

butyrate, 109-21-7; hexyl acetate, 142-92-7; butyl 2-methylbutyrate, 15706-73-7; propyl hexanoate, 626-77-7; butyl pentanoate, 591-68-4; pentyl butyrate, 540-18-1; hexyl propionate, 2445-76-3; butyl hexanoate, 626-82-4; hexyl butyrate, 2639-63-6; hexyl 2-methylbutyrate, 10032-15-2; hexyl pentanoate, 1117-59-5; hexyl hexanoate, 6378-65-0; pentyl propionate, 624-54-4; pentyl 2-methylbutyrate, 68039-26-9; pentyl 2-methylpropionate, 2445-72-9.

LITERATURE CITED

Bartley, I. M.; Hindley, S. J. *J. Exp. Bot.* 1980, 31, 449.
 Bertsch, W.; Zlatkis, A.; Liebich, H. M.; Schneider, H. J. *J. Chromatogr.* 1974, 99, 673.
 Brandt, E.; Heymann, E.; Mentlein, R. *Biochem. Pharmacol.* 1980, 29, 1927.
 Daemen, J. M. H.; Dankelman, W.; Hendriks, M. E. *J. Chromatogr. Sci.* 1975, 13, 79.
 De Pooter, H. L., State University of Gent, Faculty of Agricultural Sciences, Laboratory of Organic Chemistry, unpublished results, 1979.
 De Pooter, H. L.; Dirinck, P. J.; Willaert, G. A.; Schamp, N. M. *Phytochemistry* 1981, 20, 2135.
 De Pooter, H. L.; Montens, J. P.; Dirinck, P. J.; Willaert, G. A.; Schamp, N. M. *Phytochemistry* 1982, 21, 1015.
 Dirinck, P. J.; De Pooter, H. L.; Willaert, G. A.; Schamp, N. M. *J. Agric. Food Chem.* 1981, 29, 316.
 Eriksson, C. E. In "Progress in Flavour Research"; Land, D. G.; Nursten, H. E., Eds.; Applied Science Publishers, Ltd.: Barking, England, 1979; p 159.
 Knee, M.; Hatfield, S. G. S. *J. Sci. Food Agric.* 1981, 32, 593.

Kramer, A.; Twigg, B. A. "Fundamentals of Quality Control for Food Industry", revised and augmented ed.; Avi Publishing Co., Inc.: Westport, CT, 1966; p 142.
 Mazliak, P. In "The Biochemistry of Fruits and their Products"; Hulme, A. C., Ed.; Academic Press: London, 1970; Vol. 1, p 234.
 Novotny, M.; Lee, M. L.; Bartle, K. D. *Chromatographia* 1974, 7, 333.
 Paillard, N. *Phytochemistry* 1979, 18, 1165.
 Sae, S. W.; Kadoum, A. M.; Cunningham, B. A. *Phytochemistry* 1971, 10, 1.
 Shatat, F.; Bangerth, F.; Neubeller, J. *Gartenbauwissenschaft* 1978, 43, 214.
 Willaert, G. A.; Dirinck, P. J.; De Pooter, H. L.; Schamp, N. M. *J. Agric. Food Chem.* 1983, in press.
 Yamashita, I.; Iino, K.; Nemoto, Y.; Yoshikawa, S. *J. Agric. Food Chem.* 1977, 25, 1165.
 Yamashita, I.; Nemoto, Y.; Yoshikawa, S. *Agric. Biol. Chem.* 1975, 39, 2303.
 Yamashita, I.; Nemoto, Y.; Yoshikawa, S. *Phytochemistry* 1976, 15, 1633.

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Effect of Parboiling on Texture and Flavor Components of Cooked Rice

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Parboiling of *japonica* and *indica* rice affected the cooking properties of milled rice and resulted in a harder and less sticky texture of the cooked rice and reduced extractability of protein in the rice grain. During the parboiling process, the unbound lipid and free fatty acid in milled rice decreased, whereas the lipid bound to starch and protein and free phenolic acid increased. The results of GC analyses of the headspace volatiles of cooked rice and the steam-distilled volatiles of milled rice revealed that, after parboiling, *trans*-2-alkenals, *trans*-2,*trans*-4-decadienal, phenylacetaldehyde, and 4-vinylphenol had increased whereas 1-alkanols had decreased.

Parboiled rice has been conventionally produced by the process of presoaking, steaming, and drying with the use of rough rice. An effect of parboiling is improvement of the milling degree, and firmer and less cohesive qualities of cooked, parboiled rice were desired by people in many countries other than Japan. Consequently, parboiled rice is now produced in India, Thailand, the United States, Italy, and other countries by using modern mechanical methods. Japanese, however, prefer sticky cooked rice in general, and there is no necessity to parboil to improve the milling degree and other qualities in the case of *japonica* rice. Therefore, parboiled rice has not been commercially produced in Japan until now, and few investigations on parboiling of *japonica* rice have been reported.

Many studies concerning the changes in the rice grain resulting from parboiling have been done with the use of

indica rice samples. Subba Rao and Bhattacharya (1966) and Padua and Juliano (1974) reported the effect of parboiling on the thiamin content of rice. Bhat Sondi et al. (1980) reported the effect of processing conditions on the oil content of parboiled rice bran. Reyes et al. (1965) and Alary et al. (1977) investigated the effects of amylose on some characteristics of parboiled rice. Raghavendra Rao and Juliana (1970) investigated the effect of parboiling on some physical properties of rice, and they reported the protein fraction was less efficiently extracted from parboiled rice and the changes in amylographic characteristics on parboiling were influenced by the amylose content of the rice sample. Pillaiyar and Mohandoss (1981) reported that the cooking qualities of parboiled rice are related to the parboiling temperature, and Priestley (1976, 1977) suggested that amylose complexed with fatty acids induced by parboiling affected gelatinization and solubilization of starch.

These reports were concerned mainly with physico-chemical properties of parboiled rice, and no papers relating to the flavor of cooked, parboiled rice have been presented. This work was conducted on both parboiled *japonica* and *indica* rice samples to investigate the effect

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of parboiling on the texture and flavor of cooked rice and also on some chemical components of rice grain.

MATERIALS AND METHODS

Materials. Samples of Nakateshinsemon variety of rice (*Oryza sativa* L. *japonica*) and Bluebonnet variety of rice (*Oryza sativa* L. *indica*) harvested in Hiroshima prefecture, Japan, and that of Koshihikari variety of rice (*Oryza sativa* L. *japonica*) harvested in Niigata prefecture, Japan, were used.

Parboiling. In Japan, rice commercially circulates as brown rice. Therefore, brown rice samples of the above-mentioned three varieties were parboiled. Only the Bluebonnet sample was parboiled by using both brown and rough rice. An experimental process line was used for parboiling of these rice samples. Brown or rough rice was soaked in water at 50 °C under atmospheric pressure for 170 min and steamed at 115 °C under 0.5 kg/cm² for 15 min. After the rice was aerated at 45 °C for 7 min until the moisture content had decreased to 29%, the steamed rice was dried in two steps, that is, first at 50 °C for 10 h to a 20% moisture content and second at 30 °C for 10 h up to a 15% moisture content.

The raw Bluebonnet rice sample was dehulled and milled with a Satake Test Mill Model TM 05. Other raw and parboiled brown rice samples were milled with a Satake Two-in-One Pass Rice Whitening & Caking Machine. The milling yield was 91–92% of the brown rice basis for each sample. The milled, parboiled rice thus obtained had a pale amber and transparent appearance, which indicated that it had been completely parboiled. The milled rice samples were stored at 4 °C in polyethylene film bags.

Physical Measurement. Cooking qualities of milled rice and textural characteristics of cooked rice were measured by the methods described in a previous paper (Tsugita et al., 1983). The experimental method for the former was based on the reports of Batcher et al. (1957) and Chikubu et al. (1960) and that for the latter on the paper of Okabe (1979).

Extractability of Protein. Brown and milled rice samples were crushed with a disintegrator to obtain the brown rice flour and milled rice flour through a 60-mesh sieve. The protein contained in the rice flour was extracted by a modification of the percolation system described by Cagampang et al. (1966). That is, 10 g of rice flour was defatted with diethyl ether, and then sea sand, Celite, defatted rice flour, and Celite, in that order, were packed into the percolation column (50 cm × 3.5 cm) plugged with glass wool. All layers except the sample were about 1 cm thick. The column was covered at the top with glass wool and was then leached successively with 1 L each of the three solvents: distilled water to extract albumin, 5% NaCl for globulin, and 60% v/v aqueous ethanol for prolamin. The residual rice flour was then taken out from the column, and glutelin was extracted from the rice flour with 0.1 N NaOH (500 mL) under stirring. These four extracts of protein and original rice flour were analyzed for Kjeldahl nitrogen.

Free Fatty Acids. The milled rice flour (100 g) prepared as described above was extracted with chloroform-methanol (2:1 v/v) according to the method of Yasumatsu and Moritaka (1964). The crude lipid was then treated according to the method of Lee and Mattick (1961) to obtain the free fatty acid fraction.

Fat by Hydrolysis. According to the method described by Yasumatsu and Moritaka (1964), the milled rice flour (20 g) was extracted with diethyl ether and petroleum ether successively, each for 30 h, by using a Soxhlet apparatus, to obtain the unbound lipid fraction. The rice flour free

from unbound lipid was then hydrolyzed with diluted hydrochloric acid (1:3), neutralized, dried at 50 °C, and then extracted with diethyl ether to obtain fat by hydrolysis according to the method of Taylor and Nelson (1920).

Lipid Bound to Protein. This was estimated by the modified method of Shimada et al. (1979). The milled rice flour (50 g) was extracted with water-saturated butanol (200 mL) for 2 h with stirring and then centrifuged. This treatment was repeated 3 times. The combined supernatant was concentrated and extracted with diethyl ether to obtain the unbound lipid fraction. The butanol-extracted residue was air-dried, suspended in 500 mL of 0.1 N Na₂CO₃-NaHCO₃ buffer solution (pH 9.93) and then incubated with Pronase P (70 mg, Kaken Kagaku, Tokyo) at 37 °C for 24 h. The hydrolysis degree of protein with this incubation was 62–64%, when calculated as the ratio of 3.3% trichloroacetic acid soluble nitrogen to total nitrogen. After the incubation, the mixture was lyophilized, extracted again with water-saturated butanol, and centrifuged. The supernatant was concentrated and then extracted with diethyl ether to obtain the lipid bound to protein.

Free Phenolic Acids. Free phenolic acids contained in the milled rice flour were extracted with 70% v/v aqueous methanol and analyzed by HPLC according to the method previously reported (Tsugita et al., 1983).

Headspace Volatiles of Cooked Rice. Japanese style cooked rice for headspace analysis was prepared according to the method previously reported (Tsugita et al., 1980), and headspace volatiles trapped by the Tenax GC trapping tube were directly injected into a gas chromatograph according to the procedure described in previous papers (Tsugita et al., 1979, 1980).

Steam-Distilled Volatile Concentrate of Milled Rice. Volatile concentrates of milled rice samples were obtained by the simultaneous steam distillation-ether extraction (SDE) method described in a previous paper (Tsugita et al., 1983) using the apparatus reported by Schultz et al. (1977).

GC and GC-MS Analysis. Analytical conditions for GC and GC-MS were the same as those reported in the previous paper (Tsugita et al., 1983).

RESULTS AND DISCUSSION

Physicochemical Characteristics. Table I shows the cooking qualities of milled rice and textural characteristics of cooked rice prepared from raw (unparboiled) and parboiled samples of Nakateshinsemon (*japonica*) and Bluebonnet (*indica*) rice. Milled, parboiled rice from a brown rice sample of Nakateshinsemon showed a significantly smaller expanded volume and water-uptake ratio than milled, unparboiled rice. Similar results have been reported by Raghavendra Rao and Juliano (1970) with the use of rough samples of *indica* rice. Cooked, parboiled rice had a harder, more cohesive, and less sticky texture than cooked, unparboiled rice in the case of both Nakateshinsemon and Bluebonnet. Cooked, parboiled and unparboiled Bluebonnet rice showed greater hardness and cohesiveness and less stickiness than in the case of Nakateshinsemon. There was no remarkable difference between the parboiled brown and parboiled rough Bluebonnet rice in the above-mentioned cooking properties.

Okabe (1979) reported a "texturogram" showing the relation between the textural characteristics of cooked rice and acceptability, as judged by a trained panel of Japanese. According to the method of Okabe (1979), cooked, unparboiled Nakateshinsemon rice was evaluated as being excellent for Japanese, and cooked, parboiled Nakatesh-

Table I. Difference of Cooking Qualities and Texture of Milled Rice among Unparboiled Rice and Parboiled Rice^a

property	unparboiled	parboiled brown rice	parboiled rough rice
Nakateshinsemon			
cooking qualities			
expanded volume, mL	33.1 ± 0.6	30.8 ± 1.0**	
water-uptake ratio	3.01 ± 0.13	2.74 ± 0.07*	
pH of residual water	6.43 ± 0.06	6.33 ± 0.06	
iodine blue value of cooking water (OD at 600 nm)	0.036 ± 0.003	0.033 ± 0.004	
solids in cooking water, g	0.212 ± 0.016	0.180 ± 0.014	
texture of cooked rice ^b			
hardness	3.04 ± 0.22	3.44 ± 0.17**	
stickiness	0.59 ± 0.19	0.35 ± 0.12*	
cohesiveness	0.632 ± 0.035	0.676 ± 0.017	
Bluebonnet			
texture of cooked rice ^b			
hardness	3.58 ± 0.388	4.62 ± 0.164**	4.55 ± 0.428**
stickiness	0.10 ± 0.049	0.05 ± 0.031*	0.05 ± 0.17*
cohesiveness	0.706 ± 0.022	0.767 ± 0.022	0.738 ± 0.080

^a The asterisk shows the significance of the difference between unparboiled rice and parboiled rice with the Student's *t* test [(*) *p* = 0.05; (**) *p* = 0.01]. ^b Texturometer unit.

Table II. Contents of Total Protein and Soluble Protein Fractions in Raw and Parboiled Rice (Nakateshinsemon)

protein fraction	protein content ^a and extraction efficiency ^b			
	brown rice		milled rice	
	raw, %	par-boiled, %	raw, %	par-boiled, %
total protein	7.29	7.13	6.14	6.08
soluble protein				
albumin	0.89	0.33	0.13	0.12
globulin	0.55	0.09	0.54	0.02
prolamin	0.13	0.06	0.16	0.04
glutelin	4.61	2.82	3.90	2.48
total	6.18	3.30	4.73	2.62
extraction efficiency	84.8	46.3	77.0	43.8

^a Crude protein percent in defatted rice flour. ^b (Total soluble protein/total protein) × 100.

insemon rice was slightly poor but acceptable, and further, both cooked, parboiled and unparboiled Bluebonnet rice were evaluated as being unacceptable for Japanese, though the latter was preferable to the former. This objective evaluation indicates the acceptability of parboiled *japonica* rice and the unacceptability of parboiled *indica* rice for Japanese, and these results also agree with the actual sensory evaluation by members of our laboratory for the respective cooked rice.

Nonvolatile Constituents. In order to investigate the factors involved in the above-mentioned changes of physicochemical properties on parboiling, some chemical constituents were analyzed.

Table II shows the effect of parboiling on the contents of total protein and soluble protein fractions in brown and milled Nakateshinsemon rice samples. The slight reduction of total protein content in both brown and milled rice after parboiling is considered to be caused by dissolution of water-soluble nitrogenous compounds during the soaking process of parboiling. The reduced extractability of protein on parboiling was shown in both brown and milled rice. Especially, the glutelin fraction, which is the principal protein of rice grain, was remarkably reduced in quantity. The reduced ratio of extractability was most pronounced in the globulin fraction. These changes in protein extractability resulting from parboiling are supposed to be caused by heat denaturation of protein, the greater adhesion/cohesion between starch granules and protein bodies in parboiled rice (Raghavendra Rao and

Table III. Changes in Lipid Composition on Parboiling (Nakateshinsemon)

lipid composition	lipid content, %, of milled rice	
	raw	parboiled
unbound lipid with ether and petroleum ether	0.479	0.421
free fatty acid	0.158	0.065
fat by hydrolysis	0.580	0.788
unbound lipid with water-saturated butanol	0.481	0.380
lipid bound to protein	0.132	0.166

Table IV. Amounts of Free Phenolic Acids in Raw and Parboiled Rice

phenolic acid	amount of free phenolic acid ^a in milled rice		
	raw	par-boiled brown rice	par-boiled rough rice
Nakateshinsemon			
<i>p</i> -hydroxybenzoic acid	41	111	
vanillic acid	154	303	
syringic acid	3	10	
caffeic acid	68	304	
<i>p</i> -coumaric acid	21	120	
ferulic acid	47	86	
Bluebonnet			
<i>p</i> -hydroxybenzoic acid	110	63	224
vanillic acid	107	276	592
syringic acid	50	26	70
caffeic acid	59	373	1458
<i>p</i> -coumaric acid	28	266	1826
ferulic acid	134	269	303

^a μg/100 g of rice flour.

Juliano, 1970), the interaction between protein and other components, and so on.

Changes in lipid composition in milled rice after parboiling are shown in Table III. Both the unbound lipid with diethyl ether and petroleum ether and that with water-saturated butanol in milled rice were reduced by parboiling. These results correspond to those of Bhat Sondi et al. (1980); i.e., the oil content of residual milled kernel was consistently lower after parboiling and that of rice bran was higher in parboiled than in raw rice bran. Table III also shows the decrease of free fatty acid, the

Table V. Relative Amounts of Identified Volatile Components of Cooked Rice

peak no., compound ^c	headspace analysis of cooked rice ^a						simultaneous distillation-extraction of boiled rice ^b					
	Koshihikari			Bluebonnet			Koshihikari			Bluebonnet		
	unpar-boiled	parboiled	unpar-boiled	parboiled brown rice	parboiled rough rice	parboiled	unpar-boiled	parboiled	unpar-boiled	parboiled brown rice	parboiled rough rice	
alkanals												
9, butanal	73	107	17	21	206							
13, pentanal	175	259	85	110	146							
24, hexanal	1421	1919	866	318	603							
35, heptanal	84	90	32	27	64							
50, octanal	57	50	33	18	46							
63, nonanal	50	188	37	27	57							
79, decanal	10	12	2	3	12							
alkanols												
39, <i>trans</i> -2-hexenal	12	16	3	9	14							
54, <i>trans</i> -2-heptenal	32	90	19	33	46							
67, <i>trans</i> -2-octenal	23	66	9	20	31							
84, <i>trans</i> -2-nonenal	4	23	trace	4	5							
106, <i>trans</i> -2, <i>trans</i> -4-decadienal	trace	45	trace	13	18							
aromatic aldehydes												
82 benzaldehyde	15	16	5	7	14							
95 phenylacetaldehyde	trace	3	trace	trace	15							
ketones												
7, acetone	32	75	9	29	49							
34, 2-heptanone	22	22	9	5	15							
49, 2-octanone	19	13	8	6	9							
56, 6-methyl-5-hepten-2-one	11	8	4	2	9							
62, 2-nonanone	2	trace	trace	trace	trace							
alkanols												
43, 1-pentanol	188	trace	42	trace	trace							
57, 1-hexanol	380	24	59	6	43							
70, 1-heptanol	24	12	5	2	10							
86, 1-octanol	7	3	trace	3	6							
96, 1-nonanol	trace	trace	trace	trace	8							
other alcohols												
69, 1-octen-3-ol	13	27	10	9	16							
108, benzyl alcohol	trace	trace	trace	trace	trace							
miscellaneous												
30, ethylbenzene	21	4	6	trace	trace							
42, 2-pentylfuran	83	302	92	100	175							
155, 4-vinylphenol												
total peak area ^d	3901	4757	1632	1280	2287							

^a Relative amount of each volatile component in the headspace vapor of cooked rice (peak area on the gas chromatogram). ^b Relative amount of each volatile component in the extract obtained by simultaneous distillation-extraction of boiled rice (peak area of each volatile component $\times 100$ /peak area of the internal standard). ^c All compounds were identified by GC and GC-MS analyses. ^d Including unidentified peaks on the gas chromatogram.

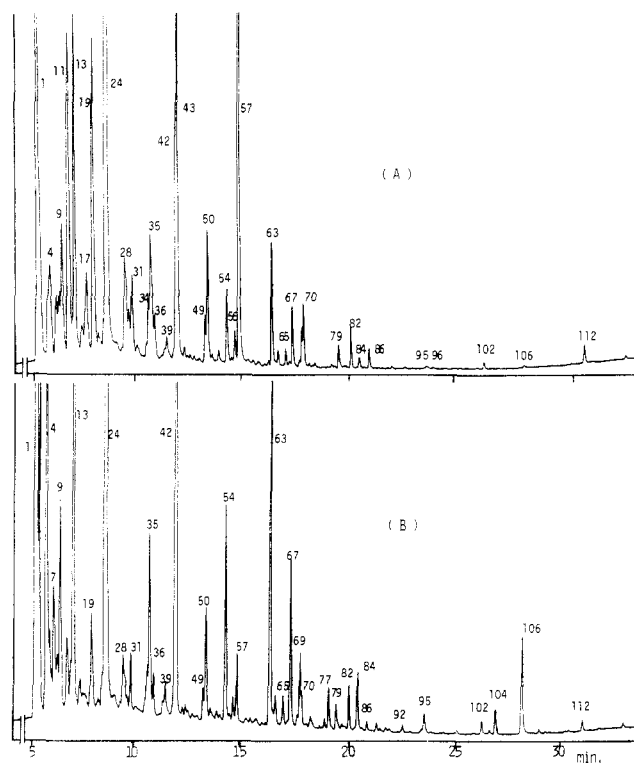


Figure 1. Gas chromatograms of headspace volatiles of cooked rice prepared from unparboiled (A) and parboiled (B) rice (Koshihikari).

increase of fat by hydrolysis and the lipid bound to protein. These results and reduction of protein extractability described above suggest that interaction between free fatty acid and starch and/or protein occurs on parboiling, and this interaction may partly account for the characteristic texture of cooked, parboiled rice.

Table IV shows free phenolic acids identified in milled rice flour of raw and parboiled rice and their amounts. Though a little decrease of *p*-hydroxybenzoic acid and syringic acid in parboiled Bluebonnet brown rice compared to the raw Bluebonnet rice was observed, an increase in other phenolic acids, especially *p*-coumaric acid, after parboiling was observed in milled samples of both Nakatshinsembon and Bluebonnet rice. The increase of phenolic acids was more remarkable in parboiled rough rice. *p*-Coumaric acid was tentatively detected in chaff and rice bran in a larger amount, and alkali-hydrolyzable bound phenolic acids were also detected in a larger amount in milled rice (Ohta et al., 1982). These results suggest that free phenolic acids are formed from bound phenolic acids occurring in the cell wall (Markwalder and Neukom, 1976; Harris and Hartly, 1980) on parboiling and that both these free phenolic acids and originally occurring free phenolic acids diffuse from chaff and bran into the inner layer of the rice grain during parboiling as in the case of thiamin (Pauda and Juliano, 1974). Since phenolic compounds have been reported to interact with protein in wheat flour (Gallus and Jennings, 1971), phenolic acids identified in this study may partly contribute to the characteristic texture of cooked, parboiled rice.

Volatiles of Cooked Rice. Since cooked, parboiled rice had a characteristic flavor, volatile components of cooked rice prepared from parboiled and unparboiled rice samples were analyzed and compared.

Figure 1 shows gas chromatograms of headspace volatiles in cooked, parboiled and unparboiled Koshihikari rice with the use of Tenax GC trapping and direct injection techniques (Tsugita et al., 1979, 1980). The gas chromatogram

pattern of samples of Nakatshinsembon rice was essentially the same as that of Koshihikari rice samples. The relative amounts of identified components in the gas chromatograms obtained for samples of Koshihikari and Bluebonnet rice are shown in Table V. In comparison with cooked, unparboiled rice, larger amounts of pentanal, hexanal, *trans*-2-alkenals, *trans*-2,*trans*-4-decadienal, and 2-pentylfuran and smaller amounts of 1-pentanol, 1-hexanol, and 1-heptanol were present in cooked, parboiled rice.

Table V also shows the relative amounts of identified components in the volatile concentrates obtained by the SDE method from parboiled and unparboiled Koshihikari and Bluebonnet rice. The similar tendency of changes in these volatiles to that of headspace volatiles was recognized. On the other hand, some middle- to high-boiling components, which were not detected or only detected in small amounts in the headspace volatiles, were found with the SDE method. 4-Vinylphenol, *trans*-2,*trans*-4-decadienal found, and phenylacetaldehyde were present in a larger amount in parboiled rice.

Among these identified volatile components, 4-vinylphenol is considered to be formed by heating from *p*-coumaric acid, which was present in parboiled rice in a larger amount (Table IV), and the formation of alkanals is considered to be caused by enzymatic reactions from lipid in rice grain during the soaking process of parboiling.

The cooking flavor of both parboiled and unparboiled samples of Bluebonnet rice was sensorially different from that of unparboiled Koshihikari rice whose cooking flavor was desirable for Japanese. However, the difference in gas chromatographic patterns of volatiles between cooked, unparboiled Koshihikari rice and cooked, parboiled or unparboiled Bluebonnet rice was not remarkable. These results suggest that the cooking flavor of rice is formed by a mixture of various volatile components and that the difference in cooking flavor between parboiled and unparboiled rice or the difference between *japonica* and *indica* rice is based on the proportions of volatiles constituting the respective flavor.

ACKNOWLEDGMENT

The Koshihikari rice sample was kindly supplied by the Niigata Food Research Institute.

Registry No. *p*-Hydroxybenzoic acid, 99-96-7; vanillic acid, 121-34-6; syringic acid, 530-57-4; caffeic acid, 331-39-5; *p*-coumaric acid, 7400-08-0; ferulic acid, 1135-24-6; butanal, 123-72-8; pentanal, 110-62-3; hexanal, 66-25-1; heptanal, 111-71-7; octanal, 124-13-0; nonanal, 124-19-6; decanal, 112-31-2; *trans*-2-hexenal, 6728-26-3; *trans*-2-heptenal, 18829-55-5; *trans*-2-octenal, 2548-87-0; *trans*-2-nonenal, 18829-56-6; *trans*-2,*trans*-4-decadienal, 25152-84-5; benzaldehyde, 100-52-7; phenylacetaldehyde, 122-78-1; acetone, 67-64-1; 2-heptanone, 110-43-0; 2-octanone, 111-13-7; 6-methyl-5-hepten-2-one, 110-93-0; 2-nanone, 821-55-6; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; 1-nonanol, 143-08-8; 1-octen-3-ol, 3391-86-4; benzyl alcohol, 100-51-6; ethylbenzene, 100-41-4; 2-pentylfuran, 3777-69-3; 4-vinylphenol, 2628-17-3.

LITERATURE CITED

- Alary, R.; Laignelet, B.; Feillet, P. *J. Agric. Food Chem.* **1977**, *25*, 261.
 Batcher, O. M.; Deary, P. A.; Dawson, E. H. *Cereal Chem.* **1957**, *34*, 277.
 Bhat Sondi, A.; Mohan Reddy, I.; Bhattacharya, K. R. *Food Chem.* **1980**, *5*, 277.
 Cagampang, G. B.; Cruz, L. J.; Espiritu, S. G.; Santiago, R. G.; Juliano, B. O. *Cereal Chem.* **1966**, *43*, 145.
 Chikubu, S.; Iwasaki, T.; Tani, T. *Eiyo to Shokuryo* **1960**, *13*, 137.
 Gallus, H. P. C.; Jennings, A. C. *Aust. J. Biol. Sci.* **1971**, *24*, 747.
 Harris, P. J.; Hartley, P. D. *J. Sci. Food Agric.* **1980**, *31*, 959.
 Lee, F. A.; Mattick, L. R. *J. Food Sci.* **1961**, *26*, 276.
 Markwalder, H. V.; Neukom, H. *Phytochemistry* **1976**, *15*, 836.

- Ohta, T.; Tsugita, T.; Kato, H., Department of Agricultural Chemistry, The University of Tokyo, Japan, unpublished results, 1982.
- Okabe, M. *J. Texture Stud.* 1979, 10, 131.
- Padua, A. B.; Juliano, B. O. *J. Sci. Food Agric.* 1974, 25, 697.
- Pillaiyar, P.; Mohandoss, R. *J. Sci. Food Agric.* 1981, 32, 475.
- Priestley, R. *J. Food Chem.* 1976, 1, 5.
- Priestley, R. *J. Food Chem.* 1977, 2, 43.
- Raghavendra Rao, S. N.; Juliano, B. O. *J. Agric. Food Chem.* 1970, 18, 289.
- Reyes, A. C.; Albano, E. L.; Briones, V. P.; Juliano, B. O. *J. Agric. Food Chem.* 1965, 13, 438.
- Schultz, T. H.; Flath, R. A.; Mon, T. R.; Egging, S. B.; Teranishi, R. *J. Agric. Food Chem.* 1977, 25, 446.
- Shimada, A.; Yazawa, E.; Yoshimatsu, F.; Kato, H.; Fujimaki, M. *Nippon Nogei Kagaku Kaishi* 1979, 53, 5.
- Subba Rao, P. V.; Bhattacharya, K. R. *J. Agric. Food Chem.* 1966, 14, 479.
- Taylor, J. C.; Nelson, J. M. *J. Am. Chem. Soc.* 1920, 42, 1726.
- Tsugita, T.; Imai, T.; Doi, Y.; Kurata, T.; Kato, H. *Agric. Biol. Chem.* 1979, 43, 1951.
- Tsugita, T.; Kurata, T.; Kato, H. *Agric. Biol. Chem.* 1980, 44, 835.
- Tsugita, T.; Ohta, T.; Kato, H. *Agric. Biol. Chem.* 1983, 47, 543.
- Yasumatsu, K.; Moritaka, S. *Agric. Biol. Chem.* 1964, 28, 257.

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Cooked Rice Aroma and 2-Acetyl-1-pyrroline

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The concentration of 2-acetyl-1-pyrroline has been determined in the steam volatile oils of 10 different varieties of rice. From these data the amount present in the cooked rice was calculated. This varied from less than 0.006 parts per million (ppm) for Calrose rice to 0.09 ppm for Malagkit Sungsong variety rice based on the dry weight of the rice. Odor panel evaluation described the odor of 2-acetyl-1-pyrroline as "popcorn"-like. Odor evaluation of the amount of popcorn-like odor in the different rice varieties ranked them in the general order of the concentration of this compound. Other odor quality evaluation tests confirmed the importance of this compound to the aroma of the more aromatic rice varieties.

Knowledge of the identities of the volatile aroma components of rice is important in the understanding of both human and insect perception of rice. Pest insects probably locate stored rice by keying in on the associated volatile (aroma) compounds. Volatile compounds found in cooked foods frequently occur in the "raw" foods also, although usually at a much lower concentration.

A considerable number of different varieties of rices are grown throughout the world. American consumers seem to prefer the more bland varieties such as the Texas Long Grain rice or Calrose rice. However, in Southeast Asia, India, and some Middle East countries, a number of more aromatic rices are highly favored and command much higher prices than the more bland varieties. A selection of these more aromatic rice varieties was studied by the authors and a potent aroma component, 2-acetyl-1-pyrroline, was identified for the first time (Buttery et al., 1982). The present work compares the concentration of this compound in the different rice varieties and reports some additional information on its chemical and odor properties.

The volatile components of rice have been studied previously by a number of researchers. Studies up until about 1978 were reviewed by Maga (1978). Some more recent studies include those of Yajima et al. (1978, 1979) and Tsugita et al. (1980).

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EXPERIMENTAL SECTION

Materials. Most rice varieties were obtained through the International Rice Research Institute (IRRI) in Manila, Philippines. These are 1981 crops of Azucena, IR841-76-1 (a line derived from Khao Dawk Mali 105), and Milagrosa from the Philippines, Basmati 370 from Pakistan, Hierl from Japan, Khao Dawk Mali 105 from Thailand, and Seratus Malam from Indonesia and the 1982 crop of Malagkit Sungsong from the Philippines. These were obtained as brown rices and milled in the laboratory removing ca. 10% of the outer layers. Calrose rice (milled) was obtained from local markets in Berkeley, CA, in 1982. Texas Long Grain rice (milled) obtained from the Comet Rice Mills in Houston, TX, and is probably Labelle variety.

Synthesis of 2-Acetyl-1-pyrroline. This followed very closely the method used by Büchi and Wüest (1971) for the synthesis of the related 2-acetyl-1,4,5,6-tetrahydropyridine. 2-Acetylpyrrole (1.7 g) in methanol solution (50 mL) was hydrogenated by using 5% rhodium on alumina catalyst (2.0 g) at room temperature under 10 psi of H₂ for 15 h with stirring. Filtration and removal of the solvent by distillation gave 1.8 g of the crude intermediate 2-(1-hydroxyethyl)pyrrolidine [cf. Hess (1915)]. This intermediate showed a mass spectrum with a molecular ion at 115 and other important ions at 70 (M⁺ - 45), 68, 97 (M⁺ - 18), and 82 (M⁺ - 33) and infrared and ¹H NMR spectra consistent with the structure of this compound. The 2-(1-hydroxyethyl)pyrrolidine (1.8 g) was added to a stirred suspension of silver carbonate on Celite (16 g) in benzene (100 mL) under a nitrogen atmosphere. The mixture was refluxed under nitrogen for 15 h. Filtration removal of the silver carbonate and concentration by distillation to 5 mL gave a benzene solution of 2-acetyl-1-pyrroline which was