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Some chemical components of Nigerian cassava cultivars and of the processed product

Eine Untersuchung von nigerianischen Cassava Sorten und deren Produkte auf einige chemische Bestandteile

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1. Introduction

Cassava, **Manihot esculenta**, Crantz, forms one of the most important food crops in the tropics. Apart from being a major staple for millions of people in the tropics, cassava is fulfilling new roles in the compound feeds industry where principal markets like West Germany import ca. 600 000 tons of sliced roots annually and the U.S.A. around 100 000 tons of cassava flour annually (Phillips, 1974). Cassava leaves are very rich in protein, vitamins and minerals; they are utulized as vegetables by various communities in Africa and fed to local livestock. In Nigeria, Oyenuga (1959) showed that cassava leaves are capable of serving as protein supplement to ruminants and recently in Thailand (Ciat, 1977) cassava leaf pellets have been successfully manufactured as a protein source for export to West Germany. The peels which constitute 14–16% of the whole tuber are also extensively used for fattening cattle and hogs. The most popular form in which cassava is consumed in West Africa is gari, the staple foodstuff of Nigerians.

The wholesomeness of cassava as a food crop has, however, been a subject of diverse interest and considerable concern (Boorsma, 1905; Bolhuis, 1954; Oyenuga and Amazigo, 1957) and a workshop in London (Nestel and MacIntyre, 1973) reviewed in depth the subject of chronic cassava toxicity. The cassava plant is cyanophoric, the plant synthesizes and accumulates in its edible leaves and tubers, cyanogenic glucosides – linamarin and lotahstralin – which on hydrolysis produce moderate to lethal concentrations of prussic acid (HCN).

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Cassava and its products also contain mannitol which in low concentration is used clinically for treating acute renal failure and for inducing diuresis in surgical cases (Fearnley & Roberts, 1966) but excessively high concentrations of mannitol in the body have adverse effects on the kidney by causing histological lesion known as mannitol nephrosis (Moore, 1963).

Previous reports on the composition of cassava utilized for food and feed in Nigeria (Oyenuga 1959; Oke, 1968) did not sufficiently elaborate on the cultivars nor specify their origin or changes in composition of the processed product. The present study was undertaken to assess the protein, HCN and mannitol content of the best local and hybrid cassava cultivars popularly grown and utilized in major ecological areas of Nigeria. Mannitol determinations were made on the processed gari while the crude protein and HCN contents were investigated in the leaves, raw cassava tubers and the gari processed therefrom.

2. Materials and Methods

2.1 Collection of cassava cultivars.

In April 1975 a survey of the major cassava growing areas of Southern Nigeria was undertaken when stem cuttings of cassava cultivars most popularly grown in each location were collected. They were planted for multiplication at the University of Ibadan Teaching and Research Farm together with three of the improved cassava cultivars currently recommended by the Federal Department of Agricultural Research (Anon, 1971). The accession numbers of the improved cultivars were used in this study while the local names of the best local cultivars were retained. Table 1 shows the sources and names of the cultivars.

Table 1. Cassava cultivars and sources of collection

	Cassava cultivars	Species	Sources of collection
1.	53101 (OLORONTO)	M. esculenta	Western Nigeria
2.	60447) F_1-hybrids	M. esculenta	Fed. Dept. of Agricultural
3.	60506) of 53101	M. esculenta	Research, Ibadan
4.	ISU-NIKAN-KIYAN	M. palmata	Western Nigeria
5.	„Sweet Cassava"	M. palmata	Uyo, Cross River State
6.	Ozu-Nwangwe	M. esculenta	Bendel State
7.	Imo	M. palmata	Imo State
8.	Okobo	M. esculenta	Cross River State
9.	Uboma II	M. esculenta	Anambra State
10.	Nwugo	M. esculenta	Anambra State
11.	IFE	M. esculenta	Oyo State
12.	Ogbomosho	M. esculenta	Oyo State

In May 1977 about 100 stem cuttings (23–30 cm) of the enlarged material now available from each cultivar were repropagated in larger plots for comparative study of their performance. It was from these plots that the present samples were taken for investigation.

2.2 Field sampling and Laboratory Analysis

Tuberous roots of each cultivar were dug from the 12 months old plants to obtain about 50 kg fresh tuber for gari processing. Mature and fully expandet but not senescent leaves, usually leaf numbers 4–5 from the top, were randomly plucked from several plants of each cultivar, put into polythene bags, sealed and transferred to the laboratory where they were washed with distilled water after removing the stalks and blotted dry between blotting papers. They were then subsampled and divided into two lots of 200 g each; one lot was oven dried at 105° C and finely ground for nitrogen determination while the HCN content was determined in 20 g of the fresh leaf samples. Samples of tubers carried to the laboratory were washed free from soil, carefully weighed, peeled and cut longitudinally into two equal halves, one half was used for dry matter and N determination and the other half for cyanide analysis. The weight of the peels and pulp were similarly obtaind. The pulp was then grated over a 5 mm perforated aluminium mesh and the peels marshed in a mortar. The HCN content was estimated iodometrically, according to the method described by Knowles and Watkins (1950) as adopted since 1957 (Oyenuga & Amazigo, 1957) in the Animal Science Department of the University of Ibadan.

About 50 kg of cassava tubers were given to experienced local processors to process into gari. This involved peeling the roots, grating to give a fine mash, fermentation in a fibre sack for 3–4 days, dewatering (dehydration) under heavy weights followed by sifting and frying over a hot fire in an open cast iron pan. Gari samples from each cultivar were analysed for HCN and mannitol content as described below. Crude protein (6.25 x % total N) was determined in the oven dried leaf, peel and pulp as well as in gari samples by the micro-kjeldahl method.

2.3 HCN determination

At each determination, duplicate samples of each material (20 g fresh leaves, peel or gari or 50 g pulp) were weighed into incubation flasks, rinsed down with 250 ml distilled water and about 3 drops of toluene were added. The flask was then stoppered tight with rubber bung and incubated at 37° C in Gallenkamp 1H–270 incubator for 2 hours. After incubation the sample was steam-distilled and distillate collected for 30

minutes in 50 ml of saturated solution of sodium bicarbonate. The distillate was transferred to a 250 ml volumetric flask and made to mark with distilled water. 50 ml portions of the distillate were pipetted and titrated with N/50 iodine solution to a bluish end point using 1 ml starch solution as indicator. The percentage HCN is given by the equation:

$$\% \text{ HCN} = 100/50 \times \text{titre} \times \text{iodine factor} \times 0.00027$$

The iodine factor was determined by titrating the iodine solution with a standard solution of sodium-thiosulphate.

2.4 Mannitol determination

Known weights (about 25 g) of gari samples were extracted in Erlenmeyer flasks with four volumes of 95% ethanol. The extract was filtered and then concentrated in a rotary evaporator. This concentrate containing the sugar alcohols was subjected to thin-layer chromatography on silica-gel G plates in butanol-acetic and water (4:1:1) and the various components were detected by spraying with sodium periodate-KI reagent (Eibel and Lands, 1970). Mannitol spot was identified by running a drop of a solution of pure substance alongside the tests, was eluted in alcohol and its concentration determined spectrophotometrically according to the modified method of Eibel and Lands (1970).

3. Results

3.1 Crude protein content

A distinctive feature of the crude protein contents of the cassava plant parts (leaf, peel and pulp) presented in Table 2 is the high protein content in the leaf which averaged 21.4 percent and the extremely low and negligible amount in the peel (0.17%). The decambiated edible cassava tuber (pulp) contained an average of 2.1 percent crude protein. Cassava leaves are thus about 10 times richer in crude protein than the peeled tuber (pulp) which is also about 12 times higher in crude protein than the peel. Thus cassava leaves and not the peel which is often fed to fatten livestock provide a more suitable protein source. There was a rather low and insignificant linear relationship between leaf crude protein content (Y) and peel protein (X), the regression equation being

$$Y = 23.63 - 12.73\,x;\ r = 0.44$$

Similarly, the crude protein content in the leaf (Y) correlated very

Table 2. Crude Protein Content of 12 Cassava Cultivars (% dry weight basis)

	Cassava cultivar	LEAF	PEEL	PEELED TUBER (PULP)
1.	53101	23.85	0.16	2.01
2.	60447	20.1	0.15	2.18
3.	60506	22.4	0.22	2.13
4.	Isunikankiyan	23.5	0.12	2.10
5.	Sweet Cassava	22.1	0.13	1.94
6.	OZU-NWANGWE	21.0	0.23	2.14
7.	IMO	20.1	0.20	2.03
8.	OKOBO	20.5	0.17	2.22
9.	UBOMA II	20.7	0.18	2.16
10.	NWUGO	19.6	0.26	1.95
11.	IFE	21.0	0.10	2.17
12.	OGBOMOSHO	22.6	0.13	2.15
	Mean	21.4	0.17	2.10
	SD ±	1.7	0.05	0.09
	CV (%)	7.5	29.3	4.4

poorly with the protein in the peeled tuber (X) where the linear regression equation was given by

$$Y = 25.45 - 1.92\,x;\ r = 0.13$$

Leaf and pulp protein data obtained in this work are comparable with 25.8–27.3 percent in leaf dry matter reported by Rogers and Miller (1963).

3.2 Cyanogenic glucoside content

The distribution of the cyanogenic glucoside (HCN) in leaf, peel and pulp portions of the plant shown in Table 3, indicates the highest HCN concentration in the leaf which constitutes the principal loci for HCN synthesis (Nartey, 1968). Foliar HCN content was at least 10 times as much as in the pulp, while the peel contained about 4 times as much HCN as that in the pulp. The high coefficient of variation in the HCN content of leaf, peel and pulp (Table 3) is attributed to the wide differences among the cultivars ($P = 0.05$). A significant positive correlation between leaf HCN (Y) and pulp HCN content (X) was established, the linear repression equation being:

$$Y = 840.5 + 4.47\,X,\ r = 0.60,\ n = 12.$$

Table 3. Distribution of Cyanogenic Glucoside (mg HCN per kg fresh Weight) in different parts of 12 Cassava cultivars.

	Cassava cultivar	LEAF	PEEL (mg HC C/kg)	PULP
1.	53101 (OLORONTO	2236	724	243
2.	60447	2101	1053	187
3.	60506	2060	756	114
4.	ISU-NIKAN-KIYAN	1288	621	93
5.	SWEET CASSAVA	1355	700	91
6.	OZU-NWANGWE	1463	586	108
7.	IMO	1422	157	61
8.	OKOBO	780	626	113
9.	UBOMA II	1287	793	173
10.	NWUGO	678	577	108
11.	IFE	1152	177	155
12.	OGBOMOSHO	2060	520	297
	Mean	1490	607,5	145,3
	SD ±	519	247.7	69.3
	CV (%)	34.8	40.8	47.8

Linear Regression Equation between leaf HCN (Y) and pulp HCN (X) is given by $Y = 840.5 + 4.47\ X$; $r^2 = 0.36$, $r = 0.60^*$ (P–0.05)

This suggests that cassava leaf samples could be used in breeding, to screen cassava cultivars for low cyanidecontent in edible tuber. Peel HCN content, however, correlated very poorly (r = 0.37) with leaf HCN, indicating that the cyanogenic glucoside content of the peel would in no way reflect the content in the pulp. In fact, with the exception of cultivars IFE and IMO (Table 3) the cultivars with the lowest HCN content in the pulp (e.g. Isunikankiyan and sweet cassava) had relatively high HCN concentration in the peel, their peel HCN being about 4–7 times that of the peeled tuber. Among the 12 cultivars investigated, only three had low cyanide content (<100 ppm) in the fresh peeled tuber. The significance of this in the diet of the growers are discussed later.

3.3 Crude protein, mannitol and cyanogenic glucoside content of gari

Some of the chemical components of gari samples processed from the 12 cassava cultivars are shown in Table 4. Scarcely 5 out of the 12 cultivars yielded gari with crude protein contents of over 1% indicating that gari is practically devoid of protein when compared with other

carbohydraterich food items like yams (5–8%) sweet potato (7–9%) or Irish potato (8–9%).

Mannitol, a sugar alcolhol which is widely distributet in plants was found to be present in all the various cassava cultivars investigated, and its level ranged from 293 to 464 mg per 100 g dry weight (Table 4).

Table 4. Crude protein, Mannitol and Cyanogenic Glucoside Content of gari processed from 12 Cassava Cultivars

	Cassava cultivar	Crude protein per cent	Mannitol mg/100 g	Cyanogenic glucoside mg HCN per kg
1.	53101 (OLORONTO)	1.24	321	28.5
2.	60447	0.98	417	19.2
3.	60506	1.94	351	21.7
4.	ISU-NIKAN-KIYAN	0.58	319	23.6
5.	SWEET CASSAVA	0.24	464	26.7
6.	OZU-NWANGWE	1.22	335	16.8
7.	IMO	0.93	357	11.8
8.	OKOBO	1.04	410	13.5
9.	UBOMA II	0.21	293	26.7
10.	NWUGO	0.42	311	25.0
11.	IFE	1.14	386	19.5
12.	OGBOMOSHO	0.14	340	20.3
	Mean	0.84	358.5	21.11
	SD ±	0.52	50.0	5.30
	CV (%)	6.2	13.9	25.1

It is remarkable that the mannitol content of the sweet cassava cultivar was the highest. This observation however could not be said to be peculiarly indicative of differences between sweet and bitter cultivars since the bitter cultivars Okobo and 60 447 contained 410 and 417 mg mannitol per 100 g gari respectively.

Happily the much dreaded cyanogenic glucoside content of cassava tubers was only present at very low levels in gari processed therefrom, ranging between 11.8 and 28.5 mg HCN/100 g with a mean value of 21.1 mg/100 g (Table 4). A comparison of the data in the last columns of Table 3 and Table 4 would show that most of the cyanide in the fresh pulp (ranging from 75–93.2% with a mean of 83.3%) was lost during processing into the traditional food, gari. The data (Table 4) also show that the quantities of the toxic component varied greatly between

cultivars and even though the gari processed from the so-called „sweet" cultivars (e.g. Isunikankiyan, Sweet cassava, Imo) were generally lower in HCN than the „bitter" ones (e.g. 53 101, 60 447, Ogbomosho), the correlation was not exact.

4. Discussion

Cassava is mostly known for its starchy tubers and mainly utilised as such. The results of this investigation re-emphesise the need to direct more attention to the crop as a potential and cheap protein source for animal and human nutrition (Terra, 1964; Eggum, 1970; Ahmed, 1973).

The values obtained for the leaf protein content (Table 1) were similar to the range of 20.6% to 30.4% reported by Rogers (1959) for Jamaica cultivars of about the same age, although his average value of 30% for more than 60 cultivars was slightly higher. Average protein content of the gari samples investigated in this study (Table 4) was about the same as that reported by Oke (1966). Protein level in the leaves was about 25 times higher than that in the roots.

It is known (Roggers and Miller, 1963; Luyken et. al., 1961) that 75 percent of cassava leaf protein consists of true protein of high biological value and good digestibility (up to 80%) containing satisfactory amounts of essential amino acids (sulpho-amino acids centent = 1.2–2.9 g/100 g protein). Since leaf yields are high (7–20 t/ha/year) cassava leaves are a good source of supplementary protein for livestock and human diet in regions of acute protein shortage.

The data on the distribution of HCN in the leaves and roots of the cassava cultivars (Table 3) confirm the general observation that the leaf has a much higher HCN content, since leaves constitute the synthetic sites of the cyanogenic glucosides (Conn, 1973). The range of 678 ppm to 2236 ppm observed in cassava leaves in this study was much higher than any of the figures hitherto reported. For example, Chew (1972), using the silver nitrate titration method reported that 174–622 ppm HCN were present in fresh cassava leaves from 18 Malaysian cultivars. The average value of 1490 ppm HCN found in the leaves of the 12 cultivars studied was higher than the average of 1040 ppm reported for 15 clones from the Ivory coast (De Bruijn, 1973). Sinha & Nair (1968) had observed that the amount of cyanide alone did not seen to be the deciding factor for bitterness of cassava roots. The HCN values (Table 3) obtained in the peeled tubers were comparable with the reported normal range of 150 to 400 mg/kg fresh weight (Coursey, 1973; Yeoh and Chew, 1974).

Cases of cyanide poisoning of livestock fed on cassava rations have not been reported in Nigeria and in Australia where 180 ppm is the safe limit, incidence of HCN poisoning of livestock fed on tapioca leaves is rare (Lim, 1968; Mahendranathan, 1971).

The traditional techniques of cassava preparation for human consumption remove most of the poisonous cyanide during processing. Boiling, for example, drives off the volatile HCN and destroys the enzyme linamarase that could liberate more HCN from the cyanogenic glucoside. Bassir and Fafunso (1976) reported that up to 99.9 percent of the cyanide content of fresh leaves was eliminated by boiling. Our work shows that up to 93 percent of the cyanide in the edible tuber was eliminated during processing into gari with an average of 21.1 mg HCN/kg which, compared with 30 mg HCN/kg regarded as acceptable in the product (Akinrele et al., 1962) are within safe levels.

Mannitol is widely distributed in plant foods and its excessive amounts are injurious to the Kidneys. Data in Table 4 show the range of 11.8 mg to 28.5 mg mannitol per 100 g gari, processed from the 12 cultivars. It is noteworthy that the gari processed from sweet cassava cultivars contained higher amounts of mannitol, a sugar alcohol, than the bitter cultivars. Unfortunately, the literature contains scanty information to facilitate a comparison. The levels of mannitol in the various gari samples, however, could be said to be sub-lethal, accepting the observation of Tonster and Shaw (1962) that 10 to 20 g of mannitol could be ingested without any deleterious effect.

5. Summary

A study of the protein, HCN and mannitol contents of the leaves and tuberous roots as well as gari preparations from different cassava varieties cultivated in the major cassava growing areas of Nigeria was undertaken. Leaf protein content averaged 21.4 percent, tuber protein ranged between 1.95–2.18 percent and gari protein content averaged 0.84 percent of dry weight.

The cyanogenic glucoside (HCN) content of the leaf was about ten times that of the peeled tuber while the peel contained 4–6 times as much HCN as the edible cassava tuber. Although leaf HCN content significantly correlated with the HCN content in the tuber ($P = 0.05$), no linear relationship was found between leaf protein and tuber protein content. Most of the cyanide in the fresh material is eliminated during processing.

The gari processed from the cassava cultivars contained safe levels of prussic acid and there was practically no difference in the HCN content (11.8–28.5 ppm) of the gari prepared from the so-called sweet and bitter cassava cultivars.

Zusammenfassung

Blätter, Wurzelknollen und zubereitetes Gari von verschiedenen Cassava Sorten aus den Hauptanbaugebieten Nigerias wurden auf den Gehalt an Protein, Blausäure (HCN) und Mannitol untersucht.

Die Blätter enthielten im Durchschnitt 21,4% Protein, der Proteingehalt der Wurzeln lag zwischen 1,95–2,18% und der Proteingehalt des Gari lag im Durchschnitt bei 0,84% der Trockensubstanz.

Der Blausäuregehalt der Blätter war etwa 10 mal so hoch wie der der geschälten Wurzelknollen, während die Schale 4–6 mal mehr Blausäure enthielt als die eßbare Wurzelknolle. Während der HCN-Gehalt der Blätter signifikant korreliert mit dem HCN-Gehalt der Wurzel ($P = 0{,}05$), wurde keine lineare Verbindung zwischen Blattprotein- und Wurzelproteingehalt gefunden. Ein großer Teil des Zyanids frischer Cassava wird bei der Verarbeitung entzogen.

Gari, hergestellt von Cassava Sorten mit gesundheitlich unbedenklichen Mengen an Blausäure, und Gari, zubereitet von sogenannten süß und bitter Cassava Sorten, ließen praktisch keinen Unterschied im HCN-Gehalt (11,8–28,5 ppm) erkennen.

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