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ANTIOXIDANT ACTIVITY AND AROMA PROFILE OF WILD-TYPE BLACKBERRY FRUITS GROWNING IN ARAPGİR

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ABSTRACT

This research aimed to describe the physicochemical and pomological characteristics of blackberry fruits of the wild-type variety growning in the region of Arapgir (town of Malatya). The investigation focused on determining the indicators of bioactive characteristics, antioxidant activity, total phenolic and anthocyanin content of the blackberry fruits. The blackberry samples exhibited a higher total phenolic content (2132.66 mg GAE $100g^{-1}$) compared to several studies, although their total anthocyanin content (356.19 mg cyn-3-O-gly $100g^{-1}$) was determined to be similar to earlier research findings. The methanolic extracts exhibited significant radical-scavenging activity, suggesting superior antioxidant capacity. The $ABTS^{+\bullet}$ and $DPPH^{\bullet}$ capacities were determined to be 19.38 mmol TE $100g^{-1}$ and 26.88 mmol TE $100g^{-1}$, respectively. Furthermore, the aroma profile was assessed by conducting volatile component analysis using the SPME/GC-MS technique As a result of volatile component analysis, a total of 67 components were identified, including 13 aldehydes, 4 ketones, 20 alcohols, 24 esters, 4 terpenes and 2 miscellaneous components.

Keywords: *Blackberry, Bioactive compounds, Antioxidant activity, Aroma, Volatiles*

ARAPGİR'DE YETİŞEN YABANİ BÖĞÜRTLEN MEYVELERİNİN ANTİOKSİDAN AKTİVİTESİ VE AROMA PROFİLİ

ÖZET

Bu çalışmada Arapgir'de (Malatya ilinin ilçesi) yetişen yabani tip böğürtlen meyvelerinin bazı fizikokimyasal ve pomolojik özellikleri belirlenmiştir. Bunun yanında meyvelerin biyoaktif özelliklerini ifade eden toplam fenolik, toplam antosiyanin ve antioksidan aktivitesi araştırılmıştır. Böğürtlen örneklerinin toplam antosiyanin içerikleri (356.19 mg Cyn-3-O-Gly $100g^{-1}$) daha önceki çalışmaların sonuçlarına yakın tespit edilirken, toplam fenolik içeriği (2132.66 mg GAE $100g^{-1}$) daha önce yapılan birçok çalışmadan yüksek bulunmuştur. Metanolik ekstraktların antioksidan özellikleri ise oldukça iyi bir radikal giderici aktivite göstermiştir. $ABTS^{+\bullet}$ ve $DPPH^{\bullet}$ değerleri sırasıyla 19.38 mmol TE $100g^{-1}$ ve 26.88 mmol TE $100g^{-1}$ olarak saptanmıştır. Ayrıca örneklerin, aroma profilini belirlemek üzere SPME/GC-MS tekniği ile uçucu bileşen analizi yapılmıştır. Uçucu bileşen analizi sonucunda, 13 aldehit, 4 keton, 20 alkol, 24 ester, 4 terpen ve 2 çeşitli bileşen olmak üzere toplamda 67 bileşen tanımlanmıştır.

Anahtar Kelimeler: *Böğürtlen, Biyoaktif bileşenler, Antioksidan aktivite, Aroma, Uçucu bileşenler*

1. Introduction

Due to the numerous advantageous effects attributed to phenolic compounds, there has been an increase in the search for identifying plant species characterised by a substantial phenolic content and related biological activity. Berries are an well-known food source of phenolic compounds, which have both antioxidant and bioactive qualities [1]. Epidemiological and clinical research suggest that phenolic compounds in berries may lower the obesity risk, coronary disease, degenerative illnesses, and cancer. Research has examined the health effects and processes of anthocyanins in vitro and in animal models.

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Blackberries ('*Rubus fruticosus* L.') have a rich and storied history that dates back thousands of years. Native to Europe, Asia, and North America, diets of people have included blackberry since the dawn of time. Native Americans were known to use blackberries for medicinal purposes, while the ancient Greeks and Romans used them for culinary delights and even fermented them into wine [2]. Blackberry plants are characterized by their perennial growth habit. They belong to the '*Rubus'* genus and are part of the 'Rosaceae' family. Blackberry plants typically have long, thorny canes that arch and trail along the ground. Some cultivated varieties have been developed with reduced thorniness for easier harvesting. Blackberries develop from the flowers of the blackberry plant. The fruit starts green and gradually turns red, then deep purple to black as it ripens. The harvest season for blackberries varies by region but is generally in the summer months, typically from May to August, depending on the climate. There are numerous blackberry cultivars with varying characteristics in terms of fruit size, flavor, yield, and growth habit. Popular cultivars include 'Marion', 'Boysen', 'Chester', and 'Thornless Evergreen' [3-5].

Blackberries have garnered attention as a fruit of significance due to their large quantities of anthocyanins, ellagitannins, and other phenolic compounds, which together contribute to their considerable antioxidant capacity. Blackberries have been the subject of multiple investigations due to their superior oxygen radical absorption capability compared to other fruits, which has resulted in the identification of their strong antioxidant activity. In Europe, blackberries have been used to cure eye and mouth infections since the 16th century because of their renowned therapeutic properties [6]. Consuming blackberries regularly can offer a wide range of health benefits. Thanks to their high vitamin C content, blackberries can strengthen the immune system, helping the body fend off illnesses. The fiber, potassium, and antioxidants in blackberries contribute to heart health by reducing blood pressure and cholesterol levels. Blackberries' fiber content aids in digestion and may help prevent constipation. Antioxidants in blackberries combat free radicals, which can lead to premature aging, making your skin look and feel better. Several studies have indicated that the existence of antioxidants in blackberries may potentially contribute to a decrease in the likelihood of developing specific types of cancer [7-11]. The content and quantities of phenolic compounds in blackberries have been observed to be altered by various factors, including genetics, growing circumstances, and maturation [12]. The blackberry fruit offers diversity in its consumption, as it can be enjoyed in its fresh form or undergo various processing methods to create a range of products such as juice ice-cream, frozen treats, dry snacks, cake, jam, marmalade, wine and liqueur [13]. The current information about the metabolism of blackberry phenolic compounds is restricted and there is a lack of research dedicated to exploring their potential health benefits, digestion, bioavailability, and the underlying mechanisms responsible for delivering these advantages. In this study, some physicochemical properties and aroma profiles, as well as antioxidant properties, of blackberries grown in Arapgir were characterized.

Figure 1. The collection of blackberry fruits (wild type) took place in Arapgir.

2. Material and Method

2.1. Blackberry Fruits

Blackberry fruits (Figure 1) were gathered from wild species growing in Arapgir district of Malatya province. The fruits were promptly stored in a freezer set at a temperature of -86 °C.

The act of keeping in the freezer is employed as a means of safeguarding phenolic components, particularly anthocyanins, from potential harm or degradation.

2.1. Physicochemical Qualities of Blackberry Fruits

The pomological features, including size and weight measurements, were evaluated using a digital micrometer and an analytical balance, respectively. Before conducting the tests, the blackberry fruits were subjected to a cleaning and pitting procedure to ease the mash production using a mixer. Following that, a homogenate was prepared using a homogenizer in order to carry out several specified analyses. A comprehensive examination was conducted on a representative group to determine the total acidity, pH, and °Brix levels. To the previously mentioned description of the sample preparation procedure for chemical analysis, a homogenate with a mass of 10 g was diluted by adding 100 mL of Milli-Q water (Millipore, Bedford, Mass., U.S.A.). Subsequently, the pH of each homogenate was assessed using a pH meter (Mettler-Toledo, Greifensee, Switzerland). The samples' overall acidity was evaluated using titration, utilizing a solution of 0.1 M NaOH. The chromameter (model CR-5, Konica Minolta, Osaka, Japan) was used to quantify the surface color attributes, namely L^*, a^*, b^*, Chroma (C^*), and hue angle ($h°$). The measurements were performed utilizing a petri dish with a diameter of 3 mm, employing illuminant D-65 and an observer angle of 10°.

2.2. Analysis of Total Anthocyanin and Total Phenolics

The method published by Serradilla et al. [14] was used to determine the total anthocyanin contents of sweet cherries. The methanolic extracts of the samples utilized for determining the total phenolic content were subjected to measurement at a wavelength of 520 nm using a precise spectrophotometer. The quantification was accomplished by employing the standard calibration curve of cyanidin-3-O-rutinoside, obtained from Sigma-Aldrich, located in St. Louis, Missouri, United States. The total amounts of anthocyanin were quantified and reported as mg cyanidin-3-O-rutinoside equivalent per 100 grams of fresh weight (FW). The quantification of total phenolic compounds in blackberries was conducted using the 'Folins' method utilizing a UV-spectrophotometer (model: UV-1800, Shimadzu, Kyoto, Japan), as previously described by Singleton et al. [15].

2.3. Antioxidant Capacity of Blackberry Fruits

The scavenging radical activity of blackberry samples was determined using two experimental methods: $ABTS^{+\bullet}$ (2,2-azino-di-(3-ethylbenzothialozine-sulphonic)) and $DPPH^{\bullet}$ (2,2-diphenyl-1-picrylhydrazyl) assays. The $ABTS^{+\bullet}$ solution was made by combining 2.45 mmol of potassium persulphate. The resulting solution was then diluted with methanol until it reached an absorbance of 0.70±0.02 at a temperature of 30 °C, using a precise spectrophotometer. The cherries that underwent homogenization were subsequently diluted with ethanol in a ratio of 1:50. Following the procedure outlined in the sample preparation section, a 0.1 mL aliquot of the homogenate was combined with 3.9 mL of ABTS. Subsequently, the resulting solution was incubated in darkness for a duration of 10 minutes. The absorbance of the samples was then determined at a wavelength of 734 nm, as described by Xu et al. [16]. The samples' absorbance was measured and compared to the Trolox® standard, which ranged from 5 to 100 µg g^{-1}. The findings were then represented as mg Trolox equivalent (TE) per gram of fresh weight (FW). The analysis of $DPPH^{\bullet}$ radical scavenging capacity was conducted by producing a solution of 2.5 mg of DPPH in 100 mL of methanol, as described by Lucena et al. [17]. A volume of 100 µL of blackberry extract was diluted with pure methanol and thereafter combined with 3.9 mL of

DPPH$^{\bullet}$ solution. The resulting mixture was allowed to rest for a duration of 45 minutes at a temperature of 20 °C. The measurement of absorbance at 517 nm was conducted on the combination using a precise spectrophotometer. The absorbance values of the samples were then compared to those of Trolox, ranging from 5 to 500 μg g^{-1}. The findings were quantified in mgs of Trolox equivalents per gram of FW.

2.4. Aroma Profile of Blackberry Fruit

The volatile compounds of blackberries were extracted by solid-phase microextraction (SPME) using a DVB/CAR/PDMS (Divinylbenzene/Carboxen/Polydimethylsiloxane; 50/30 μm coating thickness; 2 cm length; Supelco, Bellefonte, Pa., U.S.A.) fiber. A lab blender homogenized approximately 50 g of blackberries. Three grams of the homogenized sample were promptly transferred in triplicate into 15 mL SPME vials (Supelco, Bellefonte, Pa., U.S.A.) within 2 minutes. Subsequently, 10 μL of an internal standard solution containing 81 mg/kg of 2-methyl-3-heptanone (for all volatiles except acids) and 2-methyl pentanoic acid (for volatile acids; Sigma-Aldrich Co., U.S.A.) in methanol was added as an internal standard. The vials were manually agitated and thereafter placed on a heater set at a temperature of 40 °C for a duration of 30 minutes in order to facilitate the accumulation of volatile substances in the headspace. Following that, fiber was introduced into a vial with the purpose of absorbing volatile chemicals for a duration of 30 minutes. The temperature at which desorption occurred in the MS sampler was measured to be 250 °C.

The volatiles present in the blackberries were collected through hand sampling using a solid-phase microextraction (SPME) fiber. The collected samples were then analyzed using a gas chromatography-mass spectrometry (GC-MS) system, namely the Shimadzu GC-2010 gas chromatography and QP-2010 mass spectrometry system manufactured by Shimadzu Corporation in Kyoto, Japan. The separation process was conducted using a DB-Wax column (60 m × 0.25 mm × 0.25 mm; J&W Scientific, Folsom, Calif., U.S.A.) under splitless mode. The carrier gas utilized in the experiment was helium, with a flow rate of 1.0 mL/min. The temperature protocol was executed in accordance with the methodology outlined by Yildiz et al. [18], with minor adjustments. The experimental protocol involved a heating gradient procedure, wherein the temperature was initially set at 40 °C for a duration of 2 minutes, followed by a further increase at a rate of 3 °C per minute until reaching a final temperature of 80 °C, which was maintained for 1 minute. Subsequently, the temperature was elevated to 240 °C at a rate of 5 °C per minute, and maintained at this level for a duration of 6 minutes. The chromatograms were evaluated and the peaks were identified using the Wiley 8 and NIST05 mass spectrum libraries. The n-alkane series, ranging from C_{10} to C_{26}, was employed under identical experimental settings in order to validate the retention indices. The results were determined by quantifying the peak area of each chemical as μg kg^{-1} of the sample.

3. Results And Discussion

3.1. Chemical and physical characteristics

Table 1 offers data on the physicochemical and some of the pomological characteristics of blackberry fruits. The °Brix value is a measure of the sugar content in a solution, including fruit juices. It is commonly used to assess the sweetness of fruits and their potential for producing high-quality juice or other processed products. Brix is expressed as a percentage, and it indicates the grams of sucrose (table sugar) in 100 grams of juice or fruit. °Brix is often used as an indicator of fruit ripeness. As fruits mature and sugars accumulate, the °Brix value tends to increase. However, it's important to note that other factors, such as acidity and aroma, also effect the overall acceptance of the fruits. The °Brix value of blackberry fruit is estimated to be approximately 14. Nevertheless, the overall dry matter content was found to be 22%. The experimental findings indicated that the quantity of insoluble dry matter dissolved in water was comparatively lower in relation to the quantity of soluble matter. It's important to note that while °Brix is a useful indicator of sweetness, it doesn't provide a complete picture of fruit quality.

Other factors such as aroma, texture, and overall flavor profile are also important considerations in assessing fruit quality.

Table 1. Some physicochemical and pomological properties of blackberry fruit grown in Arapgir

Physicochemical and pomological values *Rubus fruticosus* L.					
Humidity	77.26	±0.71	*L**	20.14	±5.88
a_w	0.959	±0.001	*a**	8.09	±4.69
°Brix	13.92	±0.13	*b**	3.31	±2.80
pH	4.053	±0.01	*C**	9.12	±4.80
Titratable acidity (mg citric acid $100g^{-1}$)	0.91	±0.01	*h°*	20.80	±16.75
			Length (mm)	13.41	±0.68
			Weight (g)	1.21	±0.19

Averages; ± Standard deviations

The color of blackberries is primarily due to existence of anthocyanins, which give them their deep purple to black hue. The color may vary slightly depending on the cultivar and ripeness. The quality of dark-colored berry fruits and processed foods is significantly influenced by the color of the fruit, which is mostly determined by the presence of anthocyanins. Anthocyanins are a category of pigments that are soluble in water and are recognised for their antioxidative properties. The primary anthocyanin found in blackberries is cyanidin-3-glucoside [19]. The *L** (20.14) and *a** (8.09) values of blackberry fruit have been attributed to its anthocyanin composition. The acidity of fruits is an essential component of their flavor profile and plays a significant role in determining their taste. The acidity of fruits is predominantly attributed to the existence of organic acids, wherein citric acid, malic acid, and tartaric acid are the prevalent acids commonly observed in fruits. The optimal proportion between sweetness and acidity plays an essential part in determining the comprehensive sense of fruit flavour. Fruits with a good balance between sweetness and acidity are often considered the most palatable. We found the pH value of blackberry samples to be 4.05 and the titratable acidity to be 0.91 mg/100 g. In their study, Wang and Xu [20] determined the pH and titratable acidity levels of blackberry juice and concentrate to be 2.86 and 1.65 mg/100 g, respectively.

Table 2. Total phenolic and total anthocyanin content and antioxidant activity of blackberry fruit grown in Arapgir

	Rubus fruticosus L.	
ABTS (mmol TE $100g^{-1}$ d.w.)	19.38	±0.42
DPPH (mmol TE $100g^{-1}$ d.w.)	26.88	±0.55
Total phenolics (mg GAE $100g^{-1}$ d.w.)	2132.66	±104.11
Total anthocyanins (mg Cyn-3-O-Gly $100g^{-1}$ d.w.)	356.19	±27.52

Averages; ± Standard deviations; TE: Trolox® equivalent; GAE: Gallic acid equivalent; Cyn-3-O-Gly: cyanidin-3-O-glycoside equivalent; d.w.: dry matter

The study conducted by Yilmaz et al. [21] aimed to assess various physico-chemical properties of blackberry genotypes. The study centered around a comprehensive analysis of a total of sixteen selected wild-type blackberries and nine cultivated and varieties that are grown in Türkiye. The findings indicated that cultivated blackberries had greater average fruit weight and greater fruit dimensions compared to wild blackberry specimens. Nevertheless, the total soluble solids, acidity levels, and pH values exhibited greater measurements in the wild samples. The findings of our study agree with the findings of previous research carried out in Türkiye at the same time [21].

3.2. Antioxidant Activity, Total Anthocyanin and Phenolic Content of Blackberry Fruit

Blackberries are popular due to their antioxidant properties, which are related to their high anthocyanin and phenolic content. [22]. The overall anthocyanin and phenolic content of blackberry fruit depends on cultivar, ripeness, growing conditions, and extraction and analysis procedures. Blackberries contain several compounds that contribute to various health benefits. Table 2 presents the findings on the total anthocyanin content, the total phenolic content, and the antioxidant activity of blackberry fruits.

Anthocyanins have also been proven to be capable of inhibiting cellular growth and inducing apoptosis in cancer cells through in vitro research [23, 24]. Therefore, the anthocyanins that are found in the blackberry extract are able to exert various protective actions against the pleurisy that is caused by carrageenan [25].The measured quantity of anthocyanins in our sample was found to be 356.19 mg $100g^{-1}$, while its total phenolic content was confirmed to be 2132.66 mg $100g^{-1}$ dry weight. Siriwoharn et al. [26] have studied three blackberry cultivars in Oregon, (U.S.). The anthocyanin content exhibited a significant increase, rising from 74.7 to 317 mg100 g^{-1} FW for 'Marion' and from 70 to 164 mg 100 g^{-1} FW for 'Evergreen'. The study found that the levels of total anthocyanin in 'Marion' berries grew dramatically as they ripened. At the underripe stage, the total anthocyanin content of 'Marion' berries were comparable to that of 'Evergreen' berries. However, in the ripe and overripe stages, the total anthocyanin content of 'Marion' berries was about twice as high as that of 'Evergreen' berries [26]. The total anthocyanin content in blackberries can vary widely but is typically in the range of 100 to 300 mg per 100 grams of fresh weight. However, specific cultivars and growing conditions can lead to higher or lower anthocyanin levels. Upon conducting a thorough analysis and comparison of our results with those of other studies, we observed that our performance metrics were significantly higher [26, 27]. Anthocyanin levels tend to increase as blackberries ripen, which is why ripe blackberries have a deeper color. Environmental factors, such as sunlight exposure, can also impact anthocyanin production in the fruit [3, 28]. Bowen-Forbes et al. [29] studied the anthocyanin contents of four cultivated blackberry genotypes in Michigan were examined and found the results 146-2200 mg 100 g^{-1}. Also it has been known that the blackberry anthocyanins cyanidin-3-glucoside and cyanidin-3-rutinoside are the primary and minor anthocyanins in blackberries [30]. Throughout the method of preparing our results, we conducted calculations based on the compound cyanidin-3-O-glucoside.

Blackberries contain flavonoids, phenolic acids and tannins. Antioxidants in blackberries come from phenolic chemicals. Blackberry phenolic compounds may reduce chronic disease risk and enhance cardiovascular health, according to research. [2, 31]. The total phenolic content of blackberries is typically higher than that of many other fruits. It can range from 500 to 1500 mg of gallic acid equivalents (GAE) per 100 grams of fresh weight. It's important to note that the total anthocyanin and phenolic content of blackberries can vary not only between different cultivars but also between individual berries within the same harvest [2, 29]. Koca and Karadeniz [32] conducted research on ten different cultivars of blackberry fruit that are grown in Türkiye. The observed ranges for the total anthocyanin and total phenolic contents of the samples under investigation were as follows: blackberries exhibited values ranging from 95 to 197 mg $100g^{-1}$ for total anthocyanin content, and from 173 to 379 mg $100g^{-1}$ for total phenolic content. In our study, the fruits of the blackberry have been measured to have a total phenolic content of 2132 mg $100g^{-1}$. In their study, Siriwoharn et al. [26] found that the levels of a certain compound were measured to be 1541 mg $100g^{-1}$ and 1035 mg $100g^{-1}$ throughout overripe phase of 'Marion' and 'Evergreen' cultures, respectively. Our values higher than these ideals in terms of value and significance. Yilmaz et al. [21] evaluated the blackberry cultivars and wild genotypes exhibited a range of total phenolic contents, with values ranging from 584 mg 100 g^{-1} ('cv. Bartin') to 788 mg 100 g^{-1} ('cv. Chester') and from 610 mg 100 g^{-1} ('Genotype R2') to 1455 mg 100 g^{-1} ('Genotype R16'), expressed as gallic acid equivalents (GAE), based on fresh weight measurements. When compared to the findings of other studies, the results we obtained came in at a quite high level. Akin et al. [12] researched fruits of wild blackberry, black and white mulberries grown in southern Bulgaria. The findings demonstrate that black mulberries indicated the highest level of antioxidant activity, with a measured value of 122.30 mmol TE $100g^{-1}$. White mulberries followed closely with a measurement of 86.13 mmol TE $100g^{-1}$, while blackberries demonstrated a lower antioxidant activity of

44.90 mmol TE 100g^{-1} [12]. Despite the fact that our findings fall below these benchmarks, they exhibit a degree of familiarity.

In a study, Gündoğdu et al. [33] utilized a total of eleven blackberry cultivated in Malatya. In the study where the Trolox equivalent antioxidant capacity was determined, the blackberry cultures showed antioxidant results ranging from 3.08 to 4.89 mmol 100g^{-1}. Yilmaz et al. [21] determined the antioxidant activity of blackberry fruits, both cultivated and wild, ranged from 72.15% (cv. Arapaho) to 89.75% (cv. Bursa 3) and from 59.85% (R1) to 87.42% (R10), respectively. The measured antioxidant activity of the standard BHA compound was determined to be 85.07%. Consistently, various cultivars cultivated in the same geographical area shown notable variations in their antioxidant activity [21]. Oszmiański et al. [34] conducted a study in which twenty-three distinct samples of wild blackberry fruit were examined to evaluate their phenolic profiles, contents, and antioxidant activity using two different extraction methods, namely FRAP and ABTS. A total of thirty-four phenolic compounds were identified. The findings of the ABTS test that was carried out on samples of blackberries that had been subjected to pressurized liquid extraction showed that the value ranged anywhere from 4 mmol TE 100g^{-1} to 9 mmol TE 100g^{-1} as dry weight. The observation that our data exhibit greater values compared to those obtained using pressurised liquid extraction indicates notable differences in extraction efficiency and impact.

3.3. Aroma Profile of Blackberry Fruits

The formation of fruit taste is attributed to the varying quantities of volatile components. Furthermore, fragrance components play a crucial role in discerning the sensory distinctions among fruits, exerting a considerable impact on fruit quality. The technique known as Solid-Phase Microextraction (SPME) was introduced in the novel researches as a viable method for separating volatile molecules from non-volatile matrix components that may cause interference. In addition to several benefits, SPME can be regarded as a rapid, straightforward, cost-effective, highly sensitive, solvent-free, and easily automatable method. The choice of SPME fibre coating primarily affects recovery of volatile compounds. The application of SPME in the investigation of food flavour components has been extensively employed [35]. The main organic constituents contributing to the flavour profile of fruit berries contain numerous volatile chemicals, including aldehydes, ketones, alcohols, esters, furanones, sulphur compounds and terpenoids [36]. Table 3 displays the fragrance profile associated with blackberry fruits. Based on the analysis of the volatile component composition of the samples, a total of 67 components were identified. These components included 13 aldehydes, 4 ketones, 20 alcohols, 24 esters, 4 terpenes, and 2 miscellaneous components.

Du et al. [37] analyzed the volatile composition of 'Marion' and 'Black Diamond' fruits to explore differences in their aroma. Despite a similar overall profile, some compounds differed significantly in concentration. For example, 'Marion' had a stronger berry, fruity, and strawberry aroma, while 'Black Diamond' had a more pronounced floral aroma. The cultivar known as 'Thornless Evergreen' exhibited a higher overall concentration of volatiles, primarily consisting of alcohols, terpenoids, and phenols, in comparison to the cultivar 'Marion', which displayed a greater abundance of organic acids. Qian and Wang [38] identified ethyl hexanoate, β-ionone, linalool, 2-heptanone, 2-undecanone, α-ionone, and hexanal as compounds with strong smell activity in 'Marion' and 'Thornless Evergreen', compounds with strong odour activity included ethyl hexanoate, 2-heptanone, 2-methylbutanoate, 2-heptanol, 3-methylbutanal, α-pinene, limonene, p-cymene, linalool, (E)-2-hexenal, myrtenol, hexanal, 2-methylbutanal, and Our blackberry samples showed a significant presence of (E)-2-hexenal (115.16 µg kg^{-1}), which appeared to be the most prominent component, followed by ethanol (42.87 µg kg^{-1}), hexanal (27.22 µg kg^{-1}), (E)-2-hexene-1-ol (21.29 µg kg^{-1}), linalool (11.95 µg kg^{-1}) and 1-hexanol (11.82 µg kg^{-1}).

Table 3. Volatile components of blackberry fruits grown in Arapgir

Aldehydes (13)	**RI**	**µg kg^{-1}**		***Alcohols (20)***	**RI**	**µg kg^{-1}**	
Ethanal	673	2.01	±0.59	Ethanol	907	42.87	±1.60
2-Methylbutanal	871	0.36	±0.06	2-Butanol	1008	0.27	±0.09

3-Methylbutanal	878	0.65	±0.19
Hexanal	1066	27.22	±14.73
(*Z*)-3-Hexenal	1118	1.06	±0.79
2-Methyl-4-pentenal	1123	0.99	±0.22
(*E*)-2-Hexenal	1214	115.16	±38.32
Octanal	1275	0.13	±0.08
Nonanal	1385	0.89	±0.08
(*E,E*)-2,4-Hexadienal	1400	1.16	±0.35
(*E,E*)-2,4-Heptadienal	1460	0.27	±0.03
Decanal	1490	0.71	±0.25
(*E*)-2-Decenal	1637	0.15	±0.07
Esters (24)			
Methyl acetate	764	0.49	±0.17
Ethyl acetate	833	6.44	±2.15
Methyl propionate	861	0.38	±0.09
Methyl butyrate	960	0.59	±0.09
methyl carbonate	965	0.17	±0.02
Methyl-2-methylbutyrate	990	0.37	±0.04
3-Methyl-methyl butanoate	1001	1.48	±0.53
Ethyl butyrate	1019	0.16	±0.02
Ethyl isovalerate	1051	0.93	±0.29
Isobutyl isobutyrate	1073	0.48	±0.16
Methyl 3-methylpentanoate	1114	0.16	±0.04
Isobutyl isobutyrate	1130	0.38	±0.07
2-Methylpropyl Butanoate	1143	0.22	±0.03
Butyl isocyanatoacetate	1200	0.31	±0.15
Hexyl acetate	1261	0.23	±0.16
Pentyl 3-methylbutanoate	1284	1.79	±0.54
(*E*)-4-Methyl-ethyl-2-pentenoate	1319	0.51	±0.18
Methyl octanoate	1379	0.69	±0.45
Ethyl-octanoate	1423	0.15	±0.04
Methyl nonanoate	1481	0.56	±0.20
Maltyl isobutyrate	1484	0.39	±0.09
Methyl caprate	1582	0.12	±0.01
Methyl benzoate	1623	0.30	±0.04
Methyl Salicylate	1782	0.72	±0.32
3-Methyl-1-butanol	1201	0.58	±0.02
2-Heptanol	1309	8.38	±0.98
2-Methyl-3-heptanol	1324	7.82	±5.87
1-Hexanol	1344	11.82	±6.53
(*Z*)-3-Hexen-1-ol	1377	2.51	±0.96
(*E*)-2-Hexene-1-ol	1397	21.29	±18.65
1-Octen-3-ol	1436	0.24	±0.03
6-Methyl-5-hepten-2-ol	1450	9.97	±0.50
2,6-Dimethyl-7-octen-2-ol	1455	3.30	±4.45
Pinacol	1472	0.67	±0.24
(*E*)-2-Heptene-1-ol	1499	0.26	±0.03
2-Nonanol	1503	0.14	±0.03
1-Octanol	1544	1.31	±0.09
(*Z*)-2-Octen-1-ol	1601	0.19	±0.02
1-Nonanol	1644	0.55	±0.12
2-Tridecanol	1698	0.33	±0.04
Benzyl Alcohol	1870	0.54	±0.01
Phenylethyl Alcohol	1908	0.38	±0.09
Ketones (4)			
2-Heptanone	1173	2.17	±0.84
3-Octanone	1245	0.43	±0.10
Acetoine	1286	1.46	±0.25
6-Methyl-5-heptene-2-one	1330	0.57	±0.18
Terpene Compounds (4)			
L-Limonene	1184	1.06	±0.07
Linalool	1531	11.95	±1.64
Tetrahydro linalool	1736	0.24	±0.06
Isogeraniol	1795	0.21	±0.07
MiscellaneousComponent (2)			
Anisole	1338	0.22	±0.10
Methyleugenol	1996	0.15	±0.04

Averages; ± Standard deviations; Retention Index (RI): calculated in DB-Wax 60m column with C8-C20 alkane series.

Table 3. Continue

The synthesis of volatile molecules that contribute to aroma is closely linked to the process of pigment formation during ripening. Nevertheless, it is important to acknowledge that specific molecules, especially hexanal and (*E*)-2-hexenal, can be generated via the process of oxidation or the lipoxygenase-catalyzed oxidative degradation of fatty acids [13]. Du et al. [37] focused on the examination of glycosidically bound volatiles and precursors in genotypes that represent a predecessor of the 'Marion' blackberry. The mix of volatile precursors in the genotypes within the 'Marion' pedigree exhibited a high degree of similarity to their corresponding distribution of free volatiles. Meret et al. [39] analyzed the composition of free and glycosidically bound volatiles in purees derived from the fruit of 'Andean blackberry' ('*Rubus glaucus* Benth.'). They identified and quantified a total of 55 volatile compounds using solvent extraction. Additionally, a separate investigation was conducted utilising HS-SPME, focusing on the identification of seventy-one compounds.

Esters are synthesised subsequent to converting amino acids into certain extended aliphatic compounds during catabolic reactions, a characteristic fruity aroma in fruits. Esters were the most common in our samples regarding the number of volatile compounds. Nevertheless, the quantities of each of these substances are quite small. Following esters, alcohols exhibit a comparatively greater diversity and abundance. The process of alcohol formation in fruits involves the conversion of amino acids through a series of processes, including decarboxylation or reduction. In contrast, aldehydes possess the capability to undergo reduction to become alcohols within cellular environments, facilitated by the enzymatic action of aldehyde reductases or alcohol dehydrogenases. Ethanol is a byproduct of fermentation that is made without oxygen by the alcohol dehydrogenase enzyme in fruit and yeast. It is the starting point for many aroma compounds that start with acetaldehyde. It has been said that acetaldehyde and ethanol levels rise as oranges and pears dissolve before they are harvested [40, 41]. Terpenes and terpineols, which are composed of isopropene units, are synthesised through the metabolic processes of carbohydrates and lipids in fruits. These molecules are essential in generating the characteristic fruity and floral aromas [42]. Linalool, which is responsible for the blackberry aroma [43], was found in high concentrations.

4. Conclusion

Blackberries are widely cultivated, and there are numerous cultivated varieties with distinct flavors, sizes, and colors. They belong to the rose family and grow on thorny bushes. Blackberries provide a high nutritional value, as they include a significant amount of vital vitamins, minerals, and antioxidants. Some physicochemical properties, bioactive properties and aroma profiles of wild-type blackberry fruits grown in Arapgir, were investigated. In this way, it could be compared with blackberries grown in Türkiye and other countries. The fact that wild-type fruits are smaller than cultured fruits does not mean that they cannot compete with them in terms of content.

Conflict Of Interest

The authors declare that they have no conflict of interest.

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