INFLUENCE OF ROASTING PROCESS ON CHANGES IN CONTENT OF SELECTED MINERAL COMPOUNDS IN CHOCOLATES OBTAINED FROM BEANS FROM DIFFERENT REGIONS OF THE WORLD

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Summary. The aim of the study was to compare the mineral compounds content (potassium, phosphorus, magnesium, iron and sodium) in chocolates obtained from roasted and unroasted cocoa beans. Six types of unroasted beans, five types of roasted beans, and the resulting chocolates were investigated. The tested cocoa bean varieties were from Ghana, Venezuela, Dominican Republic, Colombia and Ecuador. Mineral compounds such as potassium, phosphorus and magnesium were found in both grains and chocolates at a much higher level than iron and sodium. The content of mineral components in the final product was significantly lower compared to their content in the raw material from which it was produced. However, the majority of unroasted grains were characterised by lower content of mineral components than roasted grains, which indicates the influence of roasting process on the content of analysed mineral compounds.

Key words: cocoa beans, chocolate, mineral components

INTRODUCTION

Mineral components are essential for proper functioning of the body [Nebesny and Żyżelewicz 2007]. Studies show that cocoa powder and chocolate are a good source of iron, sodium, potassium, manganese, zinc and magnesium [Ieggli et al. 2011, Cinquanta et al. 2016]. Magnesium increases the strength of heart muscle contraction, regulates blood clotting, has a positive effect on blood pressure, regulates enzymatic

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reactions, lipid metabolism and DNA synthesis. Another important macroelement is potassium, which affects the condition of the cardiovascular system and is responsible for its proper functioning [Vlachopoulos et al. 2006]. Also important is iron, an essential element in the production of red blood cells and in the transport of oxygen. Iron deficiency in the body can cause fatigue, anemia, disorders of the immune and nervous systems [Orkusz et al. 2018] The bioavailability of iron is much higher in chocolate than in other vegetables due to the low level of phytic acids contained in it [Cinquanta et al. 2016]. Phosphorus, in turn, takes part in the mineralisation of bones and teeth [Foster et al. 2008].

The chemical composition of cocoa beans is complex and varied, depending not only on how they are processed, but also on the geographical location of the crops, the type of beans and even the soil composition [Rehman and Husnain 2012, Araujo 2017]. One of the post-harvest processes affecting the mineral content of cocoa beans are fermentation and alkalisation processes, cause the extraction of elements and their leaching, which may result in a lower content of mineral components in the final product. Currently, many studies are being conducted, which are aimed at, among others, to obtain chocolate products with the least reduced content of bioactive compounds. An example is raw chocolate, which, is produced from raw unroasted cocoa beans, and the production process is conducted at a temperature not exceeding 45°C.

The aim of this study was to compare the content of selected mineral elements (K, P, Mg, Na, Fe) in roasted and unroasted cocoa beans and chocolates obtained from them.

MATERIAL AND METHODS

Experimental material

The experimental material consisted of roasted and unroasted cocoa beans from the Dominican Republic, Ghana, Venezuela, Colombia and Ecuador, as well as the bitter chocolate obtained from the beans.

Analytical methods

The determination of mineral content in test material [N-90/A-75101.07] was performed at the Analytical Centre of the Warsaw University of Life Sciences – SGGW in accordance with the PB 34 research method, published on 17 February 2011.

The content of K, P, Mg, Fe and Na was determined in roasted and unroasted grains and chocolate made from them. The mineralisation process was carried out by dry combustion in the CARBOLITE CSF 1200 muffle furnace at 550°C for 48 h. The principle of the method was based on burning the sample by heating it in crucibles in excess air (the sample had to be free of traces of carbon). The content of analysed mineral compounds was determined by method of high-performance liquid chromatography with UV VIS detector, according to an internal validated procedure. The chemical analysis was carried out in at least three replications.

Statistical analysis

Microsoft Excel 2013 for Windows 10 was used to calculate the average values of the obtained results and to make graphs. Statistical analysis of the obtained results, correlation and significance of differences using Tukey's test was conducted with use of Statistica 13.0 program.

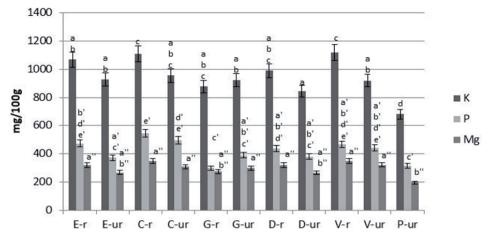
RESULTS AND DISCUSSION

Minerals in cocoa beans

The determined content of mineral compounds K, P, Mg, Fe and Na in the test material. The study also included cocoa beans that were cultivated under organic conditions from Peru and processed at temperatures below 45°C.

The highest potassium content from 682 (e.g. Peru) to 1,120 mg·100 g⁻¹ (roasted grains of Colombia) was determined in the tested samples (Fig. 1). In all analysed grains from different regions of the world, potassium content was higher in roasted grains than in unroasted ones. The only exception was roasted grains grown in Ghana. In the studies by Cinquant et al. [2016], the potassium content in the grains from Ghana was at the level of 720 mg \cdot 100 g $^{-1}$, which is more than 20% lower than in the current studies. In the literature, the level of potassium content in cocoa beans ranges from 566 to 2,552 mg 100 g⁻¹ [Afoakwa et al. 2013, Pinto et al. 2013, Bertoldi et al. 2016, Louriero et al. 2016]. Pinto et al. [2013] and Araujo et al. [2017] show that the average potassium content in cocoa beans from Brazil can reach up level of 782-1,452 mg·100 g⁻¹. Differences in the average potassium content of cocoa beans according to the authors could be related to different levels of availability of this element in soils in different places of cultivation. Louriero et al. [2016] argue similarly. Research by Djikeng et al. [2018] shows that traditional roasting of beans for 10 min at 180°C is the best way to increase the amount of potassium in cocoa beans (947.22 mg·100 g⁻¹). According to Pinto et al. [2013], potassium is the most bioavailable mineral element in cocoa beans.

The second mineral which was characterised by a high content of grains was phosphorus. It was determined as an amount from 316 (unroasted grains of Peru) to 544 mg·100 g⁻¹ (roasted grains of Colombia) – Figure 1. Similarly to the case of potassium, all roasted grains with the exception of Ghana had more potassium. About 21% more phosphorus was determined in roasted grains grown in Ecuador in comparison with unroasted grains. However, similarly as in the case of potassium, higher phosphorus content was determined in unroasted grains in Ghana compared to the amount determined in unroasted grains. The difference was approximately 30%. In the literature the average potassium content in cocoa beans was determined between 196 and 583 mg·100 g⁻¹ [Afoakwa et al. 2013, Pinto et al. 2013, Bertoldi et al. 2016, Cinquanta et al. 2016, Louriero et al. 2016]. In a study by Araujo et al. [2017], the total phosphorus content was 266 mg·100 g⁻¹ for cocoa beans grown in Brazil. In the same region, the content of this element in the beans grown in semi-moisture and wet zones was even higher and amounted to 501 and 507 mg·100 g⁻¹ respectively.



E-r – Ecuador – roasted beans; **E-ur** – Ecuador – unroasted beans; **C-r** – Colombia – roasted beans; **C-ur** – Colombia – unroasted beans; **G-r** – Ghana – roasted beans; **G-ur** – Ghana – unroasted beans; **D-r** – Dominican Republic – unroasted beans; **V-r** – Venezuela – roasted beans; **V-ur** – Venezuela – unroasted beans;

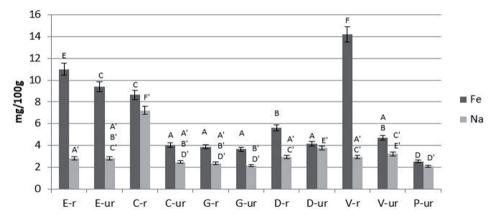
E-r – Ekwador – prażone ziarna; **E-ur** – Ekwador – nieprażone ziarna; **C-r** – Kolumbia – prażone ziarna; **C-ur** – Kolumbia – nieprażone ziarna; **G-r** – Ghana – prażone ziarna; **G-ur** – Ghana – nieprażone ziarna; **D-r** – Republika Dominikany – prażone ziarna; **D-ur** – Republika Dominikany – nieprażone ziarna; **V-r** – Wenezuela – prażone ziarna; **P-ur** – Peru – nieprażone ziarna

- Fig. 1. Total minerals (K, P, Mg) content in roasted and unroasted grains from different regions of the world (the same letter a, b or a', b' or a'', b'' means no statistically significant differences between the analysed products at the level of significance $\alpha = 0.05$)
- Rys. 1. Całkowita zawartość minerałów (K, P, Mg) w prażonych i nieprażonych ziarnach pochodzących z różnych regionów świata (ta sama litera a, b lub a', b' bądź a", b" oznacza brak statystycznie istotnych różnic między analizowanymi produktami na poziomie istotności $\alpha = 0,05$)

Magnesium content in the examined grains ranged from 197 (raw grains from Peru) to 351 mg·100 g⁻¹ (roasted grains from Cameroon) – Figure 1. The magnesium content in roasted grains was higher in all types of grains originating from different regions of the world than in unroasted grains. The only exception were grains cultivated in Ghana, in which the magnesium content in unroasted grains was determined to be approximately 9% higher than in roasted grains. The average values of magnesium in cocca beans might range from 167 to 383 mg·100 g⁻¹ [Afoakwa et al. 2013, Pinto et al. 2013, Bertoldi et al. 2016, Cinquanta et al. 2016, Louriero et al. 2016]. In the studies Araujo et al [2017] magnesium content of 208 mg·100 g⁻¹ was much lower than in the studies Pinto et al [2013], which was 377 mg·100 g⁻¹ and concerned the same growing region – Brazil. Araujo et al. [2017] concluded that the magnesium level in cocca beans depends on the relative abundance of this element in the soil solution. The release of Mg from the clay exchange-able soil complex is lower than the plant requirement, which implies the need for large amounts of available Mg for good plant growth. Djikeng et al. [2018] showed that the magnesium content in all roasted samples increased significantly in comparison with

the sample subjected only to preliminary drying (45°C; 48 h) and is in the range of 500– $-600 \text{ mg} \cdot 100 \text{ g}^{-1}$, which is much higher than in the present study.

The iron and sodium content was significantly lower. Iron content ranged from 2.53 (grains from Peru) to 14.2 mg \cdot 100 g⁻¹ (roasted grains from Venezuela) – Figure 2. In the literature we can find a number of studies where iron content in dry cocoa beans varies between 1.0 and 18.3 mg·100 g⁻¹ [Afoakwa et al. 2013, Bertoldi et al. 2016, Cinquanta et al. 2016, Loureiro et al. 2016]. Studies by Arajuo et al. [2017] show that the average iron content in Brazilian grains may be even less than 1 mg \cdot 100 g⁻¹. Studies by Pinto et al. [2013] show that farms in the same region can contain iron levels from 1.0 (semi-moisture zone) to 1.9 mg \cdot 100 g⁻¹ (wet zone). In addition, these studies have shown the influence of the environment on the iron content of dry cocoa beans. A study by Djikeng et al. [2018] showed higher content of iron after traditional roasting (59.12 and 53.78 mg \cdot 100 g⁻¹) compared to pre-dried beans (51.11 mg·100 g⁻¹) and later roasted. However, roasting significantly reduced the concentration of this mineral. The increase in iron recorded with traditional roasting can be attributed to the fact that the traditional roasting temperature increases the digestibility of cocoa beans and then initiates the release and growth of iron. The amount of iron has decreased with the processing time. The iron content of cocoa beans is a result of the geographical origin of cocoa beans [Bertoldi et al. 2016].



E-r – Ecuador – roasted beans; **E-ur** – Ecuador – unroasted beans; **C-r** – Colombia – roasted beans; **C-ur** – Colombia – unroasted beans; **G-r** – Ghana – roasted beans; **G-ur** – Ghana – unroasted beans; **D-r** – Dominican Republic – roasted beans; **D-ur** – Dominican Republic – unroasted beans; **V-r** – Venezuela – roasted beans; **V-ur** – Venezuela – unroasted beans; **P-ur** – Peru – unroasted beans

E-r – Ekwador – prażone ziarna; **E-ur** – Ekwador – nieprażone ziarna; **C-r** – Kolumbia – prażone ziarna; **C-ur** – Kolumbia – nieprażone ziarna; **G-r** – Ghana – prażone ziarna; **G-ur** – Ghana – nieprażone ziarna; **D-r** – Republika Dominikany – prażone ziarna; **D-ur** – Republika Dominikany – nieprażone ziarna; **V-r** – Wenezuela – prażone ziarna; **P-ur** – Peru – nieprażone ziarna

- Fig. 2. Total minerals (Fe, Na) content in roasted and unroasted grains from different regions of the world (the same letter A, B or A', B' means no statistically significant differences between the analysed products at the level of significance $\alpha = 0.05$)
- Rys. 2. Całkowita zawartość minerałów (Fe, Na) w prażonych i nieprażonych ziarnach pochodzących z różnych regionów świata (ta sama litera A, B lub A', B' oznacza brak statystycznie istotnych różnic między analizowanymi produktami na poziomie istotności $\alpha = 0,05$)

The sodium content was determined from 2.1 for Peru beans to 7.2 mg·100 g⁻¹ for roasted beans from Cameroon. Based on the sodium content of cocoa beans, it can be concluded whether these were treated with more alkali. In a study by Djikeng et al. [2018] no significant difference was observed between sodium concentrations in beans pre-dried at 45°C and those dried traditionally or in the oven for 5 min. On the other hand, significantly low sodium content was determined in dried and roasted grains 10 min at 180°C (51.00 mg·100 g⁻¹). The biggest difference was found in Ghana beans and it was almost 30% higher before roasting, while in Venezuela the difference was about 4% in favour of unroasted beans.

To sum up, in most roasted beans a higher content of mineral components was determined in comparison to unroasted beans.

Mineral compounds in chocolates

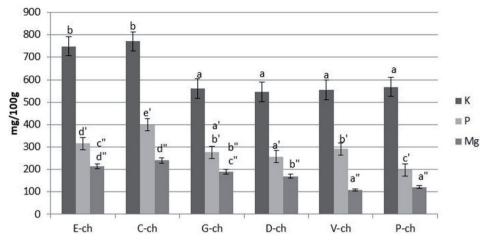
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The content of the elements in six types of chocolate from the same regions as the beans is shown in Figures 3 and 4. Similarly to cocoa beans, potassium, phosphorus and magnesium were indicated in much larger amounts than iron and sodium. However, as a result of the chocolate production process, the mineral content has decreased in comparison with the beans from which it was made.

The highest sodium content was determined in the analysed chocolates from among the analysed elements. Its content ranged from 546 (chocolate from Dominican Republic beans) to 771 mg·100 g⁻¹ (chocolate from Colombia beans) – Figure 3. Also in the studies by Grembecka and Szefer [2012] the content of potassium in bitter chocolate was the highest and was at a similar level as in these studies and amounted to 721 mg·100 g⁻¹. Also a similar level was noted in studies by Ieggli et al. [2011] and Cinquanta et al. [2016]. In the studies by Kruszewski and Obiedziński [2018] potassium content ranged from 5 to 9 g·kg⁻¹. Higher values were recorded in chocolates produced with the use of fully automated production lines, while the lowest values were characteristic for chocolate samples produced with the traditional method.

The phosphorus content of the chocolates studied ranged from 198 (chocolate obtained from raw beans from Peru) to 399 mg·100 g⁻¹ (chocolate from Colombia) – Figure 3. Also in grains from Colombia a much higher amount of this element was determined in comparison to other regions. In a study by Grembecka and Szefer [2012] the phosphorus content was at a much lower level of 107 mg·100 g⁻¹. Other results were obtained by Cinquanta et al. [2016], who determined 515 mg·100 g⁻¹ of potassium in bitter chocolate. Sager [2012] in turn report on the content of this element in bitter chocolates in the range of 1,880–3,392 mg·kg⁻¹, which is very similar to the research in this study. Whereas Mrmošanin et al. [2018] determined the content of potassium in the amount of 236 mg·100 g⁻¹. Approximate level (244 mg·100 g⁻¹) was obtained by Musioł et al. [2018].

The content of magnesium in the chocolates studied ranged from 109 (chocolate based on Venezuelan beans) to 240 mg·100 g⁻¹ (chocolate from Colombia) – Figure 3. In the literature, the content of this element is determined in wide ranges [Ieggli et al. 2011, Sager et al. 2012, Kruszewski et al. 2018, Mrmošanin et al. 2018]. According to Musioł et al. [2018], the content of magnesium in bitter chocolates is at the level of 165 mg·100 g⁻¹.



E-ch – Ecuador – chocolate – roasted beans; C-ch – Colombia – chocolate – roasted beans; G-ch – Ghana – chocolate – roasted beans; D-ch – Dominican Republic – chocolate – roasted beans; V-ch – Venezuela – cho-colate – roasted beans; P-ch – Peru – chocolate – roasted beans

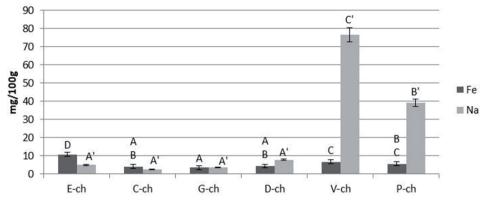
E-ch – Ekwador – czekolada – prażone ziarna; C-ch – Kolumbia – czekolada – prażone ziarna; G-ch – Ghana – czekolada – prażone ziarna; D-ch – Republika Dominikany – czekolada – prażone ziarna; V-ch – Wenezuela – czekolada – prażone ziarna; P-ch – Peru – czekolada – prażone ziarna

- Fig. 3. Comparison of the minerals (K, P, Mg) content in the chocolates (the same letter a, b or a', b' or a'', b'' means that there are no statistically significant differences between the analysed products at a confidence level of $\alpha = 0.05$)
- Rys. 3. Porównanie zawartości składników mineralnych (K, P, Mg) w czekoladach (ta sama litera a, b lub a', b' bądź a", b" oznacza brak statystycznie istotnych różnic między analizowanymi produktami przy poziomie ufności α = 0,05)

Cinquanta et al. [2016] determined in bitter chocolates (with 90% cocoa content) as much as 252 mg \cdot 100 g⁻¹, but in chocolates with lower cocoa content (60%) it was determined only 158 mg \cdot 100 g⁻¹.

Iron content in the chocolates studied ranged from 4.2 (Colombian chocolate) to $10.8 \text{ mg} \cdot 100 \text{ g}^{-1}$ (Ecuador chocolate) – Figure 4. Similarly, in Kruszewski and Obiedziński [2018] the lowest content of this element was determined in chocolate based on Ecuadorian beans (3.6 mg $\cdot 100 \text{ g}^{-1}$). The studies by Güldaş et al. [2008] and Rehman and Husnain [2012] showed a very low iron level of only 1.8–3.6 mg $\cdot 100 \text{ g}^{-1}$. However, studies by Ieggli et al. [2011], Grembecka and Szefer [2012], and Sager [2012] show a wide range of iron content similar to the results obtained in this study. The bioavailability of iron is much higher in chocolate than in vegetables due to the low level of phytic acids contained in it [Cinquanta et al. 2016]. This mineral is an essential part of respiratory pigments, myoglobin, haemoglobin and many other enzymes.

Sodium content in the chocolates studied ranged from 2.7 (Colombian chocolate) to 39.1 mg·100 g⁻¹ (Peru chocolate) – Figure 4. High sodium contents were determined by Güldaş et al. [2008] at range of 25–36 mg·100 g⁻¹ in chocolates from Turkey and at range of 2–48 mg·100 g⁻¹ in chocolates from Colombia by Rehman and Husnain [2012]. On the



E-ch – Ecuador – chocolate – roasted beans; **C-ch** – Colombia – chocolate – roasted beans; **G-ch** – Ghana – chocolate – roasted beans; **D-ch** – Dominican Republic – chocolate – roasted beans; **V-ch** – Venezuela – chocolate – roasted beans; **P-ch** – Peru – chocolate – roasted beans

E-ch – Ekwador – czekolada – prażone ziarna; **C-ch** – Kolumbia – czekolada – prażone ziarna; **G-ch** – Ghana – czekolada – prażone ziarna; **D-ch** – Republika Dominikany – czekolada – prażone ziarna; **V-ch** – Wenezuela – czekolada – prażone ziarna; **P-ch** – Peru – czekolada – prażone ziarna

- Fig. 4. Comparison of the minerals (Fe, Na) content in the chocolates (the same letter A, B or A', B' means that there are no statistically significant differences between the analysed products at a confidence level of $\alpha = 0.05$)
- Rys. 4. Porównanie zawartości składników mineralnych (Fe, Na) w czekoladach (ta sama litera A, B lub A', B' oznacza brak statystycznie istotnych różnic między analizowanymi produktami przy poziomie ufności α = 0,05)

other hand, leggli et al. [2011] examined seven dark chocolates with different cocoa mass contents, in which the sodium content ranged from 5.9 to 50.9 mg \cdot 100 g⁻¹. Literature data suggest that from a nutritional point of view chocolate is not a preferred source of sodium [Cinquanta et al. 2016].

Differences in the content of the tested elements, depending on the type of chocolate, between the results of own research and those presented by other authors may result primarily from different composition of raw materials used in their production. To summarise, the content of mineral components in chocolates was lower than in cocoa beans. Most of the components are found in the husk, which is removed before the bean milling process. As a result, the components contained in the outer layer are also lost. Grains are often subjected to the process of alkalisation, i.e. bathing in acidic carbonates. This process may cause the extraction of elements and their leaching, which may result in a lower content of mineral components in the final production. Unroasted grain and raw chocolate had one of the lowest mineral content. Similar values were obtained for the beans and chocolates obtained from them originating in the Dominican Republic and Venezuela. The regression analysis at 95% confidence interval showed that there is a positive correlation between the iron, potassium, magnesium and phosphorus content in chocolate and the type of grain used for its production (p = 0.00000). However, a negative correlation was found for sodium.

CONCLUSIONS

Potassium, phosphorus and magnesium were found in both grains and chocolates at a much higher level than iron and sodium. The content of mineral components in the final product was significantly lower compared to their content in the raw material from which it was produced. On the other hand, most unroasted grains had a lower content of mineral components than roasted grains. The lowest contents of analysed elements were determined in raw chocolate. Similar values were also determined for chocolates produced from beans grown in Ghana, Venezuela and the Dominican Republic. It can be assumed that the content of mineral components depends mainly on the region in which the beans are grown.

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WPŁYW PROCESU PRAŻENIA NA ZMIANY ZAWARTOŚCI WYBRANYCH ZWIĄZKÓW MINERALNYCH W CZEKOLADACH OTRZYMYWANYCH Z ZIAREN POCHODZĄCYCH Z RÓŻNYCH REGIONÓW ŚWIATA

Streszczenie. Celem badań było porównanie zawartości związków mineralnych (potasu, fosforu, magnezu, żelaza i sodu) w czekoladach otrzymanych z prażonych i nieprażonych ziaren kakaowych. Zbadano sześć rodzajów ziaren nieprażonych, pięć rodzajów ziaren prażonych oraz powstałe w ich wyniku czekolady. Badane odmiany ziaren kakaowych pochodziły z Ghany, Wenezueli, Republiki Dominikany, Kolumbii i Ekwadoru. Związki mineralne takie jak potas, fosfor i magnez stwierdzono zarówno w ziarnach, jak i w czekoladach na znacznie wyższym poziomie niż żelazo i sód. Zawartość składników mineralnych w produkcie końcowym była istotnie mniejsza w porównaniu z ich zawartością w surowcu, z którego został on wytworzony. Jednak większość ziaren nieprażonych charakteryzowała się mniejszą zawartością składników mineralnych niż ziarna prażone, co wskazuje na wpływ procesu prażenia na zawartość analizowanych związków mineralnych.

Słowa kluczowe: ziarno kakaowe, czekolada, składniki mineralne