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The role of cyclic amides in the formation of antioxidant capacity of bakery products

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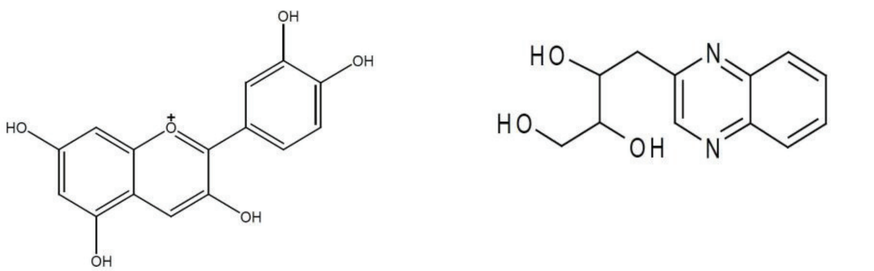
Abstract. This paper discusses the possibility of using of additives of vegetable raw materials in the manufacture of bakery products with antioxidant capacity. The optimal doses of additives in the recipe of bakery products were established. These were 3% for blueberry powder and 6% for pine nuts flour. Antioxidant capacity of hydrophilic fractions of blueberries powder, pine nuts flour, bakery crusts and crumbs were studied in vitro by chemiluminescence technique. Cyclic amides (lactams) were also identified. The antioxidant capacity of hydrophilic fraction of crust of bakery products with pine nuts flour was in 1.7 times higher than that obtained by calculation, for crumb in 1.5 times. For crust of bakery products with blueberry powder the antioxidant capacity of hydrophilic fraction was in 2.2 times higher, and for crumb in 1.3 times higher. The antioxidant capacity of hydrophilic fraction of crust of bakery products with blueberry powder was in 1.2 times higher and for bakery products with pine nuts flour, conversely was higher the antioxidant capacity of the hydrophilic fraction of crumb – in 1.3 times. The antioxidant capacity of hydrophilic fraction of crumb of bakery products with pine nuts flour was in 1.1 times higher in comparison with bakery products with a blueberry powder. The amount of mono-heterocyclic γ-lactams in the crumb of bakery products with pine nuts flour was higher than in the product with blueberries powder, but less than in the control sample. Thus, the formation of antioxidant capacity of hydrophilic fractions of crumb and crust occurs due to Maillard reaction intermediates.

Key words: bakery products; blueberry powder; pine nuts flour; antioxidant capacity; cyclic amides (lactams).

INTRODUCTION

The creation and launching of functional food products is one of the directions of the human nutrition program initiated by the UN (Nadtochii et al., 2014). One of the trends of healthy food development is creating products with antioxidant properties. Such products can minimize an oxidative stress, or prevent 'breaking' in the body, which occur as a result of negative effects of free radicals.

Natural antioxidants give a preventive effect only through regular consumption with food. Therefore, it is necessary to enrich the products of mass consumption that are used every day, which include bakery products. It is known, that in order to create antioxidant properties of bakery products it is necessary to use wheat and rye flour with high extraction rate (Horszwald et al., 2010) or whole-grain flour (Belyavskaya et al., 2014). Buckwheat, corn and amaranth flour (Antiochia et al., 2012, Chlopicka et al., 2012), vegetable powders (Belyavskaya et al., 2013), buckthorn (Nilova, 2012) and other derivatives of vegetable origin which are used in the recipes of bakery products create and improve their antioxidant capacity. Antioxidant capacity of enriched bakery products is associated with introduction of botanical derivatives to recipes. They have increased levels of antioxidant substances such as phenolic compounds, tocopherols and tocotrienols, carotenoids, ascorbic acid. At the same time there is evidence that products of the Maillard reaction (melanoidins), which are cyclic amides (lactams) formed in the process of bread baking also have antioxidant properties (Borelli & Fogliano, 2005, Chawla et al., 2009). The experiment proved that the dark brown crusts ethanol extracts have high antioxidant capacity. In crusts ethanol extract cyclic amides – pirrolinon-reductones are formed. Among them the highest antioxidant capacity has the pyrrolinone reductonyl-lysine (shortly pronyl-lysine) (Lindenmeter et al., 2002). Cyclic amides which are formed during baking, have a structure similar to the flavonoids. They contain a system of conjugated double bonds in the heterocyclic and quinoid links (Fig. 1). Flavonoids which have in their composition fragments of quinoid and sugar residues are also reductones (Selemenev et al., 2008). Molecules of these substances have one or more aromatic (benzene) ring bearing one or more hydroxyl groups. Antioxidant capacity of phenolic compounds is based on their ability to give an electron or proton and to pass into form of stable phenoxyl radical, which are capable to delocalize the unpaired electron (Korulkin et al., 2007). Due to the presence of flavonoids rings and cyclic amides in the structure of generalized π-electron system, occurs the displacement of the negative charge on the oxygen or nitrogen. As a result of this hydrogen atom quite easily separates with formation of radicals.



Anthocyantin - cyanidine

Intermediate product of Maillard reaction–2 (2,3,4-trihydroxybutil) (Martins S.,2003)

Figure 1. Comparison of the structural formulas of flavonoids and intermediate products of Maillard reactions.

Cyclic amides divided into two groups: soluble in alcohol and soluble in water. In order to exclude the influence of alcohol-soluble cyclic amides formed during bread baking, and fat-soluble antioxidants of pine nuts flour on antioxidant capacity, it is necessary to determine the antioxidant capacity of aqueous extracts of bakery products. There are various methods of determination of antioxidant capacity: photometric, electrochemical, volumetric, fluorescent, chemiluminescent, and others. Methods are based on chemiluminescence, are widely used in biological systems in Russia. These methods are known as highly informative and are used for investigation of the kinetics of antioxidants and radicals interaction (Izmailov et al., 2011).

The aims of this research were:

- the study of the antioxidant capacity of aqueous extracts of blueberry powder and pine nuts flour additives and crumbs and crusts of bakery products;
- the study of formation of cyclic amides in bakery products by IR spectroscopy;
- definition of relation between antioxidant capacity and the formation of cyclic amides (lactams).

MATERIALS AND METHODS

For the development of bakery products from patent wheat flour (fancy white wheat-flour) with antioxidant capacity we used natural sources of antioxidants – the powder of wild blueberry from the North-West of Russia and pine nuts flour (a content of fat was 20%) produced by LLC (Limited liability company) 'Specialist', Biysk, Altai Territory. Blueberries were picked up in the forest area, dried at 50–55°C to 6% of moisture and floured to a powder.

Optimization of doses of blueberry powder and pine nuts flour in the recipe was carried out by a laboratory test baking. The formulation of control bakery products was: wheat flour (ash content was 0.55%; gluten was 28.9%); sugar 5%; refined deodorized sunflower oil 4%; salt 1.5%. Enrichiment of backery products is achieved by adding blueberry powder and nuts flour instead of wheat flour. The content of additives varied from 1 to 5% with the increment of 1% for blueberry powder and from 2 to 8% with the increment of 2% for pine nuts flour. All test samples were prepared by using the straight dough method. Test bakery products weighing 100 g were baked in laboratory at the temperature of 220°C during 23 minutes (Nilova, 2012).

Assessment of bakery products quality was carried out by following properties:

- organoleptic – appearance (shape, surface, crust color), condition of crumb (elasticity, porosity), taste and smell;
- physico-chemical and physical - mass proportion of moisture was determined by drying at a temperature of 13°C during 40 minutes, acidity was determined by titration, using 0.1 n. solution of NaOH, porosity – was determined as the ratio of pore volume to the total volume of products, pore volume – as the difference between the volume of product and the volume of non-porous mass, specific volume – as the ratio of product volume to 100 g of flour; dimensional stability – as the ratio of height of the product to diameter.

Obtained samples were compared with control sample of bakery products without additives.

The antioxidant properties of the crust and crumb of bakery products with additives were determined in water extracts by using chemicoluminescence method with biochemiluminometer BCL-06M (Nizhny Novgorod, Russia).

After baking, bakery products were cooled to room temperature during 4 hours. Then crumb was separated of crust and both were dried at a temperature of 40°C to a moisture content of 6.5–7.0%.

For the research was taken 1 ml of the extract, made of: milled sample in an amount of 250 mg and 10 ml of distilled water, which were centrifuged for 10 minutes at 3,500 rev min^{-1}.

Antioxidant capacity was determined in a model system in vitro, comprising riboflavin, hydrogen peroxide and a divalent iron. Chemicoluminescence reaction of riboflavin (substrate for oxidation) was used in the presence of ferrous ions and hydrogen peroxide. 610 µl of potassium phosphate buffer solution (pH 7.5), 40 µl of 10 mM solution of riboflavin, 100 µl of physiological solution, 25 mM of iron sulfate solution (II) (model system) were introduced into the measuring cuvette of biochemiluminometer BKL 06M. In order to intensify the process, 0.1% solution of H_2O_2 was introduced to the mixture. In determining of antioxidant capacity of the samples, physiological solution was replaced by relevant extracts of different concentrations (Putilina et al., 2006). The calibration curve was built up for ascorbic acid (AA). It was chemically pure, obtained from 'Spectrum-Chem', Russia. An aqueous solution of ascorbic acid 100 ug ml^{-1} was used; each succeeding dilution was 1:2.

Calculation of theoretical antioxidant capacity of crumb and crust of enriched bakery products was based on the number of additives in the formulation (in percentage terms).

Cyclic amides (lactams) were studied by FTIR spectroscopy in 1,680–1,800 cm^{-1} (Bellami, 1971, Silverstein, 2011). Study of the spectral curves was carried out by FT-IR spectrometer 'FSM 1202' LLC 'Infraspektr' (Russia), with automatic calculation of absorption intensity. The absolute error in calibration of the scale of wave numbers is no more than ± 0.1 cm^{-1}. The deviation of 100% transmission line from the nominal value (1,950–2,050 cm^{-1}, definition 4 cm^{-1}, 20 scans), is no more than ± 0.5 (in percentage terms). Standard deviation of 100% transmission line (1,950–2,050 cm^{-1}, definition 4 cm^{-1}, 20 scans), is no more than, 0.025 (in percentage terms). Parameters of recording spectra were: spectral range – 400–4,000 cm ^{1}; number of scans – 20; resolution of 4 cm^{-1}; mode – the interferogram. The resulting interferograms were converted into absorption spectra. In order to prepare the samples for analysis powders were compressed with potassium bromide. To prepare the tablets, potassium bromide and powder (1.5 g) were triturated in the agate mortar. 100 mg of a mixture were selected and pressed in moulds for 15 minutes for each side.

Identification of heterocyclic compounds was carried out by peak areas in relative standard units, calculated in relation to the base line, carbonyl absorption bands: γ-lactam monocyclic – 1,700 cm^{-1}; polycyclic in the range between 1,700–1,750 cm^{-1}; ß-lactams monocyclic in the range between 1,760–1,730 cm^{-1}; polycyclic lactams, which condensed with other rings – in the range between 1,770–1,800 cm^{-1}; cyclic amides (lactams), with large rings – near 1,680 cm^{-1} (Bellami, 1971).

Baking of bakery products, evaluation of their quality, antioxidant capacity and removal of the IR spectra were carried out in the laboratory of examination of consumer goods, St. Petersburg State University of Trade and Economic. All bakery products were baked three times. Each bakery product sample been researched 3 times. The accuracy of experimental data was evaluated by using methods of mathematical statistics in Microsoft Excel. These data are presented with a confidence coefficient of 0.95.

RESULTS AND DISCUSSION

For the production of bakery products with antioxidant capacity blueberries powder as a source of water-soluble antioxidants (anthocyanins, phenolic acids, ascorbic acid) (Wang et al., 2009, Gupta-Elera et al., 2012) and pine nut meal as a source of fat-soluble antioxidants (tocopherol) were taken (Nilova, 2012).

Using a method of test laboratory baking we established the optimal doses of additives of natural raw materials in the compositions of bakery products, it was 3% for blueberry powder and 6% for pine nuts flour (by weight of flour).

Addition of blueberry powder to wheat dough changed organoleptic characteristics, particularly the colour of finished products. The colours of crusts changed from golden-brown in bakery products with 1% of powder to a brown, and even with small particles of blueberry powder in products with 5% of powder, crumb colour was from light grey to dark brown with a purple tinge. But blueberry taste and flavour in bakery products was felt only with introduction from 3% of powder. With introduction of 4% of blueberry powder products crumb began to lose its elasticity and became more rubbery and porosity was uniform, but pore wall thickness increased. Blueberry powder had an impact on the physicochemical properties of bakery products, especially on the porosity and specific volume. With introduction up to 3% of powder, these parameters were gradually increased, and when the doses were 4, and 5% parameters started to decline. Most of all, these changes were expressed in determination of the specific volume. Thus, for the production of bakery products from wheat flour the most optimal dose of blueberry powder was 3% provided the use of 4% of vegetable (sunflower) oil in the recipe.

The use of pine nut flour had no effect on the shape and surface of bakery products of various recipes. Bakery products with pine nut flour became higher, rounded, with a convex crust. Pine nut flour oil and sunflower oil included in the formulation of products, made the dough more elastic, and contributed to a more equal distribution of carbon dioxide in the process of maturation of dough and its knock-back. As a result, finished products had a better structure of porosity; it was more uniform and thin walled. However, with the addition of pine nut flour in the amount of 7% crumb of bakery products became jammed. The products crumb colour had a cream tint. Gentle cedar smell was felt only at introduction into recipe of bakery products 5% or more of pine nut flour. It was found that bakery product with 6% of pine nuts flour had the best quality. This product had a specific volume of 79.6 cm^3 $100g^{-1}$ higher than the product with blueberry powder and of 109.5 cm^3 $100g^{-1}$ higher than control sample. The porosity of the sample with pine nut flour was higher of 4.9% than the product with blueberry powder and of 7% in comparison with the control sample. Shape stability of bakery products with pine nuts flour was the highest in comparison with other samples

The results of research of physical and chemical parameters of obtained enriched bakery products are presented in Table 1.

Table 1. Physical and chemical quality of enriched bakery products

Chemical components	Bakery products		
	control	with blueberry	with pine nuts flour
Mass fraction of moisture, %	40.1	39.8	40.4
Acidity, deg.	2.1	2.0	2.4
Porosity, %	69.7	71.8	76.7
Specific volume, cm^3 $100g^{-1}$	375.6	405.5	485.1
Shape stability ($h\ d^{-1}$)	0.53	0.58	0.63

Water extracts of additives had the following antioxidant capacity (mg of ascorbic acid (AA) per g dry basis (DB)): wild blueberry powder – 14.47; pine nut flour – 1.74. A high blueberries powder antioxidant capacity is provided by using of soft modes of drying. All antioxidants of blueberry powder, in particular phenolic compounds retain their activity. In contrast pine nut flour does not substantially contain water-soluble antioxidants. Therefore, its water extract has low antioxidant capacity.

Determination of the antioxidant capacity of water extracts of bakery products crust and crumb showed that even products with traditional composition (without additives) had an antioxidant capacity. Moreover the antioxidant capacity of the crumb of control sample is in 1.4 times higher as compared with the crust. (Table 2). It can be connected with the fact that the heating temperature of crust reaches 180°C and for crumb does not exceed 100°C. (Auerman, 2005) Therefore, the reaction of melanoidins formation has a greater rate in the crust and it is forming final products without antioxidant properties.

Table 2. The antioxidant capacity of 1 g of bakery products in a model system in vitro, mg AA per g DB

Type	Crust	Crumb
Bakery products (control)	9.69	13.91
Bakery products with blueberry:		
theoretical	9.83	13.93
actual	21.27	18.08
Bakery products with pine nuts flour:		
theoretical	9.21	13.18
actual	15.50	20.09

Antioxidant capacity of hydrophilic fractions of crumb and crust of enriched bakery products exceeded the data obtained by calculation. The hydrophilic fraction of crust of bakery products with pine nut flour had an antioxidant capacity in 1.7 times more than that obtained by calculation, and the crumb – in 1.5 times; crust of bakery products with blueberry powder – in 2.2 times, crumb – in 1.3 times. Bakery products with blueberry powder had antioxidant capacity of hydrophilic fraction of crust in 1.2 times higher in comparison with the crumb, and conversely bakery products with pine nut flour had higher antioxidant capacity of crumb hydrophilic fraction, it was in 1.3 times higher in comparison with the crust. Antioxidant capacity of hydrophilic fraction of crumb of bakery products with pine nuts flour was in 1.1 times higher in comparison with bakery products with blueberry powder. Increase of antioxidant capacity of the crumb can be associated with the formation of intermediate products of the Maillard reaction (lactams).

Formation of the products of the Maillard reaction (melanoidins) can be studied by IR spectrum. Melanoidins in crust and crumb of enriched bakery products give a large number of sharp characteristic bands during IR spectroscopy (Fig. 2).

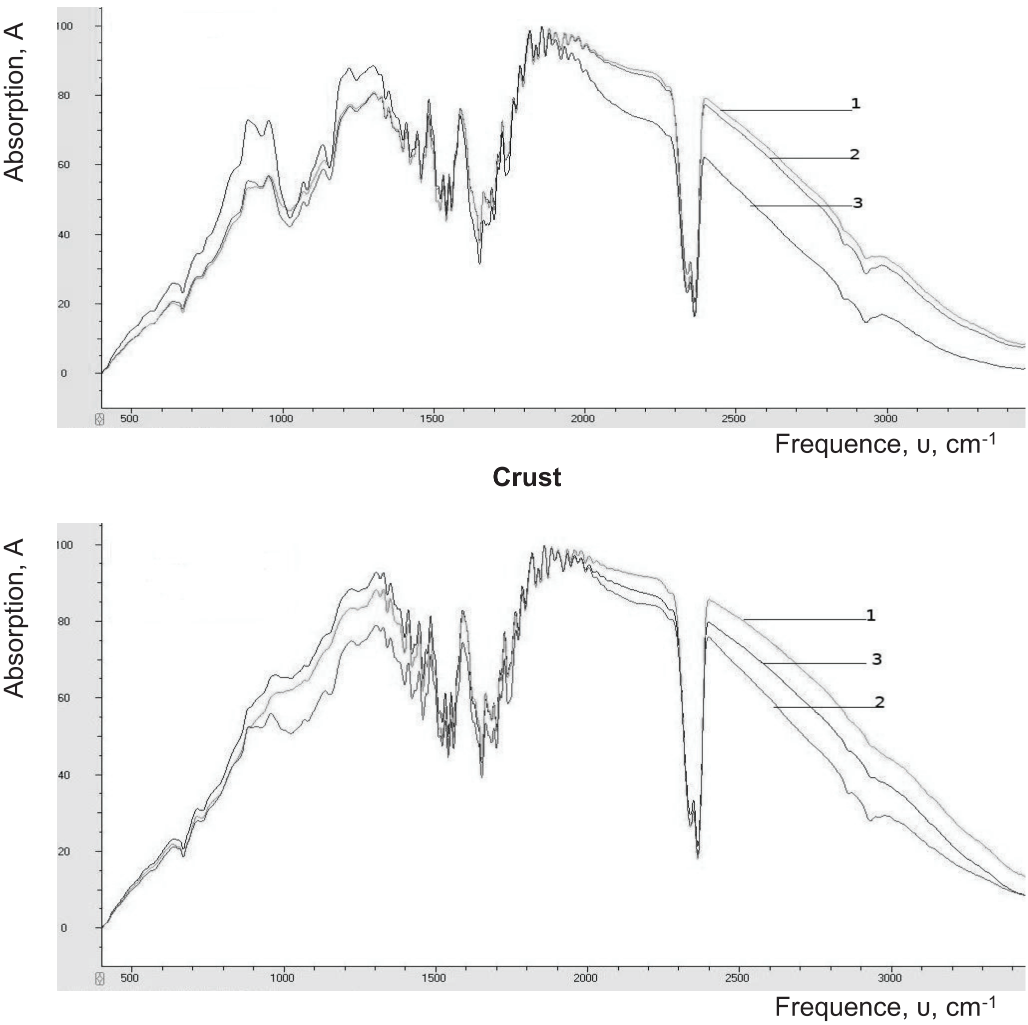


Figure 2. IR-spectrum of crust and crumb of bakery products: 1 – traditional recipe (control); 2 – with blueberry powder; 3 – with pine nuts flour.

The structure of aromatic type is best recognized by the presence of bands of stretching vibrations of the C = C in the 1,600–1,500 cm^{-1} (Bellami, 1971). However, the heterocyclic aromatic compound with six members also give two bands at 1,600 cm^{-1} corresponding to C = C and C = N bonds. It is impossible to separate them in this field. Identification of heterocyclic compounds (lactams) carried out by the intensity of the absorption bands of the carbonyl group in 1,680–1,800 cm^{-1}. Reducing of number of members in the ring leads to displacement of bands towards to high frequencies. The results of research of melanoidins formation by IR spectroscopy as an example of mono- and polycyclic γ- and ß-lactams in the crust and crumb of enriched bakery products are presented in Table 3. Peak area was calculated automatically in relative standard units relative to the baseline.

Table 3. Characteristics of cyclic amides (lactams) of enriched bakery products (relative standard units)

Lactams	Absorption lines, cm^{-1}	Bakery products			
		Type (component)	Control	with blueberry	with pine nuts flour
with large rings	Near 1,680	crust	11.264	9.945	4.043
		crumb	17.849	9.020	13.879
mono γ-lactams	1,700	crust	19.831	18.428	7.821
		crumb	29.723	16.179	24.412
poly γ- lactams	1,700–1,730	crust	44.520	38.438	11.601
		crumb	65.004	33.967	34.881
mono ß- lactams	1,750–1,760	crust	29.489	37.007	16.138
		crumb	43.367	21.753	50.078
poly ß- lactams	1,770–1,800	crust	32.845	28.416	13.123
		crumb	45.718	25.589	35.658

The nature of formation reaction of heterocyclic compounds depended on both components of bakery products (crust and crumb) and used products of processing of plant raw materials. The structure of bakery products with a powder of blueberry includes anthocyanins and the number of lactams in the crust was more than in the crumb. In bakery products with flour of pine nuts and traditional recipe (control) was noted the predominance of lactams in the crumb. The flow rate of melanoidins formation associate with the influence of temperature during baking, which leads to different moisture crumb and crust. Warming of the surface layers of dough at a temperature of 200°C (baking chamber) leads to formation of crusts in the first few minutes of baking and accompanies by a dehydration of the surface layer of dough. (Auerman, 2005). In these conditions the caramelization reaction and melanoidins formation proceed rapidly, and further increase of baking temperature can cause partial pyrolysis of polyphenol of herbal supplements and lactams (Steele, 2006). Warming of crumb is slow towards the end of baking at 95°C and it creates favourable conditions for the formation of heterocyclic compounds (intermediates melanoidins). Perhaps, the higher intensity of the absorption lines of lactams in the crust bakery products with a blueberry powder associated with the presence in them of pentoses (ribose, arabinose and xylose) (Selemenev et al., 2008). As a result, bakery products with blueberry powder have the largest number of mono γ-lactams in the crusts. But despite the fact that there was a great intensity of the process in crust compared to the crumb, the largest number of polymer γ and β-lactams was in bakery products of traditional recipes, which indicates a favourable course of melanoidins formation.

The intensity of stretching vibrations, which are inherent to four-membered monoheterocyclic compounds (ß-lactams), in the crumb of bakery products with pine nuts flour was higher than in the control sample and in bakery products with blueberry powder. In the crumb bakery products with pine nuts flour has more than in the product of a blueberries powder, and less than in the control sample.

Crumb of bakery a product with pine nut flour has more monoheterocyclic γ-lactams, than products with blueberry powder, but has less than in the control sample

In bakery products crumb formation of heterocyclic compounds proceeded rapidly in the control sample and in enriched with pine nuts flour sample. But the ratio of mono- and poly-lactams fractions was different. Poly γ-lactams predominated in the control sample, they were in 2 times higher in comparison with mono γ-lactams and almost in 1.5 times more than the poly β-lactams. In bakery products with pine nuts flour mono β-lactams predominated and the number of polymer γ and β-lactams was approximately the same. Blueberry powder did not have significant effect on the ratio of different lactams fractions, although it slowed their formation compared to the control sample.

CONCLUSION

Antioxidant capacity of aqueous extracts of blueberry powder and pine nuts flour additives and crumbs and crusts of bakery products was established. Antioxidant capacity of water extracts of blueberry powder (AA mg per DB g) was 14.47; for pine nuts flour – 1.74. Antioxidant capacity of enriched bakery products was more than antioxidant capacity of bakery products without additives. Aqueous extracts of crust of bakery products with blueberry powder had in 2.2 times higher antioxidant capacity in comparison with the control, aqueous extracts of crumb – in 1.3 times. Aqueous extracts of crust of bakery products with pine nuts flour had in 1.6 times higher antioxidant capacity in comparison with control, crumb aqueous extracts – in 1.4 times;

Cyclic amides (lactams) have been studied by IR spectroscopy. The largest amount of polymer γ- and β-lactams, without antioxidant capacity was in bakery products without additives (control), especially in the crumb. In aqueous extracts of the crumb of these products were in 1.91 times more poly γ-lactams in comparison with aqueous extracts of bakery products with blueberry powder and in 1.86 times higher in bakery products with pine nuts flour. In bakery products without additives are formed more polycyclic amides, which haven't antioxidant capacity.

In bakery products with pine nuts flour are formed more monocyclic amides with antioxidant capacity. In aqueous extracts of crumb observed in 1.15 times more mono β-lactams in comparison with the control. Enrichment of bakery products with blueberry powder reduces the formation of cyclic amides, especially in the crumb. Aqueous extracts of the crumb of bakery products with blueberry powder contain in 1.14 times less mono γ-lactams and in 1.72 times mono β-lactams in comparison with the crust.

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