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Original Research Article

Ascorbic Acid Concentration and Functional Groups in Aqueous Extracts of Tropical Fruits Sold in Owerri, Imo State, Nigeria

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Abstract

Extracts of orange, pineapple, pawpaw and watermelon bought at local and super markets within Owerri were investigated for vitamin c content and functional groups. Standard titrimetric method using iodine solution and Buck 530 FTIR spectrometer were used for vitamin C and functional group identifications respectively. Vitamin c content ranged from 77.62 ± 227mg/100g from fruits in open markets to 13.14 ± 6.39 mg /100g for fruits in supermarkets. Fruits in open markets showed vitamin c content in the following decreasing order: orange (75.46 ± 1.72) > pawpaw (65.90 ± 2.39) > pineapple (16.14 ± 1.39) > water melon (13.14 ± 0.59) for fruits in the open market. While orange (77.62 ± 2.27) > pawpaw (62.99 ± 2.79) > water melon (23.50 ± 2.90) > pineapple (14.45 ± 3.92) were generally for fruits in supermarkets. Functional groups identified include carboxylic acids, amines, amides, phenolics, thiols, alcohols, and isothiocyanates in some cases free hydroxyl groups in carboxylic acid functional group was not found in pineapple, free hydroxyl groups were equally not found in pineapple and pawpaw. Several functional groups were present in varying forms and could the basis for therapeutic and medical uses.

Keywords: Vitamin C, Functional groups, Tropical, Nutritional, Therapeutic, medical.

INTRODUCTION

The contribution of fruits and it constituent to human nutrition cannot be overstated. In Africa, fruits are on high demand. This is because they are complemented with food to ensure balanced diet, and some serve as raw materials to industries. Fruits serve as sources of vitamins and minerals hence, they also become important when the functions of these vitamins and minerals, are being considered in the body [1]. Some of these fruits are used in folk medicine as cure for some diseases [2, 3, 4]. The ability of such fruits to remedy diseases is a consequence of bioactive constituents, which are generally present in plants [3, 5, 6, 7]. However, some of these bioactive substances are anti-nutrients since they provide some of the essential nutrients unavailable in the body, for human metabolism [5]. Fruits have been part of human diet and food supplement over the years. They are considered as healthy food supplements because they contain high amount of water, carbohydrates, proteins, vitamin A, B1, B2, C, D, and E, minerals such as Ca, Mg, Zn and Fe [8] and organic compounds which are required in small amounts, to make the body function properly. Fruits represent a major source of dietary antioxidants. Studies have shown that the consumption of natural sources of antioxidants can protect humans against oxidative damage by inhibiting or quenching free radicals and Reactive Oxygen Species (ROS)[8,9]. More so, they are more advantageous to health than their synthetic counterparts/supplements.[8] The demand for these antioxidants, like ascorbic acid, carotenoids, lycopene, polyphenols, is more pronounced in this era of increased number of non-communicable diseases (NCD's) worldwide. This is especially so for developing nations where the rise in the NCD's is being battled alongside the menace of infectious disease [10]. Low fruit intake is the main contributor of micro nutrient deficiencies in the developing world. [11] FAO estimated that low intake of fruits and vegetables caused about19% gastro intestinal cancers, about 31 % of ischemic heart disease, 11% of stroke, 85% of CVD'S and 15% of cancers.[11]. According to Food and Agriculture Organization, [12] approximately 1.0% disability adjusted life years (DALYs); a measure of the potential life lost due to premature mortality and the years of productive life lost due to disability and 2.8% of deaths worldwide, are attributed to low fruit and vegetable consumption.[12]

A shift has been noticed in the worldwide food demand from basic cereals and grains to products with a higher added value such as fruits, vegetables and fats [13]. FAO 2004 reported that the production of high value agricultural commodities such as fruits, vegetables and milk is growing fast. Developing countries account for about 98% of total production while developed countries account for 80% of world import trade. [12] Also the major tropical fruits account for approximately 75% of global tropical fresh fruit production. However, in many developing countries like Nigeria and Brazil, the shift to more value-added products is less pronounced and statistics showed a decline. Von Braun reported that the decline in value added products in Brazil, Kenya and Nigeria could probably be due to the growing inequality in some of the countries. [13, 14] Tanko et al, [15] averred that Nigeria's deficient situation has been be worsened by declining farm productivity owing to inefficient production techniques, poor resource base and declining soil productivity among others. [15] According to FAO 2004, the set population nutrient goals and recommended intake was put at a minimum of 400 g of fruits and vegetables per day for prevention of chronic heart diseases, cancer, diabetes and obesity, [14] but more than three quarter of adults in less developed countries consume less than the minimum recommended five daily servings of fruits and vegetables. Ruet et al [16] reported that the average consumption (in kg per capita per year) is lower for fruits than vegetables in most countries. [16] Generally, situations suggest a significant gap in the mean consumption of fruits and vegetables across countries, sectors/locations and economic groups. Abundant intake of fruits is clearly a positive solution to problems of poor diet quality in the developing world. Fruits are relatively cheap sources of essential micronutrient and therefore a cost-effective way to prevent micronutrient deficiencies and protection against the main killers associated with these deficiencies. Nevertheless, in spite of the growing body of evidence on the protective effect of fruits their consumption is still grossly inadequate. The African continent is blessed with a rich tropical flora. Nigeria produces a variety of fruits such as mangoes, watermelon, paw-paw, pineapples, guava, oranges, tangerines and many other indigeneous fruits.[17] These fruits are consumed in different ways, some eat them fresh or process them to make juice, jam or desert and sometimes some of the fruit pulps are dried and used as flour to make porridge.

Owerri is the capital city of Imo state in Nigeria; it is also the largest city in the state. Imo State is one of the states located in the eastern zones of Nigeria. The state covers an area of about 5,067.20 km^2 with a population of 3,934,899 [18 19] and population density of about 725 km^2. [20]. The state has an average annual temperature of 28 °C, an average annual relative humidity of 80%, average annual rainfall of 1800 to 2500 nm and an altitude of about 100m above sea level. [21]

The state's economy depends primarily on agriculture and commerce and some of their cash crops include oil palm, melon, groundnut, food crops such as yam, cassava, cocoyam and maize are also produced in large quantities. [22] The location of Imo State within the tropical rain forest gives it the ecological basis for the production of a range of tropical agricultural crops within extensive potentials for industrial usage. Due to some constraints in fruit farming, most fruits are not grown in the state in large commercial scales. Fruits grown in the state come from the wild, homestead gardens and traditional cropping system and because of the high demand of fruits by the consumers and juice makers there is the struggle to satisfy demand.[22] As a strategy for enhancing agricultural development in the state, private investors are been invited to participate in direct agricultural production. [23]The increasing awareness on health and nutritional potential of fruits and encouragement of agro allied industries by the federal government of Nigeria, calls for the need for better utilization of these fruits in our everyday diet.

Unhealthy lifestyle, bad habits and some environmental conditions, promote free radical formation in the human system, and an increased level of these radicals in the body could put one at the risk of organ degradation paving way for disease and illness. Some studies have shown that diets rich in fruits can protect the body against oxidative damage. For better utilization of fruits in human diet and in production of value added products, a clear understanding of the nutritive, chemical properties and content estimation is of essence.This study aims at determining ascorbic acid content and functional groups in the fruit extracts of *Citrullus lanatus* (watermelon), *Carica papaya* (paw-paw), *Ananas comosus* (pineapple) and *Citrus cinnesis* (orange), sold in Owerri Metropolis. To achieve the aim of this study, the followed objectives were set: (1) to compare the results of fruits purchased from the local market and that of the Owerri shopping mall and comparing both results obtained with United State Department of Agriculture (USDA) standards(2) to test statistically differences between results obtained for local market and shopping mall (3) to identify the functional groups present in *Citrullus lanatus* (watermelon), *Carica-papaya* (paw-pgaw), *Ananas comosus* (pineapple), *and Citrus cinesis* (orange)using Fourier Transform InfraRed spectroscopy.

Consumers are increasingly becoming aware of the relationship between food and healthy living and scientists and researchers are also responding by identifying products and creating healthy food formulas for consumers. Similar studies have been done on analysis of different fruits to identify and evaluate the nutrient composition, estimate the concentration of compounds present but no previous study of this type has been done before now with the selected fruits of study from this city and at the different locations of purchase. Therefore, this study will directly benefit the people of Owerri, because these fruits to be analyzed are readily available in their locality and more precise information on the composition of these fruits will help to integrate them in the food based approach for correcting micronutrient deficiency. Furthermore, this could be used as source material for further study. This study reportsascobic acid and functional groups of four different fruits; *Citrullus lanatus* (watermelon), *carica papaya* (paw-paw),*ananas comosus* (pineapple) and *citrus cinesis* (orange) from two different sources in Owerri (Owerri relief market and Owerri shopping mall).

Materials and methods

Field Survey

The survey was carried out at Owerri Relief Market and Owerri Shopping Mall. These locations were selected since they are the major sale points to the people of the city. The designation of "Market" and "S. Market" (super market) is used in the remainder part of this study represent the fruits from Owerri Relief Market and Owerri Shopping Mall respectively.

Fruits used for analysis

A total of 18 fruits were used for this study comprising of 8 sizeable oranges, 4 pineapples, 2 watermelons and 4 paw paw fruits. Watermelon (*Citrullus lanatus*) specie used for study is the red fleshed seed watermelon called "*sugar baby".* The paw paw (*Carica papaya*) used for study is the *"Carica"*, the pineapple (*Ananas comosus*) used for the study is the Del-Monte Gold or MD2 variety, the orange (*Citrus cinensis*) used is the common *"sweet orange"* of the Valencia variety.

Study Area

The study was conducted in Owerri, Imo State Nigeria. It is the state's largest city and consists of 3 LGA's, Owerri municipal, Owerri North and Owerri West. Owerri has an estimated population of about 1,401,873 as of 2016 and is approximately 100 square km (40 SQ m) in area and coordinates 5◦28'34.7160"N and 7◦1'33.0708"E [24]. The city is situated at an elevation 73 meters above sea level. The city also has a large market, the Relief Market. The choice of city for study was selected because of proximity, familiarity and cost.

Figure 3.1: Map of Owerri

Collection of the sample

Fully matured ripe fruits of *Citrullus lanatus* (watermelon), *Carica papaya* (paw-paw), *Ananas comosus* (pineapple) and *Citrus cinesis* (orange) were procured from Relief Market Owerri, and Owerri shopping mall Imo State, Nigeria. Collected samples were fresh, matured, well-shaped and free from insect's bites and other organoleptic deterioration. The freshly collected samples were washed with de-ionized water to eliminate visible dirt and removed the water quickly with a blotting paper. They were transported to the Chemistry Laboratory, Imo State University, for analysis. The photographs of the studied tropical fruits in presented in Figure 3.2 and 3.3.

(1a)

(1b)

Figure-1a: Watermelon, Paw-Paw, Pineapple and Orange purchased from the market.
Figure-1b: Pineapple, Paw-Paw, Watermelon and Orange purchased from the super market.

Sample preparation

The fruits were washed thoroughly with distilled water and weighed. The outer parts were peeled off and the flesh was separated from the rind and the seeds removed. The fruit pulps were homogenized in a blender and filtered with a muslin cloth. This was done separately for each fruit. The juice was stored in air tight screw cap bottles and refrigerated at 5^0C prior to analysis.

(a) Extracts of fruit form open market

(b) Extracts of fruit form super market

Figure-3(a): The fruit juice extracts. From left to right we have pineapple, pawpaw, watermelon and orange from the open market. (b) Fruit extracts. From left to right: Orange, Watermelon, Pineapple and Pawpaw purchased from the supermarket.

Determination of Functional Groups present in the fruits using FTIR

The Fourier Transform Infrared Spectroscopy is one of the most widely employed techniques for functional group identification. FTIR spectra of the crude extracts of *Ananas comosus, Carica papaya, Citrullus lanatus and Citrus cinensis* were recorded on a Buck 530 FTIR spectrophotometer. Each sample of extract mixed with potassium bromate (KBr) salt to form paste. The paste was loaded on the KBr plate and placed in the chamber of FT-IR spectrophotometer and scanned at room temperature (25 ± 2 °C) with a scan range from 500 to 4000 cm^{-1} at a resolution of 2 cm^{-1} for 4 mins.

Data Analysis

Results for triplicate analysis were reported as mean and standard using IBM SPSS version 20. One way analysis of variance (ANOVA) was used to test for statistically differences at 5 % level of significance for mineral composition and characteristic wave number of absorption for the different fruit studied. Charts was also used were appropriate to compare and show data distributions.

Results and discussion

Ascorbic acid

In present study we observed that, *citrus cinensis* contain highest amount of vitamin C (market; 75.46 ± 1.72 mg/100g < S. market; 77.62 ± 2.27 mg/100g) and *citrullus lanatus* contain lowest amount of vitamin C (13.14 ± 0.39 mg/100g) for market while *Ananas comosus* for 14.45±3.92 mg/100g for S. market. Nutrient database by USDA [26] showed the range of vitamin C in the tropical fruits from 9.01 to 210.47 mg/100g which has been analyzed by using HPLC method whereas the information revealed from this study on vitamin C has been estimated by visual titration method according to AOAC instead of HPLC method. The North American Dietary Reference, recommended daily intake of vitamin C 90 mg and not more than 2 gm [27] and whereas in case of adult (19-65 years) population group recommended nutrient intake (RNI) for vitamin C is 45 mg/day [28]. The result of the current study is comparable to that of some other fruits. Taylor [29] reported 47.6 mg/100g for “Agbalumo” pulp, 48 mg/100g for papaya, Kennedy *et al.*, [30] reported 62 mg/100g for freshly squeezed orange juice, while Lee *et al.*, [31] reported 40.6 mg/100ml for Florida citrus (freshly squeezed and unpasteurized).

Comparing the two fruit sources for vitamin C content; for *Citrus cinensis*: S. market > market; *Ananas comosus*: Market > S. market; *Citrullus lanatus*: S. market > market while for *Carica papaya*: market > S. market respective (Table 1). The value obtained for this research could have been affected by factors such as the cultivar, oxygen, soil and some other environmental factors that lead to higher ascorbic acid.

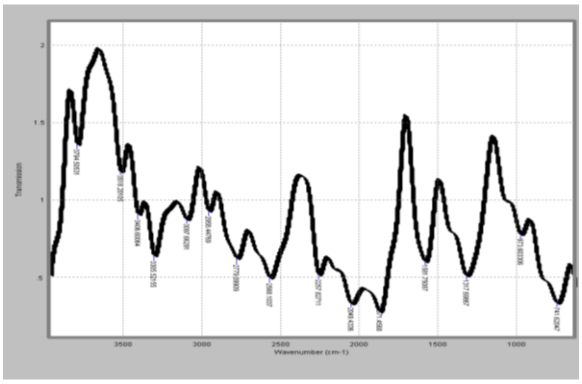
Table-1: Ascorbic acid (AA) concentrations

Parameters	*Citrus cinensis*		*Ananas comosus*		*Citrullus lanatus*		*Carica papaya*	
	Markets	**S. Market**	**Markets**	**S. Market**	**Markets**	**S. Market**	**Markets**	**S. Market**
AA (mg/100 g)	75.46±1.72	77.62±2.27	16.14±1.39	14.45±3.92	13.14±0.59	23.50±2.90	65.90±2.39	62.99±2.79

Values reported as mean ± SD for n=4

Functional group analysis

The FTIR spectrum was used to identify the functional groups of the active components present in the fruit samples based on the peaks values in the region of Infrared radiation either directly or by inference. When the fruit samples were passed into the FTIR, the functional groups of the components were separated based on its peaks ratio[32]. The associated changes in the spatial arrangement of the groups involved are reflected in the infrared spectrum as additional bands and added complexity. The FTIR spectrums for the different fruits are presented in Figure 6-9.



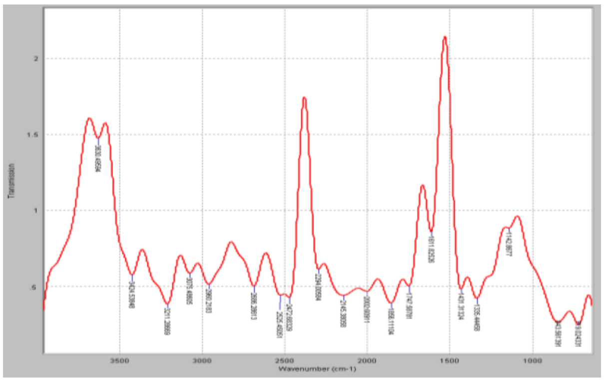
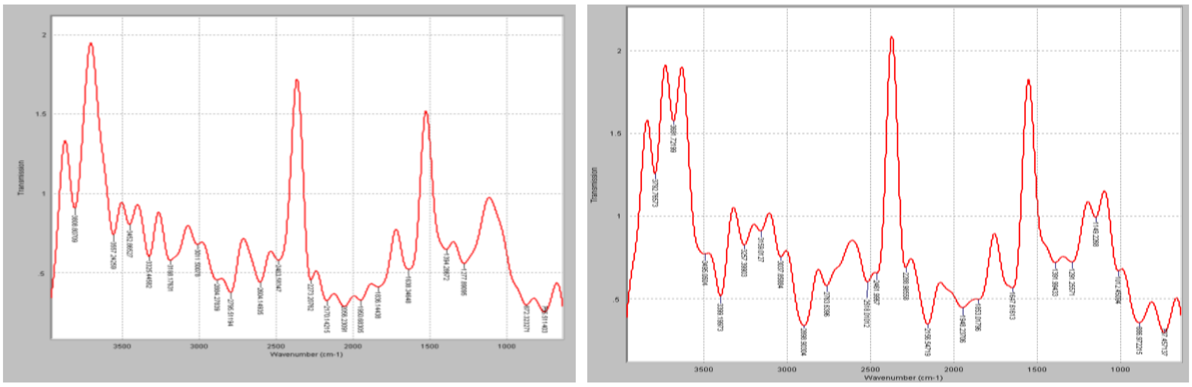
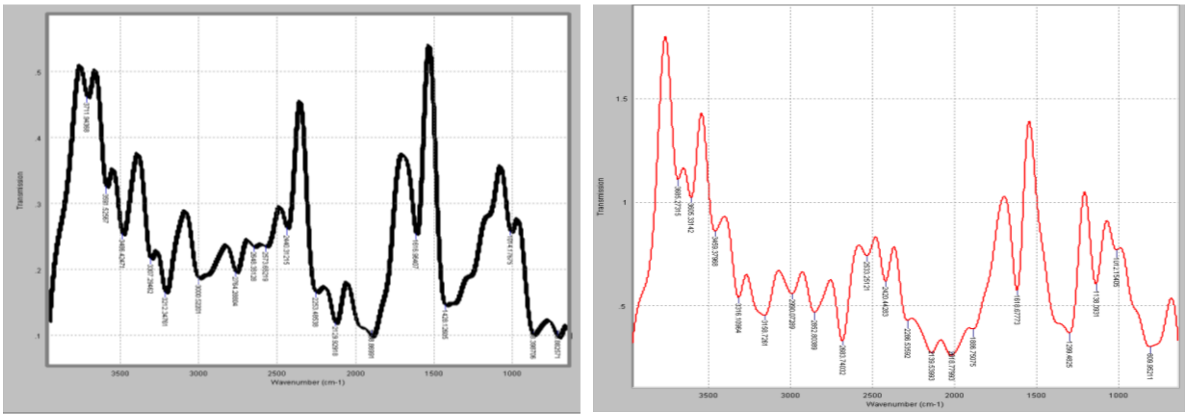


Figure-6: FT-IR spectrum of *Ananas cosmosus* crude extract



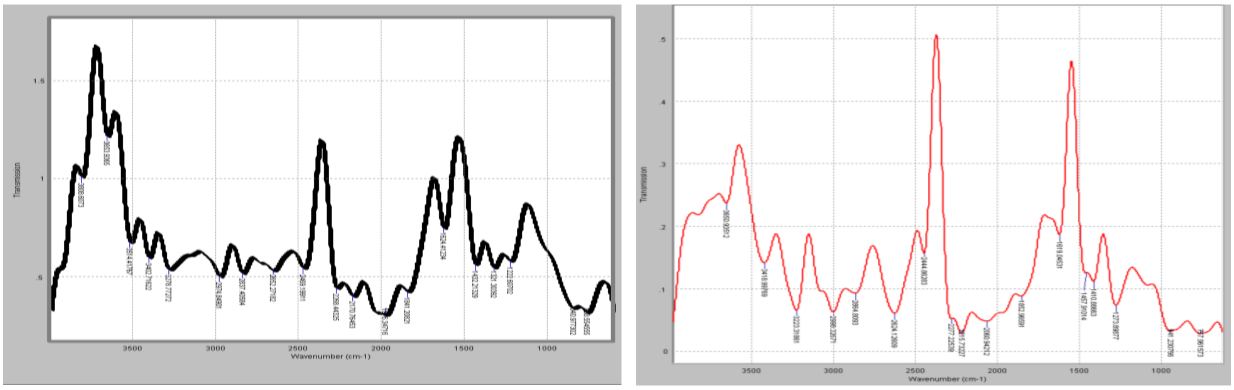
(a) Market **(b) Super market**

Figure-7: FT-IR spectrum of *citrus cinensis* crude extract



(a) Market **(b) Super market**

Figure-8: FT-IR spectrum of *Carica papya* crude extract



(a) Market **(b) Super market**

Figure-9: FT-IR spectrum of *cirtullus lanatus* crude extract

The interpretations of the spectrum are presented in Tables 2- 5. In Tables 2-5, the peaks of absorption and respective functional groups for *Ananas comosus*, *Carica papaya*, *Citrus cinensis* and *Citrus lanatus* respectively for markets and super markets fruits is shown. The intensity of the absorption is similar for the four tropical fruits studied.

Pineapple (Ananas comosus)

From the spectral analysis results for pineapple (Table 2), the characteristic peak area ranges from 741.62 cm^{-1} to 3794.50 cm^{-1} obtained from market while the supermarket showed peak area which ranged from749.02 cm^{-1} to 3630.56 cm^{-1},with 10 distinctive functional groups identified for the fruits. The peak area of 741.62 – 749.02 cm^{-1} represents a characteristic area for the absorption corresponding to vibrations characteristic to the C-H bonds. Other characteristic area from the spectral absorption corresponds to vinyl at 843.56 and 973 cm^{-1}, aromatic amine at 1142.87 to 1335.44 cm^{-1}, primary amine at 1581.75 cm^{-1}, acid halide at 1871 cm^{-1}, alkyne, thiols, aldehyde, alkane, and alcohols at 2294 to 3630.56 cm^{-1}.

Table-2: FTIR analysis of *Ananas comosus* crude extract

Market			Super Market		
Wavenumber (cm^{-1})	**Functional group**	**Remarks**	**Wavenumber (cm^{-1})**	**Functional group**	**Remarks**
741.62	C-H (broad)	Out-of-plane, bend	749.02	C-H (broad)	Out-of-plane, bend
973.60	Vinyl C-H	Out-of-plane, bend	843.56	Vinyl C-H	Out-of-plane, bend
1317.70	Aromatic amine, CN	Stretching	1142.87	Aromatic amine, CN	Stretching
1581.75	Primary amine, NH	Bend	1335.44	Aromatic amine, CN	Stretching
1871.46	Acid halide, C=O	Stretching	1431.31	Acid halide, C=O	Stretching
2049.43	Alkane, C-H	Stretching	1611.83	Alkane, C-H	Stretching
2257.83	Alkyne, C≡C	Stretching	1747.59	Acid halide, C=O	Stretching
2568.10	Thiols, S-H	Stretching	1856.11	Acid halide, C=O	Stretching
2779.09	Aldehyde, C-H	Stretching	2002.61	Acid halide, C=O	Stretching
2958.45	Alkane, C-H	Stretching	2145.38	Aldehyde, C-H	Stretching
3097.66	Alcohol, OH	Broad, Stretching	2294.00	Alkyne, C≡C	Stretching
3305.52	Alkyne, C≡C	Sharp	2472.68	Alkyne, C≡C	Sharp
3406.60	Primary Amine, NH	Stretching	2572.45	Thiols, S-H	Stretching
3518.20	Alcohol, OH	Broad, Stretching	2686.29	Alcohol, OH	Broad, Stretching
3794.50	Alcohol (Free), OH	Sharp, stretching	2960.22	Alkanes, C-H	Stretching
-	-	-	3075.49	Alcohol, OH	Broad, stretching
-	-	-	3211.29	Alkyne, C≡C	Stretching
-	-	-	3424.54	Primary Amine, NH	Stretching
-	-	-	3630.56	Alcohol, OH	Sharp Stretching

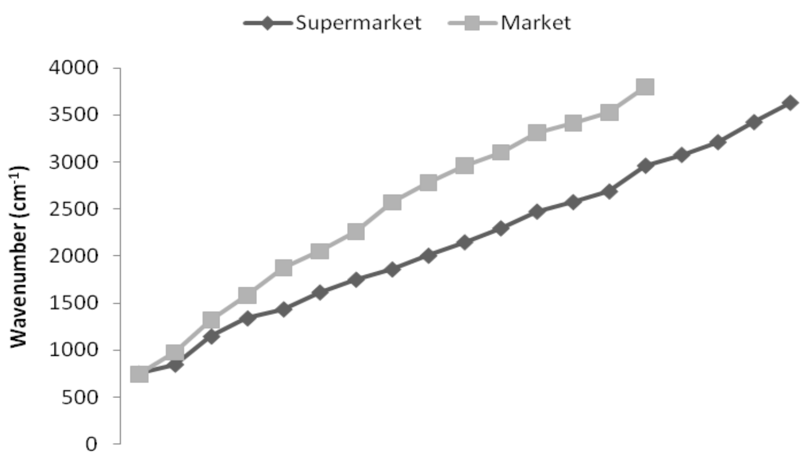


Figure-10: Characteristic wave number comparison for *Ananas comosus*

In Figure 10, the wave number of absorption showed significant differences ($p>0.05$) between the two fruits although the absorptions reveal similar functional groups but at different wavelength. These variations could be due to the different storage procedure while the fruits were still on the shelf. Joseph [33] observed that some functional compounds in fruits can be altered by storage techniques such as in the refrigerator.

Orange (Citrus cinensis)

The FTIR result for Citrus Cinensis is presented in Table 4.5. For market Orange (Citrus cinenesis) results band ranged from 755.51 cm^{-1} to 3808.51 cm^{-1} while s. market ranged from 787.46 to 3792.77 cm^{-1}. 21 functional groups were identified generally in the two Citrus cinensis extracts. Skeletal (C-C) vibrations were observed at 755.51 cm^{-1} and 787.46 cm^{-1} for both market and s. market, which is an indicative of a long-chain linear aliphatic structure. The band at 872.32 cm^{-1} and 886.97 cm^{-1} showed vinyldene (C-H) which are both out of plane and bending; the band at 1277.89cm^{-1} showed aromatic amine (CN) stretch for market while s. market showed stretching aromatic amine (CN) at band 1012.45 cm^{-1} and 1291.26 cm^{-1} respectively; the band at 1394.29 cm^{-1}, 2884.28 cm^{-1} and 3011.50cm^{-1} showed alkane groups for market while for s. market stretching band at1149.27cm^{1}, 1391.99 cm^{-1}, 2898.90 cm^{-1} and 3037.86 cm^{-1} respectively for alkanes (CH).

The band at 1638.35 cm^{-1} and 1647.62 cm^{-1} showed alkene (C=C) for both markets and s. market fruits respectively; the band at 1836.14 cm^{-1} and 1853.02 cm^{-1} showed aromatic (C-H) for both markets and s. market fruits respectively; the band at 1950.68 cm^{-1} and 1948.24 cm^{-1} showed allene (C=C=C) group for both markets and s. market fruits respectively; the band at 2056.23cm^{-1} and 2288.99 cm^{-1} showed isothiocyanate (N=C=S) group for both markets and s. market fruits respectively; the band at 2170.14 cm^{-1} and 2156.55 cm^{-1} showed alkyne (C≡C) group for both markets and s. market fruits respectively; the band at 2273.21 cm^{-1} showed isocyanate (N=C=O) for market while isocyanate was not assigned in s. market; the band at 2483.58 cm^{-1} and 3325.45 cm^{-1} showed carboxylic acid (OH) stretch for market while carboxylic acid group was assigned at band 2461.96 cm^{-1} and 3399.20 cm^{-1} respectively for s. market.

Table-3: FTIR analysis of *Citrus cinensis* crude extract

Market			Super Market		
Wave number (cm^{-1})	**Function group**	**Remarks**	**Wave number (cm^{-1})**	**Function group**	**Remarks**
755.51	Skeletal vibrations	Stretching	787.46	Skeletal vibrations	Stretching
872.32	Vinylidene C-H	Out-of-plane, bend	886.97	Vinylidene, C-H	Out-of-plane, bend
1277.89	Aromatic amine, CN	Stretching	1012.45	Aromatic amine, CN	Stretching
1394.29	Alkane, C-H	Stretching	1149.27	Alkane, C-H	Stretching
1638.35	Alkene, C=C	Strong, stretching	1291.26	Aromatic amine, CN	Stretching
1836.14	Aromatic, C-H	Stretching	1391.99	Alkane, CH	Stretching
1950.68	Allene, C=C=C	Stretching	1647.62	Alkene, C=C	Strong, stretching
2056.23	Isothiocyanate N=C=S	Stretching	1853.02	Aromatic, C-H	Stretching
2170.14	Alkyne, C≡C	Stretching	1948.24	Allene, C=C=C	Stretching
2273.21	Isocyanate, N=C=O	Stretching	2156.55	Alkyne, C≡C	Stretching
2483.58	Carboxylic acid, OH	Stretching	2288.99	Isocyanate, N=C=O	Stretching
2604.15	Thiols, S-H	Stretching	2461.96	Carboxylic acid, OH	Stretching
2795.51	Aldehyde, CH	Stretching	2518.01	Thiols, S-H	Stretching
2884.28	Alkane, CH	Stretching	2763.64	Aldehyde, CH	Stretching
3011.50	Alkane, CH	Stretching	2898.90	Alkane, CH	Stretching
3188.18	Alcohol, OH	Broad, Stretching	3037.86	Alkane, CH	Stretching

3325.45	Carboxylic acid, OH	Stretching	3159.01	Alcohol, OH	Broad, Stretching
3452.87	Heterocyclic amine, NH	Stretching	3257.40	Heterocyclic amine, NH	Stretching
3557.24	Hydroxy group, OH	Broad, stretching	3399.20	Carboxylic acid, OH	Stretching
3808.81	Free Alcohol, OH	Stretching	3495.05	Heterocyclic amine, NH	Stretching
-	-	-	3792.77	Free Alcohol, OH	Stretching

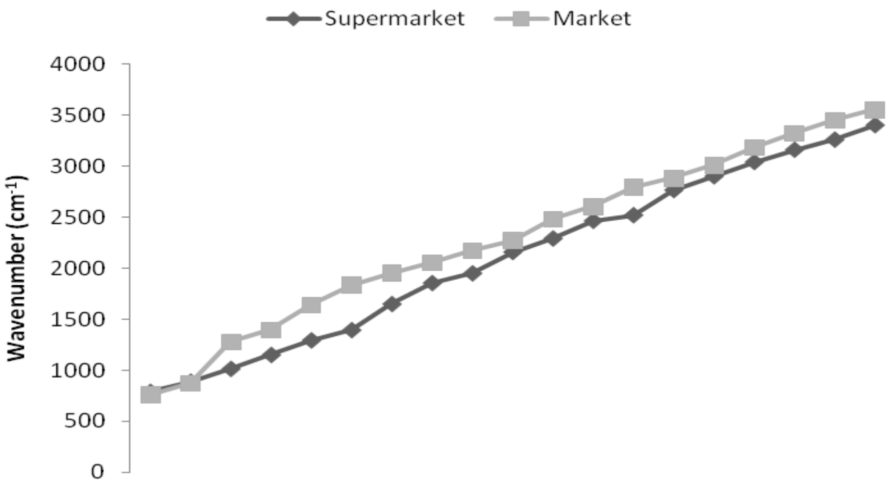


Figure-11: Characteristic wave number comparison for *citrus cinensis*

The band at 2604.15 cm^{-1} and 2518.01 cm^{-1} for market and s. market showed thiols (S-H) group respectively; the band 2795.51 cm^{-1} and 2763.64 cm^{-1} for market and s. market showed aldehyde (CH) group respectively; the band at 3188.18 cm^{-1} and 3159.01 cm^{-1} for market and s. market showed alcohol (-OH) group respectively; heterocyclic amine (NH) was observed at band 3452.87 cm^{-1} for market while at 3257.40 cm^{-1} and 3495.05 cm^{-1} respectively for s, market; the band at 3557.24cm^{-1} and 3808.81cm^{-1} showed hydroxyl group and free OH group stretching. The latter observed at band 3792.77 cm^{-1} for s. market fruit extract.

Statistically, there was no significant differences ($p<0.05$) using one-way ANOVA for the wavenumbers of the fruits from market and s. market. The two fruit samples also follow similar trend (Figure 11).

Pawpaw (*Carica Papaya*)

Pawpaw showed characteristic peak area which ranged from 710.88 cm^{-1} to 3711.94 cm^{-1} for market and from 609.95 cm^{-1} to 3685.27 cm^{-1} for s. market with 16 distinctive functional groups identified.

Skeletal (C-C) vibrations were observed at 710.88 cm^{-1} and 609.95 cm^{-1} for market and s. market respectively, which is an indicative of a long-chain linear aliphatic structure. A C-H characteristic of the vinylidene group was observed at 868.39 cm^{-1} for market whiles no observation for the super market. Cyclohexane was observed at 1014.18 cm^{-1} for market and 1012.15 cm^{-1}, 1138.09 cm^{-1} for super market.

Table-4: FT-IR analysis of *Carica papaya* crude extracts

Market			Super Market		
Wave number (cm^{-1})	**Function group**	**Remarks**	**Wave number (cm^{-1})**	**Function group**	**Remarks**
710.88	Skeletal vibrations	Vibrations	609.95	Skeletal vibrations	Vibrations
868.39	Vinylidene (C-H)	Out-of-plane, bend	1012.15	Cyclohexane	Ring vibrations

1014.18	Cyclohexane	Ring vibrations	1138.09	Cyclohexane	Ring vibrations
1428.13	Carboxylic acid, OH	Bending	1299.48	Carboxylic acid, OH	Bending
1616.96	Secondary amine, NH	Bending	1618.68	Secondary amine, NH	Bending
1898.87	Aromatic, C-H	Bending	1886.75	Aromatic, C-H	Bending
2129.93	Alkyne, C≡C	Stretching	2018.78	Alkyne, C≡C	Stretching
2253.49	Alkyne, C≡C	Stretching	2139.54	Alkyne, C≡C	Stretching
2440.31	Phosphine, PH	Sharp	2266.54	Alkyne, C≡C	Stretching
2573.66	Thiol, SH	Stretching	2420.44	Phosphine, PH	Sharp
2648.36	Phosphonic acid, (O=)P-OH	Sharp	2533.25	Thiol, SH	Stretching
2764.29	Aldehyde, CH	Stretching	2663.74	Phosphonic acid, (O=)P-OH	Stretching
3000.52	Alkene, CH	Stretching	2852.80	Aldehyde, CH	Stretching
3212.35	Alcohol, OH	Broad, Stretching	3158.73	Alcohol, OH	Broad, Stretching
3307.29	Alcohol, OH	Broad, Stretching	3316.11	Alcohol, OH	Broad, stretching
3486.42	Dimeric Alcohol, OH	Stretching	3459.38	Dimeric Alcohol, OH	Stretching
3591.53	Tertiary Alcohol, OH	Strong, Stretching	3605.33	Tertiary Alcohol, OH	Strong, Stretching
3711.94	Free Alcohol, OH	Stretching	3685.27	Free Alcohol, OH	Stretching

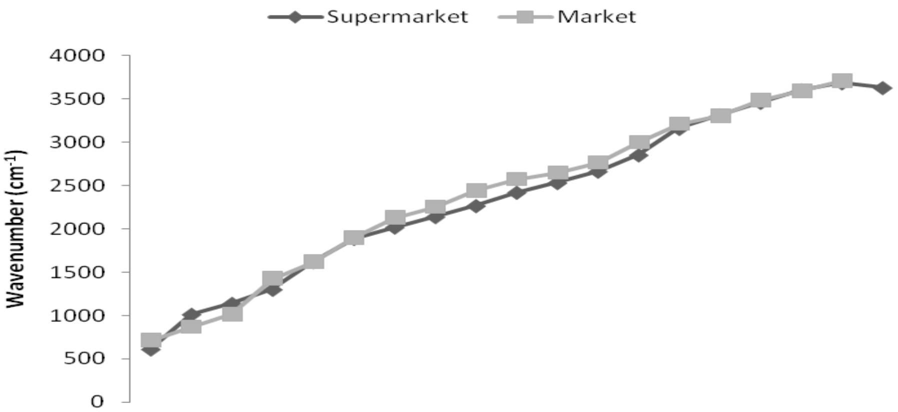


Figure-12: Characteristic wave number comparison for *carica papaya*

Hydroxyl (OH) characteristics of carboxylic acid were observed at 1299.48 cm^{-1} and 1428.13 cm^{-1} for s. market and market respectively, secondary amine (NH) were observed at 1616.96 cm^{-1} and 1618.68 cm^{-1} for market and s. market. aromatic (C-H) were observed at 1886.75 cm^{-1} and 1898 cm^{-1} for s. market and market respectively. Alkyne (C≡C) peaked at 2129.93 cm^{-1} and 2253.49 cm^{-1} respectively for market while it peaked at 2018.78 cm^{-1}, 2139.54 cm^{-1} and 2266.54 cm^{-1} respectively for s. market. The band at 2440.31cm^{-1} and 2420.44 cm^{-1} showed phosphine (PH) group; thiol (SH) was observed at 2573.66 cm^{-1} and 2533.25 cm^{-1}, phosphonic acid at 2648 cm^{-1} and 2663.74 cm^{-1}, aldehyde peaked at 2764 cm^{-1} and 2852.80 cm^{-1}.

Alkene was only observed at 3000 cm^{-1} for market, while alcohol, dimeric alcohol, tertiary alcohol and free (OH) were observed at characteristic peak range of 3212.35 to 3711.94 cm^{-1} for market and 3158.73 cm^{-1} to 3685.27 cm^{-1} for s.

market (table 4.5). Similar observation for pawpaw leaves extract was reported by Omotioma and Onukwuli [34]. The analysis of the extract revealed the presence of C-H bend in plane, C=O stretch, C-H stretch and O-H stretch [32, 33].

Statistically, there was no significant differences ($p<0.05$) using one-way ANOVA for the wavenumbers of *carica papaya* from market and s. market. The fruit samples also followed similar pattern (Figure 4.20). These suggest insignificant variations and thus no storage effect on the functional groups present in the fruit.

Watermelon (Cirtullus lanatus)

Watermelon showed characteristic band which ranged from 758.55 cm^{-1} to 3808.61 cm^{-1} for market and 757.96 cm^{-1} to 3650.94 cm^{-1} for s. market.

Table-5: FTIR analysis of *Cirtullus lanatus* crude extract

Market			Super Market		
Wave number (cm^{-1})	**Function group**	**Remarks**	**Wave number (cm^{-1})**	**Function group**	**Remarks**
758.55	Alkane, C-H (broad)	Out-of-plane, bend	757.96	Alkane,C-H (broad)	Out-of-plane, bend
840.98	Alkane, C-H	Bending	841.73	Alkane, C-H	Bending
1222.61	Tertiary alcohol, CO	Stretching	1273.89	Tertiary alcohol, CO	Stretching
1321.30	Aromatic amine, C-N	Stretching	1410.89	Aromatic amine, C-N	Stretching
1432.21	Carboxylic acid, OH	Bending	1457.91	Carboxylic acid, OH	Bending
1624.41	Absorbed water, OH	Stretching	1619.04	Absorbed water, OH	Stretching
1841.21	Aromatic compound	Stretching	1852.97	Aromatic compound	Stretching
1976.35	Allene, C=C=C	Stretching	2060.94	Allene, C=C=C	Stretching
2170.76	Alkyne, CΞC	Stretching	2215.73	Nitrile, N≡N	Stretching
2268.44	Nitrile, CΞN	Stretching	2277.23	Nitrile, N≡N	Stretching
2469.19	Carboxylic acid, OH	Stretching	2444.86	Carboxylic acid, OH	Stretching
2652.27	Carboxylic acid, OH	Stretching	2624.13	Carboxylic acid, OH	Stretching
2837.41	Amine salt	Broad	2864.81	Amine salt	Broad
2974.85	Alkane, CH	Stretching	2998.33	Alkane, CH	Stretching
3278.77	Alkyne	Stretching	3223.32	Alkyne, C≡C	Stretching
3402.72	Primary amine, NH	Stretching	3418.99	Primary Amine, NH	Stretching
3514.42	Intermolecular bonded alcohol, OH	Broad, stretching	3650.94	Free Alcohol, OH	Stretching
3653.94	Free alcohol, OH	Stretching	-	-	-
3808.61	Free alcohol, OH	Stretching	-	-	-

Bands 758.55 cm^{-1} to 840.98 cm^{-1} and again at 2974.85cm^{-1}showed alkanes (CH) for the market fruit while s. market showed alkane (CH) at band 757.96 cm^{-1} (broad), 841.73 cm^{-1} and2998.33 cm^{-1} respectively. The band at 1222.61 cm^{-1} and 1273.89 cm^{-1} showed tertiary alcohol C-O stretch for both market and s. market; the band at 1321cm^{-1} showed aromatic amine C-N for market while s. market peaked at 1410.89 cm^{-1}.

The bands at 1432.21 cm^{-1}, 2469.19 cm^{-1} and 2652.27 cm^{-1} showed OH group of carboxylic acid for market while s. market was observed at band 1457.91 cm^{-1}, 2444.86 cm^{-1}, and 2624.13 cm^{-1} respectively; absorbed water was observed at band 1624.41 cm^{-1} and 1619.04 cm^{-1} respectively for market and s. market.

The band at 1841.21 cm^{-1} and 1852.97 cm^{-1} showed combinations of aromatic compounds for market and s. market respectively; the band at 1976.35cm^{-1} and 2060.94 cm^{-1} showed allene (C=C=C) stretching for market and s. market respectively; the band at 2170.76cm^{-1} and 3278.77 cm^{-1} showed alkyne groups for market while alkyne only peaked at 3223.32 cm^{-1} for s. market; the band at 2268.44 cm^{-1} for market and at 2215.73 cm^{-1}, 2277.23 cm^{-1} for s. market showed nitrile (C≡N) group streching; the band at 2837.41cm^{-1} and 2864.81 cm^{-1} showed salt of an amine group both for market and s. market. Primary amine (NH) was observed at band 3402.72 cm^{-1} and 3418.99 cm^{-1} for market and s. market respectively. intermolecular bonded alcohol (OH) was observed at 3514.42cm^{-1} while at band range of 3653.94cm^{-1} to 3808.61cm^{-1} free OH group were observed (Table 5).

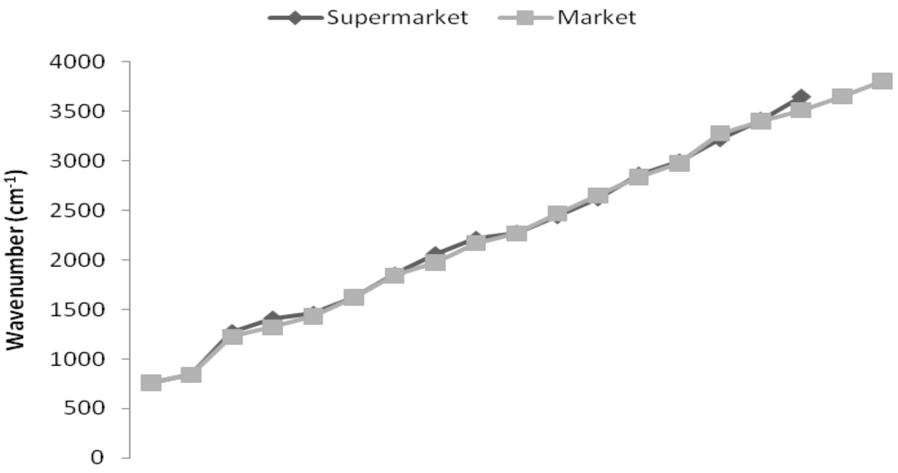


Figure-13: Characteristic wave number comparison for *citrullus lanatus*

In fig. 13, *citrullus lanatus* from the different sources followed similar trend. No significant differences ($p < 0.05$) between the two characteristic wave number of absorption.

Major Functional Groups

The major functional groups present in the fruit extracts are summarized in table 4.10. Some studies on FTIR analysis of fruits done have obtained similar results to the present study. Ramya [34], Ancilla and Judia [35], recorded similar peaks of absorbtion for *Citrus sinensis* and *Ananas Comosus* fruit. FTIR spectral analysis of showed the presence of characteristic functional groups of carboxylic acids, amines, amides, sulphur derivatives, polysaccharides, nitrates, chlorates, and carbohydrate that are responsible for various medicinal properties of the plants [32, 34].

Table-6: Major functional groups in the fruit extracts

Fruit extracts	Major groups
Ananas comosus	Aromatic Amine, Thiols, Alcohol, Aldehyde, Acid halides
Citrus cinensis	Carboxylic acid, aldehyde, hydroxy group, heterocyclic amine, isocyanate, isothiocyanate, allene, thiols, free hydroxy group.
Carica papaya	Carboxylic acid, aldehyde, alcohol, secondary amine, phosphine, phosphonic, thiols

Citrullus lanatus	Carboxylic acid, aromatic amine, amine salt, allene, thiols, free hydroxy group

The various functional groups observed in fruit juice extracts of the studied fruits reflected the biochemical compositions, especially the phenolic compounds, carboxylic acids, and alcohols responsible for several medicinal properties and biological activities.

Aromatic amines have been useful in producing no steroidal anti-inflammatory drugs. Thus, suggesting possible anti-inflammatory properties for extracts of *Ananas comosus*,*Citrus cinensis* and *Citrullus lanatus* respectively. Thiols are important antioxidants, and recent studies showed that their contents vary depending on the groups of fruits. *Ananas comosus* and *Citrullus lanatus* showed richness for thiol groups. Biological thiols such as glutathione (L-glutamyl-L-cysteinly glycine, GSH), N-acetylcysteine (NAC), captopril [CAP ($C_9H_{15}NO_3S$)], homocysteine (HCYS), cysteine (CYS), and gamma-glutamyl cysteine (GGC) has been reported for fruits [37]. Biothiols are well-known beneficial antioxidants that protect cells from oxidative damage that potentially leads to cancer and Alzheimer's disease.

Phosphonic acid is a functional group featuring two hydroxy moieties, one P=O double bond and one P–C bond. The group was identified in *Carica apaya*. It was reported that the aforementioned group has numerous applications in biology and medicine to mimic the phosphate group leading to antiretroviral drugs (e.g., tenofovir), isoprenoid biosynthesis inhibitors, antibiotics (e.g. fosfomycin), tyrosine phosphatase inhibitors, antimalarial, antihypertensive drugs (e.g., K4 and K2) or the anti-osteoporosis compounds alendronate and zoledronate [38]. Only *Citrus cinensis* contain isocyanate and Isothiocyanates. Isothiocyanates also has been reported to exhibit antioxidant and anti-inflammatory activities and interfered with numerous cancer-related targets and pathways.

The presence of phytochemicals carrying hydrogen functional group –OH bonded, found that the hydroxyl functionality is an integral part of most of phenolic phytochemicals such as polyphenols and flavonoids to provide a relative ranking of extracts in term of antioxidant activity. Therefore, the presence of characteristic functional groups that are responsible for various medicinal properties may influence considerably the biological properties and contribute significantly to their solubility, partition coefficient, stereochemistry and inherent acid–base properties [36]. From the results obtained in the present study, it could be concluded that the the fruit juice extracts may act as source of therapeutic agent. The diversity of functional groups observed probably indicate the presence of carbohydrates, carotenoid, glycogen, amino acids, amides, starch, calotropin, calotropogenin, phosphates, lipids, glycogen and cellulose. The richness of the samples–OH group enhances its ability for forming hydrogen bonding capacity and confirmed therefore, the higher potential of its antioxidant activity. [39]

Conclusion

Present study indicates that the studied fruits sold in Owerri are affluent sources of ascorbic acid and as well as many important organic compounds. The best source of ascorbic acid is orange followed by pawpaw, pineapple and then by watermelon. The physicochemical analysis revealed the studied tropical fruits are of good quality. The mineral element composition of the samples indicates that the fruits are rich in the mineral elements analyzed hence, can be good sources of mineral nutrients as they are of great importance and contribute to the well being of the body. The various functional groups observed in fruit juice extracts of the studied fruits reflected the biochemical compositions, especially the phenolic compounds, carboxylic acids, alcohols, and carbohydrates, responsible for several medicinal properties and biological activities. Also, from the results the fruit juice extracts may act as source of therapeutic agent. This study will help the people to maintain their dietary requirements through consumption of tropical fruits. Due to the richness in mineral composition, functional groups and the physicochemical quality of the studied fruits, it is recommended that inhabitants of Owerri metropolis should consume more these fruits. Numerous studies have been reported on fruits. However, different fruit qualities vary with geographical location and are affected by factors such as the cultivar, oxygen, soil and some other environmental factors. From the study there was no significant difference between the properties of the fruits purchased from the different locations of study (the Owerri Relief market and the Owerri shopping mall). Therefore, the study contributes to the knowledge of fruits with regards to the quality of the studied fruits (*Citrus cinensis, Ananas comosus, Citrullus lanatus* and *Carica papaya*) sold in Owerri metropolis. The information will be a good resource for the food composition table as well as providing information on possible nutrient deficiency from the low daily intake of these fruits. Other tropical fruits not covered here should also be analyzed for physical and chemical composition, functional groups identified in the fruits should be isolated and further studied and heavy metal analysis should be conducted on the fruits to determine their toxicity.

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