Improved Canning Stability of Rice by Chemical Modification

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ABSTRACT

The process developed involves intra- and intermolecular cross-linking of rice starch by epichlorohydrin. Reinforcing the bonds holding the granules together within the kernel results in marked changes in the swelling behavior of the rice grain, and its subsequent resistance to overcooking. The process would eliminate the need for parboiling rice for use in heat-processed formulations such as canned soups. Solids losses were 78% less than those obtained from commercial parboiled rice suitable for canning.

Prior to the development of commercial parboiling in the 1940's, the texture of canned rice in semi-liquid media such as soups was largely unacceptable (1). Parboiling certain varieties of rice, such as Bluebelle and Belle Patna, has enabled canners to produce commercially acceptable products only when processing conditions are not too severe; for example, as is the case with agitated retorts owing

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to improved heat transfer. Conventional retorting equipment can be used if the rice is canned in a limited-moisture media (2). However, in many cases it would be desirable to use rice in a number of products processed with conventional equipment but having too high a moisture content to ensure the stability of the rice kernel.

Canned rice in soups and other semi-liquid media should be white, with separate, noncohesive kernels, and with minimum amounts of longitudinal splitting and fraying of edges and ends. The canning liquor should be clear and devoid of excessive starch (1,2,3).

The purpose of this investigation was to develop a rice which could withstand retorting at 240°F. for 60 min. in a liquid media and maintain the characteristics described above.

MATERIAL AND METHODS

The process involves modification of the rice grain or kernel by cross-linking. Reinforcing the bonds holding the granules together within the kernel results in marked changes in the swelling behavior of the rice grain and its subsequent resistance to overcooking.

Activation

Fifty grams of white milled rice (Starbonnet, obtained from Dore Rice Mill, Inc., Crowley, La.) was washed with tap water in a 250-ml. Erlenmeyer flask to remove the adhering talc and glucose. Fifty milliliters of 0.2N sodium hydroxide and 3.0 g. of sodium chloride were added, and the mixture was allowed to stand for 2 hr.

Cross-Linking

After soaking, 13.0 ml. of a freshly prepared 1% epichlorohydrin solution (1 ml. epichlorohydrin made up to 100 ml. with 0.2N sodium hydroxide) was added to the flask and allowed to react on a shaker for 4 hr. The flask was closed with a rubber stopper to prevent loss of the volatile epichlorohydrin.

Neutralization

After cross-linking, the alkali-salt-epichlorohydrin mixture was decanted. The rice was washed several times with tap water, resuspended in 50 ml. of water, and neutralized slowly by adding drops of 4N hydrocloric acid. The neutralization step was carried out for 8 hr., after which the rice was washed thoroughly with tap water and air-dried at room temperature.

Evaluation

The following samples or treatment variations were employed in the course of evaluating the stability of the cross-linked rice: a) the rice cross-linked in the manner described previously; b) the original untreated rice; c) rice treated in the same manner as the cross-linked, except that the cross-linking reagent was omitted; and d) a commercial parboiled rice (Bluebelle) suggested for canning.

Twenty grams of rice from each treatment was weighed and placed in a 211 × 400 C-enameled can. Each can was filled with boiling water (pH 7), after which the cans were sealed and retorted at 240°F. for 60 min. and quickly cooled in running tap water. The evaluation process was carried out as follows:

a) Solids loss. The solids loss was obtained by calculating the difference in weight between the dry-matter content of the original sample and the dry-matter content of the sample retained after washing over a 1.68-mm. wire-mesh screen, as outlined by Webb and Adair (4).

b) Elongation ratios. Length of canned rice was divided by the length of the raw rice.

c) Subjective rating. Rice samples were grouped subjectively into five categories based on general appearance and condition of surface, using the standards recommended by Webb and Adair (4).

The extent of cross-linking of starch with epichlorohydrin was determined by measuring the quantity of unreacted epichlorohydrin in reaction filtrates. The unreacted epichlorohydrin was converted to glycerol by hot alkali. Periodate oxidation of the glycerol solutions yielded formaldehyde, which was estimated colorimetrically by the chromotropic acid color reaction (5).

RESULTS AND DISCUSSION

The development of new and improved long-grain rice (*Oryza sativa* L.) varieties having the parboil-canning stability required for use in heat-processed formulations, such as canned soups, has been an important part of rice-breeding programs for a number of years (4). Jojutla, a Mexican variety not adapted in the U.S., has been shown by Webb and Adair (4) to have one of the lowest percentages of solids loss (9%), while showing excellent kernel stability for parboil-canning processes. Belle Patna and Bluebelle are the U.S. varieties commonly used in parboil-canning processes. According to Webb and Adair (4) these varieties show a solids loss of 18 to 17%, respectively.

In this investigation, the cross-linked rice was found to have a solids loss of 5.2% (Table I), which was 78% less than that obtained from commercial parboiled samples. The low solids loss of the cross-linked samples is evidenced by the clarity of the canning liquor seen in Fig. 1. Figures 1, 2, and 3 also demonstrate that the cross-linked rice had a greater resistance to overcooking while maintaining kernel stability. Less distortion of the grain was reflected in the elongation ratio (Table I) and is clearly evident in Fig. 2. Extensive checking was noted in the treated samples during the activation process, however; no problems were encountered with the grains breaking during subsequent processing or canning.

TABLE I. CANNING STABILITY WITH VARIOUS TREATMENTS[a]

Treatment	% Solids Loss	Elongation Ratio	Subjective Rating
Cross-linked	5.2	1.89	1 (Excellent)
Untreated (control)	25.5	1.28	5 (Poor)
Treated (control)	32.5	...[b]	5 (Poor)
Commercial parboiled (Canners Quality)	23.7	1.58	3 (Fair)

[a]Average of six analyses.

[b]Grains were too distorted for measurement.

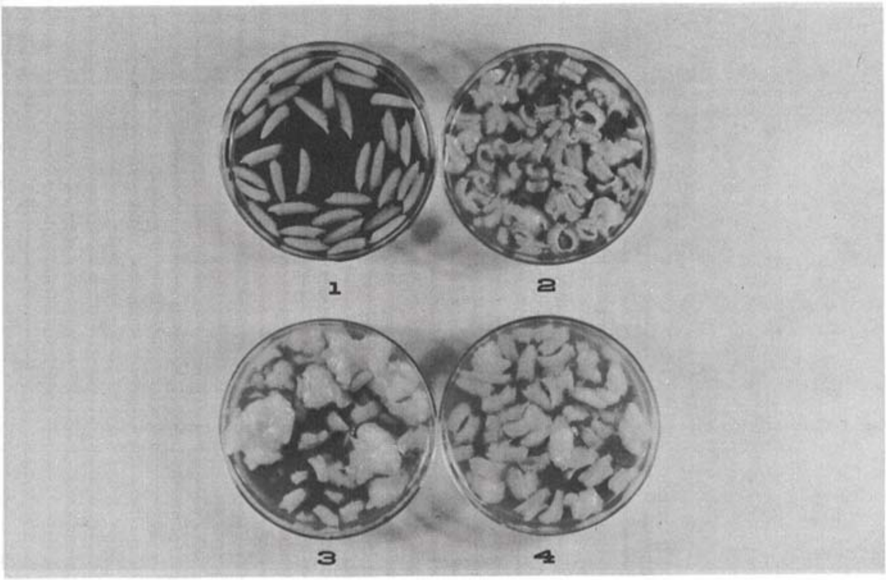


Fig. 1. Canning stability of cross-linked rice. 1. Cross-linked. 2. Treated control. 3. Untreated control. 4. Commercial parboiled.

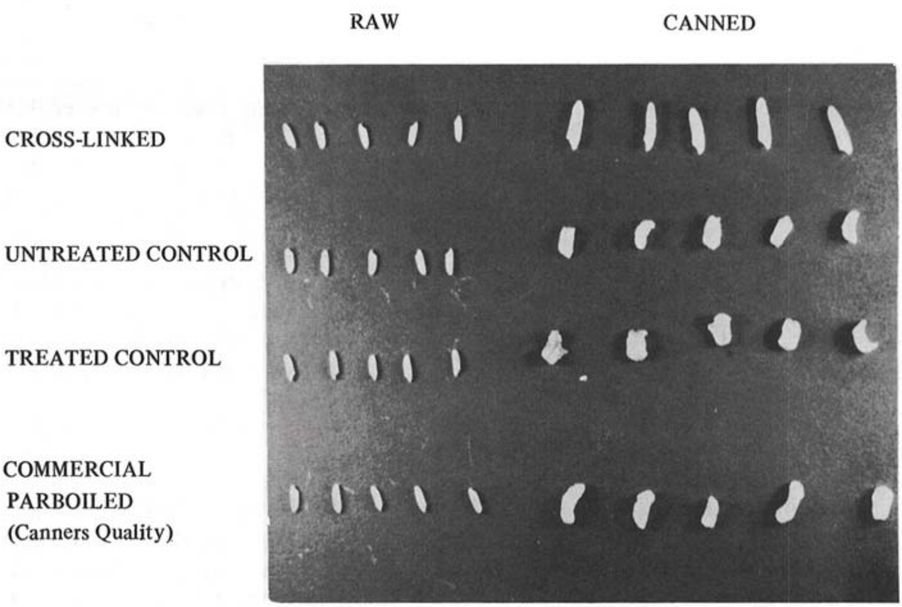


Fig. 2. Distortion of rice grains during canning.

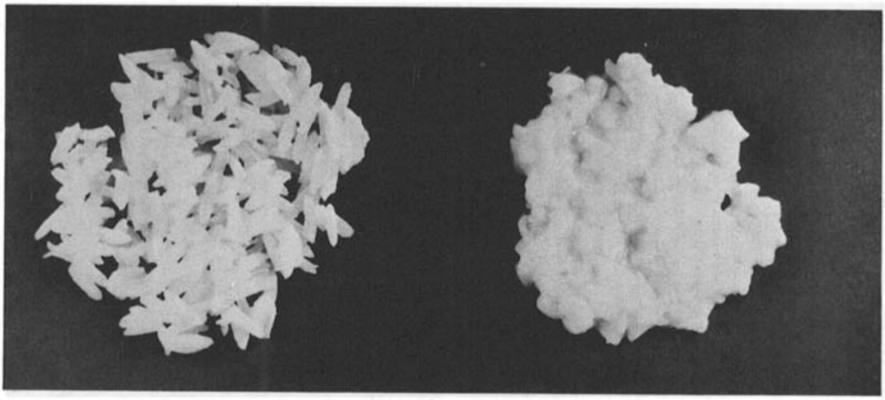


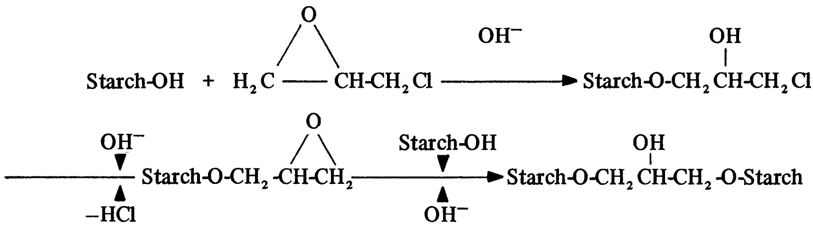
Fig. 3. Canned rice after draining off the liquid. Left: cross-linked; right: untreated control.

From the standpoint of time and expense involved in breeding programs for developing rice varieties suitable for canning, perhaps faster gains can be made through chemical modifications which result in improved cooking and canning characteristics. The textural quality of canned rice has been shown by various researchers (2,4,6,7) to be influenced by varietal differences, age, parboiling treatment, pH, fat content, salt concentration, and blanch time. However, these factors should be of less importance in cross-linked rice.

The difficulties met in the canning of rice have been due to the behavior of the starch in the rice grain when exposed to heat in liquid media. The starch granules of rice are 3 to 5 μ in diameter, with intermolecular hydrogen bonds responsible for their integrity. When the starch is heated in water, a point is reached where the hydrogen bonds holding the granules together are weakened and an irreversible swelling occurs. If heating is continued, the granule will finally rupture. The basic idea behind cross-linking starch in rice is to enhance the strength of the swollen granules so that they will be more resistant to rupture. This is accomplished by treating the starch with small amounts of di- or polyfunctional agents capable of reacting with hydroxyl groups on two or more different molecules within the granule. By this technique, the hydrogen bonds responsible for holding the granule intact are reinforced with ether bonds. As a result, when cross-linked rice is cooked in water at temperatures which weaken or destroy the hydrogen bonds, the integrity of the swollen granule is still maintained by virtue of the chemical cross-links.

The cross-linking of starch in rice is very similar to cross-linking in dispersed granular starch, with the exception that the starch in rice is still maintained in the kernel form. Owing to the high degree of organization within the kernel, activation and cross-linking times are longer than those required for dispersed starch granules. For most cross-linking reactions, starch is activated by strong bases. Although rice starch granules can be completely gelatinized in aqueous alkali, the degree of granule swelling depends upon the nature of the alkali; the relative amounts of starch, alkali, and water; the temperature; and the presence or absence of neutral salts. The reactivity of starch in aqueous alkali is increased by the addition of neutral salts (8). These salts shift the adsorption equilibrium such that alkali adsorption is increased, probably by decreasing the effective water concentration through solvation. In addition, these neutral salts in alkaline slurries reduce the tendency of the starch granules to swell at higher alkali concentrations or to gelatinize as they become increasingly disorganized by the introduction of substituent chemical groups (8). The function of the salts may also retard the hydrolysis of the cross-linking reagent epichlorohydrin, thus permitting greater penetration of the reagent into the granule and more uniform cross-linking (9).

Epichlorohydrin has been extensively used to produce inhibited or cross-linked starches (10,11,12). In its reaction with hydroxyl groups of starch, mono- and diethers are formed, the diethers being either inter- or intramolecular. It probably cross-links starch in an alkaline system in a sequence of three reactions (5).



Under the alkaline conditions required for the cross-linking of starch, partial hydrolysis of epichlorohydrin to glycerol occurs. Thus, it is important that the epichlorohydrin reagent be made only a few minutes prior to its addition to the rice.

Under regulations of the Federal Food, Drug, and Cosmetic Act, starch can be etherified with epichlorohydrin in concentrations up to, and including, 0.3%. Consequently, this particular restriction was employed in the treatment of the rice samples. However, analysis of the reaction filtrates revealed that 48.7% of the 0.3% epichlorohydrin added (based on the weight of rice) remained unreacted.

The alkali used in the activation step causes a yellow discoloration of the grain, which appears to be pH-dependent. In the course of alkali neutralization, the yellow color disappears. Neutralization required 8 hr. because of the slow leaching of the alkali from the grain.

It should be noted that all reactions described in the process take place at room temperature (72°F.), employing the minimum amount of equipment. If on a commercial scale, the drying of the rice after processing would probably represent the larger cost.

Acknowledgment

Appreciation is expressed to Continental Can Company, Inc., for supplying the cans for the above research.

Literature Cited

1. DEMONT, G. I., and BURNS, E. E. Effects of certain variables on canned rice quality. Food Technol. 22: 1186 (1968).
2. ROBERTS, R. L., HOUSTON, D. F., and KESTER, E. B. Process for canning white rice. Food Technol. 7: 78 (1953).
3. KESTER, E. B. Rice processing. In: The chemistry and technology of cereals as food and feeds, ed. by S. A. Matz, p. 451. Avi Pub. Co.: Westport, Conn. (1959).

4. WEBB, B. D., and ADAIR, C. R. Laboratory parboiling apparatus and methods of evaluating parboil-canning stability of rice. Cereal Chem. 47: 708 (1970).
5. HAMERSTRAND, G. E., HOFREITER, B. T., and MEHLTRETTER, C. L. Determination of the extent of reaction between epichlorohydrin and starch. Cereal Chem. 37: 519 (1960).
6. FERREL, R. E., KESTER, E. B., and PENCE, J. W. Use of emulsified oils to reduce cohesion in canned white rice. Food Technol. 14: 102 (1960).
7. GHOSH, B. P., and SARBAR, N. Effect of some inorganic salts on water absorption by rice during cooking. Ann. Biochem. Exp. Med. 19: 83 (1959).
8. ROBERTS, H. J. Non-degradative reactions of starch. In: Starch chemistry and technology, ed. by R. L. Whistler and E. F. Paschall; vol. 1, p. 442. Academic Press: New York (1965).
9. WETZSTEIN, H. L., and LYON, P. Modified starches. U.S. Patent 2,754,232. (1956). [Chem. Abstr. 50: 13490 (1956).]
10. KONIGSBERG, M. Ungelatinized starch ethers from polyfunctional etherifying agents. U.S. Patent 2,500,950 (1950). [Chem. Abstr. 44: 6666 (1950).]
11. HOFREITER, B. T., MEHLTRETTER, C. L., BENNIE, J., and HAMERSTRAND, G. E. Cross-linked dicarboxyl starch of stable viscosity. U.S. Patent 2,929,811 (1960). [Chem. Abstr. 54: 13704 (1960).]
12. SENTI, F. R., MELLIES, R. L., and MEHLTRETTER, C. L. Preparation and physical characteristics of cross-linked hypochlorite oxidized cornstarch. U.S. Patent 2,989,521 (1961). [Chem. Abstr. 59: 3000 (1961).]

[Received June 28, 1971. Accepted February 3, 1972]