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Research Article/Araştırma Makalesi

Some properties of fruit juice produced by black raisins by traditional methods in Erbil region and changes during storage

Erbil bölgesinde geleneksel yöntemlerle siyah kuru üzümden üretilen meyve sularının bazı özellikleri ve depolama süresince meydana gelen değişimler

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ABSTRACT

Grape (*Vitis vinifera*) is one of the most grown fruits in Iraq and is evaluated in different ways. This study aimed to determine some properties of the fruit juice that is traditionally produced from dried black grapes in the Erbil region and consumed directly, to make it durable by various methods, as well as to examine the changes that may occur during storage. For this purpose, some of the grape juices were pasteurized and the other part was stored using Na-benzoate in 500 ml glass bottles, at room temperature, under dark and light conditions for 6 months. In the stored products, pH, acidity, total dry matter, soluble dry matter, ash, color, total antioxidant (DPPH), Hydroxymethylfurfural (HMF) and browning reaction and total phenolic substance (folin-ciocalteu) analyzes as well as sensory evaluations were made periodically. As a result of the statistical evaluations, There is no difference between the applications in terms of color, but there is a slight decrease in the L value after the 4th month, depending on the storage period, while the pasteurized samples show higher values in terms of HMF and browning levels, the browning levels increase significantly in all samples after the 2nd month, and TFM values were decreased. It has been determined that all products are highly appreciated in terms of sensory properties, pasteurized samples are more appreciated, and the storage time does not have a significant effect on the sensory properties of the samples. In addition, it has been determined that beverages can be easily stored for a long time at room temperature with or without the addition of preservatives, only by pasteurization, and such a product will be in demand.

Key Words: Grape, Storage, Phenolic compounds, Antioxidant, Juice

ÖZ

Üzüm (*Vitis vinifera*) Irak'ta en çok yetiştirilen meyvelerden biri olup farklı şekillerde değerlendirilmektedir. Bu çalışmada geleneksel olarak Erbil yöresinde kuru siyah üzümlerden üretilerek doğrudan tüketilen meyve suyunun bazı özelliklerinin belirlenmesi ve çeşitli yöntemlerle dayanıklı hale getirilmesi yanında depolanması sırasında ortaya çıkabilecek değişikliklerin incelenmesi amaçlanmıştır. Bu amaçla üzüm sularının bir kısmı pastörize edilerek, diğer kısmı da Na-benzoat kullanılarak 500 ml'lik şişelerde, oda sıcaklığında, karanlık ve aydınlık koşullarda 6 ay depolanmıştır. Depolanan ürünlerde periyodik olarak pH, asitlik, toplam kuru madde, çözünür kuru madde, kül, renk, toplam antioksidan (DPPH), HMF, esmerleşme ve toplam fenolik madde (folin-ciocalteu) analizleri yanında duyusal değerlendirmeler yapılmıştır. Yapılan istatistiksel değerlendirmeler sonucunda; renk bakımından uygulamalar arasında bir fark olmadığı, ancak depolama süresine bağlı olarak özellikle L değerinde 4. aydan sonra az da olsa bir azalma olduğu, Hydroxymethylfurfural (HMF) ve esmerleşme düzeyleri bakımından pastörize örnekler daha yüksek değerler verirken, 2. Aydan sonra esmerleşme düzeylerinin

tüm örneklerde belirgin şekilde arttığı ve TFM (toplam fenolik madde) değerlerinde bir azalma olduğu görülmüştür. Duyusal özellikler açısından tüm ürünlerin çok beğenildiği, pastörize edilin örneklerin daha fazla beğeni aldığı, depolama süresinin örneklerin duyusal özellikleri üzerine önemli bir etkiye sahip olmadığı tespit edilmiştir. Ayrıca içeceklerin koruyucu ilavesiyle veya koruyucu ilave edilmeden sadece pastörizasyon işlemi ile oda sıcaklığında uzun süre depolanabileceği ve böyle bir ürünün talep göreceği belirlenmiştir.

Anahtar Kelimeler: Üzüm, Depolama, Fenolik bileşikler, Antioksidan, Meyve suyu

Introduction

Grapes botanically known as *Vitis vinifera*, and they are the oldest cultivated fruit in the Near East and Europe (USAID, 2005).

Grape is one of the most grown products and according to the data of 2020, 4 208 908 tons of 78 034 332 tons of grapes produced in the world are produced in Turkey. World raisin production is 1 327 450 tons, of which 261 000 tons are provided by Turkey (Sümbül ve Yıldız, 2022; TÜİK 2021; FAO, 2020).

The region occupied by grapes in Iraq is 48 000 hectares with a yield of 184 000 tons (FAO, 2022). Rashmiree, Bae-dank-seedless, Rashmiree Wazha, Thomsonseedless, Tre-Rash, Rash-Miow, Taefee, RashMiow, Kamali, Kazhaw, Sarquola, Soor Ssinaee, Zarek, Soraw, Halwani, Awilka, Hejazi-Spee varieties are mostly grown in the region (USAID, 2005). The grape is mainly grown in Duhok, Erbil and Sulaymaniyah in Iraq. Grape processing provides jobs and income to hundreds of thousands of families in Erbil, Duhok and Sulaymaniyah.

In addition to being consumed as fresh fruit, grapes can also be used to produce many products such as wine, raisins, pomace, seed oil, grape must. Likewise, sweet grape varieties are used to produce raisin juice. Drying is one of the oldest methods used to preserve fruits by reducing moisture contents. In the same way, it increases the shelf life of product by reaction rate slows down to. (Karabina, 2016; Karimi, 2015; Barona et al., 2012; Mary and Michael, 2003).

The shelf life of fresh fruit juice can be limited to a few days during storage in a refrigerator due to natural and artificial contamination (Soliva-Fortuny and Martin Belloso, 2003).

Basically, depending on a variety of grapes and environmental conditions, the chemical properties of grape juice are altered, as is the processing of juice. In general, the phytochemical composition of grape juice is 28.85% total soluble solids, 0.69% protein, 1.10% carbohydrate, and 0.82% fat. (Abdrabba and Hussein, 2015; Sani, 2013; Huang and Ough, 1989).

Raisin juice contains approximately 70% inverted sugar and about 2% protein. It is also rich in trace elements, especially Ca, Mg, P, Na, and K, as well as vitamins such as A, B3, and C (Papadakis et al., 2006). Phenolic acids, flavones and stilbenes are other compounds isolated from whole grapes, juices, or pomaces by enzyme hydrolysis. Twelve phenolic compounds were identified and quantified in grape juice. The content ranges from 0.07 - 910 mg kg^{-1} dry weight. The major phenolic compounds are gallic acid and catechin in grapes and pomace, while cyanidin and petunidin 3-O-glucoside are mainly anthocyanin glucosides in juice (Ramirez-Lopez, et al., 2014).

Phenolic compounds are raisin chemical compound that is involved in sensory properties such as color, taste, astringency, and bitterness (Fischer and Noble, 1994; Anlı, 2006). As anti-cancer and antiviral agents, these compounds play an important role (Hogan et al., 2010; Kammerer et al., 2004) and inhibit in vitro human low-density lipoprotein (LDL) oxidation (Teissedre and Chervin, 2011).

In general, many factors affect the consistency of fruit juice in grape or raisin juice, such as the environmental condition of the production of grapes, the variety of grapes, the drying methods for the production of raisins, and the extraction and processing methods (Bates et al., 2001). Some compounds, including some quercetin and caffeoyl tartaric acid and kaempferol derivatives, are present at a higher level in raisins compared to grapes on a wet weight basis (Morris, 1989;

Timmermans et al., 2011; Falguera, et al., 2011; Schilling, et al., 2008; Cemeroğlu, 2009, Karadeniz et al., 2000).

For raisin juice extraction, hot and cold extraction, two models are used; both methods have many advantages and disadvantages. In red fruits such as grapes, cherries, and berries, the hot break process is widely used to optimize juice yield and extraction of color flavor. Crushed fruit or mash is heated using a tubular heat exchanger to 40 °C to 60 °C. This step is referred to as the hot break method and is intended to remove a significant amount of color from the skin into juices. The extraction of both phenols and anthocyanins is also enhanced by heating (McLellan and Acree, 1993).

A large amount of grapes are grown and dried in Iraq's Erbil and Sulaymaniyah regions. The traditional black raisin juice is produced from dried black grapes. Black raisin juice cannot be stored for a long time. No scientific study has yet been found about this traditional product, which is produced and consumed in high quantities in the region. This study, it was aimed to make raisin juice durable, determine its quality characteristics, and raise awareness among the public about raisin juice.

Material and Method

Material

In this study, black grape juice obtained from black raisins produced with local techniques in Northern Iraq Erbil region was used.

Method

Raisin juices were obtained from a local company that makes traditional production. Raisin juices are produced by mixing the black raisins in an aqueous medium at 40 °C, as stated by McLellan and Acree (1993), and separating the obtained extract from coarse particles by filtration. The black grapes used are Vitis vinifera / Tre-rash varieties.

The raisin juice divided to two parts. First part of the raisin juice was pasteurized at 100±1 ºC and was bottled and storage by two ways in dark and light and other part were added Sodium Benzoate and storage in dark and light for 6 months in room temperature.

pH, titratable acidity (%), water soluble dry matter, total dry matter (%), ash, water activity (a_w), HMF (Hidroksimetil Furfural), color (L*, a*, b* values) (AOAC, 2005; Cemeroğlu, 2007), browning index (Wrolstad 1976), total phenolic substance (Medina-Remon et al., 2009) and total antioxidant (DPPH) (Sharma et al., 2011) analyzes were made in the produced black raisen Juice during the storage period. In addition, sensory evaluations were made by panellists in terms of features such as appearance, color, odor, taste-aroma, sweetness, acidity, mouth fullness and aftertaste to measure consumer taste (Altuğ and Elmacı, 2011). Trials were made in three replications and two parallels, and the SPSS package program was used in the evaluation ($P \leq 0.05$). The differences between the means in the groups were determined by Duncan test. Sensory evaluation data were made using ANOVA repeated measurement (Curran et al., 1996).

Results and Discussion

Some characteristics of locally produced raisin juices were determined and given in Table 1. As can be seen from Table 1, pH 3.66 titration acidity was determined as 0.75 (%) in raisin juices used in the study. The fact that the pH is below 4.5 makes it possible to make the samples stable by pasteurization, as in other fruit juices (Cemeroğlu, 2009).

The amount of soluble dry matter in the samples was determined as 32.10 (Brix), the total dry matter was 33.21 (%), and the ash ratio was 0.43 (%). The high dry matter and ash rates in the samples are due to the use of dried grapes in production and the low water content and high sweetness depending on consumption habits.

The water activity in the samples was determined as 0.95. In the samples used, the antioxidant values were determined as 25.263 mM Trolox, while the total amount of phenolic substances was found to be 351.26 GAE.

Table 1. Some properties of locally produced raisin juices

Properties	Value
pH	3.66
Acidity %	0.75
Water Sol. Solid (Brix)	28.95
Tot. Dry Mater. %	33.21
Ash %	0.43
a_w	0.95
DPPH (mM Trolox)	25.263
Tot. Phenolic. GAE (mg 100mL^{-1})	351.26
L*	24.15
a*	4.18
b*	1.41

Considering the CIE color values of the samples used, the L* value was found to be 24.15, the a* value 4.18, and the b* value 1.41. Here, the a* value indicates the redness of the samples, while the low L* value is due to the dark color and pulpy structure of the samples. Shao et al. (2016) reported that dark raisins contain more polyphinolics and antioxidant in their study, while Vidinamo et al. (2020) stated that antioxidant activity increased after drying.

Table 2. Some color properties of locally produced raisin juices

Source	L*	a*	b*
Str.Period (month)			
1	24.39^{abc}	4.10^{a}	1.37^{b}
2	24.18^{bc}	3.96^{a}	1.57^{b}
3	24.78^{a}	3.54^{c}	1.35^{b}
4	24.47^{ab}	3.66bc	1.50^{b}
5	23.9^{c}	3.95^{a}	1.53^{b}
6	21.41^{d}	3.74^{b}	2.42^{a}
Application			
Pasteurization	23.44^{b}	3.74^{b}	1.75^{a}
Chemical	24.27^{a}	3.91^{a}	1.50^{b}
Ambiance			
Light	23.76^{a}	3.82^{a}	1.65^{a}
Dark	23.94^{a}	3.83^{a}	1.59^{a}

The means with the same letter are not significantly different ($p < 0.05$).

As seen in Table 2, it was determined that there was a decrease in the L* value and a* value, and an increase in the b* value at the end of the 6-month storage period. It is thought that this is due to the destruction of anthocyanins in raisin juice, which is rich in anthocyanins, depending on the storage period. It was seen that the color change that occurred depending on the storage time was statistically significant ($P<0.05$). Similarly, the effect of pasteurization and sodium benzoate application on color was found significantly different ($P<0.05$). Average L*, a*, b* values were 23.44, 3.74, 1.75 in pasteurized samples, and 24.27, 3.91, 1.50 in sodium benzoate applied samples, respectively. According to the values obtained, we can say that the effect of pasteurization on the color is more than the sodium benzoate application. It was determined that the effect of the storage environment (light-dark) on L*, a* and b* values in raisin juices was not statistically significant.

One of the most important quality characteristics that reveal the stability of bioactive components in fruit juice is pH. Organic acids are responsible for the low pH value in fruit juices (Tasnim et al., 2010). As can be seen from Table 3, pH values at the beginning of storage were determined as 3.76 in pasteurized samples and 3.75 in samples treated with Na-benzoate. Although there is a difference between the pH values depending on the applications, it was determined that pasteurization and Na-benzoate application did not have a statistically significant effect on the pH values. The same situation remained valid in terms of storage in dark and light environments.

Although there was an increase in the pH values of the samples during the 6-month storage period in terms of the applied preservation method and storage conditions, it was determined that this increase was not statistically significant.

In terms of total acidity values, it is seen that there is a decrease in acidity values depending on the storage time. As can be seen from Table 3, while the total acidity was 0.76 g 100ml^{-1} at the beginning of storage, it was determined as 0.73 g 100ml^{-1} at the end of 6 months of storage. Similarly, Mgaya-Kilima et al. (2014) stated in their study on roselle fruit juice that there was an increase in pH value due to the decrease in acidity during storage. Similar results were obtained in

studies on different fruit juices and juice mixtures (Ibrahim, 2016; Kumar et al., 2012).

The change in pH and acidity values in fruit juices and similar products depending on the storage period may be caused by the formation of potassium bitartrate due to the reactions occurring between the acids and mineral substances in the products (Wisal et al., 2013; Boulton 1980).

Table 3. Some properties of raisin juices samples

St. Time (mon)	pH		Acidity (g 100ml^{-1})		TSS (Brix)		TDM (%)		Ash		a_w	
	Past	Na-B	Past	Na-B	Past	Na-B	Past	Na-B	Past	Na-B	Past	Na-B
1	3.76^a	3.74^a	0.76^a	0.76^a	29.00^a	28.95^a	30.20^a	30.20^a	0.47^a	0.47^a	0.96^a	0.96^a
2	3.77^a	3.75^a	0.76^a	0.76^a	29.00^a	28.95^a	30.20^a	30.20^a	0.47^a	0.47^a	0.96^a	0.96^a
3	3.77^a	3.76^a	0.74^a	0.75^a	29.00^a	28.95^a	30.20^a	30.20^a	0.47^a	0.47^a	0.96^a	0.96^a
4	3.78^a	3.77^a	0.75^a	0.75^a	28.95^a	28.90^a	30.20^a	30.20^a	0.47^a	0.47^a	0.96^a	0.96^a
5	3.78^a	3.78^a	0.73^a	0.74^a	28.95^a	28.90^a	30.20^a	30.20^a	0.47^a	0.47^a	0.96^a	0.96^a
6	3.78^a	3.78^a	0.73^a	0.73^a	28.95^a	28.90^a	30.20^a	30.20^a	0.47^a	0.47^a	0.96^a	0.96^a

The means with the same letter are not significantly different ($p < 0.05$).

The amount of soluble dry matter (TSS) in the raisin juice samples was determined as 29.00 Brix in pasteurized samples at the beginning of the storage, while 28.95 Brix was found in the samples to which sodium benzoate was added (Table 3). The difference is thought to be due to the moisture loss during pasteurization, and this difference was found to be statistically insignificant.

It was observed that there was a 0.05 decrease in brix values in all samples after the third month of storage. It is thought that the decrease in soluble dry matter ratio is due to the conversion of soluble components into insoluble form due to chemical reactions in raisin juice, depending on the storage period, and it was not found to be statistically significant. This is in line with the studies of Wisal et al. (2013) in strawberry juices, Bull et al. (2004) in orange juices, and Arin and Akdemir (2004) in raisin juices. The researchers stated that there was a decrease in the amount of soluble dry matter in fruit juices during storage.

It was determined that this decrease started after 2 months in the light environment, and it was seen in the 4th month in the samples kept in the dark environment, and it was determined that the storage conditions did not have a significant effect on the amount of soluble dry matter.

It was determined that the water activity values were not affected by the applied production methods, storage conditions, and storage time. Water activity ($\mathbf{a_w}$) values were found to be 0.96 in all the raisin juice samples.

It was determined that the total dry matter (TDD) and ash ratios in the raisin juice samples were not affected by the applied production methods, storage conditions, and storage time. In all the raisin juice samples, the total dry matter ratios were 30.20 % and the ash ratios were 0.47 %, and they did not change during the 6-month storage period.

HMF is a cyclic aldehyde formed by the breakdown of sugars during heat treatment and/or long-term storage of foods (Shapla et al., 2018). While HMF is not found in fresh fruits and vegetables, HMF is formed in processed and stored products depending on processing and storage conditions. HMF is one of the most commonly used indexes in non-enzymatic browning studies on fruit juices and fruit products. The level of HMF is important because it reflects the degree of heating of processed products, and quantification of this molecule is considered a quality parameter for concentrated food products (Kus et al., 2005).

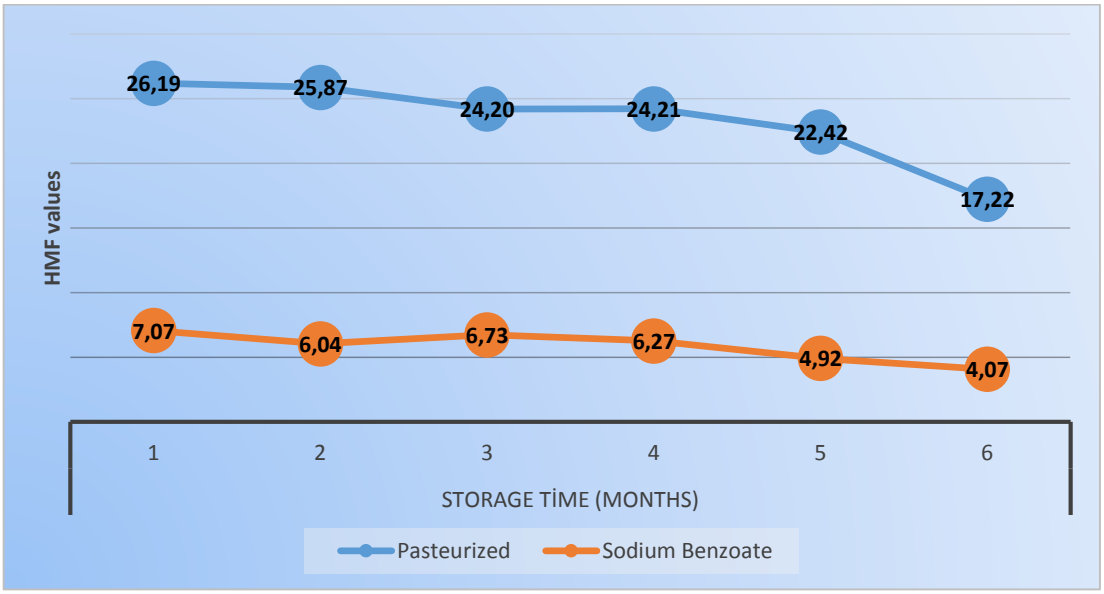

Figure. 1. Changes in HMF values during storage of raisin juice (mg L^{-1})

At the beginning of storage, the amounts of HMF in the samples were determined as 26.19 mg L-1 in pasteurized samples and 7.07 mg L-1 in samples with sodium benzoate added (Figure 1). The difference is thought to be due to the heat treatment applied during pasteurization. Due to HMF increase, color change, and similar negativities, preservatives can be used instead of heat treatment in the beverage industry. It was determined that there was a decrease in HMF values depending on the storage period.

The change in HMF values was found to be statistically significant from the 3rd month in pasteurized samples and from the 5th month in Na-benzoate applied samples ($P<0.05$). At the end of the six-month storage period, HMF values were determined as 17.22 mg L^{-1} in pasteurized samples and 4.07 mg L^{-1} in Na-benzoate applied samples. The effect of storage conditions on HMF values was found to be statistically insignificant. In a study conducted by Hepsağ and Hayoğlu (2017), it was stated that the amount of HMF in jams offered for sale in the Mediterranean region varies between 33 mg kg^{-1} and 100 mg kg^{-1}. It is thought that the decrease in HMF values is due to the decomposition of HMF due to chemical reactions in grape juice during storage and its transformation into brown colored compounds by participating in the Maillard reaction, as Cemeroğlu (2009) stated. This is in agreement with the increase in the browning index.

Browning index values (Abs_{420}) were determined as 0.14 in pasteurized samples at the beginning of storage, while it was 0.13 in sodium benzoate-added samples (Figure 2). It was determined that there was an increase in the browning index values during storage, and this increase was found to be statistically significant ($P<0.05$). Browning index values were determined as 1.96 in pasteurized samples and 1.71 in Na-benzoate applied samples at the end of the six-month storage period. The effect of storage conditions on Browning index values was found to be statistically insignificant.

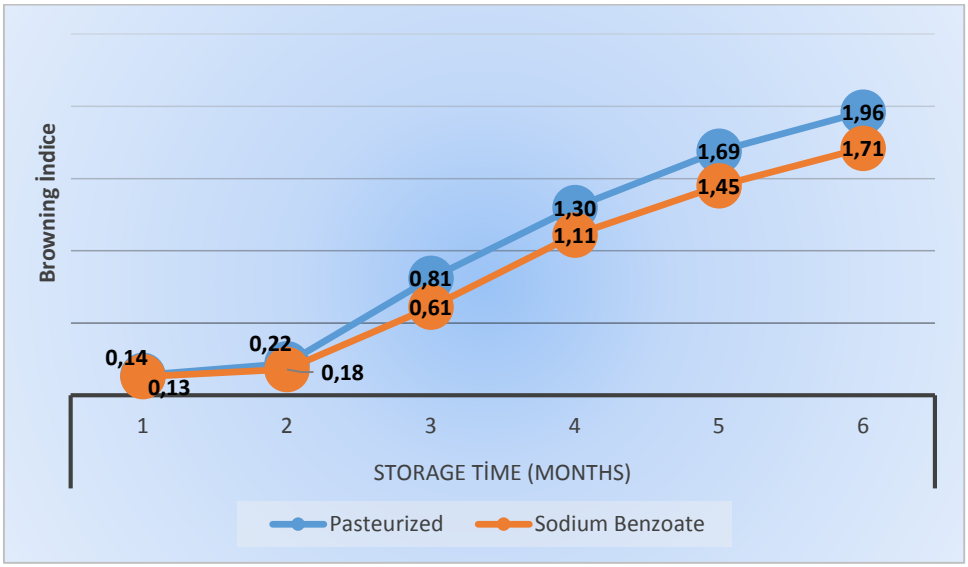

Figure 2. Changes in browning indices during storage of raisin juice (Abs_{420})

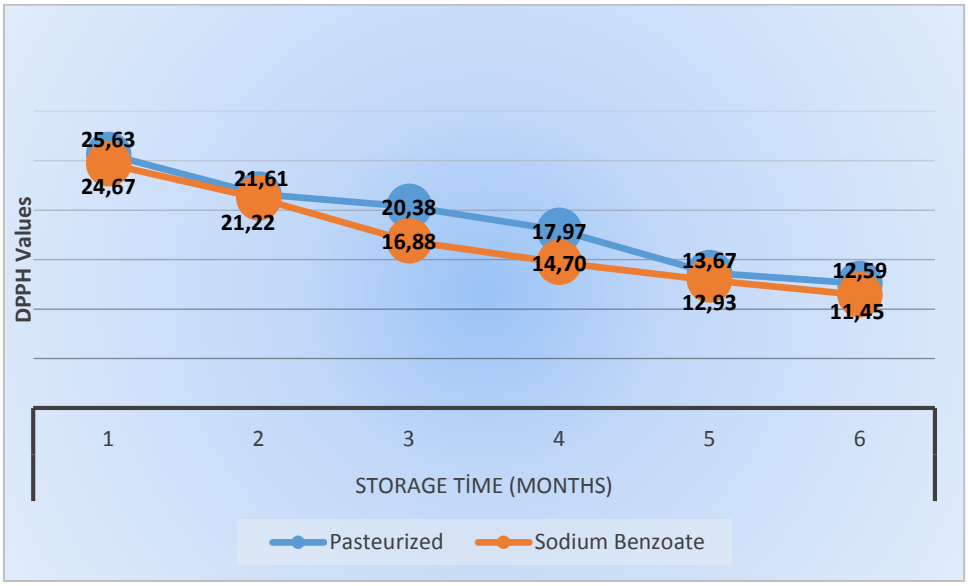

Figure 3. Changes in DPPH values during storage of raisin juice (Mm Trolox)

DPPH values of raisin juice samples were determined as 25,632 (Mm Trolox) in pasteurized samples and 24.670 (Mm Trolox) in samples treated with Na-benzoate at the beginning of storage (Figure 3). The antioxidant values of the samples showed a regular decrease depending on the storage period, and at the end of the 6-month storage period, the DPPH values were found to be 12.585 and 11.44 (Mm Trolox) in pasteurized and Na-benzoate applied samples, respectively. It was determined that there was a decrease in DPPH values during storage, and this decrease was found to be statistically significant ($P<0.05$). In a study on isotonic beverages by Toğrul and Hayoğlu (2020), it was stated that DPPH values decreased depending on the storage period. Although DPPH values were found to be higher in the samples stored in the dark environment than in the samples stored in the light environment, this difference was not statistically significant.

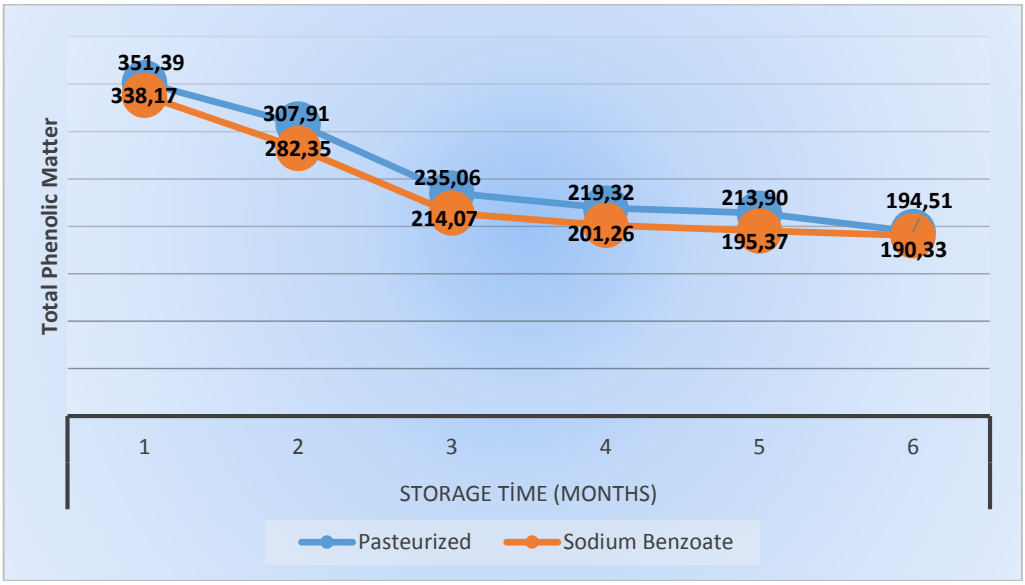

Figure 4. Changes in total phenolic matter values during storage of raisin juice (mg gallic asit/g)

Kähkönen et al. (2001) stated that grape juices are rich in phenolic substances and have great importance in terms of health.

The phenolic content of grape juices varies depending on the variety, processing conditions, and storage times (Eyduran et al., 2015; Shi et al., 2003). The total amount of phenolic substances in the dried grape juice samples was found to be 351.39 mg gallic acid/g in pasteurized samples and 338.17 mg gallic acid/g in Na-benzoate applied samples at the beginning of storage (Figure 4).

In parallel with the DPPH values, a decrease was observed in the total amount of phenolic substances during storage.

In the 6th month, the total amount of phenolic substance was found to be 194.51 mg gallic acid g^{-1} in pasteurized samples and 190.33 mg gallic acid g^{-1} in the samples to which Na-benzoate was added. It was determined that the decrease rate in the total amount of phenolic substances was fast in the first 3 months of storage, and the decrease slowed down in the following period. This decrease was found to be statistically significant ($P<0.05$). The effect of the difference between dark and light environments on the total amount of phenolic substance was not found to be statistically significant. These results are consistent with the results of Hayoğlu et al. (2009)'s study on verjuice.

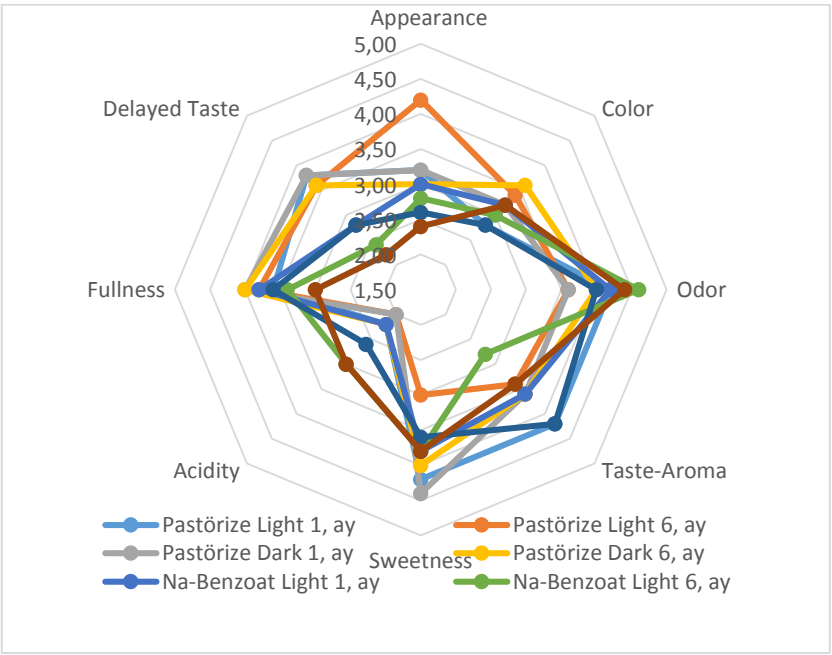

Figure 5. Average values of sensory properties of raisin juice samples

In the sensory evaluation, the samples were evaluated over 5 points in terms of appearance, color, smell, taste aroma, sweetness, acidity, saturation, and delayed taste. It was determined that all samples preserved their sensory properties for 6 months. Although the samples received low scores in terms of appearance because they are structurally sedimentary, it was determined that all samples scored above 3 points in total and were liked by the panelists (Figure 5). It was stated that pasteurized samples kept in a bright environment had a more vivid appearance in terms of their appearance properties. The most liked samples were pasteurized samples. While raisin juice samples generally scored high in terms of sweetness in accordance with their high soluble solids content, similar results were observed in terms of fullness and odor. The samples retained their odor and fullness throughout the 6-month storage period. In general, samples containing Na-benzoate scored low for aftertaste. It is thought that this situation is caused by the feeling of Na-benzoate in the mouth, although at low levels. The preference of pasteurization instead of preservative chemicals in the fruit juice industry is in parallel with this situation. The fact that the samples score high in terms of sweetness and low in terms of acidity shows that the sugar: acid ratio should be well adjusted in these products produced in accordance with local characteristics.

Conclusions and Recommendations

As a result of the research;

- Grape juice produced from raisins with local techniques can be made durable by sodium benzoate and pasteurization,
- The effect of production method and storage conditions on antioxidant level is not important, but the effect of storage time is important,
- It was determined that there was a decrease in the total amount of phenolic substances depending on the storage period, but the storage conditions did not have a significant effect.
- Products are highly appreciated in terms of their sensory properties, samples that are pasteurized and made durable are more appreciated, storage conditions and storage time do not have a significant effect on sensory properties,
- It has been determined that if the sugar: acid balance is created well, the products can be liked more.

was determined.

With the new studies to be done, it will be possible to bring the local grape juice produced from raisins to the beverage sector and provide added value to the regional economy.

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Author Contribution: Soz Dildar MAJEED and İbrahim HAYOĞLU designed, planned and conducted the experimental studies. Soz Dildar MAJEED, İbrahim HAYOĞLU and Ahmet Sabri ÜNSAL contributed to the evaluation of the experimental study results and writing the article.

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