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Comparative Analysis of Commercial and Homemade Grape Pekmez: Antioxidant Contents and HMF Levels

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ABSTRACT. Grape pekmez (molasses) is one of the most traditional food products consumed in Azerbaijan, Türkiye and the Middle East, especially in regions where viticulture is widespread. The present study compared the levels of total phenolics (TPC), flavonoid contents (TFC), antioxidant activities, and 5-hydroxymethyl furaldehyde (HMF) contents in grape pekmez samples, both commercially produced (n = 5) and homemade (n = 19). Although TPC, TFC, and antioxidant activity were similar in both types of pekmez, homemade samples had notably higher HMF content (242.24 mg L^{-1}) compared to the legal limits of 75mg L^{-1} in Turkish Food Codex and 40 mg kg^{-1} in non-heat treated honey as per Codex Alimentarius. Commercial samples had a significantly lower average HMF content (26.24 mg L^{-1}) compared to homemade pekmez because, in industrial production, water evaporation is carried out under vacuum, unlike homemade pekmez, which is prepared under uncontrolled atmospheric pressure. Additionally, approximately 74% of the homemade samples had total soluble solid contents (°Brix) below the codex minimum requirement of 68%. In commercial production, water evaporation is usually carried out at about 60°C under vacuum, whereas in homemade production, it occurs at around 100°C under atmospheric pressure. Homemade samples exhibited an HMF content nearly ten times higher than commercial samples ($p < 0.05$). Pearson's correlation test indicated a positive and significant correlation between TPC and DPPH values ($R = 0.738$, $p < 0.01$). Principal component analysis (PCA) indicated that commercial pekmez production is more effective in preserving grape antioxidative components and minimizing HMF content compared to homemade production. In summary, producing grape pekmez under vacuum conditions ensures better quality by lowering HMF levels and adhering to regulatory standards.

Keywords: Molasses; HMF; pekmez; phenolic; antioxidant; principal component analysis[1].

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Introduction

Pekmez, also known as grape molasses, is a traditional delicacy commonly made by condensing the juices of various grape types and consumed widely across regions like Türkiye, Azerbaijan, and the Middle East. Typically prepared through a simple process of boiling grape syrup without any added sugars or food additives, it features a prolonged shelf life due to this concentration method (Alpaslan and Hayta, 2002). Grape pekmez, a thick and dark-colored syrup made from grapes, is also sold in combination with ingredients like honey, condensed milk powder, tahini, or egg whites. Its production includes washing, crushing then pressing the grapes for juice which the juice concentration can be made in open containers or under vacuum, acid reduction stage and use of pekmez earth with calcium carbonate, along separation and clarifying stages (Batu, 1993; Kaya and Belibağlı, 2002). In regional markets, pekmez is available both in its pure form and as a blend with tahini particularly during winter breakfasts due to their high energy content, both being popular choices for consumers. With high levels of carbohydrates, especially fructose and glucose as all sweet fruits, pekmez has a good calorie long lasting fast energy supply; which may be suitable for individuals with an advantage to quickly take in extra calories when needed. Additionally, grape pekmez is rich in minerals and organic acids, making it valuable in human nutrition, particularly as a source of iron. Grape and its products contribute to the dietary intake of calcium, potassium, and magnesium, which are essential for the proper functioning of the blood and nervous systems (Batu et al.,

[1]Abbreviations: TPC, Total phenolic content; ABTS, Antioxidant activity determined by the ABTS method; TFC, Total flavonoid content; CE, Catechin equivalent; HMF, 5-hydroxymethyl furaldehyde; DW, Dry weight; GAE, Gallic acid equivalent; TE, Trolox® equivalent; CV, coefficient of variation; R, Pearson's correlation coefficient; TSS, Total soluble solid; PCA, Principal component analysis

2007). Pekmez can also be a natural source of antioxidants because it contains phenolic compounds, especially in the red grape varieties. The phenolic content of red-grape pekmez products has been reported higher than that of white-grape pekmez varieties (Batu, 1993; Arslan et al., 2005).

Antioxidants are molecules that contain mostly phenolics in their structure and prevent the damage of cells by blocking the formation of free radicals or removing the existing radicals. The most important factors to determine the significance of antioxidants in human health are their chemical structure, solubility and their ability to be obtained from the natural resources (Kruk et al., 2022; Matsumura et al., 2023). Phenolic compounds, products of plant secondary metabolism, are highly complex structures with more than 8000 phenolic structures. Flavonoids, a subgroup of polyphenolics, are important secondary metabolites found mostly in fruits, vegetables, and legumes, and are subdivided into six main subgroups (anthocyanins, flavanones, chalcones, flavones, flavonols, and isoflavonoids) (Panche et al., 2016; Altemimi et al., 2017). Phenolics and flavonoids, with their antioxidant and antimutagenic properties, are highly beneficial to human health. Additionally, phenolic compounds contribute to the taste and aroma of numerous plant-derived food items, imparting bitterness and astringency. Flavonoids, also responsible for food coloration, exhibit antioxidative effects and may prevent some diseases such as cancer, diarrhea, ulcers, and cardiovascular and hypertensive diseases (Rahman et al., 2021; Matsumura et al., 2023). Typically found in fruits, vegetables, and tea, flavonoids cannot be synthesized by humans and are known for their antioxidant and chelating properties. The avoiding of diseases like coronary heart disease and cancer has heightened interest in these compounds (Capanoğlu and Boyacıoğlu, 2009). Pekmez acquires its dark color through the reaction of reducing sugars during heat treatment. Hydroxymethyl furaldehyde (HMF), a quality indicator, must be monitored in pekmez products to prevent excessive heat application. Its formation results from the reaction of amino acids with reducing sugars during heat treatment and changes in the food's acidity (Yıldız et al., 2010). HMF accumulation, a significant determinant of pekmez quality, can reduce the final product's quality. The concentration step under vacuum during the production process can yield non-caramelized pekmez with desirable color, taste, and aroma properties. Vacuum application not only reduces the required temperature and process duration, typically 4-5 hours in open vessels, but also enhances the final product's quality (Batu, 1991; Karababa and Develi Isikli, 2005).

Numerous studies have explored the sensory, textural, and physicochemical properties of pekmez samples (Kaya and Belibağlı, 2002; Alpaslan and Hayta, 2002; Arslan et al., 2005; Akbulut and Özcan, 2008; Sengül et al., 2007). However, there is a gap in the literature comparing the antioxidative properties and hydroxymethyl furfural (HMF) contents of commercial and homemade grape pekmez samples. Thus, this study aims to determine and compare the total phenolic content (TPC), antioxidant activity using the DPPH method, total flavonoid content (TFC) and HMF values in both types of pekmez samples. To distinguish differences among samples and identify significant variables, this study used the PCA statistical tool and Pearson's correlation test.

Materials and methods

Materials

In this research, a total of 19 homemade grape pekmez samples were collected from various regions across Türkiye, while 5 commercial samples were purchased from national markets, primarily located in Istanbul. Typically, commercial pekmez is made from white grapes, although red grapes or a mix of both may also be utilized, and there are no regulatory requirements regarding grape type labeling on the products. Details regarding the codes, origins, and production methods of the pekmez samples used in the study are provided in Table 1. Prior to chemical analyses, all samples were stored in a refrigerator (+ 4 ± 1°C), with duplicate analyses conducted for each sample.

Table 1. Locations and production types of grape pekmez samples used in the study.

Production Type	Sample Code	Grape Type/Variety	Location (Türkiye)
Homemade	H1	Çalkarası	Denizli/Bekilli
	H2	Çalkarası	Denizli/Cal
	H3	Hacıefe	Denizli/Bekilli
	H4	Alphonse Lavallée	Denizli/Bekilli
	H5	Red	Antalya
	H6	Öküzgözü	Denizli/Bekilli
	H7	White	Uşak/Paşalar Village
	H8	Red	Burdur/Mamak

	H9	Blend	Karaman/Karapınar
	H10	Red	Isparta
	H11	Red	Karaman/Kazancı
	H12	Blend	Karaman/Ermenek
	H13	Blend	Burdur/Yassıgüme
	H14	Blend	Karaman/Ermenek
	H15	White	Karaman/Ermenek
	H16	Blend	Isparta
	H17	Blend	Isparta
	H18	Red	Isparta
	H19	Blend	Karaman/Kayaönü
Commercial*	C1	Unknown	Denizli/Bekilli
	C2	Unknown	Istanbul
	C3	Unknown	Istanbul
	C4	Unknown	Istanbul
	C5	Unknown	Istanbul

*For commercial products, locations indicate where processing plants are located.

Trolox®, Folin-Ciocalteu reagent, barbituric acid, *p*-toluidine, catechin, gallic acid, $AlCl_3.6H_2O$ and NaOH were obtained from Sigma-Aldrich (St. Louis, MO, USA). Chromatographic grade ethanol and $NaNO_2$ were obtained from Merck (Darmstadt, Germany). Sodium carbonate was purchased from Riedel-de Haen (Seelze, Germany). All chemicals used were of analytical grade unless stated.

Methods

Total soluble solid contents (°Brix)

Total soluble solid (TSS) contents of pekmez samples were determined at 24 ± 1°C by a digital refractometer (PAL-3, Atago Co., Ltd., Tokyo, Japan) and were expressed as °Brix (Cemeroğlu, 2007).

Preparation of extracts

For the extraction process, pekmez samples (5 g) were dissolved in 5 mL of distilled water, and the solution was transferred to a volumetric flask (100 mL), with the volume adjusted using distilled water and then vigorously shaken. Approximately 2 mL of this extract was transferred into Eppendorf® tubes and centrifuged at 12,225×g for a minute using a centrifuge (WiseSpin CF-10, Daihan Scientific Co. Ltd., Wonju, Gangwon, South Korea). Clear supernatants were used for subsequent chemical analyses.

Bioactive contents of grape pekmez samples

Total phenolic content

The total phenolic content (TPC) of pekmez samples was determined using the Folin-Ciocalteu (FC) method as described by Cemeroğlu (2007). Clear supernatants of each extract (1 mL) were mixed with FC reagent (5 mL), followed by the addition of 20% Na_2CO_3 (4 mL). The volume was then adjusted to 10 mL with distilled water, and the mixture was incubated in dark for two hours. After incubation, a spectrophotometer (Optizen Pop, Mecasys Co., Ltd., Daejeon, South Korea) was used to determine the absorbances at 760 nm. The TPC of the pekmez samples was expressed as mg gallic acid equivalent (GAE) per 100 g on wet or dry bases.

Antioxidant activity

DPPH assay described by Thaipong et al. (2006) was used to determine the antioxidant activities of pekmez samples. The absorbances of the colored solutions were measured using a spectrophotometer at a wavelength of 515 nm. A calibration curve of Trolox® solution, ranging from 10 to 50 μM concentrations, was used to calculate the antioxidant activity of the samples. Samples were diluted if necessary. Results were expressed as μmol Trolox® equivalents (TE) per 100 g on wet or dry bases.

Total flavonoid content

The method described by Zhishen et al. (1999) was used to determine the total flavonoid content (TFC) of samples, and catechin solutions were used to obtain the calibration curve. Briefly, clear supernatant or standard solution (1 mL) was pipetted into test tubes, then diluted with distilled water (4 mL) immediately.

Later, $NaNO_2$ (0.3 mL) was added and the mixture was vortexed. After 5 min, $AlCl_3$ (0.3 mL) was added and the mixture was vortexed, and NaOH solution (2 mL) was added after a minute. Distilled water (2.4 mL) was then added immediately and shaken. Then, the absorbances of pink-colored solutions were determined by a spectrophotometer (Optizen Pop, Mecasys Co., Ltd., Daejeon, South Korea) at 510 nm, and results were expressed as mg catechin equivalent (CE) per 100 g on wet or dry basis.

Hydroxymethyl furaldehyde analysis

The HMF content of grape pekmez samples was determined using a colorimetric assay, as described by Cemeroğlu (2007). The absorbances of the red color produced by HMF with barbituric acid and p-toluidine were obtained at 550 nm. For this purpose, each sample (20 g) was dissolved in 30 mL of distilled water at room temperature, and the mixture was transferred into a volumetric flask. The volume was then adjusted to 100 mL with distilled water. Subsequently, 2 mL of this mixture and 5 mL of *p*-toluidine solution were added to two test tubes. Barbituric acid (1 mL) was added into one of the tubes while distilled water (1 mL) was added into another as a blind. The HMF content of pekmez samples was calculated by subtracting the absorbance and applying a correction factor as described by Cemeroğlu (2007).

Statistical analysis

Data were evaluated by the SAS package program (The SAS System for Windows 9.0, Cary, North Carolina, USA) with the significance level of $\alpha = 0.05$. Student's t-test was used to compare the means of two pekmez groups to determine whether there was a statistically significant difference between them. Results were presented as mean ± standard deviation. Additionally, Pearson's correlation coefficients (R) were calculated by using PROC CORR procedure, while principal components analysis (PCA) was performed to evaluate the data patterns and define the similarities and differences within the dataset assessed on the basis of the component matrix, which captures the linear relationships between variables.

Results and discussion

Total soluble solid contents (°Brix)

The mean TSS contents of homemade and commercial pekmez samples were determined as 65.66 ± 3.08 and 71.06 ± 0.72 (°Brix), respectively (Table 2). According to the Communiqué on Grape Molasses (No: 2017/8) of the Turkish Food Codex [TFC] (2017), liquid and solid pekmez samples must have minimum TSS contents of 68 and 80%, respectively. In this study, all samples were in a liquid form, and all commercial samples were in good accordance with the legal requirement. However, nearly 74% of the homemade samples (H2-4, H7-10, H12, H13, and H15-19) had a TSS content lower than 68%, which was expected due to uncontrolled conditions in their production. During the traditional production of pekmez at home, the viscosity of liquid pekmez is usually monitored visually, and its TSS content is not controlled. Unlike homemade production, in commercial production of pekmez, °Brix values are critical and monitored by a refractometer during the vacuum evaporation step of processing. This is more likely to be the main reason of commercial samples being in good accordance of the legal requirement for the TSS content of pekmez samples. Katırcı et al. (2020) reported that commercial tomato pastes had higher TSS contents than homemade tomato pastes, and they found that high variations were noticeable in the °Brix values of homemade type tomato pastes in comparison to their commercial counterparts due to uncontrolled production conditions. In a study by Türkben et al. (2015), some physical and chemical attributes of traditionally produced grape molasses from 14 different grape varieties were determined, and the range for the water-soluble dry matter contents of samples was from 66.19 to 80.57%.

Bioactive and HMF contents of pekmez samples

The results of chemical analyses on the bioactive and HMF contents of pekmez samples are presented in Table 2. The study included 19 homemade and 5 commercial samples. The differences in mean TPC, TFC, and DPPH radical scavenging values between homemade and commercial pekmez samples were found insignificant ($p > 0.05$) (Table 2), possibly due to high variation within the two groups of pekmez samples. On a dry matter basis, the mean TPC and TFC values of homemade samples were 661.40 mg GAE $100g^{-1}$ and 441.81 mg CE $100g^{-1}$, respectively. Likewise, the mean TPC and TFC values for commercial samples were 610.72 mg GAE $100g^{-1}$ and 455.26 mg CE $100g^{-1}$ on a dry basis, respectively. The TPC values of commercial pekmez samples on a dry basis (coefficient of variation (CV): 26.5%) showed lower variability compared to homemade samples (CV: 40.9%), indicating more consistent and controlled processing steps in the commercial production of pekmez.

Table 2. Total phenolic (TPC), flavonoid (TFC) and HMF contents of homemade (H) and commercial (C) grape pekmez samples as well as their DPPH radical scavenging activities

Sample	TSS* (°Brix)	TPC (mg GAE 100g^{-1})		TFC (mg CE 100g^{-1})		DPPH (µmol TE 100g^{-1})		HMF (mg L^{-1})
		Dry Basis	Wet Basis	Dry Basis	Wet Basis	Dry Basis	Wet Basis	
H1	70.00	230.58	32.28	160.98	22.54	18.01	12.61	456.03
H2	60.50	500.32	60.54	693.62	83.93	86.97	52.62	144.99
H3	63.90	703.79	44.97	664.14	84.88	112.05	71.60	415.53
H4	64.30	694.98	89.38	634.63	81.61	107.80	69.32	305.37
H5	70.70	153.78	55.82	229.23	16.64	13.09	9.50	481.14
H6	72.60	810.11	52.01	144.45	18.55	169.73	108.61	366.12
H7	64.20	442.54	58.50	489.80	64.75	66.77	44.13	43.74
H8	66.10	623.07	40.38	214.35	27.78	130.08	84.29	66.42
H9	64.80	633.31	82.96	361.53	23.68	101.81	66.69	86.67
H10	65.50	912.65	63.34	317.42	22.03	106.47	73.89	373.41
H11	69.40	700.79	91.38	707.65	92.28	42.90	27.97	101.25
H12	65.20	1226.62	80.59	385.00	50.59	152.20	100.00	541.08
H13	65.70	1048.48	74.55	370.29	52.66	152.20	97.00	400.14
H14	71.10	208.17	12.87	227.13	23.39	91.02	56.25	11.34
H15	61.80	690.80	87.32	251.06	31.73	141.64	89.52	289.98
H16	63.20	762.08	49.91	647.36	84.80	113.20	74.14	305.37
H17	65.50	767.60	100.10	844.44	55.06	116.40	75.90	63.99
H18	65.20	757.02	48.30	429.90	54.86	94.99	60.60	124.74
H19	63.80	700.58	90.80	621.42	40.27	98.75	63.99	32.40
C1	70.70	559.47	79.11	747.09	75.46	111.05	78.51	19.44
C2	71.00	856.17	60.79	1144.37	81.25	115.15	81.76	17.01
C3	70.50	616.72	43.48	235.80	16.62	51.68	36.44	16.20
C4	72.30	405.32	29.31	136.70	19.77	22.61	16.35	51.03
C5	70.80	615.84	43.60	587.96	41.63	79.36	56.19	27.54
Homemade (n = 19)								
Min.	60.50	153.78	12.87	144.45	16.64	13.09	9.50	11.34
Mean	65.66 ± 3.08^{A**}	661.40 ± 270.47^{A}	434.04 ± 183.31^{A}	441.81 ± 216.60^{A}	287.99 ± 136.60^{A}	96.77 ± 38.11^{A}	63.12 ± 25.14^{A}	242.24 ± 175.85^{A}
Max.	72.60	1226.62	100.10	844.44	92.28	152.20	108.61	541.08
Commercial (n = 5)								
Min.	70.50	405.32	29.31	136.70	16.62	22.61	6.35	16.22
Mean	71.06 ± 0.72^{B}	610.72 ± 162.11^{A}	433.45 ± 113.55^{A}	455.94 ± 257.91^{A}	323.16 ± 182.04^{A}	75.97 ± 39.41^{A}	53.85 ± 27.84^{A}	26.24 ± 14.56^{B}
Max.	72.30	856.16	79.11	1144.37	81.25	115.15	81.76	51.03

*TSS:Total soluble solid, TPC, total phenolic content; TFC, total flavonoid content; DPPH, antioxidant activity; HMF, hydroxymethyl furaldehyde. **A-B:Different letters in the same column represent the significant differences of the mean values ($p < 0.05$).

The TFC of commercial pekmez samples was slightly higher than that of homemade samples; however, the difference was statistically insignificant ($p > 0.05$). This result could likely be attributed to variations in the raw materials used, such as white grapes, red grapes, or their mixtures. For antioxidant activity (DPPH), commercial pekmez samples showed a value of 75.9 µmol TE 100g^{-1} on a dry basis, compared to 96.7 µmol TE 100g^{-1} for homemade samples. Similarly, the difference in DPPH radical scavenging activities between homemade and commercial pekmez samples was also insignificant ($p > 0.05$).

Selcuk et al. (2011) determined the TPC, TFC, and antioxidant activity of grape seeds as 54.61 mg GAE g^{-1}, 49.20 mg CE g^{-1}, and 40.79 µmol TE g^{-1} on a dry basis, respectively. In a study by Alasalvar et al. (2005), the TPC of cherry laurel (kiraz variety) and its pekmez were 454 and 1444 mg 100 g^{-1} as ferulic acid equivalents, respectively, while the antioxidant activity value of pekmez determined by the oxygen radical absorbance assay was reported about six times higher than that of fruits. Katırcı et al. (2020) reported that the TPC and TFC values of commercial tomato pastes were significantly higher than those of homemade tomato pastes.

The HMF content was determined as 26.24 mg L^{-1} in commercial pekmez and 242.24 mg L^{-1} in homemade pekmez (Table 2), showing nearly a tenfold difference in HMF contents between homemade and commercial pekmez samples ($p < 0.05$). According to TS 3792 (Turkish Standard) and the Communiqué on Grape Molasses (No: 2017/8) of the Turkish Food Codex, the HMF content of liquid grape pekmez must not exceed 75 mg L^{-1}.

In this study, the mean HMF content of commercial pekmez was 26.24 ± 14.56 mg L^{-1}, well below the legal limit, whereas the mean HMF content of homemade samples was 242.62 mg L^{-1}, approximately 3.2 times higher than the permissible limit. Among the homemade samples, only H7, H8, H14, H17, and H19 had HMF contents below 75 mg L^{-1}, while all commercial samples complied with the legal limit.

Commercial pekmez production involves an evaporation step of grape juice under vacuum, leading to lower HMF contents compared to homemade production, which typically occurs under atmospheric conditions. The HMF content of pekmez is highly influenced by the processing method and the degree of heating. Commercial production, which is typically carried out under more controlled conditions and at lower temperatures using vacuum technology, likely resulted in lower HMF contents despite the higher TSS levels in commercial pekmez samples. According to Batu (2001), there are significant variations in the color and HMF content of pekmez samples produced under vacuum versus those produced in an open boiler that the vacuum application during boiling reduced the HMF content of pekmez samples from 681.40 (in an atmospheric boiler) to 35.25 mg kg^{-1}. In a study by Türkben et al. (2015), HMF content of traditionally produced molasses from different grape cultivars were reported in the range of 5.93-762.22 mg kg^{-1}.

A study by Ersus et al. (2020) investigated HMF formation during the heating treatment (200°C) of red and white grape juices, as well as pomegranate juice. Their results showed that the HMF contents of red and white grape juices increased by 103 and 153 times, reaching 2741.61 mg kg^{-1} and 3292.01 mg kg^{-1}, respectively, compared to their initial levels. This significant increase in HMF content was attributed to the acceleration of Maillard reaction rates during prolonged heating under atmospheric pressure. Storage conditions can also influence HMF content, as reported by Tosun and Ustun (2003), who reported an increase in the HMF content of white grape pekmez after storage. Similarly, Batu (1991) demonstrated that the HMF content of pekmez produced using the vacuum method was 35.25 mg kg^{-1}, which increased significantly to 681.4 mg kg^{-1} when produced using an atmospheric boiler. These findings indicate that the HMF content of pekmez is influenced by several factors, including the type of raw materials, fruit variety, ripening conditions, and the specific processing steps used during production.

The results of the current study indicate that homemade pekmez production is particularly prone to HMF formation due to the evaporation step being conducted under atmospheric conditions, whereas this step is carefully controlled using vacuum technology in commercial production. Therefore, in terms of HMF content, commercial pekmez samples appear to be safer than their homemade counterparts.

Principle component analysis

Correlations between the quality characteristics of pekmez samples were determined and interpreted by correlation coefficients in PCA, and eigenvalues, cumulative variance % and variance % values are shown in Table 3.

Table 3. Effects of quality properties of grape pekmez samples on principle components (PCs) used in the principal component analysis of component matrix.

Variables*	Component**	
	PC1	PC2
TPC	0.919	0.156
DPPH	0.898	0.053
HMF	0.179	0.878
TFC	0.490	-0.711
Eigenvalues	1.924	1.305
Percentage of Variance	48.102	32.621
Percent Cumulative	48.102	80.723

*TPC, total phenolic content; DPPH, antioxidant activity; HMF, 5-hydroxymethyl furaldehyde; TFC, total flavonoid content. **Two components (PC1 and PC2) were extracted.

Eigenvalue is a numerical value, representing the magnitude of variance explained by each principal component in a PCA. Higher eigenvalues indicate that the corresponding principal component describes more variance in the data, making it more important in explaining the underlying structure of the dataset. Eigenvalues higher than 1.0 were extracted as principal components, resulting in the identification of two principal components (PC1 and PC2). These components accounted for 80.70% of the total variance, with PC1 and PC2 explaining 48.10 and 32.62% of the variance, respectively. A two-dimensional component plot was generated, depicting only PC1 and PC2 (Figure 1).

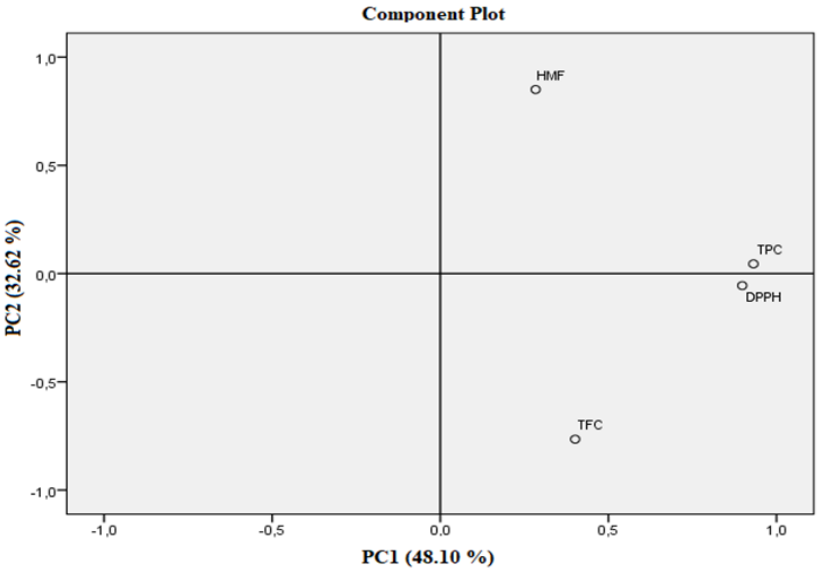

Figure 1. Loadings and plot of the principle components analysis (TPC: total phenolic content in dry basis, TFC: total flavonoid content in dry basis, DPPH: antioxidant activity in dry basis, HMF: 5-hydroxymethyl furaldehyde content).

Table 3 and Figure 1 illustrate that the TPC and DPPH radical scavenging activity of pekmez samples emerged as principal attributes. All five patterns exhibited positive loadings for PC1, while for PC2, only HMF and TPC displayed positive loadings. Specifically, PC1 was strongly associated with TPC and DPPH radical scavenging activity and weakly correlated with HMF content, whereas PC2 primarily reflected variations in HMF content.

The negative factor loading between PC2 and TFC (-0.711), as observed in Table 3 and Figure 1, suggested that pekmez samples positioned on the right-hand side of the plot had lower flavonoid concentrations compared to those on the left-hand side.

Similar approaches utilizing PCA have been applied in various studies to analyze complex datasets. For example, Fidelis et al. (2017) used PCA to describe the physicochemical properties, total phenolics, and antioxidant activity of different juices, where two principal components explained 72% of the variance. Kalaycıoğlu et al. (2017) applied PCA to evaluate the organic acids, sugars, minerals, and antioxidant activities of Turkish honeybee pollens, with three principal components accounting for 71% of the variance. Furthermore, Wang and Hu (2011) employed PCA to determine the significance of different antioxidant assays for mulberry extracts, finding that the principal components collectively explained 81% of the total variance. In the present study, PCA revealed that TPC and DPPH radical scavenging activity were the primary attributes influencing pekmez samples, with PC1 strongly associated with these parameters, while PC2 primarily reflected variations in HMF content and its negative correlation with TFC.

Correlations of components

The results of the Pearson's correlation test are shown in Table 4, presenting correlation coefficients and their corresponding significances.

Table 4. Pearson's correlation coefficients (R) among the quality characteristics of grape pekmez samples.

Variables	HMF	TFC	DPPH	TPC
HMF	1.000	-0.315	0.106	0.245
TFC		1.000	0.270	0.290
DPPH			1.000	0.738*
TPC				1.000

*TPC, total phenolic content; DPPH, antioxidant activity; HMF, hydroxymethyl furaldehyde; TFC, total flavonoid content. **Correlation coefficient is statistically significant ($p < 0.01$).

The TPC and DPPH values of pekmez samples exhibited a positive and significant correlation ($p < 0.01$), indicating a strong relationship between these two parameters. In contrast, the HMF content showed a negative correlation with TFC, though this relationship was not statistically significant ($p > 0.01$). This aligned well with the results of Wang and Hu (2011), who reported significant correlations among different antioxidant assays in mulberry extracts.

Conclusion

In this study, the TPC, TFC, HMF content, and DPPH radical scavenging activity of commercial and homemade pekmez samples were analyzed and compared. Results showed that, while the differences in TPC, TFC, and DPPH radical scavenging activities between the two groups were not statistically significant, there were significant differences in their HMF contents. Specifically, the mean HMF content in homemade samples exceeded 75 mg L^{-1}, which is the maximum limit permitted by the Turkish Food Codex. The elevated HMF levels in homemade grape pekmez are likely due to traditional boiling methods using atmospheric evaporators under uncontrolled conditions, as well as incomplete or improper acid removal processes. In contrast, commercial production typically involves evaporation under vacuum conditions, which helps minimize HMF formation during processing. A significant positive correlation was observed between TPC and antioxidant activity in pekmez samples, whereas a negative but insignificant correlation was found between HMF and flavonoid contents. PCA analysis was employed to classify and assess the interdependence of the quality attributes of pekmez samples. The results suggest that commercial pekmez samples are healthier and safer due to their significantly lower HMF levels compared to homemade samples.

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