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BIOPOLYMER FOOD COMPOSITIONS BASED ON CARAMELIZED HONEY, WAX AND PROPOLIS FOR PREVENTION OF PERIODONTOSIS

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Abstract. *For the first time, the processes occurring during caramelization of honey are studied and the biochemical properties of the obtained substances are studied. Infrared spectra, humidity and viscosity were analyzed, the size and size distribution of nanoparticles, elemental composition, oxymethylfurfural content and diastase number of caramelized honey were studied. As a result of research, the difference between the sizes of nanoparticles of natural and caramelized honey was established: caramelized honey is characterized by much smaller (1.5–2.0 times) particle sizes than for natural bee honey. Smaller particle sizes of caramelized honey, after thermochemical treatment in the presence of specially selected catalysts, increase its biochemical activity.*

The paper also describes a new method of processing crystallized honey and the characteristics of the obtained liquid honey for a long shelf life (at least 1 year). It is shown that with the help of a new method of low-temperature isothermal accelerated processing in a microwave reactor MWR-SPR, it is possible to dissolve the crystallized honey to a liquid state. The proposed method reduces the time for the dissolution of honey in comparison with the known method of heat transfer by 250 times. The properties and structure of particles of crystallized and liquid honey after low-temperature, isothermal, accelerated processing with the help of microwave technology of ultrahigh frequencies at 50 °C, for 60's are investigated. The number and particle size of pollen in honey is reduced by 10 times, and the size of the crystals of glucose and sucrose after processing is reduced by 2–5 times. The method of angular distribution of the laser beam shows a reduction of the average size of sugar macromolecules in the processed honey in 2 times, compared with crystallized honey.

It is proved that the proposed low-temperature, isothermal, accelerated processing of honey in a microwave reactor helps to maintain a high diastase Gotha number – 10–11, and the content of hydroxymethylfurfural does not exceed 3–6 mg/kg of honey. The results of X-ray fluorescence spectroscopy confirm that the chemical and element-oxide composition of honey after treatment is almost unchanged. Analyzes of data on chemical and biological oxygen consumption show that in samples of liquid honey, after dissolution by the proposed method, the biochemical activity of honey is reduced only twice, which is much less than during the dissolution of honey by traditional heat transfer. All this has a positive effect on the stabilization of liquid honey after dissolution, on its stability during long-term (up to 1 year) storage. The chemical properties of wax, propolis, honey before and after the caramelization process have been studied. Based on the results obtained from caramelized honey, wax and propolis created a chewing gum with biologically active components for the prevention and treatment of periodontal diseases (gingivitis, periodontitis and periodontitis). Clinical studies using chewing gum based on honey, wax and propolis for the treatment of periodontal tacine in dentistry confirmed a positive effect in 72.5% of patients.

Key words: honey, wax, propolis, caramelization, microwave, biochemical properties, particle size, diastase number, hydroxymethylfurfural, chewing gum, periodontitis, treatment.

БІОПОЛІМЕРНІ ХАРЧОВІ КОМПОЗИЦІЇ НА ОСНОВІ КАРАМЕЛІЗОВАНОГО МЕДУ, ВОСКУ І ПРОПОЛІСУ ДЛЯ ПРОФІЛАКТИКИ ПАРОДОНТОЗУ

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Анотація. *В роботі вперше досліджено процеси, що відбуваються при карамелізації меду та вивчено біохімічні властивості отриманих речовин. Проаналізовано ІЧ спектри, вологість та в'язкість, вивчено розміри та розподіл за розмірами наночастинок, елементний склад, вміст оксиметилфурфуролу і діастазне число карамелізованого меду. В результаті досліджень встановлено різницю між розмірами наночастинок натурального та карамелізованого меду: для карамелізованого меду характерними є значно менші (в 1,5–2,0 рази) розміри частинок, ніж для натурального бджолиного меду. Менші розміри частинок карамелізованого меду, після термохімічної обробки в присутності спеціально підібраних каталізаторів, зумовлюють підвищення його біохімічної активності.*

В роботі також описано новий спосіб обробки закристалізованого меду та характеристики отриманого рідкого меду, на протязі тривалого терміну зберігання (не менше 1 року). Показано, що за допомогою нового способу низькотемпературної ізотермічної прискореної обробки в мікрохвильовому реакторі MWR-SPR, можна провести розпуск закристалізованого меду до рідкого агрегатного стану. Запропонований спосіб скорочує час на розпуск меду у порівнянні з відомим методом теплопередачі в 250 раз. Досліджено властивості та порівняно структуру частинок закристалізованого і рідкого меду після низькотемпературної, ізотермічної, прискореної обробки з допомогою мікрохвильової технології надвисоких частот при 50 °С, за 60 с. При цьому кількість і розмір частинок пилку в меді знижується в 10 разів, а розміри кристалів глюкози і сахарози після обробки зменшуються в 2–5 разів. Методом кутового розподілу лазерного променю показано зменшення середнього розміру макромолекул цукрів у обробленому меді в 2 рази, порівняно із закристалізованим медом.

Доведено, що запропонована низькотемпературна, ізотермічна, прискорена обробка меду в мікрохвильовому реакторі сприяє збереженню високого діастазного число по Готе – 10–11, а вміст гідроксиметилфурфуролу не перевищує 3–6 мг/кг меду. Результати Х-променевої флуоресцентної спектроскопії підтверджують, що хімічний та елемент-оксидний склад меду після обробки майже не змінюється. Все це позитивно впливає на стабілізацію рідкого меду після розпуску, на його стабільність при довготривалому (до 1 року) зберіганні. Вивчено хімічні властивості воску, прополісу, меду до та після процесу карамелізації. На основі отриманих результатів з карамелізованого меду, воску і прополісу створена жувальна гумка з біологічно-активними компонентами для профілактики та лікування захворювань тканин пародонту (гінгівіту, пародонтиту і пародонтозу). Проведені клінічні дослідження із застосуванням жувальної гумки на основі меду, воску і прополісу для лікування такнин пародонту в стоматології підтвердили позитивний ефект у 72,5 % пацієнтів.

Ключові слова: мед, віск, прополіс, карамелізація, НВЧ, біохімічні властивості, розміри частинок, діастазне число, гідроксиметилфурфурол, жувальна гумка, пародонтоз, лікування.

Introduction. Problem formulation. Beekeeping products are an exceptional food product, an excellent medicine, a good cosmetic product. Due to its antiseptic properties, bee honey is widely used in medicine, which has the ability to stop the growth of pathogenic microorganisms, helps in the treatment of ulcers and wounds, diseases of internal organs, eyes, skin, lowers blood pressure, treats neuroses, insomnia. Natural bee honey is part of traditional medicine in many cultures, although it is most widely used as a sweetener and sugar substitute. It contains at least 180 components and is mainly a solution supersaturated with sugars, fructose (≥ 38%) and glucose (≥ 31%). The moisture content in me is about 17.7–21%, the total acidity – 0.08% (pH = 3.4–4.3) and ash – 0.18%. In addition, honey contains a large number of other components, including phenolic acids and flavonoids, glucose oxidase and catalase enzymes, ascorbic acids, carotenoids, organic acids, amino acids, proteins and α-tocopherol.

Beeswax is a product of the wax glands of bees, formed by the use of pollen, perga and honey. From wax plates bees build honeycombs in a beehive. Beeswax contains many components, namely: esters of ceric acid – 76.0% esters of cholesterol 1.0%. bavniki dyes 0.3%. lactones 0.6%. free alcohol 1.25%. free cerin to-you 13.5%, and higher carbohydrates 10.5–13.5%. Pure wax is lighter than water, with a melting point of 62–69 °C and a density of 0.96 g / cm^3. it is insoluble in water, but soluble in gasoline, chloroform, ether, and boiling alcohol. [1] The chemical composition of wax is similar to fats and oils, but much richer and more diverse. Currently, beeswax is already known in dentistry, it is used to clean the mouth and strengthen the gums.

Propolis is a unique natural substance that has the biological properties of antibiotics, which cannot be synthesized artificially, its taste is bitter, slightly burning. At a temperature of 20–40 °C wax is a plastic product, and at a temperature less than 20 °C – solid. The wax content in propolis is less than 28%, the oxidation index is 22%, the iodine value is less than 35. Bees in the process of their life, like no other, need powerful antiviral and bactericidal drugs. Therefore, bees use propolis as an antiseptic to treat the inner surface of the hive and mummify other insects that have got inside. The composition of propolis includes: natural resins (40–55%), beeswax and fatty acids (20–35%), aromatic oils (about 10%), pollen (about 5%) and other components. At present, it is experimentally proven that propolis has a wide range of pharmacological activity. The most common use at the moment of propolis is in dentistry: 2–4% alcohol extracts of propolis are effective in the treatment of fungal diseases of the oral cavity, abscesses on the gums and in the treatment of periodontitis, gingivitis. Due to the local anesthetic effect, propolis can be used as an analgesic for hypersensitivity of the tooth.

Bee pollen (pollen) contains the following minerals in mg / 100 g: ascorbic acid – 1.4–205.2 mg / 100 g, phosphorus 50–610 mg / 100 g, vitamin B (thiamine) 0.4–1.5 mg / 100 g, potassium 130–1140 mg / 100 g, riboflavin 0.54–1.9 mg / 100 g, calcium 30–1180 mg / 100 g, B5-nicotinic acid 4.8–21.0 mg / 100 g, magnesium 60–380 mg / 100 g, B6 (pyridoxine) 0.5–0.9 mg / 100 g, sodium 28–44 mg / 100 g, folic acid 0.1–0.68 mg / 100 g, copper 0.6–1.57 mg / 100 g, H (-biotin) 0–0.25 mg / 100 g, iron 0.2–4.2 mg / 100 g, pantothenic acid 0.32–5.0 mg / 100 g, E (á-tocopherol) 0.3–170, water 3–4%, reduced sugars 20–40%, non-reduced sugars 0–20%, fats 1–20%, proteins 11–35%, amino acids 10–45%, antibiotics + vitamins 5.75–10.8 μg / g, riboflavin 16.3–19.2 μg / g, pyridoxine 0–9 μg / g. The main active components of bee pollen are derivatives of phenolic acids and polyphenolic compounds, mainly flavonoids and glycosides. The most well-known effect of phytosterols is the ability to lower blood cholesterol by preventing its absorption in the intestine. Pollen supports the immune system: helps increase the content of vitamins, minerals and phytochemicals. In addition, pollen can act as a vaccine and normalize fever, regulate metabolism in the body, have antimicrobial, antioxidant and anti-inflammatory effects. Maintains oral hygiene and removes bad breath. [1].

The antibacterial property of honey was first recognized in 1892 and it was found that the concentration of honey should be from 1.8% to 10.8% (rpm). Therefore, natural honey must be diluted at least nine times [2]. Important factors that affect the antibacterial effectiveness of honey are: hygroscopic properties: based on this effect, high osmotic properties for extracting water from bacterial cells, which causes the possibility of causing their death. Honey, like other rich honey syrups and pastes, has the property sufficient to inhibit the growth of microbes. Honey has a fairly acidic environment, its pH is from 3.2 to 4.5, which is sufficient to inhibit many pathogens. The optimal pH value for their development is usually 7.2–7.4. Hydrogen peroxide (H_2O_2) or hydrogen peroxide: the main antibacterial activity in honey is associated with hydrogen peroxide, which is enzymatically produced in honey. The enzyme glucose oxidase is secreted from the bee's hypopharyngeal gland into nectar and promotes the formation of honey from nectar. Hydrogen peroxide and gluconic acid are formed by the reaction of oxidative hydrolysis of glucose in honey:

$$C_6H_{12}O_6 + H_2O + O_2 = C_6H_{12}O_7 + H_2O_2 \qquad (1)$$

It is these substances that contribute to the preservation of honey. The formed hydrogen peroxide H2O2) can be effective as a sterilizing agent only during the maturation of honey. Whole honey has a small amount of hydrogen peroxide, because this substance is unstable. In the presence of transition metal ions and ascorbic acid in copper, they catalyze the decomposition of hydrogen peroxide H2O2 to oxygen and water:

$$2H_2O_2 \text{ (+кат.)} = 2H_2O + O_2\uparrow \qquad (2)$$

The practical inactivity of the enzyme in "mature" honey, causes the formation of hydrogen peroxide only when the honey is diluted. When honey is diluted, the activity increases (coefficient from 2500 to 50 000), which gives an antiseptic "slow release" of hydrogen peroxide H_2O_2 at a level that is antibacterial, but does not damage the tissue [3].

The materials described in the article relate to the scientific field of food processing in the food industry and other industries related to the dilution, decrystallization of various solid and pasty products. Namely, the dissolution and study of the properties of solid, crystalline and liquid bee honey, which can be used in dentistry, for the prevention and treatment of gum disease in gingivitis, periodontitis and periodontitis. Natural bee honey, especially May, linden and acacia, contains a lot of fructose and can remain liquid in honeycombs sealed for 1–3 years. But honey extracted from honeycombs has a shelf life of only a few months, depending on the type and variety of honey. This is because honey contains up to 80% or more of fructose and glucose in a ratio of about 1:1. Over time, honey crystallizes, the consumer characteristics of honey almost do not change, but its appearance becomes less attractive to the consumer who wants to see and consume it liquid and transparent. Therefore, the use of new methods and special conditions for the dissolution of crystallized honey and prevent its natural crystallization, as well as conditions and means of storing honey in a liquid state for at least 1 year is an urgent problem in the food industry. Scientific activity and discussion of the achievements of ONAHT and the Department of Chemistry of Vasyl Stefanyk Precarpathian National University (Ivano-Frankivsk), contributed to the implementation of joint research and the introduction of a new type of food product – chewing gum "Honeycomb-Honeycomb". Which was made on the basis of dissolved, liquid caramelized honey, which has a therapeutic and prophylactic effect and has pronounced therapeutic, anti-inflammatory, astringent, anti-infective, antimicrobial and antibacterial properties. The research provides for the possibility of creating and implementing new types of chewing gum based on liquid, dissolved honey, for the treatment, protection and prevention of dental diseases of periodontal gum tissue, especially gingivitis, periodontitis and periodontitis, which lead to loss of healthy teeth.

Analysis of recent research and publications. Honey is a unique product of natural origin, the value of which is extremely high for human health. It contains many useful substances: wax, propolis, bee pollen and actually honey. These substances have anti-inflammatory, antimicrobial, general strengthening effect on the body and are widely used in medicine [4]. Honey pumped out by beekeepers from honeycombs has a shelf life of only 1–6 months, depending on the type and variety of mono- and polyfloral honey. Elite acacia honey contains more than 40% fructose, so it remains transparent and liquid for 8–12 months [5], while sunflower honey crystallizes a month after honey collection by beekeepers. Honey becomes thick, opaque, hard, but no less sweet and useful. This is because honey contains a predominant amount of glucose, which crystallizes. Valuable and useful properties of honey are almost unchanged, but its appearance becomes less attractive to the consumer, who visually better perceives and consumes liquid, transparent honey [5]. According to biological origin, there are monofloral, polyfloral, padeva and mixed honey. There are more than 21 species of honey (see table 1), which bees produce from the nectar of mainly one species of plants, such as monofloral: acacia, heather, linden, or polyfloral (herbaceous), collected from the flowers of various plants, such as forest, field, meadow, and padevy. But all types and varieties of liquid honey with a storage time of 2–6 months begin to thicken and crystallize, losing some consumer properties and attractiveness, but not losing their medicinal properties.

The process of crystallization of honey is influenced by various factors. The most important factor in the crystallization of honey is the ratio of glucose and fructose in honey, which varies in the range: (fructose 21.7–53.9 %, glucose 20.4–44.4 % [6]. In the process of crystallization fructose is in a liquid state, and the crystallization centers are crystals glucose and sucrose.The density of glucose crystals is 1.54 g / cm^3, and the density of honey varies from 1.45 g / cm^3 to 1.40 g / cm^3, depending on the water content and type of honey. Therefore, honey crystallizes from top to bottom. At a lower density of honey formed Honey passed through sand filters or special clay grades does not crystallize for a long time because it does not contain crystallization centers: pollen grains, protein and mucous substances, but significantly reduces the diastase number of honey, its biological activity, taste and quality [7] Fig. 1 and Table 1. show photos and characteristics of 19 most famous varieties (monofloral and polyfloral) of honey in crystallized form.

Crystallization of honey is a rather complex phenomenon. The process of uncontrolled crystallization, which occurs during storage of honey, leads to a change in the appearance of honey to an opaque and solid physical state, and therefore the product is less attractive to the consumer [8]. This creates problems during the packaging and processing of honey [9]. Uneven crystallization of honey also affects the preservation of quality, because the non-crystallized part of honey will contain a higher moisture content, which makes honey vulnerable to yeast growth [7]. The rate of nucleation and growth of crystals depends on temperature. Honey, which is stored at very low (−20 °C) temperatures and temperatures close to the environment (+ 18 °C), leads to the production of small crystals and coarse crystals, respectively [10].

When stored in a moderate temperature range (+4 – +10 °C) the formation of crystals of mixed type is observed. The decrease in temperature promotes the formation of small crystal sizes due to the limited mobility of sugar macromolecules [11]. The second factor influencing the crystallization of honey is the mass fraction of water. At a water content of 16–20% in honey, crystallization proceeds quickly, with a larger amount – 21% H_2O – honey remains liquid, transparent and almost colorless for a long time (for example, acacia and linden) [11]. The third factor influencing the process is the presence of crystallization centers.

Figure 1 – Appearance of samples of different varieties of monofloral and polyfloral crystallized bee honey

Table 1 – Characteristics of species of mono- and polyfloral bee honey

№	Types of mono- and polyfloral bee honey	Characteristics of different varieties of honey during crystallization
1.	Acacia honey	Transparent, slowly crystallizes into fine-grained crystals, acquires a milky color.
2.	Flower honey	Greenish-yellow color, smells like almonds, has a wonderful taste with bitterness.
3.	Heather honey	Viscous honey also quickly precipitates during storage.
4.	Thyme honey	Golden-yellow color, crystallizes into small grains, settles.
5.	Dandelion honey	Light amber to white with a greenish tinge, with a vanilla aroma.
6.	Blackberry honey	Transparent as water honey, with a pleasant taste.
7.	Chestnut honey	Dark in color, has a faint aroma of chestnut flowers and a rather bitter taste. Crystallizes slowly, has an oily appearance.
8.	Clover honey	Colorless, transparent, pleasant to smell. Crystallizes slowly into a solid mass.
9.	Lime honey	Transparent, pale yellow or greenish colors. It has a linden aroma, very sweet taste. Upon crystallization gives a dense fine-grained precipitate.
10.	Alfalfa honey	It crystallizes quickly, acquiring a white color and the consistency of thick cream. It has a pleasant aroma and a specific taste of bitterness.
11.	Strawberry and raspberry honey	Very light color, has a pleasant aroma and excellent taste. It crystallizes slowly.
12.	Thistle (thistle) honey	Very thick, viscous, yellow with a strong odor and unique taste, crystallizes quickly.
13.	Sunflower honey	Golden-yellow or light amber in color, tastes very sweet, a little tart. Crystallizes small grains, sometimes acquires a greenish tinge.
14.	Phacelia honey	It has a delicate aroma and a pleasant delicate taste. Upon crystallization acquires a doughy consistency.
15.	Rhododendron honey	Light pink or golden yellow. It has a strong rich aroma and excellent taste.
16.	Forest honey (hawthorn, willow, mountain ash, walnut)	From light yellow to dark brown, sweet in taste with a pleasant aroma. Upon crystallization, it forms a small and medium precipitate
17.	Meadow honey (clover)	Light yellow or brown, pleasant to the taste and very fragrant.
18.	Field honey (cornflower, chicory, valerian)	Has a pronounced antimicrobial and anticystitis effect. The range of shades – from almost colorless to orange-yellow. It tastes sweet, the aroma is delicate and pleasant
19.	Padevy honey	Dark, almost black, with a greenish tinge, or dark brown. The aroma is weak, sometimes unpleasant. Taste, sometimes bitter or sour.

Storage of honey in the temperature range +4 – +10 °C promotes the formation of crystals of mixed type. The formation of small crystal sizes with decreasing temperature is explained by the limited mobility of sugar macromolecules [11]. The second factor influencing the crystallization of honey is the water content. At a water content of 16–20%, honey crystallizes rapidly, and at a content of more than 21%, honey remains liquid, transparent, and almost colorless for a long time (for example, acacia and lime) [11]. The third factor influencing the process is the presence of crystallization centers.

The process of crystallization of honey depends on the number of crystallization centers (germ crystals), around which the crystallization of glucose. However, the greatest influence on the size of crystals and their number has the presence of pollen grains of plants. One of the most important factors in the crystallization of honey is the presence of bee pollen, ie pollen, which significantly accelerates the crystallization of honey. According to organoleptic parameters, bee pollen is a powdery, granular mass of hard lumps 8–200 μm in size, which are glued by bees with the secretion of salivary glands and nectar into lumps with multicolored granules 1–3 mm in size. The color of pollen – from yellow to purple (depending on the honey plant), the smell – pronounced, has a floral aroma and almost tasteless, gives a specific color to each variety of honey (Fig. 1, Table 1). Approximate composition of pollen: water (8–10%), carbohydrates (20–40%), proteins (25–35%), fats (5–7%) [6]. Pollen particles, the content of which can be in honey from 60 to 28,000 / g units of pollen grains are the main centers of crystallization of honey. In addition, pollen has a significant effect on the amount of biochemical activity of honey – its diastasis number. The largest number of pollen grains is found in phacelia (about 11000 / g) and buckwheat (about 5500 / g), the least pollen in acacia and linden honey (about 20 / g) [12].

The results of the literature and patent review show that the problem of crystallization and acceleration of improving the efficiency of dissolution of honey by heating, using alternative methods, including microwave processing of honey, requires additional study.

The purpose of the study was to find new technological methods, alternative means and selection of special technological conditions (temperature, time) and equipment for dissolving crystallized honey, as well as further stabilization of liquid honey when stored in this state for at least 1 year.

The task of the study was as follows:

– to study the effect of particle size and amount of pollen in honey on its crystallization and stability during storage before and after heat treatment in different conditions;
– compare the influence of heat treatment conditions of crystalline honey by heat exchange and microwaves on the size and size distribution of sugar macromolecules in honey depending on the technological parameters and equipment of the process;
– to study the influence of heat treatment parameters of honey in different conditions on the value of its diastase number, Goethe number, oxymethylfurfural content, quantitative and qualitative composition of honey, biochemical activity;
– try the possibility of using dissolved liquid honey to create biologically active honey for the needs of periodontology and dentistry when creating preventive chewing gum.

Thus, the study of the properties of food compositions based on caramelized honey and their changes associated with the particle size of macromolecules of sugars and polysaccharides in the caramelization of honey is a very important issue for both chemistry and food technology.

Materials and methods of research

To study the process of crystallization, standard samples of natural crystallized honey (FOP "Sviy Med" Kyiv region of Ukraine) were used, which met the requirements of DSTU 4497: 2005 Natural honey. Characteristics of polyfloral honey before and after low-temperature, isothermal, accelerated processing (dissolution), are presented in table 2. During the study, an alternative method of dissolving crystallized honey was used [12]. For this purpose, honey was treated with microwave waves at low temperature (40–60 ° C) and the minimum processing time, not more (60 ° C), which was carried out in a special rotating glass reactor in a microwave isothermal chamber MWR-SPR: "Microwavereactor for Solid-phase reactions", Milestone, Italy ", (Faculty of Industrial Technology, O. Dubčak University of Trenčín, Pukhov, Slovak People 's Republic) [14], which is shown in Fig. 2.

Studies of the structure and properties of crystalline and liquid honey were performed using a MBS-20 light laboratory microscope. IR spectra of natural honey were recorded using an IR spectrophotometer FTIR spectrometer Nicolet iS50. Quantitative changes in the composition of sugars in honey were determined by the size distribution of sugar microparticles by the method of angular distribution of the laser beam (NANODS CILAS), under dynamic and static conditions. Analyzes of samples of aqueous solution of honey on the indicators of chemical (HSC) and biological consumption (BSC) of oxygen were made in accordance with the methods (DSTU 4175:2003) for the determination of HSC and BSC in water

Table 2 – Organoleptic characteristics of honey taken for research before and after heat treatment

№ з/п	Indicator	DSTU requirements 4497: 2005 Natural honey	Honey is natural, crystallized, polyfloral (від 04.2018.)	Polyfloral honey, dissolved after heat treatment in a microwave reactor MWR-SPR
1.	Color	Colorless, white light yellow	Light yellow, sunflower	Dark yellow
2.	Taste	Sweet, tender, pleasant, tart	Sweet, tender pleasant	Sweet, pleasant, without extraneous flavors
3.	Aroma	Specific, pleasant without foreign odors	Pleasant without odors	Pleasant without odors
4.	Consistence	Liquid, viscous, dense	Dense, crystalline, with pollen particles	Liquid, without available pollen particles
5.	Crystallization	From fine to coarse-grained	Coarse-grained	Missing
6.	Signs of fermentation	Not allowed	Not found	Not found
7.	Mechanical impurities	Not allowed	Not found	Not found
8.	Mass fraction of water, not more than%	18.5–21.0	20.7	19.7
9.	Diastasis number (Goethe unit), no less	15–10	13.88	11.0

Figure 2 – Microwave laboratory rotary reactor for solid-phase reactions, including for dissolving crystallized bee honey with automatic temperature and time controller. MWR-SPR: «Microwave reactor for Solid-phase reactions, Milestone, Italy»

The diastasis number according to Gotha (biological activity of honey) and the content of hydroxymethylfurfural were determined according to DSTU 4497:2005 Natural honey (see table 2). Analysis of honey samples for the content of individual elements and their oxides was performed by X-ray fluorescence spectroscopy using the instrument EDX-7000 [14], the mass fraction of sugars and water in honey was determined using a special refractometer-saccharometer WALCOM REF 107/117. During the study, a dental examination and determination of the intensity of the carious process with the help of: CPV index, Fedorov-Volodkina index, gum bleeding index, periodontal index, saliva pH. Microbiological examination of patients before and after chewing gum was also performed.

For reference. When using the drug provides the body with components of bee honey, wax, propolis, perga and pollen; the ingredients of residual food and other ingredients are automatically removed from the mouth, teeth and gums during chewing. It should be borne in mind that the patient decides when to use the chewing gum «Honeycomb» «Honeycomb-Honeycomd», and the drug already helps him in this, reducing contamination of the oral cavity, teeth and periodontal tissues from external factors of food and others.

Periodontal diseases (gingivitis, periodontitis and periodontitis) often develop against the background of comorbidities: digestive disorders, cardiovascular and endocrine disorders, which affect the psycho-emotional state of patients. Therefore, it is not only a general medical but also a social problem. Although Medivnik-Honeycomd prophylactic chewing gum suppresses the symptoms and manifestations of periodontal disease, behavioral factors and social causes can re-cause the disease. The Medivnik-Honeycomd preventive gum should be used according to the instructions as soon as the first symptoms of periodontal disease, increased sensitivity and inflammation of the gums, as well as their bleeding during brushing to maintain normal oral periodontal tissues. Chewing gum "Honeycomb-Honeycomd" should be used continuously for the first 3 months if symptoms of periodontal disease are detected. Then, the drug should be discontinued. However, you should always have a certain amount of chewing gum in stock, as symptoms of gingivitis and periodontitis may suddenly reappear. As a rule, it is not recommended to use Chewing Gum «Medivnik-Honeycomd» for more than 6 months. However, some patients may need longer treatment to prevent moderate to severe periodontitis and periodontitis. Medivnik-Honeycomd prophylactic chewing gum based on honey, wax and propolis should not be prescribed to persons under 4 years of age without a doctor's recommendation.

Pharmacokinetics. In the process of chewing gum «Honeycomb» «Honeycomb-Honeycomd» components of bee honey, wax, propolis and pollen are slowly released and absorbed in the mouth and periodontal tissues. The maximum concentration in plasma is observed after 3015 minutes. after chewing. In comparison with chewing gums on a synthetic (polymeric) basis, the degree of absorption and adsorption of the active components of the drug during chewing is higher, their concentration increases faster geometrically and has a much higher value.

Indications for use. Prevention and treatment of gingivitis, periodontitis and periodontitis: relief of symptoms of gingivitis, pain when chewing food, bleeding gums during brushing, inflammation and destruction of periodontal tissues and reduction of dystrophic periodontal damage, which leads to impaired gingival attachment and healthy teeth.

Dosing and administration. Medivnik-Honeycomd chewing gum contains natural beeswax, honey, propolis, perga and pollen. In the process of chewing there is a gradual release of these components of chewing gum, which are then absorbed through the mucous membrane of the oral cavity. If the patient wants to prevent or cure the symptoms of periodontal disease, chewing gum «Honeycomb» «Honeycomb» «Honeycomb-Honeycomd» can help overcome malaise, irritability and pain by natural chewing. The Medivnik-Honeycomd chewing gum should be chewed slowly following the instructions. For children, adult patients, including the elderly, c. Depending on age and severe severity of periodontal disease can be used chewing gum with different greater or lesser concentration of active substances. As a rule, for patients with gingivitis, Medivnik-Honeycomd chewing gum is indicated at a dose of 1–3 chewing gums a day after meals. If the patient has periodontal disease – periodontitis, then for the treatment of progressive destruction of the periodontium and bones of the alveolar process of the jaws, a recommended dose of 3–4 chewing gum a day after meals and at bedtime, after brushing your teeth with toothpaste and brush. In the prevention and treatment of periodontitis (only mild and moderate forms), the recommended dose is 4–5 chewing gums a day after meals and at bedtime, and in the morning after brushing your teeth with toothpaste and brush. Medivnik-Honeycomd chewing gum should be used in all cases to prevent gingivitis, periodontitis and periodontitis at least once a day. Do not use more than 1 chewing gum at a time and more than 10 chewing gums a day.

Periodontal diseases (gingivitis, periodontitis and periodontitis) often develop against the background of comorbidities: digestive disorders, cardiovascular and endocrine disorders, which affect the psycho-emotional state of patients. Therefore, it is not only a general medical but also a social problem. And although Medivnik preventive chewing gum suppresses the symptoms and manifestations of periodontal disease, behavioral factors and social causes can again cause the corresponding diseases. Medivnik prophylactic gum should be chewed according to the instructions as soon as the first symptoms of periodontal disease, increased sensitivity and inflammation of the gums, as well as their bleeding during brushing to maintain the normal condition of periodontal tissues of the oral cavity. For prevention, you should take a sufficient amount of chewing gum daily, a maximum of 1–2 pieces. Medivnik chewing gum should be used continuously for the first 3 months if symptoms of periodontal disease are detected. Then, the drug should be discontinued. However, you should always have a certain amount of gum in stock, as symptoms of gingivitis and periodontitis may suddenly reappear. As a rule, it is not recommended to use Chewing Gum "Medivnyk" for more than 12 months. However, some patients may need longer treatment to prevent moderate to severe periodontitis and periodontitis. Honey, wax and propolis prophylactic chewing gum should not be prescribed to people under 4 years of age without a doctor's recommendation.

Side effect. It has been established that Medivnik-Honeycomd prophylactic chewing gum based on honey, wax and propolis in the recommended doses does not cause any side effects. Honey, wax, propolis and pollen products released from chewing gum can sometimes cause light salivation. When swallowing dissolved honey, wax and other components in the recommended amounts (5–6 g) nae causes no side effects in the digestive system. However, it should be noted that the risk of side effects (allergies) when using chewing gum "Medivnik" "Medivnik-Honeycomd" in the recommended doses is much lower than when using bee products honey, propolis wax and pollen in other forms, in particular when using them in the form food in much larger quantities. Contraindication. The presence of hypersensitivity to the components of the drug (honey, wax, propolis, perga and pollen).

Overdose. Overdose can occur in cases of consumption of several chewing gums simultaneously or one after another. There is no risk of poisoning when swallowing chewing gum, because all the components of Medivnik-Honeycomd chewing gum, namely honey, wax and propolis and pollen, are natural products produced by honey bees. Measures in case of overdose. Chewing gum should be stopped and chewed immediately. Features of application. Patients who wear dentures may have difficulty chewing Medivnik-Honeycomd by destabilizing denture fixation. Some allergic reactions have also been reported, as with excessive, more than 50g, bee consumption of honey, wax, propolis and pollen. Medivnik-Honeycomd should be used with caution in patients with diabetes. Pregnancy. According to the results of research within the program for the use of chewing gum «Medivnik» «Medivnik-Honeycomd» in these doses does not pose a danger to the fetus. But the use of chewing gum can be started only after consulting a doctor. Conditions and shelf life. Store at a temperature not exceeding +12 – +21 °C, out of reach of children. Shelf life – 2.5 years. All patients who underwent a course of prevention and treatment with chewing gum «Honeycomb-Honeycomd» signed an informed consent to participate in the next stages of testing.

Stomatoflor – the study consists of the following stages: DNA isolation (sample preparation) and PCR amplification of DNA in real time using a set of reagents ParodontoSkrin. The set of Parodonto Screen reagents includes: a mixture for PCR amplification, specific for all bacteria (total bacmas), mixtures specific for opportunistic pathogens of the oral cavity and a mixture for amplification of human genomic DNA (clinical sampling control (CVM)). In samples of biological material in which human genomic DNA is present, the detecting amplifier must register an exponential increase in the level of fluorescence in the appropriate test tube. In samples of biological material in which there is no genomic human DNA, during the amplification of the level of exponential growth in the corresponding test tube is absent. The material for analysis is gingival fluid from the gingival sulcus, the contents of the pathological pocket, as well as a smear containing dental plaque. Before taking material for laboratory examination from the oral cavity, the use of antiseptics is contraindicated 5–7 days before the study. Do not brush your teeth before the examination. Biomaterial sampling was performed using sterile disposable applicators. To obtain correct results, the quality of taking a sample of biomaterial for research, storage, transportation and pre-treatment is of great importance.

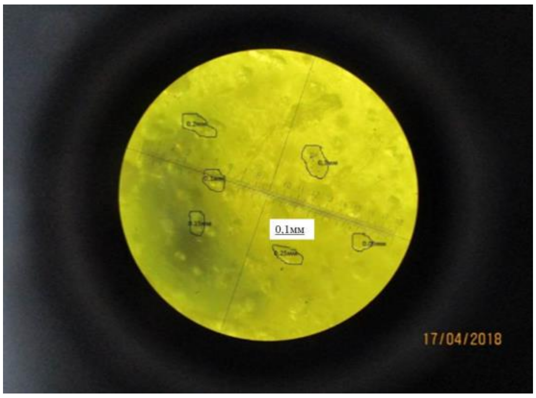
Detection of opportunistic pathogens of the oral cavity by PCR is a direct method of laboratory research, so the collection of biological material was carried out from the site of the infectious process. The contents of periodontal pockets should be selected from the deepest areas. During the removal of the absorbent, its contact with the mucous membrane of the oral cavity was completely excluded. Accounting and interpretation of the reaction results is carried out automatically using software supplied with the detector amplifier. If the DNA of the microorganisms in the test sample is detected by the Parodonto Screen set, the number of the microorganism (decimal logarithm of the concentration) is indicated in the line of this microorganism. In the results of the analysis it is necessary to take into account the value of material sampling control (KVM) and internal control sample (VK).

Research results and their discussion. For the most part, special equipment is used to dissolve crystallized solid honey, in which heat transfer takes place from water heated to 70–80 °C to crystallized honey through the wall of the tank with stirring devices (stirrers). It is possible to use devices with electric heating for a long period of 4–12 hours, given in the literature [10]. Classical equipment for dissolving honey allows dissolving (crystallization) of solid honey by heat exchange through the reactor wall with stirring, heated by electric heating or by means of a so-called water jacket, to a temperature of 50–60 °C, for 8–12 hours. Pasteurization of honey is recommended to be carried out at 57–63 °C for 60–10 minutes. To destroy the spore forms of microorganisms, it is recommended to heat the honey at 63–800C for 30–40 minutes. [6] There is a method of dissolving honey using an installation equipped with a microwave microwave oven, but it is not effective enough [12]. An advanced, rotating glass reactor in a MWR-SPR microwave isothermal chamber was used for our research (Fig. 2).

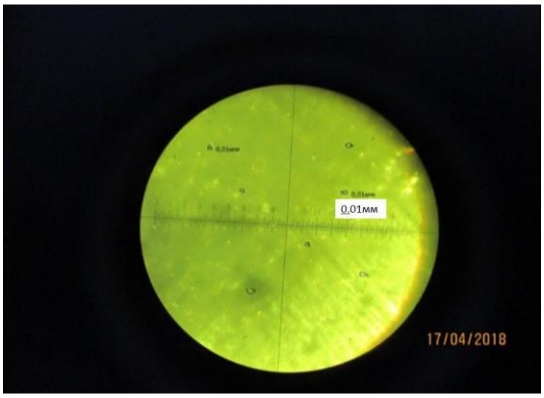
Initially, the effect of heat treatment on the size and number of pollen particles (pollen), which is known to be the center of honey crystallization, was studied. In Fig. 3. depicts microphotographs of samples of natural bee honey (Table 2) after 6 months of storage at a temperature of 16–21 °C, which is recommended by the authors [9]. A sample of such honey is opaque, partially crystallized with pollen particles (Fig. 3.1). A sample of natural honey was compared with a sample of the same variety of honey after low-temperature, isothermal express treatment in a special microwave reactor (Fig. 3.2).

As can be seen from Fig. 3.1. the size of pollen in honey before processing (Dchast. = 50–100 microns) is 10–20 times larger than the size of pollen particles in honey after low-temperature express processing in a microwave reactor, when honey becomes transparent and the size of pollen decreases to (Dchast. = 10–20 μm). The approximate composition of pollen given in the literature [6] confirms that it contains water (8–10%), carbohydrates (20–40%), which are very susceptible to microwave waves.

Additionally, samples of honey were examined under a microscope MBS-20 (×256), the results are shown in Fig. 4. Fig. 4.1 shows photographs of crystals (glucose and sucrose) of crystallized bee honey after 6 months of storage, at 16–21 °C (Dcris. = 500–1000 μm). In Fig. 4.2 you can see the same crystals of glucose in honey, after low-temperature, isothermal, accelerated processing of the honey sample in a microwave reactor MWR-SPR, after storage for 6 months – (Dcryst. = 100–200 μm). Therefore, as can be seen from the data obtained, after the dissolution of crystallized honey, the average size of glucose crystals decreased by 2–5 times.



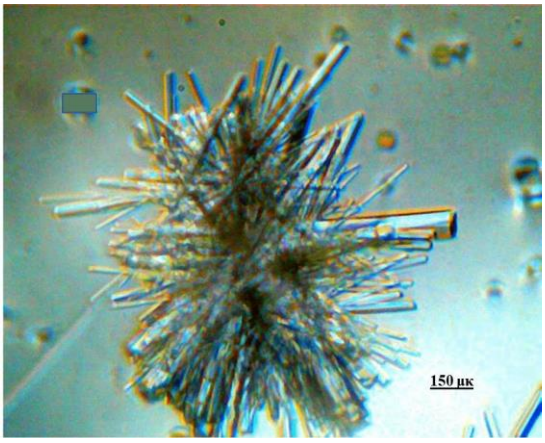
3.1



3.2

Fig. 3.2 – **Sample after low-temperature, isothermal, accelerated treatment in a microwave reactor, with pollen particles Dchast. = 0.01–0.02mm. Microscope MBS-20 (x56):**

Figure 3 (1, 2) – Natural bee honey (see table 1) after 6 months of storage, at 16–21 °C;
Fig. 3.1 Sample of honey before heat treatment with pollen particles Dchast. = 0.05–0.1mm



4.1

4.2

Figure 4 (1, 2) – Microphotographs of crystals (glucose and sucrose) of natural bee honey (Table 2) after 6 months of storage, at 16–21 °C), (Fig. 4.1) crystalline honey Dkris. = 500–1000 μm, (Fig. 4.2) – honey after low-temperature (50 °C), isothermal, accelerated processing in microwave (60 sec.) And storage for 6 months, (Dcryst. = 100–200 μm), Microscope MBS-20 (×256)

In accordance with the requirements of DSTU4497: 2005, the value of the number of diastases according to Gotha (biological activity of honey) and the content of another undesirable component in honey – hydroxymethylfurfural (GMF) before and after heat treatment were analyzed. According to the authors, the concentration of GMF increases sharply after the classical heat treatment of honey [13]. In fig. 5 (1, 2, 3, 4). The results of the analysis of the number of diastases (Fig. 5.1) And the content of hydroxymethylfurfural (Fig. 5.2) During the dissolution of crystallized honey by heating (8 hours) during heat exchange (50 °C) on classical heat exchange equipment [7] with hot (80 °C) water.

For comparison, samples were analyzed for these indicators (diastasis number and GMF content) of honey (table 2) after isothermal low-temperature (40–60 °C) express heating (60s) in a microwave reactor MWR-SPR, the results are presented in (Fig. 5.3, 5.4). The results of experimental studies (Fig. 5.1–5.4) allow us to conclude that the classical dissolution of crystallized honey by electric heating or warm water from 30 to 80 °C for 1–8 h, the diastase number according to Gotha (bioactivity) of honey samples decreases by 2–12 times. Yes, after 8 o’clock at 80 °C, the diastasis number decreases to zero, which is much lower than the permissible norms of DSTU (10 units. Goethe), (see Fig. 5.1).

This increases the content of unwanted hydrosimethylfurfural (Fig. 5.2) in 3–4 times, reaching a value of 20 mg / kg of honey, which significantly exceeds the permissible norms of DSTU (10 mg / kg). At the same time, when heated by the proposed method of low-temperature, isothermal express heat treatment in a microwave reactor, at temperatures (40–60 °C), for only 1–3 minutes, (60–160 times reduced processing time compared to the classical method), there is a decrease in the diastasis number by only 2–3 units to 11 (see Fig. 5.3). The content of hydroxymethylfurfural increases only 2 times to 6 mg / kg, which is permissible (according to DSTU 4497:2005) (Fig. 5.4).

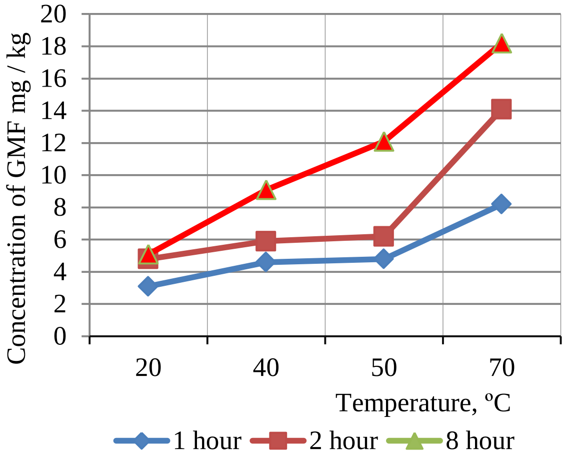


Figure 5.1 – Dependence of the diastase number of honey in Gotta units on temperature and heating time during heat transfer from hot water (80 °C)

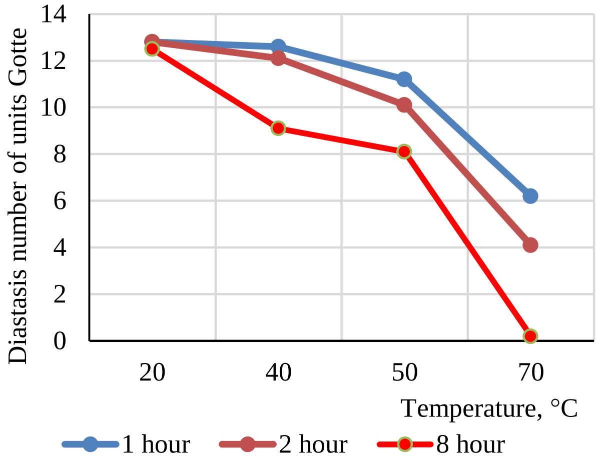


Figure 5.2 – Dependence of the content of hydroxy-methylfurfural on the temperature and heating time of honey, with heat transfer from hot water (80 °C)

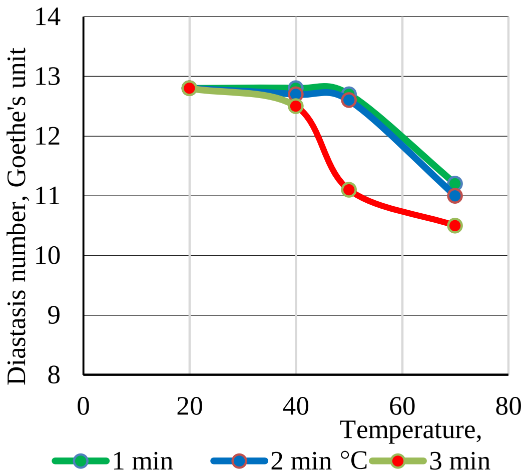


Figure 5.3 – Dependence of the diastase number of honey in Gotta units on temperature and heating time under isothermal conditions in a microwave reactor MWR-SPR

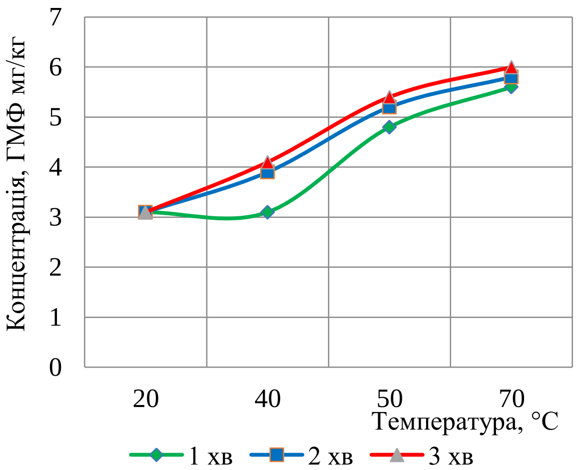


Figure 5.4 – Dependence of hydroxymethylfurfural (GMF) content in honey on temperature and heating time in isothermal conditions in the MWR-SPR microwave reactor

Studies on changes in the chemical composition and structure of honey after low-temperature express treatment in a microwave reactor MWR-SPR by IR spectroscopy on FTIR spectrometer Nicolet iS50, the spectra are shown in Fig. 6. As can be seen from the figure, the IR spectra of samples of natural honey (Fig. 6, 1-red line) and honey after low-temperature express treatment (Fig. 6, 2-blue line) are almost identical, which indicates the same chemical composition 2-x test samples.

A detailed comparison of the IR spectra of ordinary (2-red curve) and caramelized honey (1-blue curve) after low-temperature isothermal treatment, suggests that there is almost no significant difference in the chemical composition of the products. Infrared spectra differ only in the frequency range 1600–500 cm-1, which can be explained by the appearance of supramolecular changes in the structure of caramelized honey, namely condensed, caramelized mono-, di- and polysaccharides into cyclic monosaccharides, in which the chemical structure of honey is almost unchanged, and changes the supramolecular mass and the degree of polymerization and polycondensation of sugars. In this case, intramolecular and intermolecular processes of sugar cycling can occur. Subsequent heating leads to condensation of sugars and the formation of anhydrides. As a result of long-term heating and caramelization, a system of condensed (colored) compounds is formed, among which 3 main products are distinguished: terrasaccharide – caramel ($C_{24}H_{36}O_{18}$), hexasaccharide – caramel ($C_{36}H_{50}O_{25}$), and eicosan saccharide – caramel ($C_{125}H_{188}O_{80}$). Therefore, after carrying out low-temperature, isothermal express processing of honey samples by the method proposed in the work, its qualitative composition almost does not change.

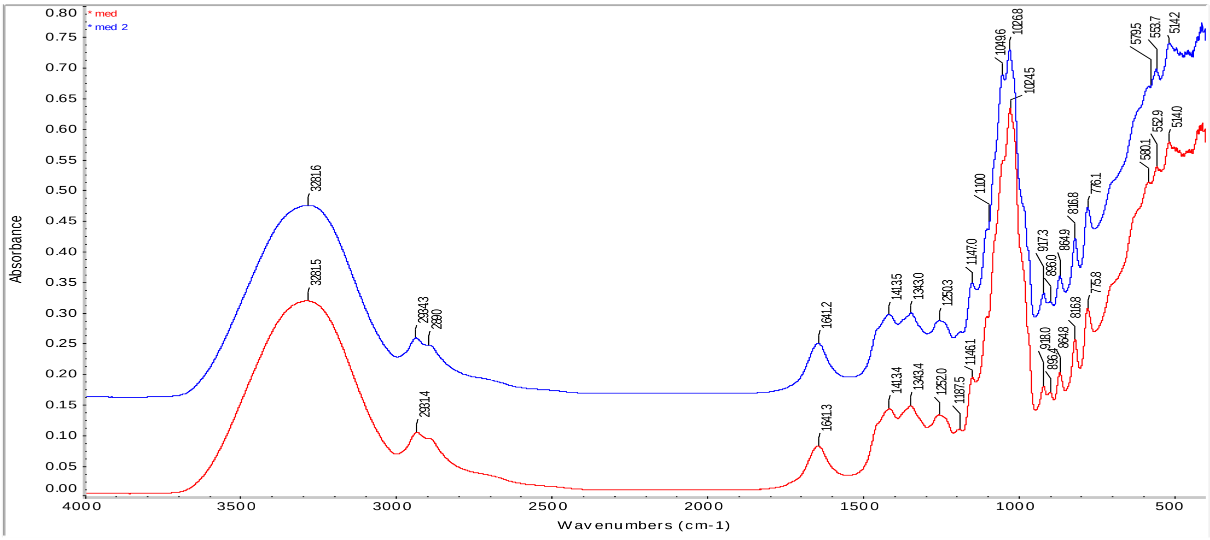


Figure 6 – IR spectra of natural honey (2-red spectral line) and honey after low-temperature (50 °C) processing of honey (1-blue spectral line). FTIR spectrometer Nicolet iS50

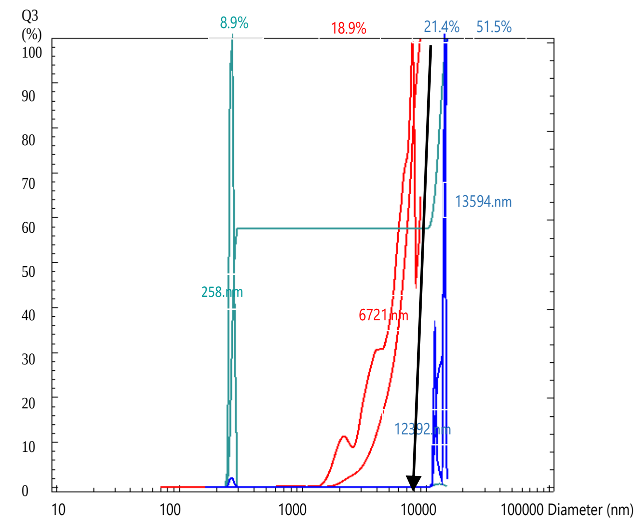


Figure 7.1 – Mass distribution of particles of natural unprocessed honey, average particle diameter Dc = 12000 nm. (NANO-DS CILAS)

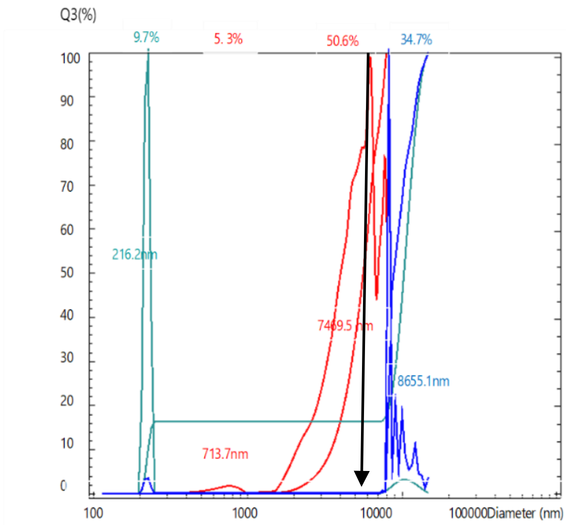


Figure 7.2 – Mass distribution of heat-treated honey particles in the MWR-SPR microwave reactor (50 °C, 1 min.) Average particle diameter Dc = 6000 nm. (NANODS CILAS)

To study the supramolecular structure of caramelized honey in more detail and compare it with the structure of ordinary honey, the method of determining the size of nanoparticles and size distribution of macromolecules of oligomeric honey compounds, including polysaccharides, was used on an automatic light scattering analyzer.

The size and distribution of nanoparticles in static and dynamic states were determined by laser scattering of particles (400–700 nm) particles in aqueous solutions, dispersions, emulsions and solids, sizes from 0.3 nm to 10000 nm (10 μm), (Particle size analyzer Nano DS from CILAS is an innovative optical device that allows you to measure the size of nanoparticles without the need to replace the optics or calibrate the device). As a result of researches curves of distribution of particles which are represented on (see Fig. 7.1, 7.2) are received. From the obtained data we can assume that natural bee honey has 4 types of macromolecules, which differ by much larger (1.5–2.0 times) the size of nanoparticles, compared with caramelized honey (Fig. 3). The highest content is 51.5% of particles with an average diameter of 13,594 nm (13.59 μm) (blue curve in Fig. 7.1, 7.2). The particle size distribution is shown on the device (PPM on NANODS CILAS) of macromolecules of sugars and polysaccharides of natural unprocessed honey (Fig. 7.1). And honey treated by low-temperature isothermal express method in a microwave reactor MWR-SP at 50 ° C for 1×C. (Fig. 7.2). Therefore, as can be seen from the figures, the average value of microparticle size of a sample of honey treated by low-temperature isothermal express method in a microwave reactor MWR-SPR is 2 times (Dser. = 6.0 μm) less than untreated crystallized natural honey (12.0 μm, Fig. 7.1). The results of molecular weight distribution show that in the heat-treated liquid honey there are microparticles of sugars with a size of 0.1–0.7 μm, the content of which exceeds 50% (Fig. 7.2). It is important to note that such small particles were absent in the crystallized copper (Dser. = 12.0 μm) (see Fig. 7.1). It is also possible to observe the presence of smaller nanoparticles (blue curve, Fig. 3) – 21.4% – 12392 nm (12.39 μm) and even smaller particles of honey sugars (red curve, Fig. 3) 18.9% – 6721 nm (6.72 μm), and the smallest nanoparticles (green curve Fig. 3) – 8.9% – 258 nm.

According to the results of particle size analysis of caramelized honey (see Fig. 7.2) We can conclude that such honey is characterized by 4 types of macromolecules, which differ in much smaller particle size than ordinary honey (Fig. 7.1). The highest content – 50.6% is accounted for by particles with an average diameter of 7469.5 nm (7.47 μm) (red curve Fig. 7.2.), 34.7% – is accounted for by larger particles 8655.1 nm (8,655 μm) (blue curve Fig. 7.2) and even smaller (216.2 nm) – 9.7% (green curve Fig. 7.2). As can be seen from the above distribution of nanoparticles (see Fig. 7.1, 7.2), a new peak appears in caramelized honey in the region of smaller nanoparticle sizes – 713.7 nm, the percentage of such particles – 5.3%. The total content of nanoparticles of caramelized honey (Fig. 7.2), Which have a size of more than 1000 nm is 85%, which is much less than in natural honey – 92% (Fig. 7.1).

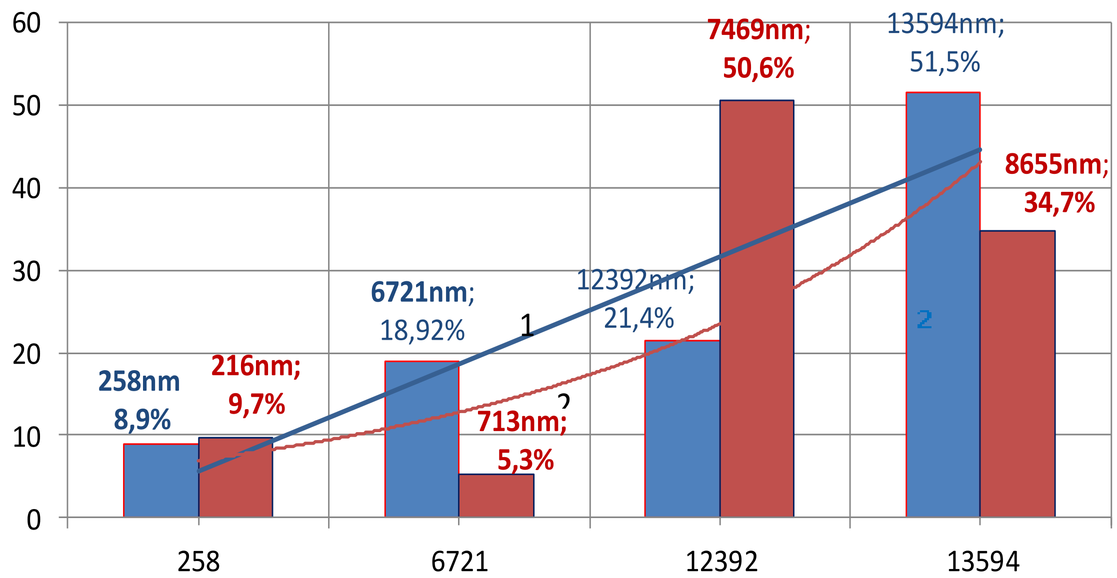


Figure 7.3 – Histograms of the comparative size distribution of nanoparticles of ordinary (1-blue histogram curve) and caramelized honey (2-red histogram curve).

To better illustrate the results obtained on the mass distribution curves, histograms of the particle size distribution of ordinary and caramelized honey were constructed (Fig. 7.3). Therefore, we can conclude that during the caramelization of honey there are two types of reactions: on the one hand there is a depolymerization of polysaccharides with a decrease in particle size, which is confirmed by the red diagrams in Fig. 7.3, Which have smaller values in the three ranges. Only in the range 6721–7469.2 nm there is a small (748 nm) increase in the size of macromolecules of caramelized honey, due to a decrease in its number from 51.5% to 34.7% in the range 8655–13594nm, which can be explained by the possible polymerization and polycondensation of mono- and disaccharides (reaction schemes in Fig. 7.4.1 and 7.4.1, 2). In other ranges of histograms, the particle sizes of macromolecules of caramelized honey decrease. The average particle size of caramelized honey is 2 times smaller than 6000nm (Fig. 7.2) than natural raw honey-12000nm (Fig. 7.1). These results confirm our previous light microscopy data that the treatment of honey in a microwave reactor at 50 ° C for 1 min, gives a positive result and promotes the dissolution and stabilization of liquid honey with a reduction in particle size by 2 times.

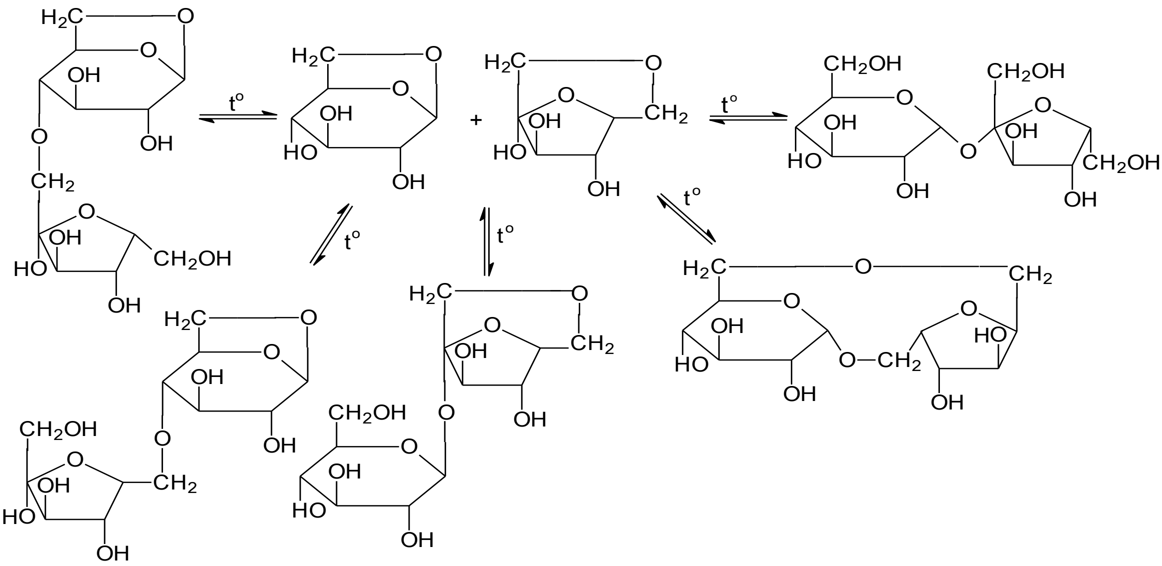


Figure 7.4.1 – Reactions and possible products of cycle formation and condensation during caramelization of sugars in honey

At a heating temperature of another 170 °C, oxymethylfurfural (OMF) can be formed, and many other compounds, for example, maltol, isomaltol [7] (reaction 7.4.2), The formation of hydroxymethylfurfural was identified by analysis of (DSTU 4497: 2005) (see Fig. 5.2, 5.4)

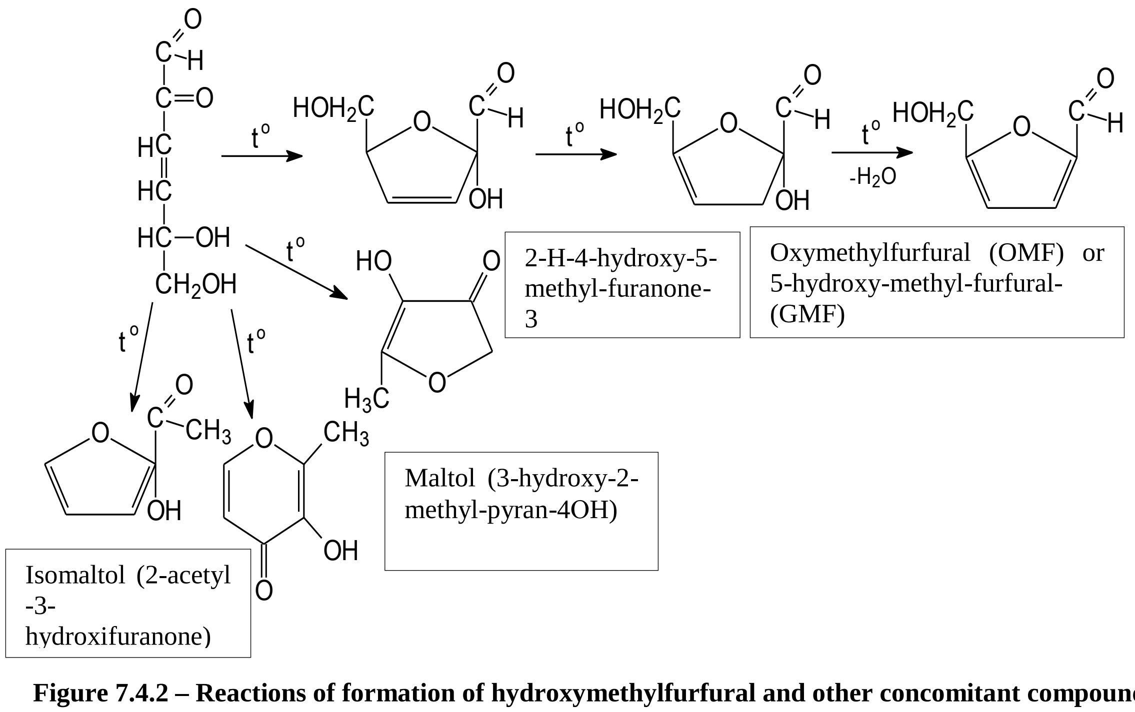


Figure 7.4.2 – Reactions of formation of hydroxymethylfurfural and other concomitant compounds (maltol, isomaltol) during caramelization of honey.

Figure 8 shows the results of X-ray fluorescence spectroscopy of the elemental content of samples of ordinary honey before and after its low-temperature isothermal express treatment in a microwave MWR-SPR (50 °C, 1 min), as well as caramelized honey at heat transfer from the carrier). According to the results of X-ray fluorescence analysis, which are shown in the histograms of the elemental (see Fig. 8) and oxide (see Fig. 9) composition of samples of natural (N) and caramelized honey (N1, N2, N3) we can conclude that that at low-temperature catalytic caramelization of honey its elemental composition almost does not change, but at the same time the supramolecular structure and structure of macromolecules (di- and polysaccharides present) change. From the histograms shown in fig. 8 shows that in all samples of natural and caramelized honey the content of basic elements (Oxygen (26–40%), Silicon (5–12%), Potassium (23–31%), Aluminum (4–6%) and Phosphorus) (3–6%)) is quite stable. It can also be noted that the content of iron (Fe) in honey samples is doubled during caramelization, which is due to the use of a steel catalyst [18].

Figure 9 shows histograms of the content of oxides present in natural and caramelized honey. From the histograms it can be concluded that all samples of honey contain a significant amount of the following oxides: SiO2-11 – 26%, K2O-27 – 37%, Al2O3-4 – 6% and P2O5-6 – 13%. It should be noted that the oxide content of most elements changes insignificantly during caramelization, except for oxides: SO3, Fe2O3, and ZnO, the content of which increases compared to their content in natural honey (N), which is associated with the use of steel catalyst [18].

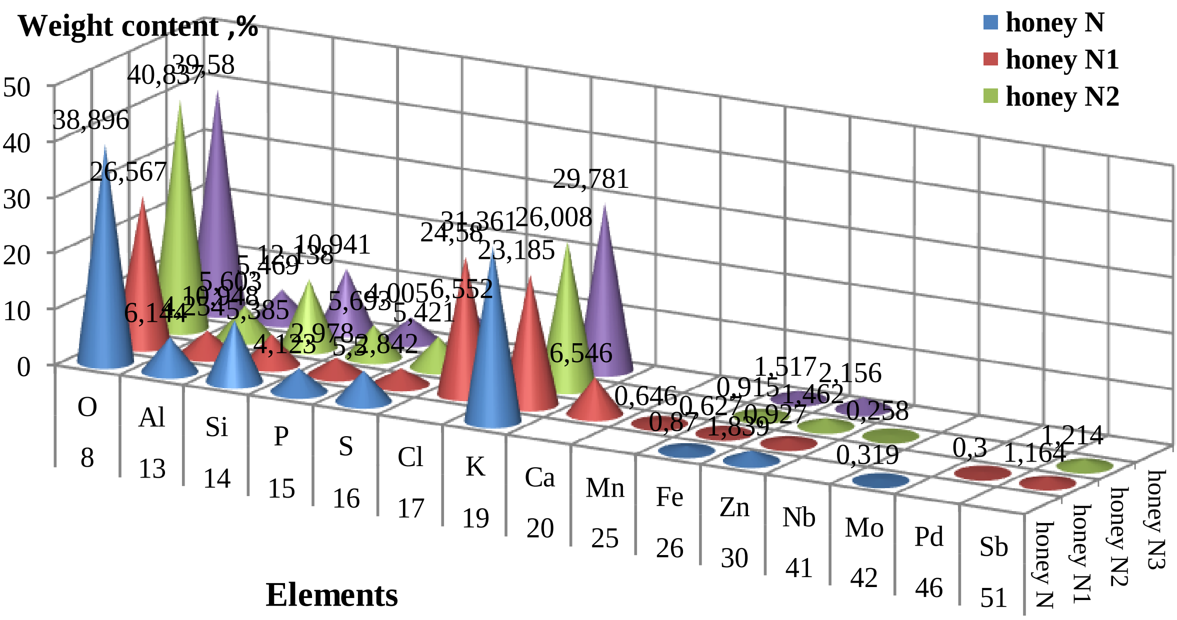


Figure 8 – The results of X-ray fluorescence analysis of the elemental composition of natural N and caramelized honey: N1, N2, N3. (EDX-7000 energy dispersive x-ray fluorescence spectrometer, Shimadzu Na-U, vacuum)

The results of analyzes of the composition of oxides of chemical elements of the studied samples of honey confirm that the qualitative content of elements in honey before and after processing in a microwave reactor is almost no different from raw honey, but differs in quantitative composition, especially after caramelization of honey in an unconventional way [18].

Experimental studies and the results of caramelization of honey with its simultaneous decrystallization made it possible to create a new food product – chewing gum with therapeutic and prophylactic properties. Samples of dissolved, liquid, caramelized honey in a MWR-SPR microwave reactor were used for this purpose [14].

According to the WHO, which is based on a survey of 53 countries (including Ukraine), the highest level of periodontal disease occurs at the age of 35–44 years (65–98%) and 15–19 years (55–89%). 80% of children on Earth are diagnosed with the first stage of periodontitis – gingivitis. Generalized periodontitis in adulthood occurs in 90–95% of patients. In Ukraine, the problem with periodontal disease is also quite relevant, so according to the Ministry of Health, Ukrainians under the age of 40 years, the frequency of periodontal disease is 50–60%, and after 40 years – 100% (see Fig. 10). In Ivano-Frankivsk region, according to the results of a comprehensive clinical and laboratory examination of residents of the Carpathian region, a high frequency of generalized periodontitis was found in 94.77% of patients [15].

Based on the synthesized liquid, caramelized honey, we created new samples of chewing gum containing a composition of liquid and caramelized honey, wax and propolis in the form of chewing candies (Fig. 11). This chewing gum has undergone successful clinical studies at the Research and Training Center for Molecular Microbiology and Immunology of Mucous membranes of Uzhhorod National University, in 2018–2019. [13] Samples of prophylactic chewing gum are recommended for use in production, as they give a positive therapeutic effect in 72.5% of patients [16] who had periodontal disease: gingivitis, periodontitis and periodontitis (Fig. 10). "Medivnik-Honeycomd" chewing gum (Fig. 11) has pronounced prophylactic, anti-inflammatory, astringent, anti-infective, antimicrobial and antibacterial properties, especially on periodontal tissues of the oral cavity of gums and other dental diseases of patients, copyright is protected by a patent for an industrial design [17] and a method of caramelizing honey [18].

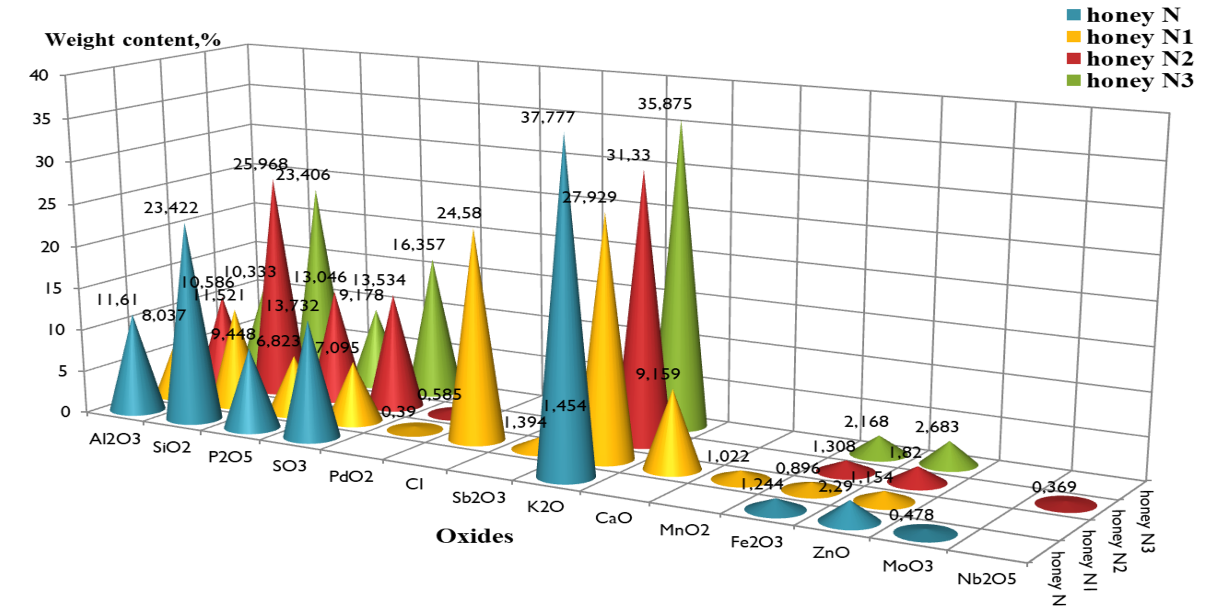


Figure 9 – The content of oxides of chemical elements according to the results of X-ray fluorescence spectroscopy EDX-7000: Sample 1-honeycomb; Sample 2-heat-treated in microwave honey in (50 °C, 1 min.); Sample 3-liquid dissolved in heat transfer honey; Sample 4-caramelized honey (at 60 °C, 10 min.) [14]

Figure 10 – Photos of healthy (1) and patients with periodontitis (2) periodontal tissues and teeth [15]

Figure 11 – Prophylactic chewing gum, based on liquid crystallized and caramelized honey, wax and propolis for the treatment of periodontal disease (gingivitis, periodontitis, periodontitis), which has passed clinical trials and showed a positive result in 72.5% of patients.

As a result of research and detailed study of the method and mode of low-temperature isothermal accelerated treatment in a microwave reactor of crystallized honey, it is proposed to create new biopolymer food compositions from honey wax and propolis for the prevention of periodontitis.

Combinations of the most virulent pathogens are important for destructive forms of periodontitis. 5–8 periodontal pathogens have been identified, which are most common in the places of the greatest destruction of the periodontium – atrophy of the gums and alveolar bone. These include: Porphyromonas gingivalis, Actinobacillus actinomycetemcomitans, Prevotella intermedia, Eikenella corodens, Fusobacterium nucleatum [19].

Modern concepts of the etiopathogenesis of periodontal disease suggest the presence of major, predominant bacterial pathogens, which are associated with clinical forms and severity of the disease. These pathogens are present in minimal quantities at the beginning of each inflammatory and destructive process of the periodontium. Different reactivity of the body's defenses to different degrees can cause this process [20].

One of the tasks of this study was to establish the relationship between the deviation of the number of microorganisms after consumption of chewing gum " "Medivnik-Honeycomd" from the initial number of oral microorganisms (Table 3 "Stomatoflor 1, 2") and depending on the indices (CPV, RI, GI, RVI) and pH (Table 4 "Intensity of the carious process"). The combination of caramelized honey, wax and propolis has the ability to inhibit certain pathogenic or opportunistic microorganisms of the oral cavity. All subjects after 7 days of using chewing gum "Medivnik-Honeycomd" noted a decrease in plaque and eliminate discomfort / pain when brushing teeth. 65% of respondents reported no bleeding gums while brushing their teeth, although at the beginning of the study, this symptom was noted by about 90% of people.

Table 3.1 – Test «Stomatoflor» Before treatment

№	Name of the microorganism	Patient 1	Patient 2	Patient 3	Patient 4	Patient 5	Patient 6	Patient 7	Patient 8	Patient 9
1	Total bacterial mass	8.4 Lg	7.8 Lg	6.1 Lg	8.5 Lg	8.8 Lg	8.9 Lg	8.9 Lg	8.1 Lg	7.0 Lg
2	Actinobacillus Actinomycetemcomitans	–	5.6 Lg	–	–	–	–	5.8 Lg	–	–
3	Porphyromonas gingivalis	7.0 Lg	5.9 Lg	–	6.9 Lg	7.3 Lg	8.2 Lg	7.6 Lg	6.4 Lg	6.0 Lg
4	Prevotella intermedia	7.2 Lg	3.7 Lg	–	7.1 Lg	–	–	2.5 Lg	6.6 Lg	4.7 Lg
5	Tannerella forsythensis (Bacteroides forsythus)	6.7 Lg	5.1 Lg	–	6.0 Lg	6.3 Lg	7.1 Lg	6.6 Lg	6.0 Lg	4.4 Lg
6	Treponema denticola	6.3 Lg	4.4 Lg	–	6.3 Lg	5.9 Lg	7.0 Lg	6.7 Lg	6.0 Lg	3.3 Lg
7	Candida albicans	–	–	2.6 Lg	4.6 Lg	4.5 Lg	–	–	–	–

Table 3.2 – Test «Stomatoflor» After treatment

№	Name of the microorganism	Pat.1 peas	Pat.2 oros	Pat.3 selesh	Pat.4 leco	Pat.5 chubirko	Пац.6 мигович	Pat.7 chuberk aa	Pats.8 beleykanich	Pat.9 pozho
1	Total bacterial mass	8.7 Lg	7.4 Lg	6.7 Lg		8.4 Lg	8.0 Lg	8.2 Lg	7.8 Lg	
2	Actinobacillus Actinomycetemcomitans	0.5 Lg	4.3 Lg	–		–	–	6.1 Lg	–	
3	Porphyromonas gingivalis	6.5 Lg	5.8 Lg	–		7.1 Lg	7.0 Lg	7.4 Lg	4.8 Lg	
4	Prevotella intermedia	7.8 Lg	4.3 Lg	–		–	–	2.2 Lg	2.4 Lg	
5	Tannerella forsythensis (Bacteroides forsythus)	6.7 Lg	4.7 Lg	–		6.0 Lg	6.4 Lg	6.6 Lg	3.9 Lg	
6	Treponema denticola	6.6 Lg	4.3 Lg	–		5.6 Lg	5.8 Lg	6.2 Lg	2.5 Lg	
7	Candida albicans	–	–	3.3 Lg		0.6 Lg	–	–	–	

Table 4 – «Intensity of the carious process»

Patient	CPV index	Fedorov-Volodkina index		Periodontal index		Bleeding index of the gums		pH of saliva	
Patient 1	18	2,5	2,0	1,8	1,5	1,5	1,1	6,5	7,0
Patient 2	17	2,5	2,2	3,5	3,2	1,4	0,4	6,0	6,5
Patient 3	12	2,1	1,6	1,0	0,7	0,4	0,2	7,5	7,0
Patient 4	21	2,6	2,3	4,2	3,5	1,3	0,7	5,5	5,5
Patient.5	18	3,1	2,6	5,6	4,8	1,2	0,9	6,0	6,5
Patient 6	17	2,2	1,9	2,9	2,5	0,8	0,3	6,5	6,5
Patient 7	19	3,3	2,8	2,6	2,1	0,9	0,4	7,0	6,5
Patient 8	14	2,4	2,0	4,0	3,6	1,6	1,1	5,5	6,5
Patient 9	17	3,2	2,6	2,5	1,9	2,0	0,8	6,5	7,0

That is why all the information we obtained experimentally about the effect of chewing gum on the human oral microbiome demonstrated the clinical effectiveness of the introduction of chewing gum "Medivnik-Honeycomd".

Conclusions:

1. A new technology of honey caramelization using the method of low-temperature thermochemical heating using a special microwave technology is proposed. Reactions of caramelization of honey and other bee products in this way have been studied for the first time. The biochemical properties of the obtained products and the ability to convert biologically active honey compounds during the thermochemical process in the presence of catalysts and microwave waves were also studied.
2. The chemical, physicochemical and structural characteristics of liquid and crystallized (solid) honey depending on its thermochemical treatment and shelf life have been studied. There are 3 main factors that affect the rate of crystallization of honey: water content, pollen content and the ratio of glucose and fructose in honey. It is shown that with the help of low-temperature isothermal accelerated treatment in a microwave reactor type MWR-SPR at 40 °C, for 60s, it is possible to dissolve crystalline honey to a liquid state, which reduces the time for its dissolution in the classical method by heat transfer through the reactor wall. electric heating from 4–12 hours. at the same temperature 50 °C to 1 min, ie 240–600 times faster.
3. The properties, structure, qualitative and quantitative composition of the obtained liquid honey were studied and compared with the properties of the original crystalline and liquid honey without processing. It is proved that the proposed accelerated treatment in a microwave reactor type MWR-SPR at 50 °C, for 60s, retains

a high diastase number in Goethe units – 10–11. The content of hydroxymethylfurfural, however, did not exceed 3–6 mg / kg of honey, which meets the requirements of DSTU. And consumer organoleptic indicators of honey in a liquid state are stored for at least 1 year. At the same time, with the traditional method of crystallization (dissolution) of honey, these indicators are much worse, the diastase number decreases to 0–6, and the content of hydrosimethylfurfural increases to 12–18 mg / kg, which significantly exceeds the permissible norms (DSTU 4497: 2005).

4. Analysis of the qualitative and quantitative composition of honey after low-temperature isothermal accelerated treatment in a microwave reactor type MWR-SPR (at 50 °C, for 60s), performed by IR spectroscopy, showed no significant changes compared to untreated honey. Microscopic studies confirmed a 10-fold reduction in the number and size of pollen particles. The size of the crystals of glucose, sucrose and other sugars after such treatment is also reduced by 5 times. At the same time, the analysis of the mass distribution of sugar macromolecules by the method of angular distribution of the laser beam (NANODS CILAS) showed a decrease in the average particle size in treated honey by 2 times compared to crystallized samples, which has a positive effect on stabilization year.

5. On the basis of samples of crystallized liquid honey obtained by the new technology, a preventive chewing gum "Medivnik-Honeycomd" was created for the treatment of periodontal disease (gingivitis, periodontitis and periodontitis). Clinical studies of chewing gum samples based on a composition of liquid caramelized honey, which were conducted at the Research and Training Center for Molecular Microbiology and Immunology of Mucous membranes of Uzhhorod National University in 2018–2019, for the prevention and treatment of gingivitis, periodontitis and periodontitis in dentistry efficacy and positive result in 72.5% of patients.

6. The mechanisms of directed correction of the oral microbiome in diseases of the oral cavity of different etiology and taking into account individual characteristics have been studied. It is proved that the use of chewing gum based on caramelized honey, wax and propolis is an effective means of prevention and treatment of gingivitis, periodontitis, periodontitis and other dental diseases. It has been confirmed that the systematic use of chewing gum "Medivnik-Honeycomd" helps to restore the normal oral microbiome and reduces the number of pathogenic and opportunistic microorganisms.

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