

Analyzing and Comparing the Physico-Chemical and Mineral Component of Cocoa (*Theobroma Cacao L.*) Pod and Bean

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To cite this article

Oguntokun Michael Ogunmola, Oguntokun Esther Adeola, Nwaokobia Kingsley, Adeola Emmanuel Abiodun. Analyzing and Comparing the Physico-Chemical and Mineral Component of Cocoa (*Theobroma Cacao L.*) Pod and Bean. *International Journal of Agriculture, Forestry and Fisheries*. Vol. 7, No. 2, 2019, pp. 18-24.

Received: June 12, 2019; **Accepted:** August 5, 2019; **Published:** September 17, 2019

Abstract

Cocoa (*Theobroma cacao L.*) is a major, essential economic, global crop and has several nutritional benefits. This study evaluated the physical, chemical and nutritive properties of the pod and bean of cocoa. Colour, Length, width, thickness, sphericity, roundness, porosity, mass, true and bulk densities were the physical properties observed. While Mineral Ash, Volatile Matter, Fixed Carbon, Crude Fibre, Crude Fat, Moisture Content, Crude Protein and Total Carbon, Hydrogen, Oxygen, Sulphur, Nitrogen were the parameters observed in Proximate and Ultimate analysis respectively. It was observed that the bean of cocoa the highest amount in all the Proximate and Ultimate analysis assayed except in mineral Ash and oxygen where the pod has 10.78% and 70.69±0.07 respectively. These values were analyzed using AOAC methods. The physical properties of cocoa (shape, size, weight, volume, density, surface area, colour and sphericity) which are relevant to engineering and industrial application were selected for study. These were determined using standard tests and experiments. It is observed that the bean has the highest values in all the physical properties studied except in thickness and sphericity where the pod has the highest. The moisture content of the cocoa pod and beans was between the range of 51.39 and 87.65 (% wb) and the ash content was between the range of 10.78% and 8.87% (wb) respectively. Noticeably, the fat content ratio (the most important value of cocoa bean) found was over 10%, thus nutritional, pharmacological and industrial importance to man cannot be over emphasized.

Keywords

Theobromine, Cocoa, Proximate Analysis, Ultimate Analysis, Bean Dimension, Chemical Property

1. Introduction

Theobroma cacao L. also known as “the food of the gods” is widely grown in tropical and subtropical areas around the world including in Africa, such as Ghana, Côte d'Ivoire, Cameroon, and Nigeria, in American countries, like Ecuador, Brazil, Mexico, and Columbia, in Caribbean and South

western Pacific countries, such as the Papua New Guinea and Dominican Republic, and in Southeast Asian countries, like Malaysia, Indonesia and Vietnam. Total cacao bean production is estimated worldwide to be about 4.0 million tonnes as at 2013, with a value about \$12 billion [12]. It is very rich in Theobromine also known as xanthose, this is a bitter alkaloid of the cacao plant, with the chemical formula $C_7H_8N_4O_2$ [25].

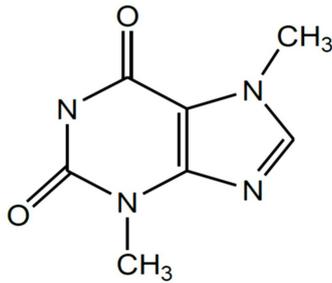


Figure 1. Theobromine Chemical structure [16].

Cacao beans are the source of cocoa, beverages, cocoa butter and chocolate. Fermented beans are roasted, broken and grounded to powdery form in which fat is extracted. Residues or wastes from the cacao processing industry consist of cacao pod shell, pulp/mucilage, husk and hull, which account for a high proportion, approximately 85% by fresh weight of total cacao pod mass [17], this waste is abundant, been considered as inexpensive, and renewable theobromine source, which exhibits stimulatory effects on the gastrointestinal, central nervous, renal, cardiovascular, and respiratory systems [9].

Cocoa is a common raw material in the cosmetics, food and pharmaceutical, industries. Studies have shown that the cocoa bean has flavonoids with antioxidant properties that can the risk of stroke and cardiovascular attacks and reduce blood clot [13]. The crop is very low in cholesterol and a good source of protein, zinc, dietary fibres, potassium and other elements.

The physical properties of cocoa beans (size, mass, sphericity, volume, thickness and length) are factors that influence the quality of beans during the time of transportation, processing and preservation [7]. These factors have been investigated on soya beans [26] date seed [19], avocado seeds [20] and several other seeds.

The knowledge of physical properties provides the basis for avoiding failure in engineering applications and as well design equipments that can handle the wastes generated from cocoa. From an engineering view point, data and information on the physical properties of cocoa beans are necessary in the mechanization of various unit operations involved in the post-harvest processing. It also helps in the development of optimization parameters for efficient and effective processing equipment [8]. Therefore, this study aimed to determine, analyze and compare the physical, proximate, Ultimate and Chemical composition of cacao pod and bean in order to provide adequate levels of nutritional, pharmacological and industrial importance to man.

2. Methodology

2.1. Experimental Location

The experiment was carried out at the Nutrition Laboratory, Department of Animal Production and Health, Federal University of Technology, P.M.B 704, Akure, Ondo state, Nigeria.

2.1.1. Experimental Material

Samples of cocoa pod and bean used for this analysis were obtained from Oja Oba Market in Akure, Ondo State, Nigeria.

2.1.2. Collection of Sample and Preparation

The beans were thoroughly screened to remove the bad ones. The plant materials (Pod and Bean) were identified and authenticated by Nutrition Laboratory, Department of Animal Production and Health, Federal University of Technology, Akure, Nigeria. The identified Pod and bean were cleaned and individually fermented in wooden barrels (6-7 days' duration). After fermentation, the pod and bean were naturally dried under the sun light, varying greatly according to seasons of the year (approximately 30°C in the summer) for 7-8 days. They were subjected to conditioning. In conditioning these beans, they were sorted in group of two and three. Each group was labeled accordingly.

2.1.3. Bean Mass

The dehydrated cocoa pods and beans were randomly selected and weighed on an electronic balance with 0.01g accuracy. The experiments were randomly repeated (5 x 100 random beans) and mean values were calculated [5]. The final values were divided by 100 to acquire the bean mass.

2.1.4. Physical Properties

Length, width, thickness, sphericity, roundness, porosity, mass, true and bulk densities were the physical properties determined in this study. A sample of 100 pods and beans were randomly selected following Dutta procedure [10]. A Vernier caliper reading to 0.01mm accuracy (Stainless Steel Electronic LCD Digital Vernier Caliper Gauge Micrometer 0-6" Range) was used to measure the length, width, Shape, diameter and thickness of each bean.

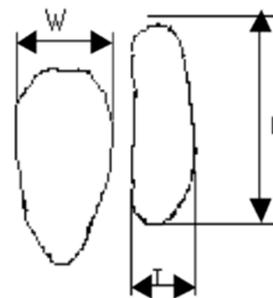


Figure 2. Pictorial view of Cocoa bean's length, width and thickness measurement.

Water displacement method as described by Aviara was used to obtain true density [5]. The size distribution for the fruit was determined by classifying the fruits into large, medium and small after which the percentage average length, width, mass and pulp thickness in each class [22]. Bulk density was determined using the AOAC recommended methods [2-3]. This involved filling a 1500mL cylinder with sample from a height of 15cm and weighing its content. Color was determined by reflectivity and absorptive character using electromagnetic radiation.

Sphericity was calculated by using the data on geometric

mean diameter and the length of the bean.

$$\emptyset = \frac{(LWT)^{1/3}}{L} \quad (1)$$

The porosity (ϵ) was calculated using the values of bulk density and true density as stated by Jain [14].

$$\text{Porosity} = \frac{\text{True Density} - \text{Bulk Density}}{\text{True Density}} \times 100 \quad (2)$$

$$\text{Roundness} = \frac{A_p}{A_c} \quad (3)$$

Where, A_p =Largest projected area of object in natural rest position,

A_c =Area of smallest circumscribing circle.

2.1.5. Frictional Properties

The frictional properties of cocoa pod and bean determined in this study were repose angle and static coefficient of friction. Angle of repose was determined using the procedure employed by Aviara [6]. This involved filling an open ended box of 150×150×150mm in size having removable front panel with sample. The front panel was swiftly detached to allow sample to slide and assumed its natural slope in bulk. The angle of repose was calculated from the depth of the free surface of the sample to the horizontal distance from the side having the free surface. Static coefficient of friction of the cocoa pod and bean was determined on four different structural surfaces namely, galvanized iron sheet, glass, hessian bag, plywood with wood grains perpendicular to the direction of movement and plywood with wood grains parallel direction of movement.

2.2. Analysis of Theobroma Cacao L. Pod and Bean

In analyzing Theobroma cacao L. Pod and Bean, two basic methods were involved; ultimate and proximate analysis. The ultimate analysis covers solid, gaseous and all component elements of the product while proximate analysis covers the fixed carbon, volatile matter and moisture content and ash percentages. Both the ultimate and proximate analysis were carried out at the Department of Animal Production and Health Laboratory, Federal University of Technology, Akure, Nigeria.

2.2.1. Proximate Analysis

Moisture Content Determination

2g of the fresh sample of crude extract of pod and bean were placed in the crucible and heated at 105°C until a constant weight was attained. The moisture content of the pod and bean was calculated as loss in weight of the original sample and expressed as percentage moisture content [2].

2.2.2. Determination of Crude Protein

The crude protein was determined by the Kjeldahl method with slight modification. 0.5g of the powdery form of each sample was digested with 5ml of concentrated sulphuric acid in the presence of Kjeldahl catalyst. The nitrogen from the

protein in the sample was converted to ammonium sulphate that reacted with 2.5ml of 2.5% Brucine reagent, 5ml of 98% sulphuric acid to give a coloured derivative and the absorbance read at 470nm. The percentage nitrogen was calculated and multiplied by 6.25 to obtain the value of the crude protein [22].

2.2.3. Estimation of Crude Fat

The crude fat in the powdered sample was determined using Soxhlet extraction method (AOAC Official Method 920.39) as mentioned by Ogboru [21]. In this extraction method, fat is extracted with petroleum ether. Samples (3.0g) weighed accurately into labeled thimble and 150ml of petroleum ether (boiling point 40-60°C) was taken in a 250ml boiling flasks. The extraction thimbles were plugged tightly with cotton wool. After that, the Soxhlet apparatus was assembled and allowed to reflux for 24hrs. The thimble was removed with care and petroleum ether collected from the top container and drained into another container for re-use. After that, the boiling flask was heated in a hot air oven until it was almost free of petroleum ether. After drying, it was cooled in desiccators and weighed.

2.2.4. Determination of Carbohydrate

The carbohydrate content was calculated using following: available carbohydrate (%), =100-[protein (%)+Moisture (%)+Ash (%)+Fibre (%)+Fat (%)] [27].

2.2.5. Determination of Crude Fiber

The estimation was done using the AOAC standard method [1]. Five grams (5g) of the powdery form of each sample and 200 ml of 1.25% H₂SO₄ were heated for 30mins and filtered with a Buchner funnel. The residue was washed with distilled water until it was acid free. 200 ml of 1.25% NaOH was used to boil the residue for 30 min, it was filtered and washed several times with distilled water until it was alkaline free. It was then rinsed once with 10% HCl and twice with ethanol. It was finally rinsed with petroleum ether three times. The residue was put in a crucible and dried at 105°C in an oven overnight. After cooling in a desiccator, it was ignited in a muffle furnace at 550°C for 90 minutes to obtain the weight of the ash [18].

2.2.6. Ash Content Determination

This was done using the AOAC standard method [1]. The total ash content of a substance is the percentage of inorganic residue remaining after the organic matter has been ignited. 2 g of the pulverized samples was placed in a crucible and ignited in a muffle furnace at 750°C for 6 hours. It was then cooled in a desiccator and weighed at room temperature to get the weight of the ash.

2.2.7. Determination of Volatile Matter

This is the loss in weight of moisture free Powdered sample when heated in a crucible fitted with cover in a muffle furnace at 950°C for 7min.

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight of Moisture free sample}}{\text{Weight of moisture free sample}} \times 100$$

2.2.8. Determination of Fixed Carbon

It is determined indirectly by deducting the sum total of

$$\text{Fixed carbon of sample} = 100 - (\% \text{ moisture} + \% \text{ volatile matter} + \% \text{ ash})$$

2.2.9. Determination of Energy Value

The energy value (kcal) of the samples was estimated by multiplying percentage crude protein, crude lipid and carbohydrate by the recommended factor (3.44, 8.37 and 3.57 respectively) used in vegetable and seed analysis [4].

3. Ultimate Analysis

The ultimate analysis indicates the range of rudimentary chemical constituents such as Carbon, Hydrogen, Oxygen, Sulphur and Nitrogen. It is useful in determining the quantity of air required for combustion and the volume and composition of the combustion gases [21].

3.1. Estimation of Carbon and Hydrogen

This was estimated using the Liebig's method. 5g of the sample was heated in a current of dry oxygen thereby converting C and H of the sample into CO₂ (C+O₂) and H₂O (H₂+1/2O₂) respectively. The products of combustion (CO₂ and H₂O) are passed over weighed tubes of anhydrous calcium chloride and potassium hydroxide which absorb H₂O and CO₂ respectively. The increase in the weight of CaCl₂ tube represents the weight of water (H₂O) formed while increase in the weight of KOH tube represents the weight of CO₂ formed. Percentage of H and C in the sample was calculated as follows:

3.1.1. Carbon

$$\text{Amount of carbon} = \frac{12 \times Z}{44}$$

Since, 44 g of CO₂ is produced from 12g of carbon and 32g of oxygen

$$\% \text{ Amount of carbon} = \frac{12 \times Z}{44 \times x} \times 100$$

3.1.2. Hydrogen

Similarly, amount of hydrogen in the cocoa sample $\frac{12 \times y}{18}$.

Since 18g of water is formed by 2g of hydrogen and 16g oxygen.

$$\% \text{ Amount of carbon} = \frac{12 \times y}{44 \times x} \times 100$$

where: =

x=weight of cocoa sample taken,

y=increase in the weight of CaCl₂ tube

z=increase in the weight of KOH tube

3.1.3. Determination of Sulphur and Oxygen

10g of cocoa bean and pod were heated with Eschka mixture (which consists of 2 parts of MgO and 1 part of

moisture, volatile matter and ash percentage from 100%.

anhydrous NaCO₃) at 800°C. The sulphate formed was precipitated as BaSO₄ (by treating with BaCl₂) and the Sulphur in cocoa was computed as follows:

32g Sulphur in the sample pod and bean will give 139g and 256g BaSO₄ respectively.

Amount of sulphur in the pod and bean = $\frac{32y}{139} = 0.2302y$
and $\frac{32y}{256} = 0.125y$ respectively

% of sulphur in the pod and bean = $\frac{100}{x} \times 0.2302y$ and $\frac{100}{x} \times 0.125y$ respectively

where: x=weight of cocoa pod and bean sample taken

y=weight of BaSO₄ precipitate formed.

oxygen was deduced indirectly as follows:

% oxygen in cocoa pod and bean = 100 - (% C + H + N + S + Ash)

3.1.4. Determination of Nitrogen

Micro Kjeldahl method was used to determine the nitrogen content of cocoa pod and bean along with 10cm³ of concentrated H₂SO₄ and pipetted with 5cm³ of 2% boric acid [24].

3.2. Determination of Mineral Composition

The minerals investigated were phosphorus, calcium, magnesium, potassium, sodium, Zinc, Silicon, Aluminum, chlorine, Sulphur, Hydrogen and Iron. Phosphorus, potassium, sodium, chlorine, Sulphur, Hydrogen were determined using Jaway digital flame photometer, while iron was determined using the Spectrophotometric method. Other Element such as Al, Ca, Fe, Mg, Si, and Zn were analyzed with a Perkin-Elmer 2001 Model Inductively Coupled Plasma-Optic Emission Spectrometry (ICP-OES).

4. Result and Discussion

Statistical Analysis

Statistical analysis was carried out to obtain the means and standard deviation of the triplicate results obtained from both analyses while hypothesis was tested using t-test statistics to compare means at 5% alpha level between the cocoa pod and bean. SPSS Version 16 was used for this analysis.

Physical Properties

Table 1. Effect of sample treatments on physical properties of cocoa pod and bean.

Parameters	Unit	Pod	Bean
Moisture content	(% d. b)	51.39±0.57	87.65±0.27
Width	(mm)	2.46±0.18	12.76±1.08
Length	(mm)	2.11±0.41	19.78±2.00
Thickness	(mm)	13.54±3.01	8.41±1.06
Sphericity	%	32.75±0.13	2.40±1.03
Roundness	%	3.04	3.72
True density	(g cm ⁻³)	78.82	97.34
Colour		Yellowish green	Brown
Mass	(g)	0.19	1.94

Parameters	Unit	Pod	Bean
Bulk density	(g cm ⁻³)	26	65
Porosity	(%)	0.67	0.33
Coefficient of static friction			
Glass		0.67±0.04	0.91±0.11
Plywood		0.25	0.76
Galvanized iron steel		0.62	3.12
Surface area	(mm ²)	700.04	1030.11
Repose Angle	(°)	14.53	51.47

Each value represented mean ±SD of n=3.

Table 2. Result of Proximate and Ultimate Analysis of cocoa pod and bean in %.

Parameters	Pod	Bean
Proximate Analysis		
Mineral Ash	10.78±0.03	8.87±0.02
Volatile Matter	6.26± 0.12	12.32±0.05
Fixed Carbon	7.58± 0.03	23.17±0.02
Crude Fibre	16.01±0.06	20.31±0.10
Crude Fat	3.86± 0.03	6.62±0.11
Moisture Content	51.39±0.57	87.65±0.27
Crude Protein	11.19±1.23	13.38±0.92
carbohydrate	6.77±0.07	15.67±0.10
Calorific value	120±11.01	187.98±6.01
Ultimate Analysis		
Total Carbon	7.83±0.01	35.49±0.03
Hydrogen	0.60±0.03	2.15±0.04
Oxygen	70.69±0.07	44.95±0.10
Sulphur	11.51±0.06	6.25±0.50
Nitrogen	1.54±0.08	2.29±0.04

Each value represented mean ± SD of n=3

Table 3. Mineral analysis of cocoa pod and bean in mg/100g.

Parameters	Pod	Bean
Macro minerals		
Pottasium	65.75±0.51	93.970.26
Sodium	15.95±0.75	28.49±0.34
Magnesium	25.24±0.28	34.56±0.29
Phosphorus	254.34±0.04	479.29±0.04
Calcium	4.38±0.71	3.30±0.48
Micro minerals		
Copper	0.11±0.04	0.60±0.04
Iron	2.96±0.11	3.21±0.19
Silicon	ND	ND
Aluminum	ND	ND
Zinc	±0.31	18.44±0.45

Each value represented mean ± SD of n=3 ND=Not Detected.

Table 4. T-test of means for Proximate, Ultimate and mineral Analysis of cocoa pod and bean.

Sample	Mean	T-Test Value	Df	Remark
Proximate Analysis				
Bean	X1	0.377	12	NS
Pod	X2			
Ultimate Analysis				
Bean	X1	0.0011	12	NS
Pod	X2			
Mineral Analysis				
Bean	X1	2.516**	12	S
Pod	X2			

NS: Not significant x1=Means of bean Proximate parameters, X2=Means of pulp Proximate parameters, **=Significant at 5%.

5. Discussion

Table 1 shows the effect of sample treatments on physical properties of *cocoa pod and bean*. The moisture content of the bean (87.65±0.27% d b) was found to be higher than that of the pod (51.39±0.57% d b). Three major dimensions i.e. length, width and thickness of the bean and pod were determined. For bean, average values of W, L and T were 12.76±1.08mm, 19.78±2.00mm and 8.41±1.06mm while 2.46±0.18mm, 2.11±0.41mm and 13.54±3.01mm for the pod respectively. The pod has higher values in thickness and sphericity (13.54±3.01 and 32.75± 0.13mm), Cocoa bean is small in size, which resulted in lesser values of sphericity. The static coefficient of friction on various surfaces, namely, glass, plywood, galvanized iron steel also increased linearly with increase in moisture content. The bean has the highest static coefficient of friction and Angle of repose on all the surfaces.

Table 2 represents the proximate and Ultimate analysis of the sample pod and bean. It shows that the bean has the highest amount in all the proximate and Ultimate analysis assayed except in moisture, oxygen and sulphur where the pod has 10.78±0.03, 70.69±0.07 and 11.51±0.06 respectively. In the investigated samples, the bean of cocoa yielded the highest fat of 6.62±0.11 than the pod. This implies that it is an oily fruit and the dietary fat quality can exert a protective effect on cardiovascular diseases. The consumption of foods rich in monounsaturated fatty acids (MUFA), dietary fibers, and antioxidants has been associated with lipid profile improvement and body weight loss as reported by Silva Caldas [23].

The ash content was very little (10.78±0.03 g/100g) in the pod and much lesser in the bean (08.87±0.02g/100g). It shows that the bean and pod can hinder the growth of micro-organism. Fahimdanesh had similar results in the Ash content of Iranian Mango Seed [11]. All of this in accordance with the T-test of means for Proximate, Ultimate and mineral Analysis of cocoa pod and bean as presented in Table 4. The richness of cocoa in percentage oxygen is in the Pod (70.69±0.07) as the bean could only hold 44.95±0.10%. This is just about 20-fold increase in percentage of oxygen in Pod than in bean, comparable to the work done by Ogboru on *Irvingia gabonensis* [21]. Table 3 shows the Mineral analysis of *cocoa pod and bean* in mg/100g. Result showed the presence of Na, K, Mg, Ca, Fe, P, Cu and Zn in bean and Pod assayed. These important minerals are found in the theobromine which is used to make chocolate which are needed by living cells for proper functional activities in the body. These essential minerals help to fight against ailments like cancer. Lack and inadequate Potassium, Sodium and Zinc have been associated with poor electrolyte balance of blood fluid and distorted activities of enzymes [22]. According to an article in the Chicago Sun Times, people who suffer extreme depression as victims of unrequited love have an irregular production of phenylethylamine. Such individuals often go on chocolate binge during periods of depression. Chocolate is particularly high in

phenylethylamine, perhaps serving as medication.

Aside from Calcium that was higher in the bean ($4.38 \pm 0.71 \text{ mg/100g}$), the other minerals were higher in the pulp. All of this is also confirmed in the T-test of means for Proximate, Ultimate and mineral Analysis of *cocoa pod and bean* as presented in Table 4. It is imperative to note that the Pod that is low in sodium makes it a nutritionally ideal source of dietary sodium for hypertensive patients and acts as cardiovascular stimulant with diuretic and bronchial smooth muscle relaxant properties. It helps in preventing and treating apnea in premature infancy [11]. The potassium in cocoa is needed to keep cell water balanced, helps in retaining proper body pH and useful in carbohydrate and protein metabolism and also reduces blood pressure to approximately 3.2 mmHg, thereby reducing death cases by over 7% [22]. The bean contains good amount of calcium, a mineral known to be very important in bone formation and other physiological systems in the body. The result also shows that cocoa contains relatively low level of Iron ($3.21 \pm 0.19 \text{ mg/100g}$) in Pulp and was not detected in the bean. The relatively low level of iron in cocoa in general prevents being prone to liver failure that is connected with high amount of iron in the body [22].

6. Conclusion and Recommendation

Physico-Chemical and Mineral component of Cocoa (*Theobroma cacao L.*) Pod and Bean has shown that cocoa contains proximate, ultimate and essential minerals that are useful for man when consumed or used industrially. The physical properties study could provide data used in the design of mechanical, storage, handling and processing equipment. Generally, the bean contains higher level of these materials than the pod which makes it nourishing to man. The results of this study will highly inspire people to utilize cocoa seed in food preparation particularly beverage product. so, one of the most convenient ways to utilize cocoa seed is to prepare beverages which can help to minimize protein malnutrition among the people in a developing country like ours.

Conflict of Interest

The authors declare that they have no conflict of interest.

Acknowledgements

The Authors would like to acknowledge the Laboratory Technologists in the Nutrition Laboratory, Department of Animal Production and Health, Federal University of Technology, Akure, Ondo state, for their technical assistance in the analysis of this study.

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