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ORIGINAL RESEARCH ARTICLE

Nutritional, Phytochemical and Antioxidant Evaluation of Fresh and Dried *Zanthoxylum zanthoxyloides* Leaves: A Traditional Leafy Vegetable Consumed by Some Igbo Clans in Southeast Nigeria

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ABSTRACT

Zanthoxylum zanthoxyloides foliage is utilized as a traditional leafy vegetable by some human populations in clans south east Nigeria. The foliage is dried as a postharvest measure during its seasonal peak usually between late March and April to produce *'Ukpo Nka'*. The impact of air and oven drying at varied temperatures on nutrient, phytochemical and antioxidant potentials of the leaves were evaluated. Results indicated that drying had varied effects on the parameters analyzed. Fresh vegetables had moisture content of 70.80% while it was 14.10% for the air-dried foliage and a range of 10.50 and 12.40% for the oven dried samples. Oven drying at 50 °C increased vitamins and phytochemicals of Z. *zanthoxyloides* leaves more than the other drying methods adopted in the study. The impact of drying on nutrients and phytochemicals was in this order: oven drying at 50 °C >air drying > oven drying at 40 °C > oven drying at 60 °C > oven drying at 70 °C. Antioxidant activity was evaluated in the methanol and aqueous extracts of the fresh and the various dried vegetable samples using ferric reducing antioxidant power (FRAP). Peak antioxidant activity was slightly higher in the water extracts than in the methanol extracts. Samples oven dried at 40 and 50 °C had higher antioxidant potentials than the other dried samples. It is therefore concluded that oven drying at 50 °C can be adopted to produce "*Upko Nka*" that will retain nutrients especially vitamins and phytochemicals with good antioxidant potentials to ensure good health, reduce post-harvest losses and ensure food security.

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INTRODUCTION

Vegetables are an indispensable part of a healthy diet and they are rich sources of vitamins, minerals, dietary fiber and a host of beneficial non-nutrient substances including plant sterols, flavonoids and antioxidants (Azlan *et al*., 2022). They are herbaceous plants whose part or parts are consumed as side or main dishes and they may be aromatic, bitter or tasteless (Mensah *et al*., 2008). Leafy vegetables form part of Africa's cultural heritage and they play significant roles in the tradition and food habits of African ancestry (Otitoju *et al*., 2014). Nigeria is a country made of many tribes and clans whose human population consume various plants parts as vegetables either in the dried or fresh state and these form part of their indigenous or traditional leafy vegetables. These traditional leafy vegetables are sold quite cheap in their localities and they serve as sources of macro- and micro nutrients as well as phytochemicals which contribute to the overall wellbeing of such human populations and food security. However, the availability of these leafy vegetables is seasonal, and most times they are dried to preserve them. Hence the need to evaluate the impact of drying on their nutrient content.

Indigenous vegetables feature prominently in food security, socio-economy and livelihood activities of rural people (Ukom *et al*., 2023). Some indigenous vegetables serve as spice for their aromatic flavour, bitter, hot or pepperish taste (Ukom *et al*., 2023). The nutritional contribution of these vegetables in local diets have health maintenance and protective roles but have not been fully harnessed for their bio-diverse nutritional and health resources in addressing the detailed intricate food, nutritional and health problems of the indigenous population (Agbugba and Thompson, 2021). Many plants foliage is not commonly eaten as conventional or exotic vegetable by most human populations due to the lack of knowledge of their edibility (Amaechi *et al*., 2021). One of such foliage eaten as a traditional/indigenous leafy vegetable is *Zanthoxylum zanthoxyloides*.

The genus *Zanthoxylum* grows as a tree shrub of 6 to 12m tall, has gray beige bark with a rough surface, having large, sharp claw-shaped prickles (Guendehou *et al*., 2018). It is a woody plant found in the savannah of West Africa and in coastal areas from Senegal to Nigeria and Cameroon (Hawthrone and Jongkind, 2006). It belongs to the family Rutaceae and comprises parts of aromatic, therapeutic deciduous shrubs and tree species (Ahmad *et al*., 1993). Spines are located on all parts of the tree including the leaves (although they are very tender on the foliage eaten as vegetable). The leaves are consumed in different forms either as decoction or as vegetable used in culinary in various parts of Africa. In Cote d'Ivoire, its leaf decoction is used as mouth-wash to soothe toothache or chewed; pulped leaves are applied to leprous sores (Guendehou *et al*., 2018). The leaves have been reported to relieve inflammation and pain (Diatta *et al*., 2014). In some climes such as Tanzania, *Zanthoxylum chalybeum* Engl leaves are dried and used as a vegetable powder by local communities (Balama *et al.,* 2015). Z. *zanthoxyloides* leaves are consumed as a traditional leafy vegetable by some clans south east Nigeria such as parts of Abia state namely Arochukwu and some parts of Ebonyi state especially Izzi clan. Izzi people call it ''Nka'' while Yoruba call it 'Orin ata'/ 'Rere' and ''Senegal prickly ash'' in English. Peak production of soft edible foliage begins in early March (a period marking the end of the hot weather and following early rainfall) through April and sparingly throughout the year during the rainy and early dry harmattan seasons. It is consumed most times in its fresh state or as dried vegetable locally known as "Ukpo Nka". In Izzi clan, Z. *zanthoxyloides* leaves is used as vegetable in soups such as 'ogbono' (soup made of ground *Irvingia* kernels used as thickener), 'egusi' (soup made of ground melon seeds), groundnut' soup or in dried okro soup and for cooking yam porridge. These soups are used for eating stiff dough like 'Garri', 'Fufu', 'Pounded yam' etc (**Figure 1**).

Drying is one of the oldest methods used to enhance the shelf-life of fruits and vegetables and constitute a relevant component of food processing (Mieszczakwoska-Frac *et al*., 2021). Drying food commodities make them available when they are off season, reduces postharvest losses by controlling enzymatic and microbial activities in them, hence increasing their shelf life. Under controlled environmental conditions, drying ensures food safety along with good retention of nutrients. The most regularly used drying process is hot air current convective drying which is used on a large scale in the food drying industry for economic reasons and controlled process (Mieszczakwoska-Frac *et al*., 2021). The production of *'Ukpo nka'* is a postharvest measure which aids consumers in such localities to preserve the leaves by drying excess harvest during the peak period of foliage production. Most times, locals air dry the fresh vegetable foliage to produce '*Ukpo nka'*. It is important to evaluate the impact of air drying as it is commonly practiced by the consumers and oven drying as a modified method of food preservation on nutrient and phytochemicals of these vegetables so as to enable both consumers and processors choose the processing method that has good impact on the vegetable when compared with the nutrients on fresh weight basis. It is in view of this that this research work was done to evaluate the impact of air drying and oven drying (which utilizes hot air convective current) at varied temperatures on the nutrient and phytochemicals as well as antioxidant properties of dried and fresh Z. *Zanthoxyloides* leaves to produce 'Ukpo Nka'.

2. MATERIALS AND METHODS

2.1.1 Source of vegetable samples

Fresh *Zanthoxylum zanthoxyloides* leaf foliage was sourced from farms in Iboko and Iboko main market in Izzi local Government Area of Ebonyi State, South east Nigeria in the month of March, 2023 (**Figure 2**).

2.1.2 Sample preparation

The leaves were picked to remove inedible portions, washed in clean tap water and drained of water before dividing into six (6) portions of 2 kg each. One portion was set aside as control to be analyzed for its nutrient and phytochemical contents on fresh weight basis while the remaining 5 portions were air dried, oven dried at 40,50, 60 and 70 °C respectively. Drying was done by placing the washed vegetable samples in a uniform thickness of 0.5 cm on a perforated stainless-steel tray respectively for each sample treatment. For the air-dried samples, drying was done in a relative humidity that fluctuated between 61 and 72% because the weather at that time in March and early April transits from dry season to early rainfall as it is typical in Umuahia, south east Nigeria. Oven temperatures were varied but relative humidity of the environment and air velocity in the oven were 32±2% and 0.6m/s respectively. For

the oven dried samples, drying was done continuously for the first 2h for each sample treatment after which, moisture loss was evaluated by weighing after 1h interval until a constant weight was obtained. For the air-dried samples, drying was done continuously for the first 72h and subsequently, the samples from the lot were weighed to monitor moisture loss at 24h interval until a constant weight was obtained. After drying, each sample was stored in a clean dry container and kept at ambient temperature prior to analysis for nutrient and phytochemical contents as well as antioxidant activities of water and methanol extracts respectively. The air-dried samples took 6 days to dry to a constant weight, while the samples oven dried at 40,50,60 and 70 °C took 76h, 55h, 48h and 35h to dry to a constant weight respectively.

2.2 Evaluation of proximate composition

Proximate composition of the various vegetable samples was analyzed by established AOAC protocols (AOAC, 2012). Crude protein was determined by the micro Kjeldahl method (AOAC 939.02). The nitrogen content of the sample digest was multiplied by 6.25 and expressed as percentage protein. Ash content was determined gravimetrically after muffle furnace (SX2-2.5-12 England) incineration at 550^{o}C for 6 h. Crude fat was also determined gravimetrically after solvent extraction using hexane. Crude fiber was determined by the Weende method while moisture determination was done by drying the pulverized vegetable samples in a convection oven at 105^{o}C for the first 2h before moisture loss was monitored at 1h interval until a constant weight was obtained. Nitrogen free extract (carbohydrate) was calculated by applying the formula: 100 - [%Moisture + %Ash + %Fat + %Crude fiber + % Crude protein].

2.3 Analysis of vitamin content

The B vitamins, vitamin A and Vitamin E contents of the vegetable samples were estimated spectrophotometrically (UV/Vis Spectro Art 200, Wealtec Bioscience, New Taipei City, Taiwan) using 1 cm pathlength cuvette, according to the methods described by Okwu and Emenike (2006). 5 g of each vegetable sample was homogenized using various solvents to extract the respective B vitamin groups. For vitamin B_1, 50 mL ethanol containing sodium hydroxide (10:1) was dispensed into each sample and homogenized for 5min on a rotary shaker. They were filtered into 100 mL conical flasks before a 10 mL of each sample filtrate was dispensed into another 100 mL conical flask and 10 mL potassium dichromate was added to them respectively. For vitamin B_2, 50% ethanol was dispensed into each vegetable sample in a 100 mL conical flask and homogenized on a rotary shaker for 5mins respectively. Each sample solution was allowed to stand for 1h before filtration into 100 mL conical flasks respectively. Subsequently, a 10 mL of each sample filtrate was dispensed into a 50 mL conical flask before 10 mL of 5% potassium permanganate and 10 mL 30% hydrogen peroxide were added and shook vigorously. These sample solutions were allowed to stand in a hot water bath for 30mins before 2 mL of 40% sodium sulphate solution was added for color development. Vitamin B_3 in each vegetable sample was extracted by dispensing 20 mL of 1N sulphuric acid and homogenized for 30mins on a rotary shaker before filtering respectively. 10 mL of each sample filtrate was dispensed into a 100 mL conical flask and 5 mL potassium cyanide was added before acidifying with 5 mL of 0.02N sulphuric acid respectively. Vitamin standards were prepared in the carrier solvents and serial dilutions of 0.00, 0.2,0.4,0.6,0.8 ppm were prepared. Their absorbance was read and used to create the calibration curves used to calculate the concentration of the vitamin. The absorbance of the vitamins was monitored as follows: thiamin (vitamin B_1) at 360 nm, riboflavin (vitamin B_2) at 510 nm, niacin (vitamin B_3) at 470 nm, vitamin A at 450 nm and vitamin E at 295 nm.

Vitamin C was determined by titrimetry after homogenizing each sample in 50mL5.6 mM EDTA solution. The homogenized samples were filtered using Whatman no.1 filter paper. Approximately 10 mL of 30% potassium iodide was added to 20 mL of filtrate and mixed thoroughly. The mixture was titrated against 0.1M $CuSO_4$ to a dark end point using1% starch solution as the indicator (Okwu and Emenike, 2006).

2.4 Mineral content determination

Ash obtained from the ash content experiment was used for the mineral's assay (James, 2013). Briefly, each ash sample was transferred to 100 mL glass tubes and 2 mL of 2M hydrochloric acid was added. The digest in each tube was made up to mark with deionized water. The diluted digest was used to analyze the different mineral elements. Sodium and potassium were analyzed using Type 128 Flame photometer (Systronics, Gujarat India). Phosphorus and zinc were analyzed by determining the absorbance of color complex formed with molybdovanadate and Zincon, respectively. The absorbance read at 400 nm for phosphorus and 615 nm for zinc (Sabel *et al*., 2010) using UV/Vis SpectroArt 200 spectrophotometer (Wealtec Bioscience, New Taipei City, Taiwan). EDTA titration was used for the determination of calcium and magnesium. Iron was analyzed by Orthophenanthroline red ferrous complex method. The analysis was carried out and reported as the mean ± standard deviation of each parameter analyzed reported in mg/100 g edible portion.

2.5 Phytochemical analysis

Phytochemicals in each sample were investigated. Total polyphenols were determined by the Folin–Ciocalteu assay (Waterhouse, 2001), while oxalate was determined by titrimetry as described by (Gupta *et al.,* 2005). Total tannins, cyanides and phytic acid contents were determined by Folin-Dennis assay, alkaline picrate assay, and 2,2-bipyrimidine solution assay, respectively, described by (Yasmin *et al.,* 2008). Gravimetric estimations of total alkaloids, total saponins and total flavonoids were carried out following the protocols described by (Harbone, 1998). Phytosterol was determined spectrophotometrically after precipitation (Kasal *et al*., 2010).

2.6 Antioxidant determination by Ferric Reducing Antioxidant Power (FRAP) assay

FRAP assay of both methanol and aqueous extracts of the vegetable samples was determined by the method described by Pulido *et al.* (2000) with slight modifications. Water and methanol extracts of each vegetable sample was prepared by weighing a 5 g sample into 250 mL conical flask before dispensing 100 mL water and absolute methanol respectively. These resultant solutions were homogenized on a rotary shaker for 5mins and allowed to stand for 24h at ambient temperature. After this period, each sample solution was filtered and the filtrates were recovered and used for antioxidant analysis. The extracts were diluted to concentrations of 10,20 and 40 mg

GAE/100g respectively. A 0.25 mL of the respective leaf extract in the varied concentrations were dispensed into labelled test tubes. Afterwards, 0.25 mL of 200mM sodium phosphate buffer (pH 6.6) and 0.25 mL of 1% potassium ferrocyanide were dispensed into the tubes. These were incubated at 50 °C for 20mins, thereafter, 0.25 mL of 10% trichloroacetic acid was added to stop the reaction before they were centrifuged at 2000 rpm for 10min. One mL of the respective sample supernatants was mixed with 1 mL distilled water and a 0.2 mL of ferric chloride was added and incubated for 10min. Gallic acid was used as the standard. Gallic acid standard solutions containing 10,20,40,60,80 mg GAE/100g was prepared. These were treated just as the test samples. A plot of absorbance against concentration of the standard was used to generate a calibration curve. The absorbance was measured at 595 nm in a UV-Visible spectrophotometer (Genesys 10-S, USA).

2.7 Statistical analysis

Statistical analysis of data obtained from the parameters analyzed was evaluated using one way analysis of variance (ANOVA) using SPSS 20. Results were expressed as mean ± standard deviation. Means were separated using Duncan's Multiple Range Test at $p < 0.05$.

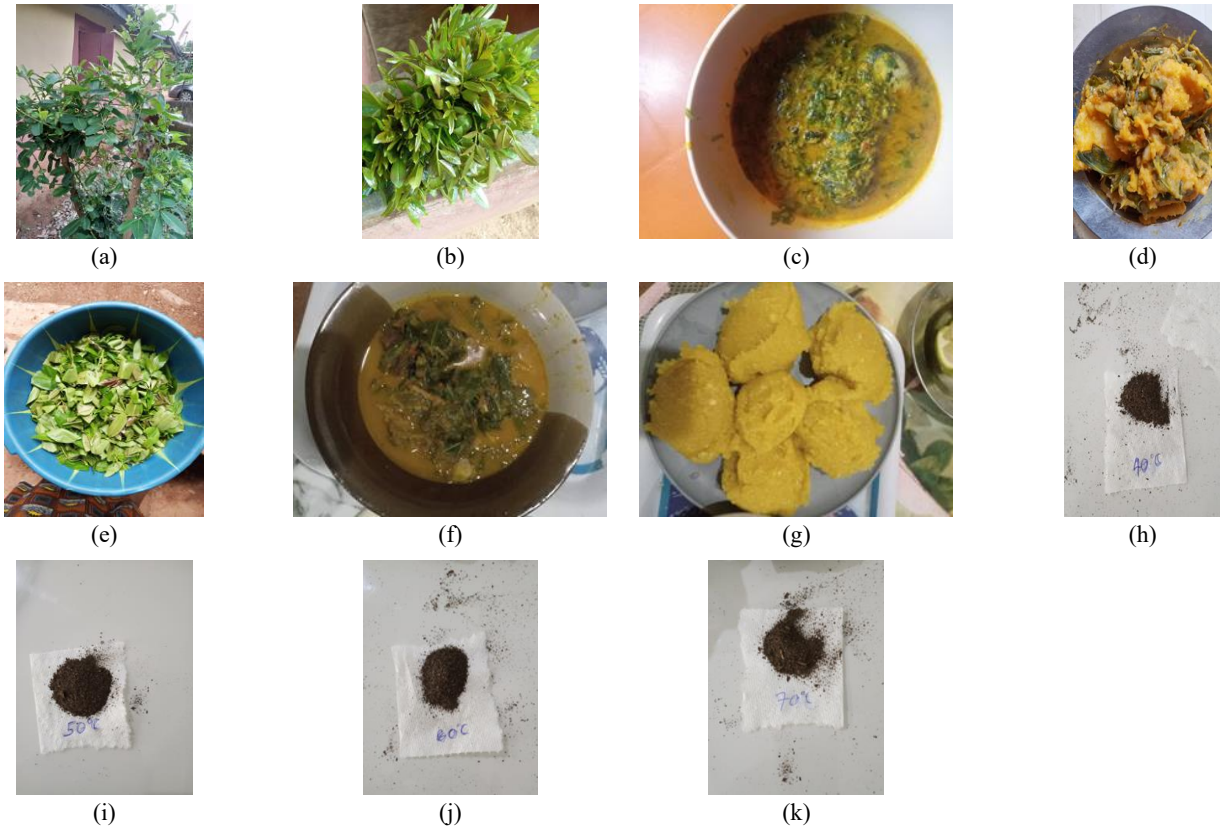


Fig. 1: (a) *Zanthoxylum zanthoxyloides* tree (b)&(e) Fresh *Zanthoxylum zanthoxyloides* leaves/foliage (c) Fresh *Zanthoxylum zanthoxyloides* leaves in ogbono soup (d) Fresh *Zanthoxylum zanthoxyloides* leaves used in cooking yam porridge (f) Fresh *Zanthoxylum zanthoxyloides* leaves in egusi soup (g) Garri (a stiff dough) (h-k) *Zanthoxylum zanthoxyloides* oven dried at 40, 50, 60 and 70 °C

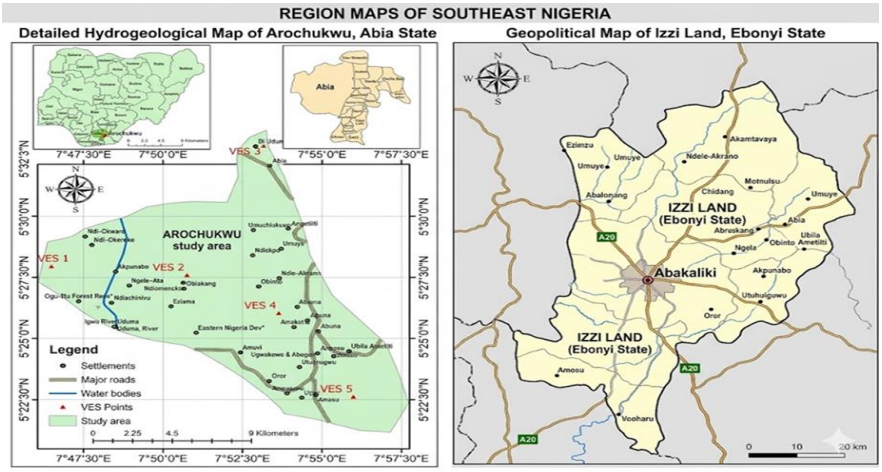


Fig. 2. Maps showing locations of Arochukwu in Abia State and Izzi clan in Ebonyi State

3. RESULTS AND DISCUSSION

3.1 Proximate composition of fresh and dried *Zanthoxylum zanthoxyloides* leaves

Table 1 shows results on proximate composition of fresh and the various dried vegetable samples. Generally, Results indicated that there were significant differences ($p < 0.05$) in the various proximate components analyzed for the fresh and dried samples. A gradual change in oven temperature resulted in a gradual change in proximate component. Fresh *Z. zanthoxyloides* leaf sample had a moisture content of 70.80% while the various dried samples had moisture which ranged between 10.50 and 14.10%. Udo *et al*. (2013) reported that leafy vegetables have a moisture content ranging between 72 and 93%. Moisture in fresh Z. *zanthoxyloides* leaves was quite lower than moisture range of 85.19 and 96.00% reported for *Telferia occidentalis, Celosia argentea, Amaranthus caudatus, Solanum macrocarpon and Talinum triangulare* respectively (Edeh *et al*., 2013). A high moisture content of vegetables indicates freshness and perishability (Adepoju and Oyewole, 2008). The air-dried vegetable samples had slightly higher moisture content than the oven dried samples. As oven temperature increased gradually so did moisture decrease. Moisture in food items is the main factor which affects the quality of storage hence reducing post-harvest losses (Zambrano *et al*., 2019). A decrease in water content and hence water activity is targeted at reducing microbial activity and the extent of their reactions, thereby extending the shelf life of foods (Zhao *et al*., 2025). Moisture content of the dried vegetable samples was within the safe moisture threshold for dried fruits and vegetables of 0-22% (Afolabi, 2014).

Crude protein of the fresh vegetable was 5.73% while the dried vegetable samples ranged between 11.90 and 13.78%. The crude protein content of fresh *Z. zanthoxyloides* was slightly lower than crude protein of *Moringa oleifera* leaves (6.7 g) reported by Yang *et al*. (2023)] as well as crude protein of fresh vegetables namely *Amaranthus viridis* (9.73%), *Aeschules glabra* (9.48%), *Alphanostylis leptantha* (9.39%), *Culcasia saxatilis* (9.18%) and *Lonchocarpus sericeus* (9.39%) reported by (Ukam *et al*., 2016). However, crude protein of the fresh vegetable sample was slightly higher than what was reported for *Amaranthus hybridus* (morogo) with a value of 3.58 g/100 g (Medoua and Oldewage-Theron, 2011) as well as that of *Zanthoxylum chalybeum* (4.909%) (Balama *et al.,* 2015). Air dried *Z. zanthoxyloides* leaves had the least crude protein content when compared with the oven dried *Z. zanthoxyloides* vegetable samples. Crude protein of the vegetable was slightly lower than crude protein of locally dried and solar dried *Z. chalybum* leaves which had values of 13.74% and 14.35% respectively (Balama *et al.,* 2015).

Crude fiber of the fresh leaves sample was 9.70%. This was quite higher than the range of 1.04-1.14% reported by (Ukam *et al*., 2016) for fresh wild green vegetables as well as those of *Telferia occidentalis* (2.23%) and *Talinum Triangulare* (1.21%) reported by (Orhuamen *et al*., 2012). Drying increased crude fiber content of the dried vegetable samples by 46.41 to 50.26% when compared with the fresh sample. Fiber exhibits physiological functions such as reducing the risk of obesity, diabetes, cancer and intestinal diseases (He *et al*., 2021). Ash content of fresh *Z. zanthoxyloides* leaves compared well with ash content of fresh wild green vegetables reported by (Ukam *et al*., 2016) except that of *Alphanostylis leptantha* which had a value of 2.39%. Drying increased ash content of these vegetables significantly ($p < 0.05$) by well over 57.50 to 66%. Ash in foods is an index of mineral content which is needed for various biological activities, most often as cofactors to many enzymes in the body.

Fat content of fresh *Z. zanthoxyloides* leaves was 2.50%; This was higher than what was reported by Ukam *et al*. (2016) for fresh wild green vegetables which ranged between 0.40 and 1.01%. Drying gradually increased fat content of this vegetables sample in the range of 58.68 and 62.4% when compared with the fresh vegetable sample. Carbohydrate i.e. nitrogen free extract (NFE) of the fresh sample was 9.58%. Drying resulted in a gradual increase in NFE. Carbohydrate ranged between 44.58% for oven drying at 70 °C and 46.63% for oven drying at 40 °C. Drying increased dry matter content of the vegetables which was most evident with increased oven temperatures. Dry matter content of foods is an index of nutrient density.

Table 1: Proximate composition of fresh and dried *Zanthoxylum zanthoxyloides* leaves

Samples	Moisture (%)	CP (%)	Fat (%)	CF (%)	Ash (%)	CHO (%)	DM (%)
Fresh	$70.80^{a}\pm0.18$	$5.73^{f}\pm0.11$	$2.50^{e}\pm0.14$	$9.70^{e}\pm0.14$	$1.70^{e}\pm0.14$	$9.58^{e}\pm0.42$	$29.20^{f}\pm0.18$
Air Dried	$14.10^{b}\pm0.14$	$11.90^{e}\pm0.00$	$6.05^{d}\pm0.07$	$18.10^{d}\pm0.14$	$4.00^{d}\pm0.00$	$45.85^{c}\pm035$	$85.90^{e}\pm0.14$
OVD $_{40}$	$12.40^{c}\pm0.00$	$12.28^{d}\pm0.18$	$6.20^{cd}\pm0.00$	$18.30^{cd}\pm0.14$	$4.20^{cd}\pm0.14$	$46.63^{a}\pm0.18$	$87.60^{d}\pm0.00$
OVD $_{50}$	$11.90^{d}\pm0.14$	$12.73^{c}\pm0.11$	$6.30^{bc}\pm0.07$	$18.60^{bc}\pm0.00$	$4.40^{bc}\pm0.00$	$46.08^{ab}\pm0.25$	$88.70^{c}\pm0.14$
OVD $_{60}$	$11.30^{e}\pm0.14$	$13.05^{b}\pm0.00$	$6.48^{b}\pm0.07$	$18.90^{b}\pm0.14$	$4.65^{b}\pm0.07$	$45.65^{c}\pm0.14$	$88.70^{b}\pm0.014$
OVD $_{70}$	$10.50^{f}\pm0.14$	$13.78^{a}\pm0.11$	$6.65^{a}\pm0.07$	$19.50^{a}\pm0.14$	$5.00^{a}\pm0.14$	$44.58^{d}\pm0.18$	$89.50^{a}\pm0.14$

Values are means ± standard deviation. Values with different superscripts in the same column are significantly different ($p < 0.05$). CP: Crude Protein, CF: Crude Fiber, CHO: Carbohydrate, DM: Dry Matter, $OVD_{40,50,60,70}$: Oven drying at 40,50,60,70 °C.

3.2 Vitamin content of fresh and dried *Zanthoxylum zanthoxyloides* leaves

Table 2 shows results on vitamin content of both fresh and the various dried vegetable samples. Drying significantly caused a change ($p < 0.05$) in vitamin content of the dried samples when compared with the fresh samples. Generally, both vitamins B_1 and B_2 of the fresh and dried vegetable samples were lower than vitamin B_3 content. Vitamin B_1 content of fresh *Z. zanthoxyloides* was lower than B_1 content of *Amaranthus gangeticus* (0.16 mg/100 g), *Centella aslatica* (0.13 mg/100 g) and *Trigonella foenum graecum* (0.42 mg/100 g) (Gupta *et al*.,

2011). Fresh *Z. zanthoxyloides* leaves had lower vitamin A content when compared with those of *Amaranthus viridis, Aeschylea glabra, Alphanostylis lepthantha, Culcasia saxatilis and Lonchocarpus sericeus* which ranged between 1.04 and 1.24 mg/100 g (Ukam *et al*., 2016).

Vitamin C content of the fresh vegetable was 29.62 mg/100 g. Drying increased it for the air-dried samples, oven drying at 40 and 50 °C respectively. A similar trend was observed for Vitamins A and E. There were no significant differences ($p > 0.05$) in vitamin C contents of the air dried and the sample oven dried at 50 °C. It was reported that changes in vitamin C content are affected by drying time, air temperature as well as moisture content (Erenturk *et al*., 2005). Vitamin C is usually selected as an index of nutrient quality because of its labile nature as compared to other nutrients in foods (Rojas and Geshenson., 2001). Kurozawa *et al*. (2014) reported that a lower hot air temperature of 40 and 50 °C at lower air velocity induced higher retention of vitamin C than temperatures of 60 and 70 °C respectively. Vitamin C is known for its low heat stability and is prone to oxidize easily, therefore various processes utilizing high temperatures results in a loss compared to the fresh food item (Mieszczakwoska-Frac *et al*., 2021). Both vitamins C and E have antioxidant roles, hence can scavenge free radicals in lipid bilayers of body cells. Vitamin C being water soluble, scavenges free radicals in the hydrophilic section of lipid bilayers while vitamin E being fat soluble, scavenges free radicals in the hydrophobic section of lipid bilayers of cells. Drying resulted in variations in vitamin concentrations in the vegetable and was in this order: OVD50 °C > Air drying > OVD 40 °C > OVD 60 °C > OVD 70 °C. This entails that oven drying at 50 °C had profound effect in vitamin retention. Drying above 50 °C resulted in a gradual decrease in vitamin content of this vegetable. This is in agreement with the findings of Gupta *et al*. (2011) who reported a decrease in vitamins of green leafy vegetables oven dried at 60 °C.

Table 2: Vitamin content of fresh and dried *Zanthoxylum zanthoxyloides* leaves

Samples	Vitamin B_1 (mg/100 g)	Vitamin B_2 (mg/100 g)	Vitamin B_3(mg/100 g)	Vitamin C (mg/100 g)	Vitamin E (µg/100 g)	Vitamin A (µg/100 g)
Fresh	$0.05^{c}\pm0.001$	$0.30^{e}\pm0.004$	$1.83^{c}\pm0.04$	$29.62^{c}\pm0.66$	$0.48^{e}\pm0.06$	$0.72^{d}\pm0.00$
Air Dried	$0.07^{ab}\pm0.004$	$0.61^{b}\pm0.03$	$2.64^{b}\pm0.07$	$36.41^{a}\pm0.00$	$1.20^{b}\pm0.02$	$1.14^{b}\pm0.00$
OVD 40	$0.065^{b}\pm0.005$	$0.53^{c}\pm0.00$	$2.55^{b}\pm0.09$	$35.03^{b}\pm0.93$	$0.99^{c}\pm0.08$	$1.03^{c}\pm0.06$
OVD 50	$0.081^{a}\pm0.003$	$0.73^{a}\pm0.004$	$2.89^{a}\pm0.00$	$37.23^{a}\pm.29$	$1.41^{a}\pm0.00$	$1.27^{a}\pm0.03$
OVD 60	$0.042^{d}\pm0.002$	$0.38^{d}\pm0.04$	$1.94^{c}\pm0.10$	$29.79^{c}\pm0.48$	$0.63^{d}\pm0.00$	$0.65^{d}\pm0.00$
OVD 70	$0.02^{e}\pm0.001$	$0.24^{e}\pm0.02$	$0.93^{d}\pm0.06$	$14.49^{d}\pm0.39$	$0.20^{f}\pm0.04$	$0.23^{e}\pm0.06$

Values are means ± standard deviation. Values with different superscripts in the same column are significantly different ($p < 0.05$).
$OVD_{40,50,60,70}$: Oven drying at 40,50,60,70 °C.

3.3 Mineral content of fresh and *dried* vegetable samples of Zanthoxylum *zanthoxyloides* leaves

Table 3 shows results on the effect of drying on the minerals of both fresh and the dried vegetable samples. The fresh leaf samples had mineral content of 80.84, 56.45, 89.78, 40.91, 193.07, 3.92 and 3.05 mg/100 g for calcium, magnesium, phosphorus, sodium, potassium, iron and zinc respectively. Increased oven temperature resulted in a gradual increase in mineral content of the various dried vegetable samples when compared with the fresh sample. Calcium content of the various dried vegetable samples increased within the range of 31.73 and 37.06%, magnesium was 35.03 and 39.84%, phosphorus was 30.19 and 34.65%, sodium was 39.88 and 46.09%, potassium was 21.58 and 27.72%, iron was 28.47- 46.30% while zinc was 23.56 and 49.59%. Oven drying concentrated the minerals more than air drying. It was observed that potassium had the highest concentration of the minerals analyzed in the fresh and dried vegetable samples. The concentration of minerals analyzed was in this order: potassium >phosphorus>calcium>magnesium>sodium> iron > zinc. A high consumption of potassium was reported to have protective effects against many pathologic conditions affecting the cardiovascular system, kidneys, bones and it has alkalinizing effects through $KHCO^{-3}$ generation which helps to neutralize fixed acidity in urine (Demigńe *et al*., 2004).

Iron content of both fresh and the dried vegetable samples were lower than 68.02 mg/100 g reported by Alemu Gobena *et al*. (2023) for Chaya leaves. However, zinc content of the oven dried *Z. zanthoxyloides* leaf samples compared well with that of dried Chaya leaves (4.85 mg/100 g) (Alemu Gobena *et al*.,2023). Iron and zinc are some of the essential micronutrients whose deficiency in diets results in hidden hunger in vulnerable individuals' especially young females and children. Iron is required for psychomotor development, maintenance of physical activity and work capacity alongside resistance to infection Stoltzfuz (2001) while zinc is required for growth, maintenance of immune function, hence enhancing both prevention and recovery from infectious diseases (Black, 2003).

Table 3: Mineral content of fresh and dried *Zanthoxylum zanthoxyloides* leaves

Sample	Calcium (mg/100 g)	Magnesium (mg/100 g)	Phosphorus (mg/100 g)	Iron (mg/100 g)	Zinc (mg/100 g)	Sodium (mg/100 g)	Potassium (mg/100 g)
Fresh	$80.84^{f}\pm0.55$	$56.45^{e}\pm0.00$	$89.78^{f}\pm0.00$	$3.92^{e}\pm0.14$	$3.05^{e}\pm0.17$	$40.91^{f}\pm0.45$	$193.07^{e}\pm0.98$
Air Dried	$118.41^{e}\pm0.00$	$86.89^{d}\pm0.07$	$128.89^{e}\pm0.07$	$5.48^{d}\pm0.23$	$3.99^{d}\pm0.04$	$68.05^{e}\pm0.23$	$246.21^{d}\pm0.00$

Sample	Calcium (mg/100 g)	Magnesium (mg/100 g)	Phosphorus (mg/100 g)	Iron (mg/100 g)	Zinc (mg/100 g)	Sodium (mg/100 g)	Potassium (mg/100 g)
OVD 40	121.13^{d}±0.46	89.16^{c}±0.79	132.08^{d}±0.53	6.06^{C}±0.18	4.22^{d}±0.00	70.61^{d}±0.33	249.45^{c}±1.06
OVD 50	124.14^{c}±0.62	91.38^{b}±0.21	133.72^{c}±0.00	6.42^{c}±0.00	4.89^{c}±0.04	72.45^{c}±0.00	252.89^{b}±0.38
OVD 60	126.11^{b}±0.00	92.75^{ab}±0.00	134.98^{b}±0.26	6.90^{b}±0.00	5.33^{b}±0.19	74.08^{b}±0.19	265.89^{a}±0.00
OVD 70	128.43^{a}±0.38	93.84^{a}±0.34	137.69^{a}±0.00	7.30^{a}±0.16	6.05^{a}±0.18	75.89^{a}±0.00	267.13^{a}±0.00

Values are means ± standard deviation. Values with different superscripts in the same column are significantly different ($p < 0.05$).
$OVD_{40,50,60,70}$: Oven drying at 40,50,60,70 °C

3.5 Phytochemicals of fresh and dried *Zanthoxylum zanthoxyloides* leaves.

Table 4 shows results on phytochemical content of fresh and dried vegetable samples from *Zanthoxylum zanthoxyloides* leaves. The fresh samples had lower values for the phytochemicals analyzed when compared with the dried vegetable samples. Drying caused a significant difference ($p < 0.05$) in phytochemical content. Peak phytochemical content was attained with oven drying at 50 °C before it gradually decreased with increase in temperatures at 60 and 70 °C respectively. Both fresh and the various dried samples had low hydrogen, cyanide, oxalate and phytate contents respectively. Hydrogen cyanide content of fresh *Z. zanthoxyloides* leaves was lower than hydrogen cyanide content of fresh Chaya (*Cnidoscolus aconitifolus*) leaves grown in Ethiopia which had a value of 102.07 mg/100 g (Alemu Gobena *et al*., 2023). Hydrogen cyanide content of the dried vegetable samples ranged between 0.08 and 0.42 mg/kg. These values were quite lower than values reported as hydrogen cyanide content of both fresh and dried cassava leaves (Modesto Junior *et al*., 2019). Phytate and oxalate content of the dried vegetable samples ranged between 0.41-1.89 mg/100 g and 0.13-0.88 mg/100 g respectively.

Alkaloid and saponin content of the fresh vegetable samples were 5.80 and 5.06 mg/100 g respectively. The dried vegetable samples had values which ranged between 2.58 -10.79 mg/100 g for alkaloids and 2.93-11.43 mg/100 g for saponins. Alkaloids and saponins contain nitrogen in their structures and they are biologically active secondary metabolites. Alkaloids have a wide range of activities such as being antimalarial, antimicrobial, anti-diarrheal, analgesic, demulcent, hepatoprotective, anti-cholinergic, ant-psychotic, antioxidant, anti-nociceptive to mention but a few of its activities (Debnath *et al*., 2018). Saponins seem to be a good alternative as natural emulsifier, foaming agent, stabilizing and drug delivery agent in the food and pharmaceutical industry (Sharma *et al*., 2023).

Phenol and tannin contents of the fresh vegetable sample was 4.22 and 11.18 mg/100 g respectively. These values were quite lower than that of *Cnidoscolus acontifolius* (ie Chaya) leaves grown in Ethiopia which was reported to have phenol content of 1916.66 mg/100 g and 176.533 mg/100 g respectively (Alemu Gobena *et al*.,2023). With drying, phenol and tannin contents of the various dried samples reduced drastically at 70 °C. Phenols are reductive and easily oxidized during drying process hence a higher drying temperature results in a faster reaction rate (El-Gamal *et al*., 2023). Therefore, lower drying temperatures are preferable to achieve higher retention of phenols. Phenols play important roles in defense responses such as anti-aging, anti-inflammatory, antioxidant and antiproliferative activities; the antioxidant activities of phenolic compounds inadvertently reduce the occurrence of some chronic diseases such as diabetes, cancers and cardiovascular diseases (Lin *et al*., 2016). Tannins are polyphenolic in structure and have reactive hydroxyl groups in the phenolic rings and this influences their biological activities. Tannins are associated with anti-inflammatory, anti-aging and anti-proliferative health benefits, can reduce the risk of cancer, neurodegenerative diseases, cardiovascular diseases and Alzheimer's respectively (De'Melo *et al*., 2023).

Flavonoid content of the fresh leaves was 8.33 mg/100 g. The range of flavonoids was 4.79 mg/100 g for oven drying at 70 °C and 16.57 mg/100 g for oven drying at 50 °C. Flavonoids are also polyphenolic compounds. They are reported to have antioxidative activity, free radical scavenging capacity, cardioprotective, antidiabetic, anti-inflammatory, anti-allergic, antiviral and lately, are proven to be the most effective as anticancer agent through apoptosis by induction of cell cycle arrest and inhibition of key enzymes involved in tumor promotion (Karak, 2019). Results also indicated the presence of steroids in *Z. zanthoxyloides* leaves. The fresh sample had steroid content of 1.22 mg/100 g, while the dried samples had steroid content which ranged between 0.98 mg/100 g for samples oven dried at 70 °C and 6.87 mg/100 g for samples oven dried at 50 °C. Plant sterols have cholesterol lowering properties, anticancer, anti-inflammatory, anti-atherogenicity and anti-oxidation activities (Berger *et al*., 2004). The effect of drying on phytochemical content of *Z. zanthoxyloides* leaves was in this order: oven drying at 50 °C > Air drying > oven drying at 40 °C > oven drying at 60 °C > oven drying at 70 °C.

Table 4: Phytochemical Content of fresh and *Ukpo Nka* from *Zanthoxylum zanthoxyloides* leaves

Parameter	Fresh	Air dried	OVD 40 °C	OVD 50 °C	OVD 60 °C	OVD 70 °C
HCN (mg/kg)	0.16^{d}±0.02	0.35^{b}±0.00	0.30^{c}±0.03	0.41^{a}±0.00	0.17^{d}±0.03	0.08^{e}±0.02
Oxalate (mg/100 g)	0.36^{d}±0.05	0.75^{b}±0.00	0.70^{b}±0.02	0.88^{a}±0.04	0.46^{c}±0.00	0.13^{e}±0.00
Alkaloid (mg/100 g)	5.80^{e}±0.00	9.78^{b}±0.00	9.24^{c}±0.26	10.79^{a}±0.00	6.31^{d}±0.25	2.58^{f}±0.18
Saponin (mg/100 g)	5.06^{e}±0.13	10.47^{b}±0.00	9.63^{c}±0.31	11.43^{a}±0.28	7.32^{d}±0.00	2.93^{f}±0.15
Phytate (mg/100 g)	0.78^{d}±0.11	1.60^{b}±0.04	1.46^{b}±0.10	1.89^{a}±0.05	1.15^{c}±0.10	0.41^{e}±0.09
Phenol (mg/100 g)	4.22^{e}±0.00	7.82^{b}±0.00	7.36^{c}±0.00	8.61^{a}±0.26	4.93^{d}±0.00	1.75^{f}±0.00
Tannin (mg/100 g)	11.18^{d}±0.32	18.20^{ab}±0.04	17.61^{b}±0.34	18.64^{a}±0.00	15.08^{c}±0.22	7.43^{e}±0.31

Parameter	Fresh	Air dried	OVD 40 °C	OVD 50 °C	OVD 60 °C	OVD 70 °C
Flavonoid(mg/100 g)	8.33^{e}±0.11	15.23^{b}±0.00	14.57^{c}±0.00	16.57^{a}±0.27	8.88^{d}±0.23	4.79^{f}±0.00
Steroid (mg/100 g)	1.22^{e}±0.00	5.32^{b}±0.13	4.94^{c}±0.15	6.87^{a}±0.09	4.08^{d}±0.09	0.98^{e}±0.09

Values are means ± standard deviation. Values with different superscripts in the same row are significantly different ($p < 0.05$). HCN: Hydrogen cyanide. $OVD_{40,50,60,70}$: Oven drying at 40,50,60,70 °C

3.6 Antioxidant activity determined by FRAP assay

Results on Ferric reducing antioxidant power (FRAP) showed variations among samples from extracts of both fresh and dried *Zanthoxylum zanthoxyloides* leaves (Figs 3 & 4). The fresh samples had higher FRAP values at the various concentrations than the air-dried samples for the water extracts. This could be as a result of oxidation by atmospheric oxygen and enzymatic degradation due to exposure to air during drying. Oven drying at varied temperatures could have inactivated oxidative enzymes at varying degrees and this had profound effects on compounds with antioxidative potentials. For the methanol extract, FRAP results showed that the fresh samples had comparable values with results of the air-dried samples at 10 & 20 mg GAE/100 g. Be that as it may, the ability to reduce ferric ions indicated that the fresh and the various dried *Zanthoxylum zanthoxyloides* leaves contained compounds capable of serving as reducing agents which is a crucial antioxidant function in biological systems. FRAP values of both extracts increased in a dose dependent manner. With increase in concentration, scavenging potency of the samples increased gradually with peak at 50 °C, while it began to decrease for samples oven dried at >60 °C. Our findings are in agreement with those of Yen and Vu (2017) whose study on the effect of convective drying at varied temperatures of 40, 50, 60 °C on *Limnophila aromatica* leaves using FRAP assay, reported that antioxidant activity was highest for samples oven dried at 50 °C; but is in contrast with the findings of Kolla *et al* .(2021) who reported that antioxidant activity were high in oven dried samples of *Hyphaene thebaica* (ie doum) fruit at a temperature of 40 °C. Scavenging potential of plant bioactive molecules depends on the nature and class of antioxidant compounds present in the plant and how they react to heat temperatures during processing.

Peak antioxidant activity was higher in the water extracts than in the methanol extracts. The reducing ability of the various dried vegetables samples could be attributed to the effect of drying on the concentration of phytochemicals and nutrients such as the vitamins present in them. Phytochemicals are bioactive compounds and these interact in various ways to scavenge free radicals. Solvents used for extraction have their various polarities and this contributed to their influence in extracting phytochemicals and nutrients which have varied bioactivities in scavenging free radicals. Phytochemicals known to have antioxidative potentials are phenols, flavonoids, carotenoids, sterols, tannins (depending on the class of tannins) and alkaloids. Vitamins known to have antioxidant activities are mainly vitamins A, C and E as well as some minerals.

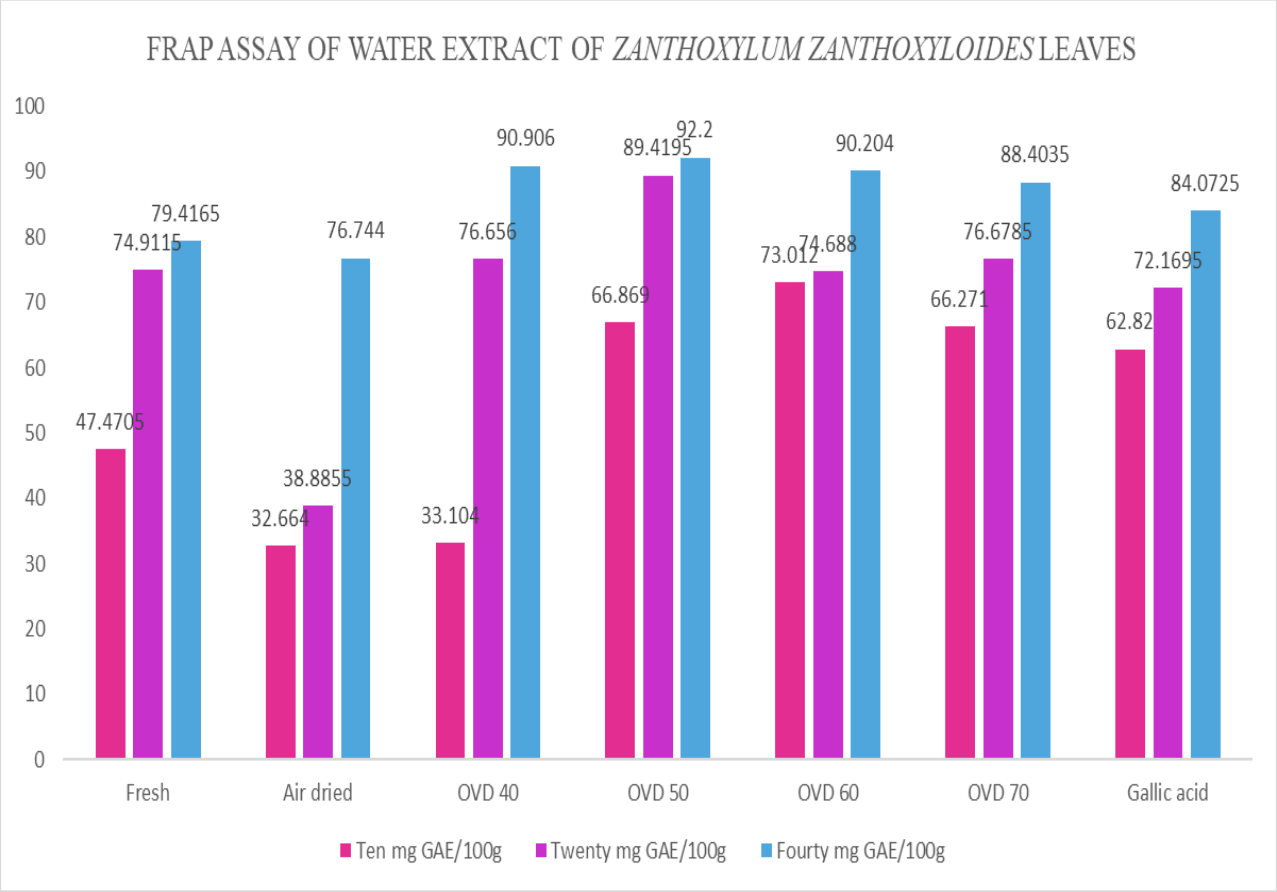


Fig.3: Column charts showing results on FRAP assay of water extract of *Zanthoxylum zanthoxyloides leaves*

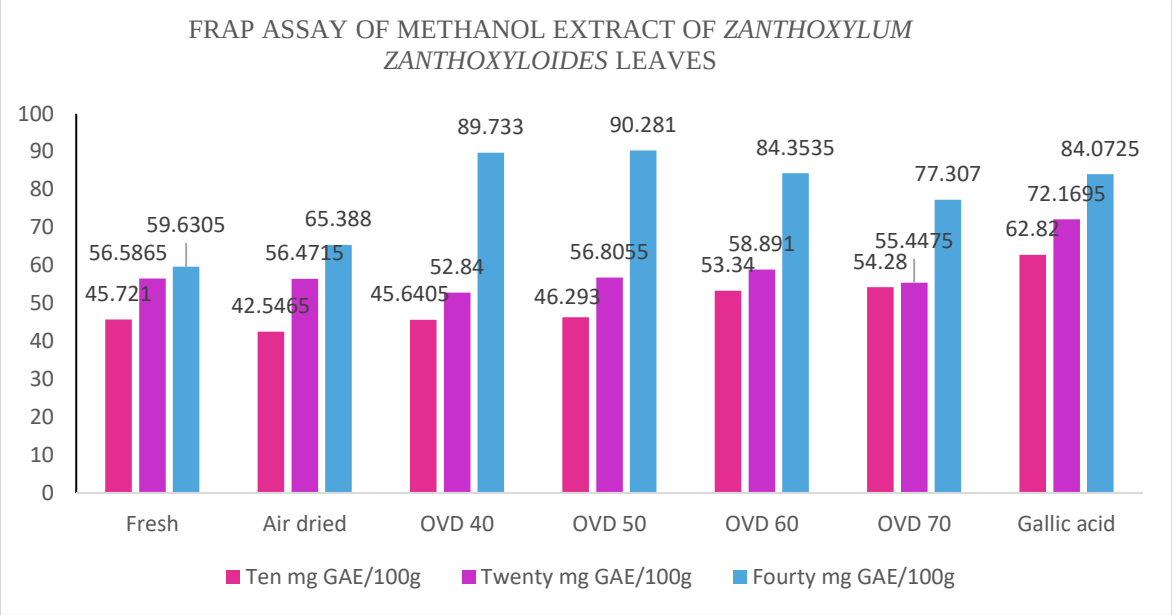


Fig.4: Column charts showing results on FRAP assay of methanol extract of *Zanthoxylum zanthoxyloides leaves*

CONCLUSION

This study presents one of the first detailed scientific information about the nutritional value of *Zanthoxylum zanthoxyloides* leaf foliage locally called *Nka* that is eaten as a traditional leafy vegetable in some clans south east Nigeria and the impact of drying to produce the dried leaves called '*Ukpo Nka'* as a postharvest measure in time of abundance. This study evaluated the impact of controlled drying process using convective oven drying at varied temperatures and compared with air drying as is practiced locally to produce *Ukpo Nka*. Both fresh and the dried leaves were low in phytate, hydrogen cyanide and oxalates. Drying *Zanthoxylum zanthoxyloides* leaf foliage at varied oven temperatures and air drying resulted in variation in nutrient, phytochemical and antioxidant activities of fresh and the various dried leaves. *Ukpo Nka* as a traditional leafy vegetable is nutritious and processing to retain beneficial nutrients such as vitamins, phytochemicals as well as having good antioxidant activities can be best achieved by drying at 50 °C. Drying at this temperature as a postharvest measure can be adopted to ensure nutrition security and promote good health.

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CONFLICT OF INTEREST

The authors confirm that they have no conflict of interest to disclose regarding the publication of this manuscript.

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