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NEW TECHNOLOGICAL APPROACHES TO CANNING CEPHALOPOD MOLLUSKS

L. V. Shul'gina[1], N. V. Dolbnina[1], L. Yu. Lazhentseva[2], and Yu. P. Shul'gin[3]

[1] Pacific Research Fisheries Center,
Shevchenko alley 4, Vladivostok, 690091 Russia
phone:: +7 (4232) 400-921, e-mail: shulgina@mail.ru;
[2] Far Eastern Technical Fisheries University,
str. Lugovaya 56b, Vladivostok, 690950 Russia
phone:/Fax: +7 (4232) 44-03-06, e-mail: lazhenceva.lyubov@mail.ru
[3] Far Eastern Federal University (FEFU),
str. Sukhanov 8, Vladivostok, 690091 Russia
phone:/Fax: +7 (423) 243-23-15, e-mail: yuriyshulgin@mail.ru

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Abstract: With significant stocks and catches of cephalopod mollusks in the Far Eastern seas, their small output as canned goods is due to a low yield of the finished product. Research was conducted on the rational use of frozen raw cephalopod mollusks in the production of sterilized canned goods. New technological approaches to canning cephalopod mollusks that ensure canning profitability and replenish the consumer market of functional seafood are justified. It was established that the exclusion of the skinning of cephalopod mollusks from the canning technology could significantly increase the output and reduce the cost of the finished product. Oil extracts of spices used in the canning of cephalopod mollusks improve their quality by reducing the thermal effects on food during sterilization and the degree of thermal damage to nutrients.

Keywords: cephalopods, canned food, technology, quality

INTRODUCTION

Cephalopod mollusks make up a massive group of sea bioresources broadly spread in the world ocean [1]. A short life cycle and quick growth of cephalopod mollusks, as well as their ability to form compact clusters determine a high level of their commercial harvesting [2, 3].

Cephalopod mollusks are easily processable, allowing for the use of various processing methods and a wide range of products, including fermented ones [4–11].

The main commercial species of cephalopod mollusks in the Far Eastern seas are octopuses (*Octopus dofleni)* and the Commander (*Berryteuthis magister*) and Pacific (*Todarodes pacificus)* squids [12]. Annual squid catches are at least 240 000 t, and those of octopuses, 800 000–900 000 t. Despite these solid catches, the current highly processed goods of cephalopod mollusks are produced in amounts insufficient for the country's population. In the consumer market, they are represented mainly by fresh frozen products. In small amounts, cephalopod mollusks are processed into dried, seasoned, and culinary products and preserves, filled with various sauces, but these products have limited storage life and conditions, causing difficulties in their transportation and marketing. The annual output of canned squids is no more than 1.6 million standard cans, and canned octopuses are not produced domestically.

At the same time, the nutritive tissues of cephalopod mollusks are characterized by high organoleptic properties, the presence of complete proteins, and insignificant amount of lipids, as well as a complex of mineral substances [13–20].

Various biologically active substances, including those that are rarely found in terrestrial animals and plants [21–27], have been found in the tissues of cephalopod mollusks; therefore, cephalopod-based products are very useful for various groups of the population and are recommended by nutritionists as ingredients of many diets. In recent decades, biologically active food additives and enzymatic preparations have been developed on the basis of cephalopod mollusks [28–31].

One of the reasons for the low use of raw materials from cephalopod mollusks in canning is the low yield of end products due to high losses of their nutritive part during processing, which makes them unprofitable as canned food under current conditions. The loss of raw materials during canning is explained by the fact that the traditional cephalopod canning technologies require thermal, enzymatic, or mechanical removal of skin integuments from the heads, pallia, and tentacles of cephalopods. At the same time, the skin of cephalopod mollusks belongs to nutritive tissues, containing amino acids, such as proline and oxyproline, which are collagen components [14, 32]. China has developed a technology of producing collagen from the cephalopod skin left after the core production [33]. The preservation of cephalopod skin integuments during canning would increase the utilization factor of this valuable raw material and its end-product yield.

Another important factor of the low motivation of producers in cephalopod canning is the worsening of organoleptic characteristics of the product after sterilization due to the interaction of reducing sugars with amino acids during thermal conditioning (the Maillard reaction) and the formation of melanoidins. As is known, melanoidin formation leads to the browning of sterilized mollusk meat, the appearance of a caramelization smell, and the loss of its inherent flavor characteristics [34, 35]. A decreased thermal effect on the product during sterilization makes it possible to reduce the activity of the Maillard reaction and improve the quality of canned goods.

The goal of this study was to justify and develop new technological approaches to cephalopod canning that reduce raw-material losses and ensure the high quality of end products.

OBJECTS AND METHODS OF RESEARCH

The object of research was frozen raw materials of squids and octopuses. Additional materials used were edible salt, vegetables, legumes, vegetable oil, olives, and spices. Glass jars III-5-58-120-00 with a capacity of 120 cm^3 (Germany) with twist-off tin lids were used for canning. When developing sterilization regimes for canning cephalopods, we used the spores of the *Cl. sporogenes-25* test strain, obtained at the laboratory of microbiology of OAO Giprorybflot (St. Petersburg).

Samples for analysis, the general chemical composition, and the safety indicators of raw materials and end products were obtained by standard methods. An atomic adsorption photometer, Nippon Jarall Asl, model AA-855 (Japan), was used to detect mineral substances. The amino-acid composition of proteins was identified with an ammo-acid analyzer, Hitachi L-8800 (Japan). The biological value of proteins was evaluated by the amino-acid score in line with the recommended composition of the "ideal" protein according to the FAO/WHO scale. The taurine amino acid was detected by the spectrophotometric method [36]. The biological value of raw materials and products was determined by the relative biological value (RBV) indicator using ciliated infusorian *Tetrahymena pyriformis* in line with the recommendations of Yu.P. Shul'gin et al. [37]. The output of intermediate products and canned goods was determined by the results of control tests.

RESULTS AND DISCUSSION

Studies on frozen raw materials from commercial catches in recent years show that the average mass of a squid specimen is no more than 0.3 kg, and that of an octopus, no more than 3.2 kg. The general chemical composition of the nutritive part of cephalopod mollusks is given in Table 1. The mollusks somewhat differed in protein and moisture contents: the Commander squid (a deepwater species) has tissues more watery than those of the Pacific squid and octopuses and contains fewer proteins.

Table 1. Chemical composition of the nutritive part of cephalopods

Substances	Quantity, % of the total body mass		
	Todarodes pacificus	Berryteuthis magister	Octopus dofleni
Moisture	75.3±4.1	82.1±4.8	78.7±4.3
Protein	19.5±1.8	12.5±1.5	16.1±1.4
Carbohydrates	2.1±0.3	2.3±0.3	2.5±0.5
Fat	1.4±0.2	1.3±0.5	0.5±0.2
Minerals	1.7±0.2	1.8±0.2	2.2±0.3

The traditional preparation of semiproducts for canning included the cutting of cephalopod mollusks, during which the insides and skin were removed. It was established that the nutritive part of mollusks before skin removal was about two-thirds of their total body mass. After skinning, it was observed that nutritive mass losses during cephalopod skinning were from 18.8±1.3 to 33.6±2.0%. The highest processing losses were characteristic of octopuses, whose skin with suckers on their arms comprises a substantial share in the total mass of their nutritive part.

The investigation of the general chemical composition of skinned and unskinned cephalopod semiproducts did not reveal any actual differences in the content of individual nutrients.

Comparative analysis of the amino-acid composition of skinned and unskinned cephalopod semiproducts also showed their similarity. The sum of essential amino acids (EAAs) in the squid tissues was practically the same and exceeded slightly the sum of essential amino acids of the reference protein (Table 2). Threonine was a deficient essential amino acid in the squid proteins, and valine, in the octopus proteins.

Table 2. Essential amino acids in the nutritive tissues of cephalopods

Amino acid	FAO/WHO reference	Content in semiproducts (g/100 g of protein) from		
		Berryteuthis magister	*Todarodes pacificus*	*Octopus dofleni*
Valine	5.0	5.0	6.3	2.9
Isoleucine	4.0	5.1	5.9	4.0
Leucine	7.0	10.2	9.4	6.9
Lysine	5.5	7.3	8.2	5.7
Methionine + cystine	3.5	3.4	4.5	5.0
Threonine	4.0	3.1	1.7	5.8
Phenylalanine + tyrosine	6.0	8.4	6.9	6.7
Triptophane	1.0	1.0	1.0	1.1
Sum of EAAs	36.0	39.9	39.9	38.1

The characteristic feature of the squid and octopus proteins' composition was high contents of proline, taurine, and other nitrogenous matters, which take part in the osmoregulation of mollusks [38].

Proline is a major amino acid that ensures the synthesis of collagen in the human organism, which, in turn, is the main building material for bones, tendons, ligaments, and the skin, ensuring the formation of strong and elastic tissues on the surface of mechanical damages of various organs [39].

Taurine is a sulfur-containing amino acid, which is contained formlessly in the cardiac-muscle cells, skeletal muscles, central nervous system, retina, and other tissues [40, 41]. In the human organism, it suppresses the increase in the level of cholesterol in the blood, normalizes the functions of the visual organs, prevents a high aggregation of thrombocytes and the convulsive activity of the brain, and displays antitoxic and antioxidant properties, having powerful adaptogenic and health-improving effects.

As is known, taurine is present in the cephalopod tissues in amounts exceeding 100 times and more its content in plants and other animals [21, 42].

The skinned meat and skin integuments of cephalopod mollusks did not differ much in proline and taurine contents (Table 3). The muscle tissue of squids contained more of them than their skin. In octopuses, high amounts of taurine were detected both in the muscle tissue and in the skin. The proline content in the octopus tissues was smaller than in squids, but its amount in different parts of octopuses was equal.

Table 3. Proline and taurine contents in cephalopod tissues

Cephalopods	Quantity, g per 100 g of proteins			
	proline		taurine	
	skinless meat	skin	skinless meat	skin
Todarodes pacificus	3.9–7.3	2.8–4.9	0.5–1.3	0.4–1.1
Berryteuthis magister	2.4–5.6	1.2–4.8	0.5–1.1	0.3–1.0
Octopus dofleni	1.8–3.8	1.4–3.9	1.2–2.6	1.0–2.5

It follows from the above data that, if the cephalopod skin is preserved during the preparation of semiproducts for canning, the factor of raw material use will increase, as well as the output of mass consumer and directed-action products with high contents of rare nutrients, valuable for humans.

To assess the possibility of producing more high-quality preserves from a unit of raw materials on the basis of unskinned semiproducts, "natural," "blanched in oil," and "blanched and smoked in oil" samples of canned goods were manufactured.

Taking into account the proposed assortment, after the cutting of mollusks and the careful washing and removal of excess moisture, the semiproducts underwent additional preprocessing. In order to obtain a natural sample, a raw cephalopod semiproduct was sliced: the pallium, into slices of no more than 7–8 mm wide; the octopus arms, into rings; and the squid tentacles were left intact for prepacking. For the samples blanched in oil, a dressed semiproduct was blanched; squid semiproducts were blanched in boiling water for three minutes; the octopus samples were blanched for 40 min. After blanching and additional dewatering, a semiproduct was cut into pieces of no more than 10×40 mm. The samples smoked in oil were obtained from blanched semiproducts that were grilled until the meat had a slight smoking flavor. The soft-smoked cephalopod meat was cooled on grills to 30–35°C and then cut into pieces of no more than 10×40 mm.

To compare the yield and quality indicators of the end products, reference samples of canned products were made from skinned semiproducts obtained according to the traditional technology.

The appearance of a sliced semiproduct from unskinned squids differed slightly from samples of skinned mollusks. A semiproduct from an unskinned octopus differed from a skinned sample in its characteristic purple tincture.

The quantity of semiproducts obtained for canning reference (skinned) and test (unskinned) cephalopod samples depending on the canning method is given in Fig. 1.

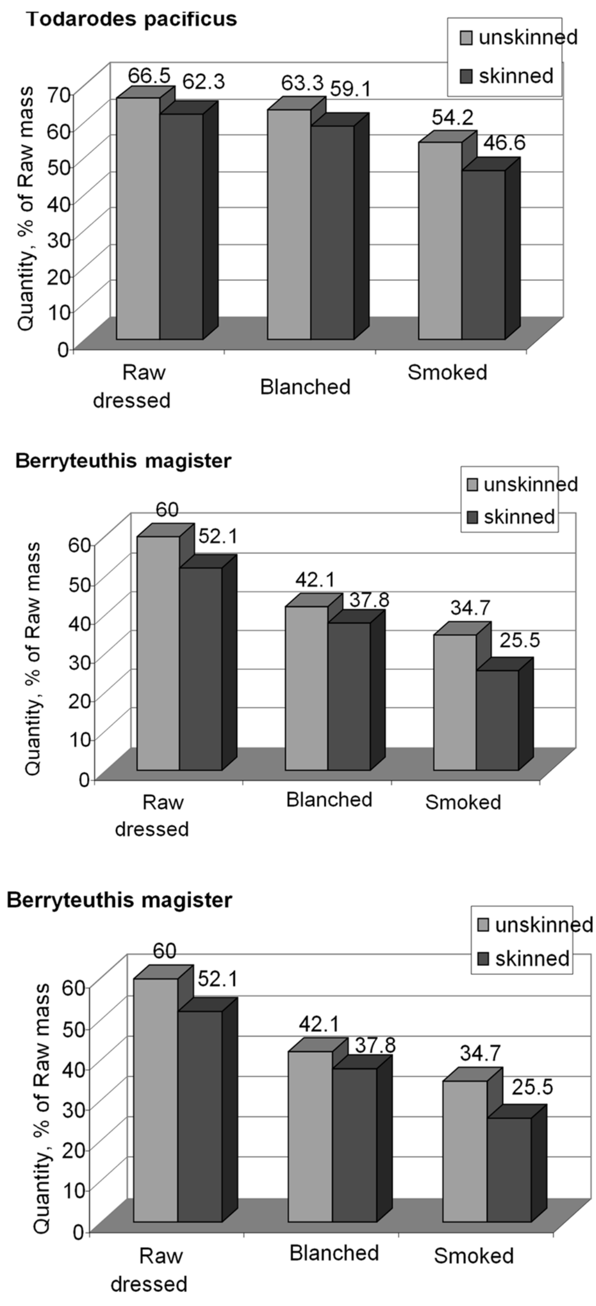

Fig. 1. Quantity of cephalopod semiproducts unskinned and skinned for various canning assortments.

As we see, if skinning is excluded from the technology of cephalopod canning, the semiproduct yield for various assortments will be much greater than after skinning, improving economic performance.

A prepared sliced cephalopod semiproduct was packed in glass jars. The packing rates for components for the proposed canning assortments are given in Table 4.

Table 4. Packing rates for glass-jar components for various cephalopod canning assortments

Canned goods	Component mass, g					
	Cephalopods	saline solution	oil	salt	olives	paprika
Natural unskinned squid	90	20	-	-	-	-
Natural unskinned octopus	90	20	-	-	-	-
Natural mixed octopus and surf clam	90	20	-	-	-	-
Octopus in oil	89	-	20	1	-	-
Octopus with paprika in oil	88.3	-	20	1	-	0.7
Octopus with olives in oil	70	-	20	1	19	-
Squid in oil	70	-	20	1	19	-
Soft-smoked octopus in flavored oil	89	-	20	1	-	-
Soft-smoked squid in flavored oil	89	-	20	1	-	-

To obtain natural preserves, jars with a sliced blanched semiproduct (the pallium, squid tentacles, and octopus arms) were filled with 20 cm^3 of filtered 2 % salt brine.

For mixed natural octopus and serf clam preserves, we used a bivalve mollusk, the Sakhalin serf clam, prepared in the following way: after unfreezing, cleaning, and washing, the surf clam muscle together with the pallium was loaded into a boiling 2% salt brine at a ratio of 1 : 3, four minutes after the simmer, the surf clam muscle was taken out of the salt brine, cooled, and cut into two-to-three parts. Fifty grams of octopus cut into pieces and 40 g of surf clam were packed into a jar, and the jar was filled with salt brine.

The preserves were sterilized at no more than 115°C, since a higher temperature has a negative effect on the protein and carbohydrate components of seafood [43]. The preserves were sterilized and cooled in water with back pressure (0.18 MPa) in an AB-2 autoclave; all preserves were cooled in water with back pressure.

Rational formulas of sterilization regimes were developed to ensure the commercial sterility of preserves. The values of the normative sterilizing effect (F_n) for the test and reference canned samples were estimated after determining the heat resistance of the spores (constants $D_{121.1}$°C and Z°C) of the test strain, *C. sporogenes-25,* in an extract from unsterilized jars with products for each assortment separately. It was established that the time of sterilization proper to obtain commercially sterile natural preserves was at least 45 min. and at least 50 min. for other types.

The amount of preserves made from unskinned cephalopods was much larger than that made from skinned semiproducts. Table 5 shows that the exclusion of the skinning operation from the cephalopod canning technology increased the yield of the end product, depending on the product assortment and type, by 12.9–52.8%.

Table 5. Increased output of preserves made from cephalopod unskinned semiproducts

Canned cephalopods	Increased output (%) of preserves from		
	squid		octopus
	Commander	Pacific	
Natural	12.9	19.1	42.1
Blanched in oil	14.8	27.1	52.8
Soft-smoked in oil	31.1	37.2	50.2

The raw material saving per unit of end product helped improve cephalopod canning profitability. Thus, the economy of raw materials to produce 1000 standard cans of natural preserves from Pacific squid amounted to 2523.48 rubles; from Commander squid, 15 146.3 rubles; and from octopus, 9292.0 rubles.

The like finished preserves from unskinned and skinned cephalopods had no significant differences in their nutritive and energy values.

When evaluating the amino-acid composition of preserves from unskinned semiproducts, high contents of proline and taurine were established. Table 6 shows that 100 g of unskinned cephalopod preserves meet the daily requirement for these substances of 10% and higher. The high contents of proline and taurine in the new cephalopod preserves make them functional products.

Table 6. Proline and taurine contents in unskinned cephalopod preserves

Variants of preserves	Recommended daily consumption for humans	Content in preserves, g per 100 g of product	Share of recommended daily consumption, %
proline			
Natural unskinned (Commander)	4.5 g	0.64±0.5	14.2
Natural unskinned octopus		0.48±0.04	10.7
(Pacific) squid in oil		1.2±0.3	26.6
taurine			
Soft-smoked squid in oil	400.0 mg	234.0±0.51 mg	58.5
Natural unskinned octopus		321.0±0.22 mg	80.25

In preserves from skinned semiproducts, the cephalopod meat was more compact and less juicy compared to the test samples, which was due to the loss of tissue juice during preprocessing. In the samples of preserves in oil, whose sterilization time was 5 min.

longer than that of natural preserves, a slight caramelization flavor was present due to thermal damage of sterilized objects and to the formation of Maillard reaction products.

A known method of reducing the heat resistance of the spores of microorganisms and, consequently, of reducing the severity of preserve sterilization regimes is to create an acidic medium of canned products, which is of little use for the assortment of preserves in oil. Therefore, we should seek techniques to reduce the excessive thermal load on products during sterilization, to diminish the thermal resistance of microorganisms, but at the same time to guarantee their commercial sterility.

It has been established previously that the oily extracts of spices used in the fish canning technology have a marked antimicrobial activity and can inhibit the development of the vegetative cells of microorganisms and reduce the thermal resistance of spore microorganisms in canned goods [44, 45]. Therefore, to ensure the full reduction of the values of the normative sterilizing effect (*F_n)* and, consequently, of the thermal load (heat damage) on the product, oil was replaced with a spicy–oily extract, the so-called flavored oil, during canning.

Flavored vegetable oil, prescribed for canning recipes, was prepared as follows: ground spices were mixed with oil, heated to 100°C, at a ratio of 5 : 100 and seasoned for 24 h, after which the liquid part was separated from the lees [44]. The flavored oil acquired a tincture characteristic of the spice used (cadmium orange, orange, or other).

The reference samples of preserves were filled with the vegetable oil used to produce spice–oily extracts.

The lethal time (constant $D_{121.1^{\circ}C}$) for the spores of the test strain, *C. sporogenes-25,* in the extractions of all preserves in spicy–oily extract was lower than for the like preserves in vegetable oil. Figure 2 shows that the test samples of "Octopus in oil" had a value of constant $D_{121.1^{\circ}C}$ lower by 0.11 conventional minute than in the like reference samples. Taking into account the obtained values of constant $D_{121.1^{\circ}C}$, we calculated indicators F_n for the test samples of preserves that were lower compared to the reference samples.

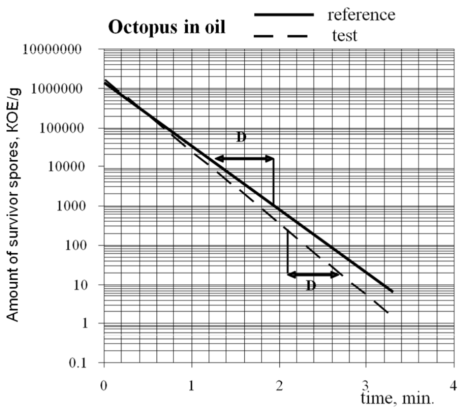

Fig. 2. Survivability and lethal-time curves ($D_{121.1^{\circ}C}$) of the *C. sporogenes-25* spores in the reference and test samples of "Octopus in oil."

The obtained data were used to determine the duration of the sterilization proper of preserves, which ensured the necessary values of the actual sterilizing effect (F_a.) during the sterilization of preserves.

It was established that, to reach the necessary sterilizing effect, the duration of the sterilization proper of the test samples of preserves was 5 min. shorter compared to the reference samples (Table 7).

Table 7. Duration of sterilization and the actual sterilizing effect (F_f) for the test and reference samples of preserves

Preserves	Preserves in					
	vegetable oil			spicy–oily extract		
	F_n, conv. min.	Sterilization time, min.	F_f, conv. min.	F_n, conv. min.	Sterilization time, min.	F_f, conv. min.
Blanched in oil	5.28	20–50–20	6.9	4.50	20–45–20	5.68
Soft smoked in oil	5.28	20–50–20	6.9	4.64	20–45–20	5.8

The reliability of the preliminary developed sterilization regimes was confirmed by the results of laboratory testing by the method of artificial inoculation of preserves in which vegetable oil was fully replaced with the spicy-oily extract. To this end, 30 jars were taken and spores of *C. sporogenes*-25 were introduced into the center of each jar, after which the jars were sterilized, and their commercial sterility was analyzed. To compare the quality of preserves, five jars of each assortment, not inoculated with bacterial spores, were sterilized, as well as preserves in vegetable oil. After sterilization, all the preserves were commercially sterile, which indicated the reliability of regimes with shortened sterilization times.

Sterilized preserves in spicy–oily extracts did not differ from samples in vegetable oil and were characterized by attractive appearance and low spicy flavor. All the test samples of preserves were free from the caramelization flavor.

Thus, the use of spicy–oily extracts in the production of preserves "in oil" made it possible to reduce the duration of the sterilization proper of preserves, which led to a reduced thermal load on the product and, consequently, a reduced intensity of the Maillard reaction.

The efficiency of the positive effect of replacing vegetable oils in the composition of cephalopod preserves "in oil," caused by the reduced duration of their sterilization by 5 min., was evaluated by the effect of heat damage on microbial and raw-material cells, including the survivability of protein and biologically valuable nutrients.

During the sterilization of preserves, part of spore-forming cells of *Bacillus subtilis* (*B. subtilis*) is able to survive and remain viable for the whole storage period [45]. However, the presence of bacilli, even in a dormant state, affects the quality of preserves and leads to the "aging" of protein structures. The sanitary standards permit the presence of *B. subtilis* within the "residual" microflora in sterilized preserves, but their number in sterilized preserves of group A should not exceed 11 cells per 1 g of the product.

Therefore, the number of *B. subtilis* cells was determined before and after the sterilization of the newly developed preserves in which spicy–oily extracts were used. Preserves with the vegetable oil used to obtain the spicy–oily extracts were used as reference products. It was established that before sterilization the average number of bacilli in 1 g of preserves was 320 ± 64 cells. After sterilization, 1 g of commercially sterile cephalopod preserves in vegetable oil revealed from 3 to 13 viable *B. subtilis* cells. Bacilli were not found in preserves with spicy–oily extracts, which indicated the expressed sporicidal effect of the oil filling.

An indicator of the degree of survival of the nutritive value of a product during sterilization is heat damage to proteins, which affects their digestibility. To evaluate the effect of spicy–oily extracts and sterilization regimes on the digestibility of the protein component of preserves developed for assortments on various oil bases, special research was conducted by biotesting. Figure 3 shows the results of digesting protein products before and after sterilization in the test and reference samples of preserves.

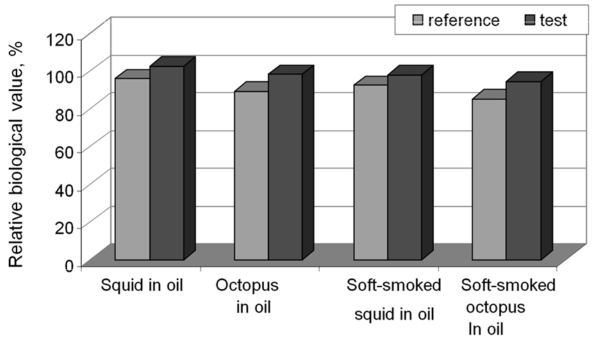

Fig. 3. Digestibility of canned cephalopod products in oil (reference) and in spicy–oily extracts (test).

As is seen from the figure, the replacement of vegetable oil with spicy–oily extracts was accompanied by increased bioavailability of the protein component of preserves. It is possible that minor liposoluble components of spices affected positively the digestion of proteins in products filled with spicy–oily extracts.

As is known, high-temperature processing destroys fatty acids [46]. The effect of spicy–oily extracts on the stability of the lipid component in cephalopod preserves filled with oil was assessed by comparing the fatty–acid composition of the reference and test samples of sterilized products. Table 8 shows the results of the study of the fatty–acid composition of the oil component in the reference (with vegetable oils or their blends) and test (filled with spicy–oily extracts prepared on the same oils or their blends) samples of cephalopod preserves.

Table 8. Comparative characteristics of the fatty–acid composition of the oil base of the reference and test samples of seafood preserves

Fat phase of preserves	Sum of fatty acids in preserves (% of the total amount of fatty acids)					
	in vegetable oil			in spicy–oily extract		
	saturated	monounsaturated	polyunsaturated	saturated	monounsaturated	polyunsaturated
Squid in oil						
Corn oil	17.2	27.6	55.2	14.9	26.7	58.4
Sunflower oil	17.5	26.4	56.1	14.0	25.6	61.1
Octopus in oil						
Sunflower oil	21.7	26.1	52.2	17.3	25.4	57.3
Soft-smoked squid in flavored oil						
Soybean oil	20.8	25.5	55.7	16.6	22.1	61.3
Soybean and corn oil blend (55:45)	16.5	25.7	57.8	15.9	24.6	59.5
Soybean and sunflower oil blend (60:40)	17.6	24.1	8.3	16.2	23.7	60.1
Soft-smoked octopus in flavored oil						
Olive oil	21.0	16.3	62.7	17.2	12.5	70.3
Soybean and sunflower oil blend (60:40)	21.2	24.5	54.3	17.6	23.4	59.0

The quoted results show that the oil component in the reference and test samples of preserves differed in fatty acid contents. In all the assortments of preserves in vegetable oils, the sum of polyunsaturated fatty acids was much lower than their amount in preserves filled with spicy–oily extracts. This indicates that a longer duration of the sterilization proper of preserves (the reference preserves by 5 min.) leads to the largest heat damage to the carbon chains of high-molecular unsaturated fatty acids. During their destruction, fatty acids with smaller carbon chains are formed and accumulated. Oil blending improves the resistance of the oil component in the composition of preserves to the sterilization temperature, especially when they are used in spicy–oily extracts. Consequently, the full replacement of vegetable oils with spicy–oily extracts makes it possible to reduce the degree of heat damage to the nutrient material of products when cephalopod preserves are sterilized.

The research results were implemented during the development of technological instructions and technical specifications for the production of new preserves. Regional and industry degustations pointed to their high consumer attributes. The fish-canning enterprise ZAO APK Slavyanskii-2000, Primorski krai) manufactured batches of new cephalopod preserves that were in demand among buyers.

CONCLUSIONS

New technological approaches have been developed to the canning of cephalopod mollusks that ensure canning profitability and replenish the consumer market with functional seafood.

The exclusion of the skinning process from the cephalopod canning technology helps increase considerably the yield of high-quality products, reducing their cost, and broaden the range of products.

The use of spicy–oily extracts as an oil filling in the cephalopod canning technology improves product quality by reducing the necessary level of thermal effect on products during sterilization and the degree of heat damage to their nutrients.

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