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Comparison of total phenolic content and antioxidative activities of EU PDO Malatya apricot (*Prunus armeniaca* L.) kernels

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Abstract

This study investigates the bioactive content of kernels from four apricot varieties: Hacihaliloglu, Hasanbey, Kabaasi, and Zerdali, grown in Malatya over two consecutive years, 2018 and 2019. The research addresses the need to understand how harvest timing and varietal differences influence total phenolic content and antioxidant activity, which are critical for health-related applications. Antioxidant activity was assessed using DPPH, ABTS, and FRAP assays. The findings revealed that sweet apricot varieties Hasanbey, Hacihaliloglu, and Kabaasi exhibited higher total phenolic and antioxidant content than the bitter Zerdali variety. Among these, Hasanbey kernels had the most favorable bioactive profile, while Hacihaliloglu and Zerdali generally exhibited the lowest levels. Harvest timing significantly impacted the bioactive content, except for the FRAP assay results, underscoring the role of developmental stages in kernel quality. Furthermore, year-to-year variations in bioactive content suggest that external factors such as soil composition, climate, and growing conditions also play a critical role. A strong positive correlation was observed between FRAP and both total phenolic and DPPH antioxidant activity, indicating shared reactive compounds. These results highlight the potential of sweet apricot kernels as a bioactive rich resource and underscore the influence of genetic, environmental, and temporal factors on their nutritional value.

Keywords*:* Antioxidant activity; apricot; Prunus aremeniaca L.; total phenolic content

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1. INTRODUCTION

The apricot is a fruit that belongs to the genus Prunus of the rose family. It is generally grown in warm regions and is mainly produced in the Mediterranean area. It can therefore only be grown in a few places. The homeland of apricot cultivation in Central Asia, Western China, and Iran-Caucasus. Only a limited number of countries, including Turkiye, can grow apricots commercially (Kan & Karaat, 2019). Apricot varieties differ from each other by their characteristics, such as color, taste, sweetness, acidity, and nutritional content. Different apricot varieties can be grown in Turkiye. Malatya (province in Türkiye) is the leader in annual apricot production (Yigit et al., 2009; Durmaz & Ağır 2024). Malatya apricot was geographically labeled in 2017. The most produced apricot variety every year is Hacihaliloglu. 60% of the total apricots produced annually in Turkiye belong to this variety (Kan and Karaat, 2019).

The apricot kernel, which is located inside the apricot fruit, is a hard and shelled product. About 15% of the apricot fruit consists of apricot seeds. Inside the kernel, there is a structure called apricot seed, which makes up 40% of the kernel (Gomaa, 2013). The kernel is an economically valuable by-product of fruit processing. It contains a large number of bioactive compounds including phenolic and antioxidant compounds (Keçe et al., 2024). It has also been used as a cancer treatment, although there is no firm scientific evidence for its use against the disease. In addition, the seed contains a toxic compound, called amygdalin. Therefore, it is unsafe to consume large amounts. The seeds of the sweet Malatya apricot have been found to have a very high level of amygdalin content and are safe enough for consumption.

Antioxidants and phenolic compounds are very important for human health. In recent decades, phenolic and antioxidant compounds in natural foods have attracted great interest in food science. They are plant secondary metabolites that carry an aromatic ring with at least one hydroxyl group. Phenolic compounds are electron donors. This means that their hydroxyl groups can have an antioxidant effect (Bendary et al., 2013). In addition, some phenolic compounds can promote the synthesis of endogenous antioxidant compounds in the cell (Cote et al., 2010). Phenolic compounds have been reported to inhibit free radicals, degrade peroxides, inactivate metals and bind oxygen in biological systems. These effects lead phenolic compounds to prevent the burden of oxidative diseases (Babbar et al., 2015).

The components found in the structure of foods continue to be intensively researched for a nutrient-rich, healthy diet (Soliman, 2023). Free radicals and antioxidants are structures that are widely distributed in nutrients. Free radicals, which show their reactivity in foods, react with cells when they enter the human body, causing cell destruction and deterioration of cell structure (Christopoulos and Tsantili, 2011). This is because the radicals contain unpaired electrons in their outer orbitals, making them unstable molecules. They cause unwanted oxidative decay as they constantly try to eliminate the unstable structure (Coco & Vinson, 2019). Antioxidant substances react by donating electrons to these free radicals and bonding with them (Yildiz et al., 2023). In this way, the negative effects of these radical groups on the cell are prevented (Korekar et al., 2011). The components contained in nutrients can have varying degrees of antioxidant effects. Antioxidant levels can vary even from the same source when they enter the human body. For example, different studies reported very different levels of antioxidants in apricot seeds (Taiti et al., 2023; Chen et al., 2020; Gomaa, 2013; Korekar et al., 2011).

1.1. Purpose of study

The main objective of this study was to investigate the effects of harvest time and variety on the total phenolic content and antioxidant content of Malatya apricot kernels. For this purpose, four different apricot varieties; namely Hacihaliloglu, Kabaasi, and Hasanbey the sweet apricot type, and Zerdali the bitter apricot type; were analyzed for their total phenolic content and antioxidant content during the period (2018 and 2019).

2. MATERIALS AND METHOD

2.1. Plant material

In this study, apricot kernels of Hacihaliloglu, Kabaasi, Hasanbey, and Zerdali varieties obtained from the apricot trees in the garden of the Apricot Research Institute Directorate in Malatya province in the months from June to August in two consecutive years of 2018 and 2019 were used.

2.2. Preparation of sample

Each apricot kernel variety was weighed (250 g), then separately pulverized and mixed. The powder was extracted with water at 40^0C for 3 h (1:9 v/w). The extracts were filtrated with filter paper and the filtrate was used for analysis.

2.3. Total phenolic content (TPC)

The TPC content in the extracts of Malatya apricot kernels was measured according to a previous study (Korekar et al., 2011). The results were expressed as mg gallic acid equivalent (GAE)/ 100 g dry weight (dw). The standard curve of gallic acid was established in a concentration range of 1 to 40 mg/L, resulting in the calibration curve of y = 0.0183x - 0.0018 (R^2 = 0.9965).

2.4. Antioxidant activity

The antioxidant activities of Malatya apricot kernel extracts were evaluated using three different antioxidant assays including ABTS, DPPH, and FRAP.

ABTS antioxidant activity was performed according to the study of Rice-Evans et al., (1997). The results were expressed as mg Trolox (TE)/ g dry weight (dw). The standard curve of Trolox was used with a concentration range of 50 to 500 mg/L, resulting in the calibration curve of y = -0.001x + 0.4891 (R^2 = 0.9998). Trolox was also used as a standard for DPPH assay, which was implemented according to a previous study (Brand-Williams et al., 1995). The results were shown as mg Trolox (TE)/ g dry weight (dw). The standard curve of Trolox was applied with a concentration range of 50 to 500 mg/L, resulting in the calibration curve of y = -0.2076x + 0.5503 (R^2 = 0.9929). In the FRAP assay, ferric (II) sulfate was used as standard, and the analysis was performed according to the study of Korekar et al., (2011). The results were expressed as μmol FE II/g dry weight (DW). The standard curve of Fe (II) was applied with a concentration range of 100 to 500 μmol/L, resulting in the calibration curve of y = 0.0007x + 0.0973 (R^2 = 0.9995).

2.5. Statistical evaluation

The statistical methods were based on the study by Sen and Yildirim (2022) using SPSS 29 statistical software. The results presented in the tables were the mean value of triplicate measurements following a randomized block design and were reported as descriptive statistical methods (mean, standard deviation). For all analyses, at least $p<0.05$ was accepted as the level of error (significance level) in all analyses. Using Duncan's multiple range test or Dunnett's C test.

Shapiro Wilk or Kolmogorov Smirnov tests were used to determine homogeneous distribution. The data that showed a homogeneous distribution were analyzed using parametric tests while non-parametric tests were used for the data that showed an inhomogeneous distribution. Pearson's (r) or Spearman's (rho) correlation tests were used to show the possible correlation between two quantitative data.

3. RESULTS

TPC and antioxidant activities of Malatya apricot kernels are presented in Table 1 and Table 2. Harvest year and variety had a significant effect on TPC (Table 1). Even though there were exceptions, such as the result of the FRAP assay, harvest time and variety had a significant effect on the antioxidant activities of Malatya apricot kernels, showing the importance of variety on the bioactive compounds of fruit kernels.

Table 1

TPC of Malatya apricot kernels.

TPC	The harvest year of 2018	The harvest year of 2019	t- Test
Hacihaliloglu	7.8 ± 0.2a	8.4 ± 0.4a	0.04
Hasanbey	12.7 ± 0.5c	14.1 ± 0.3d	0.01
Kabaaşı	10.1 ± 0.4b	13.1 ± 0.7c	0.01
Zerdali	8.3 ± 0.6a	11.0 ± 0.2b	<0.001
ANOVA	<0.001	<0.001	
t-Test for year variance	0.02		

Note: Different letters in the same column show a significant difference (p<0.05).

Mean value ± standard error (n=3). Results are mean values of triplicate measurements.

The kernels of the Hasanbey variety significantly had higher TPC and antioxidant content while the kernel of the Hacihaliloglu variety had the lowest TPC, and the kernel of the Zerdali variety had the lowest antioxidant content than those in the kernels of the other apricot varieties. In general, the sweet apricot kernels had better bioactive contents than those of the bitter (Zerdali) apricot kernel.

Table 2

Antioxidant activities of Malatya apricot kernels.

ABTS	The harvest year of 2018	The harvest year of 2019	t- Test
Hacihaliloglu	720.5 ± 130a	1105.5 ± 150a	0.01
Hasanbey	780.5 ± 135a	1130.5 ± 105a	0.01
Kabaaşı	755.5 ± 170a	1125.5 ± 100a	0.02
Zerdali	820.5 ± 75a	1560.5 ± 75b	<0.001
ANOVA	0.82	0.01	
t-Test for year variance	<0.001		
DPPH			
Hacihaliloglu	173.8 ± 6a	166.3 ± 1a	0.04
Hasanbey	188.3 ± 6b	180.4 ± 5b	0.09
Kabaaşı	185.3 ± 4b	185.3 ± 6b	0.50
Zerdali	186.3 ± 5b	178.1 ± 2b	0.03
ANOVA	0.04	0.01	
t-Test for year variance	0.04		
FRAP			
Hacihaliloglu	61.6 ± 0.5c	63.4 ± 0.9c	0.04
Hasanbey	64.3 ± 0.9c	65.1 ± 0.4c	0.50
Kabaaşı	30.9 ± 0.1b	30.7 ± 0.2b	0.04
Zerdali	12.2 ± 0.2a	14.0 ± 0.4a	0.50
ANOVA	0.02	0.02	
t-Test for year variance	0.55		

Note: Different letters in the same column show a significant difference (p<0.05).

Mean value ± standard error (n=3). Results are mean values of triplicate measurements.

The apricot kernels had a total phenolic content of 7 to 15 mg GAE/ 100 g dw; and the antioxidant content was between 700 and 1200 mg TE/ g dw in their ABTS assay, between 165 and 190 mg TE/ g dw in the DPPH assay, and between 12 and 66 µmol FE II/ g dw in FRAP assay. The bioactive contents of each apricot kernel variety changed significantly with the harvest time, showing that some other factors can affect the bioactive contents of the kernels.

4. DISCUSSION

The TPC of Malatya apricot kernels is shown in Table 1. As the results of previous studies (Juhaimi et al., 2018; Kan and Karaat, 2019; Yigit et al., 2009) showed, the variety significantly affected the total phenolic content. In addition, the varieties investigated in this study had a higher TPC than those used in previous studies (Horozic et al., 2020; Kan and Karaat, 2019; Yigit et al., 2009). This may be due to the influence of many factors, including the variety, extraction method, type of solvent, and extraction conditions (Horozic et al., 2020).

The possible correlations of the TPC of the seeds were investigated, and the correlation between the TPC and the antioxidant activity of the kernels was found only for the FRAP assay (Rho=0.9). In other words, the correlation showed that phenolics were the main components responsible for the antioxidant FRAP activity of Malatya apricot kernels. However, there was no correlation between ABTS or DPPH activity and TPC of the kernels (r_{ABTS}=0.3 and r_{DPPH}=0.4), implying that not only phenolic components but also other compounds (such as sesquiterpenoids, tocopherols, phytosterols) contribute to antioxidant activity. In contrast to the results of this study, other studies reported a correlation between the antioxidant activity of the ABTS or DPPH test and the TPC for different fruit varieties (Coco and Vinson, 2019; Pitchaon, 2011). However, the study by Korekar et al., (2011) found no correlation between antioxidant activity (ABTS and DPPH) and TPC for apricot kernels harvested in the Himalayas, similar to the result of this study. The different results of the studies might be due to the effect of kernel genotype (Korekar et al., 2011).

The antioxidant activity contents of Malatya apricot kernels are shown in Table 2. The antioxidant ABTS content of the kernels changed significantly in the 2019 crop year depending on the variety, as reported in previous studies (Chen et al., 2020; Rampackova et al., 2021). However, no significant difference in the antioxidant ABTS activity of apricot kernels was found in the 2018 harvest year. A similar result was found in previous studies (Chen et al., 2020; Tareen et al., 2021). It could be due to the differences in soil structure, growing conditions, and climatic conditions (Uckun and Aksoy, 2020). In addition, the possible correlations between the antioxidant activities of the kernels were evaluated. It was found that there is no correlation between ABTS activity and DPPH or FRAP antioxidant activities ($r_{ABTS-DPPH}$ = 0.19; $r_{ABTS-FRAP}$ = -0.05), which means that the ABTS content does not change according to the DPPH or FRAP content in apricot kernels. The activity of antioxidant substances is related to their ability to scavenge free radicals, and ABTS activity shows the activity against water-soluble radicals, while other antioxidant activities are related to the activity against radicals formed from oil and alcohol (Gomaa, 2013; Horozic et al., 2020).

The content of DPPH antioxidants in Malatya apricot kernels changed significantly depending on the variety as reported in previous studies (Chen et al., 2020; Gomaa, 2013). In addition, a positive and moderate correlation was found between FRAP and DPPH activity in apricot kernels (r= 0.5), implying that the compounds reacting with the DPPH radical are responsible for a similar reaction with the Fe^{+3}-TPTZ complex (Pitchaon, 2011). A similar result was also reported for other fruit kernel varieties in previous studies (Tareen et al., 2021; Christopoulos and Tsantili, 2011). However, no correlation was found between FRAP and DPPH antioxidant activity in sweet cherry kernels (Afonso et al., 2020). It has been mentioned that genotype plays a crucial role in these correlations for fruit kernels (Korekar et al., 2011).

The antioxidant FRAP contents of Malatya apricot kernels changed significantly depending on the variety, with Hasanbey kernel having the highest antioxidant content. A similar result was also reported by previous studies (Coco and Vinson, 2019; Keser et al., 2014; Korekar et al., 2011), and the kernels examined in this study had higher FRAP antioxidant content than those used previously (7.6μg Fe II/g to 1.6 mg/g) (Gomaa, 2013; Horozic et al., 2020; Korekar et al., 2011; Tareen et al., 2021). In addition, there was a strong correlation between the FRAP content and the TPC of apricot kernels (rho = 0.9) as already found in other studies (Coco and Vinson, 2019; Korekar et al., 2011). Thus, phenols are the main contributors to the antioxidant FRAP activity in apricot seeds.

5. CONCLUSION

In this study, the influence of harvest time and variety on bioactive content in apricot kernels was investigated from 2018 to 2019. Four apricot kernel varieties were used, namely Hacihaliloglu, Hasanbey, and Kabaasi as the sweet apricot type, and Zerdali as the bitter apricot type. The bioactive ingredients investigated were total phenolic content and antioxidant activity.

Overall, the apricot kernels had a total phenolic content of 7 to 15 mg GAE/ 100 g dw; the antioxidant content was between 700 and 1200 mg TE/ g dw in the ABTS assay, between 165 and 190 mg TE/ g dw in the DPPH assay, and between 12 and 66 μmol FE II/ g dw in the FRAP assay. The seeds of sweet apricot varieties had higher bioactive content than the seeds of bitter apricots, and the seeds of the Hasanbey variety had higher bioactive content while the seeds of the Hacihaliloglu variety had lower bioactive content among the sweet apricot varieties, showing that the genotype plays a crucial role in the content of bioactive components, ($p<0.05$).

In addition to the variety, harvest time also had a significant effect on the bioactive content of apricot seeds, indicating that other factors such as soil structure, growing conditions, and climatic conditions also influence the bioactive content of fruit seeds. In addition, a correlation was found between the TPC and FRAP assay of apricot seeds, showing that phenolics are the main contributors to the antioxidant FRAP activity in apricot seeds. In addition, there was a correlation between FRAP and DPPH assays, suggesting that the compounds reacting with the DPPH radical are responsible for a similar reaction with the Fe^{+3}-TPTZ complex.

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Ethical Approval: The study adheres to the ethical guidelines for conducting research.

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