratios of 11 cultivars in each of the 7 fractions of hulled rice. The F0–6 is the same as that in Table 1.



Figure 3. Cross section of a Koshihikari kernel stained by iodine. The outermost portion was not stained because of the almost total lack of amylose



**Figure 4.** Reflected color of flours in different portions of the hulled rice of six cultivars. Standard deviations are not shown because they were much smaller than the sizes of the symbols.

center. The color of flour at F0 (bran) showed a yellowishbrown hue in white (common) cultivars, and a reddish-brown hue in Akamai and Akamochi, a purple-black hue in Kuromai, while at F6 (the innermost portion) all cultivars looked entirely pure white. When the grains were polished normally, they would turn white, losing their distinctive color. Colored rice, therefore, should be polished between 100% and 90% to retain the color in polished rice and polished to less than 80% to remove color.

The starchy endosperms in the whitest portion of the grain are generally favored because of faster cooking and because of the better taste and digestibility of cooked rice than hulled rice (20, 23). Rice is usually milled to about 90% of the weight of a hulled rice kernel prior to cooking, with some bran and germ often remaining in the surface grooves of a kernel. If polished a few percentages more, the polished rice becomes whiter in color and tastier. If polished more to about 60% or 70%, the resultant polished rice kernel consists of almost pure starch. The milling yield is often 60% or less, especially for rice for brewing high-class sake in Japan, and only white cores (milling yield of 30% to 40%) are used for extra high-class sake brewing. Water absorption is improved, and "hazekomi" (or the penetration of molded rice fungi into steamed rice) is promoted by milling the surface of rice grains to remove protein, lipids, ash, and other substances (31). In addition, to obtain highly nutritive rice flour, the outer layer is adequate because it is rich in protein, minerals, and vitamins.

Mineral content (on a dry weight basis) showed smaller variations among the cultivars in the fractions in the inner part in hulled rice, but larger in the outer part. Recently, the outermost portion of polished rice (F1 in this experiment) was shown to have an important role. Free amino acids, maltooligosaccharides, and free sugars were reported to be rich in the outermost layer of polished rice (32-34). In the case of aromatic rice, the content of 2-acetyl-1-pyrroline that is a key aroma compound decreased logarithmically from the surface to the center of rice grains (18). Therefore, rice palatability or other characteristics can be improved through controlling the degree of milling using these biased distributions of chemical constituents within a rice kernel. Either nutritious high-protein rice or low-protein rice can be obtained, suitable for the diets of those with renal disease or rice allergy, for example, using the above procedure.

Red rice is generally considered to be low-quality, although it commands a higher market price than white rice in Japan (7). Purple-black rice has attracted much attention as a natural resource for anthocyanin pigment. Recently we reported that the colored rice has antioxidative activity (35). In addition, rice germ and bran are reported to be an effective catalyst for GABA ( $\gamma$ -aminobutyric acid) from glutamate (36), and a health drink has been developed using germinated hulled rice grains of a giant-embryo cultivar. To breed new cultivars or develop new methods of utilization, we should reexamine many kinds of rice constituents and clarify both the genetic differences in the constituents of hulled rice and the distribution pattern within the grain.

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