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Mineral content and botanical origin of Spanish honeys

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Abstract

Eleven elements (Zn, P, B, Mn, Mg, Cu, Ca, Ba, Sr, Na and K) were determined by inductively plasma coupled spectrometry in 40 honey samples from different places of Spain and four different botanical origins: Eucalyptus (*Eucalyptus sp.*), Heather (*Erica sp.*), Orange-blossom (C*itrus sinensis*) and Rosemary (R*osmarinus officinalis*). K, Ca and P show the higher levels with average concentrations ranged between 434.1–1935 mg kg^{-1} for K; 42.59–341.0 mg kg^{-1} for Ca and 51.17–154.3 mg kg^{-1} for P. Levels of Cu (0.531–2.117 mg kg^{-1}), Ba (0.106–1.264 mg kg^{-1}) and Sr (0.257–1.462 mg kg^{-1}) are the lowest in all honey samples. Zn (1.332–7.825 mg kg^{-1}), Mn (0.133–9.471 mg kg^{-1}), Mg (13.26–74.38 mg kg^{-1}) and Na (11.69–218.5 mg kg^{-1}) concentrations were found strongly dependent on the kind of botanical origin.

Results were submitted to pattern recognition procedures, unsupervised methods such as cluster and principal components analysis and supervised learning methods like linear discriminant analysis in order to evaluate the existence of data patterns and the possibility of differentiation of Spanish honeys from different botanical origins according to their mineral content. Cluster analysis shows four clusters corresponding to the four botanical origins of honey and PCA explained 71% of the variance with the first two PC variables. The best-grouped honeys were those from heather; eucalyptus honeys formed a more dispersed group and finally orange-blossom and rosemary honeys formed a less distinguishable group.

Keywords: Honey; Metals; Chemometrics; Pattern recognition; Eucalyptus (*Eucalyptus sp.*); Orange-blossom (*Citrus sinensis*); Rosemary (*Rosmarinus officinalis*); Heather (*Erica sp.*)

1. Introduction

Honey is produced by bees from nectar of plants, as well as from honeydew. Bees and plants are the sources of some honey components as: carbohydrates, water, traces of organic acids, enzymes, aminoacids, pigments; and others like pollen and wax arise during honey maturation.

Honey composition depends on great extent on the nectar sources. The monosacharides, glucose and fructose are the main components of honey, mineral content ranges from about 0.04% in pale honeys to 0.2% in some dark honeys and protein content of honey is usually lower than 0.5% [1].

The Commission of European Union has adopted a new Council Directive, 2001/110/ECC, which repeals the Directive 74/409/ECC [2]. The new Directive establishes the types of honeys that can be marketed in the European Union and gives general definitions related to honey, including general and specific honey compositional characteristics such as, hydroximethyl furfural content, humidity, enzymatic activities and pesticide levels in honey, but those parameters have not been found to have a real relationship to geographical or botanical origin of honey. Pollen recognition has been the traditional method to determine the botanical origin of honey, but this technique is tedious and has limitations:

Abbreviations: ICP-AES, inductively coupled plasma-atomic emission spectroscopy; NW, North-western; PR, Pattern recognition; CA, Cluster analysis; PCA, Principal components analysis; LDA, Linear discriminant analysis; DF, discriminant function; PC, principal component

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counting procedure, identification and interpretation are difficult and requires trained analysts. Other studies [1] have sought analytical markers, such as aroma compounds, sugar profile, flavonoid pattern, non-flavonoid phenolics, isotopic relations, protein or amino acid content to honey classification.

Pattern recognition techniques have been widely applied to food chemistry in recent years [3–6]. The subject of food authenticity covers a wide range of products, and it is of a great economic and social importance, for sectors involved in food production and consumers. Authenticity helps to guarantee the characteristics and quality of food products and helps to prevent overpayment due to adulteration or consumers mislead as a result of ambiguous, improper product labelling. Honey dilution with water and addition of sugars and syrups are the main honey adulteration methods. Besides, in recent years, there has been a rising presence of monofloral honeys in markets, more expensive than multi-floral ones, so possible adulteration by honey mixtures must be controlled.

Different procedures for the determination of honey mineral content have been proposed in some previous papers [7–27]; some of them with classification purposes [24–26], but always according to geographical origin and none of them established a classification of honey according to its botanical origin. Stein [9] determined Cd, Pb and Mn in honey samples, in different seasons of the year, using atomic absorption furnace and three different methods, they obtained identical results by the three methods; Serra [11] determined the levels of Ca, Mg, K, Na, Fe, Cu, Cr and Pb in Spanish eucalyptus honey; Sevimli et al. [12] determined As, Cr, Sb, K, Br, Zn, Fe and Co in Turkish honey by neutron activation analysis; Fodor and Molnar [13] analysed seven honey samples produced in industrial areas to investigate environmental contamination, Al, B, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, Pb and Zn were determined; Rodriguez Otero et al. [14] determined Na, K, Ca, Mg, Cu, Fe, Mn and P in Galician honeys; Viñas et al. [16] determined Pb, Zn, Cu and Cd in honey samples from different type and origin by electrothermal atomic absorption spectrometry; Latorre et al. [25,26] determined 11 metals in honeys from Galicia with classification purposes, they differentiate between honeys from Galicia and non-Galician ones, and processed and industrially commercialised Galician honeys using pattern recognition methods. Despite the fact that some authors correlate the mineral content of honey only with its geographical origin [1], the aim of this paper is, first to contribute to the scarce data about mineral content of Spanish honeys and secondly establish whether mineral content can explain botanical origin.

2. Materials and methods

2.1. Apparatus

Elemental analysis was carried out on a Fisons-ARL 3410 inductively coupled plasma-atomic emission spectrometer (Fisons Instruments, Valencia, CA). Table 1 shows the analytical lines for each element, as well as the instrumental conditions.

Table 1
Operating parameters for ICP-OES

RF frequency	27.12 MHz
Operating power	650 W
Coolant argon flow rate	7.5 l min^{-1}
Plasma/nebuliser argon flow rate	0.8 l min^{-1}
Burner type	Minitorch
Nebuliser type	Meinhard
Viewing height	8 mm
Sample flow rate	2.3 ml min^{-1}
Metals	**Emision wavelength (nm)**
Zn	213.868
P	214.914
B	249.796
Mn	257.610
Mg	279.553
Cu	324.772
Ca	393.369
Sr	407.771
Ba	455.424
Na	589.003
K	766.473

2.2. Reagents and solutions

All chemicals were of analytical-reagent grade or better. Standard solutions were prepared by adequate dilution of a multi-element standard (1000 mg l^{-1}) obtained from Merck (Darmstadt, Germany). Nitric acid 65% and perchloric acid 85% were from Merck. All solutions and dilutions were prepared with ultrapure water (Milli-Q, Milipore, Bedford, MA).

2.3. Honey samples

Forty samples of honey were analysed. The samples were obtained from stores and cooperatives, representing the most common types of honey readily available to consumers in Spain, i.e. eucalyptus (*Eucalyptus sp.*), orange-blossom (C*itrus sinensis*), rosemary (*Rosmarinus officinalis*) and heather (*Erica sp.*). A palinological study of the honey samples was performed in order to guarantee the labelled botanical origin [28]. An identification code was assigned to each group of samples, E for eucalyptus, OB for orange-blossom, R for rosemary and H for heather ones. All the samples from the same botanical origin are from different geographic origin to avoid formation of natural grouping between samples due to the same geographic origin. In addition, samples from the same geographic origin but different botanical class have been analysed to guarantee classification is due to botanical origin. Table 2 shows the origin of the analysed samples.