Processing and Detoxification of Cassava

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ABSTRACT

Cassava contains the cyanogenic glucoside linamarin, which, on hydrolysis, yields hydrocyanic acid, one of the most toxic plant substances known. After processing, some of the cyanide is still left in the product and has been implicated in the etiology of such diseases as goiter and tropical ataxic neuropathy. Because of this, efforts are now being made to products that are cyanide-free.

The various methods of processing are reviewed with emphasis on the production of gari, which is one of the most typical and best studied products. The rate of detoxification in each process is shown. Experiments simulating the various processes aimed at improving the quality of the products are discussed, and the rate of detoxification is given. The detoxification problems are reviewed. On the whole, it appears that sun-drying is an inefficient method of detoxifying cassava; however, soaking in water is much more efficient. The best combination is sequential soaking, sun-drying, and cooking, which will virtually remove all the cyanide.

Introduction

One would wonder why a fibrous toxic root with hardly any protein could be the staple of millions of people in the tropics where the actual nutrient that is in short supply is protein. There is also energy shortage as only about 68% of the energy requirement is available (Gutiérrez and Anderson, 1972). Hence, it is desirable to produce more of it, and future demand will increase because it is not regarded in the tropics as an inferior food.

From the literature cassava represents about 14% to 58% of the total caloric intake in 14 countries, and when this is limited to certain areas of a particular country, the true picture will emerge. For example in south eastern Nigeria cassava contributes about 43% to 73%, and if taken with yams about 82% to 93% of the total calorie intake. Normanha (1970) reported that in Brazil in 1962-63 cassava consumption was 124 kg person per annum at the national level, representing an urban intake of 42 kg and rural intake of 200 kg. Phillips (1974) maintained that cassava will continue as an important staple in the human diet and can supply about 500 million persons with about 50% of their energy need. By 1990 it is possible in spite of the increase in production, Africa may only have about 5% surplus, although the Far East and especially Brazil would have a lot of surplus.

From reports of several investigators it could be summarized that the population which lives on cassava and its products have higher serum and urinary concentration of SCN than the control population in Europe or elsewhere with little or no consumption of cassava. Moreover differences also occur from one region to the other as well as in the methods of preparing cassava-based meals. The question then arises as to whether this SNC overload is due to the original cyanide content of the fresh cassava roots or of the cassava products eaten. It is pertinent that Bourdoux et al (1982) found distribution of cyanide content of fresh cassava roots among the Ubangi, Kivu and Bas, Zaire regions of Zaire where there is SNC overload and high cases of goitre are as follows:

The percentage of innocuous roots (HCN content less than 50 ppm) increased from 45% in Ubangi to 56% and 80% in Kivu and Bas Zaire respectively. In contrast the percentage of dangerously poisonus (HCN content higher than 100 ppm) was almost identical in Ubangi (24%) and Kivu (21%) and was markedly lower in Bas Zaire (4%).

It is therefore essential to review the various methods of preparation of cassava-based foods and find out the extent of detoxification by the various methods and also suggest means of improvement of the methods.

Detoxification

When cassava is processed into foodstuffs, not all the cyanogenic of glucosides are eliminated. Some remain and are ingested. In the absence of B-glucosidese, most glucoside is excreted unchanged in the urine and very little from the feces (Oke and Adewusi, 1981). However, if taken together with leaf components or other ingredients that may contain a B-glucosidase (in addition to the residual linamarase and cyanogenic glucoside which will react on rehydrating) then hydrolysis takes place and hydrocyanic acid (cyanide) is librated. As is well recognized cyanide is one of the most powerful poisons known. It is destructive to all forms of life in which it affects both the individual cells such as the important nerve cells, and also reasts with hemoglobin of the red blood corpuscles to form cyanohemoglobin. Death results shortly after a sufficient dose is ingested. It interferes with enzymes which play an important part in life processes and is therefore a violent protoplasmic poison for all forms of life whether they be bacteria, yeast or germinating seeds. In certain fish ova it suspends the autolytic process accompanying death so that the cells remain in condition between life and death for several days. On the other hand if the amount of cyanide released is minimal then the body has a very efficient system of detoxification to thiocyanate (SNC) through the enzyme rhodanese as has been reviewed by Oke (1969).

Toleration of hydrocyanic acid in foodstuffs and animal feeds, and methods of reducing it in fresh roots to within suitable limits, are major problems in the use of cassava products. It is difficult to remove the last traces without making the food unsuitable for consumption. Even when the sweet variety is boiled or dried or when the bitter is fermented there is still the possibility of some residual cyanide, and the range may be wide, 10 to 120 ppm, depending on the cyanide content of the fresh root.

It appears that fufu prepared by soaking and sun-drying cassava is the most efficient detoxification process (HCN sometimes less than 1 ppm) whereas those prepared by sun-drying alone e.g. fuku is less efficient (HCN about 17 ppm).

Those fermented and fried could be effective provided it is fried with palm oil while fermentation and syn-drying seems to be very effective.

Since peeled cassava root contains about 61% water and a soluble toxic cyanogenic glucoside, then the first stage in the detoxification is the removal of at least part of the water which will cary the toxin with it. This is done in several ways as already described (e.g. putting in a sack and weighing it down with stones, centrifuging as is done commercially, use of mechanical press, manual squeezing). Most of residual glucoside (and water) is then eliminated by some form of heating. In some cases there is an initial step of soaking the root for some days during which the microflora in the cassava cause fermentation which is now to be complementary to the activity of the endogenous linamarase which effectively carry out the degradation. Maduagwu and Oben (1981) found that inhibition of linamarase activity by 1,5-gluconolactone (a potent inhibitor of B-glucosidase activity) resulted in a significant lowering of the degradation of linamarin by about 35% in 24 hours and 65% in 72 hours. On the other hand when glucose is included in the above medium, there is an enchanced degradation by about 10% especially after 36 hours which is presumably due to an increase in microbial population in situ. Since various cassava species contain different amounts of sugars this may become an important factor in the relative rate of fermentation. When fermentation was inhibited by sterilization or by addition of sodium iodoacetate, the rate of disappearance of bound cyanide from the medium was similar to the control especially within the first 48 hours indicating that it is the endogenous linamarase that effectively cause the breakdown of the linamarin.

In some cases detoxification is carried out by heating only. This seems to be effective in some cases and not in others because the heat may result in the breakdown of the enzyme linamarase without affecting the glucoside. Thus cooking destroys the enzyme at about 72°C leaving about 90% of the glucoside intact. In a similar way simple drying of slices or rasped root is capable of removing about 90% of the glucoside at 60°C but is less effective if heating is carried out at 100°C due to denaturing of the enzyme. On the contrary Paula and Rangel (1939) reported that cassava containing 39 ppm was reduced to 17 ppm by sun drying and to 6 ppm by oven drying. Joachin and Panditteserkere (1944) reported that boiling a variety of cassava roots containing 103 to 232 ppm could reduce the cyanide content to 27 to 87 ppm without correlation to the initial content of cyanide in the roots. Those that did not become soft and floury on boiling were least affected. Raymond et al (1941) was able to reduce the cyanide content from 332 to 10 ppm by boiling while Paula and Rangel (1939) got rid of all the cyanide in their root by boiling only. Steeping in warm water for short periods before drying can reduce the cyanide content to a considerable degree especially if it is grated as well. Thus Razafimaherry (1953) reported that the Madagascar food product, Bournoka, which is prepared by steaming, is free of cyanide.

From the traditional processing of cassava, the glucoside is eliminated either at the soaking (fermentation) stage or else during the heating stage (especially with palm oil) or both. In Nigeria the effect of cyanide toxicity is counteracted by giving palm oil and it is interesting that gari prepared by drying the fermented cassava pulp with palm oil usually does not contain any cyanide compared 5 to 20 ppm in those fried without palm oil (Oke, 1979). The effect of palm oil on cyanide toxicity is the subject of investigation at present (Oke and Fumiyan, 1982).

Again, among various cassava products, gari is the one that has been extensively studied and so most of the mechanism of detoxification will be

inferred from it. Bark or cassava contains most of the enzyme while the inner part contains little. During peeling and grating the enzyme comes into contact with the glucoside and hydrolysis takes place librating cyanide, the rate depending on the length of time contact is made. This is probably why fermentation is allowed to proceed for days. This could, however, be accelerated if the whole root is grated as the activity of the enzyme in the bark (and leaves) is so great that hydrolysis is complete within a very short period (1 hour). A lot of work has been done in this respect by Meuser and Smolnik (1979). As is well known the first stage of breakdown of linamarin is hydrolysis to glucose and cyanohydrin, and the latter then breaks down to acetone and hydrocyanic acid. So the cyanide in cassava can occur as free hydrocyanic acid or as bound (glucoside or cyanohydrin). However, because of the high instability of cyanohydrin at pH values over 5.0 (the pH of the pulp is usually about 6.0) the equilibrium is usually to the right i.e. release of cyanide (Cooke, 1978) and so Meuser and Smolnik (1979) devised a means of getting rid of the fruit water in gari preparation to limit the cyanide content to less than 10 ppm. The next problem is getting rid of the residual cyanide by heating. Their results from different drying techniques show that freeze drying or flash drying eliminates only the free cyanide which accounted for only 50% of the total cyanide present; whereas roller drying or drum drying of the fresh pulps at pH of 5.5 to 5.8 removes all the cyanide almost completely. Here thermal decomposition of the glucoside probably takes place and the equilibrium to the right (i.e. cyanide release) is favored. On the other hand roller drying of fermented pulp or drum drying of fermented and dewatered pulp results in high residual cyanide due to the lowering of the pH to 3.8 which favors the equilibrium to the left i.e. high stability of cyanohydrin. Under this condition there is no more release of cyanide and equilibrium between bound and free cyanide is stabilized in favor of the bound cyanide in the form of cyanohydrin. The optimum condition was therefore chosen for the drying of the chips i.e. in a warm air stream.

Table 1. Composition of cassava and its products (% of dry matter).

	Cassava	Gari	Fufu	Lafun	Kpokpogari
Starch	89.3	87.8	95.8	96.4	78.1
Sugars	5.0	0.5	0.6	0.8	0.5
Protein	2.5	1.0	0.6	0.8	1.5
Minerals	2.5	1.1	0.5	2.0	5.2
Crude fiber	3.2	0.6	0.2	0.7	4.2
Ether extract	0.5	0.1	0.1	0.4	0.0
Hydrocyanic acid (ppm)	380	19	25	10	11

Another way of eliminating the cyanide is by allowing the fermentation to proceed for longer period (5 days) to allow the water binding capacity of the mash to be sufficiently changed so that the fruit water can be pressed out to a reasonable degree, carrying with it the toxic cyanide. The bound cyanide can also be eliminated from unfermented pulp by diluting the fruit water. About 50% of the fruit water can be separated as a relatively concentrated solution. This is extremely useful for the elimination of the acidic and toxic fruits water. Using this newly developed process the cyanide content of the gari prepared by Meuser and Smolnik (1979) can be eliminated almost completely.

To understand fully the mechanisms involved in detoxification processes and be able to improve on the traditional methods, the preparation of the various foodstuffs was simulated in the laboratory (Bourdoux et al, 1982; Ketiku et al, 1978). It was found that by increasing the soaking time or boiling time the detoxification process could be improved significantly. The improved method gave cyanide concentration of about 1 ppm as opposed to an average of about 10 ppm (range 1.25 ppm) for the traditional methods. As indicated for fuku, drying the roots for 1 to 2 days showed an increase in the cyanide content. This was due to removal of water from the roots which range from 14% in the first day through 51% in the second day and progressed to about 70% by the eighth day without concomitant loss of cyanide. This therefore resulted in an increase in the cyanide content. Heating in an oven to constant weight at low temperatures gave a similar result to sun-drying. Starting with the fresh root (73.5 ppm) the cyanide content increased to 116.7 ppm on heating at 60°C, but dropped to 28.5 ppm, at 105°C and less than 1% at 165°C. The latter two temperatures are higher than the decomposition temperature reported for linamarase, 72°C (Joachim and Panditteseker, 1944) and linamarin, 150°C (Cerighelli, 1955). This means that at such high temperatures, though the linamarase is destroyed, the linamarin is decomposed by heat and so this is an effective method of detoxification. Unfortunately such temperatures are never attained in practice.

More details of the reactions taking place when cassava is heated at different temperature has been given by Cooke and Maduagwu (1978).

About 29% and 26% of the bound cyanide were lost after drying at 46.5°C and 60°C, respectively, for 18 hr, while the corresponding figures for free cyanide were 82.5% and 83%, respectively. The similarities were probably due to the stability of linamarase at these two temperatures. At higher temperatures of 80° and 100°C there was a faster drying rate with a loss of about 96% free cyanide in both cases but 10% of the bound cyanide at 80°C and 15% at 100°C, the increase probably being due to enzymic browining at 100°C (McWeeny et al, 1974). Drying at lower temperatures caused a gradual drying which took longer at moisture contents and temperatures at which linamarase is active whereas at higher temperature it is very rapid with low moisture contents and above the temperature of stability of linamarase.

Bourdoux et al (1982) found that soaking cassava roots for one day decreased the cyanide content from 108.2 to 59.5 ppm and finally to 2.9 ppm in 5 days (over 97% loss). Cooke and Maduagwu (1978) on the other hand found that rapid stirring in cold water produced a negligible decrease in bound cyanide after 4 hours but about 90% of the free cyanide was removed and most all of this could be accounted for in the water. Leaving overnight caused a marked decrease in the bound cyanide accompanied by a sour smell, indicative of fermentation. However, the free cyanide had returned to about the initial concentration probably due to endogenous linamarase activity following cellular desintegration or to microbial glucosidase activity. Over 90% of the free cyanide was removed on boiling for 15 min, but the bound cyanide was removed more slowly about 55% after 25 min. The loss in bound cyanide was parallelled by an increase in the cyanide content of the water used for boiling. The free cyanide content increased initially and then decreased probably due to the volatility of the free cyanide.

On the whole it therefore appears that sun-drying is an inefficient method of detoxifying cassava while soaking is much more efficient. The best combination will be sequential soaking, sun-drying and cooking which will virtually remove all the cyanide. It therefore appears that the differences in the amount of cyanide

intake in different regions will depend on the method of processing and the cyanide content of the fresh root, and this will affect the concentration of the serum SCN level.

Conclusion

In most methods of processing cassava into foodstuffs there is usually residual cyanide which could vary from traces to high amounts. Among the population that consume these products, a high incidence of thyroid malfunction has been reported and this has been correlated with the ingestion of cassava products. It is therefore necessary to study more closely the traditional methods of processing cassava so as to detoxify the cyanide. More accurate analytical techniques would be needed in order to be able to follow the principles involved in the detoxification processes and be able to improve on it.

Finally we need to study more carefully cases of acute toxicity of cassava and its products so as to determine the factors involved in the toxicity i.e. whether it is the cyanogenic glusosides or other constituents which have not yet been isolated. We know that rapeseed contains saturated and unsaturated nitriles in which the cyanide grouping is not directly linked to sulphur, and this can also result from the hydrolysis of rapeseed glucosinolates (Lo and Hill, 1972). These substances while rather unstable, are very toxic with and LD_{50} for rats of about one-eight of that of goitrin. Thus the severe growth depression exhibited by pigs, chicks and rats consuming raw ground rapessed could be atributed to nitriles rather than the known goitrogens. Also the fact that chlorogenic acid, a potent trypsin inhibitor, has been identified in the polyphenolic fraction of rapessed (Lo and Hill, 1972) could be a pointer to the fact that there might be other potentially toxic substances in cassava not yeat discovered. In addition certain unexpected chemical reactions occur in vivo which are not always detected. For example when intact apricot kernels are steeped in cold water considerable quantities of soluble matter are extracted along with the bitter cyanogenic glycosides prunasin and amygdalin. Endogenous emulsin catalyses the hydrolysis of these two glycosides to glucose and mandelonitrile and the latter then reversibly disassociates into benzaldehyde and hydrogen cyanide. When an attempt was made to recover the extracted matter by concentrating the aqueous solution at temperatures below 40°C, there is a production of new bitterness not attributable to the original cyanogenic glycosides. Spectroscopic characterization confirmed the presence of benzyl bensoate (4), mandelamide (5), butyl B-D-glucopyranoside (6) and benzyl B-D-glucopyranoside (7). The two glucosides possessed an intensely bitter taste and the probable mode of formation was worked out by Godfredsen et al (1978).

In view of the above, one might ask whether there might be other goitrogens presents in cassava or the diets of the people in the goitre-endemic areas reported by Ekpechi (1964) and De Lange (1973). Can it be due to their diathesis? We know that not all forms of nutrient have equal activity and that, for unknown reasons, some individuals have greatly increased requirements while others are susceptible to toxicity from excess. Have these people lost the ability to dispose of the thiocyanate being formed or are they metabolizing the glucoside at such an unsual rate that there is enough thiocyanate to compete with iodine, or is the problem simply one of iodine or protein deficiency? I pose these problems so that none of the salient points will be overlooked in our subsequent interpretation of data to prove the exact causes of goitre.

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