Thiamine Partitioning and Retention in Cooked Rice and Pasta Products¹

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ABSTRACT

Cereal Chem. 64(2):116-120

Brown and enriched white rice were examined for thiamine leaching characteristics and stability under alkaline conditions during cooking. Rapid, initial thiamine leaching was followed by thiamine uptake as water was absorbed during cooking of white rice. Thiamine leached from brown rice throughout the cooking process. Thermal degradation was slower in brown than in white rice, but the extended cooking period required for tenderness in brown rice resulted in a greater percentage of thiamine loss.

Fourteen pasta samples, representing six pasta types, were examined for thiamine leaching and destruction during cooking. Thiamine loss during cooking of pasta products was evident only through leaching; thiamine retentions ranged from 47 to 66% in cooked pastas. Differences in thiamine retention among the pasta samples were related to the nature of the food matrix involved.

Current food consumption data give evidence of extensive use of cereal products in the American diet. Approximately 150 lb of flour and cereal products were consumed per capita in 1980. This includes almost 125 lb of wheat flour products (white, whole wheat, and semolina) and over 9 lb of rice (Prescott 1983). The U.S. Department of Agriculture estimates that over 42% of the thiamine in the diet is provided by grain products (Marston and Welsh 1983). Therefore, enrichment of cereal products with thiamine plays a significant role in the nutritional adequacy of the American diet.

Thiamine has long been recognized as a vitamin that is sensitive to heat and changes in pH. Using various ratios of soda to phosphate in self-rising flour biscuits, Barackman (1942) found that recovery of thiamine in the baked product was proportional to the acidity of the biscuits. Lincoln and co-workers (1944) showed that cooking farina for varied lengths of time in phosphate buffer solutions resulted in increased thiamine losses as pH and time of cooking increased. In 1955, Farrer showed that loss of thiamine due to heat often could be predicted by the first-order kinetic mechanism. This theory was applied to investigate thiamine stability at temperatures above 250°F (Mulley et al 1975). Thiamine in buffer solutions was found to be much more susceptible to heat degradation than thiamine in food systems.

Because of its water solubility, thiamine is also susceptible to losses in foods through leaching into the cooking water. In 1982, Abdel-Rahman reported thiamine losses in the range of 39 to 47% during the cooking of spaghetti. Later studies also reported appreciable losses of thiamine during the cooking of pasta products (Dexter et al 1982, Ranhotra et al 1984). Questions still remain about whether the losses of thiamine that occur during the cooking of pasta result from leaching alone or if heat degradation is also taking place, and whether the food matrix itself influences thiamine retention in cooked cereal products.

The objectives of this research were threefold. The movement of thiamine between the kernel and the cooking liquid was monitored during cooking of enriched and unenriched rice systems and compared for differences in these systems. Losses of thiamine in cooked rice systems were examined as a function of pH and compared, using rate constants, to those found in thiamine solutions. Finally, modes of thiamine loss during cooking of pasta were determined as well as effects of the food matrices on the loss of thiamine.

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MATERIALS AND METHODS

Rice Study

Samples of long-grain brown rice and long-grain white rice enriched with iron and thiamine were used to determine thiamine-leaching characteristics and stability to heat under alkaline conditions. The rice samples were purchased at a local retail store.

A sample of 10 g of rice in 60 ml of 0.1M sodium phosphate buffer solution in a 250-ml covered beaker was heated to a constant boil for specified times. This buffer system was used because phosphate is the predominant buffer anion in cereals (Farrer 1949, 1955). The excess of cooking liquid, which is not normal, allowed for cooking liquid to be collected and analyzed for thiamine content. Cooking periods of 5, 10, 15, and 20 min were used for the white rice and 5, 10, 15, 20, 35, and 50 min for the brown rice. The longer cooking time for brown rice followed package instructions. Preliminary studies showed pH levels below 6.5 to have very little effect on thiamine stability at boiling temperatures in a rice system. Therefore buffers at pH levels of 6.5, 7.0, 7.5, and 8.0 were chosen for this study. At the end of the cooking period, 10 ml of 1.0Nsulfuric acid was added to lower the pH of the samples to 2.5, which prevented further degradation of thiamine. Two replications of each heating treatment were performed. The cooking liquid was decanted from the rice, its volume was measured, and the liquid was frozen until analysis for thiamine.

Pasta Study

A variety of pasta products was used in this study to obtain information about thiamine leaching and stability among the different pasta types, including enriched egg noodles, enriched elbow macaroni, enriched spinach ribbons, and their unenriched whole wheat counterparts. All samples were purchased at local retail stores. Three replicates were cooked in the following manner. Twenty-five grams of pasta was cooked for 10 min in 250 ml of rapidly boiling deionized water in an uncovered 600-ml beaker. After cooking, the samples were drained, rinsed with 20 ml of deionized water, and again allowed to drain for 3 min. The volume of liquid was then measured and the liquid frozen until analysis for thiamine.

Freeze-Drying and Moisture Analysis of Samples

Cooked rice and pasta samples were frozen and then lyophilized in a freeze-dryer (The Virtis Company) for 48 hr, which was sufficient to reach constant weight. After freeze-drying, samples were stored in a desiccator until weighed out for duplicate air-oven moisture (AACC 1983) and thiamine analyses. Thiamine and moisture contents of uncooked samples were determined also, and results were reported as apparent retention (Murphy et al 1975).

Apparent retention =
$$\frac{\mu g \text{ thiamine/g cooked pasta (dry basis)}}{\mu g \text{ thiamine/g uncooked pasta (dry basis)}} \times 100$$

¹Published as paper no. 14,968 of the scientific journal series of the Minnesota Agricultural Experiment Station; research conducted under project no. 18-087 supported by GAR funds.

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Thiamine Hydrochloride Study

To compare thiamine degradation in a rice system to that in a model system, kinetics of thiamine loss in buffered solutions at boiling temperatures were examined. All buffers were prepared using deionized water. Solutions of 0.1M mono-, di-, and trisodium phosphate were used to adjust the pH to the desired levels. assuring a final phosphate concentration of 0.1 M. Preliminary studies showed little thiamine loss during 1 hr of heating in a boiling water bath at pH levels below 6.0, so the pH levels tested were 6.0, 6.5, 7.0, 7.5, and 8.0. To minimize temperature come-up time, 5 ml of 0.1 M sodium phosphate buffer at each pH level was preheated in a screw-capped test tube for 5 min in a boiling water bath. One milliliter of thiamine solution (20 µg thiamine hydrochloride/ml) was added to the tubes, which were heated for specified times up to 60 min. Immediately after heating, 4 ml of 1.0N sulfuric acid was added to the tubes to lower the pH of the solutions to below 3.0. After cooling the tubes to room temperature, the contents were analyzed for thiamine. Each treatment was run in duplicate.

Quantification of Thiamine

Thiamine was determined by the thiochrome method (AACC 1983) using 3.0-g samples of brown rice and whole wheat pasta products, 2.0-g samples of enriched white rice and enriched pasta products, and 10 ml of cooking liquid for the analyses. The entire contents of the tube was used for analysis of the buffer solutions of pure thiamin. Acid extraction of thiamine was followed by an enzyme digestion step at 55°C for 60 min (Wehling and Wetzel 1984). This modification to the standard procedure gave results

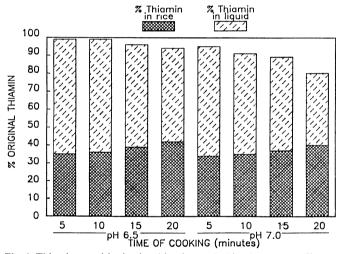


Fig. 1. Thiamine partitioning in white rice cooked in phosphate buffers at pH levels of 6.5 and 7.0 during cooking.

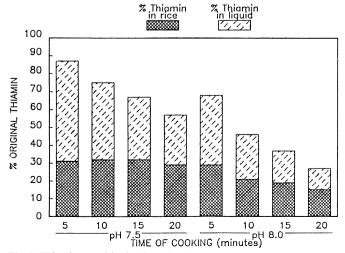


Fig. 2. Thiamine partitioning in white rice cooked in phosphate buffers at pH levels of 7.5 and 8.0 during cooking.

comparable to the standard procedure with a reduction in analysis time. Thiochrome fluorescence was measured in a Farrand ratio fluoremeter-2 (Farrand Optical Company) using quartz sample cells, an excitation filter with maximum transmittance at 365 nm, and an emission filter with maximum transmittance above 435 nm. Each sample was analyzed in duplicate.

Kinetic and Statistical Analysis

Effects of pH on thermal degradation of thiamine were determined by monitoring thiamine concentrations before and after two replications cooked for specified time intervals, all on a dry weight basis.

Thermal destruction of thiamine in foods follows first-order kinetics (Farrer 1955); therefore, logarithmic transformation of the dependent variable (percent thiamine retention) and linear regression to determine the best fit line were used to determine the rates of thermal degradation.

The effect of pasta type on thiamine retention during cooking was determined by comparing thiamine concentrations before and after pasta was cooked (three replications), all on a dry weight basis. Percent retention of thiamine after cooking was evaluated by analysis of variance (Ott 1984). All statistical analyses were done using a 5% level of significance on the mean values of duplicate thiamine analyses for each replication.

RESULTS AND DISCUSSION

Thiamine Partitioning in White and Brown Rice

The initial thiamine content of white rice samples used in this study was $6.6 \pm 0.2 \,\mu g$ per gram of rice, which is within the range specified in the Code of Federal Regulations for an enriched rice product (1985a). The brown rice samples contained $3.2 \pm 0.3 \,\mu g$ of thiamine per gram of rice, approximately one-half of the amount present in the white rice and corresponding to the published values for brown rice (Pennington and Church 1980).

The movement of thiamine into the cooking liquid was monitored by collecting liquid at various intervals during cooking. Partitioning of the thiamine between the cooking liquid and the rice kernels is expressed in terms of a percent of the original thiamine (on a dry weight basis). As seen in Figure 1, thiamine was relatively stable to heat degradation at pH 6.5 in white rice. After 5 min of cooking, nearly 65% of the thiamine leached into the cooking liquid. Gradually, as the rice absorbed water, some of this thiamine transferred back into the rice kernel, leaving only about 50% of the thiamine still in the cooking liquid. At pH 7.0, similar results were observed. But in this case, losses due to the cooking process increased more rapidly as the cooking time increased. For the most part, the increased losses resulted from lower thiamine contents of the liquid sample rather than losses from the kernels.

At the higher pH levels of 7.5 and 8.0, the transfer of thiamine back into the white rice was hindered by the fact that heat degradation in the buffer was probably also taking place (Fig. 2). At pH 7.5, the thiamine in the cooking liquid was not going back into the rice as it did at lower pH levels. The destruction of thiamine in the cooking liquid appeared to limit the amount of thiamine that could be absorbed. At pH 8.0, thiamine degradation was extensive; the thiamine in the rice as well as that in the liquid was reduced. It is unclear whether this loss of thiamine from rice resulted from pH changes in the rice kernel itself or if increased thiamine leaching resulted in its destruction in the cooking liquid at this high pH.

Unenriched brown rice showed a different pattern of thiamine partitioning. As with white rice, the brown rice was relatively stable to heat degradation at pH 6.5 (Fig. 3). The losses due to the cooking process increased at pH 7.0. Unlike white rice, the leaching of thiamine from brown rice into the cooking liquid increased with time of cooking. This was reasonable, because the native thiamine is in the rice kernel and not applied only on the surface as in enriched white rice. The thiamine leaching from brown rice was much less extensive than that from the white rice, even at the end of the 50-min cooking period. For example, at pH 6.5, 50% of the thiamine in the white rice was lost through leaching at the end of

the cooking period, but only 37% of the thiamine in the brown rice was lost through leaching.

At pH 7.5 and 8.0, the percent of thiamine retained in the brown rice as well as the percent found in the cooking liquid dropped off considerably, as seen in Figure 4. Destruction of thiamine due to heat at these pH levels more closely resembled that found in white rice. At the end of their respective cooking periods at pH 8.0, the thiamine in the white rice was reduced by 73% and the thiamine in the brown rice was reduced by 75%. Again, it is not known if this increased thiamine loss was due to pH changes in the rice kernel itself or if accelerated thiamine leaching and subsequent degradation in the cooking liquid was taking place.

A minimum amount of thiamine degradation at pH 6.5 made this level appropriate for comparing thiamine leaching characteristics in white and brown rices (Figs. 1 and 3). Initially, thiamine leached rapidly from white rice, but this changed to gradual thiamine uptake as water absorption occurred. In brown rice, on the other hand, leaching of thiamine into the cooking liquid was continuous as the grains swelled. Leaching from brown rice was never as extensive as that from white rice, however, and brown rice lost 44% of the original thiamine after 50 min of cooking whereas white rice lost 58% of the original thiamine after 20 min of cooking.

During typical cooking of rice by consumers, all of the cooking liquid is absorbed by the rice and very little thiamine loss would occur by leaching. But this leaching phenomenon could play an important role in thiamine loss in foods where part of the cooking liquid is not consumed.

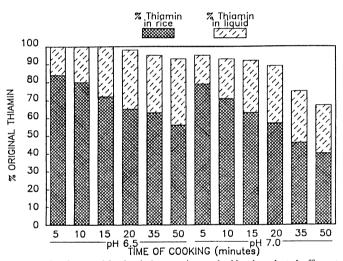


Fig. 3. Thiamine partitioning in brown rice cooked in phosphate buffers at pH levels of 6.5 and 7.0 during cooking.

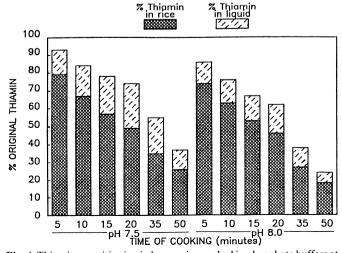


Fig. 4. Thiamine partitioning in brown rice cooked in phosphate buffers at pH levels of 7.5 and 8.0 during cooking

Thermal Degradation of Thiamine as a Function of pH

Thiamine degradation due to heat can be predicted using firstorder kinetics (Farrer 1955). Taking into account the thiamine in the rice as well as the thiamine in the cooking liquid, percent thiamine retention versus time of cooking was plotted on a semilog plot. Figure 5 presents a first-order plot for the white rice data. In white rice, increasing the pH of the cooking liquid from 6.5 to 8.0 caused an increase in the rate of thermal degradation in all cases.

A first-order plot for the brown rice data is shown in Figure 6. As with the white rice, the brown rice samples showed increased rates of thermal degradation as the pH of the cooking liquid was increased from 6.5 to 8.0. First-order plots of the thermal degradation of thiamine hydrochloride in solution are shown in Figure 7. Similar to data for both rices, increasing the pH of the water increased the rate of thermal degradation in all cases.

Table I presents calculated rate constants for thiamine loss based on the slopes of the lines in Figures 5-7 for both rice products as well as the thiamine hydrochloride solution at boiling temperatures. For each of these systems, the rate constant increased as pH increased, and at each pH level tested the rate constant was lowest for brown rice, intermediate for white rice, and highest for thiamine hydrochloride in buffer solutions. The greater heat resistance of thiamine in food systems than in aqueous solutions was also observed by Mulley and co-workers (1975). The presence of proteins that are known to protect thiamine or absorption of thiamine into starch in rice may play an important role in promoting retention during heating.

Even with the slower rate of degradation, thiamine retention in brown rice plus cooking liquid at the end of the 50-min cooking period was lower than that in white rice after the 20-min cooking

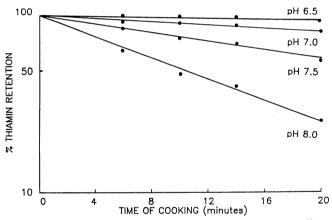


Fig. 5. Total thiamine retention in white rice cooked in phosphate buffers at various pH levels during cooking. Each regression line was determined using eight data points (four cooking times for two replicates). The data points shown are mean values of the two replications at each cooking time.

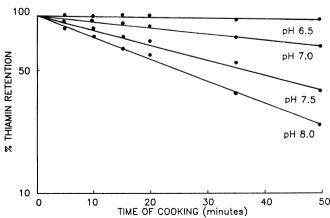


Fig. 6. Total thiamine retention in brown rice cooked in phosphate buffers at various pH levels during cooking. Each regression line was determined using 12 data points (six cooking times for two replications).

period. Therefore, the extended cooking time necessary to achieve tenderness in brown rice allowed for continued degradation of thiamine beyond that found in the white rice samples. When cooked according to package instructions (no excess cooking liquid) using deionized water, the white rice showed a thiamine retention of 92% and the brown rice showed a thiamine retention of 89%. These thiamine retention values in deionized water show that normally cooked rice has thiamine retention values somewhere between the samples cooked in buffer at pH 6.5 and pH 7.0. But many factors play a role in thiamine retention in rice, especially cooking time.

The relationship between rate constant and pH was shown to be linear in buffer solutions of thiamine (Farrer 1945). For the systems used in this experiment, this logarithmic relationship appears to be adequate. When plotted, rate constants for the thiamine solution and the white rice showed very good linearity in the range studied with r^2 values of 0.996 and 0.998, respectively. It seems reasonable that the trends in white rice would be as linear as those of the thiamine hydrochloride standard solutions. With the excessive thiamine leaching that occurred within the first 5 min of cooking in white rice, the thiamine was more closely associated with the aqueous phase than with the rice kernel. The brown rice, while still linear, deviated slightly with an r^2 value of 0.920 based on the best fit line. As with white rice, the brown rice system provided protection against thiamine destruction as compared to the thiamine hydrochloride solution. Because thiamine in brown rice is more closely associated with the rice kernel, the rate constants were lower than for white rice and may deviate from linearity because of the more complex environment of the thiamine in brown rice.

Thiamine Loss in Cooked Pasta

The initial thiamine contents of uncooked pasta samples are listed in Table II. All enriched products were within the range specified in the Code of Federal Regulations for an enriched pasta product (1985b). As might be expected, the thiamine content of the whole wheat products was less than one-half that found in the

TABLE I
First-Order Rate Constants for Thiamine Loss in Rice Products
and Thiamine Solutions Subjected to 100° C

pH Level	Rate Constant ^a		
	White Rice	Brown Rice	Thiamine Solutions
6.0	•••	***	0.002 ± 0.000
6.5	0.005 ± 0.002	0.002 ± 0.001	0.007 ± 0.001
7.0	0.010 ± 0.003	0.008 ± 0.002	0.023 ± 0.008
7.5	0.028 ± 0.004	0.020 ± 0.002	0.135 ± 0.010
8.0	0.060 ± 0.007	0.028 ± 0.002	0.516 ± 0.028

^a Rate constant ± 95% confidence interval (min⁻¹).

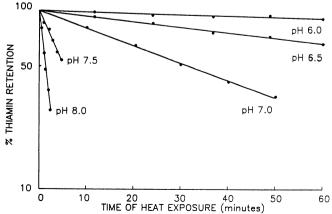


Fig. 7. Thiamine retention in standard solutions heated in phosphate buffers at various pH levels with frequent sampling. Ten data points were used to determine each regression line (five exposure times for two replications).

enriched products. The final pH of the cooking liquid for each pasta sample was in the range of 5.5–6.1.

The sum of the thiamine recovered from the cooked products and their corresponding cooking liquids ranged from 96 to 104%, relative to the amount of thiamine found in the raw counterparts. This indicated that there was minimal thermal degradation of thiamine taking place in the samples studied. Nearly all of the thiamine lost from the pasta products during cooking was accounted for in the corresponding cooking liquid samples and thus was a result of leaching. These results concur with those of Abdel-Rahman (1982), who reported only minimal losses of thiamine from cooking. Dexter and co-workers (1982) observed losses of thiamine in the range of 30-46% after 10 min of cooking. In this case, though, the pH and buffering capacity of the tap water in which these samples were cooked may have been a factor.

Thiamine retentions in the cooked products (Table II) ranged from 47 to 66% of the thiamine in the uncooked product. This range is in agreement with results of Abdel-Rahman (1982), who found thiamine retentions of 58-67% in spaghetti made from two durum wheat varieties. Significant differences among the pasta types indicated that pasta type or composition was an important factor in thiamine leaching during the cooking process.

Whole wheat egg noodles and whole wheat elbows tended to retain more thiamine than their enriched counterparts. Also, products with lower levels of enrichment generally retained a higher percentage of thiamine than did their counterparts with higher levels of enrichment. Finally, all the spinach-containing pasta products studied showed low thiamine retentions compared to the other products.

The reasons for these differences in thiamine retention among the cooked pasta products are unclear, but some factors can be identified. That whole wheat egg noodles and whole wheat elbows exhibited some of the highest thiamine retentions may indicate that thiamine retention was dependent on how thiamine was held in the product. In whole wheat pasta, the thiamine was in the bran and germ portions of the flour. Here it was bound more tightly, both chemically and physically, than in enriched pasta where it was added as a powder to the semolina mix. In egg noodles, the egg was an additional source of thiamine in the product and this thiamine apparently is more tightly bound than in regular enriched pasta. Increasing the proportion of thiamine that is tied up within the pasta matrix appeared to decrease the portion of thiamine available to leach into the cooking water.

Of the enriched products, those with lower levels of enrichment showed higher thiamine retention than their highly enriched counterparts. These products contained a lower proportion of added thiamine and a higher proportion of the more bound thiamine from other ingredients. Thus, increasing the proportion of bound thiamine in the product decreased the proportion of

TABLE II
Thiamine Content of Uncooked and Retention in Cooked Pasta Products
in Ranked Order of Percent Retention

Pasta Type ^a	Initial Content ^b	Percent Retention ^c
Egg noodle 3*	9.9 ± 0.8	66.5 ± 1.8
W.W. egg noodle	5.2 ± 0.3	63.0 ± 1.7
W.W. elbow 2	4.4 ± 0.3	58.8 ± 9.6
W.W. elbow 1	5.8 ± 0.1	58.2 ± 3.9
Elbow 2*	11.4 ± 1.1	57.8 ± 0.9
Elbow 3*	9.6 ± 1.2	56.1 ± 1.3
Spinach ribbon 2*	1.0 ± 0.7	55.5 ± 1.4
Egg noodle 1*	11.6 ± 0.5	53.1 ± 0.9
W.W. spinach ribbon 1	4.4 ± 0.3	51.5 ± 0.8
W.W. spinach ribbon 2	5.2 ± 0.5	51.0 ± 3.4
Elbow 1*	13.1 ± 0.5	50.6 ± 5.0
Egg noodle 2*	15.6 ± 1.2	49.5 ± 1.2
Spinach ribbon 3*	11.8 ± 0.5	48.2 ± 1.6
Spinach ribbon 1*	11.9 ± 1.1	47.1 ± 2.2

^a W.W. = Whole wheat; starred items are enriched products.

^b Mean \pm 95% confidence interval (µg thiamine/g dry sample).

^c Mean ± 95% confidence interval.

thiamine lost through leaching. All the spinach noodle products, enriched as well as whole wheat, had relatively low thiamine retentions. The reason for this remains unclear.

CONCLUSIONS

Enriched white rice samples leached thiamine rapidly during the initial minutes of cooking, with gradual thiamine uptake as water absorption occurred. Brown rice leached thiamine into the cooking liquid throughout the cooking period, but never as extensively as white rice.

Kinetic analysis using a logarithmic relationship between the rate constant of thiamine loss and pH showed linearity for thiamine solutions and white rice. Compared with rates of loss for thiamine hydrochloride solutions, white rice showed a tendency to protect against thiamine loss, and an even greater protection was shown by brown rice at each pH level.

In all pasta products studied, losses of thiamine from the cooked products were caused by leaching and not thiamine destruction. An analysis of variance showed a highly significant difference among the thiamine retentions in the pasta types studied. This variability was related to the thiamine enrichment level and the composition or type of pasta studied.

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[Received July 2, 1986. Revision received November 14, 1986. Accepted November 21, 1986.]