



Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: <http://chemistry.dnu.dp.ua>



UDC 664.8.037.1: 581.192

CHANGES IN PECTIC SUBSTANCE CONTENT DURING PEAR FRUIT STORAGE AFTER ANTIOXIDANT COMPOSITION TREATMENT

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Received 24 September 2018; revised __; accepted __; available online __

Abstract

Aim. The research is devoted to determination of the regularities of pectic substance changes in pears during refrigeration storage after antioxidant composition treatment. **Methods.** The content of pectic substances was determined by titrimetric method, which was based on alkaline titration of the pre-selected and prepared pectic substances before and after hydrolysis. The titration results are proportional to the number of free esterified carboxylic groups, and when multiplied by the corresponding equivalents, they indicate the content of polygalacturonic acid residues in the pectic substances of the product. **Results.** The research showed that late ripening pears had greater content of pectic substances when put to storage. During the first 30 days of storage an insignificant (1..4%) increase of pectic substance content was observed in the fruit of control variants, during further storage (130 ... 180 days) a decrease was recorded. The loss of pectic substances by the control fruit amounted to 49 % for the entire storage period. During fruit storage after antioxidant composition treatment the increase of pectic substance content had been lasting for 2-4 months longer than of the control variants fruit, and further transfer of protopectin to the soluble pectin was taking place at a slower rate. It provided for the best preservation of pectic substances during storage. The loss of pectic substances by fruit treated with antioxidants amounted to 15 % for the entire storage period. **Conclusions.** Minimal losses of pectic substances (7%) were found out at the storage of pears of the varieties Victoria, Conference, Cure, Izyuminka Crimea, which had been treated with the antioxidant composition DL.

Keywords: pectic substances; protopectin; pectin; antioxidants; pear fruit; refrigerated storage.

ЗМІНИ ВМІСТУ ПЕКТИНОВИХ РЕЧОВИН ПРИ ЗБЕРІГАННІ ПЛОДІВ ГРУШІ ЗА ОБРОБКИ АНТИОКСИДАНТНИМИ КОМПОЗИЦІЯМИ

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Анотація

Дослідження присвячені визначенню закономірностей змін пектинових речовин плодів груші протягом холодильного зберігання за обробки антиоксидантними композиціями. В результаті досліджень встановлено, що в період закладання плодів на зберігання більшим вмістом пектинових речовин характеризувалися плоди груші пізнього терміну достигання. Протягом перших 30 діб зберігання у плодах контрольних варіантів спостерігалася незначне збільшення вмісту суми пектинових речовин, при подальшому зберіганні зафіксоване її зниження. При зберіганні плодів за обробки антиоксидантними композиціями зростання вмісту пектинових речовин тривало на 2 – 4 місяці довше, ніж у плодів контрольних варіантів, а подальший перехід протопектину у розчинний пектин відбувається більш повільними темпами. Це забезпечувало кращу збереженість пектинових речовин протягом зберігання. Основною тенденцією зміни показника динамічної твердості плодів було зменшення його кількісного значення протягом усього терміну зберігання незалежно від варіанту обробки. Однак, швидкості його зниження у плодів контрольних варіантів були істотно вищими. Найбільший позитивний ефект для всіх сортів плодів встановлений при використанні композиції ДЛ.

Ключові слова: пектинові речовини; протопектин; пектин; антиоксиданти; плоди груші; холодильне зберігання.

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doi: 10.15421/081905

ИЗМЕНЕНИЯ СОДЕРЖАНИЯ ПЕКТИНОВЫХ ВЕЩЕСТВ ПРИ ХРАНЕНИИ ПЛОДОВ ГРУШИ С ОБРАБОТКОЙ АНТИОКСИДАНТНЫМИ КОМПОЗИЦИЯМИ

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Аннотация

Исследования посвящены определению закономерностей изменений пектиновых веществ в плодах груши в течение холодильного хранения с обработкой антиоксидантными композициями. В результате исследований установлено, что в период закладки плодов на хранение большим содержанием пектиновых веществ характеризовались плоды груши позднего срока созревания. В течение первых 30 суток хранения в плодах контрольных вариантов наблюдалось незначительное увеличение содержания суммы пектиновых веществ, при дальнейшем хранении зафиксировано ее снижение. При хранении плодов с обработкой антиоксидантными композициями увеличение содержания пектиновых веществ продолжалось на 2 - 4 месяца дальше, чем у плодов контрольных вариантов, а последующий переход протопектина в растворимый пектин происходил более медленными темпами. Это обеспечивало лучшую сохранность пектиновых веществ при хранении. Основной тенденцией изменения показателя динамической твердости плодов было уменьшение его количественного значения в течение всего срока хранения независимо от варианта обработки. Однако, скорости его снижения у плодов контрольных вариантов были существенно выше. Наибольший положительный эффект для всех сортов плодов установлен при использовании композиции ДЛ.

Ключевые слова: пектиновые вещества; протопектин; пектин; антиоксиданты; плоды груши; холодильное хранение.

Introduction

Pectic substances (PS) are present in almost all plants. Fruit are especially rich in them. Pectic substances form part of the fruit cell walls, participate in the regulation of the water regime of tissues, regulate transpiration [1]. Their transformation during ripening and storage, the transition from an insoluble form to a soluble one and reverse determines the consistency of fruit pulp. In this regard, the rate of the fruit ripening and their keeping capacity are determined by the nature of the metabolism of pectic substances [2].

However, the study of pectic substances conversion processes was carried out with a limited amount of fruit products. The apple fruit, used as raw materials in the canning and confectionery industry to produce products with a jelly-like consistency were studied in the majority of scientific works. Difficulties in extracting individual fractions, their stabilization and separation from other substances have led to the fact that existing data on post-harvest metabolism of pectic substances are inadequate and contradictory. Data on the intensity of the processes of pectic substance conversion during the storage of pear fruit in general are absent.

From this point of view, the research of post-harvest metabolism of pectic substances under the influence of antioxidant compositions during the pear fruit refrigeration is an actual one.

Analysis of literary data and problem statement. Pectic substances have the properties of lyophilic colloids and are high-molecular compound of

carbon nature. They are considered to be the main components of the primary cell membrane matrix, and are also contained in the intercellular substance. This substance forms a middle blade and glues the walls of adjacent cells [3].

Pectinic acid is in the basis of the pectic substance molecule structure (Fig.1). It is formed from the remnants of galacturonic acid coupled with ($\alpha 1 \rightarrow 4$)- link. Pectic acid can be found in the cell walls in a free state or in the form of salts and ethers [4].

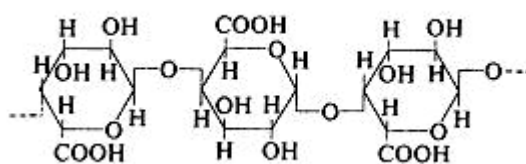


Fig.1. Part of the pectic (polygalacturonic) acid molecule

Carboxyl groups of pectinic acid easily form ethers with methyl alcohol. Methylated pectinic acid is called soluble pectin. Due to the presence of free carboxyl groups of galacturonic acid, soluble pectin is capable of binding both heavy metals and radionuclides, with the formation of insoluble complexes that are excreted from the organism [5].

Besides soluble pectin, pectic substances in fruit are presented by propectine, pectin and pectic acid.

Protopectin molecule consists of a large number of polygalacturonic acid molecule remnants, which are joined in long chains. These

chains are interconnected through calcium and magnesium ions. Replacing Ca^{2+} i Mg^{2+} ions with monovalent ions of sodium and potassium leads to a break in the bonds between the chains and the transition of protopectin into the soluble form – pectin [6].

Unripe fruit are characterized by high content of protopectin. As they ripe, protopectin transfer into pectin under the action of enzymes, and the fruit become softened. With the beginning of the post climacteric period, the amount of pectic substances in the fruit significantly decreases and they acquire an unpleasant puffy consistency [7].

When overripe and aged, the pectin under the action of enzymes turns into pectin and pectinic acids. As a result, the fruit become overly sour taste [8].

When stored pectic substances take an active part in the carbohydrate metabolism of fruit. At the same time, they, together with hemicelluloses and cellulose, undergo significant quantitative changes in the direction of decline. Pectic substance content reducing is connected with their hydrolysis and the cost of respiration. [9].

It is known that pear fruit contain less pectic substances than apple fruit do. Along with this, the conversion of protopectin into pectin in pears occurs in a shorter time than in apples [10].

In fruit that genetically have high keeping capacity, the transition of protopectin into pectin occurs at a slower pace, due to the weak activity of pectolytic enzymes. Fruit of late term ripening even after 4 months of storage were characterized by a dominant content of protopectin over soluble pectin, which is evidence of a high potential of variety preservation [11].

Along with this, there are assertions that the content of pectic substances during the fruit products storage may increase. It occurs due to the oxidation of monosaccharides to galacturonic acid, as well as due to the complex compounds decomposition, which include pectin, with the activation of hydrolytic enzymes, for example, protopectinase [12].

Pectic substances also serve as protective colloids that regulate the transpiration process rate during fruit storage, and cause the turgor to be preserved.

Thus, the main task during fruit products storage is to reduce the rate of pectic substances post-harvest metabolism.

The dynamics of pectic substances changes during the pear fruit storage was studied by Kaur, K., Dhillon, W.S., & Mahajan, B.V. [1]. At the same time, various packaging materials were used to store pear fruit. The authors determined that the

best packaging material which promotes the pectin solubilization rate reducing and which prevents fruit softening are high density polyethylene lined CFB boxes (see annotation below).

A promising way of slowing down the pectic substances conversion is the use of antioxidant compositions. The antioxidant compositions reduce the rate of post-harvest metabolism and they will contribute to the valuable phytonutrients preservation [13, 14].

The effect of edible coatings such as shellac and Semperfresh™ (sucrose-polyester based coating) on the pectic substances metabolism in pear fruit has been studied [15]. However, the authors do not reveal the question of the regulation of after-harvesting metabolism of the pectin complex rates.

Thus, the analysis of literary sources showed that many issues of after-harvesting metabolism of pectic substances have not been studied enough and remain controversial ones.

Purpose and objectives of the research. The conducted studies aimed at determining the patterns of changes in pectic substances of pear fruit during their refrigeration after the antioxidant composition treatment.

To achieve this goal it was necessary to solve the following tasks:

to determine changes in the content of pectic substances during the refrigeration of pear fruit;

to investigate the effect of antioxidant compositions on the intensity of post-harvest metabolism of pectic substances in pear fruit;

to determine the dynamic hardness of the pear fruit at the stages of storage;

to substantiate scientifically the correlation of the pectic substances conversion intensity and changes in the consistency of fruit during refrigeration after the antioxidant composition treatment.

Materials and methods

Experimental researches were carried out in the laboratory of technology of primary processing and storage of crop products by the Research Institute of Agro-technologies and Ecology of the Tavria State Agrotechnological University (Melitopol, Ukraine). The objects of the research were the pear fruit of medium term ripening varieties Victoria and Conference and of the late term ripening – Cure and Izyuminka Crimea.

The fruit were processed by immersion in the following antioxidant compositions (AOC): ACM – a mixture of dimethyl sulfoscid, ionol and

polyethylene glycols; AARL – a mixture of ascorbic acid, routine and lecithin; DL – a mixture of dimethylsulphoside, ionol and lecithin. For control (C) fruit was treated with water. The exposure was 10 seconds. The replicate was fivefold. The mass of one replicate was 25 kg.

The storage was carried out at a temperature of 0 ± 1 °C, relative humidity of 90-95%. The shelf storage of the fruit of the pear varieties Victoria, Conference: control – 160 days, ACM - 210 days, AARL and DL – 220 days; Cure and Izyuminka Crimea Crimea varieties: control -- 215 days, ACM, AARL and DL – 260 days.

The content of pectic substances was determined by titerometric method, which was based on alkaline titration of the pre-selected and prepared pectic substances before and after hydrolysis. The titration results are proportional to the number of free esterified carboxylic groups and when multiplied by the corresponding equivalents, they indicate the content of polyuronides in the pectic substances of the product.

To determine separately pectin and protopectin from the prepared median sample of two hinges of 30–50 g each was taken. To degrease the selected hinges, they were placed in a cartridge of filter paper and dried at a temperature of 70–80 °C. The dried sample was placed in a flask of 250 or 500 cm³ volume with a slice, poured 30–40 cm³ of ether and heated in a water bath at a temperature of 40–50 °C with a reflux condenser for 20–30 minutes. Then the ether was carefully drained or filtered through a paper filter. Fat separation was repeated four or five times. The degreasing of the sample can be carried out in the Soxhlet's apparatus.

The fat-free remnants of the filtered sample were added to a flask of the fat-free hinge, poured 100 cm³ of distilled water heated to 60–70 °C and then the extraction of pectic substances was held.

To remove water-soluble pectin, the hinge of the test product was placed in a flask of 250 or 300 cm³ volume, poured 100 cm³ of distilled water heated to 60–70°C and shaken for 30 minutes. Then the contents were transferred quantitatively to distilled water into a volumetric flask of 200 or 250 cm³ volume, cooled, kept to the mark, carefully mixed and separated the liquid by centrifugation. The resulting extract of water-soluble pectin was transferred to a dry dish.

The total content of pectic substances was determined in another hinge of the product after hydrolysis of hydrochloric acid to convert protopectin into a soluble state. For this, the hinge of the test material was placed in a flask of 250 or

300 cm³ volume, poured 100 cm³ of a hydrochloric acid solution at a concentration of 0.05 mol / dm³ (pH of the mixture 1.8–2.0) and heated in a water bath for 30 minutes at a temperature of 85–90 °C. Then the contents of the flask quantitatively to distilled water was transferred to a volumetric flask of 200 or 250 cm³ volume, cooled, kept to the mark, stirred and left for 1–1.5 h. to level the concentration of pectic substances in the liquid and solid phases. The extract was separated by centrifugation and collected into a dry dish.

The resulting solutions of pectic substances were purified by precipitation with an alcoholic-acid mixture. For this purpose, 25, 50 or 100 cm³ of extract (depending on the pectin content) were added to the chemical bottle with a pipette, a double amount of the alcohol-acid mixture was added, carefully mixed and left for 1–1.5 h. to form a precipitate.

The precipitate was filtered through a funnel with a porous plate with a layer of 0.5–0.7 cm sand. The bottle and the precipitate were washed with a solution of 70% ethyl alcohol acidified with hydrochloric acid for three times at 15–20 cm³, then with a solution of 70% ethyl alcohol to a negative reaction to chlorine ion with silver nitrous oxide. For one sample washing 90–100 cm³ of 70% solution of ethyl alcohol was spent.

The funnel with the washed precipitate was set in a clean flask with a tube of 250 cm³ volume and quantitatively dissolved the pectin containing precipitate with water at a temperature of 60–70 °C. The bottle, where the precipitation was conducted, was also washed twice or three times with warm water. The solution was cooled to room temperature; 6 drops of the Hinton indicator were added and titrated with a solution of sodium hydroxide in a concentration of 0.05 mol / dm³ before the transition of yellow coloration into the crimson one, which did not disappear within 20–30 seconds. Then to the solution in the flask with the help of a pipette or a burette, 20 cm³ of sodium hydroxide solution in a concentration of 0.1 mol / dm³ was added, corked and left for 30 minutes. Then, with a burette, the solution of hydrochloric acid in a concentration of 0.1 mol / dm³ was added, the exact amount of which was determined by preliminary titration of 20 cm³ of sodium hydroxide in a concentration of 0.1 mol / dm³ with the same acid solution with the Hinton indicator. The mixture in the flask was again titrated with a solution of sodium hydroxide in a concentration of 0.05 mol / dm³.

The mass concentration of polyuronides (X) was calculated by formula 1:

$$X = \frac{(m_1 \cdot V_1 + m_2 \cdot V_2) c V}{V_3 m} \cdot 10^{-1}, \quad (1)$$

where V_1, V_2 are the volumes of sodium hydroxide solution, which are spent on the first and second titrations, cm^3 ; V_3 is the volume of the extract selected for precipitation and titration, cm^3 ; c is the exact concentration of the sodium hydroxide solution used for titration, mol / dm^3 ($0.05 \text{ mol} / \text{dm}^3$, multiplied by the correction factor); V is a total volume of extract, cm^3 ; m is the weight of a hinge, g; m_1 is the molecular weight of polygalacturonic acid chain, $m_1 = 176 \text{ g} / \text{mol}$; m_2 is the molecular weight of the etherified chain of polygalacturonic acid, $m_2 = 190 \text{ g} / \text{mol}$.

The degree of extracted pectic substances etherification (ε) in percentagewise is calculated by formula 2:

$$\varepsilon = \frac{V_2}{V_1 + V_2} \cdot 100 \quad (2).$$

The amount of protopectin is determined by the difference between the total content of pectic substances and the content of water-soluble pectin.

The calculations were carried out with three significant figures. As the final outcome the arithmetic mean of the results of two parallel determinations, the allowable absolute difference between which should not exceed 0.10% during the determination of polyuronides and 4.0% in determining the degree of etherification was taken. To determine the dynamic hardness, at least 30 fruit were selected and 3 punctures in the equatorial region were made on each variant with

a penetrometer GY-3 with a cylindrical steel probe of 11 mm.

The calculation of the conversion of pectic substances rate constant was carried out using formula 3, the mathematical calculation of which is given in the previous publications [16]:

$$k = \frac{\ln \frac{PS_1}{PS_2}}{\tau_2 - \tau_1}$$

where k is a constant rate of pectic substances conversion, % per day⁻¹, PS_1, PS_2 is the initial and final content of pectic substances, %, τ_1, τ_2 is the initial and final moment of time, days.

The processing and analysis of the experiments were carried out using standard methods of variation statistics using the computer programs "MSoffice Excel 2007", the package "Statistica 6" and the personal computer.

Results of the study of the antioxidant compositions effect on the pectic substances metabolism during the storage

When placed fruit in storage, the pear fruit of late term ripening were characterized by the highest content of pectic substances (Table 1). The average long-term content of pectic substances in pear fruit of medium term ripening was 1.15% and was 12% lower than that of late term ripening pears. This indicator was characterized by low variability, as evidenced by the coefficient of variation V (see Table 1). The highest content of pectic substances among all four varieties was recorded in the fruit of pears of the Izyuminka Crimea variety.

Table 1

The content of pectic substances in pear fruit when placed in storage

Pomological variety	The content of pectic substances, %		
	average value	min max	V on an annual basis
Fruit of medium term ripening			
Victoria	1,170±0,055	1,212 1,107	4,7
Conference	1,122±0,039	1,157 1,079	3,5
Mean for varieties	1,146±0,047	1,212 1,079	4,1
Fruit of late term ripening			
Cure	1,285±0,058	1,327 1,219	4,5
Izyuminka Crimea	1,317±0,038	1,345 1,274	2,9
Mean for varieties	1,301±0,048	1,345 1,219	3,7

It should also be noted that during placing on storage the protopectin content exceeded over the soluble pectin content in the fruit of all the

analyzed varieties. During the first 30 days of storage a slight increase in the content of the

pectic substances amount in all control variants of the fruit was observed.

In the fruit of the experimental variants, the increase of pectic substance content lasted for 2 - 4 months (depending on the variety and variant of treatment) longer than in the control ones. Moreover, the increase in the total content of pectic substances took place due to increased protopectin content. According to some authors [17, 18], such an increase is connected with the transformation of the hemicellulose which contains remnants of glucuronic and galacturonic acids into protopectin.

In the further storage of both control and experimental fruit, there was a decrease in the content of pectic substances. This decrease takes place due to the enzymatic hydrolysis of insoluble protopectin into a soluble form – pectin, which, in its turn, is consumed as a result of participation in carbohydrate metabolism.

During storing fruit with AOC treatment, the transition of protopectin into soluble pectin takes

place at a slower pace, as evidenced by the calculated rate constants (Tab. 2). The highest rate constants of protopectin hydrolysis were obtained for all varieties of control fruit. Moreover, the maximum values are set for the fruit characterized by less keeping capacity, that is, pears of medium term ripening, somewhat lower – for fruit with high keeping capacity – pears of late term ripening.

The positive influence of antioxidant compositions was expressed in the reduction of k_{pp} during the storage of pears of late term ripening with treatment of antioxidant composition ACM in 2.2 times, with AARL treatment – in 3 times, with the DL treatment – in 5 times compared with the fruit of control variants. The highest positive effect of antioxidant compositions was observed for pear fruit of medium term ripening. At the same time, the value of k_{pp} in pears was lower than in the control variant, respectively, in 2, 3.4 and 9.3 times.

Table 2

Rate constants of the protopectin mass fraction reduction in fruit during storage with AOC treatment

Pomological variety	Rate constants of the protopectin mass fraction reduction in fruit with different types of treatments, k_{pp} , day ⁻¹ , $\times 10^{-2}$			
	C	ACM	AARL	DL
Pear fruit of medium term ripening				
Victoria	-0,81	-0,41	-0,24	-0,12
Conference	-1,05	-0,51	-0,30	-0,07
Mean for varieties	-0,93	-0,46	-0,27	-0,10
Pears fruit of late term ripening				
Cure	-0,77	-0,36	-0,24	-0,14
Izyuminka Crimea	-0,61	-0,28	-0,20	-0,14
Mean for varieties	-0,69	-0,32	-0,22	-0,14

After prolonged storage the pear fruit of late term ripening varieties Cure and Izyuminka

Crimea were characterized by the the highest number of pectic substances (Fig. 2).

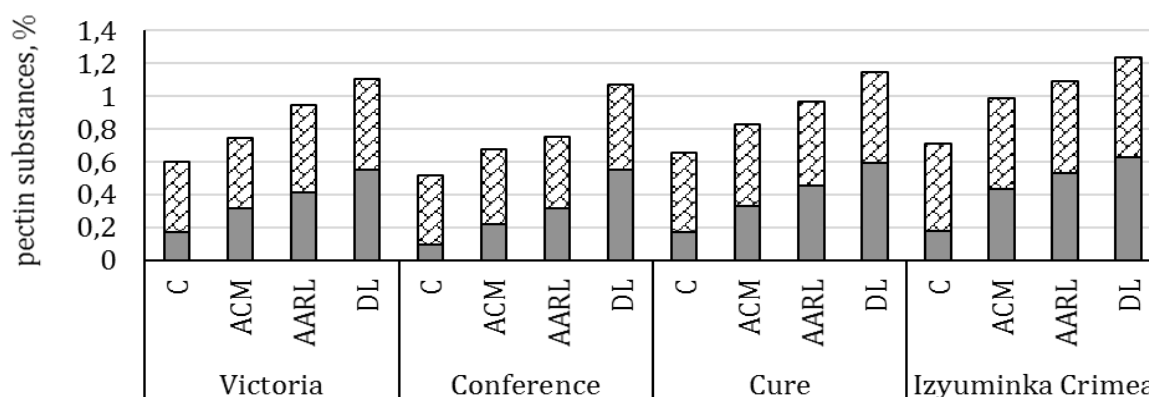


Fig. 2. The content of pectic substances in pears after prolonged storage after the antioxidant composition treatment

The treatment of the fruit with AOC contributed to the better preservation of pectic

substances during storage, which is explained by the inhibitory effect of antioxidants on oxidative-reduction processes, and first of all on respiration. The greatest positive effect for all varieties of pear fruit is defined with using DL composition (Fig. 2).

Correlated analysis confirmed the participation of pectic substances in the processes of post-harvest metabolism of the pear fruit of late term ripening.

A strong correlated connection between the content of pectic substances and the amount of sugars is defined only during the storage of pears of Izyuminka Crimea variety with all antioxidant composition treatment (correlation coefficients r range from -0.66 to -0.8 depending on the treatment variant) and Cure variety DL composition treatment ($r = -0.75$). A strong negative connection between the content of pectic substances and the intensity of respiration was observed during the storage of the experimental pear fruit of Cure variety with the DL composition treatment ($r = -0.84$). Negative connections of average strength between the indicated indices were defined in the pear fruit of the other analysed varieties.

So, the treatment with antioxidant compositions balances the catabolic and anabolic processes of the transformation of carbohydrates, resulting in the use of pectic substances as the main spare substance for the synthesis of sugars. And negative correlated dependences between the intensity of respiration and pectic substances

confirms the active involvement of the latter in the respiratory metabolism of the fruit.

The rate of interconversion of pectic substances during post-harvest fruit ripening affects their consistency. Hydrolysis of protopectin into soluble pectin is accompanied by softening of fruit, which is explained by the separation of adjacent cells from each other. However, with high content of soluble pectin, due to its ability to swell and maintain a large amount of moisture, the turgidity of the fruit tissues remains high. At the last stage of storage, with the rapid consumption of soluble pectin, the fruit lose their succulence and become friable.

According to some authors [19, 22], the decrease in the dynamic hardness of fruit is mainly determined by the protopectin content ratio to the soluble pectin, or the so-called protopectin index (PPI).

The main tendency of dynamic hardness index change of the fruit was the decrease in its quantitative value throughout the shelf life, regardless of the treatment variant. However, the rates of decrease in control and experimental variants were different (Table 3). They were the maximum in the fruit of control variants with the variation of rate constants k_{ph} (PH – pulp hardness) from $-0.31 \cdot 10^{-2}$ in pears of Izyuminka Crimea variety, up to $-0.58 \cdot 10^{-2}$ in pears of Conference variety, minimum – during the storage of all sorts of fruit with DL antioxidant composition treatment.

Table 3

Rate constants of fruit firmness reduction during storage with AOC treatment

Pomological variety	Rate constants of fruit firmness reduction with different kinds of treatment, k_{ph} , day ⁻¹ , $\times 10^{-2}$			
	C	ACM	AARL	DL
Pear fruit of medium term ripening				
Victoria	-0,48	-0,19	-0,14	-0,07
Conference	-0,58	-0,32	-0,14	-0,06
Mean for varieties	-0,530	-0,255	-0,140	-0,065
Pear fruit of late term ripening				
Cure	-0,37	-0,14	-0,07	-0,05
Izyuminka Crimea	-0,31	-0,08	-0,04	-0,03
Mean for varieties	-0,340	-0,110	-0,055	-0,040

Correlated analysis confirmed the existence of close feedback between PPI and the percentage of reduction in the firmness of fruit pulp with correlation coefficients $r = -0.95 \dots -0.98$ depending on the fruit variety and the variant of treatment.

So, the results of our studies proved that the content of pectic substances, including protopectin, in the fruit treated with antioxidant compositions, in comparison with the control

ones, was kept at a higher level throughout the period of storage (220...260 days), which had a positive effect on their qualitative properties.

The after-harvest processing of the fruit and their preparation for storage were carried out according to the developed technological scheme.

At the same time, during the fruit-picking, inspection, sorting and calibration were carried out. Fruit-picking should be done carefully, always with the stalk, in order to preserve the wax

coating. Fruit of the highest and first commercial grade were selected for storage. Then the fruit were immediately transported to the refrigerator. Delaying fruit in the garden for more than 3 hours is not recommended.

Processing products with antioxidant compositions and their simultaneous pre-cooling were performed in the preparatory section of the refrigerator. Pre-cooling was carried out in 2 stages. At the first stage, pear fruit in boxes or containers were loaded into a bath with a working solution of the antioxidant composition with a temperature of 1.5 ± 0.5 °C and kept for 1.5 hours. The temperature of the working solution and the exposure time were determined by experimental studies [14]. Baths with working solutions were installed in refrigerated rooms at a temperature of 2 ... 5 °C. After the end of stage 1, the fruit in the container were raised out of working solutions and placed above the trays to drain the excess solution for 10 ... 15 minutes.

The purpose of the second stage of pre-cooling was to reduce the temperature of the fruit to 1 °C and to remove completely the remaining moisture from their surface. This stage was carried out in the intensive cooling chambers with regime parameters: temperature minus 2 ... minus 5 °C, relative air humidity 95%, air velocity 3 m/s.

The composition of the AOC is determined by the results of studies [21]. The consumption of the preparation was 25 liters of working solution per 1 ton of fruit.

Then the fruit were transported to the storage chamber where the following operating parameters were maintained: temperature 0 ± 1 °C, relative air humidity 90 ... 95%.

The application of the proposed technology for the pear fruit storage with AOC processing, despite the additional explicit costs of the preparation, contributed to an increase in the yield of standard production, a reduction in costs for losses, and, as a result, ensured a high economic effect.

Thus, an increase in the profitability level during the storage of pear fruit of medium term ripening with ACM composition was 59% with an economic effect of 8287.019 UAN/t, with an AARL treatment – 77% with an economic effect of 10838.74 UAH/t and with a DL composition - 92% with the economic effect of 12455.72 UAH/t.

When storing pear fruit of late term ripening, profitability growth was for variants 27% with an economic effect of 3864.095 UAH/t, 42% with an economic effect of 5972.059 UAH/t and 52% with an economic effect of 7034.996 UAH/t respectively.

Thus, the economic indicators analysis of fruit storage has shown that the most effective is the technology of fruit storage after the DL composition treatment.

Conclusions

When put to storage, pear fruit of the late term ripening varieties was characterized by high content of pectic substances. During the first 30 days of storage a slight increase in the content of pectic substance amount was observed in the control samples. During further storage, a decrease in the content of pectic substances was registered.

During the fruit storage after the antioxidant composition treatment, the growth of pectic substance content had been lasting for 2 - 4 months longer than in the fruit of the control variants, and the further transition of protopectin into the soluble pectin was taking place at a slower rate. This provided for the better preservation of pectic substances during the storage. The greatest positive effect for all fruit varieties was achieved by treating with the DL composition.

The main tendency of dynamic hardness index change of the fruit was the decrease in its quantitative value throughout the shelf life, regardless of the treatment variant. However, the rates of decrease in the fruit of control variants were significantly higher. They were minimal when storing all varieties of pear fruit after the antioxidant DL composition treatment.

The results show that the antioxidant composition DL balances the catabolic and anabolic processes of carbohydrate transformation, resulting in the use of pectic substances as the main storage compound for the synthesis of sugars and pectic substances take place in the respiratory metabolism of the fruit. Along with this, the degree of pectic substances participation is based on varietal features of the fruit. From this point of view, there is a need to conduct the research with a wider range of varieties. This will be the task of our further research.

Bibliography

- [1] Kaur K. Changes in pectin methyl esterase activity with different packaging materials and stages of fruit harvesting during cold storage of pear cv. Punjab beauty / K. Kaur, W. S.Dhillon, B. V. C.Mahajan // *Journal of food science and technology*. – 2014. – Vol. 51, N 10. – P. 2867-2871.
- [2] Кварацхелия В. Н. Изменение аналитических характеристик пектиновых веществ яблок зимнего срока созревания при длительном влиянием низких температур / В. Н. Кварацхелия, Л. Я. Родионова //

- Политематический сетевой электронный научный журнал Кубанского государственного аграрного университета. – 2014. – №100(06). [Электронный ресурс] – Режим доступа: <http://ej.kubagro.ru/2014/06/pdf/49.pdf>.
- [3] Светличенко В. Изменение содержания пектиновых веществ в плодах яблони под влиянием пленкообразующего состава «PELECOL» при длительном хранении / В. Светличенко // *Studia Universitatis Moldaviae-Științe Reale și ale Naturii*. – 2016. – № 6 (86) – P. 33–36.
- [4] Oechslin R. Pectic substances isolated from apple cellulosic residue: structural characterisation of a new type of rhamnogalacturonan I / R. Oechslin, M. V. Lutz, R. Amadò // *Carbohydrate Polymers*. – 2003. – Vol. 51, N 3. P. 301–310.
- [5] Yapo B. M. Pectic substances: From simple pectic polysaccharides to complex pectins – A new hypothetical model / B. M. Yapo // *Carbohydrate Polymers*. – 2011. – Vol. 86, N 2. – P. 373–385.
- [6] Strasser G. R. Pectic substances from red beet (*Beta vulgaris conditiva*). Part I. Structural analysis of rhamnogalacturonan I using enzymic degradation and methylation analysis / G. R. Strasser, R. Amado // *Carbohydrate Polymers*. – 2001. – Vol. 44, N 1. – P. 63–70.
- [7] Billy L. Relationship between texture and pectin composition of two apple cultivars during storage / L. Billy, E. Mehinagic, G. Royer, C. M. Renard [et. al.] // *Postharvest Biology and Technology*. – 2008. – Vol. 47, N 3. – P. 315–324.
- [8] Segonne S. M. Multiscale investigation of mealiness in apple: an atypical role for a pectin methylesterase during fruit maturation / S. M. Segonne, M. Bruneau, J. M. Celton [et. al.] // *BMC plant biology*. – 2014. – Vol. 14, N 1. – 375 p.
- [9] Lapasin R. The polysaccharides: sources and structures / R. Lapasin, S. Priss // *In Rheology of Industrial Polysaccharides: Theory and Applications*. – 1995. – P. 1–133.
- [10] Zhou, R., Su, S., & Li, Y. (2008). Effects of cushioning materials on the firmness of Huanghua pears (*Pyrus pyrifolia* Nakai cv. Huanghua) during distribution and storage / R. Zhou, S. Su, Y. Li // *Packaging Technology and Science: An International Journal* / - 2008. – V 21, № 1. – P. 1–11.
- [11] Созаева Д. Р. Содержание пектинов в различных видах плодовых культур и их физико-химические свойства / Д. Р. Созаева, А. С. Джабоева, Л. Г. Шаова, О. К. Цагоева // *Вестник Воронежского государственного университета инженерных технологий*. – 2016. – № 2(68). – С. 170–174.
- [12] Deuel H. Pectic substances and pectin / H. Deuel, E. Stutz // *Advances in Enzymology and Related Areas of Molecular Biology*. – 2009. – Vol. 20. – P. 341.
- [13] Priss O. Effect of heat treatment with antioxidants on oxygen radical scavenging during storage of zucchini squash / O. Priss, V. Kalitka // *Eastern-European Journal of Enterprise Technologies*. – 2015. – № 6/10 (77). – P. 47–53.
- [14] Serdyuk M. Substantiation of selecting the method of precooling of fruit / M. Serdyuk, D. Stepanenko, S. Baiberova, N. Gaprindashvili, & A. Kulik // *Eastern-European Journal of Enterprise Technologies*. – 2016. – T. 4. – № 11 (82). – С. 62–68.
- [15] Zhou R. Effect of edible coatings on enzymes, cell-membrane integrity, and cell-wall constituents in relation to brittleness and firmness of Huanghua pears (*Pyrus pyrifolia* Nakai, cv. Huanghua) during storage / R. Zhou, Y. Li, L. Yan, J. Xie // *Food Chemistry*. – 2011. – № 124(2), P. 569–575.
- [16] Serdyuk M. The study of mass loss intensity of plum fruit during storage / M. Serdyuk, D. Stepanenko, S. Kurchev // *Eastern-European Journal of Enterprise Technologies*. – 2016. – № 1/10 (79). – P. 42–48.
- [17] Voragen A. G. Pectin, a versatile polysaccharide present in plant cell walls / A. G. Voragen, G. J. Coenen, R. P. Verhoef, H. A. Schols // *Structural Chemistry*. – 2009. – Vol. 20(2). – P. 263.
- [18] Новикова О. А. Динамика содержания пектиновых веществ в плодах яблони в процессе хранения / О. А. Новикова, Н. А. Голикова, Р. И. Овчинникова // *Аграрный вестник Урала*. – 2009. – №12(66). – С.49–50.
- [19] El-Ramady, H. R. Postharvest management of fruit and vegetables storage / H. R. El-Ramady, É. Domokos-Szabolcsy, N. A. Abdalla, H. S. Taha, M. Fári // *In Sustainable agriculture reviews*. – 2015. – P. 65–152.
- [20] Салина Е. С. Пектиновые вещества как технологический показатель пригодности плодов яблони для производства сока / Е. С. Салина, Н. С. Левгерова, Л. А. Грюнер, И. А. Ильина // *Достижения науки и техники АПК*. – 2010. – № 9. – С. 30–31.
- [21] Serdyuk M. Substantiation of the choice of optimal concentrations of active ingredients of the antioxidant composition for fruit treatment before storage / M. Serdyuk, I. Velichko, O. Priss, O. Danchenko, L. Kurcheva, S. Baiberova // *Technology audit and production reserves*. – 2017. – № 3 (3). – P. 44–49.

References

- [1] Kaur, K., Dhillon, W. S., Mahajan, B. V. C. (2014). Changes in pectin methyl esterase activity with different packaging materials and stages of fruit harvesting during cold storage of pear cv. Punjab beauty. *Journal of food science and technology*, 51(10), 2867–2871. <https://doi.org/10.1007/s13197-012-0773-1>.
- [2] Kvaratskheliya, V. N., Rodionova, Y. A. (2014). Izmenenie analiticheskikh kharakteristik pektinovykh veshhestv yablok zimnego sroka sozrevaniya pri dlitel'nom vliyaniem nizkikh temperatur. *Politematicheskij setevoy ehlektronnyj nauchnyj zhurnal Kubanskogo gosudarstvennogo agrarnogo universiteta*, 100(06) (in Russian). <http://ej.kubagro.ru/2014/06/pdf/49.pdf>.
- [3] Svetlichenko, V. (2016). Izmenenie soderzhaniya pektinovykh veshhestv v plodakh yablони pod vliyaniem plenkoobrazuyushhego sostava «PELECOL» pri dlitel'nom khraneniі. *Studia Universitatis Moldaviae-Științe Reale și ale Naturii*, 6 (86), 33–36 (in Russian).
- [4] Oechslin, R., Lutz, M. V., Amadò, R. (2003). Pectic substances isolated from apple cellulosic residue: structural characterisation of a new type of rhamnogalacturonan I. *Carbohydrate Polymers*, 51(3), 301–310. [https://doi.org/10.1016/S0144-8617\(02\)00214-X](https://doi.org/10.1016/S0144-8617(02)00214-X).
- [5] Yapo, B. M. (2011). Pectic substances: From simple pectic polysaccharides to complex pectins—A new hypothetical model. *Carbohydrate Polymers*, 86(2), 373–385. <https://doi.org/10.1016/j.carbpol.2011.05.065>.
- [6] Strasser, G. R., Amado, R. (2001). Pectic substances from red beet (*Beta vulgaris conditiva*). Part I. Structural analysis of rhamnogalacturonan I using enzymic degradation and methylation analysis. *Carbohydrate Polymers*, 44(1), 63–70. [https://doi.org/10.1016/S0144-8617\(00\)00190-9](https://doi.org/10.1016/S0144-8617(00)00190-9).

- [7] Billy, L., Mehinagic, E., Royer, G., Renard, C. M., Arvisenet, G., Prost, C., Jourjon, F. (2008). Relationship between texture and pectin composition of two apple cultivars during storage. *Postharvest Biology and Technology*, 47(3), 315–324. doi.org/10.1016/j.postharvbio.2007.07.011.
- [8] Segonne, S. M., Bruneau, M., Celton, J. M., Le Gall, S., Francin-Allami, M., Juchaux, M., Renou, J. P. (2014). Multiscale investigation of mealiness in apple: an atypical role for a pectin methylesterase during fruit maturation. *BMC plant biology*, 14(1), 375. <https://doi.org/10.1186/s12870-014-0375-3>.
- [9] Lapasin, R., Pricl, S. (1995). The polysaccharides: sources and structures. In *Rheology of Industrial Polysaccharides: Theory and Applications*, 1–133.
- [10] Zhou, R., Li, Y., Yan, L., Xie, J. (2011). Effect of edible coatings on enzymes, cell-membrane integrity, and cell-wall constituents in relation to brittleness and firmness of Huanghua pears (*Pyrus pyrifolia* Nakai, cv. Huanghua) during storage. *Food Chemistry*, 124 (2), 569–575 (in Russian).
- [11] Sozaeva, D. R., Džaboeva, A. S., Šaova, L. G., Cagoeva, O. K. (2016). Soderžanie pektinov v različnyh vidah plodovoyh kul'tur i ih fiziko-himičeskie svoystva. *Vestnik Voronežskogo gosudarstvennogo universiteta inženernykh tehnologij*, 2(68), 170 – 174. <http://doi.org/10.20914/2310-1202-2016-2-170-174>.
- [12] Deuel, H., Stutz, E. (2009). Pectic substances and pectic. *H. Deuel, E. Stutz//Advances in Enzymology and Related Areas of Molecular Biology*, 20, 341.
- [13] Priss, O., Kalytka, V. (2015). Effect of heat treatment with antioxidants on oxygen radical scavenging during storage of zucchini squash. *Eastern-European Journal of Enterprise Technologies*, 6(10), 77. <https://doi.org/10.15587/1729-4061.2015.56188>.
- [14] Serdyuk, M., Stepanenko, D., Baiberova, S., Gaprindashvili, N., Kulik, A. (2016). Substantiation of selecting the method of pre-cooling of fruit. *Eastern-European Journal of Enterprise Technologies*, 4 (11 (82)), 62. <https://doi.org/10.15587/1729-4061.2016.76235>.
- [15] Zhou, R., Li, Y., Yan, L., Xie, J. (2011). Effect of edible coatings on enzymes, cell-membrane integrity, and cell-wall constituents in relation to brittleness and firmness of Huanghua pears (*Pyrus pyrifolia* Nakai, cv. Huanghua) during storage. *Food Chemistry*, 124(2), 569–575.
- [16] Serdyuk, M., Kurchev, S. (2016). The study of mass loss intensity of plum fruit during storage. *Eastern-European Journal of Enterprise Technologies*, 1 (10/79), 42–48. <https://doi.org/10.15587/1729-4061.2016.59694>.
- [17] Voragen, A. G., Coenen, G. J., Verhoef, R. P., & Schols, H. A. (2009). Pectin, a versatile polysaccharide present in plant cell walls. *Structural Chemistry*, 20(2), 263. <https://doi.org/10.1007/s11224-009-9442-z>.
- [18] Novikova, O. A., Golikova, N. A., Ovchinnikova, R. I. (2009). Dinamika soderzhaniya pektinovykh veshhestv v plodakh yabloni v protsesse khraneniya. *Ovchinnikova, Agrarian herald of the Urals*, 12, 49–50 (in Russian).
- [19] El-Ramady, H. R., Domokos-Szabolcsy, É., Abdalla, N. A., Taha, H. S., & Fári, M. (2015). Postharvest management of fruit and vegetables storage. In *Sustainable agriculture reviews*, 65–152. <https://doi.org/10.1007/978-3-319-09132-7>.
- [20] Salina, E. S., Levgerova, N. S., Gryuner, L. A., Ilina, I. A. (2010). Pektinovy veshhestva kak tekhnologicheskij pokazatel' prigodnosti plodov yabloni dlya proizvodstva soka. *Dostizheniya nauki i tekhniki APK*, 9, 30–31 (in Russian).
- [21] Serdyuk, M., Velichko, I., Priss, O., Danchenko, O., Kurcheva, L., & Baiberova, S. (2017). Substantiation of the choice of optimal concentrations of active ingredients of the antioxidant composition for fruit treatment before storage. *Technology audit and production reserves*, (3 (3)), 44–49. <https://doi.org/10.15587/2312-8372.2017.105630>.