WEST GEORGIAN HONEY CATIONS

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Abstract: The present study was conducted to determine the content of four mineral elements in honeys originating from different regions of West Georgia. Sodium (Na), Potassium (K), Calcium (Ca), magnesium (Mg), and Ammonium (NH4+) were analyzed by HPLC-Conductivity, column "Cation" (3.9x150mm) solvent 0.1 mM EDTA 3mM HNO_3, following the microwave digestion of the honey. High mineral contents were observed in the investigated honeys with K, Na, Ca and Mg being the most abundant elements with mean concentrations in Chestnut honey 5000-7000 ppm, 56-150 ppm, 40-230 ppm, 25-130 ppm, respectively. In Lime (Tilia) honey - 2400-2600 ppm, 30-50 ppm, 160-180 ppm, 45-60 ppm, Acacia honey 300-500 ppm, 35-45 ppm, 85-95 ppm, 15-25 ppm, Field honey -750-930 ppm, 35-45 ppm, 75-130 ppm, 25-35 ppm, Spring polyflora honey - 630-650 ppm, 45-50 ppm, 280-300 ppm, 25-35 ppm, Autumn polyflora Honey – 2500-3000 ppm, 80-100 ppm, 250-300 ppm, 80-100 ppm respectively. The correlation dependence was between the content of cations in the honey and conductivity (Chestnut honey 1.4 μs/cm, Lime (Tilia), honey 0.5 μs/cm, Acacia honey 0.16 μs/cm, Field honey 0.55 μs/cm, Spring polyflora honey 1.2 μs/cm, Autumn polyflora Honey 1.3 μs/cm)

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Keywords: Chestnut, Lime (Tilia), Acacia, Spring and Autumn Polyfloral Honey, cations, HPLC, conductivity

Introduction

Honey is not only a source of carbohydrate, it also contains many essential substances necessary for human health, including minerals, the composition of which significantly changes due to the geographical location of the collected honey, its botanical origin and the results of falsification. Special demand in the world market is enjoyed by monopoly honey. Different compounds are used as botanical markers to establish the naturalness of honey. Georgia, especially its western part, is historically known for its variety of honey productions. Among the dominant varieties are: chestnut honey, linden honey, acacia honey, as well as field and polyfloral honey. Determination of botanical origin of honey is quite difficult (Uršulin-Trstenjak et al., 2017, Bogdanov S. et al. 2007). Numerous studies have recently been carried out to establish chemical indices for determining the botanical origin of honey (Gonzralez-Miret et al., 2014, Gonzalez-Miret et al., 2005) among them there are a lot of studies in which the botanical origin and the mineral content are interconnected (Vanhanen L.P. et al., 2011, Wieczorek et al. 2014, Marcelo Enrique Conti et al. 2014, Marcelo Enrique Conti et al., 2007, Fernandez-Torres R.et al. 2005, Terrab A. et al. 2004).

Unfortunately, we do not have similar staff in our reality and conscientious beekeepers and consumers are not protected from falsification.

The purpose of our work was to study the cationic composition of honey of various botanical origins with a HPLC method and to establish a correlation between the chemical composition and botanical origin.

Methods and materials

Standards were obtained for Lithium hydroxide monohydrate (Li^+), Sodium chloride (Na^+), Ammonium chloride ($NH4^+$), Potassium chloride (K^+), Magnesium nitrate hexahydrate (Mg^{2+}), Calcium nitrate tetrahydrate (Ca^{2+}), Strontium nitrate tetrahydrate (Sr^{2+}), Barium chloride dihydrate (Ba^{2+}) (Fisher Scientific), EDTA (Serva). Isocratic HPLC pump (Waters 1515), Detector Waters 432 (Conductivity) Column IC-Pak CationMD, Eluent 3 mM HNO_3/0.1 mM EDTA, Blancconductivity 1250 ± 50 μS, Base Sensitivity 2000 μS, Integrator Sensitivity μS, column temperature 35^0C, Polarity-negative.

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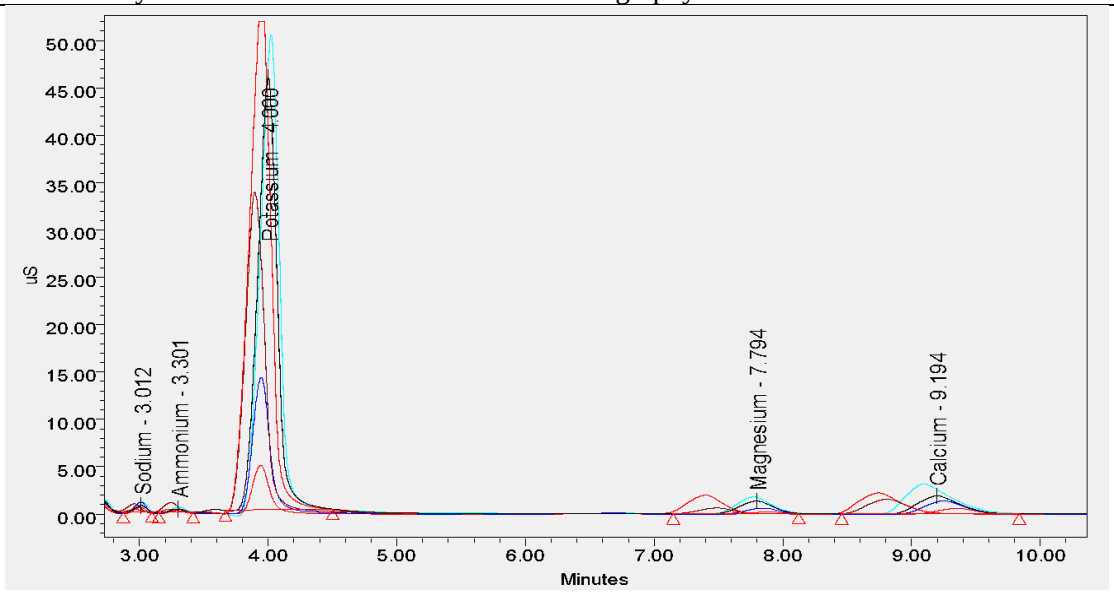
Conductivity mS/cm – Conductometer (Mettler Toledo) samplers added deionized water (1:5) (Chudzinska and Baralkiewicz, 2010, Yücel and Sultanoğlu, 2013)

The samples of Chestnut Honey were taken in places of intensive production of honey - in Adjara, Samegrelo, Imereti, Guria (in total 115 samples, among them the results were generalized for 17 samples (the samples fully complied with the standards of Euro regulations).

Results and their review

In Western Georgia Chestnut Honey is distinguished with potassium content. Its content in natural honey is approximately up to 5000 mg / kg. Regions do not play a significant role in this regard. The honey, collected in the mountainous village located at 300 m above sea level, was particularly interesting. Potassium content in it exceeded 7000 mg / kg. In all the samples of natural honey, the share of potassium in the total composition of cations is more than 90%. The conductivity of the studied honey ranged from 1.41 to 1.96 S / cm. It is interesting to note, that there was established a certain correlation between the total composition of cations and the conductivity in Chestnut Honey. In natural honey this indicator ranges from 0.3 to 0.44. The quantitative ratio of potassium to the total amount of cations and conductivity can be used as markers for the identification of naturalness of chestnut honey.

Figure 1: Honey cations characteristics HPLC chromatography



Source: Authors

As the results have shown, the total content of cations in Chestnut honey isn't more than 8-9 %. In most of the samples, the indicators of calcium are from 14 mg/kg to 500 mg / kg, which is 0.33-7.2 % of the total content of cations, while magnesium is from 51 to 130 mg/kg, which is 0.88-1.95% of the total content of cations. As for the sodium, its content is from 26 to 140 mg/kg, which is 0.45-2.1% of the total content of cations. The content of the ammonium varies quite a lot in a large range between 24 and 197 mg / kg (Tables 1, 2).

In Lime (Tilia) honey potassium is the dominant-cation, with a quantitative content of minimum 2377 ppm and maximum of 2747 ppm. Its content significantly changes (min 5167.94 ppm-max 6516.32 ppm) when the honey is collected with simultaneous flowering of chestnut and linden (Table 3). The content of total potassium cations is about 90%. The content of potassium in the analyzed Tilia honey varies very strongly (min 1660.38 ppm, max 3444.5 ppm) (Table 3).

In the spring and autumn, honey is polyfloral, and the potassium content in it is quite high. The amount of the total potassium cations is at least 87.9%. Among the other ions in the studied types of honey (in Chestnut honey as well), Ca2 + varies from 43.6 to 378 ppm, and Mg^{2+} is 29,8 to 94,1 ppm, that is 1.77-8.44% of the total amount of cations. The content of Na^{+} cations is 28.2 – 134.3 ppm, that is only about 1.12 to 2.9% of cation total content (Table 4). The conductivity is not less than 0.81 s/cm and the total amount of cations (%) and conductivity is from 0.23 to 0.41.

Table 1: Chestnut honey Cations, Conductivity and Ratio

Name	Samplers	Na^+ ppm	$NH4^+$ ppm	K^+ ppm	$Mg2^+$ ppm	$Ca2^+$ ppm	Total ppm	Total cations %	**Conds/cm**	Ration Cation /conduct
H 9	Chestnut honey Mengrelia min	86.34	54.32	5050.06	74.76	13-44	5278.92	0.53	1.41	0.37
H 21	Chestnut honey Mengrelia max	63.26	43.84	5839.40	65.82	247.14	6259.46	0.63	1.75	0.36
H 18	Chestnut honey Guria max	112.18	52.28	5154.04	58.18	267.66	5644.34	0.56	1.41	0.40
H 17	Chestnut honey Guria min	112.14	73.50	6840.42	110.32	307.34	7443.72	0.74	1.71	0.44
H 24	Chestnut honey Imeretia min	122.82	51.78	5401.38	51.22	220.74	5847.94	0.58	1.67	0.35
H 19	Chestnut honey Imeretia max	26.50	6.28	5661.02	114.38	42.08	5850.26	0.59	1.96	0.30
H82	Chestnut honey Adjara min	52.82	45.50	5054.06	94.10	198.86	5445.34	0.54	1.42	0.38
H86	Chestnut honey Adjara max	108.68	197.80	7248.30	134.08	302.18	7991.04	0.80	1.93	0.41
H38	"Datunia"- Mix Chestnut honey commercial	64.38	47.90	6879.26	92.30	503.22	7587.06	0.76	1.73	0.44

Source: Authors

Table 2: Percentage distribution of chestnut honey cations

Name	Samplers	Na+	NH4+	K+	Mg2+	Ca2+
H 9	Chestnut honey Mengrelia min	1.64	1.03	95.66	1.42	0.25
H 21	Chestnut honey Mengrelia max	1.01	0.70	93.29	1.05	3.95
H 18	Chestnut honey Guria max	1.99	0.93	91.31	1.03	4.74
H 17	Chestnut honey Guria min	1.51	0.99	91.90	1.48	4.13
H 24	Chestnut honey Imeretia min	2.10	0.89	92.36	0.88	3.77
H 19	Chestnut honey Imeretia max	0.45	0.11	96.77	1.96	0.72
H82	Chestnut honey Adjara min	0.97	0.84	92.81	1.73	3.65
H86	Chestnut honey Adjara max	1.36	2.48	90.71	1.68	3.78
H38	"Datunia"- Mix Chestnut honey commercial	0.85	0.63	90.67	1.22	6.63

Source: Auhors

Table 3: Linden (Tilia), Acacia and Polyfloral honey Cations, Conductivity and Ratio

Name	Samplers	Na+	NH4+	K+	Mg2+	Ca2+
H 8	Tilia (Clion) Honey Adjaria min	1.55	0.86	93.94	1.92	1.72
H70	Tilia (Clion) Honey Adjaria max	1.82	0.45	88.66	1.30	7.77
H81	Chestnut and Tilia honeyAdjariamin	2.36	0.00	90.97	1.03	5.64
H36	Chestnut and Tilia honeyAdjaria max	1.32	0.40	91.69	1.26	5.32
H78	Acacia honeyAdjaria min	1.13	0.34	88.90	1.19	8.44
H90	Acacia honeyAdjaria max	1.12	0.42	90.94	1.90	5.62
H51	Spring honey Adjaria min	1.36	0.24	89.85	2.27	6.28
H52	Spring honey Adjaria max	2.90	1.49	87.91	2.18	5.52
H63	Autumn honey Adjaria min	2.19	0.00	89.94	1.58	6.29
H60	Autumn honey Adjaria max	2.18	0.00	90.36	1.67	5.79

Source: Authors

Table 4 Percent distribution of cations in Linden (Tilia), Acacia and Polyfloral honey

Name	Samplers	Na+ ppm	NH4+ ppm	K+ ppm	Mg2+ ppm	Ca2+ ppm	Total ppm	Total cations %	**Conds/cm**	Ratio Cation /conduct
H 8	Tilia (Clion) Honey Adjaria min	39.32	21.86	2377.34	48.56	43.64	2530.72	0.25	0.81	0.31
H70	Tilia (Clion) Honey Adjaria max	56.42	13.84	2746.58	40.24	240.86	3097.94	0.31	1.33	0.23
H81	Chestnut and Tilia honeyAdjariamin	134.32	0.00	5167.94	58.34	320.24	5680.84	0.57	1.70	0.33
H36	Chestnut and Tilia honeyAdjaria max	94.16	28.66	6516.32	89.36	378.42	7106.92	0.71	1.75	0.41
H78	Acacia honey Adjaria min	28.20	8.58	2220.22	29.78	210.68	2497.46	0.25	0.91	0.27
H90	Acacia honey Adjaria max	42.26	16.06	3444.50	72.08	212.94	3787.84	0.38	1.05	0.36
H51	Spring honey Adjaria min	44.76	7.88	2961.72	74.78	207.00	3296.14	0.33	0.96	0.34
H52	Spring honey Adjaria max	118.78	60.76	3595.44	89.04	225.96	4089.98	0.41	1.71	0.24
H63	Autumn honey Adjaria min	93.98	0.00	3856.28	67.58	269.62	4287.46	0.43	1.43	0.30
H60	Autumn honey Adjaria max	122.80	0.00	5092.18	94.06	326.44	5635.48	0.56	1.87	0.30

Source: Auhors

Conclusion

From the above data and analysis, we can conclude that the quantitative content of potassium is dominant in all types of honey of botanical origin collected in western Georgia. The potassium content in the cation total amounts of Chestnut, Tilia, Acacia and Polyfloral honey and the ratio of cations total amounts and conductivity represent one of the markers to determine the naturalness of honey.

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