Electrical conductivity of hungarian honeys

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Abstract. The aims of this present study were the determination of electrical conductivity and mineral content of different honey types and the examination of the relation among the floral origin, electrical conductivity and element content. Electrical conductivity and 13 elements (K, Ca, Mg, Na, P, S, Al, B, Ba, Cu, Fe, Mn and Zn) were determined with digital conductivity meter and ICP-OES) in seven honey types (acacia, lime, silk grass, sunflower, rape, chestnut and forest). The values of the electrical conductivity ranged between 0.101 and 1.036 mS/cm. The lowest values were measured in the acacia, silk grass and rape honey samples and the chestnut and forest honey samples showed the highest values. The electrical conductivity showed strong correlation with K, Mg and S (r = 0.975, 0.856 and 0.802). It was possible to determine the botanical origin of the case of the lime and sunflower honey types was able to determine by measuring their electrical conductivity.

INTRODUCTION

The honey production in the European Union (EU) was 191,119 tons in 2012. The greatest producers were Spain (29,735 tons) and Romania (23,062 tons). Hungary was the third most important honey producer in the EU with 17,000 tons in 2012 (FAO). About 80% of total amount of Hungarian honey is exported to abroad, to the different countries of the world.

Honey plays an important role in the human nourishment. This food contains many important constituents such as sugars, acids, proteins, vitamins, enzymes, micro and macro elements. The honey is not only a food but it is a very good environmental indicator. Honey can provide environmental data from the collecting area that is about 7 km^2 (Pisani et al., 2008).

Electrical conductivity is a very important property of a honey because it is used to distinguish between floral and honeydew honeys (Kaškonienė et al., 2010). The electrical conductivity is closely related to the mineral salts, organic acids and proteins (Terrab et al., 2004). According to many authors the measurement of electrical conductivity instead of the time-consuming gravimetric method is an indirect technique to the determination of mineral content in some food (Acquerone et al., 2007).

The aims of this present study were: (i) determination of electrical conductivity and micro and macro element content of different honey types (acacia, rape, lime, sunflower, silk grass, chestnut and forest); (ii) examination of the connection among the botanical origin, electrical conductivity and mineral content.

MATERIALS AND METHODS

Samples

Fifty honey samples were examined in this study. All samples were collected from Hungarian beekeepers. The collecting areas were different counties of Hungary. The samples were not heated or treated. The botanical origin was verified with pollen analysis that were: acacia *(Robinia pseudoacacia)* (18 samples); lime *(Tilia sp.)* (7 samples); rape *(Brassica napus)* (8 samples); sunflower *Helianthus annuus)* (7 samples); silk grass *(Asclepias sp.)* (3 samples); chestnut *(Aesculus hippocastanum)* (3 samples) and honeydew (4 samples). The samples were stored at room temperature in dark.

Methods

Electrical conductivity (EC)

The determination of EC was carried out with Bogdanov et al. (1997) method, in 20% (v/w) honey solution at 20°C, using a digital electrical conductivity meter (Mettler Toledo Five Easy™ FE30, Switzerland) with an electrode (Mettler Toledo LE703). Ultrapure water produced by Milli-Q water purification system (Millipore SAS, Molsheim, France) was used for the preparation of solutions. The results were expressed in millisiemens per centimetre (mS/cm).

Element content

The determination of aluminium (Al), boron (B), barium (Ba), calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), phosphorous (P), sulphur (S) and zinc (Zn) was carried out with an inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Scientific iCAP 6300, Cambridge, UK). The used reagents to the digestion were high-purity concentrated nitric acid (VWR® International BVBA, Belgium) and hydrogen-peroxide (VWR® International S.A.S., France) based on method of Kovács et al. (1996). The standard solutions were prepared from monoelemental standard solutions (1000 mg/dm^3, Sharlau Chemie, Spain).

Statistics

All examination was carried out in triplicate. The applied statistical program was the SPSS version 13.0 for Windows. Applied statistical methods were the general statistics (mean, standard deviation, minimum and maximum values), and Pearson correlation. The hierarchical cluster analysis and linear discriminant analysis (LDA) were applied to categorize the honey types.

RESULTS AND DISCUSSION

Results of the determination of electrical conductivity and element content

According to the floral origin the electrical conductivity showed great variability (Table 1). The values of this parameter ranged between 0.101 and 1.036 mS/cm. The measured values were corresponding to the Codex Alimentarius Hungaricus. In floral origin honey samples (except the chestnut honey) the electrical conductivity was lower than 0.800 mS/cm. The acacia, rape and silk grass honeys showed very similar results (0.140±0.026, 0.220±0.070 and 0.196±0.029 mS/cm). In the sunflower honeys the measured values were higher (0.396±0.065 mS/cm). The lime honeys showed the highest results (0.604±0.060 mS/cm) among the floral origin honeys (except the chestnut honey). The electrical conductivity of chestnut and forest honey samples was higher than 0.800 mS/cm. The measured values were similar (0.935±0.076 and 0.965±0.063 mS/cm).

Table 1: The analysis of electrical conductivity and macro elements

Honey types	Statistics	EC (mS/cm)	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)
Acacia	range mean±std	0.101-0.185 0.140±0.026	100-255 164±54.2	17.6-59.6 20.9±16.7	1.90-15.9 6.57±3.96
Lime	range mean±std	0.519-0.680 0.604±0.060	1027-1883 1374±291	15.2-67.4 50.2±19.6	19.8-30.2 24.2±3.67
Rape	range mean±std	0.143-0.301 0.220±0.070	103-288 209±63.9	23.7-60.4 38.6±12.3	13.5-27.6 18.3±4.78
Sunflower	range mean±std	0.311-0.470 0.396±0.065	245-552 412±120	58.2-153 93.1±32.2	10.2-36.6 22.3±9.71
Silk grass	range mean±std	0.168-0.225 0.196±0.029	149-165 157±8.00	17.2-35.8 28.0±9.67	3.00-11.3 7.87±4.33
Chestnut	range mean±std	0.850-0.998 0.935±0.076	2136-2281 2197±75.2	51.6-59.7 55.5±4.06	25.4-31.7 27.6±3.58
Forest	range mean±std	0.901-1.036 0.965±0.063	2155-2391 2259±108	55.8-78.8 66.7±9.44	34.7-43.6 39.9±3.96
Total	range mean±std	0.101-1.036 0.370±0.289	100-2391 664±767	17.6-153 44.1±30.3	1.90-43.6 17.1±11.4

Honey types	Statistics	Na (mg/kg)	P (mg/kg)	S (mg/kg)
Acacia	range mean±std	1.60-11.5 5.23±3.53	27.7-92.3 49.9±20.4	6.92-30.4 17.6±8.76
Lime	range mean±std	5.12-7.43 6.03±0.76	23.0-42.4 30.7±7.83	31.4-39.3 35.5±3.08
Rape	range mean±std	6.27-16.9 11.2±4.19	50.9-71.1 63.7±10.5	20.3-43.0 33.2±8.22
Sunflower	range mean±std	4.66-24.5 9.18±5.72	59.8-144 81.7±30.6	17.3-35.9 26.9±7.96
Silk grass	range mean±std	3.49-11.6 7.94±4.10	27.1-74.7 45.2±25.7	11.5-32.7 23.2±10.8
Chestnut	range mean±std	10.8-18.3 13.7±4.00	66.4-84.7 77.8±9.95	38.6-44.9 42.3±3.36
Forest	range mean±std	12.0-19.4 15.9±3.57	115-156 129±19.4	85.8-89.8 87.4±1.86
Total	range mean±std	1.60-21.5 8.38±5.02	23.0-156 61.6±31.4	6.92-89.8 31.3±19.9

The macro and micro element content in the examined honey types was very various (Table 1 and Table 2). In each samples the potassium showed the highest concentration. Similarly to the electrical conductivity the lowest potassium concentrations were measured in acacia, rape and silk grass (164±54.2, 209±63.9 and 157±8.00 mS/cm) honeys following by sunflower (412±120 mS/cm), lime (1374±291 mS/cm), chestnut (2197±75.2 mS/cm) and forest (2259±108 mS/cm) honeys.

Table 2: The analysis of micro element contents

Honey types	Statistics	Al (mg/kg)	B (mg/kg)	Ba (mg/kg)	Cu (mg/kg)
Acacia	range	0.083-1.14	2.43-8.57	<LD-0.193	0.009-0.282
	mean±std	0.481±0.307	4.89±1.96	0.052±0.064	0.146±0.090
Lime	range	0.126-1.720	3.36-5.70	<LD-0.170	0.080-0.340
	mean±std	0.762±0.578	4.92±0.96	0.072±0.059	0.216±0.097
Rape	range	0.279-1.960	5.05-15.7	<LD-0.086	0.050-0.642
	mean±std	0.717±0.579	10.0±3.89	0.030±0.034	0.251±0.192
Sunflower	range	0.103-1.540	4.46-9.88	0.007-0.238	0.098-0.457
	mean±std	0.565±0.510	6.36±2.37	0.081±0.080	0.292±0.142
Silk grass	range	0.590-0.814	3.65-5.74	<LD-0.061	0.259-0.269
	mean±std	0.696±0.112	4.92±1.12	0.039±0.034	0.265±0.006
Chestnut	range	1.06-1.56	2.86-4.08	0.335-0.551	0.304-0.384
	mean±std	1.37±0.274	3.40±0.619	0.429±0.110	0.352±0.042
Forest	range	1.77-2.56	1.70-6.71	0.078-0.995	0.649-1.030
	mean±std	2.29±0.36	4.95±2.24	0.384±0.413	0.839±0.161
Total	range	0.083-2.559	1.70-15.7	<LD-0.995	0.009-1.030
	mean±std	0.781±0.642	5.83±2.91	0.104-0.171	0.268±0.215

Honey types	Statistics	Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)
Acacia	range	0.033-1.78	<LD-0.470	0.234-6.661
	mean±std	0.679±0.432	0.134±0.149	1.82±1.71
Lime	range	0.389-1.16	0.075-1.521	1.58-2.79
	mean±std	0.736±0.247	0.610±0.603	2.15±0.541
Rape	range	0.473-3.35	<LD-0.343	0.271-5.603
	mean±std	1.62±1.09	0.142±0.137	2.39±1.84
Sunflower	range	0.123-2.45	<LD-0.183	0.379-4.690
	mean±std	0.968±0.750	0.073±0.074	2.43±1.65
Silk grass	range	0.896-1.320	<LD-0.298	1.16-7.67
	mean±std	1.07±0.22	0.164±0.151	3.52±3.60
Chestnut	range	1.17-1.71	14.5-16.1	0.637-0.918
	mean±std	1.45±.0.27	15.4±0.58	0.798±0.145
Forest	range	2.93-3.78	2.72-21.9	0.776-1.929
	mean±std	3.37±0.38	8.27±9.11	1.42±0.54
Total	range	0.033-3.795	<LD-21.9	0.234-7.67
	mean±std	1.16±0.94	1.76±4.70	2.06±1.65

The forest honeys showed the highest calcium, magnesium, phosphorus, sulphur, aluminium, copper and iron concentrations. The lowest sodium and phosphorus content was determined in the lime honeys and the lowest magnesium content was measured in the acacia and silk grass honeys.

Evaluation of the Pearson correlation

The electrical conductivity is closely related to the mineral content. The correlation values is indicated in Table 3 (that were highest than 0.600). These correlations were significant at the 0.01 level. The highest correlation value was determined between the electrical conductivity and potassium content (r=0.975). This value was also high in the case of magnesium (r=0.856) and sulphur (r=0.802).

Table 3: Results of the Pearson correlation ("r" values)

	EC	Al	B	Ba	Ca	Cu	Fe
EC		0.654		0.60		0.656	
Al	0.654					0.851	0.831
B							
Ba	0.603						
Ca							
Cu	0.656	0.851					0.803
Fe		0.831				0.803	
K	0.975	0.632		0.628		0.616	
Mg	0.856	0.632			0.624	0.741	
Mn	0.671			0.901			
Na						0.603	
P		0.606				0.730	0.614
S	0.802	0.732				0.830	0.682
Zn							

	K	Mg	Mn	Na	P	S	Zn
EC	0.975	0.856	0.671			0.802	
Al	0.632	0.632			0.606	0.732	
B							
Ba	0.628		0.901				
Ca		0.624					
Cu	0.616	0.741		0.603	0.730	0.830	
Fe					0.614	0.682	
K		0.786	0.697			0.779	
Mg	0.786			0.636		0.861	
Mn	0.697						
Na		0.636				0.605	
P						0.703	
S	0.779	0.861		0.605	0.703		
Zn							

Therefore these elements had strong influence to the electrical conductivity. Other element such as aluminium, barium, copper and manganese had also important effect to this parameter. Very strong correlation (r>0.800) was determined between aluminium and copper; aluminium and iron; barium and manganese; copper and iron; sulphur and copper; sulphur and magnesium.

Evaluation of the Linear Discriminant Analysis (LDA)

First, the electrical conductivity and potassium content were used to the LDA (Figure 1.a.). The values of Wilks' Lambda were 0.29 (EC) and 0.25 (K), so the values of independent variables were similarly assisted to the function (both were significant). The first function explained the 97.6% of the variance of the independent variable and this value was 71.0% in the case of second function. The value of group centroid of acacia honeys had low values in both dimension. The values of group centroids of rape and silk grass honeys had similarly low values in the first dimension but their other values were higher. Therefore these three honey types were not separated based on these two parameters. In the case of chestnut and forest honey types the results of the LDA were similar.

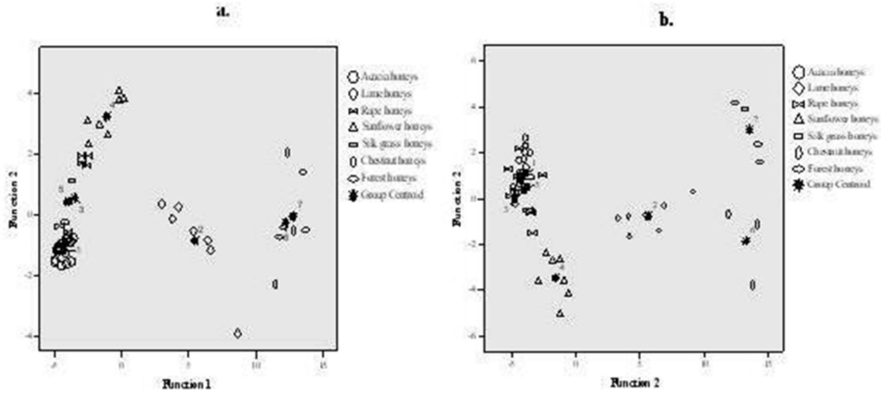

Figure 1
The results of the LDA

These two groups could not be discriminated but these honey types were squarely separated from the other honey types. The sunflower and the lime honeys were absolutely separated from the other honey types. Taking the sulphur and magnesium into the LDA analysis the sunflower and lime honeys were squarely separated; the forest and chestnut honeys divorced from each although these samples showed similar group centroid values in the first dimension (Figure 1.b).

CONCLUSIONS

The electrical conductivity is important parameter of a honey. Due to the various botanical origins the examined samples showed different element content. The electrical conductivity was strong relation to the potassium, magnesium and sulphur content but other elements, such as aluminium, barium, copper and manganese were influence to this parameter. The determination of mineral content is a very expensive method however the measure of electrical conductivity may be enough to the verification of the botanical origin.

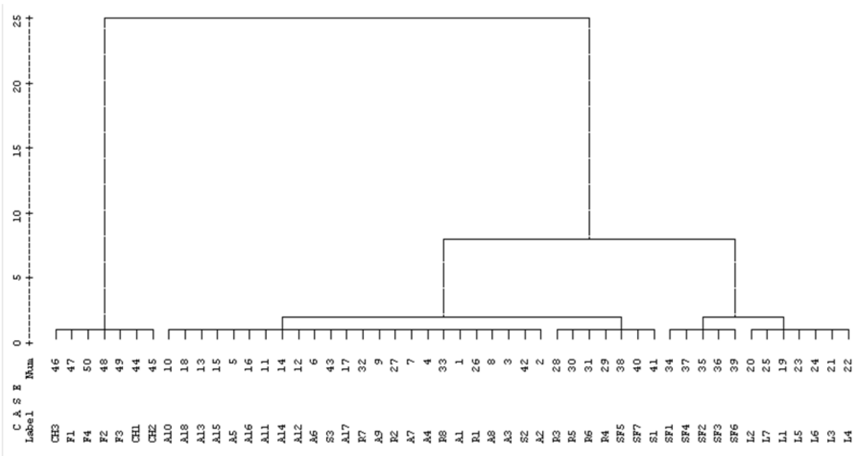

Figure 2
Result of the Cluster analysis

Based on the electrical conductivity the lime and the sunflower honeys could be differentiated from the other honey types. The forest and chestnut honeys showed one separated groups from the other types but this parameter did not allow to the discrimination of this two types. The electrical conductivity values of this two honey types were very similar to each other and the very high values (> 0.800 mS/cm) showed the botanical origin of these two honey types.

The acacia, rape and silk grass honeys did not showed difference but studying together the electrical conductivity, colour and consistence of these honeys the authentication of botanical origin is possible. The rape honeys are crystallized (because of the ratio of fructose and glucose) but the acacia and silk grass honeys are not crystallized. The rape honeys are white or jonquil (it depends on the clarity of honey), the acacia honeys are greenish and the silk grass honeys are yellow.

The examination of great number samples may permit of the determination of minimum and maximum electrical conductivity limit values in the case of each honey types. The knowledge of the electrical conductivity and appearance of different honeys types may be enough to the determination the botanical origin.

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