

Physico-Chemical Study of Pomegranates of Different Degrees of Maturity

S. G. Hafizov and G. K. Hafizov*

Research Institute of Fruit and Tea Growing of the Ministry of Agriculture, Guba, Azerbaijan

*Corresponding Author

G. K. Hafizov, Research Institute of Fruit and Tea Growing of the Ministry of Agriculture, Guba, Azerbaijan.

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Abstract

The results of physico-chemical studies of individual fruit parts, including crusts, partitions, juice and seeds themselves, extracted from immature (green), unripe and mature fruits of three harvest periods are presented: 20.VII, 01.IX and 15.X. The analyses were carried out in 2019-20 during the period of active growth and ripening of fruits in the varieties Spring, Iridanaly, Guleisha pink and wild pomegranate from the Geokchay region (Azerbaijan) using standard and generally accepted physico-chemical methods. The ripe fruit (130-288 g) consisted of 60-113% of the peel (peel together with partitions), 53-140% of the juice and 17-85% of the seeds themselves. The edible part of the ripened fruits (53.85-73.2) of the total weight of the fruit consisted of 58.54-78.65% juice and 21.35 -41.46% seeds, fresh juice contained 15.7-17.7% solids, including 12.04-13.84% sugar, 0.17-0.30% protein, 0.15—0.23% pectin, 0.30-0.40% ash and 0.26-0.57% total polyphenols. The concentrations of solids, protein, ash and total polyphenols in the seeds themselves, remaining after the extraction of juice from the grains of ripe fruits, were 50.0-58.2, 4.13-5.75, 0.60-1.0 and 0.08-0.32%, respectively. There were fewer total polyphenols, flavonoids, chlorogenic acids, catechins and leucoanthocyanins in ripe fruits, and more ascorbic acid, anthocyanins and proanthocyanins than in unripe ones. The period from the second half of July to the beginning of September is the time of a real "boom" of common polyphenols.

Keywords: Pomegranate, Separation of Varieties by Taste, Degree of Maturity, Fruit Weight and Ratio of its Individual Parts, Chemical Composition, Sugar, Protein, Ascorbic Acid, Common Polyphenols, Flavonoids

1. Introduction

Pomegranate (*Punica granatum* L.) is one of the important commercial fruits in Azerbaijan and, as a rule, is very well adapted to the climate of the dry subtropics of the republic [1]. Here it is cultivated mainly in the Shirvan natural and economic zone, which includes several districts, including the Geokchay district. Fruits are consumed directly in the form of fresh grains, as well as freshly squeezed juice, they are used in the preparation of narsharab, a product of boiling the juice of sour fruits with the addition of spices, beverages, as well as flavorings and dyes [2-4]. The edible part of the pomegranate fruit contains a significant amount of acids, sugars, vitamins, polysaccharides, polyphenols and important minerals. Phytochemical studies allow various parts of pomegranate fruits as a promising source of new medicines [5]. They contain unique substances that can lower cholesterol and regulate blood pressure, reduce inflammatory processes, prevent infectious and fungal infection, disinfect the stomach and intestines, have an antidepressant effect, lighten skin pigmentation, exhibit antidiabetic properties, reduce the risk of cancer [7-13].

The results of the study of some morphological and technological features of Taifi pomegranates of varying degrees of maturity grown on the territory of the experimental station of KSU Agricultural College (Riyadh, Saudi Arabia) were reported [14]. These signs of a very green, immature and ripe fruit in the above order have changed as follows: the weight of the fruit is 163.51 g; 193.82 g and 216.50 g, respectively; the weight of the peel is 48.34 g; 54.43 g and 69.01 g (its share in the total weight of the fruit is 29.56%; 28.08% and 31.87%); the weight of juicy grains is 90.01 g; 111.95 g and 129.27 g (their share in the total weight of the fetus is 55.05%; 57.77% and 59.71%); the weight of the juice is 59.99 g; 68.76 g and 81.03 g (its share in the total weight of the fruit is 30.57%; 30.32% and 32.86%). The analyses showed a difference in the chemical composition of the grains of very green, unripe and ripe fruits: water - 79.45 (green); 80.66 (unripe) and 77.20 (ripe) g/100 g of raw mass; protein -3.99; 3.74 and 4.45 g/100 g of raw mass; ash-0.2; 0.01 and 0.25 g/100 g of crude mass; total polyphenols -3.65; 3.22 and 1.90 g/100 g of crude mass,

respectively.

Although there have been several reports in the literature about pomegranate flavonols, among them there is only one report on their changes related to fruit development, which states that during the period July 25 – September 13, the content of flavonols in fruits decreased: in the Hongbaoshi cultivar from 187.90 ± 22.02 to 143.52 ± 21.7 mg / 100 g; in the Lvbaoshi cultivar from 91.37 ± 8.47 to 57.84 ± 7.55 mg/100 g and in the Motilium cultivar from 134.37 ± 5.25 to 98.39 ± 7.25 mg/100 g of their raw mass. The authors consider this concentration of flavonols to be high, indicating that in onions - the richest source of flavonols – their concentration is 120 mg/100 g, in blueberries 16.7 mg/100 g, apples 4 mg/100 g, parsley 185 mg/100 g, celery 14 mg/100 g [15]. Changes in the chemical composition of the peel and bare seeds of fruits of such pomegranate cultivars as Wonderful and Rosh-Hapered during the initial and late periods of their maturation were also studied [16]. However, this work is of a slightly different direction, and the task it solved was to determine the optimal date of fruit removal, taking into account the time of maximum accumulation of nutrients in fruits.

Qualitative and quantitative changes of polyphenols in Taishanhong fruits in China were traced. 18 compounds were found in the phenolic complex, with punicalagin being the main phenol of both green and ripe pomegranate, and protocatechic acid being the main phenolic acid. The nature of changes in benzoic acid, floridzine, luteolin, floretin and vanillin in the peel and cinnamic acid in the juice, as well as ferulic and cinnamic acids, quercetin, floridzine, floretin, taxifolin and vanillin in the seeds, turned out to be the same: the content of these compounds was high at first, and decreased by the end of maturation [17]. Another work by Chinese authors reported that during the transition of the pomegranate fruit from a state of low maturity to a state of high maturity, the content of total phenols in its crust and partitions (dried samples) decreased by 29% and 44%, respectively [18]. In the process of studying the changes in the composition of pomegranates of the Hicaznar cultivar during their ripening in Turkey, it was found that during the period from August 15 to October 30, the fruit weight of this variety increased 2.1 times (from 208.8 g to 438.5 g). The content of total polyphenols in them decreased from 8308 mcg/g to 5696 mcg/g, gallic acid - from 97.2 mcg/g to 29.5 mcg/g, chlorogenic acid – from 83.9 mcg/g to 66.3 mcg/g, ellagic acid – from 13.6 mcg/g to 4.5 mcg/g [19]. As can be seen, the total content of phenols has noticeably decreased to the level of their content in ripe fruit 0.57 g / 100 g (considering that 1 mcg = 0.000001 g).

In a study conducted by an Egyptian-Indian group of authors using the HPLC method, it was found that in the methanol extract of pomegranate peel, the main phenolic compounds are rutin (with a mass fraction of 4.828% of the total number of extracted compounds) and chlorogenic acid. In addition, coumaric acid, pyrogallol, ferulic acid, benzoic acid, catechin and cinnamic acid were present in the extract in concentrations 1.297%, 0.529%,

0.077%, 0.025%, 0.019 % and 0.018% of the total number of extracted compounds, respectively [20]. Another published work concerns the quantitative content of catechins and chlorogenic acid in the dried fruit peel of two Turkish pomegranate cultivars with a residual moisture content of 6.35 and 7.71 wt.%. In this study, the analyses were carried out using the HPLC method after preliminary separation of the initial extract on Watman paper. Depending on the pomegranate variety, the content of catechins in their peel after drying varied from 27.7 mg/100 g to and 50.0 mg/100 g, chlorogenic acid – from 327.0 mg/100 g to 493.0 mg/100 g [21]. It has also been reported that the concentration of anthocyanins in the juices of ripe fruits of intensely colored pomegranate varieties can reach 59.3 mg/100 cm³ [22].

Using mobility coefficients (Rf) on Watman paper in a system of butanol/ acetic acid/ water solvents (40/12/29) and taps, it was found that the fruits of the Guleisha pink cultivar contain up to 10 flavonols. In this cultivar, two rutin isomers with Rf 0.44 and 0.46, avicularin (Rf 0.71), quercetin (Rf 0.76) and two more with Rf 0.10 and Rf 0.30 were found in the juice; rutin was found in the peel. Quercetrin (Rf 76), isoquercetrin (Rf 60), rutin (Rf 0.46) and avicularin (Rf 71) were found in the peel of wild pomegranate fruits. In the Iridanal variety, quercitrin (Rf 0.61) and isoquercitrin (Rf 0.66) were present in the juice, and in addition to them, several other flavonols with Rf 0.03; 0.04; 0.09; 0.78 [23]. It was also found that in the total number of polyphenols per pomegranate fruit of the Kyrmyzy Kabuk cultivar weighing 183.74 g, the proportion of juice polyphenols was 8.1% (or 4.9 g), seeds -1.9% (3.5 g), peel – 3.8 g or 90% [24]. Changing the nutritional value of pomegranates depending on the degree of maturity, varietal affiliation and soil and climatic conditions requires more work with pomegranates from individual regions of their cultivation. The purpose of this study was to determine the ongoing physico-chemical changes in pomegranate fruits at various stages of their maturation in the Geokchai region. Knowledge of changes in the content of phenolic and other substances would be very useful for determining the quality of fruits.

2. Materials and Methods

2.1 Objects of Research

In Azerbaijan and neighboring Turkey, it is customary to divide pomegranate cultivars into three groups: sour, sweet-sour and sour. In each of these groups there are varieties of early, medium and late ripening periods, which allows harvesting in the Mediterranean region in three periods from August 20 to October 20 [25]. Therefore, in this work, the fruits of the cultivars Spring, Iridanal, Guleisha pink and wild pomegranate, representing different taste groups, starting from the group of sweet pomegranates (Spring) and ending with the group of sour pomegranates, which in this study was represented by wild pomegranate, were selected as objects of research. Since morphological and technological signs are responsive to the climatic conditions of the year, the fruits were harvested two years in a row in 2019-20 and in three different terms: 20.VII; 01.IX and 15.X. These were fruits grown in the

experimental-industrial garden of the Geokchai stronghold of the Research Institute of Fruit and Tea Growing of the Ministry of Agriculture of the Republic of Azerbaijan. Only fruits were taken that started in the first half of the pomegranate flowering period with a peak in mid-May - early June and X. This is due to the fact that the fruits tied here on the shoots of the current year in the second half of the general flowering period (which begins here on 25.06 and ends on 10.07) are defective fruits with a certain lag in growth and development.

In Geokchaysky district, the soils are mainly light brown and meadow type, and the annual precipitation rate here ranges between 220 - 443 mm, the sum of active temperatures is between 4445 – 4550o C. Here, it takes 10 -15 days from the bud to the opening of the flower, and the beginning of flowering most often falls on 05.05. Pomegranate fruits, which began in the first half of their mass flowering period on branches older than one year, account for about 60-70% of the total harvest. According to the chosen

time for the collection and analysis of fruits, this work of ours is close to the work that was devoted to the study of changes in the composition of pomegranates of the Taifi cultivar from Riyadh in three different periods of their ripening: the first time at a time when the fruits were still with a hard texture and green color; the second time at a time when the texture remained still firm, and the cover color became light green; for the third time when the fruits acquired a reddish hue and became softer, that is, ripe [14].

2.2 Organization of Work and Place of its Holding

The work was carried out in the laboratory of Processing and storage Technologies in accordance with the program and calendar plan of research for doctoral students approved by the Scientific Council of the Research Institute of Fruit and Tea Growing of the Ministry of Agriculture of the Republic of Azerbaijan. The collected fruits in the amount of 20 pieces (average sample) from each cultivated variety and wild pomegranate were delivered to the laboratory on the same day.

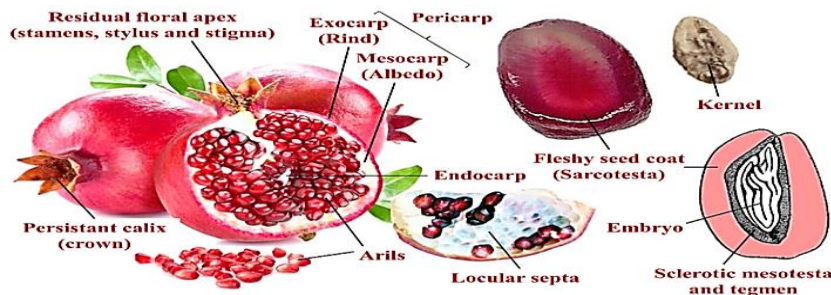


Figure 1: Anatomy of a Typical Pomegranate Fruit and Arils [26]

The next morning, the fruits were washed under the tap, then wiped with a soft dry cloth and divided manually into several parts according to their anatomical structure (Fig. 1). As a result of their manual separation, the crust (exocarp, rind), covering the fruit with a thin layer from the surface (1st part), internal light partitions (mesocarp, albedo), along with the filmy outgrowths of the placenta (endocarp) and seed nests (local septa) were first separated [2nd part] and juicy grains (arils), consisting of seeds and the surrounding fleshy shell (sarcotesta). Then, juice was obtained from juicy grains using a juicer of the Kenwood JE290 citrus press type (3rd part) and in the remainder – the bare seeds themselves (the 4th part). Then each of these parts was weighed on electronic scales BJ 610C Precisa (Switzerland) with a discreteness of 0.1 g in order to determine their shares in the total weight of a sample of 10 fruits randomly selected from an average sample. Sampling and their preparation for chemical analyses was carried out according to GOST (State Standard of Russia) 26313-84 and GOST 26671-85, respectively.

3. Methods of Quantitative Analysis of Hydrophilic Substances

Determination of the content of individual groups of nutrients and the amount of polyphenols was carried out using standard

and generally accepted chemical analysis methods. The mass fraction of dry substances was determined by drying the suspension of the material to a constant weight according to GOST 33977-2016, simple sugars - according to the Bertrand method according to GOST 8756.134-87, which is based on the ability of the aldehyde group of sugars to interact with the Fehling reagent and restore copper oxide to copper oxide precipitating in the form of a red precipitate. The mass fraction of titrated acids was determined by titration in the presence of a color indicator according to the interstate standard ISO 750-2013 (0.0064 is the conversion coefficient of 0.1 N NaOH solution to citric acid). The determination of the mass fraction of ascorbic acid was carried out by the iodometric method according to GOST 24556-89. To determine the mass fraction of total protein, a method was used, consisting in the determination of nitrogen by Kjeldahl, followed by conversion ($N \cdot 6.25$) to protein, ash - a standardized method according to GOST 25555.4-91. The mass fraction of pectin substances was determined by a method based on the precipitation of pectin acids in the form of calcium salts and taking into account their amount by weight [27]. Determination of the mass fraction of total polyphenols was carried out by a method based on titration with 0.1 N potassium permanganate solution of the indigo carmine

residue not consumed for the oxidation of phenolic substances. This principle underlies the method of determining tannins in medicinal raw materials according to GOST 24027.2-80 and the corresponding article of the State Pharmacopoeia of Russia, which is also devoted to the definition of these substances in medicinal raw materials.

The term "polyphenols" used here usually refers to an extensive family of naturally occurring compounds and includes phenols and polyphenols. Phenols are a class of chemical compounds consisting of a single phenolic link in their structure. Despite the fact that they are similar to alcohols, phenols have unique properties, including relatively higher acidity due to the aromatic ring closely associated with oxygen and the relatively weak bond between oxygen and hydrogen. Examples of phenolic compounds in this group include ellagic acid and gallic acid. Polyphenols are a group of compounds characterized by the presence of more than one phenolic group. Polyphenols include tannins (e.g., ellagitannins and Gallo tannins), flavonoids (e.g., anthocyanins and isoflavones) and stilbenes (e.g., resveratrol). With such a variety of this class of compounds, it is not surprising that the data on the content of common polyphenols in the same object vary greatly from different authors. After all, we are talking about a complex of substances with different responsiveness to the reagents used and methods of their determination in general.

In this study, the determination of the amount of polyphenols was carried out by the Leventhal method, based on titration of the indigo carmine residue, not consumed for the oxidation of phenolic substances, with 0.1 N KMnO₄. Not only polyphenols, but also some other compounds react with permanganate. Therefore, first, all substances oxidized by this reagent are titrated, then only that part of them that remained in the extract after processing it with activated carbon capable of adsorbing polyphenols. According to the difference in the amount of potassium permanganate, which went to oxidation for the first and second time, the phenol content is determined using 0.004157 as the conversion factor of 0.1 N KMnO₄ into grams of phenols. The use of activated carbon, on the one hand, helps to distinguish the polyphenols themselves from other substances that can also react with permanganate. However, the degree of absorption of polyphenols by activated carbon depends a lot on its brand and composition and structure of the polyphenols in the object under study, and some other factors. The functional groups of their molecules have a great influence on the sorption of polyphenols with activated carbon. In a review article devoted to this issue, the most important aspects of the irreversible adsorption of this group of substances and the effect of various phenolic substituents on their absorption by activated carbon were considered [28]. It shows that some substituents in the phenolic ring lead to inhibition of absorption, others to increased adsorption: p-nitrophenol, m-chlorophenol and p-cresols having a hydrophobic group are adsorbed more intensively than phenol and m-aminophenol, both of which have a hydrophilic group. Polyphenolic compounds with low solubility are adsorbed by activated carbon to a greater extent than other phenolic

compounds. The polymerization factor enhances adsorption under oxygen conditions. And this means that if, for example, as the pomegranate fruit matures, the balance between the oligomeric forms of polyphenols contained in its crust and their monomeric forms changes in favor of monomeric forms, then the Leventhal method will give a slightly lower result than it would have been with earlier analyses, and vice versa.

An effective sorbent for the extraction of polyphenols from water-alcohol solutions is the unique activated carbon BAU-A according to GOST 6217-74, which is made from environmentally friendly raw materials (birch wood), which was used in this study for the sorption of polyphenols from the extract when determining their quantitative content by the Leventhal method [29]. Determination of the mass fractions of anthocyanins, leucoanthocyanins (flavan-3,4-diols), catechins (flavan-3-ols) and proanthocyanidins (water-soluble oligomers containing from two to six catechin units) is usually carried out using methods based on measuring the optical density of colored extracts [30,31].

In this study, the method of determining anthocyanins was used, the feature of which is the measurement of the optical density of the tested solutions before and after their treatment with weak hydrogen peroxide. After such treatment, the anthocyanins are discolored, which makes it possible to subtract its optical density from the optical density of the test solution before treatment after treatment with weak hydrogen peroxide and determine the content of the anthocyanins themselves from the resulting difference. A sample of the test material in an amount of 10 g is poured with absolute methyl alcohol and extracted in a boiling water bath until the flavonoids are completely extracted (4 drains after 30 minutes). The extraction is repeated until the residue ceases to give staining when treated with a solution of 1% HCl. The volume of the solution is adjusted to 100 cm³ and filtered through a Schott filter with a pore diameter of 16 microns. To 1 cm³ of the filtrate, 9 cm³ 0.5 N HCL is added in 80-85% methanol, from here 4.5 cm³ is taken into two test tubes. 1.5 cm³ 3 N HCL in methanol is added to one of them, 1.5 cm³ of a reagent consisting of 9 cm³ 3 N HCL and 1 cm³ 30% hydrogen peroxide is added to the other. The optical density of solutions is measured at a wavelength of 540 nm in a cuvette L = 1 sm. Methyl alcohol is used as a comparison solution. The mass fraction of anthocyanin pigments is calculated according to a calibration schedule compiled according to the pure cyanidin-3-glucoside preparation Chroma Dex, USA.

The determination of leucoanthocyanins is based on the redness of these compounds when heated with mineral acid. Take 1 cm³ of the filtered extract obtained in the determination of anthocyanins, add 1 cm³ of distilled water to it (to reduce the alcohol concentration), then the diluted extract is divided into two equal parts of 1 cm³, 10 cm³ of the reagent in the composition of absolute butyl alcohol / HCL 20:1 is added to both of them. The resulting mixture is thoroughly mixed and the first tube is heated at 97 ° C for exactly 40 minutes, cooled and the optical density is measured at a wavelength of 540 nm in a cuvette L = 1 cm.

The same mixture from the second test tube is used as a control (without heating it). The mass fraction of leucoanthocyanins is calculated using a calibration curve compiled for a pure cyanidin-3-glucoside preparation (ChromaDex, USA).

Determination of the total content of catechins is based on their reaction with vanillin. From the alcohol extract obtained during the extraction of the sum of anthocyanin pigments, 1 cm³ is measured into a test tube and diluted with distilled water, bringing the total volume of the diluted extract to 6 cm³. 3 cm³ of the diluted extract is measured in two test tubes. 3 cm³ of hydrochloric acid with a concentration of HCl 37% is added to one of them (control), and 3 cm³ of vanillin reagent prepared at the rate of 25 mg of vanillin per 10 cm³ of hydrochloric acid of the same concentration is added to the other tube. The contents of the test tubes are mixed and the optical density is determined exactly after 3 minutes at a wavelength of 490-500 nm in a cuvette L = 1 cm. The mass fraction of catechins is calculated according to the schedule compiled according to the pure epicatechin preparation Sigma-Aldrich, CAS No: 490-46-0. Proanthocyanins exist in the form of water-soluble oligomers containing from 2 to 6 catechin units, as well as in the form of polymers with a degree of polymerization of 7 and higher.

The extraction of oligomeric proanthocyanins was carried out according to the method, which includes holding a mixture of the test material and deionized water (1:5) for 20 minutes in a water bath at 50 ° C [32]. The liquid extract was separated from solid particles by centrifugation at 2000 rpm for 10 minutes. The supernatant is transferred to a 10 ml flask and deionized water is added to obtain a final volume of 10 cm³. Lipids are then eluted by washing the raw extract with hexane.

The mass fraction of proanthocyanins was determined by a method based on the formation of a color complex during the reaction of vanillin with condensed tannins in an acidic medium. The aliquot of the raw extract in a volume of 1 cm³ is mixed with 4 cm³ of the reagent (1% vanillin solution in 70% aqueous sulfuric acid by volume) and left for 15 minutes in an ice bath. The optical density is measured at a wavelength of 490 nm in a cuvette L = 1 cm (control: 1 cm³ of extract + 4 cm³ of 70% aqueous sulfuric acid by volume). The concentration of proanthocyanins in the test solution is determined by a standard curve constructed from a pure preparation of catechin (+) Sigma-Aldrich, CAS No: 225937-10-0. The mass fraction of flavonols and hydroxycinnamic acids is now often carried out using spectral analysis, ultra-high-performance liquid chromatography and other methods [33]. In this study, quantitative analysis of flavonols and hydroxycinnamic acids was carried out by methods including chromatographic separation of individual substances (within each of the above groups), taking into account their different mobility on paper in different solvent systems [34]. After overlocking, the locations of the desired substances are identified on paper [due to complexation with reagents such as AlCl₃, Pb(CH₃COO)₂, etc.], the identified spots

are eluted and their concentration in the eluate and in the starting material is determined by photometry and comparison of its results with the previously obtained results for standard samples.

Due to the three-stage cyclic extraction of a sample of fresh material of 50% (flavonols) and 70% (hydroxycinnamic acids) with aqueous ethyl alcohol at slow heating to 70 ° C, only 25 cm₃ of the extract from 2.5 g of raw material was obtained at first. An amount of extract corresponding to 0.05 – 0.1 g will be applied to Filtrak Ahlstrom Munkell paper strips (4-5 sm wide each) 1g of the source material. The paper in the column is positioned so that the lower part of the strip is evenly (by 1 mm) immersed in the solvent system. Chromatography is carried out in an ascending mode for 23-24 hours in a solvent system butyl alcohol: acetic acid: water 4:2.5:1 (flavonols) and 4:1:3 (hydroxycinnamic acids). After sublimation, the chromatogram is removed and dried using a desktop fan. The detection of flavonol stains on the paper tape is carried out using a roller moistened with a 10% aqueous solution of Pb-acetate. The yellowed sections of the tape as a result of complexation are cut out, crushed and placed in a dry test tube. Similarly, Pb-acetate-treated pieces of paper are cut out from a colorless section of the tape on which the extract was not applied (control), and so that their total area is equal to the area of the cut yellowed sections. The paper in test tubes is moistened with 2-3 drops of 10% aqueous H₂SO₄ (colored pieces turn white from this), after which a 3-4-fold extraction of flavonols 1.2-1.5 cm₃ of 50% aqueous ethyl alcohol is carried out with careful heating in a water bath before it boils to obtain 5 cm₃ of the total extract for measurements. Before measuring the optical density at a wavelength of 360 nm, the extract is centrifuged to increase its transparency. The concentration of the sum of flavonols is determined by the curve constructed according to the results of preliminary experiments with the application of 90-95% purity rutin standard from Chromadex, CAS No: 153-18-4 on the chromatogram.

When determining hydroxycinnamic acids, a paper tape is used, divided by a slit (slightly not reaching the end of the tape) of 0.5 sm into two strips of 4-5 sm wide. The test solution is applied in equal amounts to both strips. After overlocking, one of these strips is treated with Hopfner reagent (5 sm³ 5% NaNO₂ + 2 sm³ 10% H₂SO₄) and 5% KOH aqueous solution. As a result of such processing, the places of paper where chlorogenic acids (and caffeic acid) are located turn red, they are immediately cut out and placed in distilled water. With the second strip, which is not treated with Hopfner reagent and KOH, they do the same thing (control). The eluates are separated and brought to a certain volume (10 cm³) with water. Their optical density is measured at a wavelength of 520 nm. The calculation of the content of hydroxycinnamic acids is carried out on a scale constructed according to the standard of chlorogenic acid 95% purity from Sigma-Aldrich, CAS No: 327-97-9.

3.1 Processing of Primary Data

In this study, it was reduced to calculating the average of the definitions in three repetitions (a total of 6 definitions for two years of research on each parameter) and identifying statistical reliability using Excel software so that it was possible to give an approximate estimate of the obtained data set for each studied trait and substance [35].

4. Results and their Discussion

The study of the technical composition of fruits of different maturity showed that in the studied varieties and wild pomegranate, the ripened fruit (130-288 g) consisted of 60-113% of the peel (peel together with partitions), 53-140% of the juice and 17-85% of the seeds themselves (Fig. 2). The juice yield of the sweet and sour Guleisha pink variety, a little sweet - Iridanally and sour wild in

the time interval between 20.VII and 15.X increased from 38.9; 47.4 and 27.9% to 48.6; 54.0 and 40.8% of the fruit weight, and in the sweet variety Spring - decreased from 46.4 to 42.9% of the the weight of the fetus, respectively. The yield of the peel (the crust together with the partitions) in the varieties Spring, Guleisha pink, Iridanal and wild pomegranate decreased from 35.7; 44.2; 35.7 and 53.5% to 26.8; 39.2; 28.0 and 46.2% of the total weight of the fruit, respectively. The situation was different with the output of the actual seeds, the remaining extraction of juice from juicy grains. If in the Guleisha pink cultivar and wild pomegranate, it decreased from 16.8 and 18.6% to 12.2 and 13.0% of the total fruit weight, respectively, then in the Iridanally and Spring cultivars, on the contrary, it increased from 16.9 and 17.9% to 18.0 and 30.3% of the total fruit weight, respectively.

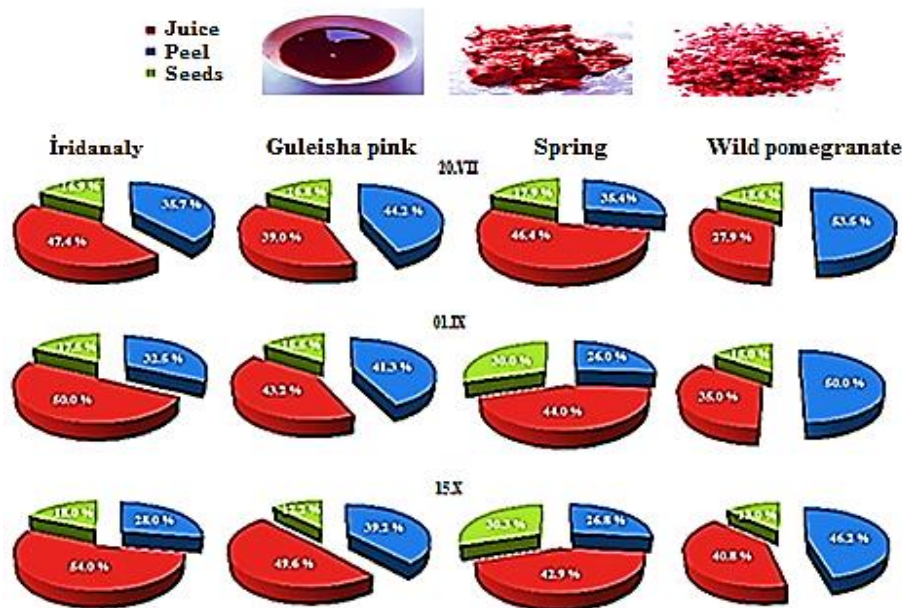


Figure 2: The Change in the Percentage Ratio Between the Juice, Peel (Crusts Together with Partitions) and Kernels (Seeds Themselves) in the Fruit of the three Studied Varieties and wild Pomegranate in Different Periods of its Maturation

The amount of peel per fruit increased over the same period of time as follows: Guleisha pink - from 42 to 113 g, that is 2.7 times; wild pomegranate - from 23 to 60 g, that is 2.6 times; Iridanally - from 55 to 70 g, that is 2.7 times; Spring - from 50 to 75 g, that is 2.6 times. The number of actual seeds per fruit in the Guleisha pink cultivar increased from 16 to 37 g, that is, 2.3 times; in wild pomegranate - from 8 to 17 g, that is, 2.1 times; in the Iridanal variety - from 26 to 45 g, that is, 1.7 times; in the Spring cultivar - from 25 to 85 g, that is, 3.4 times. In the Guleisha pink cultivar, along with an increase in the weight of the fruit from 95 to 288 g, in the above-mentioned period of time, the amount of juice that fell on it increased from 37 to 140 g, that is, by 3.8 times. In the Spring honeycomb and wild pomegranate, the weight of the fruit increased from 154 and 43 g to 250 and 130 g, respectively, and the amount of juice that fell on it – from 65 and 12 to 120 and 53

g, that is, 1.8 and 4.4 times. In the Iridanally variety, the weight of the fruit increased from 154 g to 250 g, and the amount of juice falling on it - from 73 g to 135 g, that is, 1.8 times. This means that the accumulation of juice (starting from July 20) in the fruit of the sweet and sour Guleisha pink cultivar and sour wild pomegranate took place at a much higher rate (the amount of juice increased by 3.8 and 4.4 times, respectively) than in the slightly sweet Iridanally cultivar (1.8 times) and the sweet Spring variety (1.8 times).

But, despite this, the Iridanally variety, due to the lowest rates of accumulation of peel and bare seeds during the same period, the yield of juice from the ripe fruit in mid-October is higher (54.0% of its weight) than the other two aforementioned cultivars and wild pomegranate (40.8 - 48.6% of its weight). It was found that there is a statistically significant relationship between the weight of the

fetus and the juice yield as a percentage of its weight ($r = -0.732$). Variables such as the weight of the peel per fruit and the juice yield as a percentage of the weight of the fruit ($r = -0.658$), as well as the weight of the juice per fruit and the juice yield as a percentage of the total weight of the fruit ($r = +0.640$) are also closely related. And the correlation between two variables such as the total weight of the bare seeds after extracting the juice from the grains that fell on one fruit, and the juice yield as a percentage of its total weight is not so high ($r = -0.413$) that we can talk about the presence of reliable conjugacy in this pair of signs. The ratio between the individual fruit parts and their chemical composition at the time of analysis are given in Tables 1-4.

Table 1 shows that the total sugar content in the crust and partitions of sweet pomegranates Spring on September 1 (14.03 and 13.22 g / 100 g of their raw mass, respectively) is slightly lower than it was on July 20 (14.64 and 14.84 g / 100 g of their raw mass). But by October 10, it rises again to 14.34 and 13.84 g/100 g of their raw mass, thereby becoming higher than not only the September,

but also the July level. The total sugar content in their seeds and juice of this variety is constantly growing (in July 1.16 and 7.36; September 3.95 and 10.96; in October - 4.16 and 12.25 g / 100 g, respectively), and in juice and seeds (especially seeds) it is always much lower than in the crust and partitions. Thus, although the total sugar content in the analyzed objects increased in October compared to July, in the peel and partitions, unlike seeds and juice, this was not permanent. This may be due to the simultaneous decrease in the content of the total amount of dry substances in the crust and partitions in the period from July to October, while their content in seeds and juice has been increasing all the time. Due to such trends, in terms of the concentration of total sugar, the juice of the fruits of the October harvest is inferior to the crust and partitions not as much as it was in July and September. Another feature is that in the sum of simple sugars, the "lion's" share belongs to monosaccharides, and sucrose accounts for very little in it. By the time the pomegranates were fully ripe, the sucrose content in their juice had already become so insignificant that it remained beyond the sensitivity of the Bertrand method.

Parameters	The fruit as a whole	Part of the fruit			
		Crust	Partitions	Seeds	Juice
<i>20.VII: crust 35 g, partitions 15 g, juice 65 g, seeds 25 g.</i>					
Mass fraction of dry substances, %	24.85	38.4	36.20	35.10	11.0
Mass fraction of the sum of sugars, %	8.87	14.64	14.84	1.16	7.36
Acidity (titrated)	1.61	3.65	2.17	0.83	1.76
Mass fraction of protein (N x 6.25), %	2.36	1.88	2.50	8.48	0.23
Mass fraction of pectin substances, %	0.53	0.64	0.48	1.54	0.09
Mass fraction of mineral substances, %	0.70	1.0	0.44	0.70	0.60
Mass fraction of total polyphenols, %	4.71	13.05	12.73	0.03	0.17
Mass fraction of ascorbic acid, mg/100 g	4.03	5.46	4.93	4.05	3.05
Mass fraction of anthocyanins, mg/100 g	8.93	8.07	8.00	2.5	2.07
Mass fraction of leucoanthocyanins, mg/100 g	0.05	3.0	0.10	0.0	0.04
Mass fraction of proanthocyanidins, mg/100 g	1.72	6.48	0.78	0.072	0.0004
Mass fraction of catechins, mg/100 g	9.6	19.65	17.7	3.12	4.8
Mass fraction of flavonoids, mg/100 g	169.25	455.0	310.0	12.0	42.5
Mass fraction of hydroxycinnamic acids, mg/100 g	38.25	62.5	84.5	5.8	27.13
<i>01.IX: crust 45 g, partitions 20 g, juice 67 g, seeds 75 g.</i>					
Mass fraction of dry substances, %	29.87	35.0	32.0	48.28	14.8
Mass fraction of the sum of sugars, %	9.59	14.03	13.22	3.95	10.96
Acidity (titrated)	1.02	2.03	1.89	0.64	0.70
Mass fraction of protein (N x 6.25), %	2.18	0.88	1.31	6.06	0.23
Mass fraction of pectin substances, %	0.89	1.09	0.88	1.86	0.16
Mass fraction of mineral substances, %	0.56	0.54	0.45	0.85	0.4
Mass fraction of total polyphenols, %	3.72	12.28	11.69	0.11	1.25
Mass fraction of ascorbic acid, mg/100 g	7.51	18.98	14.61	3.82	4.05
Mass fraction of anthocyanins, mg/100 g	10.23	10.93	9.13	3.87	4.87
Mass fraction of leucoanthocyanins, mg/100 g	1.92	9.06	1.24	0.0	0.44
Mass fraction of proanthocyanidins, mg/100 g	3.80	16.2	4.2	1.0	0.6
Mass fraction of catechins, mg/100 g	15.56	39.85	24.08	3.26	12.45
Mass fraction of flavonoids, mg/100 g	64.5	195.0	287.5	6.2	10.31
Mass fraction of hydroxycinnamic acids, mg/100 g	22.98	56.80	58.3	2.5	16.69

<i>15.X: crust 50 g, partitions 25 g, juice 120 g, seeds 85 g.</i>					
Mass fraction of dry substances, %	30.54	30.0	29.6	52.1	15.7
Mass fraction of the sum of sugars, %	10.31	14.34	13.84	4.16	12.25
Acidity (titrated)	1.39	0.48	1.54	1.06	1.98
Mass fraction of protein (N x 6.25), %	2.42	1.63	2.88	5.75	0.3
Mass fraction of pectin substances, %	0.91	2.59	1.72	2.89	0.21
Mass fraction of mineral substances, %	0.57	0.5	0.56	1.00	0.30
Mass fraction of total polyphenols, %	1.27	4.36	3.95	0.08	0.26
Mass fraction of ascorbic acid, mg/100 g	16.9	60.9	20.77	4.05	6.87
Mass fraction of anthocyanins, mg/100 g	11.06	12.0	9.52	8.8	12.6
Mass fraction of leucoanthocyanins, mg/100 g	0.59	3.28	0.0	0.0	0.0
Mass fraction of proanthocyanidins, mg/100 g	15.88	86.4	2.4	0.42	0.255
Mass fraction of catechins, mg/100 g	5.6	23.37	7.73	0.81	1.14
Mass fraction of flavonoids, mg/100 g	49.56	150.0	218.7	5.8	3.48
Mass fraction of hydroxycinnamic acids, mg/100 g	6.57	21.5	21.8	1.2	1.0

The arithmetic mean of each parameter in a row of 20 fruits of each harvest period marked in the table- is 6 repeated measurements over 2 years of research ($p \leq 0.05$).

Table 1: Changes in the Physico-Chemical Parameters of the Pomegranate as the Process of its Maturation Deepens (cv. ‘Spring’)

Tables 2 - 3 show that the period from July 20 to September 01 was a period of a significant decrease in the quantitative content of titrated acids in the crust, partitions and seeds of slightly sweet (Iridanals) and sweet-sour pomegranates (Guleisha pink). By October, it began to rise again, but by October 10 it still had not reached the original July level. This is clearly seen by the example

of data on the Iridanal variety placed in Table 2. As can be seen from this table, in July the content of titrated acids in the crust, partitions, seeds and juice was the highest (6.24; 3.16, 1.10 and 2.43 g/100 g, respectively). In September, it fell to 2.05; 1.90; 0.77 and 1.31 g/100 g, and in October it increased to 3.52; 2.43; 0.90 and 1.76 g/100 g of crude mass, respectively.

Parameters	The fruit as a whole	Part of the fruit			
		Crust	Partitions	Seeds	Juice
<i>20.VII: crust 40 g, partitions 15 g, juice 73 g, seeds 26 g.</i>					
Mass fraction of dry substances, %	23.42	36.0	32.0	35.1	10.6
Mass fraction of the sum of sugars, %	7.22	11.75	10.97	1.74	5.91
Acidity (titrated)	3.27	6.24	3.16	1.10	2.43
Mass fraction of protein (N x 6.25), %	1.92	2.60	1.56	5.61	0.31
Mass fraction of pectin substances, %	0.49	0.64	0.41	1.58	0.04
Mass fraction of mineral substances, %	0.58	1.1	0.4	0.4	0.4
Mass fraction of total polyphenols, %	3.53	8.31	10.83	0.05	0.67
Mass fraction of ascorbic acid, mg/100 g	7.38	15.8	6.86	4.58	3.87
Mass fraction of anthocyanins, mg/100 g	5.47	13.93	6.53	2.40	1.67
Mass fraction of leucoanthocyanins, mg/100 g	1.88	5.82	0.38	0.0	0.66
Mass fraction of proanthocyanidins, mg/100 g	22.63	82.8	7.9	0.9	0.006
Mass fraction of catechins, mg/100 g	35.0	116.45	20.3	1.5	4.8
Mass fraction of flavonoids, mg/100 g	209.13	448.0	287.0	12.2	131.5
Mass fraction of hydroxycinnamic acids, mg/100 g	31.35	45.0	75.0	4.5	24.63
<i>01.IX: crust 47 g, partitions 18 g, juice 100 g, seeds 35 g.</i>					
Mass fraction of dry substances, %	25.51	30.5	28.0	48.1	14.8
Mass fraction of the sum of sugars, %	9.93	12.6	11.0	3.72	10.66
Acidity (titrated)	1.44	2.05	1.9	0.77	1.31
Mass fraction of protein (N x 6.25), %	1.44	0.93	2.65	4.88	0.26
Mass fraction of pectin substances, %	0.79	1.2	1.02	2.06	0.12
Mass fraction of mineral substances, %	0.49	0.8	0.48	0.5	0.35
Mass fraction of total polyphenols, %	3.75	9.15	8.65	0.21	1.25

Mass fraction of ascorbic acid, mg/100 g	8.42	20.38	7.75	5.34	4.0
Mass fraction of anthocyanins, mg/100 g	7.19	14.93	8.8	3.6	4.13
Mass fraction of leucoanthocyanins, mg/100 g	5.13	17.82	2.9	0.0	0.8
Mass fraction of proanthocyanidins, mg/100 g	14.87	54.0	4.36	1.1	1.44
Mass fraction of catechins, mg/100 g	25.11	56.5	21.6	1.87	18.22
Mass fraction of flavonoids, mg/100 g	85.27	170.0	245.0	5.1	38.75
Mass fraction of hydroxycinnamic acids, mg/100 g	21.08	34.8	33.8	2.0	18.75
<i>15.X: crust 50 g, partitions 20 g, juice 135 g, seeds 45 g.</i>					
Mass fraction of dry substances, %	25.0	26.4	26.0	50.0	16.0
Mass fraction of the sum of sugars, %	10.07	9.38	12.3	3.96	12.04
Acidity (titrated)	2.01	3.52	2.43	0.9	1.76
Mass fraction of protein (N x 6.25), %	1.52	2.5	1.87	4.13	0.23
Mass fraction of pectin substances, %	1.41	2.69	2.4	3.1	0.23
Mass fraction of mineral substances, %	0.54	0.7	0.8	0.98	0.3
Mass fraction of total polyphenols, %	1.16	3.12	2.49	0.16	0.57
Mass fraction of ascorbic acid, mg/100 g	17.95	67.23	8.8	5.7	5.14
Mass fraction of anthocyanins, mg/100 g	11.06	20.3	8.96	9.6	29.2
Mass fraction of leucoanthocyanins, mg/100 g	1.84	8.06	2.88	0.0	0.0
Mass fraction of proanthocyanidins, mg/100 g	21.49	105.0	4.0	0.34	0.21
Mass fraction of catechins, mg/100 g	4.78	18.1	6.88	0.2	1.06
Mass fraction of flavonoids, mg/100 g	43.96	142.5	162.5	4.6	3.03
Mass fraction of hydroxycinnamic acids, mg/100 g	9.54	31.3	29.0	1.5	1.28

The arithmetic mean of each parameter in a row of 20 fruits of each harvest period marked in the table- is 6 repeated measurements over 2 years of research ($p \leq 0.05$).

Table 2: Changes in the Physico-Chemical Parameters of the Pomegranate as the Process of its Maturation Deepens (cv. 'Iridanaly')

At the same time, in very sweet (Spring) and sour (wild pomegranate) pomegranates, quantitative changes in titrated acids had a slightly different character. This was reflected in the fact that in the crust and partitions of the fruits of the Spring cultivar, the maximum amount of activated acids was contained in July, amounting to 3.65 and 2.17 g/100 g of their raw mass, respectively, and by October it had decreased to 0.48 and 1.54 g/100 g of the

crust and partitions (Table 1). Titrated acidity of wild pomegranate seeds and juice in July was low (0.77 and 1.09 g/100 g of their raw weight). In September, it became lower than in July, and by October it increased to the maximum value: in seeds - up to 1.25 g/100 g of their raw mass; in juice - up to 3.20 g/100 g of raw mass (Table 4).

Parameters	The fruit as a whole	Part of the fruit			
		Crust	Partitions	Seeds	Juice
<i>20.VII: crust 33 g, partitions 9 g, juice 37 g, seeds 16 g.</i>					
Mass fraction of dry substances, %	27.5	40.5	37.5	35.5	10.0
Mass fraction of the sum of sugars, %	8.35	14.35	15.38	1.78	4.14
Acidity (titrated)	3.39	3.68	3.1	1.25	4.14
Mass fraction of protein (N x 6.25), %	1.59	1.56	2.52	4.50	0.14
Mass fraction of pectin substances, %	0.78	1.2	0.55	1.66	0.09
Mass fraction of mineral substances, %	0.65	0.7	0.4	0.8	0.6
Mass fraction of total polyphenols, %	4.16	8.56	12.66	0.11	0.17
Mass fraction of ascorbic acid, mg/100 g	9.19	14.78	6.69	3.62	7.22
Mass fraction of anthocyanins, mg/100 g	3.95	11.3	6.93	2.4	3.47
Mass fraction of leucoanthocyanins, mg/100 g	3.47	8.72	2.18	0.0	0.56
Mass fraction of proanthocyanidins, mg/100 g	31.13	86.4	8.0	1.12	0.007
Mass fraction of catechins, mg/100 g	43.46	111.0	19.65	3.0	6.01
Mass fraction of flavonoids, mg/100 g	204.78	363.0	450.0	12.8	87.5

Mass fraction of hydroxycinnamic acids, mg/100 g		112.5	86.3	5.9	11.63
<i>01.IX: crust 44 g, partitions 20 g, juice 67 g, seeds 24 g.</i>					
Mass fraction of dry substances, %	29.6	36.4	35.4	53.4	14.8
Mass fraction of the sum of sugars, %	10.18	12.78	12.3	5.28	9.6
Acidity (titrated)	2.02	2.39	2.4	0.77	2.13
Mass fraction of protein (N x 6.25), %	1.63	1.63	2.88	4.69	0.16
Mass fraction of pectin substances, %	1.01	1.65	0.95	2.31	0.14
Mass fraction of mineral substances, %	0.53	0.5	0.5	0.7	0.5
Mass fraction of total polyphenols, %	5.84	12.89	11.64	0.42	1.25
Mass fraction of ascorbic acid, mg/100 g	11.32	18.98	14.61	3.82	8.0
Mass fraction of anthocyanins, mg/100 g	7.06	12.4	7.06	5.05	4.13
Mass fraction of leucoanthocyanins, mg/100 g	4.62	14.48	3.0	0.0	0.07
Mass fraction of proanthocyanidins, mg/100 g	15.16	48.0	2.82	1.43	1.50
Mass fraction of catechins, mg/100 g	23.01	47.1	16.05	2.52	16.35
Mass fraction of flavonoids, mg/100 g	126.41	240.0	395.0	6.5	11.25
Mass fraction of hydroxycinnamic acids, mg/100 g	24.64	45.0	54.3	2.8	9.81
<i>15.X: crust 85 g, partitions 28 g, juice 140 g, seeds 37 g.</i>					
Mass fraction of dry substances, %	26.4	28.0	27.0	57.3	16.8
Mass fraction of the sum of sugars, %	11.89	11.3	13.3	4.16	13.84
Acidity (titrated)	1.77	2.82	2.6	1.06	1.12
Mass fraction of protein (N x 6.25), %	1.39	1.5	2.13	5.06	0.18
Mass fraction of pectin substances, %	1.38	2.58	1.91	2.84	0.15
Mass fraction of mineral substances, %	0.5	0.5	0.8	0.66	0.4
Mass fraction of total polyphenols, %	1.39	3.33	2.49	0.32	0.31
Mass fraction of ascorbic acid, mg/100 g	24.83	60.9	20.77	4.05	8.87
Mass fraction of anthocyanins, mg/100 g	25.05	24.5	9.3	21.33	29.2
Mass fraction of leucoanthocyanins, mg/100 g	2.05	6.82	0.48	0.0	0.0
Mass fraction of proanthocyanidins, mg/100 g	17.78	58.8	2.58	0.50	0.285
Mass fraction of catechins, mg/100 g	10.56	31.26	5.53	1.02	1.47
Mass fraction of flavonoids, mg/100 g	66.67	170.0	163.8	5.5	3.19
Mass fraction of hydroxycinnamic acids, mg/100 g	14.16	37.3	27.3	1.4	1.2

The arithmetic mean of each parameter in a row of 20 fruits of each harvest period marked in the table - is 6 repeated measurements over 2 years of research ($p \leq 0.05$).

Table 3: Changes in the Physico-Chemical Parameters of the Pomegranate as the Process of its Maturation Deepens (cv. ‘Guleisha pink’)

The change in the mass fraction of protein in the crust and partitions of sweet-sour and sour pomegranates of Guleisha pink and Wild pomegranate occurred according to the same pattern: by the beginning of September it is slightly higher than in July, then by October it falls again, although not so significantly. Moreover, all these decreases and increases in the crust and partitions occur in a rather narrow range, differing from the level of the previous period by a minimum - maximum of 0.06 - 0.75 g / 100 g of their

raw mass. In a slightly sweet cultivar of Iridanaly and a very sweet cultivar of Spring, in the period from July to October, the protein concentration in seeds and juice decreases all the time. In the same varieties, the mass fraction of protein in the crust and partitions of fruits of the September harvest is significantly lower than in the crust and partitions of fruits of the July harvest, and by mid-October it rises again, but not so much as to correspond to the highest July level.

Parameters	The fruit as a whole	Part of the fruit			
		Crust	Partitions	Seeds	Juice
<i>20.VII: crust 19 g, partitions 4 g, juice 12 g, seeds 8 g.</i>					
Mass fraction of dry substances, %	32.84	46.24	39.4	33.5	9.0
Mass fraction of the sum of sugars, %	11.43	18.23	17.35	1.12	5.58
Acidity (titrated)	3.02	5.12	3.37	0.77	1.09
Mass fraction of protein (N x 6.25), %	1.67	1.19	2.69	4.63	0.13
Mass fraction of pectin substances, %	0.86	1.25	0.48	1.39	0.03
Mass fraction of mineral substances, %	0.91	1.2	0.45	1.0	0.55
Mass fraction of total polyphenols, %	8.06	15.13	12.32	0.21	0.68
Mass fraction of ascorbic acid, mg/100 g	7.6	8.98	7.04	3.87	8.1
Mass fraction of anthocyanins, mg/100 g	8.45	15.4	8.0	2.67	1.45
Mass fraction of leucoanthocyanins, mg/100 g	6.38	13.48	2.2	0.0	0.27
Mass fraction of proanthocyanidins, mg/100 g	40.75	91.2	3.2	0.83	0.009
Mass fraction of catechins, mg/100 g	56.12	116.45	30.15	1.0	6.01
Mass fraction of flavonoids, mg/100 g	299.67	528.0	578.0	13.0	36.5
Mass fraction of hydroxycinnamic acids, mg/100 g	57.05	104.3	89.5	4.8	6.25
<i>01.IX: crust 35 g, partitions 15 g, juice 35 g, seeds 15 g.</i>					
Mass fraction of dry substances, %	29.88	39.6	33.0	43.0	13.2
Mass fraction of the sum of sugars, %	11.46	16.35	12.74	2.4	9.89
Acidity (titrated)	3.13	1.82	1.54	0.52	0.83
Mass fraction of protein (N x 6.25), %	1.62	1.25	2.89	4.69	0.14
Mass fraction of pectin substances, %	0.97	1.39	0.81	2.0	0.18
Mass fraction of mineral substances, %	0.67	0.75	0.53	0.95	0.52
Mass fraction of total polyphenols, %	6.85	14.17	10.22	0.42	0.83
Mass fraction of ascorbic acid, mg/100 g	12.26	10.57	33.26	4.2	8.4
Mass fraction of anthocyanins, mg/100 g	12.25	17.87	8.67	4.0	1.47
Mass fraction of leucoanthocyanins, mg/100 g	7.78	20.8	2.44	0.0	0.37
Mass fraction of proanthocyanidins, mg/100 g	42.0	63.0	3.12	0.95	1.26
Mass fraction of catechins, mg/100 g	45.04	106.0	21.8	1.15	12.86
Mass fraction of flavonoids, mg/100 g	151.22	245.0	407.5	7.1	9.38
Mass fraction of hydroxycinnamic acids, mg/100 g	31.15	61.3	50.8	3.0	4.63
<i>15.X: crust 40 g, partitions 20 g, juice 53 g, seeds 17 g.</i>					
Mass fraction of dry substances, %	28.21	30.0	27.0	58.2	17.7
Mass fraction of the sum of sugars, %	10.89	12.51	10.96	3.05	12.16
Acidity (titrated)	3.12	3.81	3.1	1.25	3.2
Mass fraction of protein (N x 6.25), %	1.36	0.94	2.5	4.75	0.17
Mass fraction of pectin substances, %	1.38	1.97	1.97	3.01	0.2
Mass fraction of mineral substances, %	0.63	0.8	0.9	0.6	0.4
Mass fraction of total polyphenols, %	2.29	4.99	3.53	0.31	0.42
Mass fraction of ascorbic acid, mg/100 g	49.68	126.72	49.63	4.87	8.98
Mass fraction of anthocyanins, mg/100 g	18.63	21.0	9.0	12.33	24.0
Mass fraction of leucoanthocyanins, mg/100 g	2.31	7.5	0.04	0.0	0.0
Mass fraction of proanthocyanidins, mg/100 g	24.72	78.0	3.0	1.2	0.26
Mass fraction of catechins, mg/100 g	10.36	23.37	14.81	0.33	2.07
Mass fraction of flavonoids, mg/100 g	65.09	120.0	172.5	4.1	2.69
Mass fraction of hydroxycinnamic acids, mg/100 g	16.12	34.3	31.3	1.6	1.34

The arithmetic mean of each parameter in a row of 20 fruits of each harvest period marked in the table - is 6 repeated measurements over 2 years of research ($p \leq 0.05$).

Table 4: Changes in the Physico-Chemical Parameters of the Pomegranate as the Process of its Maturation Deepens (wild Pomegranate)

In the exposed seeds, after extracting the juice from the juicy grains of fully ripened fruits, the protein concentration varied from 4.13 to 5.75 g / 100 g of raw seed mass. The protein concentration in the bare seeds decreased all the time: in the Spring cultivar - from 8.48 g/100 g (in July) to 6.06 g/100 g (in September) and 5.75 g/100 g (in October); in the Iridanaly cultivar - from 5.61 g/100 g to 4.88 g/100 g and 4.13 g/100 g. At the same time, in the seeds of sweet and sour fruits of the Guleisha pink cultivar and sour fruits of wild pomegranate in the period limited to the 20th of July - the 15th of October, the protein content, on the contrary, increased. This is probably one of the features of pomegranates belonging to relatively sweet and relatively sour groups of varieties. As sweet pomegranates ripened in Spring, the protein concentration in their juice increased slightly, while in other varieties and wild pomegranate, on the contrary, decreased. However, the quantitative content of protein in juices is so small compared to its content in solid fruit parts that it may not be taken into account when assessing the total potential of fruits for protein. The concentration of the sum of pectin substances in all parts of the fruits of the studied cultivars and Wild pomegranate increased during their maturation. In the hard parts of fruits in mid-October, the concentration of total pectin varied from 1.72 g/100 g of their raw mass (Spring, partitions) to 3.10 g/100 g of their raw mass (Iridanals, seeds).

Between July 20 and September 01, the concentration of ascorbic acid in the crust and partitions of all the studied cultivars and wild pomegranate increased, especially strongly - between September 01 and October 15. If in September the mass fraction of ascorbic acid in the crust and partitions of wild pomegranate was 10.57 and 33.26 mg/100 g of their crude mass, respectively, then in October it increased to 126.72 mg/100 g and 49.63 mg/100 g of their crude mass. The quantitative content of ascorbic acid in juice and bare seeds also increased, but only slightly (Table 4). The results show that proanthocyanidins are concentrated mainly in the crust, and their concentration in this part of the fruit of the early September period is significantly lower than their concentration in this part of the ripe October fruit. In the peel of fruits of the Iridanaly cultivar in July, September and October, the quantitative content of proanthocyanidins was 82.8; 54.0 and 105.0 mg/ 100 g of its raw mass, respectively, and in the crust of fruits of the Spring cultivar - 64.8; 16.2 and 86.4 mg/ 100 g of its raw mass. As can be seen, the content of proanthocyanides in the fruit crust of these two varieties increased significantly in the time interval between September 01 and October 15. At the same time, there are more proanthocyanidins in the juice and seeds of fruits of the early September period than in the juice and seeds of the October and especially July periods. But there are so few of them in the juice and seeds that this has almost no effect on the overall proanthocyanidin potential of the fruits.

Recently, there has been an increased interest in biologically active additives containing the so-called "hormones of youth" - complexes

of oligomeric proanthocyanidins due to their ability to "quench" radical reactions in the body. Condensed proanthocyanidins (which are based on two monomeric units - catechin and (-) epicatechin, as well as their gallyl derivatives) are found in many plants, but their content is overwhelmingly low [36]. From the data of the above tables, it follows that in the fruit crust of the studied varieties and wild pomegranate of the October 15 period, the mass fraction of proanthocyanidins varies from 58.8 mg/100 g to 105.0 mg/100 g of its raw mass, and the average value of this indicator is 82 g/100 g of raw crust. Simple calculations show that as a result of the conversion of the crust into an air-dry state, its anthoprocyanidin - raw potential can be raised to ≈ 250 mg/ 100 g or 0.25%. This is a good indicator, given that there are not many proanthocyanidin-bearing plants, and their yield from *Vitis vinifera* grape seeds and *Pinus maritime* coniferous bark used in the industrial production of proanthocyanidins does not exceed 0.1-0.5% of the mass of the feedstock.

From the data in Tables 1-4, it is also clear that in July-October, the concentration of anthocyanins increased not only in the juices, but also in the solid parts of the fetus. For example, in the crust and partitions of pomegranates, the concentration of anthocyanins on September 01 was equal to 13.93 mg and 6.53 mg/100 g of their raw mass, respectively, and by October 10 it was up to 20.30 and 8.96 mg/100 g of their raw mass. The mass fraction of anthocyanins in the juices of the studied cultivars and wild pomegranate was maximum on October 15 (12.6 - 29.2 mg/100 g of raw juice mass). The concentration of anthocyanins in the juice of ripe fruits of intensely colored local varieties can be 39.0 mg/ 100 g or higher [37]. Comparison of these values with the values of anthocyanin concentrations in pomegranate juices indicated by other authors showed that the content of anthocyanins in the juices of ripe fruits of intensely colored pomegranate varieties can reach 59.3 mg/100 cm³ [38].

The concentration of anthocyanins in the seeds of fruits of the July 20 period is almost the same (2.4 - 2.67 mg/100 g of their raw mass) as in their juices of the July 20 periods (1.45 -3.47 mg/100 g of raw juice mass) and September 01 (1.67 - 4.87 mg/100 g of raw juice mass). In the first two studied periods, there are still few anthocyanins in juices (maximum 4.87 mg/100 g). The crust of the fruits of the July 20 period contains much more anthocyanins (10.03 - 15.4 mg/ 100 g of its raw mass), by the beginning of September it increased to 10.93 - 17.87.8 mg/100 g of its raw mass, and by October 15 - up to 12.0 - 24.5 mg / 100 g of its raw mass. By October 15, there are already more anthocyanins in the juice (12.6 - 29.2 mg / 100 g of its raw mass) than in the crust (12.0 - 24.5 mg/ 100 g of its raw mass). In this and other cases, when talking about the composition of seeds, it should be borne in mind that the seeds for analysis were taken in the form in which they remain after squeezing juice from juicy pomegranate seeds. Initially, they are surrounded by succulent sarcotesta rich in anthocyanins, covered from the surface with a strong and thin film shell (all

together - aryls). When the grains are pressed, the integrity of the aril is violated, the juice flows out of them, after which the seeds remain covered with a film-like shell rich in anthocyanins, which had previously covered the juicy pomegranate seeds and did not go anywhere. In this process, the seeds also come into contact with the juice itself, from which they are enriched with anthocyanins even more. Therefore, this sample for analysis actually included a part of the juice and a thin film shell rich in anthocyanins pressed to the surface of the seeds themselves.

Leucoanthocyanins are concentrated mainly in the crust, and the maximum of their content in it was at the beginning of September. In the crust and partitions of the fruits of the studied varieties and wild pomegranate from the beginning of September, the quantitative content of leucoanthocyanins varied as follows: the crust - from 9.06 - 20.8 mg /100 g of raw mass, the partitions - from 1.24 to 3.0 mg / 100 g of raw mass. The maximum amounts of flavonols were found in certain parts of the fruits of the July 20 period, and the crust (363.0 – 528.0 mg/100 g of its raw mass) and the partitions (287.0 - 578.0 mg/100 g of their raw mass) of fruits of this early period were practically not inferior to each other in this respect. By September 01, the content of flavonols decreased in the fruit crust of the studied cultivars and wild pomegranate to 170 - 245 mg/ 100 g of its raw mass, in the partitions - to 245 – 407.5 mg/ 100 g of their raw mass. By October 15, the quantitative content of flavonols decreased to 120 - 170 mg/100 g (crust) and 162 - 218 mg/100 g (septum). That is, during the period from September 01 to October 15, the concentration of flavonols in these parts of the fetus decreased by 1.4 - 2 times (crust) and 1.5-1.8 times (partions). In very sweet Spring pomegranates, the mass fraction of catechins in the crust and partions in July was 19.7 mg/100 g and 17.7 mg/100 g of their raw mass, respectively. By September 01, it increased - in the crust to 39.9 mg/100 g of its raw mass, in the partitions - to 24.8 mg/100 g of their raw mass, and by October 15 it fell again to 23.37 mg/100 g in the crust and 7.73 mg/100 g in the partitions.

In other studied cultivars and wild pomegranate, there was a constant decrease in the concentration of catechins in all parts of the fruit as the process of its maturation deepened. Slightly sweet pomegranates have Iridanaly partitions of July and September fruits with a catechin content of 20.3 mg/100 g and 21.6 mg/100 g of their raw mass, respectively, and the peel of fruits of the same periods contains more catechins - 116.5 mg/100 g and 56.5 mg/100 g of its raw mass, respectively. By October 15, the mass fraction of catechins in this cultivar had fallen to 18.1 mg/100 g in the crust and 6.88 mg/100 g in the partitions. In this and two other studied cultivars, the concentration of catechins on October 15 was lower than their concentration on September 01, in the crust by 1.5-3.1

times, in the partitions - by 2.9 -3.1 times; in wild pomegranate - by 4.5 (crust) and 1.5 times (partitions). It can also be seen from the data in Tables 1-4 that, quantitatively, the main flavonoids of pomegranates are flavonols, and their concentration in the crust and partions (as well as catechins and leucoanthocyanins) until September 01, it is at a fairly high level, after which it begins to fall sharply.

As the process of fruit growth and development deepens on the tree, the concentration of hydroxycinnamic acids (chlorogenic acid + caffeic acid) in all their parts of the pomegranate, including in the crusts and partitions, decreases all the time. However, as of September 01, it is still quite high (34.8 - 61.3 mg/100 g of the raw mass of the crust and 33.8 - 53.8 mg/100 g of the raw mass of the partitions). By October 10, the mass fractions of hydroxycinnamic acids fell in the crust to 21.5 – 37.3 mg/100 g, in the partitions - to 21.8 - 31.3 mg/100 g. Also in this process, there was a significant decrease in the concentration of total polyphenols in all fruit parts during the period limited from July 20 and October 15. The concentration of total polyphenols in the crust and partitions of fruits of the September 01 period was much higher than in the crust and partitions of fruits of the October 15 period: during this time, the concentration of total polyphenols decreased in the Spring cultivar from 12.28 to 4.36 g/100 g (crust) and from 11.69 to 3.95 g/100 g (partitions); Iridanaly 9.15 - 3.12 g/100 g (crust) and 8.65 - 2.49 g/100 g (partitions); Guleisha pink 12.89 - 3.33 g/100 g (crust) and 11.64 - 2.49 g/100 g (partitions); wild pomegranate 14.17- 4.99 g/ 100 g (crust) and 10.22 - 3.53 g/100 g (partitions).

Economic feasibility requires such a comparative assessment of the quantitative changes in the content of polyphenols in connection with the increase in the weight of individual fruit parts and the total weight of the fetus. From the data of the above tables, it can be seen that the concentration of polyphenols in the crust and partitions of fruits of the tested varieties and wild pomegranate by the final date (October 15) is on average 3.1 (crust) and 3.5 (partitions) times lower than on September 01. From the same tables it can be seen that in the time interval between September 01 and October 15, the studied cultivars and wild pomegranate fruit weight increased as follows: Spring - from 140 g to 280 g, Iridanaly - from 154 to 250 g, Guleisha pink - from 95 g to 288 g and wild pomegranate - from 43 g to 130 g; on average - 2.4 times. Taking into account the lag in the rate of weight gain by fruits from the rate of reduction in the quantitative content of total polyphenols in them, the productivity of each hectare of a pomegranate orchard by polyphenols will clearly not be in favor of the fruits of the October harvest. This conclusion is also confirmed by the data in Figure 2, which shows the total number of polyphenols (in g), which falls on one whole fruit of the periods July 20, September 01 and October 15 (Fig. 3).

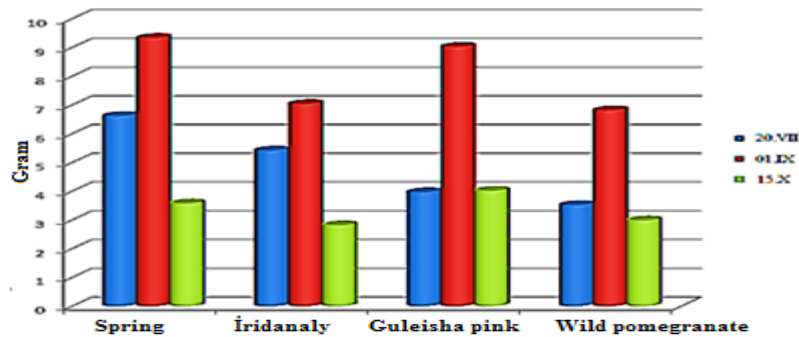


Figure 3: The Number of Total Polyphenols (in g), Which Falls on one Fruit of the Studied Cultivars and wild Pomegranate of the Periods of July 20, September 01 and October 15, Taking into Account the Lag in the Rate of Increase in its Weight From the Rate of Decrease in the Quantitative Content of Total Polyphenols in it

From this figure it can be seen that for each individual fruit of the September 01 period, the Spring cultivar has 9.3 g of total polyphenols; for the same variety, 3.6 g of total polyphenols account for each individual fruit of the October 15 period. That is, in this cultivar, one single fruit of the September 01 period accumulated 2.5 times more total polyphenols than each individual fruit of the October 10 period accumulates in itself. From the same comparison of the data of this figure for two other studied cultivars and wild pomegranate, it becomes clear that the September fruit, despite its smaller size, is on average able to accumulate 2.6 times more polyphenols in itself than the October one. Thus, one immature, semi-ripe and mature fruit of the studied cultivars and wild pomegranate accounts for a completely different amount of polyphenols. This is due to the fact that during the studied period, the total weight of the fruit increased not so much due to the peel, in which the main part of the total polyphenols is concentrated, as due to the juice. The vitality of this trend is also confirmed by a published study by Egyptian authors concerning quantitative changes in total polyphenols in pomegranates of the local Taifi cultivar; the maximum amount of total polyphenols was in the green fruit - 3.65%, while in the ripe it decreased to 1.90% [14]. Our data are also consistent with the data of Turkish authors, who showed that the concentration of total polyphenols in Hicaznar pomegranates in the time interval between August 15 and October 30 decreased from 8308 mcg/g to 5696 mcg/g; this occurred simultaneously with a decrease in the concentration of gallic acid from 97.2 mcg/g to 29.5 mcg/g, chlorogenic acid – from 83.9 mcg/g to 66.3 mcg/g, ellagic acid – from 13.6 mcg/g to 4.5 mcg/g [19]. As can be seen, the quantitative content of total polyphenols in 100 g of raw decreased during this time from 0.83 to 0.57 g / 100 g (considering that 1 mcg = 0.000001 g).

The decrease in concentration as the maturation process deepens concerns not only total polyphenols, but also some individual flavonoids (flavonols, leucoanthocyanins, catechins) and oxycoric acids. From the data in Tables 1-4, it can be seen that in the Guleisha pink cultivar, in the total amount of flavonoids per 100 g of raw fruit of the September 01 period (flavonols 126.4 mg +

leucoanthocyanins 4.62 mg + catechins 23.0 mg + anthocyanins 7.06 mg = 161.8 mg), the proportion of flavonols is 78.4%; whereas the proportion of flavonols in the total amount of flavonoids per 100 g of raw fruit of the period of October 15 (flavonols 66.7 mg + leucoanthocyanins 2.05 mg + catechins 10.6 mg + 25.05 mg = 104.4 mg), significantly lower - 63.9 %. Using the data from the same tables, it can be calculated that over the same period of time in the fruits of the studied cultivars and wild pomegranate, the quantitative content of flavonoids decreased on average as follows: 01.September: flavonols 106.85 mg + leucoanthocyanins 4.86 mg + catechins 27.18 mg + anthocyanins 9.18 mg = 148.1 mg/100 g of raw fruit; October 15: flavonols 56.32 mg + leucoanthocyanins 1.70 mg + catechins 7.83 mg + anthocyanins 16.45 mg = 82.3 mg/100 g of raw fruit. This means that as we approach the consumer stage of maturity, the percentage of flavonols in the total amount of flavonoids becomes smaller.

This trend was also noted by Chinese authors, who showed that in the time interval between July 25 and September 13, the mass fraction of flavonols in the fruit as a whole, depending on the pomegranate cultivar, decreased from 91.37- 187.90 to 57.24-143.52 mg/100 g [15]. Almost the same changes in the concentration of flavonols were noted by us in the fruits of the periods July 20 and September 01 (see Table 1-4). From the results of the Egyptian-Indian group of authors using the HPLC method, it follows that flavonols and oxycoric acids play a leading role in the formation of the polyphenolic potential of pomegranate, which is consistent with the data of the tables given in this work [20]. Another published work concerns the quantitative content of catechins and chlorogenic acid in the dried peel of the fruits of two Turkish pomegranate cultivars with a residual moisture content of 6.35 and 7.71 wt.%. In this study, analyses were carried out using the HPLC method after preliminary separation of the initial extract on Watman paper. Depending on the pomegranate cultivar, the content of catechins in their peel after drying varied from 27.7 mg/100 g to and 50.0 mg/100 g, chlorogenic acid – from 327.0 mg/100 g to 493.0 mg/100 g [21]. This is slightly higher than the values of the concentrations of catechins and hydroxycinnamic

acids in the crust and partitions of fruits, which, as an example, we noted above for the Spring cultivar. However, this is not surprising, given the different sensitivity of calorimetric analysis and the HPLC method. Table 5 presents data on the quantitative

content of total polyphenols per dry matter of crusts and partitions of pomegranates of varying degrees of maturity, which may be of interest to manufacturers of pomegranate polyphenols working with dried raw materials.

Pomegranate variety	Date of analysis	Crust	Partions	Peel (crust together with partitions)
Spring	20.VII	37.46	35.16	36.77
	01.IX	35.08	36.53	35.53
	15.X	13.08	14.53	13.56
İridanaly	20.VII	23.08	33.84	26.54
	01.IX	30.0	30.89	30.25
	15.X	11.82	9.57	11.18
Guleisha pink	20.VII	21.13	33.76	23.84
	01.IX	35.41	32.88	34.62
	15.X	11.89	9.22	11.23
Wild pomegranate	20.VII	32.72	31.26	32.46
	01.IX	35.78	30.97	32.20
	15.X	16.63	13.07	15.44

The arithmetic mean of each parameter in a row of 20 fruits of each harvest period marked in the table - is 6 repeated measurements over 2 years of research ($p \leq 0.05$).

Table 5: Percentage of Total Polyphenols in the Dry Matter of Crusts and Partitions of Pomegranates of Different Degrees of Maturity

From the data in this table, it can be seen that the percentage of polyphenols in the dry matter of the peel of the fruits of the studied cultivars and wild pomegranate on 01.IX was 30.25 - 35.53, on July 20 - 23.84 - 36.77, and by October 15 it became an order of magnitude lower (11.18-15.44). It follows from this that for the Geokchay pomegranate, the second half of July - the beginning of September is the time of the "polyphenolic boom". Thus, ripe fruits have their own morphological, technological and chemical characteristics that distinguish them from unripe fruits, in particular, it concerns the quantitative content of total polyphenols and individual flavonoids and the ratio between the most oxidized (and, therefore, the most resistant to thermal and other influences) flavonols and anthocyanins, leucoanthocyanins and catechins.

5. Conclusions

This study provides important data on changes in the quantitative content of sugar, protein, pectin, ascorbic acid, minerals and polyphenols that occur during the maturation of sweet, slightly sweet, sweet-sour and sour pomegranates, emphasizing that there are certain differences between them in terms of the "structuring" of the final set of morphological, technological and chemical signs. Since it covered only one representative from each of the above-mentioned groups, it is necessary to investigate the physical and chemical relationships between other varieties of the same and different tastes.

Contribution

S. G. Hafizov and G. K. Hafizov performed the research.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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