HERBS AS A SOURCE OF NATURAL PRESERVATIVES AGAINST RANCIDITY IN THE LOW-MOISTURE BAKERY PRODUCTS

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In recent years, it is a global trend of avoiding the use of synthetic ingredients for the food products quality enhancement. In this case it is actual task to search for the alternative natural raw materials, which provide the stabilization the products quality during storage. Due to their chemical composition, physiological and functional-technological properties the usage of herbs is a perspective solution of this problem. The aim of the study was to evaluate the effectiveness of natural ingredients based on herbs (powder and extracts) on the rancidity retardation. The antioxidant effect of herb raw-materials (hop, chamomile, nettle) was studied for the low-moisture bakery products with high fat content. These products are the ideal type of “food on the go” with long term of storage, which characterized with increasing popularity among modern consumers. The study was conducted at the Odessa National Academy of Food Technologies labs. The peroxide value of samples was determined by iodometric method (ISO 3960:2017). The results revealed that addition of natural antioxidants to the bakery goods in comparison to products without additives reduced this indicator up to the 37…52 % for the samples with herbs. It has been determined that hop, chamomile and nettle incorporation have pronounced antiseptic properties also. The use of herbs in the low-moisture bakery products technology leads to the quality stabilization during their shelf life, improvement of nutritional value and it may be more attractive to consumers due to their natural origin.

Keywords: herbs, low-moisture bakery products, quality, rancidity.

INTRODUCTION

Preservation of the original high-quality product characteristics during the whole period of storage is a consumer preference that determines their demand and, therefore, the competitiveness of products on the market. During storage a number of changes lead to the products quality deterioration. The factors, which provide negative effect on the qualitative characteristics of bread, are caused by the moisture loss, aging of high polymeric substances - starch and proteins - as a result of complex physical, chemical and colloidal processes and microbial spoilage (Cauvain, 2015; Hebeda, 1996). Also, the lipid oxidation is a major problem for the quality stabilization of baked goods during their shelf-life, especially, for products with high fat content and long storage term.

Lipid oxidation is a process that results in rancidity and deterioration of fats and progresses via free-radical propagated chain reactions. Primary lipid oxidation provides forming of hydroperoxides that cause a variety of secondary reactions with evolution of aldehydes, ketones, acids, and other low-molecular-weight volatile substances (Ramis-Ramos, 2003). The presence of oxygen and metal ions, heat and light catalyze these processes (Dhartiben et. Al., 2016). Oxidative changes can cause rancidity such as of flavor, loss of color, altered nutrient value, which limits the shelf life of baked products, and may produce toxic compounds with mutagenic, carcinogenic and cytotoxic properties, which have detrimental consequences on consumer's health (Frankel, 2012; Mukhtar et. Al., 2016). Due to this oxidation of lipids is a serious concern for food industry, especially for long-term flour products.

Application of antioxidants is one of the most effective ways for the oxidation prevention and food shelf-life prolongation. Antioxidants are classified according to their origin, type of action and source of solubility (Butnariu, 2012; Pisoschi, 2015). Synthetic antioxidants, such as BHA, BHT, TBHQ etc., perhaps, are the most extensively used additives for...
the rancidity prevention in the food industry (Nanditha, 2008; Anbudhasan, 2014; Hermund, 2018). Some authors summarized the main advantages of their usage. Among them are low price, easy application to food systems, stable quality, antimicrobial effect and greater antioxidant activity compared with natural compounds (Akbarirad, 2016; Nanditha, 2008). At the same time according to the global consumer demands towards clearly labeled products that are totally safe and free of artificial ingredients the addition of synthetic antioxidants in the products recipe causes concerns.

In this case there is an increasing need of the alternative natural raw materials, which provide the flour products quality stabilization with high fat content during storage and potential nutritional effect. It should be mentioned that herbs due to their chemical composition can be the potential source of natural origin antioxidants (Akbarirad, 2016; Ingvild, 2011; Kyung, 2008). In their research Dimov et. Al., (2018) show that adding of herbal mixtures (thyme, oregano and lemon balm) to the wheat flour leads to the antioxidant activity increase of the final wheat products. Herbs enriched bread characterized with higher healthy status and sensory characteristics compared with control sample. Some authors (Das et. Al., 2012) observed that powder coriander leaf usage effects positively on the flour products. Suggested natural raw-material characterized with high content of the polyphenolic compounds and its addition enhances health benefit for the flour products and prolongs their shelf life. In a study by Frutos (2005), the influence of rosemary extract on the bread with an oil and garlic/parsley dressing was evaluated. It is shown that usage of this herb extract retards the rancidity process, which is confirmed with lower peroxide value after 8 days of storage for enriched samples. The supplementation of 1...4% rosemary and mints to the cookie recipe is also the effective way for the antioxidant activity product increase (Myeong-Sook, 2006). The obtained results indicated that 1% rosemary herb cookies has the highest sensory test characteristics (overall acceptability, taste, etc.).

Despite existing results of herbs usage in bread making, there is lack of the experimental data of the natural antioxidants enrichment of the low-moisture bakery products with high fat content, such as rusk. Currently these types of bakery goods are in a high demand because they are the ideal type of “food on the go” with long term of storage. It should be mentioned that in rusk technology the fats and their oxidative stability play the key role in the quality formation. Due to this the purpose of the study was to determine the effectiveness of herbs (hop, chamomile, nettle) water extracts on the rancidity retardation of the rusks during their storage.

MATERIALS AND METHODS

The dry leaf of nettle (Urtica dioica) and flower-stalk part of chamomile (Matricária recutita) were used for water extraction, 10 g herbs was grounded into a powder in a mill and was mixed with 100 ml boiling water by magnetic stirrer during fifteen minutes, next the extract was filtered over Whatman No.1 paper.

Hop (Humulus lupulus) extract was made in a different way because it needs special condition for extraction of isohumulone, which is the valuable substance in the hop. It has antiseptic properties and takes part in redox reactions. We have used granulated hops type 90 local crop «UA-AROMA». It is a granulated powder of dry hops, ground to a particle size of 1-5 mm. The hop pellets were poured into the water with the temperature of (90-95 °C) in the ratio of 1:100, after that it was boiled during 90 min. with slow steering, next the extract was filtered over Whatman No.1 paper. For extraction all herb raw materials, the water were used with next quality characteristics: pH=6.7; hardness - 5.9 mg/l.

The total flavonoids content (TFC) was determined using aluminium chloride colorimetric method according to Chang et. al. (2002). The total flavonoid content was calculated from a calibration curve, and the result was expressed as mg rutin equivalent per g of dry weight. The vitamin C concentration was determined in the herbs extract by a redox titration with potassium iodate in the presence of potassium iodide. The method for determining the isohumulone based on isoctane (2, 2, 4-trimethylpentane) extraction and determination of the optical density of isoctane extract on a spectrophotometer at the wavelength of 275 nm (Rigby, Bethune, 1955).

Total phenolic content (TPC) of extracts were analyzed as presented in research work of Singleton and Rossi (1965) with some changes. 0.03 ml of all samples was taken in a test tube with 1 ml of distilled water. After that 0.5 ml Folin-Ciocalteau reagent (1:1) and 10 ml 7.5% sodium carbonate solution were added. The contents were mixed and after that incubated under dark at room temperature for 30 min. For blank preparation, 1 ml of distilled water was taken instead of the sample. For determination, was used the spectrophotometer where the absorbance of the samples was measured at 750 nm. These results were converted into mg of GAE (Gallic acid equivalent) per 100 g.

Rusk for research was made according to “National bakery recipe collection” the recipe of rusk, since the amount of butter in them reached up to 15%. The control sample was prepared according to the recipe, which contained 100% of wheat all-purpose flour, 15% of butter, 10% of sugar, 4% yeast by weight of dry ingredients, liquid part according to the calculation based on the moisture content of the recipe. The water in the dough recipe was replaced by hop, nettle and chamomile extracts in the amount of 25, 50, 75% respectively, according to previous research based on sensor evaluation of baked dough sample. One sample has been prepared with the addition of butylated hydroxyanisole (BHA) 0.01% by weight of butter in the recipe. The conditions of kneading, proofing and baking were the same as described below. The rusk technology consists of several operations: dough mixing, dough fermentation, forming, proofing, baking, cooling, cutting and drying at 120 °C during 20-30 min until the moisture content of the rusk decreased to the level 8-9%. To speed up the rancidity the suggested (used) storage conditions were: no packaging used, the ambient temperature (t) was 40±1 °C, and the relative humidity (φ) of the air was 65-70%, with the access of sunlight.
The fat was separated from the product by solid-liquid extraction using diethyl ether/petroleum ether mixtures (1:1 v/v). In particular, ground rusks and solvent mixture in the ratio of 1:2.5 w/v were stirred at room temperature for 1 h. After filtration through filter paper (Whatman no. 1), the fat was separated from the solvent by evaporation. Determination of peroxides content was conducted according to ISO 3960:2017 standard method by assaying the peroxide value (PV) with the titration method.

A twenty persons (both male and female) who has experience in sensor assessment were evaluated the rusks aroma profile and flavor were asked to describe aroma and taste in line with next statements “free of any foreign smell and/or taste”: “have foreign smell”, “have foreign taste”, “have foreign smell and taste”. To determine the physical and chemical characteristics of rusks we have used standard DSTU 7045:2009 Bakery products. Methods of determination of physical and chemical characteristics.

Statistical data were processed using Microsoft "Excel" and "STATISTICA 7.0" software packages. The differences between the values were considered to be significant at p≤0.05.

RESULTS AND DISCUSSION

Additives of natural origin based on medicinal and spicy raw materials can be successfully used as inhibitors of biochemical and microbiological processes leading to spoilage of products. Extracts are natural complex of biologically active substances, which include substances with antioxidant and antimicrobial properties that are safer than additives of artificial origin.

Phenolic compounds have redox properties that allow them to act as antioxidants (Soobrattee, M.A., et. al., 2005). The most important property of phenolic and polyphenolic compounds is their participation in redox reactions and in the process of neutralization of reactive oxygen species. Herbs have a different chemical compound, but all of them contain polyphenols, flavonoids, which are well known as substances with antioxidant activity. The vitamin C is also considered one of the most active antioxidants (Kukić, Z. Z. et al., 2012).

In order to establish patterns of relationship between the composition-concentration of active ingredients of herbs extracts such as TFC, TPC, Vitamin C, Isohumulon, and the speed of the rancidity in the bakery products with low-moisture content which have been determined in extracts (Table 1). Since vitamin C is present in large quantities in nettles, its presence was determined only for this extract, a similar for the determination of isohumulone.

Table 1. The content of substances with antioxidant activity in extracts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total flavonoid content, mg rutin eq. 100 g⁻¹ DW</th>
<th>Total phenolic content, Gallic acid eq. 100 g⁻¹ DW</th>
<th>Vitamin C, mg 100 g⁻¹ DW</th>
<th>Isohumulon, mg (dm³)⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hop extract</td>
<td>23,2</td>
<td>67,4</td>
<td>wasn’t an object</td>
<td>135</td>
</tr>
<tr>
<td>Chamomile extract</td>
<td>5,7</td>
<td>18,3</td>
<td>wasn’t an object</td>
<td>wasn’t an object</td>
</tr>
<tr>
<td>Nettle extract</td>
<td>11,2</td>
<td>48</td>
<td>0,87</td>
<td>wasn’t an object</td>
</tr>
</tbody>
</table>

The results show that hop extract has more TPC than nettle and chamomile extracts. This result can be explained by the fact that hop polyphenolic substances have high antioxidant properties, dissolve in water at any temperature and, as shown by research in the brewing industry, retain their activity after brewing (Knez Hrnčič, 2019). The research work (Pereira, 2018), in which the total content of phenolic compounds in chamomile was studied, obtained comparable results. An insignificant content of vitamin C was found in the finished nettle extract, which is most likely due to the temperature conditions of extraction, Rutto et. al. (2013) and Wolska, (2016) reported a loss of ascorbic acid from 1.1 mg 100 g⁻¹ in fresh leaves to 0.6 mg 100 g⁻¹ in cooked leaves. Considering the fact that it is necessary to provide antioxidant activity in baked and dried flour products undergoing severe temperature conditions, the predicted result will be the loss of almost the entire extracted vitamin C. From our point of view, in such situation, it is still worth concentrating on polyphenolic compounds.

The content of substances with antioxidant properties is influenced by both the extraction conditions and the region of origin of certain herbs, nevertheless, the aim of this work was to study the possibility of using the simplest extraction conditions to obtain plant extracts containing a sufficient amount of antioxidant substances and capable of compete with synthetic antioxidants. According to (Kukić, 2012), ethanol nettle extract had a 20 times weaker total antioxidant ability compared to control antioxidants such as vitamin C and BHA (butylated hydroxyanisole). At the same time, according to (Gülcin, 2004), nettle extract was more active in absorbing superoxide radicals than BHA. It is quite difficult to compare the total antioxidant activity in the simulated systems; it is even more difficult to predict the effect that the extracts will have on the final product; therefore, it seemed necessary for us to evaluate the result of their action in the final products.

Changes in the lipid component that lead to rancidity can be associated or accompanied by an increasing of their moisture content and acidity. These indexes were studied in assessing the properties of finished products, which are shown in table 2.

An increase in titratable acidity occurs as a result of the accumulation of organic acids and acid-reactive compounds formed during oxidative hydrolytic processes occurring with lipids. The titratable acidity for all storage samples increased compared to the initial value but the intensity of these processes was different. Thus, the increase in titratable acidity relative
to the starting point was 28% for the control, 17% for the sample with chamomile extract, 7% for the sample with nettle extract, and 3% for the sample with BHA. The only sample that did not change its performance relative to the starting point was a sample with hop extract. Obtained data naturally correlates with a significant content of polyphenolic compounds in comparison with other extracts that were selected for research.

Table 2. Characteristics of rusk

<table>
<thead>
<tr>
<th>Storage time in special conditions</th>
<th>Control</th>
<th>With hop extract</th>
<th>With chamomile extract</th>
<th>With nettle extract</th>
<th>With 0.01 % butylated hydroxyanisole (BHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titratable acidity, °Н</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st day</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
</tr>
<tr>
<td>After 2 weeks</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
</tr>
<tr>
<td>After 4 weeks</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
</tr>
<tr>
<td>After 6 weeks</td>
<td>3,2</td>
<td>2,8</td>
<td>3,0</td>
<td>3,0</td>
<td>2,9</td>
</tr>
<tr>
<td>After 8 weeks</td>
<td>3,6</td>
<td>2,8</td>
<td>3,3</td>
<td>3,0</td>
<td>2,9</td>
</tr>
<tr>
<td>Moisture content, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st day</td>
<td>9,0</td>
<td>9,0</td>
<td>8,8</td>
<td>9,0</td>
<td>9,0</td>
</tr>
<tr>
<td>After 2 weeks</td>
<td>9,2</td>
<td>9,2</td>
<td>8,8</td>
<td>9,0</td>
<td>9,0</td>
</tr>
<tr>
<td>After 4 weeks</td>
<td>9,2</td>
<td>9,2</td>
<td>8,8</td>
<td>9,0</td>
<td>9,0</td>
</tr>
<tr>
<td>After 6 weeks</td>
<td>9,5</td>
<td>9,3</td>
<td>8,8</td>
<td>9,3</td>
<td>9,2</td>
</tr>
<tr>
<td>After 8 weeks</td>
<td>9,5</td>
<td>9,3</td>
<td>9,0</td>
<td>9,3</td>
<td>9,2</td>
</tr>
<tr>
<td>Sensor evaluation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st day</td>
<td>free of any foreign smell and/or taste</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 2 weeks</td>
<td>free of any foreign smell and/or taste</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 4 weeks</td>
<td>free of any foreign smell and/or taste</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 6 weeks</td>
<td>foreign smell and taste free of any foreign smell and/or taste</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>After 8 weeks</td>
<td>foreign smell and taste free of any foreign smell and/or taste</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Deterioration of sensory characteristics in the control sample and the sample with chamomile extract may indirectly indicate the formation of reaction products such as aldehydes, ketones, acids, and alcohols. Since, as lipids are oxidized, hydroperoxides are formed, which are the subjects to further oxidation or decomposition to the aforementioned secondary reaction products. It is these compounds, which negatively effect on the taste, aroma, nutritional value and overall quality of the products. High molecular fatty acids have no taste or smell, and therefore, with increasing of their amount in the product, there is no noticeable change. Because of the action of oxygen in fats, primary and secondary oxidation products accumulate. Their presence causes the appearance of a characteristic unpleasant taste and smell in fats. The number of peroxides and hydroperoxides characterizes the peroxide number determined in the samples and shown in Fig. 1.

Figure 1. Dynamics of change of lipid peroxide value during special storage conditions

Storage conditions: unpacked, \( t=40\pm1 \, ^{\circ}\text{C} \), \( \varphi=65 \ldots 70\% \), with access of sunlight
The dynamics of changes peroxide value during storage in bakery products with low moisture content showed that the oxidation processes in the control sample proceeded more intensively than in the sample with the addition of herbs extracts and BHA. It was noted that the hop extract usage was more effective compared with other extracts but less effective than synthetic BHA. The obtained results are naturally consistent with both the data on the assessment of sensory characteristics and overlap with the quantitative content of polyphenolic substances, the more they were found in extracts, the lower the final peroxide value of fat in the product on the 56th day of storage was.

CONCLUSIONS

The obtained data suggest that the extracts of the selected herbs do not exclude, prevent the process of fat oxidation during storage of products; nevertheless, they can significantly inhibit them. This process is more effective the more polyphenols and flavonoids they contain. It has been found that synthetic antioxidants such as BHA can be more effective, in comparison with herbal extracts with a low content of flavonoids and phenolic compounds, in preventing oxidation in the finished product during storage.

The use of natural plant ingredients as a method of inhibiting oxidative spoilage of products will not only have a positive effect on consumer health, but also allow enterprises to follow the trend of a clean label that will bring significant economic benefits.

Further research should be aimed not only for rancidity prevention in products with a low moisture and a high fat content by using natural antioxidants derived from plant extracts, but at studying the technological aspects of their use, as well as the problems of rational dosage of such raw materials.

It seems possible to use a strategy to improve extraction parameters or to create a combination of various extracts to enhance their activity against hydrolytic fat spoilage in low-moisture flour-based products for long-term preservation, their nutritional value and consumer properties.

REFERENCES