al Kimiya: Jurnal Ilmu Kimia dan Terapan
p-ISSN: 2407-1897, e-ISSN: 2407-1927
Vol. 12, No. 1 (54-61), June 2025/Muharram 1447

EFFECT OF COPPER-BASED FUNGICIDE ON CHEMICAL COMPOSITION OF COCOA SEEDS

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Article Information

Received: Jan 29, 2025
Revised: May 05, 2025
Accepted: Jun 16, 2025
Published: Jun 30, 2025

DOI:
10.1557/ak..v12i1.43696

Keywords:
Chemical Composition; Cocoa; Copper-based Fungicide; Proximate Analysis

Abstract

Production of cocoa seeds, one of Nigeria's major non-oil foreign exchange earners as well as a major raw material for the beverage industry, is greatly hindered by diseases caused by various species of the genus Phytophthora. To avert this, copper-based fungicides are sprayed on the leaves of cocoa trees to control or prevent the survival of this organism by the farmers without paying attention to the effects of this chemical on the proximate composition of cocoa seeds. This study, therefore investigated the effects of a copper-based fungicide (Ridomil Gold Copper) on the quality of the cocoa seeds by spraying cocoa trees, including the pods, with 50.00 g/L of copper-based fungicide. The results obtained showed that cocoa seeds from the control trees showed significantly higher contents of fiber (4.51%), protein (15.1%), and fat (36.1%) when compared to the respective values of 3.45, 3.95, and 7.59% obtained for the cocoa seeds harvested from the fungicide-treated cocoa trees. All other proximate compositions did not show any statistical difference, except for carbohydrate and calorific values, which were significantly higher in cocoa seeds from fungicide-treated cocoa trees. Seeds from fungicide-treated trees showed significantly higher potassium, phosphorus, and magnesium contents but lower zinc and copper contents. However, phytochemicals such as phenols, alkaloids, flavonoids, and tannins were significantly lower in content in the seeds of fungicide-treated cocoa trees. The contents of glycosides and antioxidants in the cocoa seeds were statistically similar for both the control and treatment, except for ascorbic acid, which showed a significantly lower value (4.8 mg/100 ml) in cocoa seeds from fungicide-treated cocoa trees, compared with the value recorded for the control in this study (13.33%). The foregoing results showed that the use of copper-based fungicides for the control of black pod disease in cocoa adversely affected the quality of cocoa seeds from the treated trees.

INTRODUCTION

Cocoa (*Theobroma cacao L.*), is the primary raw material for numerous chocolate industries and is one of the most significant cash crops in the majority of the nations in the West and Central African sub-regions (primarily Cote d'Ivoire, Ghana, Nigeria, and Cameroon). Nigeria is the world's fifth-largest producer of cocoa behind Cote d'Ivoire, Ghana, Indonesia, and Cameroon [1]. In terms of generating foreign exchange, generating revenue at the national level, and generating revenue for socioeconomic provision, cocoa as a crop boosts the economy of the nation where it is grown [2]. In Nigeria, cocoa plantations employ 300,000 farmers and the purchase of 800,000 hectares of land. Nigeria produced 328,263 tons of cocoa in 2017, which made up around 2% of the nation's exports. Ondo, Ogun, Osun, Oyo, and Ekiti are the cocoa-growing regions, and they account for 60% of the nation's total production [3]. Before 1970, Nigeria was the second-largest producer of cocoa in the world, but this position fell on account of significant amounts of crude oil that were discovered [4].

The main problems facing cocoa seed production are pests and diseases, with Phytophthora pod rot or "black pod" being the most serious cocoa disease in Nigeria [5]. The disease is caused by Phytophthora palmivora and Phytophthora megakarya [6]. The majority of fungicides used in Nigeria to treat this disease are copper-based fungicides [7]. Long-term usage of this fungicide has led to copper contamination of numerous cocoa farms across the country because soil microorganisms are unable to degrade copper

[8]. By the interaction between humic compounds and the oxides of Cu, Sn, and Fe, metal binding is a common occurrence in soil [9]. These heavy metal fractions, Fe, Sn, and Cu, along with their integrated oxides and organic matter complexes, are thought to comprise the active component [10].

However, it has been shown that, for heavy metals, the most bioavailable and active forms are those that are exchangeable and soluble in water [11]. The term "bioavailability" refers to the chemicals released to living receptors, such as plant roots, from a medium of interest [12]. When soil has a high concentration of bio-available metals, it has a propensity to accumulate in the cocoa seeds, which will lower the quality of the product on the global market [13]. Spraying copper-based fungicides on cocoa plants for the treatment or control of black pod disease is another practical way for copper to reach the cocoa seeds [14]. This study was aimed at determining the impact of copper-based fungicides on the nutritional and phytochemical compositions of cocoa seeds harvested from the treated trees.

EXPERIMENT

This Study Area

This research was conducted in Adejubu town situated between Longitude 5°.5’1’’ – 5° 29’39’’ E and Latitude 7°3’40 – 7°26’38’’ N in the Southeast of Akure North. It is bordered by Imafon District to the south and Baba-Sale District to the north. Adejubu town has several locations of lowlands and rough mountains with granite outcrops.

Field Work

The fieldwork was conducted on two cocoa farms; one farm was used for the control experiment, while the other farm was sprayed with copper-based fungicide (Ridomil Gold Copper). To carry out the study, twenty (20) cocoa trees were chosen randomly on each of the farm sites. Twenty cocoa trees were treated with a copper-based fungicide on the experimental or treatment farm site, while twenty trees were not sprayed with a copper-based fungicide on the control farm site. The research work was carried out between July and October 2022.

Mineral Analysis

The procedures of the Association of Official Analytical Chemists [15], were employed to determine the mineral content. Atomic absorption spectroscopy was used to determine the concentrations of Mg, Cu, Mn, Fe, Co, and Zn, while the concentrations of Ca, K, and Na were determined in triplicate using a flame photometer.

Proximate Analysis

AOAC procedures were followed for the proximate analysis (moisture, ash, fat, protein, and carbohydrate content, respectively) [16]. The thermogravimetric method was used to determine the content of ash and moisture; the Kjeldahl technique and oxhlet extraction technique were used to determine the protein and fat contents, respectively, while the amount of carbohydrates was calculated by difference. All analysis were carried out in triplicate.

Quantitative Phytochemical Analysis

Using standard protocols as stated by S. O. Oyedemi et al. (2010), the alkaloids, glycosides, saponins, phenols, flavonoids, and tannins contents of the cocoa seeds were determined [17].

Statistical Analysis

Data were analyzed by Analysis of Variance using Statistical Package of Social Sciences (SPSS) software version 20.0. Means were separated using Duncan Multiple Range Test (DMRT) at 5 % level of probability.

RESULT AND DISCUSSION

Effect of Copper-based Fungicide on Proximate Composition of Cocoa Seeds

As shown in **Table 1**, significant differences were observed in all the proximate compositions except for moisture and ash in this study. The recorded values for moisture and ash were higher in the cocoa seeds that were not sprayed with copper-based fungicide (control). The crude fiber, fat, and protein in the control had respective values of 4.61%, 36.10%, and 15.10% % which were statistically higher when compared to values recorded in the cocoa seeds from copper-based fungicide-treated cocoa trees. The fungicide-treated cocoa seeds had fat and protein content of 7.59% and 3.95% respectively, which can be considered to be extremely low compared to the control, 36.10% and 15.10%, respectively. Cocoa seeds from cocoa trees sprayed with copper-based fungicide had a carbohydrate value (56.00%) that was significantly greater than that recorded for cocoa seeds from the untreated cocoa trees (14.5%). The results of calorific value followed the same pattern as recorded for the carbohydrate content.

Table 1. Proximate composition of cacao seeds as influenced by copper-based fungicide.

Proximate	Treatment (%)		t-test value
	Control (0.00)	Copper-based fungicide (50.00)	
Moisture	25.60±0.09^{a}	25.30±0.04^{a}	0.088
Ash	4.02±0.05^{a}	3.62±0.11^{a}	0.199
Crude fibre	4.61±0.04^{a}	3.54±0.07^{b}	0.004
Crude fat	36.10±0.06^{a}	7.59±0.03^{b}	<0.001
Protein	15.10±0.05^{a}	3.95±0.03^{b}	<0.001
Carbohydrate	14.54±0.08^{b}	56.00±0.19^{a}	<0.001
Energy (Kcal)	516.17±0.77^{b}	588.24±1.56^{a}	<0.001

Data were expressed as means ±SE of three replicates. The means within a row followed by the same superscripts are statistically the same at $p \leq 0.05$

Effect of Copper-based Fungicide on Macro - and Microelements Present in Cocoa Seeds

The effect of copper-based fungicide on the presence of macro and microelements in cocoa seeds is presented in **Table 2**. Spraying of copper-based fungicide significantly enhanced the contents of potassium (34.00 ppm), phosphorus (12.39 ppm), and magnesium (3.52 ppm), respectively, when compared to those recorded for the control (**Table 2**). A significant difference was observed in the contents of magnesium, potassium and phosphorus, while there was no significant difference in the calcium content of cocoa seeds in this study. Microelements such as copper, sodium and zinc were significantly higher in content in the cocoa seeds from the control than those in the seeds from treated cocoa trees. A significant difference was observed in the contents of copper and zinc, while all the other micro-elements did not show any statistical difference at $p \leq 0.05$. It should be noted that though the presence of cobalt was investigated in this study, it was absent in the cocoa seeds from both the treatments and controls.

Effect of Copper-based Fungicide on Phytochemical Constituents of the Cocoa Seeds

The phytochemical constituents of cocoa seeds as affected by spraying of copper-based fungicide are presented in Table 3. Phenol is the highest phytochemical found in the copper-based fungicide-treated seeds, with a value of 11277.68±436.53 µg/ml and 14252.32±145.71 µg/ml in control and treated cocoa seeds, respectively. This was followed in decreasing order of magnitude by those of tannins (1858.55±8.73 and 1210±0.91 µg/ml), flavonoids (1291.30±39.97 and 676.81±39.97 and 676.81±7.23 µg/ml), saponins (0.426±0.053 and 0.399±0.05 µg/ml) and glycosides (0.418±0.67 and 0.380±0.01 µg/ml) (**Table 3**). Alkaloids showed the lowest quantity when compared to other phytochemicals (**Table 3**). A significant difference was observed in alkaloids, saponins, phenols, flavonoid and tannin content of the copper-based fungicide-treated seeds, while all other phytochemicals such as glycosides and saponins did not show a significant difference in this study. Phytochemicals such as flavonoids, tannin and alkaloids in cocoa seeds from the control plants showed values that were significantly higher than those recorded from seeds whose plants were sprayed with copper-based fungicide.

Effect of Copper-based Fungicide on Vitamins Content of Cocoa Seeds

As shown in **Table 4**, the ascorbic acid content of cocoa beans was found to be higher compared to lycopene and beta-carotene content in this study. A closer look at the data indicated that the use of copper-based fungicide had an adverse effect on the accumulation of the vitamins that were determined. Cocoa seeds obtained from the control plants showed a significant amount of ascorbic acid (13.33 g/L), lycopene (0.22 g/L) and beta-carotene (0.33 g/L), compared to those recorded in cocoa seeds from trees sprayed with a copper-based fungicide, 4.80, 0.15 and 0.20 g/L, respectively.

Table 2. Macro and microelements of cocoa seeds as influenced by copper-based fungicide.

	Elements	Treatment (g/L)		t test – value
		Control (0.00)	Copper-based fungicide (50.00)	
Macroelements	Mg	3.13±0.05^{b}	3.52±0.01^{a}	<0.003
	Ca	0.10±0.01^{a}	0.11±0.01^{a}	0.225
	K	26.00±1.00^{b}	34.00±2.00^{a}	<0.005
	P	10.97±0.08^{b}	12.39±0.17^{a}	<0.010
Microelements	Cu	1.69±0.07^{a}	0.22±0.01^{b}	<0.001
	Mn	0.30±0.00^{a}	0.30±0.00^{a}	0.432
	Fe	0.35±0.01^{a}	0.05±0.00^{a}	0.386
	Na	3.24±0.19^{a}	2.52±0.17^{b}	0.071
	Co	0.00±0.00^{a}	0.00±0.00^{a}	-
	Zn	1.70±0.07^{a}	0.87±0.03^{b}	<0.001

Data were expressed as means ±SE of three replicates. The means within a row followed by the same superscript are statistically the same at p≤0.05.

Table 3. Phytochemical constituents (µg/ml) of cocoa seeds as influenced by copper-based fungicide.

Phytochemical	Treatment g/L		t- test value
	Control (0.00)	Copper-based fungicide (50.00)	
Alkaloids	0.182±0.03^{a}	0.084±0.04^{b}	<0.001
Glycosides	0.418±0.67^{a}	0.380±0.01^{a}	0.631
Saponins	0.426±0.03^{a}	0.399±0.05^{a}	0.010
Phenols	11277.68±436.53^{b}	14252.32±145.71^{a}	0.010
Flavonoids	1291.30±39.97^{a}	676.81±7.23^{b}	0.003
Tannins	1858.55±8.73^{a}	1210.45±0.91^{b}	<0.001

Data were expressed as means ±SE of three replicates. The means within a row followed by the same superscript are statistically the same at p≤0.05.

Table 4. Vitamins (mg/100ml) of cocoa seeds as influenced by copper-based fungicide

Vitamin	Treatment (g/L)		t-test value
	Control (0.00)	Copper-based fungicide (50.00)	
Ascorbic acid	13.33 ± 0.67^{b}	4.80 ± 0.40^{b}	0.002
Lycopene	0.22 ±0.001^{a}	0.15 ± 0.0007^{a}	<0.001
B- carotene	0.33 ±0.02^{a}	0.20 ± 0.0004^{a}	0.011

Data were expressed as means ±SE of three replicates. The means within a row followed by the same superscript are statistically the same at p≤0.05

Discussion

The proximate composition analysis showed that the percentage moisture content in the control seeds was higher than that of the treated seeds. The percentage moisture content obtained in this study (25.30±0.04%), disagrees with the results of M. Djali et al. (2023), who reported moisture content of 14.14 % in fresh cocoa and 7.86% in roasted cocoa as well as those of E. I. Adeyeye (2013) and E. O. Afoakwa et al. (2013), who reported an average of 4.43% and 6.65% in unfermented cocoa and natural cocoa powder respectively [18-20]. Excessive moisture content can make a cocoa seed lose its flavor and deteriorate because it is hygroscopic in nature22.

The percentage ash content in the control seeds is numerically higher than that of the treated seeds, which aligns with the reports of E. O.

Afoakwa et al (2013) and M. Djali et al (2023), who reported 4.27 % and 3.2%, respectively. The percentage of crude fiber in the experimental seeds is lower than that of the control seeds. The level of crude fat as reported in this study disagrees with the reports of E. O. Afoakwa et al. (2013) who reported an average crude fat of 53.33%, but aligns with M. Djali et al. (2023), who reported an average crude fat of 4.20% in fresh cocoa [18][20].

The percentage of crude fat reported in this study disagrees with the study of E. I. Adeyeye (2013), who reported 14.5 % [19]. The percentage of carbohydrates as reported in this study aligns with that of M. Djali et al. (2023), who reported an average carbohydrate of 43.26% in fresh cocoa, and that of E. I. Adeyeye (2013), who also reported 48.9% carbohydrate content in natural cocoa powder, while it disagrees with the results of E. O. Afoakwa et al. (2013), who reported an average carbohydrate content of 18.43% in unfermented cocoa. Carbohydrate plays a vital role in the building up of energy [18-20]. It also provides immediate energy unlike other classes of food [20]. The crude protein content observed in this study disagrees with the study of E. O. Afoakwa et al. (2013), who reported an average protein content of 20.63%. This is an indication that the copper-based fungicides might interfere with the accumulation of protein in the seeds [21].

The components present in the growing soil and the potential availability of nutrients from the application of different fungicides during the growth process have a significant impact on the presence of macro and microelements in cocoa [22]. Potassium was the most abundant mineral in cocoa seeds in this study as compared to the other minerals. This observation goes in line with the reports of E. O. Afoakwa et al. (2013). The presence of micronutrients is necessary for the maintenance of certain physiochemical processes that are essential to life [23].

The concentration of calcium reported in this study disagrees with the studies conducted by E. I. Adeyeye (2013), A. Assa (2019), and E. O. Afoakwa et al. (2013), who reported concentrations of 1.02, 2.34 and 145.58 mg/100g, respectively [19] [20] [22]. Calcium works as a constituent of bone and teeth, a source of regulation of nerve and muscle function. It is necessary for the conversion of prothrombin to thrombin during blood coagulation. The concentration of phosphorus observed in this study is higher than what was reported by E. I. Adeyeye (2013), who reported 5.80 mg/100 g in natural cocoa powder, but lower than the concentration reported by E. O. Afoakwa et al. (2013), who reported an average concentration of 293 mg/100g in unfermented cocoa seeds. The potassium content reported in this study is far lower than that of E. O. Afoakwa et al. (2013), who reported 2,347.73 mg/100 g, but higher than the concentration of 2.39 mg/100 reported by A. Assa et al. (2019) [19] [20] [22]. Potassium helps in acid-base balance, regulation of osmotic pressure, conduction of nerve impulses and muscle contraction and it also helps in glycogenesis. High potassium content leads to dilation of the heart, cardiac arrest, small ulcers, paralysis, and muscular weakness [24].

Potassium and phosphorus have the highest concentrations in this study, with the concentration of potassium being twice as much as that of phosphorus (Table 2). The concentration of magnesium obtained in this study aligns with the report of E. I. Adeyeye (2013) who also reported a concentration of 3.13 mg/100 g, but disagrees with a concentration of 286 mg/100 g reported by E. O. Afoakwa et al. (2013) [19-20].

A potent class of substances found in plants' secondary metabolites, phytochemicals contain a wide variety of chemical substances like polyphenols, saponins, tannins, flavonoids, alkaloids and glycoside [25]. Phytochemical analysis (Table 3), shows that the percentage of glycoside in the control seeds is higher than that of the experimental bean. The concentration of tannin in the control seeds is greater than that of the experimental seeds. There is a higher percentage of alkaloids and saponins in the control seeds than in the treated seeds. These results are in agreement with those of P. Kumah et al. (2023); they also reported higher percentage of phenols in ethylacetate-purified cocoa leaf extracts, compared to the other phytochemicals [26]. Saponin helps to reduce blood cholesterol and it is used as an antioxidant, helping to reduce the risk of cancer [27].

The level of Vitamin C in the control seeds is higher than that of the treated seeds. High levels of Vitamin C leads to bleeding of the gum. Vitamin C is an essential nutrient that helps to repair worn-out tissues and production of certain enzymes [28]. The concentrations of lycopene and β-carotene in the control seeds were higher than those in the treated seeds. These results align with the results of Nascimento da Silva et al. (2014), who reported 10.90 mg/L of ascorbic acid in cocoa honey [29].

This further indicated that the consumption of cocoa beans treated copper-based fungicide might limit the functionality of these chemicals as potential antioxidants that help to protect humans against heart disease and certain types of cancer. P. E. Aikpokpodion et al. (2010), also reported that the excessive presence of copper can cause oxidative stress in plants and also cause an increase in antioxidant response due to increased production of highly toxic oxygen free radicals [30]. Thus, at high concentrations, copper can become extremely toxic resulting in the yellowing of leaves and premature death of cells in the living tissues of young plants. At the cellular level, toxicity may result from the binding to sulfhydryl groups in proteins.

CONCLUSION

The finding of this study has established that copper-based fungicide (Ridomil gold copper) may not necessarily lead to the accumulation of copper in cocoa beans but may adversely affect the quality of cocoa beans in terms of limiting the ash, fiber, protein, fat, vitamins and mineral elements and the majority of phytochemical constituents that have tremendous advantage in the normal functioning of a human being.

ACKNOWLEDGEMENT

Briefly describe the people/institutions involved and supporting the research. For example: financing or contributing the results of the analysis, and others.

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