Study of natural honey of group 04 TN VED: identification examination and physical and chemical properties

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Abstract. For the export of manufactured products, it is necessary to consider its classification according to the commodity nomenclature. The classification code of goods following the commodity nomenclature of foreign economic activity is one of the most common tools used by participants in foreign economic activity to minimize costs and expenses. This code, related to the information indicated in column 33 of the cargo customs declaration for goods, is of great importance since it determines the import (export) customs duty amount. In addition, in the lists of goods approved at the legislative level, in respect of which prohibitions and restrictions are established or tax benefits and exemptions are determined, the goods are determined exclusively by the CNFEA code, and the name of the goods is given only for ease of use. The use of some lists involves the use of both the product code and its name. CNFEA codes are also used when maintaining customs statistics. Also, new code numbers for natural honey according to the commodity nomenclature of foreign economic activity were recommended for the first time based on botanical origin, chemical composition, and consumer properties.

1 Introduction

Product classification is dividing a set of objects into several subsets by difference or similarity following accepted methods. Following the goals set by the developers of the product classification system, the latter can be grouped according to different criteria. Accurate systematization of the characteristics of goods makes it possible to avoid double classification and to streamline the levels of significance of information for individual groups of objects.

The composition of honey in terms of chemical composition may vary depending on the source of nectar collection, the area where nectar-bearing plants grow, the maturity of honey, the maturity of honey, time of collection, bee species, weather, and climatic conditions, etc. it is also necessary to take into account the fact that some characteristics of the composition honey are typical. The composition of honey is very complex; it contains

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over 300 different components, 100 of which are present in each form and are permanent [1, 2].

Also, honey contains vitamins K, B12, choline, and carotene. The content and amount of vitamins in natural honey can directly depend on the pollen in its composition. Removal of pollen by filtration can lead to the complete removal of vitamins. Vitamins are also slowly destroyed during storage due to the acidic environment of honey. Bee honey has a wide range of flavors, which depend on the source of nectar, the degree of heat treatment, and the shelf life. It has a specific aroma peculiar only to it, which can be well expressed or veiled by a stronger floral smell. In enzymatic processes, aromatic substances are formed, so the aroma does not appear immediately after the bees seal the comb but for a certain time.

It should be noted that during long-term storage, natural honey does not mold under favorable conditions for developing microorganisms and retains its valuable food and nutritional qualities. Based on this, we can argue that all types of natural honey have antimicrobial effects. Honey contains in its composition substances that have antimicrobial properties. Its antimicrobial property can be seen by its action on mold fungi and gram-positive bacteria.

To carry out export-import operations of manufactured products, it is necessary to consider its classification according to the commodity nomenclature. The product code, classified following the commodity nomenclature of foreign economic activity, is one of the most common tools participants use to reduce costs and expenses. This code, related to the information to be indicated in column 33 of the cargo customs declaration for goods, has a significant role because it determines the amount of customs duty charged [3]. Any goods entering the country will require a classification code indicating what is included in the shipment. This is usually a six- to ten-digit code that informs customs officers of the general goods category and their specific details. These classifications are vital for determining the amount of import duties and tariffs that businesses will be required to pay, as well as for completing import or export declarations and other important paperwork. Import duties are calculated using this classification code and the country of origin and value of the goods [4].

It is important to remember that although the first six digits are constant, the remaining two to four may vary. This can cause problems if vendors in different parts of the world use their own codes, so it is vital that entities have systems in place to ensure consistency[5].

Natural honey is included in group 04 of the CNFEA in heading 0409 "Natural honey". This heading covers honey produced by bees (Apis mellifera) or other insects, centrifuged, may be in a comb, or may contain pieces of comb, provided that it is free from additives containing sugar or any other substance. This honey can be named after the melliferous plants, flowers, and places of its origin. However, honey, as mentioned above, classified in Chapter 04, may also occur in other groups of the Nomenclature; for example, natural honey containing royal jelly in its composition is classified in heading 2106. The name "honey" may also occur in other sweet products, in which it is usually difficult to determine the differences by the organoleptic method[6].

These types of honey have a chemical composition and biological value much less than a natural product. These include sugar, fruit and vegetable, and vitamin honey, which bees produce from sugar and fruit and vegetable juices. In medicinal honey varieties, special ingredients have been introduced that have a therapeutic and prophylactic effect (pumpkin fruits, nuts, flower pollen, ginseng, etc.). Artificial honey products are made based on glucose, and invert sugars, which, to imitate natural honey, color, and flavor natural honey. Artificial honey and artificial and natural honey mixtures are classified in heading 1702 of the CNFEA. [7].

Group 17 "Sugar and sugar confectionery", consisting of 4 commodity items, is divided according to chemical and physical characteristics, also according to production technology and origin. This group includes the following products 1) sugar in it includes sucrose, glucose, lactose, maltose, and fructose), also sugar syrup that does not contain flavoring additives, artificial honey, and maple syrup. The concept of "artificial honey" is defined as a mixture of sugars based on sucrose, glucose, or invert sugar. Often flavorings or dyes are added to it to imitate natural honey. This group also includes a mixture of natural and artificial honey [8].

2 Objects and methods of research

The objects of the study are the classification features of natural and artificial honey. When performing research on the classification of natural honey according to the commodity nomenclature, an analytical research method was used[9,10]. This method is used to substantiate the necessary norms in the conditions of the current production based on observations and experiments. Based on the data received, relevant standards are being developed. The high complexity of collecting primary information leads to using this method to develop various regulatory materials. To determine proline in honey, a method of its determination has also been developed. According to the methodology, solutions for testing are prepared as follows:

To prepare a standard solution of L-proline, 15.7 mg of L-proline (accurately weighed) are weighed into a 100 ml volumetric flask, then it is dissolved in water, and the volume is adjusted to the mark and mixed.

Pour 10 ml of the solution into a 25 ml volumetric flask, dilute to the mark with water, and mix [11].

2 ml of the obtained solution is poured into a volumetric flask with a capacity of 25 ml, 2 ml of a saturated sodium bicarbonate solution, 1 ml of a derivatizing agent are added and mixed well. Derivatize this solution (Place the pre-filtered desired sample in a 60°C water bath for 1 hour with frequent stirring), then cool, bring the volume to the mark with pH 7.0 phosphate buffer, and mix thoroughly [12,13].

To prepare the test solution, 7000 mg of a selected sample of honey is placed in a glass, dissolved in water until dissolved, and transferred to a 50 ml volumetric flask; the volume of the solution is adjusted to the mark with water and mixed well.

5 ml of the resulting solution is transferred to a 25 ml volumetric flask, 2 ml of a saturated sodium bicarbonate solution, 1 ml of a derivatizing agent are added and mixed well. Derivatize as indicated in the method, cool, bring the volume to the mark with phosphate buffer pH=7.0, and mix thoroughly.

Conditions for chromatographic analysis*:*

The test is carried out on an Agilent Technologies 1200 high performance chromatograph or equivalent.

- a column with a size of 4.6 mm x 15 cm, filled with a sorbent Zorbax Eclipse XDB C-18, with a particle size of 5 microns, or similar;
- wavelength 361 nm;
- sample volume 20 µl.

The ratio of mobile phases along the gradient is given in the following table:

Table 1. Mobile phase ratios

Time (min)	A	B
0	75%	25%
6	70%	30%
6.1	60%	40%
12	60%	40%
12.0	40%	60%
23	40%	60%
29	20%	80%
29.1	5%	95%
34	5%	95%
36	75%	25%

The reference and test solutions are injected alternately, obtaining at least 3 chromatograms for each, and the peak area is calculated.

The calculation of the content of amino acids (X), in%, is made according to the formula:

$$X = \frac{S_1 \cdot m_0 \cdot 50 \cdot 25 \cdot 10 \cdot 2 \cdot P \cdot 1000}{S_0 \cdot m_1 \cdot 100 \cdot 25 \cdot 25 \cdot 5 \cdot 100}$$

Where:
S_0 is peak area of a standard sample on a chromatogram;
S_1 is proline peak area on the chromatogram of the test sample;
m_0 is proline standard sample, mg;
m_1 is weighing of the tested sample of honey
P is proline content (purity), in%.
1000 is content of L- proline in 1 kg of honey

Note. 1. Preparation of the mobile phase. Phase A. 4.10 g of anhydrous sodium acetate is placed in a 1000 ml volumetric flask, dissolved in water, DMF (N,N-dimethylformamide) is added in a ratio of 100:1, shaken well, and the pH value is adjusted to 6.4 with ice-cold acetic acid. The resulting solution is filtered.

Phase B. Mix acetonitrile (for HPLC) with phase A in a ratio of 1:1.

Preparation of the derivatizing agent. 1 ml of 2,4 - dinitrofluorobenzene with a pipette should be placed in a 100 ml volumetric flask; the volume is adjusted to the mark with acetonitrile (for HPLC) and mixed.

3 Results and Discussion

The amino acid content in the studied honey samples is given separately in Table 2 [14].

Table 2. Quantitative analysis results of honey samples (mg/g)

Name of amino acids	Sample №1	Sample №2	Sample №3	Sample №4
Aspartic acid	0	0.015952	0	0
Glutamine acid	0.488041	0	0.987044	1.516942
Serine	0.037403	0.072078	0.16039	0.027532
Glycine	0.0318	0.045332	0	0.127368
Asparagine	0.031006	0.046041	0	0.131074

Continuation of table № 2.

Name of amino acids	Sample № 1	Sample № 2	Sample № 3	Sample № 4
Glutamine	0.008859	0.311621	0.475899	0
Cysteine	0	0.612462	0	0
Threonine	0	0	0	0.051881
Argenin	0	0.014805	0	0
Alanine	0.075345	0.176303	0.027262	0
Proline	0.023424	0.679296	0.013601	0.032275
Tyrosine	0.227171	1.098241	1.177957	0
Valine	0.188342	0.253972	0.206304	0.211485
Methionine	0	0	0	0
Isoleucine	0.006883	0.031031	0	0
Leucine	0.001683	0	0	0
Histidine	0.046101	0.0625	0.040634	0
Tryptophan	0.069252	0.009142	0.016709	0
Phenylalanine	0.975756	1.078372	1.167794	1.112201
Lysine HCl	0.017908	0.016403	0.026387	0.026941

For detailed specification, we have proposed additional commodity codes for their inclusion in the commodity nomenclature of foreign economic activity of the Republic of Uzbekistan, used for customs purposes [15].

The content of amino acids in honey depends on various natural factors, particularly the botanical origin of honey. Free amino acids are included in the components of nectar and pollen of plants, which must necessarily be in them and serve as a source of odor for pollinating insects. Since proline is the main amino acid that characterizes the maturity and authenticity of honey, its values have been studied to classify honey [16]. Thus, we recommended new commodity codes, considering honey's botanical origin (Table 3).

Table 3. Recommended new code numbers for bee honey according to the Commodity Nomenclature of Foreign Economic Activity

Valid CNFEA codes for natural honey	Recommended new CNFEA codes for natural honey	Name	Proline content in honey, mg/kg
0409 00 000 0		- Floral:	
	0409 00 000 1	- - from cotton	from 300 to 500
	0409 00 000 2	- - from buckwheat	from 500 to 600
	0409 00 000 3	- - from linden	from 250 to 300
	0409 00 000 5	- - polyfloral	from 250 to 400
	0409 00 000 6	- honeydew	from 100 to 200
	0409 00 000 9	- Other	

"Artificial honey," which may be mixed with natural honey or not mixed with it, is in Section IV, group 17 in heading 1702, subheading 1702 90 and subheading 1702 90 950 0 of the CNFEA of the Republic of Uzbekistan. Accordingly, the new codes for honey recommended by us are shown in Table 4.

Table 4. Recommended new code numbers for artificial honey according to the Commodity Nomenclature of Foreign Economic Activity

Valid CNFEA codes for artificial honey	Recommended CNFEA codes for artificial honey	Name
1702 90 950 0		- - artificial honey:
	1702 90 950 1	- - - mixed with natural honey
	1702 90 950 2	- - - other
	1702 90 950 9	- - other

Therefore, taking into account the physical and chemical indicators of natural bee honey, we have proposed new commodity codes to the customs authorities for use in the commodity nomenclature of foreign economic activity of the Republic of Uzbekistan, with the help of which honey can be classified in more detail for customs purposes [17].

The amount of amino acids in honey is one of the main indicators of maturity and naturalness. Amino acids are one of the important indicators of honey, as they contain many enzymes, pollen grain proteins, and free amino acids. Among the amino acids in honey, proline dominates and contains alanine, arginine, aspartic acid, glutamic acid, valine, leucine, lysine, threonine, and phenylalanine. According to I.P.Chepurnoy, 20 free amino acids have been identified in honey, including ornithine and glutamine, discovered for the first time [17].

It is known that according to the composition of amino acids, honey has no equal among all-natural food products. Daily 100 g of honey consumption satisfies 5% of the required daily requirement for essential and non-essential amino acids. The range of amino acids depends on the botanical origin of honey, and the amount depends on the conditions of honey collection and processing of nectar by bees. Thus, the basis of free amino acids in flower honey is phenylalanine and proline - 969 and 548 mg/kg, respectively. For example, sage honey has a high phenylalanine content - from 1600 to 2300 mg/kg. In natural flower honey, proline accounts for 45–85% of the total content of free amino acids (67% on average) [19].

The proline content in honey is normalized following the requirements of GOST 19792-2017 [29] “Honey is natural. Specifications". The mass fraction of proline must be at least 180 mg/kg.

The proline content in natural flower honey indicates the naturalness and maturity of honey. Also, it depends on the conditions of honey collection and processing of nectar by the bee colony. Bees secrete proline of their own metabolism into honey. It can, like enzymes, catalyze the conversion of honey sugars. The amount of proline in honey correlates with an increase in the acidity of honey and increases its resistance to fermentation [20].

4 Conclusion

As a result of the research, the criteria for the quality and safety of honey were studied using modern physical and chemical methods, thereby proving that the amino acid proline is an important indicator for determining the maturity and authenticity of honey, as a result of which a methodology for determining the amino acid proline was developed and introduced into the activities of customs authorities. This makes it possible to confirm the quality of honey in disputable cases at the consumer's or regulatory organizations' request.

Also, for the first time, new code numbers for natural honey according to the commodity nomenclature of foreign economic activity were recommended based on botanical origin, chemical composition, and consumer properties: 0409 00 000 1 - obtained from cotton flowers, 0409 00 000 2 - obtained from buckwheat flowers, 0409 00 000 3 - obtained from linden flowers, 0409 00 000 5 - polyfloral; 0409000006 - honeydew, 0409 00 000 9 - other. The following new code numbers for artificial honey are recommended according to the commodity nomenclature of foreign economic activity, based on consumer properties: 1702 90 950 0 - artificial honey, 1702 90 950 1 - honey mixed with natural, 1702 90 950 2 - "other". As a result, it became possible to ensure the economic security of the country and the introduction of correct customs statistics due to the correct determination of the code numbers of natural and artificial honey.

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