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Contribution to the study of avocado honeys by their mineral contents using inductively coupled plasma optical emission spectrometry

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Abstract

Avocado honey samples were analyzed by inductively coupled plasma optical emission spectrometric. First, the botanical origin of the honeys was confirmed by melissopalynological analysis. Twenty-four minerals were quantified for each honey sample. The elements Al, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Se, Si and Zn were detected in all samples; seven elements were very abundant (Ca, K, Mg, Na, P, S and Si), six were not abundant (Al, Cu, Fe, Li and Zn) and 11 were trace elements (As, Ba, Cd, Co, Cr, Mo, Ni, Mo, Pb, Se, Sr and V).

Keywords: ICP-OES; Minerals; Honey; Avocado

1. Introduction

The mineral content of honey has been the subject of many studies. A flow injection analysis, coupled with atomic spectroscopy in order to determine the mineral elements of honey, was used (Salinas, Montero, Osorio, & Lozano, 1994). The mineral contents of some honeys from Galicia (Spain) were analyzed by flame atomic absorption spectrometry (Rodríguez-Otero, Paseiro, Simal, & Cepeda, 1994). High-performance ionic chromatography was used to quantify minerals in some unifloral honeys of Italian origin (Poiana, Fudo, Manzin, Postarino, & Mincione, 1996). The mineral content of Moroccan honey was also studied using inductively coupled plasma atomic emission spectrometric (Terrab, González, Diez, & Heredia, 2003).

Avocado honey is one of the less studied types, Israel and Spain being the main producers of this honey type in the Mediterranean area. A avocado-growing was introduced to Spain in the 1980s, Granada, Málaga and Canary Islands being the main producing regions. Although there are some melissopalynological studies on avocado honey (Orantes, Torres, & Delgado, 2002; Ramos, Pérez, & Ferreras, 1998), the physicochemical work on the characterization of this honey type is unknown, contrary to the various studies carried out on other honey types, such as acacia, berseem clover, chestnut, citrus, eucalyptus, lavender and mustard, (Conti, 2000; Nanda, Sarkar, Sharma, & Bawa, 2003; Poiana et al., 1996; Serra Bonvehi, 1988, 1989; Terrab, Díez, & Heredia, 2003a, Terrab, Díez, & Heredia, 2003b).

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This study is part of a series referring to the mineral characterization of the unifloral honeys produced in the Mediterranean area (Terrab, Hernanz, & Heredia, 2004). Thus, the goal of the present study is a contribution to the characterization of avocado honey, analyzing the mineral content of this honey type produced in Spain, by inductively coupled plasma optical emission spectrometry (ICP-OES).

2. Materials and methods

2.1. Samples

The present study made use of eleven avocado honey samples from *Persea americana* Mill., collected in Spain, between 2002 and 2003. The samples were taken directly from the beekeepers, all professionals, and the extraction of honey from combs was done by centrifugation. For the site of collection, see Appendix A and Fig. 1. All samples were unpasteurised and were taken no more than three months after extraction, stored in holders and immediately transferred to the laboratory and kept at 0 °C. Analyses were done within a 6-month time period after harvesting.

2.2. Pollen analysis

The quantitative analysis of the samples was carried out using the light microscope (LM) on slides prepared without any chemical treatment, according to the method described by Maurizio (1979); all the pollen grains (PG) and honeydew elements (HDE) were counted for each honey sample in four different slides, covering the whole surface of each slide. The botanical elements (BE) represent the addition of the pollen grains and the honeydew elements. The qualitative analysis was carried out using acetolysed slides prepared according to the method described by Erdtman (1960) and always using a subsample of 10 g of honey. Following the results obtained by Behm, VonderOhe, and Henrich (1996), at least 500 pollen grains were counted among four different slides for each honey sample. For the identification of the pollen grains, the general key to pollen types was used (Díez, 1987). Due to the fact that the pollen from the *Persea americana* and Lauraceae families, in general, is

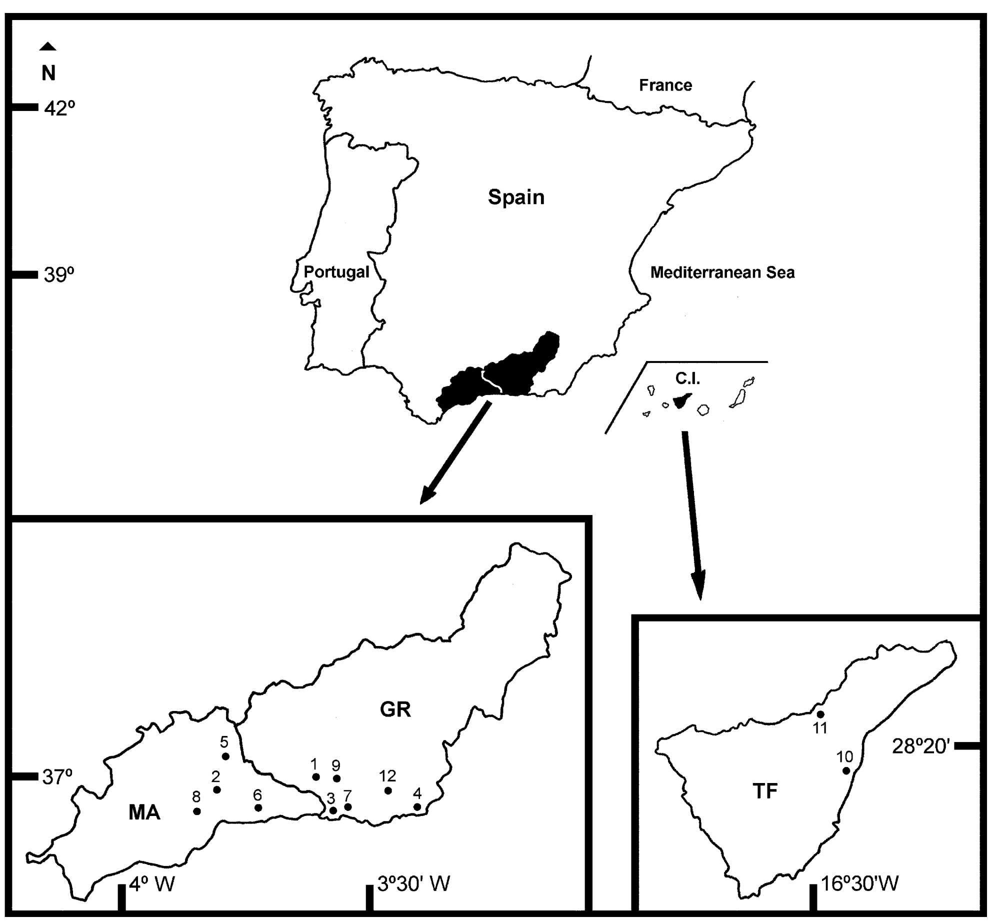

Fig. 1. Distribution of the honey samples. GR, Granada Province; MA, Málaga Province; TF, Tenerife Province; C.I., Canary Islands.

destroyed by the acetolysis treatment, the counting of these pollen grains for the spectra was done on natural preparations. As reported previously (Terrab, Pontes, Heredia, & Díez, 2004), the low pollen representation is due to the special characteristics of avocado plants, which have a short flowering period, low pollen production and very large pollen grains. Furthermore, the bees tend to remove many of these pollen grains from avocado nectar before returning to the hive. So, a minimum of 5% pollen from *Persea americana* was required to consider these honeys as unifloral from a melissopalynological point of view according to the same authors.

2.3. Apparatus

A Jobin-Yvon Ultima 2 ICP optical emission spectrometer and an Ultrasonic nebulizer (U6000 AT^{+}, Cetac) were used for metal determination. The instrument were operated under the following conditions (Table 1).

2.4. Reagents and solutions

Distilled, deionised water of 18 $M\Omega\,cm^{-1}$ resistivity, obtained from a Milli-Q system (Millipore), was used to prepare all solutions. A 10% v/v solution of nitric acid (Panreac, Spain) was used for digestion of the samples. Spex plasma standard (1000 $mg\,l^{-1}$) was used to prepare Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sr, V and Zn reference solutions.

2.5. Procedures

The ashes were obtained by calcinations (600 °C) of approximately 5 g samples honey to constant weight (AOAC, 1990). Nitric acid (0.1 M, 5 ml) was added to the resultant ashes, and the mixture was stirred on a heating plate to almost complete dryness. Then 10 ml of the same acid was added and the mixture was made up to 25 ml with distilled water. The emission wavelengths used, the correlation coefficients for the calibration straight line, and the working linear ranges found for each metal in the ICP-OES determination, are presented in Table 2. Results were expressed as mg of metal per kg of honey.

Table 1
Operational parameters for ICP-OES measurements

Parameters	
Power (kW)	1.2
Radio-frequency (MHz)	27
Plasma gas flow rate ($l\,min^{-1}$)	2
Auxiliary gas flow rate ($l\,min^{-1}$)	2
Nebulizer gas flow rate ($l\,min^{-1}$)	0.02
Nebulizer pressure (bar)	1
Rinsing time (s)	35
Rinsing pump speed	High
Transfer time (s)	60
Stabilization time (s)	20
Transfer pump speed	High

Table 2
Emission wavelength, linear working range and correlation coefficient of the calibration, for each mineral determined

Mineral	Wavelength (nm)	Correlation coefficient	Linear range ($mg\,l^{-1}$)
Al	266.039	0.99996	0–20.7
As	189.042	0.99993	0.018–5.20
Ba	455.403	0.99998	0.001–0.53
Ca	422.673	1	0–51.3
Cd	228.802	0.99999	0–0.52
Co	228.616	1	0–0.52
Cr	267.716	1	0–0.51
Cu	213.598	1	0.003–5.10
Fe	262.167	0.99991	0.022–5.10
K	766.490	0.99985	2.83–518
Li	670.784	0.99999	0.009–5.10
Mg	382.935	1	0.05–210
Mn	259.373	0.99995	0.001–0.52
Mo	204.598	0.99997	0.001–0.51
Na	589.592	0.99998	0.374–204
Ni	221.647	1	0–0.52
P	255.493	0.99897	2.16–102
Pb	220.353	0.99999	0–0.52
S	181.978	0.99369	2.01–41.5
Se	196.026	0.99996	0.016–5.10
Si	212.412	0.99919	0.724–49.9
Sr	407.771	0.99993	0.001–0.53
V	311.838	0.99995	0–0.52
Zn	334.502	0.99969	0.086–5.20

3. Results and discussion

The results of pollen analysis of the sediment for the honey samples used in this work have been published previously by Terrab et al. (2004) and briefly summarised. Percentages are always referred to pollen from nectar plants (excluding in the spectra the anemophilous and nectarless plants). Avocado honeys contained between 5% and 60% pollen of *Persea americana*, according to under-representative presence of this pollen type in the honeys. The most characteristic accompanying species are *Echium* sp. and *Genista* f. (*Chamaecytisus proliferus*, *Stauracanthus genistoides*, *Retama sphaerocarpa*) (present in more than 90% of the samples), and *Eucalyptus* sp. *Olea europaea*, *Mentha* sp. and *Reseda* sp. (in more than 80% of the samples). Other taxa were Compositae (mainly *Helianthus annuus*), *Cistus monspeliensis Ononis* sp. and *Papaver* sp. Our results agree with data reported by other authors (Orantes et al., 2002; Ramos et al., 1998) who analyzed the pollen contained in one avocado sample from La Palma (Canary Islands).

Table 3
Descriptive statistical data for mineral contents in avocado honeys

	Mean[a]	Range	SEM[b]
Al	9.91	4.45–25.4	2.24
As	0.52	0–1.93	0.15
Ba	0.57	0.28–1.16	0.10
Ca	113	52.3–318	25.6
Cd	0.04	0–0.05	0
Co	0.02	0.01–0.04	0
Cr	0.10	0.02–0.44	0.04
Cu	4.18	2.62–7.80	0.45
Fe	9.19	4.92–24.1	1.95
K	1778	1221–246	100
Li	19.6	11.7–27.7	1.63
Mg	136	103–209	9.95
Mn	1.14	0.40–3.16	0.23
Mo	0.01	0–0.03	0.09
Na	279	135–693	55.1
Ni	0.33	0.17–0.66	0.04
P	148	67–190	10.3
Pb	0.08	0.03–0.26	0.02
S	92.5	40.1–120	6.42
Se	0.05	0.02–0.09	0.09
Si	68.2	27.8–289	23.2
Sr	0.41	0–1.01	0.09
V	0.01	0–0.08	0.09
Zn	5.65	0.07–16.8	1.27

[a] mg kg^{-1}.
[b] Standard error of mean.

The results of the 24 minerals determined in avocado honey samples are summarized in Table 3, where three mineral groups can be differentiated: elements that are very abundant, elements in a medium concentration and trace elements.

The first group is composed of seven minerals (K, Ca, Mg, Na, P, S and Si), potassium being quantitatively the most important; it accounts for 72% of the total minerals quantified, which coincides with most authors, who consider this mineral to be the most abundant in honey (White, 1978). The sodium content is different from those reported in Spanish eucalyptus honeys (Serra Bonvehi, 1989), and in Italian eucalyptus and Spanish lavender honeys (Poiana et al., 1996; Serra Bonvehi, 1988), the mean value being 279 mg kg^{-1}, which represents around 11% of the total mineral content. The third most abundant mineral was phosphorus, with a average value of 148 mg kg^{-1}; this value is slightly higher than that of heather honeys (Salinas et al., 1994). Magnesium and calcium are present in average quantities (136 and 113 mg kg^{-1}, respectively). Finally, with quantities never greater than 100 mg kg^{-1}, sulphur, and silicon are present, which agree with the results found in Spanish commercial honeys (Rodríguez-Otero et al., 1994).

The second mineral group is composed of six elements (Al, Cu, Fe, Li and Zn), lithium being the most abundant, with 19.6 mg kg^{-1} as a mean, while the other minerals are found with values of less than 10 mg kg^{-1}.

The third mineral group is composed of As, Ba, Cd, Co, Cr, Mn, Mo, Ni, Pb, Se, Sr and V, always present in concentrations of less than 1 mg kg^{-1}, except for the manganese (1.14 mg kg^{-1}). It is worth nothing the low levels of cadmium and lead, minerals appropriate for testing the contamination of the environment (Przybylowski & Wilcznska, 2001), which show the low levels of contamination in the atmosphere and water in the area where the avocado honey is produced (Stocker & Seager, 1981).

4. Conclusions

Avocado honeys produced in Spain are characterized by a total average content of around 2454 mg kg^{-1}, potassium, sodium, phosphorus, magnesium, calcium, sulphur and silicon being the most abundant elements, representing more than 97% of the total mineral; this content places them between very dark and dark-amber honeys, which coincides with their intrinsic very dark brown colour.

Appendix A. Collection sites

1, Otívar (Granada); 2, Benamargosa (Málaga); 3, Almuñecar (Granada); 4, Calahonda (Granada); 5, Periana (Málaga); 6, Frijiliana (Málaga); 7, Almuñecar (Granada); 8, Almáchar (Málaga); 9, Otívar (Granada); 10, Güimar (Tenerife); 11, Santa Úrsula (Tenerife); 12, Motril (Granada).

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