Hooker, A. L. In "Proceedings of the Thirty-first Annual Corn Sorghum Research Conference", Chicago, 1977; pp 167–182.
Huggins, C.; Lapides, J. *J. Biol. Chem.* **1947**, *170*, 467–482.
Laemmli, U. K. *Nature (London)* **1970**, *227*, 680–685.
Lai, H.-Y.; Axelrod, B. *Biochem. Biophys. Res. Commun.* **1973**, *54*, 463–468.
Lipps, P. E. *Plant Dis.* **1983**, *67*, 102–104.
Lowry, O. H.; Rosebrough, N. J.; Farr, A. L.; Randall, R. J. *J. Biol. Chem.* **1951**, *193*, 265–275.
Merril, C. R.; Switzer, R. C.; VanKeuren, M. L. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 4335–4339.
Nicholson, R. L.; Moraes, W. B. C. *Phytopathology* **1980**, *70*, 255–261.
Orten, J. M.; Neuhaus, O. W. In "Human Biochemistry", 10th ed.; C. V. Mosby Co.: St. Louis, 1982; p 532–533.
Pastor-Corrales, M. A.; Frederiksen, R. A. In "Sorghum Diseases A World Review"; International Crops Research Institute for the Semi-Arid Tropics: Patancheru, A. P., India, 1980; pp 289–299.
Reid, L.; Bhaskar, K.; Coles, S. In "Mucus in Health and Disease-II"; Chantler, E. N., Elder, J. B., Elstein, M., Eds., Plenum Press: New York, 1982; pp 369–391.
Reid, L.; Clamp, J. R. *Br. Med. Bull.* **1978**, *34*, 5–8.
Weber, P. L.; Carlson, D. M. *Anal. Biochem.* **1982**, *121*, 140–145.
Zinn, A. B.; Marshall, J. S.; Carlson, D. M. *J. Biol. Chem.* **1978**, *253*, 6761–6767.

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Composition of Raw and Parboiled Rice Bran from Common Sri Lankan Varieties and from Different Types of Rice Mills

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The levels of protein, fat, crude fiber, starch, and ash in bran obtained from raw and parboiled rice belonging to six popular Sri Lankan varieties were determined. Also, the contents of these nutrients in raw and parboiled rice bran obtained from three types of rice mills, namely, traditional mill (Engelberg stell huller), semimodern mill (rubber roll sheller and steel huller), and modern mill (rubber roll sheller, separator, and a battery of abrasive and friction type polishers) were compared. Significant varietal influence on the chemical composition of bran was observed. In all varieties the parboiled rice bran contained, on an average, 26% higher fat than raw rice bran. Traditional and semimodern mills produced bran with high fiber and ash contents probably due to contamination with paddy husk. Contamination of bran with husk resulted in a reduction in the levels of protein and fat in both raw and parboiled rice bran. Even though the starch content was also reduced in parboiled rice bran obtained from the traditional mill due to husk admixture, this reduction was not observed in raw rice bran because of its contamination with portions of the starchy endosperm.

INTRODUCTION

Rice bran, which is a byproduct formed during polishing of dehusked rice, consists of the outer most layers of the rice grain, namely fragments of pericarp, tegmen, aleurone layer, the germ, and sometimes portions of the endosperm. The total bran constitutes 8–10% of the weight of rice. It is widely used as an animal feed and for oil extraction. It is also mixed to a limited extent in human food preparations.

The chemical composition of rice bran varies significantly among varieties (Mc Call et al., 1953; Limcango-Lopez et al., 1962). Also, parboiling results in compositional changes in rice bran (Houston et al., 1969). The composition of bran may also vary according to the type of machinery used for milling. In traditional types of rice mills where the operations of dehusking (removal of hulls from paddy) and polishing (removal of bran from brown rice) are not clearly demarcated, the bran gets mixed to varying amounts with paddy husk resulting in a poor quality byproduct with limited usage. On the other hand, in improved modern rice mills, processing is carried out in stages by separate machines and hence contamination of bran with husk is minimal.

Scientific data on the chemical composition of rice byproducts obtained from different sources become important in order to maximize their utilization. This study was undertaken to determine the influence of variety and machinery used for processing on the chemical composition of bran from raw and parboiled rice.

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MATERIAL AND METHODS

Freshly harvested paddy free from varietal admixture and foreign matter from six popular Sri Lankan varieties were used in the study. Bran from the different varieties were obtained by dehusking 200 g of samples of paddy by using a "Satake" laboratory dehusker and polishing the brown (unpolished) rice with a Mc Gill miller no. 2 to obtain a bran removal of 8 ± 0.5% by weight of brown rice. To obtain bran from different mills, 100 kg of samples of paddy belonging to the variety BG 276-5 were milled with the following types of machinery to obtain a bran removal of 8 ± 0.5%.

Traditional Mill. The paddy was milled with a steel huller (Engelberg) where both operations of dehusking and polishing were done in one pass. The byproduct formed during the milling operation was collected for analysis.

Semimodern Mill. The paddy was dehusked with a rubber roll sheller with husk aspirator and the brown rice containing 5% unhusked grains was polished with a steel

Table I. Composition of Raw and Parboiled Rice Bran from Six Popular Sri Lankan Varieties[a,b]

	protein		fat		starch		crude fiber		ash	
variety	raw	parboiled	raw	parboiled	raw	parboiled	raw	parboiled	raw	parboiled
B.G. 90–2	11.53[cd]	14.18[b]	26.17[a]	30.37[c]	25.76[ab]	18.65[ab]	9.90[c]	11.63[a]	10.85[d]	13.56[a]
B.G. 34–8	11.87[cd]	13.75[c]	23.71[b]	31.42[a]	29.10[a]	15.57[b]	10.49[b]	10.02[c]	12.21[a]	13.40[a]
B.G. 11–11	12.83[b]	15.05[a]	23.99[b]	30.92[b]	20.12[b]	18.96[ab]	12.33[c]	10.00[c]	10.78[d]	11.46[e]
B.G. 276–5	10.43[e]	13.25[d]	22.23[c]	30.14[c]	20.93[b]	17.95[b]	9.60[c]	11.05[b]	11.42[c]	12.73[b]
B.G. 400–1	11.94[c]	12.19[e]	23.64[b]	30.04[c]	22.42[b]	22.20[a]	10.81[b]	9.75[c]	11.79[b]	11.79[c]
B.G. 94–1	15.54[a]	13.22[d]	23.55[b]	28.55[d]	24.25[ab]	21.61[a]	10.00[c]	11.55[a]	11.64[be]	11.49[ce]

[a] Values given as g per 100 g of dry material. [b] Means within a column followed by the same letter are not significantly different at the 0.05 level according to DNMRT.

Table II. Composition of Raw and Parboiled Rice Bran from Different Types of Mills[a,b]

	protein		fat		starch		crude fiber		ash	
type of mill[c]	raw	parboiled	raw	parboiled	raw	parboiled	raw	parboiled	raw	parboiled
modern	10.04[b]	10.01[a]	23.36[a]	31.61[a]	26.90[a]	25.89[a]	12.59[c]	12.91[c]	14.26[b]	12.76[c]
semimodern	10.95[a]	8.99[a]	19.23[b]	19.70[b]	27.13[a]	24.44[b]	15.36[b]	15.87[b]	14.13[b]	15.03[b]
traditional	7.51[c]	7.30[b]	8.58[c]	6.64[c]	28.74[a]	20.22[c]	29.26[a]	30.86[a]	15.47[a]	20.40[a]

[a] Variety of paddy is BG 276–5. Values are given in g per 100 g of dry material. [b] Means within a column followed by the same letter are not significantly different at the 0.05 level according to DNMRT. [c] Modern mill: rubber roll sheller, separator, two abrasive polishers, and one friction polisher. Semimodern mill: rubber roll sheller and Engelberg huller. Traditional mill: Engelberg steel huller.

huller similar to that used in the traditional mill. The byproduct formed during the polishing operation was collected for analysis.

Modern Mill. The paddy was dehusked with a rubber roll sheller similar to that used in the semimodern type of mill. After separating unhusked grains from brown rice in a compartment type separator, the brown rice fraction was polished in stages with two horizontal abrasive-type polishers and one friction-type polisher. The bran from the three polishers was collected for analysis.

Paddy parboiled in the following manner was used to obtain parboiled rice bran from different varieties and different types of mills; paddy was immersed in water preheated to 100 °C and allowed to soak for 18 h without maintaining the water temperature. The soaked paddy was steamed for 25 min and dried in the sun to 14% grain moisture.

The samples of bran were stored in the dark at refrigeration temperature in moisture-proof screw-capped glass bottles for analysis. Moisture content of the bran samples was determined according to method no. 44-40 of AACC 1976, protein by Kjeldahl method no. 46-10 of AACC 1976, fat by method no. 30-20 of AACC 1976, ash by method no. 08-01 of AACC 1976, fiber by method no. 32-15 of AACC 1975, and starch by method no. 76-10 AACC 1976.

RESULTS AND DISCUSSION

The levels of nutrients analyzed in raw and parboiled bran varied significantly among varieties (Table I). This supports the observation of Mc Call et al. (1953) that varietal influence could cause considerable variation in the nutrient content of rice bran. In all varieties the oil content of parboiled rice bran was higher, on an average, by 26% than raw rice bran. However, parboiling had no significant effect on the protein, fiber, and ash contents of bran. The high oil content in parboiled bran is probably due to effective removal of oil-rich bran layers from the hardened parboiled rice grain during milling, unlike in raw rice where portions of the soft endosperm, rich in starch, also get milled out into the bran. Siriwardane (1969) observed that the oil content of parboiled rice bran is 39% higher than that of raw rice bran, even though no differences were observed in the contents of ash and protein. Differences in composition between raw and parboiled brans depend upon the degree of milling and parboiling condition. (Benedito de Barber et al., 1977).

The compositional data of raw and parboiled rice bran from different mills are given in Table II. The presence of high fiber and ash contents in bran from the traditional mill is probably due to contamination of bran with paddy husk, which is rich in fiber and silica, because in this type of mill both operations of dehusking and polishing are performed by one machine in one pass and the byproduct obtained is a mixture of husk and bran. In a semimodern type of mill, too, there is husk admixture to a certain extent resulting in a slight increase in the fiber content of bran because, even though the dehusking and polishing operations are performed separately, for efficient polishing a mixture of unhusked paddy grains and brown rice at a ratio of 1:19 has to be fed into the steel huller. On the other hand, in a modern mill the two operations are performed separately and only brown rice enters the polishing stage. Therefore, mixing of the two byproducts namely, husk and bran, is minimum in a modern mill. While the levels of fiber and ash were increased, contamination with husk resulted in a reduction in the contents of protein and fat in both raw and parboiled rice bran. The starch content was also reduced in parboiled rice bran obtained from the traditional type of mill due to husk admixture. However, this reduction in the starch content was not observed in raw rice bran obtained from the traditional mill probably because of contamination of the bran with portions of the starchy endosperm which gets fragmented due to the high pressure exerted by the steel huller on the grain during milling unlike in the modern mill where the pressure is distributed over a number of machines and, hence, damage to the endosperm is minimum. On the other hand, parboiled rice bran does not get contaminated with starch even in traditional mills because the hardened endosperm of the parboiled grain resist breakage and fragmentation during milling. According to Barber and Benedito de Barber (1969) the fiber content of rice bran can vary between 6.2% and 26.9%, and the ash content between 8% and 22.3% depending on the type of mill used for bran production.

The significant variation observed in the levels of different nutrients, especially in the levels of protein and fat, among varieties indicates that when rice bran is used for oil extraction or as a feed, varietal selection becomes important. Further, the increase in the levels of fiber and ash, and the corresponding reduction in the levels of other nutrients due to husk admixture, makes rice bran from traditional and semimodern mills unsuitable for use as a feed and for oil extraction. The results of the study also indicate that even though parboiling results in a high oil content in rice bran, the use of parboiled bran for oil extraction will be advantageous only if it is obtained from a modern type of rice mill where contamination of bran with husk could be minimized.

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LITERATURE CITED

Barber, S.; Benedito de Barber, C. In "Rice Production and Utilization"; Luh, B. S., Ed.; AVI Publishing Co. Inc.: West Port, CT, 1980; p 790.

Benedito de Barber, C.; Martinez, J. Barber, S. In "Proceedings of the Rice Byproducts Utilization International Conference" Valencia, Spain, 1977.

Houston, D. F.; Allis M. E.; Kohler, G. O. *Cereal Chem.* **1969**, *46*, 527.

Limcango-Lopez, P. D.; Achacoso, F. S.; Costilla, L. S. *Philipp. Agric.* **1962**, *46*, 324.

Mc Call, E. R.; Jurgens, J. F.; Hoffpauir, C. L.; Pons, W. A.; Stark, S. M.; Cucullu, A. P.; Heinzelman, D. C.; Cirino, V. O.; Murray, M. D. *J. Agric. Food Chem.* **1953**, *1*, 988.

Siriwardane, J. A. de S. *Ceylon Vet. J.* **1969**, *17*, 73.

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Determination of Aspartame and Its Breakdown Products in Soft Drinks by Reverse-Phase Chromatography with UV Detection

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A rapid and simple analytical method is presented for the determination of aspartame and its breakdown products in carbonated soft drinks which had been stored at 22 ± 1 °C for various periods. The samples were analyzed by high-performance liquid chromatography (HPLC) with a reverse-phase column and UV detection at 214 nm under isocratic conditions. Four breakdown products were identified and their relative proportions determined. No aspartame condensation product, such as benzaldehyde–aspartame, was observed. The data showed that aspartame is relatively unstable in carbonated soft drinks over extended periods of storage, and that the breakdown products from hydrolysis and cyclization accounted for the aspartame lost.

INTRODUCTION

Aspartame (*N*-L-α-aspartyl-L-phenylalanine methyl ester), a high potency noncarbohydrate sweetener, is currently used in tabletop sweeteners, chewing gums, breakfast cereals, and carbonated soft drinks as well as powdered drinks and dessert mixes in the United States. It is claimed to have a sweetness profile similar to that of sucrose, which should give it a subtantial advantage over saccharin (Cloninger and Baldwin , 1974; O'Sullivan, 1983; Stegink and Filer, 1984).

Almost every major soft drink manufacturer in the United States now uses both aspartame and saccharin, usually in combination, to sweeten diet drinks. The blending of these two noncarbohydrate sweeteners serves to hold down the cost and helps to prolong the shelf life of the beverages, against the cost and shelf life of aspartame alone. Aspartame hydrolyzes slowly in the low pH range used in soft drinks, so products containing exclusively aspartame become less sweet on prolonged storage (Homler, 1984).

Aspartame is the methyl ester of the dipeptide aspartyl phenylalanine and under a wide range of stressful conditions (heat, moisture, and pH) may be susceptible to degradation. The stability of this high potency sweetener in various media was reported recently by Homler (1984). This author showed that aspartame-based cola, stored at 20 °C for 6 months, remained acceptably sweet relative to saccharin-sweetened beverages. The levels of aspartame left in the carbonated beverages and its breakdown and condensation products, however, were not reported. A recent study by Hussein and co-workers (1984) showed that aspartame is quite reactive with aldehydes—which are the principal flavor compounds used in chewing gums and in some soft drinks.

HPLC methods for the determination of aspartame have been reported (Argoudelis, 1984; Cross and Cunico, 1984; Daniels et al., 1984; Hussein et al., 1984; Scherz et al., 1983; Tyler, 1984; Webb and Beckman, 1984). These methods allowed the determination of aspartame to be made in the presence of other additives in beverages such as saccharin, caffeine, and sodium benzoate. No attempts, however, have been made by the above authors other than Scherz to identify any of the hydrolysis or degradation products of aspartame. Scherz and co-workers (1983) developed a reverse-phase HPLC method using gradient elution to separate aspartame, aspartylphenylalanine (AP), and 5-benzyl-3,6-dioxo-2-piperazineacetic acid (DKP).

In this paper, the effects of storage on aspartame are investigated in soft drinks after standing at 22 ± 1 °C for varying periods of time. Soft drinks were analyzed for aspartame and its breakdown products with a simple isocratic HPLC procedure. This work is particularly relevant because of the growth in use of this new noncarbohydrate sweetener in carbonated soft drinks.

EXPERIMENTAL SECTION

Chemicals and Reagents. Organic-free water was obtained from a Milli-R/Q water purifier (Millipore Co., Bedford, MA). LC quality acetonitrile (Burdick & Jackson

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