PRODUCTION AND ANALYSIS OF *CERATONIA SILIQUA* L. POWDERS

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Abstract
The powder of Ceratonia siliqua fruit pulp is important for the food industry because it is used as a component of various food products, mainly in confectionery, bakery and beverages. The raw and roasted carob powders are used in foods due to the high content of sweet components and for the flavor and color of foods. The purpose of this paper was to determine the chemical composition of the raw and roasted Ceratonia siliqua pulp powders. The carob legumes were gathered from Ceratonia trees from Romania, Galati area. Three types of carob powders were produced: CR1 powder from raw carob pulp, CR2 powder from roasted carob pulp at 146 ± 3 °C and CR3 from roasted carob pulp at 195 ± 5 °C. Were determined the amount of sugars, protein, fat, ash, dietary fibers, pH and acidity for CR1, CR2 and CR3 powders. The profile of amino acids was also of interest, but only for CR1 powder. The most abundant amino acid was valine followed by threonine. By contrast, cysteine and cystine were the lowest, followed by glycine and tryptophan. CR1 powder presented a large amount of sugars and a high acidity level. When compared with CR1 powder, roasted carob powers presented a reduced amount of moisture, sugars, protein and acidity, but an increased amount of fibers and ash.

Key words: amino acids,carob pods, carob pulp, food nutrients, reducing sugars, roasting.

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1. INTRODUCTION

Ceratonia siliqua tree is growing wild on Romanian soil. It produces the carob pod or so-called the carob legume, which is the tree fruit. The pods are used in food industry to produce chocolate (as cocoa powder substitute), or as an ingredient in cookies and cakes because of its flavor and sweet taste. Thermal treatment of the carob legumes darkens the color and gives a plus for the carob use. In some countries the carob pods can be used to produce beverage, compote, liqueur and syrup (Youssef *et al*., 2013). Due to the content in sugars (glucose, fructose and sucrose)the carob powder is used as a natural sweetener. So, the carob powderis used in confectionery, bakery, beverages (Lecumberri *et al*., 2007; Wang *et al*, 2002; Koebnick*et al*, 2006; Yousif and Alghzawi 2000; Kumazawa *et al*., 2002). Other uses of carob are in medicine as laxative and diuretics, and it can be fermented to produce bioethanol (Biner *et al*., 2007; Bouzouita *et al*., 2007; Dakia *et al*., 2007; Turhan *et al*., 2006; Roukas, 1994).

Carob pods are made from pulp and seeds. Carob powder is produced from the carob pulp by drying, roasting and milling. According to many researchers, the general chemical composition of carob pulp contains carbohydrates, fat, protein, dietary fibres, polyphenols, minerals and vitamins. Battle and Tous (1997) say that the carob pulp has a high amount of total sugars between 48 and 56 %, of which sucrose is 32 to 38 %, glucose is 5 to 6 %, fructose is 5 to 7 % and maltose which has also been found. Fat content is between 0.2 to 0.6 % and ash between 2 and 3 %. Also, ripe carob pods contain a large amount of condensed tannins (16 to 20% dry weight). Insoluble dietary fiber content is 18% and is made by cellulose and hemicellulose.Ayaz (2007) analysed carob pods with removed seeds (carob pulp) and found 87.5 % sugars (with 43.7 % sucrose, 39.5 % glucose, 4.2 % fructose), 4.5 % protein, organic acids, phenolic compounds and mineral elements (K,P, Ca, Mg, Fe, Mn, Zn, Cu). Morton (1987) reported for carob powder amounts of 80.7 % carbohydrates of which sugar is 72 %, fiber 7.7 %, 4.5 % protein, 1.4 % fat, 2.2 % ash.

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According to these findings, can be observed that *Ceratonia siliqua* pulp have a high amount of carbohydrates, followed by a good content of fibres and small amounts of proteins, fat, minerals and other compounds.
The purpose of this paper was to determine the chemical composition of the raw and roasted *Ceratonia siliqua* pulp powders. The interest of making the carob powders is to later use them in various food combinations such as confectionery, bakery, beverages etc.

2.MATERIALS AND METHODS

Carob powder production

Carob pods were gathered from Galati area when fully riped, in November. They were washed, cleaned, air-dried for two days at 22 ± 2 °C, and then the carob seeds were removed manually from the pulp. The carob pulp was dried using Etuva 50 (ITM, Romania). The raw carob pulp powder (CR1) was produced by grinding the dried pulp using the electric grinder HB-7562 (Hausberg, Germany), followed by sieving with no. 14 sieve according to ASTM E11 (2015), or through 1.4 mm sieve according to ISO 3310-1 (2000),and finally packaging the fine carob powder in food jars. Another carob pulp powder (CR2) was produced starting from dried carob pulp that was roasted at 146 ± 3 °C for 15 minutes (with heating level one) using Evsan oven (Evsan, Turkey), then grinded, sieved with no. 14 sieve (1.4 mm) and packaged as mentioned before. The third carob powder (CR3) was produced as mentioned for CR1, but the roasting was at 195 ± 5 °C for 5 minutes (using heating level one and two).

Physicochemical evaluationof carob powder

Themoisture was determined using ITM 50 oven (Bucuresti, Romania) according to AOAC 925.09 (2005) method. The total sugars were determined by the Luff-Schoorl method according toEC 152 (2009), the total protein was determined using UDK 130 D distilling unit (Velp Scientifica, Italy) by AOAC 960.52 (2005) (calculated with a converting factor of 6.25), the fatby AOAC 920.39C (2005) using SER 148Soxhlet extractor (Velp Scientifica, Italy)and the ash by AOAC 923.03 (2005). The amino acids such as alanine, arginine, aspartic acid,cystine and cysteine,glutamic acid,glycine, histidine, isoleucine, leucine, lysine, methionine,phenylalanine, proline,serine,threonine,tyrosine, valine were determined according to ISO 13903 (2005) and tryptophan was determined according to EC 152 (2009). The pH was determined using theautomatic titrator (Metrohm, Switzerland). The dietary fibers were determined using the formula: % dietary fibers = % dry matter – (% reducing sugars + % protein + % lipid + % ash). Carob powder acidity was determined by AOAC 920.92 (2005) method.

Statistical analysis

Mean values and standard deviations for physicochemical parameters were determined with Microsoft Excel 2010 in the case of three replications for each physical and chemical parameter analysed.

3.RESULTS AND DISCUSSIONS

Raw carob powder physicochemical characteristics were presented in table 1.

Table 1. Physicochemical parameters for CR1 powder

Composition of raw powder (CR1)	Mean ± SD (n = 3)
Moisture*	9.85 ± 0.19
Sugars*	57.88 ± 2.33
Protein*	5.44 ± 0.53
Fat*	0.83 ± 0.01
Ash*	2.85 ± 0.05
Dietary fibers*	23.15 ± 0.39
pH	4.34 ± 0.01
Acidity	36.04 ± 1.91

*-calculated on dry weight (d. w.) basis and expressed as g/100g d. w.

The moisture of the powder is around 10 %, the percent being a relative value, as it can be either lower or higher. The CR1 carob powder value is acceptable according to literature, because Khlifa (Khlifa et al., 2013) found a medium value of 10.2 % and Youssef (Youssef et al., 2013) determined a lower value, of 5.3 %. The variation of moisture in carob powder is caused by preparation and storage. The sugars are around 58 %, being the major constituent of CR1. Ayaz (Ayaz et al., 2007) found an amount of 88 % sugars, Youssef (Youssef et al., 2013) of 76 % and Khlifa (Khlifa et al., 2013) a lower value, of only 45 %. Biner and Kumazawa (Biner et al., 2007, Kumazawa et al., 2002) stated that the sugars which can be found in carob pods are mostly glucose, fructose and sucrose. Fat amount of CR1 powder is low, being under 1 % of carob composition. Similar values were found by Sigge and Khlifa (Sigge et al., 2011; Khlifa et al., 2013) but Youssef (Youssef et al., 2013) found a higher value of fat that approached 2 %. Ash amount comply with the literature limits of 2 to 3 % (Khlifa et al., 2013;Sigge et al., 2011;Youssef et al., 2013). According to literature reports, the fiber amount of carob powder vary from 7 to 40 % (Khlifa et al., 2013; USDA, 2016), and from the data obtained, it can be seen that the CR1 content of fibers is within the limits. The values of pH and the acidity of the CR1 powder indicate a product with high acidity.

Table 2.Amino acids profile of carob pulp powder CR1

Amino acid	CR1 powder (mg/g d. w.)
Alanine	2.20 ± 0.10
Arginine	1.06 ± 0.47
Aspartic acid	2.92 ± 0.76
Cysteine and cystine	0.36 ± 0.44
Glutamic acid	2.73 ± 0.50
Glycine	0.41 ± 0.11
Histidine	0.79 ± 0.29
Isoleucine	1.37 ± 0.38
Leucine	2.50 ± 0.56
Lysine	2.44 ± 0.37
Methionine	0.50 ± 0.14
Phenylalanine	0.54 ± 0.16
Proline	2.10 ± 0.40
Serine	2.85 ± 0.46
Threonine	3.57 ± 0.43
Tryptophan	0.45 ± 0.25
Tyrosine	1.10 ± 0.30
Valine	3.70 ± 0.34
Σ amino acids	30.99 ± 1.78

As mentioned above, the protein was calculated as total nitrogen multiplied by 6.25, thus an amount of 5.4 % being obtained. By determining the amino acids profile of the carob powder (Table 2), there was a total of 3.1 % for the protein content. Other researchers mentioned that they obtained a sum of the amino acids of 2.6 for raw carob powder (Ayaz et al., 2009). For CR1 powder the most abundant amino acid was valine followed by threonine. By contrast, cysteine and cystine were the lowest, followed by glycine and tryptophan.

As mentioned before, the CR2 and CR3 powder were produced by means of thermal treatment (roasting). The studied parameters are presented in tables 3 and 4.

In the case of CR2 carob powder the color was darker then CR1, due to Maillard reactions (Cepo et al., 2014).

Table 3.Physicochemical parameters for CR2 carob powder

Composition of roasted powder (CR2)	Mean ± SD (n = 3)
Moisture*	4.54 ± 0.01
Sugars*	53.44 ± 1.73
Protein*	4.50 ± 0.05
Fat*	0.75 ± 0.03
Ash*	3.48 ± 0.31
Dietary fibers*	33.29 ± 1.37
pH	4.72 ± 0.01
Acidity	27.72 ± 1.52

*expressed as g/100g d. w.

Because of the thermal treatment, the moisture of CR2 powder was 54 % lower than CR1. The amount of protein and sugars decreased with 17 % and respectively 20 %. After roasting the ash and pH values increased. Compared with the values for CR1, the dietary fibers value for CR2 increased due to the reduced amount of the sugars, proteins and moisture. The thermal treatment seems to reduce the carob powder acidity, CR2 having with 23 % less acidity than CR1. The chemical composition of CR2 powder is due to the new chemical compounds formed after Maillard reactions (Cepo et al., 2014), removal of the volatile acidity and other reactions at high temperatures.

As revealed in table 4, there was a loss in reducing sugars, protein, fat and moisture for CR3 powder when compared with CR1 powder. So, the reducing sugars decreased with

45 %, followed by fat with 30 % and protein with 26 %.

Table 4.Physicochemical parameters for CR3 powder

Composition of roasted powder (CR3)	Mean ± SD (n = 3)
Moisture*	2.60 ± 0.04
Sugars*	31.88 ± 2.65
Protein*	4.01 ± 0.01
Fat*	0.68 ± 0.06
Ash*	3.57 ± 0.22
Dietary fibers*	57.26 ± 1.37
pH	5.03 ± 0.02
Acidity	13.90 ± 2.10

*expressed as g/100g d. w.

The reducing of CR3 acidity with 61 % toward CR1 seems to fasten the Maillard reactions, but the reduced amount of water and the acid medium don't favor the Maillard reactions, therefore the losses of nutrients being probably caused by the intensive thermal treatment that burnt, caramelized and denaturalized many of the chemical components of the CR3 powder. This can be proven by the increase in the ash amount of CR3 with 20 % compared to CR1. After the intense thermal treatment the amount of the most important nutrients in CR3 powder decreased when compared with the values determined for CR1 and CR2 powders.

4.CONCLUSIONS

The values of the most important nutrients of raw carob powder from Galati area are within the limits of research literature. The roasting of the carob pulp went to a reduced amount of studied physicochemical parameters. Intense thermal treatment (around 200 °C) caused the destruction of some nutritive components of the carob powder. Our study must be followed by a sensorial analysis of various food matrices containing the carob powders.

5.REFERENCES

[1] Youssef, M. K. E., El-Manfaloty, M. M., Ali, H. M. Assessment of proximate chemical composition, nutritional status, fatty acid composition and phenolic compounds of carob (Ceratonia siliqua L.).Food and Public Health,3(6),2013, 304-308.

[2] Lecumberri, E., Mateos, R., Izquierdo-Pulido, M., Rupérez, P., Goya, L., Bravo, L. Dietary fibre composition, antioxidant capacity and physico-chemical properties of a fibre-rich product from cocoa (Theobroma cacao L.).Food Chemistry,104(3),2007,948-954.

[3] Wang, J., Rosell, C. M., de Barber, C. B. Effect of the addition of different fibres on wheat dough performance and bread quality.Food chemistry,79(2), 2002, 221-226.

[4] Koebnick, C., Gruendel, S., Garcia, A. L., Otto, B., Weickert, M. O. Carob pulp preparation rich in insoluble fiber and polyphenols enhances lipid oxidation and lowers postprandial acylated ghrelin.The FASEB Journal,20(4), 2006, A599.

[5] Yousif, A. K., Alghzawi, H. M. Processing and characterization of carob powder.Food Chemistry,69(3), 2000, 283-287.

[6] Kumazawa, S., Taniguchi, M., Suzuki, Y., Shimura, M., Kwon, M. S., Nakayama, T. Antioxidant activity of polyphenols in carob pods.Journal of agricultural and food chemistry,50(2), 2002, 373-377.

[7] Biner, B., Gubbuk, H., Karhan, M., Aksu, M., Pekmezci, M. Sugar profiles of thepods of cultivated and wild types of carob bean (Ceratonia siliqua L.) in Turkey. Food Chem., 100(4), 2007, 1453–1455.

[8] Bouzouita, N., Khaldi, A., Zgoulli, S., Chebil, L., Chekki, R., Chaabouni, M.M., Thonart,P. The analysis of crude and purified locust bean gum: a comparison of samples from different carob tree populations in Tunisia. Food Chem. 101(4),2007, 1508–1515.

[9] Dakia, P.A., Wathelet, B., Paquot, M. Isolation and chemical evaluation of carob (Ceratonia siliqua L.) seed germ. Food Chem., 102(4), 2007, 1368–1374.

[10] Turhan, I., Tetik, N., Aksu, M., Karhan, M., Certel, M. Liquid-solid extraction of soluble solids and total phenolic compounds of carob bean (Ceratonia siliqua L.).J. Food Process. Eng., 29 (5), 2006, 498–507.

[11] Roukas, T.Solid-state fermentation of carob pods for ethanol production. Applied Microbiology and Biotechnology, 41(3), 1994, 296–301.

[12] BATLLE, I., TOUS, J. Carob tree. Ceratonia siliqua L. Promoting the conservation and use of underutilized and neglected crops. Institute of Plant Geneticsand Crop Plant Research, Gatersleben, 1997, 17.

[13] Ayaz, F. A., Torun, H., Ayaz, S., Correia, P. J., Alaiz, M., Sanz, C., Gruz, J., Strnad, M. Determination of chemical composition of Anatolian carob pod (Ceratonia siliqua L.): sugars, amino and organic acids, minerals and phenolic compounds.Journal of Food Quality,30(6), 2007, 1040-1055.

[14] MORTON, J. F.Fruits of Warm Climates. Julia F. Morton, Miami, Florida, USA,1987, 65-69.

[15] ASTM E11. Standard Specification for Woven Wire Test Sieve Cloth and Test Sieves, ASTM International, West Conshohocken, PA, 2015.
[16] ISO 3310-1:2000.International Organization for Standardization.Test Sieves, Technical Requirements and Testing, Part 1: Test Sieves of Metal Wire Cloth, 4th edition, Geneva,2000.
[17] AOAC. Official method of analysis. 18th ed. Association of Official Analytical Chemists (AOAC), Washington, DC, USA, 2005.
[18] EC 152. Commission Regulation 152/2009. The methods of sampling and analysis for the official control of feed. Determination of total sugars; Determination of tryptophan, 2009.
[19] ISO 13903. International Organization for Standardization. Animal feeding stuffs. Determination of amino acids content, 2005.
[20] Khlifa, M., Bahloul, A., Kitane, S. Determination of Chemical Composition of Carob Pod (Ceratonia Siliqua L.) and its Morphological Study.J. Mater. Environ. Sci. 4(3), 2013, 348-353.
[21] Sigge, G. O., Iipumbu, L., Britz, T. J. Proximate composition of carob cultivars growing in South Africa.South African Journal of Plant and Soil, 28(1), 2011, 17-22.
[22] USDA. United States Department of Agriculture Agricultural Research Service, National Nutrient Database for Standard Reference Release, Basic Report: 16055,Carob flour, 2016, http://ndb.nal.usda.gov/ndb/foods/show/4794?fgcd=&manu=&lfacet=&format=&count=&max=35&offset=&sort=&qlookup=carob
[23] Ayaz, F. A., Torun, H., Glew, R. H., Bak, Z. D., Chuang, L. T., Presley, J. M., Andrews, R. Nutrient content of carob pod (Ceratonia siliqua L.) flour prepared commercially and domestically.Plant foods for human nutrition,64(4), 2009, 286-292.
[24] Čepo, D. V., Mornar, A., Nigović, B., Kremer, D., Radanović, D., Dragojević, I. V. Optimization of roasting conditions as an useful approach for increasing antioxidant activity of carob powder.LWT-Food Science and Technology,58(2), 2014, 578-586.