

Physico-Chemical Properties of Honey and Sunflower Flowers of Various Soil and Climatic Zones of The Republic of Moldova

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Introduction

Sunflower honey is the most common honey in the southern regions of Russia, Ukraine and Moldova. It is nutritious and enriched with the elements such as amino acids and minerals, showing antimicrobial and antioxidant properties [3].

The honey is golden in color, becoming light amber with crystallization, sometime with a greenish hue. It has a mild aroma and slightly tart flavor [5].

Sunflower is cultivated as the main oil-bearing plant in the Republic of Moldova; its seeds have an oil content of 40-41%. It blooms for 2-3 weeks in the second half of June. The duration of flowering of calotidiums (baskets) is 10 days, beginning with the outermost flowers. Honey production of this crop varies from 30 to 120 kg/ha, depending on soil and climatic conditions, and used farming equipment.

The sunflower sown area averaged 223910.6 ha in the last 5 years by regions of the country. Sunflower occupies an area of 95492.8 ha or 42.65% in the Northern Zone, 76810.2 ha or 34.30% in the Southern Zone, - 51607.6 ha or 23.05% in the Central Zone. [1, 2].

The objective of this work was to study the physico-chemical properties, the content of micro- and macroelements and the presence of heavy metals in honey and sunflower flowers.

Research Material and Methodology of The Study

The object of the study was presented by samples of honey and sunflower flowers selected from different soil and climatic zones of the Republic of Moldova, in all of which physical and chemical parameters were determined. The content of micro- and macroelements and the presence of heavy metals were determined by atomic absorption spectrometry at the Institute of Chemistry, ASM. Analysis of the amino acid composition of linden flower and honey was carried out by liquid chromatography with ion exchange on an amino acid analyzer AAA T 339M [4]. The obtained data were processed by the variational statistics method and with the help of Microsoft Office Excel computer software.

Research results

The obtained results showed that the mass fraction of water in sunflower honey averaged 17.5% with a variation of 16.2-18.2%, inverted sugar - 76.5% (76.5-80.0%), sucrose - 2.22% (1.87-3.25%), diastase number 17.22 units of Gote (11.19-24.29 units), oxymethylfurfural 3.65 mg/kg

(1.92-3.94 mg/kg), and total acidity 2.52 cm³ NaOH per 100 g honey (2.08-2.73 cm³ NaOH solution per 100 g honey) (Table 1).

Table 1. Physico-chemical properties of sunflower honey

Indicators	Permitted number	2020 r		2021 r		X ± Sx
		Northern zone	Southern zone	Central zone	Southern zone	
Mass fraction of water, %	max 20,0	16,2	18,2	18,0	17,6	17,5±0,451
Mass fraction of inverted sugar, %	min 60,0	80,0	79,0	76,63	76,5	76,5±0,872
Mass fraction of sucrose %	max 7,0	1,0	3,25	1,87	2,75	2,22±0,496
Diastase number , unites of Gote	min 6,5	24,29	16,81	16,59	11,19	17,22±2,691
Oxymethylfurfural, mg/kg	max 20,0	4,8	1,92	3,94	3,94	3,65±0,611
Total acidity, cm ³ NaOH solution (milliequivalents) per 100 g of honey	max 4,0	2,53	2,73	2,73	2,08	2,52±0,153

It was found that sunflower honey contains Cr - <1.5 mg/kg and Ni - <2.5 by the content of chromium and nickel, regardless of the year and location of honey collection (Table 2).

Table 2. Content of microelements in sunflower honey, mg/kg

Microelements	2020 year		2021 year		X ± Sx
	Northern zone	Southern zone	Central zone	Southern zone	
Manganese (Mn)	0,63	0,68	<0,5	<0,5	0,58 ± 0,046
Zinc (Zn)	0,68	0,74	1,65	0,85	0,98 ± 0,226
Copper(Cu)	<0,8	0,89	1,49	1,24	1,10 ± 0,160
Iron(Fe)	2,03	2,18	2,48	1,98	2,17 ± 0,113
Chromium(Cr)	,<1,5	<1,5	<1,5	<1,5	<1,5 ± 0,00
Nickel (Ni)	<2,5	<2,5	<2,5	<2,5	<2,5 ± 0,00
Total amount	8,14	8,49	10,12	8,57	8,83

In 2021, the amount of Zinc in sunflower honey in the Central zone was 1.94 times greater than in the Southern zone, Copper was 1.20 times greater, and iron was 1.25 times greater than in the Southern zone.

The total amount of microelements studied in sunflower honey from the Central zone was 10.12 mg/kg or 1.55 mg/kg greater than in the Southern zone. The average amount of Manganese in honey regardless of the collection location was 0.58 mg/kg, Zinc 0.98 mg/kg, Copper 1.10 mg/kg, Iron 2.17 mg/kg.

It was found that the total amount of microelements in sunflower flowers collected from the Southern zone was 225.55 mg/kg or 2.25 times more than those from the Central zone, including manganese content of 1.61 times, iron 4.29 times and nickel 2.03 times more than those from the Central zone.

Sunflower flowers averaged 15.6 mg/kg manganese concentrations, 32.9 mg/kg zinc, 12.7 mg/kg copper, 79.6 mg/kg iron, 1.1 mg/kg chromium, and 2.3 mg/kg nickel (Table 3).

Sunflower honey was found to contain an average of 363.2 mg/kg calcium with a range of 82.5-1217.16 mg/kg, 48.8 mg/kg magnesium (21.0-111.2 mg/kg), 686.4 mg/kg potassium (319.3-778.1), 29.5 mg/kg sodium (16.0-45.9) and 219.1 mg/kg phosphate (208.4-232.0 mg/kg).

Table 3: Content of microelements in sunflower flowers, mg/kg

Microelemenets	2020 year		2021 year		X ± Sx
	Central and Southern zone		Central zone	Southern zone	
Manganese (Mn)	11,2		13,7	22,0	15,6±3,264
Zinc (Zn)	36,8		32,9	29,2	32,9±2,194
Copper (Cu)	11,6		14,0	12,4	12,7±0,706
Iron (Fe)	44,6		36,7	157,5	79,6±39,017
Chromium (Cr)	0,3		<1,5	<1,5	1,1±0,400
Nickel (Ni)	2,5		1,45	2,95	2,3±0,444
Total amount	107,00		100,25	225,55	144,2

The highest amount of studied macronutrients was found in sunflower honey collected from the Northern zone - 2347.96 mg/kg, and less in the Southern zone - 6.72.3 mg/kg (Table 4).

Table 4. Content of macronutrients in sunflower honey, mg/kg

Macronutrients	2020 year		2021 year		X ± Sx
	Northern zone	Southern zone	Central zone	Southern zone	
Calcium (Ca ²⁺)	1217,16	87,3	65,7	82,5	363,2 ± 284,7
Magnesium (Mg ²⁺)	111,2	34,2	21,0	28,8	48,8 ± 20,976
Potassium (K ⁺)	778,1	1278,4	369,9	319,3	686,4 ±222,450
Natrium (Na ⁺)	33,1	45,9	23,1	16,0	29,5 ± 6,488
Phosphates (P ₂ O ₅)	208,4	210,2	232,0	225,7	219,1 ± 5,800
Total amount	2347,96	1656,0	711,7	672,3	1347,0

The total amount of macronutrients in sunflower flowers collected in 2020 was 48869.3 mg/kg or 13591.5 mg/kg more than in 2021 from the Central zone and 14452.9 mg/kg from the Southern zone (Table 5).

Table 5. Content of macronutrients in sunflower flowers, mg/kg

Macronutrients	2020 year		2021 year		X ± Sx
	Southern and Northern zone	Central zone	Southern zone		
Calcium(Ca ²⁺)	19465,1	4723,8	4582,2		9590,4
Magnesium (Mg ²⁺)	1246,8	1384,4	1412,2		1347,8
Potassium(K ⁺)	22457,0	16552,3	16620,2		18543,2
Natrium (Na ⁺)	19,4	42,5	67,7		43,2
Phosphates (P ₂ O ₅)	5681,0	12574,8	11734,1		9996,6
Total amount	48869,3	35277,8	34416,4		39521,2

The average amount of calcium in sunflower flowers collected from different soil and climatic zones averaged 9590.4 mg/kg with variation of 4582.2-19465.1 mg/kg, potassium 18543.2 mg/kg (16552.3-22457.0 mg/kg), phosphate 9996.6 mg/kg (5681.0-12574.8 mg/kg). It was found that the amount of magnesium in sunflower flowers of the Southern zone was higher by 27.8 mg/kg than in the Central zone, and sodium by - 25.2 mg/kg respectively.

The amounts of lead and cadmium in sunflower honey were found to be <0.5 and <0.06 mg/kg regardless of the collection area, while zinc and copper were higher by 0.80 mg/kg and 0.14 mg/kg. The total amount of heavy metals in sunflower honey ranged from 2.19 mg/kg (Southern zone) to 3.7 mg/kg (Central zone) (Table 6).

Table 6: Content of heavy metals in sunflower honey, mg/kg

Heavy metals	2020 year		2021 year		X ± Sx
	Northern zone	Southern zone	Central zone	Southern zone	
Lead (Pb)	<0,5	<0,5	<0,5	<0,5	<0,5±0,00
Cadmium (Cd)	<0,06	<0,06	<0,06	<0,06	<0,06±0,00
Zink(Zn)	0,68	0,74	1,65	0,85	0,98±0,226
Copper (Cu)	<0,8	0,89	1,49	1,24	1,10±0,160
Total amount	2,04	2,19	3,7	2,65	2,64
Ash content , %	0,17	0,24	0,29	0,23	0,23±0,025

The total amount of heavy metals in sunflower flowers ranged from 42.16 mg/kg to 48.96 mg/kg (Table 7).

In 2021, the total amount of heavy metals in sunflower honey collected from the Central zone was 1.05 mg/kg higher than from the Southern zone, and in flowers by 5.30 mg/kg respectively. Ash content in honey averaged 0.23% (0.17-0.29%) and in flowers 7.27% (5.62-9.64%).

Table 7. Content of heavy metals in sunflower flowers, mg/kg

Heavy metals	2020 year		2021 year		X ± Sx
	Northern and Southern zone	Central zone	Southern zone		
Lead (Pb)	<0,5	<0,5	<0,5		<0,5±0,00
Cadmium (Cd)	0,06	<0,06	<0,06		<0,06±0,00

Zink(Zn)	36,8	32,9	29,2	32,9±2,194
Copper (Cu)	11,6	14,0	12,4	12,7±0,706
Total amount	48,96	47,46	42,16	46,16
Ash content, %	5,62	9,64	6,56	7,27±1,214

Amino acids are one of the important indicators of honey because it contains a large number of enzymes, pollen grain proteins and free amino acids [7].

It was found that the total amount of nitrogen in sunflower honey is 0.2302 mg/g (Central zone) and 0.2972 mg/g (Southern zone). The total amount of amino acids in sunflower honey varies from 1.8616 mg/g to 2.4028 mg/g.

Proline is the most concentrated of the amino acids, averaging 0.578 mg/g (0.5395-0.6164 mg/g) or 26.19% of the total, glutamic acid 0.030 mg/g (0.022-0.037 mg/g) or 11.19% and asparagic acid 0.231 mg/g (0.1732-0.2888 mg/g) or 10.47%.

Honey contains on average 8.20% taurine, 4.22% serine, 3.90% alanine, 3.40% lysine, 3.22% threonine, 3.12% cysteic acid, 3.08% phenylalanine, 2.72% glycine, 2.54% valine, 2.40% leucine, 1.81% arginine and 1.77% isoleucine (Figure 1).

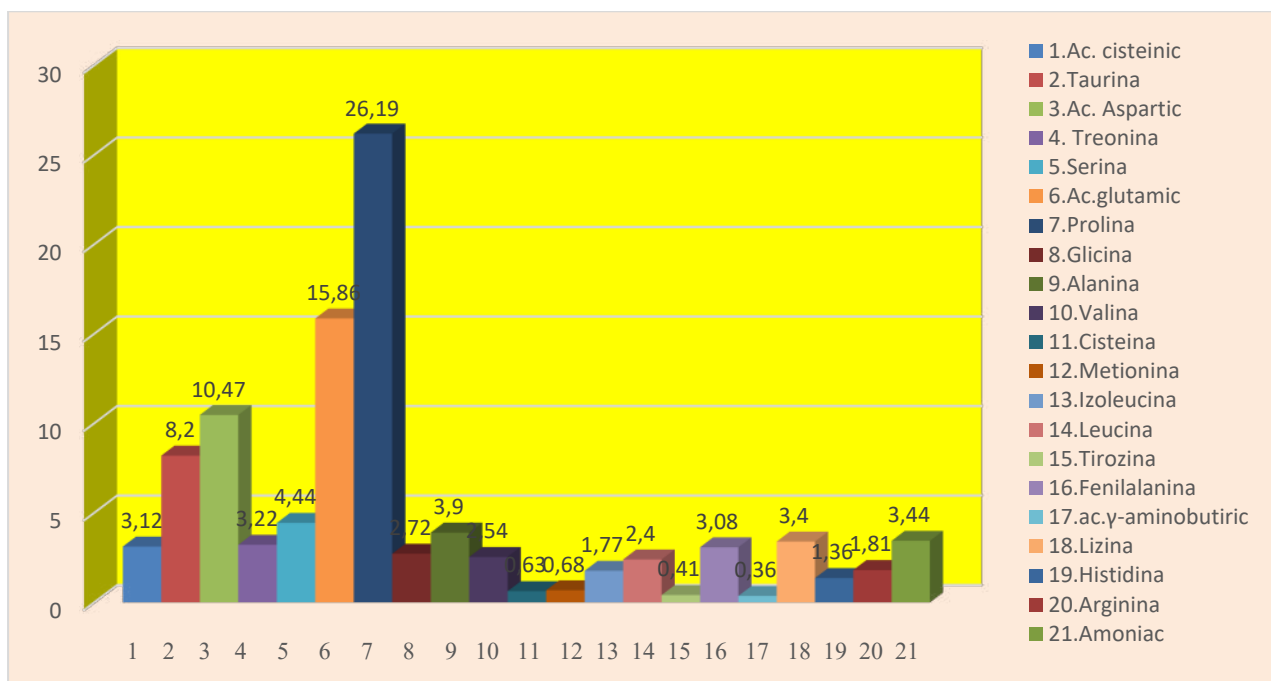


Figure 1: Amino acid content in sunflower honey, % of the total amount

The lower amounts of γ -aminobutyric acid - 0.36%, tyrosine - 0.41%, cysteine - 0.63% and methionine - 0.68% were found respectively.

The total amount of nitrogen in Central zone's sunflower honey was found to be 0.2302 mg/g and 0.2972 mg/g in the Southern zone. The total amount of amino acids in sunflower honey ranged from 1.8616 mg/g to 2.4028 mg/g. It was found that the total amount of amino acids in sunflower honey collected from the Southern zone is 0.5412 mg/kg higher than from the Central zone.

The amount of essential amino acids in sunflower honey averaged 0.447 mg/g (0.3776-0.5168 mg/g), substitutable - 1.426 mg/g (1.2507-1.6016 mg/g), immunoreactive - 0.914 mg/g (0.6903-1.1377 mg/g), glycolytic 0.902 mg/g (0.4778-0.7263 mg/g), ketogenic 0.244 mg/g (0.2198-0.2677),

proteinogenic 1.873 mg/g (1.6283-2.1184 mg/g) and sulfuric 0.280 mg/g (0.2417-0.3185 mg/g) (Table 8).

The content of essential amino acids represents the biological value and palatability of the product [6].

Table 8: Content of total amino acids in sunflower honey

Amino acid	Southern zone		Central zone		On average mg/g±
	mg/g	nitrogen, mg/g	mg/g	nitrogen, mg/g	
Σ amino acids	2,4028	0,2972	1,8616	0,2302	2,207
Σ metabolic nitrogen indices	2,4752	0,3567	1,9405	0,2951	2,208±0,267
Σ essential amino acids	1,6016	0,1895	1,2507	0,1499	1,426±0,175
Σ substitutable amino acids	0,5168	0,0786	0,3776	0,0563	0,447±0,070
Σ anionic amino acids	1,1377	0,1285	0,6903	0,0787	0,914±0,224
Σ glycogenic amino acids	0,7263	0,0929	0,4778	0,0613	0,902±0,124
Σ ketogenic amino acids	0,2677	0,0333	0,2198	0,0279	0,244±0,024
Σ proteinogenic amino acids	2,1184	0,2681	1,6283	0,2061	1,873±0,245
Σ sulfur-containing amino acids	0,3185	0,0347	0,2417	0,0257	0,280±0,038

It was found that the total amount of amino acids in sunflower flowers collected from the Southern zone was 7.02 times higher than in honey and, respectively, 13.93 times higher than in Central zone. The sum of total amino acids in sunflower flowers averaged 21.713 mg/g (16.8582-25.9375 mg/g) and nitrogen was 2.1927-3.4978 mg/g.

The most abundant amino acids found in sunflower flowers were glutamic acid (16.62% of the total amount), proline (11.51%), and asparagine acid (11.27%).

Alanine content - 6.95%, serine - 6.42%, lysine - 6.11%, glycine - 5.85%, threonine - 5.84%, valine - 5.63%, leucine - 5.45%, phenylalanine - 4, 51%, arginine 2.97%, tyrosine 2.58%, histidine 2.36%, isoleucine 1.46%, methionine 1.22%, and cysteine 1.11% of the total (Figure 2).

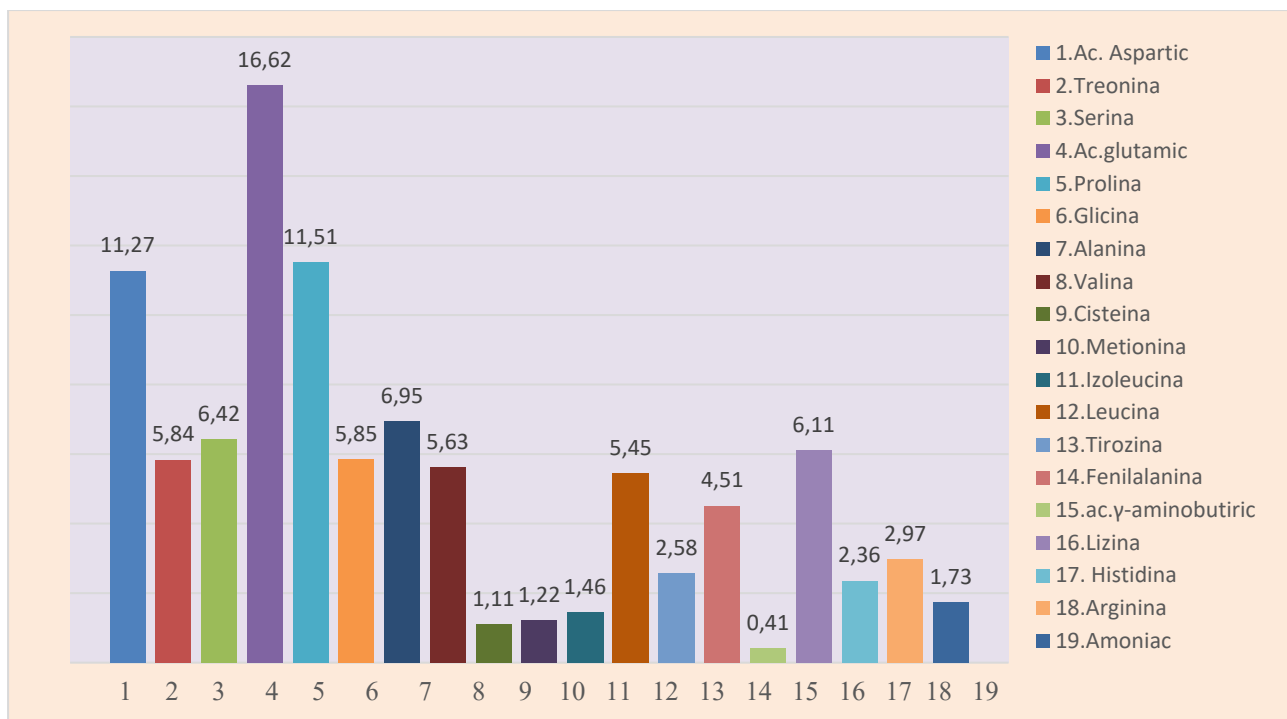


Figure 2: Amino acid content in sunflower flowers, % of the total amount

The amount of substitutable amino acids in sunflower flowers averaged 13.528 mg/g (10.8791-16.1776 mg/g), essential amino acids 7.781 mg/g (5.8819-9.6805 mg/g), immunoactive amino acids 11.778 mg/g (10.3391-13 2163 mg/g), glycogetic - 9.112 mg/g (8.1851-10.0379 mg/g), ketogenic - 4.428 mg/g (3.1948-5.6612), proteinogenic - 21.310 mg/g (16.7610-25.8581 mg/g) and sulfuric - 0.506 mg/g (0.2633-0.7481)(Table 9).

Table 9. Content of total amino acids in sunflower flowers

Amino acid	Southern zone		Central zone		On average, mg/g
	mg/g	nitrogen, mg/g	mg/g	nitrogen, mg/g	
Σ amino acids	16,8582	2,1927	25,9375	3,4978	21,713
Σ metabolic nitrogen indices	17,3228	2,5746	26,2249	3,7341	21,774±4,451
Σ essential amino acids	10,8791	1,3098	16,1776	2,0176	13,528±2,649
Σ substitutable amino acids	5,8819	0,8697	9,6805	1,4694	7,781±1,899
Σ anionic amino acids	10,3391	1,1918	13,2163	1,5817	11,778±1,439
Σ glycogetic amino acids	8,1851	1,0562	10,0379	1,3685	9,112±0,926
Σ ketogenic amino acids	3,1948	0,3970	5,6612	0,6970	4,428±1,233
Σ proteinogenic amino acids	16,7610	2,1795	25,8581	3,4870	21,310±4,549

Σ sulfur-containing amino acids	0,2633	0,0428	0,7481	0,1191	0,506±0,242
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The research was conducted within the framework of project no. 20.80009.5007.17 of the National Agency for Research and Development of Moldova (ANCD).

Conclusion

1. It was found that the mass fraction of water in sunflower honey averaged 17.5% water, inverted sugar - 76.5%, sucrose - 2.22%, diastase number - 17.22 unite of Gote, oxymethylfurfural - 3.65 mg/kg and total acidity - 2.52 cm³ NaOH in (miliequivalents) per 100 g of honey (2.08-2.73 cm³ NaOH solution per 100 g of honey).

2. It was shown that the total amount of microelements in sunflower honey averaged 8.83 mg/kg, in flowers - 144.2 mg/kg and macronutrients in honey - 1347.0 mg/, in flowers - 39521.2 mg/kg and depends on soil and climatic zones of the collection.

3. The amount of lead and cadmium in sunflower honey and in flowers was determined to be <0.5 and <0.06 mg/kg regardless of the collection location, while the zinc content in honey averaged 0.98 mg/kg and copper 1.10 mg/kg and in flowers Zn - 32.9 mg/kg and Cu - 12.7 mg/kg respectively.

4. It was found that the total amount of amino acids in sunflower honey averaged 2.207 mg/g. Proline is the largest amino acid, averaging 0.578 mg/g or 26.19% of the total, glutamic acid 0.030 mg/g or 11.19% and asparagic acid 0.231 mg/g or 10.47%. Taurine is 8.20%, serine 4.22%, alanine 3.90%, lysine 3.40%, threonine 3.22%, cysteic acid 3.12%, phenylalanine 3.08%, glycine 2.72%, valine 2.54%, leucine 2.40%, arginine 1.81% and isoleucine 1.77% of their total amount in average amounts. The amount of essential amino acids in sunflower honey averaged 0.447 mg/g, substitutable 1.426 mg/g, immunoactive 0.914 mg/g, glycogenic 0.902 mg/g, ketogenic 0.244 mg/g, proteinogenic 1.873 mg/g and sulfuric 0.280 mg/g.

The sum of total amino acids in sunflower flowers averaged 21.713 mg/g. The largest amount of amino acids was found glutamic acid - 16.62% of the total amount, proline - 11.51% and asparagine acid - 11.27%. Alanine - 6.95%, serine - 6.42%, lysine - 6.11%, glycine - 5.85%, threonine - 5.84%, valine - 5.63%, leucine - 5.45% were found in average amounts, phenylalanine - 4.51%, arginine - 2.97%, tyrosine - 2.58%, histidine - 2.36%, isoleucine - 1.46%, methionine - 1.22%, cysteine - 1.11% of their total.

Bibliography

1. Eremia N. Apicultura. Chişinău, Ediția a II. Tipogr. „Print-Caro”, 2020. – 455 p.
2. Eremia N. Particularitățile tehnologiei creşterii măcilor de albine și stupăritului pastoral / Eremia N. Zagareanu A., Modvala S. Monografie. – Chişinău, 2018. – 356 p.
3. Бурмистров А.Н. Энциклопедия пчеловода / Бурмистров А.Н., Кривцов Н.И., Лебедев В.И., Чупахина О.К. – М.: ТИД Континент-Пресс, Континенталь- Книга, 2006. – С. 480.
4. Гараева С.Н., Редкозубова Г.В., Постолати Г.В. Аминокислоты в живом организме. Кишинев, 2009. 550 с.
5. Красочко П.А. Продукты пчеловодства в ветеринарной медицине / Красочко П.А. Еремия Н.Г. Монография. Минск. ИВЦ Минфина. – Минск, 2013. 669 с.

6. Мелконян М.В. Наследование свойства накопления в ягодах аминокислот гибридным потомством винограда / Мелконян М.В., Марутян С.А. – Доклады ВАСХНИЛ, 1978, № 12.
7. Омаргалиева Н.К. Изучение аминокислотного состава разных сортов меда из Восточно-Казахстанской области. Молодой ученый, 2017, № 6.1 (140.1), с. 39-42. URL: <https://moluch.ru/archive/140/39419/> (дата обращения: 17.12.2020).