The effect of cold maceration on the phenolic composition of red wines

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Abstract. In this study, it was aimed to reveal the effect of cold maceration on the phenolic composition according to classical maceration in Cabernet sauvignon wines. For this purpose; total phenol, total anthocyanin and biologically active eight different phenolic compounds were determined by HPLC in Cabernet sauvignon wines produced with two different maceration techniques during the 2009 and 2010 harvest years. According to the results obtained; wines produced in 2009 and 2010 with classical maceration showed the highest total phenol content with 1529.09 mg GAE/L and 2051.81 mg GAE/L, respectively. The highest total anthocyanin content in Cabernet sauvignon wines were determined in classic maceration wine (149.95 mg/L), cold maceration wine (279.50 mg/L) in 2009 and 2010. The amount of catechin in classic and cold maceration wines was determined as 58.30 mg/L; 51.30 mg/L in 2009 and 140.98 mg/L; 86.45 mg/L in 2010, respectively. According the results, catechin was the highest individual phenolic compound among gallic acid and epicatechin in all maceration types in 2009 and 2010. (–) - Epicatechin and gallic acid were the most present phenolic compounds respectively after (+) - catechin. Malvidine 3-glycoside content was higher than cyanidin 3–5 diglucoside content in all kinds of different maceration types in 2009 and 2010.
Keywords: red wine, maceration, phenolic, anthocyanins

1. Introduction

The researches on positive effects of wine on human health are increasing in the leading wine producing countries of the world (Lin 2000, Pervaiz 2001). In addition to alcohol, sugar, organic acids, ester compounds, cations, anions, amino acids, nitrogenous compounds, color compounds, enzymes, polypeptides, polysaccharides and colloidal substances, wine contains phenolic compounds which have considerable effects on human health (Ribereau-Gayon et al., 2000). Among these compounds, phenolic acids, flavanoids, antociyanins, flavones having antioxidant features, have proven to lower thromboses formation and prevent hazards caused by the free radicals (Martinez and Moreno 2000). Phenolic compounds pass into the wine through seed and peel during maceration and affect on the color, flavor and taste of wine (Ribereau-Gayon et al., 2000). In this study, it was aimed to reveal the effect of cold maceration on the phenolic composition according to classical maceration in C.Sauvignon wines.

2. Material and method

Grapes from Cabernet sauvignon variety were manually harvested at optimum maturity in the 2009 and 2010 vintage in Tokat province and transported to the Diren Winery. Grapes were destemmed and crushed in a commercial grape destemmer-crusher. They were then homogeneously transferred into three stainless-steel tanks for the maceration and added with 30 mg/kg sulfur dioxide. Wines were produced by two different macerations (classic maceration, cold maceration). In classical maceration; The must and marc were left to maceration-fermentation at $24 \pm 2^{\circ}$C for 10 days. After maceration-fermentation, they were pressed with a 10000 L hydraulic Bucher press and the fermentation were completed at $\sim 24^{\circ}$C temperature in controlled stainless steel tanks. In pre-cold maceration; the maceration temperature was adjusted at 4–6°C for 96 hours. The fermentation was then carried out by adding 20 g / hL yeast to the medium. After maceration-fermentation, they were pressed with a 10000 L hydraulic Bucher press and the fermentation were completed at $\sim 24^{\circ}$C in temperature controlled stainless steel tanks.

Saccharomyces cerevisiae as yeast strain (Oenoferm Rouge, Erbslöh Gerseheim, France) and *Oenococcus oeni* as malolactic bacteria (Geisenheim, Germany) were used in C.sauvignon wines.

2.1. Determination of total phenolic content (TP)

Spectrophotometric determination of the TP content was done with the Folin–Ciocalteu micro method as adapted for wine analysis (Waterhouse, 2009) using gallic acid as the standard. The calibration curve of absorbance concentration of standard was used to quantify phenolic content. Results were expressed as mg gallic acid equivalents per litre of wine (mg GAE/L).

Table 1. Gradient elution program for phenolic compounds.

Time(min)	A Concentration % (v/v)	B Concentration % (v/v)
0	0	100
3	5	95
18	20	80
25	20	80
30	25	75
35	30	70
40	40	60
55	50	50
65	60	40
67	0	100
68	0	100

2.2. Determination of total anthocyanin content (TA)

TA contents of the samples were determined using the pH-differential method described by Giusti and Wrolstad (1976). The obtained wines were diluted with buffer to give an absorbance reading between 0.4 and 0.6 U. The pH values of the diluted wines were 1.0 (0.025 M potassium chloride buffer) and 4.5 (0.4 M sodium acetate buffer), respectively. Absorbance was measured, by using a Shimadzu spectrophotometer at 520 nm. Results were expressed as mg malvidin 3-glicoside equivalent per litre of wine (mg /L).

2.3. Determination of some individual phenolic compunds

Catechin, epicatechin, gallic acid and other standards were purchased from Sigma-Aldrich (Steinheim, Germany). Detection and quantification of phenolic compounds were carried out with a CBM-20A Prominence System controller, a SIL-10 AXL Autosampler, a 1C–20 AT Prominence pump, a DGU-20 A5 Prominence degasser, a CTO-10A column heater and a diode array detector with wavelengths set at 280 nm. Intersil ODS-3 column ($5\,\mu m - 25 \times 4.6\,mm$) were used for detection of phenolic compounds. The flow rate was 1 ml/min, injection volume was 10 μl and the column temperature was set at 30°C. Gradient elution of two solvents was used: Solvent A consisted of: acetic acid (Sigma-Aldrich,Germany)–water (2:98 v/v), solvent B: methanol (Sigma-Aldrich,Germany) and the gradient programme used is given Table 1. The wine samples, standard solutions and mobile phases were filtered by a 0.45-μm pour size membrane filter. The amount of phenolic compounds in the extracts was calculated as μg/l wine using external calibration curves, which were obtained for each phenolic standard (Özkan ve Göktürk Baydar 2006).

2.4. Determination of some individual anthociyanin compounds

Anthocyanins of the samples were determined using the OIV method (2003) with some modifications. Malvidine 3-glicoside were purchased from Extrasynthese (France), cyanidine 3–5 diglicoside were purchased from Sigma-Aldrich (Germany). The chromatographic separation was carried out in a C_{18} column with water/Formic acid/Acetonitrile (87:10:3, solvent A) and water/formic acid/acetonitrile (40:10:50, solvent B) as the mobile phase. Gradient elution program is given Table 2.

Table 2. Gradient elution program for anthocyanin compounds.

Time(min)	A Concentration % (v/v)	B Concentration % (v/v)
0	94	6
15	70	30
30	50	50
35	40	60
41	94	6

Table 3. Total phenolic content of C. sauvignon wines in different maceration types (2009).

	Classic	Cold
2009	1529.09± 12.334bA	1501.81± 5.056aA
2010	2051.81± 19.285bB	1715.45± 19.285aB

(n:3), Results were calculated as mg/L gallic acid equivalent. Different letters in the same column and row indicate significant differences between years and different maceration types respectively ($P<0.05$).

2.5. Statistical analyses

All data were analyzed by ANOVA using Statistical Analysis System. The Least Significant Difference (LSD) was used to compare the significance among means. Significant levels were chosen at 5% ($p<0.05$).

3. Results and discussion

3.1. Total phenolic content

The highest total phenolic content was identified in Cabernet sauvignon wines with the classic maceration (1529.09 mg/L) samples in 2009 and in classic maceration (2051,81 mg/L) samples in 2010 (Table 3, Table 4).

Classic maceration wines had the highest total phenolic content for both years. Long maceration times have a positive effect on the level of total phenolic content (Anlı, 2004). The results indicated that wines produced from classical maceration methods had significantly higher total phenolic content than wines produced from cold maceration methods which is consistent with the research of Salinas et al. (2005). Also Joscelyne (2009) sign that a low maceration temperatures leads to a decrease in phenols.

3.2. Total anthocyanin content

The highest total anthocyanin content in Cabernet sauvignon wines were determined in classic maceration wine (149.95 mg/L), cold maceration wine (279.50 mg/L) in 2009 and 2010 respectively. But the amount of anthocyanin in wines obtained from Cabernet sauvignon grapes by applying classical and cold maceration did not show any statistical difference in same year (Table 4). Sacchi et al. (2005) sign that cold maceration (low temperature extraction in the absence of alcohol), produced little difference in anthocyanin and tannin levels, or sometimes, produced even less anthocyanins, color intensity, and flavonols than non cold-maceration wines (Pinot noir).

Table 4. Anthocyanin content of C. sauvignon wines in different maceration types (2009).

	Classic	Cold
2009	149.95± 5.626aA	134.76± 2.648aA
2010	268.26± 12.511aB	279.50± 7.158aB

(n:3), Results were expressed as mg malvidin 3-glicoside equivalent per litre of wine (mg /L). Different letters in the same column and row indicate significant differences between years and different maceration types respectively (P<0.05). (P<0.05).

Table 5. Individual phenolic compounds of C. sauvignon wines in different maceration types (2009).

	Classic	Cold
Gallic acid	18.68± 0.487b	16.64± 0,771a
Catechin	58.30± 1.052b	51.28± 0,455a
Vanilic acid	0.98± 0.022a	0.67± 0,022a
Caffeic acid	0.32± 0.068a	0.60± 0,055a
Epictechin	25.97± 1.652b	18.06± 0,081a
p-coumaric acid	1.28± 0.074a	1.04± 0,059a
Ferulic acid	0.73± 0,061a	0.61± 0,024a
Hydroxycinnamic acid	5.15± 0,221b	2.82± 0,745a
Quercetin	<LOQ	<LOQ

(n:3), Results were calculated as mg/L. Different letters in the same row indicate significant differences between different maceration types (P<0.05).

Table 6. Individual phenolic compounds of C. sauvignon wines in different maceration types (2010).

	Classic	Cold
Gallic acid	62.57± 0.442b	40.99± 1.420a
Catechin	140.98± 1.198b	86.45± 2.263a
Vanilic acid	3.16± 0,056b	1.75± 0.157a
Caffeic acid	<LOQ	<LOQ
Epictechin	59.51± 0.177b	40.89± 2.355a
p-coumaric acid	2.63± 0,452b	1.48± 0.028a
Ferulic acid	0.84± 0,009a	0.91± 0.160a
Hydroxycinnamic acid	1.86± 0,160a	1.16± 0.518a
Quercetin	0.92± 0,297a	0.63± 0.076a

(n:3), Results were calculated as mg/L. Different letters in the same row indicate significant differences between different maceration types (P<0.05).

3.3. Individual phenolic compounds

Individual phenolic compounds of C. sauvignon wines in different maceration types according to years are given in Table 5 and Table 6.

Catechin was the highest individual phenolic compound in all maceration types in 2009 and 2010 (Tables 5, 6). Epicatechin and gallic acid were the most present phenolic compounds respectively after (+)− catechin. In classical maceration wines the amounts of gallic acid, catechin and epicatechin were found higher than cold maceration wines for both year. The differences between catechin, gallic and epicatechin amounts in classical and cold maceration wines were determined to be statistically significant.

3.4. Individual anthociyanin compounds

The amounts of malvidin 3-glucoside in classic maceration and cold maceration wines were determined as

Table 7. Individual phenolic compounds of C. sauvignon wines in different maceration types (2009).

	Classic	Cold
Malvidin 3-glycoside	75,26± 3,016a	66,96± 1,979a
Cyanide 3-5diglycoside	0,53± 0,033a	0,53± 0,000a

(n:3), Results were calculated as mg/L. Different letters in the same row indicate significant differences between maceration types respectively (P<0.05).

Table 8. Individual phenolic compounds of C. sauvignon wines in different maceration types (2010).

	Classic	Cold
Malvidin 3-glycoside	95,82± 3,697a	99,45± 0,632a
Cyanide 3-5diglycoside	1,25± 0,025a	0,96± 0,009a

(n:3), Results were calculated as mg/L. Different letters in the same row indicate significant differences between maceration types respectively (P<0.05).

75.26 mg/L, 66.96 mg/L in 2009, 95.82 mg/L, 99.45 mg/L in 2010, respectively (Tables 7, 8). Malvidine 3-glycoside content is higher than cyanidine 3–5 diglucoside content in all kinds of different maceration types in 2009 and 2010. The differences between the amounts of malvidin 3-glycoside in classical and cold maceration wines were statistically insignificant for both years.

4. Conclusion

Total phenolics, total anthocyanins, phenolic composition and anthocyanin composition changes during wine process treated by different maceration methods like classic maceration, cold maceration. The results indicate that maceration methods are important factors to control quality of wine made from C.sauvignon grapes. The anthocyanin and total phenolic content of C. sauvignon wines were not increased by the cold pre-fermentative maceration. On the other hand individual phenolic compounds of classical maceration wines were found higher than pre-fermentative maceration wines. In conculison, the maceration types play a role on the individual phenolic composition and anthocyanin content of C. sauvignon red wines. On the other hand, according to the research results “classsic maseration” seems to be more suitable application with the richness of individual phenolic compounds compare to the other process.

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