International Journal of Food Science and Nutrition Engineering 2013, 3(3): 40-47
DOI: 10.5923/j.food.20130303.04

Phenolic Composition and Antioxidant Capacity of Some Red Wines from Turkey

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Abstract In this research, three different red wines (Boğazkere, Öküzgözü and Shiraz) from different terroir of Turkey were investigated for their phenolic composition and antioxidant capacity. The objective of the study was to evaluate the influence of different enological application on the antioxidant capacity and phenolic content of wines. The wine samples were taken from the specific stages of winemaking process such as after alcoholic fermentation, before malolactic fermentation, after malolactic fermentation, after sulfur treatment and after clarification. ABTS + and $DPPH^{\cdot}$ assays were used for determination of the antioxidant capacity of wine samples. A slight reduction of total phenol, total anthocyanins and antioxidant capacity of wines observed with the subsequent treatments in all wine samples. Also, we observed that a strong positive correlation between the antioxidant capacity measured by DPPH and ABTS assays and total anthocyanins, Malvidin-3-glucoside, total phenolics and especially some of the individual phenolic compounds (gallic acid, (+)-catechin, (-)-epicatechin, p-coumaric acid, o-coumaric acid).

Keywords Polyphenols, Red Wine, DPPH, ABTS

1. Introduction

Regular and small amount of red wine consumption reduces the risk of coronary heart disease. “French Paradox” has been proposed as an explanation for the protection from coronary heart disease death in France since French people have a relatively low incidence of coronary heart disease, despite having a diet rich in saturated fats[1]. Phenolic compounds play a major role in wine quality, since they contribute to organoleptic properties such as colour and astringency. Also, polyphenols have antioxidant properties that have beneficial influence on health especially in the prevention of cardiovascular disease and cancer[2-4]. The health benefits associated with phenolic antioxidant compounds in wines are commonly studied[5-8].

Phenolic compounds can be divided into two major groups based on carbon skeletons: the flavonoids and non-flavonoids. The major flavonoids in wine include; flavonols (quercetin and myricetin); flavan-3-ols ((+)-catechin and (-)-epicatechin); and anthocyanins. The non-flavonoids include the hydroxybenzoates (p-hydroxybenzoic acid and gallic acid); the hydroxycinnamates (caffeic, caftaric, and p-coumaric acids); and the stilbenes[9]. The phenolic composition of wines is dependent on several factors; such as the grape variety, viticultural and environmental factors, winemaking techniques, ageing process[10-13].

Winemaking process such as maceration, alcoholic fermentation, pressing, maturation, fining and bottle aging are factors that affect the phenolic composition of wines[3]. The number of studies about the influence of different enological practices on the phenolic composition and antioxidant activity of wines has been increased[14-18]. Throughout winemaking process particularly during aging, different chemical reactions occur that produce changes in both the phenolic composition and antioxidant capacity of wine[10],[14-15],[19-22].

Several studies on antioxidant capacity have been published and a number of methods have been developed for this purpose. Analytical methods which determine antioxidant capacity gives different results, therefore two methods ($ABTS^{\cdot+}$ and $DPPH^{\cdot}$ assay) which are frequently used in various studies of wines were preferred. In addition, at least two methods were recommended for the detection of antioxidant activity of foods[15],[23]. Among various analytical methods to evaluate total antioxidant capacity of wines, ABTS[2],[15],[24-27] and DPPH methods[9],[15],[26-31] were commonly preferred.

The aim of this study was to evaluate the phenolic composition and antioxidant capacity of *Boğazkere, Öküzgözü and Shiraz* wines from the various stages of winemaking. Also, the correlation between antioxidant capacities and total phenol content, total anthocyanins, free anthocyanin as Malvidin-3-glucoside and individual phenolic compounds (phenolic acids and flavanols) of wines has been investigated.

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Published online at http://journal.sapub.org/food

2. Materials and Methods

2.1. Materials

2.1.1. Wine Samples

Red wines from the Vitis vinifera cv. Boğazkere (Denizli, GPS Coordinates: 38.162636, -29.080811), Öküzgözü (Elazığ, GPS Coordinates: 38.460041, -39.885864) and Shiraz (Denizli, GPS Coordinates: 38.162636, -29.080811) were produced in "Doluca Winery S.A./Turkey" following the 2011 harvest. All the analysis was carried out in triplicate. Samples were taken from five different stages of winemaking such as after alcoholic fermentation, before malolactic fermentation, after malolactic fermentation, after sulfur treatment and after clarification. Block chart of wine sampling is shown in Fig 1.

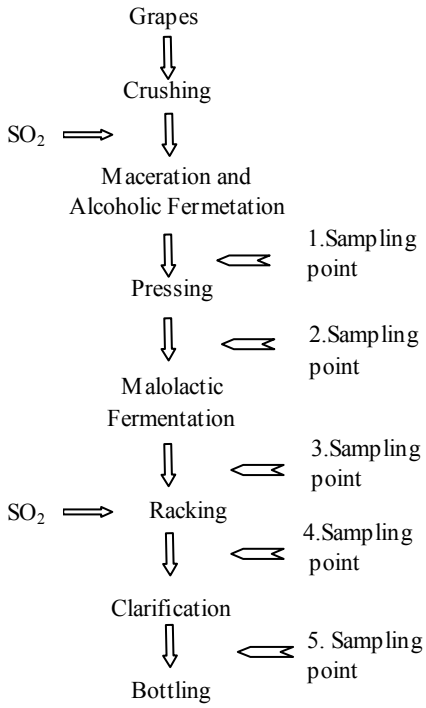


Figure 1. Block chart of wine sampling

2.1.2. Chemicals

Folin-Ciocalteu reagent, sodium carbonate anhydrous, 2,2-Diphenyl-1-picrylhydrazyl radical ($DPPH^{\cdot}$), 2,2'-azinobis-(3-ethylbenzothiazoline)-6-sulfonic acid ($ABTS^{\cdot+}$), potassium persulfate, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), gallic acid, p-coumaric acid, (+)-catechin, (-)-epicatechin, o-coumaric acid were obtained from Sigma (St. Louis, MO, USA); and malvidin-3-glucoside was from Extrasynthese (France). HPLC-grade water from Merck (Germany); formic acid, acetonitrile, methanol, and acetic acid from Sigma-Aldrich (Germany) were purchased.

2.2. Methods

2.2.1. Determination of Total Phenolic Compounds

The total phenolic content of samples was determined by the Folin-Ciocalteau method[32]. The quantification of total phenols was carried out using a calibration curve prepared with known amounts of gallic acid. Results were expressed as mg gallic acid equivalents per litre of wine (mg GAE/L). Absorbance measurements were performed on a Model UV-1700 spectrophotometer (Shimadzu, Japan).

2.2.2. Determination of Total Antioxidant Capacity (TAC)

The antioxidant capacity of wines was investigated by the 2,2-Diphenyl-1-picrylhydrazyl ($DPPH^{\cdot}$) radical assay and 2,2'-azinobis-(3-ethylbenzothiazoline)-6-sulfonic acid ($ABTS^{\cdot+}$) radical assay. The reaction was monitored by a Model UV-1700 spectrophotometer (Shimadzu, Japan).

2.2.2.1. $DPPH^{\cdot}$ Method

The $DPPH^{\cdot}$ method was modified from the method of Nixdorf and Hermosin-Gutierrez[33]. 100 µl of wine diluted with methanol (1:10 v/v) was added to 2.9 ml of a $DPPH^{\cdot}$ radical methanolic solution ($6x10^{-5}$ mol L^{-1}), and after 30 min, the absorbance was measured against a blank (methanol) at 517 nm. Antioxidant activity was defined as the percentage inhibition of the initial concentration of $DPPH^{\cdot}$ radical caused by each diluted wine sample according to equation (1):

$$\% \text{ Inhibition} = [(A_{DPPH} - A_{wine}) / A_{DPPH})] \times 100 \quad (1)$$

2.2.2.2. $ABTS^{\cdot+}$ Method

Antioxidant activity was determined using the $ABTS^{\cdot+}$ method described by Re et al.[34] with some modifications. The colored $ABTS^{\cdot+}$ radical cation stock solution was prepared by reaction of a 7 mM solution of $ABTS^{\cdot+}$ in water with 2.45 mM of potassium persulfate for 12-16 h at room temperature. $ABTS^{\cdot+}$ radical solution was prepared freshly on the day of analysis by diluting the stock solution with phosphate buffer (PBS), to an absorbance of 0.70 ± 0.02 at 734 nm. Different volumes of each wine sample (at a dilution of 1:50 in PBS) was added to 1.0 ml of a $ABTS^{\cdot+}$ radical cation and the absorbance at 734 nm was measured at 0 and 6 min. of reaction. Standard Trolox solutions (5–20 mM) were also evaluated against the radical in order to obtain a calibration curve. Results are expressed as Trolox Equivalent Antioxidant Capacity (TEAC).

2.2.3. Determination of Monomeric Anthocyanins

The total monomeric anthocyanin (TMA) content was measured using pH-differential method according to colour variation in function of pH as described by Giusti and Wrolstad[35]. Wine samples were diluted with aqueous pH 1.0 and pH 4.5 buffers and absorbance was measured at λ= 700 nm and λ_{max} for each grape variety. The result was calculated as mg of malvidin-3-glucoside using equation (2) and expressed as mg per litre (mg/L)

$$\text{TMA (mg/L)} = [(A \times MW \times DF \times 1000)] / (\varepsilon \times 1) \quad (2)$$

where by $A = (A_{max} - A_{700})pH_{1.0} - (A_{max} - A_{700})pH_{4.5}$, ε is the malvidin-3-glucoside molar absorptivity (28000 $L.cm^{-1}.mol^{-1}$), MW is the molecular weight for malvidin-3-glucoside (493.5 g/mol), and D is a dilution factor (100).

2.2.4. HPLC Analysis of Some Individual Phenolic Compounds and Malvidin-3-glucoside

High performance liquid chromatography seperation of phenolic compounds (gallic acid, (+)-catechin, (-)-epicatechin, p-coumaric acid, o-coumaric acid) was performed according to modified method of Özkan and Göktürk Baydar [36]. Shimadzu LC10A liquid chromatograph equipped with diode array dedector was used. 20 µl of wine samples were directly injected after filtration through a 0.45 µm syringe filter. Seperation was achieved on an Intersil ODS-3 reversed phase column (25 cm x 4.6 mm, 5 µm particle size). A flow rate of 1 ml/min was used. Solvent A was (%2) (v/v) acetic acid and Solvent B was methanol. The gradient conditions were; 0 min, 100% B; 3 min, 95% B; 18 min, 80% B; 25 min 80% B; 30 min, 75% B; 35 min, 70% B; 40 min, 60% B; 55 min, 50% B; 65 min, 40% B; 68 min, 100% B. Compounds were identified by comparing their UV spectra recorded with DAD and those reported in the literature. The detection wavelength was 280 nm for gallic acid, (+)-catechin, (-)-epicatechin, o-coumaric acid and p-coumaric acid.

Malvidin-3-glucoside content of wines also was determined by a modified version of OIV method[37]. Shimadzu LC10A liquid chromatograph equipped with diode array dedector was used. 20 µl of wine samples were directly injected after filtration through a 0.45 µm syringe filter. Seperation was achieved on an Intersil ODS-3 reversed phase column (25 cm x 4.6 mm, 5 µm particle size). A flow rate of 1 ml /min was used. The Solvent A was water/formic acid/acetonitrile (87:10:3), Solvent B was water/formic acid/acetonitrile (40:10:50). The gradient used was 0 min, 6% B; 15 min, 30% B; 30 min, 50% B; 35 min, 60%B; 41 min, 6% B. Chromatograms were recorded at 520 nm.

2.2.5. Statistical Analysis

All data were subjected to analysis of variance (ANOVA). Statistical analyses were performed using the Statistical software XLSTAT (Addinsoft).

3.Results and Discussion

3.1. Total Phenolic Content and Antioxidant Capacity

Red wines were investigated for total phenolic content and total antioxidant capacity to evaluate the influence of some of the winemaking stages. The variation of total phenols of wines in different processes of winemaking is presented in Figure 2.

The variance of all wines is similar in phenolic changes during winemaking. At the end of alcoholic fermentation, the maximum values of total phenol content were achieved for *Öküzgözü* (2679.09±36.36 mg GAE/l), *Boğazkere* (3300.30±27.77mg GAE /l) and *Shiraz* (4236.66 ±59.15 mg GAE /l) wines owing to the extraction of more phenols from the skin, seed and stem of the grapes. High values for the total phenolic content at the same stage of process have also been reported[15],[19]. At the end of the clarification, a 7.01%, 4.96%, 9.24% decrease of total phenol content of *Öküzgözü, Boğazkere* and *Shiraz* wines was observed respectively compared to the end of alcoholic fermentation.

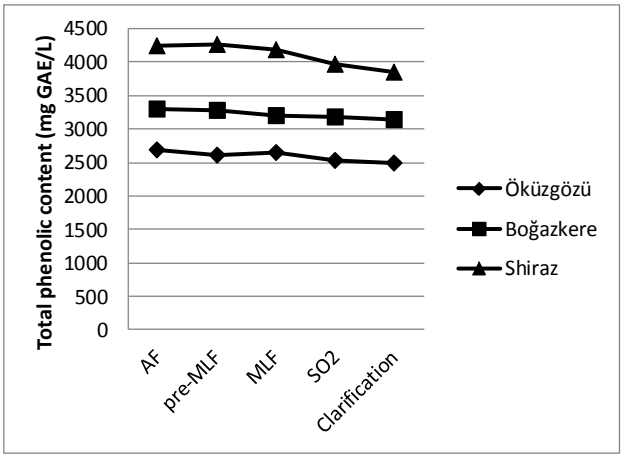


Figure 2. Effect of some winemaking process on the total phenol content

The reduction of antioxidant capacity of *Öküzgözü* wines (from 70.19±0.62 % to 60.68±1.07 % in DPPH assay; from 26.81±0.63 mM to 19.24±0.56 mM in ABTS assay); *Boğazkere* wines (from 87.58±0.55% to 84.55±0.22 % in DPPH assay; from 29.61±0.56 mM to 24.15±0.69 mM in ABTS assay) and *Shiraz* wines (from 74.64±0.87 % to 64.69±0.45 % in DPPH assay; from 24.33±0.84 mM to 16.94±0.57 mM in ABTS assay) during process were obtained (see Fig.3).

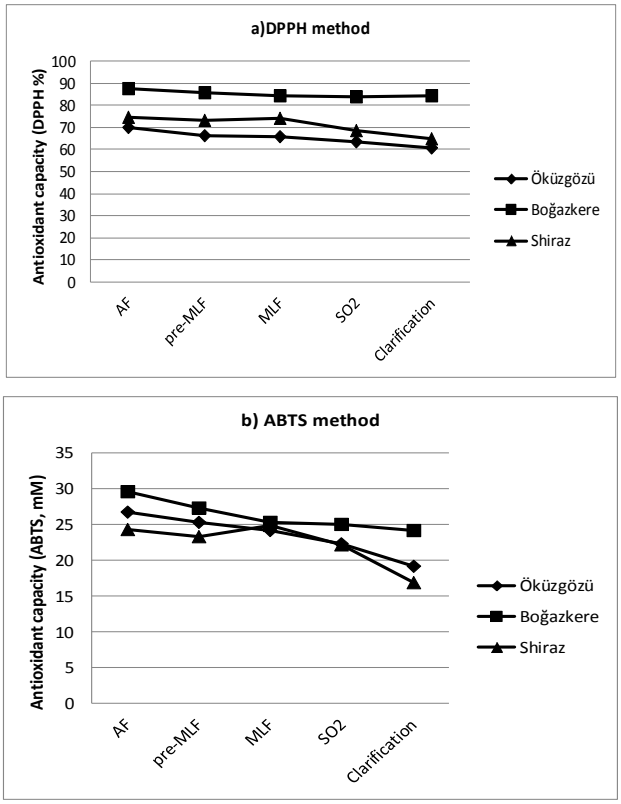


Figure 3. Effect of some winemaking process on the antioxidant capacity of wines as measured by a)DPPH method and b) ABTS method

In spite of the differences between the results obtained by the two adopted methods, a very good correlation was obtained between the results measured by DPPH and ABTS assay (R^2=0.989, p=0.006 for *Öküzgözü*, R^2=0.716, p=0.154

for *Boğazkere*, R^2=0.912, p=0.045 for *Shiraz* wines).

The antioxidant properties of many compounds are directly related to their phenolic composition. Once the phenolic content of wines has diminished during process, a decrease in the results of antioxidant capacity (DPPH and ABTS) of wine samples at subsequent processes of winemaking was observed. There is a good correlation between total phenol content and antioxidant capacity of red wines during processing. The correlation observed with the antioxidant capacity results by the ABTS method (R^2=0.992, p=0.004) was even stronger for *Boğazkere* wines than that measured by the DPPH method (R^2=0.632, p=0.205). High correlation coefficients were found between the total phenol content and antioxidant capacity measured by DPPH for *Öküzgözü* (R^2=0.876, p=0.064) and *Shiraz* wines (R^2=0.907, p=0.048). However the correlation coefficient of ABTS values with total phenol content is lower (R^2=0.803, p=0.104; R^2=0.727, p=0.147, respectively). Similar results of good correlation between antioxidant capacity and total phenol content of wines have been reported. Porgalı and Büyüktuncel[30] observed that a good relationship between antioxidant capacity and total phenolic content determined by HPLC (R^2=0.817) and Folin-Ciocalteu method (R^2=0.992) in the red wines from local stores of Turkey. According to Paixao et al.[3], the high correlation (R^2=0.927) of total phenolic content and antioxidant activity of commercial table wines from Madeira Island was obtained. Seruga et al.[27] analyzed the correlation (R^2=0.995 for ABTS method and R^2=0.989 for DPPH method) of total phenolic content and antioxidant activity of Croatian red wines.

3.2. Total Monomeric Anthocyanins and Antioxidant Capacity

Among polyphenols, anthocyanins which are present in red grape skins are the major components responsible for red wine color[38]. The content of anthocyanins in grape skins was largely influenced by variety[39]. Anthocyanin composition and also the color of red wine can be affected by winemaking process. Monagas et al.[40] observed that numerous chemical reactions such as hydrolysis, oxidation, and polymerisation involving phenolics especially anthocyanins occur during winemaking. Anthocyanins take place in these reactions with the other phenolic compounds and results the formation of new polymers that effect wine colour intensity and stability. This can be explained as the transformation of monomeric anthocyanins to more stable polymeric forms during winemaking[21],[41]. All wines exhibited much higher amount of anthocyanins at the alcoholic fermentation which is attributed to extraction of grape skin during maceration. As reported in the studies[28],[39] the content of monomeric anthocyanins decreased accordingly formation of polymeric forms from the alcoholic fermentation throughout the subsequent stages analyzed. The highest content of anthocyanins for *Öküzgözü, Boğazkere* and *Shiraz* wines (322.71±4.49, 431.81±4.66, 592.2±8.07 mg/l respectively) was found at the alcoholic fermentation stage and the lowest (304.32±2.69, 377.17±8.07, 555.77±8.32 mg/l respectively) at the clarification stage of winemaking.

Our findings show that the monomeric anthocyanin content is important for antioxidant potential of wines since an important correlation was confirmed between total anthocyanins and the results of DPPH and ABTS assays. It was obtained a correlation of R^2 =0.880, p=0.062 for DPPH assay and R^2=0.828 p=0.090 for ABTS assay of *Öküzgözü* wines; R^2 =0.806, p=0.102 for DPPH assay and R^2=0.987, p=0.007 for ABTS assay of *Boğazkere* wines; R^2 = 0.969, p=0.016 for DPPH assay and R^2=0.849, p=0.079 for ABTS assay of *Shiraz* wines. Our results are generally in agreement with the literature[26],[28],[31] supporting that anthocyanins are important antioxidants among polyphenols. Nevertheless, some authors suggest that total monomeric anthocyanins showed non-significant correlation with antioxidant capacity[11],[29],[42]. It was also determined that a linear relationship (R^2= 0.965, p=0.018 for *Öküzgözü*, R^2= 0.961, p=0.019 for *Boğazkere*, R^2= 0.977, p=0.011 for *Shiraz* wines) was observed between total phenolic content and monomeric anthocyanins corroborating the results (R^2= 0.996) of Radovanovic et al.[28].

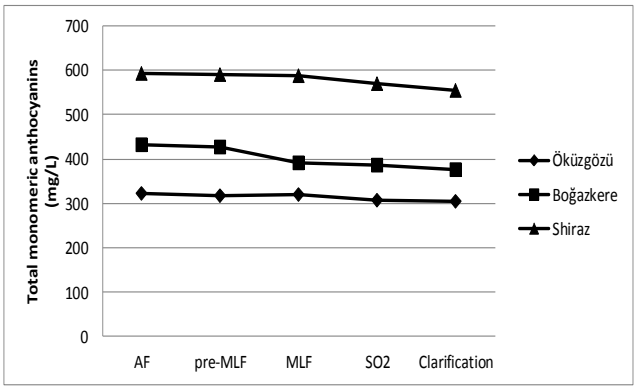


Figure 4. Effect of some winemaking process on the total monomeric anthocyanins of wines

3.3. HPLC Determination of Phenolic Compounds and Antioxidant Capacity

Wine samples were also analyzed for the variation and correlation of the individual phenolics with the antioxidant capacity. Gallic acid, (+)-catechin, (-)-epicatechin, p-coumaric acid, o-coumaric acid were used as phenolic standards for the characterization of the phenolics by HPLC.

The variation of these phenolics during process can be seen in Fig.5

Generally, the decrease in the concentration of the phenolics from the alcoholic fermentation to the end of the clarification stage can be seen in Fig.5 according to biochemical reactions between wine flavanols and anthocyanins to form oligomeric and polymeric compounds. Nevertheless, some phenolics such as gallic acid and (-)-epicatechin increased at the first stage in accordance with literature. Mazza et al.[39] determined the increase of colorless phenolics during alcoholic fermentation, then reaching maximum values at the time of pressing, and remaining stable during malolactic fermentation and subsequent storage. In another research, the concentrations of individual phenolics generally increase with the degree of pressing[15]. According to Burns et al.[14], (+)-catechin,

(-)-epicatechin, gallic acid, coumaric acid levels in the juice increased from day 0 to day 7 during vinification and then decreased slightly or remained relatively steady. Also, the reason of high gallic acid concentration can be explained such a way that it is principally formed by hydrolysis of flavonoid gallate esters due to skin extraction[43].

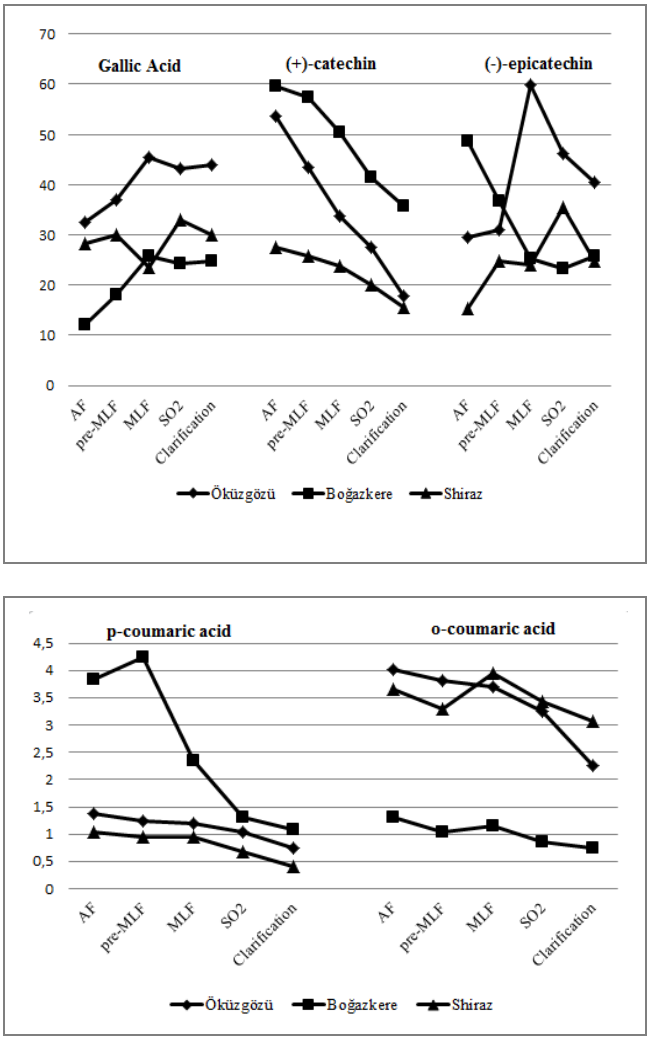


Figure 5. Effect of some winemaking process on the individual phenolic compounds of wines (a) gallic acid, (+)-catechin, (-)-epicatechin, (b) coumaric acid, o-coumaric acid

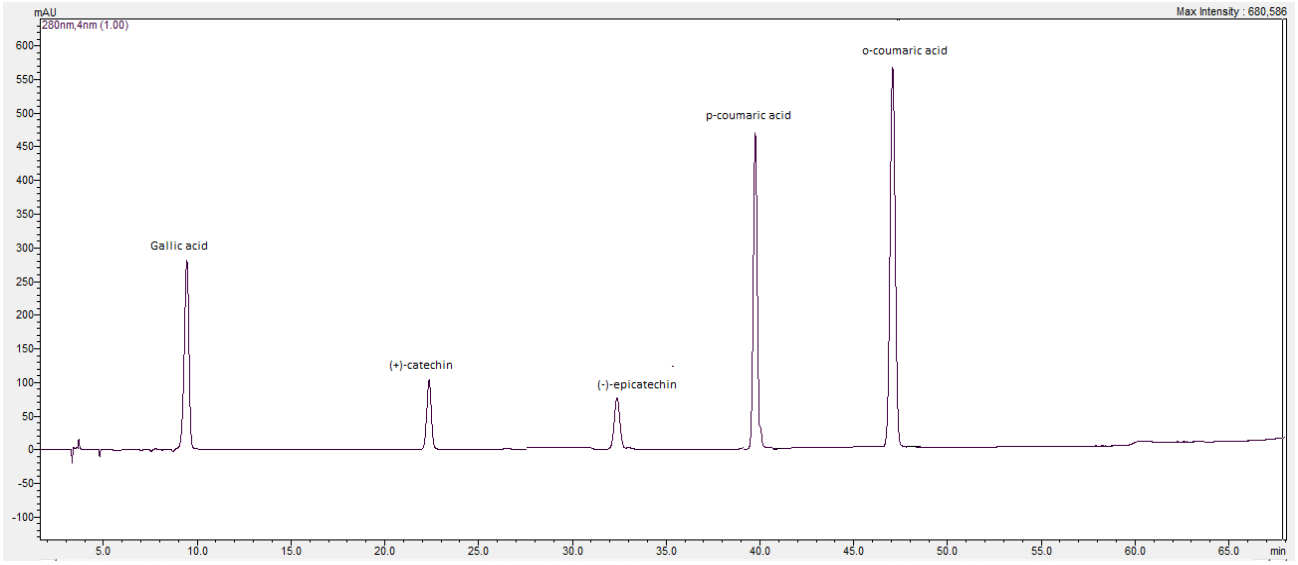
HPLC chromatogram of phenolic standards and Boğazkere wines after MLF stage at 280 nm are shown in Fig. 6.

It is important to determine the group of phenolic compounds which is most significant in antioxidant capacities of wines. The relationship with individual phenolics content and antioxidant capacity was measured and high correlations was found for different group of phenolics for three types of wine (see Table 1). It is concluded from Table 1 that the most potential antioxidant individual phenolics were identified as (+)-catechin, p-coumaric acid and o-coumaric acid for *Öküzgözü* wines; gallic acid, (+)-catechin, (-)-epicatechin and p-coumaric acid for *Boğazkere* wines; (+)-catechin and p-coumaric acid for *Shiraz* wines.

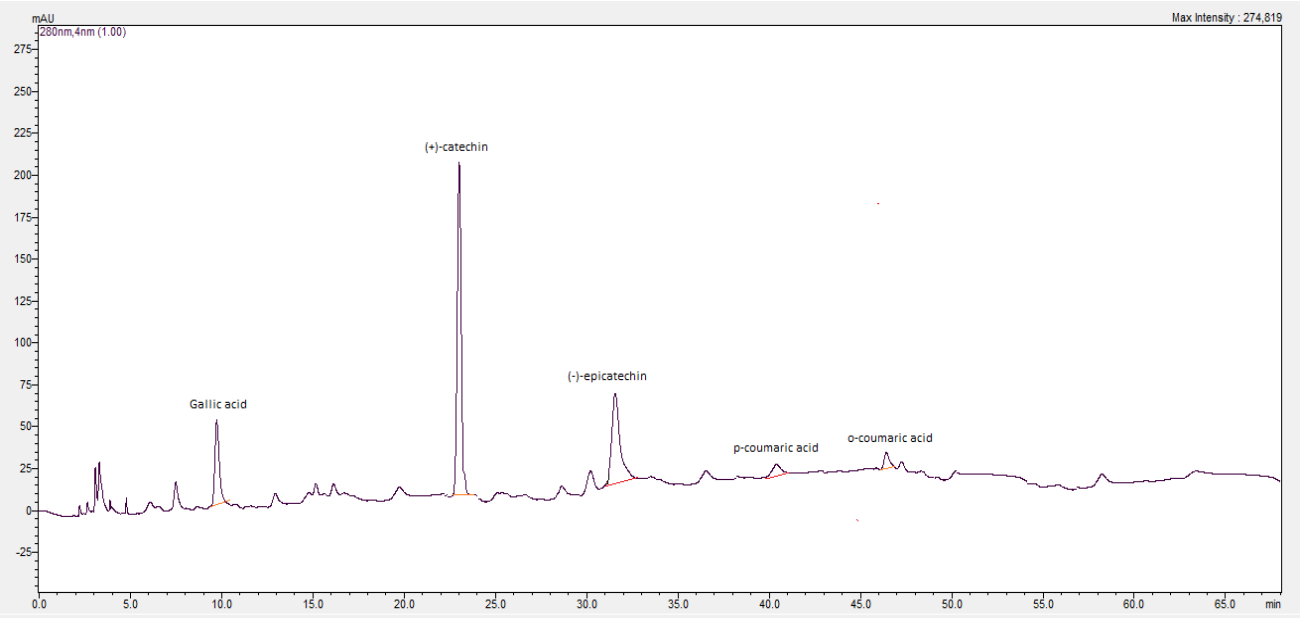
These results are in agreement with other studies in the literature. It is reported by Minussi et al.[2], the correlation of TAC with the concentrations of gallic acid (R2=0.957), epicatechin (R2=0.958), catechin (R^2=0.917) were found higher. Tenore et al.[23] showed that the antioxidant activity (DPPH and FRAP) was mainly correlated with quercetin-3-O-glucorinide (R ranging from 0.972 to 0.998), laricitrin-3-O-rhamnose-7-O-trihydroxycinnamic acid (R ranging from 0.964 to 0.999), kaempferol-3-O-caffeoylate (R ranging from 0.986 to 0.992) and kampferol-3-O-glucoside (R ranging from 0.689 to 0.874) among the flavonols. Porgalı and Büyüktuncel[30] reported that, a good correlation between p-coumaric acid (R^2=0.9585), kampferol (R^2=0.885), myricetin (R^2=0.868), quercetin (R^2=0.722), t-resveratrol (R^2=0.569), (+)-catechin (R^2=0.529), rutin (R^2=0.506) and gallic acid (R^2=0.386) contents and the antioxidant activity (DPPH) was obtained. According to Granato et al.[11]; quercetin, rutin, myricetin, gallic acid, catechin, ferulic acid, and kaempferol were highly correlated; however; trans-resveratrol, p-coumaric acid, epicathechin, caffeic acid, vanillic acid were not significantly correlated with ORAC or DPPH assays.

As reported in the studies, Malvidin-3-glucoside was the major anthocyanin in red wines[44],[45]. The decreased concentration of Malvidin-3-glucoside was observed (see Fig.7). This can be explained as the transformation of monomeric anthocyanins such as malvidin-3-glucoside to form polymeric anthocyanins during process. The variation in the Malvidin-3-glucoside content of three wines appears to be associated to the antioxidant capacities measured by ABTS rather than DPPH. The results of correlation between Malvidin-3-glucoside and total antioxidant capacities (ABTS) were determined highly for *Öküzgözü* (R^2= 0.845, p=0.081), *Boğazkere* (R^2= 0.861, p=0.072) and *Shiraz* (R^2= 0.970, p=0.015) wines.

There is scarce research about the relationship between individual anthocyanins and antioxidant capacity of wines. Tenore et al.[23] determined that, whereas delphinidin-3-O-glucoside (in FPAP test, R= 0.913; in DPPH test, R=0.750), peonidin-3-O-glucoside (in FPAP test, R=0.869; in DPPH test, R=0.683) demonstrated a higher reducing capacity; malvidin-(6-O-caffeoyl)-glucoside (in FPAP test, R=0.766; in DPPH test, R =0.923) and peonidin-3-(6-O-coumaroyl)-glucoside (in FPAP test, R=0.764; in DPPH test, R=0.922) were more powerful radical scavenger. In another study, the relative antioxidant activity correlation with the concentration of malvidin -3-glucoside (r = 0.380) was found[43].



(a)



(b)

Figure 6. HPLC chromatogram of (a) phenolic standards and (b) Boğazkere wine after MLF at 280 nm

Table 1. The correlations between total antioxidant capacity and some individual phenolic compounds

	Gallic acid	(+)-catechin	(-)-epicatechin	p-coumaric acid	o-coumaric acid
DPPH $_{Boğazkere}$	R^2=0.770 (0.122)	R^2=0.589 (0.233)	R^2=0.967 (0.017)	R^2=0.848 (0.079)	R^2=0.190 (0.564)
ABTS $_{Boğazkere}$	R^2= 0.802 (0.104)	R^2=0.864 (0.071)	R^2=0.787 (0.113)	R^2=0.946 (0.027)	R^2=0.391 (0.375)
DPPH $_{Öküzgözü}$	R^2=0.198 (0.555)	R^2=0.905 (0.048)	R^2=0.011 (0.893)	R^2=0.993 (0.003)	R^2=0.979 (0.010)
ABTS $_{Öküzgözü}$	R^2=0.283 (0.468)	R^2=0.953 (0.024)	R^2=0.000 (0.994)	R^2=0.986 (0.007)	R^2=0.974 (0.013)
DPPH $_{Shiraz}$	R^2=0.344 (0.413)	R^2=0.916 (0.043)	R^2=0.071 (0.733)	R^2=0.980 (0.010)	R^2=0.577 (0.241)
ABTS $_{Shiraz}$	R^2=0.210 (0.542)	R^2=0.819 (0.095)	R^2=0.000 (0.982)	R^2=0.890 (0.057)	R^2=0.670 (0.181)

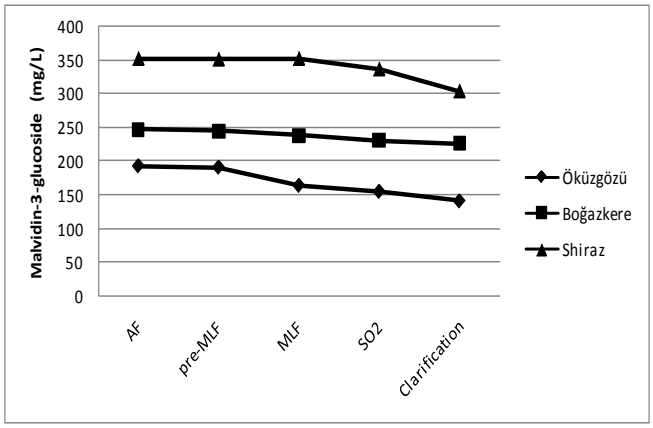


Figure 7. Effect of some winemaking process on the concentration of Malvidin-3-glucoside of wines

4. Conclusions

Total phenolic content, total monomeric anthocyanins, individual phenolics and their relation with antioxidant capacity of *Boğazkere, Öküzgözü* and *Shiraz* wines from Turkey were determined. The evolution of phenolic composition and antioxidant capacities of wine samples from the specific stages of winemaking showed progressive changes. It was obtained that a reduction of total phenolic, total anthocyanin, malvidin-3-glucoside and some of the studied individual phenolic compounds of *Boğazkere, Öküzgözü* and *Shiraz* wines from at the end of the alcoholic fermentation to the end of the clarification stage. In addition, total antioxidant capacity measured by DPPH and ABTS assays of three wines showed similar changes. The research of major phenolics responsible for antioxidant capacity of wines is an important issue. It was observed strong positive correlation with the total antioxidant capacity and the total phenol content, total anthocyanins and especially some of the individual phenolic compounds such as gallic acid, (+)-catechin, (-)-epicatechin, p-coumaric acid and o-coumaric acid depending on the grape variety.

ACKNOWLEDGMENTS

The authors would like to thank Aysun PİRDEL (Board Member-Production Supervisor) and Gülcan BOZ (Production Manager) from DOLUCA Winery for their kind help during this study.

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