Chemistry Research Journal, 2020, 5(6):256-265

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Chemical and Nutritive Composition of Buffalo Thorn (*Ziziphus mucronata*) Seeds from Kwami LGA of Gombe state, Nigeria

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Abstract The proximate and mineral analyses of Buffalo Thorn (*Ziziphus mucronata*) were carried out on both seeds. The proximate analysis recorded the concentrations (In percentage) of seed samples as Moisture (5.75±0.25), Ash (35.00±2.5), Crude fiber (6.1±0.1), Crude protein (18.9±0.16), Crude lipids (20.1±0.1), Carbohydrate (8.4± 0.4). The mineral content of the seed was found to be: Sodium (78.15±0.48 mg/kg), calcium (380.56±6.19 mg/kg), iron (50.19±0.74 mg/kg) and magnesium (621.69±0.88 mg/kg. The seeds contained a high percentage of calcium and magnesium. The result showed that *Z. mucronata* seed is useful to both man and animal's food supplements.

Keywords Proximate Analysis, Buffalo Thorns, *Ziziphus mucronata*, Food Supplements

1. Introduction

Buffalo thorn (*Ziziphus mucronata*) is a small to medium-sized tree, 3–10m high with a spreading canopy. The main stem is green and hairy when young, year-old branches often zigzag. The bark is reddish-brown or roughly milk grey, leaves are simple, alternate, ovate, or broadly ovate; very enormous in size from tree to tree 30-90 x 20-50mm tapering. The leaves of *Z. mucronata* often turn golden yellow in autumn. Flowers are borne in dense clusters in leaf axis, green to yellow; ±4mm in diameter. The fruit is a smooth, shiny lathering, spherical, drupe, 12-20mm in diameter, reddish-brown or deep red when ripe, slightly sweet, the pulp is dry. The fruit sometimes stays on the plant long after the leaves have fallen (March-August). The seeds are usually solitary, elliptic and compressed. *Z. mucronata* is commonly found in northern Nigeria [1]. The species of tropical Africa and the leaves from the plant provide a good source of forage for domestic and wild animals [2]. The buffalo thorn is distributed throughout the summer rainfall areas of Sub-Saharan Africa extending from South Africa northwards to Ethiopia and Arabia. It grows in areas dominated by thorny vegetation in both temperate and tropical climates. It is also found in scrubland, rocky koppies and open grasslands on a variety of soils along streams, nutrient-rich valley bottoms, and forest margins. It reaches its largest size on the margins of the scrub forest and on deep alluvial soils near water. Its presence is said to indicate the presence of groundwater. There are 49 genera and 900 species in the family *Rhamnaceae* [3] the Genus *Ziziphus* include some 86 species of which the one discussed here is among the commonest and the best-known trees of southern Africa. Another well-known species is the *Z. mauritiana.* The *Jujube* tree fruit is commonly found in shops that sell Asian food-stuff. A decoction of the *Z. mucronata* is commonly administered as pain killers as well as a remedy for dysentery. A concoction of the bark of leaves is used

for respiratory ailments and another septic swelling of the skin. The paste of the roots and leaves can be applied to treat boils, swollen glands, wounds, and sores. Steam baths from the bark are used to purify and improve the complexion [4]. In east Africa, roots are used for snake bites [5]. All the above can be attributed to the peptide alkaloids and antifungal properties isolated from the bark and leaves. The berries are edible and were used by the Transvaal in making porridge or as a coffee substitute. Africans have many superstitions about this tree, Zulus and Swazis use it in connection with burial rites. It was once customary that when Zulu Chief died, the tree was planted on his grave as a reminder. In other parts, the branch was dragged around the village to protect it from evil spirits. Wood from this tree is used for wagon making and fence post as it yields a yellow fine-grained, heavy wood that contains 12.2-15.7% tannin matter [6]. The elasticity of the shoots makes it suitable for bows and whips as well as being used as hedges that protect the lives of livestock. The fruit of *Z. mucronata* is spherical-shaped with a shiny brown skin that cannot be easily separated from the sweet whitish brown-yellow edible flesh. The fruit contains a hard woody nut that encloses the seed [7]. The buffalo thorn is browsed by stock animals as well as antelopes, giraffes, Cheema baboon, and velvet monkey also visit this tree for the ripe fruit.

Omosuli *et al* [8] determined the proximate and mineral composition of roasted and defatted cashew nut flour. Cashew nut was roasted, defatted and treated into flour. The flour was assessed for its physicochemical characteristics (proximate and minerals). The proximate composition (in %) was as follows: moistness (5.52 ± 0.2), ash (4.41 ± 0.1), crude fat (34.95 ± 0.2), crude protein (27.31 ± 0.0), crude fibre (1.42 ± 0.2), carbohydrate (by subtraction) 25.39 and energy (kcal) (534.35). The composition of the mineral makeup (in mg/100g) showed that roasted and defatted cashew nut flour contains calcium (ca) (21.± 0.23), potassium (38.5 ± 0.1), magnesium (36.4 ± 0.3), iron (0.8 ± 0.1), Zinc (0.9 ± 0.1)8), sodium (22.6 ± 0.2), Copper (0.4 ± 0.1). It is obvious that the flour is a good source of energy, protein, and minerals. Proximate compositions determination was done by the recommended methods of association of officials analytical chemist [9] energy value was obtained using the method of Osborne and Vogt [10] and carbohydrate content determined by difference. Mineral determination: the minerals: calcium, magnesium, iron, Zinc, Copper, were determined by atomic absorption spectrophotometry [11]. Akinhanmi *et al* [12] determined the proximate composition and mineral concentration of cashew nut (*Anacardium occidentale*) were investigated using standard analytical methods. The physicochemical characteristics of cashew nut shell liquid were also determined. The proximate composition (in %) was as follows moisture (7.2), ash (2.8), crude fat (49.1), crude protein (36.3), crude fiber (3.2), and carbohydrate (by difference) (1.4). The mineral composition (in mg/100g) of cashew nut showed potassium (27.5 ± 0.4) to be the highest, calcium (21.5 ± 0.0), magnesium (19.3 ± 0.1), sodium (8.2± 0.2), and phosphorus (14.0 ± 0.2). Zinc and iron concentrations were lower. The physicochemical properties of cashew nut oil were as follows color (yellow), refractive index (1.458), specific gravity (0.962), acid value (10.7 mgKOH/g), iodine value (41.3 mg iodine/100g), saponification value (137 mgKOH/g) and free fatty acid (5.4 mgKOH/g). This is an indication that the oil non-drying, edible and may not be used for soap making. The cashew nut shell liquid (CNSL) extracted was dark brown in color. Ash and moisture content (%) were 1.2 and 3.9 (for Brazilian species) and 1.3 and 6.7 (for African species). Specific gravity and refractive index were 0.941 and 1.693 (for BRZ variety) and 0.924 and 1.686 (for AFR variety) saponification, acid, free fatty acid (mgKOH/g) and iodine (mg iodine/100g) values were (58.1, 12.1, 6.1, 21.s respectively) (for BRZ species) and 47.6, 15.4, 7.8, 235 (for AFR species). The investigation showed that CNSL is a drying oil and it is useful in industries for paints, varnishes and surface coatings.

Hassan *et al* [13] worked on the nutritive value of Garden cress (*Lepidium sativum* leaves), a vegetable commonly consumed by the people of North-Western Nigeria. The sample was subjected to proximate, amino acids, minerals, and anti-nutritional analysis. The results of the proximate analysis indicate that the leaves had high crude protein (18.25%), crude fiber (9.31%) and ash (15.38%). The mineral analysis showed that the leaves are particularly high in potassium (1850.00mg/100g), calcium 829.13 mg/100g), sodium 141.13 mg/100g) and iron (63.47 mg/100g) with low level of phosphorus (4.10 mg/100g), manganese (5.74 mg/100g) copper (0.39mg/100g) and chromium (0.36mg/100g). The amino acid profile revealed that the leaf protein is generally low in lysine, sulfur-containing amino acids (methionine and cysteine), and the threonine. Lysine was the limiting amino acid in the leaves. In terms

of anti-nutritional factors, the leaves had low concentration of phytate (10.95mg/100g), nitrate (0.05mg/100g) and HCN (31.54mg/100g) with moderate amount of oxalate (337.50mg/100g)

Statement of the Problem

There is a need to evaluate the proximate analysis of the seeds of *Z. mucronata* to help supplement the nutrients needs and demand of man and other domestic animals.

Aim and objectives

The aim of this research is to carry out the proximate analysis of the seeds of *Z. mucronata*. The objectives are as follows:

(i) To determine the moisture content of the seeds of *Z. mucronata.*
(ii) To determine the ash content of the seeds of *Z. mucronata.*
(iii) To determine the crude fiber content of the seeds of *Z. mucronata.*
(iv) To determine the crude lipid content of the seeds of *Z. mucronata.*
(v) To determine the crude protein content of the seeds of *Z. mucronata.*
(vi) To determine the carbohydrates content of the seeds of *Z. mucronata*.
(vii) To determine the mineral content (Na, Mg, Ca, Fe,) of the seeds.

Significance of the Study

This research serves as a source of additional data to all who will be embarking on further research on seeds of *Z. mucronata*. The result will also serve as a basis for other researchers regarding the mineral and chemical contents of the seeds and fruits with the oil content of the seeds. This could also help in assessing the actual nutrient composition of the seeds, to supplement the nutrients needs of animals and mankind obtained from the seeds of *Z. mucronata.*

Scope and Limitation

This research is restricted to the proximate analysis of *Z. mucronata* Seeds it is also limited to the analysis of the minerals - Na, Ca, Mg, & Fe, only of the seeds.

2. Experimental

2.1 Sampling (Collection and Treatment)

Dry fruit of *Ziziphus mucronata* was obtained in the nearby bush from Bojude village in Kwami and Bajoga in Funakaye, Local Government Area of Gombe State northern Nigeria. The matured fruits were collected from two different trees of the *Z. mucronata* plant. The fruits were crushed mildly (carefully) in a clean wooden mortar to release the fruits. The seeds were dried for better cracking of the woody seed shell and were later crushed into powder, further dried for two days and then package in a clean well-ventilated cupboard.

2.2 Proximate Analysis

All the analyses were carried out in triplicate.

2.3 Determination of Moisture Content

The method is based on drying a sample in an oven and determining moisture by the weight difference between dry and wet materials. 5 g of the sample of *Z. mucronata* seed and fruits were weighed (W_1) into a pre-weighed crucible (W_0) and placed into a hot drying oven at 105 ^oC. The process of drying, cooling and weighing were repeated until a constant weighed (W_2) was obtained. The weighed loss due to moisture content was obtained by the equation.

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_2 - W_0} X100$$

Where
W_0= weight of empty crucible, (g)
W_1 = weight of fresh sample +empty crucible, (g)
W_2= weight of dried sample +empty crucible, (g)

2.4 Determination of Ash Content

This method is used to determine ash foodstuff by calcination. The method followed was described by James [14], where 2 g of the powdered sample was weighed (W_1) into a pre-weighed crucible (W_0) and placed in a muffle furnace and was allowed to completely ash at 600 ^oC. The ash was removed and cooled in a desiccator and weighed (W_2). The weight of the sample was determined by the difference between the ash sample and pre-weighed crucible;

$$\text{Ash content (\%)} = \frac{W_2 - W_0}{W_1 - W_0} X100$$

Where
W_0= weight of empty crucible, (g)
W_1 = weight of fresh sample +empty crucible, (g)
W_2= weight of dried sample +empty crucible, (g)

2.5 Determination of Crude Lipid Content

In this method, the fats are extracted from the sample with n-hexane and evaluated as a percentage of the weight. The crude lipid content in the sample was extracted using Soxhlet extractor procedure as described by Udo and Ogunwele [15]. 5 g of the sample was folded in filter paper and placed in an extractor and extracted into a pre-weighed round bottom flask with low boiling n-hexane (69 ^oC) using solvent extractor for about 8 hours. The solvent was recovered by a rotator evaporator. Finally, the flask and its content were placed in an oven at 90 ^oC for 2 hours and it was cooled in a desiccator and weighed. The percentage of crude lipid was calculated as follows:

$$\text{Crude Lipid Content (\%)} = \frac{W_1 - W_2}{W_0} X100$$

Where
W_0= weight of clean dry flask (g)
W_1= weight of flask with fat (g)
W_2= weight of the sample (g)

2.6 Determination of Crude Fibre Content

This method gives the crude fiber content of the sample after it has been digested in sulphuric acid and sodium hydroxide solution and the residue calcined. The difference in weight after calculations indicates the quality of the fiber present. The percentage of crude fiber was determined by the method described by Udo and Ogunwele [15]. 2 g of the sample was weighed (W_0) into a 1dm^3 conical flask and 20% of H_2SO_4 acid was added and boiled gently for 30 minutes. The content was filtered through Whatman No 1 filter paper. The residue was scrapped back to the flask with spatula and filter paper rinsed with distilled water. 20cm^3 of 10% NaOH was added and allowed to boil gently for 30 minutes. The content was filter and the residue was washed with HCl and rinsed with petroleum ether. It was allowed to dried and scrapped into a crucible and allowed to dry overnight at 100^{0}C in an oven. It was then removed and cooled in a desiccator. The weighed W_1) was ash at 600^{0}C for 90 minutes. It was removed and cooled in a desiccator and reweighed (W_2). The percentage of crude fiber was calculated as follows;

$$\text{Crude Fibre Content (\%)} = \frac{W_1 - W_2}{W_0} X100$$

Where
W_0= weight of the sample, (g)
W_1 = weight of the dried sample, (g)
W_2= weight of ash sample,(g)

2.7 Determination of Crude Protein Content:

The crude protein of the sample was determined using the micro Kjeldahl method described by Association of Official Analytical Chemists (AOAC) [16]. The principle of this method is based on the transformation of protein nitrogen-containing organic compounds, other than nitriles and nitrates into ammonium sulfate by acid digestion.

Sample nitrogen + $H_2SO_{4(aq)} \xrightarrow{\text{catalyst}} (NH_4)_2SO_{4(aq)}$

$(NH_4)_2SO_{4(aq)} + 2NaOH \longrightarrow 2NH_{3\,(aq)} + 2H_2O + Na_2SO_{4(aq)}$

$NH_{3(aq)} + H_3BO_{3(aq)} \longrightarrow NH_4^+{}_{(aq)} + H_2BO_{3(aq)}$

$H^+{}_{(aq)} + H_2BO_{3(aq)} \longrightarrow H_3BO_{3(aq)}$

2 g of the sample was weighed along with 20cm^3 of distilled water into the micro Kjeldahl digestion flask. It was shaken and allowed to stand for some time and the tablet of selenium catalyst was added followed by the addition of 20cm^3 concentrated sulphuric acid. The flask was heated on the digestion block until the content became clear. The flask was removed from the block and allowed to cool. The content was transferred into a 50cm^3 volumetric flask and diluted to the mark with distilled water. An aliquot of the digestion (10cm^3) was transferred into another micro Kjeldahl flask along with 20cm^3 of distilled water and placed in the distilling outlet of the micro Kjeldahl distillation unit. A conical flask containing 20cm^3 of the boric acid indicator was placed under the condenser outlet. Sodium hydroxide solution (20cm^3, 40%) was added to the content in the Kjeldahl flask by opening funnel stopcock. The distillation started and heat supplied was regulated to avoid sucking back. When all the available distillate was collected in 20cm^3 of boric acid; the distillation was stopped ed. The nitrogen in the distillate was determined by titration with 0.01M of H_2SO_4. The endpoint was obtained when the color of the distillate change from green to pink.

Crude protein is the measure of nitrogen in the sample. It was calculated by multiplying the total nitrogen content by a constant 6.25. This is based on the assumption that protein contains about 16% nitrogen which includes both protein and non-protein nitrogen and does not make a distinction between available and unavailable protein. The crude protein was calculated using the equation;

% crude protein= % nitrogen× 6.25

The nitrogen content is given by the formula;

$$\% \text{ N} = \frac{T_V \; X \; N \; X \; 0.014 \; X \; V_1}{G \; X \; V_2} X100$$

Where T_v=titre value of acid (cm^3)
N = concentration of acid
V_1 = volume of distilled water used for distilling the digest (50cm^3)
V_2 = volume of the aliquot used for distillation (10cm^3)
G = original weight of sample used in gram.

2.8 Determination of Carbohydrate Content

The method described by James [14] was adopted where the total proportion of carbohydrates in the seed sample was obtained by calculation using the percentage weight by subtracting the % sum of the food nutrient; %crude lipids, % crude protein, % crude fiber and % ash from 100%. This is done by using the equation;

% Carbohydrate = 100 ─ (% crude protein + % crude fibre + % ash + moisture)

2.9 Calorific Value

The calorific value was determined by multiplying the percent of crude protein, crude lipid, and carbohydrate by the recommended factor (2.44, 8.37, and 3.57) respectively reported by Asibey-Berko and Tayie [17]. Energy (Kcal/100g) = (% Carbohydrate × 3.57) + (% crude protein × 2.44)+ (%crude lipid × 8.37)

2.10 Sample Digestion

The triple digestion method of AOAC [16] was adopted. The dried samples (2g) were weighed into a micro Kjeldahl digestion flash to which 24cm^3 of a mixture of concentrated HNO_3, H_2SO_4 and 60% $HClO_4$ were added. The flask was put on a heating block and digested to a clear solution, cooled and the content transferred into a 50cm^3 volumetric flask and made-up to the volume mark with water. The solution was used for the determination of the mineral elements, sodium potassium, calcium, and iron.

2.11 Elemental Determination

Atomic absorption spectrophotometry (AAS) model 210VGP Buck Scientific was used for this analysis it gives a good precision and accuracy. The principle of the method is based on nebulizing a sample solution into the air acetylene flame where it is vaporized. Elemental ions were atomized and atoms then absorb radiation of characteristics wavelength from the hallow-cathode lamp. The absorbance measured is proportional to the amount of analyte in the sample solution this atomic absorption spectrophotometer has a computer containing software attached to it. The software interprets the absorbance and concentration of the standard solutions and gives the result of the samples as concentrations.

3.0 Results

The nutritive mineral and oil content of the *Z. mucronata* seeds and fruits have been given in the following tables and figures.

Table 1: Proximate composition of *Z. mucronata* seed

Parameters	Result (%)
Moisture Content	5.75 ± 0.25
Ash Content	35.00 ± 2.5
Crude Fibre	6.1 ± 0.1
Crude Lipid	20.1 ± 0.1
Crude Protein	18.9 ± 0.16
Carbohydrate	18.00 ± 0.05
Energy (Kcal/100g)	2008.58 ± 0.58

Table 2: Mineral composition of *Z. mucronata* seed

Element	Composition (mg/100g)
Sodium (Na)	7.815 ± 0.48
Calcium (Ca)	38.056 ± 0.056
Magnesium (Mg)	62.169 ± 0.88
Iron (Fe)	5.019 ± 0.74

3.1 Proximate Analyses

3.1.1 Moisture Content

The moisture content of *Z. mucronata* seed is 5.75 % (Table 1) and is closely related to those of *Moringa oleifera* seed and *Terminalia catappa* with 5.00 % and 5.52 % as reported by Aja *et al* [18] and Akpabio [19]. The low moisture content of the seeds normally hinders the growth of microorganisms and the storage life will be high [20].

3.1.2 Ash Content

The ash content determined for *Z. mucronata* seed was 35.00% compared to *Z. mauritiana* with 3.01% [21]. The high ash content of the seed showed that the seeds contained more mineral elements.

3.1.3 Protein Content

The protein content was 18.9% in *Z. mucronata* seed. The value is low when compared to that of almond seed which is 33.69 % [19], melon seed which is 30.8% [22], African oil bean with 28.1%, and cashew nuts with 21.2% [23]. The dietary allowance for protein is 56g for a 70kg man. Therefore a 70Kg man needs about 296.29g of *Z. mucronata* seed to supplement the protein need. It can be used as a dietary supplement for people who need a lot of protein, especially those who require plant protein e.g. people suffering from hypertension. However, it may be incorporated into animal feed to increase the protein content. Protein content for *Z. mucronata* fruit is 8.94% and is higher compared to 6.68% for *Z. Mauritiana* [21].

3.1.4 Fibre Content

The fiber content of *Z. mucronata* seed was 16.6%. This is significantly high when compared to 0.8% obtained from cashew nut [23], almond seed 3.11% [19] and 2.5% for African oil bean and melon seed [24]. The high Fibre content can act better on the digestive system without giving many problems of constipation. The Fibre content of *Z. mucronata* seed is high even when compared to the value of 8.2% obtained for African mango [25].

3.1.5 Carbohydrate Content

The carbohydrate content of *Z. mucronata* seed was 18%. This value is high when compared to the value of melon seed with 7.3%. However, it is lower when compared to African mango 19.2% and African oil bean with 15.3% [24] as well as almond seed 25.47% [19].

3.1.6 Caloric Value

The caloric value of *Z. mucronata* seed was 2008.58 kcal. This value is high and as such could be recommended as a dietary supplement for people who require a lot of energy, for example, the athletes.

3.1.7 Lipid Content

Z. mucronata seed has a lipid content of 20.10 %. The lipid content of the seeds is normally low when compared to almond seed with 32.73% [19], melon seed which contains 51.1% lipid [22] and African mango, with 55% [24], Cashew nut with 48.1% [23] and African oil bean with 34.9%

3.2 Mineral Elements

3.2.1 Sodium

The value of sodium in *Z. mucronata* seed was 7.815 mg/100g (Table 2). This value is high when compared to 5.0mg/100g obtained for almond seed [19], 1.96 mg/100g obtained for cocoa bean [26]. The dietary allowance for sodium is 110mg - 3300mg for adults. Hence adults need to take 426.48mg/day of *Z. Mucronata* seed in order to serve as a dietary supplement for sodium.

3.2.2 Magnesium

The magnesium content for seed was 62.169 mg/100g (Table 2). This value is low when compared to 520 mg/100g obtained for cocoa beans [26]. The value is also low when compared to 300 mg/100g reported for *Benni* seed [27]. It is, however, high when compared to almond seed 26.40mg/100g [19]. Recommended dietary allowance for magnesium is 210-320 mg/day, pregnant women 20mg/day, lactating mothers 60mg/day. Therefore, the categories of people above need about 514.72mg/day, 32.17mg/day and 96.51mg/day of *Z. mucronata* seed respectively.

3.2.3 Calcium Content

The calcium content in *Z. mucronata* seed was 38.056mg/100g (Table 2). This value is high when compared to 36.1 mg/100g obtained for almond seed [19] and 2.17 mg/100g obtained for cocoa bean [26], but low when compared to 900 mg/100g obtained for Benni seed [27]. The dietary allowance for calcium is 800mg for 70kg man. This means that a 70kg man requires about 2102.16mg of *Z. mucronata* seed per day as a supplement for Calcium. The recommended dietary allowance for calcium is 1200 mg for pregnant and lactating women throughout pregnancy and lactation period. That is to say, they need about 3153.24mg of Z. mucronata seed throughout pregnancy and lactation period.

3.2.4 Iron content

The value of 5.019mg/100g was obtained for *Z. mucronata* seed (Table 2). The Iron content is high when compared to 1.94 mg/100g obtained for cocoa bean [25]. However, the iron content of *Z. mucronata* seed is low when compared to 37.5mg/100g for almond seed [19] and 50 mg/100g obtained for Benni seeds [27]. The dietary allowance for iron is 10g for 70kg. Therefore, a 70kg man needs about 200mg of *Z. mucronata* seed per day, and so can be recommended as a dietary supplement for people who need iron. From figure 2, it is evident that the mineral content of the fruit is very negligible as compared to the mineral content of the seed. The mineral content observed in the seed was high in the case of calcium and magnesium elements and low in the case of sodium and iron elements. Table 2 shows the results for the mineral analyses seed of *Z. mucronata*.

4. Conclusion

From the results of the analyses carried out on *Z. mucronata*, the seeds show appreciable contents of ash, fiber, protein, lipid, and carbohydrate but show low moisture content. The seeds show high mineral composition in terms of their calcium and magnesium content. From the result of this analysis, it can be concluded that *Z. mucronata* seeds can be a useful dietary supplement.

5 Recommendations

On the basis of this research, the following recommendations are made;

a. Further analyses should be done for other mineral composition e.g magnesium, potassium, etc.
b. Analyses should also be carried out on the anti-nutritive content of the *Z. Mucronata* seed to ascertain its consumption viability.
c. Further analyses are also required to be done on the oil of *Z. mucronata* seed like saponification value, iodine value, etc.
d. Protein needs to be analyzed to ascertain the category of protein contained in the seeds of *Z. mucronata.*

Acknowledgment

The researchers are grateful to the Gombe state university and Abubakar Tafawa Balewa University Bauchi (ATBU) for their kind permission to use their chemicals, equipment, and apparatus during the research.

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