The effect of sterilization modes used for pork preserved in polymeric consumer packaging on the destruction of fatty acids

V B Krylova, T V Gustova and L S Kudryashov
V. M. Gorbatov Federal Research Center for Food Systems of RAS, Moscow, Russia

E-mail: v.krylova@fncps.ru

Abstract. The article is devoted to solving an actual problem aiming at substantiating the rational modes of sterilization of preserved meat in order to minimize destructive effects on the main components of the products, including fats. The authors emphasized mainly on the change of polyunsaturated fatty acids (PUFAs) more specifically, essential fatty acids, which are under the close attention of researchers, both in our country and abroad. Particular attention is paid to the influence of sterilization modes on changes in the quality composition of fatty acids of meat lump in preserved pork. The article summarizes the new material on the effect of sterilization modes of preserved food on the degree of hydrothermal destruction of fat and the formation of free fatty acids on the total content of saturated, monounsaturated and polyunsaturated fatty acids. In this article, the approach for assessing the degree of destruction of the fat component of preserved meat from the point of separation of volatile substances, the content of which, as studies have shown, either decreases with sterilization, is completely destroyed, or increases after sterilization. It is established that most of the compounds, the proportion of which decreases with sterilization, belongs to the class of carboxylic acids, including heptadecanoic, decanoic, eicosanoic and octanoic acids. The idea is that the main factors influencing the change in the initial chemical composition of the product lipids are the presence of moisture in the raw food, the sterilization temperature and the pressure. It is shown that the free fatty acids identified in the raw food: arachidonic acid and hexane are absent in the finished product. As a research task, the authors evaluated the effect of gentle sterilization modes on the safety of oleic acid, which can inhibit the formation of cholesterol plaques in the blood vessels, preventing the development of atherosclerosis. A small amount of nervonic acid was found with a dietary value. It was shown that irrespective of the sterilization modes, γ-linolenic acid was preserved, which contributes to the strengthening of the structure of cell membranes. In conclusion, analysis results obtained indicated a shallow destructive change in the fat content of the preserved food under the influence of gentle thermal loads.

1. Introduction
Preserved meat, including pork, belong to the group of products of mass consumption by all categories of the population, that are a source of essential nutrients and play an important role in the provision of the health of the population. The works aiming at justifying rational modes of heat treatment for preserved food with the purpose of minimizing destructive influences on the main substances of products, including fats still remain in actuality.
Fat components undergo various negative changes during any technological process, which significantly affect their composition and consequently, can reduce the nutritional and biological value of the finished product. Such changes include hydrolysis, oxidation and interaction of fats with proteins and carbohydrates.

Factors determining the depth of destruction of fatty components include the water content of the processed raw materials, the presence of oxygen and the influence of light, the activity of tissue enzymes, the microbiological contamination of raw materials, mechanical influences and the processing temperature [1–5]. With a combination of these factors, destructive changes can be amplified, having a negative effect first on the organoleptic characteristics and then on the safety of the products [6,7]. The process of oxidation of lipids is classically a free-radical, chain, autocatalytic mechanism consisting of several stages [1–3].

With regard to animal raw materials, the processes of destruction of lipids in the preparation of edible animal fats have been most thoroughly studied. As a criterion for the correctness of such operations, as preliminary cooling and subsequent heat treatment, the acidic value is taken, which characterizes the depth of hydrolytic changes in fat and indicates the formation of free fatty acids in the product.

Formed during hydrothermal destruction, free fatty acids are activators of subsequent chemical transformations, including when preserving products. Oxidation, polymerization and cyclization are primarily polyunsaturated fatty acids. It is possible to form six-membered unsaturated cyclic compounds, oxidized polymers and other substances harmful to the human body. Because of their poor absorption, the primary oxidation products of fat-peroxide and hydroperoxide when ingested with food into the intestine are less toxic than the final oxidation products - aldehydes, ketones, which, due to the carbonyl group in their composition, are readily absorbed in the intestine [8–10].

When the product is exposed to high temperatures, oxidative processes that are usually impossible under normal conditions, begin to occur with the formation of specific peroxidation products. Moreover, every 10 °C increase in temperature doubles the rate of the reaction [11]. The presence of proteins in the product slightly suppresses oxidative and hydrolytic processes, it is assumed that this is due to the antioxidative property of some amino acids.

Works aiming at justifying rational modes of heat treatment to preserve food with the purpose of minimizing destructive influences on the main substances of products, including fats still remain in actuality. It is known that the process of sterilization, which creates conditions for long-term storage of the product, can be accompanied by hydrothermal decomposition of fats with the formation of free fatty acids.

Sterilized preserved meat is traditionally produced in metal cans and glass jars. In recent years, the technologies to sterilize preserved meat in consumer packaging from combined materials (lamister and sterilkon) with an inner layer of aluminium foil, possessing high barrier properties ensuring leak tightness of consumer packaging have become increasingly widespread. However, the packaging of such materials is strongly deformed under physical influences, which requires an additional individual transport packaging to prevent deterioration of its appearance. More sustainable were consumer packages of modern multi-layer polymer barrier materials without a layer of aluminium foil.

During sterilization of preserved food, which usually happens at temperatures of 115–120 °C, processes that substantially change the initial chemical composition of lipids begins to occur. To date, the results of studying the fatty acid composition of meat lump in preserved food, developed in new polymer consumer packages, are fragmentary and not systematized.

The purpose of this study is to research the effect of sterilization modes developed on the dynamics of the content of fatty acids and their derivatives in preserved meat made from pork produced in polymer consumer packaging.

2. Research methods
As an object of research, experimental samples of preserved pork "Stewed pork extra class" were taken, consisting of pork veined with a mass fraction of fatty tissue, not more than 30% amounting to
87%, onion, salt, black pepper and bay leaf. Food is preserved from one batch of raw materials, in a high-barrier polymer consumer packaging amounting to 600 cans. When preparing the intermediate sample of the preserved food, the meat portion of the product was crushed, after pre-draining the broth from the can into the beaker, and then both parts were combined, mixed and ground in a mortar to form a homogeneous mass.

Sterilization modes: hard (1) - with a sterilizing effect $F = 18$ conventional minutes and gentle (2) - with a sterilizing effect $F = 12$ conventional minutes. The value of the achieved sterilizing effect was determined using a device that monitors the process of sterilization of preserved food PKPSK-1, developed at the Gorbaty ARRIMI" (now FSBSU "Gorbaty FSC of food systems" RAS) in 2001, which automatically implements the following functions:

- measure the temperature of air in the autoclave;
- measure the temperature inside three cans containing the product;
- measure sterilization time;
- calculate sterilizing effect;
- indicate all listed parameters on a digital display;
- register these parameters and print them.

Thermocouples of resistance with a nominal statistical characteristic (NC) Pt100, in which the change in resistance is directly proportional to the temperature change, were used as temperature sensors for the cans with the product and the autoclave. Thermal converters were placed in a stainless-steel tube with a diameter of 3 mm, on which there is a washer and a fitting to attach the sensors inside the cans to the product. The device makes it possible to measure the temperature inside the cans with the product and the temperature of the heating medium in the autoclave for a temperature range from 0 °C to 150 °C and an accuracy of 0.2 °C.

The content of natural fatty acids and their derivatives, the appearance of which is associated with the thermal processing of the preserved food, was determined by gas chromatography with mass spectrometric detection. This method requires additional chemical treatment in order to give optimal volatility to all analytes at the temperature of the analysis performed. As a processing method, a combination of the Folchu extraction method and methylation was used, which allowed to expand the list of identified components and accordingly, to increase the level of the established content of the minor components in the mixture.

The fatty acid composition was determined on a gas chromatograph HP 6890 from Hewlett Packard (USA). Chromatography conditions: a 0.2 μl hexane extract containing methyl esters of fatty acids extracted from the sample was introduced into the vaporizer of a gas chromatograph with a flame ionization detector and analyzed with a programmable change in column temperature from 120 °C to 240 °C (6 °C/min), evaporator temperature 250 °C, detector temperature 300 °C, inert gas flow rate to a packed column of 75 ml/min.

The acid value (AV) was determined using a titrimetric method based on the titration of free fatty acids with a solution of potassium hydroxide.

The processing of experimental data was carried out using mathematical statistics. The experiment was repeated three to five times. Hypotheses were tested with a probability of 0.95.

3. Results and discussion
Sterilization of meat pieces in the preserved pork was carried out after sealing the cans at a temperature of 120 °C and the system pressure was set within the autoclave. The main factors affecting the degree of destruction of preserved fat include the moisture content in raw meat, the sterilization temperature and the pressure. After sealing the can there was an air space not exceeding 5 mm between the lid and the surface of the mixture, including oxygen. Consequently, oxygen can be considered a possible factor of fat oxidation, but only as a secondary one due to its low availability.
To assess the effect of sterilization modes on the degree of hydrothermal destruction of fat and the formation of free fatty acids, the acid values of fat and the total content of saturated, monounsaturated and polyunsaturated fatty acids were determined. The results are shown in Table 1.

The results of the studies showed that the sterilization process leads to the accumulation of free fatty acids, as evidenced by the increase in the acid value of fat. It should be noted that the hard sterilization mode (mode 1) exerts a more destructive effect on pork lipids than mode 2.

Table 1. Indicators of preserved fat quality.

| Name of indicator | Indicator value |
|-------------------|-----------------|
| Acid value of fat, mg KOH/1g | Before sterilization | when sterilized in mode 1 | when sterilized in mode 2 |
| Amount of saturated fatty acids (SFA), % | 47.68 | 38.85 | 43.42 |
| Amount of monounsaturated fatty acids (MUFA), % | 29.35 | 39.38 | 35.69 |
| Amount of polyunsaturated fatty acids (PUFA), % | 20.36 | 15.05 | 19.35 |
| Other unidentified compounds | 2.61 | 6.76 | 1.54 |

Prior to heat treatment, the pork fatty tissue used for the production of preserved food consisted predominantly (more than 97%) of a mixture of triglycerides of various fatty acids, with the ratio of PUFA:MUFA:SFA at 1:1.4:2.3. The sterilization process resulted in a decrease in the total content of SFA and PUFA in the product, and in the growth of the percentage of MUFA. Moreover, the harder the sterilization mode, the higher the degree of destruction of saturated and polyunsaturated fatty acids. The net decrease in the PUFA content was 5.31% and 1.01% for modes 1 and 2, respectively, compared to the initial raw material data prior to sterilization. In saturated fatty acids, the decrease was 8.83% and 4.26%, respectively.

Table 2 provide data on the content of free fatty acids and their derivatives in preserved food that underwent sterilization under different heat loads, which manifested with high probability (80-99%) in chromatographic-mass spectrometry. A total of 128 chemical compounds were identified. Of these: 49.2% carboxylic acids; 21.1% esters; 3.1% ethers; 1.6% alkanes; 0.8% alkenes; 1.6% heterocyclic amides; 0.8% nitrile; 1.6% alkatrienes; 2.3% alcohols; 0.8% alkadienes; 0.8% ketones; 1.6% silicones and 10.9% unidentified compounds.

The detected substances can be conditionally divided into four groups: 1st group - substances, the content of which decreased upon sterilization (Table 2); 2nd group - substances that were completely destroyed after sterilization; 3rd group - substances whose concentration increases after sterilization; 4th group - substances that are identified in the product only after sterilization of the preserved food.

Most of the substances, whose concentration decreased with sterilization, belong to the class of carboxylic acids, their isomers and, in smaller fractions, esters (Table 2).

Table 2. Content of 1st group substances.

| Name of free fatty acids and their derivatives | Content, mg/kg |
|-----------------------------------------------|---------------|
|                                              | Before sterilization | After sterilization: | mode 1 | mode 2 |
| Cyclotrisiloxane, hexaethyl-                  | 0.76 | 0.07 | - |
| Methyl tetracosanoate                          | 5.78 | 2.22 | 1.02 |
| 3-(3-Methoxyphenyl)propenitrile               | 0.01 | 0.01 | - |
| Pentadecanoicacid                             | 0.17 | 0.10 | 0.05 |
| Cis-10-Heptadecenoic acid                     | 0.73 | 0.60 | 0.23 |
The content of esters was heptadecanoic, decanoic, urated fatty acid of preserved food showed a small amount of nervonic acid, which has a dietary value, like a plaques in the vessels, preventing the development of atherosclerosis. As a result, mode 2 sterilization recorded. It is known that monounsat

Table 2 clearly shows a significant decrease in saturated fatty acids such as heptadecanoic, decanoic, dodecanoic, eicosanoic and octanoic in the product after sterilization. Before sterilization, 18 chemical compounds were detected in the raw materials, of which carboxylic acids accounted for 83.3%; alkanes, nitriles and aldehydes - 5.6% each; esters - 11.1%; Unidentified compounds - 5.6%. The sterilization process resulted in a change in the content of the substances to be determined in the finished product. Thus, the thermal treatment of preserved food in mode 1 led to a decrease in the content of carboxylic acids to 80.0%, esters to 5.6% and an increase in the content of alkanes and nitriles to 6.7% of their original value. Sterilization mode 2 identified 14 compounds, whereby carboxylic acids - 71.4%; aldehydes - 7.1%, esters - 14.3%; while the share of unidentified substances increased to 7.1%.

It is known that carboxylic acids are the starting compounds for the preparation of intermediate products of organic synthesis, in particular ketones, halides, vinyl ethers, halogen acids. The data in Table 2 clearly shows a significant decrease in saturated fatty acids such as heptadecanoic, decanoic, dodecanoic, eicosanoic and octanoic in the product after sterilization.

The discovery of ω-7 MUFA (C16:1n7) – palmitoleic acid by scientists at Harvard University led to serious research aimed at studying this acid as a means of treating metabolic disorders that lead to the risk of diabetes and cardiovascular diseases. It has been suggested that this acid is the only regulating composition of serum fatty acids in exact accordance with the existing disorders of lipid metabolism in adipose tissue. As a result of the study, data were obtained on the positive effect of palmitoleic acid on liver function and plasma lipid profile [12].

In the preserved samples tested, the effect of high temperature during sterilization led to the accumulation of palmitoleic acid, on average, 13.1% compared to the initial data on the raw material before sterilization. The presence of monounsaturated fatty acids in preserved food has a positive effect on lowering cholesterol in the blood, promoting the formation of an insoluble complex with cholesterol and, thus, interfering with the absorption of the latter [12].

When sterilizing preserved food in mode 1, finished products contained carboxylic acids 40.0%; esters - 26.7%; others - 13.3%; heterocyclic compounds - 13.3% and alcohols - 6.7%. With sterilization mode 2, the proportion of carboxylic acids was higher by 2.1%; the content of esters was lower by 10.9%; others by 8.0%. 5.3% of alkenes, stigmasterol and aldehydes were identified.

With gentle sterilization mode a substantial amount of oleic acid, relating to the family of ω-9 was recorded. It is known that monounsaturated fatty acid ω-9 prevents the formation of cholesterol plaques in the vessels, preventing the development of atherosclerosis. As a result, mode 2 sterilization of preserved food showed a small amount of nervonic acid, which has a dietary value, like arachidonic
and eicosapentaenoic acids. It was established that irrespective of the sterilization modes, $\gamma$-linolenic acid is preserved, which contributes to the strengthening of the structure of cell membranes.

According to the researchers [3,5], one of the possible mechanisms leading to the formation of the most characteristic products of oxidation, aldehydes, is the decomposition of hydroperoxides or cyclic peroxides of acids, resulting in the formation of two aldehydes with molecular weights less than the initial acid. In the preserved food, free aldehydes were identified in trace amounts (0.01% of the number of identified acids, determined with a probability of more than 80%) $E$-11-Hexadecenal and 9-Octadecenal, (Z), indicating a shallow destructive change in the fat component of the preserved food studied, under the influence of thermal loads.

Aldehydes are reactive substances and form primary alcohols upon reduction. In the preserved food prepared in a hard mode, Z, Z, Z-Octadekatriene-9,12,15-ol-1-saturated monohydric alcohol was found. Alcohols are isolated in small amounts and do not exceed the established threshold concentration (for alcohols with a content of more than 10 carbon atoms, 1-5 mg/l).

Stigmasterol (plant sterol), found in the preserved food, belongs to the group of steroid alcohols naturally present in plants. Since the preserved food used onions, it is possible that the formation of this alcohol is associated with its presence.

Small amounts of heterocyclic compounds detected after sterilization mode 1 may enter a substitution reaction instead of addition, so as to preserve the double bond system. These compounds can affect the smell and flavour of the finished product.

4. Conclusion
It was found that the process of sterilization led to a decrease in the content of carboxylic acids by 2.0–3.3%; increased the proportion of esters by 2.0 - 2.2%; alkanes, nitriles and aldehydes - on average 1.1% compared with their content in raw materials; the share of unidentified substances also increased.

It was shown that arachidonic acid was not identified in preserved pork, regardless of sterilization modes, while its derivatives were identified.

It was found that gentle sterilization modes promoted the preservation of mono- and polyunsaturated fatty acids in the product, including oleic, $\gamma$-linolenic and nervonic acids, which play an important biological role.

Analysis of the results indicated shallow destructive changes in the fat component of the preserved food under the influence of gentle thermal loads.

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