

PHYSICOCHEMICAL PROPERTIES AND THE PRESENCE OF HEAVY METALS IN THE ACACIA HONEY

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ABSTRACT

The work presents the research results of the Acacia honey on physicochemical properties, the presence of heavy metals and radionuclides over a period of years. It was established that the mass fraction of water in the Acacia honey was ranging from 15,71% up to 16,93%, the mass fraction of the invert sugar—from 77,65% up to 84,50%, the mass fraction of sucrose from 2,27% up to 4,7%, the diastatic number—from 9,25 up to 20,7 Gothe units, the mass fraction of hydroxymethyl furfural was ranging from 3,69 up to 10,72 mg/kg, the total acid number—from 0,96 up to 1,96 cubic centimeters, the NaOH solution (in milliequivalent) per 100 grams of honey and the ash content was ranging from 0,007 up to 0,2%. It was identified that the lead content in the Acacia honey was varying annually from 0,010 mg/kg up to 0,025 mg/kg, the cadmium—from 0,004–<0,01 mg/kg, the arsenic—from <0,01–0,020 mg/kg, the cesium-137—from 0,030 up to 0,6 Bq/kg and the strontium-90 was varying from 1,0 up to 7,6 Bq/kg.

Keywords: The Acacia honey, physicochemical properties, heavy metals.

INTRODUCTION

Nowadays the production issues of qualitative safe food products and alimentary raw materials are quite relevant and widely discussed all over the world. It is well-known, that 40–50% of harmful substances are ingested with the food products, 20–40% of them are ingested with water. They are accumulated in the human organs and tissues changing the process of their vital activity and causing various types of poisoning.

Attention is being given to the production issues on the hive products that is safe for humans, because of the environmental deterioration.

The problem of honey quality and naturalness are pretty relevant. The consumer must be sure that he or she buys a good quality product. Since honey is a multicomponent product, there is no an integral index, that can show the quality and naturalness of the product.

Bee honey is a product produced by honey bees from the nectar of flowering plants. The bees put the collected and processed nectar in honeycomb cells, where the nectar ripens. The main constituent of honey are carbohydrates: glucose and fructose, as well as enzymes and minerals. The Acacia honey is almost transparent, colorless, slowly crystallized, so it is

suitable for the bees' wintering (Staletich M., 2016).

The presence of diastase in honey should not be lower than 8.3. Its activity is reliably reduced in a year. The diastase activity changed in acacia honey the least of all and this indicator fell below the rate specified by GOST after storage at room temperature (Efimov V., 2004).

It was established that the amount of microelements in flower honey ranges from 1.82 mg/kg up to 5.70 mg/kg, and macronutrients range from 443.37 mg/kg to 2154.3 mg/kg (Eremiya N.G., Eremiya N.M., Naraevskaya I., 2016).

The composition of the mineral part of honey is very complex, unstable and depends on geographical entities according to the microelements content. Honey contains radioactive elements of phosphorus, iodine, lead and cesium, strontium, radium, etc. Zinc, lead, fluoride, arsenic, cadmium are dangerous for the bees.

Honey that was harvested in the places located next to motorways, mines and diggings is dangerous for bees and the human body. It can be used only as an indicator of the pollution degree of the environment (Akimov I.A., Naumkin V.P., 2000).

The production problems of high-quality and safe hive products are discussed around the

world. Increasing technogenic pollution issues of the natural environment requires researching of the effects on the bees and the hive products in different zones and regions. The sources of pollution can be water, air and soil, that can cause negative effects (Pichushkin I.S., Pichushkin S.I., Mordvinova E.I., 2005).

About 40 macro- and microelements have been found in honey, but their composition depends on a number of conditions, including the botanical origin of the product and the fertility of the soil where the nectariferous plants grow (Ivashevskaya E.B and others, 2007).

The pollution of the surrounding atmosphere caused by harmful emissions of industrial enterprises and road transport has a direct impact on the bees and their products of life.

The heavy metals belong to a group of potentially hazardous substances for human health. The chemical elements are divided into three classes by the degree of hazard:

1–Highly hazardous substances—arsenic, cadmium, mercury, lead, zinc.

2–Moderately hazardous—molybdenum, copper, tin, chrome.

3–Low hazardous—barium, tungsten, manganese, strontium.

All the substances are brought into the bee's nest together with the nectar, honeydew, pollen and water and they are emitted to honey, propolis, wax and beebread (Rusakova T.M., Repnikova L.V., Martynova V.M., 2001).

The most hazardous heavy metals (HM) are cadmium, chromium, mercury, lead, nickel, copper, etc. for the biosphere. Their dynamics in the biocenosis process can serve as a factor that determines its development and stability. The chronic exposure of small doses of the toxic substances, as low levels of radioactivity, can cause disturbances in the metabolic processes, immunological status, neurohumoral systems, hereditary properties and etc.

Cadmium, lead and mercury that accumulated in the soil are absorbed by plants and enter the animal and human body through the trophic chains in increasing concentrations.

The plants accumulate the heavy metals not only from the soil, but also from air, so the heavy metals concentration in plants can be exceeded in the soil. All the honey indicators on the heavy metals content are much lower than the threshold limit value. Thus, the amount of Cu is equal to 0.85, Zn is 1.81, Cd is 6.16, Pb is 0.21, Co is 11.77 $\mu\text{g/l}$ (Eskov E.K., 2006).

It was established that the amount of microelements in the soil is equal to 1012.8 mg/kg, in leaves of the honey plants—319.3 mg/kg, in honey—4.23–5.01 mg/kg, in pollen loads—165.97 mg/kg, in propolis—468.74 mg/kg and in the body of bees—158.34 mg/kg (Eremiya N.G., Dabizha T.A., Eremiya N.M., Dodon I., 2010).

The maximum amount of lead in honey was 0.46 mg/kg, the cadmium content exceeded the limits (1.0 mg/kg) and was more than 4 times higher in some samples. The amount of copper and zinc was much higher. The average content of copper was 2.29 mg/kg, and zinc—1.33 mg/kg (Rusakova T.M., Burmistrova L.A., Repnikova L.V., Vakhonina E.A., Kharitonova M.N., Martynova V.M., Budnikova N.V., 2006).

Based on the above, the purpose of this work was to study the physicochemical properties, the content of micro and macro elements and the presence of the heavy metals in the Acacia honey.



Figure 1. Robinia

METHODS AND PRODUCT OF OUR RESEARCH

The research object was presented by the acacia honey samples, selected in the countryside and in the Chisinau municipality area, represented by the economic agents to the Republican Veterinary Diagnostic Center laboratory, where the physicochemical properties were determined.

The content of water, invert sugar, sucrose, diastase number, hydroxymethylfurfural and total acidity in the honey samples were determined according to the GOST 1992–2001.

Ash, insoluble substances and the presence of cereal cultivars, gelatin and starch in honey were

determined according to the sanitary–veterinary examination.

The content of micro and macro elements and the presence of toxic elements in the Acacia honey were determined using the atomic absorption spectrometry method at the Institute of Chemistry of the ASM.

The obtained results were processed by the variational statistics methods according to Merkurev E.K. (1970), Plokhinsky N.N. (1971) and using some computer programs

RESULTS OF THE RESEARCH

Robinia is an important plant since it is the main spring plant during the honey flow for the bees (Figure 1). Honey production depends on the density of trees planting: the thin sown trees produce 1100–1700 kg of honey/ha, the thick set trees produce 900–1500 kg/ha, on average of 800–1000 kg/ha, the young trees produce 300–700 kg/ha.

The total area of the Robinia trees planted in the Republic of Moldova is equal to 98630 ha, of which 20.20% is located in the Northern area, 42.80% in the Central area and 37.00% in the

Southern area. The Robinia blossoms from mid–May till early June.

Different factors (temperature and humidity, wind power, drought, humidity and soil fertility, etc.) influence the nectar emission. Plants do not exudate the nectar under unfavorable conditions (temperature below 10°C and above 35–38°C) at all (Eremiya N.G., Eremiya N.M., 2011).

The daily gain of the control beehive varied from 0.7 to 9.7 kg during the honey flow of the Robinia. The total amount of collected honey during the flowering period was between 37 and 71 kg.

We have studied the chemical composition of the Acacia honey to achieve the desired goal. The results of the research showed that the total amount of honey of all the investigated batches for the year varied from 2941 to 45880.6 kg. The mass fraction of water averaged from 15.71 to 16.93%, with an allowable maximum of 20% (Table 1) over the years. The mass fraction of the invert sugar ranged from 77.65% up to 84.50%, with a minimum amount of 65.0%, the mass fraction of sucrose varied from 2.27% up to 4.7%.

Table 1. Physicochemical properties in the Acacia honey by years

Indicators	Amount allowed	2007	2008	2009	2010	2011	2012	2013
The total amount of honey of all studied batches, kg	–	37340	2941	40226	12169,5	45880,6	9168,8	40783,0
Mass fraction of water, %	max. 20,0	16,17	16,1	16,34	16,93	15,71	15,92	16,08
Mass fraction of invert sugar, %	min. 65,0	91,0	93,67	94,50	90,44	92,37	90,75	77,65
Mass fraction of sucrose, %	max. 8,0	4,67	4,25	2,27	3,22	4,12	4,7	3,75
Diastatic number units go to	min. 8,0	13,61	12,62	20,7	13,38	12,83	9,25	9,83
The content of hydroxymethyl furfural, mg/kg	max. 20,0	8,24	10,72	7,18	3,69	4,78	4,47	5,65
Total acidity, cm ³ solution of NaOH in (milliequivalent) per 100 g of honey	max. 4,0	1,02	1,12	1,96	1,08	0,96	1,0	–
Ash content, %	max. 0,5	0,07	0,08	0,08	0,07	0,07	0,07	0,2
Insoluble substances, in water, %	max. 0,2	absent	absent	absent	absent	absent	0,003	absent
Grain flour	absent	absent	absent	absent	absent	absent	absent	absent
Gelatin	absent	absent	absent	absent	absent	absent	absent	absent
Starch	absent	absent	absent	absent	absent	absent	absent	absent

The diastatic number was ranging between 9.25 and 20.7 Gothe units, with a minimum of 8.0 Gothe units. The content of hydroxymethyl furfural varied from 3.69 to 10.72 mg/kg, the total acidity—from 0.96 up to 1.96 cm³ NaOH solution in (milliequivalents) per 100 g of honey. The Ash content of the Acacia honey—was

ranging between 0.007 and 0.2%, with a maximum of 0.5%.

Cadmium, chromium, mercury, lead, nickel and copper are the most hazardous heavy metals for the biosphere.

The research results showed that the lead content in the Acacia honey varied from 0.010

mg/kg (2010) up to 0.025 mg/kg (2012), with an allowable maximum of 1.0 mg/kg (Table 2).

It was identified that the amount of cadmium was 5–12.5 times less than the allowable amount (maximum 0.05 mg/kg), it was equal to 0.004–<0.01 mg/kg.

The arsenic amount in the Acacia honey was ranging between <0.01 and 0.020 mg/kg, with an allowable maximum of 0.5 mg/kg. The

radionuclides–cesium–137 content was 0.030–3.6 Bq/kg and strontium–90 varied from 1.0 up to 7.6 Bq/kg.

Analyzing the data it can be noted that lead content averaged 0.017 mg/kg, cadmium–0.008 mg/kg, arsenic–0.012 mg/kg, cesium–137–2.766 Bq/kg and strontium–90–2.621 Bq/kg. The coefficient of the indicators varied from 33.81% up to 91.41%.

Table 2. The heavy metals and radionuclides content in the Acacia honey by years

Years	Heavy metals			Radionuclides	
	Plumbum (Pb) mg/kg	Cadmium (Cd) mg/kg	Arsenic (As) mg/kg	Cesium–137 Bq/kg	Strontium–90 Bq/kg
Permissible amount	max. 1,0	max. 0,05	max. 0,5	max. 100	max. 80,0
2007	0,015	< 0,01	< 0,01	< 3	< 1,0
2008	0,015	< 0,01	< 0,01	< 3	< 1,0
2009	0,012	0,010	0,010	0,030	1,222
2010	0,01	0,010	0,010	3,0	1,267
2011	0,017	0,010	0,015	3,0	3,35
2012	0,025	0,004	0,010	3,6	7,6
2013	0,024	0,004	0,020	3,46	2,91

Table 3. The heavy metals and radionuclides average content and limits of in the Acacia honey by years (2007–2013)

Heavy metals and radionuclides	Permissible amount	$X \pm S_x$	V, %	Limits (min.–max.)
1. Plumbum (Pb), mg/kg	max. 1,0	0,017±0,002	33,81	0,010–0,025
2. Cadmium (Cd), mg/kg	max. 0,05	0,008±0,001	35,33	0,004–0,01
3. Arsenic (As), mg/kg	max. 0,5	0,012±0,001	39,40	0,01–0,02
4. Cesium–137, Bq/kg	max. 100	2,766±0,422	40,36	0,3–3,6
5. Strontium–90, Bq/kg	max. 80,0	2,621±0,906	91,41	1,0–7,6

CONCLUSIONS

1–It was established that the mass fraction of water in the Acacia honey varied from 15.71 up to 16.93%, the mass fraction of invert sugar was from 77.65% up to 84.50%, the mass fraction of sucrose was from 2.27% to 4.7%, the diastatic number–from 9.25 up to 20.7 Gothe units, hydroxymethyl furfural–from 3.69 up to 10.72 mg/kg, the total acidity varied from 0.96 up to 1.96 cm³ NaOH solution in (milliequivalents) per 100 g of honey and the ash content varied from 0.007 up to 0.2%.

2–It was revealed that the lead content in the Acacia honey varied from 0.010 mg/kg (2010) up to 0.025 mg/kg, cadmium was 0.004–<0.01 mg/kg, arsenic–<0.01–0.020 mg/kg, cesium–137 varied from 0.030 up to 3.6 Bq/kg and strontium–90 was ranging between 1.0 and 7.6 Bq/kg.

3–The mineral composition of honey can depend on the region of the honey plants origin, including soil and climatic conditions.

4–It must be noted that the acacia honey produced in the Republic of Moldova meets the requirements on the physicochemical properties and the heavy metals and radionuclides content.

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