Determination of the chemical composition of commercial carob products and evaluation of the results using Chemometrics

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1. Introduction

Carob tree is cultivated in most Mediterranean countries, mainly in mild and dry areas. Its scientific name (*Ceratonia siliqua*) derives from the Greek word "Kera", which relates to the keratomorphic shape of the fruit and the Latin word siliqua, which refers to the pods' hardness and shape. World production of carob is estimated at around 160 000 tonnes per year. Spain produces the largest quantities, followed by Italy, Portugal, Morocco, Turkey, Greece, Cyprus and Lebanon [1].

Many studies have shown that carobs and their products can promote human health and assist to prevent the treatment of some chronic diseases. Carobs contain antioxidants and polyphenols (ingredients that help cancer prevention and hyperlipidemia), improve cholesterol levels in the blood, treat diarrhea, contain vitamins and many minerals. The carob is effective in regulating blood glucose levels (due to the high content in fibers), thus improving digestion. Therefore, it is a safe food for people with diabetes [2]. Carob can be eaten raw and it has a sweet taste. It has its own unique flavor and provides a variety of healthy and natural food products such as bread, beverages (coffee substitutes, liqueurs, tea), nuts, can be combined with tahini, honey and/or chocolate. In Cyprus, a lot of carob products are produced and the most widely known is the carob syrup (charoupomelo). Carob is known as a substitute for chocolate, since it is a natural chocolate-like sweetener. It has advantages over chocolate, since it has fewer calories and contains neither caffeine nor theobromine [1,3]. Carob flour (from the seeds) is used to manufacture dietetic products and products for celiac patients (gluten free products) [4].

2. Experimental part

Twenty commercially available carob products were analysed for the determination of carbohydrates, proteins, caffeine/theobromine, dietary fibers, fat, moisture, ash and minerals composition and the results were compared to that of domestic carob fruits, widely found in the island of Cyprus (*cultivars: Koumpota, Kountourka and Tylliria*). The analyses took place in an accredited laboratory using, either official or accredited/validated methods. The results for the moisture and ash analysis of carob fruits and carob powders are presented in detail.

Fig. 1: Commercially carob products that were analysed.

3. Results and Discussion

The nutritional composition of the 3 carob cultivars and all the 20 products that were analysed is shown in Figure 2.

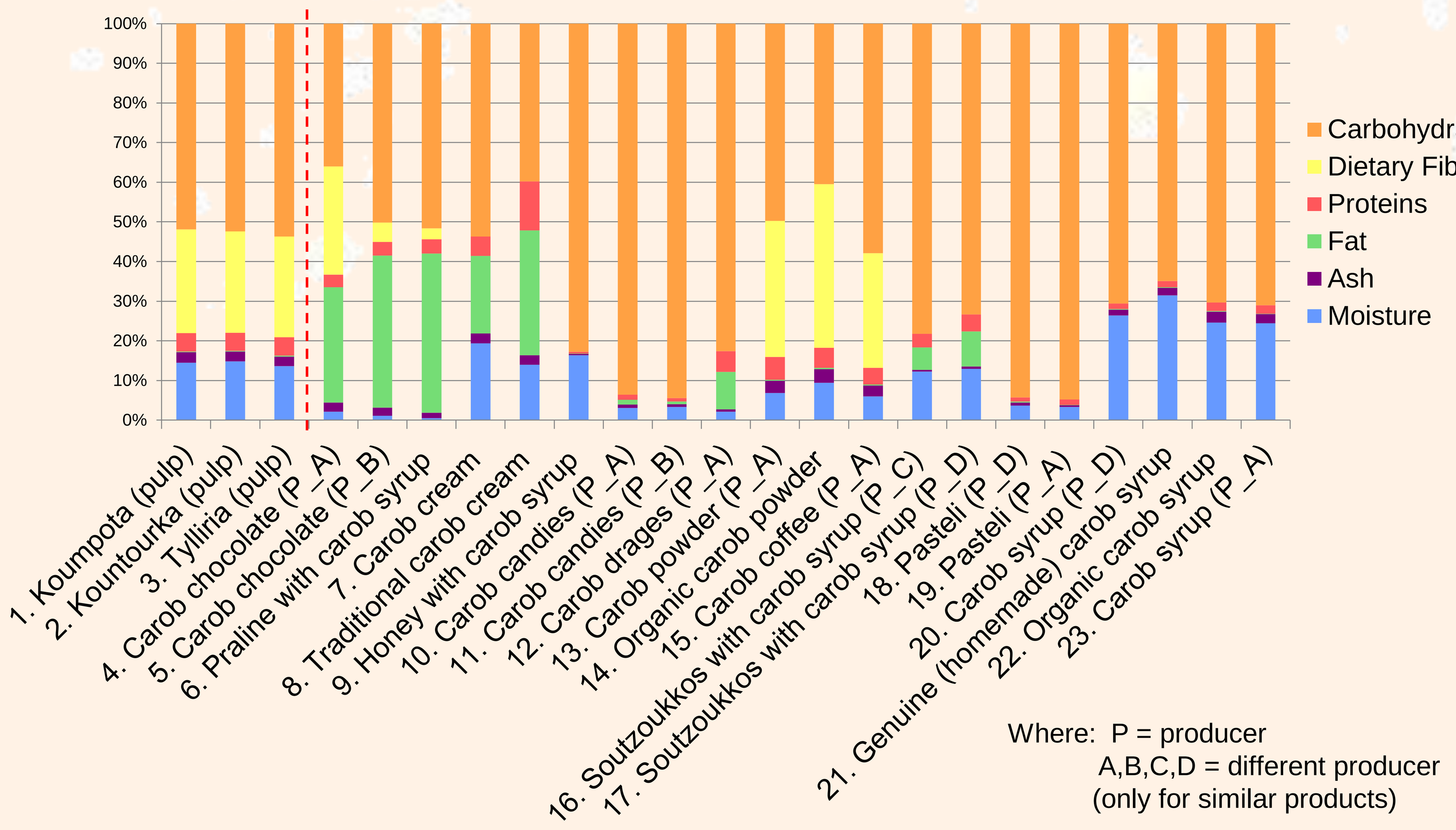


Fig. 2: Chemical composition of carobs and carob products.

3.1. Moisture

For the moisture measurement the combined standard uncertainty (u_c) was used and the result was expressed as x±2u_c (for 95% confidence level), where:

$$\frac{u_c}{c} = \sqrt{\left(\frac{u(m)}{m}\right)^2 + (U_{RSD})^2 + (U_{BIAS})^2}$$

Table 1: Moisture of carobs and carob powders.

Product	Moisture (%) ± U (N=3)
Koumpota (pulp)	14,48 ± 0,12
Kountourka (pulp)	14,80 ± 0,13
Tylliria (pulp)	13,59 ± 0,20
Carob powder P_A	6,05 ± 0,11
Organic carob powder	8,49 ± 0,78
Carob coffee P_A	7,21 ± 0,55

3.2. Ash

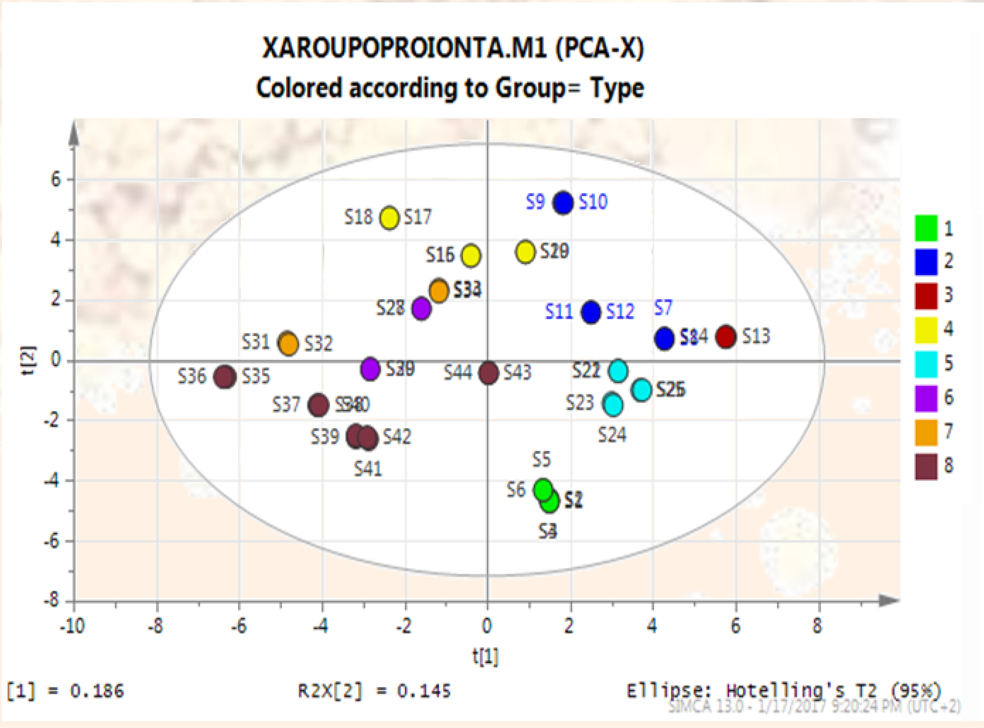
The uncertainty (U) of the ash measurement is expressed as standard deviation and the result as x±2S/$\sqrt{N}$, where S=S_L=1,6 S_r (for 95% confidence level).

Table 2: Ash of carobs and carob powders.

Product	Ash (%) ± U (N=3)
Koumpota (pulp)	2,63 ± 0,07
Kountourka (pulp)	2,49 ± 0,05
Tylliria (pulp)	2,46 ± 0,03
Carob powder P_A	2,74 ± 0,02
Organic carob powder	3,15 ± 0,06
Carob coffee P_A	3,24 ± 0,05

3.3. Chemometrics

Different chemometric techniques were performed with SIMCA 13.0 software (Umetrics, Sweden), for the differentiation of the carob products. Principal component analysis proved able to distinguish the samples according to their type. In the plot below (Figure 3), the 8 pre-defined groups are present in the space to be close to similar types of samples: a well-defined group consisting of the pulp samples, appear to be close to the carob powder/coffee group. Carob chocolate and carob cream samples are close to the traditional carob cream samples belong to the same group. Carob candies, soutzoukkos and pasteli are presented in the same quadrant of lack, so they have a great deal of similarity. Finally, carob syrup samples were slightly distinguished from the last group.



1: Carobs' pulp
2: Carob chocolate (P_A, P_B), carob cream
3: Traditional carob cream
4: Carob candies (P_A, P_B), carob drages
5: Carob powder (P_A), organic carob powder and carob coffee (P_A)
6: Soutzoukkos with carob syrup (P_C, P_D)
7: Pasteli (P_D, P_A)
8: Carob syrup (P_D, P_A), genuine (homemade) carob syrup, organic carob syrup

Fig. 3: PCA scatter plot (PC1 vs PC2).

4. Remarks

Each result for moisture and ash of the samples was expressed with its uncertainty as the uncertainty indicates possible errors in the measurement and therefore is an important part of the result.

Uncertainty is important for the development of models that may differentiate carob products from different types. In any case, a larger number of samples, from different production years, is needed to produce safer conclusions.

References: [1] Goulas V, Stylos E, Chatziathanasiadou M V., Mavromoustakos T, Tzakos AG. Functional components of carob fruit: Linking the chemical and biological space. Int. J. Mol. Sci. (2016) 17. [2] Youssef MKE, El-Manfaloty MM, Ali HM. Assessment of proximate chemical composition, nutritional status, fatty acid composition and phenolic compounds of carob (Ceratonia siliqua L.) Food and Public health (2013) 3 304-308. [3] Khlifa M, Bahloul A, Kitane S. Determination of chemical composition of carob pod (Ceratonia siliqua L) and its morphological study. J. Mater. Environ. Sci. (2013) 4 348-353. [4] K. Tsatsaragkou, G. Gounaropoulos IM. Development of gluten free bread containing carob flour and resistant starch. Food Sci. Technol. (2014) 58 124-129.

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