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THE PRESENCE OF OXALATES IN THE COCOA POWDER FROM ORGANIC AND CONVENTIONAL PLANTATIONS

Summary

The objective of this study was to assess the content of oxalates in the samples of cocoa powder available on Polish market, obtained from the cocoa beans from organic and conventional farms. The cocoa is an important food product, which is used for immediate consumption as well as for chocolate production. It is also used in confectionery. The cocoa is of high sensory and nutritional value. However, it also contains antinutrients, including oxalates. It was hypothesised that cocoa beans from conventional cultivation contain more oxalates. The study is aimed to describe cocoa as a commodity product and discuss the presence of oxalates in food products as well as their toxicological aspects. The contents of soluble oxalates in cocoa powder with regard to the method of cocoa farming have been presented therein. The oxalates content in cocoa obtained from organic beans ranged from 322±10 to 1173.52 ± 21.28 mg/100g and from 727.5 ± 53.03 to 1477.5 ± 31.82 mg/100g in cocoa beans from a conventional farm. The statistical analysis showed that the method of farming significantly influenced the content of oxalates.
***Key words**: cocoa, cocoa powder, organic plantations, conventional plantations, oxalate*

OBECNOŚĆ SZCZAWIANÓW W PROSZKU KAKAOWYM Z PLANTACJI EKOLOGICZNYCH I KONWENCJONALNYCH

Streszczenie

Celem pracy była ocena zawartości rozpuszczalnych szczawianów w próbkach proszku kakaowego dostępnego na polskim rynku pochodzącego z ziarna kakaowego z plantacji ekologicznych i konwencjonalnych. Kakao jest ważnym produktem spożywczym, który służy do bezpośredniego spożycia, jak również jest składnikiem do produkcji czekolady oraz wykorzystywania w cukiernictwie. Jest to produkt atrakcyjny sensorycznie o wysokich walorach odżywczych. Trzeba jednak pamiętać, że zawiera on również związki antyodżywcze, do których należą szczawiany. Postawiono hipotezę iż ziarno kakaowe z konwencjonalnego systemu uprawy zawiera więcej szczawianów. W pracy dokonano charakterystyki towaroznawczej kakao i omówiono występowanie szczawianów w żywności oraz ich toksykologiczne aspekty. Zaprezentowano wyniki zawartości szczawianów rozpuszczalnych w proszku kakaowym w zależności od sposobu uprawy. Kakao z ziarna organicznego zawierało od 322±10 do 1173.52 ± 21.28 mg/100g, a kakao z ziarna konwencjonalnego od 727.5 ± 53.03 do 1477.5 ± 31.82 mg/100g szczawianów. Analiza statystyczna wykazała, że na zawartość szczawianów wpływał w sposób istotny sposób uprawy.
***Słowa kluczowe**: kakao, proszek kakaowy, plantacja ekologiczna, plantacja konwencjonalna, szczawiany*

1. Introduction

Food is the fundamental element of human existence and it is a source of energy, building and nutritional components which influences the health and mental condition as well as human behaviour. The composition of food includes the basic nutrients as proteins, lipids, saccharides and micronutrients which are vitamins, mineral nutrients, enzymes, pigments, polyphenolic compounds and others. The presence of these compounds determines the quality of healthy food. Apart from these elements, food also contains a number of other compounds - natural antinutrients and non-nutrients.

The natural antinutrients include a great number of compounds of diverse structure. The oxalic acid and its salts are the examples of antinutrients. The oxalic acid influences the mineral balance of the body. The excessive amount of the oxalic acid may cause renal diseases [1-3]. Oxalic acid is present in vegetables and fruits as well as their preserves, e.g. spinach, dock, rhubarb, coffee, tea, cocoa, sesame seeds, cauliflower, numerous herbs and spices, beer and cider [2, 4].

The objective of this study was to assess the content of soluble oxalates in the cocoa powder available on Polish market, obtained from the cocoa beans from organic and conventional farms.

2. Cocoa as a commodity product

Cocoa is extracted from the seeds of cocoa tree *Theobroma cacao* L. (*Sterculiacae*). The largest plantations of cocoa trees are located in Africa (comprising 70% of the world production, of which 40% is cultivated in the Ivory Coast). There are several varieties of cocoa trees, however, the following varieties: *criollo*, *forastero*, *trinitario* and *national* are of the greatest significance [5-6].

Cocoa pods are the main raw material. They contain from 30 to 40 seeds which are set in a soft pulp. After being deshelled, the seeds undergo natural fermentation or fermentation with *Lactobacillus* sp. The seeds are subsequent-

ly dried and roasted, separated from their skins, cracked, partially deoiled, and ground to powder. The cocoa beans are the source of various products, such as cocoa powder, cocoa paste (mass), coarsely ground cocoa and theobroma oil, also called cocoa butter. Apart from chocolate, cocoa powder is the most popular product made of cocoa beans. It contains numerous beneficial compounds and nutrients.

The excellent properties of cocoa have been known for several thousand years. Nowadays, the cocoa trees are cultivated in about 60 countries, however, only a few of the countries are the main exporters of cocoa [5]. Cocoa trees are cultivated on the area of over 70 000 km^2. About 70% of the world's cocoa production is located in Africa (mainly *forastero*), 20% in Asia (mainly *tirnitario*), and 10% in South America (mainly *trinitario* and *forastero* as well as some of the types of *criollo*) (Figure 1).

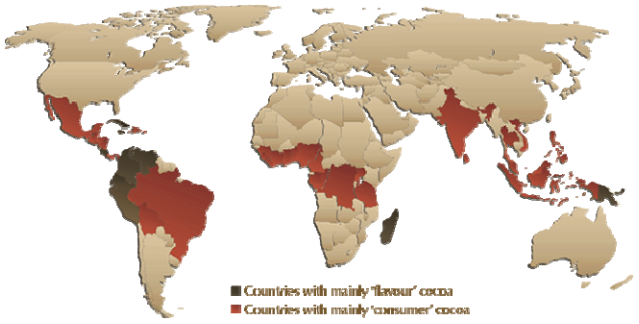
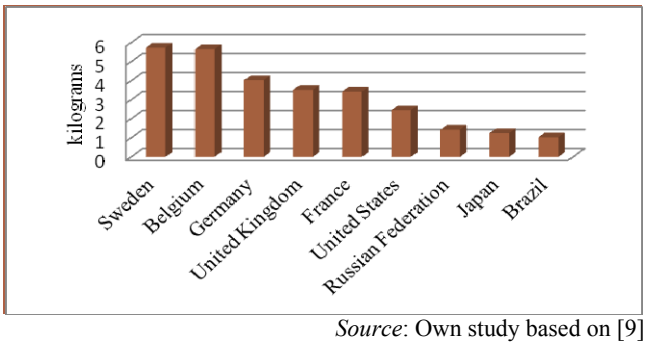


Fig. 1. The main areas of cultivation of cocoa [7]
Rys. 1. Główne obszary upraw Theobroma cacao L. [7]

The following countries were the world's leading producers of cocoa in the years 2012/2013: Ivory Coast (36.9%), Ghana (21.3%), Indonesia (10.4%), Cameroon (5.7%), Nigeria (5.7%), Ecuador (4.9%) and Brasil (4.7%) [8].

The kilogram per capita consumption of cocoa beans in different countries as of 2011/2012 are presented in Figure 2.



Source: Own study based on [9]
Fig. 2. Apparent consumption of cocoa per capita (in 2011/12)
Rys. 2. Spożycie kakao na świecie w 2011/12 [kg/mieszk.]

The cocoa bean comprises various components. The majority of fat is in the bean's kernel and it is partially removed from the kernel in the process of pressing. The extracted paste (mass) contains 8-23% of fat and is used in the production of cocoa powder. There are three types of cocoa powder, with regard to the fat content: whole fat (20-22%), fat (15-17%) and skimmed (9-11%). The components of cocoa beans are used in the production of food, cosmetics and medicines [10].

The cocoa beans also contains saccharides, proteins, purine compounds (caffeine and theobromine) and polyphenolic compounds [11]. During fermentation, the cocoa bean undergoes a number of various changes, which form the cocoa bean's sensory properties. The aroma is developed fully in the process of roasting [6, 12].

The up to date research has confirmed the cardioprotective effect of cocoa - as the source of compounds of antioxidant properties, mainly proanthocyanidins occurring in the form of monomers as catechins and epicatechins or in the form of oligomers of catechins and epicatechins as procyanidin, which have beneficial effect on the function of the endothelium of blood vessels, prevent inflammation and thrombosis processes which leads to the development of arteriosclerosis [13-15].

The research has also showed that cocoa and chocolate are free radical scavengers which is of great importance in cancer prevention [16]. Cocoa and its products also reduce the cholesterol level and the regular consumption of bitter chocolate may increase the concentration of HDL cholesterol (high density lipoprotein) [17]. The research also showed the beneficial effect of cocoa and its preserves on the nervous system. Cocoa contains three main alkaloids, caffeine, theobromine and theophylline. Each of these compounds demonstrates different effect on the nervous system. The content of caffeine in cocoa varies from 0.2 to 0.3% [18]. The regular consumption of caffeine may have a beneficial effect on endocrine, nervous, urinary and respiratory systems [19]. The studies also showed that the caffeine may demonstrate neuroprotective properties in the Alzheimer's and Parkinson's diseases. Caffeine reduces the feeling of tiredness, boosts and improves the mood and may have anticarcinogenic effect. Theophylline demonstrates the strongest diuretic effect, but it also causes dilation of bronchi and bronchioles [19]. Theobromine, occurring in cocoa in the biggest amount, is the most typical alkaloid of cocoa. The cocoa powder comprises about 2-4% of theobromine, the content of theobromine in chocolate is about 1% [20]. Theobromine improves concentration, boosts and partially reduces the effect of tiredness. The positive aspect of the theobromine consumption is that, in comparison to caffeine consumption, it does not cause cardiac arrhythmia and does not increase the blood pressure [21]. It also has a diuretic effect and releases the bronchi muscles [18]. Some of the research also showed that theobromine has an antitussive effect [22].

The amount of 100 g of cocoa contains 1400 mg of flavonoids and procyanidins [23]. Some of the researchers claim that cocoa may contain more polyphenols than wine and tea [24]. Cocoa may also include antinutrients or compounds of negative effect such as oxalates.

3. The oxalates in food of plant origin

The oxalic acid is a common component of plants and animals. This compound is regarded as antinutrient as it inhibits the bioavailability of minerals. Some plants have the ability to cumulate high concentrations of dicarboxylic acids. There are several precursors of the oxalic acid in plants, including glyoxylate and L-ascorbic acid [25].

The function of the oxalate acid in plants has not been fully known. There are some indications that a high content of oxalate acid may protect plants against animals, insects and contagia, due to its influence on the taste, texture, acidi-

ty and the availability of calcium. It has been also suggested that it may serve as a pH regulator and osmoregulator in plants [2].

The oxalates are a common substance and are the end-products of metabolism in plants. Simultaneously, they are undesirable in the human diet due to their negative effects [2]. They are found in the form of salts soluble in water, combined with Na^+, K^+ and NH_4^+ ions whereas the insoluble salts are formed by combining with Ca^{2+}, Fe^{2+} and Mg^2 ions. They are generally described as insoluble oxalates and they are not absorbed in the digestive tract. A regular high consumption of the oxalates with food is alarming due to their negative effects on health [26].

Table 1. Range of published oxalate values [mg/100 g] for foods
Tabela 1. Zawartość szczawianów w żywności [mg/100 g]

Food (100 g)	Description	Range of published values [mg]
Spinach	Raw	400-900
Rhubarb	Raw or cooked	260-1235
Star fruit (carambola)	Raw	80-730
Beet	Roots	76-675
Beet	Leaves	121-916
Tea (100 ml)	Black, brewed	48-92
Tea (100 ml)	Green, brewed	6-26
Tea (100 ml)	Herbal, brewed	0-8
Chocolate	Cocoa powder (baking)	170-623
Chocolate	Milk chocolate Candy	42-123
Tree nuts	Almonds	431-490
Tree nuts	Cashews	231-262
Tree nuts	Hazelnuts	167-22
Tree nuts	Walnuts	74
Tree nuts	Pecans	64
Tree nuts	Pistachios	49-57
Tree nuts	Macadamia	42
Bran	Wheat	457
Legumes	Beans, cooked	8-91
Legumes	Peanuts	96-705
Legumes	Soybeans, dried	2-21
Legumes	Tofu	3-280
Legumes	Textured vegetable protein	58-150
Legumes	Meat substitutes, links, patties	87-154

Source: Own study based on [2, 28]

The soluble oxalates are absorbed by the human body and they enhance the increase in the oxalic acid concentration in urine [27], whereas the insoluble oxalates are directly excreted with faeces. In case of oversaturation of urine with oxalates, the urine may crystallize in the form of insoluble salt, as calcium oxalates, and as gall stones in the kidneys. The oxalates may cause bone decalcification, arthritis or impair the muscle contraction and heart beat [28].

The available research [29] have stated that the acceptable daily intake (ADI) of oxalates for adults is about 250 mg per day. In the countries of Western Europe the average consumption of oxalates in food ranges from 100 to 150 mg per day. It should be noted that about 50% of the calcium oxalates from food dissolve in stomach and the calcium ions and oxalic acid are absorbed into blood stream and internal organs in the upper section of small intestine. A certain amount of the acid passes to the muscle tissue and bones, and the rest undergoes partial oxidation or is excreted with urine. The excessive excretion of the oxalates with urine, above 60 mg per day, contributes to crystallization of calcium oxalate in the urinary tract and therefore one of the most common type of renal calculus is the calcium oxalate renal calculus. 80% of the persons suffering from this disease is diagnosed with this type of renal calculus (kidney stones) [30].

The content of oxalates in food products is diversified and it depends on numerous factors. Table 1 presents the content of oxalates in certain food products.

4. Material and methods

The analysis of the oxalate content was performed on 12 samples of cocoa, 6 from organic production and 6 from conventional production. The organic cocoa was manufactured by the following manufacturers: Naturata, NatVita, Natubio, Terra etica, Surovital and Symbio. The majority of the manufacturers of organic cocoa could define the place of origin of the cocoa. The organic cocoa originated from Ecuador, Dominican Republic, three samples were from Peru, two of which were Criollo. All samples of the organic cocoa were certified and included the names of the certifying units.

The manufacturers of the conventional cocoa were Magnetic, Sweet, Celiko, Deco Morreno, E. Wedel and Van Houten. Three manufacturers of the conventional cocoa stated the place of origin of the product. The samples originated from Ghana, Australia and Africa. None of the conventional cocoa package included the information of the variety of cocoa tree. Both organic and conventional cocoa was mostly a skimmed product in the range of 9-14% of fat and the samples (O1, C1) contained 21% of fat.

All the cocoa samples were encoded. The samples of the organic cocoa were labeled with the symbols from O1 to O6 and the conventional cocoa samples were labeled with symbols from C1 to C6.

The content of soluble oxalates was marked with hot water extraction method and, next, it was precipitated by means of $CaCl_2$ calcium salt and next dissolved in H_2SO_4 acid. After the dissolution it was hot titrated with the solution of $KMnO_4$ until pink colour was obtained and maintained for about 1 minute [31].

5. Test results and discussion

The results of the analyses regarding the general assessment of cocoa as a commodity as well regarding the content of oxalates in cocoa samples coming from organic and conventional plantations have been presented in Table 2.

It has been confirmed that the conventional cocoa available on Polish market is in most cases labeled inappropriately. No country of origin has been found on the label. The consumer purchasing the product does not know where the product originates from. This is incompliant with the applicable regulations [32].

Most of the conventional cocoa powder available on Polish market is a skimmed cocoa type. Only one product was a full fat cocoa. Among the samples of organic cocoa only one product was a full fat cocoa and one fat cocoa whereas the rest of products were skimmed cocoa. The full

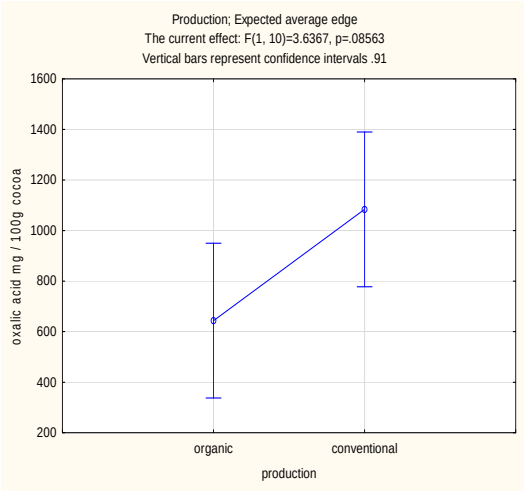
fat and fat cocoa requires special protection against light and oxygen in order to prevent the rapid fat oxidation.

Table 2. The soluble oxalic acid in cocoa
Tabela 2. Rozpuszczalne szczawiany w kakao

Sample number	Origin	The content of oxalic acid [mg/100g]	The fat content [%]
ORGANIC COCOA			
O1	Ecuador	330 ± 21.21	21
O2	Dominican Republic	1173.52 ± 21.28	10-12
O3	Peru (variety Criollo)	360 ± 21.21	12
O4	Peru (variety Criollo)	1327.5 ± 31.82	14
O5	Dominican Republic	352.5 ± 10.61	9.5
O6	Peru	322.5 ± 10.61	10
COCOA CONVENTIONAL			
C1	no data	727.5 ± 53.03	21
C2	no data	1110 ± 21.21	10.5
C3	Ghana	1477.5 ± 31.82	11
C4	no data	1410 ± 21,21	10.5
C5	no data	787.5 ± 53.03	11
C6	no data	990 ± 21.21	10-12
		Value F 3.636*	
* statistically significant p = 0.09			

Source: Compiled on the basis of own results
/ *Źródło*: Opracowano na podstawie badań własnych

The content of the soluble oxalates in the tested samples was very much differentiated. The organic cocoa contained from 322±10 to 1173.52 ± 21.28 mg/100g (of oxalates). However, a higher content of the soluble oxalates has been confirmed in the conventional cocoa, from 727.5 ± 53.03 to 1477.5 ± 31.82 mg/100g. The statistical analysis confirmed this dependency to be statistically significant (Fig. 3).



Source: Compiled on the basis of their own
/ *Źródło*: Opracowano na podstawie badań własnych

Fig. 3. The content of oxalate in organic and conventional cocoa
Rys. 3. Zawartość szczawianów w kakao ekologicznym i konwencjonalnym

The research of Schroder et al. [33] has confirmed the presence of the soluble oxalates from 360 ± 1.7 to 567 ± 8.9 mg/100g in the tested cocoa purchased in organic stores and supermarkets in different countries.

However, it had been proved in the earlier research that systematically drunk cocoa could increase the risk of renal calculus [34]. Still, it has to be taken into account that only 10-20% of the oxalates entering human body with food get absorbed whereas the remaining 40-50% of the oxalate anion present in blood plasma is created from glycine and the other 40–50% from ascorbic acid [35-36].

Conclusions

The research conducted within this study has shown that the method of farming has significantly influenced the content of oxalates in cocoa. The cocoa powder obtained from the organic cocoa grains contained remarkably less oxalates than the cocoa from a conventional plantation. The toxicological aspect of oxalates causes that the consumption of food rich in oxalates should be limited, especially for the people suffering from kidney stones. Cocoa and cocoa processed products belong to the food group with a high oxalate content. Therefore, nutritional education and dietetic limitations are important for people suffering from urinary system disorders, especially from renal calculus.

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