



Assessment of Nutritional Composition, Vitamin C Content and Toxic Heavy Metals Concentration in Some Local Drinks Made in the Northern Part of Nigeria

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Abstract: Five different locally prepared drinks (Kunun Acha, Kunun Gyada, Kunun Masara, Kunun Tsamiya, and Kunun Kanwa) were analyzed for proximate content and heavy metals concentration using Association of Official Analytical Chemists method and atomic absorption spectrophotometer respectively. The result indicated that moisture, ash, fat, protein and carbohydrate ranges from 81.90 to 94.90, 0.06 to 3.51, 0.05 to 1.32, 0.18 to 1.14, and 10.0 to 15.8 mg/L, respectively. Furthermore, vitamins are within 0.78 to 21 mg/L, while those of mineral elements are 35.675 to 124.725 mg/L Ca, 0.025 to 2.700 mg/L Cu, 0.350 to 3.700 mg/L Mn, 53.900 to 298.425 mg/L Mg, 4.750 to 99.930 mg/L Fe, and ND to 0.550 mg/L Pb. The locally made Kunun from Masara (maize) recorded the highest value for acceptability of overall moisture content with a better aroma, taste and appearance, while Kunun made from Acha had the highest ash content. Kunun made from kanwa (potash) recorded the highest vitamin content. Kunun made from gyada (groundnut) had the highest fat, carbohydrate and protein contents. Heavy metal concentrations in the local beverages are all within the recommended dietary intake for human, except for Kunun Masara with Pb content of 0.55 ± 0.00 mg/L. Based on this result, the five locally produced Kunun analyzed are adjudged to be good for the human body and can contribute to the growth and stability of the body system. The consumption of Kunun made from masara with lead contaminant of 0.550 mg/L above WHO and NAFDAC recommended limit should be discouraged.

Keywords: Assessment, Nutritional, Composition, Heavy Metals, Vitamin C

1. Introduction

In Nigeria, local drinks are consumed daily in large amounts by both the young and old due to its accessibility, characteristic taste, and thirst quenching potential. They are the usually served during most festivities and celebrations across the country. The hot weather conditions in the country contribute immensely to the patronage of these drinks [1]. Cereal food products constitute the bulk of foods of the daily main dishes of the average individual in North-Eastern Nigeria and Africa as a whole. There have been reported cases of heavy metal contamination of local drinks made in Nigeria [1]. The increasing demand for food safety is stimulating research regarding the benefits and risks associated with consumption of foodstuffs and drinks [1].

The important measure of averting food/drinks contamination and poison is therefore to mount up a surveillance study in order to assess the quality of foods and drinks locally produce and consumed in the rural areas of developing countries like Nigeria. The knowledge of the mineral elements composition of foods is of interest because some are essential, while others are toxic to human. The widespread roles of metals in health and diseases range from the requirement for intake of essential trace elements to toxicity associated with metal overload. In small quantities, certain metals such as Fe, Cu, Mn, Cr, Co and Zn are nutritionally essential for a healthy life. However, these metals can still cause ill effects when ingested in high amounts. Metals like Pb, Cd, Hg and As are considered non-nutritive and toxic and are known to have deleterious effects

even in small quantities [1]. Several cases of human disease, disorders, malfunction and malformation of organ due to metals toxicity has been reported [1].

2. Related Work

Many metals and other chemicals accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted [2]. Daily intakes requirement of some of the heavy metals includes; Manganese (2–5 mg/day), Chromium (0.005 mg/day), Cobalt (0.0001 mg/day), Zinc (15–20 mg/day of which 99% is found intracellular and 1% in the plasma), Iron (1–2 mg/day of which 75% is found in the blood and the rest 25% in the bone marrow, liver etc.), and Copper (2–5 mg/day of which 50% is absorbed from the gastrointestinal tracks) [3].

There is limited information on the composition of most of the local drinks produced in northern Nigeria. For the purpose of acquiring full knowledge of the nutritive value of some of our local Kununn types, their chemical analysis is necessary. Thus, the aim of this study is to access the total nutritional composition and the toxic heavy metals concentration in five locally made drinks Kunun Acha (KAC), Kunun Gyada (KGD), Kunun Masara (KMS), Kunun Tsamiya (KTM), and Kunun Kanwa (KKW) from northern Nigeria.

3. Methodology

3.1. Sample Collection

The raw materials (main substrates and ingredients) were processed into five homemade drinks (Kununn Type) namely; Kunun Tsamiya, Kunun Acha, Kunun Gyada, Kunun Kanwa and Kunun Masara) and packaged in 50ml plastic bottles and stored in cool environment prior to analysis.

3.2. Sample Digestion Procedure

The samples (5ml) were measured into conical flask each and 5 ml of concentrated nitric acid and deionized water were added to each of the flask. The mixtures were heated over steamed water-bath until the red fume nitrous oxide ceased and the sample solution turns clear. The sample solution was allowed to cool and then diluted with deionized water, filtered into 50ml volumetric flask and made up to the mark and transferred into labeled capped plastic bottle and submitted for the elemental analysis. Blank sample was prepared following the sample preparation process without introduction of the sample analyte.

3.3. Procedure for Heavy Metal Analysis

The concentrations of heavy metals (Cu, Fe, Mn, Mg and Pb) in the digested samples solutions were determined using Atomic Absorption Spectrometer (GBC Avanta version 2.0 Model). The Atomic Absorption Spectrometer equipped with all the necessary components was switched- on, optimized and calibrated using the prepared standard solutions of the

metals of interest after running the prepared blank solution, followed by the sample analyte consecutively. The data obtained were processed by calculating the actual concentrations in the samples analyzed using the relation:

$$\text{Metal (Mg/L)} = C \times V \times D.f$$

where C is the concentration obtained from the AAS machine (mg/L); V is the volume of the undiluted sample solutions in mL; and $D.f$ is the dilution factor.

3.4. Determination of Moisture Content [4]

Empty crucibles and lid were dried in the oven at 105°C for 3 hours and then transferred to the desiccators to cool and weighed; 3 g of each samples were weighed into the crucibles and were placed in the oven to dry for 3 hours at 105°C. After which they were transferred to the desiccator to cool with partially covered lid. The crucible and its dried sample were weighed again.

3.5. Determination of Protein Content by Kjeldahl Method

1g of the sample was weighed into a digestion flask and 10 g of K_2SO_4 salt, 1 tablet of Kjeldahl catalyst and 20 ml of conc. H_2SO_4 acid were added. 0.1 of the solution was heated on a heating mantle at an inclined angle until frothing subsided, and it was boiled for three hours till the solution cleared. The flask and content were cooled and 90 ml of distilled water, 25 ml of 4 sulphide solution, few pieces of anti-bumping and 80 ml of 40 NaOH were added. The sample was tilted to form two layers, the condenser and water inlet were then connected immediately. 0.4 of the distillate was heated and were distilled to 50 ml saturated boric acid/1 ml indicator solution. 50 ml of the distillate was titrated with 0.1N HCl solution.

3.6. Determination of Ash Content [4]

The crucible and lid were placed in the furnace at 550°C overnight so as to ensure that impurities on the surface of crucible were burnt off. There were cooled in the desiccators for 30 minutes and weighed; 5 ml of the samples were weighed into the crucible and heated over low Bunsen flame with lid half covered till the fumes were no longer produced. The crucible and lid were returned to the furnace and heated at 550°C overnight. During heating, the lid was not covered. The lid was then placed back after it was completely heated to prevent loss of fluffy ash and it was cooled down in the desiccator. The ash with crucible and lid were weighed after the sample turned gray.

3.7. Determination of the Fat Content [4]

5ml of each of the samples were measured and poured into the separating funnels, 2ml of NH_3 solution was added to each of the samples inside the separating funnel and shaken, 10 ml of ethanol was also added and shaken, then 25 ml of diethyl ether was added and shaken, then 25 ml of petroleum ether was added and shaken for 1 minute, then 25

ml of a mixture of diethyl ether and petroleum ether (12.5 ml both) and shaken for 30 seconds. It was then allowed to settle and the ether layer was collected, dried and then weighed.

3.8. Determination of Carbohydrate Content

100 ml of each of the samples were weighed into a boiling tube and were hydrolyzed by keeping it in boiling water bath for 3 hours after adding 5 ml of HCl and cooled to room temperature. It was neutralized with solid sodium carbonate until the effervescence ceased and the volume was made up to 100 ml and was centrifuged. 0.2, 0.4, 0.6, 0.8, and 1 ml of the working standard were pipette into a series of test tube, 0.1 and 0.2 ml of the sample solution were also pipette into two separate test tubes and were made up to 1 ml with water in each test tube. 1 ml of phenol solution was added to each tube, 5 ml of 96 sulphuric acid was further added to each tube and was shaken thoroughly. After 10 min the content in the tubes were shaken again and were placed in water bath at 25-30°C for 20 min [5]. The color was read by UV-Visible

Spectrophotometer at 490 nm and the amount of total carbohydrate present in the sample solution was calculated using calibration equation obtained from standard calibration graph [13, 14].

Determination of Vitamins

Vitamins C was determined using the AOAC (2000). A sample solution of 20 ml was put in a pipette and poured into a 250 ml conical flask and about 150 ml of distilled water was added with 1 ml of starch indicator solution to each conical flask. The samples were titrated with 0.005 mol L⁻¹ iodine solution. The end point was identified as the first permanent trace of a dark blue-black colour due to the starch-iodine complex; same was repeated with further sample solutions until a concordant result was obtained.

4. Results and Discussion

The result of nutritional analysis for the determination of moisture, ash, protein, fat, carbohydrate and Vitamin C in the local drinks are shown below in table 1.

Table 1. Proximate and Vitamin C Content of Kununn Products Made from Sorghum, Acha, Maize, Potash, Millet.

SAMPLE CODE	Moisture	Ash	Fat	Protein	Carbohydrate mg/L	Vitamin C mg/L
KAC	91±6.93	3.51±0.29	0.06±0.01	0.96±1.00	11.5	0.86
KGD	81.9±7.9	0.57±0.07	1.32±0.11	1.14±1.09	15.8	5.94
KMS	94.9±1.69	0.08±0.05	0.13±0.01	0.61±1.00	12.5	0.78
KTM	94.3±6.15	0.06±0.02	0.05±0.01	0.18±0.20	10.0	2.6
KKW	92.5±4.53	3.24±0.05	0.12±0.15	1.09±1.00	11.2	21
RDA Value	-	-	ND	56 g/d	130 g/d	75 g/d

Key: KAC = Kunun Acha, KGD = Kunun Gyada, KMS = Kunun Masara, KTM = Kunun Tsamiya, KKW = Kunun Kanwa ND = Not Detected.

Moisture is in abundance as a result of the presence of high level of water content (84-94%) in locally prepared types of Kununn drinks. Ash is present due to the presence of inorganic matter such as silica in the mixture of all the local drinks (Kununn). All local drinks have fat ranging from 0.00 to 1.0. Carbohydrate is present in all five samples. All samples have protein content which ranges from 0.18 to 1.14. Vitamin C is also present in all five samples analyzed.

The moisture content ranges between 81.9 to 94.9 for the five locally made drinks. The result of this study showed that Kununn made from Masara (maize) recorded the highest value for acceptability of overall moisture content (94.9±1.69) with a better aroma, taste and appearance compared to the other types of Kununn which are Kununn Acha, Kununn Tsamiya (sorghum/tamarind), Kununn Kanwa (Potash) and the least value observed was in Kununn Gyada (millet) (91±6.93, 94.3±6.15, 92.5±4.23, 81.85±7.9) respectively. The high level of moisture could be attributed to high water retention capacity of Maize. Ash content is a measure of inorganic matter or mineral content of a sample. The results of the percentage ash content of Acha, Maize, Potash, Sorghum, Millet were found to be within the range of 0.06 to 3.51 with sorghum having the least value and Acha having the highest ash content (Table 1). The results indicated only samples KTM (0.06±0.02) and KMS (0.08±0.05) have ash values lower than the result (0.2)

reported for a similar study by Otaru *et al.* [6] and Innocent *et al.* [7], while samples KAC (3.51±0.29) and KKW (3.24±0.05) falls outside the range of the result (2.00 to 3.00) reported [8]. (2011). The percentage fat content of Kunun Acha, Kunun Gyada, Kunun Masara, Kunun Tsamiya, Kunun Kanwa obtained falls within the range of 0.00 to 1.0. Fat content of Kunun Acha, Kunun Gyada, Kunun Masara, Kunun Tsamiya, Kunun Kanwa obtained are 0.06±0.01, 1.32±0.11, 0.13±0.01, 0.05±0.01, 0.12±0.15 respectively (Table 1). Kunun Gyada has the highest and Kunun Tsamiya has the least content. There is no definite recommended level of intake for fat but as recommended dietary allowances and adequate intakes, fat is estimated to be in the range of 30-35 g/d [8]. Dietary fats are essential to the body for energy and to support cell growth. The level of carbohydrate obtained ranged from 10.0 to 15.80 mg/L. The carbohydrate content of the Kunun Acha, Kunun Gyada, Kunun Masara, Kunun Tsamiya, Kunun Kanwa having 11.5, 15.8, 12.5, 10.0, 11.2 mgL⁻¹, respectively, as shown in Table 1. Kunun Tsamiya has the least and Kunun Gyada has the highest level. They are all under the recommended dietary intake for men and women. Men and female both have a maximum recommendation of 130 g/d [9]. The sugar concentration of the drinks is within the recommended carbohydrate intake. It aids in the digestion of food and keeps blood cholesterol levels in check. Low carbohydrate can lead to low blood sugar, which can lead to

hypoglycemia. The protein content of the Kunun Acha, Kunun Gyada, Kunun Masara, Kunun Tsamiya and Kunun Kanwa are; 0.96 ± 1.00 , 1.14 ± 1.09 , 0.61 ± 1.00 , 0.18 ± 0.20 , 1.09 ± 1.00 respectively, as shown in Table 1. Kunun Tsamiya has the least and Kunun Gyada has the highest percentage of protein. The recommended dietary allowance for the intake of protein is 56 g/day for male and 46 g/day for female. They are all within the recommended intake for both sexes [10]. The body uses protein to build and repair tissues, it can also be used to make enzymes, hormones, and other body chemicals. The vitamin C content obtained from Acha, Maize, Millet, Sorghum and Potash were found to be 0.86

mgL^{-1} , 0.78 mgL^{-1} , 5.94 mgL^{-1} , 2.6 mgL^{-1} , and 21 mgL^{-1} , respectively. Potash has the highest concentration of vitamin C and maize has the lowest concentration. This implies that Potash may be used as an antioxidant as it is good for the human body because it helps maintain tissues, muscles, organs and it is essential for growth. The values fall within the recommended intake as the normal intake required is 75 mg for women and 90 mg for men [11].

The result of the determination of Manganese, Iron, Lead, Magnesium and Copper in the five locally made drinks from Sorghum, Acha, Maize, Potash, Millet are shown in table 2 below;

Table 2. Heavy Metal and Mineral Content of Kununn Products Made from Sorghum, Acha, Maize, Potash, Millet Local Drinks.

Sample Code	Mn (mg/L)	Fe (mg/L)	Pb (mg/L)	Mg (mg/L)	Cu (mg/L)
KAC	ND	41.38 ± 0.10	ND	114.10 ± 0.11	0.98 ± 0.01
KGD	1.88 ± 0.01	14.75 ± 0.01	ND	210.88 ± 0.32	0.93 ± 0.01
KMS	0.35 ± 0.00	25.13 ± 0.05	0.55 ± 0.00	95.88 ± 0.10	0.35 ± 0.00
KTM	0.85 ± 0.02	20.78 ± 0.03	ND	53.90 ± 0.11	0.03 ± 0.00
KKW	3.70 ± 0.04	99.93 ± 0.10	ND	298.43 ± 0.52	2.70 ± 0.06
WHO	2.3	1.0	0.01	50	2.0
NAFDAC	0.0	0.0	0.0	30	0.0

Note: KAC = Kunun Acha, KGD = Kunun Gyada, KMS = Kunun Masara, KTM = Kunun Tsamiya, KKW = Kunun Kanwa, ND = Not Detected.

Lead is detectable in only one sample which is Kunun Masara with the concentration of $0.55 \pm 0.00 \text{ mg/L}$, while Manganese, Iron, Magnesium and Copper are present in all samples except for Kunun Acha which did not contain Manganese. Manganese ranged from 0.35 ± 0.00 to $3.70 \pm 0.04 \text{ mg/L}$, Iron ranged from 14.75 ± 0.01 to $99.93 \pm 0.10 \text{ mg/L}$, Magnesium ranged from 53.90 ± 0.11 to $298.43 \pm 0.52 \text{ mg/L}$ and Copper ranged from 0.03 ± 0.00 to $2.70 \pm 0.06 \text{ mg/L}$ (see in Table 2).

Kunun Masara has a lower concentration of manganese compared to Kunun Kanwa. They are within the range of recommended dietary allowances for intake [11]. The concentration of manganese in all samples detected were below the maximum acceptable concentration of 2.3 mg/L recommended by WHO except Kunun Kanwa which had the highest concentration of $3.70 \pm 0.04 \text{ mg/L}$ manganese but it is still below the dietary allowance intake [10].

Kunun Gyada has the least concentration of Fe and Kunun Kanwa has the highest concentration as shown in Table 2. All the samples have iron concentration higher than that of the WHO acceptable level which is 1.0 mg/L and the NAFDAC acceptable level of 0.00 mg/L . Kunun Acha, Kunun Gyada, Kunun Masara, Kunun Tsamiya with iron concentrations of 41.375 mg/L , 14.750 mg/L , 25.125 mg/L , 20.775 mg/L respectively are within the tolerable upper intake level of iron [11] but the value of Kunun Kanwa is higher with 99.925 mg/L . The tolerable upper intake for children is 40 mg/L , males 45 mg/L and that of females is also 45 mg/L .

Lead concentration was detectable in only Kunun Masara, all the other samples did not show the presence of lead. Kunun Masara which has 0.550 mg/L Pb is higher than the maximum acceptable level by WHO for lead which is 0.01 mg/L and it is also higher than NAFDAC acceptable level which is 0.00 mg/L .

Kunun Tsamiya has the least value of Magnesium and Kunun Kanwa has the highest concentration of Magnesium. The concentrations are within the estimated average intake of magnesium in the dietary reference intake (DRI) [12]. For males the estimated reference intake is from $200\text{--}350 \text{ mg/d}$ and for females it is from $200\text{--}265 \text{ mg/d}$. When compared with the maximum acceptance intake of the Krishnaveni, et al [13], only Kunun Tsamiya is within that range, the other samples are higher than the acceptance level of 50 mg/L . All the samples are above the required intake of 30 mg/L maximum acceptance level by the NAFDAC.

The concentration of copper ranged from 0.025 mg/L – 2.700 mg/L . The sample of Kunun Tsamiya has the least value and Kunun Kanwa has the highest. All the samples as seen in Table 2 fall within the range of the maximum acceptance level of 2.0 mg/L by WHO and that of 0.0 mg/L by NAFDAC. The tolerable upper intake for children is $3000 \text{ }\mu\text{g/d}$, males' $5000 \text{ }\mu\text{g/d}$ and for females it is also $5000 \text{ }\mu\text{g/d}$ [14].

5. Conclusion

The presence of moisture, ash, fat, carbohydrate, protein and vitamin C in local drinks in Nigeria gives it the characteristic taste which justifies its frequent consumption. However, this high consumption gives room for the risk of heavy metal contamination and intoxication as manganese, iron, lead, magnesium and copper were found to be present in most of the local drinks and some of the values were above the accepted limits for consumption. From this study, people need to be educated and given proper awareness on the benefits and risk associated with these drinks. The water and feedstock used for the production of local beverages should be pure and free of heavy metals in order not to pose as

sources of contamination to the process. The grinding machine should be properly clean before and after use to minimize the level of contamination of the locally made beverages. The packaging materials should be investigated for possible regulation in heavy metal constituents. Agencies, such as the National Agency for Food and Drug Administration and Control and SON should the concentration of heavy metals found in local drinks produced, sold and consumed in Nigeria.

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