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Journal of Agricultural Sciences

Journal homepage:
www.agri.ankara.edu.tr/journal

Physical and Chemical Properties of Pekmez (Molasses) Produced with Different Grape Cultivars

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ARTICLE INFO

Research Article

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Received: 04 November 2014, Received in Revised Form: 12 February 2015, Accepted: 13 April 2015

ABSTRACT

In this study, some physical and chemical properties of pekmez samples produced using the traditional method with fourteen different grape cultivars were investigated. The water-soluble dry matter, pH, titratable acidity and hydroxymethylfurfural (HMF) content of the samples were determined to be 66.19-80.57%, 3.59-5.23, 0.27-1.81 g 100 g⁻¹ and 5.93-762.22 mg kg⁻¹, respectively. The mean fructose and glucose contents of the pekmez samples were determined to be 28.42 g 100 g⁻¹ and 31.67 g 100 g⁻¹, respectively. The densities and electrical conductivities varied between 1.33-1.43 g cm⁻³ and 1.96-4.51 mS cm⁻¹, respectively. The content of the macro element K identified in the pekmez samples (4449.86 mg kg⁻¹) was greater than that of Ca (1275.52 mg kg⁻¹), P (369.96 mg kg⁻¹), Mg (344.79 mg kg⁻¹) and Na (119.56 mg kg⁻¹). The pekmez samples have antioxidant activities, ranging between 38.20 to 64.45 µmol TE g⁻¹. Six phenolic compounds, caffeic acid, ellagic acid, ferulic acid, gallic acid, *p*-coumaric acid and rutin hydrate, were identified in the pekmez samples, and significant differences were observed between samples (P<0.01).

Keywords: Grape; Antioxidant activity; Phenolic composition; Mineral; Pekmez

Farklı Üzüm Çeşitleri ile Üretilen Pekmezlerin Fiziksel ve Kimyasal Özellikleri

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Geliş Tarihi: 04 Kasım 2014, Düzeltmelerin Gelişi: 12 Şubat 2015, Kabul: 13 Nisan 2015

ÖZET

Bu çalışmada on dört farklı üzüm çeşidinden geleneksel olarak üretilen pekmez örneklerinin bazı fiziksel ve kimyasal özellikleri incelenmiştir. Örneklerin suda çözünür kuru madde miktarı, pH, titrasyon asitliği ve hidroksimetilfurfural (HMF) içerikleri sırasıyla % 66.19-80.57, 3.59-5.23, 0.27-1.81 g 100 g⁻¹ ve 5.93-762.22 mg kg⁻¹ olarak belirlenmiştir. Pekmez örneklerinin ortalama fruktoz ve glikoz içerikleri sırasıyla 28.42 g 100 g⁻¹ ve 31.67 g 100 g⁻¹ olarak saptanmıştır.

Yoğunluk ve elektriksel iletkenlik değerlerinin sırasıyla 1.33-1.43 g cm⁻³ ve 1.96-4.51 mS cm⁻¹ aralığında olduğu belirlenmiştir. Pekmez örneklerinde belirlenen makro element K miktarı (4449.86 mg kg⁻¹), Ca (1275.52 mg kg⁻¹), P (369.96 mg kg⁻¹), Mg (344.79 mg kg⁻¹) ve Na (119.56 mg kg⁻¹) miktarından daha olmuştur. Pekmez örneklerinin antioksidan aktivitesi 38.20 ile 64.45 µmol TE g⁻¹ aralığında değişmiştir. Pekmez örneklerinde kafeik asit, ellajik asit, ferulik asit, gallik asit, *p*-kumarik asit ve rutin hidrat olmak üzere altı adet fenolik bileşik tanımlanmış ve örnekler arasında önemli farklılıklar olduğu belirlenmiştir (P<0.01).

Anahtar Kelimeler: Üzüm; Antioksidan aktivite; Fenolik kompozisyonu; Mineral; Pekmez

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1. Introduction

Pekmez (molasses), which has been produced for a long time in Turkey, is one of the popular and traditional Turkish foods (Tosun & Üstün 2003). Pekmez is a concentrated and extended shelf-life form of several fruit juices, and it is formed by boiling without the addition of sugar or other food additives (Yoğurtçu & Kandaşlı 2006). Pekmez is produced primarily from grapes by concentrating juices with a soluble dry matter content of up to 70-80% (Alpaslan & Hayta 2002; Batu et al 2007). In Turkey, approximately 4185.126 tons of grapes are produced per year (TUIK 2012), and approximately 30% of the grapes produced in Turkey are used for pekmez, wort and sausage with pekmez production in a year. Furthermore, some fresh or dried fruits that contain high amounts of sugar, such as fig, mulberry, carob, juniper, sugar beet, sugar cane, melon, watermelon, apple and apricot, can also be used to produce pekmez (Karababa & Isikli 2005; Akbulut et al 2008). Fresh fruits are directly squeezed, whereas dried fruits are subjected to extraction in an aqueous medium and then pressed and derived extract called as must is homogenized (Aliyazıcıoğlu et al 2009).

Pekmez samples are produced in all regions of Turkey and are named after the geographic locations in which they are produced, such as Zile Pekmez in Zile, Ağda in Gaziantep, Çalma in Kırşehir, Bulama in Balıkesir and Masara in Kahramanmaraş (Tosun & Üstün 2003). However, the varieties of grapes and processing techniques used in pekmez production can be different in these regions. Pekmez is produced using traditional and vacuum evaporation methods in

Turkey. However, most of rural regions that do not have modern processing units use the traditional production method (Arici et al 2004; Batu 2006). Pekmez processing techniques vary according to the species of fruits used during production (Kaya & Belibağlı 2002; Arici et al 2004).

Pekmez is a good energy and carbohydrate source due to its high sugar content (up to 50-80%) in the form of glucose and fructose; therefore, it easily passes into the blood without digestion. The average energy value of pekmez is 293 kcal 100 g⁻¹ (Simsek & Artık 2002; Tosun & Ustun 2003). It contains organic acids and, essential minerals such as Fe (2.62-16.30 mg 100 g⁻¹), P (0-95.06 mg 100 g⁻¹), Ca (50.9-206.1 mg 100 g⁻¹) and K (792-929 g 100 g⁻¹) (Üstün & Tosun 1997; Yoğurtçu & Kandaşlı 2006; Batu 2011). The high Fe content makes pekmez a recommended supplement for anemia (Öztürk & Öner 1999). Pekmez, which is an important product for human nutrition due to its composition (Batu & Gök 2006), is consumed at breakfast as jams and marmalades by mixing with tahini as a dessert, used in place of sugar in several traditional products such as halva and it is also processed for snacks such as sweet tarhana, köfter and köme (Yoğurtçu & Kandaşlı 2006; Koca 2014).

There is little information about the physical and chemical properties of grape pekmez. The purpose of this study was to determine the physical and chemical properties of grape pekmez produced using the traditional (classical) method with fourteen different grape cultivars as well as to determine the phenolic composition and antioxidant activity.

2. Material and Methods

2.1. Materials

In this study, fourteen different grape varieties (Alphonse Lavallée, Müşküle, Razakı, Eksenez, Erenköy Beyazı (Bursa), Pafi, Hatun Parmağı, Horoz Karası (Hatay), Şıra Üzümü 1, Narince (Tokat), Parmak Üzümü (Nevşehir), Izabella (Giresun), Siyah Dimrit (Manisa) and Şıra üzümü 2 (Amasya)) were used for the production of Pekmez samples. Pekmez samples were prepared from these grape varieties according to traditional (classical) method.

Standards and chemicals: rutin hydrate (R5143), quercetin hydrate (337951), and gallic acid (G7384) were purchased from Sigma-Aldrich (St. Louis, USA); caffeic acid (822029), *p*-coumaric acid (800237), erulic acid (822070), methanol, hydrochloric acid, oxalic acid, formic acid and acetonitrile were purchased from Merck (Darmstadt, Germany); and ellagic acid (45140) was purchased from Fluka (Buchs, Switzerland). All chemicals used were of analytical grade.

2.2. Methods

Pekmez preparation: Traditional method was used preparation of pekmez samples. At first, grapes were crushed by human power to obtain must. Pekmez earth (75.84% CaCO₃) was added to must and kept for one night to acid reduction and clarification. The obtained liquid must was boiled in open boilers till pekmez sample become optimum consistency. The samples arriving to the laboratory were placed in jars with a volume of 100 mL and stored at 20 °C in darkness.

Chemical analyses: The water-soluble dry matter content of the pekmez samples was determined using a refractometer (Kem RA-500N, Tokyo, Japan) at 20 °C. The titratable acidity was determined (tartaric acid g 100 g⁻¹) using the potentiometric method (0.1 N NaOH solution up to a pH of 8.1), and the pH was determined using a pH meter (Mettler Toledo Seven Easy, Switzerland).

Determination HMF content: The HMF was quantitatively determined following the procedure described by the International Honey Commission (IHC 2002) based on the colorimetric reaction between barbituric acid, *p* toluidine and HMF, which forms a red-colored complex. The intensity of the red color was measured at 550 nm using a UV-Vis-NIR-5000 spectrophotometer.

Determination sugar content: The fructose (g 100 g⁻¹) and glucose (g 100 g⁻¹) contents of the pekmez samples were determined according to the International Honey Commission (IHC 2002) with HPLC. HPLC was conducted using a system composed of a Shimadzu LC-10 A pump and a RID-10A detector using a reversed-phase waters carbohydrate column (300 mm × 3.9 mm). The mobile phase consisted of 80% acetonitrile and 20% water, with a flow rate of 0.9 mL min⁻¹. The retention times (t_r) of fructose and glucose were determined to be 4.8 and 5.2 min, respectively.

Determination mineral content: Approximately 0.5 g of each completely homogenized sample was placed into a Teflon crucible with 6 mL of pure HNO₃+1 mL H₂O₂. The samples were incinerated in a Milestone microwave oven, and the incinerated samples were diluted to 25 mL with distilled water. The mineral elements (Ca, Fe, K, Mg, Na, and P) were analyzed using ICP-OES (Yıldız et al 2009).

Determination antioxidant activity: The antioxidant activities of the pekmez samples were determined using the 2,2-diphenyl-2-picrylhydrazyl (DPPH) method (Türkben et al 2010) with some modifications. Approximately 1 g samples were extracted with 80% aqueous methanol (4.5 mL) on a mechanical shaker for 2 h. The mixture was centrifuged at 10,000 rpm for 15 min, and the supernatant was decanted into polypropylene tubes. The pellets were extracted under identical conditions. The supernatants were combined and filtered, and the clear extracts were analyzed for antioxidant activity. A 1.5 mL aliquot of 0.1 mM DPPH radical in methanol was added to a test tube with 0.5 mL of the sample extracts. Pure methanol, rather than the methanolic extract of the samples, was used as a

control. The reaction mixture was vortex mixed and allowed to stand at room temperature in the dark for 1 h before the decrease in absorbance (A) at 517 nm by Shimadzu UV/VIS 1800 model (Kyoto, Japan) spectrophotometer was measured. The results were expressed as $\mu\text{mol Trolox equivalents } (\mu\text{mol TE g}^{-1})$.

Determination phenolic compounds: The methanol extraction method was applied with some modifications as described by the International Honey Commission (IHC 2002). HPLC was conducted using a system composed of a Shimadzu LC-10 A pump and a SPD-M10AVP detector using a reversed phase Nucleodur C18 column (250 mm \times 4.0 mm i.d, 5.0 μm). The mobile phase consisted of 0.05% formic acid and methanol (Table 1), and the flow rate was 0.9 mL min^{-1} at 250-280 nm. The retention times (t_R) of each compound are presented in Table 2.

Table 1- HPLC conditions for the determination of phenolic compounds

Çizelge 1- Fenolik bileşiklerin belirlenmesi için kullanılan HPLC koşulları

Time (min)	HPLC conditions
0.01	95% formic acid 5.0% methanol
50.00	50% formic acid 50% methanol
55.00	100% formic acid 0.0% methanol
57.00	100% formic acid 0.0% methanol
60.00	5.0% formic acid 95% methanol
65.00	5.0% formic acid 95% methanol

Table 2- Retention times (t_R) of standard phenolic compounds

Çizelge 2- Standart fenolik bileşiklerin alıkonma zamanları (t_R)

Phenolic compounds	t_R (min)
Gallic acid	9.95
Cafeic acid	27.4
p-Cumaric acid	34.9
Ferrulic acid	37.5
Rutin hidrat	45.3
Ellagic acid	46.0
Quercetin	56.5

Physical analyses: The electrical conductivity of a 20% pekmez solution (dry matter basis) in CO_2 -free deionized distilled water was measured at 20 $^\circ\text{C}$ using a WTW InoLab Cond Level 1 Digital Ec-meter (Weilheim, Germany) and the result was expressed as mS cm^{-1} (AOAC 1990).

The density determinations of the pekmez samples were performed using the oscillating U-tube method. For this purpose, approximately 1 g of pekmez was placed into a temperature-controlled sample cell, and oscillation frequency data obtained from the density-meter (KEM-DA-505, Tokyo, Japan) were saved. By measuring the oscillation frequency of a calibration fluid with a known density and using predetermined cell coefficients, the densities of the samples (g cm^{-3}) were calculated.

2.3. Statistical analyses

The experiment was conducted in a completely randomized design with three replications. The results were statistically evaluated by one-way analysis of variance (ANOVA) using the JMP software package version 7.0 (SAS Institute Inc. NC, 27513). The significance of the treatments was determined at the 0.01 probability level using the F-test.

3. Results and Discussion

Some physical and chemical properties of grape pekmez samples produced from fourteen different grape varieties are given in Table 3. The water-soluble dry matter content was found to be 66.19-80.57%. The water-soluble dry matter in fruits is primarily formed by sugars, including fructose, glucose and sucrose, and by acids, such as citric acid and malic acid (Cemeroğlu 2010). Alpar (2011) estimated the water-soluble dry matter content in white grape pekmez processed using the traditional method to be 61.50%. Koca et al (2007) and Üstün & Tosun (1997) also reported that the water-soluble dry matter content in grape pekmez ranged from 69.00-73.90% and 68.60-78.30%, respectively.

The pH in grape pekmez was found to range from 3.59 to 5.23. The titratable acidity (in terms of tartaric acid) was determined to be the highest

and lowest in the Pafi (0.27 g 100 g⁻¹) and Izabella (1.81 g 100 g⁻¹) samples, respectively (P<0.01). Titratable acidity is inversely proportional to pH. Acidity may vary depending on the herbal sources and producing regions (Batu et al 2013). According to Grape Pekmez Notification (2007), pekmez is classified as sweet pekmez if their pH range is from 5 to 6, and they are classified as sour pekmez when their pH range is from 3.5 to 5. Therefore, while Eksenez, Erenköy Beyazı, Pafi, Hatun Parmağı, Horoz Karası, and Şıra Üzümü 2 pekmez are sweet pekmez samples, the other samples are classified as sour pekmez. The pH and titratable acidity of grape pekmez have been identified in several studies as 4.36 to 5.12 and 0.08-0.97% (Üstün & Tosun 1997), 5.20 to 5.33 and 0.71-0.79% (Simşek & Artık 2002), 8.11 and 0.59% (Alpar 2011), respectively.

HMF is not naturally found in fruits; rather, it is formed from monosaccharides by the action of heat

and acid and is a limited compound for preventing the application of excess heat in many products. It is an important quality factor that reflects the severity of heat treatment (temperature and time) that were applied to the foods thickened with the application of a heat treatment (Tosun & Üstün 2003; Cemeroglu 2010). The HMF contents of the grape pekmez samples varied from 5.93 mg kg⁻¹ (Pafi) to 762.22 mg kg⁻¹ (Izabella). According to Pekmez Standards, the allowed formation of HMF in liquid pekmez is 75 mg kg⁻¹, whereas in solid pekmez, 100 mg kg⁻¹ is allowed. This value in pekmez samples derived from grape varieties such as Alphonse Lavallée (380.08 mg kg⁻¹), Müşküle (116.93 mg kg⁻¹), Razakı (206.31 mg kg⁻¹), Erenköy Beyazı (333.37 mg kg⁻¹), Izabella and Şıra Üzümü 1 (163.10 mg kg⁻¹) were quite high. A study conducted on the traditional methods in homes with found an HMF content that was approximately 20 times higher in high

Table 3- Physical and chemical properties of traditionally processed grape pekmez samples

Çizelge 3- Geleneksel olarak üretilen pekmez örneklerinin fiziksel ve kimyasal özellikleri

Grape cultivars	Water-soluble dry matter (%)	Titratable acidity (g 100 g ⁻¹)	pH	HMF (mg kg ⁻¹)	Electrical conductivity (mS cm ⁻¹)	Density (g cm ⁻³)
Alphonse Lavallée (Bursa)	68.38 d	0.79 d	4.73 g	380.08 b	4.07 b	1.363 c
Müşküle (Bursa)	69.43 cd	0.53 g	4.84 f	116.93 f	3.59 d	1.380 b
Razakı (Bursa)	69.54 cd	0.82 c	4.70 g	206.31 d	3.85 c	1.347 de
Eksenez (Bursa)	66.19 f	0.35 j	5.04 c	57.21 ij	3.02 g	1.327 f
Erenköy Beyazı (Bursa)	68.10 de	0.45 h	5.05 c	333.37 c	1.96 i	1.337 ef
Parmak Üzümü (Nevşehir)	68.52 d	0.42 i	4.95 de	60.85 gh	2.97 g	1.340 def
Izabella (Giresun)	68.86 cd	1.81 a	3.59 i	762.22 a	2.48 h	1.340 def
Pafi (Hatay)	66.33 f	0.27 k	5.23 a	5.93 l	3.26 f	1.350 cde
Hatun Parmağı (Hatay)	66.73 ef	0.37 j	5.13 b	44.13 k	3.41 e	1.340 def
Horoz Karası (Hatay)	66.30 f	0.41 i	5.00 cde	58.13 hi	3.09 g	1.350 cde
Siyah Dimrit (Manisa)	80.57 a	1.02 b	4.17 h	46.87 k	3.01 g	1.430 a
Şıra Üzümü 1 (Tokat)	74.27 b	0.69 e	4.75 g	163.10 e	3.70 d	1.393 b
Narince (Tokat)	68.59 d	0.56 f	4.94 e	63.61 g	4.05 b	1.353 cd
Şıra Üzümü 2 (Amasya)	70.07 c	0.43 hi	5.00 cd	54.57 j	4.51 a	1.363 c
LSD	1.47	0.02	0.06	1.00	0.13	0.01
CV (%)	1.27	2.26	0.73	1.23	2.39	0.63

*, mean values within a column with different superscript letters were significantly different (P<0.01); CV, coefficient of variation

temperature-produced pekmez (681.40 mg kg⁻¹) compared with the pekmez produced under vacuum (35.25 mg kg⁻¹) commercially (Batu 1991). The high content of HMF in the grape pekmez samples is a result of the boiling process in an open vessel at high temperature. In the literature, the amounts of HMF in grape pekmez samples range from 7.38 to 166.05 mg kg⁻¹ (Üstün & Tosun 1997), from 18.4 to 200 mg kg⁻¹ (Kus et al 2005) and from 29.56 to 801.80 mg kg⁻¹ (Koca et al 2007).

The sugar contents of the pekmez samples are given in Figure 1. In the study of grape pekmez, the amount of fructose changed from 22.34 g 100 g⁻¹ of (Hatun Parmağı) to 34.69 g 100 g⁻¹ (Parmak Üzümü) and was determined to be 28.42 g 100 g⁻¹ on average. On the other hand, the glucose ratios ranged from 27.57 g 100 g⁻¹ (Hatun Parmağı) to 41.11 g 100 g⁻¹ (Siyah Dimrit), with an average value of 31.67 g 100 g⁻¹. Simşek & Artık (2002) reported that the fructose

and glucose contents of 25 commercially produced grape pekmez samples changed from 30.14 to 34.42% and from 30.73 to 34.99%, respectively. The densities of the pekmez samples were found to range between 1.33 g cm⁻³ (Eksenez) and 1.43 g cm⁻³ (Siyah Dimrit). The electrical conductivity values also showed variations between 1.96 mS cm⁻¹ (Erenköy Beyazı) and 4.51 mS cm⁻¹ (Şıra Üzümü 2). Electrical conductivity provides more information about mineral salts, organic acids, and protein concentrations. When the product contains high contents of mineral salts, organic acids, and proteins, the electrical conductivity is higher (Akbulut & Özcan 2008). Akbulut et al (2008) reported that the density and electrical conductivity values of *Juniperus drupacea* (andız) pekmez were 1.34 g cm⁻³ and 6.14 mS cm⁻¹, respectively. In another study, the electrical conductivity of sweet sorghum pekmez was identified as 13.53 mS cm⁻¹ (Akbulut & Özcan 2008).

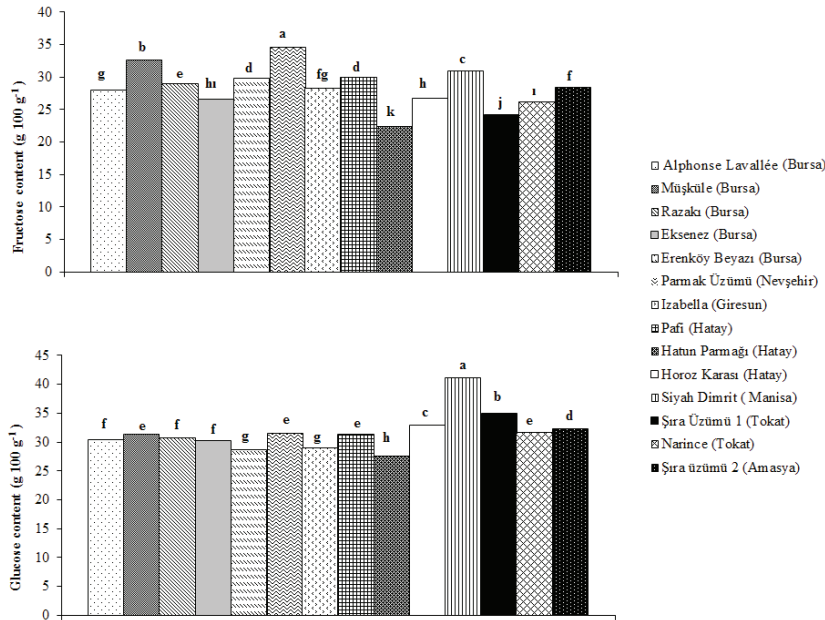


Figure 1- The sugar contents of traditionally processed grape pekmez samples. Bars with different superscript letters were significantly different (P<0.01)

Şekil 1- Geleneksel olarak üretilmiş üzüm pekmezi örneklerinin şeker içerikleri. Farklı harflerle belirtilen değerler istatistikî açıdan farklıdır (P<0.01)

Minerals are food ingredients that are vital. The mineral contents of the grape pekmez samples are given in Table 4. The contents of macro elements found in grape pekmez samples produced from different grape varieties were determined to range from 48.70 mg kg⁻¹ (Horoz Karası) to 5109.56 mg kg⁻¹ (Horoz Karası) (P<0.01). In terms of the average values of macro elements, the highest amount was found for K, with the value of 4449.86 mg kg⁻¹, followed by Ca (1275.52 mg kg⁻¹), P (369.96 mg kg⁻¹), Mg (344.79 mg kg⁻¹) and Na (119.56 mg kg⁻¹). Several studies have reported that the K content was highest in grape pekmez (Yumlu 2006; Akbulut & Özcan 2009; Alpar 2011; Çoklar & Akbulut 2012). The micro element Fe was identified in the pekmez samples (average 46.91 mg kg⁻¹), and it was found in lower amounts than other minerals. The pekmez sample produced from Şıra Üzümü 2 has the highest Ca content (4973.93 mg kg⁻¹), the Müşküle sample has the highest Fe (403.67 mg kg⁻¹) and P (597.87 mg kg⁻¹) contents, the Izabella sample has the highest Mg (612.83 mg kg⁻¹) content, and the Narince

sample has the highest Na (344.28 mg kg⁻¹) content with statistical significance (P<0.01). The pekmez samples produced from Horoz Karası varieties have the highest K content (5109.56 mg kg⁻¹), and there is no significant difference between Erenköy Beyazı (5063.11 mg kg⁻¹) and Izabella (5045.81 mg kg⁻¹) (P>0.01). Alpar (2011) determined that the Ca, K, Mg, Na, P and Fe contents of pekmez samples produced from white, black and red grapes using the traditional method ranged from 1.56 to 1491.65 mg kg⁻¹, from 1811.79 to 9581.34 mg kg⁻¹, from 187.34 to 332.33 mg kg⁻¹, from 153.14 to 248.86 mg kg⁻¹, from 192.44 to 492.43 mg kg⁻¹ and from 49.53 to 132.13 mg kg⁻¹, respectively. On the other hand, Yumlu (2006) reported that the most abundant mineral in the grape pekmez was K (302.50 mg 100 g⁻¹), followed by Ca (153.49 mg 100 g⁻¹), Mg (62.19 mg 100 g⁻¹) and Na (54.84 mg 100 g⁻¹). Aliyazicioglu et al (2009) determined the Ca, K, Na, P and Fe contents in grape pekmez to be 186, 831, 1353, 48 and 3.4 mg kg⁻¹, respectively.

Table 4- Mineral contents of traditionally processed grape pekmez samples (mg kg⁻¹)

Çizelge 4- Geleneksel olarak üretilen pekmez örneklerinin mineral içerikleri (mg kg⁻¹)

Grape cultivars	Ca	Fe	K	Mg	Na	P
Alphonse Lavallée (Bursa)	265.50 ı	10.95 f	4007.93 h	412.16 d	84.67 g	307.09 gh
Müşküle (Bursa)	894.62 f	403.67 a	4560.95 d	257.62 h	133.64 e	597.81 a
Razakı (Bursa)	528.12 g	7.42 g	4693.47 cd	476.88 c	80.82 g	367.19 e
Eksenez (Bursa)	507.17 g	13.56 e	4059.66 gh	241.67 ı	153.55 d	331.81 f
Erenköy Beyazı (Bursa)	3515.88 b	42.51 b	5063.11 ab	553.52 b	84.05 g	303.08 h
Parmak Üzümü (Nevşehir)	1322.33 e	9.89 fg	4933.78 b	191.97 j	173.36 c	401.94 d
Izabella (Giresun)	1743.63 c	34.04 c	5045.81 ab	612.83 a	107.39 f	370.70 e
Pafi (Hatay)	404.39 h	40.25 b	3370.58 ı	250.08 hı	52.59 hı	226.76 j
Hatun Parmağı (Hatay)	163.12 j	15.80 e	4396.53 e	250.29 hı	52.59 hı	272.31 ı
Horoz Karası (Hatay)	564.17 g	2.27 h	5109.56 a	308.17 g	48.70 ı	513.04 b
Siyah Dimrit (Manisa)	271.58 ı	26.08 d	3961.60 h	328.27 f	51.44 hı	361.69 e
Şıra Üzümü 1 (Tokat)	1405.18 d	10.84 f	4206.90 f	320.89 fg	249.39 b	489.56 c
Narince (Tokat)	1297.67 e	15.93 e	4191.56 fg	370.53 e	344.28 a	316.21 gh
Şıra Üzümü 2 (Amasya)	4973.93 a	23.52 d	4696.66 c	252.13 hı	57.32 h	320.30 fg
LSD	78.99	2.59	132.67	13.46	7.13	13.62
CV (%)	3.71	3.30	1.79	2.34	3.58	2.21

*, mean values within a column with different superscript letters were significantly different (P<0.01); CV, coefficient of variation

Grapes are one of the richest sources of phenolic substances in fruits, and the antioxidant activity of these fruits results from the abundance of phenolic substances (Revilla et al 1997). The antioxidant activities and contents of phenolic compounds of the grape pekmez samples are given in Table 5. The antioxidant activities of the pekmez samples changed from 38.20 to 64.45 $\mu\text{mol TE g}^{-1}$, and significant differences were observed between samples ($P < 0.01$).

In this study, six phenolic compounds, caffeic acid, ellagic acid, ferulic acid, gallic acid, *p*-coumaric acid and rutin hydrate, were determined in pekmez samples. The HPLC chromatograms of standards and the Narince (Tokat) sample are shown in Figure 2. The caffeic acid, ferulic acid, *p*-coumaric acid, rutin hydrate and gallic acid contents of the samples changed from 1.95 (Hatun Parmağı) to 14.69 (Narince) mg kg^{-1} , from 0.35 (Parmak Üzümü) to 2.62 (Şıra Üzümü 1) mg kg^{-1} , from 0.41 (Şıra Üzümü 1) to 20.4 (Alphonse Lavallée) mg kg^{-1} ,

from 0.51 (Alphonse Lavallée) to 7.48 (Parmak Üzümü) mg kg^{-1} , and from 0.35 (Eksenez) to 10.14 (Müşküle) mg kg^{-1} , respectively. Quercetin hydrate was not determined in any of the pekmez samples, whereas ellagic acid was determined only in the samples produced from Izabella (0.20 mg kg^{-1}), Şıra Üzümü 1 (0.23 mg kg^{-1}) and Narince (0.32 mg kg^{-1}). Phenolic compounds in grapes are affected by many factors, such as properties of the varieties, cultivation conditions, the location of the production area and the degree of ripeness of the grapes (Revilla et al 1997). Alpar (2011) determined that the antioxidant activity changed from 86.44% to 93.40% and that the total phenolic content changed from 20.447 mg L^{-1} to 24.188 mg L^{-1} in pekmez produced using the traditional method. Kelebek et al (2012) reported that the contents of gallic acid, *p*-coumaric acid and caffeic acid in white grape pekmez were 8.93, 0.03 and 0.20 mg kg^{-1} , respectively, and similarly, they were 5.50, 0.03 and 0.25 mg kg^{-1} in black grape pekmez, respectively.

Table 5- The antioxidant activities and contents of phenolic compounds (mg kg^{-1}) of traditionally processed grape pekmez samples

Çizelge 5- Geleneksel olarak üretilen pekmez örneklerinin antioksidan aktivite değerleri ve fenolik bileşikleri (mg kg^{-1})

Grape cultivars	Caffeic acid	Ferulic acid	<i>p</i> -coumaric acid	Rutin hydrate	Gallic acid	Ellagic acid	Antioxidant activity ($\mu\text{mol TE g}^{-1}$)
Alphonse Lavallée (Bursa)	12.50 b	1.58 b	20.04 a	0.51 g	2.59 d	nd	61.52 b
Müşküle (Bursa)	10.69 c	1.35 c	1.39 j	nd	10.14 a	nd	55.36 f
Razakı (Bursa)	6.60 e	0.58 g	1.87 h	nd	nd	nd	58.59 d
Eksenez (Bursa)	9.46 d	0.84 e	3.78 e	0.84 f	0.35 e	nd	54.94 f
Erenköy Beyazı (Bursa)	9.56 d	0.73 f	3.30 f	nd	3.75 c	nd	59.76 c
Parmak Üzümü (Nevşehir)	4.45 g	0.35 ı	1.73 hı	7.48 a	nd	nd	50.53 g
Izabella (Giresun)	5.76 f	0.54 g	1.87 h	2.83 d	nd	0.20 b	45.42 h
Pafi (Hatay)	9.69 d	2.62 a	6.32 d	nd	nd	nd	56.53 e
Hatun Parmağı (Hatay)	1.95 ı	0.83 e	2.65 g	1.10 e	nd	nd	61.37 b
Horoz Karası (Hatay)	nd	1.36 c	1.51 ij	nd	nd	nd	63.65 a
Siyah Dimrit (Manisa)	12.42 b	1.33 c	9.67 b	3.37 c	9.68 b	nd	38.20 ı
Şıra Üzümü 1 (Tokat)	3.36 h	2.62 a	0.41 k	2.73 d	nd	0.23 b	64.45 a
Narince (Tokat)	14.69 a	1.17 d	7.57 c	4.66 b	0.49 e	0.32 a	61.52 b
Şıra Üzümü 2 (Amasya)	4.68 g	0.45 h	1.33 j	0.66 fg	nd	nd	63.48 a
LSD	0.15	0.14	0.14	0.15	0.15	0.17	0.31
CV (%)	2.27	3.90	4.06	5.49	3.32	6.93	1.12

*, mean values within a column with different superscript letters were significantly different ($P < 0.01$); nd, not detected; CV, coefficient of variation

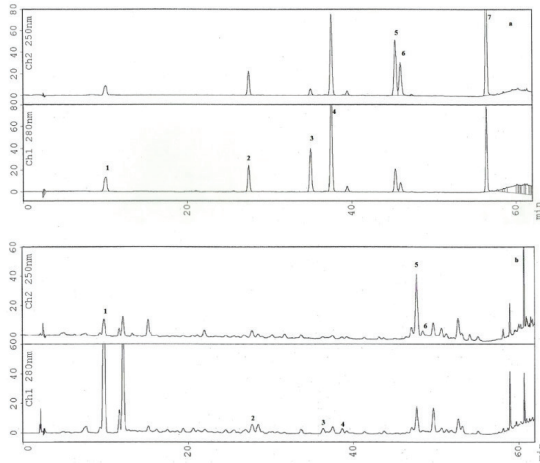


Figure 2- HPLC chromatograms of standard phenolic compounds (a) and the Narince (Tokat) pekmez sample (b). (1, Gallic acid; 2, Caffeic acid; 3, *p*-coumaric acid; 4, Ferulic acid; 5, Rutin hydrate; 6, Ellagic acid; 7, Quercetin hydrate)

Şekil 2- Standart fenolik bileşiklerin (a) ve Narince (Tokat) (b) pekmez örneğinin HPLC kromotogramları. (1, Gallik asit; 2, Kafeik asit; 3, p-kumarik asit; 4, Ferulik asit; 5, Rutin hidrat; 6, Ellajik asit; 7, Kuersetin hidrat)

4. Conclusions

Grape pekmez is routinely produced in Turkey, and open vessels are used with traditional methods in many areas for the production of grape pekmez. With the use of traditional methods for the production of pekmez and the absence of any standard implementation, the quality of the pekmez is decreased, and compounds that are harmful to human health, such as HMF, are also formed in large amounts. To produce better quality pekmez, standardization in production should be applied by using modern technology, and traditional production should be adapted to this technology.

Acknowledgements

The authors would like to acknowledge the financial support from the Uludag University Research Foundation for financial support (Project

No. UAP(Z)-2011/62), likewise to Dr. Önder KAMILOĞLU (Department of Horticulture, Faculty of Agriculture, Mustafa Kemal University, 31034 Antakya-Hatay, Turkey) for his help with the material supplied.

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