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Reduction of cyanide content of cassava flour in Mozambique by the wetting method

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Abstract

Fifty cassava flour samples from Mogincual District of Nampula Province in Mozambique were found to contain, on average, 43 mg HCN equivalents/kg flour (ppm), of total cyanide, which is typical for a year of average rainfall. Five gram samples of the 30 flour samples of highest cyanide content were mixed with water and left for 5 h at 30 °C and it was found that the mean% retention of cyanide was 16.7%. Using 500 g instead of 5 g samples caused an increase in the % retention due to accumulation of the very weak acid, HCN, in the damp flour mass, which also decreased its pH and somewhat reduced the rate of breakdown of linamarin catalysed by linamarase. This problem was overcome by spreading out the damp flour in an approximately 0.5 cm thick layer on a tray, which allowed the release of HCN.

If the wetting/spreading method is acceptable to users it could greatly reduce the cyanide intake of the population of eastern, southern and central Africa and has the potential to eliminate konzo from Africa.

Keywords: Cyanide; Cassava flour; Wetting method; Konzo; Linamarin; Linamarase; Mozambique

Article Outline

1. Introduction

Cassava is the most important food source in the tropics after rice and maize. The plant produces two cyanogenic glucosides, linamarin and a small amount of lotaustralin (methyl linamarin). If the plant is attacked by predators, an enzyme, linamarase, catalyses breakdown of the glucosides to give hydrogen cyanide. Processing of the roots to give a stable product, causes removal of most of the cyanogens. However, in cassava flour produced in eastern, southern and central Africa, there is still 12–33% retention of cyanide (Cardoso et al., 2005), whereas with gari produced in west Africa and farinha in central and southern America the retention of cyanide is an order of magnitude lower at 1.8–2.4% (Dufour, 1994 and Oke, 1994). The relatively high retention of cyanide in the former case is due to the inefficient removal of cyanide by the processing methods, sun drying or heap fermentation. Our previous studies have shown average cyanide levels of 40–46 mg HCN equivalents/kg flour (ppm) in normal years (Cardoso, Ernesto, Cliff, Egan, & Bradbury, 1998). In a year of low rainfall, we found a mean cyanide content of cassava flour of 100–148 ppm (Cardoso et al., 2005 and Ernesto et al., 2002), more than 10 times the WHO safe level of 10 ppm for cassava flour (FAO/WHO, 1991).

High intake of cyanide from consumption of high cyanide cassava flour is associated with konzo, an irreversible paralysis of the legs in children and women of child-bearing age, which occurs in many countries of southern, eastern and central Africa (Howlett et al., 1990 and Ministry of Health Mozambique, 1984). Konzo has not been reported from west Africa, presumably because gari and other cassava products used there contain much less cyanide than the flour used in southern, eastern and central Africa (Cardoso et al., 2005). Bradbury (2006) recently reported a simple, new wetting method that is applied, just prior to cooking, which substantially reduces the cyanide content of cassava flour. In this paper we report the successful laboratory trial of this method in Mozambique, using flour samples collected from an area where konzo has occurred recently. If acceptable to users, the method could contribute to a large reduction of cyanide intake in communities dependent on a diet of high cyanide cassava.

2. Materials and methods

2.1. Collection and preparation of flour samples

Fifty cassava flour samples were collected in plastic bags from 50 rural producers in Mujocojo, in Mogincual District of Nampula Province in northern Mozambique. They were transported by air to Beira and were analysed on the subsequent day. Flour samples used in Canberra for pH experiments were prepared from cassava grown in the Plant Culture Facility at the Australian National University. The peeled roots were weighed and dried at

50 °C for one week to constant weight. The dry roots were ground in a coffee grinder.

2.2. Methodology of experiments to measure cyanide loss by wetting method

Preliminary analyses of the 50 flour samples from Mujocojo were carried out using the picrate kit B2 for determination of the total cyanide content of cassava flour (Bradbury et al., 1999 and Egan et al., 1998). Thirty samples, with the highest cyanide contents, were chosen for further study, using the simple wetting method (Bradbury, 2006). A 5 g sample of flour in a beaker was well mixed with 6.25 ml water and two 100 mg samples were placed in plastic vials for analysis. The beaker was placed in an oven at 30 °C for 5 h, after which two more 100 mg samples, were taken for analysis. In some cases, larger samples of flour, ranging up to 500 g, were thoroughly mixed with 1.25 times their weight of water and left in bowls (depth of damp flour about 4 cm) or spread out on trays in layers of 0.5–1.5 cm thick. Flour samples were analysed at zero time and after 5 h at 30 °C. The % retention of cyanide of the damp flour after 5 h at 30 °C was calculated.

2.3. Analysis for total cyanide

A 100 mg flour sample was placed in a plastic vial, a small filter paper impregnated with pH 6 buffer, and linamarase was added, followed by 0.5 ml of water and a yellow picrate paper. The vial was immediately closed and left at 30 °C overnight. The next day the yellow–brown picrate paper was separated from the plastic backing strip and placed in 5.0 ml of water. The absorbance of the solution was measured at 510 nm and the total cyanide content in ppm was calculated by multiplying by 396 (Bradbury et al., 1999).

2.4. pH-dependence of cyanide loss from wet flour

Five grams of flour were thoroughly mixed with 6.25 ml of 1 M phosphate buffer, the pH of which had been adjusted with base or acid to give the desired pH after mixing with the flour. The pH of the damp flour was measured at zero time, and after 5 h, by taking 0.5 g damp flour, adding 5 ml of distilled water and determining the pH of the mixture using a pH meter checked against two pH standards. Two 100 mg samples of the damp flour were taken for cyanide analyses (see Section 2.3) at zero time and after 5 h at 30 °C. The % retention of cyanide of damp flour after 5 h was calculated at various pH values.

3. Results and discussion

3.1. Cyanide loss by the wetting method

The cyanide contents of the 50 cassava flour samples from Mogincual District ranged from 8 to 85 ppm, with an average of 43 (SD 20) ppm, which agrees well with previous results from that district of 45 ppm in 1996 (Cardoso et al., 1998) and 41 ppm in 1999 (Cardoso et al., 2005). The mean cyanide content of the 30 cassava flour samples of highest cyanide content was 30 (9) ppm straight after mixing with water and 5 (3) ppm 5 h later, which gave a % retention of 16.7%. This cyanide removal is about twice that obtained in the earlier study by Bradbury (2006), presumably because the Mujocojo flour samples had a greater linamarase content than those in Australia. Bradbury (2006) showed that flour samples that contained only a small amount of linamarase lost very little cyanide over the 5 h period of wetting, but if exogenous linamarase was added then rapid breakdown of linamarin occurred.

3.2. Effect of increased sample weight on % retention

From five different samples of flour, the mean % retention of cyanide after 5 h of treatment using 500 g flour was 59 (11) but, using 5 g flour, was only 26 (11). It was thought that this may have resulted from partial entrapment of water-soluble HCN in the damp flour mass, which may also have reduced the pH of the damp flour.

3.3. Measurements of pH of damp cassava flour

Measurements in Beira of the pH of six damp flour samples (2 of 5 g and 4 of 300 g) showed a decrease of pH, from an average of 6.3 at zero time to 5.8, 5 h after wetting. This decrease of pH is almost certainly due to the liberation of HCN in the flour/water mass, since HCN is a water soluble very weak acid with $K_a = 4.93 \times 10^{-10}$ (Weast, 1974). Calculations show that a 0.002 M solution of HCN in water, that would be liberated from 70 ppm cassava flour under the conditions of the experiment, would have a pH of 5.95.

Similar measurements made in Canberra on 5 g samples of 19 different flour samples, each mixed with 6.25 ml of water, showed no decrease of pH from 6.4 over a 5 h period with no evidence of spoilage, but there was an average decrease to pH 5.4 over a 22 h period, with evidence, in some cases, of mold growth and flour spoilage. The zero change of pH found over 5 h with the Canberra flour samples would be due to their slower release of cyanide (Bradbury, 2006) compared with the Beira samples and their small sample size (5 g), that would allow HCN to escape readily. The average decrease of pH of one unit found over 22 h in these samples is due to lactic acid fermentation such as occurs in heap fermentation, during cassava processing in Mozambique (Tivana, Bvochora, Mutukumira, Owens, & Zvauya, 2003).

3.4. Effect of pH on % cyanide retention in flour

For three different cassava flour samples, 6.25 ml of 1.0 M buffer solution, of various pH values, were mixed with 5 g flour and the pH and cyanide content of the damp mass were measured at zero time and after standing for 5 h at 30 °C. The minimum % retention was at pH 6.3–6.7, which agreed reasonably well with the pH optimum of linamarase of about 6.0 (Yeoh, 1989), that catalyses hydrolysis of linamarin to acetone cyanohydrin. From the data for three different flour samples, the mean ratio (% retention at pH 5.8/% retention at pH 6.3) is 1.5, which could partially explain the increased retention of cyanide with 500 g as compared with 5 g samples (see Section 3.2). The decreased rate of production of HCN below pH 6.3 is due to the decreased activity, at lower pH values, of linamarase in breaking down linamarin to acetone cyanohydrin, plus the progressively decreased rate of breakdown of acetone cyanohydrin to HCN as pH falls below 6 (White, Mc Mahon, & Sayre, 1994).

3.5. Spreading damp flour on a tray to achieve loss of cyanide

Samples of the same cassava flour were mixed with 1.25 times their weight of water and left at 30 °C and the cyanide content was measured at zero time and 5 h later. The treatment and results were as follows: (a) triplicate 5 g samples in a beaker, % retention was 14(4); (b) duplicate 500 g samples in a bowl with damp flour about 4 cm deep, % retention was 38 (5); (c) triplicate 500 g samples spread on a tray in a layer about 0.5 cm thick, % retention was 18 (3) and (d) single 500 g sample spread on a tray in a layer about 1.5 cm thick, % retention was 27%.

The % retentions of the 5 g and 500 g samples in a 0.5 cm layer on a tray were about the same and less than that using a thicker (1.5 cm) layer of damp flour and less than that using a bowl with a 4 cm thick lump of damp flour. Clearly, it is important to facilitate the removal of water-soluble HCN gas (b.p. 26 °C) from the damp flour mass by spreading it out in a layer about 0.5 cm thick. Any accumulation of the weakly acidic HCN in the damp flour mass would also reduce the pH and have the effect of lowering the rate of breakdown of linamarin catalysed by linamarase (see Section 3.4).

4. Conclusions

The results of this study with cassava flour in Mozambique show that the cyanide level is reduced to about one sixth of its former value by mixing with water and spreading it out in a thin layer for 5 h at 30 °C. In a normal year, with an average cyanide content in Mogincual District of Nampula Province of 43 ppm, this reduction would lower the cyanide content to 7 ppm, below the 10 ppm WHO safe limit (FAO/WHO, 1991). However, in a year of low rainfall, the cyanide content of flour is more than doubled to an average level of

>100 ppm (with consequent incidence of konzo, Ernesto et al., 2002). A six-fold reduction in cyanide content on processing would give a cyanide level of 16 ppm, unless the linamarase content of cassava also increased due to low rainfall, in which case the increased amount of enzyme present could decrease the cyanide level to <16 ppm.

The wetting/spreading method therefore has the potential to greatly reduce the cyanide intake of the cassava flour-eating population of eastern, southern and central Africa, with the possible elimination of konzo. The acceptability of the method among communities dependent on high cyanide cassava is being evaluated.

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