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GROUPS OF HONEY - PHYSICOCHEMICAL PROPERTIES AND HEAVY METALS

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Abstract

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The aim of the study was to obtain the physicochemical characteristics and the content of Cd, Pb, Hg, Cu and Zn in three groups of honey (blossom, blends and honeydew). Physicochemical constituents were examined according the European Honey Commission recommended methods and heavy metals were determined by atomic absorption spectrometry. Among the groups of honey significant differences in the amount of mineral substances, pH, electrical conductivity ($P < 0.01$) and free acidity ($P < 0.05$) were found. Differences were not found in water content and insoluble matter. The average concentration of hydroxymethylfufural (HMF) and sucrose varied in individual groups of honey, however, these differences were not statistically conclusive. Concentrations of risk elements (Cd 0.5-77.4 µg/kg, Pb 0.02-1.0 mg/kg, Hg 0.67-2.93 µg/kg, Cu 0.06-1.55 mg/kg and Zn 0.2-22.9 mg/kg) were far below the allowable limits and showed statistically significant differences ($P< 0.01$) for Cd, Hg Cu in the individual groups of honey. The content of Pb and Zn did not differ significantly in individual groups, however, significant correlations between HMF and Pb ($r = 0.63$, $P < 0.05$) and HMF and Zn ($r = 0.5$, $P < 0.05$) were found.

Quality, risk elements, physicochemical characteristics, correlation

Honey is an easily digestible foodstuff containing a range of nutritiously important complementary elements. Besides a high content of a range of saccharides, there are also organic acids, amino acids, mineral matter, colours, aromatic substances and a trace amount of fats (Redtke and Hadtke 1998; Bogdanov et al. 1998). Beside these honey contains very valuable but unstable compounds, such as enzymes, substances of hormonal character, some vitamins and a few minor compounds (Yilmaz and Yavuz 1999; Qiu et al. 1999). Individual groups of honey (blossom, blends and honeydew) vary significantly in colour, aroma and taste. There are also differences in the chemical composition which are reflected in many physicochemical properties, such as in the content of ash, the spectrum of saccharides, the activity of enzymes, electrical conductivity, pH and optical rotation (Bogdanov et al. 1987, 1999; Golob and Plestenjak 1999; Sanjuan et al. 1997). The manipulation of honey and its possible adulteration is reflected in many of these characteristics.

Pollen, which can also serve as a bioindicator of environmental pollution, is one of the sources of honey. The concentration of cadmium, lead, copper and zinc, however, does not have to correspond with the pollution of the environment (Bohačenko et al. 1994). The concentration of mercury in honey, on the other hand, depends on the contamination of the environment by this element (Toporčak et al. 1992).

The aim of this work was to evaluate the quality of some samples of honey from the market from the point of view of physicochemical properties and content of heavy metals and comparing these samples with others, analysed honeys in literature, from countries which

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do not belong to locations with heavy pollution. Our work was also aimed to find some relationships among individual groups of honey and the correlation among individual constituents.

Materials and Methods

A collection of 30 samples of honey were analysed. All samples were from the Czech market and from different suppliers, the year of filling being 1999. Honey, labelled outlandish origin, were not included in the study. The blossom, blends and honeydew types were equally represented in the groups. The physicochemical properties were determined according to methods in agreement with the EU (Bogdanov et al. 1997). The individual constituens were determined as follows:

- moisture – refractometrically (Abbé refractometer, AR 2, A-Krüss Optronic, Germany)
- pH – with a ROSS combination spear-tip pH electrode and pH-meter (model 250A, Orion Research, Inc., USA)
- free acidity – by titration to pH 8.3
- hydroxymethylfurfural (HMF) – spectrophotometrically according to Winkler (spectrophotometer UV-VIS, Lambda 11, Perkin-Elmer, USA)
- apparent sucrose – method according to Lane and Eynon
- conductivity – with the help of a thermostatic conductive cell and conductometer (model LF 315, WTW GmbH, Germany)
- ash – by burning in a muffle furnace (LM 312.11, MLW Germany)

Cadmium, lead and copper were determined by electrothermal atomisation AAS (atomic absorption spectrometry) with Zeeman background correction on the apparatus Z-5000 (Perkin-Elmer, USA) after mineralization of the sample with a concentrated nitric acid in a laboratory autoclave with microwave heating (type UNICLEVER, manufactured by Plazmatronica, Poland). Zinc was measured with the help of the flame technique AAS after the dissolution of ash in 0.2 mol/l HCl. The apparatus was set to the conditions recommended by the producer, the temperature program was optimised for the individual elements. The used method AAS showed the following detection limits (defined as the concentration equivalent to 3 times the standard deviation of the analytical blank signal, n = 10): Cd = 0.25 µg/kg, Pb = 4.5 µg/kg, Cu = 0.003 mg/kg and Zn = 0.06 mg/kg.

The accuracy of methods was verified using the recovery test, which ranged from 93.5 to 104.1% for individual elements. The measurement of mercury was done on an Advanced Mercury Analyzer AMA – 254 (ALTEC ltd, the Czech Republic).

The obtained results were processed with the help of a statistic programme STAT Plus (Matoušková et al. 1992).

Table 1
Physicochemical characteristics of honey and the limits given by the legislation of the Czech Republic 334/1997 Sb. (x = average, s = standard deviation, n = 10)

Honey	Moisture *(%)*	Acidity *(mekv/kg)*	pH	Conductivity *(mS/m)*	Sucrose *(%)*	HMF *(mg/kg)*	Ash *(%)*	Insoluble matter *(%)*
Blossom								
x	15.9	13.2	3.70	23.9	1.42	17.7	0.14	0.023
s	1.2	8.3	0.36	10.3	0.80	20.6	0.16	0.021
variance	1.5	68.8	0.13	106.4	0.64	422.5	0.03	0.000
min	13.2	6.0	3.16	11.2	0.39	0.8	0.02	0.002
max	17.6	34.0	4.40	42.0	2.90	63.8	0.59	0.070
limit	20.0	40.0		55.0	5.00	40.0	0.60	0.100
Blends								
x	15.9	22.8	4.15	61.3	1.97	20.4	0.29	0.026
s	1.2	6.0	0.18	11.1	0.85	17.5	0.11	0.032
variance	1.5	35.7	0.03	122.1	0.72	306.9	0.01	0.001
min	13.0	13.0	3.83	49.6	0.70	0.0	0.16	0.002
max	17.1	33.0	4.46	87.3	3.14	59.3	0.58	0.098
limit	20.0	40.0		50-105	10.00	40.0	1.00	0.100
Honeydew								
x	15.6	32.7	4.53	107.8	2.54	30.1	0.58	0.036
s	1.7	10.6	0.16	13.2	1.93	37.5	0.10	0.030
variance	1.4	47.7	0.03	88.9	3.73	132.3	0.01	0.001
min	13.0	14.3	4.22	90.0	0.10	0.6	0.40	0.002
max	19.8	53.5	4.76	129.2	5.69	99.0	0.80	0.084
limit	20.0	40.0		90-130	10.00	40.0	1.00	0.100

Results and Discussion

The results of physicochemical characteristics of different groups of honey and the boundary values given by regulations (Edict in Czech 334/1997 Sb.) are summarised in Table 1. Among the three observed groups statistically significant differences were in mineral substances (ash), pH, electrical conductivity ($P < 0.01$) and free acidity ($P < 0.05$). Differences were not found in water content (moisture) and insoluble matter. The average concentration of HMF and sucrose varied in individual groups of honey, however, these differences were not statistically conclusive. Our results are in accordance with the published results of Golob and Plestenjak (1999) and Bogdanov et al. (1987). Only five samples (16.6%) concerning HMF and two samples (6.6%) concerning free acidity exceeded the boundary values for physicochemical requirements.

Figs 1, 2 and 3 show average concentration of metals and standard deviation in the individual groups of honey. The found level of metals were below the tolerable amount prescribed by the Czech Bylaw (298/1997 Sb.: Cd - 0.5 mg/kg, Pb - 8.0 mg/kg, Hg - 0.5 mg/kg, Cu and Zn - 80.0 mg/kg). The concentration of Cd of the investigated samples ranged between 0.5-77.4 g/kg, Pb 18.4-1000.3 µg/kg, Hg 0.67-2.93 µg/kg, Cu 0.057–1.55 mg/kg and the concentration of Zn 0.190–22.9 mg/kg. Our results are partly in accordance with the works of Golob, Plestenjak (1999) and Bohačenko et al. (1994) and tended to move at the bottom boundaries of the ranges of concentrations found by the above mentioned authors. The concentrations of metals in our samples more or less correspond with Turkish (Yilmaz and Yavuz 1999), Spanish (Bonvehi and Coll 1993), Italian (Caroli et al. 1999) and Slovenian honeys (Kump et al. 1996). Data from literature (Crane 1990) show that individual groups of honey vary in the mineral content (especially in relation to

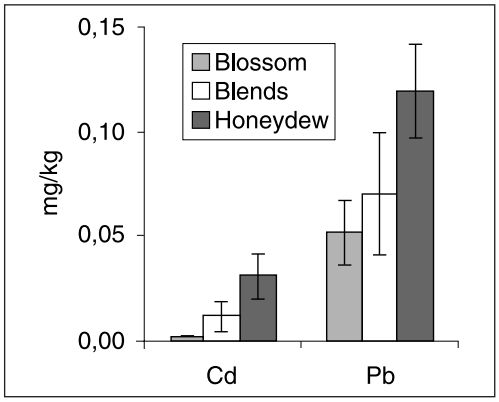

Fig. 1. Average concentrations of Cd, Pb and standard deviations in the individual groups of honey

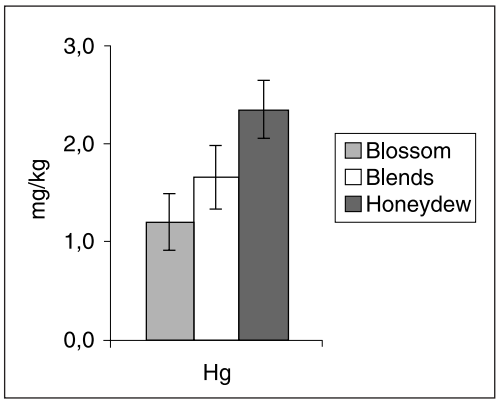

Fig. 2. Average concentrations of Hg and standard deviations in the individual groups of honey

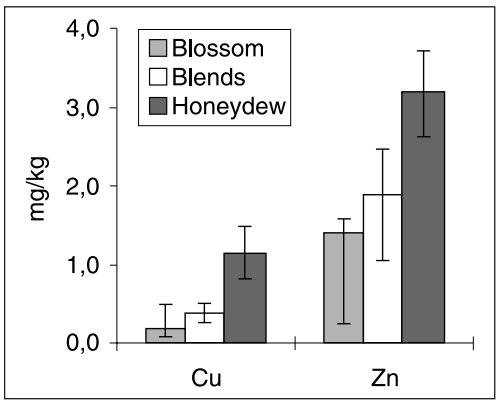

Fig. 3. Average concentrations of Cu, Zn and standard deviations in the individual groups of honey

Table 2
Correlations of physicochemical constituents of honey (statistical significance $^{**}P < 0.01$, $^{*}P < 0.05$).

Parameter	Acidity	Conductivity	pH	Ash	HMF
Acidity	–	0.73**	0.57*	0.58*	0.68*
Conductivity		–	0.75**	0.80**	0.22
pH			–	0.73**	0.01
Ash				–	0.07
HMF					–

ash and conductivity). Our results showed statistically significant differences ($P< 0.01$) for Cd, Hg Cu in the individual groups of honey. The concentrations of Pb and Zn varied in individual groups of honey, however, these differences were not statistically conclusive. If we consider the fact that the concentration of mercury in honey reflects the contamination of the environment by this element (Toporčak et al. 1992) as well as other heavy metals originating from immissions, then we can assume that our samples of honey probably came from areas not contaminated by industry.

In order to express relations, correlation coefficients including levels of significance were calculated for the individual set of constituents for honey. These are shown in Table 2. Beside the assumed correlation relations, there was found a statistically significant correlation between the concentration of lead and HMF ($r = 0.63$, $P < 0.05$) and zinc and HMF ($r = 0.5$, $P < 0.05$). The last one is described by Anam and Dart (1995). The correlations found by us, however, are in incipiency. To confirm them, a larger amount of samples would have to be analysed.

Skupiny medu - fyzikálně-chemické vlastnosti a těžké kovy

Cílem studie bylo získat údaje o fyzikálně-chemických vlastnostech a obsahu Pb, Cd, Hg, Cu a Zn u třech skupin medů (květových, smíšených a medovicových). Fyzikálně-chemické vlastnosti byly stanoveny metodami doporučenými Evropskou komisí pro med a těžké kovy byly stanoveny metodou atomové absorpční spektrometrie. Mezi jednotlivými skupinami medů byly nalezeny signifikantní rozdíly v obsahu minerálních látek, pH, elektrolytické konduktivitě ($P< 0.01$) a kyselosti ($P < 0.05$). Nebyly nalezeny rozdíly v obsahu vody a ve vodě nerozpustných látek. Průměrné koncentrace hydroxymethylfurfuralu (HMF) a sacharózy se lišily u jednotlivých skupin medů, avšak rozdíly nebyly statisticky významné. Koncentrace rizikových prvků (Cd 0.5-77,4 g/kg, Pb 0.02-1.0 mg/kg, Hg 0.67-2.93 g/kg, Cu 0.06-1.55 mg/kg a Zn 0.2-22.9 mg/kg) byly hluboko pod přípustným množstvím a vykazovaly rovněž statisticky významné rozdíly ($P < 0.01$) u Cd, Hg a Cu v jednotlivých skupinách medů. Obsah Pb a Zn se v jednotlivých skupinách medů statisticky významně nelišil, nicméně byly nalezeny signifikantní korelace mezi HMF a Pb ($r = 0.63$, $P < 0.05$) a HMF a Zn ($r = 0.5$, $P < 0.05$).

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