

## PHYTOCHEMICAL PROFILES OF WILD GROWN BLACKBERRY AND MULBERRY IN TURKEY

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**Abstract.** Blackberry and mulberry are main berry crops grown in Black Sea region mostly in humid shade forest areas and its important for local people's diet and also important for the maintenance of their health and prevention of disease. Present study aimed to determine the content of vitamin C, organic acids (citric acid, tartaric acid, oxalic acid, malic acid, succinic acid, fumaric acid), sugars (glucose and fructose) and phenolic compounds (catechin, rutin, quercetin, chlorogenic acid, ferulic acid, o-coumaric acid, p-coumaric acid, caffeic acid, syringic acid, vanillic acid, and gallic acid), as well as antioxidant capacity (Trolox Equivalent Antioxidant Capacity, TEAC assay) in the wild grown blackberry and mulberry fruit. Among phenolic acids, chlorogenic acid was the predominant for all wild grown blackberries, white and black mulberries. The presence of oxalic acid was only detected in the wild blackberry genotype. As a result, the phytochemical recognition of the wild grown blackberry, black and white mulberries might contribute to forthcoming investigations for developing the efficiency of food industry.

**Key words:** Antioxidant, berries, organic acids, phenolic compounds

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## INTRODUCTION

Horticultural plants including berries have long been valued as part of a nutritious and tasty diet and there is increasing scientific awareness that fruits play an important role for human nutrition and health [Ozturk et al. 2009, Bacvonkralj et al. 2014, Rop et al. 2014].

Berry crops contain high non-nutritive antioxidants called phytochemicals, which help to reduce the risk of chronic diseases such as heart disease, diabetes, obesity, cancer and neurodegenerative diseases. Antioxidants are involved in the prevention of free-radical-induced damage to the DNA, eliminating free radicals and influencing enzyme actions in the cells and organs. These are the events that cause aging and damage to blood vessel walls and internal organs and can then lead to chronic diseases. [Herrera et al. 2009, Contessa et al. 2013].

Phenolic compounds and vitamins are among the healthy phytochemicals indispensable in human diet. Organic acids are another constituent of the phytonutrients beneficial for human health and organoleptically important in fruit flavor characterization together with sugar content [Eyduran et al. 2015a].

Recent years berry crops in particular blackberry, raspberry, blueberry, mulberry, strawberry etc. are especially preferred by increase of consumer's conscious because of these fruits possess rich phytochemical composition and antioxidant capacity which could vary with species and environmental conditions [Espin et al. 2007, Huang et al. 2012, Contessa et al. 2013, Eyduran et al. 2015a].

Therefore, in recent studies on phytochemical content and antioxidant properties of berries cultivated in diverse parts of the world like Turkey [Ercisli and Orhan 2007, Koca and Karadeniz 2009, Yilmaz et al. 2009, Yildiz et al. 2010], Italy [Contessa et al. 2013], Serbia [Stajcic et al. 2012], Slovenia [Mikulic-Petkovsek et al. 2012], USA [de Sousa et al. 2014] and New Zealand [Connor et al. 2005] the non-genetic and genetic effects were also underlined.

Blackberry and mulberry worldwide are preferable as functional foods in food industry with the goal of reducing disease risk and their acceptability should be inquired in food industry and breeding strategies. Therefore, more elaborated investigations on characterization of the species currently available in Turkey are still unsatisfactory from the point of conservation of germplasm when considered from these aspects. In addition, there is lack of information on phytochemical properties of blackberries and mulberries grown wild in the Giresun province of Black Sea Region of Turkey. Herewith, the objective of this research was to identify the total antioxidant capacity and phytochemical profiles of blackberries and mulberries grown wild in the Giresun province of Black Sea Region/Turkey, which has a mild climate with high precipitation rate.

## MATERIALS AND METHODS

**Plant Material.** To ascertain phytochemical properties of wild blackberries (*Rubus fruticosus* L.), white mulberries (*Morus alba* L.) and black mulberries (*Morus nigra* L.) fruit samples were collected in the summer of the year 2013 from the villages Bülbüllü and Nefsişiraziz of Giresun province located in the Black Sea Region of northeastern Turkey. The coordinate of Giresun is 40.9153°N, 38.3894°E.

**Analysis of organic acids.** Slightly modified method of Bevilacqua and Califano [1989] was adopted to analyze succinic, citric, malic, fumaric and tartaric acid content as also indicated by Eyduran et al. [2015a]. Berries were mashed within cheesecloth and the juice samples were stored at (-20°C), and prior to analyzing they were thawed overnight in room temperature. 5 ml of each sample was blended with 20 ml 0.009 N H<sub>2</sub>SO<sub>4</sub> (Heidolph Silent Crusher M, Germany) on a shaker (Heidolph Unimax 1010, Germany) for 1 hour, after that the pulps were centrifuged for 15 min at 15000 × g. The supernatants were filtrated twice by 0.45 µm membrane filter (Millipore Millex-HV Hydrophilic PVDF, Millipore, USA), and run on SEP-PAK C18 cartridge using Aminex column (HPX-87 H, 300 × 7.8 mm, Bio-Rad Laboratories, Richmond, CA, USA). The absorbance range was adjusted as 214 and 280 nm and Agilent package with DAD detector was utilized.

**Analysis of phenolic compounds.** Modified method of Rodriguez-Delgado et al. [2001] was handled to determine gallic acid, catechin, chlorogenic acid, caffeic acid, p-coumaric acid, o-coumaric acid, ferulic acid, vanillic acid, rutin, oxalic acid, syringic acid and quercetin phenolic compounds as described by Eyduran et al. [2015b]. Sample juices were diluted with distilled water in a ratio of 1 : 1, and centrifuged for 15 min at 15000 × g. Supernatants were filtered twice through 0.45 µm membrane filter (Millipore Millex-HV Hydrophilic PVDF, Millipore, USA) prior to loading to 1100 (Agilent) HPLC system with DAD detector (Agilent, USA) and 250 × 4.6 mm, 4 µm ODS column (HiChrom, USA). Methanol : acetic acid : water (solvent A) in a ratio of 10 : 2 : 28 eluted by methanol:acetic acid:water (solvent B) in a ratio of 90 : 2 : 8 with 1 mL/min flow rate and 20 µL injection volume at 254 and 280 nm wavelengths were arranged for equilibration.

**Sugar analysis.** A modification of the method described by Melgarejo et al. [2000] and Eyduran et al. [2015c] was used for sugar analysis. Fructose and glucose were used as standards. After homogenized on a shaker, juice samples from berries were centrifuged for 2 min at 12000 × g. Supernatants were filtrated and run on SEP-PAK C18 column. 85% solvent B (acetonitrile liquid phase) within µbondapak-NH<sub>2</sub> column of HPLC device with a refractive index detector was employed for elution. Sugar composition from the assessed berries was determined with fruit juice standards.

**Analysis of ascorbic acid.** From the berries, 5 ml of each sample juice was blended with M-phosphoric acid solution, and centrifuged for 10 min at 6500 × g and 4°C. 0.5 ml of each supernatant was complemented to 10 ml with % 2.5 M-phosphoric solution, after that filtrated with 0.45 µm teflon filter. Samples were loaded to HPLC device with C18 column (Phenomenex Luna C18, 250 × 4.60 mm, 5 µ) at 25°C. Ultra distilled water at acidic 2.2 pH was arranged as a mobile phase. Readings were made by DAD detector at 254 nm wavelength. Diverse concentration levels of L-ascorbic acid (SigmaA5960) (50, 100, 500, 1000, and 2000 ppm) were considered to determine ascorbic acid composition [Cemeroglu 2007].

**Determination of trolox equivalent antioxidant capacity (TEAC).** For TEAC analysis ABTS acetate was dissolved with potassium persulphate in a buffer [Ozgen et al. 2009]. ABTS<sup>+</sup> was diluted with 20 mM sodium acetate buffer at 4.5 pH and 734 nm wavelength, 0.700 ± 0.01 for long storage. Spectrophotometric readings were implemented with mixture of 3 ml ABTS<sup>+</sup> solution and 20 µl fruit extract which were incubated for 10 min.

**Statistical analysis.** A total 100 fruits (25 fruits per replicate) sampled from per species and used for analysis. Descriptive statistics were calculated as mean  $\pm$ SE for all the phytochemical characteristics evaluated in the study.

Table 1. Phytochemical contents of blackberry and mulberries from Black Sea Region of Turkey

	White Mulberry	Black Mulberry	Blackberry
Citric acid (g 100 g <sup>-1</sup> )	0.840 $\pm$ 0.015	1.163 $\pm$ 0.026	0.953 $\pm$ 0.014
Tartaric acid (g 100 g <sup>-1</sup> )	0.371 $\pm$ 0.009	0.233 $\pm$ 0.018	ND
Malic acid (g 100 g <sup>-1</sup> )	2.107 $\pm$ 0.037	1.947 $\pm$ 0.009	0.910 $\pm$ 0.021
Succinic acid (g 100 g <sup>-1</sup> )	0.360 $\pm$ 0.011	0.140 $\pm$ 0.006	0.297 $\pm$ 0.014
Fumaric acid (g 100 g <sup>-1</sup> )	0.033 $\pm$ 0.003	0.023 $\pm$ 0.003	0.020 $\pm$ 0.000
Oxalic acid (g 100 g <sup>-1</sup> )	ND	ND	0.087 $\pm$ 0.003
TEAC	8.613 $\pm$ 0.027	12.230 $\pm$ 0.064	4.490 $\pm$ 0.120
Vitamin C (mg 100 g <sup>-1</sup> )	16.686 $\pm$ 0.023	13.160 $\pm$ 0.032	13.330 $\pm$ 0.049
Fructose (g 100 g <sup>-1</sup> )	5.270 $\pm$ 0.035	8.610 $\pm$ 0.046	16.186 $\pm$ 0.272
Glucose (g 100 g <sup>-1</sup> )	6.143 $\pm$ 0.055	9.180 $\pm$ 0.043	8.507 $\pm$ 0.133
Catechin (mg g <sup>-1</sup> )	0.035 $\pm$ 0.001	0.063 $\pm$ 0.003	0.082 $\pm$ 0.004
Rutin (mg g <sup>-1</sup> )	1.114 $\pm$ 0.005	1.334 $\pm$ 0.005	0.842 $\pm$ 0.062
Quercetin (mg g <sup>-1</sup> )	0.082 $\pm$ 0.002	0.065 $\pm$ 0.001	0.141 $\pm$ 0.003
Chlorogenic acid (mg g <sup>-1</sup> )	1.663 $\pm$ 0.003	2.126 $\pm$ 0.008	2.324 $\pm$ 0.008
Ferulic acid (mg g <sup>-1</sup> )	0.065 $\pm$ 0.002	0.024 $\pm$ 0.001	0.097 $\pm$ 0.004
o-coumaric acid (mg g <sup>-1</sup> )	0.051 $\pm$ 0.002	0.166 $\pm$ 0.003	0.098 $\pm$ 0.003
p-coumaric acid (mg g <sup>-1</sup> )	0.045 $\pm$ 0.001	0.061 $\pm$ 0.001	0.098 $\pm$ 0.003
Caffeic acid (mg g <sup>-1</sup> )	0.122 $\pm$ 0.001	0.108 $\pm$ 0.001	0.178 $\pm$ 0.002
Syringic acid (mg g <sup>-1</sup> )	0.049 $\pm$ 0.001	0.037 $\pm$ 0.001	0.159 $\pm$ 0.004
Vanillic acid (mg g <sup>-1</sup> )	0.040 $\pm$ 0.002	0.036 $\pm$ 0.001	0.052 $\pm$ 0.002
Gallic acid (mg g <sup>-1</sup> )	0.141 $\pm$ 0.002	0.430 $\pm$ 0.004	0.312 $\pm$ 0.003

Phytochemical composition of blackberry, white and black mulberry fruits under wild condition of Black Sea Region of Turkey are given in Table 1. The content of citric acid, glucose, o-coumaric acid, and gallic acid in descending order, was black mulberry > blackberry > white mulberry. The phytochemical compounds with the order white mulberry > black mulberry > blackberry were malic acid and fumaric acid. The descending order white mulberry > blackberry > black mulberry was recorded for succinic acid and vitamin C. The highest quantities of quercetin, ferulic acid, caffeic acid, syringic acid, and vanillic acid were detected in blackberry. The order of numerical magnitude, blackberry > black mulberry > white mulberry was satisfied for fructose, catechin, chlorogenic acid, and p-coumaric acid. The order of black mulberry > white mulberry > blackberry was appeared possible for antioxidant capacity (TEAC), and rutin. Oxalic acid was only extracted in blackberry fruits. In the Melekli district of Iğdir province of Turkey, Eyduran et al. [2015c] biochemically remarked that the predominant phenolic compound for mulberries was chlorogenic acid, followed by rutin. With the survey of Table 1, several fluctuations were appeared in levels of the bioactive compounds among blackberry and mulberries consumed preferably for medical objectives by virtue of the variability of genotypic or climatic conditions.

**White mulberry.** Mulberries are attractive and salubrious fruits due to the availability of sugar, organic and phenolic acids. Gundogdu et al. [2011] reported greater glucose and fructose contents for white mulberry fruits at harvest time (6.864 and 6.269 g 100 g<sup>-1</sup>, respectively) with compared to corresponding contents obtained in the present work. Sanchez et al. [2014] made a phytochemically examination of eight Spanish white (MA1, MA2, MA3, and MA4) and black mulberry (MN1, MN2, MN3, and MN4) clones, and they recorded the following values for Spanish white mulberry clones: 4.88, 4.22, 5.05, and 5.37 g 100 g<sup>-1</sup> for glucose content; 7.41, 6.53, 7.68, and 8.55 g 100 g<sup>-1</sup> for fructose content; 0.04, 0.14, 0.07 and 0.18 g 100 g<sup>-1</sup> for citric acid; 0.66, 0.58, 0.68, and 0.79 g 100 g<sup>-1</sup> for malic acid, and 0.02, 0.03, 0.03, and 0.03 g 100 g<sup>-1</sup> for tartaric acid, respectively. In the phytochemical valuation of two white mulberry genotypes (76-IGD-4 and 76-IGD-5) under Melekli district wild condition of Iğdir province of the Eastern Anatolia Region of Turkey, Eyduran et al. [2015c] detected of citric acid (0.687–0.480 g 100 g<sup>-1</sup>, respectively), tartaric acid (0.153–0.430 g 100 g<sup>-1</sup>, respectively), malic acid (2.103–1.130 g 100g<sup>-1</sup>, respectively), succinic acid (0.267–0.437 g 100 g<sup>-1</sup>, respectively), fumaric acid (0.100–0.123 g 100 g<sup>-1</sup>, respectively), glucose (9.437–5.337 g 100 g<sup>-1</sup>, respectively), and fructose contents (7.700–4.057 g 100 g<sup>-1</sup>, respectively).

In the study of Gundogdu et al. [2011], TEAC content of the white mulberry (4.494 mg 100 g<sup>-1</sup>) was nearly half of the wild mulberry TEAC content declared in our study (tab. 1). For antioxidant activity (TEAC) of two white mulberry genotypes, Eyduran et al. [2015c] found it as 6.170 and 9.273 μmol TE g<sup>-1</sup>, respectively (P < 0.05). The TEAC content of available white mulberry in our study was between those notified by Eyduran et al. [2015c]. Whereas, Gundogdu et al. [2011] obtained higher content for vitamin C (24.422 mg 100 g<sup>-1</sup>) than that obtained in the present study. The wild white mulberry tested in our study produced either greater or lower content compared to the vitamin C content of 76-IGD-4 or 76-IGD-5 white mulberry genotypes (18.220 mg 100 g<sup>-1</sup> or 13.400 mg 100 g<sup>-1</sup>) reported by Eyduran et al. [2015c]. The vitamin C level of the wild grown white mulberry genotype under Iğdir micro-climate condition was lower in comparison to the vitamin C levels of the prominent white and red mulberries (25.20 and 30.60 mg 100 g<sup>-1</sup>, respectively) of Pakistan [Iqbal et al. 2010]. Several phenolic compounds; namely, catechin (0.032–0.070 mg g<sup>-1</sup>), rutin (0.750–0.925 mg g<sup>-1</sup>), quercetin (0.101–0.045 mg g<sup>-1</sup>), chlorogenic acid (2.667–0.980 mg g<sup>-1</sup>), ferulic acid (0.110–0.141 mg g<sup>-1</sup>), o-coumaric acid (0.062–0.026 mg g<sup>-1</sup>), p-coumaric acid (0.065–0.127 mg g<sup>-1</sup>), caffeic acid (0.094–0.134 mg g<sup>-1</sup>), syringic acid (0.115–0.060 mg g<sup>-1</sup>), vanillic acid (0.074–0.017 mg g<sup>-1</sup>), and gallic acid (0.206–0.214 mg g<sup>-1</sup>) were extracted from two wild white mulberry genotypes (76-IGD-4 and 76-IGD-5) in studies performed by Eyduran et al. [2015c]. Higher content of quercetin, chlorogenic acid, ferulic acid, o-coumaric acid, p-coumaric acid, vanillic acid, and gallic acid in the fruit of 76-IGD-4 white mulberry genotype was found compared to the results obtained for wild grown white mulberry in our study, whereas higher content of catechin, o-coumaric acid, p-coumaric acid, syringic acid, and gallic acid was also found for 76-IGD-5 white mulberry genotype.

**Black Mulberry.** The vitamin C level of the wild grown black mulberry genotype under Black Sea condition was far less than the vitamin C levels of 32.25 and 30.60 mg

100 g<sup>-1</sup> for the prominent black and red mulberries in Pakistan reported by Iqbal et al. [2010]. In the work conducted before on phytochemical properties of black mulberry fruits at various harvest time, Gundogdu et al. [2011] enunciated lower glucose and fructose contents with 7.748 and 5.634 g 100 g<sup>-1</sup> compared with corresponding contents depicted in Table 1. On the other hand, Mikulic-Petkovsek et al. [2012] reported much higher values of glucose (36.8 g kg<sup>-1</sup>) and fructose content (39.9 g kg<sup>-1</sup>) in the fruits of cultivated black mulberry from the central Slovenia. The same authors also detected the following organic acids in this fruit: citric acid (4.50 g kg<sup>-1</sup>), malic acid (0.74 g kg<sup>-1</sup>), and fumaric acid 67.7 mg kg<sup>-1</sup>. Ozgen et al. [2009] reported several ranges for fructose (4.86 to 6.41 g 100 mL<sup>-1</sup>), glucose (5.50 to 7.12 g 100 mL<sup>-1</sup>), malic acid (0.10 to 0.23 g 100 mL<sup>-1</sup>), vitamin C (0.003 g 100 mL<sup>-1</sup>) and citric acid (1.45 to 2.68 g 100 mL<sup>-1</sup>) extracted from fruits of 14 black mulberry accessions fully matured in the framework of a nationwide mulberry selection program conducted in Turkey. According to Sanchez et al. [2014], four Spanish black mulberry (MN1, MN2, MN3, and MN4) clones, contained glucose (3.19, 4.91, 7.45, and 7.21 g 100 g<sup>-1</sup>), fructose (4.82, 7.59, 11.70, and 11.40 g 100 g<sup>-1</sup>), citric acid (0.66, 0.25, 0.14, and 0.18 g 100 g<sup>-1</sup>), malic acid (0.41, 0.69, 0.72, and 0.79 g 100 g<sup>-1</sup>) and tartaric acid (0.04, 0.04, 0.04, and 0.03 g 100 g<sup>-1</sup>), respectively. Lower glucose (3.99 g 100 g<sup>-1</sup>) and fructose (3.68 g 100 g<sup>-1</sup>) levels of the black mulberry under the wild Slovenia condition were identified by Mikulic-Petkovsek et al. [2012]. Eyduran et al. [2015c] confirmed the presence of citric acid (0.877, 0.733 and 1.033 g 100 g<sup>-1</sup>), tartaric acid (0.147, 0.223, and 0.297 g 100 g<sup>-1</sup>), malic acid (1.210, 2.713 and 3.040 g 100 g<sup>-1</sup>), succinic acid (0.280, 0.360, and 0.117 g 100 g<sup>-1</sup>), fumaric acid (0.010, 0.057, and 0.107 g 100 g<sup>-1</sup>), glucose (6.173, 6.247, and 8.573 g 100 g<sup>-1</sup>), and fructose (5.620, 4.163, and 7.167 g 100 g<sup>-1</sup>) contents ( $P < 0.05$ ) for the wild grown three black mulberry genotypes, 76-IGD-1, 76-IGD-2, and 76-IGD-3, under microclimate condition in the Eastern Anatolia Region of Turkey, respectively. The variability could be explained by various extraction methods, in contrast to those used in this study.

With the extensive investigation of bioactive compounds of the wild mulberry genotypes, Koyuncu [2004] found malic acid (35.55 to 198.50 mg g<sup>-1</sup>), citric acid (8.80 to 23.40 mg g<sup>-1</sup>), tartaric acid (3.05 to 5.95 mg g<sup>-1</sup>), oxalic acid (0.348 to 1.176 mg g<sup>-1</sup>), and fumaric acid (0.015 to 0.033 mg g<sup>-1</sup>) for the wild blackberries taken from Mahmatlar district located in Isparta province of Turkey. The author stated malic acid (35.40 to 93.90 mg g<sup>-1</sup>), citric acid (5.50 to 9.60 mg g<sup>-1</sup>), tartaric acid (2.95 to 4.05 mg g<sup>-1</sup>), oxalic acid (0.344 to 0.847 mg g<sup>-1</sup>), along with fumaric acid (0.010 to 0.018 mg g<sup>-1</sup>) for Sutculer district of Isparta province of Turkey where the wild black mulberries were discovered. Ercisli and Orhan [2007] reported that malic acid contents (123 to 218 mg g<sup>-1</sup>) were almost 5-fold higher than citric acid contents (21 to 41 mg g<sup>-1</sup>) for five black mulberry genotypes in respect of Northeast Anatolia Region of Turkey.

Within the scope of a special mulberry breeding program in Turkey, TEAC of 14 fully matured black mulberry accessions, was identified ranging from 6.8 to 14.4  $\mu\text{mol TE g}^{-1}$  [Ozgen et al. 2009]. Antioxidant activity (12.230  $\mu\text{mol TE g}^{-1}$ ) of the wild black mulberry detected in this study was lower than that reported by Gundogdu et al. [2011] for black mulberry of Van province located in the Eastern Anatolia Region of Turkey; however, TEAC contents with reference to half of the black mulberry accessions evaluated by Ozgen et al. [2009] were greater than the content of the wild grown blackberry

genotype in this investigation. Ercisli et al. [2010] found vitamin C levels of four black (MN1, MN2, MN3 and MN4) along with four purple (MR1, MR2, MR3, and MR4) mulberry genotypes of Coruh valley with the corresponding orders: 22.60, 18.10, 21.35 and 21.10 mg 100 ml<sup>-1</sup> as well as 19.02, 18.71, 18.12 and 19.64 mg 100 ml<sup>-1</sup>, respectively.

In the study of the phytochemical properties of the black mulberry genotypes (76-IGD-1, 76-IGD-2, and 76-IGD-3) conducted by Eyduran et al. [2015c], there were a great number of phenolic compounds accounted for free radical scavenging mechanism such as: catechin (0.085, 0.046 and 0.066 mg g<sup>-1</sup>), rutin (0.820, 1.365, 1.238 mg g<sup>-1</sup>), quercetin (0.119, 0.067 and 0.137 mg g<sup>-1</sup>), chlorogenic acid (2.339, 1.641 and 0.759 mg g<sup>-1</sup>), ferulic acid (0.036, 0.023 and 0.063 mg g<sup>-1</sup>), o-coumaric acid (0.034, 0.129 and 0.043 mg g<sup>-1</sup>), p-coumaric acid (0.111, 0.062 and 0.035 mg g<sup>-1</sup>), caffeic acid (0.114, 0.094 and 0.158 mg g<sup>-1</sup>), syringic acid (0.119, 0.053 and 0.085 mg g<sup>-1</sup>), vanillic acid (0.035, 0.011 and 0.062 mg g<sup>-1</sup>), and gallic acid (0.122, 0.410 and 0.105 mg g<sup>-1</sup>), respectively.

**Blackberry.** Kafkas et al. [2006] analyzed sugars, organic acids, and vitamin C contents of five blackberry cultivars (C. Thornless, Bursa 2, Navaho, Jumbo and Loch Ness) in Adana province in the Mediterranean Region of Turkey with HPLC and presented evidence that the predominant organic acid was malic acid, and fructose was the sugar with the most ample content for the blackberries grown. For the cultivated and wild grown blackberries, Mikulic-Petkovsek et al. [2012] designated glucose (26.70 and 35.30 g kg<sup>-1</sup>), fructose (26.90 and 35.40 g kg<sup>-1</sup>), citric acid (5.60 and 4.10 g kg<sup>-1</sup>), malic acid (2.05 and 1.11 g kg<sup>-1</sup>), tartaric acid (ND and ND), and fumaric acid (34.1 and 30.7 mg kg<sup>-1</sup>) at commercially harvest time.

In the current study, the blackberry genotype from Black Sea Region of Turkey had the vitamin C level of 13.330 mg 100 g<sup>-1</sup>, which was slightly lower than those documented by Yildiz et al. [2010], who extracted vitamin C for ten wild (ART1 = 16.70 mg 100 g<sup>-1</sup>, ART2 = 17.15 mg 100 g<sup>-1</sup>, ART3 = 15.36 mg 100 g<sup>-1</sup>, ART4 = 14.15 mg 100 g<sup>-1</sup>, ART5 = 14.05 mg 100 g<sup>-1</sup>, ART6 = 16.70 mg 100 g<sup>-1</sup>, ART7 = 15.10 mg 100 g<sup>-1</sup>, ART8 = 15.40 mg 100 g<sup>-1</sup>, ART9 = 16.20 mg 100 g<sup>-1</sup> and ART10 = 14.70 mg 100 g<sup>-1</sup>), and one cultivated (Chester = 14.30 mg 100 g<sup>-1</sup>) blackberries from Coruh valley of Turkey. Ochmian et al. [2009] identified p-coumaric acid (0.9 mg 100 g<sup>-1</sup>) and vitamin C (11 mg 100 g<sup>-1</sup>) lower amounts of the wild blackberry) at full ripening stage from a forest near Szczecin of Poland. Similarly, Mikulic-Petkovsek et al. [2012] did not identified tartaric acid in the cultivated and wild blackberries as also highlighted in Table 1, but they recorded much higher quantities in the total phenolics of the wild grown blackberries, compared to the cultivated ones. The knowledge is precious for conscious consumers who pay attention to their own health and food safety as well as for plant breeders to pick more phytochemically valuable plants agreeable to food industry. Attending Choctaw and Kiowa blackberry cultivars of Georgia in USA, Sellappan et al. [2012] detected the presence of caffeic acid (1.38 and 3.64 mg 100 g<sup>-1</sup>), p-coumaric acid (2.08 and 0.40 mg 100 g<sup>-1</sup>), ferulic acid (2.51 and 2.99 mg 100 g<sup>-1</sup>), and catechin (312.86 and 265.75 mg 100 g<sup>-1</sup>) as a flavonoid, which were extremely lower than the values obtained for wild grown blackberry discussed in Table 1, and keynoted that total anthocyanins and polyphenols of blackberries were very strongly associated with TEAC values. Kafkas et al. [2006] mentioned that antioxidant activity was liable

for recovering metabolic disorders, and the presence of fructose (33.8, 25.1, 25.5, 21.1 and 30.2 mg g<sup>-1</sup>), glucose (26.1, 16.9, 16.6, 15.8 and 20.3 mg g<sup>-1</sup>), and sucrose (2.6, 1.5, 1.4, 1.2 and 2.0 mg g<sup>-1</sup>) of Navaho, Chester Thornless, Jumbo, Bursa 2, and Loch Ness blackberry cultivars grown in Mediterranean Region of Turkey, respectively ( $P < 0.05$ ). In Brazos and Tupy blackberries cultivated in Southern Brazil, Zielinski et al. [2015] detected much lower contents of glucose (3.11 and 3.30 g 100 g<sup>-1</sup>, respectively) and fructose (2.86 and 2.49 g 100 g<sup>-1</sup>, respectively). The markedly lower amounts of the sugars were also noted by Zielinski et al. [2015]. The variability might be due to the presence of the changeableness of agro-climatic conditions [Eyduran et al. 2015a, b, c], hereditary variation (cultivar, species), and cultural applications.

## CONCLUSION

In literature, phytochemical compounds and antioxidant activity of the wild grown blackberry, white and black mulberry genotypes under the wild conditions of Black Sea Region of Turkey have been insufficiently detected. However, the first investigation for these bioactive compounds of the wild blackberry and mulberries has been elaborated herein. The salient results with the investigation can be summarized that:

1. The predominant organic acid for the wild grown white and black mulberry genotypes was malic acid.

2. More remarkable antioxidant activity was reported for the black mulberry compared to white mulberry. Among the studied phenolic acids, chlorogenic acid ranked the highest for blackberry, white and black mulberries under the wild condition. The presence of oxalic acid was only in the wild blackberry genotype.

Most wild grown blackberries undiscovered in phytochemical properties and antioxidant activities were still available for developing more profitable genotypes in plant breeding and more qualified food products in the enrichment of present food products in the human health. The nature introduces unlimited options to breeders in this regard.

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## FITOCHEMICZNY PROFIL DZIKIEJ CZARNEJ JAGODY I MORWY W TURCJI

**Streszczenie.** Czarna jagoda i morwa należą do głównych owoców jagodowych uprawianych w rejonie Morza Czarnego w wilgotnych cieniistych obszarach. Są one też ważne w diecie lokalnych mieszkańców, dla utrzymania zdrowia oraz zapobiegania chorobom. Celem niniejszego badania jest określenie zawartości witaminy C, kwasów organicznych (cytrynowego, winowego, szczawiowego, jabłkowego, bursztynowego, fumarowego), cukrów (glukozy i fruktozy), związków fenolowych (katechiny, rutyny, kwercetyny, kwasów: chlorogenowego, ferulowego, o-kumarowego, p-kumarowego, kawowego, syryngowego, wanilinowego i galusowego), a także pojemności antyoksydacyjnej (pojemność przeciwutleniająca wyrażona w równoważnikach, test TEAC) w owocach dziko rosnącej czarnej jagody i morwy. Dominującym kwasem wśród kwasów fenolowych dla wszystkich uprawianych czarnych jagód oraz białej i czarnej morwy był kwas chlorogenowy. Obecność kwasu szczawiowego była wykryta tylko w genotypie dzikiej czarnej jagody. Fitochemiczna analiza dziko rosnącej czarnej jagody oraz czarnej i białej morwy może zatem przyczynić się do kolejnych badań zmierzających do zwiększenia wydajności przemysłu spożywczego.

**Słowa kluczowe:** antyutleniacz, jagody, kwasy organiczne, związki fenolowe

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