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Mineral content of the honeys produced in Galicia (North-west Spain)

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Sodium, potassium, calcium. magnesium, copper, iron, manganese, phosphorus (phosphate), chlorine (chloride), silicon (silica), sulphur (sulphate), and ash contents of 91 samples of raw honey from Galicia (NW Spain) were determined. The mean ash content was 0·408%. Potassium was the most abundant of the elements determined, with an average content of 1572 mg/kg (38·5% of the ash).

All mineral contents showed high coefficients of variation, ranging from 0·34 (sodium, calcium, and sulphur) to 0·71 (iron). In general, the Galician honeys studied have high mineral contents in comparison with honeys reported in the literature.

INTRODUCTION

Galicia is a region of 29 434 km^2 on the Atlantic seaboard of north-western Spain. Total annual precipitation exceeds 1000 mm; isotherms range between 4 and 8°C in winter, and 18 and 22°C in summer. Vegetation cover is characterized by oak, birch, pine, and eucalyptus, abundant pasture, and scrub formed by heather, broom, and gorse (Anon., 1988).

Apiculture in Galicia is in a state of expansion. In 1987, there were 102 100 hives, representing an increase of 7·6% on the year before and accounting for 6·4% of the Spanish total. Honey production in that year was 929·1 tonne, up to 17·9% as compared with the preceding year and accounting for 4·17% of the Spanish total (Fernández, 1990).

The sugar content, colour (Huidobro *et al.*, 1984), and protein profiles (Rodríguez-Otero *et al.*, 1990) of Galician honeys have been studied previously. Mineral content, however, has been largely ignored until now; hence it seemed of interest to determine this parameter in Galician honeys.

MATERIALS AND METHODS

Samples

The samples were 91 raw, strained, liquid honeys supplied by the Centro Regional de Extensión Agraria of Santiago de Compestela and obtained in accordance with Spanish legislation (BOE, 1986).

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Ash determination

Ash content was determined by heating 20 g of honey at 550°C to constant weight, after desiccating with an infra-red lamp to prevent foaming (AOAC, 1984).

Preparation of samples for mineral analysis

Sodium, potassium, calcium, magnesiur , copper, iron, silica, phosphates, sulphates, and manganese were determined in solutions obtained by dissolution of the ash in 20 ml of hydrochloric acid (0·1N) and subsequent dilution to 100 ml with distilled water. Chlorides were determined directly in aqueous solutions of honey.

Mineral analysis

Sodium and potassium were determined by emission spectroscopy at 598·0 and 766·5 nm, respectively, by using an air–acetylene flame, after dilution (1:50 for sodium and 1:500 for potassium) of the ash solution. Interference was corrected for by a method based on multiple linear regression (Rodríguez-Otero *et al.*, 1992*a*).

Calcium was determined with complexona III in 10 ml of ash solution buffered to pH 12, by using calconcarboxylic acid as an indicator. Calcium and magnesium ions were determined simultaneously in 10 ml of ash solution buffered to pH 10 by using eriochrome black T as an indicator, and the magnesium content was determined by calculating the difference (Rodier, 1981).

Copper was determined directly in the ash solution by atomic-absorption spectroscopy at 324·7 nm with an air–acetylene flame (Rodier, 1981).

Iron was reduced to the ferrous ion by hydroxylamine chlorohydrate and the red colour produced by the reaction between the ferrous salts and the reagent $\alpha\alpha'$-dipyridyl, in a pH-5·2 acetic acid–ammonium acetate buffer solution, was measured at 510 nm (Rodier, 1981).

The silicon anhydride in ash was reacted with ammonium molybdenate in acid medium to give silicomolybdic acid, which was reduced to the anhydride by oxalic acid. The reaction with 1-amino-2-naphthol-4-sulphonic acid gives a blue coloration, which can be measured at 610 nm (Rodier, 1981).

Phosphates were determined by measuring the yellow colour developed by the reaction in acid medium of phosphates with molybdate–vanadate reagent at 465 nm (Vogel, 1978).

Sulphates were precipitated as barium sulphate in hydrochloric acid medium in the presence of a stabilizer containing glycerine and sodium chloride. The turbidity of the solution was measured at 420 nm (Vogel, 1978).

Manganese was oxidized with periodate and the violet colour of the permanganate ion measured at 525 nm (Hach, 1973).

Chlorides were determined potentiometrically after the addition of silver nitrate to an aqueous honey solution (Simal *et al.*, 1976).

RESULTS AND DISCUSSION

Mean mineral contents (expressed as mg/kg of honey), and ash contents (expressed as % w/w), together with the corresponding standard deviations and coefficients of variation, are shown in Table 1.

It can be seen that Galician honeys generally have a high ash content: higher, for example, than ash contents reported from various European countries by Duisberg (1967), from Hungary by Varju (1970), from North America by White (1978), from south-west Spain by Serra (1989), and for commercial Spanish honeys in general by Rodríguez-Otero (1992*a*).

Table 1. Statistical analysis of mineral content in mg/kg and ash in % (w/w) of Galician honeys

Variable	Number of samples	Mean	Standard deviation	Coefficient of variation
Na	91	138	47·3	0·34
K	91	1 572	670·0	0·43
Ca	91	102	34·2	0·34
Mg	91	106	73·2	0·69
Cu	91	1·11	0·393	0·35
Fe	91	5·12	3·620	0·71
Mn	91	4·02	2·514	0·63
P	91	110	50·7	0·46
Cl	91	245	134·9	0·55
Si	91	9·16	5·765	0·63
S	91	68	23·1	0·34
Ash	91	0·408	0·147	0·36

Potassium, which accounts on average for 38·5% of ash weight, was the most abundant of the elements determined; the mean content of 1572 mg/kg is much higher than that reported by Serra (1989) and by Rodríguez-Otero *et al.* (1992*a*), but similar to that reported by White (1978).

Sodium, accounting on average for 3·4% of ash weight, is only exceeded in the honeys from south-west Spain analysed by Serra (1989).

Magnesium, copper, and manganese contents also exceed the values reported in the literature (Varju, 1970; White, 1978; Serra, 1989; Rodríguez-Otero *et al.*, 1992*a*). Calcium and iron contents, on the other hand, were intermediate.

Anion contents of honeys have, to date, received little attention. The most abundant anion-forming element in the Galician honeys was chlorine, with chloride contents exceeding those reported by Rodríguez-Otero *et al.* (1992*b*) but lower than those reported by White (1978). The next most abundant was phosphorus, with phosphate contents exceeding those reported by both authors.

Sulphur (sulphate) and silicon (silica) were more abundant in the Galician honeys than in the honeys analysed by Rodríguez-Otero *et al.* (1992*b*) but less abundant than in the honeys analysed by White (1978).

Use of the t test to compare the mean mineral contents of the Galician honeys and of the commercial Spanish honeys studied by Rodríguez-Otero *et al.* (1992*b*) indicates that sodium, potassium, magnesium, copper, manganese, phosphorus, silicon, sulphur, and total ash contents are all significantly higher in the Galician honeys ($p \leq 0{\cdot}05$). In the case of calcium, iron, and chlorine, the differences were not significant.

Comparison of the mean mineral contents of the Galician honeys and the honeys from south-west Spain analysed by Serra (1989) indicates that potassium, magnesium, copper, and total ash contents were all significantly higher in the Galician honeys ($p \leq 0{\cdot}05$), whereas sodium, calcium, and iron contents were significantly lower ($p \leq 0{\cdot}05$).

As has been the case in the majority of previous studies, mineral contents in the Galician honeys showed very high coefficients of variation (up to 71% in the case of iron).

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