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# ANALYSIS OF THE INFLUENCE OF ROSEMARY AND GRAPE SEED EXTRACTS ON OXIDATION THE LIPIDS OF PEKING DUCK MEAT

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*Для гальмування окислювальних процесів у фарші з м'яса качки Пекінської використовували композицію з екстрактів розмарину та виноградних кісточок, яка містить комплекс антиоксидантів. Внесення композиції до фаршу з м'яса качки дозволяє уповільнити гідролітичне та перекісне окислення ліпідів. Отримані результати доводять перспективність використання композиції у технології фаршевих виробів з високим вмістом жиру*

*Ключові слова: окислення ліпідів, екстракт розмарину, виноградні кісточки, кислотне число, перекісне число*

*Для торможения окислительных процессов в фарше из мяса утки Пекинской использовали композицию экстрактов розмарина и виноградной косточки, которая содержит комплекс антиоксидантов. Внесение композиции в фарш из мяса утки позволяет замедлить гидролитическое и перекисное окисление липидов. Полученные результаты доказывают перспективность использования композиций в технологии фаршевые изделий с высоким содержанием жира*

*Ключевые слова: окисление липидов, экстракт розмарина, виноградные косточки, кислотное число, перекисное число*

## 1. Introduction

Qualitative properties of meat products may deteriorate due to lipid oxidation during processing of meat raw materials and storing finished products. The oxidative processes in the lipid fraction of meat products lead to the accumulation of primary and secondary oxidation products, which affects the nutritional value and quality of the food products [1].

The most common way of solving the problem of oxidative damage to meat products is the use of a variety of antioxidant food additives that allow the purposeful regulation of the processes of oxidation of the lipid fraction of meat systems.

The use of nutritional additives and plant components with antioxidant effect can purposefully provide the necessary technological outcome, minimizing the introduction of these substances to stabilize the quality of meat products [2, 3].

Important directions of research are the substantiation of the expediency of using antioxidants of natural origin, the influence of these substances on the oxidation processes

in various meat products, and the determination of effective and optimal concentrations of the active substances.

## 2. Literature review and problem statement

Oxidation of lipids, which represents a complex and difficult process, is initiated in subcellular membranes in the fraction of highly unsaturated phospholipids. Unsaturated fatty acids of membrane phospholipids are oxidized by the formation of hydroperoxides. Oxidation products tend to decompose into secondary oxidation products such as short-chain aldehydes, ketones, and other compounds. Accumulation of such products can adversely affect the overall quality and compliance of meat products with standards [4].

Antioxidants are compounds that are donors of hydrogen ( $H^+$ ), which suppresses the chain reaction of free radical oxidation. It effectively inhibits the oxidative processes of lipids without any negative changes in the nutritional and

organoleptic properties of meat products, and it prolongs their shelf life [4].

In the living muscles of animals, there are many factors preventing oxidation. However, these factors disappear during the processing of meat, which in turn requires further supplementation of meat products with additional doses and/or sources of antioxidants [5].

Taking into account the aforementioned, the meat industry for a long time has used synthetic antioxidants such as butylhydroxytoluene (BHT) and butylhydroxyanisol (BHA) to suppress the formation of free radicals effectively. However, concern about the safety of these substances has given rise to a number of studies of new natural sources of antioxidants for delayed oxidative degradation of lipids [1, 2, 4–6].

Natural antioxidants have a high potential for applying them in the meat industry, but the use of such elements has certain limitations due to the lack of data on their efficacy in different types of meat raw materials. Therefore, the search for various types of natural antioxidants and a study of the effects of these substances on the oxidative processes in meat products are important present-day tasks.

In order to inhibit oxidative processes in meat products, various types of antioxidant preparations of plant origin are proposed [7, 8]. The effectiveness of such complexes is determined by the high content of phenolic and other active ingredients that can effectively prevent the initiation or propagation of oxidative reactions. At the same time, some of them (rosemary and oregano) have shown higher antioxidant activity than the synthetic BHT and BHA [9].

The effectiveness of using spice extracts in the production of meat foods has been demonstrated by a number of researchers [10, 11]. Various natural antioxidants (including *Rosmarinus officinalis* and *Origanum vulgare*) have also shown a positive effect on the color and sensory characteristics of meat products.

The antioxidant action of natural herbal substances occurs due to the presence of various groups of biologically active elements. Plants belonging to the Labiatae family (rosemary, oregano, sage, marjoram, etc.) have high contents of flavonoids, phenolic acids, rosemary and caffeine acids, carnosol, and carnosine acid. Red grape processing products, namely, the skin, seeds and extracts of red grapes are known for high concentrations of gallic acid, catechins (routine and quercetin), anthocyanins, and resveratrol [12]. This gives reason to consider winemaking wastes as effective sources of antioxidant substances for using in the food industry.

There have been studies [13–16] that consider the use of medicinal plant extracts, including dihydroquercetin, as sources of antioxidants.

The efficiency of using thistle to improve the quality and to increase the storage time of sausage products was studied in [13, 14]. In the conducted research, the authors found that the shelf life of sausages made from mechanically separated meat (MSM) of poultry complied with the normative documentation of preserving for 15 days at a temperature of 6 °C. However, after 5 days of storage, the peroxide value (PV) of the control samples exceeded 0.1 % J<sub>2</sub>. The use of the thistle extract in the maximum allowable dose (40 mg per 100 g of minced meat) made it possible to slow down the undesirable processes: the peroxide value in the experimental sausages reached a critical level only after 10 days. The antioxidant effect is explained by the presence of phenolic compounds, including flavonoids and phenolic acids, in the thistle extract.

Studies [15, 16] are devoted to the use of dihydroquercetin (DHQ) to increase the usefulness of semi-finished meat products. This compound belongs to the group of vitamin P, the raw material for obtaining which can be Siberian larch wood, grapes, eucalyptus, rose petals, and other plant varieties. The DHQ substance inhibits oxidation of fat of meat samples, which is confirmed by a lower peroxide value. At the beginning of storage, there is no development of secondary oxidation products. The comparative estimation of the antioxidant efficacy of various concentrations of DHQ (0.02 %, 0.08 %, and 0.2 %) and BHT showed that in samples with adding DHQ in the amounts of 0.08 % and 0.2 %, there is complete inhibition of oxidation processes during the whole storage time. The peroxide values in the samples at these concentrations were 97.3 % and 98.2 % lower than in the reference [15, 16].

Investigation of the effect of encapsulated forms of oleoresin spices showed that essential oils also exhibit both antioxidant and bacteriostatic characteristics, which helps achieve effective extension of the shelf life of cooked sausage products [17].

The authors of [18, 19] developed a polyfunctional additive Maltovin. It is based on the extract of polyphenolic compounds of grape seeds and maltodextrin as a carrier of biologically active compounds. The additive was developed for semi-finished meat products. Investigation of the influence of Maltovin on the functional and technological properties of minced meat has shown that the additive Maltovin exhibits high functional properties necessary for the production of meat products (especially for chopped semi-finished products). In addition to improving the functional characteristics of products, Maltovin prolongs the shelf life of fat-containing products due to antioxidant properties [18, 19].

The authors of [20, 21] provide data on the antioxidant properties of such phytoplankton supplements as extracts of the Baikal skullcap (*Scutellaria baicalensis*), the cynarrhodium fruit, the rowanberry, hawthorn berries (fresh and frozen), as well as dry herbs of tutsan and thyme (leaves and flowers).

Of considerable interest are phenolic compounds of grapes, both of seeds and skin, due to the antioxidant properties and the ability of these compounds to absorb free radicals. Clinical studies have proven that antioxidant properties and the ability to absorb free radicals of oligomers of procyanidins of grape seeds are 20 times stronger than of vitamin C and 50 times stronger than of vitamin E [22]. The phenolic substances of grape seeds protect vitamins from early oxidation and allow vitamins to perform their functions where necessary. Procyanidines have been proven to prevent the growth of cancer cells and to have anti-mutagenic activity [23].

Some studies [24, 25] are devoted to the efficiency of using imported extracts of medicinal and spice-aromatic plants such as salvia, rosemary, ginger, and green tea. As a result of studying the antioxidant properties of the plant extracts, it was found that the highest content of total fat-soluble and water-soluble antioxidants is in the extracts of rosemary and green tea. It has been shown that using rosemary and green tea extracts to stabilize the lipids of minced semi-finished meat products can reduce the rate of forming products of hydrolysis, as well as primary and secondary oxidation of lipids [25].

The Department of Technology of Milk and Meat of Sumy National Agrarian University (Ukraine) researched the effectiveness of using cranberry and blackcurrant ex-

tracts in the production of cooked sausages from Peking duck meat. It has been proved that the use of the extracts of cranberry and blackcurrant in the technology of meat-containing sausage can slow down the flow of oxidative processes. The most effective concentrations of the substances were the extract of cranberry in the amount of 0.02 % and the extract of blackcurrant in the amount of 0.01 %. Sensory evaluation revealed that adding the cranberry extract in the amount of 0.1–0.3 % did not aggravate the organoleptic characteristics of the cooked sausages. The study of the microbiological indicators demonstrated safety of the cooked sausages during the production and storage of the meat products [26].

### 3. The aim and objectives of the study

The aim of the research is to determine the effectiveness of using the extracts of rosemary (RE) and grape seed (GSE) in the technology of minced Peking duck meat with high lipid content, which will help inhibit oxidative processes and improve the quality of products.

To achieve this aim, the following objectives were set to be solved:

- to determine the antioxidant properties of a mixture of rosemary and grape seed extracts;
- to study the influence of the RE and the GSE on the course of oxidative processes in minced duck meat (acid value, peroxide value, and thiobarbituric acid value);
- to establish the optimal concentration of the RE and the GSE for inhibiting oxidative processes in the minced duck meat.

### 4. Materials and methods of studying the influence of rosemary and grape seed extracts on the oxidation of Peking duck meat lipids

To solve the problems as a model for studying the influence of the RE and the GSE on the process of oxidative processes in meat products, the raw material was Peking duck meat (DSTU 3143:200. Poultry meat (carcass). General technical conditions), which has a high content of lipids – 37–40 %, including polyunsaturated fatty acids (PUFAs) – 17.5 %. The duck meat was prepared according to the standard technological scheme. The duck meat was crushed, shredded and minced on a meat mincer with the grille hole diameter of 2–3 mm. The minced meat was supplied with a rosemary extract (Food Ingredients Mega Trade, USA). As the second antioxidant preparation, a grape seed extract was added to the minced meat. The substance had been extracted by water-alcohol extraction (1:4) in a 60 % solution of ethyl alcohol of grape seed powder from the Isabelle red grapes, Mak-Var, Ukraine.

In more detail, the methods of studying the influence of rosemary and grape seed extracts on the oxidation of the duck meat lipids are presented in [27].

### 5. Results of studying the influence of rosemary and grape seed extracts on the oxidation of Peking duck meat lipids

To characterize the effect of antioxidants of the composition on the course of hydrolytic processes in the lipid fraction of the duck meat, the AV was determined, as shown in Fig. 1.

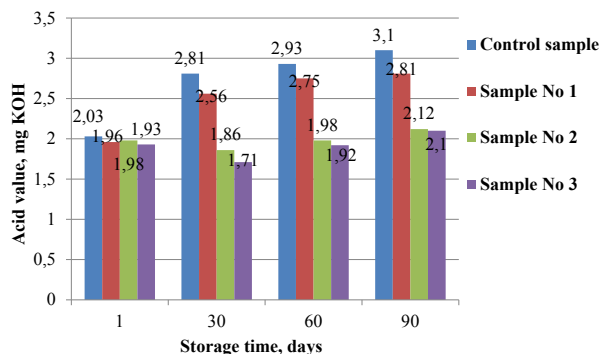


Fig. 1. The dependence of the acid value on the concentration of the added antioxidant composition

The decomposition of fats with the formation of fatty acids can accelerate the oxidation process, since the primary oxidation happens to free acids, not bound into triglycerides. The processes of fat hydrolysis in the experimental samples throughout the storage period were slower than in the reference. In the control sample, the AV on the 30th day of storage was  $2.81 \pm 0.13$  mg KOH; on the 60th day, it was  $2.93 \pm 0.09$ ; at the end of the storage period, it was  $3.10 \pm 0.12$  mg KOH. This tendency indicates a direct proportional dependence of the rate of accumulation of free fatty acids on the concentration of the antioxidant composition [28, 29].

Among the experimental samples, the smallest amount of free fatty acids was observed at the concentration of antioxidant composition in sample 3: after a month of storage, the AV in sample 1 reached  $2.56 \pm 0.12$  mg KOH; in sample 2, it was  $1.86 \pm 0.14$ , and in sample 3, it was  $1.71 \pm 0.13$ , which was 40 % lower than in the control sample. At the end of the storage period, the AV in the experimental samples was  $2.81 \pm 0.13$  mg KOH in sample 1;  $2.12 \pm 0.01$  in sample 2; and  $2.10 \pm 0.12$  mg KOH in sample 3. The obtained results indicate that the introduced complex inhibits fat hydrolysis by combining the flavonoids with the extract of rosemary and polyphenols of the grape seed extract. The most effective variant was the composition of sample 3. This is due to the fact that the increased concentration of extracts in the composition inhibits the hydrolytic decomposition of acylglycerides.

The dynamics of the AV shift in the minced duck meat is shown in Fig. 2.

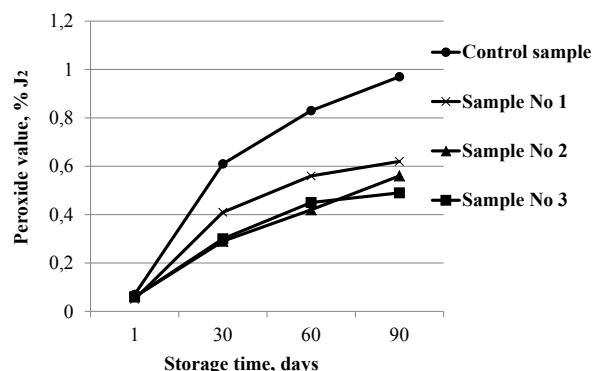


Fig. 2. The dependence of the peroxide value on the concentration of the added antioxidant composition

The study of the peroxide oxidation dynamics in the samples shows that among the experimental samples of minced meat, the PV increased more intensively in the

sample without supplementation, and the addition of the antioxidant compositions in all three concentrations slowed down the oxidative processes. The largest stabilizing effect was produced by the concentration composition in sample 3. The PV in this sample on the expiration date was  $0.43 \pm 0.001 \% J_2$ , whereas in the control sample, this value was  $0.97 \pm 0.002 \% J_2$ .

The antioxidant action of the additives is also manifested in the accumulation of mono and di-aldehydes that react with 2-thiobarbituric acid. To determine the volume of accumulation of secondary oxidation products on the last day of storing the fat samples, the thiobarbituric acid (TBA) value of the fat was studied, and the TBA results are presented in Fig. 3.

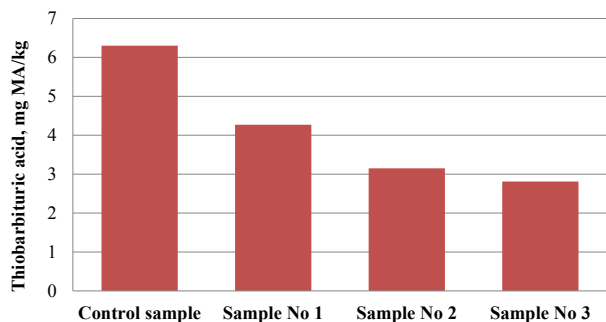


Fig. 3. The influence of bioflavonoids of the antioxidant composition on the accumulation of secondary products of oxidizing the lipids of the minced duck meat

Secondary oxidation products, namely, peroxides and hydroperoxides, are carriers of unpleasant taste and odor of oxidized fats. Adding a composition of antioxidants helps slow down the accumulation of secondary oxidation products. At the end of the storage period, the amount of secondary oxidation products in the control sample was  $6.30 \pm 0.17$  mg MA/kg of the minced meat, whereas in the experimental samples it had reached the following values:  $4.27 \pm 0.21$  mg MA/kg in sample 1,  $3.15 \pm 0.11$  mg MA/kg in sample 2, and  $2.81 \pm 0.15$  mg MA/kg in sample 3.

The composition of the extracts of rosemary and grape seeds was the most effective in sample 3, where the amount of malonic aldehyde in the minced meat at the end of its shelf life was the lowest; it was 2.24 times lower than in the control sample.

## 6. Discussion of the results of studying the influence of rosemary and grape seed extracts on the oxidation of Peking duck meat lipids

The research findings confirm the high antioxidant activity of rosemary and grape seed extracts, whose effectiveness is due to the presence of flavonoids, phenol acids, terpenoids, and polyphenolic compounds [12, 30, 31]. The combination of the extracts in the antioxidant composition contributed to the inhibition of the oxidation of the Peking duck meat lipids.

The process of hydrolysis of fat in the experimental samples proceeded more slowly than in the control but at practically the same speed. The obtained results testify that the introduced complex of the plant extracts essentially influences the hydrolysis of fat in addition to inhibiting the action of lipolytic enzymes.

This is due to the fact that flavonoids effectively inhibit freely radical chain reactions and significantly affect the lipolysis of acylglycerols – not as individual components but in the complex, showing the effect of synergism. A similar view is made by the authors of [9, 32], who show that the extract of rosemary has a higher antioxidant activity than individual phenol compounds separately (carnosine acid or carnosol). The contents of catechin, epicatechin, routine and resveratrol in the grape seed extract also produce high antiradical activity. In particular, resveratrol is a potent antioxidant that can inhibit oxidative processes with antioxidant activity higher than of BHA [33].

The study of the dynamics of the peroxide values in the samples indicates that adding the antioxidant compositions of the extracts of rosemary and grape seeds produces an optimal ratio of biologically active compounds. The inhibition of lipid peroxidation is associated with high contents of carnosine and rosemary acids in the rosemary extract; therefore, the activity is twice as high as the activity of the synthetic antioxidants of BHT and BHA [32]. When adding the antioxidant composition, the components of the extracts of rosemary and grape seeds make it impossible to add oxygen to the glycerides, thereby inhibiting the flow of oxidizing processes in the minced meat. The arnosic acid and carnosol block the peroxide radicals particularly effectively in systems based on the high content of lipid components.

The research on the content of secondary oxidation products has helped estimate the depth of the oxidative processes occurring in the minced meat samples during storage for 90 days at a temperature of  $-10^{\circ}\text{C}$ . The concentration of the secondary oxidation products was the highest in the control sample, whereas in the experimental samples, it was reduced proportionally to the concentration of the introduced antioxidant composition. Catechin and epicatechin of the grape seed extract are active absorbers of oxygen, which prevents the formation of hydroperoxides and propanal [31]. The effectiveness of the composition depended on the concentration. The extracts in the composition were in the ratio of 0.06 % of the rosemary extract and 0.3 % of the grape seed extract.

According to studies [7, 12], phenol carboxylic acids effectively inhibit anions of free radicals, whereas carnosic acid and carnosol effectively block metal chelates, which increases the antioxidant capacity of plant phenols. The antioxidant activity of individual compounds depends on the number of  $-\text{OH}$  groups in the aromatic ring. As a result, the combination of active substances with higher content of hydroxyl groups in the cyclic structure increases the effect of inhibiting free radical oxidation of lipids in meat systems. The results show that the composition of the rosemary and grape seed extracts has a high antioxidant effect, and the magnitude of the effect is directly proportional to the concentration of the rosemary and grape seed extract in the minced duck meat. The highest effect is obtained by using the composition of sample 3, with the extracts in the composition being present in the ratio of 0.06 % of the rosemary extract and 0.3 % of the grape seed extract, which is associated with the highest concentration of antioxidants in the composition of different chemical nature.

Adding the composition of the rosemary and grape seed extracts did not alter the organoleptic properties of the minced meat due to the low concentration of the studied substances.

The obtained results can be applied in the technologies of producing semi-finished products from minced meat, in particular minced duck meat.

A possible interest in further research may be posed by a combination of the extract compositions of antioxidant properties with active packaging elements [33], which also provides a certain perspective on the use of long-term storage product technologies.

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## 7. Conclusions

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1. The conducted research has confirmed the high antioxidant activity of the composition of rosemary and grape seed extracts and the effective inhibition of the oxidation process of duck meat lipids.

2. Adding the RE and the GSE in the form of a composition in the amount of 0.12–0.36 % helps slow down the hydrolytic oxidation of the minced meat lipids by 10.5–32.5 %. As a consequence, the stabilization of the peroxide oxidation of the minced Peking duck meat inhibits the formation of secondary oxidation products such as pentanal, hexanal, malonic aldehyde and others, which is confirmed by the results. The amount of secondary oxidation products reacting with thiobarbituric acid was the lowest at the end of the storage period for the minced meat in the sample with the composition concentration of 0.36 %, when the TBA value was  $2.81 \pm 0.11$  mg MA/kg, which was more than twice as low as the control.

3. The strongest effect was obtained when using the additive in the amount of 0.36 %, which reduced the oxidized fat spoiling more than twice.

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