



Physicochemical and Sensory Quality Properties of Yellow Hawthorn Fruit (*Crataegus tanacetifolia*) Vinegar Produced by Traditional Fermentation Method

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Abstract

In this study, some physical, chemical and sensory properties of vinegar produced from hawthorn (*Crataegus tanacetifolia*) by conventional method were investigated. According to the results of the analyses performed, dry matter, pH, total acidity, ash and conductivity values were determined to be $2.08 \pm 0.09\%$, 2.69 ± 0.08 , 20.49 ± 0.13 g/L, 2.2 ± 0.10 g/L and 1.36 ± 0.08 μ S/cm, respectively. As a result of the alcohol analysis performed after 9 months of storage, no alcohol was detected in the samples. Furthermore, total antioxidant activity and total phenolic content in vinegar samples were determined to be 86.23 ± 8.12 μ g trolox equivalent (TE)/mL and 751.11 ± 15.71 mg gallic acid equivalent (GAE)/L, respectively. In hawthorn vinegar samples, it was determined that the brix value was 2.24 ± 0.07 , density was 1.018 ± 0.02 g/cm³, mean color values; L* values were 27.80 ± 0.51 ; a* values were 1.33 ± 0.04 and b* values were -0.30 ± 0.13 . 47.30 ± 0.76 ppm Na, 3.38 ± 0.04 ppm Mg, 197.14 ± 3.50 ppm K, 2.59 ± 0.47 ppm Ca, 83.20 ± 0.43 ppm P, 0.42 ± 0.01 ppm Fe, 0.02 ± 0.01 ppm Cu, 0.33 ± 0.00 ppm B, 0.18 ± 0.00 ppm Zn, 0.75 ± 0.01 ppm Al, 0.02 ± 0.00 ppb Cr, 4.42 ± 0.01 ppb Sn were found in hawthorn vinegar, which is rich in mineral content. According to the sensory analysis results, it was determined that the color scores of vinegar samples were 7.20 ± 0.28 , the aroma value was 6.25 ± 0.32 , the odor value was 6.75 ± 0.37 , the appearance value was 6.25 ± 0.22 , and the general appreciation value was 7.25 ± 0.53 .

Keywords: Hawthorn, Vinegar, Fermentation, Antioxidant activity, Phenolic content.

Geleneksel Fermantasyon Yöntemiyle Üretilen Sarı Alıç Meyve (*Crataegus tanacetifolia*) Sirkesinin Fizikokimyasal ve Duyusal Kalite Özellikleri

Öz

Bu çalışmada geleneksel yöntemle alıçtan (*Crataegus tanacetifolia*) üretilen sirkenin bazı fiziksel, kimyasal ve duyusal özellikleri araştırılmıştır. Yapılan analiz sonuçlarına göre; kuru madde, pH, toplam asitlik, kül, iletkenlik değerleri sırasıyla $2.08 \pm 0.09\%$, 2.69 ± 0.08 , 20.49 ± 0.13 g/L, 2.2 ± 0.10 g/L, 1.36 ± 0.08 μ S/cm olarak belirlenmiştir. 9 aylık depolama sonrasında yapılan alkol analizi sonucunda örneklerde alkol tespit edilmemiştir. Ayrıca sirke örneklerinde toplam antioksidan aktivite ve toplam fenolik madde miktarı sırasıyla 86.23 ± 8.12 μ g troloks eşdeğeri (TE)/mL ve 751.11 ± 15.71 mg gallik asit eşdeğeri (GAE)/L olarak belirlenmiştir. Alıç

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sirkesi örneklerinde; briks değeri 2.24 ± 0.07 , yoğunluk (g/cm^3) 1.018 ± 0.02 , ortalama renk değerleri; L^* değerleri 27.80 ± 0.51 ; a^* değerleri 1.33 ± 0.04 ve b^* değerleri -0.30 ± 0.13 olarak saptanmıştır. Mineral içeriği bakımından zengin olan alıç sirkesinde; 47.30 ± 0.76 ppm Na, 3.38 ± 0.04 ppm Mg, 197.14 ± 3.50 ppm K, 2.59 ± 0.47 ppm Ca, 83.20 ± 0.43 ppm P, 0.42 ± 0.01 ppm Fe, 0.02 ± 0.01 ppm Cu, 0.33 ± 0.00 ppm B, 0.18 ± 0.00 ppm Zn, 0.75 ± 0.01 ppm Al, 0.02 ± 0.00 ppb Cr, 4.42 ± 0.01 ppb Sn belirlenmiştir. Duyusal analiz sonuçlarına göre ise sirke örneklerinin renk skorları 7.20 ± 0.28 , aroma değeri 6.25 ± 0.32 , koku değeri 6.75 ± 0.37 , görünüş değeri 6.25 ± 0.22 , genel beğeni değeri 7.25 ± 0.53 olarak tespit edilmiştir.

Anahtar Kelimeler: Alıç, Sirke, Fermantasyon, Antioksidant aktivite, Fenolik içerik.

1. Introduction

Vinegar is a fermented food produced by successive ethyl alcohol and acetic acid fermentation of fruits and vegetables containing sugar or starch (FAO/WHO, 2000; Plessi, 2003). The first stage of vinegar production is the alcohol fermentation in which sugars that can be fermented by yeasts, usually of *Saccharomyces* species are converted to ethanol and CO_2 under anaerobic conditions. In the stage, the resulting ethanol is converted to acetic acid and water by acetic acid bacteria of *Acetobacter pastorianus*, *Acetobacter aceti*, and *Acetobacter hansenii* species under aerobic conditions (Plessi, 2003; Aktan & Kalkan, 2011). The positive effect of vinegar on health is due to the bioactive components it contains originating from the raw material used in vinegar production (Tan, 2003). It is reported that bioactive components including vitamins E and C, phenolic compounds and carotenoids and phytosterols, which are responsible for the antioxidant activity of vinegar, have preventive effects on chronic diseases and oxidative stress (Cullum, 2003; Charoenkiatkul et al., 2016). It is known that vinegar containing various and different amounts of polyphenols may have positive effects especially on cardiovascular diseases (Soleas et al., 2002; Verzelloni et al., 2007).

Hawthorn (*Crataegus*), one of the members of the *Rosaceae* family, has been used as food and medicine for centuries in the world (Rigelsky & Sweet, 2002). While *Crataegus* species, most of which have edible fruits, are known by the name hawthorn among people in Turkey, they are also known by different region names such as bird food, wormwood, goshawk hawthorn, and godan hawthorn (Ergezen, 1999). The composition of hawthorn fruits contains chemical components such as 0.1-1% flavonoids, 1-3% oligomeric proanthocyanidins (OPC), 0.5-1.4% triterpene acids, 2-6% organic acids, vitamin C, sterols and trace amounts of cardioactive amines. Among the components, flavonoids and OPCs constitute the two most important groups of bioactive components. Furthermore, hawthorn fruits also have high amounts of Ca, P, Mg, Na and K minerals (Petkov, 1979; Baytop, 1984; Bahorun et al., 1994; Chang et al., 2002; Ozcan et al., 2005). It is considered that the main benefit of hawthorn, which is used in the treatment of diseases such as depression, gout and kidney stone for centuries, is to support cardiovascular health (Chang et al., 2002; Gaby, 2006; Caliskan et al., 2012).

In this study, it was aimed to investigate some physical, chemical, and sensory properties of vinegar obtained from hawthorn, which is an extremely useful fruit for health, by conventional method.

2. Material and Method

2.1. Material

In this study, yellow hawthorn fruits of *Crataegus tanacetifolia* species picked from the orchards and mountain slopes in the city center of Afyonkarahisar were used as a material.

2.2. Methods

The kernels of hawthorn fruits (*Crataegus tanacetifolia*) were removed, and then they were washed and cleaned, and crack. Then, they were allowed to be aired in the laboratory environment for 1 day. The hawthorns prepared were added in 1/3 of 10-liter jars. Then, 100 g flower honey and 100 g grape molasses were added to them for the natural fermentation process to take place. The creation of fermentation conditions was ensured by adding 150 mL of natural fermented hawthorn vinegar and 50 g chickpeas. Water was added to the prepared product to complete 10 L. The samples in the jars prepared were covered with cheesecloth to be aired for 30 days. Furthermore, they were mixed twice a day to be aired. This process was continued for approximately 30 days until a vinegar mother appeared on the surfaces of the jars. After the formation of the vinegar mother following the fermentation process, filtration was performed, and the raw material and vinegar were separated from each other. Then, the jars were sealed and stored without exposing to light at room temperature for 9 months. At the end of the storage period, samples were analyzed under laboratory conditions. This study was conducted in triplicate were used for each repetition.

2.3. Analyzes

While the oven (Ecocell 55, Germany) was used in determining the dry matter content of hawthorn vinegar samples, the electromag (M 1811, Turkey) ash furnace was used in ash analyses (AOAC, 2000). In hawthorn vinegar samples, pH values were determined by Hanna (HI 2215, Germany) pH meter, brix analysis was performed by a hand refractometer (N-1E, Japan), density was determined using a pycnometer, and titration acidity values were determined according to AOAC (1990). Alcohol measurements of the samples were performed using a vinometer. The conductivity values of the samples were measured by hand conductivity, and the results were determined as $\mu\text{S/cm}$. Total antioxidant capacity and total phenolic content analyses were performed according to Chu and Chen (2006). While the color measurements of hawthorn vinegar samples were performed using a colorimeter (Minolta Chroma meter, CR-400, Japan) according to Voss (1992), the determination of mineral matter was performed using a microwave burning unit

(CEM MARS 6) according to Fu et al. (2013). Sensory evaluation (color, aroma, odor, appearance and general appreciation) of hawthorn vinegar samples were made according to Ilik (2019).

3. Results and Discussion

In hawthorn vinegar samples, it was determined that the brix value was 2.24 ± 0.07 °Brix, the density value was 1.018 ± 0.02 g/cm³, the color values were (L^* : 27.80 ± 0.51 , a^* : 1.33 ± 0.04 and b^* : -0.30 ± 0.13), and with respect to sensory analysis scores, it was determined that the color value was 7.20 ± 0.28 , the aroma value was 6.25 ± 0.32 , the odor value was 6.75 ± 0.37 , the appearance value was 6.25 ± 0.22 , and the general appreciation value was 7.25 ± 0.53 (Table 1).

In similar studies, °Brix values in hawthorn vinegar samples were determined to be 5.33 ± 0.4 (Kadas et al., 2014), 1.26 ± 0.02 (Ozturk et al., 2015) and 5.9 (Taslipinar, 2018). The °Brix values obtained in our study were found to be generally lower than the results obtained in other studies.

The density value of hawthorn vinegar was determined to be 1.018 ± 0.02 g/cm³. In the studies carried out with apple cider vinegar samples, it was found that specific gravity values ranged between 0.9987-1.0517 g/mL (Budak, 2010), 1.013-1.024 g/cm³ (Plessi, 2003). The results obtained in our study and the results obtained from apple cider vinegar were similar.

In the study, it was determined that the L^* values of hawthorn vinegar samples were 27.80 ± 0.51 ; a^* values 1.33 ± 0.04 and b^* values -0.30 ± 0.13 . In similar studies, the color values (L^* , a^* and b^*) of hawthorn vinegar samples were determined to be 31.4 ± 5.2 , 20.48 ± 3.7 and 40.08 ± 4.87 (Kadas et al., 2014), 18.10 ± 0.11 , 1.96 ± 0.02 , 10.67 ± 0.04 (Ozturk et al., 2015), respectively. L^* value, which refers to the brightness to darkness, takes a value between 0-100, including 0=black and 100=white (Anonymous, 1979). In our study, the brightness value of hawthorn vinegar samples was generally found to be lower than the results obtained in similar studies. While $+a^*$ indicates change to redness, $-a^*$ indicates change to greenness (Anonymous, 1979). Vinegar obtained from *tanacetifolia* species of hawthorn in yellow-green colors has a lower a^* value compared to vinegar produced from other hawthorn species. This difference is thought to be caused by the color of the hull of the hawthorn species. While $+b^*$ indicates change to yellowness, $-b^*$ indicates change to blueness (Anonymous 1979). When kinds of hawthorn vinegar were compared in terms of b^* values, b^* values of vinegar samples produced from hawthorn fruits used in our study were found to be lower compared to other samples.

In the study, the dry matter value of hawthorn vinegar was determined to be $2.08 \pm 0.09\%$ (Table 2). In their study carried out in twelve different kinds of apple cider vinegar, Gerbi et al. (1998) found that the total amount of dry matter was 16.38 g/L on average.

The mean pH values of the samples after 9 months of storage were determined to be 2.69 ± 0.08 (Table 2). In similar studies, the pH values of hawthorn vinegar were determined to be 3.28 ± 0.56 (Kadas et al., 2014), 3.76 ± 0.02 (Ozturk et al., 2015), 2.75 (Bilginer, 2018). The pH value obtained in our study was found to be lower when compared to other studies.

The mean ash value in hawthorn vinegar samples was determined to be 2.2 ± 0.1 g/L. Budak (2010) reported that the ash value in apple cider vinegar samples ranged between 1.70-4.70 g/L. The results of the analysis indicated that the hawthorn used as the raw material of vinegar had a lower mineral matter content than apple.

The mean conductivity value was found to be 1.36 ± 0.08 µS/cm in our samples. In similar studies, the conductivity value was determined to be 3.86 ± 0.45 µS/cm (Kadas et al., 2014). The conductivity values of our samples were found to be lower when compared to the conductivity values of other studies.

No alcohol was detected in our samples after nine months of storage (Table 2). In a similar study, Taslipinar (2018) reported that no alcohol was detected on the 60th day of hawthorn vinegar fermentation. It was considered that the reason why alcohol was not detected in the product was the long-term storage of vinegar.

The mean total acidity values of hawthorn vinegar samples were 20.49 ± 0.13 g/L. In similar studies, the titration acidity values of the samples were reported to be 3.7 ± 0.3 g/100 mL (Kadas et al., 2014), $0.82 \pm 0.03\%$ (Ozturk et al., 2015) and 41.75 g/L (Bilginer, 2018) in acetic acid. The analysis results obtained in our study were found to be lower compared to other similar studies.

The total amount of antioxidants in the samples was determined to be 86.23 ± 8.12 (µg TE/mL) on average. In the study carried out by Kadas et al. (2014) on hawthorn vinegar, the total antioxidant capacity was found to be 76.27±4.6%. In another study, DPPH radical scavenging activity was determined to be 55.59±3.86% (Ozturk et al., 2015).

The total phenolic content of hawthorn vinegar was determined to be 751.11 ± 15.71 (mg GAE/L). In similar studies, the total phenolic content in hawthorn vinegar samples was determined to be 5.02 ± 0.23 mg/100 mL (Kadas et al., 2014), 306.80 ± 5.07 mg GAE/ L (Ozturk et al., 2015) and 683.78 ± 12.7 mg GAE/ L (Taslipinar, 2018).

The mineral matter contents of the hawthorn vinegar were determined to be 47.30 ± 0.76 ppm Na, 3.38 ± 0.04 ppm Mg, 197.14 ± 3.50 ppm K, 2.59 ± 0.47 ppm Ca, 83.20 ± 0.43 ppm P, 0.42 ± 0.01 ppm Fe, 0.02 ± 0.01 ppm Cu, 0.33 ± 0.00 ppm B, 0.18 ± 0.00 ppm Zn, 0.75 ± 0.01 ppm Al, 0.02 ± 0.00 ppb Cr and 4.42 ± 0.01 ppb Sn (Table 3). The analysis results indicated that hawthorn vinegar was an important source of mineral matter.

Table 1. Physical and Sensory Analysis Results of Hawthorn Vinegar

Analyzes										
Samples	Brix (°Brix)	Density (g/cm ³)	Color			Sensory Scores			General Appreciation	
			L*	a*	b*	Color	Aroma	Odor		Appearance
Hawthorn Vinegar	2.24±0.07	1.018±0.02	27.80±0.51	1.33±0.04	-0,30±0,13	7.20±0.28	6.25±0.32	6.75±0.37	6.25±0.22	7.25±0.53

Table 2. Chemical Analysis Results of Hawthorn Vinegar

Analyzes								
Samples	Dry Matter Content (%)	pH	Ash (g/L)	Conductivity (µS/cm)	Alcohol (%)	Total Acidity (g/L)	Total Antioxidant (µg TE/mL)	Total Phenolic (mg GAE/L)
Hawthorn Vinegar	2.08±0.09	2.69±0.08	2.2±0.10	1.36±0.08	-	20.49±0.13	86.23±8.12	751.11±15.71

Table 3. Mineral Analysis Results of Hawthorn Vinegar

Analyzes												
Samples	Na (ppm)	Mg (ppm)	K (ppm)	Ca (ppm)	P (ppm)	Fe (ppm)	B (ppm)	Cu (ppm)	Zn (ppm)	Al (ppm)	Cr (ppb)	Sn (ppb)
Hawthorn Vinegar	47.30±0.76	3.38±0.04	197.14±3.50	2.59±0.47	83.20±0.43	0.42±0.01	0.33±0.00	002±0.01	0.18±0.00	0.75±0.01	0.02±0.00	4.42±0.01

In the study carried out by Kadas et al. (2014), K, Ca, Mg, Fe, Na, Zn and Cu values in hawthorn vinegar were determined to be 6638.7±452.7, 521.4±39.5, 241.9±43.7, 240.0±28.3, 123.1±21.3, 40.1±9.8 and 0.273±0.5 ppm, respectively. In this study, hawthorn vinegar was found to be very rich in K, Ca, Mg, Fe, Na and Zn.

Cr, Mg, Mn, Zn, Fe, Cd, Ni, Pb, Ag contents of hawthorn vinegar samples were determined to be 0.040, 0.060, 0.1, 0.500, 0.210, 0.060, 4.600, 0.240 and 0.035 µg/mL, respectively (Salman & Shamar, 2013). Se, Cr, Cu, Mg, Co, Zn, Na, K, Ca, Ni, Mn amounts of hawthorn vinegar samples were determined to be 0.09±0.01, 0.04±0.00, 0.03±0.00, 61.40±3.80, 0.00±0.00, 1.50±0.36, 73.90±4.30, 864.90±42.60, 156.30±15.20, 0.07±0.01 and 0.38±0.03 mg/L, respectively (Ozturk et al., 2015).

It is considered that general differences that emerged with the comparison of the results on hawthorn vinegar in our study with similar studies were due to fruit variety, fruit species, the quantity used, fermentation conditions, and storage time.

According to the sensory analysis scores of hawthorn vinegar, it was determined that the mean color value was 7.20±0.28; the aroma value was 6.25±0.32; the odor value was 6.75±0.37; the appearance value was 6.25±0.22; and the general appreciation value was 7.25±0.53. The sensory analysis results of hawthorn vinegar in our study indicated that the product had consumable properties.

4. Conclusions

The results obtained from the study indicated that hawthorn vinegar had high phenolic content and high antioxidant capacity. Furthermore, this study revealed that hawthorn vinegar was also rich in mineral matter.

It is known that bioactive components in hawthorn fruit have positive effects on human health, which indicates that hawthorn can be processed into different functional products in addition to its consumption as a fruit. Thus, the recognition and economic value of the fruit will increase, and it will be an alternative product to apple cider vinegar and grape vinegar that are commonly used in our country.

Consumers should be encouraged to regularly use hawthorn vinegar since it has very strong metabolic effects in patients with cardiovascular risk and numerous beneficial effects on health such as lowering cholesterol, LDL, and triglyceride levels.

The fact that further studies are carried out to support previous studies on the health benefits of hawthorn vinegar and to find the best way to use vinegar as a possible functional food product is considered to contribute to the national economy.

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