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# RESEARCH ON A NEW APPROACH TO LOW-TEMPERATURE DEODORIZATION AND ITS EFFECT ON OXIDATIVE DETERIORATION OF FISH OIL

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## Abstract

**The high content of docosahexaenoic acid and eicosapentaenoic acid in fish oil explains the benefits of this type of fat, especially for the health of the cardiovascular system and the brain.**

**However, the incorporation of fish oil into foods and beverages is often challenging, as fish oil oxidizes very easily and can cause undesirable flavors. An alternative method for deodorizing fish oil has been proposed and investigated. The method is based on the chemical transformation of the main odoriferous compounds of fish oil - aldehydes and ketones. Under the influence of ethyl alcohol and an acid catalyst, more volatile acetals and ketanals are formed. The obtained fish oil tastes and smells in accordance with the requirements for deodorized oils. Aldehydes are also the main secondary products of fish oil oxidation, which are responsible for the so-called "rancidity". The possibility of restoring the sensory characteristics of oxidized fish oil has been proven: the taste and smell of rancid oil disappears, the sensory profile corresponds to fresh fish oil.**

*Keywords:* fish oil; deodorization methods; sensory evaluation; peroxides; aldehydes.

# ДОСЛІДЖЕННЯ НОВОГО ПІДХОДУ ДО М’ЯКОГО ДЕЗОДОРУВАННЯ ТА ЙОГО ВПЛИВУ НА ОКИСНЕ ПСУВАННЯ РИБ’ЯЧОГО ЖИРУ

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## Анотація

**Високий вміст у риб’ячому жирі докозагексаєнової та ейкозапентаєнової кислот пояснює користь цього виду жиру, особливо для здоров’я серцево-судинної системи та мозку. Однак включення риб'ячого жиру в продукти харчування та напої часто є складним завданням, оскільки риб'ячий жир дуже легко окиснюється і може вносити неприємні аромати. Запропонований та досліджений альтернативний метод дезодорування риб’ячого жиру. Метод заснований на хімічному перетворенні основних одоруючих сполук риб’ячого жиру – альдегідів та кетонів. Під впливом етилового спирту та кислотного каталізатору утворюються більш леткі ацеталі та кетаналі. Смак та запах риб’ячого відповідає вимогам до дезодорованих жирів. Альдегіди також є основними вторинним продуктами окиснення риб’ячого жиру, які відповідають за появу відчуття згіркнення. Доведена можливість відновлення сенсорних характеристик окисненого риб’ячого жиру: зникає смак та запах згіркненого жиру, сенсорний профіль відповідає свіжому риб’ячому жиру.**

*Ключові слова:* риб’ячий жир; методи дезодорації; сенсорна оцінка; гідропероксиди; альдегіди.

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# ИССЛЕДОВАНИЯ НОВОГО ПОДХОДА К МЯГКОЙ ДЕЗОДОРАЦИИ И ЕГО ВЛИЯНИЯ НА ОКИСЛИТЕЛЬНУЮ ПОРЧУ РЫБЬЕГО ЖИРА

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Аннотация
**Высокое содержание в рыбьем жире докозагексаеновой и эйкозапентаеновой кислот объясняет пользу этого вида жира, особенно для здоровья сердечно-сосудистой системы и мозга. Однако включение рыбьего жира в продукты питания и напитки часто является сложной задачей, поскольку рыбий жир очень легко окисляется и может привносить неприятные ароматы. Предложенный и исследован альтернативный метод дезодорации рыбьего жира. Метод основан на химическом преобразовании основных одорирующих веществ рыбьего жира – альдегидов и кетонов. Под влиянием этилового спирта и кислотного катализатора образуются более летучие ацетали и кетанали. Вкус и запах полученного рыбьего жира соответствует требованиям к дезодорированным жирам. Альдегиды также являются основными вторичными продуктами окисления рыбьего жира, которые отвечают за появление чувства прогорклости. Доказана возможность восстановления сенсорных характеристик окисленного рыбьего жира: исчезает вкус и запах прогорклого жира, сенсорный профиль соответствует свежему рыбьему жиру.**
*Ключевые слова:* рыбий жир; методы дезодорации; сенсорная оценка; гидропероксиды; альдегиды.

## Introduction

Fish oil is a functional food because it is a source of polyunsaturated fatty acids (PUFA). Especially important is the content of eicosapentaenoic acid (EPA, C20: 5 n-3) and docosahexaenoic acid (DHA, C22: 6 N-3), ie omega-3 fatty acids. They play an important role in human cardiovascular health [1]. However, crude fish oil also contains undesirable compounds that impair its stability and quality. These include moisture, phospholipids, free fatty acids, pigments and volatile compounds. Another problem is the unpleasant tastes and aromas that characterize fish oil and are primarily related to its easy oxidation ability. The quality of fish oil is improved by its refining – successive stages of Degummming, Deacidification, Decoloration and Deodorization.

High temperatures (180–270 °C) are used in deodorization, which is why it should be noted that PUFAs are unstable and heat treatment leads to side reactions, such as oxidation, polymerization, cyclization, geometric isomerization and double-bond migration [2]. Therefore, it is especially important, particularly for fish oil, on the one hand to carry out deodorization due to its specific organoleptics, on the other – to carry it out at the lowest possible temperature.

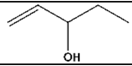
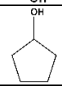
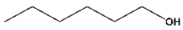
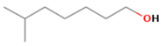
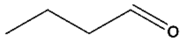
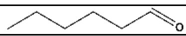
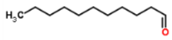
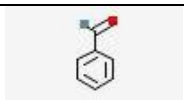
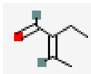
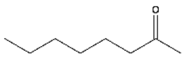
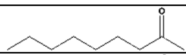
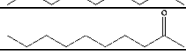
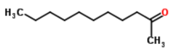
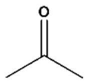
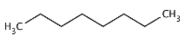
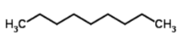
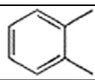
In recent years, there has been a search for ways to deodorize fish oil at lower temperatures. For example, the known technology of short-path distillation. Short-path distillation is characterized by the short residence time of the product in the evaporator under very low operating pressure [3]. A significant reduction in odor was achieved by extraction of tuna and squid fat with n-hexane and nanofiltration using membranes with atomic mass units of 360 Da. The value of odor activity (VOCs) of volatile components in tuna and squid fats was significantly reduced by removing about 80 % of the odorous components. In [4] liquid-liquid extraction (LLE) was proposed as a deodorization method.

The taste and smell of fish oil are determined by its volatile components (Volatile organic compounds). They are characterized by low molecular weight (less than 300 Da) [5]. The composition of volatile compounds of fish oil is given in table. 1. It should be remembered that fish oil is a concept that summarizes the lipid part of many fish and other marine organisms, so it has significant differences in its composition (depending on the source), including the volatile part. It is also important that the content and composition of volatile compounds of various fatty products cannot be considered separately from the oxidative status of the product, because a significant amount of volatile substances is formed in the oxidation process – aldehydes, ketones, alcohols, etc.

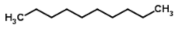
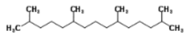
The mass fraction of hydrocarbons is the largest of all the volatile components of fish oil (40 % of the total amount of volatiles in raw fat, 35 % in deodorized fat) [8]. However, due to the high threshold for the perception of hydrocarbons, it is unlikely that they affect the taste and smell of fish oil.

*Table 1*

**The composition of the main volatile compounds of fish oil and their sensory characteristics**

| Name of volatile compounds | Flavor description [6] | Sensory threshold (mg*L$^{-1}$) [7,8] | Structure [6] | Relative content of volatile compounds, % | |
|---|---|---|---|---|---|
| | | | | Crude fish oil [7] | Deodorized fish oil [7] |
| **Alcohols** | | | | | |
| 1-Penten-3-ol | Fishy | 400 |  | 0.89 | 0.15 |
| Cyclopentanol | green, leaf, pleasant | 125 |  | 0.79 | - |
| 1-Pentyn-3-ol | Camphor | - | | 1.20 | - |
| 1-Hexanol | flower, fruit, green, herb, wood | 250 |  | 1.03 | 0.47 |
| Isooctanol | - | - |  | 0.25 | 1.38 |
| 4-ethyl-Benzenemethanol | - | - | | 1.78 | 1.11 |
| **Aldehydes** | | | | | |
| Butanal | banana, green, pungent | 9 |  | | |
| Hexanal | Fishy, grassy | 4.5 |  | 2.13 | 0.75 |
| Nonanal | citrus, fat, floral, green, paint | 1 |  | 2.76 | 2.52 |
| Undecanal | citrus, fat, oil, pungent, sweet | 5 |  | 1.27 | 1.75 |
| Benzaldehyde | almond, fruity, powdery, nutty | 350 |  | 0.74 | 0.53 |
| 2-Ethylcrotonaldehyde | pungent | - |  | 1.14 | 0.20 |
| **Ketones** | | | | | |
| 2-Heptanone | bell pepper, blue cheese | 140 |  | 0.31 | 0.18 |
| 2-Octanone | fat, fragant, mold, overripe fruit, soap | 50 |  | 0.42 | 0.42 |
| 2-Nonanone | Fruity, sugary | 5.5 |  | 5.93 | - |
| 2-Decanone | fat, fruit | 35 |  | 0.32 | 0.52 |
| 2-Undecanone | fresh, green, orange, pineapple, rose | 7 |  | 1.45 | 2.44 |
| Acetone | chemical, ether, hay, nauseating, pungent | 20 |  | 0.85 | - |
| **Hydrocarbons** | | | | | |
| Octane | alkane, fat, flower, oil, sweet | 940 |  | 2.29 | - |
| Nonane | alkane | 2150 |  | 1.03 | 0.29 |
| o-Xylene | Geranium | 450 |  | - | 0.08 |
| Ethylbenzene | strong | 2205 |  | - | 0.33 |

*Continued Table 1*

| | | | | | |
|---|---|---|---|---|---|
| Cycloheptane | - | - |  | 0.39 | - |
| Decane | alkane | 4000 |  | 0.31 | - |
| Pentadecane | alkane | >13000 |  | 17.73 | 19.91 |
| Hexadecane | alkane, root | >13000 |  | 0.41 | 0.46 |
| Heptadecane | alkane, biting, pungent | - |  | 5.93 | 6.12 |
| 2,6,10,14-tetramethylpentadecane | - | - |  | 8.80 | 5.56 |

Butanal, hexanal, nonanal, undecanal, 2-nonanone, and 2-undecanone undecanone are the key volatile components of fish oil [8]. These compounds make a major contribution to the sensory characteristics of fish oil, giving it fishy, herbal scent, earthy, floral scent, etc. [9]. In addition, three ketones (2-heptanone, 2-octanone, and 2-decanone) are contained in fish oil in amounts above the thresholds of perception [8], giving it a fruity, soapy, sweet, fried flavor.

Thus, it is necessary to distinguish between the concepts of "volatile" and "odorizing" substances. Aldehydes make up only about 13% of the sum of all volatile compounds of fish oil [10], however, as can be seen from the analysis of sensory characteristics of volatiles (Table 1), only aldehydes and some ketones are characterized by low thresholds of perception. Namely, these compounds are those that probably make the greatest contribution to the perception of the specific smell and taste of fish oil.

The reaction between aldehydes and alcohols is known to result in the formation of acetals. Acetals are characterized by different sensory profiles and lower boiling points than the corresponding aldehydes [11], that is, they are easier to remove from the fat composition, and they themselves are characterized by pleasant floral aromas (Fig. 1).

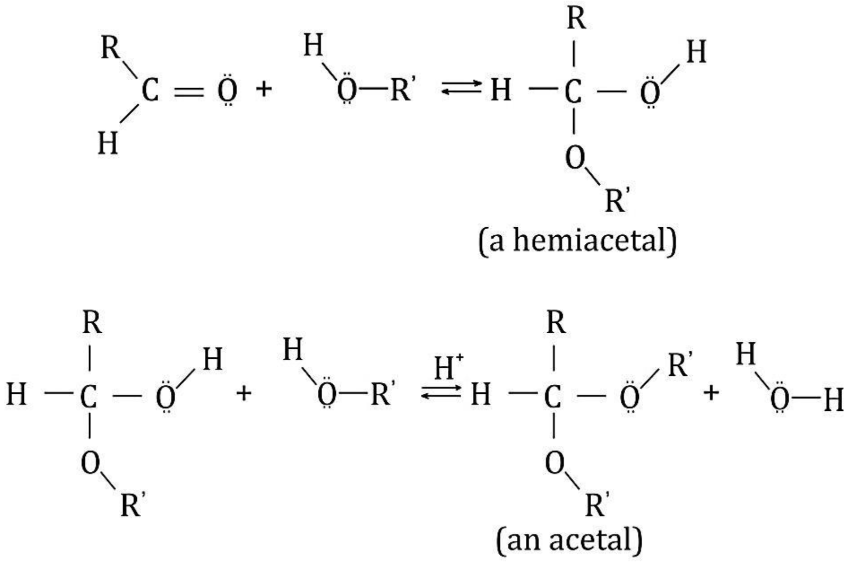



**Fig. 1. Obtaining hemiacetal and acetal [12]**

A similar reaction with the formation of hemiketals and ketal is characteristic of ketones (Fig. 2):

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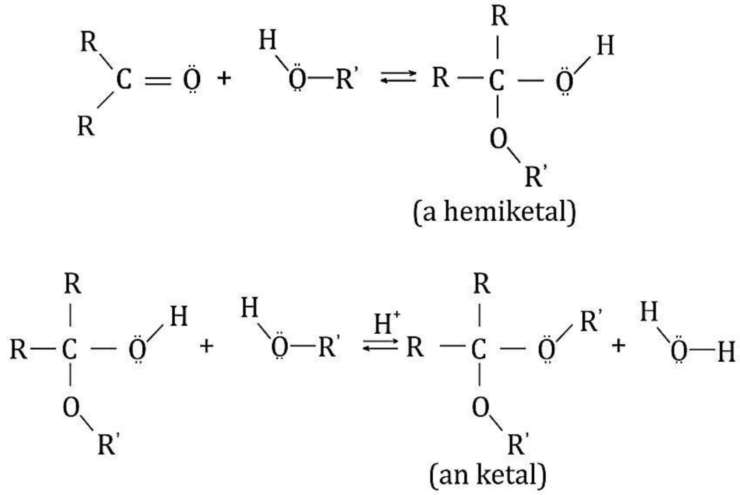


**Fig. 2. Obtaining hemiketals and ketals [12]**

Acetal synthesis is usually carried out under conditions of catalysis using strong liquid inorganic acids, such as sulfuric and phosphoric acids as catalysts [13].

In our previous studies, a decrease in the aroma of fish oil was observed due to the addition of ethyl alcohol and acid catalyst. This result looks very interesting in terms of the potential possibility of developing an alternative method of low-temperature deodorization, which can be carried out at significantly lower than traditional deodorization temperatures (less than 100 °C). The possibility of obtaining less energy-intensive deodorized fish oil with intact omega-3 fatty acids requires further research.

The purpose of the study is to establish the possibility of low-temperature deodorization of fish oil.

In accordance with the use, it is necessary to establish the location of low-temperature deodorization, the rational conditions of this process, to investigate the change in taste and smell of fish oil and its quality indicators.

## Materials and methods

Samples of fish oil from various manufacturers (№ 1 – "Omega 3, 6, 9", "Adrien Gagnon", Canada and № 2 – "Fish oil for children" LLC WTF PHARMACOM, Ukraine) were purchased in pharmacies in Ukraine. Immediately before the start of the study, the required amount of fat was removed from the capsules with a syringe in low light to glass vials made of dark glass. Fish oil № 3 O.L.KAR was purchased at a veterinary pharmacy. It was filtered and hydrated using a magnetic stirrer with a thermocouple at a temperature of 60 °C, with constant stirring (160 rpm). The sample volume was 50 $cm^3$, the temperature was controlled with an error of ± 0.1 °C. During all experiments, a magnetic stirrer was used (RIVA – 04.4, Riva Stal, Ukraine). The amount of water for degumming – 2 %, the amount of citric acid - 0.3 %. A centrifuge (MPW-340, CHEMARGO, Blachownia, Poland) operated at 1000 * g was used to separate the wet gum and to reduce the content of Insoluble impurities. The obtained fat (sample №3) was stored in dark glass vials after treatment of the vials with inert gas (nitrogen) at a temperature of –20 °C (in the freezer).

The conversion of aldehydes and ketones with fish oil into acetals and ketanals was carried out in a laboratory round-bottom reactor with a capacity of 50 $cm^3$, to which an air reflux condenser was connected hermetically. Stirring the reaction mixture (250 rpm) and maintaining the temperature (90 °C, the temperature was controlled with an error of ± 0.1 °C) was carried out on a laboratory magnetic stirrer with a thermocouple (RIVA-04.4, RIVA-STAL, Ukraine). The acetal formation reaction is reversible in the presence of water. Therefore, anhydrous magnesium sulfate was added to the reaction vessel in an amount of 0.5 % with respect to the fat. After the reaction, the fat was cooled and transferred to a laboratory separatory funnel, where it was washed from acid residues to neutral pH. The removal of water and alcohol residues was carried out on a rotary laboratory evaporator IKA RV 10 digital V-C for 30 min, the pressure was less than 5 mbar.

Fish oil oxidations were carried out in a 50 $cm^3$ round bottom flask. The flask was placed in a water bath, in which the temperature was maintained at 90 °C. Stirring and temperature control were carried out on a laboratory magnetic stirrer with a thermocouple (RIVA – 04.4, RIVA-STAL, Ukraine). Oxygen (99.5 % pure) was passed through the fish oil by submerging a bubbler into the bottom of the flask, which was attached to an oxygen cylinder. Oxidation was carried out for 2 hours.

Analysis of the taste and smell profile of fish oil samples was performed according to standard methods [14]. 10 participants of the tasting commission (4 men, 6 women, aged 20–60 years), voluntarily included in the group during the week were trained. At least 10 hours of training were devoted to establishing the organoleptic characteristics of fish oil and the intensity of its taste. A sensor panel was developed, with the following odor descriptors: fishy, fatty, cucumber, earthy, flowery, rancid, green and boiled potato odors. To study the effectiveness of deodorization, a touch panel was used, where 1 is the complete absence of a shade of smell and taste, 5 is a clearly expressed saturated shade of taste and smell. The fat samples were placed in a transparent glass (Petri dish), covered before serving and labeled with coded numbers. The samples were kept at room temperature and analyzed in daylight. Samples were randomized and tested on different days.

The acid value of oils was determined according to the official method of AOCS Cd 3a - 63 (AOCS, 1997). The peroxide number was determined according to the official AOCS method Cd 8b-90 (AOCS, 2017). PAV was determined spectrophotometrically according to AOCS official method Cd 18–90 (AOCS Official Method Cd 18-90, 2011). All measurements were repeated three times. The significance of the differences between the average values of all measurements was determined at the level of $p = 0.05$ (5 %).

## Results and their discussion

It was decided to use only ethyl alcohol as an alcohol for the formation of acetals and ketals. Other monohydric alcohols (propanol-2, methanol, etc.) are more toxic than food ethyl alcohol. Polyhydric food alcohols (glycerin, sorbitol, etc.) according to previous studies have shown a significantly worse effect on the deodorization of fats.

A series of studies have been performed to establish rational conditions for mild deodorization in the presence of ethyl alcohol and acid catalyst. An active experiment with 3 factors of variation was performed. Feedback is a sensory result of deodorization on a 5-point scale, where 1 is the complete impersonality of the taste and smell of fish oil, 5 is the characteristic taste and smell of raw fish oil without changes. Intervals of variation: the amount of ethyl alcohol (X1) – from 1 to 20 %, the reaction time – from 1 to 40 minutes, the deodorization temperature – from 70 to 90 °C. In all samples was present concentrated sulfuric acid (98 %) in the amount of 0.03 %. In previous studies, the need for the presence of a strong acid was found, and sulfur was the most effective of the studied. In the absence of an acid catalyst, the deodorizing effect of fish oil does not occur under any conditions.

As a result of processing the results of the experiments obtained the following regression equation:

$$Y = -71.23 - 6.57 \cdot X_1 + 1.75 \cdot X_2 + 2.38 \cdot X_3 + 0.074 \cdot X_1^2 + 0.001 \cdot X_2^2 - 0.017 \cdot X_3^2 + 0.026 \cdot X_1 \cdot X_2 + 0.055 \cdot X_1 \cdot X_3 - 0.021 \cdot X_2 \cdot X_3$$

The correlation coefficient of the equation $R^2 = 0.745$.

The resulting function reaches a minimum point:

$X_1 = 5$; $X_2 = 7.24$; $X_3 = 90$.

The minimum response value in this case $Y = 0.26$.

Thus, the rational conditions for mild deodorization are as follows: the amount of ethyl alcohol – 5 %, the reaction time – 7.24 min., the deodorization temperature – 90 °C, concentrated sulfuric acid (98 %) in the amount of 0.03 %. The results of changes in the sensory characteristics of fish oil after deodorization under certain rational conditions are shown in Fig. 3.

The intensity of the taste and odor of fish oil has sharply decreased after low-temperature deodorization. Fish oil could not be identified. Saturated shades such as rancid (it is responsible for the presence above the threshold of perception of 2,4-Heptadienal), fish, fat and floral (they are created by 3-Pentanone 1-Penten-3-ol 2-Penten-1-ol) have completely disappeared [16]. There are barely noticeable shades of smell and taste of cucumber (2-Nonenal) and boiled potatoes (Heptanal), which is probably due to the low thresholds of perception of these volatile.

The tasting committee commended the deodorized fish oil, its taste and aroma were barely noticeable and pleasant. The commitee concluded that the resulting deodorized fish oil could be included in food and beverages.

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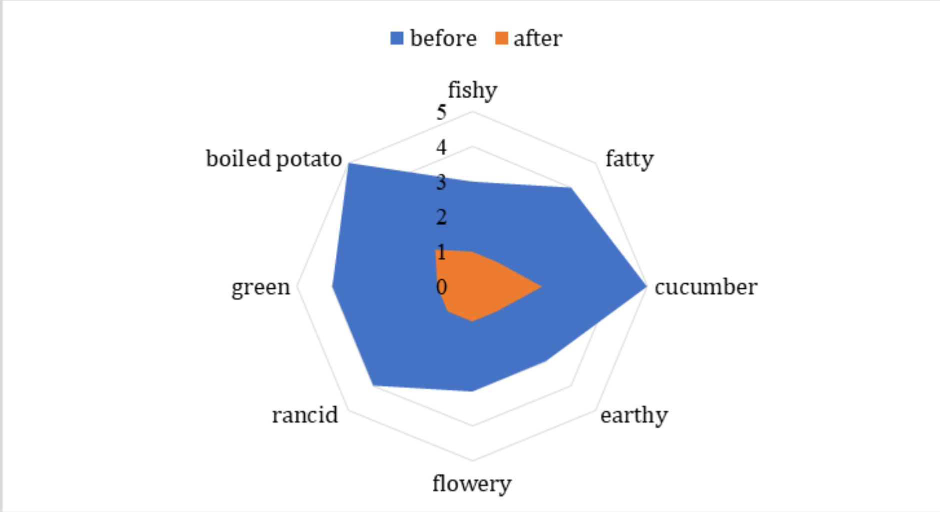


**Fig. 3. Change in intensity and odor profile after "mild" deodorization of fish oil**

It should also be noted that the mixture removed during drying under reduced pressure after low-temperature deodorization contains alcohol and acetals; the mixture is characterized by a pleasant aroma and can be used as a source of additional income. Thus, acetals are used in the aromatic industry [15].

The results of establishing the effect of low-temperature deodorization on the quality of fish oil are given in table. 2. Today in the EU the content of hydroperoxides (peroxide number), aldehydes (anisidine number) in fish oils is not standardized. The criterion is 60 mg of total volatile basic nitrogen (TVB-N) / 100 g for whole fish. However, according to EFSA, it has no scientific basis. At present, the methods to determine the peroxide and anisidine values are the most reliable chemical methods for rancidity measurements in fish oils [17] and it is better to use the value of Peroxide value, P-anisidine value (PAV) to control fat oxidation during storage.

*Table 2*

**Qualitative indicators of fish oil before after low-temperature deodorization**

| Quality indicators of refined fish oil | Fish oil № 1 (before deodorization) | Fish oil after deodorization | Standard requirements [16] |
|---|---|---|---|
| Moisture, % | 0.5 ± 0,35 | 0.41 ± 0.41 | < 1 |
| Colour | Yellow | Yellow | <3.0 Red, 30 Yellow |
| Insoluble impurities, % | 0.12 | 0.03 | <0.05 |
| Peroxide value, mmol1/20/kg | 6.32 ± 0.11 | 3.22 | <10 |
| Free fatty acid, s% (as oleic acid) | 1.21 | 1,25 | <0,10 |
| P-anisidine value | 12.22 | 13,45 | <20 |
| Odour and taste | Inherent in fish oil | Deodorized fat | Soft |

From the data shown in Table 2, we can conclude that the quality of fish oil samples after low-temperature deodorization has not deteriorated. The acid number after washing is practically equal to the initial one. Color does not change. Of course, the resulting fish oil is deodorized, but not completely refined. To fully meet the requirements for refined deodorized fish oil, deacidification and bleaching must be carried out.

The developed method of low-temperature deodorization should be carried out after bleaching, because during this process hydroperoxides are destroyed on molecules of activated bleaching clay with the formation of aldehydes and it is possible deterioration of sensory characteristics of fish oil, which minimizes the proposed method of deodorization. When Bleaching does not adversely affect the fat, deodorization should be carried out after the stage of Settling and degumming before deacidification, while the fat does not need to be further washed from the residues of acid catalyst - it will be neutralized at the stage of deacidification, drying is also carried out after this stage.

The noticeable decrease in the peroxide number can be explained by the destruction of hydroperoxides on the catalyst molecules (98 % sulfuric acid). However, hydroperoxides decompose with the formation of primarily aldehydes. This point needs to be investigated more carefully. Table 3 shows the results of changes in peroxide and anisidine numbers as a result of deodorization.

*Table 3*

**Fish oil oxidation indicators before and after low temperature deodorization**

| Sample fish oil | PV, meq/kg before deodorization | PV, meq/kg after deodorization | PAV before deodorization | PAV after deodorization | TOTOX before deodorization | TOTOX after deodorization |
|---|---|---|---|---|---|---|
| 1 | 2.3 ± 0.05 | 1.29 ± 0.04 | 3.43 ± 0.15 | 2.36 ± 0.21 | 8.03 | 4.94 |
| 2 | 2.01 ± 0.08 | 1.15 ± 0.04 | 11.05 ± 0.38 | 8.65 ± 0.18 | 15.07 | 10.95 |
| 3 | 6.32 ± 0.11 | 3.22 ± 0.07 | 12.22 ± 0.41 | 10.45 ± 0.33 | 24.86 | 16.89 |

In all the samples studied, a decrease in peroxide numbers was observed, which is probably due to the destruction of hydroperoxides under the influence of sulfuric acid. To determine how much aldehydes would be formed without undergoing the acetal conversion reaction, fat samples were treated under the same conditions, but without ethyl alcohol (only in the presence of an acid catalyst). The results are shown in Fig. 4.

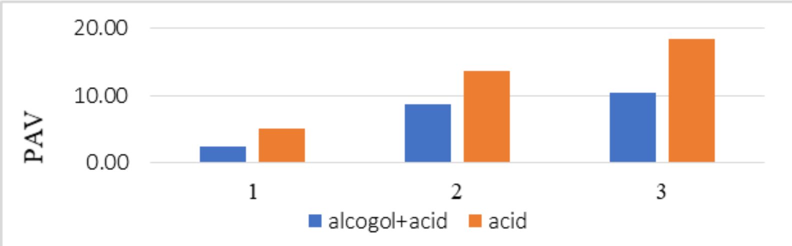


**Fig. 4. Change in anisidine number as a result of the reaction of formation of acetals and only under the influence of sulfuric acid (0.03 %), where 1,2,3 - fish oil samples**

The difference in PAV values of fish oil after deodorization (Fig. 4 three blue histograms) compared with treatment with acid alone (yellow histograms) can be explained by the conversion of aldehydes by reactions with the formation of acetals. These reactions may involve aldehydes already present in fish oil, those formed during the oxidation of fat and those formed during the destruction of hydroperoxides. In general, it should be noted that all obtained samples improved their oxidative state (the value of the TOTOX number, table. 3).

Fish oil is easily autoxidized due to its high content of polyunsaturated fatty acids. The oxidized lipids that are formed can cause adverse effects on human health [18]. Also, the taste and smell of rancid fish oil is very unpleasant, it is characterized by the possibility of deterioration of sensory characteristics, even at low oxidation levels [19].

Primary oxidation products – hydroperoxides in the subsequent stages of oxidation are destroyed with the formation of secondary oxidation products – for such unsaturated fats as fish it is mainly aldehydes, ketones, alcohols, hydroxy acids, etc. can also be formed. The oxidative status of omega-3 supplements is commonly determined by analyzing the peroxide (PV) and the para-anisidine value (PAV). The Global Organization for EPA and DHA Omega-3 s (GOED) representing the worldwide EPA and DHA omega-3 industry has set thresholds for PV, PAV as well as the total oxidation value (TOTOX = 2 × PV + PAV) to be followed by their members. It is suggested by the GOED Voluntary Monograph [20] that the PV must be under 5 meq/kg, the PAV under 20 and the TOTOX below 26 in the final product to be of acceptable quality [21].

Most of the aldehydes of fish oil (Table 1) are generated in the process of lipid autooxidation [22]. For example, hexanal is mainly formed during the oxidation of linoleic acid, it is more in deodorized fish oil compared to crude [8]. High deodorization temperatures can cause oxidation of linoleic acid.

Therefore, given the data in table. 3 (the higher the initial values of PV and PAV, the more effective their reduction after mild deodorization) was the task to investigate the possibility of restoring already oxidized fish oil (according to PV and PAV) using the developed method.

Samples of pre-oxidized deodorized fish oil were characterized by the following sensory defects: rancidity (maximum level - 5), fishy odor (maximum level - 5). One sample was pre-oxidized (№ 4), another deodorized sample (№ 5) was stored with access to oxygen at ambient temperature for two months, which is associated with a high value of its peroxide value (at elevated temperatures (eg, 90 °C). ) peroxides are destroyed).

The samples were processed under the above rational conditions. Importantly, the samples were pre-deaerated and the acetal and ketal formation reaction took place in an inert gas atmosphere to prevent oxidation. The results of changes in oxidation parameters are given in table. 4, the results of organoleptic evaluation - in Fig. 5.

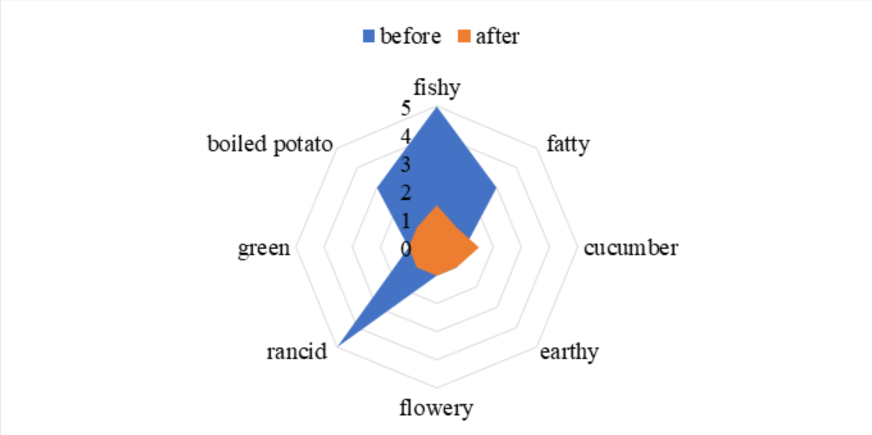


**Fig. 5. Change in odor profile of oxidized fish oil after treatment with ethyl alcohol and acid**

Aldehydes are the main odorous substances that cause a rancid odor and fishy odor in oils [22]. After treatment with ethanol and acid, these pronounced sensory characteristics of oxidized fish oil disappeared. The intensity of the smell also decreased greatly. There was a floral hue and taste of cucumber became slightly more apparent (probably as a result of incomplete excretion of aldehydes). The taste and smell of "regenerated" fish oil was pleasant, equal to the organoleptic characteristics of fresh fat.

*Table 4*

**Oxidized fish oil oxidation indicators before and after low temperature deodorization**

| Sample of oxidized fish oil | PV, meq/kg before processing | PV, meq/kg after processing | PAV before processing | PAV after processing | TOTOX before processing | TOTOX after processing |
|---|---|---|---|---|---|---|
| 4 | 18.10 ± 0.05 | 4.39 ± 0.09 | 18.87 ± 0.21 | 15.26 ± 0.30 | 55.07 | 24.04 |
| 5 | 81.45 ± 0.12 | 8.74 ± 0.11 | 9.22 ± 0.15 | 11.65 ± 0.18 | 172.12 | 29.13 |

In order to study in more detail the effect of the proposed method of deodorization on the oxidation products, the kinetics of changes in the content of hydroperoxides in the oxidized sample was studied (Fig. 6).

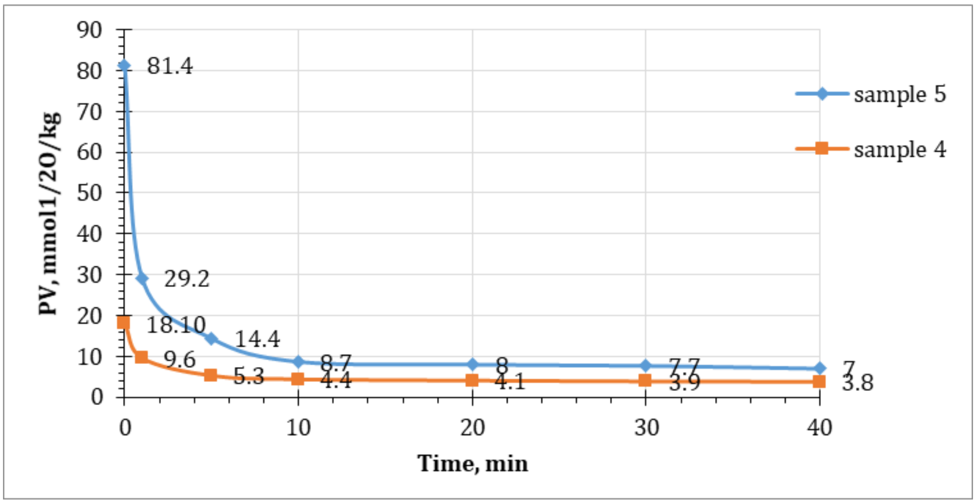


**Fig. 6. Kinetics of reducing the content of hydroperoxides in oxidized fish oil under the influence of ethyl alcohol (5 %) and concentrated sulfuric acid (0.03 %)**

The PV kinetics curve of sample 5 is explained by its high peroxide value (81.45 meq/kg), peroxides are destroyed with the formation of significant amounts of aldehydes, most of which, however, react with the formation of acetals.

Given the results of the kinetics of changes in the content of oxidation products, the feasibility of using a certain rational time of treatment of fish oil (10 min) with ethyl alcohol in the presence of an acid catalyst is confirmed.

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Significant reduction of accumulated oxidation products in this process makes it interesting not only for deodorization, but also as a method of restoring the quality of fish oil, extending its shelf life, etc.

The new method makes it possible to significantly reduce the deodorization temperature (up to 90 °C under normal conditions or lower under reduced pressure), which leads to the following positive results:

- energy saving, simplification of equipment used for deodorization. The use of the method makes it possible to deodorize fish oil in small industries;

- reducing the content of oxidation products. The first oxidation products - hydroperoxides in the process of mild deodorization decompose to form secondary oxidation products - aldehydes and ketones. Aldehydes and ketones are mainly converted to acetals and ketans and do not participate in further oxidation reactions. In this way, the rate of oxidative processes is slowed down, which allows you to get more stable fish oil. Also under the influence of high temperatures of traditional deodorization (180–270 °C), under the influence of sharp steam PUFA are unstable, enter into reactions of polymerization, cyclization, migration of double bond which do not occur at temperatures less than 100 °C.

- no formation of trans-isomers of fatty acids, which are formed at high temperatures, typical of traditional deodorization. Their content in deodorized fish oil is usually equal to 1–3 % [23];

- absence of MCPD-esters and esters of glycidyl. It is known that 3-MCPD-esters and glycidyl esters are formed at the stage of fat deodorization at a temperature: for 3-MCPD esters - from about 140 °C and above, for glycidyl esters - from 230 °C [23]. That is, when using the method of low-temperature deodorization, they simply can not be formed in appreciable quantities, even in the presence of precursors;

- proved the possibility of restoring oxidation, initial taste and odor as a result of processing of rancid fish oil by low-temperature deodorization.

## Conclusion

A fundamentally new method of deodorization of fish oil is proposed, based on the possibility of chemical transformations of the main donating components of fish oil

The rational conditions for mild deodorization are as follows: the amount of ethyl alcohol – 5 %, the reaction time – 10 min., the deodorization temperature – 90 °C, concentrated sulfuric acid (98 %) in the amount of 0.03 %.

When using a new method of low-temperature deodorization there is no deterioration of the quality of fat. However, there is a significant reduction in the content of oxidation products - hydroperoxides and aldehydes, which allows you to use the method to improve the quality of fish oil. The taste and smell of the obtained fish oil meets the requirements for deodorized fats.

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