Available online free at www.futurejournals.org

The Future Journal of Agriculture

Print ISSN: 2687-8151 Online ISSN: 2687-8216

Future Science Association

Future J. Agric., 4 (2021) **10-19** **OPEN ACCES**

DOI: 10.37229/fsa.fja.2021.12.15

COCOA AND COCOA BUTTER

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ABSTRACT: Cocoa is a source of biologically active compounds, especially flavonoids such as epicatechin, catechin and procyanidin monomers, which positively affect health and aging, reduce the risk of chronic diseases such as cardiovascular diseases, metabolic disorders and cancer, as well as containing it vitamins, minerals, fats, proteins, stimulants and organic acids. Cocoa trees are classified into Forastero, Criollo, Trinitario and Nacional, differing from each other in the shape and color of the pods, the type and flavor of the cocoa produced from them, with different chemical composition. Fermentation, drying, roasting and alkalization are the most commonly used processing steps in the cocoa industry. Depending on the alkaline treatment, different types of modified and natural cocoa powders are produced that differ among themselves in color, taste, solubility and purpose of use. They may be used in the manufacture of many types of chocolate, including milk, dark and white chocolate, Nutella, cakes, pastries, hot drinks, ice cream and others. Cocoa butter is produced from a mixture of saturated (palmitic and stearic) and unsaturated (oleic) fatty acids. Its quantity and its melting or hardening properties depend on the type of cocoa bean, fermentation and drying conditions and environmental conditions.

Key words: Cocoa, butter, industry, fermentation, drying, roasting, alkalization.

INTRODUCTION

The cultivation of cacao trees dates back to the Mayan and Aztec tribes of Central America 2000-4000 years before the arrival of the Spaniards in South America **(Powis *et al.*, 2011)**, the scientific name of the cocoa tree Theobroma cacao, the scientific name of the cocoa tree Theobroma cacao, gained importance that became known as the gods' foods **(De Souza *et al.*, 2018)**. Its almond-like kernels are used in the cocoa and chocolate industry, while the color of flowers are pink to white and smell good. The cocoa tree tolerates various hot and dry weather conditions, and is one of the most important crops in the world that has a high economic value, as it contains a stock of biologically active substances useful in medicine and natural therapy **(Voora *et al.*, 2019)**.

Cocoa beans types

1- Forastero is one of the most cultivated types of cocoa beans, representing 95% of the world production, and the regions of Southeast Asia, West Africa and Brazil are the main production centers. The cocoa tree gives this species a higher yield of cocoa beans compared to criollo. The resulting cocoa is characterized by its mild bitter taste, strong flavor and pleasant taste that remains for a short time, so it is used in the manufacture of chocolate **(Afoakwa *et al.*, 2012)**.

2- Criollo is widely cultivated in South and Central America, Ecuador and Venezuela. The cocoa beans of this type occupy the highest rank in the world markets, because of their preferred flavor over the rest of the cocoa beans, and because of their meager production, which represents 5% of global production, the resulting cocoa is characterized with its complex, nutty and flowery flavour, it stays in the mouth for a longer time **(Rusconi and Conti, 2010)**.

3- The Trinitario is a cross between Criollo and Forastero, with colorful horns.

4- Nacional is grown in Ecuador. It has distinctive flavor and aroma characteristics, but it is less cultivated and represents 5% of the world production. Varieties of this species are currently rare **(Afoakwa *et al.*, 2008)**. It can be said that all cocoa produced in the last five decades is of the Forastero or Trinitario species **(Fowler, 2009)**.

The chemical composition of cocoa beans

The chemical composition of cocoa beans varies according to its type and cultivation conditions. Raw cocoa beans contain vitamins A, B1, B2, B3, C, E, D, pantothenic acid and minerals such as magnesium, calcium, iron, phosphorous, zinc, copper, potassium and manganese. It also contains fats, which are the highest reliable indicator in determining the price of cocoa **(Afoakwa *et al.*, 2013)** and are in the form of saturated fatty acids such as palmitic and stearic acids and unsaturated ones such as oleic acid, in addition to containing proteins that in form amino acids such as Phenyl ethyl amine and Tyramine. Tryptamine and serotonin, which decrease during roasting, due to microbiological and enzymatic reactions **(Bertazzo *et al.*, 2011)** and due to non-enzymatic Maillard reactions **(Torres-Moreno *et al.*, 2021)**. It is increased through the interactions of Maillard **(Marseglia *et al.*, 2020)**, as well as containing flavonoids as antioxidants and stimulants such as theobromine, caffeine, and serotonin, and organic acids such as citric, acetic, succinic and malic, the following table shows the amount of theobromine in cocoa and its products.

Table 1. Amount of theobromine in cocoa and its products

Type	Theobromine component mg/ml
Cocoa	**20.3**
Cocoa beans or seeds	**0.695**
Chocolate baked goods	**1.47**
Chocolate decorations	**1.95**
Cocoa drinks	**2.66**
ice cream	**0.621**
Chocolate milk	**0.226**

Craig and Nguyen (1984)

Bioactive Compounds in Cocoa

The bioactive compounds in cocoa include polyphenols and methylxanthines as shown in Figure (1).

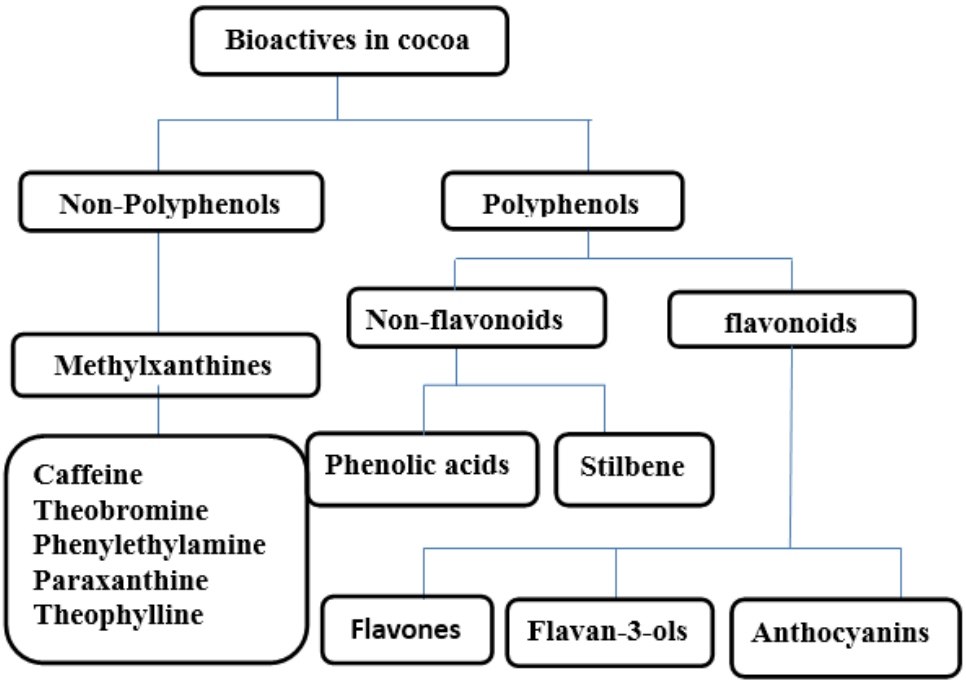

Figure 1. Bioactive Compounds in Cocoa (Massaro *et al.*, 2019)

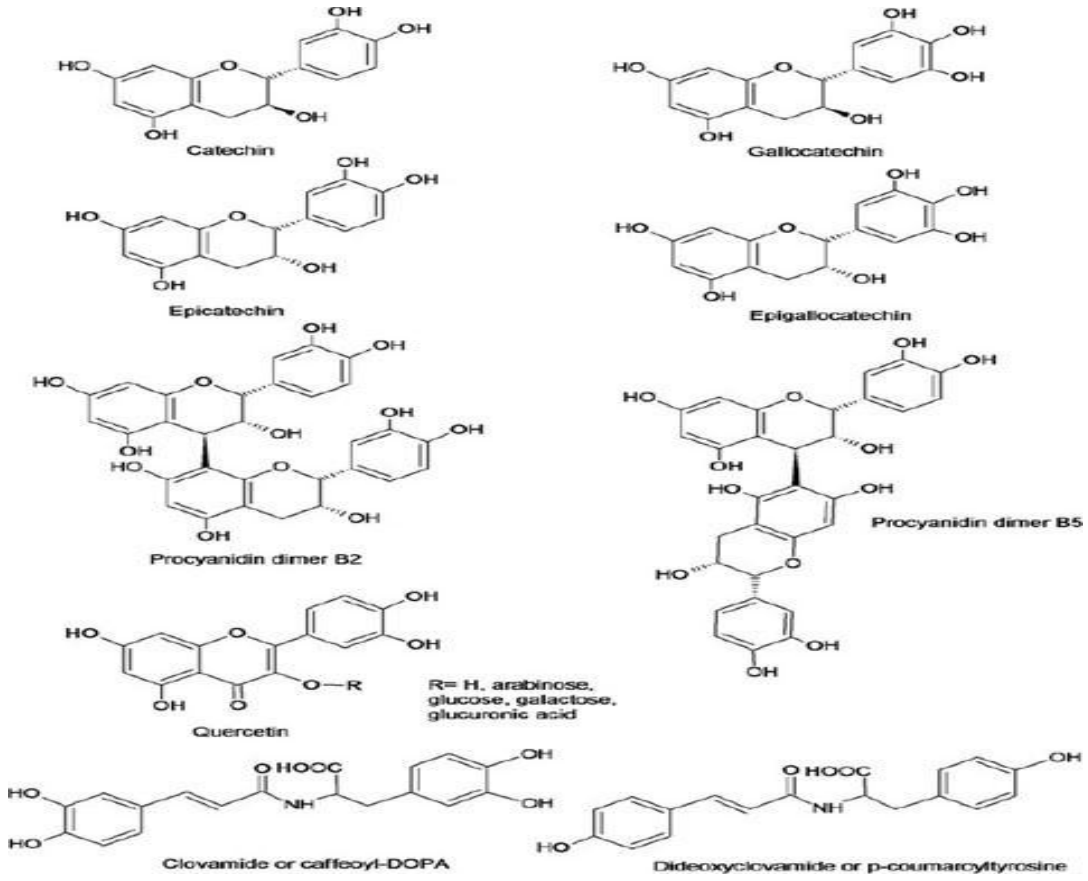

Figure 2. The chemical structure of the types of flavanols (Poli *et al.*, 2012)

Cocoa powder manufacturing process

Picking cocoa pods and fermenting the beans

Cocoa pods are harvested, opened, stacked and left for 24-36 hours to start the fermentation process in an anaerobic phase Cereals are exposed to many microorganisms, including yeasts, lactic acid bacteria, acetic acid bacteria, bacilli and fungi. The main types that control in the fermentation process are Hanseniaspora guilliermondii, Pichia kudriavzevii, Kluyveromyces marxianus, Lactobacillus plantarum, L. fermentum lacticacid bacteria, Acetobacter pasteurianus and Gluconobacter frateurii aceticaci **(Zhao and Fleet, 2014)**. Sucrose, glucose and fructose from acid (pH less than 4) pulp are subject to an alcoholic fermentation process catalyzed by yeasts to produce ethanol **(Afoakwa, 2012 & Nigam and Singh, 2014)**. The aerobic phase begins after 48-96 hours, then the yeast activity Inhibits, alcohol concentrate and The pH rises as a result of the consumption of citric acid in the yeast metabolism, which leads to the growth of lactic acid bacteria. The fermentation of pulp sugars produces lactic, acetic, ethanol and carbon dioxide acids. Then the acetic acid bacteria oxidize the ethanol to The acetic acid bacteria then oxidize the ethanol to acetic acid, which is responsible for the formation of cocoa's distinctive flavor compounds. Fully fermented grains are brown in color due to enzymatic brown discoloration that catalyzed by the enzyme polyphenol oxidase **(Aculey *et al.*, 2010)**.

Drying and roasting cocoa beans

Cocoa beans are dried immediately after the end of the fermentation process by placing them in the sun for 5-7 days or using hot air fans, after which they are dried in special dryers to reduce the moisture content in the beans to a maximum of 7- 7.5% to prevent fermentation and mold contamination during storage, as well as reducing the feeling of bitter, astringent, sour taste and preventing the development of brown color **(Merkus, 2014)**. Well-dried kernels of good quality are brown in color, have little bitterness and does not contain flavors such as smoky flavor and excessive acidity **(Afoakwa *et al.*, 2008)**. Cocoa beans are roasted to develop flavour, get rid of unwanted volatiles (acetic acid) and reduce moisture content to 1-2% **(Giacometti *et al.*, 2015)**. Free amino acids and reducing sugars are involved in non-enzymatic Maillard reactions **(Jumnongpon *et al.*, 2012)**. Roasting temperature ranges from 120-140°C for 10-35 minutes. The seeds are turned over to absorb moisture and turn dark brown. Non-volatile flavor compounds are created during roasting as Methylxanthines, Polyphenols, Theobromine, Caffeine, and small amounts of Theophylline contribute to raw cocoa beans' distinctive flavor and bitter taste **(Franco *et al.*, 2013)**.

Removing grain husks, crushing, grinding and softening

The husks represent 12% of the total weight of the kernels. The husks are removed by applying light pressure to the unhulled seeds through cylinders that are close to space. The husks are removed by sifting or airing the kernels **(Afoakwa *et al.*, 2008)**. The brown pulp is crushed into 4-5 cylinders. Overlapping cylinders with less space between them from top to bottom. At this stage, the embryo is separated to prevent cocoa rancidity. The crushed cocoa is passed between the smoothing cylinders, which consist of 3-5 cylinders placed on top of each other so that the cocoa groats turn into a liquid paste that is collected in a steam-heated double-walled tank to turn it into a liquid paste. A viscous liquid containing 40% butter and 60% cocoa powder, which is transferred to tanks equipped with steam-heated stirrers. The temperature of the liquid is raised to 100°C for 24-36 hours. The increase in heat

associated with good stirring leads to an increase in the proportion of the resulting butter to obtain a liquid. Cocoa **(Giacometti *et al.*, 2015)**.

Cocoa Butter

Cocoa butter is composed of a mixture of unsaturated fatty acids such as oleic acid and saturated fatty acids such as palmitic and stearic acid, as well as containing a high percentage of natural antioxidants such as flavonoids and phenolic compounds that preserve cocoa butter for a long time without damage and make it resistant to natural storage conditions. Cocoa butter solidifies at room temperature **(Kamphuis, 2017)**.

Cocoa Butter Separation

Cocoa butter is separated by squeezing after transferring the cocoa mass to a mill with a capacity of 1500 kg heated with steam, raising its temperature to 80°C and adding to it potassium salts and a little citric acid with stirring and leaving the cocoa mass for 24 hours. 96 kg, the pressing process takes 10-20 minutes, depending on the proportion of cocoa butter in the mass. After separating the butter, the butter is taken into special tanks and left to rest for 24 hours, then cooled to a temperature close to freezing, packed in suitable containers and stored. Or it may be separated with organic solvents such as hexane permitted for use by the Codex Alimentarius Commission and according to the standard amended in 2016 that allows the use of 1 mg/kg of cocoa mass. After the 47-56% of the butter has been extracted, the cocoa remains in the form of pressed tablets **(Kamphuis, 2017)**.

Cocoa Butter Hardness

The amount of fat and its melting or hardening properties depend on the type of cocoa bean, fermentation and drying conditions and environmental conditions. The daily temperature in the last months of cocoa pods growing affects the hardness of cocoa butter. In addition to the effect of free fatty acids resulting from rotting cocoa beans which should not exceed 1.75% according to the laws of the European Union **(Beckett, 2009)**.

Alkali treatment

Alkaline treatment of cocoa pods is carried out after separation of butter to improve cocoa color, increase cocoa dispersion in drinks, reduce astringent taste by complex polymerization of polyphenols and eliminate bitter taste **(Afoakwa *et al.*, 2008)**.

Cocoa tablet grinding

The remaining cocoa is grinded to obtain cocoa powder, by passing the pressed cocoa in the form of a disk through a number of cylinders separated from each other by varying distances, with the necessity of cooling the cylinders with water in order to maintain the solidity of the product. Cocoa powder granule size ranges between 35-70 microns, packed in special drums **(Kamphuis, 2017)**.

Types of cocoa powder

There are different types of cocoa powders and they have certain uses (Dyer, 2003) which are:

1- Modified cocoa powder (Slightly alkaline-treated)

To obtain this type of powder, soak a cocoa pod in an alkaline solution; In order to reduce bitterness and increase solubility and to make the resulting powder a brown color slightly darker than natural cocoa and less prone to clumping. Its pH value is 6.1-6.8, making it reactive with sodium bicarbonate, so it is used in pastries or cakes with yogurt or milk added.

2- Natural cocoa powder (unmodified)

Natural cocoa (Nestlé cocoa powder) has a very concentrated, sharp flavour, with a high

bitterness. The pH value is 1.5-4.5, which is the natural acidity of cocoa as a result of lactic acid from fermenting the seeds, it is light brown in color, this type of cocoa is used with cake or cookies, it works excellent with sodium bicarbonate.

3- Black modified cocoa powder (treated with alkali)

This type of cocoa is intensely alkaline, pH 6.8-8.1 The alkaline process reduces bitterness and improves solubility. Cholesterol is very low, this type of cocoa is used in Oreo products, and in other products by mixing it with another type of cocoa powder, it has a distinct flavor.

Cocoa products

First: the chocolate

One of the best cocoa products is chocolate, its industry has developed and is now produced in different types and shapes. The proportion of solids in chocolate is 70% represented by cocoa powder, sugar and milk, and fats from cocoa butter and milk fat, the proportions of the ingredients vary depending on the specific composition **(Fernandes *et al.*, 2013)**.

The main sources of cocoa that used in the manufacture of chocolate

It is used to make milk and dark chocolate, cocoa from Forastero beans, as well as fine or flavored cocoa from Criollo, Trinitario and Nacional beans. In order to produce chocolate with a stable quality from a variable raw material, cocoa beans from different sources must be mixed before or after roasting to obtain a consistent product of the required quality **(Beckett, 2009)**.

Kinds of chocolate

The type of chocolate varies depending on the percentage of cocoa in the final product, being 70-85% in dark chocolate, 35% in semi-sweet or bitter chocolate, 20% in white chocolate, and 10-12% in milk chocolate **(Callebaut, 2017)**. as well as the type and proportions of ingredients used in its manufacture **(Beckett, 2010)**.

- Dark Chocolate: Consists of 14% fat-free cocoa powder, sugar (35% cocoa solids and sugar total) and 18% cocoa butter. This type of chocolate has a bitter and sweet taste. It contains antioxidants such as polyphenols in a high percentage **(Rousseau, 2007& Brillo and renzo, 2015)**. The US Department of Agriculture divides dark chocolate into three types according to the amount of stimulants caffeine, theobromine and the proportion of cocoa powder shown in Table (2).

Table 2. Amount of Caffeine and Theobromine and Percentage of Cocoa Powder in Dark Chocolate

Cocoa powder %	Theobromine/mg	Average amount of caffeine/gm	dark chocolate type
45-59	493 mg	45 mg/100 g	**Low-darkness**
60-69	632 mg	80 mg/100 g	**dark**
70-85	802 mg	86 mg/100 g	**black**

(USDA, 2014)

- White chocolate: consisting of cocoa powder and partly or fully dried whole milk with a ratio of 14%, cocoa butter can be replaced with cream or milk fat with a content of at least 3.5% **(EU Commission, 2000)**.

-Milk chocolate: consists of sugar, cocoa butter, milk, a small amount of skimmed cocoa powder or cocoa liquor, and flavoring agents **(Rousseau, 2007 & Brillo and Renzo, 2015)**.

Second: Nutella

The first Nutella formula was prepared in Italy, consisting of sugar, vegetable oil, 13% of ground hazelnut paste, 7.4% of low-fat cocoa, 6.6% of skimmed milk powder, lactose, lactose whey powder and soy lecithin added as an emulsifying agent and stabilizing agent for Nutella with vegetable oils at the stage of Smoothing or smoothing in order to give it a specific smoothness and a creamy character **(Cova and D'Antone, 2016)**.

Third: Cocoa is used in the manufacture of cakes, pastries, hot drinks, ice cream, and others.

The effect of some components of cocoa and chocolate on health

- Antioxidant effect

There has been increased interest in the health effects of antioxidants in cocoa powder and its products, especially dark chocolate. More than 200 studies have found bioactive compounds in cocoa and its products such as flavonoids and flavanols, which contribute to the protection of the heart and blood vessels from disease, and the mechanism lies in the activation of nitrite oxide (NO), as well as the anti-cancer and anti-inflammatory effects of these compounds and their role in improving endothelial function. In other studies, cocoa powder was found to be the richest dietary source of bioactive flavanols such as procyanidin, catechin, and epicatechin, which have immune regulatory effects and modulate the immune response **(Colombo *et al.*, 2012)**.

- Fat effect

The proportion of saturated fatty acids in cocoa butter is high, stearic acid 35% and palmitic 25%, and the proportion of unsaturated fatty acids is low, oleic acid 35% and linoleic 3%. Cocoa butter is used in the manufacture of chocolate, Nutella and other products. Sterols and stanols contribute to the improvement of the level of lipids in the blood by competitive inhibition of the absorption of dietary cholesterol in the gastrointestinal tract. Sterols, such as sistosterol and stigmasterol present in very small amounts, have a limited effect on cholesterol absorption **(Colombo *et al.*, 2012)**.

- Metal effect

Cocoa and its products such as chocolate are a rich source of essential minerals important for the health of the body. Copper is involved in multiple enzymatic reactions including the synthesis of collagen and neurotransmitters. Iron is necessary for the production of heme compounds. Magnesium is involved in stimulating many biological reactions, including protein synthesis, nerve transmission, muscle relaxation and energy production. Calcium is important in the formation of bones and teeth, muscle contraction, and transmission of nerve signals. Cocoa does not contain a large amount of calcium, but milk chocolate is rich in calcium whose presence, along with the oxalic acid in cocoa, leads to the formation of calcium oxalate stones. And potassium, which maintains the permeability of the cellular membranes of the heart and blood vessels. And selenium, which acts as a cofactor in the formation of the enzyme glutathione peroxidases, thioredoxin reductase and iodothyronine deiodinases, as well as zinc. The amount of minerals depends on the amount of cocoa solids, so dark chocolate contains high amounts of minerals. Some compounds in cocoa such as oxalic and phytic acids and one of the procyanidins polyphenols can interfere with mineral absorption **(Colombo *et al.*, 2012)**, as shown in Table (3).

Table 3. Chemical Composition of Cocoa Powder and Dark Chocolate/ 100gm

Nutrient	Cocoa powder	Chocolate dark 70-85% cacao solids
Protein	19.60 g	7.79 g
Total lipid	13.70g	42.64 g
Fatty acids, total saturated	8.07g	24.489 g
Fatty acids, total monounsaturated	4.57 g	12.781 g
Fatty acids, total polyunsaturated	0.44 g	1.257 g
Ash	5.80	2.32 g
Carbohydrate	57.90	45.90 g
Total dietary fiber	33.2 g	10.9 g
Total sugars	1.75 g	23.99 g
Minerals		
Calcium, Ca	128 g	73 mg
Iron, Fe	13.86 mg	11.90 mg
Magnesium, Mg	499 mg	228 mg
Phosphorus, P	734 mg	308 mg
Potassium, K	1524 mg	715 mg
Sodium, Na	21 mg	20 mg
Zinc, Zn	6.81 mg	3.31 mg
Copper, Cu	3.788 mg	1.766 mg
Manganese	3.837 mg	1.948 mg
Selenium, Se	14.3mg	6.8 mg
Others		
Caffeine	230 mg	80 mg
Theobromine	2057 mg	802 mg

(USDA,2014)

CONCLUSIONS

In general, studies show that daily consumption of small amounts of flavanols and procyanidins from cocoa or chocolate, along with the usual intake of flavonoids from different food sources, can provide a natural therapeutic approach to improving an individual's health status.

Modern techniques in cocoa processing can be used in order to manufacture cocoa products with a high content of biologically active substances and suitable flavor properties.

Cocoa and its butter are a good food source, rich in energy and important essential compounds such as phenolic compounds, minerals and fatty acids.

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