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Cherry chemical composition and antioxidant activity under freezing comprehensive relations assessment

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Abstract: Cherry is a successful combination of sugars, acids, attractive color and taste. However, its shelf life is limited and can be prolonged only with the help of new freezing technologies. Therefore, the gool of this work was to investigate changes in component composition of fresh and frozen cherry. The objects of the research were cherries of the varieties of Shpanka and Lotovka. The studies were carried out with cherries grown in the Central region of Ukraine at the Department of Technology of storage and processing of fruits and vegetables at Uman National Horticulture University. For cherries of both varieties were kept in 20% sugar solution with the addition of 4% ascorutin 1% chitosan for 30 minutes, dried with air flow, frozen at –25°C, packed in 0.5 kg plastic bags, and stored at –18°C. For control purposes, nontreated cherries were packed in plastic bags of respective volume. According to the research, preprocessing with 20% sugar solution with the addition of 1% chitosan contributes to preservation of quality and biological value of frozen cherries. Thus antioxidant activity in frozen cherries of Shpanka and Lotovka varieties is 27 and 18 mmol/dm^3, ascorbic acid content – 17.6 and 20 mg/100g. So the indexes of quality of cherries for freezing are interrelated and constitute one correlation pattern in which the major index indicator is the content of dry soluble substance and antioxidant activity.

Keywords*:* Frozen cherries, tanning and coloring substances, ascorbic acid, antioxidant activity

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INTRODUCTION

Cherry is a successful combination of sugars, acids, attractive color and taste. Formation of the chemical composition of fruits, including cherries, depends on the species, variety, degree of ripeness, growing area, weather conditions, etc. To a large extent these change food quality and nutritional value [1–5].

The total sugar content is 6.5–21.5%, of which glucose is 3.8–5.3%, fructose is 3.3–4.4%, and sucrose – 0.8%. Acidic component is 0.7–3.0%, mainly containing malic and citric asids, and in a small amount – succinic, formic, and traces of salicylic acid. Combined with sugars, acids determine the sweet and sour taste of cherries. As for vitamins, the fruit contains vitamin C in the amount of 10–50 mg/100 g, as well as vitamins B_1, B_2, B_9, and PP. Tannins in the amount of 0.05–0.34% provide the tart flavor. However, the number of useful substances is 0.8% [1–3].

Moisture regime, minimum and maximum temperatures at different periods of the tree growth are the main factors that determine the yield of cherries. The ripening conditions of fruits, including cherries, depend on the cultivation characteristics. For example, warm weather in June and July contributes to early ripening of the berries while low temperatures with heavy rains cause later ripening of fruits [4–6].

Weather conditions, especially before harvesting, affect cultivation of fruits and the yield. Warm weather during the flowering period with temperatures above 16°C promotes the production of good flower pollinate [7].

Temperature lowering during flowering within some years to –2.4°C causes decrease in crop productivity of cherry [8]. High rainfalls reduce productivity due to cracking of the fruit. High daytime temperatures (33°–37°C) during the harvest are unfavourable [7].

Cherries quality has a varietal character and changes during the growing season. Different varieties of cherries display various reactions to change in weather conditions, including hydrothermal coefficient (HTC), especially in the last ripening period of 10–15 days before removal [22].

Increased temperatures and reduced humidity increase the content of soluble dry substances, including sugars [10, 11]. In years with high temperatures and minimal rainfall during ripening acidity is reduced while in years with a cool and humid ripening period it is, conversely, increased [12].

Rainfalls, temperature and humidity affect accumulation of ascorbic acid. Cool weather with lots of rainfalls is one of the positive factors for accumulation of ascorbic acid [6, 13]. Temperature lowering during fructification increases its content in cherries [10].

The number of tannins in cherries varies depending on weather conditions, but less than the amount of ascorbic acid [13]. The total content of phenolic compounds depends on the temperature of growing fruits. Black cherry grown at a temperature of 25–30°C have a higher content of anthocyanins and phenols. The formation of basic phenols (anthocyanins) observed within the last few weeks before harvest contributes to the antioxidant activity [14].

Antioxidant activity most significantly correlates with the content of total phenolic compounds and anthocyanins, while ascorbic acid significantly impacts the total antioxidant activity [17].

Antioxidants determine the color of fruits and exhibit antiradical and antioxidant activities. However, during processing they are lost. We know about the 88% change of anthocyanins in cherries frozen at −23°C for six months.

Therefore, to reduce the loss of anthocyanins and the antioxidant activity, ways of enriching and adding antioxidants to food products are used. It is possible to extend storage by slowing lipid peroxidation, which is one of the reasons for food quality reduction during processing and storage [16–19].

M.S. Shaheen suggested the use of complex chitosan-fructose to prevent lipid oxidation in meat [20].

However, the period of cherry consumption is limited to the period of maturation, only 10–15 days. And it is possible to continue the period of maturation by using new technologies, in particular freezing. However, at the stage of defrosting of raw materials a significant amount of sugars and acids is lost, thus deteriorating the appearance. So before the freezing process, antimicrobial substances, antioxidants and film-forming substances are used. One of these substances is chitosan. This polysaccharide is a biopolymer that is widely used in agriculture, biotechnology, food industry and has antibacterial and antifungal properties [21–29].

According to the literature, coating based on chitosan and 5% calcium gluconate or chitosan with the addition of 0.2% tocopherol acetate reduces fruit disease and weight loss, delays discoloration, loss of density, and deterioration of texture during storage [30]. So, according to Begon a de Ancas [31], in frozen berries of raspberry treated with a chitosan solution the content of phenolic compounds by the end of the freezing decreased by 14–21%, ascorbic acid by 33–55%.

Also according to Yan Jiang et al. [32], the mixture of 3% chitosan, 0.75% glycerol, 0.25% sapn, 40.5% corn syrup, 3% pectin solution, 88% distilled water was used for pre-freezing blueberries. Thereby loss of density and juice reduced, and product quality improved.

It is also known From the literature that to calculate statistical research results is to use evaluation of appropriate dependency and statistical comparison of the variance/covariance. Correlation matrix, sometimes visualized, using correlation galaxy is among principal components of the analysis [33–38].

The goal set is to investigate changes in the composition of cherry to establish correlations between the components of fresh cherry and frozen cherry treated with chitosan solution [36, 39–42].

STUDY OBJECTS AND METHODS

The objects of research were cherries of the varieties of Shpanka and Lotovka. The studies were carried out during 2015–2016 with cherries grown in the Central region of Ukraine. The variety is zoned in the forest steppe, Polesye and Western Ukraine. For this research, cherry varieties of Shpanka and Lotovka were harvested 2–3 days before the consumer maturity stage. These conditions of cultivation affected the long ripening periods in 2015 and 2016 years.

A significant difference in growing season length of cherries in 2015–2016 (Table 1) was caused by hydrothermal conditions within 15 days of ripening before harvesting. In particular, in the last 15 days of ripening the sum of effective temperatures in 2016 was 143.2°C less than in 2015.

This happened alongside with the amount of precipitation reduction to 12.8 and 30.7 mm and with increase in HTC to 0.4 and 2.1 in 2015 and 2016, respectively.

Obviously, the total rainfall has more influence on cherries than the temperature during the growing season. Specifically, comparing hydrothermal conditions, the sum of effective temperatures during the growing season in 2016 was lower by 166°C to 2015. But rainfall was only 42.8 mm less than in 2016. While rainfall for the 15-day period of maturation in 2015 was 12.8 mm, in 2016 its index was 30.7 mm, respectively HTC 4.1 and 4.8. Thus, fruits ripen more effectively at lower precipitation and lower temperatures (2015).

Reduced amount of effective temperatures and increased precipitation at the final stage prolong the period of ripening.

Table 1. Agroclimatic indexes during the growing season of cherries (According to Uman weather station)

Year	Growing season	The sum of effective temperatures,°C		Rainfall, mm		HTC	
		growing season	phase of ripening 15 days	growing season	phase of ripening 15 days	growing season	phase of ripening 15 days
2015	89	564.2	286.8	233.9	12.8	4.1	0.4
2016	80	398.2	143.6	191.1	30.7	4.8	2.1

Table 2. The content of some components in the chemical composition of the cherries

Year	Dry soluble substances, %	Acid (in terms of malic), %	Tanning and coloring substances, %	Ascorbic acid, mg/100g	Antioxidant activity mmol/dm^3
			Shpanka		
2015	16.4	1.02	0.66	20.0	26
2016	15.8	0.72	0.68	17.2	28
Average	16.1	0.87	0.67	17.6	27
			Lotovka		
2015	15.2	1.40	1.03	18.0	17
2016	14.8	0.90	1.04	22.0	19
Average	15.0	1.15	1.04	20.0	18
NSD_{05}	0.7	0.70	0.50	0.5	1.0

The study of cherry varieties was conducted at the Department of Technology of storage and processing of fruits and vegetables at Uman National Horticulture University during 2015–2016. Cherries were kept in 20% sugar solution with the addition of 4% ascorutin or 20% sugar solution with the addition of 1% chitosan for 30 minutes, dried with air flow and frozen at –25°C, packed in 0.5 kg plastic bags and stored at –18°C. For control purposes, nontreated cherries were packed in plastic bags.

Contents of dry soluble substances in cherries before and after freezing were determined by refractometric method [43], acids by alkali titration (GOST 25555.0-82) [44], the content of tannins and coloring substances – by Neubauer and Leventhal methods [43], ascorbic acid – by iodometric method [43], and antioxidant activity – by FRAP [48]. Weight of the analysis material was 2 kg. The procedure was repeated three times.

By the method of correlation pleiades [39, 45, 46], the correlation between the components of the chemical composition of the cherries was determined. For this:

(1) Using modern statistical analysis software, correlation coefficients were calculated between the set attributes for a specific number of connections, whose number

$$C = N (N–1) 2,$$

where C is the number of connections; N is the number of characters, of = 5 (5 – 1) : 2 = 10.

(2) Correlation matrix of dependencies was built in which correlation coefficients significant at confidence level of $p < 0.05$ were extracted .

(3) Correlation ring was built in which primary connections centers were defined.

(4) Degree of dependence between the following qualitative characteristics was set:

– CSS is the content of soluble substances, %;

– TA is content of titrated acids (on conversion to malic acid), %;

– AA is ascorbic acid content, mg/100g;

– TC is the content of tannins and coloring substances, %;

AOA is antioxidant activity, mmol/dm^3.

Mathematical processing of data held by Dospyehov B.A. (1979) [47] on the PC using the programs “Excel 2000” and “Statistica”.

RESULTS AND DISCUSSION

The chemical composition of the cherry (Table 2, Fig. 1) depends on climatic parameters in the last 15 days of maturation.

A high content of soluble dry matter was observed in the cherries in 2015 (15.2% and 16.4%). High temperatures and almost no rain over the 15 days of ripening contributed to this. The sum of effective temperatures within the 15 days of ripening amounted to 286.8°C which was 143.6°C more than in 2016. Over the 15 days of cherry ripening in 2015 there was little rain – 12.6 mm.

Significant reduction of dry soluble substances (14.8% and 15.8%) was recorded in cherry harvested in the years of 2016 and 2015 which were characterized by a low amount of effective temperatures, especially in the last 15 days of ripening, while rainfall rates amounted to 12.8 and 30.7 mm. This confirms the increasing value of HTC (2.1 and 1.6) in the last 15 days of maturation. As compared to 2015, in 2016 the content of dry soluble substances decreased by 4.0 and 4.2%.

The level of generalized quality indicator of fruits − dried soluble substances − significantly increased by 0.4 and 0.6% with the increase of effective temperatures to 286.8 and 143.6°C and the reduction of rainfall to 12.8 and 30.7 mm in the last 15 days of maturation.

An important component of the chemical composition of the fruits is acids. Their level in cherries is 0.72−1.4%. However, the level of acids depends on environmental indicators. Given that there was no significant difference (1.4%) between the acid content in the cherries harvested in 2015 and 2016, the increase in the fruit harvested in 2015 (1.4%) was ruled by its own laws in synthesis and accumulation.

Dry conditions during ripening and much rain influence acid accumulation and, being a synthetic material, it is rapidly accumulated. Acid content increased by 29–35% in 2016 compared with 2015 yield. Conversely, it decreased significantly in the cherry in 2016 due to the increase in rainfall. The results of research of Kaldmae et al. (2013) [6] and Chernozubenko (1993) [13] confirm that low temperatures and adequate moisture contribute to longer ripening and higher levels of acid accumulation.

Biologically active substances of cherries are represented by polyphenolic substances and ascorbic acid.

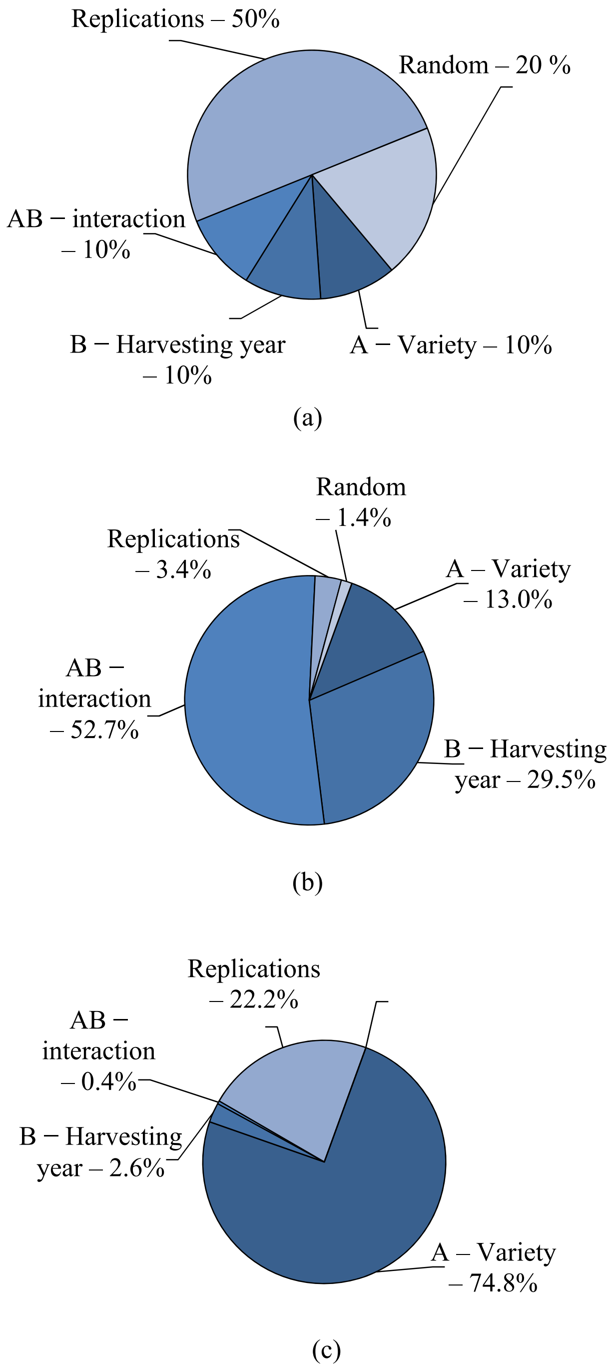

Fig. 1. Influence of factors A (variety) and B (harvesting year) on: (a) tanning and coloring substances, (b) ascorbic acid, (c) antioxidant activity of cherry.

The total content of tannins and coloring substances was consistently high averaging 0.66–1.04%. Weather conditions had no significant effect on this indicator.

The content of ascorbic acid in cherries was 17.2–22% mg/100g, changing under the influence of weather conditions during the growing season and the 15-day period of maturation. High concentrations of ascorbic acid reached 22 mg/100g in 2016 and 17.2 mg/100g in 2015. In 2015 and 2016, respectively, the decrease of effective temperatures by 1.1 and 2.3 times exceeds the rainfall by 3.4 and 2.0 times as compared to 2015, HTC reaching 0.4 and 2.1.

In 2015 and 2016 the highest amount of effective temperatures was observed, precipitation was practically unavailable in 2015. Thus, the high content of ascorbic acid in cherries correlated with conditions during ripening. Drought was extreme conditions for cherry in 2015, and the content of ascorbic acid was the lowest – 18.0 mg/100g. This confirms the results of Kaldmae et al. (2013) [6] .

Antioxidant activity of cherries depends on polyphenolic substances and ascorbic acid contents. Antioxidant activity is not only consistently high averaging 17–22 mmol/dm^3.

In order to emphasize the contribution of each factor, they were represented as the proportion of total changes attributable to each factor. For each chemical characteristic, a pie chart was used for displaying the proportion of total change that corresponds to experimental factors and interactions (Figs. 1 and 2).

The impact of each factor is demonstrated in Fig. 1 which shows the influence of the harvesting year and the varieties of the chemical composition of the cherries. The analysis of variance revealed that the main effects – harvesting year and varieties of the phase – indicated highly significant differences ($p < 0.05$) for all chemical characteristics analyzed, as shown in Fig. 1. The influence of various pre-treatment methods was the most effective. The influence of A (variety), B (harvesting year) and AB (interaction) was 13, 29.5 and 52.7% for ascorbic acid; 74.8, 2.6 and 0.4% for antioxidant activity; 10% each for tanning and coloring substances.

For the tanning and coloring substances the main effects were the harvesting year and features of the varieties. As for ascorbic acid, the statistical tests performed showed the influence of the features of the varieties (which explained 13% of the variability) and the importance of the harvesting year (29.5%). Among the most important interactions were the features of the variety, which registered 74.8% of the antioxidant capacity, while the remaining interactions altogether had less than 3%.

The contents of some components of the chemical composition of cherry before and after storage are shown in Table 3. It is seen that content of soluble dry matter in fresh cherry varieties of Shpanka and Lotovka is 16.1 and 15.0%, titrated acids – 0.87 and 1.15%, tanning and coloring substances – 0.67 and 1.04%, and ascorbic acid – 17.6 and 20.0 mg/100g. After six months of freezing, the content of dried soluble substances in processed cherries increased by 2.0–28.0% which was caused by processing in sugar solution with added chitosan or ascorutin and diffusion process.

Table 3. The contents of some components of the chemical composition of cherries

Type of treatment	Dry soluble substances, %	Titrated acid (in terms of malic), %	Tanning and coloring substances, %	Ascorbic acid, mg/100 g	Antioxidant activity, mmol/dm^3
Shpanka Before freezing					
	16.1 ± 0.2	0.87 ± 0.02	0.67 ± 0.02	17.6 ± 0.2	27 ± 2
After freezing:					
Without treatment (control)	16.1 ± 0.3	0.86 ± 0.03	0.51 ± 0.03	11.0 ± 0.2	23 ± 3
20% sugar solution with 4% ascotutin	16.4 ± 0.3	0.80 ± 0.02	0.60 ± 0.02	11.0 ± 0.3	24 ± 2
20% sugar solution with 1% chitosan	20.0 ± 0.2	0.75 ± 0.02	0.65 ± 0.01	17.6 ± 0.2	27 ± 1
Lotovka Before freezing					
	15.0 ± 0.2	1.15 ± 0.02	1.04 ± 0.02	20.0 ± 0.2	18 ± 2
After freezing					
Without treatment (control)	15.0 ± 0.1	1.14 ± 0.02	0.88 ± 0.01	13.3 ± 0.2	14 ± 1
20% sugar solution with 4% ascotutin	15.4 ± 0.2	1.08 ± 0.02	0.96 ± 0.02	13.4 ± 0.3	15 ± 2
20% sugar solution with 1% chitosan	9.2 ± 0.1	1.00 ± 0.03	1.03 ± 0.03	20.0 ± 0.1	18 ± 1
NSD_{05}	0.4	0.20	0.40	0.6	0.4

Obviously, the content of titrated acids also changed. In particular, in the control batch as compared to the fresh fruits these contents remained almost unchanged. In the cherries processed by 20% sugar solution with the addition of 4% ascorutin it decreased to 7% and those processed by 20% sugar solution with the addition of 1% chitosan to 13%. Apparently, this is due to osmotic processes and diffusion of solutions.

The content of tannins and coloring substances in frozen cherries decreased slightly. After a six months of freezing, it decreased by 23 and 15% in the control variant of cherry varieties Shpanka and Lotovka while in the processed cherries, compared to the fresh ones, it decreased by 3 and 10%. Obviously, for tanning and coloring substances preservation pre-treatment before freezing is preferable. Confirming the results of research of Scibisz et al. [35], it is shown that the loss of phenolic compounds in cherries after six months of freezing amounted to 20–50%.

The content of ascorbic acid in the control variant, compared to fresh cherries varieties decreased by 37.5 and 37.9 %, except for the cherries processed with 20% solution of sugar with the addition of 1% chitosan, in which the content of ascorbic acid remained the same as in fresh cherries. This confirms the results of Begon a de Ancos' research [31], according to which after freezing the content of ascorbic acid is reduced by 33–55%.

Antioxidant activity of Shpanka and Lotovka cherry varieties is caused by fruit tannins and coloring substances and averages 27 and 18 mmol/dm^3 for fresh cherries, decreasing after freezing by 11−22%. It remained the highest for cherries processed with 20% solution of sugar with the addition of 1% chitosan, which is confirmed by the research of Scibisz et al. [35] stating that freezing does not result in significant losses of antioxidant activity.

The impact of each factor is shown in Fig. 2 that shows the influence of various pre-treatment methods and varieties after freezing. The influence of various pre-treatment methods was the most effective.

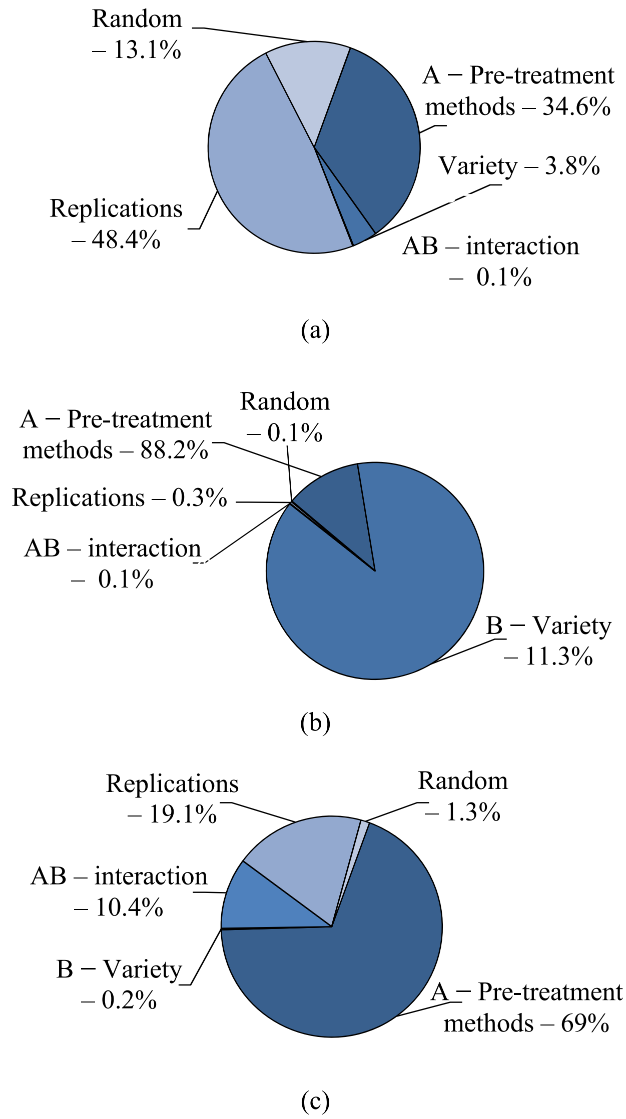

Fig. 2. The share of influence of factors A (pre-treatment methods) and B (variety) on: (a) tanning and coloring substances, (b) ascorbic acid, (c) antioxidant activity of cherry.

Table 4. The matrix of pairwise correlations between some parameters of the chemical composition of frozen cherry

Indicator	Dry soluble substances	Titrated acid	Tanning and coloring substances	Ascorbic acid	Antioxidant activity
		Shpanka			
Dry soluble substances	1	**0.87**	0.40	0.55	0.55
Titrated acid	**0.87**	1	–0.30	–0.21	–0.29
Tanning and coloring substances	0.40	–0.30	1	**0.85**	**0.93**
Ascorbic acid	0.55	–0.21	**0.85**	1	**0.98**
Antioxidant activity	0.55	–0.29	**0.94**	**0.98**	1
		Lotovka			
Dry soluble substances	1	**0.87**	–0.47	0.60	–0.58
Titrated acid	**0.87**	1	–0.37	–0.29	–0.36
Tanning and coloring substances	–0.47	–0.37	1	**0.90**	**0.97**
Ascorbic acid	0.60	–0.29	**0.90**	1	**0.98**
Antioxidant activity	–0.58	–0.36	**0.97**	**0.98**	1

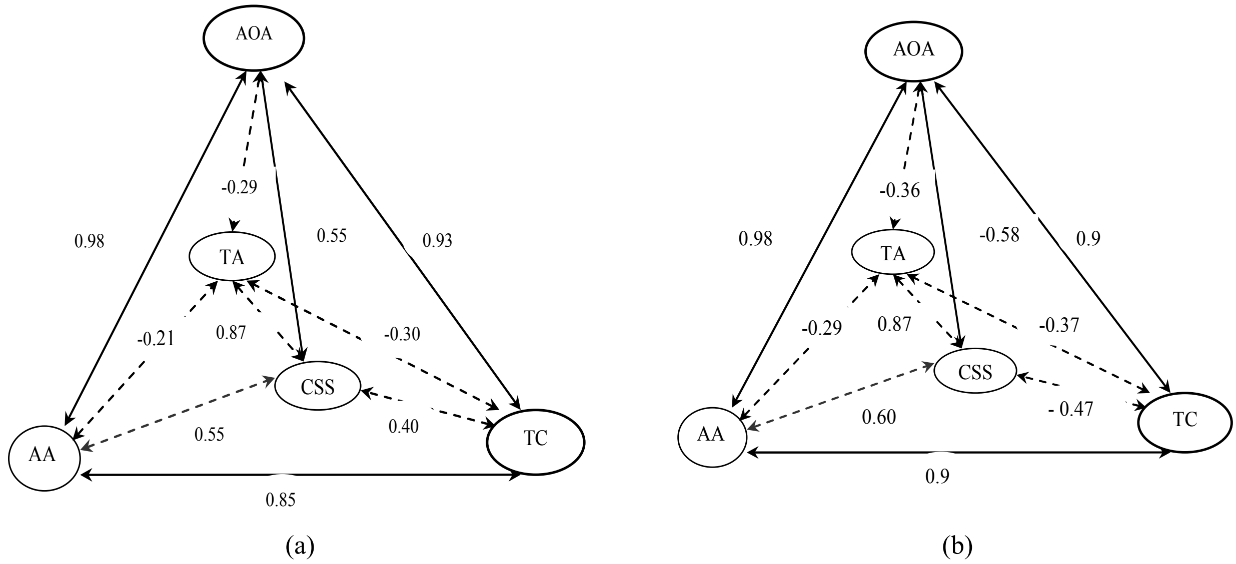

Fig. 3. Correlation galaxy of relationship between the content of dry soluble substances (CSS), titrated acids (TA), tanning and coloring substances (TC), ascorbic acid (AA) and antioxidant activity (AOA) in cherry varieties of (a) Shpanka, (b) Lotovka during freezing.

The analysis of variance revealed that the main effects of the pre-treatment methods and varieties phase indicated significant differences ($p < 0.05$) for all studied chemical characteristics as shown in Fig. 2.

The influence of A (pre-treatment methods), B (variety) and AB (interaction) was 34.6, 3.8 and 0.1% for tanning and coloring substances; 88.2, 11.3 and 0.1% for ascorbic acid; 69.0, 0.2 and 10.4% for antioxidant activity.

Among the most important interactions were the pre-treatment methods which registered 34.6% of the tanning and coloring substances while the remaining interactions altogether had less than 4%.

The experimental factor of the pre-treatment methods explained 88.2% of the total ascorbic acid, indicating, as expected, the high significance of pre-treatment methods on the ascorbic acid content. For the antioxidant capacity the main effects had the pre-treatment methods and varieties. These positions explain 69% and 0.2%, respectively, indicating the particular significance of the pre-treatment methods while the remaining interactions contribute less than 10.4%.

For the determined correlation coefficients of the chemical composition of cherry see Table 4.

To study the relationship between these components of the chemical composition in cherry varieties of Shpanka and Lotovka after freezing, the correlation ring (Fig. 3) was built by means of correlation pleiades [39, 45, 46].

The figure shows the relations of cherry quality indicators. Thus, the content of dry soluble substances has inverse and high dependence on acid content ($r = –0.87$) and average dependence on ascorbic acid ($r = 0.55$ and $r = 0.60$) and tanning and coloring substances ($r = 0.4$ and $r = –0.47$).

And it is natural because mainly acids, tannins and coloring substances and ascorbic acid were involved in the formation of the chemical composition of dry soluble substances. Besides, the content of dry soluble substances is a significant indicator of antioxidant activity.

There is a strong correlation dependence between antioxidant activity, content of tannins and coloring substances ($r = 0.93$; $r = 0.97$), ascorbic acid ($r = 0.98$), and dry soluble substances ($r = 0.55$; $r = −0.58$). Such dependence is apparently connected with processes of deterioration and transformation, which affect cherries during freezing and storage.

CONCLUSION

Thus, the quality indexes of cherries during freezing are interrelated and constitute one correlation galaxy in which the main indicators are the content of dry soluble substances and antioxidant activity.

The content of dry soluble substances is determined by the content of acids, while the content of ascorbic acid, tannins, and coloring substances determines antioxidant activity of raw materials.

According to the research, preprocessing with 20% sugar solution with the addition of 1% chitosan contributes to preservation of the quality and biological value of frozen cherry. Herewith antioxidant activity in frozen cherry varieties of Shpanka and Lotovka is 27 and 18 mmol/dm^3, ascorbic acid content is 17.6 and 20 mg/100g, respectively.

CONFLICTS OF INTEREST

The author declares no conflict of interest.

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