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STUDY OF HEAT TREATMENT EFFECT ON THE BIOLOGICAL VALUE OF PINE NUTS KERNELS

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Abstract: *The aim of the research was to determine the optimal modes of heat treatment of pine nut kernels in order to preserve their biological value to the optimal, which will allow in the future to use this type of raw material in the technology of various types of sauces with the addition of dry whey. The article analyzes the drying kinetics of Pinus pinea Linneus pine nut kernels for 120 minutes under 4 heat treatment regimes: 20, 40, 60 and 80 ˚C. The effect of heat treatment on the composition of essential amino acids, the content of vitamin C and β-carotene was studied. Thus, the temperature of 20 and 40 ˚C ensures the maximum preservation of the biological value of the raw material, but it does not allow to achieve a significant decrease in the mass fraction of moisture, which will negatively affect the microbiological indicators of the raw material. During processing at 60 ˚C, the mass fraction of moisture in the kernels of pine nuts decreases from 7 to 5.28 %, which is likely to reduce water activity and positively affect the duration of storage. An increase in temperature to 80 ˚C significantly reduces the content of essential amino acids and β-carotene, as well as makes it impossible to achieve a technological effect (a significant decrease in moisture content) with the irrational use of energy resources. It was established that the optimal mode of heat treatment of pine nut kernels is drying at a temperature of 60 ˚C, which ensures the preservation of the biological value of the raw material and meets the recommendations for achieving satisfactory microbiological indicators.*

Keywords: *drying kinetics, moisture content, amino acid composition, vitamin C, β-carotene.*

1. Introduction

Today, the most important task of the food industry is the manufacturing of products with increased biological value in order to overcome the deficiency of protein, vitamins, minerals, dietary fiber in the human diet [1-2]. The most economically expedient is the development of technologies for food products of mass consumption [3-4], which, due to the use of plant raw materials, special methods of processing of individual ingredients or the product as a whole, will increase the amount of biologically active substances, protein and ensure food safety. Nut raw materials are one of the largest branches of the agricultural sector, cultivated in most countries of the world [5].

The seeds of the Siberian pine *Pinus pinea Linneus*, or as it is also called – pine nuts, are a source of biologically active substances and contain, on average, 13.69 % protein, 68.37 % fats, 13.08 % carbohydrates, 3.7 % dietary fiber, mineral and vitamin substances [6]. The fatty fraction of pine nut kernels is characterized by a high content of polyunsaturated fatty acids, such as linoleic and linolenic [7]. According to the amino acid profile, they are rich in arginine, lysine, methionine, and tryptophan [8]. Pine nuts are widely consumed in Eastern Europe, Asia, the USA and India. The most widely studied

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representatives of nut raw materials are peanuts, almonds, walnuts, cashews and hazelnuts [9-10].

Despite the high biological value of pine nuts, they have not been widely used in the production of food products [11], which is due to the issue of food safety and the need to find ways of their preliminary preparation [12]. At the same time, the seeds of the Siberian pine still remain a promising raw material for use in the food industry [13], as it can perform the role of a flavor additive, which ensures the manufacturing of a product with original taste properties, as well as a fortifier capable of increasing the biological value.

That is why it is promising to search and research different methods of processing pine nuts in order to avoid the risks of microbiological contamination in the case of their use in the recipe composition of food products [14].

Microwave irradiation of nuts can cause the inactivation of pathogenic microorganisms under the influence of heat due to the destruction of the cell walls of bacteria. However, this mechanism and the factors affecting it have not been fully studied [15]. Heat treatment is capable of reducing microbiological contamination, enzymatic and oxidative degradation, as well as facilitating its further processing, storage and quality, which will undoubtedly affect the shelf life of the finished product. In addition, such processing can create favorable conditions for the intensification of the fatty acid composition of nuts [16], which affects the texture of the food product in which they will be used. However, exposure to high temperatures over a long period of time leads to the loss of essential vitamins and other substances [17], while low temperatures may not have a significant effect on microbiological indicators [18]. Thus, short-term preparation of nuts at a temperature of 200 ˚C allows obtaining a high-quality product due to the removal of 70...80 % of surface films, but at the same time, the mass fraction of protein decreases by 15...20 %, the content of fatty acids decreases to a level that does not contribute to their assimilation [19]. Moisture-temperature processing allows to reduce the content of phytates to 45 % [20], however, this process is long-term, since only the soaking stage can take up to 10 hours, and the obtained raw materials have significantly worse indicators of microbiological purity.

The aim of the study was to determine the optimal modes of heat treatment of pine nut kernels for the maximum preservation of biologically active substances, which will allow them to be used in the technology of various types of sauces with the addition of whey in the future.

To achieve the goal, the following tasks were defined: 1. To study the kinetics of drying pine nut kernels at different heat treatment temperatures; 2. Determine and compare the amino acid composition, vitamin C and β-carotene content of pine nut kernels before and after drying under different conditions; 3. Choose the most appropriate mode of heat treatment, which contributes to the maximum preservation of biologically valuable substances in the kernels of pine nuts.

2. Matherials and methods

Raw material for research

Siberian pine seeds *Pinus pinea Linneus* of the 2020 harvest were chosen as the raw material for research. The chemical composition according to the manufacturer's specification was as follows and met the requirementsща ISO 6756: mass fraction of moisture - 7 %, mass fraction of protein - 13.8 %, mass fraction of fat - 63.9 %, mass fraction of ash - 2.44 %. Pine kernels were shelled, weighed and placed on a metal sheet, which was then placed in a drying cabinet.

The study of drying kinetics was carried out under 4 modes of heat treatment for 120 minutes: 1st sample - 20 ˚C, 2nd sample - 40 ˚C, 3rd sample - 60 ˚C, 4th sample - 80 ˚C. Weighing of pine nut kernels was carried out at 10-minute intervals during the entire drying period.

Research methods

Study of drying kinetics

When studying the drying process, an important aspect is the determination of physico-mechanical forms of moisture connection with the material. Quantitatively, the content of moisture in the material is estimated by its humidity. Relative humidity (ω, %) is distinguished, that is, the mass of moisture contained in the material (W, kg), attributed to the total mass of the sample (G, kg) [21]:

$$\omega = \frac{W}{G} = \frac{W}{G_{ac} - W},$$

and absolute humidity (ω_c), which is determined in relation to 1 kg of absolutely dry matter in the material under study (G_{ac}, kg):

$$\omega_c = \frac{W}{G_{ac}},$$

Both relative and absolute humidity are expressed in fractions of a unit or in percentages. When analyzing the drying process, it is more convenient to use absolute humidity, because the amount of absolutely dry matter in the sample remains constant under any conditions. When calculating humidity according to the above formulas, its average value in this material is obtained. The values of relative ω and absolute ω_c of humidity are connected by the following dependencies [22]:

$$\omega_c = \frac{\omega}{1-\omega}, \qquad \omega = \frac{\omega_c}{1+\omega_c}.$$

When studying the kinetics of drying, it is necessary to establish the influence of various external and internal factors on the speed of the process.

The drying speed υ is determined by the decrease in humidity $d\omega_c$ by some an infinitesimal time interval dτ, i.e. [22-23]:

$$v = \frac{d\omega_c}{d\tau}$$

Determination of vitamin C content

Determination of vitamin C content in the kernels of pine nuts before and after drying was carried out by the titrometric method [24], which is based on the acid extraction of vitamin C (with solutions of hydrochloric, metaphosphoric, or a mixture of acetic and metaphosphoric acids) followed by titration with a solution of sodium 2.6-dichlorophenolindophenolate until a light pink color.

The mass fraction of ascorbic acid (A) in percent was calculated according to the formula:

$$A = \frac{(V_1 - V_2) \cdot T \cdot V_3 \cdot 100}{V_4 \cdot m},$$

where V_1 is the volume of sodium 2.6-dichlorophenolindophenolate solution used for titration of the sample extract, cm^3;

V_2 is the volume of sodium 2.6-dichlorophenolindophenolate solution used for the control test, cm^3;

T is titer of sodium 2.6-dichlorophenolindophenolate solution, cm^3;

V_3 is the volume of the extract obtained during the extraction of vitamin C from the sample product, cm^3;

V4 is the volume of extract used for titration, cm^3; m - weight of the product, g.

Determination of β-carotene content

The content of β-carotene was determined by the accelerated UV-VIS method [25], according to which an acetone extract was prepared from the kernels of pine nuts and scanned with a UV-VIS spectrum at wavelengths from 350 to 600 nm. The content of β-carotene in the experimental

samples was calculated according to the calibration curve.

Determination of amino acid content

The amino acid composition of pine nut kernels before and after heat treatment was determined by ion-exchange liquid column chromatography on the T339 amino acid analyzer in automatic mode [26-27].

Statistical data processing

Statistical data processing was carried out using the Statistica 10 program and Microsoft Excel 2016. Construction of experimental drying curves was carried out in the Microsoft Excel 2016 editor. The results of the experimental part were obtained by conducting three times of research under the same conditions to ensure accuracy.

3. Results and discussion

Kinetics of pine nut kernel drying

On the basis of an analytical review of literature sources on the issue of drying various types of nuts, "soft" modes of heat treatment were determined, which will contribute to the maximum preservation of the protein fraction, in particular amino acids.

The first stage was to study the kinetics of heat treatment of pine nut kernels during convective drying. Based on the obtained data, drying curves were constructed at different processing temperatures (Fig. 1).

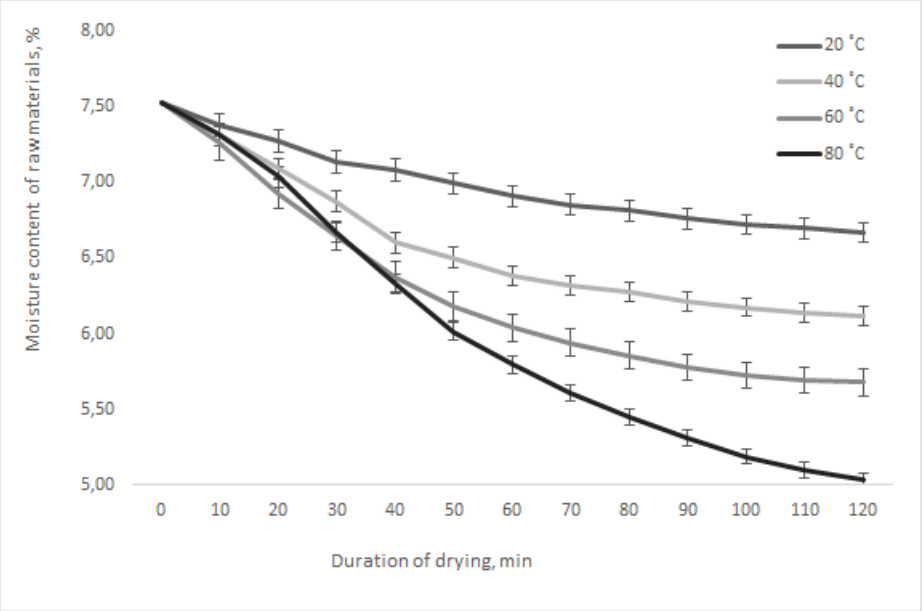

Fig. 1 – Drying curves of pine nut kernels at different processing temperatures

As can be seen from Fig. 1, the process of drying pine nut kernels depends on the temperature. Drying at low temperatures - 20 and 40 ˚C is long-term and there is no significant difference in the dynamics of the process. The drying kinetics of pine nut kernels at a temperature of 20 ˚C is the lowest, which is probably justified by strong bonds between water molecules [28], which require the expenditure of a greater amount of thermal energy to intensify the drying process. Under such heat treatment modes, the value of moisture content during the entire duration of drying decreases by 11.4 % (at a temperature of 20 ˚C) and 18.7 % (at a temperature of 40 ˚C) from the initial value.

The use of higher temperatures - 60 and 80 ˚C accelerates the removal of free moisture from raw materials. This can be explained by the fact that the greater amount of heat that comes from the heated air to the food material in the drying chamber increases the rate of movement of moisture from the inside of the kernels to the surface [29], which significantly reduces the time to reach a constant humidity. At a temperature of 60 ˚C, the initial moisture content during the process decreases by 24.6 %, and at 80 ˚C by 33.2 %. A further decrease in drying efficiency is associated with the presence of hydrophobic lipid molecules [30], which act as a certain limiting factor when the maximum mass fraction of moisture in the food material is reached. Thus, drying at a temperature of 80 ˚C is impractical from the point of view of using an excessive amount of energy resources for the possibility of significantly increasing the effect of the technological process.

A characteristic feature of the drying curves of this type of raw material is the absence of a horizontal section at the beginning of the heat treatment process [31], which is called the period of constant drying speed (or the 1st period). This makes further use of traditional methods of calculating the duration of drying impossible. That is why it was decided to investigate the effect of temperature treatment under different regimes on the biological value.

The effect of heat treatment on the biological value of pine nut kernels

Considering the fact that pine nuts are characterized by a high content of essential amino acids, the effect of heat treatment on their final content was investigated in order to determine the optimal mode of their processing, which will ensure a significant preservation of the amount of amino acids. The amino acid composition of pine nut kernels before and after drying under different modes of heat treatment is given in Table 1.

Table 1

Amino acid composition of pine nut kernels before and after heat treatment (P ≤ 0.05%, n = 3)

The name of an essential amino acid	Content, mg/100 g				
	Before drying	After drying			
		20 ˚C	40 ˚C	60 ˚C	80 ˚C
Tryptophan	107.542	101.412	94.548	88.657	75.28
Isoleucine	522.708	500.541	480.854	449.083	405.956
Valin	667.874	648.504	601.579	553.876	468.527
Leucine	981.52	949.389	906.844	851.009	785.216
Threonine	378.988	369.024	360.629	349.989	337.54
Lysine	540.215	534.873	525.207	513.693	485.678
Methionine + cysteine	259.058	237.01	219.924	196.551	140.851
Phenylalanine + tyrosine	514.66	498.807	469.791	438.02	395.654

An increase in heat treatment temperature reduces the content of essential amino acids in pine nut kernels, which becomes more significant as it increases. The
percentage of reduction in content for each essential amino acid at different processing temperatures is shown in Fig. 2.

Thus, at a temperature of 20 ˚C, a decrease in the content of amino acids is observed from 0.99 to 8.51 %, depending on the essential amino acid, at 40 ˚C from 2.78 to 15.11 %, at 60 ˚C from 4.91 to 24.13 %, at 80 ˚C from 10.1 to 45.63 %.

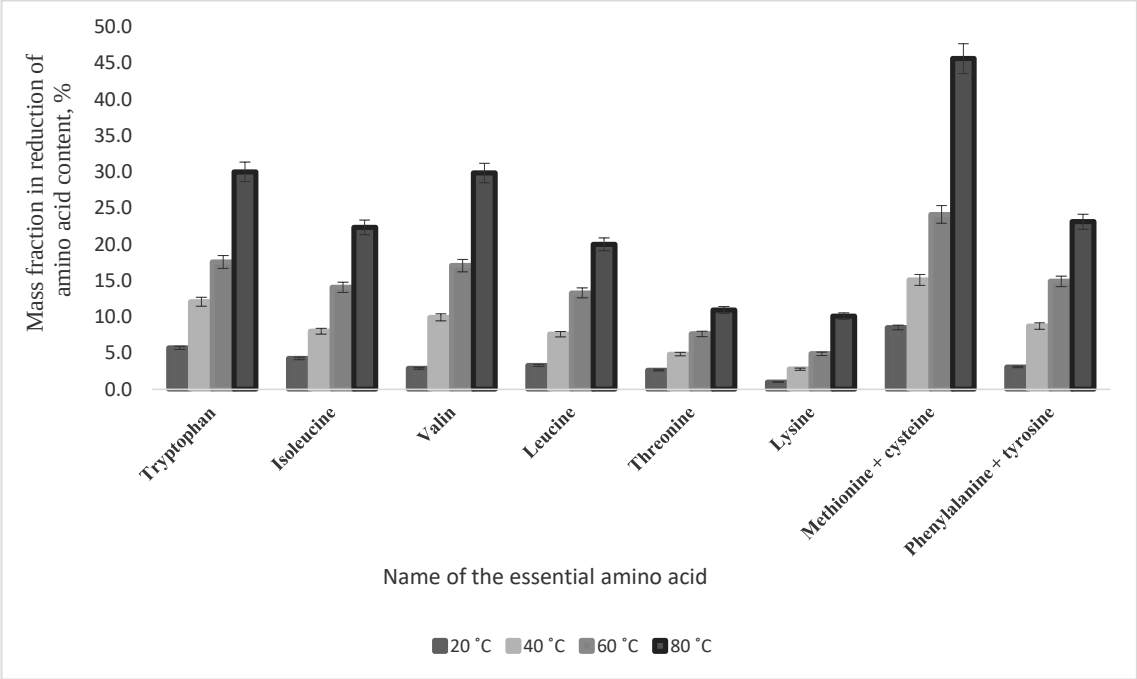

Fig. 2 - Dependence of the decrease in the content of essential amino acids of pine nut kernels on the processing temperature

Tryptophan, valine and methionine+cysteine undergo the greatest destruction, which is consistent with the data of the scientific literature [32].

The minimal effect on the content of amino acids occurs at heat treatment temperatures of 20 and 40 ˚C, while a significant decrease in biological components occurs at a temperature of 80˚C, which is explained by the partial denaturation of proteins [33] and the subsequent decrease in biological value.

The content of vitamin C and β-carotene before and after heat treatment of pine nut kernels is illustrated in Fig. 3.

Despite reports on the particular instability of vitamin C under thermal action on it in the temperature range of 70...90 ˚C [34-35], it can be seen (Fig. 3) that its decrease after drying of pine nut kernels at a temperature of 80 ˚C decreases by 30.96 % of the initial content, which is significant compared to the results of exposure to other regimes, but most of it still remains in the raw material after processing.

The content of β-carotene significantly depends on the drying temperature: during processing at 20 ˚C, 10.71 % of the initial content is destroyed, at 40 ˚C – 25 %, at 60 ˚C – 42.86 %, and at 80 ˚C – 67.86 %, which corresponds to with well-known information about the effect of temperature on the stability of β-carotene [36].

Taking into account the study of changes in the amino acid composition, the content of vitamin C and β-carotene in the kernels of pine nuts after heat treatment under different modes, the optimal treatment temperature is 60 ˚C, which allows reducing the mass fraction of moisture in the product from 7 to 5.28 %, which is more effective in compared with the processing temperature of 20 and 40 %. A decrease in the moisture content of pine nut kernels will contribute to a decrease in the water activity index [37], which will

have a positive effect on the microbiological state of the raw material, which requires additional scientific research.

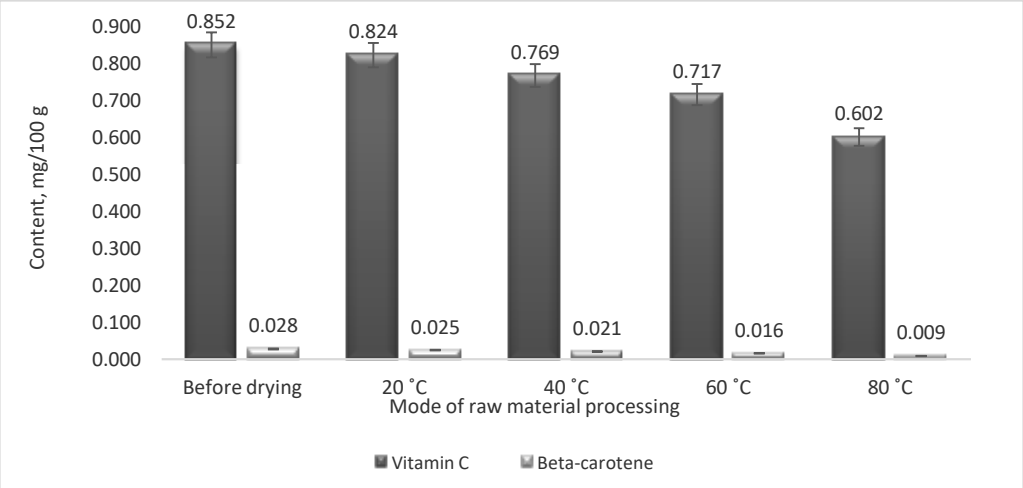

Fig. 3 – Content of vitamin C and β-carotene before and after heat treatment of pine nut kernels

4. Conclusion

The paper examines the kinetics of pine nut kernel drying under different modes of heat treatment and its effect on the biological value of the raw material. It was established that the best drying mode is a temperature of 60 ˚C, which ensures a significant decrease in the mass fraction of moisture in the raw material, helps to preserve a significant part of essential amino acids, vitamin C and β-carotene.

The perspective of further scientific work consists in determination of unsaturated fatty acids content after processing, the development of original recipes of sauces using the kernels of pine nuts that have undergone heat treatment, and the study of the quality of the obtained products.

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