

Cynarin, Chlorogenic and Caffeic Acid Flavonoids, Cyanidin, Peonidin Anthocyanidins in Head, Heart, Bractes of Artichokes as Antioxidative Quality Indicators: Alterations By Boiling, Steaming and Frying

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Abstract

In edible parts- bracte leaves, heart, head of artichoke varieties (Turkish *var.Sakız*, *var.Bayrampaşa*), proximate composition, antioxidative major phenolic acids [cyanarin-(1,3-dicaffeoylquinic acid), chlorogenic acid-(5-O-caffeoylquinic acid), caffeic acid], anthocyanidins (cyanidin, peonidin), total phenolic acids-TPA, total flavonoids-TFlav, total phenolics-TP, total antocyanins were determined ($p<0.01$), the alterations on above-mentioned bioactive constituents through heat treatment effect (boiling, steaming, frying) were put forwarded. Cyanarin-(1,3-di-O-caffeoylquinic acid) was determined the major phenolic compound of head part of artichokes. It was determined about 6.2 ; 5.6; 3.48 fold increasing in TP content with boiling, steaming, frying, respectively respect to raw-form and total anthocyanins-TA risen as 1.93 fold with boiling whereas decreased as 1.04, 3.09 fold after steaming and frying, respectively. The important alterations were established in phenolic acids -PA, total phenolics-TP, cyanarin, chlorogenic acids in boiling (B) > steaming (S) > frying (F) towards whereas 1.36; 1.28; 2.59 fold decreasing in TFlav with B,S,F processing, respectively ($p<0.01$).

Keywords: Artichoke, Phenolic acid, Anthocyanin, Antioxidant, Heat treatment

Artichoke (*Cynara cardunculus* L. *scolymus*) is an herbaceous perennial plant belonging to Composite family (Asteraceae) and widely cultivated in the Mediterranean area and adjoining parts of Europe, which accounts for 85% of the world's production. Major producers of the globe artichoke are France, Italy, Spain, Egypt, Israel, Algeria, Morocco, and Turkey in Europe whereas California Castroville-Monterey County in USA (Tokuşoğlu, 2018& Tokuşoğlu and Başay, 2009).

Artichokes are consumed as fresh, traditional meal, and canned and are also traditionally used as a medicinal plant. The artichoke heads are edible and used worldwide. The leaves have beneficial effects against liver complaints and have strong antioxidant effects. Their leaves are brewed and consumed as teas and leaves are processed into pharmaceutical preparations such as capsules, tablets and juices. Artichokes contain bioactive compounds including phenolics which protect liver and have strong positive effects on several diseases and disorders. Also, inulin form carbohydrate in artichokes, stabilize blood sugar levels in diabetes (Tokuşoğlu & Başay,2009; Fratianni et al., 2007; Costabile et.al.2010; López-Molina et.al., 2005).

Majorly, such extracts from head and leaves of artichokes have been utilized for their hepatoprotective effects (Speroni *et. al.*, 2003; Gebhardt and Fausel,1997), their benefits on the liver and their protecting against toxins and infection are important (Adzet et.al.,1987). Artichoke head and leaves have antioxidative (Miccadei et.al,2008; Gebhardt and Fausel,1997), anticarcinogenic (Agarwal andMukhtar,1996)and hypocholesterolemic activity (Rondanelli et al.,2012). The artichoke has strong choleric activity (promotes bile secretion in the liver), and choleric increase the excretion of

cholesterol and decrease the manufacture of cholesterol in the liver (Bundy et.al.,2008). It is shown that artichoke leaf consuming improved the dyspeptic symptoms who suffer dyspepsia (digestive problems) and artichoke leaf extract has potential value in relieving irritable bowel syndrome symptoms (Bundy et.al.,2004).

These strong effects are attributed to the high polyphenolic content of artichokes including phenolic acids, majorly hydroxycinnamic acids, flavones and anthocyanins (Figure 1.) Artichoke have high proportion of phenolics (Fratianni et al., 2007; Llorach et al., 2002). The phenolics include cynarin (1,3-di-O-caffeoylquinic acid), luteolin, cynaroside (luteolin-7-O-glucoside), scolymoside (luteolin-7-O-rutinoside); phenolic acids such as caffeic, coumaric, hydroxycinnamic, ferulic, caffeoylquinic acid derivatives; mono- and dicaffeoylquinic acids, including chlorogenic; acid alcohols; flavonoid glycosides, among others (Tokuşoğlu & Başay,2009,2008; Fratianni et al.,2007; Sa'nchez Rabaneda et al., 2003).

Especially, the pleasant bitter taste of the artichoke is due mostly to a plant chemical called cynarin (1,5-dicaffeoylquinic acid), which is found in highest concentration in the leaves of the plant. It is known that extracts including cynarin have positive effects on liver health, hepatobiliary diseases, hyperlipidaemia and cholesterol metabolism (Tokuşoğlu & Başay,2009, Fratianni et al.,2007). Figure 2 shows two major compounds in globe artichoke are chlorogenic acid (5-dicaffeoylquinic acid) and cyanarin (1,5-dicaffeoylquinic acid), phenolic compounds that are derivatives of caffeic acid (Figure 2).

Anthocyanin pigments are responsible for most of the blue-purple and red color intermediate hues of artichoke plant tissues and an increase in anthocyanin pigmentation is considered a positive attribute of plant. It is reported that the main major anthocyanins in artichoke heads were

cyanidin aglycone (Figure 3) and cyanidin glycosides (cyanidin 3,5-diglucoside, cyanidin 3-O- β -glucoside, cyanidin 3,5-malonyldiglucoside, cyanidin 3-(3"-malonyl)glucoside, and cyanidin 3-(6"-malonyl) glucoside (Schütz et.al.,2006). Besides peonidin aglycon (Figure 3) and the two peonidin derivatives were identified as peonidin 3-O- β -glucoside, peonidin 3-(6"-malonyl) glycoside (Schütz et.al.,2006).

Currently, the data of vegetable composition includes are mainly determined regarding raw vegetable material. The limited data are reporting on cooking processes of vegetables. Cooking processes would bring about a number of changes in the chemical composition, antioxidant activities and physical properties and vegetables (Miglio et.al.,2008; Turkmen et.al.,2005; Zhang et.al.,2004; Sahlin et.al.,2004).

It is reported that there are only two studies concerning quality parameters and antioxidant activity of some cooked vegetables including artichoke (Pellegrini et.al.,2009; Jiménez-Monreal et.al.,2009) and only one study regarding antioxidant profiles and some physical properties of artichoke (Ferracane et.al.,2008) in the literature.

The present detailed study was undertaken to determine the antioxidant activity, total phenolics, the simultaneous quantitative determination of major flavonoids cynarin (1,5-dicaffeoylquinic acid), chlorogenic acid (5-dicaffeoylquinic acid) and caffeic acids and major anthocyanidins (cyanidin, peonidin) and major quality parameters; to investigate the influences of several heat treatments including boiling, steaming and frying on these major phenolic acids (cynarin, chlorogenic acid, caffeic acid), anthocyanidin phenolics (cyanidin, peonidin), antioxidant activity, total phenolics, and some quality indicators in head and bracte leaves of breaded artichoke varieties [*Cynara Cardunculus* L. *Scolymus* var. Sakız, BayramPaşa] and to carry out the

ratio of monitored phenolics in total phenolics of raw and cooked artichokes.

2. Material and Methods

2.1. Research Material

The artichoke variety SAKIZ (Figure 4a.) was obtained from Çeşme-Karaburun via Ege University Horticultural Department, Agriculture Faculty, Izmir, Turkey. Artichoke variety BAYRAMPAŞA (Figure 4b.) was obtained from Atatürk Horticulture Institute, Yalova, Turkey.

For variety development using the clonal selection of the artichokes lineages, 2 developmental lineages and 2 control lineages were used. The material reproduction operations that were performed for the variety development experiment were set up in a randomised complete block design with 4 replications in 2 locations. In each plot containing 10 plants, 4 candidate varieties and 2 control varieties were used. Each of the experimental and the control plants had the stem weight, width, and the length, as well as the head weight, width, and height measured both at the beginning and at the end of the breeding experiment.

2.2. Chemicals

Cynarin (1,5-Di-caffeoylquinic acid) (Cat.No:30964-13-7; 10 mg) from Carl Roth GmbH & Co. (Karlsruhe, Germany), chlorogenic acid (5-O-Caffeoylquinic acid) (Cat.No:327-97-9; 1 g) and caffeic acid (Cat.No.331-39-5; 1 g) from Sigma (Germany), cyanidin (Cat.No:528-58-5; 10 mg) and peonidin (Cat.No:134-01-0; 5 mg) from Extrasynthese, Genay (France). Cyanidin-3-O-glycoside chlorur (Cat.No: 7084-24-4; 5 mg) from Sigma (Germany), luteolin 7-O-glukozid (Cat.No:5373-11-5; 250 mg) from Extrasynthese, Genay (France), 1,1-diphenyl-2-picryl-hydrazyl (DPPH) (Cat.No. D9132-1G;1g) from Sigma-Aldrich, Chemie GmbH (Munich, Germany) were obtained. All HPLC grade solvents were purchased from Merck (Darmstadt, Germany).

2.3. Preparation of Artichokes to Analysis and Processing

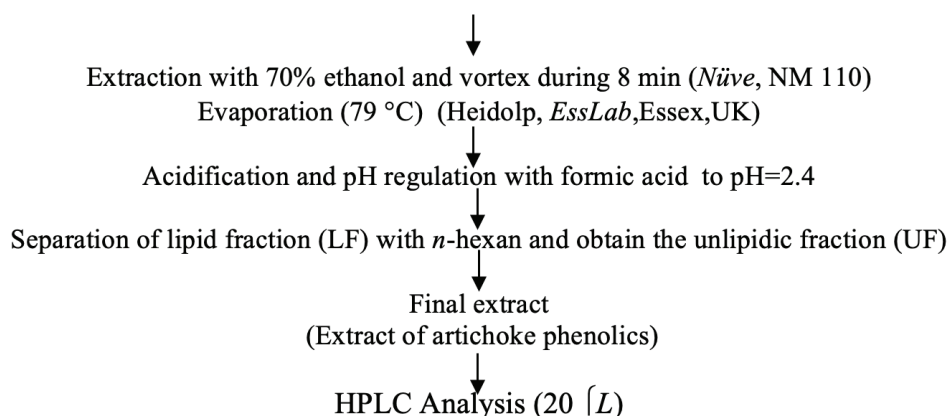
Prior to analysis and processing, artichokes were freshly transferred to laboratory (Product Chemistry and Quality Control Laboratory) at 4 °C refrigerated conditions from breeding areas and equilibrated to room temperature for about 2 h before treatments.

Artichokes were washed, cleaned and blotted by blotting paper. Outer bracte leaves and ruder parts were separated, stem parts were cut by knife which cleaned with ethanol and awns of artichokes were

discarded. Ruder parts in heads of bracte leaves were cleaned. Green parts were peeled as rolling by knife and accessed to head and heart, pileous parts were discarded by spoon. To prevent the browning of peeled parts, cut and peeled artichokes were treated with lemon-water (For lemon-water content; 2 liter (10 glass-water) water and 3 lemons were used). Separated green parts (bracte leaves) and white parts (heads-hearts) were homogenized at blender (*Waring*) apparatus. The homogenized bracte leaves and heart parts of artichokes were dried at N₂ atmosphere. Final samples were obtained for quality analyses, phenolic

2.4. Extraction Methodology of Artichoke Phenolic Acids

Artichokes (*cynara cardunculus var. scolymus*) were extracted the method as shown below (n=2). Leave (or heart) part of artichoke sample was weighed (20 g)



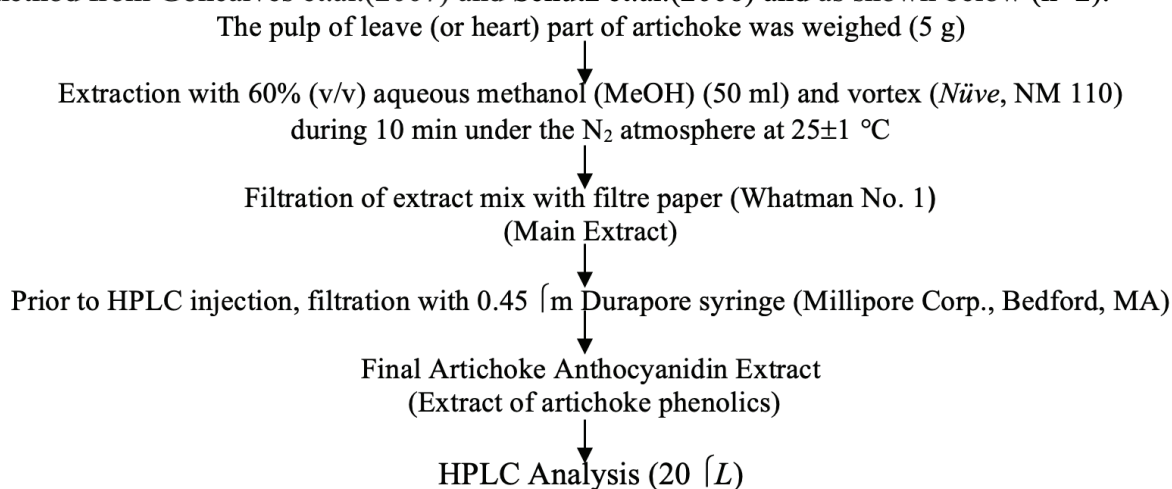
2.5. High Performance Liquid Chromatographic (HPLC) Analysis Methodology for Artichoke Phenolic Acids

Major artichoke phenolics cynarin, chlorogenic acid and caffeic acid were simultaneously determined by modified isocratic HPLC based on the procedure from Sánchez-Rabaneda et al. (2003) and Häusler et al. (2002) and as shown below (n=2).

Column : Hypersil-ODS
[(250×4.6 mm (5 µm) RP-18 (Luna, Phenomenex, CAL)]
Mobile Phase : Acetonitrile/ phosphate buffer (25:75) (v/v) [pH=2.4]
Detection : Fluorometric detection (254-370 nm) ((Shimadzu UV-1601)
Flow rate : 1 ml/min
Sensitivity : 0.05 A. U.F.

2.6. Extraction Methodology of Artichoke Anthocyanidins

Artichoke (*Cynara cardunculus* var. *scolymus*) anthocyanidins were extracted the modified method from Goncalves et.al.(2007) and Schütz et.al.(2006) and as shown below (n=2).



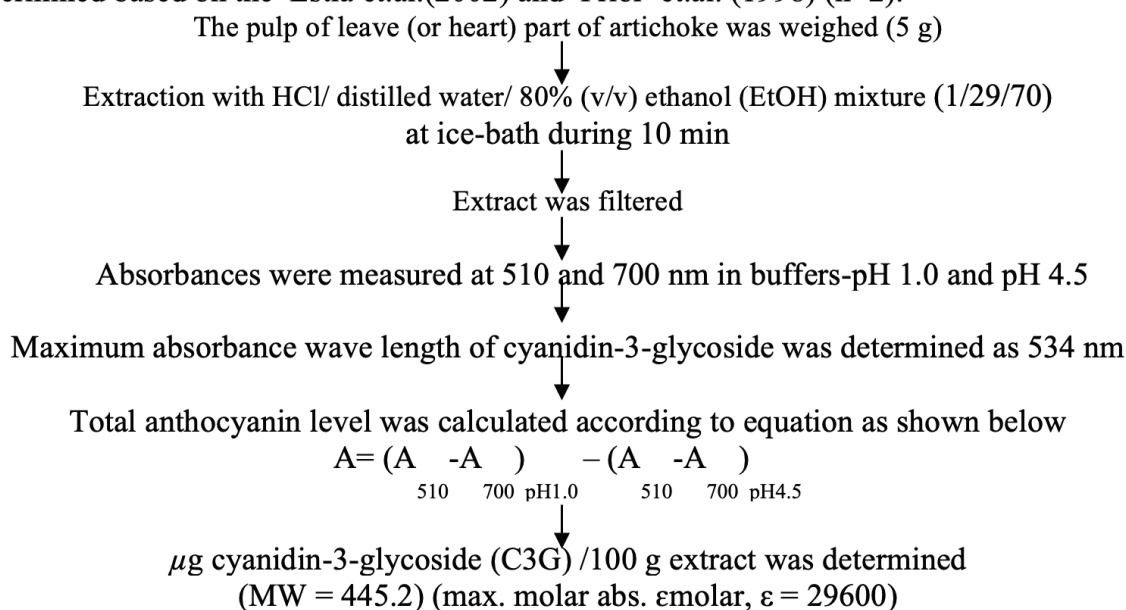
2.7. High Performance Liquid Chromatographic (HPLC) Analysis Methodology for Artichoke Anthocyanidins

Major artichoke anthocyanidins cyanidin and peonidin were simultaneously determined by modified HPLC method based on the procedure from Goncalves et.al.(2007) and as shown below (n=2).

Column : 3.9 ×150 mm NovaPak C₁₈ (Waters)
 Mobile Phase : Asetic acid HCOOH (%10) (A)
 Methanol (%50)+ TFA (%1) (B)
 Detection : UV-VIS (520 nm)
 Flow rate : 0.8 ml/min
 Column temp. : 40 °C
 Sensitivity : 0.05 A. U.F.S.

2.8. Total Anthocyanin Analyses of Artichokes

Total anthocyanins of artichokes were spectrophotometrically (*Optima SP 300*) determined based on the Estia et.al.(2002) and Prior et.al. (1998) (n=2).



2.9. Total Phenolic Analyses of Artichokes

The level of phenolic compounds in artichoke samples was determined based on the Folin-Ciocalteu method (Singleton & Rossi, 1965) and was expressed as gallic acid equivalents (n=2).

5 ml of 80% methanol including 1% HCl solution was added to 1 g artichoke leave (or heart)

The solution was mixed at 4 ± 1 °C (ice-bath) during 2 h and centrifuged at $4000 \times g$ during 15 min.

The extract was filtered and clear part was separated for phenolic analyses. 2.5 ml of clear part (supernatant) was mixed with Folin-Ciocalteu reagent (2.5 ml) + distilled water (10 ml) [in ratio 0.5/0.5/10 (v/v/v)]

2 ml of 7% sodium carbonate (Na_2CO_3) was added to the mixture

The mixture was incubated for 2 h at room temperature and obtained blue-violet colour solution was measured at spectrophotometer (*Optima SP 300*) at 760 nm.

Total phenolics was expressed as chlorogenic acid equivalents (as $\mu\text{g Clg}/100\text{g}$ fresh artichoke)

2.10. Total Flavonoid Analyses in Artichokes

Total flavonoid analyses of artichokes were carried out spectrophotometrically (*Optima SP 300*) based on the aluminum chlorur chlorimetry method according to Singleton et al. (1999) (n=2).

1 g artichoke leave (or heart) puree was treated with 5% sodium nitrite (NaNO_2), 10% aluminum chlorure ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and 1 M sodium hydroxide (NaOH) mixture during 15 min

The absorbance of extract solution was measured at 510 nm and was expressed as luteolin 7-O-glukozid (luteolin-7-G) equivalent /100 g fresh artichoke

2.11. Antioxidant Activity Analyses of Artichokes

Antioxidant activity analyses of artichokes were performed based on the 1,1-diphenyl-2-picryl-hydrazyl (DPPH) method described by Brand-Williams et al. (1995) (n=2).

5 g of leave (or heart) part of artichoke was extracted with 80% (v/v) ethanol (EtOH) at ice-bath during 10 min

900 μl of solutions in different concentration ranges (0.25–35 $\mu\text{g}/\text{ml}$) were treated with 900 μl 0.2 mM methanolic DPPH solution

The absorbance of each mixture was spectrophotometrically (*Optima SP 300*) measured at 517 nm, immediately.

After incubation at room temperature during 1,5,10,30 min, the absorbance of each mixture was again measured at 517 nm, immediately.

DPPH radical-scavenging activity was expressed as inhibition percent and calculated based on the equation as shown below.

DPPH radical-scavenging activity (%) = $(1 - \text{antioxidant OD} / \text{control OD}) \times 100$

The method was validated [$y = 12,33 x - 3,87$ ($R^2 = 0.9997$)]

2.12. Heat Treatments of Artichokes

Three types of cooking methods (boiling, steaming, frying) were used. The optimized heat treatment conditions were applied for each artichoke. Testo 922 Dual Input Type K Thermocouple (Brandt Instruments, Inc., LA, USA) was used in temperature detection measurements for all heat treatments. In all cooking processes, same water with suitable pH (Erikli brand, pH 7.25) was used for the homogenize conditions and pH control of water was performed by Testo-206PH1 Tds (LA, USA) apparatus. All cooked samples with heat treatment were equilibrated to room temperature (25 ± 1 °C) under the ice-bath (4 ± 1 °C) conditions via rapid cooling for prevent the artichoke antioxidants. All heating processes were done as twice replication.

2.12.1. Boiling

Out bracte leaves of 6 of same calibre artichoke samples (*var.*Sakız 6 item; *var.*Bayrampaşa 6 item; as different experiment set) were peeled, washed and were transferred to stainless steel pan (Edition, *TEFAL*) including $\frac{1}{2}$ pan boiled water and cooked at medium heat during 15 min. The excess water of boiled samples was decanted with colander about 40 sec, was equilibrated to room temperature (25 ± 1 °C) and was prepared to analyses.

2.12.2. Steaming

Out bracte leaves of 6 of same calibre artichoke samples (*var.*Sakız 6 item; *var.*Bayrampaşa 6 item; as different experiment set) were peeled, washed and transferred to steam cooker (VC 1002 Ultra Compact Buharlı Pişirici, *TEFAL*) and were cooked with $\frac{3}{4}$ tea glass olive oil (*Tariş Naturel Sızma*).

Firstly, $\frac{1}{3}$ proportion of water was transferred to water reservoir of steam cooker. Artichokes were placed to multilayered reservoirs of steam cooker, and olive oil was added, then cooked during 25 min and was equilibrated to room

temperature (25 ± 1 °C) after cooking and was prepared to analyses.

2.12.3. Frying

Out bracte leaves of 6 of same calibre artichoke samples (*var.*Sakız 6 item; *var.*Bayrampaşa 6 item; as different experiment set) were peeled, washed and were transferred to oiled oven tray (Oven:MF-26 GR Midi Oven, *VESTEL*) and were fried with $\frac{3}{4}$ tea glass olive oil (*Tariş Naturel Sızma*). 5 min frying was performed in adjustable oven to 170 °C. After the frying, the excess frying oil was removed with blotting paper about 15-20 sec and fried artichokes were equilibrated to room temperature (25 ± 1 °C) and was prepared to analyses.

3. Results and Discussion

Figure 6 shows the standard and separated sample HPLC chromatograms (Figure 6.). Average retention times (R.T.s) of cyanarin, caffeic acid and chlorogenic acid were 12.5 min, 15.7 min, 23.7 min, respectively in standard chromatogram whereas avg.retention times (R.T.s) of above mentioned compounds were 12.4 min, 15.6 min, 23.0 min, respectively in sample chromatogram (*var.*Bayrampaşa artichoke). It is shown that cyanarin, caffeic acid and chlorogenic acid were perfectly separated by provided HPLC procedure (Figure 6., chromatogram 1,2).

A mixture of cynarin (1,5-dicaffeoylquinic acid), chlorogenic acid (5-dicaffeoylquinic acid) and caffeic acid were perfectly simultaneously separated by an isocratic HPLC and a baseline resolutions was obtained as shown in Figure 6 first and second chromatogram (Figure 6.). Figure 6, second chromatogram shows that in artichoke sample [*var.*Bayrampaşa heart], cynarin (1,5-dicaffeoylquinic acid), chlorogenic acid (5-dicaffeoylquinic acid) and caffeic acid gave good base-line separation and were determined, simultaneously ($n=30$) (Figure 6 second chromatogram). The quantification and

concentration determination of individual artichoke phenolic acids (cynarin, caffeic acid, chlorogenic acid) were obtained through calibration curves of standards by HPLC software. Our utilized extraction methodology and chromatographic separation was shorter than that of studies and total elution time for three compounds was about 25 min. Not only was time saving but also economical determination regarding solvent consuming.

3.1. Phenolic Acids (Cynarin, Chlorogenic Acid, Caffeic Acid) Quantities

Cynarin, chlorogenic acid and caffeic acid quantities of heart, bracte leaves and head of artichoke samples as shown in Table 1.

In our study, major phenolic acid was found as cynarin (Cyn) in heart parts of artichokes and its level was found as $29483 \pm 201 \text{ mg kg}^{-1}$ in heart of artichoke *var.Sakız* and was found as $18087 \pm 21 \text{ mg kg}^{-1}$ in heart of artichoke *var.Bayrampaşa* ($p < 0.01$) (Table 1).

Cyn levels were $1512 \pm 2 \text{ mg kg}^{-1}$ ve $1058 \pm 5 \text{ mg kg}^{-1}$ in bracte leaves of *var.Sakız* and *var.Bayrampaşa*, respectively. It is shown that cynarin was the main compound of artichoke hearts and was found as 1.6 fold high in *var.Sakız* than *var.Bayrampaşa* ($p < 0.01$) (Table 1).

Figure 7 shows the phenolic acid amounts in heart and bracte leave parts of *var.Sakız* and *var.Bayrampaşa* in our study (Figure 7.).

Head part of artichokes includes heart and bracte leaves of artichokes. The present results demonstrated that both heart and bracte leaves and also sum total of heart and leaves, head part data were in our study and it has been put forwarded the importance of our study. In the literature, detailed study on phenolic compounds and polyphenols in all artichoke edible parts (head, heart and bracte leaves) are limited.

Romani et.al.(2006) were found polyphenol levels in different parts of

typical Italian artichokes (*Cynara scolymus* L.) *var.Violetto di Toscana* and *var.Terom*. Chlorogenic acid (Clg) level had determined in bracte leaves of *var.Violetto di Toscana* and *var.Terom*, avg. $8.72 \pm 6 \text{ mg kg}^{-1}$ and avg. $2.53 \pm 2 \text{ mg kg}^{-1}$ by Romani et.al (2006). In our study, chlorogenic acid (Clg) levels were found as $3197 \pm 27 \text{ mg kg}^{-1}$ and $2379 \pm 43 \text{ mg kg}^{-1}$ in heart of artichokes *var.Sakız* and *var.Bayrampaşa*, respectively. Clg levels were found as $569 \pm 3 \text{ mg kg}^{-1}$ and $1263 \pm 11 \text{ mg kg}^{-1}$ in bracte leaves of artichokes *var.Sakız* and *var.Bayrampaşa*, respectively and it is seen that bracte leaves of artichokes in our study have very high Clg existence in comparison with Italian varieties (Table 1.) (Figure 7.). Romani et.al. (2006) showed that Clg amount had determined in head of *var.Violetto di Toscana* and *var.Terom*, avg. $30.51 \pm 20 \text{ mg kg}^{-1}$ and avg. $14.25 \pm 10 \text{ mg kg}^{-1}$ (Table 1.) while $3766 \pm 30 \text{ mg kg}^{-1}$ and $3642 \pm 54 \text{ mg kg}^{-1}$ were found in heads of our artichokes *var.Sakız* and *var.Bayrampaşa*, respectively and Clg level of our artichoke heads were very high (Table 1.) (Figure 7.).

Caffeic acid (Caf) concentration was found as $452 \pm 2 \text{ mg kg}^{-1}$ ve $688 \pm 7 \text{ mg kg}^{-1}$ in artichoke *var.Sakız* heart part and bracte leaves part, respectively whereas found as $106 \pm 5 \text{ mg kg}^{-1}$ ve $881 \pm 3 \text{ mg kg}^{-1}$ in artichoke *var.Sakız* heart part and bracte leaves part, respectively. It is determined that bracte leaves part included more caffeic acid than heart of artichokes in both varieties and it is seen that Caf levels of *Sakız* variety-heart was 4.2 fold higher than that of *Bayrampaşa* variety-heart ($p < 0.01$) (Table 1.). Detailed data regarding caffeic acid which deproteinized form of chlorogenic acid in artichokes was not found in literature.

Romani et.al.(2006) stated that $63.57 \pm 48 \text{ mg kg}^{-1}$ cynarin and $27.54 \pm 21 \text{ mg kg}^{-1}$ cynarin in bracte leaves of artichoke *var.Violetto di Toscana* and *var.Terom*, respectively. In our artichokes $1512 \pm 2 \text{ mg kg}^{-1}$ cynarin and $1058 \pm 5 \text{ mg kg}^{-1}$ cynarin were detected in *Sakız* and

Bayrampaşa artichokes (Table 1.) (Figure 7.) and higher than literature data by Romani et.al.(2006).

It was reported the 253.35 ± 244 mg cynarin kg^{-1} in head of Violetto di Toscana artichoke and 95.02 cynarin ± 91 mg kg^{-1} in head of Terom artichoke by Romani et.al.(2006). In artichoke head *var.Sakız* and in artichoke head *var.Bayrampaşa*, cynarin concentration was extremely high and 30995 ± 203 mg kg^{-1} and 19145 ± 26 mg kg^{-1} of cynarin were determined, respectively (Table 1.) (Figure 8.). Figure 8 shows the phenolic acid levels in head of *var.Sakız* and *var.Bayrampaşa* in our study (Figure 8.). It has also been revealed that cyanidin was major compound in studied artichoke varieties. Especially heart part of studied artichokes were rich in cynarin and thereby cynarin profile has been determined extremely high in heads of Turkish artichokes, *var.Sakız* and *var.Bayrampaşa*. As overall, owing to the richness of their phenolic acid compositions, especially sources of cynarin compounds of Turkish artichokes, it has been stated their wealthiness of liver-hepatic functions and antioxidative availability.

3.2. Total Phenolic Acid, Total Flavonoid and Total Phenolics in Artichokes

In studied artichokes, total phenolic acid, total flavonoid and total phenolics were determined as shown in Table 2.

Total phenolic acids were determined as 33325.12 ± 85 mg kg^{-1} in heart part of artichoke *var.Sakız* and while 20992.25 ± 23 mg kg^{-1} in heart part of artichoke *var.Bayrampaşa* and 1.59 fold difference was found in each other (Table 2.). Total flavonoid levels was higher in artichoke *var.Bayrampaşa* (3302.78 ± 17 mg kg^{-1}) and was found 1.84 fold higher than artichoke *var.Sakız* ($p < 0.01$) (Table 2.). Figure 9 shows total phenolic acids, total flavonoids and total phenolics in parts of studied artichokes (Figure 9.).

Total phenolic amounts was found as $35482,64 \pm 77$ mg kg^{-1} in artichoke

var.Sakız whereas $24438,14 \pm 38$ mg phenolics kg^{-1} in *var.Bayrampaşa* and was 1.45 fold higher in *Sakız* artichokes ($p < 0.01$). It is shown that both artichokes were good sources of phenolics (Table 2.).

Total phenolic acids (TPA) were found as 36097.31 ± 90 mg kg^{-1} in head of artichoke *var.Sakız* and while 24208.47 ± 26 mg kg^{-1} in heart part of artichoke *var.Bayrampaşa*. *Sakız* head was rich as 1.49 fold in phenolic acids (Table 2.). Romani et.al.(2006) stated that 287.92 mg kg^{-1} and 109.83 mg kg^{-1} of TPA in head of artichoke *var.Violetto di Toscana* and *var.Terom*, respectively. TPA in Turkish artichoke heads were higher about 84-125 fold than the study reported by Romani et.al.(2006). Romani et.al.(2006) found that 72.99 mg kg^{-1} and 30.46 mg kg^{-1} of TPA in bracte leaves of *var.Violetto di Toscana* and *var.Terom*, respectively. Based on our data, however, total phenolic acids were lower than another parts in *var.Sakız* and *var.Bayrampaşa*, Turkish artichokes have very rich in phenolic acids. TPA in bracte leaves were 2772.19 ± 5 mg kg^{-1} and 3216.22 ± 3 mg kg^{-1} for *var.Sakız* and *var.Bayrampaşa*, respectively and at least 44 fold higher than the literature data. Detailed data concerning chlorogenic acid in artichokes was not found in literature.

Due to extremely Turkish artichoke-heart part have very high total phenolics, the total phenolic (TP) concentration of head parts have been extremely high (Table 2.) ($p < 0.01$). Total phenolics were found as 40784.96 ± 83 mg kg^{-1} in head part of *Sakız* and 29952.6 ± 54 mg kg^{-1} in head part of *Bayrampaşa* (Table 2.). Romani et.al.(2006) reported 297.50 mg kg^{-1} and 111.81 mg kg^{-1} of total phenolics in *Violette di Toscana* and *Terom* artichokes, respectively. Romani et.al.(2006) also reported that total polyphenols level was 74.65 mg kg^{-1} and 32.09 mg kg^{-1} in bracte leaves of *Violette di Toscana* and *Terom* artichokes, respectively. In our study, total phenolics of bracte leaves were found as 5302.32 ± 6 mg kg^{-1} in *Sakız* artichokes and 5514.46 ± 16 mg kg^{-1} in *Bayrampaşa*

variety ($p < 0.01$) (Table 2.), this bracte leaves data very high than Violette di Toscana and Terom. TP in heart parts of our artichokes were $35482.64 \pm 77 \text{ mg kg}^{-1}$ for Sakız and $24438.14 \pm 38 \text{ mg kg}^{-1}$ for Bayrampaşa artichokes. Detailed data study regarding TP in heart part of artichoke was not found in literature.

Total flavonoid (TF) content was also detected in bracte leaves of Sakız ($2011.53 \pm 4 \text{ mg kg}^{-1}$) and Bayrampaşa ($1697.57 \pm 8 \text{ mg kg}^{-1}$) and in our previous study, $3805.35 \pm 6 \text{ mg kg}^{-1}$ and $5000.35 \pm 25 \text{ mg kg}^{-1}$ of TF in head parts of Sakız and Bayrampaşa, respectively ($p < 0.01$) (Table 2.). In the literature, avg. 166 mg kg^{-1} of TF in bracte leaves while $198\text{-}958 \text{ mg kg}^{-1}$ of TF in heads were reported in Italian artichokes (Romani et al., 2006). As it is seen that our artichokes were rich in TF contents (Table 2). TF levels of heart part of Turkish artichokes were found as $1793.82\text{-}3302.78 \text{ mg kg}^{-1}$ while detailed data study regarding TF in heart part of artichoke was not found in literature.

As overall evaluation, Turkish artichoke head > heads > bracte leaves were very rich in phenolic compounds (Table 1 and Table 2). Especially, alongside of normal consuming of heart and leaves (totally thereby head) as meal, heart parts can be used as canned food goods, bracte leaves powder can be used as food additive and nutraceutical food.

3.3. Major Anthocyanidins and Total Anthocyanin Quantities in Artichokes

Figure 10. shows the standards and separated sample HPLC chromatogram of major anthocyanidins in studied artichoke *var. Sakız* (Figure 10.). Average retention times (R.T.s) of cyanidin and peonidin were 2.58 min [(R.T)_{peonidin} = 2.58 min] for peonidin and 5.08 min for cyanidin [(R.T)_{cyanidin} = 5.08 min] in sample artichokes.

It is seen that cyanidin and peonidin anthocyanidins were perfectly simultaneously separated by provided HPLC procedure (Figure 10). As it is seen, cyanidin and peonidin were perfectly

simultaneously determined with HPLC base-line separation ($n=30$). The sugar moieties containing glycosides were removed with the used method and were obtained aglycon forms as anthocyanidins. Total anthocyanidin content including glycosides was determined, spectrophotometrically (Table 3.).

In our study, major anthocyanidin (aglycon form) was cyanidin in both artichoke varieties. In studied artichokes, cyanidin aglycon which gives orange-red colour, amount was found as $92.73 \pm 3.1 \mu\text{g}^{-1}/100\text{g}$ ($0.92 \pm 0.03 \text{ mg kg}^{-1}$) in heart of artichoke *var. Sakız* while $101.11 \pm 4.0 \mu\text{g}^{-1}/100\text{g}$ ($1.01 \pm 0.04 \text{ mg kg}^{-1}$) in heart of artichoke *var. Bayrampaşa*. It was detected that dominant aglycon form was cyanidin and its concentration was higher in heart part than that of in bracte leaves ($p < 0.01$) (Table 3.) (Figure 11.).

Peonidin which give more colour, was found less in both varieties and was found higher concentration in bracte leaves of both artichokes (Table 3.) (Figure 11.). $156.84 \pm 9.4 \mu\text{g}/100\text{g}$ ($1.56 \pm 0.09 \text{ mg kg}^{-1}$) and $154.42 \pm 9.9 \mu\text{g}/100\text{g}$ ($1.54 \pm 0.09 \text{ mg kg}^{-1}$) of cyanidin aglycon in artichoke *var. Sakız* and *var. Bayrampaşa*, respectively and the levels of major aglycon cyanidin *var. Sakız* in accordance with *var. Bayrampaşa*. It is stated that individual aglycon levels in Turkish artichokes as shown in Table 3 and Figure 11 ($p < 0.01$). Detailed study regarding individual aglycons in bracte leaves, in heart parts and in head parts of artichokes were not found in literature.

Total anthocyanin (TA) content of artichoke *var. Sakız* was determined as $912.28 \pm 9.4 \mu\text{g}/100\text{g}$ ($9.12 \pm 0.09 \text{ mg kg}^{-1}$) and $2091.42 \pm 11.2 \mu\text{g}/100\text{g}$ ($20.91 \pm 0.11 \text{ mg kg}^{-1}$) in head parts of artichokes *var. Sakız* and *var. Bayrampaşa*, respectively. We reported that TA level was 2.3 fold higher in Bayrampaşa artichoke heart. TA amount was determined as $528.46 \pm 1.2 \mu\text{g}/100\text{g}$ ($5.28 \pm 0.01 \text{ mg kg}^{-1}$) in bracte leaves of artichoke *var. Sakız* and there was no significant differences with

TA levels in *var.*Bayrampaşa ($p<0.01$). In artichokes, total anthocyanin levels in head part (including heart and bracte leaves) was also detected as shown in Table 3 and Fig.12.

In head parts of artichokes *var.*Sakız and *var.*Bayrampaşa, total anthocyanins were found as $1440.74\pm 10.6 \mu\text{g}^{-1}/100\text{g}$ ($14.40 \pm 0.10 \text{ mg kg}^{-1}$) and $2589.78\pm 13.5 \mu\text{g}^{-1}/100\text{g}$ ($25.89 \pm 0.13 \text{ mg kg}^{-1}$), respectively and it is seen that artichokes were rich in anthocyanins. With regards to colour intensity, anthocyanidin compounds in Bayrampaşa artichokes was 1.8 fold higher than that of Sakız artichokes ($p<0.01$) (Table 3.) (Figure 12.).

Schütz et.al.(2006) had carried out anthocyanin characterization and quantification in artichokes varieties by high performance liquid chromatography-electrospray ionization mass spectrometry (HPLC-DAD-ESI-MS). Schüts et.al.(2006) reported that anthocyanin profiles (with glycoside compounds) in the heads of German artichokes (*Cynara scolymus* L.) *var.*“Camus”, *var.*“Green Globe”, *var.*“Le Castel”, *var.*“Petit Violet” and the heads of French artichokes (*Cynara scolymus* L.) *var.*“Burette” and *var.*“Poivrade”(Schütz et.al.,2006). Total anthocyanin level were determined as $8.4 - 1705.4 \text{ mg kg}^{-1}$ in the study reported by Schütz et.al. (2006) and it has been stated that major anthocyanin compound was cyanidin-3-(6''-malonyl) glycoside and delphinidin and two peonidin as the others.

In our present study, both individual anthocyanidins-cyanidin,peonidin as aglycons and also total anthocyanins were determined in bracte leaves, in hearts, in head part of artichokes and as it is seen that that is detailed research on artichoke parts. In the literature, total anthocyanins (TA) were found in head part of German artichoke *var.*“Petit Violet” as $8.4 \pm 0.0 \text{ mg kg}^{-1}$ and in head part of French artichoke *var.*“ Poivrade” as $20.8 \pm 0.2 \text{ mg kg}^{-1}$ (Schütz et.al., 2006). In our study, TA was determined as $14.40 \pm 0.10 \text{ mg kg}^{-1}$ ($1440.74\pm 10.6 \mu\text{g}/100\text{g}$) in head of

artichoke *var.*Sakız and as $25.89 \pm 0.13 \text{ mg kg}^{-1}$ ($2589.78\pm 13.5\mu\text{g}/100\text{g}$) in head of artichoke *var.*Bayrampaşa (Table 3) (Figure 11,12); especially TA level in *var.*Bayrampaşa was very high than German and French varieties. TA levels were found as $912.28 \pm 9.4 \mu\text{g}/100\text{g}$ ($9.12\pm 0.09 \text{ mg kg}^{-1}$) and $528.46\pm 1.2 \mu\text{g}/100\text{g}$ ($5.28\pm 0.01 \text{ mg kg}^{-1}$) in heart and in bracte leaves of *var.*Sakız while $2091.42 \pm 11.2 \mu\text{g}/100\text{g}$ ($20.91\pm 0.11 \text{ mg kg}^{-1}$) and $498.36\pm 2.3 \mu\text{g}/100\text{g}$ ($4.98\pm 0.02 \text{ mg kg}^{-1}$) in heart and in bracte leaves of *var.*Bayrampaşa, respectively. Detailed data study concerning total anthocyanins in bracte leaves and heart parts of artichokes were not found in literature. As it is seen, the importance of our study were revealed.

3.4. The Alterations in Artichokes by Heat Treatment Effects

In our study three different cooking methods were applied to samples (Part 2.12.) and monitored the alterations of phenolic profiles, selected parameters and antioxidant activities. The changes in phenolic profiles after boiling, steaming, frying were shown in Table 4 ($p<0.01$) (Table 4.).

3.4.1. The Alterations of Phenolic Acid Profiles After Boiling and Steaming

It is determined that after the heat treatment, especially caffeoylquinic acids levels importantly increased. Cynarin (1,3-di-*O*- caffeoylquinic acid) and chlorogenic acid (5-*O*- dicaffeoylquinic acid) of artichokes rised ($p<0.01$) (Table 4.) and it has been considered that the increasing of caffeoylquinic acids were owing the formed different dicaffeoylquinic acid isomers after heat treatments. High total phenolic acid levels of studied artichokes after heat treatments have been verified our remarks on forming of different dicaffeoylquinic acid isomers ($p<0.01$) (Table 4.). Especially via the boiling effect, phenolic acid levels of artichokes mostly increased by comparison to steaming and frying, respectively ($p<0.01$) (Table 4.) (Table 4.1.). Between

the dicaffeoylquinic acid concentrations formed after steaming and frying were not found significant difference as statistically ($p < 0.01$) (Table 4.) (Table 4.1.).

Chlorogenic acid (Clg) level in bracte leaves of *var.Sakız* was 1354.22 ± 19 mg kg⁻¹ after boiling process and was found as 2.38 fold high in comparison to raw form while its level was 6745.67 ± 152 mg kg⁻¹ in heart part of *Sakız* and was detected as 2.11 fold increased in comparison with raw heart form. In boiled head part of artichoke *var.Sakız*, 8099.89 ± 171 mg kg⁻¹ of chlorogenic acid (5-*O*-caffeoylquinic acid) was detected and was 2.15 fold higher than its raw head form ($p < 0.01$) (Table 4). After boiling process, in bracte leaves of *Bayrampaşa*, 2867.01 ± 8 mg kg⁻¹ of Clg was found and its level was 2.27 fold higher than its concentration in raw leaves whereas 6994.26 ± 93 mg kg⁻¹ of Clg was determined in heart part of *Bayrampaşa* and it was 2.94 fold high from raw heart of *Bayrampaşa* ($p < 0.01$) (Table 4).

It was found that boiled head part of *Bayrampaşa* included 9861.27 ± 93 mg kg⁻¹ of Clg and this boiled form contained 2.7 fold high in Clg ($p < 0.01$) (Table 4).

After boiling, cynarin (1,3-di-*O*-caffeoylquinic acid) content was found as 8.02 and 8.42 fold high in boiled bracte leaves and boiled heart forms, respectively. With the boiling process, the raising of major artichoke phenolic substance cynarin was considerably high in comparing to that of chlorogenic acid ($p < 0.01$) (Table 4). It is stated that due to the dicaffeoylquinic acid groups of cynarin, it has been formed more isomers, likewise chlorogenic acid (5-*O*-caffeoylquinic acid) is monocaffeoylacid group. Figure 13 shows the cynarin (1,3-di-*O*-caffeoylquinic acid) level after boiling and steaming process (Figure 13).

After boiling process, total phenolic acids (TPA) in heart parts of *Sakız* and *Bayrampaşa* were found as 63531.26 ± 163 ve 58638.56 ± 87 mg kg⁻¹ and it was found that 1.76 and 2.4 fold increasing in their concentrations, respectively after the boiling ($p < 0.01$) (Table 4.).

With steaming process, TPA in head of *var.Sakız* and *var.Bayrampaşa* was found as 75602.19 ± 66 and 70952.66 ± 61 mg kg⁻¹ and was detected 2.09 and 2.93 fold raising in their TPA amounts after steaming. In steaming forms, phenolic acid contents of *var.Sakız* and *var.Bayrampaşa* were 1.19 and 1.21 fold high, comparison to their boiled forms, respectively.

($p < 0.01$) (Table 4.).

After the cooking at steam, cynarin (1,3-di-*O*-caffeoylquinic) level was 81219.44 ± 89 mg kg⁻¹ in head of *Bayrampaşa* artichoke variety and was detected as 4.24 fold raising in cynarin concentration of steamed heads, as comparing to raw heads ($p < 0.01$) (Table 4.).

In steamed forms, cynarin contents were lower in *Sakız* and *Bayrampaşa*, comparing to boiled forms and were detected 2.34 and 2.14 fold lower ($p < 0.01$) (Table 4.). From the point of total phenolic acid (TPA) content, in artichokes, however TPA of steamed forms were high, individual cynarin contents were higher in boiled forms ($p < 0.01$) (Table 4.). The establishing of these findings were notable for our study. Due to it is known more strong antioxidant and liver protector (hepatoprotective), anti-LDL effects of cynarin which is the major phenolic compound of artichoke; regarding findings on mostly high concentration of cynarin in boiled artichokes and regarding findings on good levels of cynarin in steam cooking were notable for consumers (Table 4.).

After steaming process, chlorogenic acid was found in steamed head parts of *var.Sakız* and *var. Bayrampaşa* as 6439.86 ± 43 and 6154.98 ± 24 mg kg⁻¹ and 1.71 and 1.69 fold rising was found, respectively (Table 4.). As it is known, chlorogenic acid (Clg) is strong antioxidant, liver-gallbladder-friendly, anti-cancer and antimicrobial agent. It is shown that with boiled artichoke or steam cooked artichoke, high concentrations of Clg can be absorbed. Our study has been put forwarded the notable data. In steamed forms, cynarin contents were detected as 1.26 and 1.6 fold

lower than their boiled forms in *var.Sakız* and in *var.Bayrampaşa*, respectively, but both boiled and steamed forms can be fruitful ($p<0.01$) (Table 4.).

3.4.2. The Alterations of Total Flavonoids, Total Phenolics After Boiling and Steaming

In the head parts of *var.Sakız*, after the boiling, total flavonoid levels were found as $2782.94 \pm 23 \text{ mg kg}^{-1}$ luteolin-7-*O*-glukozid equivalent ($p<0.01$) (Table 4.). It was stated that total flavonoids level affected by boiling process and was detected 1.36 fold decreasing (Table 4.).

Total flavonoid (TF) levels of steamed *var.Sakız* was found as $2954.45 \pm 34 \text{ mg kg}^{-1}$ luteolin-7-*O*-glukozid equivalent and was 1.28 fold lower than that of raw forms. TF levels in boiled head of *var.Bayrampaşa* and in steamed head of same cultivar were $4717.31 \pm 10 \text{ mg kg}^{-1}$ and $4733.83 \pm 23 \text{ mg kg}^{-1}$ luteolin-7-*O*-glukozid equivalent and there was no significant difference regarding the cooking losses between two processing, statistically ($p<0.01$) (Table 4.). As TF quantity, the cooking losses in both method were not high, thereof, the consuming of boiled or steamed artichokes can be healthy for consumers owing to they are also good flavonoid sources with antioxidative, auxiliary of anticancer, LDL cholesterol inhibition properties (Table 4.).

Total phenolic (TP) substances in boiled head of *var.Sakız* was $252866.75 \pm 127 \text{ mg Clg/kg}$ and TP in steamed head of *var.Sakız* $228388.55 \pm 138 \text{ mg Clg/kg}$. In *Bayrampaşa* variety, TP level was 188400.43 ± 92 and $186969.12 \pm 110 \text{ mg Clg/kg}$, after boiling and steaming processes, respectively. In both varieties, with boiling and steaming, about 6.2 and 5.6 fold increasing were determined, compared to their raw forms ($p<0.01$) (Table 4.). Figure 14 shows the alterations in total phenolic acids, total flavonoids and total phenolics of studied artichokes after boiling and steaming (Figure 14).

In our study, it has been put forwarded that boiling or steaming were effective cooking methods for maximum phenolic availability from artichoke vegetable ($p<0.01$) (Tablo 4.).

3.4.3. The Alterations of Anthocyanidins (Aglycons), Total Anthocyanins After Boiling and Steaming

After boiling, in head of *var.Sakız*, total anthocyanin (Tantho) quantities were found $2780.62 \pm 105 \mu\text{g}/100\text{g}$ as cyanidin-3-glycoside (C3G) equivalent and was detected as 1.93 fold high total anthocyanin in comparing to raw form whereas Tantho quantities were $1383.11 \pm 58 \mu\text{g C3G}/100\text{g}$ in head of *var.Sakız* with steam cooking application and was detected 1.04 fold decreasing than that of raw form ($p<0.01$) (Tablo 4.). It is considered that the duration of boiling application was 15 min and the duration of steaming cooking was 25 min (parts 2.12.1. and 2.12.2.), due to the longer heating process duration in steaming, it may be ring opening in unstable anthocyanin compounds, so a far amount of anthocyanin loss may be in steam cooking of artichokes, comparing to raw form. It is stated that the proposed mechanism the conversion of cyanidin aglycon to cyanidin 3-glycosid and cyanidin 3,5-di-glycoside (Figure 15.) (Anonymous,2005).

Aglycon form (anthocyanidin) has been formed via attaching of sugar moieties from 3. and 5. sites of the molecule, cyanidin-glycoside forms has been increased with the boiling process. It has been commented that sugar (glycoside) content of vegetable may complex to colour compounds, merely, within the longer heating time, it may be the openings from O^+ position of the ring or it may be rupture from sites attached of glycosides in the ring or it may be the conversions in the molecule (Anonymous,2005;Tokuşoğlu & Başay , 20 09).

With the boiling effect, in the head of *Bayrampaşa*, total anthocyanin (TA) quantity was found as $5904.69 \pm 77 \mu\text{g}/100\text{g}$ (as cyanidin-3-glycoside,C3G,

equivalent) and was detected as 2.28 fold increasing in TA content. After the steam cooking, TA levels was determined as $2686.78 \pm 25 \mu\text{g C3G} / 100\text{g}$ in head of *var.Bayrampaşa*, comparing to raw form. As it was seen that TA levels had not decreased in steamed *var.Bayrampaşa*, compared to steamed *var.Sakız*; this result may be interpreted that the sugar content of *var.Bayrampaşa* was higher than that of *var.Sakız* ($p < 0.01$) (Table 4.).

Artichoke colour substances, anthocyanins are strong antioxidants, effective on specific cancer types and have positive effects on health of urinary system (urinary tract system and urologic system), important constituents on memory functions and eye health (Anonymous, 2008; Tokuşoğlu & Başay, 2009).

Cyanidin aglycon level was identified in boiled head of *var.Sakız* and in boiled head of *var.Bayrampaşa* as $68.19 \pm 4 \mu\text{g}/100\text{g}$ and $65.97 \pm 5 \mu\text{g}/100\text{g}$, respectively was found as about 50% of decreasing in both varieties, comparing to raw forms ($p < 0.01$) (Table 4.).

For effective availability of artichoke anthocyanins, boiling > steaming cooking were effective consuming methods, respectively ($p < 0.01$) (Table 4.). After steam cooking, $35.78 \pm 12 \mu\text{g}/100\text{g}$ of cyanidin aglycon was detected in head of *Bayrampaşa* and was determined the 4.3 fold of decreasing in raw head form ($p < 0.01$) (Table 4.). The more cyanidin decreasing in *var.Bayrampaşa* may be due to the more dark green content of *var.Bayrampaşa*. It may be interpreted that the dark green colour content of artichoke may be more increase and also its in cyanidin content may be more decrease. For our hypothesis verification, $L^*a^*b^*$ Colour-Hunter values were measured and it is determined the a values (redness) decreasing. In heart part of the artichokes, it was detected the same level of cyanin stability ($p < 0.01$) (Table 4.).

3.4.4. The Alterations of Major Phenolic Profiles After Frying

After frying (part 2.12.3.) process, cynarin was found in head of *var.Sakız* and in head of *var.Bayrampaşa* as 74078.21 ± 155 ve $43650.52 \pm 103 \mu\text{g}/100\text{g}$ and it was detected as 2.39 and 2.28 fold increasing of cynarin for *var.Sakız* and *var.Bayrampaşa*, respectively, in comparing to raw forms ($p < 0.01$) (Table 5.). With frying, chlorogenic acid quantity rised as 2.13 fold in *var.Sakız* and as 1.9 fold in *var.Bayrampaşa* ($p < 0.01$) (Table 5.).

Total phenolic acids was determined as $65697.23 \pm 42 \mu\text{g}/100\text{g}$ in fried head of *var.Sakız* and was detected 1.82 fold increasing, in comparison to raw head ($p < 0.01$) (Table 5.). After frying, total flavonoid content was 1953.26 ± 23 and $1452.42 \pm 50 \mu\text{g}/100\text{g}$ luteolin-7-*O*-glikozid in *Bayrampaşa* head and in *Sakız* head, respectively and was detected 2.56 and 2.62 fold of decreasing ($p < 0.01$) (Table 5.).

After frying process, total phenolics (TP) was determined in fried head of *var.Sakız* and was detected as 3.34 fold high ($136218.56 \pm 97 \mu\text{g}/100\text{g}$ Clg equivalent). In fried head of *var.Bayrampaşa*, TP levels was found as $104235.05 \pm 111 \mu\text{g}/100\text{g}$ and was determined 3.48 fold increasing.

After the frying, 3.14 and 3.05 fold decreaseings were obtained in total anthocyanin (TA) content ($p < 0.01$) (Table 5.). Owing to the intensity of glycosid groups of *var.Bayrampaşa*, $849.108 \pm 4 \mu\text{g}/100\text{g}$ cyanidin-3-*O*-glycosid equivalent was detected in head of *Bayrampaşa* artichokes and 1.85 fold higher than that of fried *var.Sakız* head ($p < 0.01$) (Table 5.).

Figure 16 shows total anthocyanin levels of artichoke heads after frying process (Figure 16.) Cyanidin aglycon was determined in *var.Sakız* and *var.Bayrampaşa* as 29.89 ± 5 and $30.06 \pm 2 \mu\text{g}/100\text{g}$ respectively and was found 5.25 and 5.14 fold of decreaseings, comparing to their raw forms ($p < 0.01$) (Table 5.).

After frying process, phenolics were also good levels in fried artichokes and were detected increasing levels in some phenolic profiles ($p < 0.01$) (Table 5.). Artichoke frying is alternative consuming to boiling and steam cooking of artichokes, also aroma and flavor

compounds has been formed in frying. In this point, frying time and frying temperature must be controlled and also frying oil quality must be considered for frying process.

Ferracane et.al. (2008) were determined that changing of phenolic caffeoylquinic acid isomers, apigenin derivatives of cooked Italian artichokes with various cooking procedures (Ferracane et.al.,2008). Ferracane et.al. (2008) reported that about 60% of increasings in total caffeoylquinic acids in steamed Italian artichokes. It was no significant alteration in apigenin phenolics in Italian artichokes (Ferracane et.al.,2008).

3.5. Antioxidant Activity in Artichokes

Antioxidant activity (AA) is a measurement of free radical distinctness ability of products. In our study, with DPPH method, antioxidant activities of raw, boiled, steamed, fried artichokes *var.*Sakız and *var.*Bayrampaşa were determined as Trolox equivalent ($p<0.01$) (Tablo 6.). Especially in boiled and steamed artichokes, it was determined the highest AA levels ($p<0.01$) (Table 6.).

In Turkish artichokes, the increasing of AA was about 7 fold in boiled form, was about 11 fold in steamed form and also was about 5.5 fold in fried forms of artichokes ($p<0.01$) (Table 6.) (Figure 17.). Ferracane et.al.(2008) reported that the increasing of AA was 8 fold in boiled Italian artichokes whereas that of was about 15 fold in steam cooked Italian artichokes. Several research were found on antioxidant activity of artichokes (Fратиanni et.al.,2007; Lattanzio et.al.,2005; Alamanni et.al.,2003) in literature but one research was found for comparable to our data. Our study data on AA was in accordance with that study by Ferracane et.al.(2008) however processing procedure differency was.

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4. Conclusion

In our performed study, various phenolic parameters were examined in two raw artichoke varieties and were also identified phenolic profiles after cooking processes including boiling, steaming and frying. It is seen that our study was detailed on individual phenolic acids;caffeoylquinic acids, total flavonoids,total phenolics, anthocyanidins, total anthocyanins, antioxidant activity and their alterations on cooking processing effects. This previous study on phenolic profiles of processed artichokes has been given the strong data for food science and technology literature.

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FIGURES

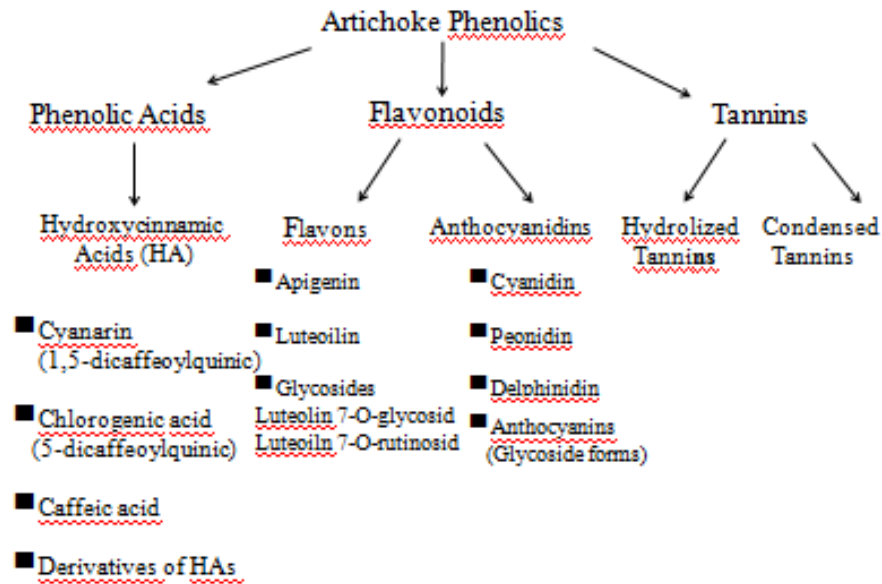


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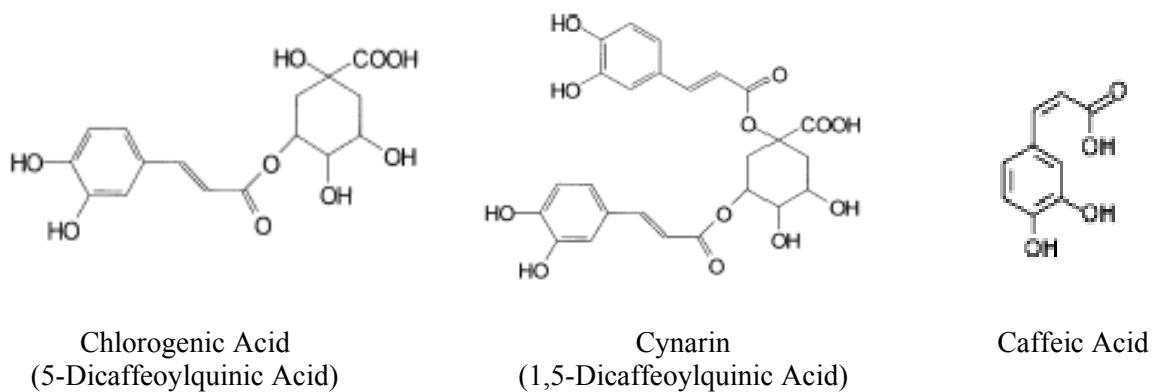
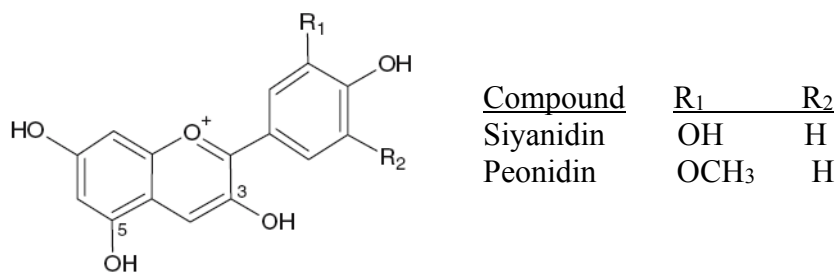
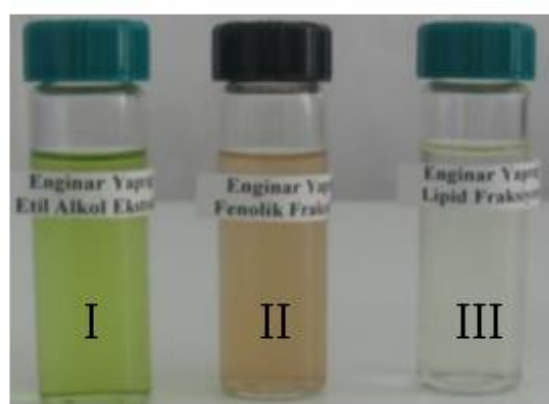
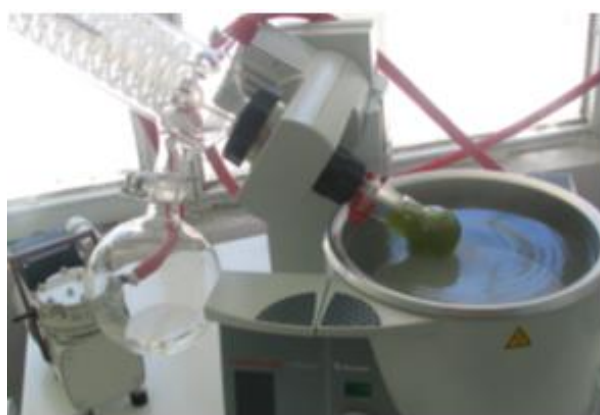


Figure 2.

**Figure 3.****Figure 4a.****Figure 4b.****Figure 5.**

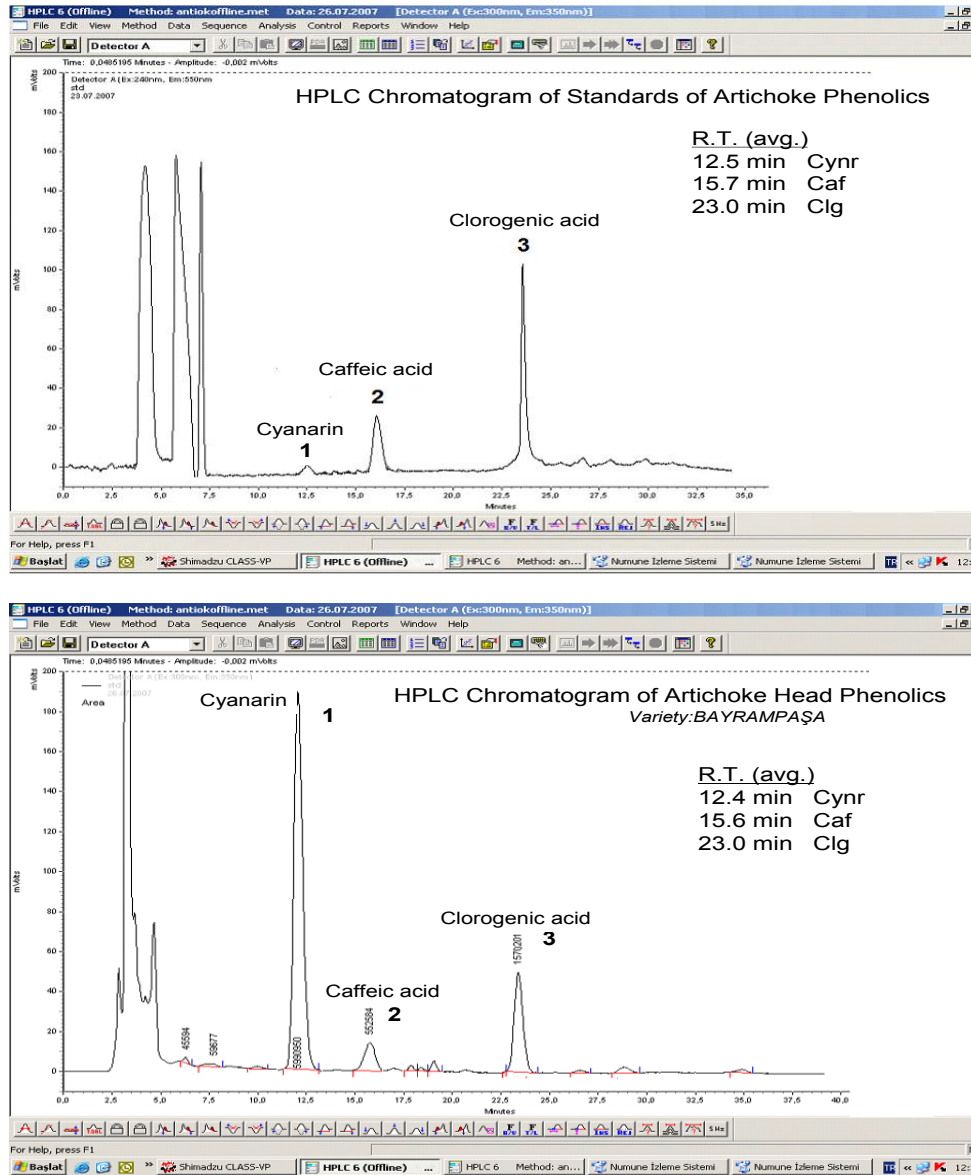


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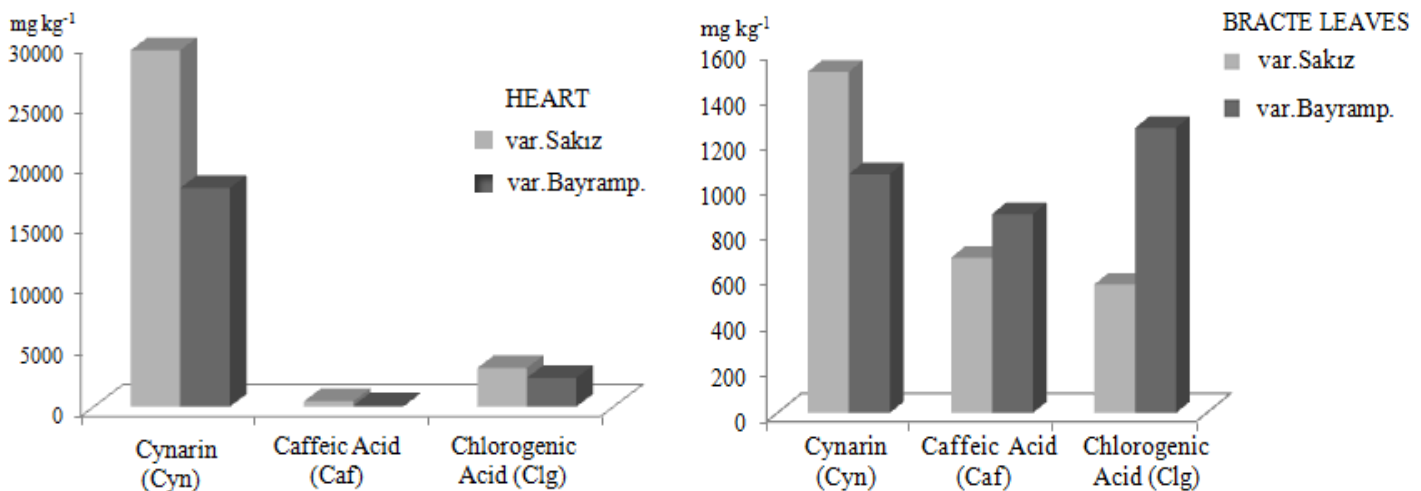


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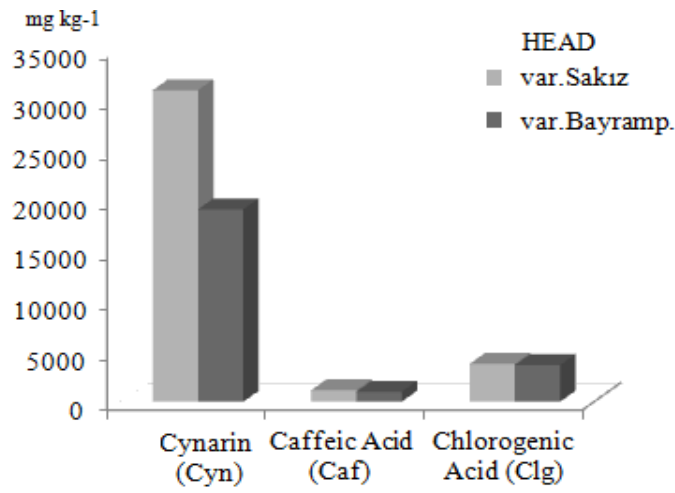


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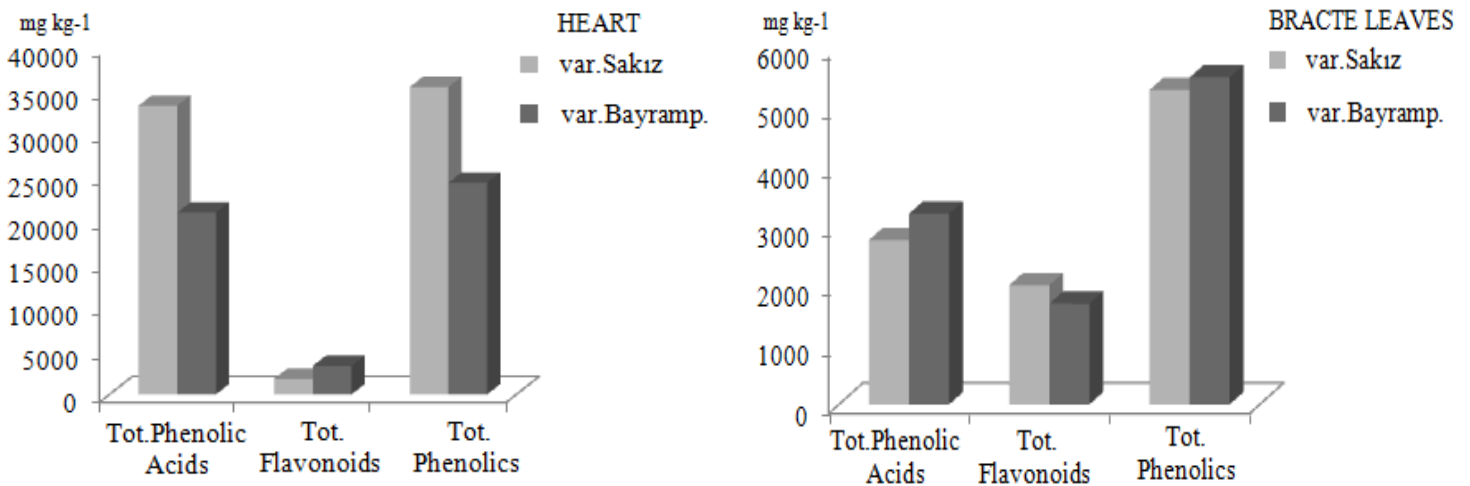


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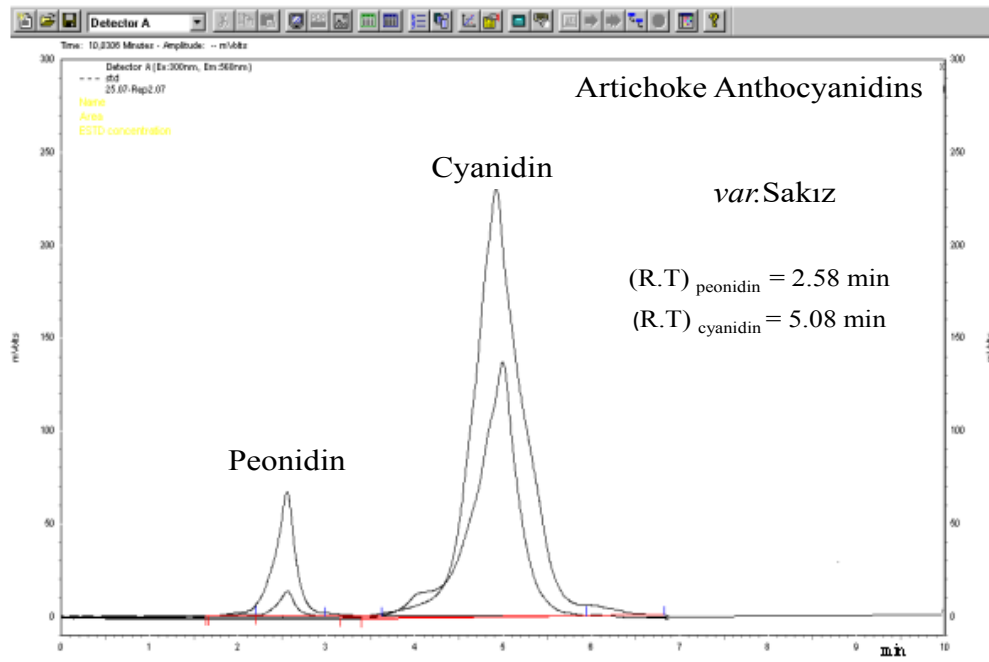


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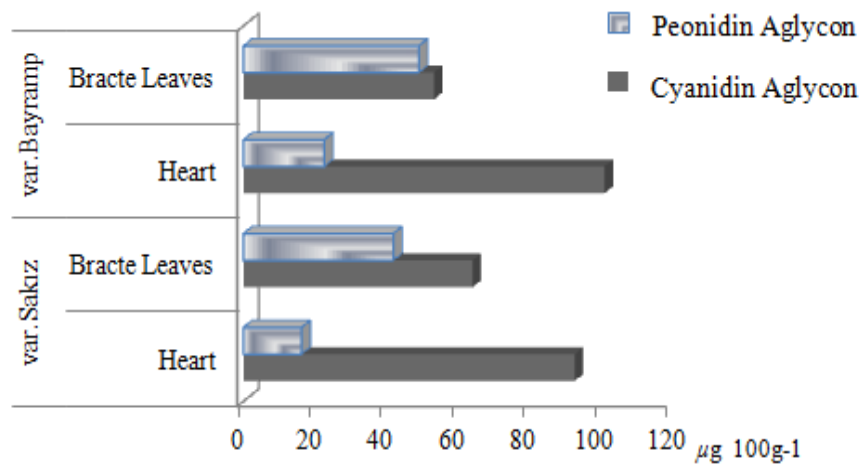


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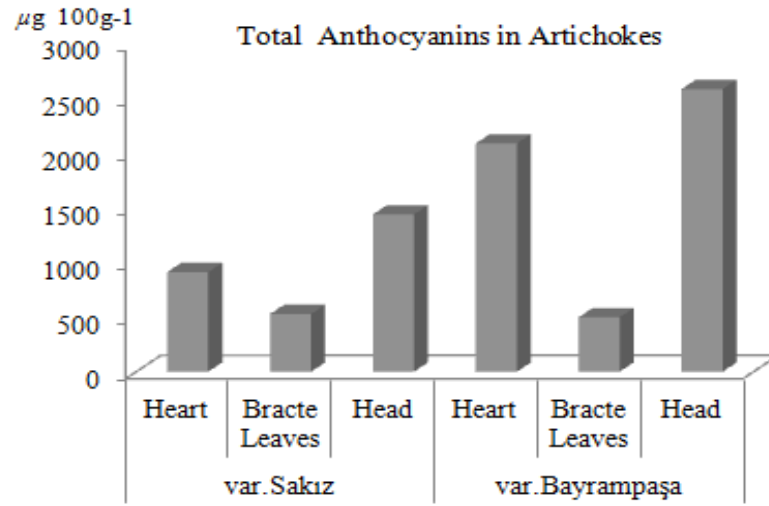


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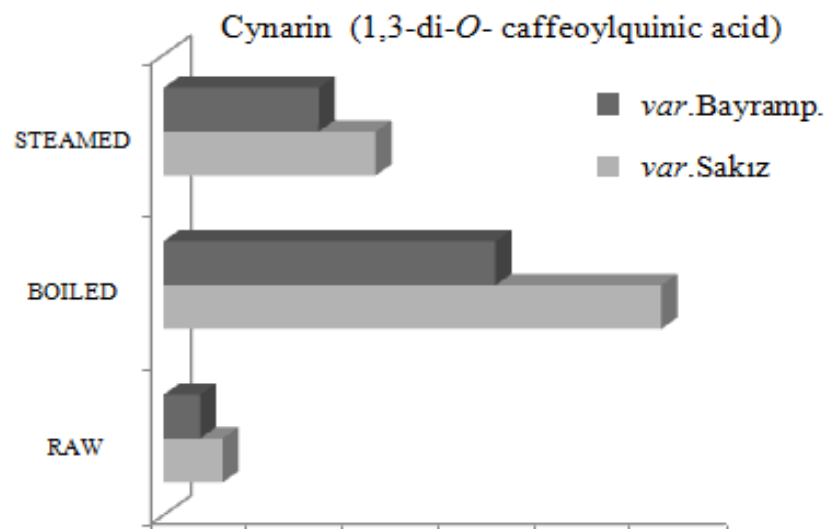


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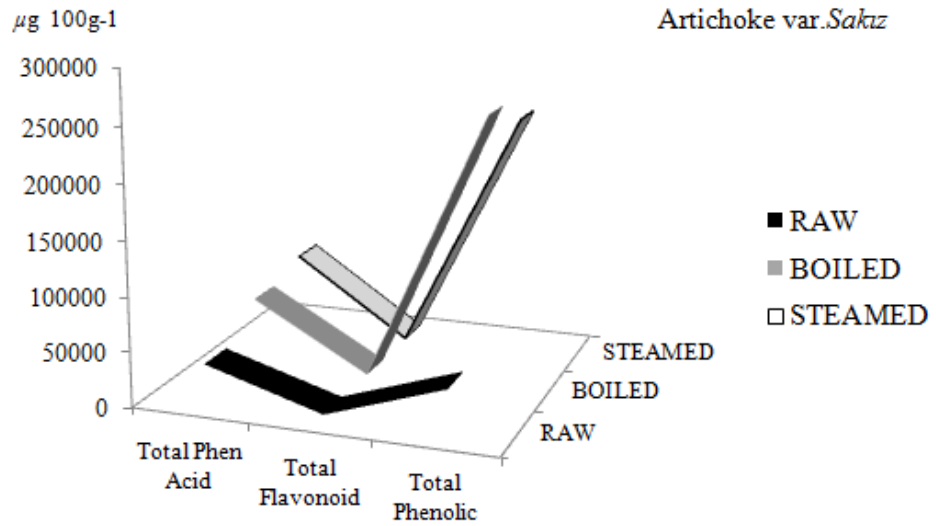


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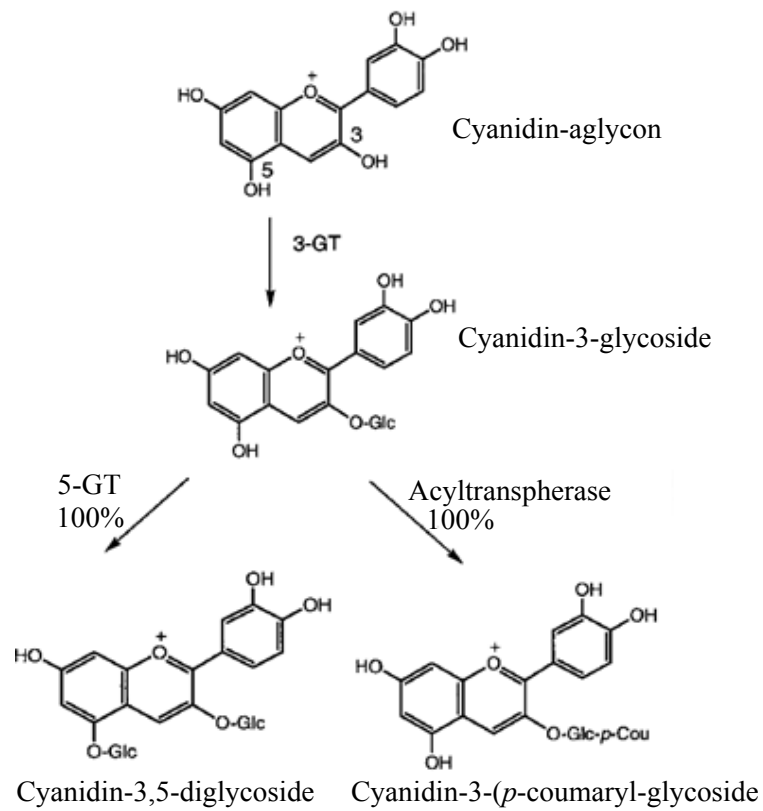


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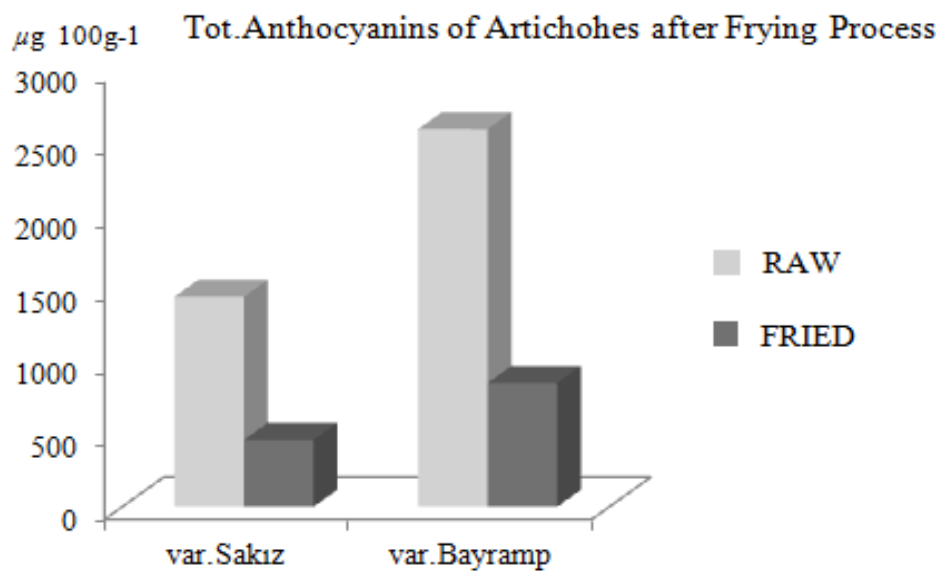


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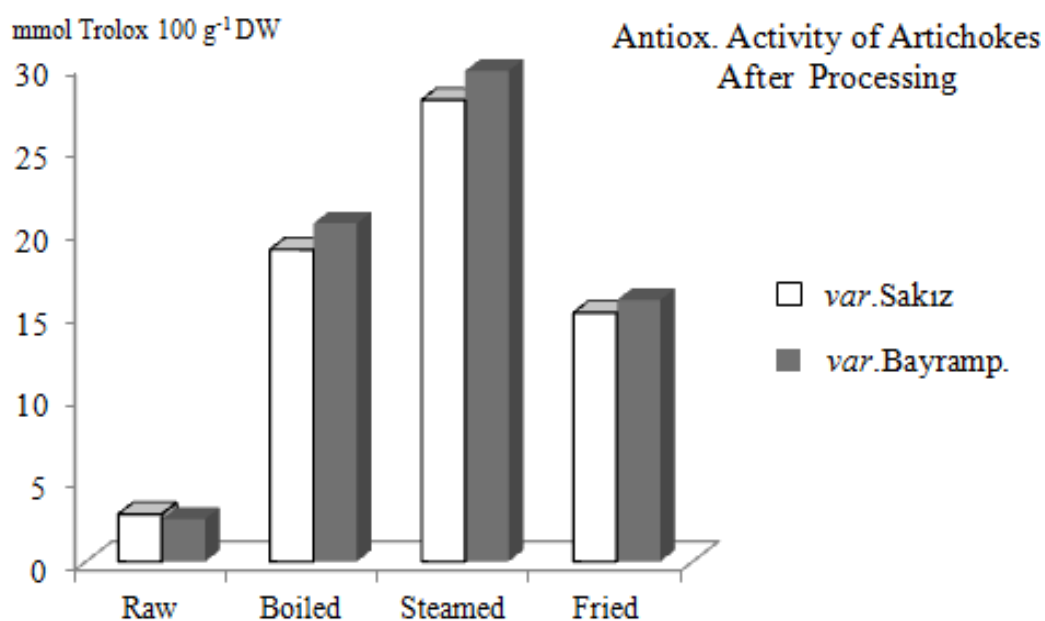


Figure 17.

Table 1. Phenolic Acid Levels of Artichokes*

Parameters	Artihocke Varieties					
	<i>var.Sakız</i>			<i>var.Bayrampaşa</i>		
	Heart	Leave	Head	Heart	Leave	Head
(mg kg ⁻¹)						
Cynarin (Cyn)	29483 ±201	1512 ± 2	30995 ± 203	18087 ± 21	1058 ± 5	19145 ± 26
Caffeic Acid (Caf)	452 ± 2	688 ± 7	1140±9	106 ± 5	881 ± 3	987±8
Chlorogenic Acid (Clg)	3197 ± 27	569 ± 3	3766 ± 30	2379 ± 43	1263 ± 11	3642 ± 54

□($p<0.01$); $n=30$; as mg kg⁻¹ FW**Table 2.** The Levels of Total Phenolic Acid, Total Flavonoid and Total Phenolics In Artichokes

Parameters	Artichoke Varieties					
	<i>var.Sakız</i>			<i>var.Bayrampaşa</i>		
	Heart	Bracte Leaves	Head	Heart	Bracte Leaves	Head
(mg kg ⁻¹)						
Total Phenolic Acids	33325.12 ±85	2772.19 ± 5	36097.31± 90	20992.25 ±23	3216.22 ± 3	24208.47 ± 26
Total Flavonoids	1793.82 ± 2	2011.53 ± 4	3805.35 ± 6	3302.78 ± 17	1697.57 ± 8	5000.35 ± 25
Total Phenolics	35482.64 ±77	5302.32 ± 6	40784.96 ± 83	24438.14 ±38	5514.46 ± 16	29952.6 ± 54

□($p<0.01$); $n=30$; as mg kg⁻¹ FW**Table 3.** The Levels of Individual Anthocyanidins and Total Anthocyanins in Artichokes*

Parameters	Artihocke Varieties					
	<i>var.Sakız</i>			<i>var.Bayrampaşa</i>		
	Heart	Bracte Leaves	Head	Heart	Bracte Leaves	Head
(µg 100 g ⁻¹)						
Cyanidin Aglycon	92.73 ± 3.1	64.11± 6.3	156.84 ± 9.4	101.11 ± 4.0	53.31± 5.9	154.42 ± 9.9
Peonidin Aglycon	16.22± 2.7	41.95± 9.0	58.17± 11.7	22.55 ± 2.2	49.07± 3.6	71.62 ± 5.8
Total Anthocyanins	912.28 ± 9.4	528.46± 1.2	1440.74±10.6	2091.42 ±11.2	498.36± 2.3	2589.78±13.5

□($p<0.01$); $n=30$; as µg 100 g⁻¹ FW; In the text, the data was also compared as mg kg⁻¹ (conversion; µg g⁻¹ = mg kg⁻¹)

Table 4. The Alterations in Major Phenolic Profiles of Boiled and Steamed Processed Artichokes(as $\mu\text{g } 100\text{g}^{-1}$)

Compound	Variety	Heat Treatments								
		Raw			Boiled			Steamed		
		Bracte Leave	Heart	Head	Bracte Leave	Heart	Head	Bracte Leave	Heart	Head
Cynarin	Sakız	1512 ± 2	29483 ± 201	30995 ± 203	12126.23± 78	248246.86 ±185	260373.09 ±263	4868.64 ±21	106093.46 ±125	110962.1 ±146
	Bayrampaşa	1058 ±5	18087 ±21	19145 ± 26	9978.55± 113	163678.41 ±92	173656.96 ±205	3159.18 ±9	78060.26 ±80	81219.44 ±89
Chlorogenic Acid	Sakız	569 ± 3	3197 ± 27	3766 ± 30	1354.22 ± 19	6745.67 ±152	8099.89 ±171	938.85 ±12	5501.01 ±31	6439.86 ±43
	Bayrampaşa	1263 ± 11	2379 ± 43	3642 ± 54	2867.01 ± 8	6994.26 ±93	9861.27 ±93	2089.29 ±7	4065.69 ±17	6154.98 ±24
Total Phenolic Acid	Sakız	2772.19 ± 5	33325.12 ±85	36097.31± 90	4684.68 ± 11	58846.58 ±56	63531.26 ± 67	5246.84 ±27	70355.35±39	75602.19 ±66
	Bayrampaşa	3216.22 ± 3	20992.25 ±23	24208.47 ± 26	5628.22 ± 17	53010.34 ±70	58638.56 ± 87	6093.64± 15	64859.02 ± 46	70952.66 ± 61
Total Flavonoid	Sakız	2011.53 ± 4	1793.82 ± 2	3805.35 ± 6	1399.18 ± 5	1383.76 ± 18	2782.94 ± 23	1418.2 ± 8	1536.25 ± 26	2954.45 ± 34
	Bayrampaşa	1697.57 ± 8	3302.78 ± 17	5000.35 ± 25	1515.66 ± 3	3201.65 ±7	4717.31 ± 10	1610.63± 14	3123.2 ±9	4733.83 ± 23
Total Phenolic	Sakız	5302.32 ± 6	35482.64 ±77	40784.96 ± 83	32988.54 ±85	219878.21±42	252866.75±127	29145.79±51	199242.11±87	228388.55± 138
	Bayrampaşa	5514.46 ± 16	24438.14 ±38	29952.6 ± 54	35123.31 ±23	153277.12 ±69	188400.43 ±92	30309.56 ±34	156659.56±76	186969.12 ±110
Tot.Anthocyanin	Sakız	528.46± 1.2	912.28 ± 9.4	1440.74±10.6	1167.89 ± 19	1612.73 ±86	2780.62 ±105	493.27 ±40	889.84 ±18	1383.11 ±58
	Bayrampaşa	498.36± 2.3	2091.42±11.2	2589.78±13.5	1041.57 ±33	4863.12±44	5904.69 ±77	510.38±19	2176.4 ±6	2686.78 ±25
Cyanidin Aglycon	Sakız	64.11± 6.3	92.73 ± 3.1	156.84 ± 9.4	22.10 ±2	46.09 ±2	68.19±4	18.94 ±4	23.67 ±3	42.61 ±7
	Bayrampaşa	53.31± 5.9	101.11 ± 4.0	154.42 ± 9.9	19.78 ±1	46.19 ±4	65.97±5	16.88 ±1	18.9 ±11	35.78 ±12

Table 5 . The Alterations in Phenolic Profiles in Artichokes After Frying (as $\mu\text{g } 100\text{g}^{-1}$)

		Raw	Frying
		Head	Head
Cynarin (1,3-dicaffeoylquinic acid)	<i>Sakız</i>	30995 \pm 203	74078.21 \pm 155
	<i>Bayrampaşa</i>	19145 \pm 26	43650.52 \pm 103
Chlorogenic Acid (5-O-caffeoylquinic)	<i>Sakız</i>	3766 \pm 30	8021.58 \pm 73
	<i>Bayrampaşa</i>	3642 \pm 54	7243.20 \pm 54
Total Phenolic Acid	<i>Sakız</i>	36097.31 \pm 90	65697.23 \pm 42
	<i>Bayrampaşa</i>	24208.47 \pm 26	42848.77 \pm 66
Top.Flavonoids (as Lutein-7-G)	<i>Sakız</i>	3805.35 \pm 6	1452.42 \pm 50
	<i>Bayrampaşa</i>	5000.35 \pm 25	1953.26 \pm 23
Total Phenolic (as Clg)	<i>Sakız</i>	40784.96 \pm 83	136218.56 \pm 97
	<i>Bayrampaşa</i>	29952.6 \pm 54	104235.05 \pm 111
Total Anthocyanin (as C3G)	<i>Sakız</i>	1440.74 \pm 10,6	458.834 \pm 15
	<i>Bayrampaşa</i>	2589.78 \pm 13,5	849.108 \pm 4
Cyanidin Aglycon	<i>Sakız</i>	156.84 \pm 9,4	29.89 \pm 5
	<i>Bayrampaşa</i>	154.42 \pm 9,9	30.06 \pm 2

Table 6. Antioxidant Activity Levels of *Sakız* and *Bayrampaşa* Artichoke Heads

Antioxidant Activity (mmol Trolox 100 g ⁻¹ DW)				
Variety	Raw	Boiled	Steamed	Fried
<i>Sakız</i>	2.87 \pm 0.03	18.87 \pm 0.22	27.92 \pm 0.83	15.04 \pm 0.58
<i>Bayrampaşa</i>	2.58 \pm 0.02	20.46 \pm 0.64	29.68 \pm 0.80	15.82 \pm 0.58

$p < 0.01$; $n = 30$