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Original Article

Assessment of Proximate Composition, Mineral Contents, and Pollution Index of Cocoa and Kola Nut Preserved with Pesticides

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ABSTRACT

Post-harvest losses of stored produce due to storage pests have been estimated at approximately 30%. Consequently, farmers rely on pesticides, whose long-term use affect the composition of the produce. This study determines the effect of aluminum phosphide pesticides on the proximate composition and mineral contents of farm produce and the level of pollution index prior. Cocoa and Kola nut samples were obtained from local farmers at Aba-Oyo, Akure, Ondo State, Nigeria. Proximate composition was determined using AOAC methods and mineral contents were evaluated by Flame Emission spectrophotometer and Atomic Absorption Spectrophotometer. The determination of theobromine, caffeine, and pesticide residues was done by GC-MS. There are considerable variations in moisture, ash, crude fat, crude protein, crude fibre, and carbohydrate contents of cocoa samples before and after preservation. Both samples contained high levels of calcium, magnesium, potassium, copper, sodium, and iron. Unpreserved cocoa contained theobromine content of 0.74 mg/g while the full tablet sample contained 0.29 mg/g. Similarly, unpreserved Kola nut contained high caffeine content of 0.24% while the full tablet preserved Kola nut contained 0.08%. Likewise, unpreserved cocoa had pesticide residue of 0.73 µg/kg, while the full tablet preserved cocoa had the highest (0.88 µg/kg). Unpreserved Kola nut had pesticide residue of 0.65 µg/kg, while the full tablet sample had 0.74 µg/kg. Unpreserved samples were highly polluted with organochlorine and other harmful pesticide groups than preserved samples. All values remained below the European Union safety limits. The findings emphasize the need to educate farmers on using approved pesticides within regulatory limits.

1.0 Introduction

Cocoa (*Theobroma cacao L.*) is a key export product in Nigeria and contributes significantly to the nation's foreign exchange revenue (Ajayi & Oyejide, 2001). It is a plant-derived food rich in vitamins and essential minerals that support human health (Taubert et al., 2007). Cocoa outputs are being threatened by the declining nature of soil fertility, and other insect and fungal infestations (Salas et al., 2003). According to the International Cocoa Organization (ICO), 450 thousand metric tons are lost annually to swollen shoot virus (CSSV), capsids, and witches broom, while 250, 200, and 50 thousand metric tons are lost to swollen shoot virus (CSSV), capsids, and witches broom, respectively. In West Africa, both the black pod and CSSV are widespread. The most prevalent insects in Africa that consume cocoa are capsids, which were initially identified as pests at the turn of the century (Mahot et al., 2005). Kola nut, derived mainly from *Cola nitida* and *Cola acuminata*, is a member of the Sterculaceae family, grown mainly in Nigeria. It is also grown in the Ivory Coast, Ghana, the West Indian Islands, and Brazil. Nigeria produces 50.2% of the kola nuts produced worldwide, with Cameroon producing 18.3%, the Ivory Coast producing 19.3%, Sierra Leone producing 3%, Benin producing 0.2% and Ghana producing 9.0% (Bassini-Cameron et al., 2007). The main chemical components of the Kola nut are xanthine derivatives caffeine, theobromine, and theophylline. Caffeine has stimulatory effects on the cardiovascular and neuroendocrine systems when eaten in large amounts. Caffeine ingestion also heightens the stress response by boosting the production of stress-related chemicals such as cortisol, adrenaline, and norepinephrine (Bassini-Cameron et al., 2007). These hormones, if found in the body, can accelerate aging by suppressing the immune system, slowing digestion and waste clearance, and hindering body repair mechanisms. Although commonly used as stimulants, kola nuts and caffeine-containing drinks may promote inflammation. Additionally, kola nuts may contain ochratoxin A, a harmful toxin that poses serious health risks, including immunotoxicity, carcinogenicity, genotoxicity, and nephrotoxicity, necessitating a reevaluation of their production and consumption (Ndagi et al., 2012). Kola trees are vulnerable to several diseases during growth and harvest, caused by various fungi such as *Pestalotia spp.*, *Botryodiplodia theobromae*, *Armillaria mellea*, and *Phomopsis spp.* (Asogwa et al., 2011). Parasitic weeds such as *Phyragmanthera incana* and *Tapinanthus bangwensis* (mistletoes) infest kola trees, reducing their photosynthetic capacity (Opoku et al., 2007). These are mainly spread by birds that consume the berries and deposit the seeds on kola branches (Opoku et al., 2007). Pesticides - either natural or synthetic - are used to control pests like fungi, weeds, insects, and rodents. They play a key role in safeguarding crops, food products, and wood materials, and are regulated to ensure safety and efficacy (KVI, 2005). However, the hazards of pesticides have surpassed their benefits. When food products have excessive levels of pesticide residue, there may be health risks for consumers. Excessive pesticide levels may lead to toxic effects in consumers (Emeribe, 2008; F.A.O., 2007). Pesticides significantly impacts ecosystems, aquatic and terrestrial food webs, biodiversity, and non-target species (Sabarwal et al., 2018). While previous studies have evaluated pesticide residues in cocoa and kola nut, limited research has been conducted on how varying pesticide concentrations influence their chemical composition and the proximate composition before and after pesticide treatment. To address these challenges, this study aims to optimize pesticide application by evaluating the effect of varying concentrations on the nutrient compositions, mineral contents and the pollution index deposited in the produce. Although previous studies have examined pesticide residues in cocoa and kola nuts and others have reported their nutritional composition, limited information exists on the combined impact of aluminum phosphide preservation on nutritional quality, mineral composition, pesticide residue accumulation, and pollution status. The study therefore evaluates the effects of aluminum phosphide preservation on the proximate composition, mineral content, pesticide residue levels, and pollution index of cocoa and kola nuts obtained from a selected location in Nigeria. This is important because both cocoa and kola nuts are major export crops in West Africa and they undergo storage after harvest. In addition, aluminum phosphide is frequently used during storage, but limited studies have evaluated its effect on the nutritional quality and residue accumulation of the crops.

2.0 Materials and Methods

2.1Sample collection and preparation

Fresh cocoa (*Theobroma cacao*) and Kola nut (*Cola nitida*) were obtained from local farmers at Aba-Oyo, Akure, Ondo State, Nigeria. The samples were subsequently transported to the Department of Crop, Soil, and Pest Management of the Federal University of Technology, Akure, Ondo State, Nigeria, for authentication and identification. The kola nuts were soaked for 24 hours to ease peeling, then cleaned, drained for three days under banana leaves, chopped, sun-dried, and ground into powder. Fresh cocoa beans were extracted from pods, sun-dried for 168 hours, and milled into powder. Each sample was split into two parts: with and without pesticide. The pesticide-treated samples were further divided into three portions (300 g each) and preserved for three months using full (2.8 g), half (1.4 g), and quarter (0.7 g) tablets of aluminum phosphide.

2.1 Determination of the proximate composition

The proximate analysis (moisture content, crude protein, crude fiber, ash, crude fat, and carbohydrate) was carried out in triplicate using methods as described in AOAC 925.10, 979.09, 962.09, 923.03, 920.39, and 941.15 respectively (Onyango et al., 2004).

2.1.1 Moisture content

An evaporating dish was washed and dried before weighing about 3 g of the sample. The dish and its content were transferred to an oven at 105 ºC for 2 hours; it was removed, cooled in a desiccator, and weighed. At 30 mins intervals, the heating, cooling, and weighing processes were continued until a constant weight was established.

% Moisture content = $\frac{weight\ loss}{weight\ of\ sample} \times 100$ --------------- eqn 1

Weight loss = weight of sample before drying – weight of sample after drying

2.1.2 Ash content

A cleaned, weighed crucible was filled with approximately 3 g of the sample, charred on a hot plate for 30 minutes to remove moisture and carbon, and then ashed in a muffle furnace at 550 ºC for 3 hours. The sample was cooled in a desiccator and weighed. The process of heating, cooling, and weighing was repeated every 30 minutes until a constant weight was obtained.

Ash content = $\frac{weight\ of\ ash}{weight\ of\ sample} \times 100$ ------------------- eqn 2

2.1.3 Crude fat

Crude fat was determined using Soxhlet extraction. Three grams of the sample were wrapped in a weighed filter paper, placed in a thimble, and inserted into the Soxhlet extractor. The extractor, connected to a reflux condenser and a round-bottom flask containing n-hexane (filled to approximately two-thirds), was heated on an electrothermal hot plate for 3 hours. After extraction, the defatted sample was air-dried to remove residual solvent, then oven-dried, cooled in a desiccator, and weighed.

% Crude fat = $\frac{weight\ of\ sample - weight\ of\ defatted\ sample}{weight\ of\ sample} \times 100$ ------- eqn 3

2.1.4 Crude fibre

The defatted sample was weighed (W1) and placed in a 250 mL beaker. It was hydrolyzed with 200 mL of 1.25% H_2SO_4, boiled for 30 minutes, and filtered. The residue was thoroughly rinsed with distilled water, returned to the beaker, and treated with 200 mL of 1.25% NaOH, boiled for 30 minutes, and filtered. The residue was further rinsed with distilled water, followed by 10% HCl and ethanol. It was then transferred to a cleaned, dried crucible, weighed (W2), ashed in a furnace at 550 ºC for 4 hours, cooled in a desiccator, and re-weighed (W3).

% Crude fiber = $\frac{(w2-w3)}{(weight\ of\ sample)} \times 100$ ------------------eqn 4

W_2=weight of sample + crucible before incineration

W_3= weight of sample + crucible after incineration

2.1.5 Crude protein

The protein content of the samples was estimated based on the organic nitrogen content determined using the Kjeldahl method. Approximately 0.5 g of the sample was digested with 15 mL of concentrated sulfuric acid and a copper catalyst tablet until a clear solution was formed. The solution was diluted to 50 mL with distilled water, and 15 mL of the digest was transferred into a distillation flask, followed by the addition of 25 mL of 40% sodium hydroxide. A receiving conical flask containing 5 mL of 2% boric acid and two drops of a mixed indicator (prepared from methyl red and bromocresol green in alcohol) was placed under the condenser. During distillation, the light brown solution turned blue, indicating the presence of ammonia. Distillation was continued until 50 mL of the distillate was collected, after which it was titrated with 0.1 M HCl until the blue color became colorless. The nitrogen content was determined from the titre value, and the crude protein content was calculated accordingly.

Digestion: $N_2 + 4H_2SO_4 \longrightarrow (NH_4)_2SO_4$ + Excess H_2SO_4

Distillation: $(NH_4)_2SO_4 \longrightarrow 2NH_3 + H_2SO_4$

Absorption: $3NH_3 + H_3BO_3 \longrightarrow (NH_4)_3BO_3$

Titration: $(NH_4)_3BO_3 + 3HCl \longrightarrow H_3BO_3 + 3NH_4Cl$

$\%\ Nitrogen = \frac{\text{Molarity of acid x 0.0014 x volume of acid used}}{\text{Weight of sample}} X\ 100$ …………. eqn 5

2.1.6 Carbohydrate

The carbohydrate was determined by difference..

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

2.1.7 Mineral Analysis

The standard procedures recommended by the Association of Analytical Chemists (AOAC 985.35) were employed in the determination of minerals (AOAC, 2010). The samples were ashed at 550 ºC, dissolved in 10% HNO_3, filtered, and made up to 100ml with deionized water. Then Na and K were determined using a flame emission photometer, while Ca, Mg, Cu, Fe, Zn, Cd, and Pb were analyzed using an atomic absorption spectrophotometer.

2.2 Extraction of Pesticide Residue

Pesticide residues were extracted using the method described by Oyekunle et al. (Oyekunle et al., 2011). Twenty grams of each powdered sample were placed in a pre-cleaned Whatman extraction thimble and subjected to Soxhlet extraction using dichloromethane (DCM) as the solvent for approximately five hours. The extract was concentrated to about 3 mL using a rotary evaporator at 41 ºC, then further reduced to approximately 2 mL under a high-purity nitrogen stream. The final extract was stored for chromatographic cleanup before gas chromatography analysis.

2.2.1 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis of Caffeine and Theobromine

The samples were subjected to chromatographic analysis using a Varian 3800/4000 gas chromatograph-mass spectrometer equipped with a BP5 capillary column (30 m × 0.25 mm × 0.25 µm) and a split/splitless injector. The carrier gas was nitrogen at a flow rate of 1.2 mL/min, with a split ratio of 1:50 and an injection volume of 1 µL. The oven temperature was initially set at 70 ºC, increased at 10 ºC/min to 300 ºC, held for 10 minutes, and then maintained for a total run time of 78 minutes. Injector and interface temperatures were set at 250 ºC and 300 ºC, respectively.

Mass spectra were acquired in the range of 30–800 m/z with a detector voltage of 1150 V. Compound identification was based on comparison of retention times and spectral data with authentic standards and the NIST MS library. Relative compound quantities were reported as area percentages from the integrator. No reaction factors were calculated. All samples and replicates were randomly injected as a single batch to minimize technical variability. Quality control (QC) samples, prepared from pooled extracts, were injected periodically throughout the run to ensure repeatability and monitor analytical consistency (Ibrahim et al., 2012).

2.2.2 Pollution Index Calculation

The Pollution Index (PI) for each pesticide was calculated using the formula:

PI = (Measured concentration of pesticide in sample) / (Maximum Residue Limit (MRL) established by the European Union for that pesticide in the respective crop)

A PI value > 1 indicates that the pesticide concentration exceeds the EU-MRL, representing a potential health risk. A PI value < 1 indicates the pesticide level is below the regulatory limit.

2.3 Statistical Analysis

Each treatment group of samples was analyzed three times (n = 3). All data were presented as mean value ± standard deviation (SD). The normality of data distribution was tested with Shapiro-Wilk test ($p > 0.05$ was regarded as normal distribution). Levene's test was used to assess homogeneity of variances. To compare means between the treatment groups, data that met normality and homogeneity assumptions was subjected to One way analysis of variance (One-way ANOVA) using GraphPad Prism 8 (San Diego, USA). The Tukey's multiple comparison test (α = 0.05) was used for the post-hoc test at 95% confidence interval (α = 0.05). The differences between the values in different alphabets when written in superscript are statistically significant at $P < 0.05$ level. If the data failed the normality assumptions, the non-parametric Kruskal-Wallis test was used and Dunn's post-hoc test performed.

3. Results and Discussion

The results of proximate composition (%) of cocoa beans and Kola nuts are presented in Tables 1 and 2, respectively. The moisture content results of preserved and unpreserved cocoa beans revealed that the unpreserved cocoa bean had the highest level (4.81%) of moisture, while the cocoa preserved by the full pellet of pesticide possessed the lowest moisture (2.46%). Also, Kola nut preserved with full pellet of pesticides possessed the lowest moisture (14.10%).

According to Onyango *et al*. (2004) and Ezeama (2007), low levels of moisture content provide a long shelf life of foods because microbial proliferation that leads to spoilage (Ezeama et al., 2007; Onyango et al., 2004).

Table 1: Proximate Analysis (%) of Preserved and Unpreserved Cocoa Beans.

Proximate (%)	**CUP**	**CF**	**CH**	**CQ**
Moisture	$4.81^{a} \pm 0.36$	$2.46^{b} \pm 0.02$	$3.20^{a,b} \pm 0.23$	$3.47^{a,b} \pm 0.17$
Ash	$3.11^{a} \pm 0.39$	$2.23^{a} \pm 1.04$	$2.42^{a} \pm 0.27$	$5.23^{a} \pm 0.82$
Crude Fat	$11.25^{a} \pm 0.30$	$17.52^{b} \pm 0.67$	$9.73^{c} \pm 0.51$	$10.86^{a,d} \pm 0.19$
Crude Protein	$27.64^{a} \pm 0.69$	$24.65^{b} \pm 0.32$	$25.76^{c} \pm 0.59$	$26.76^{c,d} \pm 0.32$
Crude Fibre	$25.77^{a} \pm 0.17$	$22.70^{b} \pm 1.89$	$23.94^{b,c} \pm 1.48$	$25.58^{a} \pm 0.74$
Carbohydrate	$27.42^{a} \pm 0.37$	$39.44^{b} \pm 3.44$	$34.95^{c} \pm 2.26$	$30.42^{d} \pm 0.60$

Values are presented as mean ± SD. Values with different letters in superscript across the rows indicate statistical significance at P< 0.05.
CUP - Unpreserved cocoa. CF - Full tablet preserved cocoa. CH - Half tablet preserved cocoa. CQ - A quarter tablet of preserved cocoa

Table 2: Proximate Analysis (%) of Preserved and Unpreserved Kola Nuts.

Proximate (%)	KUP	KF	KH	KQ
Moisture	$21.88^{a} \pm 0.09$	$14.10^{b} \pm 0.47$	$15.25^{c} \pm 0.18$	$19.66^{d} \pm 0.14$
Ash	$4.65^{a} \pm 0.16$	$4.15^{a} \pm 0.98$	$4.24^{a} \pm 0.37$	$4.78^{a} \pm 1.20$
Crude Fat	$7.38^{a} \pm 0.27$	$11.67^{b,c} \pm 0.58$	$6.55^{b,c} \pm 1.41$	$7.27^{a} \pm 0.05$
Crude Protein	$16.34^{a} \pm 0.25$	$11.25^{b} \pm 0.33$	$13.61^{c,d} \pm 0.33$	$14.58^{a,d} \pm 0.59$
Crude Fibre	$4.74^{a} \pm 1.20$	$2.94^{a,b} \pm 0.42$	$4.54^{a} \pm 1.13$	$4.68^{a} \pm 0.81$
Carbohydrate	$45.02^{b} \pm 0.97$	$61.88^{a} \pm 0.80$	$55.81^{c} \pm 2.25$	$50.77^{d} \pm 1.41$

Values are presented as mean ± SD. Values with different superscript letters across rows indicate statistical significance at P < 0.05.
KUP - Unpreserved Kola nut. KF - Full tablet preserved Kola nut. KH - Half tablet preserved Kola nut. KQ - A quarter tablet preserved Kola nut

The moisture content results from this research study are lower than 40% which is recommended by the Nigerian regulatory standard for food (Onyango et al., 2004). Low moisture content inhibits the hydrolysis of various components present in food samples and therefore the food samples can be stockpiled for long without risk of microbial attack.

The ash content in food substances varies directly with the amount of inorganic element content in such food material (Mesfin & Shimelis, 2013). The result from this present study revealed that there are no significant differences in the ash content of both preserved cocoa and kola nut. However, both cocoa and kola nut preserved with one-quarter of the pesticide possessed the highest ash content (5.23 and 4.78, respectively). Hence, the samples with high percentages of ash content would be expected to have high concentrations of various mineral elements (Habtamu et al., 2018).

The crude fat contents for the preserved cocoa bean from this present study ranged from 11.25-17.52. CF had the highest fat content (17.52), and CUP had the lowest fat content (11.25). Similarly, for Kola nut, KF has the highest fat content (11.67), and KUP has the lowest fat content (7.38). The increase in the absorption of fat-soluble vitamins A, D, E, and K is caused by fat, and body temperature is also maintained by fat. They are regarded as the most energy-dense macronutrient, providing the body with 9 calories per gram of energy (WHO/FOA/UNU, 1994). To maintain good health by reducing the risk of diseases such as obesity, atherosclerosis, cancer, and aging caused by its excess consumption, foodstuffs having crude fat value of 1-2% are sufficient. Also, to maintain glucose and lipid levels, food substances with a moderate level of crude fat can be used (Thomford et al., 2015).

The crude protein contents of both preserved samples decreased with respect to the unpreserved samples as the preservative concentration increased. Interestingly, the unpreserved cocoa and kola nut possess the highest level of crude protein (27.64% and 16.34%, respectively. For growth and maintenance of body tissues and for the production of hormones and enzymes that help to control many functions within the body, proteins are essential. Also, protein may be used as an alternative source to provide the body with energy if carbohydrates and fats are insufficiently available in the diet (Huang et al., 2018). High fibre content in food samples is of dietary advantage because crude fiber aids digestion and limits cholesterol absorption. According to the results of Mepba *et al*. and Vitaglione *et al*., who noticed that the crops with crude fiber content have an anti-diabetic effect (Mepba et al., 2007; Vitaglione et al., 2008). This experimental work showed that the fiber content from this present study ranges from 19.70-25.77 for the cocoa beans and 2.94-6.28 for the kola nut. In other words, the cocoa samples possess higher fiber content than the kola nut samples. The unpreserved cocoa beans possess the highest fiber content (25.77), while the kola nut preserved with a quarter amount of pesticide pellet has the highest fiber content (76.28) among the kola nut samples. This result gives a strong indication that each of the samples could limit cholesterol absorption and also possess a low starch digestibility effect.

The carbohydrate content ranged from 27.42-42.26 for the cocoa samples, while that of the Kola nut ranged from 39.39-51.14. The moisture, ash, and carbohydrate contents of the unpreserved kola nut are more than those of unpreserved cocoa beans, while the unpreserved cocoa bean contained more crude fat, crude protein, and crude fibre than those of the unpreserved kola nut. The moisture, ash, crude fat, crude protein, and crude fibre contents of both preserved samples decreased as compared to both unpreserved samples as the amount of the preservative increased. Mostly, preservation increases carbohydrate contents of the two samples as the amount of preservative increases.

The moisture, crude protein and carbohydrate contents (4.8, 27.64 and 27.42%) of the unpreserved cocoa bean is higher than the values (4.2, 21.6 and 15.5%) respectively reported by Emmanuel *et al*., for unfermented cocoa bean at 0-day pod storage while the ash and crude fat contents (3.50 and 55.20%) reported by them are higher than the one (3.11 and 11.25%) in this study respectively (Afoakwa et al., 2013). The moisture content (21.88%) of the unpreserved kola nut is close to the value (22.50%) reported by Ajayi *et al*. while the crude fibre, crude fat, crude protein and ash contents (4.75%, 7.38%, 16.34% and 4.65%) respectively in this study exceed that of their report (8.68%, 2.59%, 4.25% and 0.87%) (Ajayi et al., 2012). The carbohydrate content (61.11%) reported in that study is more than that obtained in this study (27.42%) (Ajayi et al., 2012).

The mineral composition results, as shown in Table 3 (cocoa bean) and Table 4 (kola nut), indicate that both unpreserved samples possessed high levels of calcium, magnesium, potassium, copper, sodium, and iron, while heavy metal content, such as lead and cadmium levels, is below the detection limit. The unpreserved cocoa bean contains higher amounts of calcium, magnesium, zinc, iron, manganese, and copper than the unpreserved kola nut, while the unpreserved kola nut has higher amounts of sodium than the cocoa bean.

The mineral content of both preserved samples decreased relative to the unpreserved samples, with a progressive decline observed as the concentration of preservatives increased. The contents of potassium, calcium, magnesium, iron, zinc, sodium and copper for the unpreserved cocoa bean in this study (41.88, 165.59, 68.64, 14.38, 3.34, 26.01 and 32.90 mg/g) respectively are higher than the values (2313.10, 140.20, 286.8, 2.7, 9.7, 3.4 and 11.10 mg/100g) reported in another study on unfermented cocoa bean at 0-day pod (Afoakwa et al., 2013). Also, the contents of potassium, calcium, magnesium, iron, and zinc for the unpreserved kola nut in this study (55.35, 141.34, 52.16, 8.60, and 1.20 mg/g) are higher than the values (3484.67, 124.40, 392.00, 16.43, and 5.24 mg/kg) reported in another similar study (Odebunmi et al., 2009). Also, the calcium, potassium, iron, sodium, and magnesium contents of kola nut in this study are higher than those reported for the minerals (0.72, 1.35, 0.28, 0.10, and 0.32 mg/g), respectively in another study (Ajayi et al., 2012).

Table 3: Mineral Content of Preserved and Unpreserved Cocoa Beans.

Mineral (mg/g)	CUP	CF	CH	CQ
Zinc	$3.34^{a} \pm 0.18$	$2.51^{a} \pm 0.03$	$2.62^{a} \pm 0.09$	$2.80^{a} \pm 0.10$
Iron	$14.38^{a} \pm 0.23$	$11.54^{a} \pm 1.11$	$13.29^{a} \pm 0.17$	$14.03^{a} \pm 0.17$
Sodium	$26.01^{a} \pm 1.87$	$22.48^{a} \pm 1.43$	$24.84^{a} \pm 0.52$	$25.28^{a} \pm 1.65$
Potassium	$41.88^{a} \pm 48.59$	$32.42^{a} \pm 29.60$	$35.15^{a} \pm 1.20$	$38.32^{a} \pm 1.53$
Manganese	$1.70^{a} \pm 0.03$	$1.32^{a} \pm 0.04$	$1.43^{a} \pm 0.04$	$1.59^{a} \pm 0.03$
Copper	$32.90^{a} \pm 0.74$	$27.88^{a} \pm 0.46$	$28.77^{a} \pm 0.18$	$29.98^{a} \pm 0.21$
Lead	BDL	BDL	BDL	BDL
Cadmium	BDL	BDL	BDL	BDL
Magnesium	$68.64^{a} \pm 0.31$	$62.67^{a} \pm 0.71$	$64.58^{a} \pm 0.28$	$66.28^{a} \pm 1.37$
Calcium	$165.59^{a} \pm 4.13$	$147.33^{a} \pm 1.44$	$151.10^{a} \pm 0.80$	$157.63^{a} \pm 0.68$

Values are presented as mean ± SD. Values with different superscript letters across rows indicate statistical significance at $P < 0.05$. CUP – Unpreserved cocoa: CF - Full tablet preserved cocoa. CH - Half tablet preserved cocoa. CQ - A quarter tablet of preserved cocoa. BDL – Below Detection Limit

Table 4: Mineral Content of Preserved and Unpreserved Kola Nuts.

Mineral (mg/g)	KUP	KF	KH	KQ
Zinc	$1.20^{a} \pm 0.04$	$1.13^{a} \pm 0.05$	$1.15^{a} \pm 0.07$	$1.18^{a} \pm 0.03$
Iron	$8.60^{a} \pm 0.12$	$7.43^{a} \pm 0.08$	$7.66^{a} \pm 0.70$	$7.89^{a} \pm 0.38$
Sodium	$37.12^{a} \pm 1.52$	$29.62^{b} \pm 1.17$	$32.61^{a} \pm 8.25$	$33.24^{a} \pm 1.18$
Potassium	$55.35^{a,b} \pm 2.88$	$50.82^{a} \pm 0.37$	$51.29^{a,b} \pm 1.63$	$53.32^{b,c} \pm 4.37$
Manganese	$0.93^{a} \pm 0.02$	$0.83^{a} \pm 0.01$	$0.85^{a} \pm 0.23$	$0.89^{a} \pm 0.06$
Copper	$20.55^{a} \pm 1.32$	$16.54^{a,b} \pm 0.54$	$17.13^{a,b} \pm 1.51$	$19.02^{b,c} \pm 11.48$
Lead	$0.07^{a} \pm 0.01$	$0.05^{a} \pm 0.01$	$0.06^{a} \pm 0.00$	BDL
Cadmium	BDL	BDL	BDL	BDL
Magnesium	$52.16^{a} \pm 0.03$	$40.99^{b} \pm 0.95$	$47.47^{a,b} \pm 1.68$	$51.94^{b} \pm 1.12$
Calcium	$141.34^{a} \pm 1.37$	$126.82^{b,c} \pm 1.48$	$131.46^{b,c} \pm 1.00$	$134.87^{a} \pm 1.86$

Values are presented as mean ± SD. Values with different superscript letters across rows indicate statistical significance at $P < 0.05$.
KUP - Unpreserved Kola nut. KF - Full tablet-preserved kola nut. KH - Half tablet preserved Kola nut. KQ - Quarter-tablet-preserved kola

There are a number of mechanisms which can explain the reduced levels of crude protein, crude fat and crude fibre found in the pesticide preserved samples when compared with the unpreserved samples. Exposure to moisture, aluminium phosphide produces phosphine gas (PH_3), which is highly reactive and can react with the various biomolecules (Misra et al., 2015). The reduction in protein content could be due to denaturation or hydrolysis of protein by phosphine that can cause a denaturation of peptide bonds or the tertiary structure of protein (Anand et al., 2016). In addition, oxidative stress caused by phosphine can cause protein carbonylation and degradation (Chaudhry et al., 2019). This reduction in crude fat content could be attributed to phosphine-mediated lipid peroxidation inducing generation of reactive oxygen species (ROS) which damage the unsaturated fatty acid chains by formation of lipid hydroperoxides and subsequent breakdown products (Gupta & Rani, 2018). This is similar to the findings of Ahmed et al. (2020) that exposure to phosphine can increase the free fatty acid content of stored grains. The decrease in crude fiber may result from partial dissolution of cellulose and hemicellulose structures through oxidative cleavage of glycosidic bonds, as reported in plant materials treated with phosphine (Singh & Sharma, 2017). The results indicate that aluminum phosphide is useful in controlling storage pests but its reactivity with organic macromolecules could affect the quality of the stored food. A dose-dependent effect of aluminium phosphide on the chemical composition of the samples is further supported by its progressive decrease with the increasing concentration of the pesticide (Kumar et al., 2021).

The results of theobromine contents in cocoa seeds are presented in Table 5. The result revealed that the theobromine content (0.74mg/g) of the unpreserved is close to the value 0.75mg/g reported for local chocolate (Ramli et al., 2001). The cocoa preserved with the full pesticide tablet possessed the lowest level of theobromine content (0.29). The theobromine contents decrease steadily from quarter-quarter-pellet preserved bean to the full pellet preserved bean relative to the unpreserved bean. Therefore, preservation decreases the theobromine contents as the amount of preservative increases.

Table 5: Theobromine Content in Preserved and Unpreserved Cocoa

Theobromine	CUP	CF	CH	CQ
(mg/g)	0.74	0.29	0.36	0.54

CUP – Unpreserved cocoa seed. CF - Full tablet preserved cocoa seed. CH - Half tablet preserved cocoa seed. CQ - A quarter tablet of preserved cocoa seed

Caffeine contents from this present study are presented in Table 6. The results revealed that the percentage composition of caffeine in the unpreserved Kola nut (0.24) was very low when compared to the value (2.4 %) reported for cola nitida (Okoli et al., 2012). Another previous study also reported a caffeine content of 2.4 % (Yalwa & Bello, 2017). Similar studies attributed caffeine content variations in the samples analyzed to origin, genetic and environmental factors, processing methods, and time of harvest (Athayde et al., 2000; Komes et al., 2009).

The caffeine contents of the unpreserved Kola nut decrease gradually with respect to the unpreserved, with the full tablet preserved Kola nut possessing the lowest value (0.08%). Therefore, preservation decreases the caffeine content as the amount of preservative increases.

The United States Food and Drug Administration (USFDA) stated that caffeine consumption below 130 – 300 mg/day is low /moderate, whereas an intake of 400mg/day is high (Ogah & Obebe, 2012). The results obtained in this study showed that the low caffeine content of the Kola nuts and several consumptions of them in a day, either by chewing or as beverages, was safe, as accumulation above the threshold limit may not be practicable.

Table 6: Caffeine Content in Preserved and Unpreserved Kola Nuts.

Caffeine (wt. %)	KUP	KF	KH	KQ
	0.24	0.08	0.11	0.14

KUP - Unpreserved Kola nut. KF - Full tablet preserved Kola nut. KH - Half tablet preserved Kola nut. KQ - A quarter tablet preserved Kola nut

This observed reduction in theobromine and caffeine content after pesticide preservation should be considered. Theobromine (3,7-dimethylxanthine) and caffeine (1,3,7-trimethylxanthine) are both methylxanthine alkaloids which are susceptible to oxidative degradation. The phosphine gas emitted from aluminum phosphide produces reactive oxygen species (ROS) such as hydroxyl radicals and superoxide anion (Nath et al., 2011). These ROS can trigger oxidative demethylation of their corresponding demethylated metabolites (methylxanthines) (Serra et al., 2018). Moreover, the acidity produced in the hydrolysis of phosphine (formation of phosphoric acid) could facilitate acid-catalyzed hydrolysis of the ring in these alkaloids (Pinto et al., 2020). Methylxanthines have been found to bind to metal ions, and changes in metal ion availability may also impact their stability as a result of the phosphine effect (Fernandes et al., 2019). These proposed mechanisms are supported by the dose-dependent decrease found in this study, as the concentration of pesticide increased, the loss of theobromine and caffeine increased. This is especially true of the quality of cocoa and kola nuts, which both have significant amounts of these alkaloids in their sensory properties and pharmacological activities (McDonald & Evans, 2017).

The GC-MS chromatogram of the samples are presented in Figures 1 to 8. The results of pesticide residues analysis, presented in Tables 7 and 8, reveal the detection of carbamate (methomyl, carbofuran, carbaryl and dilufenican), organophosphate (Phosphoric acid, 7-chlorobicyclo (3.2.0) hepta-2,6-dien-6-yl dimethylester, chlorpyrifos, diazinone, parathion, triazophos and dichlorvos), organophosphorus (penconazole, pirimiphos methyl and malathion), organochlorine (aldrin, dieldrin, heptachlor and lindane) and pyrethroid (cyfluthrin, bifenthrin and cypermethrin) in the two samples. This indicates that the farmers were applying multiple classes of pesticides during pre-harvest activities. Amitraz, malathion, parathion, diazinone, and carbofuran were not detected in the cocoa bean. Only methomyl was not detected in the Kola nut. Pirimiphos methyl occurred in the highest concentration in both unpreserved samples (0.24 and 0.13 µg/kg for cocoa bean and Kola nut).

The total residue of the pesticides in both samples increased with increasing preservative concentration compared to unpreserved samples.. The values of lindane, aldrin and dieldrin (Organochlorine) and bifenthrin and cyfluthrin (Pyrethroid) detected in the unpreserved cocoa bean were 0.01, 0.03 and 0.02 and 0.03 and 0.03µg/kg respectively and were below the maximum residue level (MRL) (1.00, 0.05 and 0.50) mg/kg and (0.10 and 0.10)mg/kg recommended by the European Union (EU). The values of pirimiphos methyl and chlorpyrifos (Organophosphorus) detected in the unpreserved cocoa bean were (0.24 and 0.03)µg/kg and were below the EU-MRL (50 and 100)mg/kg.

The values of organochlorine: lindane, aldrin, dieldrin, and heptachlor detected in the unpreserved Kola nut were (0.02, 0.02, 0.02, and 0.02) µg/kg, respectively, and were below the EU-MRL (0.01, 0.05, 0.05, and 0.02mg/kg). The values of pyrethroid: bifenthrin, cyfluthrin, and cypermethrin were 0.02, 0.01, and 0.02 µg/kg, respectively, and were below the EU-MRL (50, 100, and 100) µg/kg.

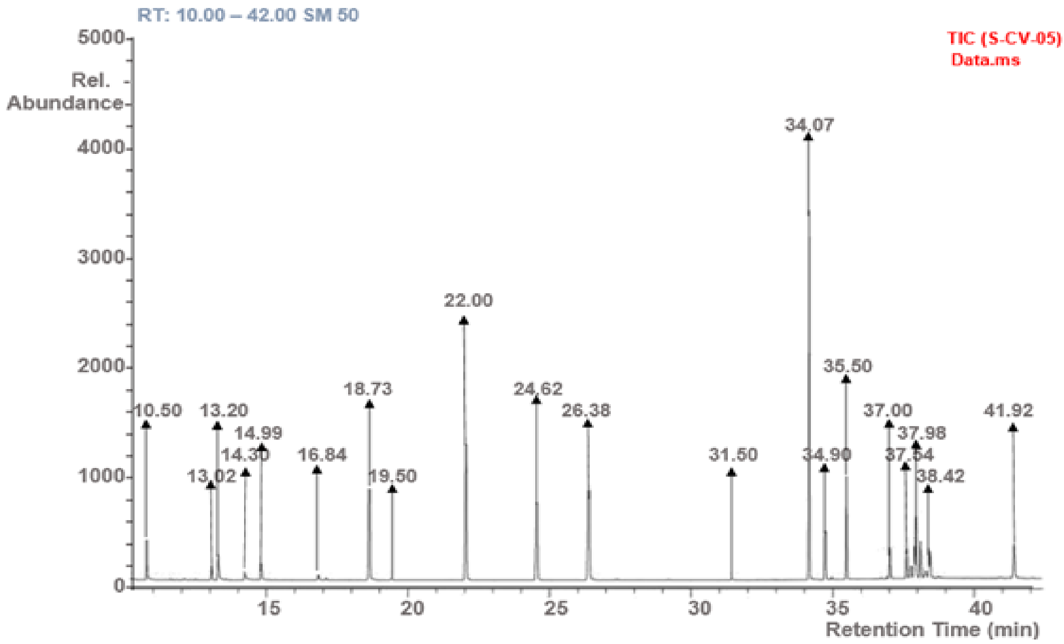

Figure 1: The GC-MS chromatogram of the unpreserved cocoa bean extract (CUP) that displays profiles of pesticide residues. The chromatographic conditions were: BP5 capillary column (30 m × 0.25 mm × 0.25 µm), carrier gas (N2), 1.2 mL/min flow rate, split ratio 1:50, oven temperature program: 70°C to 300°C with the rate of 10°C/min, total run time (TV): 78 min. Peaks matched to NIST MS library and peaks matched by retention time comparison.

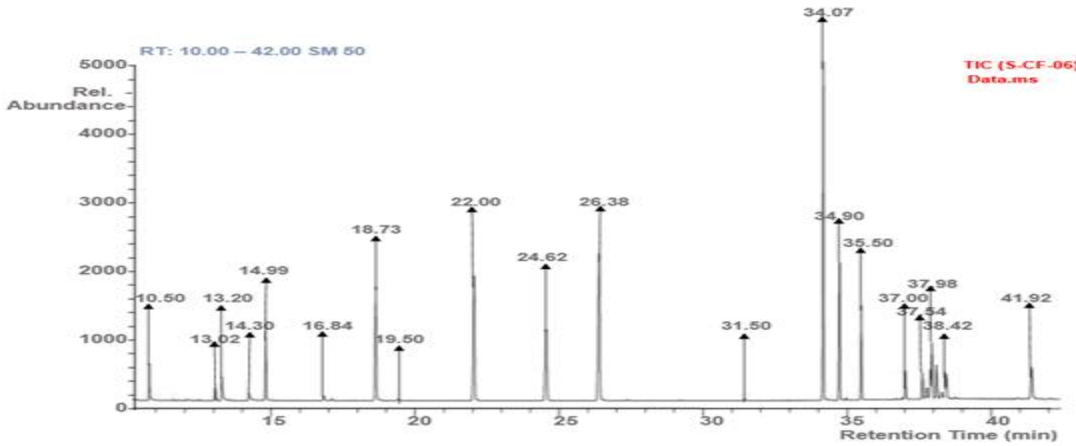

Fig 2: GC-MS chromatogram of the pesticide residue profile of full tablet preserved cocoa bean extract (CF). Chromatographic conditions: BP5 capillary column, 30 m x 0.25 mm x 0.25 µm; carrier gas – N2, 1.2 mL/min split 1:50, oven temp program 70 to 300 at 10C/min, total run time 78 min. Compare the intensities of the peaks of chlorpyrifos and cyfluthrin with those of the unpreserved sample.

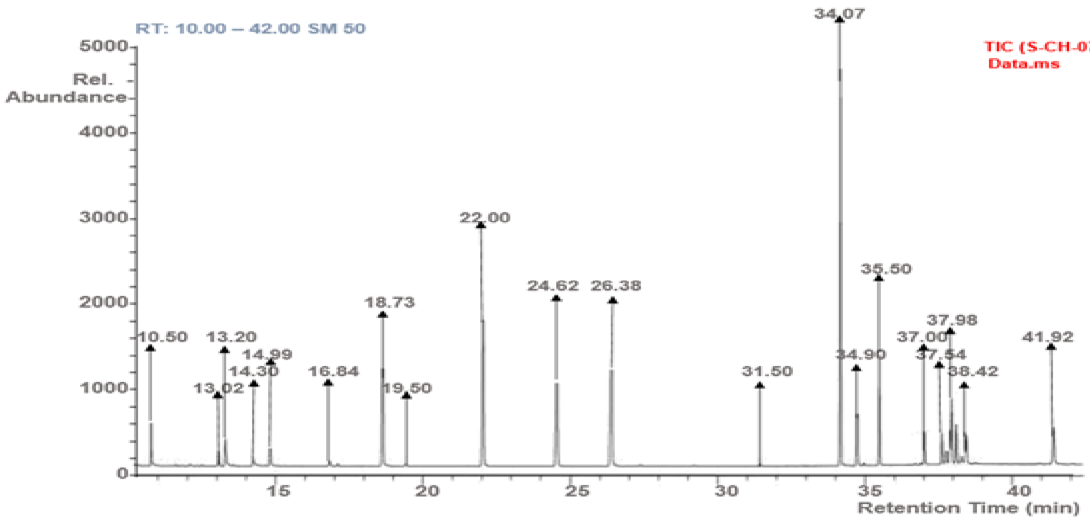

Figure 3: A GC-MS chromatogram with the residue profiles of the pesticides in the half tablet preserved cocoa bean extract (CH). The chromatographic conditions were: BP5 capillary column (30 m × 0.25 mm × 0.25 µm), split ratio 1:50, carrier gas nitrogen, flow rate 1.2 mL/min, oven temperature program: 70°C to 300°C at the rate of 10°C/min and total run time 78 min.

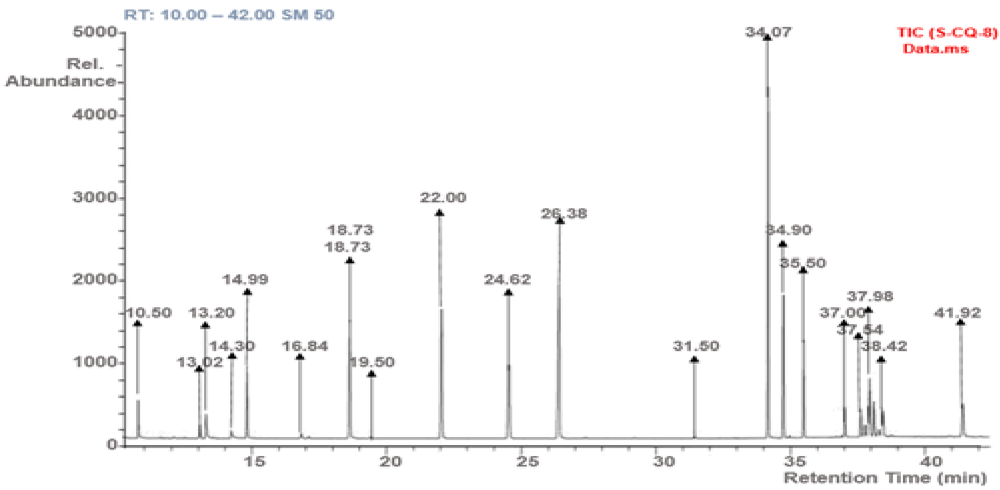

Figure 4: Pesticide residue profiles in CQ (quarter tablet preserved cocoa bean extract) by GC-MS. Chromatographic conditions: BP5 capillary column (30 m × 0.25 mm × 0.25 µm), N2 carrier gas, flow of 1.2 mL/min, split of 1:50, oven temperature program 70°C to 300°C with a ramp of 10°C/min, total run time of 78 min.

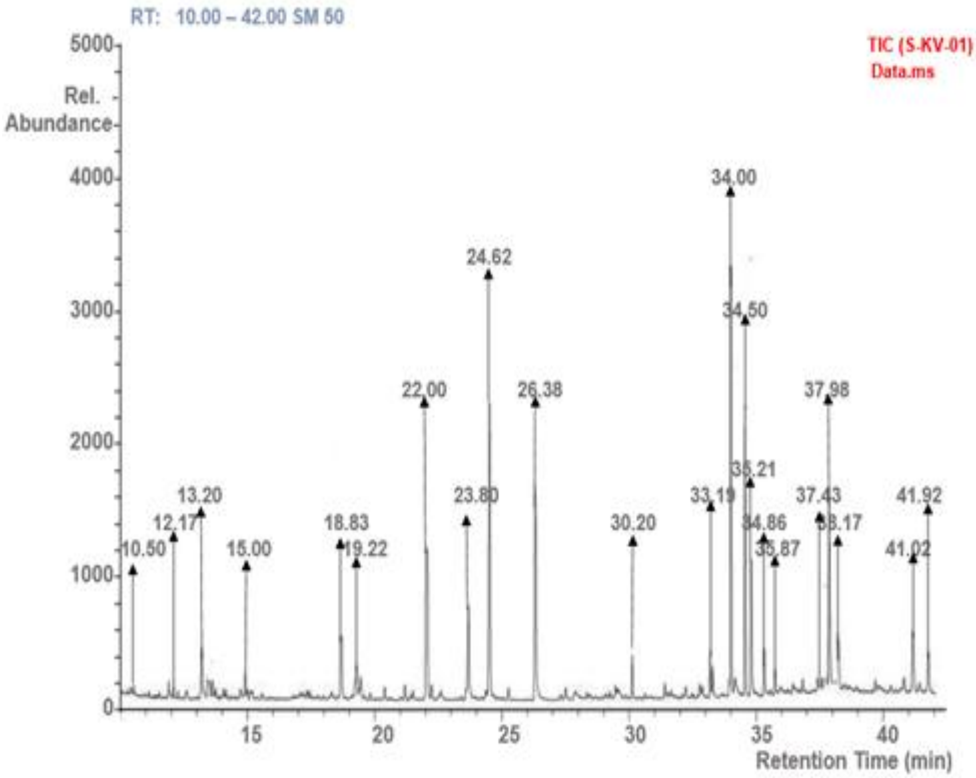

Figure 5: GC–MS chromatogram of pesticide residue profile of unpreserved Kola nut extract (KUP). Chromatographic conditions: BP5 capillary column (30 m × 0.25 mm × 0.25 µm), nitrogen carrier gas, split ratio 1:50, oven temperature program: 70°C to 300°C at 10°C/min, 78 min total run time. Record the peaks of carbofuran, amitraz and dichlorvos.

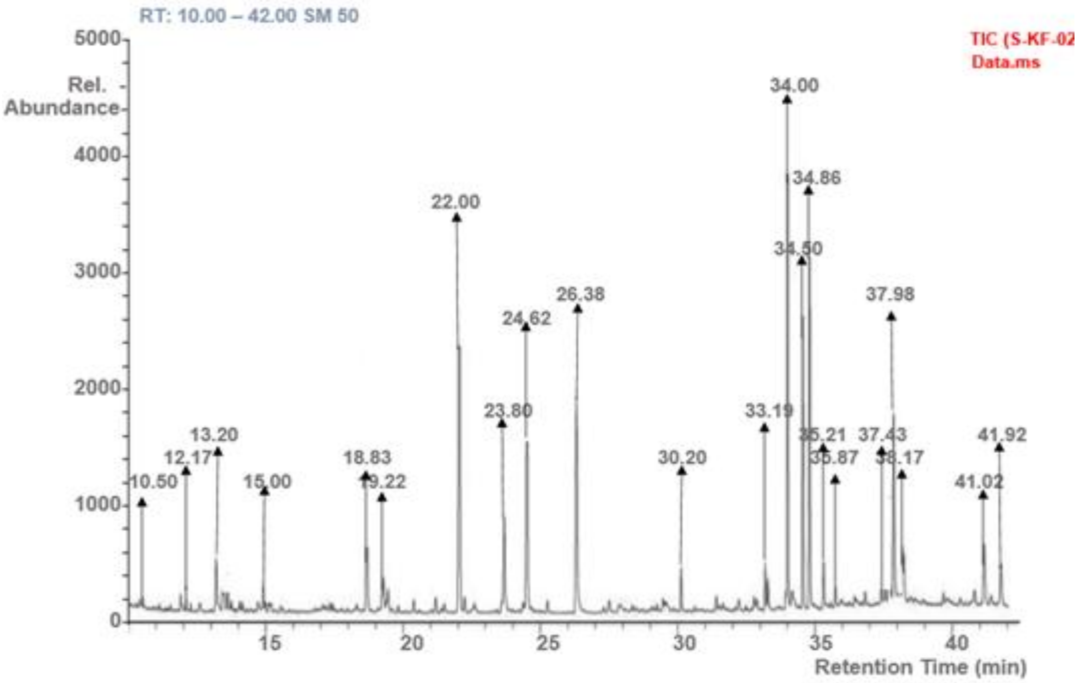

Figure 6: GC-MS chromatogram of pesticide residue profile of the full tablet preserved extract of Kola nut (KF). Chromatographic conditions: BP5 capillary column (30 m × 0.25 mm × 0.25 µm), carrier gas (N): 1.2 mL/min, split ratio 1:50, oven program temperature: 70°C to 300°C at rate of 10°C/min, 78 min total run time.

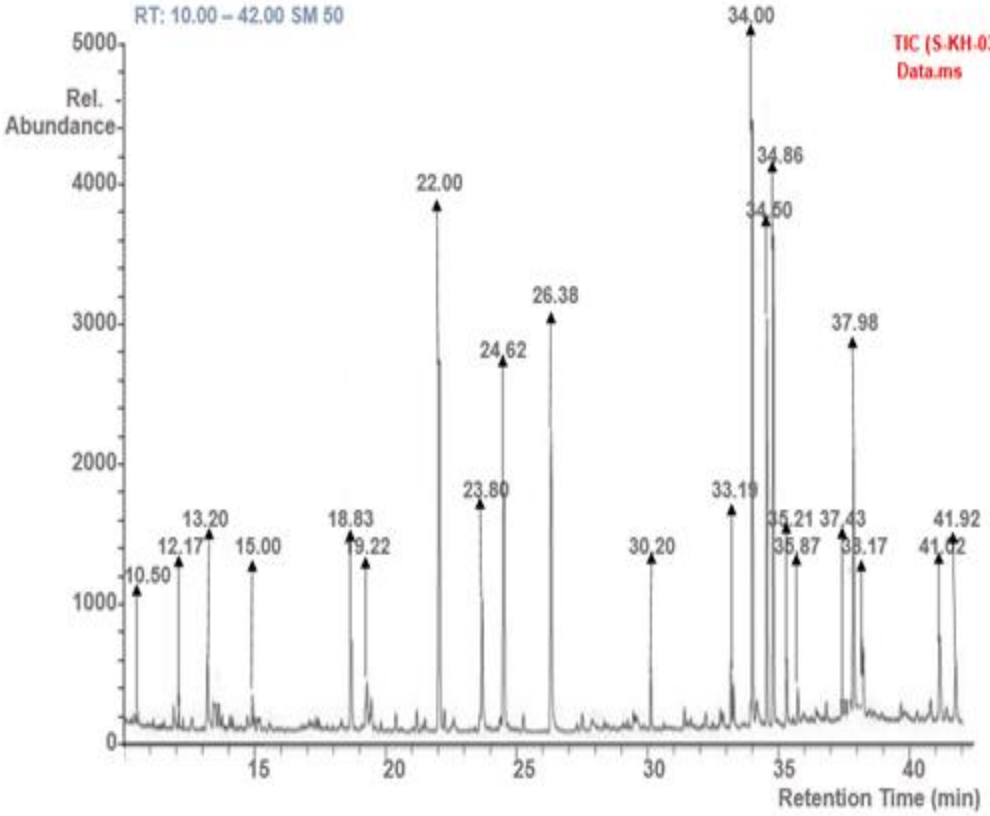

Figure 7: The GC-MS chromatograms of the pesticide residue profile in half tablet preserved Kola nut extract (KH). Chromatographic conditions: BP5 capillary column (30 m × 0.25 mm × 0.25 µm), carrier gas: nitrogen, 1.2 mL/min, split ratio: 1:50, oven temp. program: 70°C to 300°C at 10°C/min, total run time: 78 min.

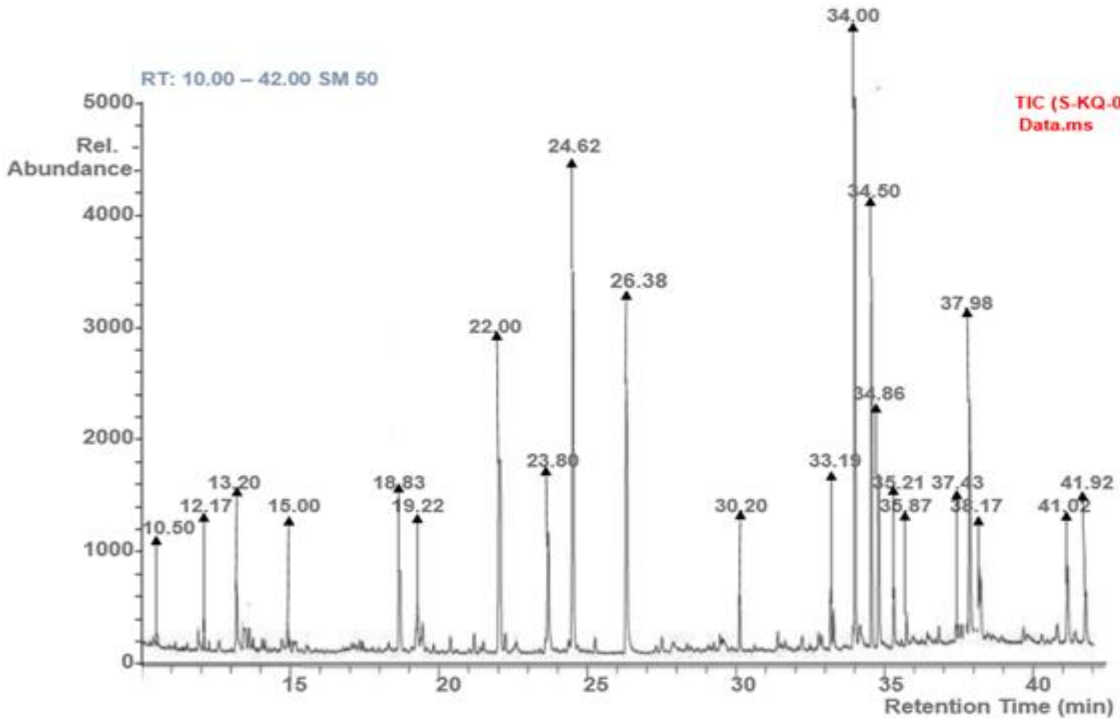

Figure 8: GC-MS chromatogram of quarter tablet preserved Kola nut extract (KQ) showing pesticide residue profile. The chromatographic conditions: BP5 capillary column (30 m × 0.25 mm × 0.25 µm), N2 carrier gas flow rate 1.2 mL/min, split ratio 1:50, oven temperature program: 70°C to 300°C at 10°C/min, 78 min total run time. Note the reduced cypermethrin peak compared to full tablet preserved sample.

Table 7: Pesticide Residue Content in Preserved and Unpreserved Cocoa Beans.

Pesticide residue	CUP	CF	CH	CQ	CU	CF	CH	CQ
	(µg/kg)				(% of total pesticide)			
Methomyl	0.03	0.03	0.02	0.02	4.11	3.41	2.56	2.67
Penconazole	0.01	ND	0.01	0.01	1.37	ND	1.28	1.33
Lindane	0.01	0.01	0.02	0.01	1.37	1.14	2.56	1.33
Malathion	ND	ND	ND	ND	ND	ND	ND	ND
Phosphoric acid, 7-chlorobicyclo (3.2.0) hepta-2,6-dien-6-yl dimethylester	0.01	0.07	0.05	0.03	1.37	7.95	6.41	4.00
Carbofuran	ND	ND	ND	ND	ND	ND	ND	ND
Cyprodinil	0.04	0.02	0.03	0.04	5.48	2.27	3.85	5.33
Amitraz	ND	ND	ND	ND	ND	ND	ND	ND
Carbaryl	0.10	0.09	0.14	0.07	13.70	10.23	17.95	9.33
Imazalil	0.03	0.03	0.03	0.03	4.11	3.41	3.85	4.00
Chlorpyrifos	0.03	0.12	0.04	0.07	4.11	13.64	5.13	9.33
Diazinone	ND	ND	ND	ND	ND	ND	ND	ND
Pirimiphos methyl	0.24	0.27	0.28	0.26	32.88	30.68	35.90	34.67
Cyfluthrin	0.03	0.13	0.02	0.06	4.11	14.77	2.86	8.00
Triazophos	0.05	0.03	0.04	0.04	6.85	3.41	5.13	5.33
Aldrin	0.03	ND	0.02	0.02	4.11	ND	2.56	2.67
Diflufenican	0.02	0.02	0.02	0.02	2.74	2.27	2.56	2.67
Dichlorvos	0.05	0.02	0.02	0.02	6.85	2.27	2.56	2.67
Dieldrin	0.02	0.01	0.02	0.02	2.74	1.14	2.56	2.67
Bifenthrin	0.03	0.03	0.02	0.02	4.11	3.41	2.56	2.67
Total	0.73	0.88	0.78	0.75	100.00	100.00	100.00	100.00

CUP for unpreserved cocoa, CF for cocoa preserved by a full pellet of pesticide, CH for cocoa preserved by half a pellet, and CQ for cocoa preserved by one quarter of a pellet.

Table 8: Pesticide Residue Content in Preserved and Unpreserved Kola Nuts.

Pesticide residue	KUP	KF	KH	KQ	KUP	KF	KH	KQ
	(µg/kg)				(% of total pesticide)			
Methomyl	ND	ND	ND	ND	ND	ND	ND	ND
Penconazole	0.01	0.01	ND	0.01	1.54	1.35	ND	1.47
Lindane	0.02	0.01	0.02	0.02	3.08	1.35	2.78	2.94
Parathion	0.01	0.01	0.02	0.01	1.54	1.35	2.78	1.47
Phosphoric acid, 7-chlorobicyclo (3.2.0) hepta-2,6-dien-6-yl dimethylester	0.01	0.02	0.01	0.01	1.54	2.70	1.39	1.47
Carbofuran	0.01	0.01	0.02	0.02	1.54	1.35	2.78	2.94
Imazalil	0.02	0.06	0.09	0.05	3.08	8.11	12.50	7.35
Amitraz	0.02	0.02	0.05	0.02	3.08	2.70	6.94	2.94
Dichlorvos	0.10	0.03	0.08	0.03	15.38	4.05	11.11	4.41
Carbaryl	0.02	0.03	0.03	0.02	3.08	4.05	4.17	2.94
Coumaphos	0.02	0.02	0.01	0.01	3.08	2.70	1.39	1.47
Diazinone	0.02	0.01	0.01	0.01	3.08	1.35	1.39	1.47
Pirimiphos methyl	0.13	0.20	0.21	0.21	20.00	27.03	29.17	30.88
Triazophos	0.12	0.11	0.07	0.05	8.46	14.86	9.72	7.35
Cypermethrin	0.02	0.10	0.01	0.11	3.08	13.51	1.39	6.18
Aldrin	0.02	0.01	0.01	0.01	3.08	1.35	1.39	1.47
Heptachlor	0.02	0.01	ND	0.01	3.08	1.35	ND	1.47
Malathion	0.01	ND	ND	ND	1.54	ND	ND	ND
Chlorpyrifos	0.02	0.02	0.04	0.03	3.08	2.70	5.56	4.41
Bifenthrin	0.02	0.02	0.01	0.02	3.08	2.70	1.39	2.94
Cyfluthrin	0.01	0.03	0.02	0.02	1.54	4.05	2.78	2.94
Dieldrin	0.02	0.01	0.01	0.01	3.08	1.35	1.39	1.47
Total	0.65	0.74	0.72	0.68	100.00	100.00	100.00	100.00

KUP for unpreserved Kola nut, KF for Kola nut preserved by full pellet of pesticide, KH for Kola nut preserved by half pellet and KQ for Kola nut preserved by one quarter of the pellet. Unpreserved cocoa bean was highly polluted with lindane, aldrin, dieldrin (Organochlorine), bifenthrin, cyfluthrin (Pyrethroid) and pirimiphos methyl (Organophosphorus) because of values greater than 1 while there was low level of pollution of chlorpyrifos because of its value less than 1 (Table 9 and 10). Cocoa with half preserved tablet has the lowest values of the high pollution index with the three classes of pesticide detected while with a quarter preserved tablet cocoa there is low pollution index of pirimisphos methyl. Unpreserved Kola nut was highly polluted with lindane, aldrin, dieldrin, heptachlor (Organochlorine) because of values of its pollution index greater than 1 (Table 10). However, it is contaminated with bifenthrin, cyfluthrin and cypermethrin (Pyrethroid) because of pollution index less than 1. A quarter preserved tablet Kola nut has low level of cyfluthrin pollution amongst the three preserved Kola nuts. Half preserved tablet Kola nut has the lowest value of all the high lindane pollution.

Table 9: Pollution Index for Organochlorine, Pyrethroid and Organophosphorus in Preserved and Unpreserved Cocoa Beans.

Organochlorine	**CU**	**CF**	**CH**	**CQ**	**Pyrethroid**	**CU**	**CF**	**CH**	**CQ**	**Organophosphorus**	**CU**	**CF**	**CH**	**CQ**
			(PI)				**(PI)**						**(PI)**	
Lindane	10	10	20	10	Bifenthrin	300	300	100	200	Pirimiphos methyl	4.8	5.4	5.6	**4.6**
Aldrin	600	-	200	200	Cyfluthrin	300	1300	200	600	Chlorpyrifos	0.3	1.2	0.3	**0.7**
Dieldrin	40	20	20	40										

Note: PI > 1 indicates high pollution; PI < 1 indicates low pollution. "-" indicates not detected

Table 10: Pollution Index for Organochlorine and Pyrethroid in Preserved and Unpreserved Kola Nut

Organochlorine	**KU**	**KF**	**KH**	**KQ**	**Pyrethroid**	**KU**	**KF**	**KH**	**KQ**
		(PI)						**(PI)**	
Lindane	2000	2000	1000	2000	Bifenthrin	0.4	0.4	0.4	0.2
Aldrin	400	200	200	200	Cyfluthrin	0.1	0.2	0.3	0.2
Dieldrin	400	200	200	200	Cypermethrin	0.2	1.1	1.0	0.1
Heptachlor	1000	500	500	----					

Note: PI > 1 indicates high pollution; PI < 1 indicates low pollution. "-" indicates not detected.

4.Conclusion

The study underscores the double edge sword effect of pesticide applications to cocoa and Kola nut farming whereby users of the pesticides were able to maintain yields and reduce pest attack but at the same time reduced the quality of farm produce in terms of chemical composition. Crude protein, crude fat, crude fibre, caffeine and theobromine contents were decreased in the preserved samples compared with the unpreserved samples. Both groups were able to absorb key minerals like calcium, magnesium, potassium, iron, sodium and copper. Pesticide residue levels in the sampled produce were also found to be below EU-MRLs, but the farmers often use various pesticides such as banned pesticides in the pre- and post-harvest activities which may pose risks to consumers of contaminated produce. The findings of this study show that the Al-P can be used for the successful postharvest preservation of cocoa and kola nuts during storage and has the potential to influence some nutritional and bioactive components. Limitations of the study are the use of one site for sample collection and one pesticide type.

The results might not be applicable in areas where agricultural practices, climatic conditions, or pesticide use differs from that of the study area. In addition, the study failed to evaluate the health effects from long-term exposure to pesticides from these products at low doses. Future research should examine the effects of aluminum phosphide on other crops and varying storage conditions, look into the possibility of creating application protocols for pesticides which minimize nutritional losses and still keep pest control at the desired level, and look into the possibility of finding some other more environmentally friendly method of preserving food which would reduce or eliminate the need for synthetic pesticides. The study recommends that to solve the current problems, five tablets of Aluminium phosphide be used for the preservation of 60kg of cocoa and Kola nuts; farmers to be educated on the safe chemical use practices to enhance their marketability; public awareness campaign should be made a regular exercise with the aim of reducing health risks from pesticide residues and some regulation of the use and importation of obsolete or banned chemicals in pest control.

Declarations

Consent to publish

All authors consented to the publication of this work. All authors confirm permission for the publication of this research work.

Declaration of competing interests

The authors declare no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author's contributions

Authors contributed equally to this work

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References

Afoakwa, E. O., Quao, J., Takrama, J., Budu, A. S., & Saalia, F. K. (2013). Chemical composition and physical quality characteristics of Ghanaian cocoa beans as affected by pulp pre-conditioning and fermentation. *Journal of Food Science and Technology*, *50*(6), 1097–1105. Crossref

Ahmed, M., Kumar, P., & Singh, R. (2020). Effect of phosphine fumigation on nutritional quality of stored grains. *Journal of Stored Products Research*, 87, 101-109. Ref

Ajayi, A. I., Ochigbo, S. S., J, J. O., Ndamitso, M. M., & Abubakar, U. (2012). Proximate and mineral compositions of different species of Kola Nuts. *European Journal of Applied Engineering and Scientific Research*, *1*, 44–47. Ref

Ajayi, S. I. O., & Oyejide, T, A. (2001). *The role of cocoa in Nigeria economic development*. The Economics of Cocoa Production and Marketing in Nigeria. Ref

Anand, R., Singh, P., & Sharma, A. (2016). Biochemical changes in stored commodities due to phosphine exposure. *Pesticide Biochemistry and Physiology*, 134, 45-52. Ref

AOAC, A. O. A. C. (2010). *Official Methods of Analysis of Association of Official Analytical Chemists* (18th ed.). Ref

Asogwa, E. U., Otuonye, A. H., Mokwunye, F. C., Oluyole, K. A., Ndubuaku, T. C. N., & Uwagboe, E. O. (2011). Kolanut production, processing and marketing in the South-eastern states of Nigeria. African Journal of Plant Science, 5(10), 547–551. Ref

Athayde, M. L., Coelho, G. C., & Schenkel, E. P. (2000). Caffeine and theobromine in epicuticular wax of Ilex paraguariensis A. St.-Hil. *Phytochemistry*, *55*(7), 853–857. Crossref

Bassini-Cameron, A., Sweet, E., Bottino, A., Bittar, C., Veiga, C., & Cameron, L.-C. (2007). Effect of caffeine supplementation on haematological and biochemical variables in elite soccer players under physical stress conditions. *British Journal of Sports Medicine*, *41*(8), 523–530; discussion 530. Crossref

Chaudhry, A., Gupta, S., & Rani, S. (2019). Oxidative stress markers in phosphine-exposed food products. *Food Chemistry*, 289, 456-463. Ref
DL, N., M, K., & OS, B. (2007). Occurrence of Ochratoxin A in Kola nuts. *Annual Report of Cocoa Research Institute of Nigeria*, *28*. Ref
Emeribe, E. O. (2008). *Safety precautions in the use of pesticides, calibrations, and application rates*. Ref
Ezeama, C. F., Keke, E., & Nwachukwu, E. (2007). Influence of brine treatment, drying methods, and storage conditions on the microbial quality of freshwater snail (Lanistes libycus) meat. *Nigerian Food Journal*, *25*, 101–111. Crossref
F.A.O. (2007). *Food and Agriculture Organization of the United Nations*. International Regulatory Co-operation and International Organisations. Crossref
Fekadu Gemede, H., Desse Haki, G., Beyene, F., Rakshit, S., & Woldegiorgis, A. (2018). Nutritional and antinutritional evaluation of indigenous Ethiopian okra (Abelmoschus Esculentus) seed accessions. *AFRICAN JOURNAL OF FOOD, AGRICULTURE, NUTRITION AND DEVELOPMENT*, *18*, 13019–13033. Crossref
Fernandes, C., Oliveira, J., & Silva, M. (2019). Metal complexation of methylxanthines: Implications for food quality. *Journal of Food Science*, 84(5), 1123-1130. Ref
Gupta, R., & Rani, M. (2018). Lipid peroxidation in stored grains during phosphine fumigation. *Food Science and Technology International*, 24(6), 512-520. Ref
Hakanson, L. (1980). An ecological risk index for aquatic pollution control - A sedimentological approach. *Water Research*, 14(8), 975-1001. Crossref
Huang, S., Wang, L. M., Sivendiran, T., & Bohrer, B. M. (2018). Review: Amino acid concentration of high protein food products and an overview of the current methods used to determine protein quality. *Critical Reviews in Food Science and Nutrition*, *58*(15), 2673–2678. Crossref
Ibrahim, M., Imran, M., Hussain, A., Aslam, M., Rehmani, F. S., & Ali, B. (2012). Phytochemical Studies on Amberboa ramosa. *Pak J Chem*, *2*, 24–28. Crossref
Komes, D., Horžić, D., Belščak, A., Kovačević Ganić, K., & Baljak, A. (2009). Determination of Caffeine Content in Tea and Maté Tea by Using Different Methods. *Czech Journal of Food Sciences*, *27*, 213–216. Crossref
KVI, J. (2005). *Agrochemical poisoning, Textbook of Forensic Medicine and Toxicology* (3rd ed.). Reed Elsevier India Private limited. Ref
Kumar, V., Singh, D., & Yadav, S. (2021). Dose-dependent effects of aluminum phosphide on grain quality parameters. *Journal of Food Safety*, 41(3), e12876. Ref
McDonald, R., & Evans, K. (2017). Methylxanthines in food: Sensory and pharmacological aspects. *Critical Reviews in Food Science and Nutrition*, 57(8), 1567-1579. Ref
Misra, U., Sharma, M., & Patel, R. (2015). Chemistry of phosphine gas release from aluminum phosphide. *Chemical Reviews*, 115(14), 6789-6824. Ref
Mahot, H., Babin, R., Dibog, L., Tondje, P. R., & Bilong, C. (2005). Biocontrol of cocoa mired Sahlbergella singularis hagl. In A. Y. Akrofi & F. Baah (Eds.), *Cameroon in Proceedings of the 5th INCOPED International Seminar on Cocoa Pests and Diseases*. Miridae. Ref
Mepba, H. D., Eboh, L., & Banigo, D. E. B. (2007). Effects of processing treatments on the nutritive composition and consumer acceptance of some Nigerian edible leafy vegetables. *African Journal of Food, Agriculture, Nutrition and Development*, *7*. Ref
Mesfin, W., & Shimelis, A. (2013). Effect of Soybean/Cassava Flour Blend in the Proximate Composition of Ethiopian Traditional Bread Prepared from Quality Protein Maize. *African Journal of Food, Agriculture, Nutrition and Development*, *13*, 7985–8003. Crossref
Nath, K., Kumar, S., & Singh, P. (2011). Reactive oxygen species generation during phosphine exposure. *Free Radical Biology and Medicine*, 51(8), 1587-1593. Ref
Ndagi, I., Babalola, F. D., Mokwunye, I. U., Anagbogu, C. F., Aderolu, I. A., Ugioro, O., Asogwa, E. U., Idrisu, M., & Mokwunye, F. C. (2012). Potentials and Challenges of Kolanut Production in Niger State, Nigeria. *International Scholarly Research Notices*, *2012*(1), 492394. Crossref
Odebunmi, O, E., Oluwaniyi, O, O., Awolola, G.V, Adediji, & D, O. (2009). Proximate and nutritional composition of kola nut (Cola nitida), bitter cola (Garcinia cola) and alligator pepper (Afromomum melegueta). *African Journal of Biotechnology*, *8*(2), 308–310. Ref
Ogah, C. O., & Obebe, O. T. (2012). Caffeine Content of Cocoa and Coffee Beverages in Lagos, Nigeria". *Journal of Innovative Research in Engineering and Sciences*, *3*, 404–411. Ref
Okoli, B. J., Abdullahi, K., Myina, O., & Iwu, G. (2012). Caffeine Content of Three Nigerian Cola. *Journal of Emerging Trends in Engineering and Applied Sciences*, *3*, 830–833. Ref
Onyango, C., Noetzold, H., Bley, T., & Henle, T. (2004). Proximate composition and digestibility of fermented and extruded uji from maize–finger millet blend. *LWT - Food Science and Technology*, *37*(8), 827–832. Crossref
Opoku, I., Akrofi, A., Appiah, A., & Appiah, A. (2007). Assessment of sanitation and fungicide application directed at cocoa tree trunks for the control of Phytophthora black pod infections in pods growing in the canopy. *European Journal of Plant Pathology*, *117*(2), 167–175. Crossref
Oyekunle, J. A. O., Ogunfowokan, A. O., Torto, N., & Akanni, M. S. (2011). Determination of organochlorine pesticides in the agricultural soil of Oke-Osun farm settlement, Osogbo, Nigeria. *Environ Monit Assess*, *177*, 51–61. Crossref
Pinto, E., Silva, A., & Costa, R. (2020). Acid-catalyzed degradation of methylxanthines. *Journal of Agricultural and Food Chemistry*, 68(23), 6432-6440. Ref
Ramli, N., Yatim, A. M., Said, M., & Hok, H. C. (2001). Food Science Program, School of Chemical Science and Food Technology,Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia. *Malaysian Journal of Analytical Sciences*, *7*, 377–386. Ref
Sabarwal, A., Kumar, K., & Singh, R. P. (2018). Hazardous effects of chemical pesticides on human health-Cancer and other associated disorders. *Environmental Toxicology and Pharmacology*, *63*, 103–114. Crossref
Salas, J. H., González, M. M., Noa, M., Pérez, N. A., Díaz, G., Gutiérrez, R., Zazueta, H., & Osuna, I. (2003). Organophosphorus pesticide residues in Mexican commercial pasteurized milk. *Journal of Agricultural and Food Chemistry*, *51*(15), 4468–4471. Crossref
Serra, A., Franco, S., & Martinez, L. (2018). Oxidative demethylation of alkaloids in food systems. *Food Chemistry*, 245, 734-741. Ref
Singh, B., & Sharma, R. (2017). Structural changes in plant cell wall components during fumigation. *Carbohydrate Polymers*, 168, 234-241. Ref
Taubert, D., Roesen, R., & Schömig, E. (2007). Effect of cocoa and tea intake on blood pressure: A meta-analysis. *Archives of Internal Medicine*, *167*(7), 626–634. Crossref
Thomford, N. E., Dzobo, K., Chopera, D., Wonkam, A., Skelton, M., Blackhurst, D., Chirikure, S., & Dandara, C. (2015). Pharmacogenomics Implications of Using Herbal Medicinal Plants on African Populations in Health Transition. *Pharmaceuticals*, *8*(3), 637–663. Crossref
Vitaglione, P., Napolitano, A., & Fogliano, V. (2008). Cereal dietary fibre: A natural functional ingredient to deliver phenolic compounds into the gut. *Trends in Food Science & Technology*, *19*(9), 451–463. Crossref
WHO/FOA/UNU (1994). Codex Alimentarius: Foods for special dietary uses (including foods for infants and children. In *Food and Agriculture Organization of the United Nations, World Health Organization*. Ref
Yalwa, I. R., & Bello, A. M. (2017). Determination of Caffeine Content in Some Varieties of Kola Nut (C. acuminate)". *Bayero Journal of Pure and Applied Sciences*, *10*, 247–251. Crossref