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Proximate, phytochemical and heavy metal levels of selected ripened fruits sold in market outlets within Enugu metropolis, Enugu State, Nigeria

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ABSTRACT

Studies were carried out to evaluate the proximate, phytochemical and heavy metal levels of selected ripened fruits (paw-paw, banana and plantain) sold in market outlets within Enugu metropolis, using standard analytical procedures and instrumentation. The parameters were evaluated in both the processed and control samples and were subjected to one way analysis of variance at 5% confidence level. The purchased ripened banana, paw-paw and plantain samples had 69.19± 3.96, 87.54± 4.20 and 79.54±1.72% respectively as moisture content compared to 58.71± 2.14, 74.66±3.01 and 70.71±3.01 % respectively obtained as moisture content in the control banana, paw-paw and plantain samples. The mean ash, protein, carbohydrate and vitamin C contents of the purchased banana, paw-paw and plantain samples were 1.71±0.21, 6.90±1.01, 8.84±2.11% ; 0.86±0.22, 0.67±0.18, 5.89±0.17% ; 2.34±0.54, 47.24 ±1.89, 40.81± 2.24 % and 11.11± 2.15, 31.12±0.34, 31.79±2.30 %, compared to 3.16±0.16, 7.61±0.46, 11.16±0.35% ; 1.24±0.39, 0.75±0.14, 6.82±0.33 % ;4.76±0.20, 50.66±3.41, 45.52±.46 % ; 16.02±1.49, 37.22±0.91, 25.21±2.71% gotten as mean ash, protein, carbohydrate and vitamin C contents in the control banana, paw-paw and plantain samples respectively. The mean moisture content was statistically higher in the investigated purchased samples than it was in the control samples. However, the mean ash, protein, carbohydrate and vitamin C contents of the control samples were higher than they were in the purchased samples. The mean flavonoids content in the control banana, paw-paw and plantain samples were 0.57±0.08, 0.87±0.26 and 0.43±0.06 mg/g respectively, but was 0.39±0.06, 0.66±0.10 and 0.38±0.02mg/g respectively in the purchased ripened banana, paw-paw and plantain samples. The mean alkaloids content in the control banana, paw-paw and plantain samples were 0.29±0.05, 0.93±0.09 and 0.32±0.05 mg/g respectively, but was 0.18±0.04, 0.85±0.06 and 0.20±0.04 mg/g respectively in the purchased banana, paw-paw and plantain samples. Lead was not detected in the control banana samples but was 0.02±0.01 and 0.12±0.05µg/g respectively in the control paw-paw and plantain samples. The mean Pb values in the purchased banana, paw-paw and plantain samples were 0.05±0.02, 0.10±0.04 and 0.33±0.08 µg/g respectively. Cadmium was not detected in the investigated control samples but had mean values of 0.07±0.02, and 0.15±0,03µg/g respectively

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in the purchased paw-paw and plantain samples. Although ripening agents generally accelerates the ripening of fruits to reduce economic loss due to possible decay, however, it could at the same time reduce the nutritive and phytochemical contents of the ripened fruits as was the suggested case with the investigated samples purchased from the market. The contaminant (heavy metal) levels of the purchased samples were equally found to be higher in the purchased samples than they were in the control samples.

Key words: Plantain, Paw-paw, Banana, Heavy metals, proximate parameters, Phytochemicals, Natural ripening and Induced ripening.

1. INTRODUCTION

According to Perotti *et al., (*2014), fruit ripening is the initiation of fruit senescence, which is programmed genetically to lead to organ transformation of fruits from unripe stage to ripe stage, which then makes the fruit attractive and consumable. The organ transformation of fruits into the ripe stage is an irreversible phenomenon, involving a series of biochemical, physiological and organoleptic changes (Tripathi *et al*., 2016). According to Maduwanthi *et al*., (2019), fruits ripening is closely associated with ethylene, a phytohormone that can trigger initiation of ripening and senescence. Thus, fruits can be classified as climacteric or non-climacteric. Climacteric fruits has strong respiratory peaks with high level of ethylene production during the ripening process while climacteric fruits have near constant respiration rate with little or no increase in ethylene production during the ripening processes. According to Maduwanthi *et al*., (2019), climacteric fruits are ethylene dependent and therefore have the ability to ripen after harvest. Examples are banana, mango, plantain and paw-paw etc. Fruit ripening is a combination of the physiological, biochemical and molecular processes in the fruit, which results to changes in the colour, sugar content, acid content, flavour, aroma and texture etc. Most climacteric fruits such as banana, plantain and paw-paw are harvested in a matured but unripe state and then subsequently allowed to ripen naturally. However, as has been experienced over time with most climacteric fruits, its natural ripening is usually slow. According to Unmesh *et al*., (2016), this slow process of natural ripening of climacteric fruits leads to high weight loss, fruits decay and invariably loss of economic value. Based on this foregoing, most fruit sellers induce the quick ripening of fruits that are climacteric, to be able to sale them at the period their economic value is still high. In the quest to quicken the ripening of fruits in order to be ready for sale and consumption, fruit sellers utilizes natural and artificial agents and this practice is common in developing countries such as Nigeria (Adewole and Duruji, 2010). Artificial ripening agents include calcium dicarbide, glycol, ethereal, ethephon etc. The natural ripening agents used to quicken the ripening of fruits include African bush mango fruit and leaves, apple and palm nut and leaves of *Irvingia gabonensis*.

According to Orisakwe *et al., (*2012), although the use of ripening agents may successfully shorten or reduce post-harvest losses however, such practices may lead to the contamination of the fruits and there by exposing the consumers to numerous health challenges such as digestive disorders, oedema, liver and kidney dysfunction, cardiovascular diseases and respiratory disorders. For instance, Nura *et al., (*2018) stated that calcium dicarbide, a commonly used ripening agent, triggers a variety of side effects on human health, ranging from irritation of the skin, eyes, chest and abdomen, vomiting to burning, seizures and even coma at low concentrations. Equally, Krishina *et al., (*2017) stated that artificial ripening agents when used inappropriately are toxic and consumption of fruits contaminated with them could result to health problems such as skin diseases, cancer, neurological disorders and organ failure. Ghandi *et al., (*2016) studied the effect of ripening agents on the quality of fruits and observed that natural ripening agents contributed to the highest sensory appeal and with the highest organoleptic quality while artificial ripening agents were the least.

Orisakwe *et al., (*2012) reported that the use of toxic and suspicious ripening agent on fruits meant for consumption have resulted to the contamination of such fruits with heavy metals. The health consequences of undue exposure to heavy metals through such food consumption is already well documented.

The three studied fruit samples (paw-paw (*Carica papaya*), banana (*Musa spp*. and plantain (*Musa paradisiaca*) are commonly consumed in various forms by people of all ages in Nigerian communities. They are blended in diets, fried as snacks (especially and plantain) and serves as the daily favourite fruit alternatives to the general public. In all the market outlets within Enugu metropolis, Enugu State, Nigeria, these fruits samples are displayed for sale at varying stages of ripening. To limit economic loss on these fruits, fruit vendors usually trigger the quick ripening of the fruits using available techniques and practices, which most often ultimately depletes the nutritive value of the fruits. The unsuspecting consumer purchases and consumes these fruits to build up essential nutrients in their body, but not knowing the possible contaminants and nutritive status of the fruits so consumed.
Hence this research became imperative.

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2. MATERIALS AND METHODS

Five samples of each of the ripened paw-paw, banana and plantain were randomly purchased in different market outlets within Enugu metropolis. Also, five samples of each of the investigated fruits were allowed to ripen naturally and hence served as the control samples. Both the purchased ripened fruit samples and the control fruit samples were washed clean with distilled water and were subsequently cut open to obtain the edible part that has been separated from the peel. The edible part was sliced into pieces and oven-dried at 60^{o}C for 24hrs. The oven-dried samples were subsequently ground into fine powder using mortar and pestle. The finely powdered samples were stored separately in well labelled air-tight containers until analysis.

Proximate Analysis

The moisture, ash, protein and carbohydrate content of both the purchased fruit samples and the control fruit samples were carried out using the methods described by (AOAC, 2002), while the vitamin C content was determined using iodometric titration as described by Silva and Barbosa, (2009). The alkaloids and flavonoids in the fruit samples were determined using standard methods of quantification as described by Tram *et al., (*2002) and Millogo *et al*., (2009) respectively. The levels of Pb and Cd were determined in the fruit samples using atomic absorption spectrophotometer as described by (AOAC, 2005). The entire experiment was performed in triplicates.

Statistical Analysis

The data obtained were expressed in mean± standard deviation and subjected to one way analysis of variance (ANOVA) at 5% level of confidence using IBM SPSS 22.0.

3. RESULTS AND DISCUSSION

Table 1: Mean proximate values of the selected ripened fruit samples sold in market outlets within Enugu metropolis.

Sample	Moisture content (%)	Ash content (%)	Protein content (%)	Carbohydrate content (%)	Vitamin C content (%)
BA_c	58.71±2.14^a	3.16±0.16^a	1.24±0.31^a	4.76±0.20^a	16.02±1.49^a
BA_{pu}	69.19±3.96^b	1.71±0.21^b	0.86±0.22^b	2.34±0.54^b	11.11±2.15^b
PW_c	74.66±3.01a	7.61±0.46^a	0.75±0.14^a	50.66±3.41^a	37.22±0.91^a
PW_{pu}	87.54±4.20^b	6.90±1.01^b	0.67±0.18^b	47.24±1.89^b	31.12±0.34^b
PL_c	70.71±3.01^a	11.16±0.35^a	6.82±0.33^a	45.52±1.46^a	25.21±2.71^a
PL_{pu}	79.54±1.72^b	8.84±2.11^b	5.89±0.17^b	40.81±2.24^b	21.79±2.30^b

BA_c, PW_c and PL_c represents banana, paw-paw and plantain samples that served as the control while BA_{pu}, PW_{pu} and PL_{pu} represents the purchased fruit samples from the market outlets within Enugu metropolis. For each of the samples, either purchased or the control, different letters in the row of each of the proximate value depicts significance at $p<0.05$.

Moisture content: Result of Table 1 shows that the mean moisture levels of the control banana samples (58.71±2.14%) was significantly lower than those of the purchased banana samples (69,19±3.96%). Also the ripened control paw-paw samples had a significantly lower mean moisture value of 74.66±3.01% than the purchased ripened paw-paw samples with a mean value of 87.54±4.20%. In the same vein, the mean moisture level of the control plantain samples (70.71±3.01%) was significantly lower than 79.54±1.72% that was obtained for the purchased plantain samples. The common observation in the moisture content of the samples was that the control samples had lower mean moisture values than the samples purchased from the market. The implication of this is that the samples purchased from the market were more readily prone to microbial decay than the control samples because of the increased moisture level. The increased moisture levels of the purchased fruit samples could have been caused by induced ripening of the fruit samples by the fruit sellers and this observation corroborates the findings of Ariyo *et al., (*2021), who observed that artificially ripened banana samples had higher moisture values than naturally ripened samples and they also opined that this phenomenon could accelerate the post-ripening deterioration and reduce market value of the samples.

Similarly, Nuhu *et al*., (2020) reported that artificially ripened fruit samples usually have higher moisture content than naturally ripened fruit samples because the chemical compound used in the ripening process causes the weakening of the fiber of the peel leading to easier moisture absorption.

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Ash content: Result of Table 1 shows that the mean ash content of the control banana samples (3.16±0.21%) was significantly higher than those gotten from the market (1.71±0.21%). Also, the paw-paw samples purchased from the market had a significantly lower mean ash content of 6.90±1.01% than the control samples with a mean ash value of 7.61±0.46%. In the same vein, the mean ash content of the control plantain samples (11.16±0.35%) was significantly higher than 8.84±2.11% gotten for the purchased plantain samples. The result of Table 1 shows that the ash content of the three investigated control samples showed a similar pattern of increasing mean values than the purchased fruit samples. Sojinu *et al*., (2021) reported a lower mean ash content (6.17±0.20%) in ripened plantain samples induced with calcium dicarbide than 6.62±0.40% obtained as mean ash content in the naturally ripened plantain samples . This report agrees completely with the findings of this research. The observed low mean ash contents shown in the purchased fruit samples compared to the control samples could have resulted from rapid metabolism of the fruits necessitated by the use of induced ripening agents.

Protein content: Result of Table 1 shows that the mean protein content of the control banana and purchased banana samples were 1.24±0.31 and 0.86±0.22% respectively. The mean protein values of the investigated banana samples showed statistical significance. The ripened control paw-paw samples had a statistically higher mean protein content of 0.75±0.14% than 0.67±0.18% obtained for the ripened purchased paw-paw samples. Similarly, the ripened control plantain samples had a mean protein content of 6.82±0.33%, which was statistically higher than 5.89±0.17% gotten for the purchased ripened plantain samples.

It was a common observation that the mean protein content of the investigated control samples were higher all round than the purchased samples. This observation could indicate that the samples purchased from the market could have had their ripening induced by various means, which could have trigerred the rapid oxidation and metabolism of the fruits' essential food nutrients such as protein. Adeyemi *et al*., (2018) reported a higher mean protein value of 0.96±0.18% in their control plantain samples than 0.78±0.07% obtained for the calcium dicarbide induced plantain samples and therefore their findings was in total agreement with the observation of this study.

Carbohydrate content: The carbohydrate content in Table 1 shows that the ripened control banana samples had a statistically higher mean value of 4.76±0.20% than 2.34±0.54% obtained for the purchased ripened banana samples. The ripened control paw-paw samples had a statistically higher mean carbohydrate value of 50.66±3.41% than 47.24±1.89% gotten for those purchased from the market. The carbohydrate content of the ripened control plantain samples (45.52±1.46%) was equally statistically higher than 40.81±2.24% reported for the ripened purchased plantain samples. The findings of this research agrees with the report of Islam *et al*., (2018), who stated that induced ripening of fruits usually triggers an increased glucogenesis, which results in decreased carbohydrate content of such fruits.

Vitamin C content: The mean vitamin C content of the control (naturally ripened) banana samples (16.02±1.49%) shown in Table 1 was statistically higher than 11.11±2.15% reported for the ripened purchased samples. Similarly, the ripened purchased paw-paw samples had a statistically lower mean vitamin C value of 31.12±0.34% compared to 37.22±0.91% gotten for the ripened control samples. The mean vitamin C value of 25.21±2.71% for the control plantain samples was statistically higher than 21.79±2.30% reported as mean vitamin C value in the purchased samples. The higher mean vitamin C values obtained in all the investigated control samples compared to the purchased samples could have been as a result of lower metabolism and oxidation of the anti-oxidant mineral (vitamin C) whereas the lower mean vitamin C values of the purchased samples could have been caused by increased oxidation from the use of artificial ripening agents. The findings of Adeyemi et al., (2018), who reported a higher mean vitamin C value of 50.12±1.23% in the naturally ripened plantain samples than 44.72±2.02% gotten for the artificially (carbide) ripened plantain samples was in agreement with the observed values of this research.

Table 2: Mean alkaloids and flavonoids content of the ripened fruit samples

Sample	Flavonoids(mg/g)	Alkaloids(mg/g)
BA_c	$0.57±0.08^a$	$0.29±0.05^a$
BA_{pu}	$0.39±0.06^b$	$0.18±0.04^b$
PW_c	$0.87±0.26^a$	$0.93±0.09^a$
PW_{pu}	$0.66±0.10^b$	$0.85±0.06^b$
PL_c	$0.43±0.06^a$	$0.32±0.05^a$
PL_{pu}	$0.38±0.02^b$	$0.20±0.04^b$

Result of Table 2 shows that the mean flavonoids content of the control banana samples and the purchased banana samples were 0.57± 0.08 and 0.39±0.06mg/g respectively. This result indicates that the control banana samples had a statistically higher mean flavonoids content than the purchased banana samples. The control paw-paw samples had a statistically higher mean flavonoids

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content of 0.87±0.26 mg/g than 0.66±0.10 mg/g reported as flavonoids content in the purchased paw-paw samples. Also, the control plantain samples had a statistically higher mean flavonoids content of 0.43±0.06 mg/g than 0.38±0.02mg/g gotten for the purchased plantain samples. Therefore the result of Table 2 indicates that the low mean flavonoids content of the purchased samples could have been caused by their hastened ripening occasioned by the use of ripening agents, which invariably accelerated the oxidation and the consequent breakdown of the phytochemical. Similar observation of reduced levels of tannins, saponins, alkaloids and phenol were observed by Ariyo et al., (2021) in their investigated artificially ripened banana samples than was found in the naturally ripened banana samples. Also, the result of Table 2 shows that the mean alkaloids content in the control banana samples (0.29±0.05mg/g) was statistically higher than 0.18±0.04mg/g obtained for the phytochemical in the purchased banana samples. The naturally ripened paw-paw samples (control) had a statistically higher mean alkaloids content of 0.93±0.09mg/g than it was reported (0.85±0.06mg/g) in the purchased paw-paw samples. In the same vein, the mean alkaloids content of the control plantain samples with a value of 0.32±0.05mg/g was statistically higher than 0.20±0.04mg/g reported for the phytochemical in the purchased plantain samples. Both alkaloids and flavonoids are two of the most important phytochemicals, that impacts therapeutic effect when ingested in the body system and could be easily metabolized and oxidized in the presence of harsh chemical environment, such as accelerated ripening of fruits using artificial ripening agents.

Table 3: Mean Pb and Cd levels in the investigated ripened fruit samples.

Sample	Pb(μg/g)	Cd(μg/g)
BA_c	ND	ND
BA_{pu}	0.05±0.02	ND
PW_c	0.02±0.01^a	ND
PW_{pu}	0.10±0.04^b	0.07±0.02
PL_c	0.12±0.05^a	ND
PL_{pu}	0.33±0.08^b	0.15±0.03

ND = non detected

Result of Table 3 shows that Cd and Pb were not detected in the naturally ripened (control) banana samples. However, the purchased ripened banana samples had a mean Pb value of 0.05±0.02μg/g, while the Cd was undetected. The mean Pb value of the control paw-paw samples (0.02±0.01μg/g) was statistically lower than 0.10±0.04μg/g gotten for the metal in the purchased paw-paw samples. The control samples could have had Pb contamination from the heavy metal contamination of the soils were the fruits grew while the metal contamination of the purchased paw-paw samples could have been from the soil heavy metal pollution where the fruits grew, improper storage, poor handling and the use of ripening agents, whose purity from pollutants such as heavy metals is not guaranteed.

Cadmium was not detected in the control paw-paw samples but had a mean value of 0.07±0.02μg/g in the purchased paw-paw samples. The control plantain samples had a mean Pb value of 0.12±0.05μg/g, which was statistically lower than 0.33±0.08μg/g obtained for the metal in the purchased plantain samples. Cadmium was not detected in the control plantain samples, but had a mean value of 0.15±0.03μg/g in the purchased plantain samples. Cadmium is a divalent metal, with oxidation state of 2 and therefore are most likely found in impure form in divalent metals such as calcium. The investigated metals (Pb and Cd) were present in the studied samples at non-toxic levels as established by WHO, (2005). The investigated heavy metals are food toxicants of concern to clinicians and food safety agencies and therefore their hazardous health effects especially at high dose exposure are well documented in literature.

4. CONCLUSION

The ash, protein, carbohydrate and vitamin C contents of the purchased fruit (paw-paw, banana and plantain) samples were all statistically lower than the naturally ripened (control) samples. The moisture content of the purchased fruit samples were observably higher than those that were ripened naturally. This observation implies that the purchased fruit samples must have had some form of induced ripening using available ripening agents and therefore the increased moisture content was an indication of onset of microbial decay. It can safely be concluded that the purchased fruit samples had lower nutrient contents compared to the control samples and induced ripening is a suggested cause. Important investigated phytochemicals such as alkaloids and flavonoids were significantly lower in the purchased fruit samples than they were in the control samples. Although, the investigated heavy metals (Pb and Cd) were within permissible limits in the studied fruit samples, however, the metals were

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detected more in the purchased fruit samples than they were in the control samples. Serious advocacy is required by both the food regulatory agencies and the general mass media, especially in conjunction with food and environmental science experts to encourage fruit sellers and the general public to ensure that fruits meant for human consumption would be safer for body well-being if allowed to ripen naturally. Health implications of the use of induced ripening agents in accelerating the ripening of fruits meant for human consumption should be advocated by government at all levels using available media space and in the peoples' mother tongue.

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Conflicts of interests

The authors declare that there are no conflicts of interests.

Data and materials availability

All data associated with this study are present in the paper.

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