

INVESTIGATION OF PHENOLIC COMPOUNDS IN FRESH AND SUN DRIED APRICOT FRUITS OF DIFFERENT CULTIVARS

Farklı Çeşitlere Ait Taze ve Gün Kurusu Kayısı Meyvelerindeki Fenolik Madde Miktarlarının İncelenmesi

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ABSTRACT

This study has been carried out to compare the amounts of phenolic compounds in fresh and sun dried fruit samples of different apricot varieties. For this purpose, fruit samples were taken from trees belonging to ‘Çataloğlu’, ‘Çöloğlu’, ‘Hacıhaliloğlu’ and ‘Kabaası’ cultivars, some of them were kept at -25°C and some were dried directly in the sun. The p-coumaric acid, epicatechin, ferulic acid, caffeic acid, chlorogenic acid and rutin (µg/g dry matter) contents in the obtained fruit samples were determined using high performance liquid chromatography (HPLC) and UV-DAD detector. Among the phenolic compounds examined, the highest amounts were detected for rutin. Apricot varieties showed statistically significant differences in the phenolic compounds examined, and the highest rutin value was found in the ‘Kabaası’ cultivar with 88.7 µg/g dry matter while the lowest value was determined in the ‘Çataloğlu’ cultivar with 52.1 µg/g dry matter. In general, fresh fruit samples showed higher amounts, and a loss of phenolic compounds was observed in dried fruits of all varieties.

Keywords: Drying, HPLC, Nutrition, Polyphenols, Prunus armeniaca L.

ÖZ

Bu çalışma farklı kayısı çeşitlerine ait taze ve güneşte kurutulmuş meyve örneklerindeki fenolik madde miktarlarının karşılaştırılması amacıyla yürütülmüştür. Bu amaçla ‘Çataloğlu’, ‘Çöloğlu’, ‘Hacıhaliloğlu’ ve ‘Kabaası’ çeşitlerine ait ağaçlardan meyve örnekleri alınmış, bir kısmı -25°C’de muhafaza edilmiş bir kısmı ise doğrudan güneşte kurutulmuştur. Elde edilen meyve örneklerinde p-kumarik asit, epikateşin, ferulik asit, kafeik asit, klorojenik asit ve rutin (µg/g kuru madde) içerikleri yüksek performanslı sıvı kromatografisi (HPLC) ile UV-DAD dedektörü kullanılarak tespit edilmiştir. İncelenen fenolik bileşikler arasında en yüksek miktarlar rutin için tespit edilmiştir. Kayısı çeşitleri incelenen fenolik bileşikler istatistiksel açıdan önemli farklılıklar göstermiş ve en yüksek rutin değeri 88.7 µg/g kuru madde ile ‘Kabaası’ çeşidinde bulunurken en düşük değer ise 52.1 µg/g kuru madde ile ‘Çataloğlu’ çeşidinde tespit edilmiştir. Genel olarak taze meyve örnekleri daha yüksek miktarlar göstermiş olup tüm çeşitlerde kurutulan meyvelerde fenolik bileşikler açısından kayıp gözlenmiştir.

Anahtar kelimeler: Beslenme, HPLC, Kurutma, Polifenoller, Prunus armeniaca L.

INTRODUCTION

Apricot has an important place among stone fruit species which is counted in the *Prunus* genus of the *Prunoideae* subfamily of the *Rosaceae* family of the *Rosales* order of the plant kingdom (Gülcan, Mısırlı, Eryüce, Demir & Sağlam, 2001).

Apricot is described as one of the foods with functional properties due to its composition and it is stated that its consumption has an important place in a healthy life. Phytochemicals are among the most important micronutrients that support human health. It is known that it has a mechanism of action on devastating diseases such as cancer and heart diseases. Polyphenols and carotenoids have the ability to alleviate chronic diseases due to their antioxidant properties (Gardner, White, Mcphail & Duthie, 2000).

Foods rich in antioxidants play an active role in preventing heart diseases, various types of cancer (Bengoechea et al., 1997; Wargovich, 2000), Parkinson's and Alzheimer's and inflammatory diseases, as well as all cellular problems that occur with aging (Prior & Cao, 2000). Researchers have stated that β -carotene and vitamin C delay the onset of clinical symptoms in patients with HIV virus, and anthocyanins reduce the occlusion of the coronary arteries feeding the heart and the risk of heart attack.

Soil quality, climate, insect and herbivorous pest pressures are effective on the nutritional levels of plants (Locasio, Wiltbank, Gull & Maynard, 1984). However, there is little information about the effects of different cultural practices on the production of secondary metabolites in plants (Brandt & Molgaard, 2001). Similarly, the content and amounts of phytochemicals vary on various factors such as sunlight, soil, season, ripening status, agricultural region and fruit cultivar (Haris, 1997). Since antioxidant content has become an important parameter for the quality of fruits and vegetables; Evaluation of changes in antioxidant contents after harvest has been a subject that has attracted considerable attention (Zavala, S. Y. Wang, C. Y. Wang & Aguilar, 2004). Being one of the fruit species having highest phenolic compound contents, various studies on phenolic compound contents of apricots has been performed.

In a study, polyphenol levels in different apricot cultivars were examined and it was reported that chlorogenic acid was the most abundant polyphenol in apricots (Macheix, Fleuriet & Billot, 1990). Other polyphenolic compounds determined in apricots are neochlorogenic acid, caffeic acid, p-coumaric acid, ferulic acid, and even catechin and epicatechin are also present (Arts, Putte & Hollman, 2000). Kaempferol and quercetin, which are flavonols in apricots, occur extensively in the form of rutinoside and glycoside. However, quercetin 3-

rutinoside (rutin) is abundant in apricots (Uzelac, Pospisil, Levaj & Delonga, 2005). In fact, aeskuletin and scopoletin have been detected to a small extent in some apricot varieties (Fernandez de Simon, Perez-Ilzabre & Hernandez, 1992). However, there are very few studies on biochemical changes in apricot fruits at different ripening stages. Amino acids decreased towards ripening and soluble carbohydrates increased (Sharaf, Ahmed & El-Saadany, 1989). The highest amount of chlorogenic acid, kaempferol-3-rutinoside changed and quercetin-3-rutinoside were obtained in the 3rd ripening stage of 11 apricot varieties (Garcia-Viguera, Bridle, Ferreres & Tomas-Barberan, 1994).

Dietary fibers found in dried apricots have many benefits on the digestive system. It has also been observed that dried apricots are rich in cellulose, which is of great importance in a healthy diet. Dried apricots, which contain low levels of B group vitamins, are an important source of β -carotene. The reason why the β -carotene level (2.50 mg/10g) is lower than the literature findings may be due to differences in the drying method applied. It has been noted that the mineral composition of dried apricots is very rich. Despite its low sodium level, it contains high amounts of potassium. With this feature, dried apricots have an important place in healthy nutrition. 1269 mg potassium was found in 100 g of dried apricots. In addition, the iron level was found to be 3.88 mg/100g, the zinc level was 0.61 mg/100g, and the calcium and magnesium levels were 22.87 and 47.08 mg/10g, respectively (Gülcan et al., 2001).

In the aspects of the mentioned factors, this study was conducted to investigate phenolic compound contents of different drying apricot cultivars and compare these compounds in fresh and sun dried fruits of different cultivars. As both fresh and dried usage of apricots is common, the results of the study would be important for consumers and traders as well as the researchers and the growers.

MATERIAL AND METHOD

In this study, 15 years old trees of ‘Çataloğlu’, ‘Çöloğlu’, ‘Hacıhaliloğlu’, and ‘Kabaası’ cultivars planted in 8 × 8 m grid in Apricot Research Institute in Malatya collection orchard were used. Apricot fruit samples were taken from three different trees of each cultivar. Some of the samples were directly kept in the deep freezer at -25°C, and some were dried under the sun. The samples were then analyzed for their p-coumaric acid, epicatechin, ferulic acid, caffeic acid, chlorogenic acid and rutin contents.

For the moisture determination, the method described by Cemeroglu (1992) were used. Then, the polyphenol amounts were determined by calculating the % moisture content in the weighed samples.

Dionex ASE-200 Model accelerated extraction device was used for polyphenol extraction from apricot samples. 50 g apricot samples were taken and extracted in a solvent mixture of methanol: water: TBHQ (70:30:0.1) at 60°C and 1500 psi pressure for 60 minutes. During the extraction process, TBHQ was added to the medium as a stabilizer and antioxidant substance, and was filtered through 0.22 µm filters. Since polyphenols oxidize very quickly, they were completely dried in a vacuum evaporator, then diluted to 2 mL with a mixture of methanol: water (50%: 50%) and passed through 0.22 µm filters again.

To prepare polyphenol standards, 0.001 g of polyphenol was dissolved in deionized pure water and the volume was completed to 1 mL with methanol: pure water (1:1) to prepare polyphenol stock solutions at a concentration of 1000 mg/L. A standard solution mixture was prepared to contain p-coumaric acid, epicatechin, ferulic acid, caffeic acid, chlorogenic acid and rutin 5, 10, 20, 40 mg/L of each polyphenol (Dragovic-Uzelac, Pospisil, Levaj & Delonga, 2005).

Agilent 1100 Series high performance liquid chromatography (HPLC) device was used in the analysis of polyphenols. DAD and UV were used as detectors. A reversed phase ACE 5 C-18-A11608 (250 × 4.6mm, ID) separation column was used.

In the HPLC analysis of polyphenols, a solvent mixture of Eluent A (3% Acetic acid: 97% water) and eluent B (3% Acetic acid: 25% Acetonitrile: 72% water) was used. This gradient profile is given in Table 1.

Table 1. HPLC Analysis Flow Chart

Analysis Duration (min)	Solvent A	Solvent B	Flow rate (mL/min)	Temperature (°C)	Wavelength (nm)
1	100	0	1	30	280, 290, 355, 310, 329
40	30	70	1	30	280, 290, 355, 310, 329
40-45	20	80	1	30	280, 290, 355, 310, 329
45-55	15	85	1.2	30	280, 290, 355, 310, 329
55-57	10	90	1.2	30	280, 290, 355, 310, 329
57-75	10	90	1.2	30	280, 290, 355, 310, 329

The obtained data as a result of the performed analyzes were subjected to Duncan's Multiple Range Test and the statistically significant differences ($P \leq 0.05$) were evaluated using SPSS for Windows 16.0 software.

RESULTS AND DISCUSSION

Within the scope of this study, phenolic compound contents in fresh and sun dried fruit samples of 'Çataloğlu', 'Çöloğlu', 'Hacıhaliloğlu' and 'Kabaşu' apricot cultivars were determined using a UV-DAD detector and HPLC device.

As the result of the analyzes, it was determined that the amounts of p-coumaric acid in fresh and sun dried fruit samples of 'Çataloğlu', 'Çöloğlu', 'Hacıhaliloğlu' and 'Kabaası' cultivars were statistically different from each other. Among the fresh samples, the highest amount of p-coumaric acid was found in the 'Hacıhaliloğlu' cultivar (0.28 µg/g dry matter), while the lowest amount of p-coumaric acid was detected in the 'Çataloğlu' cultivar (0.15 µg/g dry matter). A decrease in the amount of p-coumaric acid was observed in all sun dried samples (Table 2).

In terms of epicatechin levels, it was determined that the amounts of epicatechin in fresh and sun dried samples of 'Çataloğlu', 'Çöloğlu', 'Hacıhaliloğlu' and 'Kabaası' cultivars were statistically different from each other. Among the fresh samples, the highest amount of epicatechin was found in the 'Hacıhaliloğlu' cultivar (8.3 µg/g dry matter), while the lowest amount of epicatechin was detected in the 'Çöloğlu' cultivar (3.2 µg/g dry matter). A decrease in the amount of epicatechin was observed in all sun dried samples (Table 2).

When the apricot samples were examined in terms of ferulic acid levels, it was determined that the amounts of ferulic acid in fresh and sun dried samples of 'Çataloğlu', 'Çöloğlu', 'Hacıhaliloğlu' and 'Kabaası' cultivars were statistically different from each other. Among the fresh samples, the highest amount of ferulic acid was found in the 'Hacıhaliloğlu' cultivar (8.2 µg/g dry matter), while the lowest amount of ferulic acid was detected in the 'Çataloğlu' cultivar (1.4 µg/g dry matter). A decrease in the amount of ferulic acid was observed in all sun dried samples (Table 2).

In terms of caffeic acid levels, it was determined that the amounts of caffeic acid in fresh and sun dried samples of 'Çataloğlu', 'Çöloğlu', 'Hacıhaliloğlu' and 'Kabaası' cultivars were statistically different from each other. Among the fresh samples, the highest amount of caffeic acid was found in the cultivar 'Kabaası' (4.2 µg/g dry matter), while the lowest amount of caffeic acid was found in the cultivar 'Çöloğlu' (1.8 µg/g dry matter). A decrease in the amount of caffeic acid was observed in all sun dried samples (Table 2).

The amounts of chlorogenic acid in fresh and sun dried samples of 'Çataloğlu', 'Çöloğlu', 'Hacıhaliloğlu' and 'Kabaası' cultivars were statistically different from each other. Among the fresh samples, the highest amount of chlorogenic acid was found in the 'Hacıhaliloğlu' cultivar (8.6 µg/g dry matter), while the lowest amount of chlorogenic acid was detected in the 'Çöloğlu' cultivar (2.7 µg/g dry matter). A decrease in the amount of chlorogenic acid was observed in all sun dried samples (Table 2).

When the apricot samples were examined in terms of rutin levels, it was determined that the rutin amounts in fresh and sun dried samples of 'Çataloğlu', 'Çöloğlu', 'Hacıhaliloğlu' and 'Kabaası' cultivars were statistically different from each other. Among the fresh samples, the

highest amount of rutin was found in the cultivar 'Kabaaşı' (88.7 µg/g dry matter), while the lowest amount of rutin was detected in the cultivar 'Çataloğlu' (52.1 µg/g dry matter). A decrease in the amount of rutin was observed in all sun dried samples (Table 2).

Table 2. Detected Phenolic Compound Contents (µg/g) in Fresh and Sun Dried Fruits of the Used Apricot Cultivars

Phenolic Compounds	Çataloğlu		Çöloğlu		Hacıhaliloğlu		Kabaaşı	
	Fresh	Sun Dried	Fresh	Sun Dried	Fresh	Sun Dried	Fresh	Sun Dried
p-coumaric acid	0.15 ^c	0.09 ^d	0.22 ^b	0.14 ^c	0.28 ^a	0.17 ^{bc}	0.21 ^b	0.14 ^c
Epicatechin	7.8 ^{ab}	7.0 ^{ab}	3.4 ^c	2.5 ^d	8.3 ^a	5.1 ^b	4.8 ^b	3.2 ^c
Ferrulic acid	1.4 ^e	0.8 ^f	1.9 ^d	0.9 ^f	8.2 ^a	7.5 ^a	5.4 ^b	4.1 ^c
Caffeic acid	3.8 ^b	3.1 ^c	1.8 ^d	0.9 ^e	3.8 ^b	3.2 ^c	4.2 ^a	3.4 ^c
Chlorogenic acid	4.2 ^c	2.8 ^d	2.7 ^d	1.8 ^e	8.6 ^a	4.9 ^b	2.8 ^d	1.9 ^e
Rutin	52.1 ^c	48.5 ^d	65.5 ^b	56.9 ^b	58.8 ^b	48.5 ^d	88.7 ^a	78.3 ^b
Total	69.5 ^d	62.3 ^e	75.5 ^c	63.1 ^e	88.0 ^b	69.4 ^d	106.1 ^a	91.0 ^b

The differences among the values signed with different letters are significant at $P \leq 0.05$ level

The results indicated that the cultivars show significant variations in terms of the examined phenolic compounds. The obtained data were found in accordance with previous studies (Campbell, Merwin, & Padilla-Zakour, 2013; Garcia-Viguera et al., 1994; Gedük & Ünal, 2022). In the dried samples the phenolic compounds were found to be lower in amount which is an expected result, as the compounds could be lost due to various reasons including reactions as oxidation and biochemical changes related to ripening and the moisture changes. Besides, enzymatic browning reactions constitute another major reason of the lost since the phenolic compounds are used as substrates in the enzymatic reactions (Kaplan, Eskigün, Levent, Diraman & Atik, 2019; Radi, Mahrouz & Jaouad, 1997). Especially the some of the main phenolic compounds, catechin, epicatechin etc., were reported as polyphenol oxidase which is the major enzyme responsible for enzymatic browning of apricot during drying (Eddine Derardja et al., 2022). On the other hand, factors such as temperature, light, ventilation would be effective in the change of the phenolic composition.

When the cultivars are compared, 'Hacıhaliloğlu' was found to give highest amounts in most of the phenolic compounds both in fresh and dried samples. However, 'Kabaaşı' was found as the leading cultivar when the cumulative amounts were compared. Especially 'Hacıhaliloğlu' but also 'Kabaaşı' is more commonly grown by the farmers and these cultivars have higher Total Soluble Solids and lower Titratable Acidity which indicate higher Taste Index (Bügem, 2014; Caliskan, Bayazit & Sumbul, 2012). This fact would be interesting to note that would suggest relation of those contents with phenolic compounds in both fresh and dried

apricot samples. Supportingly, Kan and Bostan (2010) reported higher contents of phenolic compounds for the related cultivars.

CONCLUSION

In this study different drying apricot cultivars were compared in terms of main phenolic compound contents (p-coumaric acid, epicatechin, ferulic acid, caffeic acid, chlorogenic acid and rutin) in both their fresh and sun dried fruits. The study showed that there were significant differences in terms of phenolic compounds among the cultivars which indicated that the cultivar preference has an important effect on the take of phenolic compounds in the dietary. Besides, the study showed that the dried fruits include lower phenolic compounds. In the detected cultivars, ‘Hacıhaliloğlu’ was the leading cultivar in most of the examined phenolic compounds, whereas ‘Kabaası’ was the leader when the total amounts were considered. In all these aspects, the study resulted with original findings that would be beneficial for related stakeholders but also the consumers and the traders.

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