CHANGES OF NUTRITIONAL PROPERTIES OF THREE VARIANTS PEPPERS BY PROCESSING OF PICKLED RED PEPPERS

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Abstract
The pepper (Capsicum annuum L.) is an important vegetable crop due the multiple ways it can be used in the processing industry, as well as the presence of nutrients and bioactive matters that are important for health. The pepper fruits for processing is necessary to have a larger useful part, with expressed red color, a higher content of dry matter and to possess inherent sensory characteristics. The quantity and the inter-relationship of chemical components, including water, are responsible for their nutritional value. The aim of this investigation was to compare the nutritional composition of three varieties of peppers, fresh and processed, as well as pasteurized pickled peppers. As a raw material had been used pepper varieties kurtovska kapija, palanechko chudo and horgosh, harvested at their technological maturity. Blanching was done at 85-90 °C for 5 min. To the pasteurized pepper, acetic acid was added at a concentration of 1.5 % in terms of finished product, which belongs to the low marinated products. Pasteurization is carried out at T 92 °C for 30 minutes. The chemical properties were determined by analyzing the following parameters: total dry matter, carbohydrates, proteins, oils, total acids, vitamin C, β-carotene and ash, both in fresh and in pasteurized peppers. Based on the obtained results the quality and nutritional composition were determined. The variety horgosh shows the highest content of total dry matter (11.45 %), vitamin C (138.9 mg/100 g), β-carotene (22.7 mg/100 g), and the highest energy value (41.7 kcal). In the group of the pasteurized peppers, the variety of palanechko chudo has been characterized by the lowest average value of total dry matter (7.49 %) and lowest total energy value (24.6 kcal); the variety of kurtovska kapija had the lowest contents of vitamin C (52.1 mg/100 g) and β-carotene (6.09 mg/100 g).

Keywords: chemical composition, pasteurization, energy value.

Introduction
Pepper (Capsicum annuum L.) is an annual shrub belonging to the nightshade family Solanaceae and is one of the commercially important crops which is classified under vegetable fruits (Sethu et al., 1996). Growers have selected many pepper cultivars with different properties and characteristics. The result is a great number of very different cultivars showing a wide range of morphological and organoleptic characteristics, including color, which determine their use. At first all cultivars must meet a series of appropriate agronomic and industrial requirements (Hornero-Méndez et al., 2000). Peppers are becoming increasingly popular among consumers due to their broad variety of shapes (bell or tomato shaped), sizes, colours (starting from green, yellow or white for the unripe fruit, and turning to red, dark red, brown, and sometimes almost black in the ripe state) and its characteristic flavour, which mostly determines their application. They can be used to produce dehydrated products (such as paprika), in salads, pickled peppers, sliced or diced frozen peppers to be used in different products or as a food colorant (Castro et al., 2008). Peppers are very popular vegetables because of the nutritional value. They are a good source of numerous antioxidant compounds. The
chemical composition of pepper fruits vary, even within the same variety, depending on maturity, the location of production, and agricultural practices as well as on numerous environmental factors (Pérez-López, 2007). The beneficial effects of peppers have been related to the presence of vitamin C, vitamin A is present as provitamin – carotenoids, dietary fibre and other phytochemicals (polyphenols, carotenoids) in these plant food products. The intense red color of pepper fruits is due to carotenoid pigments that are synthesized mainly during fruit ripening (Guil-Guerrero et al., 2006). The red fraction contains the pigments exclusive to the Capsicum genus (capsanthin, capsanthin-5,6-epoxide, and capsorubin), and the yellow fraction comprises the rest of the pigments (zeaxanthin, violaxanthin, antheraxanthin, β-cryptoxanthin, β-carotene, and cucurbitaxanthin A), which act as precursors of the former (Hornero-Méndez et al., 2000). Some of them have provitamin A activity (β-carotene, α-carotene, β-cryptoxanthin), and some act as antioxidants. These pigments occur in non-esterified, mono- and di-esters with fatty acids (Vračar, 2007). They are more liposoluble and at the same time more stable to photo- and thermoxidative reactions and other processes (Pérez-Gálvez et al., 1999). Fresh peppers have a high content of vitamin C, and are also a good source of pro-vitamin A carotenoids. The importance of carotenoids in the diet has been recognised, as vitamin A and other retinoid precursors and antioxidants in cell protection, for the prevention of degenerative diseases and for human epithelial cell differentiation (Pérez-López, 2007). The safety and impact of industrial operations is necessary to be in balance with optimal process methods and applying the most suitable processing conditions for achieving a desired high quality products, in organoleptic and nutritional terms (Silva et al., 1993). Basically, the thermal processing of the products during preservation should be performed at the lowest possible temperature and for the shortest period of time, provided that a microbiologically stable product is obtained, which will not get spoiled during the intended shelf life (Vereš, 2004). For the success of the heating effect, the most important are: the temperature and the heating time; the type and number of microorganisms in the raw material; the chemical composition and physical properties of the product (content of: water, sugars, fats, preservatives; pH, packaging and pre-treatment of product). Pasteurization uses temperatures of up to 100 °C and heating times of up to 30 minutes. It is mainly used for vegetable products, which in the technological process of preservation have increased acidity (marinated, pickled, and fermented vegetables) (Niketić-Aleksić, 1994).

Material and methods
For this experiments we used ripe pepper fruits (Capsicum annuum L.,) of three varieties, kurtovska kapija, polanechko chudo and horgosh. They originated from different regions in R. Macedonia. The varieties kurtovska kapija and polanechko chudo came from Strumica region and the variety horgosh from Demir Kapija region. The laboratory analyses were made at the laboratories for food quality control in the Institute of Public Health in Skopje, at the laboratory of the Department for Processing Fruits and Vegetables at the Faculty of Agricultural Sciences and Food in Skopje and at the laboratory of Food Chemistry, Institute of Biochemistry, Graz University of Technology, Austria. The analyses were performed by applying standard laboratory methods, equipment and standard chemical reagents, according to the laboratory procedures.

Technology of pasteurization of pickled red peppers
The production of pasteurized pickled red peppers from the three varieties was performed industrially, at the factory "Bonum", Kumanovo. Uniform raw fruits were used for production; that is, a batch of pepper fruits with similar color, size and ripeness. The peppers were washed with water to remove impurities, partly from the microorganisms and waste parts and other substances. Afterwards the fruits were inspected and selected manually, cut of the stalk and seeds removed, and then blanched. Blanching as a pre-treatment is used to inactivate deleterious enzymes which can have a series of detrimental effects such as hydrolysis of pectin. Simultaneously the required elasticity of the pericarp is achieved (Castro et al., 2008). Also, due the blanching a series of changes of the physical-microbiological nature occur, such as a decrease in the total number of...
microorganisms and an undesirable change in the sensory properties, such as loss of colour, flavour, texture and nutrients. The changes are depending on the blanching conditions (Cruz et al., 2011; Каракашова, 2011). The process of pepper blanching is performed at a temperature of 85-90 °C for 5 min. After blanching, the raw material must be cooled in order to preserve the structure of the blanched product and to prevent the undesirable effects associated with high temperature. Only healthy blanched pepper fruits, equal in size, shape and color are used for further processing. Then the peppers are submerged in a hot solution for pickling, which contains water, salt, sugar, and acetic acid. In pasteurized pickled pepper, the acetic acid is added in a concentration of up to 1.5 %, in terms of the final product. Due to the low concentration of acetic acid this type of product is called “weakly marinated” (Каракашова, 2011). The filled jars closed and washed prior to pasteurization. The process of pasteurization of pickled peppers in jars is done in an autoclave according to the established heating regime. During heating the quality of the peppers changes to a typically cooked product meaning that texture, taste, flavour, and colour as well as nutritional quality attributes (e.g. reduction of ascorbic acid) are altered (Castro et al., 2008). The pasteurization is performed at a temperature of 92 °C for 30 minutes with a cooling cycle for 30 minutes in cold water.

**Determination of quality and nutritional value**

The determination of quality and nutritional value were performed by analyzing the following parameters: total dry matter by drying the samples in an oven dryer at 105 ºC to obtaining constant mass (AOAC 925.10, 1995); total acidity by using titration solution 0.1 M of NaOH and 1 % solution of phenolphthalein as indicator (AOAC, 942.15, 1995); content of salt in final products by titration with 0.1 M AgCl and 1 % solution of K2CrO4 as indicator (AOAC, 971.27, 1995); pH value of the pickled solution of the final products, by pH meter (AOAC, 981.12, 1995); the total ash by incineration and burning of samples in a Muffle oven, at a temperature of 550 °C; ash insoluble in HCl, by incineration and burning in a Muffle oven at a temperature of 550 °C (AOAC, 941.12, 1995); determination of sugars by applying HPLC-method with RI-detector (ASU # 35 LMBG L00.00, 1984); fats determination, according to the Soxhlet method (AOAC 960.39, 1995); the content of proteins was analyzed with the Kjeldahl method (AOAC 978.04, 1995); determination of Vitamin C was performed by using a solution of 0.1 N I2 and 1 % starch solution as an indicator (http://www.canterbury.ac.nz/media/documents/scienceoutreachvitaminC/ iodine.pdf -15.09.2017). β-Carotene was extracted by organic solvents and the analysis was performed by thin layer chromatography TLC. The quantification was performed by using Camag Scanner II.V.3.14/PC/Cats HPTLC densitometer, at 450 nm (Zeb et al., 2010). From the analysed values the energy was calculated according to (FAO, 2003). The sensory evaluation was done on basis of a linear scale with 20 points. This included the smell, taste, appearance and texture. The quality of the final products was determined in accordance with legal regulations of R. Macedonia (Official Gazette no. 69/2014). Statistics was done software supported by using SPSS (IBM Statistics 21). The obtained results were processed by statistical software package (SPSS).

**Results and discussion**

**Determination of the quality of fresh and pasteurized pickled peppers**

The term "pepper quality" as a raw material implies the affiliation to an appropriate variety of certain properties. For the fresh pepper fruits, the important quality characteristics are the different sensory properties appearance, color, taste, hardness, and texture, as well as changes that can occur under certain storage conditions before processing. The first sensorial assessment is the visual appearance. The sensory analysis of color is assessed by the intensity, tint, color uniformity, which is especially important (Каракашова, et al., 2013). The texture described as crunchiness, is also an important quality characteristic which is influenced by hardness, surface gloss, roughness/smoothness, dryness (Tijskens, 2000). The determination of the sensory properties of the pepper varieties, kurtovska kapija, palanechko chudo and horgosh, was done during the reception of
the raw material and immediately before the processing. This was necessary since the quality of the raw material had to be in accordance with the Law on the Quality of Agricultural Products (Official Gazette of RM no.140/2010) and the Law on Amending the Law on the Quality of Agricultural Products (Official Gazette of the Republic of Macedonia No. 53/2011 and 55/2012). The production of pasteurized pickled red peppers, as the processed vegetables, should be in accordance with the requirements of the Regulation on the requirements regarding the quality of processed products from fruit and vegetable, as well as mushrooms and their processed products (Official Gazette of the Republic of Macedonia No. 69/2014). These regulations reflect international norms. According to this Rulebook the term "pasteurized vegetables" is defined as a product obtained by processing the fruits of vegetables or parts thereof by pasteurization in hermetically closed packages. According to Jašić (2007), the color evaluation is often important, especially for final products, because food spoilage is regularly associated with a color change. The pickled solution in pasteurized pepper is mostly clear, with a beautiful light-yellow color, with a weak acid taste, a pleasant smell which is characteristic for pepper. The appearance of a slightly opalescent color of pickled solution in some samples is related to the degree of maturity (Марковић и Врачар, 1998).

The sensory assessments of pasteurized pickled pepper from the varieties kurtovska kapija, palanechko chudo and horgosh, were made for all sensory properties that are important for the quality. The significance of the individual properties that contributes to the total product quality can be determined by multiplying with a factor of significance (weighting factor) (Koprivnjak, 2014). The highest sensory score was given to pasteurized pickled pepper from the varieties horgosh and palanechko chudo for the best color (3.00 - average number of points); the best odour with 2.80 and best consistency 7.80 were given for the variety kurtovska kapija; best taste (5.80) had the products of the variety palanechko chudo. Regarding the overall sensory evaluation, it can be concluded that the pasteurized pickled pepper from the variety kurtovska kapija had the highest total score 18.6 (22.3 weighting factor). The lowest total score 16.8 (19.2 weighting factor) had the product from the variety horgosh. The analysis of variance (ANOVA) was made according to the obtained results for the total number of points from the sensory analysis on pasteurized pickled peppers. It showed that the interaction of factors variety/technology have a statistically significant influence on the total number of points.

**Determination of nutritional composition of fresh and pasteurized pickled peppers**

Марковић и Врачар (1998) indicate that the pepper has a specific and rich chemical composition. Water is the ingredient that is most present in the fruits of fresh pepper. From a technological point of view, an important parameter for the quality of pepper as a raw material is determining the content of total dry matter. The varieties of pepper with a better quality considered to be those that have a higher content of total dry matter, which causes also the higher content of individual ingredients leading to a higher nutritional value. The carbohydrates make up the bulk of dry matter. Together with acids they represent the basic components in the formation of flavor. Glucose and fructose are the dominating carbohydrates in pepper fruits (Niketić-Aleksić; 1994; Марковић и Врачар, 1998). Gvozdenović and co-workers (2004) point out that in comparison to the other vegetable crops, pepper is rich in nitrogen (proteins, amino acids, various peptides, etc.). The oils in peppers are present in the seeds and the pericarp. The pepper oils play an important role as a solvent of colored substances, primarily carotenoids. The content of vitamin C varies greatly and it depends on many factors. It mainly depends on the variety and the conditions of breeding, the maturity phase and the way of cultivation (Марковић и Врачар, 1998). The content of total mineral matter is actually expressed as total ash and the ash alkalinity (ash) is obtained after neutralization by hydrochloric acid. For pepper, the content of total ash is an important parameter for the quality control of the raw material as well as the appropriate technological procedure (Niketić-Aleksić, 1994). The acidity of the pepper originated from the presence of organic acids and their salts (Марковић и Врачар, 1998). For pasteurized pickled pepper a weakly acidic solution is used, to which acetic acid is added, and therefore the pH value of the pickled solution is important for the
quality and safety of the final product. By adding acetic acid, the pH of the medium decreases, thus inhibiting the growth of many microorganisms. Typically, acidic foods are pasteurized at up to 100 °C (not below 75 °C) (Vereš, 2004). Determination of the salt content (sodium chloride) in pickled peppers is one of the most important parameters (max. 2 %). The sensitivity of microorganisms towards the amount of added salt is in direct relation to the applied temperature. This means that with a combination of salt (3 - 6 %) and temperature, spores of some bacteria at lower temperatures can be destroyed (Vereš, 2004). The energy value was derived from the content of the individual nutrients, carbohydrates, fats (oils), proteins, and total acids. (Гордиев и со., 2008). The results are presented in Figure 1 and Figure 2. The variety kurtovska kapija had the highest value on: fructose (%) (4.32 ± 0.38) in fresh peppers and total acids (%) (as citric acid) (0.91 ± 0.06) in pasteurized pickled peppers. This variety had the lowest value for content of: total ash and β-carotene in fresh peppers; ash insoluble in HCl, salt, proteins, vitamin C and β-carotene in pasteurized pickled peppers. The variety palanechko chudo had the highest values for: water (%) (91.6 ± 0.13); total acids (%) (as citric acid) (0.40 ± 0.04) in fresh peppers and in pasteurized pickled peppers, for the content of: water (%) (92.5 ± 0.27); pH value (6.15 ± 0.19); salt (%) (1.10 ± 0.10). This variety had the lowest values for: total dry matter, fructose, glucose, proteins, fats, vitamin C, as well as energy value (133.3 ± 15.3 kJ or 31.8 ± 3.1 kcal) in fresh peppers; in pasteurized pickled peppers the lowest value were for: total dry matter, total acids, fructose, glucose, fats and energy value (103.3 ± 19.3 kJ or 24.6 ± 3.2 kcal). From the results presented in Figure 1 and Figure 2, it can be concluded that the variety horgosh had the highest values for: total dry matter (11.5 ± 0.15 %); total ash (0.67 ± 0.04 %); glucose (3.39 ± 0.49 %); proteins (1.43 ± 0.12 %); fats (0.49 ± 0.06 %); vitamin C (139 ± 13 mg/100 g); β-carotene (22.7 ± 2.4 µg/g), as well as energy value (174.8 ± 16.1 kJ) or (41.7 ± 5.4 kcal) in fresh peppers and total dry matter (10.2 ± 0.31 %); ash insoluble in HCl (0.08 ± 0.02 %); fructose (3.19 ± 0.25 %); glucose (2.79 ± 0.18 %); proteins (1.14 ± 0.17 %); fat (0.44 ± 0.08 %); vitamin C (69.6 ± 11.1 mg/100 g); β-carotene (19.5 ± 1.3 µg/g); as well as energy value (170.2 ± 15.9 kJ) or (40.65 ± 3.6 kcal) in pasteurized pickled peppers. The lowest values were found in the variety kurtovska kapija which included water and total acids for fresh peppers; water, total ash and pH value in pasteurized pickled peppers.

![Figure 1. Comparison of quality and nutritional parameters of fresh and pasteurized pickled peppers from varieties: kurtovska kapija, palanechko chudo and horgosh](image-url)
matter, glucose, vitamin C and total energy value. Other chemical properties were not statistically significant different.

Figure 2. Comparison of vitamin C and β-carotene content in fresh and pasterized pickled peppers from varieties: kurtovska kapija, palanechko chudo and horgosh

Conclusions
The sensory characteristics of all fresh pepper fruits: whole fruits, healthy and fresh, in a stage of technological maturity with a characteristic red color, with a characteristic surface gloss, a normal external moisture of the surface of the pepper fruits and suitable for further processing. With the lowest sensory score, were the final product produced from the variety horgosh. Statistical significant differences in final products were found for the sensory evaluation. In terms of examined chemical components, the variety horgosh had the highest content of total dry matter, as well on most constituents and therefore also the highest energy value, in fresh and in final products. Oppositely, the lowest content of dry matter, as well on most constituents and energy value, were found in fresh and in final products from the variety palanechko chudo. Among the examined varieties of red peppers, there were statistically significant differences in relation to the average energy value. Also, between the energy values of fresh and pasteurized acid peppers for each of the varieties, were noticed reduction of energy value due to the passing of some of water-soluble nutrients into the pickled solution in which the pepper fruits are dipped. The pasteurized varieties kurtovska kapija, palanechko chudo and horgosh were in accordance with the quality prescribed by the national regulations.

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