Prevention of oxidative processes in oil by the use of antioxidants during preservation process of sardines

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Prevention of oxidative processes in oil by
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Scientific studies of the nutritional value of fish
meat, rapid improvement in the fish catching techniques, and
improvement of technological processes for holding, storing,
transporting and preserving fish resulted in a considerable
increase in the consumption of fresh and canned fish, not only
by the population of the coastal region, but by continental
regions as well. The bringing in of larger fish catches and
preserving their nutritional value had noticeably improved the
quality of food and contributed to the decrease of deficiency
in albumins of organic origin.

The chemical composition of the fish meat is not
constant all the time and varies with the type, age, and sex
of fish and with the location of the catch. The quantity of water, albumins and fat varies and therefore the caloric value of individual kinds of fish meat also varies in a wide range. According to Mayer, the amount of edible portions in individual kinds of fish varies from 30 to 78% (1). Carbohydrates are contained in the fish meat in negligible quantities and, in evaluating the nutritional value of fish, can be disregarded.

While during a whole year the quantity of water and fat in fish varies, the quantity of albumins and mineral materials is, mostly, constant. The fish meat contains 17 - 20% of albumins; the amount and interrelation of individual essential aminoacids in these albumins is very favourable and, therefore, the albumins in fish meat are considered to be very valuable ingredients. The fat in the fish is not spread evenly through the whole body, and its amount depends on the age, species, and type of food used by the fish, as well as on the temperature of water; in the sardine, as the main industrial fish of our sea, it varies during a year from 4 to 21% (2). The quantities of water and fat in sardines are in reverse proportion, i.e. with the increase of the amount of fat, the amount of water decreases, while the total amount of water and fat remains approximately constant during the whole year and amounts to 76% of the body weight (2).

Since fish oils are mixed glycerides, they contain both saturated and unsaturated fatty acids. With the oxidation of the unsaturated fatty acids, the fish oils become rancid
and attain an unpleasant taste and odour. In addition to the unpleasant odour and taste, a change in colour occurs in the oxidized fish oils, depending on the specific properties of the oil and the degree of oxidation. According to Venoli et al, the darkening (brown) of fish oils is particularly accelerated in the presence of albumins (3). Obata considers that the red colour occurring in fish oils is caused by the action of trimethylamin, which enters into a reaction with aldehydes created during the process of autooxidation of highly unsaturated fatty acids (3).

According to Farmer and Sutton, unpleasant odour from the fish meat occurs because of oxidative decomposition of unsaturated fatty acids and their esters (4). Tomaya and Matsumoto consider that the volatile matters created by the decomposition of unsaturated fatty acids of sardine oil contain various acids and carbonic compounds with a very unpleasant and sharp odour (4).

The fat contained in the fish meat is subjected to faster deterioration than the extracted oil. So, during the storage of herring (Clupea harengus) and of the extracted herring oil at -20°C, the peroxide value of the oil contained in the herring increased more than that of the extracted oil (4). The same is also true for sardines with which the experiments were conducted at a temperature of -15°C. In addition, the acidity of sardine oil increases with the storage time, while the extracted oil hardly changes its acidity at all (4). After
one day of holding the anchovy at a temperature of 20°C, the acidity (expressed as oleic acid) increased 2.5 times in relation to the initial value, after two days of storage - 7.5 times, and after five days of storage - 8 times, and the oil obtained a dark reddish colour (4). The study of the oil acidity of herring stored at 2 - 4°C determined that the degree of acidity increased two-fold after two days of storage, by three times after 4 days of storage and by four times after 6 days of storage, in relation to the initial value (4). The skinning and filleting of fish creates favourable conditions for a better contact of the raw meat with air, which accelerates the process of oxidative spoilage. It is considered that dipping fillets into a brine solution prior to storing them in refrigerators favours the development of rancidity (4), likewise, freezing in a brine solution creates more favourable conditions for the development of rancidity than freezing fish in open air (4).

The admixtures in the sea salt, particularly the MgCl₂, accelerate oxidative spoilage in the fish meat. According to Venoli et al the brownish colouring of frozen fish and the colour change of canned fish could be attributed to the oxidative oil spoilage (3).

Immediately after the catch, fish must be 'iced', i.e. mixed with crushed ice and placed in a dark location. It is desirable for such 'iced' fish to be stored as soon as possible at a temperature of -20°C. A shorter interval between the catch and the 'icing' favourably affects the quality of frozen fish. If the fish is filleted, the fillets should be 'glazed', which is achieved by fast dipping of the frozen fish
and fillets in ice-cold water. The thin layer of ice which develops on the surface of fish and fillets is a good protection from oxidative spoilage, which is particularly important in the case of fat fish (4).

The oxidative spoilage of fish oils can be prevented by storing frozen fish in a CO₂ or N₂ atmosphere (1).

An important factor in stability of the fish oil is the amount of tocopherol. The study of different kinds of extracted fish oils confirmed that their stability is in direct ratio to the content of tocopherol, which varies from 40 mg/kg in sardines to 628 mg/kg in sablefish (1).

For the purpose of preventing the rancidity, experiments were conducted on the 'glazing' of cut fish with a water solution of ascorbic acid. The results obtained had shown that the use of ascorbic acid protects, to a certain extent, fish oils from the oxidative changes (4). For greater efficiency of this process — particularly in the preservation of large fish — water binding agents were added to the ascorbic acid solution (for example the extract of Irish moss), for the purpose of fuller adhesion of the icing to the surface of the processed fish (4).

For the purpose of preventing the rancidity during the storage of salted and dried fish, the effects of some antioxidants were studied, such as butylhydroxyanisol (BHA), nordihydroguaiaretic acid (NDGA), propylgallate (PG), izoamylgallate (IAG), and others. The above antioxidants
were employed individually or in combination with the citric acid as the synergist. The results of the experiments performed had shown that the BHA provides better results than the NDGA, while the esters of gallic acid proved unsatisfactory and caused colour change of the fish meat (4). According to the research by Russian scientists, conducted on the bacalar oil, favourable results were obtained by adding ethylgallate, octylgallate and butyloxyanisol in the amount of 0.05% in relation to the weight of oil (4).

**Material and methods of study**

It is known that fish oils contain natural antioxidants, but the effect of these compounds is limited, i.e. it stops as soon as the heat treatment of fish is started.

Having in mind the onset and development of the oxidative processes, fish oils should be protected from oxidation at the very beginning of the technological process of fish preservation. It could be done most conveniently by using the brine solution, with which the water-soluble antioxidants can be employed. On the other hand, in the selection of antioxidant it is also necessary to consider its stability during the process of fish preservation and the method of introducing the antioxidant into the fish.

In normal production, and particularly during the peak of the fishing season, because of limitations of the production capacity, delays in fish processing occur quite frequently and
the interval between the fish coming out from the tunnel-type oven and its packing in the cans and sterilizing is extended. It is evident, that the longer, or shorter time period between fish leaving the tunnel-oven, until its final sterilization, will have its influence on the extent of oxidative changes.

The purpose of this study was to investigate the possibility of using some antioxidants with the conventional heat-treatment method of sardine preservation. The selected antioxidants were added to the infusion oil after the heat treatment of the sardines in order to prevent oxidation of the fish oil and of the vegetable oil which is added as the infusion liquid.

In selecting the antioxidants, we have chosen the American "Griffit G-16" and domestic "RuA". Griffit G-16 contains butylhydroxytoluen (BHT), BHA, PG, citric acid, monoglycerides and mineral oils. This antioxidant is stable and completely soluble in oils, and when added to food products does not cause changes of their organoleptic characteristics. It is usually added in the amount of 0.02 to 0.1%.

The 'RuA' is a domestic antioxidant produced by the Yugoslav Institute of Meat Technology in Belgrade. It is a light-yellow powder obtained by extraction of rosemary with alcohol, readily soluble in fats and oils and partially soluble in quite a number of organic solvents. Although the chemical composition of the RuA has not been fully determined, it is considered, on the basis of typical reactions, that it contains a phenolic ingredient.
The tests were carried out on sardines under normal production conditions in the fish processing department of the "Adria" factory in Zadar.

A mixture of refined soya and sunflower oils was used as an infusion oil, which is normally used in regular production. The antioxidants were added into the oil in the amount of 0.05% of the amount of infusion oil.

The experiment was carried out in two series of tests with a total of 320 cans, 160 in each series.

Sterilized, washed and dried cans were stored for six months at room temperature and, after that, they were opened and the peroxide and thiobarbituric values were determined for each fish-can.

The peroxide value was determined by the modified Lea's method, and the thiobarbituric value by the Sedlachek's method (3).

By determining these parameters in the contents of canned fish food, we have definitely established the effect of the length of time between the baking of fish and the can sterilization, on the degree of oil oxidation in canned sardines. The results of these tests are shown on diagrams 1 and 2.

Table 1.
The arrangement of test specimens of cans of "sardines in oil" for the purpose of analyzing the peroxide and thiobarbituric values in the contents of fish cans after six months of storage.
Time elapsed from the baking of sardines until they are placed in cans and infusion oil added - in hours

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<td>Number of cans filled:</td>
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| Infusion oil without any antioxidants | 20+20 | 20+20 | 20+20 | 20+20 | 160 |
| Infusion oil with antioxidant RuA | 10+10 | 10+10 | 10+10 | 10+10 | 80  |
| Infusion oil with antioxidant G-16 | 10+10 | 10+10 | 10+10 | 10+10 | 80  |

Total number of cans used: 320

Diagram 1

1. Oil with no antioxidants
2. Oil with the RuA antioxidant
3. Oil with the G-16 antioxidant

Peroxide value
(ml 0.01N $\text{N}_2\text{S}_2\text{O}_3$ / 1 g of oil)

Length of time between the baking of fish and its sealing in the cans and sterilizing (in hours)

The variation of peroxide value in the can oil of "sardines in seed oil" in relation to the length of time between the baking of the fish and enclosing them in the cans and sterilizing.
Diagram 2

1. Oil without any antioxidants
2. Oil with the RuA antioxidant
3. Oil with the G-16 antioxidant

The thiobarbituric value (extinction)

The length of time between the baking of fish and sealing of the cans and sterilizing (in hours).

Variation of the thiobarbituric value in the can oil of "sardines in seed oil" in relation to the length of time between the baking of the fish and their sealing in the cans and sterilizing.

Results and discussion

From diagram #1 we can observe that the peroxide value curves indicate the minimum values for specimens which were canned 3 hours after baking. On the curve related to the specimens canned 20 hours after baking the effect of the antioxidant is evident, in which case the lowest peroxide value is the one for the specimens treated with G-16; it is somewhat
higher for the specimens treated with RuA, and the highest value is for the specimens to which no antioxidant was added.

It should be pointed out, that the specimens containing antioxidant RuA, when the cans were opened, produced a mild scent of rosemary, which is not desirable with this type of canned food and, for evaluation purposes, this tends to reduce its value.

It is evident from diagram #2 that the curves representing the thiobarbituric value have their minimum with the specimens which were canned 3 hours after baking, which indicates that these specimens contain the smallest amount of peroxide.

The curve obtained from testing the specimens in which no antioxidant was added has the greatest drop in the value of the thiobarbituric index, both with specimens canned 30 minutes after baking and those canned 3 hours after baking.

The initial value of the thiobarbituric index for the specimens canned 30 minutes after baking, with RuA added, is considerably lower than the one for the specimens without any antioxidant. Although this value for the specimens canned 6 hours after baking is slightly higher than for specimens without antioxidants, it shows only a minor tendency to increase, which is evident from the curve on the graph.

Specimens with G-16 added, indicate the lowest thiobarbituric values.
Conclusion

On the basis of the tests performed and the results obtained we can draw a conclusion that it is necessary to ensure the continuity of technological process during the fish preservation, in order to avoid delays, particularly after the heat treatment of fish. The addition of antioxidants G-16 and RuA, in the amount of 0.05% of the total amount of infusion oil, can partially prevent the oil oxidation and improve the organoleptic properties of the heat treated canned sardines in oil.

Bibliography:

1. W. Ludorff (1960)


3. J. Schormüller (1968)


Summary

Prevention of oxidation processes in oil by applying antioxidants, during the preservation of pilchards. Based on investigations carried out by the authors of this article and results theretfrom obtained, the conclusion was drawn that during the fish processing the continuity of the technological process should be secured, in order to avoid stoppages, particularly after the heat treatment. By the addition of 0.05% antioxidants G-16 and RuA to infusion oil, the oxidation of oil could be prevented and organoleptic properties of heat preserved pilchards improved.

Literatura:


