Comparative Studies of Four Locally Produced Rice in Wukari and an Imported Brand Based on Their Proximate, Vitamin, Mineral Composition, and Heavy Metal Contamination

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ABSTRACT: *This study analyzes four locally produced rice varieties in Wukari and one imported brand (caprice) to scientifically determine the concentration of selected heavy metals, minerals, proximate, and vitamin contents. Atomic absorption spectroscopy was used to analyze for Cd, Cr, and Pb present in the rice. From the result, Cd and Cr were not detected in all the rice brands. However, Pb concentrations ranging from 0.024 mg/kg to 0.12mg/kg, were detected. Mineral analysis was determined using flame photometry, which shows the presence of Na, K, Ca, and P in all the rice brands analyzed. Vitamins analysis results revealed the presence of B1 (thiamine), B2 (riboflavin), and B6 (pyridoxine) in all four local varieties and the imported brand. The proximate analysis revealed the mean nutritional content of (7.65 ± 0.00 - 12.86 ± 0.014) protein, (1.00±0.00 - 1.26 ± 0.014) Fat, (0.80±0.00 - 0.86 ± 0.0071) Fibre, (1.20 ± 0.00 - 1.89 ± 0.0071) Ash, (9.15±0.00 - 9.50 ± 0.00) Moisture, (76 ± 0.283 - 79.85 ± 0.00) CHO. From the present study, all four locally produced rice are very rich in nutritional contents and some of them contain more nutritional profile than the imported variety. The entire four local rice brands and the imported brand analyzed were not contaminated by heavy metals, their concentration is below the permissible level (0.2mg/kg) according to WHO and FAO*

KEYWORDS: Rice, mineral, proximate composition, metal contamination, local and imported brand

INTRODUCTION

Rice (Oryza sativa) is the most important cereal food crop in the world (Ghosh *et al.*, 2019). It is an essential staple food for more than 50% of the world's population (Hu *et al.*, 2014) and provides dietary energy. Nigeria is currently a thrice-producing producing

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country in Africa. The consumption rate is about 7.9 million tonnes and the production rate has increased from 5.5 million tons in 2015 to 5.8 million tons in 2017 (Udemezue 2018). Rice is grown in more than 100 countries worldwide (Zarei *et al.*, 2017). The rice plant is a monocot and grows to an average height of 1–1.8 m (3.3–5.9 ft) tall, which depends on the variety of the crop and soil fertility. Two major brands of rice are brown rice and white rice. Brown rice is processed into milled or white polished rice by removing the bran layer along with subaleurone, germ (embryo), and a small part of the endosperm underneath. Milled white rice is broadly accepted as it fulfills customers' preferences like lightness, softness, easy digestibility, better eating characteristics, and shorter cooking time than brown rice. However, the milling process reduces the nutrient quality of rice as the nutrients are mainly present in the outer layers of rice that are removed by the milling process. Brown rice contains vitamins like thiamin (B1), riboflavin (B2), niacin (B3), pantothenic acid (B5), pyridoxine (B6), biotin (B7), folate (B9), and a-tocopherol (E) (Ghosh et al. 2019).

Vitamins are essential organic substances required in trace amounts for normal growth, self-maintenance, and proper functioning of the human body. All vitamins (except vitamins D and K) are obtained from various food products as they are not formed in adequate amounts in our bodies. The recommended dietary allowances (RDAs) suggested by the Food and Nutrition Board of the U.S. Institute of Medicine for B1 for women and men are 1.1 and 1.2 mg/day, respectively. Similarly, for B6, RDAs for women and men are 1.2 and 1.5 mg/day, respectively (Shrivas et al., 2018).Elemental concentrations are vital for human dietary intake of essential minerals and nutrients as well as for the estimation of human exposure to toxic metals (Parengam *et al.*, 2010). It is of utmost importance to keep contaminants within permissible limits for food safety The aim of this study is to analyze the proximate, vitamins, mineral composition, and heavy metal contamination of four locally produced rice in Wukari and their comparison with an imported brand (Caprice).

MATERIALS AND METHODS

Sample collection.

Four milled rice varieties were bought from Wukari Rice-mill, in Taraba State Nigeria, and one imported variety. The local varieties were grown in Wapang-Aku, Wukari east, Mission quarters, and the new site area of Wukari while the imported brand is grown in Thailand as shown in Table 2.1.

Table 2.1: List of selected varieties and where they are grown

S/N	Name	Type	Physical characteristics	Area grown
1	Caprice	Imported brand	Long white grain	Thailand
2	Jan-bawo rice	Local brand	Short-brown grain	Wapang-Aku (Wukari)
3	Yar-hayi rice	Local brand	Short- slender brown grain	Wukari east
4	Cipi rice	Local brand	Long white grain	Mission quarters and New site (Wukari)
5	Faro rice	Local brand	Short white grain	Wukari east

Pretreatment of samples materials

The milled rice varieties were transported to the laboratory in polyethylene bags, after which they were washed with deionized water and spread in mesh-like bags, and allowed to drain. They were packed into five (5) brown envelop and kept in the oven for 48 hours at a constant temperature of 65^0C for drying, before being pulverized and stored in an airtight container for further analysis.

Digestion Procedure.

5.0g of each pulverized sample was weighed in an analytical weighing balance and transferred into a graduated beaker, and 4 mL of perchloric acid and 8 mL of nitric acid were added. The solution mixture was then placed in a hot plate at a temperature of 150 ^{o}C to break down the solid sample matrix. The resulting solution was allowed to cool and was filtered and made up to 100 mL using deionized water. It was analyzed for metal contamination using atomic absorption spectroscopy.

Proximate Analysis

The dry matter, moisture, ash, crude fat, crude protein (nitrogen x 6.25), and crude fiber contents were determined using the standard methods of the Association of Official Analytical Chemists (AOAC, 2010). Carbohydrate content was estimated based on the net difference between the other nutrients and the total percentage composition.

Determination of Moisture Content.

This involved drying to a constant weight at 105^{o}C and calculating moisture as the loss in weight of the dried rice samples. The crucible was thoroughly washed and dried in an oven at 105^{o}C for 30 min and allowed to cool inside desiccators. Then, the moisture content of the rice sample was calculated from equation (2.1)

$$\% \text{ moisture} = (W_2 - W_3)/(W_2 - W_1) \times 100 \quad (2.1)$$

Where, W_1 = Initial weight of empty crucible, W_2 = Weight of crucible + sample before drying, and W_3 = Final weight of crucible + sample after drying

Determination of Ash Content

The residue remaining after the destruction of the organic matter of feedstock is referred to as ash. The silica dish was heated at 600°C and was allowed cool in a desiccator and weighed. 4 g of dried milled rice was added to the dish. The weight of the dish and sample was taken and heated in a fume cupboard to burn off the less volatile organic materials. This is called pre-ashing and stops when the smoke stops. Place the dish in a cool muffle furnace (Vecstar ECF3, UK). The temperature of the furnace was raised to 600^0C and this temperature was maintained until whitish-ash remained. The dish was placed in a desiccator and allowed to cool and weigh.

The % ash content was calculated using equation (2.2)

$$\% \text{ Ash} = \frac{\text{Wt. of dish + ash} - \text{Wt. of dish}}{\text{Wt. of sample used}} \times 100 \qquad 2.2$$

Determination of Crude Fiber

Oil was removed from 2 g of rice sample, and ground to pass a 1 mm mesh sieve, by Soxhlet extraction or by stirring, setting, and decanting was done three times using petroleum spirit. The air-dried fat-free material was transferred into a flask or beaker. 100 ml of TCA (Trichloroacetic acid) which was measured at room temperature was added. It was boiled by refluxing gently for 30 min, maintaining constant volume by the flow of water. An 11 cm Whatman No. 541 filter paper was fitted into a Buchner funnel, at the end of the 30 min boiling period, the acid mixture was allowed to stand for approx. 1 min and pour into the prepared funnel. The insoluble matter was washed with boiling water until it becomes neutral to litmus paper. The filter paper and the residue were transferred to a crucible. The crucible and its contents were dried at 100^0C, cooled in a desiccator, and weighed. The crucible was placed in a cool muffle furnace, with the temperature increased to 500^0C, and it was maintained until the ashing is complete. The crucible was removed from the muffle furnace and was allowed to cool in a desiccator and weighed. The % crude fibre is calculated using equation (2.3)

$$\% \text{ Crude fiber} = (\text{Wt. after drying}) / (\text{Wt. of the sample}) \times 100 \qquad 2.3$$

Determination of Crude Lipid (Fats).

Total fat in the rice sample was determined using Soxhlet extraction for 4 hr starting with methanol and ethanol, respectively [AOAC 2010]. A 250 ml clean boiling flask was dried in an oven at 105 – 110 ^{0}C for about 30 min and cooled in a desiccator. 2g of samples were weighed accurately into labeled thimbles. The dried boiling flask was weighed correspondingly and filled with 300 ml of petroleum ether (boiling point 40-60° C). The extraction thimble was plugged tightly with cotton wool. After that, the Soxhlet apparatus was assembled and allowed to reflux for 6 hrs. The thimble was removed with care and petroleum ether was collected from the top container and drained into another container for re-use. After that, the flask was dried at 105 – 110 ^oC for 1 hour when it was almost free of petroleum ether. After drying, it was cooled in a desiccator and weighed. The % fat in the rice sample was calculated using equation (2.4)

% fat = Weight of fat x 100 / Weight of sample   2.4

Protein Digestion

2.0 g of the rice sample was weighed into a Kjeldahl flask and 4 tablets of Kjeldahl Catalyst were added. This was followed up with the addition of 1.0 g copper sulfate and a speck of selenium catalyst into the mixture, and 25 ml concentrated sulphuric acid was introduced. The whole mixture was subjected to heating in the fume cupboard. The heating was done gently at first and increased with occasional shaking till the solution assumed a green color. The temperature of the digester was above 420℃ for about 30min. The solution was cooled and black particles showing at the neck of the flask were washed down with distilled water. The solution was re-heated gently at first until the green color disappeared. Then, it was allowed to cool. After cooling, the digest was transferred into a 250 ml volumetric flask and was washed thoroughly, thereafter made up to the mark with distilled water followed by distillation.

Protein Distillation:

Before use, the Markham distillation apparatus was steamed through for 15 min after which a 100 ml conical flask containing 5 ml boric acid /indicator was placed under the condenser such that the condenser tip was under the liquid. About 5.0 ml of the digest was pipetted into the body of the apparatus via a small funnel aperture. The digest was washed down with distilled water followed by the addition of 50 ml of 60 % NaOH solution. The digest in the condenser was steamed through for about 5-1 minutes after which enough ammonium sulphate was collected. The receiving flask was removed and the tip of the condenser was washed down into the flask after which the condensed water was removed. The solution in the receiving flask was treated with 0.01M hydrochloric acid. Also, a blank was run through along with the sample. After titration, the % nitrogen was calculated using equation (2.5)

% Nitrogen = Vs–VB x Macid x0.01401 x 100W   2.5

Where; Vs = Volume (ml) of acid required to titrate sample; VB = Volume (ml) of acid required to titrate the blank; Macid =Molarity of acid; W=Weight of the sample (g). Then, the percentage of crude protein in the rice sample was calculated from the % Nitrogen as shown in equation (2.6)

% crude protein = % N x F   2.6

Where, F (the conversion factor), is equivalent to 6.25

Determination of Carbohydrates Content

The total percentage carbohydrate content in the rice sample was determined by the difference in feed. This method involved adding the total percentage values of crude protein, lipid, crude fiber, moisture, and ash content of the sample and subtracting it from 100. The value obtained is the percentage carbohydrate constituent of the sample as indicated in equation (2.7)

% carbohydrate=100 – (% moisture + % crude fiber +% protein+%lipid+% ash) 2.7

Determination of Vitamins

1.0 g of the prepared sample solution was put into a 25ml standard volumetric flask and made up with the mobile phase mixture, filtrate was filtered using HPLC grade filter paper.

2.0

High performance Liquid chromatography: Analysis was performed by injecting 20ul of carefully prepared sample into a Buck scientific (USA) BLC10/11 – model HPLC equipped with UV 325 nm and UV 254 nm detectors for fat and water-soluble vitamins respectively. A C18, 4.6 x 150mm, 5um column and a mobile phase of 95:5 (methanol: water) were used at a flow rate of 1.00 mL/min and an ambient operating temperature. A 0.1mg/of mixed standards was also analyzed in a similar manner for identification. Peak identification was conducted by comparing the retention times of authentic standards and those from the samples. Concentrations were calculated using a four-point calibration curve.

Mineral Determination

The mineral content (Fe, Na, K, P, and Ca) of the digested samples was analyzed using Flame photometry (Sherwood 410 model flame photometer) while the iron was analyzed using Atomic Absorption Spectrometry.

RESULTS AND DISCUSSION

Heavy metal analysis

Heavy metal analysis of the selected metals (Pb, Cd and Cr) revealed the presence of Pb ranging from 0.024mg/kg to 0.12mg/kg, while Cr and Cd were not detected as indicated in Table 2.

Table 3.1: Concentration of some heavy metals (Pb, Cr, and Cd) in the five rice varieties (mg/kg)

S/N	Sample	Cr	Cd	Pb
1	Faro rice	ND	ND	0.057
2	Yar-hayi rice	ND	ND	0.024
3	Jan-bawo rice	ND	ND	0.064
4	Foreign rice	ND	ND	0.076
5	White rice (Cipi)	ND	ND	0.12

ND = not detected

WHO/FAO permissible level for Pb is 0.2mg/kg

Table 2 shows the result of the selected heavy metals in the five rice brands. Cr and Cd were not detected. This present study revealed the presence of Pb ranging from 0.024mg/kg to 0.12mg/kg, Faro rice (0.057mg/g), Yar-hayi rice (0.024mg/g), Janbawo rice (0.064mg/kg), imported rice (Caprice) (0.076mg/kg) and Cipi rice (0.12kg/g). The results show that white rice (Cipi) has the highest Pb concentration while Yar-hayi rice has the least concentration, although the values obtained were below the permissible concentration (0.2mg/kg) according to WHO and FAO. The presence of Pd could be due to the residual effects of some agrochemicals used in protecting and ensuring the proper growth of the rice.

Mineral composition analysis
The result of the mineral composition of the selected minerals are as follows: Fe range is from 0.204 to 1.199 mg/kg, Ca range 0.329 mg/kg - 0.728 mg/kg, Na range 0.120-0.176 mg/kg, K range 0.232mg/kg - 0.188 mg/kg, P range 2.48mg/kg - 3.15mg/kg.

Table 3.2: Mineral composition of Fe, K, Na, Ca and P (mg/kg)

S/ N	**Sample**	Fe	Na	K	P	Ca
1	Faro rice	0.204	0.124	0.2	2.7	0.329
2	Yar-hayi rice	0.267	0.128	0.192	2.93	0.608
3	Jan-bawo rice	0.199	0.128	0.196	2.7	0.339
4	Imported rice	0.209	0.12	0.188	2.48	0.33
5	White rice (Cipi)	0.408	0.176	0.232	3.15	0.728

The mineral compositions in the five different varieties of rice are shown in Table 3.2 and figure 3.1. The major minerals detected in rice were Fe ranging from 0.204 to 1.199 mg/kg, Ca ranging from 0.329 mg/kg g to 0.728 mg/kg, Na ranging from 0.120 to 0.176 mg/kg, K ranging from 0.232 mg/kg to 0.188 mg/kg, P ranging from 2.48 mg/kg to 3.15mg/kg. These minerals are essential in their moderate concentration. The mineral composition of the selected metals in the five different brand brands of rice ranging from the highest to the least is as follows; Fe: Cipi > Yar-Hayi rice > Imported (Carp rice) > Faro > Janbawo rice. Na; Janbawo rice = Yar-Hayi rice > Faro > Imported (Carp rice)> Cipi. K: Cipi > Faro > Janbawo rice > Yar-Hayi rice >Imported (Carp rice), P: Cipi > Yar-Hayi rice Faro = Janbawo rice > Imported (Carp rice), Ca; Cipi > Yar-Hayi rice > Janbawo rice >Imported (Carp) > Faro. The iron content in rice is mainly affected by the iron absorption from the soil. Iron content also varies greatly based on rice cultivars or genotypes, mainly controlled by the correlated genes (Meng *et al.*, 2005). Padovani *et al*. (2007) reported 4 mg/100 g level of Ca and 1 mg/100 g Na content in Brazilian rice. The difference in the mineral composition may be a result of soil type and the different species grown. The degree of polishing has a significant effect on the

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quality and nutritional aspects of white rice, affecting properties such as the content of minerals, phytochemicals, and grain breakage (Mohapatra and Bal, 2010).

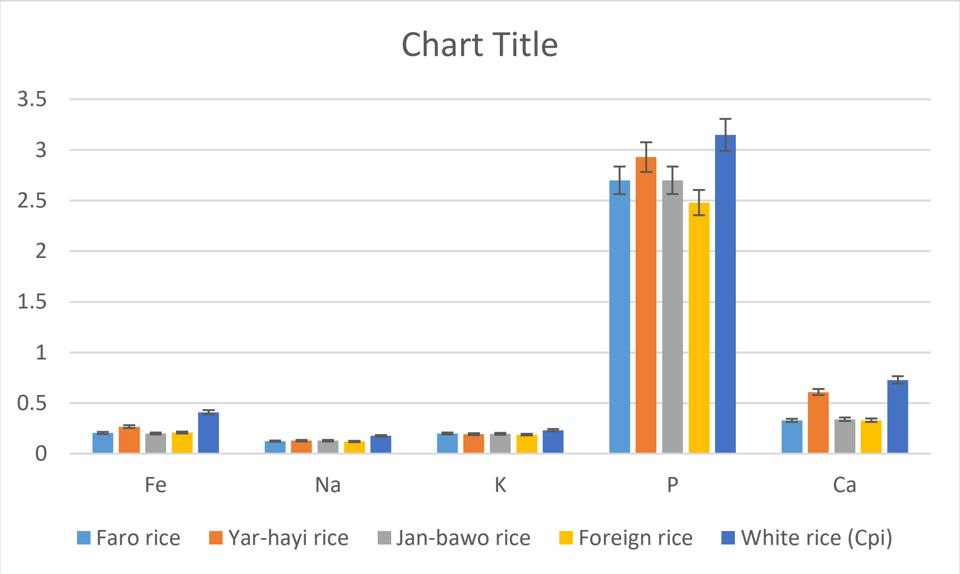

Fig 3.1: Mineral composition of Fe, K, Na, Ca, and P (mg/kg)

Proximate Composition

The proximate composition of four locally produced rice in Wukari and one imported rice is displayed in Table 3.3

Table 3.3: Proximate (%) Content of the selected five rice brand

S/ N	Sample	Crude Protein	Fat	Crude Fibre	Ash	Moisture	Carbohydrate
1	Faro rice	12.86 ±0.014	1.26 ±0.014	0.86 ±0.0071	1.89 ±0.0071	9.15 ±0.00	76 ±0.283
2	Yar-hayi rice	11.06 ±0.014	1.11 ±0.014	0.85 ±0.000	1.56 ±0.014	9.20 ±0.00	76.22 ±0.042
3	Jan-bawo rice	10.21 ±0.001	1.035 ±0.021	0.81 ±0.0141	1.40 ±0.000	9.20 ±0.00	77.345 ±0.049
4	Imported rice	9.85 ±0.000	1.00 ±0.000	0.80 ±0.000	1.38 ±0.014	9.50 ±0.00	77.47 ±0.014
5	Cipi)	7.65 ±0.000	1.00 ±0.000	0.80 ±0.00	1.20 ±0.000	9.50 ±0.00	79.85 ±0.000

From the result the moisture content range from (9.15%-9.50%) which were lower than that reported by Wireko-Manu (2017)13.30±0.18 15.17±0.26 and higher than what Ebuehi and Oyewole reported for Ofada rice (7.5 ± 0.08). Imported rice (caprice) and Cipi had the highest moisture content of 9.50% which may be attributed to their processing drying temperature. The relatively higher moisture content in rice of these two may have an effect on its storage. Faro rice had the least percentage moisture of at 9.15% while %Yar-hayi and Jan–bawo had 9.20% respectively which may be due to the parboiling process and may have the potential to store relatively longer. The significant difference observed in the moisture content of the rice varieties may be attributed to temperature and duration of drying. The crude fat values obtained ranged between 1.0-1.26% with the imported brand and Cipi having lower values compared to other local varieties. Faro rice had the highest fat content of 1.26% followed by Yar-yayi (1.11%). Rice bran, being an excellent fat source, which is lost during milling, contributes to the low-fat content in the well-polished imported rice brand. Thus the observed difference may be attributed to the degree of milling. Milling and polishing of rice remove the outer layer of the grain where most of the fats are concentrated. The values obtained for percentage ash content in this study ranged between 1.20-1.885%. Faro rice had the highest ash content of 1.885% followed by Yar-hayi which had 1.56% while the other rice varieties had the least ash contents of 1.40 and 1.38% respectively. Values obtained in this study were above the values reported by Ebuehi and Oyewole (2008) who reported ash values of 0.53% and 0.80% for raw 'aroso' and 'ofada' rice varieties respectively in Nigeria. The ash content of a food sample shows the mineral contents in the food sample. Minerals are more concentrated in the bran and thus get lost during milling and polishing when the bran is removed from the grain. The ash content of 1.20-1.885% observed in all may be due to the degree of milling/polishing which is influenced by variety.

Carbohydrate values in the varieties ranged from 74%-79.85%. Virtually all the rice varieties have appreciably high carbohydrate content. The variation in values for carbohydrates among the varieties was significant. A similar result (78.3 ± 1.64) has been reported by Ebuehi and Oyewole (2008) for raw 'ofada' and Oko *et al*.,(2011) for Sipi' rice variety (76.92±0.0) in the Ebonyi state. The observed high carbohydrate content of both local and imported rice varieties affirms that rice is a carbohydrate food source.

Generally, the local varieties had significantly higher crude fibre than the imported brand. The range of values for crude fibre observed in this study was between 0.80% - 0.85 % for the five brand rice varieties respectively. The protein contents of the rice varieties ranged from 7.65%-12.86%. The findings of this study showed that local varieties had higher protein contents of 12.86 %, 11.06 %, and 10.21% respectively. The variations observed may be due to differences in variety and environmental influences.

Vitamin analysis

The vitamin analysis revealed the presence of B1 ranging from 0.22±0.000 to 0.33±0.014, B2 ranging from 0.0514±0.000 to 0.073±0.014 and B6 ranging from 0.82±0.000 to 0.135±0.0070 in all the selected five rice variety as shown in Table 3.4

Table 3.4: Vitamins composition of selected five rice varieties (mg/100g)

S/ N	Sample	B1	B2	B6
1	Faro rice	0.330.014	0.073±0.0014	0.135±0.0070
2	Yar-hayi rice	0.32±0.010	0.063±0.0010	0.115±0.0071
3	Jan-bawo rice	0.25± 0.010	0.061±0.0000	0.12 ±0.0000
4	Foreign rice	0.22±0.000	0.057±0.0000	0.0835±0.0007
5	White rice (Sipi)	0.22± 0.000	0.050±0.0014	0.082±0.0000

Table 3.4 shows the results on vitamins for the five brands of rice. Vitamin B1 (Thiamin) shows a value ranging from 0.22±0.000 to 0.33±0.014 in the rice varieties. Thiamin was found in broken rice (0.14 mg/100 g), polished rice (0.11 mg/100 g), husked rice (unpolished) (0.38mg/100g), and parboiled rice (0.22 mg/100 g) as in the FCD report Fairulnizal et al (2015). The mean levels of B2 (Riboflavin) detected in all the rice were 0.073±0.0014 (faro) >0.063±0.0010 (Yar-hayi rice) > 0.061±0.0000 (Jan-bawo rice) > 0.057±0.0000 (Imported caprice) >0.050±0.0014 (white rice Cipi). Sood et al., (2006) reported 0.067 mg/100 g content of B2 in India (Basmati) rice. The mean levels of B6 detected in all the rice were 0.135±0.0070 (faro) > 0.12 ±0.0000 (Jan-bawo rice) > 0.115±0.0071 (Yar-hayi rice) > 0.0835±0.0007 (Foreign caprice) > 0.082±0.0000 (white rice Cipi).

CONCLUSION

This study has shown that the proximate constituents of the locally produced rice are relatively high and comparable to the imported (Caprice), such as the percentage of crude proteins, crude fiber, lipids, ash content, carbohydrates, and moisture content. Also, the vitamins B1, B2, and B6 are relatively high in locally-produced milled rice. The mineral compositions of Na, P, and K in the four locally produced rice are higher than the imported variety (caprice) while Fe and Ca are comparable with the local brands. The heavy metal contamination analysis showed that Cr and Cd were not detected while Pb was detected with a concentration range of 0.024mg/kg to 0.12mg/kg, Faro rice 0.057mg/g, Yar-hayi rice 0.024mg/g, Janbawo rice 0.064mg/kg, imported rice (Caprice) 0.076mg/kg and white rice (Cipi) 0.12kg/g these values were below the permissible limit for lead in food (0.2mg/kg) according to WHO and FAO. Therefore the selected five varieties of rice are safe for consumption and contain minerals, nutritional compositions, and vitamins that are essential to the body. Thus, the four locally produced rice are very good and should be consumed more since their nutritional profile are higher and also they are cheaper.

Conflict of interest
The authors declare no conflict of interest

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