

CHANGING THE ANTIOXIDANT ACTIVITY OF CHERRY FRUITS DURING STORAGE BY MEANS OF PRE-TREATMENT WITH POLYSACCHARIDE COMPOSITIONS

Olena VASYLYSHYNA¹

Abstract: *The article shows the effect of pre-treatment with chitosan and salicylic acid on the anthocyanin content of cherry fruits after storage. The research was conducted between 2016–2019 within the premises of the Station of Horticulture named after M.F. Sidorenko of the Institute of Horticulture of NAAS of cherry fruit varieties Alpha and Pamiat Artemenko. For the study, 15 trees of each variety were sprayed with a solution of 100 mg /l of salicylic acid; 1% chitosan with salicylic acid (100 mg /l) the day before harvest. The fruits were harvested at the consumption stage of ripeness from four different places of the crown from each tree of a certain variety and type of treatment, placed in boxes №5 weighing 5 kg for storage at a temperature of 1 ± 0.5 °C and relative humidity of $95\pm 1\%$. Non-treated cherry fruits were taken for control. The experiment was repeated three times. It was found, that the cherry fruits from the Alpha and Pamiat Artemenko varieties are dominated by anthocyanins: cyanidin-3-glucorutinoside in the amount of 204.9 and 103.5 mg/100 g and cyanidin-3-rutinoside 72 and 36.6 mg/100 g. In the period of storage, the content of cyanidin-3-glucorutinoside and cyanidin-3-rutinoside decreased by 1.6–1.7 and 1.2 times. The treatment of cherry fruits with a solution of chitosan reduced the losses of cyanidin-3-glucorutinoside by 1.56 –1.7 times and the cyanidin-3-rutinoside content to 8.7–7.6%. The content of cyanidin-3-glucorutinoside in cherries treated with a solution of chitosan with salicylic acid was the most preserved, as the losses decreased 1.5–1.25 times. The content of cyanidin-3-rutinoside decreased to 0.5-0.83%. A strong correlation ($r = 0.86$) was established between antioxidant activity and the light transmission coefficient and a regression equation was derived.*

Key words: *anthocyanins, cherry fruits, storage, chitosan, salicylic acid.*

¹ Uman National University of Horticulture, Faculty of Engineering and Technology, Institutaska,1, Uman city, 20305, Ukraine;
Correspondence: OLENA VASYLYSHYNA; e-mail: elenamila@i.ua.

1. Introduction

The cherry is a popular fruit crop, a source of anthocyanins which are pigments that render the red color of the fruit [9]. The quality of the cherry fruit is determined by its attractive color, sweet and sour taste. In cherries, the ripening process is associated with the accumulation of polyphenolic compounds. Polyphenols are secondary metabolites of plants involved in antioxidant protection against biotic and abiotic stresses. Modern epidemiological studies show the role of polyphenols in the prevention of cardiovascular diseases: cancer, osteoporosis, neurodegenerative diseases and diabetes, gastric ulcers, digestive system, eczema [1], [9]. Procyanidins contained in cherries increase nitrogen synthesis, inhibit platelet activation and stimulate anti-inflammatory cytokines. They limit the formation of free radicals by inhibiting the enzymes involved in their generation [1].

Cherry fruits include a phenolic composition consisting of flavonoids of so-called phenolic antioxidants, which include anthocyanins such as flavonols and flavan-3-oles (procyanidins) and phenolic acids [2], [10].

The total content of anthocyanins differs by variety. The main anthocyanins of cherry fruits are: cyanidin-3-glucoside, cyanidin-3-glucosidrutinoside, cyanidin-3-sophoroside [1], [9].

The total content of anthocyanins in cherry fruits ranges from 82 to 297 mg /100 g for dark and from 2 to 41 mg /100 g for light fruits [9].

Studies [6] show that the daily intake of cherries – 280 g (45 fruits) is sufficient to replenish the body with phenolic substances, including anthocyanins.

There is almost no information in the literature on the relationship between the anthocyanin content and the color of cherry fruits. Whereas, as regards the transmittance, the angle of hue is negatively correlated with the total anthocyanin content in cherries and weakly correlated in plums [6], [12].

The goal of the research was to determine the effect of treatment with chitosan and with salicylic acid on the color change of cherry fruits during storage.

2. Materials and Methods

Pre-harvest and postharvest treatments.

The research was conducted in the period of 2016–2019 in the premises of the Station of Horticulture named after M.F. Sidorenko of the Institute of Horticulture of NAAS on cherry fruits of the Alpha and Pamiat Artemenko varieties. For the study, 15 trees of each variety, were sprayed with a solution of 100 mg /l of salicylic acid; 1% chitosan with salicylic acid (100 mg/l) the day before harvest. After 24 hours, the fruits were removed at the consumption stage of ripeness from four different places of the crown from each tree of a certain variety and type of processing, placed in boxes №5 weighing 5 kg for storage at $1 \pm 0.5^{\circ}\text{C}$ and a relative humidity of $95 \pm 1\%$. Raw cherry fruits were taken for control. The experiment was repeated three times.

2.1. Analytical Methods

The criterion for the termination of fruit storage was weight loss of not more than 6% [8].

The content of anthocyanins: cyanidin-3-glucorutinoside and cyanidin-3-rutinoside

was determined by high performance liquid chromatography with a diode-matrix detector (chromatograms with absorption spectra) by means of a Waters instrument (USA).

For the research, cherries were soaked in an ethanol solution for 4–5 days, stirring thoroughly from time to time. The solution was filtered through a paper filter (white tape). The filtrate was transferred to a separatory funnel and diluted with an aqueous potassium chloride solution 20 times. The solution in the separatory funnel was extracted 4 times with ethyl acetate (pre-soaked in water) at a ratio of organic and aqueous phases 1:3. The ethyl acetate phases were discarded and the aqueous solution was purged with helium to remove ethyl acetate. Anthocyanin glycosides were removed from the aqueous solution using solid phase extraction cartridges (Sep Par Cartridges for Solid Phase Extraction (company Waters, USA). Methanol-eluted from the surface of the sorbent anthocyanin glycosides were removed by evaporation of methanol (pre-acidified to pH 1 with hydrochloric acid) in vacuum. Thus, anthocyanin glycosides were obtained in a preparative form. Because according to the literature (Guide to methods of quality control and safety of dietary supplements. P 4.1.1672-03.) [5] glycosides cyanidin-3-glucorutinoside and cyanidin-3-rutinoside are dominant in cherries. The relative content of cyanidin-3-glucorutinoside and cyanidin-3-rutinoside is defined as the ratio of the area of the chromatographic peak and the sum of the peak planes of all identified anthocyanins.

The ratio of the chromatographic peaks of these two glycosides that was discovered, was calculated according to the content of each glycoside in the

obtained preparatively isolated standard $m = S_1/S_2$, (where S_1 is the peak area of Cyd-3-glu-rut; S_2 is the peak area of Cyd-3-rut; m is the mass of glycosides).

A color analysis was performed by using a colorimeter (KFK-2, Russia) on a 30 mm thick plate, in 20 fruits of each grade. Three measurements were performed at different points on the samples, and this procedure was repeated three times to obtain average values.

Antioxidant activity was determined using the FRAP method [7].

2.2. Statistical Analysis

The data were statistically processed using a two and three factor analysis of variance (ANOVA) method at a significance level of $P < 0.05$ on the Statistica PC software.

3. Results and Discussions

Considering that the main indicator of quality and freshness of cherry fruits is color, the aim of the study was to examine its changes during storage. In studies on cherries of the varieties Alpha and Pamiat Artemenko, the content of cyanidin-3-glucorutinoside depended on the characteristics of the variety and was at the level 204.9 and 103.5 mg/100 g (Figure 1). During the period of storage, its content decreased 1.6-1.7 times.

According to the content of cyanidin-3-rutinoside, cherry fruits had lower values – namely 72 and 36.6 mg/100 g. During storage, its content remained more stable and decreased 1.16–1.2 times as compared to fresh cherries.

The treatment of cherry fruits with a solution of chitosan allowed the reduction of the loss of cyanidin-3-rutinoside by

8.7–7.6% (Figure 1). While the content of cyanidin-3-glucorutinoside slightly

decreased 1.56 and 1.7 times respectively.

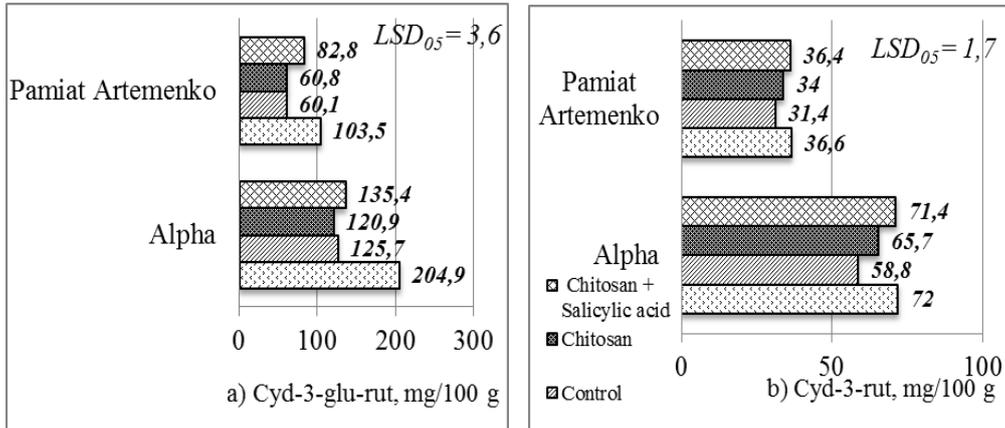


Fig. 1. Changes in anthocyanins: cyanidin-3-glucorutinoside and cyanidin-3-rutinoside in cherry fruits during the period of storage

Cherry fruits treated with a solution of chitosan with salicylic acid had a lower loss by 1.5–1.25 times (Figure 1).

The antioxidant activity of cherry fruits pertaining to the varieties Alpha and Pamiat Artemenko, which determines the content of biologically active substances was at the level of 28–27 (Figure 2). During storage is decreased 1.7 times.

The content of cyanidin-3-rutinoside decreased slightly by 0.5–0.83% and remained at the level of fresh cherries.

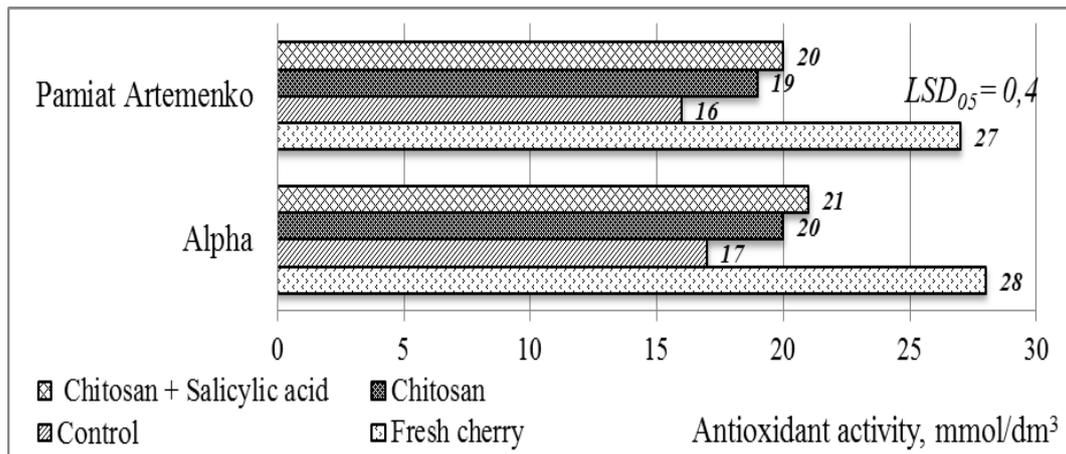


Fig. 2. Changes in antioxidant activity of cherry fruits during the period of storage

Cherry fruits treated with a chitosan solution had higher antioxidant activity as compared to fresh cherries in which it decreased 1.4 times. In cherry fruits

treated with a solution of chitosan with salicylic acid, the antioxidant activity of the fruit is higher and it decreased only 1.3–1.35 times. The change in anthocyanin

content in cherry fruits during the period of storage is confirmed by B. Goncalves [3, 4].

Thus, according to the data [4], [11] color and hue have a negative correlation with the total content of anthocyanins (Figure 3). Determination of color gives an estimate of the change in the content of

anthocyanins in cherry varieties during storage. We determined the relationship between antioxidant activity, light transmission and the content of cyanidin-3-glucorutinoside and cyanidin-3-rutinoside (Table 1 and Figure 4).

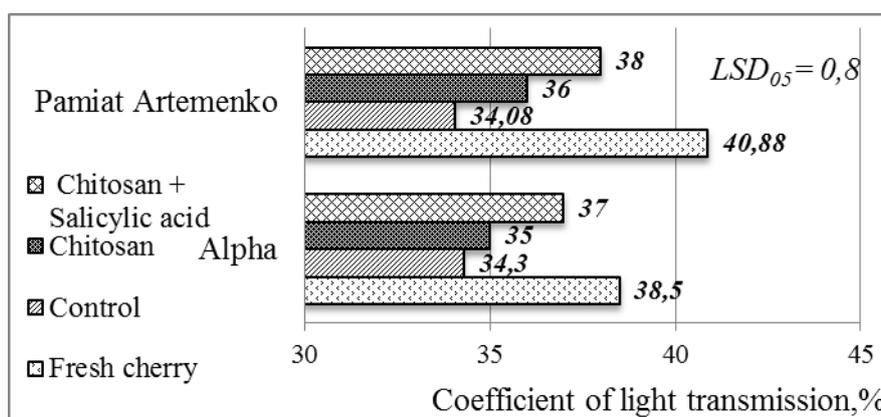


Fig. 3. Changes of the light transmission coefficient in cherry fruits during storage

Table 1

Matrix of paired correlations between storage duration, weight loss and yield of marketable cherry fruits

Indicator	The content of cyanidin -3-glucorutinoside, mg/100 g, X_1	The content of cyanidin -3-rutinoside, mg/100g, X_2	Coefficient of light transmission, X_3	Antioxidant activity, mmol/dm ³ , X_4
The content of cyanidin-3-glucorutinoside, mg/100 g, X_1	1.000	0.863	0.289	0.644
The content of cyanidin-3-rutinoside, mg/100 g, X_2	0.863	1.000	-0.054	0.297
Coefficient of light transmission, %, X_3	0.289	-0.054	1.000	0.872
Antioxidant activity, mmol/dm ³ , X_4	0.644	0.297	0.872	1.000

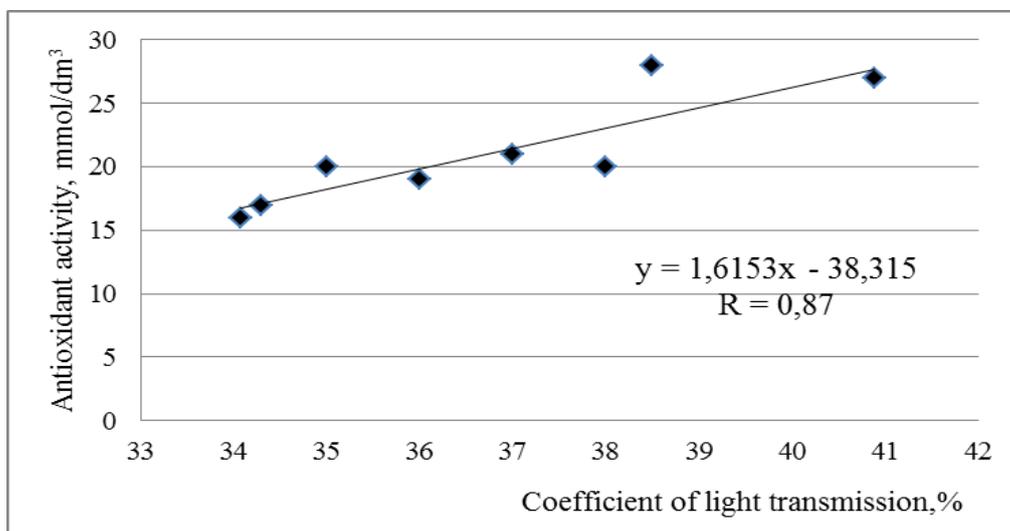


Fig. 4. Dot graphs and theoretical lines of dependence of antioxidant activity on the coefficient of light transmission of cherry fruits of the Alpha and Pamiat Artemenko varieties during storage

It's showed that there is an average correlation between the content of cyanidin-3-glucorutinoside and the antioxidant activity with a correlation coefficient $r = 0.64$.

The correlation dependence between antioxidant activity and light transmission is also strong with a correlation coefficient $r = 0.86$.

The correlation dependence between the content of cyanidin-3-glucorutinoside and cyanidin-3-rutinoside is also strong with a correlation coefficient $r = 0.87$. Based on the fact that the correlation is strong, regression equations are derived, which allow us to predict the antioxidant activity of cherry fruits according to the content of cyanidin-3-glucorutinoside or light transmission.

4. Conclusions

Thus, in the cherry fruits of the Alpha and Pamiat Artemenko varieties,

anthocyanins are predominant: cyanidin-3-glucorutinoside in the amount of 204.9 and 103.5 mg/100g and: cyanidin-3-rutinoside 72 and 36.6 mg/100 g.

During the period of storage, the content of cyanidin-3-glucorutinoside and cyanidin-3-rutinoside decreased 1.6-1.7 and 1.2 times respectively.

The treatment of cherry fruits with a solution of chitosan allowed cutting the loss of cyanidin-3-glucorutinoside by 1.56–1.7 times and of cyanidin-3-rutinoside to 8.7–7.6%.

The content of cyanidin-3-glucorutinoside in cherries treated with a solution of chitosan with salicylic acid was the most preserved, where the losses decreased 1.5–1.25 times. The content of cyanidin-3-rutinoside decreased to 0.5–0.83%.

A strong correlation dependence ($r = 0.86$) was found between the content of antioxidant activity and the light

transmission coefficient thus the regression equation was derived.

References

1. Capanoglu E., Boyacioglu D., Vosb R.C.H. et al., 2011. Procyanidins in fruit from sour cherry (*Prunus cerasus*) differ strongly in chainlength from those in Laurel cherry (*Prunus lauracerasus*) and Cornelian cherry (*Cornus mas*). In: Journal of Berry Research, vol. 1, pp. 137-146. doi:10.3233/BR-2011-015.
2. Ferretti G., Neri D., Bacchetti T., 2014. Effect of Italian sour cherry (*Prunus cerasus* L.) for the formation of advanced glycation end products and lipid peroxidation. In: Food and Nutrition Sciences, vol. 5, pp. 1568-1576. doi:10.4236/fns.2014.516170.
3. Goncalves B., Landbo A.-K., Knudsen D. et al., 2004. Effect of ripeness and postharvest storage on the phenolic profiles of cherries (*Prunus avium* L.). In: Journal of Agricultural and Food Chemistry, vol. 52(3), pp. 523-530. doi: 10.1021/jf030595s.
4. Goncalves B., Silva A.P., Moutinho-Pereira J. et al., 2007. Effect of ripeness and postharvest storage on the evolution of colour and anthocyanins in cherries (*Prunus avium* L.). In: Food Chemistry, vol. 103, pp. 976-984. doi: 10.1016/j.foodchem.2006.08.039.
5. Guide to methods of quality control and safety of dietary supplements, 2004. P 4.1.1672-03. Ministry of Health of Russia, Moscow, Russia.
6. Jakobek L., Seruga M., Voc S. et al., 2009. Flavonol and phenolic acid composition of sweet cherries (cv. Lapins) produce on six different vegetative rootstocks. In: Scientia Horticulturae, vol. 123, pp. 23-28. doi: 10.1016/j.scienta.2009.07.012.
7. Khasanov V.V., Ryzhova G.L., Maltseva E.V., 2004. Methods for the determination of antioxidants. In: The Chemistry of Plant Raw Material Academic Journal, vol. 3, pp. 63-75.
8. Naichenko V.M., 2001. Practicum on technology of storage and processing of fruits and vegetables. Pupil, Kyiv, Ukraine.
9. Pedisic S., Levaj B., Dragovic-Uzelac V. et al., 2009. Color parameters and total anthocyanins of sour cherries (*Prunus cerasus* L.) during ripening. In: Agriculturae Conspectus Scientificus, vol. 74(3), pp. 259-262.
10. Toydemir G., Capanoglu E., Kamiloglu S. et al., 2013. Jules beekwilderb changes in sour cherry (*Prunus cerasus* L.) antioxidants during nectar processing and in vitro gastrointestinal digestion. In: Journal of Functional Foods, vol. 5, pp. 1402-1413. doi.org/10.1016/j.jff.2013.05.008.
11. Vasylyshyna O., Postolenko Y., 2019. Influence of freezing method on color change and antioxidant activity in cherry fruit. In: Carpathian Journal of Food Science and Technology, vol. 11(4), pp. 133-140. doi.org/10.34302/2019.11.4.12.
12. Viljevac M., Dugalic K., Jurkovic V. et al., 2012. Relation between

polyphenols content and colour in
sour cherry fruits. In: Journal of
Agricultural Sciences, vol. 57(2),

pp. 57-67.
10.2298/JAS1202057V.

doi: