# Reduction of Phytic Acid During Breadmaking of Whole-Meal Breads<sup>1</sup>

B. FRETZDORFF and J.-M. BRÜMMER<sup>2</sup>

#### ABSTRACT

Reduction of phytate was studied in model dough systems using wholegrain coarse meals or flours and during breadmaking of coarse meal breads from wheat and rye. It was found that pH was the most important factor in reducing phytic acid content. In doughs with pHs of 4.3-4.6, adjusted with citric or lactic acid, phytic acid content was more effectively reduced than in doughs with higher pHs. Phytic acid was almost completely hydrolyzed in doughs made from whole-grain flours at pH 4.5 and 30°C after a 4-hr incubation. Reductions of phytic acid content in doughs made from coarse meals were small, but with increasing temperature

Because of increasing health consciousness in our society, whole-meal breads have become more popular. In addition to the nutritional benefits of higher vitamin, mineral, and fiber levels in whole-meal flours, concentrations of some undesirable substances such as phytic acid are also higher in whole meal than in white flours. Phytic acid can bind multivalent cations (such as calcium, copper, iron, and zinc) to form insoluble complexes, thus lowering their bioavailability. The German Nutrition Report (Deutsche Gesellschaft für Ernährung 1988) stated that reduced minerals in food should not be a general concern. However, there might be a marginal supply of essential minerals in certain sectors of the pópulation, such as vegetarians, children, and seniors.

Wheat and rye contain about 1% phytic acid, which is localized in the aleurone layer of the kernel as the magnesium-potassium salt. Phytate is important in physiological functions as an energy source and as a phosphorus and mineral reserve for the growing plant (Cosgrove 1980). In flour-milling technology, the phytic acid content of flour is significantly correlated with the ash content and the milling extraction rate (Fretzdorff and Weipert 1986). In food processing, phytic acid in flour can be hydrolyzed by the enzyme phytase, which also is localized in the aleurone, to yield myoinositol and orthophosphate. Optimum conditions for phytase activity are a pH range from 5.0 to 5.5 and a temperature range from 50 to  $55^{\circ}$ C (Rohrlich 1969).

Whole-meal breads contain considerable amounts of phytic acid. However, only a few studies have described breadmaking procedures aimed at lowering the phytate content of whole-meal breads. For example, increasing the yeast or malt in whole-meal wheat breads reduced the phytate content less than 50% (Harland and Harland 1980, Faridi et al 1983, Chhabra and Sidhu 1988). Wu et al (1984) and Meuser and Meissner (1987) separated milled grain into bran and flour and reduced the content of phytate in the bran fraction by hydrolysis catalyzed by endogenous phytase. The dephytinized wet bran was mixed into the dough before it was baked into whole-meal breads. However, this procedure has not been commercialized.

Reduction of phytic acid content during breadmaking depends on phytase action. As with other enzyme reactions, various factors contribute to phytate degradation in doughs, including phytase activity, particle size of meals, pH, temperature, water content, and fermentation time. Published reports on the fate of phytic acid during bread production were reviewed by Lasztity and Lasztity (1990). Some European publications provide further information (Blumenthal and Scheffeldt 1983, McKenzie-Parnell

Contribution 6022, Federal Centre for Cereal, Potato, and Lipid Research, D-4930 Detmold, Germany. Presented at the AACC 75th Annual Meeting, Dallas, TX, October 1990.

<sup>2</sup>Federal Centre for Cereal, Potato, and Lipid Research, D-4930 Detmold, Germany.

and Davies 1986, Meuser and Meissner 1987, Bartnik and Florysiak 1988).

(up to 55°C) phytic acid concentrations were less than 8 and 4% of original

concentrations for wheat and rye, respectively. Further increase of the

temperature (above 55°C) of the unfermented sponge resulted in smaller

reductions of phytic acid. In acidified unfermented sponges (pH 4.4-4.6),

the residual phytic acid was less than 10% of original concentrations.

From dough mixing through baking, the content of phytic acid was

reduced to about 20 and 33% for wheat and rye, respectively. Phytic

acid contents ranged from 6.3 to 10.1 mg/g (dry matter) and from 0.6

to 2.7 mg/g (dry matter) for wheat and rye meal breads, respectively.

This article reports results of a study of the effect of pH and temperature on phytic acid degradation in model dough systems. We also report on the reduction of phytic acid content in rye and wheat whole-meal breads.

## **MATERIALS AND METHODS**

## **Meals and Flours**

Whole grain coarse meals (ground using a hammer mill until about 80% of the particles did not pass through a 1.4-mm sieve) and whole-grain flours (ground using a modified Bühler laboratory mill until about 90% passed through a 250- $\mu$ m sieve and more than 50% through a 100- $\mu$ m sieve) were prepared from wheat (cv. Ralle) and rye (cv. Danko) by standard procedures of the Federal Centre for Cereal, Potato and Lipid Research, Detmold, Germany. The two products are hereafter referred to as meal and flour.

## **Preparation of Model Doughs**

Doughs for the pH study were prepared by mixing for 3 min (in a household mixer with kneading hooks) 300 g of flour or meal with 270 ml of deionized water or acid solutions of various concentrations. The solutions were 0.5, 1.0, and 2.0% citric acid; 2.0 ml of lactic acid (90%) (0.7%, v/v); and 1.0 and 2.0% tartaric acid. Doughs were kept for 2 and 4 hr at 30°C and then freezedried and ground into a fine powder.

Doughs for the temperature study were prepared by mixing for 3 min (as above) 300 g of meal with 300 ml of 0.9% citric acid solution. Doughs were kept at 25, 30, 40, 45, 50, 55, 65, or 75°C for 2 and 4 hr and then freeze-dried and ground into a fine powder.

## Breadmaking

Unfermented sponges were made by manual mixing (2 min) 300 g of meal with 300 ml of water or the same volume of 0.9% citric acid. Three sets of water and acid sponges were prepared by mixing at cold (25°C), warm (50°C), or hot (62°C)

TABLE I   Formulas and Procedures for Wheat and Rye Breads		
Ingredient	Wheat	Rye
Coarse meal	700 g	300 g
Unfermented sponge	600 g	600 g
Sourdough		800 g
Water	300 ml	50 ml
Yeast	15 g	15 g
Salt	15 g	15 g
Dough rest (23–26°C)	60 min	60 min
Proofing (32°C)	60 min	50 min
Baking (200°C)	60 min	70 min

Cereal Chem. 69(3):266-270

<sup>© 1992</sup> American Association of Cereal Chemists, Inc.

temperatures and then storing 18 hr at 22°C, 4 hr at 40°C, or 4 hr at 22°C, respectively.

Sourdoughs were prepared by mixing 1 kg of meal, 100 g of basic sourdough, and 800 ml of cold tap water. The sourdoughs

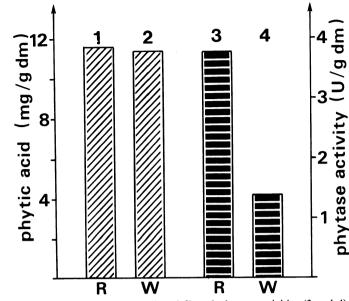


Fig. 1. Phytic acid contents (1 and 2) and phytase activities (3 and 4) in rye (R) and wheat (W) whole meals. Phytase activity was assayed by incubation of extract with sodium phytate in citrate buffer at pH 5.5 and 55°C; 1 U represents 1  $\mu$ mol of liberated inorganic phosphate per minute in 5 ml of assay solution.

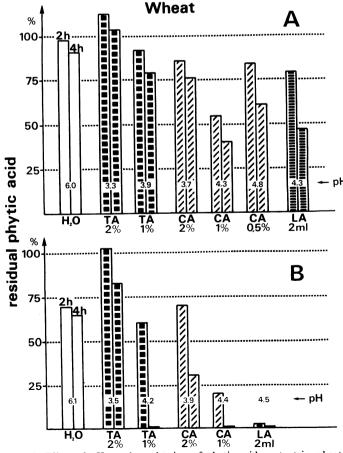


Fig. 2. Effect of pH on the reduction of phytic acid content in wheat doughs incubated at  $30^{\circ}$ C for 2 and 4 hr. A, Coarse meal doughs; B, whole flour doughs. TA = tartaric acid, CA = citric acid, LA = lactic acid.

were stored for 15–18 hr at 26°C. Wheat breads were prepared by the unfermented sponge procedure (Table I). Rye breads were produced by the Detmold one-stage sourdough process (Spicher and Stephan 1987, Table I).

#### **Analytical Methods**

Determinations of phytic acid and phytase activity were according to Wheeler and Ferrel (1971) and Fretzdorff and Weipert (1986), respectively. pH values of the doughs were measured after suspending (with magnetic stirring, 3 min) 19 g of dough in 91 ml of deionized water.

## **RESULTS AND DISCUSSION**

Phytic Acid Content and Phytase Activity of Meals and Flours

Phytic acid contents were relatively high, almost 12 mg/g or 1.2% of dry matter (dm) in both the wheat and rye samples (Fig. 1). However, phytase activity in rye was almost three times that in wheat (Fig. 1). These results are in agreement with those of Rohrlich (1969) and Harland and Harland (1980).

# Effect of pH in Model Doughs

A question arises whether the optimum pH (5.0-5.5) of phytase activity in solution is also the optimum pH for the hydrolysis of phytate in a dough system. Figures 2 and 3 show the changes of phytate in wheat and rye model doughs, respectively. Organic acids were used in the given concentrations to adjust the pH. These acids can be used for food processing and are part of acidification improvers. The lower pHs were in the range of sourdoughs.

For wheat, the flour doughs (Fig. 2B) had slightly higher pH than the meal doughs (Fig. 2A). This might have been due to a higher buffering capacity in the flour doughs, which had smaller particle sizes with larger surface area so that buffering substances were more readily extracted.

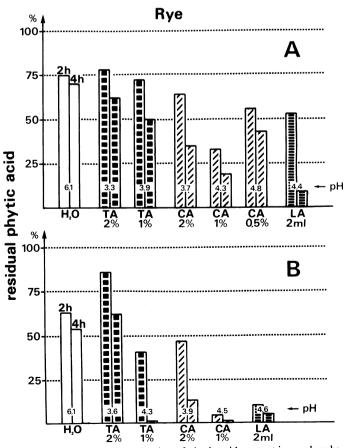
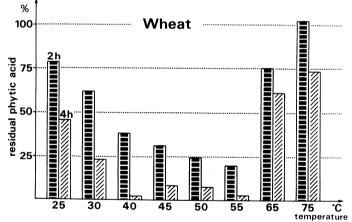


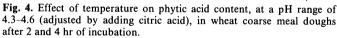
Fig. 3. Effect of pH on the reduction of phytic acid content in rye doughs incubated at  $30^{\circ}$ C for 2 and 4 hr. A, Coarse meal doughs; B, whole flour doughs. TA = tartaric acid, CA = citric acid, LA = lactic acid.

As expected, phytic acid was hydrolyzed to a greater extent in flour doughs than in meal doughs (Fig. 2). In the water doughs, there was almost no reduction of phytic acid content in the meal doughs and only about 30% in flour doughs after 4 hr. After 4 hr at pH 4.5, phytic acid was almost completely hydrolyzed in the flour doughs (Fig. 2B) as compared with 50–60% reduction at pH 4.3 in the meal doughs (Fig. 2A). Furthermore, increasing the pH to 4.8 in the meal doughs decreased the hydrolysis of phytic acid.

Hydrolysis of phytic acid in rye doughs followed a pattern similar to that in wheat doughs, except that the decreases were much greater (Fig. 3). The reason is probably the higher phytase activity of rye. The greatest decreases were at 4.3-4.6 pH for both wheat and rye doughs; this pH range is lower than the pH optimum of phytase activity in solution (pH 5.0-5.5).

On the basis of the results presented here, it is not possible to conclude which of the three organic acids used in the present study is most suitable for reducing phytic acid content in doughs. The main controlling factor appears to be the pH of the dough. The importance of acidity in doughs was reported by Wu et al (1984), Meuser and Meissner (1987), and Bartnik and Florysiak (1988). The most favorable pH was thought to be the optimal pH of phytase activity examined in solution. But a dough is a more complex system than the assay solution with soluble sodium phytate and phytase. The solubilities of the phytic acid chelate complexes with cations depend on pH and the amounts and kinds of cations. The most effective pH for phytase action in a dough need not necessarily coincide with the optimal pH of phytase activity in aqueous solution. Increasing the pH with soda (0.2





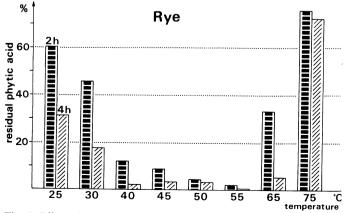


Fig. 5. Effect of temperature on phytic acid content, at a pH range of 4.3-4.6 (adjusted by adding citric acid), in rye coarse meal doughs after 2 and 4 hr of incubation.

and 0.4%) in various doughs lowered phytic acid hydrolysis (Faridi et al 1983).

# Effect of Temperature in Model Doughs

The optimum temperature for hydrolysis of phytic acid in wheat meal doughs was  $55^{\circ}$ C, at which 80% was hydrolyzed after 2 hr and more than 95% after 4 hr (Fig. 4). At temperatures higher than  $55^{\circ}$ C, the hydrolysis was significantly lower, probably because of inactivation of phytase.

The pattern for rye doughs was similar, except for a generally higher reduction of phytic acid than that in wheat doughs (Fig. 5). At  $55^{\circ}$ C and a pH of 4.5, almost all of the phytic acid in the meal doughs was hydrolyzed. In contrast to the results for wheat doughs, the content of phytic acid was still considerably reduced at  $65^{\circ}$ C in rye doughs. It appears that rye phytase may be more heat resistant than wheat phytase.

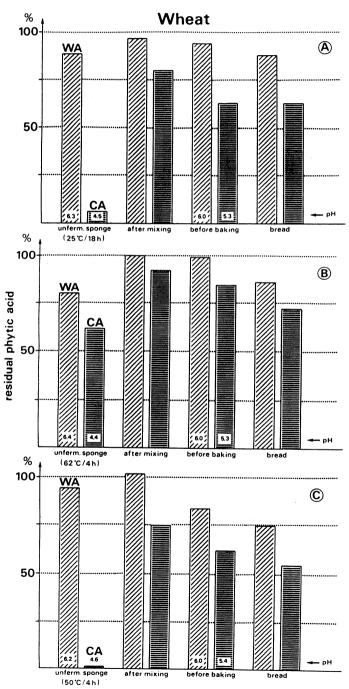


Fig. 6. Changes of phytic acid contents during breadmaking with water (WA) or citric acid (CA) unfermented sponges prepared at cold (A), hot (B), or warm (C) temperatures in wheat coarse meal doughs and breads.

## **Breadmaking Results**

As expected from previous results, the reduction of phytic acid in the cold water sponge was insignificant, while that in cold acidified sponge was almost 100% (Fig. 6A). The mixing of the acidified sponge (pH 4.5) with meal and water resulted in a pH of 5.3 (Fig. 6A). In hot sponges ( $62^{\circ}$ C), phytase appears to be inactivated (Fig. 6B). Thus very little phytic acid would subsequently be hydrolyzed in the doughs and breads at this temperature. In the warm sponges ( $50^{\circ}$ C), phytic acid was almost completely hydrolyzed in 4 hr (Fig. 6C), indicating a higher rate of the hydrolysis reaction and little, if any, phytase inactivation.

During the breadmaking process a gradual decrease in phytic acid content occurred from mixed dough to bread in all six baking experiments with wheat meal (Fig. 6A–C). Reduction of phytic acid content in doughs from acidified sponges was about 25% higher than that in the water doughs. This was presumably due to the lower phytic acid content in the acidified sponges at the time they were mixed into the bread dough. In doughs from acidified sponges, the pH dropped to 5.3, into the range of optimum pH of phytics acid occurred. The actual phytic acid contents in the breads from water sponges ranged from 8.6 to 10.1 mg/g (dm) and, in those from acidified sponges, from 6.3 to 8.3 mg/g (dm). Apparently, the pH of the wheat bread doughs was not optimum in terms of phytase action.

Rye breads are traditionally made with sourdough. The bread doughs contain 30% unfermented sponge and 40% sourdough added to meal in addition to yeast and salt. In rye sponges, the conditions for phytic acid reduction are much more favorable

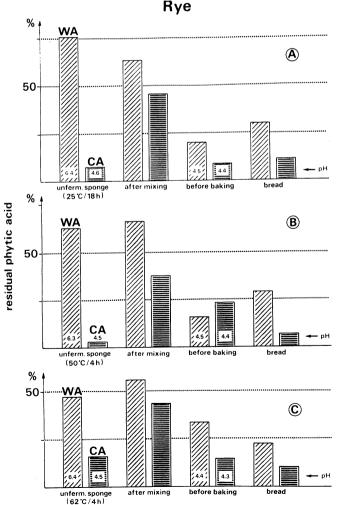


Fig. 7. Changes of phytic acid contents during breadmaking with water (WA) or citric acid (CA) unfermented sponges prepared at cold (A), warm (B), or hot (C) temperatures in rye coarse meal doughs and breads.

because the intrinsic activity is higher than that in wheat sponges. In all sourdoughs that we analyzed, phytic acid was completely hydrolyzed. In contrast, Meuser and Meissner (1987) reported a 15% residual phytic acid content in a rye sourdough that they analyzed. Thus, it seems that the low phytic acid content in the rye bread doughs analyzed in the present study was partly due to the low phytic acid content in the sourdough and the sponge.

For rye, we observed substantial difference between phytic acid losses in water sponges and in acidified sponges under cold conditions (25°C) held overnight (18 hr) (75 vs. 8%, Fig. 7A). The analogous difference for warm sponges (50°C) was similar (65 vs. 3%, Fig. 7B). Even in the hot sponges (62°C), phytic acid content reduction was more than 50% in the water sponges and about 85% in the acidified sponge (Fig. 7C). This is consistent with our earlier results, which indicate that rye phytase is more heat resistant than wheat phytase.

In comparison with wheat, the reduction of phytic acid in rye bread, from mixing through baking, was about 33% higher. This is most likely due to the relatively higher phytic acid content of wheat doughs, whether made with water or acid.

The three rye breads from water sponges contained, on average, 2.4 mg of phytic acid per gram (dm), which is a 75% reduction of the total in the meal. Breads with acidified sponges contained an average of 0.8 mg of phytic acid per gram (dm), which is a 90% reduction of the original content.

Knorr et al (1981) reported that phytate was hydrolyzed in breads with added enzymes during storage. In the present experiment, when one rye bread with 3.7 mg of phytic acid per gram and one wheat bread with 8.6 mg/g were stored for two days, no further loss of phytic acid occurred. It was concluded that cereal phytases were inactivated during baking, preventing further hydrolysis. The appearance and taste (as reported by untrained tasters) of breads with acidified sponges did not differ from that of the traditional breads.

## CONCLUSIONS

This study showed that pH and intrinsic phytase activity are the most important factors for phytic acid hydrolysis in a dough. The overall effect includes the effect of pH on phytase action and on phytate susceptibility (solubility of cation and protein complexes). On the basis of our results, we conclude that a pH of 4.5 is optimal for hydrolysis of phytic acid in wheat and rye doughs. In a dough system at optimal pH, increase of temperature to about 55°C can further increase the rate of hydrolysis. Furthermore, phytic acid in flours (which had smaller particle size) was more easily hydrolyzed than in coarse meals. Accordingly, phytic acid levels in breads made from coarse meals would be higher than in breads from whole-meal flour. Our results showed that it should be possible to bake traditional rye bread with a low phytic acid content by using the sourdough procedure and acidified sponges. For whole wheat breads, baking formulas with acidified sponges and sourdough should be considered. It is possible to produce low-phytate bread by incorporating as much as possible of the meal or flour into the unfermented sponge, provided that the satisfactory sensory quality of the bread is maintained.

#### ACKNOWLEDGMENT

We thank W. Bushuk and P. Ng for revision of the manuscript.

#### LITERATURE CITED

- BARTNIK, M., and FLORYSIAK, J. 1988. Phytate hydrolysis during breadmaking in several sorts of Polish bread. Nahrung 32:37.
- BLUMENTHAL, A., and SCHEFFELDT, P. 1983. Zum Phytinsäuregehalt schweizerischer Brote. Mitt. Geb. Lebensmittelunters. Hyg. 74:348.
- CHHABRA, P., and SIDHU, J. S. 1988. Fate of phytic acid during bread making. Nahrung 32:15.
- COSGROVE, D. J., ed. 1980. Studies in Organic Chemistry. Vol. 4. Inositol Phosphates, Their Chemistry, Biochemistry and Physiology.

Elsevier Scientific Publishing: Amsterdam.

- DEUTSCHE GESELLSCHAFT FÜR ERNÄHRUNG, ed. 1988. Ernährungsbericht 1988. Henrich: Frankfurt/Main.
- FARIDI, H. A., FINNEY, P. L., and RUBENTHALER, G. L. 1983. Effect of soda leavening on phytic acid content and physical characteristics of middle eastern breads. J. Food Sci. 48:1654.
- FRETZDORFF, B., and WEIPERT, D. 1986. Phytinsäure in Getreide und Getreideerzeugnissen. Mitt. I: Phytinsäure und Phytase in Roggen und Roggenprodukten. Z. Lebensm. Unters. Forsch. 182:287.
- HARLAND, B. F., and HARLAND, J. 1980. Fermentative reduction of phytate in rye, white, and whole wheat breads. Cereal Chem. 57:226.
- KNORR, D., WATKINS, T. R., and CARLSON, B. L. 1981. Enzymatic reduction of phytate in whole-wheat breads. J. Food Sci. 46:1865.
- LASZTITY, R., and LASZTITY, L. 1990. Phytic acid in cereal technology. Pages 309-371 in: Advances in Cereal Science and Technology.

Vol. 10. Y. Pomeranz, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.

- McKENZIE-PARNELL, J. M., and DAVIES, N. T. 1986. Destruction of phytic acid during home breadmaking. Food Chem. 22:181.
- MEUSER, F., and MEISSNER, U. 1987. Verfahrenstechnische Massnahmen zur Verbesserung des Phytatabbaus bei der Vollkornbrotherstellung. Ernährung/Nutrition 11:102.
- ROHRLICH, M. 1969. Getreideenzyme. Paul Parey: Berlin. p. 31.
- SPICHER, G., and STEPHAN, H. 1987. Handbuch Sauerteig, Biologie, Biochemie, Technologie. Behr's: Hamburg. p. 241.
- WHEELER, E. L., and FERREL, R. E. 1971. A method for phytic acid determination in wheat and wheat fractions. Cereal Chem. 48:312.
- WU, X. Q., LIANG, Y. T., WU, Y. S., and SEIB, P. A. 1984. Low phytate whole-wheat bread and muffins. Pages P-1 to P-30 in: International Symposium on Advances in Baking Science and Technology: Manhattan, KS.

[Received May 21, 1991. Accepted November 18, 1991.]