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# Phenolic Profiles of Currant (*Ribes* spp.) Cultivars

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**Abstract**: The present work aimed the study of rutin, protocatechuic, catechin, *p*- hydroxy benzoic, chlorogenic, caffeic, kuersetin, luteolin, kamferol, p-coumaric, vanilin and ferulic acids composition in different currant varieties in Turkey. Red and black currant varieties (Goliath, Red Lake, Rovada, Rosenthal, and Booskop Giant) were analyzed for phenolic acids by using reversed-phase high performance liquid chromatography (HPLC). Results showed that p-coumaric acid (1.66-0.04 µg $g^{-1}$) was the predominant phenolic acid extracted from currant varieties. In addition, other acids, namely rutin (35.41-7.23 µg $g^{-1}$), Protocatechuic (3.28-2.84 µg $g^{-1}$), Chlorogenic (65.49-2.38 µg $g^{-1}$), and kuersetin acids (2.29-1.50 µg $g^{-1}$) were obtained in extracts from currant fruit.

**Keywords:** Currant, HPLC, Phenolic compounds

## Frenküzümü (*Ribes* spp.) Çeşitlerinin Fenolik İçerikleri

**Özet:** Bu çalışmanın amacı Türkiye'de yetiştirilen farklı frenküzümü çeşitlerinin rutin, protocatechuic, catechin, p- hydroxy benzoic, chlorogenic, caffeic, kuersetin, luteolin, kamferol, p-coumaric, vanilin ve ferulic asit içeriklerinin belirlenmesidir. Kırmızı ve siyah frenküzümü çeşitleri (Goliath, Red Lake, Rovada, Rosenthal, and Booskop Giant) ters fazlı yüksek performanslı sıvı kromatografisi kullanılarak fenolik asit içeriklerini belirlemek için analizleri yapılmıştır. Sonuçlar p-coumaric asitin (1.66-0.04 µg g-1) frenküzümü çeşitlerinde baskın fenolik asit olduğunu göstermiştir. Ayrıca frenküzümü meyvelerinden elde edilen ekstraktlardan elde edilen diğer sınuçlarda rutin (35.41-7.23 µg g-1), protocatechuic (3.28-2.84 µg g-1), chlorogenic (65.49-2.38 µg g-1), ve kuersetin asit (2.29-1.50 µg g-1) fenolikleri gözlemlenmiştir.

## Introduction

There is an increasing interest in the inclusion of berries, especially currant in the human diet mainly for the health benefits associated with their consumption. Currant belonging to the genus Ribes is widely cultivated across temperate European countries, Australia, Asia and North America. Currant fruits are suitable for freezing and can be processed into concentrates, jams, jellies, fillings on pies, ice creams, flavoured mineral water, candies and desert toppings. In various countries fruits are of use in production of liqueurs (Brennan 1996).

Also in recent years there has been an increased scientific interest toward the crops belonging to the genus Ribes, not only due to their desired taste but also for the health benefits associated with their consumption (Mitchell et al. 2011). The beneficial effects in its consumption, which include skin and oral health and a reduction in the incidence of metabolic or degenerative diseases like cancer, diabetes, cardiovascular disorders, anti-inflammatory activity, and osteoporosis, among many others, have been directly related with its high content in phenolic acids (Viuda-Martos et al. 2010; Miguel et al. 2010).

Phenolic acids are secondary metabolites that belong to the group of phenolic compounds that are ubiquitously distributed throughout the plant kingdom (Naczk and Shahidi 2004; Luthria 2008). Phenolic phytochemicals play an important role in the normal growth, development and protection in plants (Søltoft et al. 2009). Phenolic acids are known to occur in free and conjugated forms within cells. In a bound form phenolic acids commonly occur as ester linked to other biomolecules. Free phenolic acids are determined by extraction of plant material with aqueous methanol, while soluble-bound phenolic acids are released by hydrolysis of the plant extract, and the total phenolic acids are determined by direct hydrolysis of the plant material (Robbins 2003; Lin and Harnly 2007; Lin and Harnly 2008; Madhujitha and Shahidi 2009).

The study was carried out in order to reveal the importance of black and white currant cultivars in terms of their phenolic compound contents. In the present study, we have evaluated the extraction of red and black currant varieties (Goliath, Red Lake, Rovada, Rosenthal, Booskop Giant) were analyzed for phenolic acids by using reversed-phase high-performance liquid chromatography (HPLC).

## Materials and Methods

HPLC analysis for the identification and quantification of phenolic acids compounds in the currant fruits was conducted at the Pomology Laboratory of the Agriculture Faculty of Suleyman Demirel University, Isparta, Turkey in 2016.

*Plant material and extraction procedure*

Black currant fruits of Rosenthal, Boskoop Giant, Goliath and red currant fruits of red lake and rovada cultivars were collected during commercial harvest time from Kestel-Bursa (40°11'04.73" N, 29°18'47.96" E, height above sea level: 439 m) district in Marmara Region of Turkey. Collected fruits were immediately transferred to the laboratory, rinsed with distilled water to removing of dust or external debris and finally dried with a clean towel. Afterward, the air-dried plant materials were grinded to obtain a fine grade powder. Lipids and waxy compounds of samples (1 g of air-dried plant material) were eliminated using n-hexane (10 ml) for 20 min in an ultrasonic (Power Sonic 505, Korea) bath. Solvent was enforced to evaporation utilizing a rotary-evaporator until dryness. The achieved extracts were treated by 100 ml MeOH:$H_2O$ (1:1) and then sonicated for 20 min. The acquired aqueous extracts were sequentially filtered and centrifuged (10 min) at 13 000 rpm. Finally, extracts were assayed for phenolic compounds constituents by analytical HPLC.

*High performance liquid chromatography (HPLC) analysis*

Phenolic acids compounds were quantified according to the method described by Caponio et al. (1999) with some modifications. Separation of phenolics was carried out with a HPLC system (Cecil Company, English) equipped with a binary pump (CE 4100), Cecil in-line degasser and UV/Vis detector (CE 4201). Phenolic compounds were separated on a symmetry C18 column (250×4.60 mm with 5 µm packing) protected with a corresponding guard column (CTO-10Avp). To avoid the same time elution of some compounds from column encountered in the primary experiments, three different binary solvent systems were employed. The first binary solvent system of the mobile phase consisted of 2% acetic acid in water/methanol, with gradient of 10-100% for the separation of flavanols and phenolcarbonic acids (except for chlorogenic acid). The flow rate and injection volume were 1 ml/min and 20 µl, respectively. Phenolic compounds constituents were detected at 280 nm in short running time of chromatography (30 min). The separated compounds were identified by comparing their retention time (Rt) and UV spectra with those of authentic standards. Quantification was based on an external standard calibration curve. All reference reagents and solvents were afforded from Sigma, Sigma Aldrich and Merck companies.

*Statistical analysis*

The data of two replications were analysed by SPSS (ver. 20) according to one-way ANOVA based on completely randomized design. Mean comparisons were carried out by Duncan's multiple range test at $P \leq 0.05$ probability level.

## Results and Conclusion

The ten phenolic acids found within the analysed currant fruit material were "rutin, protocatechuic, catechin, p- hydroxy benzoic, chlorogenic, caffeic, kuersetin, luteolin, kamferol, p-coumaric, vanilin and ferulic" acids. The black currant extracts possessed generally a much higher content of phenolic acids than the extracts from red currant (Table 1). Great variability determined among the examined currant fruits, regarding their content in Rutin acid. The highest number of Rutin acid was noted in the Rosenthal of black currant (35.41 μg $g^{-1}$ ), while the lowest number was seen in the Boskoop Giant of black currant (15.71 μg $g^{-1}$). Rutin acid was recorded in the Red Lake of red currant cultivar (18.52 μg $g^{-1}$), followed by the Rovada (7.23 μg $g^{-1}$). Protocatechuic acid value in Rosenthal and Boskoop Giant of black currant varieties was 3.28 μg $g^{-1}$ and 2.86 μg $g^{-1}$, respectively. But it wasn't found Protocatechuic acid value in Goliath variety. Protocatechuic acid value was recorded in Red Lake and Rovada of red currant varieties equal (2.84 μg $g^{-1}$). The value of Catechin was found 10.24 μg $g^{-1}$ in Rosenthal (black currant) and 7.09 μg $g^{-1}$ in Rovada (red currant). However, we didn't determine value of Catechin in Boskoop Giant, Goliath (black currant) and Red Lake (red currant) varieties. We just determined p- hydroxy benzoic 1.68 μg $g^{-1}$ in Rovada variety (red currant), it wasn't found p- hydroxy benzoic value of other varieties. Chlorogenic acid value in Rosenthal, Boskoop Giant and Goliath of black currant varieties was found 45.64 μg $g^{-1}$, 65.49 μg $g^{-1}$ and 18.35 μg $g^{-1}$ respectively. It was recorded 2.38 μg $g^{-1}$ Rovada variety (red currant) but we didn't determine Red Lake variety.

Table 1. Phenolic acids content of black and red currant varieties (μg $g^{-1}$)

| | Currant Varieties | | | | |
|---|---|---|---|---|---|
| | Black Currant Varieties | | | Red Currant Varieties | |
| | Rosenthal | Boskoop Giant | Goliath | Red Lake | Rovada |
| Rutin | 35.41 ± 0.14 a* | 15.71 ± 0.13 c | 16.12 ± 0.08 c | 18.52 ± 0.13 b | 7.23 ± 0.01 d |
| Protocatechuic | 3.28 ± 0.03 a | 2.86 ± 0.04 b | ND | 2.84 ± 0.05 b | 2.84 ± 0.13 b |
| Catechin | 10.24 ± 0.54 a | ND | ND | ND | 7.09 ± 0.12 b |
| p- hydroxy benzoic | ND | ND | ND | ND | 1.68 ± 0.05 |
| Chlorogenic | 45.64 ± 0.83 b | 65.49 ± 1.65 a | 18.35 ± 1.15 c | ND | 2.38 ± 0.18 d |
| Caffeic | ND | ND | ND | 0.57 ± 0.03 b | 0.77 ± 0.03 a |
| Quercetin | 2.20 ± 0.08 ab | 1.50 ± 0.01 c | 1.61 ± 0.02 c | 2.29 ± 0.08 a | 2.01 ± 0.01 b |
| Luteolin | ND | ND | ND | 0.63 ± 0.00 | ND |
| Kamferol | ND | ND | ND | 0.92 ± 0.01 a | 1.14 ± 0.01 b |
| Vanilin | ND | ND | ND | ND | 0.73 ± 0.01 |
| p-Coumaric | 1.64 ± 0.01 a | 1.66 ± 0.01 a | 0.71 ± 0.01 b | ND | 0.04 ± 0.00 c |
| Ferulic | ND | 0.54 ± 0.00 | ND | ND | ND |

*:There are significant differences ($p<0.05$) among the cultivars having different letters. ND:No detected

The Caffeic acid wasn't found in black currant varieties, while it was found (Rovada) 0.77 μg $g^{-1}$ - 0.57 μg $g^{-1}$ (Red Lake) in red currant varieties. Kuersetin acid was determined 2.20 μg $g^{-1}$, 1.50 μg $g^{-1}$ and 1.61 μg $g^{-1}$ in Rosenthal, Boskoop Giant and Goliath of black currant varieties, 2.29 μg $g^{-1}$ -2.01 μg $g^{-1}$ Red Lake and Rovada varieties of red currant varieties. We just determined Luteolin acid 0.63 μg $g^{-1}$ in Red Lake variety (red currant), it wasn't found Luteolin acid value of other varieties. The kamferol acid wasn't found in black currant varieties, while it was found (Rovada) 1.14 μg $g^{-1}$ - 0.92 μg $g^{-1}$ (Red Lake) in red currant varieties. We only determined Vanilin acid 0.73 μg $g^{-1}$ in Rovada variety (red currant), it wasn't found Vanilin of other varieties. It was found p-Coumaric acid value 1.64 μg $g^{-1}$, 1.66 μg $g^{-1}$ and 0.71 μg $g^{-1}$ in Rosenthal, Boskoop Giant and Goliath of black currant varieties. p-Coumaric acid was 0.04 μg $g^{-1}$ in Rovada variety (red currant), while it wasn't found in red lake variety of red currant. We only determined

Ferulic acid 0.54 μg $g^{-1}$ in Boskoop Giant variety (black currant), it wasn't found Ferulic value of other varieties.

In generally, our values data for the phenolic acids in currant are in accordance with earlier reports (Häkkinen et al. 1999; Kris-Etherton 2002; Benvenuti et al. 2004). According to Häkkinen et al. (1999), *p*-coumaric acid, ferulic acid, and quercetin were the most abundant phenolics in wild berries. Borges et al. (2010) determined that the amount of chlorogenic acid contained by black and red currants among berry fruits were 80 and 89 nmol $g^{-1}$, respectively. The same compounds were found in our studies. Chlorogenic acid was also detected in all currant varieties. This is in agreement with the study of Jakobek et al. (2007), who reported the currant varieties species to contain significant amounts of chlorogenic acid. The phenolic acids profiles of currant varieties obtained are the result of analysis of the antiradical components contained in currant and thus may help to provide a better understanding of the health benefits of different currant. The variations in the phenolic acids profiles of various currant found may be related to their significantly different variety and biological activities. Biochemical compounds may emerge at different levels due to factors such as genetic factors, cultural applications, climate conditions, and soil structure (Celik et al. 2007; Hegedus et al. 2010; Ruttanaprasert et al. 2014). Therefore, more detailed studies are necessary to evaluate the contribution of each phenolic acids of currant. This is generally considered to be dependent on their structure and content in currant.

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