Chocolate: Origins, current technology and production of antioxidants beneficial to health

El chocolate: Orígenes, tecnología actual y producción de antioxidantes benéficos para la salud

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Abstract

The current review entitled Chocolate: Origins, L current technology and production of beneficial antioxidants for health, presents us with a compilation of researchs on the origin, history and benefits of chocolate as a superfood that contributes to the daily diet not only with empty carbohydrates; but also, with a number of complex chemical antioxidants compounds such as flavonoids, theobromine, caffeine among others, wich contribute to the health and development of the human being in all stages of their life, thus also improving the cognitive and immunological capacities of those who consume this product. All the aforementioned characteristics of this product of tropical origin require a deeper knowledge of each of its possible benefits and what are the effects on its consumption in the long and short term.

Keywords: Chocolate, cocoa, health, antioxidants.

Resumen

a presente revisión titulada Chocolate: Orígenes, L tecnología actual y producción de antioxidantes beneficiosos para la salud, nos presenta una recopilación de investigaciones sobre el origen, historia y beneficios del chocolate como superalimento que contribuye a la dieta diaria no solo con carbohidratos vacíos; pero también, con una serie de compuestos químicos complejos como flavonoides, teobromina, cafeína entre otros, que contribuyen a la salud y desarrollo del ser humano en todas las etapas de su vida, mejorando así también las capacidades cognitivas e inmunológicas de quienes consumen este producto. Todas las características antes mencionadas de este producto de origen tropical requieren un conocimiento más profundo de cada uno de sus posibles beneficios y cuáles son los efectos sobre su consumo a largo y corto plazo.

Palabras claves: Chocolate, cacao, salud, antioxidantes.

Introduction

Acao (Theobroma cacao L.) belongs to the genus Theobroma; Greek word that means "food of the gods". The word cacao derives from the Mayan cacau; cac = red and cau = force and fire (Hugo *et al.*, 2011). Historical compilations indicate that the Mayans cultivated it, and the seed was used as currency (Leon-Villamar et al., 2016), Mayan merchants, in their many trips, made cacao known to the Aztec people, who in turn adopted its cultivation and began to consume it in the form of a drink made with ground cacao, water and honey; which was called xocolatl, which in Nahuatl means "sparkling water" (González et al., 2019). Cocoa was introduced to Europe after the colonization of America. In 1528 the first shipment of cocoa beans to Spain was made (Torres, 2012). Despite its bitter taste for European taste, chocolate managed to spread throughout the Old Continent, thanks to the fact that the upper classes made it a fashionable drink (snobbery and foolishness, therefore, are not recent phenomena). To its toning effects, an alleged aphrodisiac capacity was added that made it very (Medrano, 2010).

Cacao is an evergreen tree of great economic importance, with a tropical habitat that has been used for various nutritional, medicinal, ritual purposes, etc. by numerous cultures throughout history. Although still found in the wild (Waizel, *et al.*, 2012). (*Theobroma cacao* L). it is a diploid fruit species (2 n = 2 x = 20) endemic to the tropical forests of South America. Cacao was domesticated approximately 3000 years ago in Central America (Argout *et al.*, 2011). The Criollo cacao variety, which has a homozygous and almost unique genotype, was one of the first to be cultivated. Criollo is now one of two varieties of cacao that provides fine-flavored chocolate (Zarrillo *et al.*, 2018)

Cocoa And Derivatives: Origin Of Chocolate

Cocoa derivatives are defined as products that are obtained by extraction, pressing, or pulverization, and that can be chemically treated and mixed or not with sugars or other ingredients (Sánchez *et al.*,2017).

One of the most important processes carried out by the producer is fermentation, which is essential to eliminate the pulp that surrounds the grains. During this process, a consortium of natural yeasts is generated, among which are lactic bacteria and acetic acid, responsible for the production of alcohol and acid that diffuses into the grains, giving rise to complex biochemical reactions within them. (Teneda, 2016). The chocolate flavor develops from: Fermentation, drying, which is carried out by the primary producer as well as the exporting merchant, and the roasting carried out by the chocolate industry (Vera Chang *et al.*,2018). The main cocoa producers worldwide are: Ivory Coast, Ghana, and Indonesia, countries that cover around 70% of global production, despite the fact that Ecuador is currently a country with a small cocoa production worldwide (4% of production), for fine aroma cocoas, represents the first producer with a wide margin of difference, 60% of world production (Teneda, 2016).

The industrial processing of cocoa, therefore, is a complex process that requires numerous operations. The chocolate obtained from this process is defined as a semi-solid suspension of very fine solid particles of sugar and cocoa, dispersed in a continuous fat phase. (Latif, 2013).

The present bibliographic work aims to carry out an exhaustive review on the current state of the art of chocolate, its origins, the current technology available and the benefits of its consumption for human health, due to the production of antioxidants that *T. cocoa*.

Chocolate: A Food

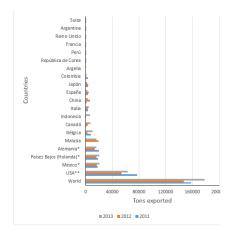
Chocolate seems to be one of the most promising foods due to its high content of polyphenols such as flavonoids, showing beneficial health properties (Delgado et al., 2018). Chocolate, the main derivative of cocoa, contains, according to experts, compounds that report beneficial antioxidant properties, especially interesting for cardiovascular health. It is convenient to specify the type of chocolate you have greater benefits, depending on whether it is black, milk or White (Amaya & Pabón, 2017). The process of producing chocolate (generic name for cocoa-based sweets) from cocoa. To make chocolate you need a mixture of cocoa, or cocoa powder, cocoa butter and sugar. Then, depending on the product you want to obtain, other ingredients such as milk, almonds, hazelnuts, fruits, etc. will be added. The phases of chocolate manufacture are: roasting, grinding, mixing, fine grinding, conching, tempering, molding and packaging. If you want to separate the cocoa butter to obtain, for example, defatted cocoa powder, we will have the additional phase of alkalization (Oliveras, 2007).

Studies have shown that chocolate provides a great energy contribution to the human body, keeping the brain part activated, achieving great mental abilities, for this reason the cocoa shell is a useful food, which is why entrepreneurs in our nation have prepared infusion envelopes, obtaining relaxation, total stress levels regulating nerve cells (Martinez, 2020).

Cocoa contains between 10 and 22% fat, consisting mainly of fatty acids: oleic, palmitic and stearic, as well as other organic acids; by various amino acids: alkaloids derived from pyrazine, others of the purine type or methylxanthines (caffeine, theophylline and theobromine); tryptamine, tyramine, hordenine, loginmesine, longimamidine, longimamine, metanephrine, octapamine, phenylephrine, methylisoquinoline, salsolin, salsolinol, and synephrine; by sulfur compounds, phenols (coumarin, esculetin and catechol), acetophenone, benzaldehyde, isopentyl benzoate; and by terpenes (essential oils), apigenin, linalol, linalool, etc. (Waizel *et al.*, 2012).

Cocoa export from Ecuador to the world

At the end of the 19th century, new trade flows led Ecuadorian cocoa beyond the Spanish "semi-periphery" and linked it to the "center" of the world economy. As early as the 1870s, part of the Ecuadorian cocoa production had found a market in France and Germany. By the 1890s, the movement from Spain to northern Europe was complete (Maiguashca, 2014). Ecuador held the position of the world's largest cocoa exporter between 1880 and 1890, between 1870 and 1910 the main cocoa exporting houses were founded, the rules for the distribution of the value of the exported bean were established, and the main world companies for the purchase of the grain, processing and marketing of derivatives, such as Nestlé, Côted'Or, Cadbury or Fry (Vassallo, 2016). Its cultivation and export was intensified, it was the basis of the economy of Ecuador between the years 1860 and 1920, a time identified as the era of the "Golden Pepa", becoming one of the countries with the largest world export of cocoa, generating wealth and allowing an important economic growth at the private level, which later served as economic support, Ecuador currently went from seventh to fourth place as an exporter of cocoa in the world and remained in the first place as a supplier of fine aroma national cocoa in 2015. During this year, total production was 265000 metric tons, breaking records for the third consecutive time. Sales reached \$ 750 million (Leon-Villamar et al., 2016).



Graphic 1. Important export destinations of dry roasted / fermented cocoa beans (quantity expressed in tonnes) Trade Map.

Varieties with greater aroma to produce chocolate

The fine and aroma cocoa of Ecuador is a unique argument for its very high quality: the Ecuadorian National cocoa is a natural outsider of the humid forest of Ecuador and appreciated at the same time as fine and aroma (Vallejo-Torres *et al.*, 2018). the fine and aroma Nacional cacao preserves a characteristic flavor and an exclusive floral aroma designated "Up". It is an essential element in the elaboration of fine chocolate of the highest quality and aroma in the world market (Vera-Chang , *et al.*, 2018).

Nacional

Fine and aroma cocoa has distinctive aroma and flavor characteristics sought after by chocolate manufacturers. It represents only 5% of the world cocoa production. Ecuador, due to its geographical conditions and its richness in biological resources, is the producer par excellence of fine and aroma Cacao Arriba (63% of world production) from the National variety whose flavor has been recognized for centuries in the international market. This type of grain is used in all refined chocolates (ANECACAO, 2017).

Sacha Gold®

Various flavor studies and cocoa harvested from trees in the Sacha Gold® selection has a fine flavor and aroma, very intense floral, characteristics that are highly desirable for customers in international markets. Theobromine / Caffeine tests in INIAP in 2014, and a T / C ratio of 6.65% was obtained, which according to INIAP in its study "Establishment of physical, chemical and organoleptic parameters to differentiate fine and ordinary cocoa" (INIAP, 2006),

INIAP-EET 103

The genetic material known as EET - 103 shows aromatic profiles of nut and cocoa, possibly this fruit profile in the National variety of Ecuador could be closely related to the sweet or caramel and nutty flavor, when this attribute is present it could be linked to the environment and hygroscopy of the almond near fruit trees, to this is added a second component that is postharvest or curing management (Vera-Chang *et al.*, 2015).

INIAP-EETP-800 'Aroma Pichilingue'

The main characteristics of this clone are: semi-erect growth, flowering in the first and third quarter of the year, green and yellow immature ear in its physiological maturity, self-compatible, early production (14 months), ear index of 18, average of 46 seeds per ear and seed index of 1.40, which according to NTE INEN 2018 (INEN, 2018), ranks it in the Superior Superior Summer Selecta (ASSS) category. Its sensory profile, at the end of four days of benefit, is made up of a moderate combination of cocoa, floral and fruity flavors, with notes of nuts and sweetness, in which highlights the floral flavor, the main characteristic of National cocoa, which identifies it as fine aroma cocoa (Loor-Solórzano *et al.*, 2019).

The Ecuadorian technical standard NTE INEN 2018(INEN, 2018) 176 (Table 1) establishes the classification for cocoa and the quality requirements that the processed bean must meet and the criteria that must be applied for its classification.

Modern technology for making chocolate

The quality of cocoa is manifested through the physical characteristics (size, weight, shell thickness, color, fat content) and the organoleptic characteristics of the almonds (Vera Chang *et al.*, 2018). The pressing of the almonds gives rise to three main products: the cocoa liquor, the cocoa butter, and the residue, the cocoa powder. The mixture of these elements originates the cocoa paste, which is the basis for the elaboration of chocolate bars and the different types of chocolate that exist today. (Palacio-Vásquez *et al.*, 2017).

Cadmium contamination and its relationship with chocolate production

The cocoa known as the 'Pepa de Oro', is one of the representative fruits as a brand of Ecuador.

In 2018, exports of these cocoa beans increased by 12.79%, with Europe being one of the most important destinations for these exports. (Mite *et al.*, 2010). At the beginning of this year, Regulation 488/2014 came into force, which was approved by the European Union and, which establishes the maximum level of cadmium that products derived from cocoa and chocolate can contain, in order to protect health public (Salous & Pascual, 2018).

Cadmium Allowable Levels

According to Ministerial 097 - Annex 2 of the Ministry of the Environment of Ecuador (MAE, 2018), Soil resource environmental quality standard and remediation criteria for contaminated soils, mention that the permissible value declared as normal is 0.5 mg / kg of heavy metal. While according to the regulations of the European Union approved since January 1, 2019, the maximum cadmium content in food products is regulated. Therefore, the limits allowed for cocoa and chocolate will be the following: Milk chocolate with a total dry matter content of cocoa less than 30% will be 0.10mg / kg. Chocolate with a total dry matter content of less than 50%, the maximum limit will be 0.30 mg / kg. Chocolate with a cocoa dry matter content greater than or equal to 50% will have a maximum limit of 0.80 mg / kg. Cocoa powder sold to the final consumer 0.60 mg / kg. The State of California in the United States will establish regulations for chocolate

Requirements	Unit	"Cacao Arriba"					CCN-
		TSSP	TSS	TS	TCS	TE	51
One hundred grains weigh	g	135- 140	130- 135	120- 125	110- 150	105- 110	135- 140
Good fermentation (minimal)	%	75	65	60	44	26	65***
Light fermentation * (minimum)	%	10	10	5	10	27	11
Fully Fermented (minimum)	%	85	75	65	54	53	76
Violet (maximum)	%	10	15	21	25	25	18
Slate / pasty (maximum)	%	4	9	12	18	18	5
Mold (Maximum)	%	1	1	2	3	4	1
Totals (analysis on 100 almonds)	%	100	100	100	100	100	100
Defective (maximum) (analysis over 500 grams)	%	0	0	1	3	4**	1
TOTAL FERMENTED	%	85	75	65	54	53	76
	. 11	1 1	C 1	100			

Table 1. NTE INEN 2018 quality requirements of cocoa above and clone CCN-51 benefited (INEN, 2018)

* Violet brown coloring ** The presence of pellets is allowed only for the type ASE

*** The coloration varies from brown to violet

TSSP: Top Summer Select Plantation. TSS: Top Summer Selecto. TS: Top Select TCS: Top Christmas Selection TE: Top Epoch that exceed these permitted levels as well, but without restricting the marketing of the product that contain high cadmium content, it will only warn of the risks of its consumption.(ANECACAO, 2017).

Cadmium remediation in contaminated soils

To reduce Cd levels in agricultural soils, it consists of applying nutrients to the soil that act antagonistically with the metal, limiting the plant to absorb it. A natural biological mechanism by which the absorption and translocation of Cd decreases occurs in the case of forest species where it has been proven that plantassociated ectomycorrhizae can reduce the amount of heavy metals absorbed by roots and their transfer to the roots. stem, thereby reducing the toxicity of the metal. An alternative for the phytoremediation of heavy metals is to incorporate plant species that carry out the phytoextraction that are capable of accumulating and tolerating high concentrations of metals in their harvestable tissues. (Armijos, 2019).

Antioxidant Effects Of Chocolate

One of its nutritional attributes is the antioxidant capacity, associated with the content of polyphenols, which is affected in different stages of industrialization. (Acevedo-Alzate *et al.*, 2017). The main phenolic compounds present in cocoa beans are located in three groups, the catechins or flavan 3-ol, which represent 37% of the total; anthocyanins with about 4% and proanthocyanidins with 58% (Gómez-Juaristi *et al.*, 2011)

Chocolate flavonoids have significant antioxidant activity, being able to protect tissues from oxidative stress. Intervention studies carried out in humans after the consumption of chocolate show a decrease in the oxidability of serum low-density lipoproteins (LDL) and an increase in the antioxidant capacity of the plasma Likewise, the consumption of chocolate rich in procyanidins leads to a decrease in plasma oxidation products (Gómez-Juaristi *et al.*, 2011).

The polyphenols of interest in cocoa are those of the group of flavonoids, such as catechins (37%), anthocyanins (4%) and procyanidins (58%). Pharmacologically, flavonoids stand out for their low toxicity and high antioxidant action, and their ability to inhibit lipid peroxidation by reducing free radicals and chelating metals. Due to these properties, cocoa is linked to the prevention of oxidative stress, biological imbalance and alteration of cell function caused by degenerative diseases such as atherosclerosis, heart disease, neurological diseases and cancer. (Negaresh & Marín, 2013).

Cocoa and its products: cocoa liquor, dark chocolate, cocoa powder or cocoa, are foods rich in

these substances, mainly in catechins (epicatechin, epigallocatechin, gallocatechin and catechin), in addition to other flavonoids such as procyanidins, anthocyanins, flavonones and glycosidic flavonol.The concentration of polyphenols in dry and fat-free cocoa beans ranges between 15-20% (w / w) and they are made up of 37% catechins, 4% anthocyanins and 58% of proanthocyanidins (Perea-Villamil *et al.*, 2009).

The Effects Of Chocolate On Cardiovascular Health

According to a study in the British Medical Journal presented at the Congress of the European Society of Cardiology, drinking chocolate is healthy, as it reduces the risk of developing heart disease by almost a third (Siswi-Wulandari, 2017). Dark chocolate contains many biologically active components, such as catechins, procyanidins, and theobromine from cocoa, along with added sucrose and lipids. All of these can directly or indirectly affect the cardiovascular system by multiple mechanisms(Kerimi & Williamson, 2015).

Cocoa flavonoids have been shown to have a modulating effect on platelet function, reducing the risk of thrombus formation. The mechanism of action of flavanols would occur at the level of platelet activation induced by ADP and by epinephrine. Furthermore, flavanols have been observed to increase the bioavailability of nitric oxide (NO) in endothelial cells. (Gómez-Juaristi *et al.*, 2011).

Other bioactive components present in chocolate, such as methylxanthines (mainly caffeine and theobromine), have been studied to a lesser extent and some authors indicate that they should be taken into account when interpreting the effects of chocolate on the cardiovascular system. On the other hand, the constituent fatty acids deserve special attention, such as stearic acid, which is considered neutral due to its effects on total cholesterol and LDL-cholesterol. (Watson *et al.*, 2013).

(Ibero-Baraibar *et al.*, 2017) showed that the ingestion of a cocoa extract (415 mg of flavanols / day) for 4 weeks resulted in a reduction of oxidized LDL levels in older people. This cocoa extract was bioavailable, since metabolites derived from its consumption were found in urine. On the other hand, this research showed that the group supplemented with cocoa extract presented a greater reduction in postprandial blood pressure levels compared to the non-supplemented group.

Numerous studies report that chocolate is one of the foods that contains active compounds such as Polyphenols and Flavonoids (such as Epicatechin, which is a molecule that acts as an antioxidant). Despite the fact that chocolate is high in fat, most of it is represented by omega-3 and omega-6, if it is consumed in moderate portions it brings health benefits (Estevan-Marín, 2015.).

Is Chocolate Addictive?

Many people claim to crave chocolate and enjoy the sensation that its consumption induces, the key to this sensation could be a chemical called anandamide, which is similar to the compounds released when consuming cannabis (marijuana), when we eat chocolate, anandamide is released in small amounts and creates a relaxing sensation (Wilson, 2015). It is identified as one of the endogenous cannabinoid neurotransmitters in humans, which is synthesized in the brain and, according to recent research, has been identified in the peripheral nervous system. It is linked to memory processes and movement control, as well as the attenuation of the sensation of pain, the regulation of appetite and cell fate (Rojas *et al.*,2018).

Chocolate contains a substance called enkephalin, which is possibly responsible for making chocolate an impossible delicacy to resist. Encephalin activates opioid receptors in the brain, the same ones that react to morphine, increasing the urge to eat. This effect works in two ways: the consumption of chocolate stimulates the production of enkephalins and this, in turn, increases the consumption of chocolate. (Badrie, *et al.*, 2015). Encephalins are a class of endogenous opioids that appear to have analgesic effects on the central nervous system. (Sinisterra, 2015).

Nowadays already the positive effects on the health of the products from chocolate are very known. Certains studies to the human health benefits are mentioned to belong, some of them, have antioxidant and antiinflammatory effects on the body in general (Table 2).

Theobromine (3,7-dihydro-3,7-dimethyl-1Hpurine-2,6-dione), the main alkaloid-purine found in the products of cocoa trees, their seeds and shells, belongs to a class of alkaloid molecules known as methyl xanthines, which occur naturally in up to 60 different plant species and also include caffeine (the main methyl xanthine in coffee) and theophylline (the main methyl xanthine in tea) (Vázquez-Ovando *et al.*, 2016).

Table 2. Some Investigations related to chocolate benefits on human health

StudyEstudio	Health benefitsBeneficios para la salud		
(Martinez, 2020)	It keeps the brain part activated, reaching great mental abilities if the cocoa shell is consumed in infusion.		
(Perea-Villamil et al.,2009)	Functional properties such as antioxidants, anticancer, anti-inflammatory, antithrombotic, antimutagenic, antibacterial and analgesicNos comenta que posee Ppropiedades funcionales como antioxidantes, anticancerígenos, antiinflamatorios, antitrombóticos, antimutagénicos, antibacteriales y analgésicos		
(Vázquez-Ovando et al., 2016)	It has three high antioxidant elements, catechins or flavan 3-ol that represent 37% of the total; anthocyanins with about 4% and proanthocyanidins with 58%.		
(Gómez-Juaristi et al., 2011)	The consumption of chocolate shows a decrease in the oxidability of serum low- density lipoproteins (LDL) and an increase in the antioxidant capacity of the plasma.		
(Ibero-Baraibar et al., 2017)	Consumption of (415 mg flavanols / day) for 4 weeks resulted in a reduction in oxidized LDL levels in older people.		
(Sinisterra, 2015)	The consumption of chocolate stimulates the production of enkephalins which are a type of endogenous opioids that seem to have analgesic effects on the central nervous system.		
(Coto-Hernández, 2019)	Cocoa is an important source of polyphenols, in the form of flavonoids, which are not only beneficial for its antioxidant capacity, but also for its positive impact on a cardiovascular level.		
(Ortiz et al., 2019)	The main methylxanthines in cocoa are theobromine $(3.7\% \text{ on a fat-free basis})$ and caffeine (around 0.2%). beneficial health properties, such as the stimulant and antidepressant properties in cocoa products.		
(Negaresh & Marín, 2013)	cocoa is linked to the prevention of oxidative stress, biological imbalance and alteration of cellular function caused by degenerative diseases such as atherosclerosis, heart disease, neurological diseases and cancer.		

Conclusions

For years there has been the consumption of cocoa, almonds and their derivatives, it is the last decade that has made us aware of the benefits and virtues of this tropical drupe, its high content of flavonoids is characterized, however, the consumption of everything Food in excess could be harmful in people with obesity or overweight, in nature we can find flavonoids in different forms such as the implantation of a diet rich in fruits and vegetables, however without neglecting the pleasure that a quality chocolate offers us greater than 60% pure cocoa.

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