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Chemical composition of food product “KalmaKS” produced from dried squid skin

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Abstract. Proteins are structure-forming agents most widely used in food technology. The most abundant protein in nature is collagen. Squid skin is remarkable for the high content of collagen. Taking into account a considerable stock of squid, the development of collagen-containing produce with the prospect of its usage in making moldings, presents itself as a promising field of research. Squid skin is known to be characterized by high biological value – it contains well-assimilated proteins, lipids, microelements and vitamins. Presumably, the usage of the like additive will make it possible both to stabilize the structural-mechanical properties of products and to enhance their biological value. A developed by the authors technology of producing a dried product “KalmaKS” from squid tegumental tissue implies drying the skin followed and grinding it to a powder. “KalmaKS” is a pulverized product with pleasant taste, colour and fragrance. The skin of the Commander Islands squid *Berryteuthis magister* (Berry, 1913) is the most numerous representative of Gonatidae squid family in the North Pacific and one of the few molluscs cephalopoda caught by the fishing companies in the Russian Federation and used as a raw material. The objective of the research was to envisage the perspectives of using a dried food product “KalmaKS” from squid skin in food technologies. For this purpose the chemical composition of “KalmaKS” was studied. The chemical composition of the dried food product from the skin of the Commander Islands squid is rich in protein and polycomponents. Mass fraction of protein in the developed product reaches 80.8%. The amount of lipids comes to 7.0%, mineral substances – 6.1%. It is demonstrated that the dried food product from squid skin is remarkable for the considerable amount of collagen (18.654%). It is proved that the food product from squid skin contains all the essential amino acids; at the same time, it is ascertained that the amino acid composition is not balanced. Among the nonessential acids, glycine (18.46 g per 100 g of the product) and proline (9.74 g per 100 g of the product) have the largest mass fraction. It has been inferred that the food product from squid skin can be used as a dresser to enrich food products, as well as an organic structure-regulating agent.

Keywords: chemical composition, amino acid content, Commander Islands squid, dried food products, biological value, structure-regulating additives, amino acid score

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Научная статья

Химический состав сушеной пищевой продукции из кожи кальмара «КальмаKS»

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Аннотация. Белки – наиболее широко применяемые в пищевой технологии структурообразователи. Самым распространенным белком в природе является коллаген. Высоким содержанием коллагена отличается кожа кальмара. С учетом значительных запасов кальмаров разработка коллагенсодержащей продукции с перспективой использования ее в производстве формованных изделий представляется перспективным направлением исследований. Известно, что кожа кальмара характеризуется высокой биологической ценностью – содержит хорошо усвояемые белки, липиды, микроэлементы и витамины. Вероятно, использование подобной добавки позволит как стабилизировать структурно-механические свойства продуктов при ее внесении, так и повысить биологическую ценность продукта. Разработанная авторами технология производства сушеного продукта из покровных тканей кальмара «КальмаKS» предполагает сушку кожи с последующим измельчением до порош-

кообразного состояния. «КальмаKS» представляет собой порошкообразный продукт с приятным вкусом, цветом и ароматом. В качестве сырья используется кожа командорского кальмара *Berryteuthis magister* (Berry, 1913) как наиболее массового представителя кальмаров семейства Gonatidae северной Пацифики и одного из немногих эксплуатируемых рыбодобывающими организациями Российской Федерации видов головоногих моллюсков. Целью настоящего исследования явилось рассмотрение перспектив использования сушеной пищевой продукции из кожи кальмара «КальмаKS» в пищевых технологиях. Проведено изучение химического состава «КальмаKS». Установлено, что пищевая сушеная продукция из кожи командорского кальмара «КальмаKS» относится к высокобелковым и поликомпонентным. Массовая доля белка в разработанном продукте достигает 80,8%, содержание липидов – 7,0 %, минеральных веществ – 6,1 %. Показано, что сушеная продукция из кожи кальмара отличается значительным содержанием коллагена – 18,654 %. Доказано, что в пищевом продукте из кожи кальмара содержатся все незаменимые аминокислоты, в то же время установлено, что аминокислотный состав не сбалансирован. Среди заменимых аминокислот наибольшую массовую долю имеют глицин (18,46 г на 100 г продукта) и пролин (9,74 на 100 г продукта). Сделан вывод о перспективности использования пищевого продукта из кожи кальмара в качестве обогатителя продуктов питания, а также в качестве натурального структурорегулирующего агента.

Ключевые слова: химический состав, аминокислотный состав, командорский кальмар, сушеная пищевая продукция, биологическая ценность, структурорегулирующие добавки, аминокислотный скор

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Introduction

In making food products, an important task is the stabilization of their function-technological properties, which allows to obtain stable food systems possessing the composition and properties that meet the consumers' demands. With the aim to create moldings, structure-forming agents are widely used [1].

Proteins are structure-forming agents most widely used in food technology. The structure-forming agents of animal origin include, in particular, fish protein concentrates and isolates. In making these components, complex technological schemes are used, which means the usage of costly equipment, treatment by chemical agents (ethanol, isopropane, ethylene dichloride et al.), and strict temperature conditions.

Collagen is the most widespread protein in nature. It is the very protein that determines the structure of skin and bones [2, 3]. This property, undoubtedly, provokes much interest on the part of researchers. The technologies of its extraction from fish skin, fins and heads imply grinding, defatting, maceration, caustic treatment of collagen-containing raw product.

Squid skin is remarkable for high content of collagen. Taking into account the considerable stocks of squid (in the Russian Federation the annual squid catch of the Pacific *Todarodes pacificus* and the Commander Islands *Berryteuthis magister* reaches up to 200 thousand tons [4, 5]), the development of collagen-containing products with the prospect of its usage in making moldings, is becoming a promising field of research. It is known that squid skin is characterized by the high biological value: it contains well-assimilated proteins, lipids, microelements and vitamins. Presumably, the usage of the like additive will make it possible both to stabilize the structural-mechanical properties of products and to enhance their biological value.

The technology of producing a dried product "KalmaKS" from squid tegumental tissue developed by the authors implies drying the skin followed by its grinding to a flowable powder [6].

"KalmaKS" is a pulverized product with a pleasant taste, colour and fragrance. As raw material there is used the skin of the Commander Islands squid *Berryteuthis magister* (Berry, 1913), which is the most numerous representative of Gonatidae squid family in the North Pacific and one of the few mollusca cephalopoda caught by Russian fishing companies. By safety indices, the dried product from squid skin corresponds to the requirements TR EEU (Technical Regulation of the Eurasion Economic Union) 040/2016 "On safety of fish and fish products" and TP TC – TR CU (Technical Regulation of the Customs Union) 021/2011 "On safety of food products".

It has been experimentally proved for the first time that the developed technology of producing dried food product from squid skin, "KalmaKS", makes it possible to obtain a high-protein product containing essential and nonessential amino acids including those generating its jellying properties.

The research objective is to envisage the perspectives of using dried food produce from squid skin, "KalmaKS", in food technologies.

The task for the current stage of research is to study the chemical composition of the dried food product "KalmaKS" from squid skin.

Materials and methods

The major object of research is the technology of obtaining a dried food product from squid skin. The subject of research is the dried product obtained from the skin of squid *Berryteuthis magister* caught in the Commander Islands. Sampling of the dried product from squid skin is carried out under Federal standard 31339 "Fish, non-fish objects and the products from them. Acceptance rules and sampling methods".

The estimation of protein and collagen mass concentration in the dried products is carried out by standard methods under Federal standard 33692 "Animal fibroproteins. General specifications". The estimation of the protein content is done by burning a sample

with concentrated sulphuric acid followed by titration with hydrochloric acid to estimate the quantity of ammonia, and the calculation of nitrogen mass concentration in the product sample, based on the quantity of the ammonia formed.

To estimate the ratio of the collagen mass to the general protein mass, in the sample of acid hydrolysate oxiproline was liberated, the hydrolysate was neutralized and oxidized with T-chloramine forming a compound of red colour, photometric measurement of the optical density with the wave length (558 ± 2) nm was taken followed by the recalculation for collagen.

Estimating the content of water, lipids and mineral substances was carried out by standard methods under Federal standard 7636 "Fish, sea mammals, sea invertebrates and the products of their processing. Analysis techniques". The water mass part was estimated by drying off till the constant mass in the drying cabinet, the mineral substances – by ashing in the muffle furnace. The estimation of the lipid content was carried out by the extraction method in the Soxhlet's apparatus.

To estimate the amino acid composition of the protein of the squid dried product, the standard method given in the Federal standard 34132 "Meat and meat products. The method of estimating the animal protein amino acid composition" was used. To state the individual amino acids mass part, the protein acid hydrolysis was performed with the following chromatographic estimation.

The statistical treatment of the findings was done on the basis of calculating average values and arithmetic error. To treat the received data and to draw graphical dependence, the operational system Microsoft Windows 2016 and the software Microsoft Office 2016 (incl. Word 2016, Excel 2016) were used. In this paper the arithmetic values are represented by average values; their assurance (P) is 0.95 at the confidence interval (Д) of ± 10%.

Results and discussion

At this stage of research, the chemical composition of the dried product obtained from the skin of the Commander Islands squid, the "KalmaKS", is studied. The chemical potential makes it possible to forecast the expedience of using the developed produce in the technologies of food products.

The content of macronutrients in the product "KalmaKS" made from the Commander Islands squid coating tissue is represented in Table 1.

Table 1

Content of macronutrients in the dried food product "KalmaKS" made from the Commander Islands squid skin

Name of the index	Index value, %
Water mass part	6.0 ± 0.025
Mineral substances mass part	6.1 ± 0.0003
Protein mass part	80.8 ± 0.2
Including collagen mass part	18.654 ± 0.077
Lipids mass part	7.0 ± 0.067

The data presented in Table 1 indicate that the developed product belongs to the high-protein products (protein content reaches 80.8%), which is conditioned by the composition of the feedstock – squid skin. Besides, the new product contains a significant amount of collagen – up to 18.654%. The test sample had a high mass part of mineral substances – 6.1%, and of lipids – 7.0%.

The high collagen content makes it possible to forecast the possibility of using the product made from squid skin as an organic structure-forming agent in food technologies. Collagen is known to reveal the properties of food fibres. It is able to enhance the gastrointestinal motor activity, to influence the protective functions of human organism against the environmental hazards. These facts testify to enhancing the biological value of food products by introducing the "KalmaKS" [7-11]. When deciding on the expediency of using the new development, one should take account of the fact that the collagen in hydrobionts is assimilated well by the human organism, for – by its structure and range of fundamental properties – it is much closer to man's collagen (to 96%) than to animals'. Of no small importance is the capacity of hydrobionts' collagen for absorption and restoration [12–16].

The nutritive value of proteins is known to be determined by the qualitative and quantitative ratio of separate amino acids forming the protein. Of great interest is the amino acid composition of the products from squid skin, the "KalmaKS" (Table 2).

Table 2

Amino acid composition of the dried products from the Commander Islands squid skin, the "KalmaKS"

Name of amino acid	Amino acid content, g per 100 g of the product*
Nonessential amino acids	
Asparaginic acid	5.55 ± 0.83
Glutaminic acid	6.30 ± 0.95
Serine	2.89 ± 0.43
Histidine	1.33 ± 0.20
Glycine	18.46 ± 2.77
Arginine	6.54 ± 0.98
Alanine	4.94 ± 0.l4
Tyrosine	0.89 ± 0.13
Cystine	0.31 ± 0.05
Proline	9.74 ± 1.46
Oxyproline	2.31 ± 0.01
Essential amino acids	
Isoleucine	1.63 ± 0.24
Leucine	6.16 ± 0.92
Lysine	4.20 ± 0.63
Methionine	2.05 ± 0.3l
Phenylalanine	1.34 ± 0.20
Threonine	2.29 ± 0.34
Tryptophan	0.47 ± 0.09
Valine	3.26 ± 0.49

* The research was carried out in Federal State Budgetary Scientific Institution "Federal scientific centre of food systems n. a. V. Gorbatov" of RAS in 2022.

Analyzing the amino acid content by the research results presented in Table 2, there should be men-

tioned the presence of the proline and oxyproline amino acids, which are most important for the jellying effect, because their total content reaches to 12.05 g per 100 g. The findings make it possible to assume that the developed product possesses structure-regulating properties, which allows to use it as a structure-regulator.

For the normalization of the human organism's activity, the basic factor is the quantity of the protein incoming with the food, especially its quality characterized by the balance of the amino acid content (the content of essential amino acids and their correspondence to the optimal ratio recommended by WHO). For the substantiation of the product's general biological value, the nonessential amino acid content in the protein is important as well. From Table 2 data, one can see that squid skin contains all the essential amino acids. Among the nonessential acids, glycine (18.46 g per 100 g of the product) and proline (9.74 g per 100 g of the product) have the largest mass fractions. In smaller quantities, protein contains the nonessential amino acids: asparaginic, glutaminic, serine, histidine, arginine, alanine, tyrosine, cystine, and oxyproline.

After estimating the amino acid balance of "KalmaKS" (Table 3), it can be seen that the limiting amino acids are phenylalanine and tyrosine, isoleucine, tryptophan, threonine, methionine and cystine, valine, lysine.

Table 3

Amino acid score in the total protein of the dried food product "KalmaKS" made from the Commander Islands squid skin

Amino acid	Content of essential amino acids in total food additive protein, g/100 g of protein	Amino acid score, % relative to the scale by WHO	Data from WHO, g/100 g of protein
Isoleucine	2.02	50.5	4.00
Leucine	7.62	108.85	7.00
Lysine	5.20	94.55	5.50
Methionine + Cystine*	2.54	72.57	3.50
Phenylalanine + Tyrosine*	1.66	27.67	6.00
Threonine	2.83	70.75	4.00
Tryptophan	0.58	58.00	1.00
Valine	4.03	80.6	5.00

* The human organism's requirement for methionine is satisfied to 80-89% by nonessential cysteine amino acid, for phenylalanine – to 70-75% by nonessential tyrosine amino acid, so amino acid data are estimated summarily.

The prevailing limiting amino acids are phenylalanine and tyrosine (the amino acid score is 27.67%). Thus, the protein of the food produce from squid skin contains all the essential amino acids, but its amino acid composition is not balanced.

On the whole, the developed product can be a source of nonessential and essential amino acids, well-assimilated collagen. Besides, taking into account a considerable amount of proline and oxyproline, one can assume the "KalmaKS"'s high jellying capacity, which holds much promise for using it as a structure-regulator in making food products.

Conclusion

The results of studying the chemical composition of the dried food product "KalmaKS" made from the Commander Islands squid skin proved that the developed product is rich in protein and polycomponents. The protein mass fraction in the product reaches 80.8%. The amount of lipids accounts for 7.0%, mineral substances – for 6.1%. It is demonstrated that the dried food product from squid skin contains a considerable amount of collagen (18.654%).

Analysis of the amino acid composition has shown that the protein of the dried product "KalmaKS" contains both nonessential and essential amino acids, which makes it promising for being used for the enrichment of food products, despite the disbalance of its amino acid composition. The presence of proline and oxyproline amino acids provides the product's jellying properties.

The results obtained are very promising in terms of including the dried product from squid skin into people's food as a source of animal protein containing nonessential and essential amino acids, as well as lipids, mineral substances and collagen. The product's composition makes it feasible to use it in food technologies for enhancing the food nutritive value. The presence of collagen in the product as well as the ascertained content of proline and oxyproline acids make it possible to forecast the possibility of using "KalmaKS" as an organic structure-regulating additive.

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