Хроматографічним методом досліджено поліфенольний склад виноградних порошків grape seeds powder (GSP) і defatted grape seeds flour (DGSF) в водно-спиртових (етанол, ізопропанол) екстрактах. Встановлено вміст антиоксидантів, що присутні в вигляді фенольних кислот (галова, елагова), стилбенів (ресвератрол) та флавоноїдів, насамперед, флаванолів (катехін, епікатехін) та флавонолів (кемпферол, мирицитин, кверцетин та його похідні гликозиди). Показано, що загальний вміст поліфенолів досягає максимальної величини – майже 4,5 % в галовому еквіваленті від маси порошку при екстрагуванні водно-етанольною сумішшю з вмістом етанолу 50 % (w/w). В якості маркерів процесу утворення згірклості, що зумовлена окисненням та гідролізом жирів, досліджено вплив фенольних антиоксидантів на перекисне (PV) та кислотне (AV) числа кондитерських жирів лауринового та нелауринового типів в модельних системах. Доведено, що завдяки високому вмісту у виноградних порошках антиоксидантів, додавання цих порошків до складу зразків суттєво уповільнює процеси автоокиснення жирів. Показано, що виноградні порошки як рослинна сировина є більш стабільними з точки зору активізації процесу гідролізу жирів у кондитерській глазурі. Про це свідчать дані з активності ферменту ліпаза, що констатують нижчі значення у зразках порошків з виноградних кісточок – 1,03 та 1,12 см^3/г для GSP та DGSF, відповідно, порівняно з такими у різних зразках какао-порошків – 0,84 та 1,87 см^3/г. Дослідження зміни кислотного числа зразків також засвідчило, що додаванням GSP та DGSF як джерела антиоксидантів значно інгібує процес гідролізу жирів до вільних жирних кислот. Отримані результати мають практичне значення для удосконалення процесу виробництва кондитерської глазурі в напрямку часткової заміни какао-порошку порошками з виноградних кісточок. Це сприятиме створенню продукту підвищеної харчової цінності та більш стійкого до псування жирів

Ключові слова: порошок з виноградних кісточок, поліфенольні антиоксиданти, автоокиснення жиру, гідроліз жирів, стабільність глазурі до окиснення, ліпаза

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INFLUENCE OF GRAPE SEEDS POWDER ON PRESERVATION OF FATS IN CONFECTIONARY GLAZE

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1. Introduction

Under current conditions, the activity of specialists in confectionery industry is aimed at resolving the issues to provide people with high-quality safe foods that have the balanced chemical composition. Given this, a special role belongs to the development of new technologies to produce healthy foods that make use of the enriching additives of plant origin. On the one hand, plant additives are a source of biologically active substances (BAS), on the other hand, they are used as thickeners, colorants, they make it possible to form a new consistency of products, as well as provide original organoleptic characteristics.

The grape is one of the most cultivated crops in the agricultural world market. According to the data of the statistical database FAOSTAT (Food and Agriculture Organization (FAO) of the United Nations), the produce worth USD 67.5 billion was manufactured in 2016 [1]. Much of this production is used in wine making industry [2]. However, according to data from [3], almost 20 % of weight of wine making material are made from waste, the so-called pomace, which is the remains of pressed grape (skin, seeds), small pieces of stems. As it is known, these wastes from production are a source of valuable BAS. Currently, there is a reviving interest in the use of these biologically active components of secondary vegetable raw materials with functional properties (texture, coloration, antioxidants, aromatization, or taste) for the needs of industry, in particular, food industry [4]. A special place among the BAS of plant origin is taken by those that contain antioxidants blocking the negative effect of free radicals on the body [5]. For economic reasons, the predominant sources of antioxidants are secondary products of processing vegetables and fruits, because they are inexpensive and often have a high concentration of biologically active substances. This approach is a part of the modern perspective concept of biorefinery as a concept of waste-free production [6]. Under this concept, the grape seeds produced in large quantities as a residue of wine making find their application in the industry.

The research into grape seed powders revealed the existence of a significant amount of substances of phenolic nature, specifically, resveratrol, catechin, epicatechin, gallic acid, quercetin, rutin, antioxidants, etc. [7, 8]. This gives a basis for the application of the specified raw materials as natural antioxidants that may inhibit the process of oxidation of lipids and act as substitutes of the known effective synthetic antioxidants, BHT, BHA and TBHQ [9].

From this perspective, the study of the application of grape powders as an antioxidant ingredient in technologies of production of confectionery fat-containing products is a promising subject.

2. Literature review and problem statement

Over the past decade, there started the tendency to use grape seeds and skins powders in the food industry [2]. This natural raw material that is the product of grape pomace processing has a high content of antioxidants in the form of phenolic substances [10, 11].

The most attractive from the economic point of view is the use of grape seeds in food technologies in the form of defatted finely ground powder (flour). This raw material is produced in the process of grinding the oil cake after cold-pressing grape oil.

The use of this flour in a non-conventional ingredient quality that is an inhibitor of fats oxidation led to positive results. This is especially true of the technology of various meat products. Thus, in paper [12], it was shown that the addition of the composition with the content of 0.6 % grape seed extract and 0.03 % of rosemary extract contributed to the inhibition of oxidation of lipids of Beijing duck. This fact was obtained thanks to the research into the influence of antioxidants of the composition on the change of acid value. Similar results, but exclusively with the addition of only grape seeds extract in a range of 100–300 ppm, were obtained for beef sausage products with addition of pork fat [13]. The authors had shown that grape seeds extract has better protective properties against oxidation of fats than well-known propyl gallate. In paper [14], low-fat finely ground powder from grape seeds was added in the amount of 1.5 % and 3.0 % to the formulation of the Turkish dry fermented smoked sausage Sucuk. The addition of the powder enabled the authors to get the results that showed increased resistance of the final product to oxidation. This fact was explained by the result of the influence of phenolic substances on the oxidation of the meat product. Antioxidant and antimicrobial effectiveness of the grape seed extract was studied in the restructured lumps of mutton under aerobic and vacuum packaging conditions during its storage in the refrigerated state [15]. The addition of the 0.1 % extract to meat improved the shelf life to at least 28 days. A comparison of the antioxidant potential with that of synthetic antioxidant BHT enabled the authors to conclude a remarkable antioxidant and antimicrobial properties of grape seed extracts. This fact is another sign of the trend on the possibility of replacing synthetic antioxidants with natural ones without deterioration of the resistance of the finished product [16].

The above papers show the high potential of grape seeds powder in inhibiting the processes of oxidation of fats of animal origin, which gives a good basis for conducting research into the products with the high content of vegetable fats. From this perspective, grape powder should be considered as one of the most promising raw materials in the technology of confectionery glaze, which is a product with a high fat content. Glaze is the most common semi-finished product to decorate many products, such as chocolates, biscuits, glazed cottage cheese, ice cream, etc. By its organoleptic quality indicators and technological properties, these powders are very similar to cocoa powder but have a richer chemical composition in comparison to them and are characterized by a higher content of the substances with antioxidant properties. This is the basis for obtaining the produce of high biological value and wellness.

Thus, it is recommended to use grape pomace powders in the technologies of flour confectionery products [17]. An undoubted advantage of this approach is that grape powder, unlike cocoa, is the raw material of local origin and has a significantly lower cost. However, there are not enough data on the composition and effect of grape powder on the oxidation of confectionery fats.

The existence of a significant content of substances with antioxidant properties makes it possible to assume that grape seeds powder can make an inhibiting effect on the processes of oxidation of fats in the glaze and affect the extension of the duration of storage of glazed products. These potential benefits of grape powders as raw material in the technology of confectionery glaze require a detailed study of the polyphenolic composition of the powders and their influence on the processes of hydrolysis and oxidation of fats in the composition of this product.

3. The aim and objectives of the study

The aim of this research was to study the influence of grape seeds powders as a source of natural antioxidants on the inhibition of the process of fats oxidation in the model fat-containing systems that make up the base for confectionery products.

To accomplish the aim, the following tasks have been set:

– to determine the phenolic composition of grape seed powders;

– to study the antioxidant properties of water-ethanol extracts of the DGSF powders to characterize the total antioxidant potential of phenolic compounds;

– with the help of the study of peroxide value of model systems with the content of lauric and non-lauric fats, to establish the effect of grape seeds powders on the fats oxidation process;

– to investigate a change in lipase activity at replacing a part of cocoa powder with the grape seeds powder in model systems;

– to explore, by measuring the acid value, the influence of lipase enzyme content in the powders on the process of fats hydrolysis in the model samples.

4. Materials and methods to study the antioxidant properties of grape seeds powders

4. 1. Reagents and materials

The following chemical reactants were used in the experiment: potassium bromide, potassium iodide, sodium hydroxide, sodium carbonate (Reachim, Russia); sulfuric acid (Khimprom, Ukraine), gallic acid (Sigma Aldrich, the United States). All of the reactants are qualified as "chemically pure".

The reagent Folin-Ciocalteu was prepared according to procedure [18] using reagents qualified as "chemically pure". For the analysis, we used the resulting 2 M solution. For the preparation of aqueous solutions and extracts, distilled water with electric productivity not worse than 0.55 mS/m was used. 96 % ethyl alcohol (Ukraine) and isopropyl alcohol (Ineos Solvents, Germany) were used to make alcoholic extracts.

Cocoa powders CP1 (brand "Mriya", Ukraine) and CP2 (ADM COCOA Polska Sp. Zo. o., Poland) were used in the study.

4. 2. Samples

For research, we selected the samples of grape seeds powders (*Vitis vinifera L.),* obtained under industrial conditions from the mixture of grape seeds of varieties *Cabernet Sauvignon, Cabernet, Muscat Blanc à Petits Grains, Muscat* of the harvest of 2015–2017, which are cultivated and processed in the region of Odessa oblast (Ukraine). Two kinds of grape powder were studied:

– the powder obtained by crushing grape seeds, separated from grape pomace of GSP (Grape Seed Powder);

– the powder, obtained by crushing the oil cake of the grape seeds, separated after cold pressing grape oil, DGSF (Defatted Grape Seed Flour), which is a commercial product under the trade mark OleoVita (Orion, Ukraine).

A precisely weighted batch of grape seed powder (according to the ratio of liquid/solid) was placed in glass test tubes of 15 ml total volume. 10 ml of an appropriate solvent was added and the test tube with screw caps. The extraction was carried out in the dark at the appropriate temperature, the ratio of solid-liquid and the extraction time. The contents of the tubes were periodically shaken. The liquid after extraction was separated from solid substances by centrifuging over 6,000 g for 10 min (OB-8UHL4.2, Russia). Each test was conducted twice and the result was averaged.

The influence of grape powders on the processes of oxidation of confectionery fats was studied in model systems. To do this, six samples were prepared: two control samples – cocoa butter substitute of lauric type (CEBESTM MC 80, AAK, Poland) and cocoa butter substitute of non-lauric type "Olivia glaze lux" (JSC "Zaporizhia oil and fat factory", Ukraine); four experimental samples: lauric fat from GSP and DGSF, cocoa butter substitute non-lauric fat with GSP and DGSF. The ratio of fat and powder in the model systems was the same as in the formulation of confectionary glaze and was 100:15. The samples for acceleration of the oxidation processes were kept in the thermostat at the temperature of 30 °C for 42 days.

4. 3. Research methods for the polyphenolic composition of grape seeds powder

The chemical composition of grape seeds powders in the extracts were studied by the chromatography method (GC-MS). The research procedure is given in detail in [19].

4. 4. Determining the total antioxidant capacity of extracts from grape seeds powders

TAC (Total Antioxidant Content) of simples was determined by galvanostatic coulometry with electronegative bromine [20, 21]. The values of TAC were expressed in mg of gallic acid in calculation per weight unit of dry matter (mg GAE/g DW) using linear regression coefficients for the dependence of the quantities of electricity on the concentration of standard aqueous solutions of gallic acid: slope 2.263 and intercept 0.2567 [21].

4. 5. Determining the total content of phenolic substances

The TPC (Total Phenolic Content) was determined by the spectrophotometric method with reactant Folin-Ciocalteu according to Singleton and Rossi [18, 22] with the transition from volume to mass concentration. The aliquot of the sample solution, the standard solution or the blank solution of the weight of 0.1 mg was mixed with 0.5 mg of reactant Folin-Ciocalteu and 2.0 mg of water. The samples of DGSF extracts were previously diluted by 10 times. The mixture was kept at the room temperature for up to 8 min, after which 1.5 mg of 20 % (w/w) aqueous solution of sodium carbonate was added. The volume of the solution was brought by water to 10.0 mg. The obtained solutions was incubated for 30 min in thermostat 1TZhH-0.03 (Russia) at 45±0.2 °temperature. After the solutions acquired blue color, measurement of absorbance was carried out in spectrophotometer SF-46 (Lomo, Russia) at wavelength of 765 nm against a blank sample. The TPC of the samples were expressed in mg of gallic acid per weight unit of dry matter (mg GAE/g DW) using linear regression coefficients for the dependence of optical density on the concentration of the standard aqueous solutions of gallic acid: slope 0.001036 and intercept 0.00262 [21].

4. 6. Studying the peroxide and acid values and the activity of lipase

PV (Peroxide Value) and AV (Acid Value) of fats were determined by standard methods [23]. PV was expressed in mmol/kg ½O, and AV was expressed in mg KOH/g of the sample.

The activity of the enzyme (AL, cm^3/g) lipase was determined by the titrimetric method [24]. The samples were prepared in accordance with [25]. We calculated the activity of lipase from formula (1)

$$AL = \frac{(a-b)k}{m}, \qquad (1)$$

where a is the amount of 0.1 mol/dm^3 of potassium hydroxide solution, consumed by the titration of the studied sample, cm^3; b is the same for the control sample; k is the correction coefficient to 0.1 mol/dm^3 of potassium hydroxide solution, k=1; m is the batch of fat, g.

4. 7. Statistical processing of results

A single-factor dispersion analysis (ANOVA) was used for a series of parallel measurements (n=3–4) was used for statistical processing. The difference in values was analyzed by the Student's t-test with statistical significance ($p<0.05$). All experimental values are given in the form $X \pm \Delta X$, where X is the mean value of the experimental magnitude and ΔX is its confidence interval. Statistical processing of the data was carried out by using Excel program of Microsoft Office 2010 (Microsoft Corp., USA) and IBM SPSS Statistic v. 20 (IBM Corp., USA).

5. Results of research into the influence of antioxidants of grape seeds powders on the processes of fats oxidation

5. 1. Studying the antioxidant properties of grape seeds powders

The CG-MS analysis [19] of isopropylic extract of GSP and DGSF (Fig. 1) was conducted earlier. The identification of chemical compounds based on the duration of aging made it possible to determine 32 individual chemicals in these powders. The existence of fatty acids, benzoic and lilac aldehydes, various representatives of phenolic compounds was detected.

Fig. 1 shows that polyphenolic compounds are represented by terpenoids, stilbenes, phenolic acids, and flavonoids in the region of the time of aging from 18.69 to 24.84 (it is indicated by a red rectangle on the chromatogram).

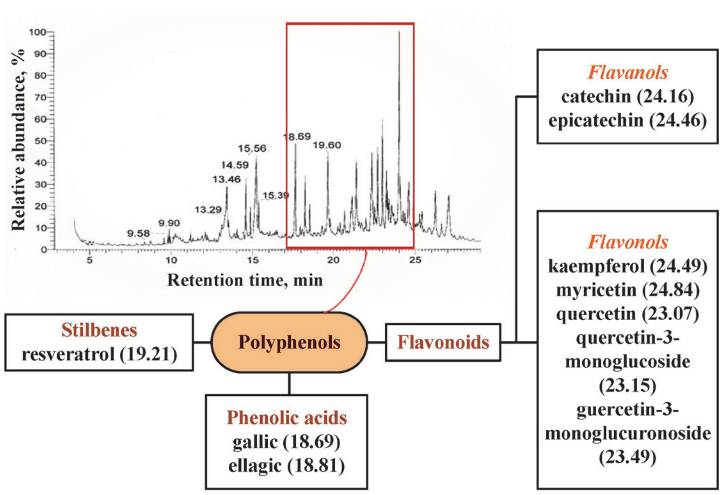

Fig. 1. Identification of antioxidants of phenolic nature based on data from GC-MS chromatogram of isopropanolic extract of DGSF (the retention time in minutes is given in brackets)

Phenolic acids are present in the form of gallic and ellagic acids, typical components of seeds of almost all varieties of grape. A flavonoids is represented by flavanols – catechin, epicatechin, and flavonols – myricetin, kaempferol, quercetin and its derivatives, and stilbenes, such as resveratrol.

Thus, the results of chromatographic studies showed the existence of a significant amount of phenolic antioxidants. However, the information about the content of separate representatives of antioxidants is not always an informative indicator. Determining the total or integrated values that corresponds to the total antioxidant potential of all components in the interaction (synergetic or antagonistic) is often more informative for practical purposes. In this evaluation, it is important that an analytical signal ideally should be determined by the existence of one-type compounds related in the structural or functional terms. For the research samples, this condition was actual, given the advantage in the content of flavonoids.

To characterize the total antioxidant potential of the samples, the total antioxidant capacity TAC and total polyphenols content TPC of the DGSF sample was studied. The techniques of research into these values are associated with the process of concentration of polyphenolic compounds by extraction. The extraction efficiency depends on the selection of a solvent. However, for food purposes, this choice is usually limited to water, ethanol, or a mixture of these solvents. That is why the study was confined to the defatted sample DGSF, the extraction of phenolic compounds from which should better occur in these polar solvents.

Fig. 2 shows the dependence of the TAC and the TPC values on ethanol content in aqueous-alcoholic extracts at the temperature of 60 °C.

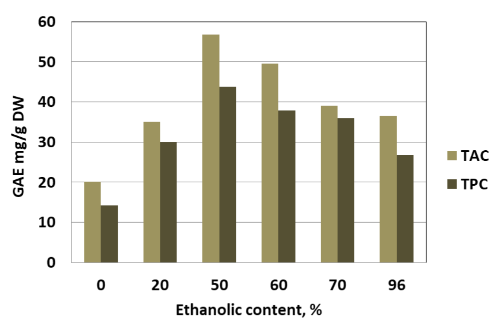

Fig. 2. Total antioxidant capacity TAC and total polyphenols content TPC in DGSF at temperature 60 °C depending on the ethanol content in water-ethanol mixture

Additional experimental research revealed that a monotonous growth at an increase in temperature was observed for TAC and TPC values. That is why the selected temperature is maximum, at which it is possible to study alcoholic extracts. This is due to the boiling point of ethanol and thermal stability of phenolic compounds.

As Fig. 2 shows, the maximum values of the studied properties are obtained for the mixture with the content of water and ethanol of 50 to 50. The TAC and the TPC values for this extract are equal to 56.8 and 43.8 mg in the equivalent of gallic acid calculated per 1 g of dry powder, respectively.

5. 2. Effect of grape seed powders on oxidation of confectionery fats of the lauric and non-lauric types

Peroxide value. The results of the research into the effect of grape seeds powders on peroxide value of fats are shown in Fig. 3, 4 (accuracy of the results shown for ΔPV did not exceed 0.02 for n=3 at p=0.05).

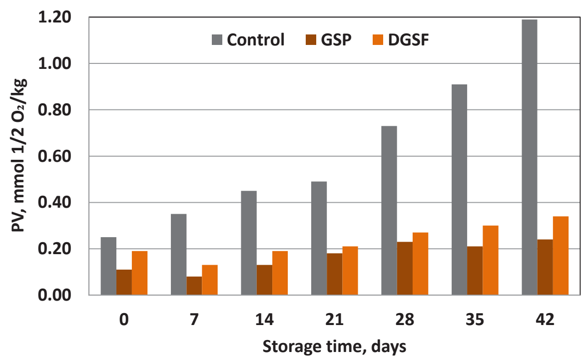

Fig. 3. Effect of antioxidants of GSP and DGSF on peroxide value of lauric fat during storage time

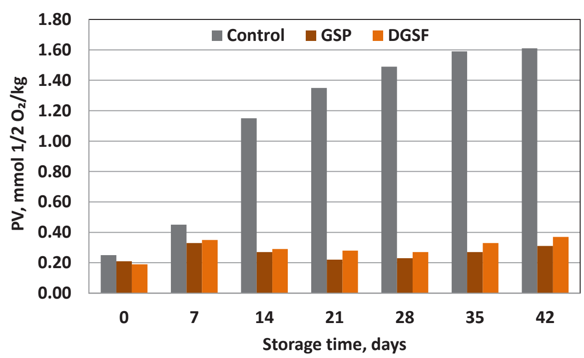

Fig. 4. Effect of antioxidants of GSP and DGSF on peroxide value of non-lauric fat during storage time

The research results reveal that peroxide compounds are most actively accumulated in the control samples of fats. The analyzed indicator starts increasing significantly after the storage term of 14 and 21 days for lauric and non-lauric fats, respectively. At the same time, we have an insignificant peroxide value for the studied samples with the addition of grape seeds powders within the studied storage term.

Lipase activity. The performed experiment enabled us to determine the activity of lipase enzyme in the grape seeds powder, which made up 1.03 cm^3/g for GSP and 1.12 cm^3/g for DGSF. For a comparative analysis, the activity of this enzyme was explored in the samples of cocoa powders. For this, cocoa powders used as formulation components of confectionary glaze were taken. The obtained values were equal to 0.84 cm^3/g for CP1 and 1.87 cm^3/g for CP2.

Acid value. Acid value of fats in the model systems and its change during the storage period were determined to explore the influence of fats hydrolysis on the product quality (Table 3).

A higher initial AV in the samples with the GSP and the DGSF is related to the fact that the grape seeds powders contain organic acids in its composition. Active acidity of the GSP and the DGSF is within 4.0–4.5 degrees. In terms of the analysis of the influence of the hydrolysis process on fats oxidation, it is more appropriate to consider the dynamics of AV instead of absolute values. To do this, the quantitative criterion associated with the rate of acid value change over the period of storage was considered for each sample including the control sample. The relative change in acid value δAV, which was calculated from equation (2), was used as such criterion

$$\delta AV = \frac{AV_t - AV_0}{AV_0}, \quad (2)$$

where AV_t, AV_0 are the acid values of the samples that correspond to the storage term of t days and the initial state.

Table 3

Acid value AV, mg KON of fats in the studied samples (accuracy of determining did not exceed the magnitude of 0.01 for n=3 and p=0.05)

Sample	Storage term, days						
	0	7	14	21	28	35	42
Fat of lauric type							
Control	0.40	0.40	0.40	0.40	0.45	0.48	0.51
GSP	1.80	1.80	1.80	1.80	1.80	1.83	1.86
DGSF	1.90	1.90	1.90	1.90	1.90	1.95	1.97
Fat of non-lauric type							
Control	0.20	0.20	0.20	0.21	0.22	0.23	0.24
GSP	1.60	1.60	1.60	1.60	1.60	1.62	1.65
DGSF	1.70	1.70	1.70	1.70	1.70	1.72	1.74

Fig. 5, 6 show dependences δAV on storage time of the samples.

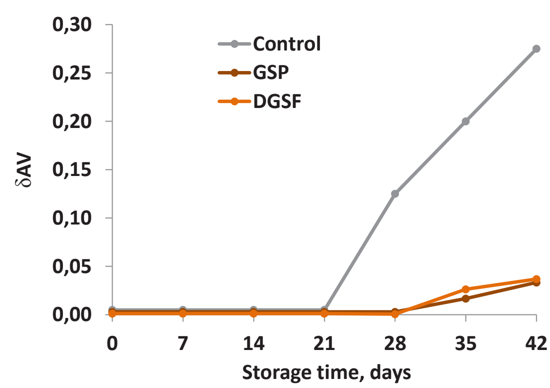

Fig. 5. Effect of antioxidants of GSP and DGSF on change in acid value of lauric fat during storage time

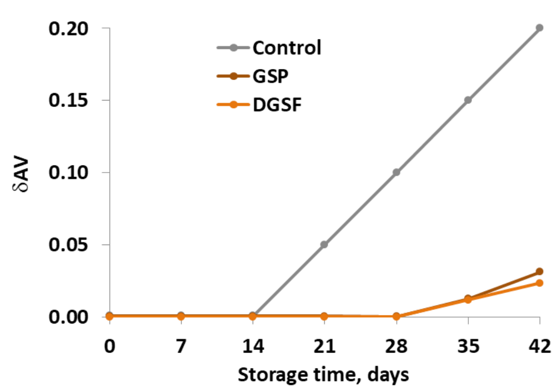

Fig. 6. Effect of antioxidants of GSP and DGSF on change in acid value of non-lauric fat during storage time

As Fig. 5, 6 show, the acid value of the experimental samples both in the case of lauric and non-lauric fats starts to grow through 28 days of storage time. For the control samples with lauric fat, the similar indicator starts to change after 21 days. In the control sample non-lauric fat, the term is shorter and makes up about 14 days.

6. Discussion of the effect of grape seeds powders on oxidative rancidity and hydrolytic rancidity

It is known that the cause of the reduction of shelf-life and appearance of negative sensory sensations (unpleasant smell, rancidity) in fat-containing food products, including confectionery products is the processes of oxidation and hydrolysis of fats.

The most vulnerable to the product quality among oxidation reaction is the reaction of auto-oxidation of fats, which happens between oxygen and unsaturated fatty acids with the involvement of autocatalytic process. Auto-oxidation of fats occurs by the free-radical chain mechanism with the existence of the initiation, propagation and termination reactions that are characteristic for this mechanism [15]. The process leads to the formation of primary products of fats oxidation – peroxides. The introduction of the synthetic or natural by nature antioxidants to the food composition prevents auto-oxidation of oils and fats. This process occurs due to giving hydrogen of antioxidant molecules to free radicals. The specified reaction happens at the stages of initiation and propagation of the oxidation process. This introduction results into the breakage of chain reaction.

The obtained results of chromatographic studies clearly demonstrate that the studied powders from the mixture of grape seeds of different varieties are rich in antioxidants of the phenolic nature. The identified types of polyphenols are in line with the numerous literary sources in terms of the availability of the basic classes of phenolic compounds in the seeds of different grape varieties, determined by the chromatographic methods (for example, [26–29]) and review publications [11, 30, 31]. Comparison of the areas of peaks on the chromatograms made it possible to obtain the quantitative relationships between the identified components in both samples. The content of the substances decreases in the following series: quercetin-3-monoglucoside > kaempferol > quercetin > myricetin > gallic acid > quercetin-3-monoglucuronoside > resveratrol ≅ ellagic acid > catechin ≅ ≅ epicatechin for both samples. Due to defatting, the content of phenolic compounds in the DGSF sample is higher per weight unit of dry matter.

It is known from the literary sources [8, 11] that all the identified phenolic compounds have antioxidant properties. Resveratrol, quercetin, catechin, which are much more powerful antioxidants than well-known ascorbic acid and carotene, are especially distinguished among them.

The explored individual antioxidants caused enough high value of total antioxidant capacity at the level of TAC and TPC values of 56.8 and 43.8 mg in the equivalent of gallic acid per 1 g of dry powder, respectively. That is, the content of antioxidants in the gallic equivalent is about 5 %. Having a quantitative expression of antioxidant potential, there is an opportunity to further optimize the structure of confectionary glaze with viewpoint of extension of storage terms.

An analysis of the absolute magnitude of TAC is somewhat limited due to the lack of such data. This is an essential drawback of the used method of studying TAC, which is possible to remove with the accumulation of information. To some extent, this also applies to the magnitude of TPC, whose determining methods are not standardized.

However, given the obtained results, it is possible to assume that the DGSP powder has a significant antioxidant potential. Such a conclusion can be made, if we pay attention, for example, to the fact that the recommended dosage of antioxidants to use in the technologies of meat products ranges from 0.01 to 0.1 % [9].

Thus, the conducted studies of the antioxidant properties of the samples made it possible to assume that grape seed powders can have an inhibiting effect on the processes of oxidation of fats in glaze and extend the duration of storage of glazed products. The marker of this process is peroxide value PV as one of the indicators of the depth of the fat oxidation process and oxidative rancidity. The magnitude of peroxide value is the specific content of peroxide compounds in fat.

The results obtained from the study of peroxide value proved the hypothesis on the influence of antioxidants of grape seeds powders on the oxidative rancidity. A retrospective look at the data in Fig. 3 and 4 makes it possible to state the fact of extending the shelf life of the samples with the addition of grape seeds powders. While a sharp increase in the process of fat auto-oxidation after 14 days is characteristic for the control samples, there is no such tendency for the samples with the addition of GSP and DGSF. Thus, for the samples with lauric fat, an insignificant increase in peroxide value is observed in 21 days. At the same time, for the sample with non-lauric fat, it is possible to state the unchanging character (within the experimental error) of PV during the period of storage. If we consider the ratio of peroxide value of the samples with confectionary fats to the similar magnitude of the control sample as a protective factor, that is, the magnitude that quantitatively characterizes the process of inhibiting fats oxidation, we obtain the following:

– an increase in this value during the period of storage by almost 2.5 times for the samples with lauric fat and by 3 times for the samples of non-lauric fat during the period of storage;

– the linear character of the increase in the protection factor after 21 days and the probability that the protective power will be increased after 42 days;

– the need for studies with longer storage of the samples.

Another important process that affects the quality of fat-containing confectionary products is hydrolytic rancidity. Firstly, this process runs under the influence of enzyme lipase. Secondly, as a result of hydrolysis occurs, fatty acids are released, which also leads to rancidity. This process leads to increased acid value of fat AV.

Enzyme lipase required for the progress of fat hydrolysis may be contained in raw material or appear as a result of vital activity of microorganisms. This fact requires the experimental evaluation of the activity of this enzyme in raw materials. The obtained results make it possible to prove that the value of activity of enzyme lipase in the samples of grape powders is almost at the same level. The difference between them is only 8 %. Compared with the GSP and DGSF, the lipase activity in the domestic cocoa powder is lower by 18 %, in cocoa powder produced in Poland – higher by 81 %. This makes it possible to state that the introduction of grape powders instead of a share of cocoa powder will not lead to a significant activation of the process of fats hydrolysis in confectionery glaze and it will even decrease in the case of using the imported cocoa powder.

The marker of the process of fats hydrolysis is the acid value, which quantitatively characterizes the concentration of free fatty acids. Fig. 5, 6 show that the significant formation of free fatty acids slows down by 7 days for the samples with lauric fat. For the samples with non-lauric fat, this slowdown is 14 weeks, which is even more. That is, the introduction of grape seeds powders as a source of antioxidants significantly inhibits the process of hydrolysis of fats.

It should also be noted that since the storage term of 28 days, slowing down of the rate of fats hydrolysis in the studied samples, compared with the control sample, is observed. Such a conclusion can be made from the analysis of the angle of inclination of the curves of increasing acid value of samples. Indeed, the magnitude of inclination angle of curve δAV over time is the relative rate of fats hydrolysis. For the quantitative expression, we will approximate the increasing part of this curve by the linear regression equation. It is an assumption for the studied range of storage time, considering the number of experimental points. Thus, we have only three points for model samples, which indicates an insufficiency of the conducted study in terms of limiting the storage term of 42 days. Based on the available data, we obtain the relative rate of fats hydrolysis of 0.013 and 0.007 1/day for the control samples with lauric and non-lauric fats, respectively. At the same time, we have a similar magnitude for the model samples of approximately 0.003 1/day for the systems with both powders and lauric fat and 0.002 with both powders and non-lauric fat.

The obtained results suggest the expediency of using grape seeds powders in the technology of confectionery glaze to prevent the negative consequences of the processes of oxidation and hydrolysis of fats during the storage of glaze and glazed products. However, the model systems containing lauric and non-lauric fats were used as objects in this study. Of course, confectionery glaze also has other components in the formulation. These components can also affect the considered processes of oxidation and hydrolysis of fats. Consideration of only the dominant factor is the limitation of this study.

On the other hand, the continuation of the research with obtaining the results of influence of antioxidants on the processes of oxidation and hydrolysis of fats in the actual food matrix is a promising development of this research.

7. Conclusions

1. The conducted GC-MS analysis of isopropyl extracts of grape seeds powders reveals the existence of phenolic compounds in them in the form of phenolic acids, stilbenes, terpenoids and flavonoids. Among the specified polyphenol, resveratrol, flavanols catechin and epicatechin, quercetin and its derivatives glycosides, kaemferol, myricetin are quite powerful antioxidants.

2. The conducted study into total antioxidant capacity and total polyphenol content of aqueous and water-ethanol extracts of grape seeds powders indicates a significant antioxidant potential of the samples.

3. A peroxide value for model samples with lauric and non-lauric fat with the addition of GSP and DGSF changes slower than that in the model samples. This indicates that the antioxidants existing in grape seeds powders inhibit the process of oxidative rancidity.

4. Activity of the enzyme lipase is less than that in the samples of grape seeds powders – 1.03 and 1.12 cm^3/g for GSP and DGSF, respectively, compared with the sample of cocoa powdexr – 0.84 cm^3/g (trade mark "Mriya", Ukraine) and 1.87 cm^3/g (ADM COCOA Polska Sp. Zo. o., Poland). This fact proves that the application of grape powders, instead of a share of cocoa powder, will not lead to the activation of a fat hydrolysis process in confectionery glaze.

5. The acid value for samples with both types of fat starts to increase in 28 days of storage term, whereas in the control sample it changes after 21 days for the sample with lauric fat and in 14 days for the sample with non-lauric fat. This fact proves that the addition of grape seeds powder as a natural source of polyphenolic antioxidants inhibits the hydrolytic rancidity.

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