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INFLUENCE OF FREEZING METHOD ON COLOR CHANGE AND ANTIOXIDANT ACTIVITY IN CHERRY FRUIT

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ABSTRACT

Showing preprocessing cherry fruit of varieties Shpanka and Lotovka by sugar solution with the addition of chitosan or ascorutin. For this studies conducted over the years 2016–2017 with the fruits of cherry varieties Shpanka and Lotovka. Prepare fruit included: sorting, inspection, washing, hold 30 minutes in solutions of 20% sugar ascorutin 4% or 20% of the sugar with the addition of 1% chitosan, remove moisture, freezing at −25°C, packing in plastic bags of 0.5 kg and storage at −18° C. By taking control of raw fruit cherries packed in plastic bags. The content of tannins and colorants in cherry fruits is a varietal feature and after freezing in the fruits of the cherry varieties of Shpanka and Lotovka is reduced by 22 and 29%. Whereas in pre-treated fruits cherries by 20% sugar solutions with addition of 4% ascorutin or 1% chitosan decreased to 10 and 12%. The number of ascorbic acid in fruits, respectively, decreased to 23 and 38%. In addition, the smallest losses were for fruits treated with 20% sugar solution with the addition of 1% chitosan. According to the research, preservation of quality and biological value of frozen fruit cherry preprocessing contributes 20% sugar solution with the addition of 1% chitosan. The color indicator is a varietal feature. Antioxidant activity during freezing did not change significantly. It has been established that antioxidant activity correlates with the content of tannins and colorants and correlates with the content of ascorbic acid inverted.

1.Introduction

Cherries are a very attractive fruit to consumers, for their taste and colour attributes, as well as for their wealth of nutrients (Serra *et al.*, 2011).

The fruit has dark red colour and high dry matter, approximately 27.3 %, specific sweet and sour aroma derived from volatile compounds such as alcohols, carbonyls, esters and terpenes (Levaj *et al.*, 2010) and therefore is valuable raw material in food industry.

Regarding their phytochemical composition, sour cherries are rich source of polyphenol compounds which strongly influence the quality and nutritional value of the fruits and contributing to their sensorial attributes (Zoric *et al.*, 2016).

Moreover, cherries are a good source of natural antioxidant substances, namely polyphenols, which are reported to have many health benefits.

Cherry polyphenols include flavonoids: anthocyanins, flavan-3-ds and flavonols hydroxychric acids and hydroxybenzoic acids (Goncalves *et al.*, 2004). Among these compounds, especial interest has been focused on anthocyanins, which are the polyphenols responsible for the red skin and flesh colour of fruits, due to their strong antioxidant and anti-inflammatory activities (Blando *et al.*, 2004; Wang *et al.*, 1999; Serra *et al.*, 2011).

The predominant anthocyanins in cherry are cyanidin-3-rutinoside and cyanidin-3-glucoside. The major polyphenols in sweet cherry are anthocyanins followed by the hydroxycinnamic acid's. Thus, at the last sampling date, the highest levels of H-TAA were found in 'Sonata' and 'Cristalina' (130 mg/100 g) and the lowest in 'Brooks' (69.67±2.50 mg/100g) (Dıaz-Mula *et al.*, 2009).

Total anthocyanins of sweet cherries are between 30 (cv. Black Gold) and 79 (cv. Cristalina)mg cyanidin-3-glucoside equivalents (CGE)/100g, whereas total anthocyanins of sour cherries were between 45 (cv.Balaton) and 109 (cv. Sumadinka) mg CGE/100g (Ferretti *et al.*, 2010).

Total anthocyanin content ranged from 82 to 297 mg/100g for dark cherries and from 2 to 41 mg/100 g for the light coloured cherries (Goncalves *et al.*, 2007).

The evaluation of antioxidant activity, performed by ORAC and TEAC assays, revealed a relatively high antioxidant capacity for the fruit extracts (from 1145 to 2592 μmol TE/100 g FW) and a lower one for the callus extract (688 μmol TE/100 g FW) (Blando *et al.*, 2004).

Several studies showed that cherry anthocyanins, and especially cyanidins, have potential to inhibit tumour growth, slow cardiovascular diseases and retard the aging process (Serra *et al.*, 2011).

The correlation between antioxidant activity and phenolic compounds has been also found in several studies comparing a wide range of fruits cherry (Dıaz-Mula *et al.*, 2009; Vasylyshyna, 2017).

The chromatic parameters L, a, b, chroma and hue angle correlated negatively ($P < 0.001$) with the total anthocyanins levels, but not with total phenols ($P > 0.05$). Therefore, for cherries for human consumption, it seems important to have a simple and non-destructive technique for anthocyanins content determination, and in this way easily and quickly assess and monitor cherry quality on a large number of cherries (Goncalves *et al.*, 2007).

Colour is one of the most important indicators of maturity and quality of fresh, stored, and processed cherries. In cherries, colour is mainly influenced by the concentration and distribution of different anthocyanins in the skin (Gao & Mazza, 1995; Pedisic *et al.*, 2009) as well as pH and levels and types of colourless phenolics in the fruits and other factors such as light, temperature, oxygen, metal ions and enzymes (Goncalves *et al.*, 2007).

Fresh sweet cherries represent an important, but fragile, commodity in the agricultural export market. The harvesting season is very short, and cold storage is used to stretch the supply period in the season. However, the effects of different storage conditions on cherry quality, including colour development, is not well studied (Esti *et al.*, 2002; Szymczak *et al.*, 2003; Goncalves *et al.*, 2007).

The freezing process triggers the formation of ice in cellular fruits, which increases the volume of the fruit and damages the integrity of the cell, leading to fruit structure breakdown. Large drip loss found in the thawed product (Han *et al.*, 2004) will have a major effect on the appearance of the product. Another adverse consequence of freezing is that nonaqueous constituents become concentrated in the unfrozen phase. Thus, besides lowering reaction rate by lowering temperature, freeze-concentration can increase reaction rates, resulting in decreased anthocyanin and ascorbic acid contents in frozen stored of fruits (Sahari *et al*., 2004; Ngo *et al*., 2007).

According to Scibisz et all., (2007) measurements of the antioxidant activity and bioactive compounds contents of blueberries showed there were no significant differences between fresh and frozen fruits. Also in the works of Begon a de Ancos *et all*., (2000) at the end of long-term frozen storage (12 months), no significant change of total phenolic content extracted was observed, but significant decreases of 14−21% in ellagic acid and of 33-55% in vitamin C were quantified.

Consequently, we have assigned task to study the change of color and antioxidant activity in cherry fruit in different ways of freezing.

2. Materials and methods

2.1. Materials

Studies conducted over the years 2016−2017 with the fruits of cherry variety Shpanka and Lotovka. Prepare fruit included: sorting, inspection, washing, hold 30 minutes in solutions of 20% sugar ascorutin 4% or 20% of the sugar with the addition of 1% chitosan, remove moisture, freezing at −25 °C, packing in plastic bags of 0.5 kg and storage at −18° C. By taking control of raw fruit cherries packed in plastic bags.

Fresh fruits and after six months of dry freezing determine soluble substances – refractometer (PAL-3 (ATAGO), Japan). Ascorbic acid was determined using the modified Tillman's method. Ascorbic acid was titrated with 2.6-dichloroindophenol under acid conditions (Naichenko, 2001). Tanning and coloring substances - by Neubauer and Leventhal (Naichenko, 2001), titrated with potassium permanganate (0.1n $KMnO_4$).

2.1.1.Antioxidant capacity. Antioxidant activity - by FRAP (Khasanov et all., 2004).

Measurements were performed on the millivoltmeter (MP 511 Lab pH Meter "Ulab", China) (mV). FRAP values were expressed as mmol 100g of dry matter, as mean value ± standard deviation (N = 3 replicates).

2.1.2.Colour analysis. Colour analysis was performed using a colorimeter (KFK-2, Russia) at by 30 mm thick plate. Three measurements were made at different points of the samples, and this procedure was repeated three times to get the average values.

Statistical analysis. The data were statistically processed using a two factor analysis of variance (ANOVA) method at significance level $P < 0.05$ on the PC program Statistica. A Fisher correlation analysis including all the parameters was also performed.

3.Results and discussions

As can be seen from Table 1, the content of dry soluble substances in fresh fruit of the cherry varieties of Shpanka averaged over two years of researching was 16.9%, while for fruit cherries variety of Lotovka – 15.2%, which is 1.7% lower, which is obvious due to the features of the variety.

As shown in Figure 1, after six months of frozen pre-processed fruit cherries in polyethylene bags, the content of dry soluble substances increased to 11–12%.

This is obviously due to the preliminary treatment of cherry fruit in sugar solutions with the addition of ascorutin or chitosan and the passage of osmotic processes.

The content of tannins and colorants in fresh fruit cherries averaged over two years of research was 0.67%, while for the fruits of the Lotovka variety, it was slightly less – 0.51%. After six months of freezing in the control version, their content decreased to 22–29%. While for fruit cherries, pre-treated with a sugar solution with chitosan addition, it decreased to 10–12%, and in processed solution of sugar with the addition of chitosan remained at the level of fresh cherry fruit. Obviously, the preservation of the content of tannins and colorants promoted to the before freezing. What is evidenced by the research results of Scibisz (2007) end Ngo et al. (2007) that the content of phenolic substances during freezing is reduced to 20–50%.

The content of ascorbic acid in the fruit of the cherry varieties of Shpanka variety was 19.8 mg/100g and Lotovka – 24.2 mg/100g. After six months of storage its contents decreased by 23 and 37.5%. This is confirmed by the results of the research of Begon a de Ancos (2000) end Ngo et al. (2007) on the reduction of the ascorbic acid content after freezing to 55%. Compared to fresh fruit cherries in pre-processed fruit cherry sugar solution with the addition of chitosan after freezing, the content of ascorbic acid remained at the level of fresh cherry fruit.

The content of tannins and colorants and ascorbic acid determines the antioxidant activity of the fruits and depends on the characteristics of the variety. For fruits, the cherry varieties of Shpanka are 38 mmoles / dm^3, and Lotovka – 23 mmoles/dm^3. After six months of freezing, antioxidant activity decreased to 15 and 18%. Whereas in the cultivated fruit, the cherry varieties of Shpanka and Lotovka with sugar solutions with the addition of ascorutin or chitosan remained at the level of fresh cherry fruit. The data obtained from studies are confirmed by Scibisz (2007) end Ngo et al. (2007) that freezing of fruits does not reduce their antioxidant activity.

Since color is one of the most important indicators of the maturity and quality of the fruits Pedišić (2009) end Gonçalves et al. (2007) was studied the change in the content of optical density and the world-propagation coefficient after freezing.

Table 1. The content of some components of the chemical composition cherry fruit varieties Shpanka and Lotovka

Varieties	**Years**	**Dry soluble substances, %**	**Tanning and coloring, substances, %**	**Ascorbic acid, mg / 100g**	**Light transmit - tance ratio**	**Optical density, %**	**Antioxi-dant activity, mmol / dm^3**
Shpanka	2016	16.1±0.2	0.67±0.03	17.6±0.2	27±2	0.62±0.22	48±2
	2017	17.6±0.2	0.67±0.02	22.0±0.3	29±1	0.54±0.24	28±3
	Average	16.9±0.2	0.67±0.02	19.8±0.2	28±2	0.58±0.23	38±2
Lotovka	2016	14.7±0.2	0.60±0.01	22.0±0.2	34±1	0.52±0.26	26±1
	2017	15.7±0.3	0.42±0.02	26.4±0.1	36±2	0.44±0.22	17±2
	Average	15.2±0.2	0.51±0.02	24.2±0.2	35±2	0.48±0.24	23±2
LSD_{05}		0.7	0.7	0.7	5.8	0.68	6.7

As can be seen from Figure 1, the change in the content of the optical density for fruit of the cherry varieties of Shpanka is 0.58, and Lotovka – 0.48.

After six months of freezing, it dropped to 48% and 14% accordingly, which is apparently due to the varietal peculiarity. After freezing of fruits cherry treated with sugar solution with the addition of ascorutin or chitosan, the optical density of the fruit of the cherry of the Spanka variety decreased to 53% and 75%, respectively, for the Lotovka variety to 83 and 79%. Similar results were obtained in the study of Gonçalves (2007).

As the color index is estimated by the world-propagation coefficient in the fruit of the Lotovka variety it was 28%, and Spanka 35%. After freezing, it increased to 11% and 46%, and in processed cherry fruit to 1.8 and 2.6 times, which is obviously due to the transfer of anthocyanins to cellular fruit juice and more intense coloration of cherry fruit. As the color is negatively correlated with the total content of anthocyanins Gonçalves (2007).

Processing of the data obtained by statistical methods of analysis allows us to show the regularity of numerical characteristics. Correlation indicators were established between the data obtained (Table 2, Figure 2). In particular, installed a strong and inverse correlation between the antioxidant activity and the content of ascorbic acid ($r = -0.72\pm0.05$), antioxidant activity and the content of tannins and colorants ($r = 0.54\pm0.05$), optical density and coefficient of light transmission ($r = –0.89 \pm 0.05$), dry soluble substances and tannins and colorants ($r = –0.78 \pm 0.05$).

Figure 2 shows the regression equation for these dependencies.

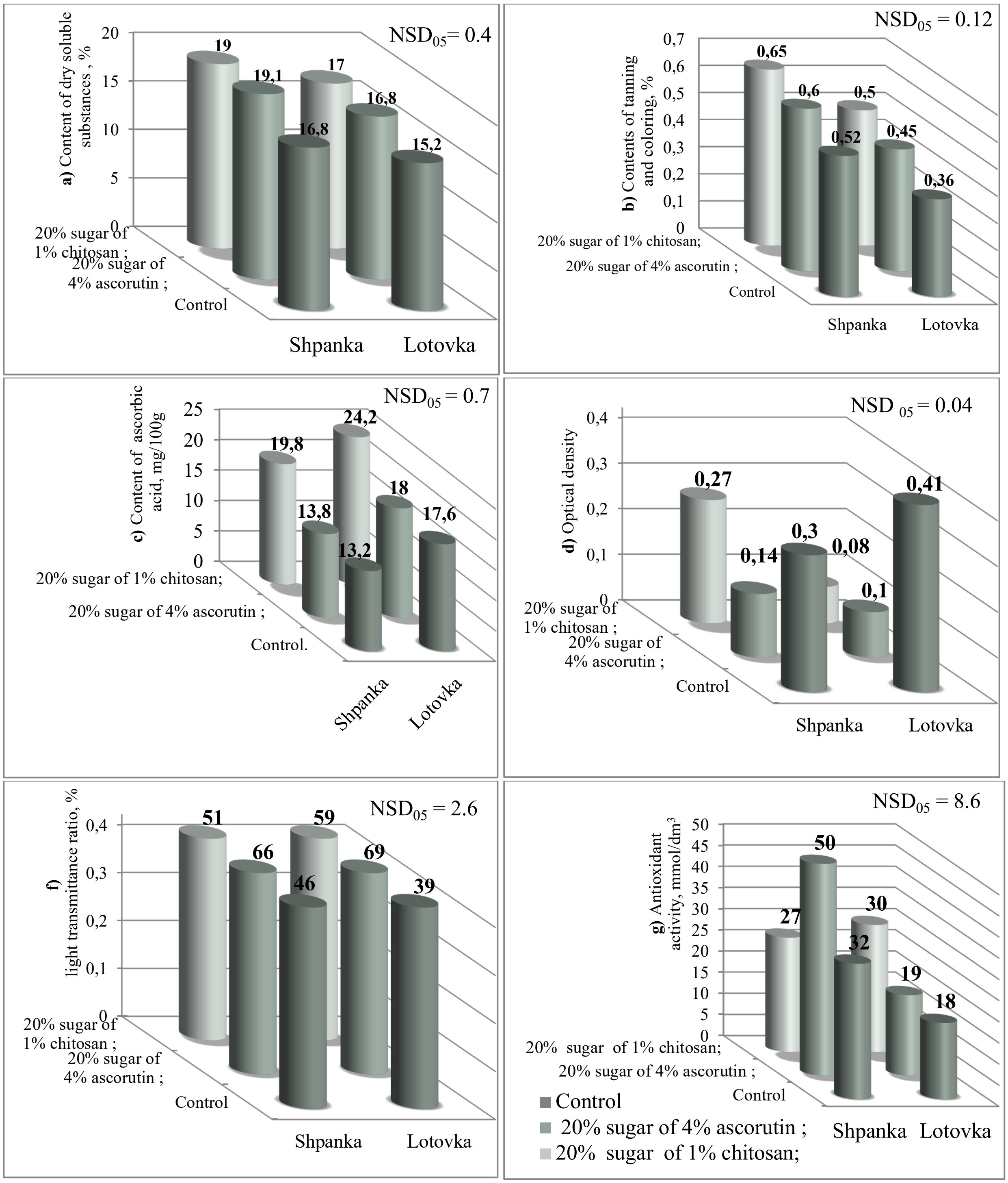

Figure 1. Contents: a) dry soluble substances; b) tanning and coloring; c) ascorbic acid; d) optical density; f) light transmittance ratio; g) antioxidant activity of fruits cherries varieties Shpanka and Lotovka

Table 2. The matrix of pairwise correlations between certain indicators of chemical composition and ability moisture-containing of frozen fruit cherries

Indicator	**Dry soluble substances**	**Tanning and coloring substances**	**Ascorbic acid**	**Light transmittance ratio**	**Optical density**	**Antioxidant activity**
Dry soluble substances	1	**0.78**	−0.10	0.46	−0.37	**0.61**
Tanning and coloring substances	**0.78**	1	−0.22	0.27	−0.22	**0.54**
Ascorbic acid	−0.10	−0.22	1	0.08	−0.39	**−0.72**
Light transmittance ratio	0.46	0.27	0.08	1	**−0.89**	0.46
Optical density	−0.37	−0.22	−0.39	**−0.89**	1	−0.17
Antioxidant activity	**0.61**	**0.54**	**−0.72**	0.46	-0.17	1

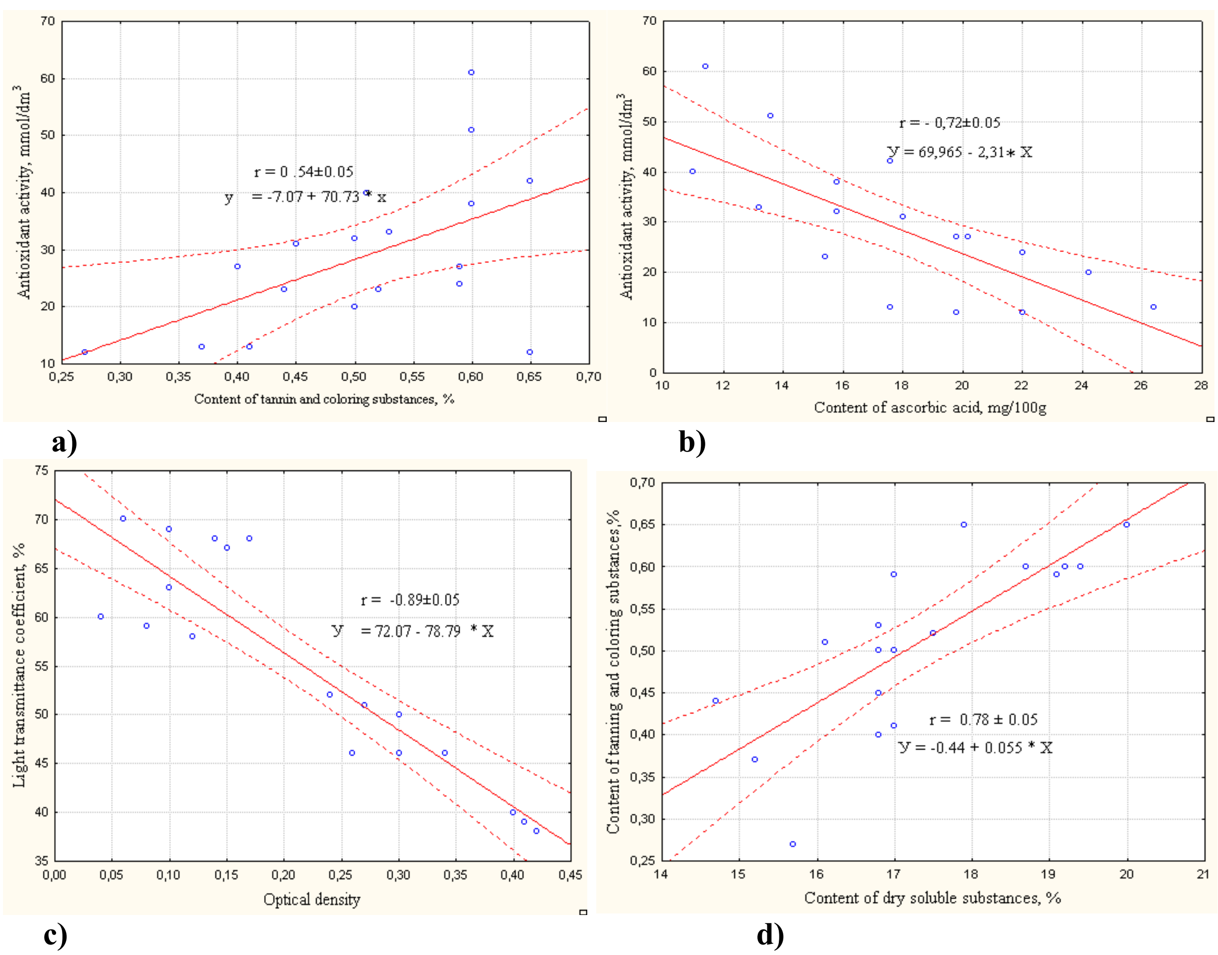

Figure 2. Regression equation and correlation between a) antioxidant activity and content: tanning and coloring agents and b) ascorbic acid, c) light transmittance ratio and optical density; d)content of soluble substances and tanning and coloring substances of fruit cherries varieties Shpanka and Lotovka

4.Conclusions

The content of tannins and colorants in cherry fruits is a varietal feature and after freezing in the fruits of the cherry varieties of Shpanka and Lotovka is reduced by 22 and 29%. Whereas in pre-treated fruits cherries by 20% sugar solutions with addition of 4% ascorutin or 1% chitosan decreased to 10 and 12%. The number of ascorbic acid in fruits, respectively, decreased to 23 and 38%. In addition, the smallest losses were for fruits treated with 20% sugar solution with the addition of 1% chitosan.

Antioxidant activity during freezing did not change significantly. It has been established that antioxidant activity correlates with the content of tannins and colorants and correlates with the content of ascorbic acid inverted.

The color indicator is a varietal feature. The optical density of the fruits of the cherry after the freezing negatively correlated and depended on the coefficient of light transmission.

5.References

Begon a de Ancos, Gonzalez, E. M., Pilar Cano, M. (2000). Ellagic acid, vitamin C, and total phenolic contents and radical scavenging capacity affected by freezing and frozen storage in raspberry fruit. *Journal Agricultural and Food Chemistry*, 48, 4565−4570.

Blando, F., Gerardi, C., Nicoletti, I. (2004). Sour cherry (Prunus cerasus L.) anthocyanins as ingredients for functional foods. *Journal of Biomedicine and Biotechnology*, 5, 253–258.

Dıaz-Mula, H.M., Castillo, S., Martınez-Romero, D., Valero, D., Zapata, P.J., Guille'n, F., Serrano, M. (2009). Sensory, nutritive and functional properties of sweet cherry as affected by cultivar and ripening stage. *Food Science and Technology International*, 15(6), 535−543.

Esti, M., Cinquanta, L., Sinesio, F., Moneta, E., Di Matteo, M. (2002). Physicochemical and sensory fruit characteristics of two sweet cherry cultivars after cool storage. *Food Chemistry*, 76, 399–405.

Ferretti, G., Bacchetti, T., Belleggia, A., Neri, D. (2010). Cherry antioxidants: from farm to table. *Molecules*, 15, 6993−7005.

Gao, L., Mazza, G. (1995) Characterization, quantification and distribution of anthocyanins and colourless phenolics in sweet cherry. *Journal of Agricultural and Food Chemistry*, 43, 343–346.

Goncalves, B., Silva, A.P., Moutinho-Pereira, J., Bacelar, E., Rosa, E., Meyer, A.S. (2007). Effect of ripeness and postharvest storage on the evolution of colour and anthocyanins in cherries (Prunus avium L.). *Food Chemistry*, 103, 976–984.

Gonçalves, B., Landbo, A.K., Knudsen, D., Silva, A.P., Pereira, J.M., Rosa, E. (2004). Effect of ripeness and postharvest storage on the phenolic profiles of cherries (Prunus avium L.). *Journal of Agricultural and Food Chemistry*, 52, 523–530.

Han, C., Zhao, Y., Leonard, S.W., Traber, M.G. (2004). Edible coatings to improve storability and enhance nutritional value of fresh and frozen strawberries (Fragaria ananassa) and raspberries (Rubus ideaus). *Postharvest Biology and Technology,* 33(1), 67–78.

Khasanov, V.V., Ryzhova, G.L., Maltseva, E.V. (2004). Methods for the determination of antioxidants. *Chemistry of Plant Raw Material*, 3, 63−75.

Levaj, B., Dragovic-Uzelac, V., Delonga, K., Kovacevic Ganic, K., Banovic, M., Bursac Kovacevic, D. (2010). Polyphenols and volatiles in fruits of two sour cherry cultivars, some berry fruits and their jams. *Food Technology and Biotechnology*, 48(4), 538–547.

Naichenko, V.M. (2001). Practicum on the technology of storage and processing of fruit and vegetables. (pp.158–162), Kyiv: FADA Ltd.

Ngo, T., Wrolstad, R.E., Zhao, Y. (2007). Color quality of Oregon strawberries − impact of genotype, composition, and processing. *Journal of food science*, 72(1), 25−32.

Pedisic, S., Levaj, B., Dragovic-Uzelac, V., Skevin, D., Skendrovic Babojelic, M.

(2009). Color parameters and total anthocyanins of sour cherries (Prunus cerasus L.) during ripening. *Agriculturae Conspectus Scientificus*, 74 (3), 259−262.

Sahari, M.A., Boostani, F.M., Hamidi, E.Z. (2004). Effect of low temperature on the ascorbic acid content and quality characteristics of frozen strawberry. *Food Chemistry*, 86(3), 357–363.

Scibisz, I., Mitec, M. (2007).The changes of antioxidant properties in highbush blueberries (Vaccinum corymbosum L.) during freezing and long term frozen storage. *Acta Scientiarum Polonorum Technologia Alimentaria*, 6(4), 75−82.

Serra, A.T., Duarte, R.O., Bronze, M.R., Duarte, C.M. (2011). Identification of bioactive response in traditional cherries from Portugal. *Food Chemistry*, 125, 318–325.

Szymczak, J.A., Rutkowski, K.P., Miszczak, A., Rozpara, E. (2003). Sensory evaluation of okordiao sweet cherry after storage. *Polish journal of food and nutrition sciences*, 12/53(3), 45−49.

Vasylyshyna E. (2017). Changes in antioxidant activity of cherry fruits and grapes during freezing. *Journal of food, agriculture & environment*, 15(2), 52−54.

Wang, H., Nair, M.G., Strasburg, G.M., Chang, Y.C., Booren, A.M., Gray, J.I. (1999). Antioxidant and anti-inflammatory activities of anthocyanins and their aglycon, cyanidin, from tart cherries. *Journal of Natural Products*, 62, 294–296.

Zoric, Z., Pedisic, S., Kovacevic, D.B., Jezek, D., Dragovic-Uzelac, V. (2016). Impact of packaging material and storage conditions on polyphenol stability, colour and sensory characteristics of freeze-dried sour cherry (prunus cerasus var. Marasca). *Journal of Food Science and Technology*, 53(2), 1247–1258.