MSc. Eng. Izabela HURKO-ROMEYKO[1]
PhD, DrSc Jolanta KOWALSKA
Dr Irina POCHITSKAYA[2]
[1]Department of Technology and Food Evaluation, Institute of Food Sciences
Warsaw University of Life Sciences (WULS), Poland
Katedra Technologii i Oceny Żywności, Instytut Nauk o Żywności
Szkoła Główna Gospodarstwa Wiejskiego w Warszawie (SGGW), Polska
[2]The Scientific and Practical Centre for Foodstufs of the National Academy of Sciences of Belarus, Republic of Belarus, Minsk

COCOA POWDER AS SOURCE OF PHENOLIC COMPOUNDS, DETERMINING FACTORS – A REVIEW®

Proszek kakaowy jako źródło związków fenolowych, czynniki determinujące – przegląd®

In recent years, there has been increasing interest in the properties of cocoa powder as sources of valuable polyphenolic compounds. Cocoa powder is obtained in a multi-stage process of cocoa beans processing, during which many valuable bio-components are lost. The aim of this article is to characterize phenolic compounds present in cocoa powder in the context of their beneficial effects on human health.

Key words: cocoa beans, cocoa powder, chocolate, polyphenols content.

W ostatnich latach wzrosło zainteresowanie właściwościami proszku kakaowego jako źródła cennych związków polifenolowych. Proszek kakaowy otrzymywany jest w wieloetapowym procesie przetwarzania ziarna kakaowego, podczas którego traconych jest wiele cennych biokomponentów. Celem niniejszego artykułu jest charakterystyka związków fenolowych obecnych w proszku kakaowym w kontekście korzystnego wpływu na zdrowie człowieka.

Słowa kluczowe: ziarna kakaowe, proszek kakaowy, czekolada, zawartość polifenoli.

INTRODUCTION

Cocoa powder, commonly called cocoa, is obtained from refined, shelled and roasted cocoa beans. In accordance with the guidelines of the Directive [11], it must contain at least 20% cocoa butter calculated on a dry matter basis and no more than 9% water. This document also allows fat-reduced cocoa with a fat content below 20%. Such cocoa is most often used by food producers, as evidenced by the information on the labels of many products, e.g. chocolate. The market offers a wide range of cocoa powders. From light brown, honey–colored powders to dark brown powders resembling dark chocolate [28]. In addition, more and more bio–powders obtained from organic plantations are available. The customer / consumer is faced with the choice of which of the offered products is the most beneficial in terms of health and utility [32]. Modern customers are aware of their expectations regarding the food they buy. More and more often, consumers' purchasing decisions are focused on pro–health products, which, apart from satisfying their nutritional needs, also have a beneficial effect on their health. The answer to these expectations is cocoa powder, a source of valuable polyphenolic components that exhibit anti–atherosclerotic, anti–carcinogenic, anti–inflammatory, anti–aging and many others [4, 15, 10, 30]. In addition, the consumers expect products that are convenient, easy and quick to prepare or for direct consumption. The food industry is facing these expectations.

GENOTYPE OF COCOA BEANS

The raw material for the production of cocoa powder is cocoa beans. Cocoa beans are obtained from the fruit of Theobroma cocoa trees, which are grown in the equatorial belt. The main producers of cocoa beans are Ivory Coast, Ghana, Indonesia, Brazil, Ecuador, Venezuela, as well as the Dominican Republic, Peru, Sri Lanka and many other countries (Fig. 1) [29, 30].

Many varieties of cocoa beans are grown, but the most famous are two, *Criollo* and *Forastero* and their hybrid *Trinitario* (Fig. 2).

Criollo is considered to be the oldest cultivated cocoa species. The fruits ferment very easily and quickly, are characterized by an excellent, delicate taste, shaped, among others, by low theobromine content and low pH [22, 30]. The flavor of *Criollo* beans is described as little chocolate, but it is characterized by rich secondary notes shaped in the processing process. Unfortunately, trees are very susceptible to disease and pest damage. Therefore, their cultivation is difficult and only accounts for about 5% of all cocoa crops. Their

Corresponding author – Adres do korespondencji: Jolanta Kowalska, Department of Technology and Food Evaluation, Institute of Food Sciences, Warsaw University of Life Sciences (WULS), 159c Nowoursynowska Str., 02-776 Warsaw, e-mail: jolanta_kowalska@sggw.edu.pl

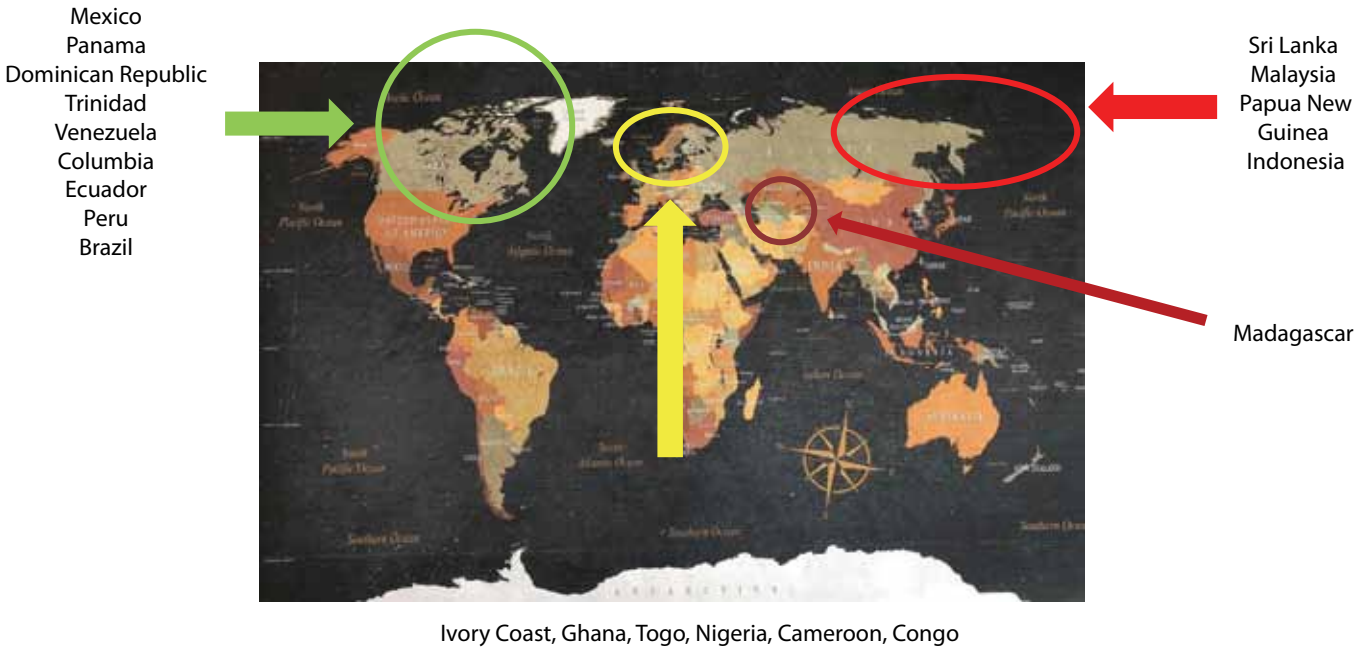


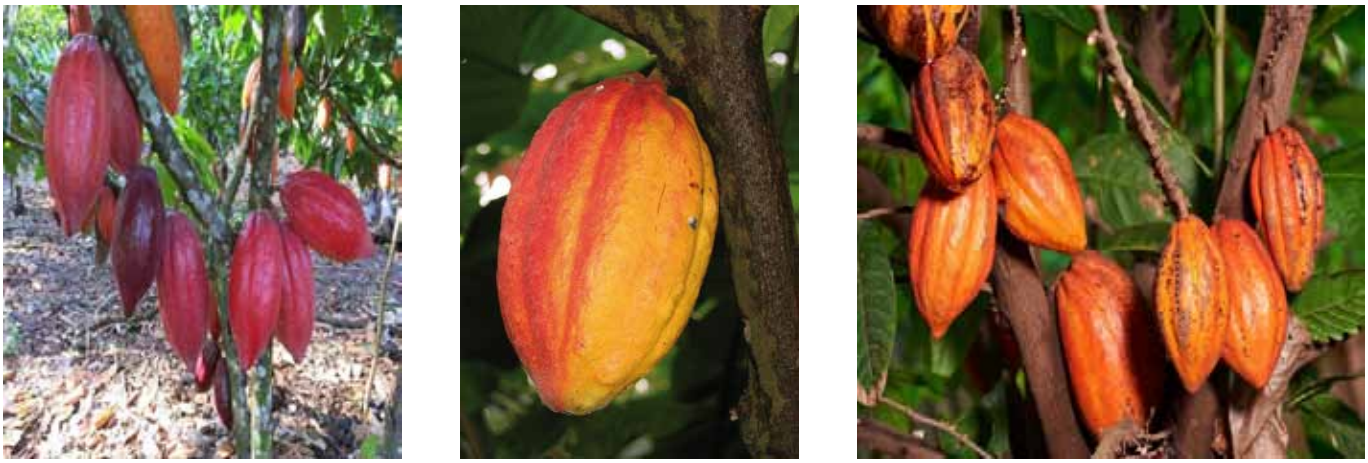
Fig. 1. Cocoa growing regions.
Rys. 1. Regiony upraw kakaowca.
Source: Own study
Źródło: Opracowanie własne

fruits are green, through red to purple, which is determined, among others, by content of polyphenol compounds, mainly anthocyanins [6]. The grains obtained from them are used primarily for the production of so-called „premium".

Forastero is often referred to as the basic grain. Plantations are mainly found in West Africa and Brazil, but there are also many wild–growing trees of this species. The trees are resistant to climatic factors and pests. This variety is productive, on average about 40 seeds are obtained from one pod. Fruits differ from other varieties in shape and size. The beans are characterized by a bitter, tart taste, without any other aromas, but quickly losing their qualities, which means that these beans are often combined with other varieties in order to obtain appropriate sensory characteristics. The intense bitterness and tartness is also felt in the products obtained from the processing of these grains [24].

A variety that combines the properties of *Criollo* and *Forastero* is *Trynitario*, characterized by the resistance and efficiency of *Forastero* and the subtle flavor of *Criollo*. *Trinitario* is characterized by high variability resulting from the different characteristics of the basic varieties from which it was created. The cultivation of this cocoa tree occurs mainly in areas where *Criollo* was or is cultivated, among others in Mexico, Venezuela, Colombia and Southeast Asia.

Another variety of cocoa beans, "ruby", from which pink chocolate is produced, is also significant. This type of beans was discovered by Barry Callebaut. The company was the first to introduce pink chocolate to the market. This product is



a) **b)** **c)**

Fig. 2. Cocoa varieties: a) Criollo, b) Forastero, c) Trinitario.
Rys. 2. Odmiany kakaowca: a) Criollo, b) Forastero, c) Trinitario.
Source: [16]
Źródło: [16]

characterized by a fruity, berry taste and aroma; it is produced without the use of dyes and flavors. The secret of these cocoa fruits lies in the specific climatic conditions in which the trees grow. The company obtains these "berry" kernels beans from the regions of Brazil, Ecuador and the Ivory Coast [16]. Moreover, within the varieties, the cocoa fruit and beans are characterized by high variability and diversity. It is associated with the presence of many subspecies, differing in physico-chemical and sensory characteristics. Many attempts have been made to classify and group the fruit, considering the appearance and morphology of the pod as a significant and distinctive feature. Unfortunately, despite many attempts, the correlation between the shape of the pod and the characteristics of the fruit and grains has not been established [6]. Research is still being conducted to develop a model that allows the use of morphological features to predict the properties of grains and, consequently, the final products obtained from them.

The variety of characteristics within a given species depending on the cultivation region, climatic conditions and grain maturity are the basic factors influencing the sensory values as well as the physico-chemical properties of products obtained from cocoa bean processing. Ławrowski [20] described the variety of flavor notes of grains obtained from crops from different regions of the world. The author pointed out that the sour–fruity note is characteristic of the beans from Madagascar, while the beans from Java have a creaminess and caramel flavor, which are preferred by producers for milk chocolates. The beans from Ecuador are characterized by a licorice-fig aroma with a noticeable scent of wood; other beans from this region have a fruity note of blackcurrant or strawberry. On the other hand, the beans from Venezuela are characterized by an earthy note, with a noticeable aroma of wood, but also fruity and nutty. According to Kowalska et al. [19] the characteristics of cocoa bean processing products are shaped, among others, by volatile and non–volatile aromatics generated in the processing of cocoa beans. Therefore, apart from natural factors, an important role in shaping sensory features is played by technological processes that the grain is subjected to, especially fermentation and roasting [7]. It is in the technological process that the precursors of taste, smell and color are created. Three factors determine the "from grain to chocolate" process: ingredients, temperature and time. How is cocoa powder made?

THE SHAPING PROPERTIES OF COCOA POWDER

As mentioned, cocoa powder is obtained in the processing of cocoa beans. The main purpose of the entire cocoa beans processing is to obtain chocolate. The process of making chocolate can be divided into three stages: plantation processes (cultivation), obtaining pulp, fat and cocoa powder (from beans to pulp) and the chocolate production (from pulp to chocolate) [4, 30]. Cocoa powder is obtained in the second stage of cocoa beans processing. The fermented and dried grains are transported to processing plants all over the world. There, after initial sorting and cleaning, they are (or not) roasted, and then rolled to a liquor. Some of the liquor is intended for the production of chocolate, while the rest is pressed, resulting in cocoa butter (cocoa butter) and cocoa cake. After drying and grinding the cocoa cakes, cocoa powder is obtained. A consumer reaching for cocoa powder or chocolate from different manufacturers may feel the difference in taste, smell, color, in the case of powder – in its flowability, granulation and solubility, and in chocolate – in hardness, gloss or breakthrough (rheological properties). Where do these differences come from?

Manufacturers carefully hide the secrets of the technological process, and more precisely the parameters used (time and temperature). In addition, the secret of the production plant is also the mixing of cocoa beans with different properties, coming from different plantations or regions, to obtain the expected and unique taste and aroma characteristic for a given producer.

COCOA BEANS

The cocoa tree blooms and bears fruit all year round. However, of the thousands of flowers, only about 40 develop into fruit. Cocoa beans are made of the husks, kernels and sprouts. The husk and sprout are removed after the roasting process, while the kernel is used for further processing [31]. Cocoa beans are a valuable source of fat (approximately 50%), carbohydrates (approximately 25%) and protein (approximately 16%), as well as phenolic compounds. The grain also contains theobromine, niacin, minerals (calcium, iron, potassium, magnesium, sodium and phosphorus) and vitamins A, B1, B2 and B6 [12]. In the technological process, some of these components are lost. Manufacturers strive to preserve as many valuable components as possible, which is why low–temperature processes are increasingly used, as a result of which "raw" products are obtained [23]. Raw products are obtained from cocoa beans that have not been roasted, but dried and conched for many hours at a temperature not exceeding 50–55°C.

POLYPHENOL COMPOUNDS IN COCOA BEANS

Cocoa beans are a rich source of polyphenols that accumulate in the so-called polyphenolic cells [3]. It should be emphasized that polyphenols are present in the non–fat components of cocoa beans. They constitute about 15% of the dry weight of the grain. Polyphenols are responsible for the color, bitter and tart taste of the beans, as well as the sensory qualities of the products obtained from their processing. However, the most important action of polyphenols is their positive effect on human health. Polyphenols have a strong anti–cancer effect, neutralizing the participation of free radicals in the human body, they can have antiviral and anti–inflammatory properties, supporting the immune system in the fight against diseases. Three groups of polyphenols dominate cocoa beans: catechins (flavan–3–ols), anthocyanins and proanthocyanidins. Catechins constitute approximately 29–38% of all polyphenols, they are represented by (–) – epicatechin, (+) – catechin, gallocatechin (–) – epigallocatechin. Another group is anthocyanins (about 4% of all polyphenols), is formed by leucoanthocyanins – L1, L2, L3, and L4, cyanidin–3–α–L–arabinoside, and cyanidin–3–β–D–galactoside [3]. Proanthocyanins constitute approximately 58–65% of all polyphenols. This group includes dimers, trimers or oligomers of flavan–3,4–diols, the most important of which

are proanthocyanidins B1, B2, B3, B4, B5, C1 and D [2]. In addition to the main and predominant groups of polyphenols cocoa beans also contain apigenin, luteolin, kaempferol and polyphenolic acids – caffeic, chlorogenic and coumaric. The composition and content of polyphenols is different and depends on the genotype, region of cultivation, degree of maturity [30]. The content of flavanols also depends on the microflora [13]. According to Aprotosoaie et al. [3] yeast, lactic acid bacteria and acetic acid bacteria have a positive effect on the content of polyphenols, while the influence of aerobic spores and molds is negative.

SHAPING THE PRO–HEALTH PROPERTIES OF COCOA POWDER IN THE TECHNOLOGICAL PROCESS

The production of cocoa powder is multistage and complex. However, some processes play a special role in shaping the properties of the final product, including health–promoting properties.

There are beans in the cocoa fruit, from about 20 in *Criollo* to as much as 50–60 in Forasterro, dipped in the flesh. After slicing by the farmer, the fruit is left for several days during which the fermentation stage takes place [8, 9]. It is the first treatment that significantly shapes the value of the final products. Most often it is a spontaneous process taking place under natural conditions leading to obtaining grains of variable quality. During fermentation (aerobic and anaerobic), the pH and bitterness the grains decreased as a result of the decomposition of tannic compounds, the formation of taste and aroma precursors, and a color change. Lowering the pH increases the enzymatic activity, including polyphenol oxidase. In the fermentation process, proteins are broken down, which in turn leads to an increase in the content of peptides and free amino acids, including: tyrosine, phenylalanine, leucine, which are precursors of the cocoa / chocolate aroma [25, 32]. At this stage, the acidity also increases, associated with the formation of volatile (acetic) and non-volatile (citric and lactic) acids that penetrate into the kernel [29]. The content of soluble polyphenols is reduced, which, on the one hand, leads to a reduction in the bitter and sharp taste and aroma of the grains, and on the other hand, to the loss of valuable antioxidant compounds [5]. After fermentation, the beans are dried, most often in natural conditions – in the sun. During this process, first of all, the water content is reduced to about 6%, the changes that occurring during fermentation are preserved, acidity is reduced, and the precursors of the characteristic taste and smell as well as brown color are further developed [1, 3]. At the drying stage, phenolic compounds are also lost, which is related to humidity, high temperature, oxygen and polyphenol oxidase. Oxidases catalyze the conversion of polyphenols into quinones, which in turn undergo further condensation with free amino and sulfhydryl groups, resulting in the synthesis of brown polymers [1]. Most studies confirm significant losses of polyphenols in technological processes. However, there are also studies that have shown the preservation of polyphenols and even an increase in their content. Rusconi and Conti [27] explained this phenomenon as a consequence of the formation of proanthocyanidins as a result of polymerization.

Roasting is considered to be one of the most important, if not the most important, process in shaping the physico–chemical and sensory characteristics, as well as health–promoting products of cocoa bean processing. This is mainly due to the high temperatures (110–160°C) used at this stage [17]. The purpose of roasting is to loosen the grain structure, reduce the water content, and deactivate the microflora. During this process, due to high temperature, protein degradation, Maillard reactions or caramelization of sugars are also stimulated [30]. Volatile compounds, including acids, are also evaporated, which reduces the acidic aftertaste in the final products. As a result of these processes, new compounds are formed that shape the characteristic sensory features, mainly taste, smell and color. At the same time, exposure to high temperature reduces the content of polyphenolic compounds, which is attributed to the epimerization of (–) – epicatechin to (–) – catechin and (+) – catechins to (+) – epicatechin. Proanthocyanidin is also epimerized, the content of which decreases at the beginning of roasting and then increases. Oracz and Nebesny [21] indicated the influence of temperature on the content of polyphenolic compounds. They showed that the use of lower temperature and humid air preserves valuable antioxidants.

Some manufacturers take one more important step, especially with regard to cocoa powder. Alkalization, also known as refining, is the treatment of grains, pulp or powder with sodium or potassium bicarbonates [18]. The purpose of this process, also colled "Dutch", is to improve – darken the color, alleviate bitterness, as well as improve the dispersion of powder particles [3]. Unfortunately, as numerous studies show, alkalization, which also increases the pH, has a negative effect on the phenolic compounds contained in the raw material. According to Rodrigez et al. [26] and Garcia et al. [14] the color of alkalized cocoa is the result of the enzymatic activity of polyphenol oxidase, for which the optimal pH is around 8. As a result of this enzyme, polyphenolic compounds are oxidized to melanoidins (brown pigments), but at the same time the phenol content is degraded.

As reported by APROTOSOAIE et al. [3] a higher degree of alkalization leads to higher losses of polyphenols; epicatechin at the level of up to 98%, and of catechins by about 80%. As the pH increases, the color of the cocoa darkens, from reddish brown to almost black. Todorowic et al. [28] showed that the content of polyphenols in the alkalized powder was about 1.8 times lower than in the untreated powder. They also showed a similar relationship by determining the antioxidant activity, which was significantly higher in natural powders.

CONCLUSIONS

To summarize the beneficial effects of cocoa powder, the EFSA report [13], issued in 2012 on behalf of Barry Callebaut should be taken into account. The opinion confirms that cocoa flavanols help maintain proper vasodilation, which in turn contributes to normal blood flow. The report **recommended a daily intake of 200 mg of cocoa flavanols, which could be achieved by consuming 2.5 teaspoons of high flavanol cocoa powder or 10 g of dark chocolate**. The content of polyphenolic compounds in cocoa bean products depends on many factors. It is already shaped in the plantations, depending on the variety, region and growing conditions, degree of

maturity, as well as technological processes, and more precisely the parameters used during cocoa beans processing. Nevertheless, as numerous studies have shown, it is possible to preserve these valuable natural compounds by modifying the made from unroasted cocoa beans are offered. It has been shown to be one of the basic processes that degrade a significant amount of polyphenols. Similarly, the alkalization process that has a destructive effect on these valuable antioxidants can be dispensed with. Although non–alkaline powders are lighter in color and have a lower cocoa–chocolate flavor or smell, they contain much more of the desired polyphenols. Dark brown cocoa powders, also called "Dutch" cocoa, are alkalized which gives them color and intense aroma and taste. It should be mentioned **that cocoa powder is also a valuable source of minerals, as well as alkaloids (theobromine or caffeine), which have a stimulating effect, especially after exercise, and also improve concentration. In addition, serotonin, dopamine and tryptophan contained in cocoa beans and its processing products have a positive effect on the work of the brain. Cocoa powder contains more polyphenols than red wine or green tea**. It is important to consume cocoa or dark chocolate regularly, especially those with high cocoa content, in the recommended amounts. Consumers should note, however, that despite the benefits of consuming these products, they are high in calories.

WNIOSKI

Podsumowując korzystne działanie proszku kakaowego, należy wziąć pod uwagę raport EFSA [13], wydany w 2012 roku w imieniu firmy Barry Callebaut. Opinia ta dotyczy potwierdzenia działania flawanoli kakaowych, które pomagają w utrzymaniu prawidłowego rozszerzenia naczyń krwionośnych, co z kolei przyczynia się do prawidłowego ukrwienia. W raporcie **zalecono dzienne spożycie 200 mg flawanoli kakaowych, co można osiągnąć, spożywając 2,5 łyżeczki proszku kakaowego o wysokiej zawartości flawanoli lub 10 g gorzkiej czekolady**. Zawartość związków polifenolowych w produktach z ziarna kakaowego zależy od wielu czynników. Kształtuje się już na plantacjach w zależności od odmiany, regionu i warunków uprawy, stopnia dojrzałości, a także procesów technologicznych, a dokładniej parametrów stosowanych podczas obróbki ziarna kakaowego. Niemniej jednak, jak wykazały liczne badania, możliwe jest zachowanie tych cennych naturalnych związków poprzez modyfikację oferowanych z nieprażonych ziaren kakaowych. Wykazano, że jest to jeden z podstawowych procesów degradacji znacznych ilości polifenoli. Podobnie, można zrezygnować z procesu alkalizacji, który ma destrukcyjny wpływ na te cenne przeciwutleniacze. Chociaż niealkaliczne proszki są jaśniejsze i mają słabszy smak lub zapach kakao-czekolady, zawierają znacznie więcej pożądanych polifenoli. Ciemnobrązowe proszki kakaowe, zwane także „holenderskim" kakao, są alkalizowane, co nadaje im kolor oraz intensywny aromat i smak. Należy wspomnieć, **że proszek kakaowy jest również cennym źródłem związków mineralnych, a także alkaloidów (teobromina, kofeina), które działają pobudzająco, szczególnie po wysiłku, a także poprawiają koncentrację. Dodatkowo serotonina, dopamina i tryptofan zawarte w ziarnach kakao i produktach ich przetwarzania wpływają pozytywnie na pracę mózgu. Proszek kakaowy zawiera więcej polifenoli niż czerwone wino czy zielona herbata**. Ważne jest regularne spożywanie kakao lub gorzkiej czekolady, szczególnie tych z dużą zawartością kakao, ale w zalecanych ilościach. Konsumenci powinni jednak pamiętać, że pomimo korzyści płynących ze spożywania tych produktów są one wysoko kaloryczne.

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