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Effect of bottle storage on changes in phenolics and antioxidant capacity of Cabernet Sauvignon red wines from five different wine-producing regions in China

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Abstract

The present worked aimed to assess the effect of bottle storage on changes in phenolics and antioxidant capacity of Cabernet Sauvignon red wines from five different wine-producing regions [including three "new regions" (NW) and two "old regions (OW)] in People's Republic of China. The phenolic contents were analysed by UV-VIS spectrophotometry, and HPLC-MS was used to identify and quantify the concentration of individual phenolic compounds. Most phenolic compounds and their antioxidant capacity exhibited a decreasing trend as the storage time progressed. Following 6- and 18-month storage, the phenolic contents and antioxidant capacity of NW1 was significantly higher than OW1 and OW2. The three "new regions" could be considered to have a big potential for producing high quality Cabernet Sauvignon wines. The obtained results can be also used in the optimisation process of wine ageing which would allow producers to time the optimal date of wine release onto the market, depending on the desired content parameters.

Introduction

Red wine is one of the most important and popular wines fermented from fruits and consumed worldwide. It is well known for its beneficial health effects; moderate drinking of wine can decrease the incidence of many diseases, such as atherosclerosis and cardiac diseases (Arranz *et al.,* 2012; Stockham *et al.,* 2013). Numerous studies have been carried out in the past 20 years which elucidated that phenolic compounds such as flavonoids and phenolic acids, originated from grape berries, are responsible for its antioxidant properties and associated with the prevention of oxidative damage (Bertelli and Das, 2009). There is a significant correlation between the phenolic contents of red wine and its antioxidant properties (Büyüktuncel *et al.,* 2014; Jiang and Zhang, 2019). In addition, the phenolic compounds also play an important role in wine quality attributes such as appearance, bitterness, astringency, and stability (Gil *et al.,* 2015; Chen *et al.,* 2018).

Besides the grape variety, the presence of phenolics in red wine mainly depends on the following factors: viticulture practices (Jackson and Lombard, 1993), winemaking techniques (Zhang *et al.,* 2015), vintage effect (He *et al.,* 2016), conditions and time of wine ageing (Makhotkina et al., 2012; Lombardi *et al.,* 2017), and the terroir (wine-growing regions) where the grapes are grown (Van Leeuwen *et al.,* 2004; Jiang and Sun, 2019). The characteristics of terroir include climatic conditions (e.g., temperature, rainfall and light), soil type, geological environments, and human activity. Each terroir reflects wine quality in its chemical composition (Lampíř and Pavloušek, 2013). Among the many factors, it is well known that wine ageing can improve red wine quality and result in continuous changes in the composition and concentration of the phenolic compounds (García-Carpintero *et al.,* 2012). Before wine is consumed, it is usually bottled. During the ageing period in the bottle, the antioxidant capacity of red wine also changes gradually. The lower phenolic levels in red wine, the more susceptible it is to oxidation (Del Caro *et al.,* 2014). In fact, several studies have shown that the phenolic content of red wine has significant losses during bottle storage, especially to flavan-3-ols and flavonols (Cejudo-Bastante *et al.,* 2013; Balga *et al.,* 2014). These chemical reactions continuously modify the phenolic composition in red wine during ageing, thus leading to some have more and others less.

China is a new world wine country. In recent years, the Chinese wine industry has been developing rapidly in terms of both consumption and production. At present, China is one of the largest 10 wine-producing countries in the world in terms wine production and grape plantation. Moreover, China's terroirs spread from east to west spanning over 2,000

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kilometres, where a wide range of pedoclimatic conditions prevail, from warm semi-humid to cold arid and semi-arid conditions. Due to the diversity of ecological conditions, the quality and style of wine vary from region to region. For this reason, many studies have reported on the sensory quality and nutritional properties of wines from different regions in China (Jiang *et al.,* 2013; Ma *et al.,* 2014; Xing *et al.,* 2015; Yue *et al.,* 2015). However, there has been no study on the effect of terroir on phenolic levels and antioxidant capacity during wine ageing in the bottle. In the present work, we assessed the phenolic content and composition as well as antioxidant capacities by DPPH and CUPRAC assays of Cabernet Sauvignon (*Vitis vinifera* L.) red wines from three "new terroirs" (namely Wuwei of Gansu province, Yuquanying of Ningxia autonomous region, and Jingyang of Shaanxi province, abbreviated as GSWW, NXYQY and SXJY, respectively) and two "old terroirs" (namely Yantai of Shandong province and Shacheng of Hebei province, abbreviated as SDYT and HBSC, respectively) during bottle storage. Both SDYT and HBCL are traditional terroirs in the east of China with over 50 years of history, and GSWW, NXYQY, and SXJY are newly developed terroirs in the northwest of China. The locations of the five terroirs are displayed in Figure 1.

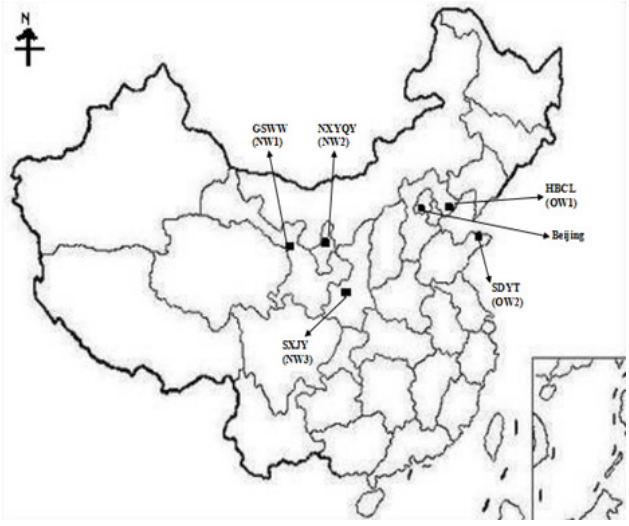

Figure 1. Distributions of five wine-grape growing regions in China.

The present work aimed at comparing three "new terroirs" phenolic levels and antioxidant capacities of Cabernet Sauvignon red wines with two "old terroirs" during bottle storage. The work may provide some valuable information for improvement of winemaking techniques from five regional wines. The findings will also contribute to the brand development of new regional wines.

Materials and methods

Chemicals, standards, and instruments

Gallic acid, procyanidin B1, cyanidin-3-galactoside, gallocatechin gallate, catechin, procyanidin B2, epicatechin, caffeic acid, syringic acid, cyanidin chloride, rutin, ferulic acid, myricetin, benzoic acid, coumarin, salicylic acid, quercetin, kaempferol, Folin-Ciocalteau phenol reagent, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), *p*-dimethylaminocinnamaldehyde (DMACA), neocuproine free base, and 2,2-diphenyl-1-picrylhydrazyl (DPPH•) were purchased from Sigma-Aldrich (St. Louis, MD, USA). Tris (base) was purchased from Sanland Chemical Co. Ltd. (Los Angeles, CA, USA). All analytical grade reagents and solvents were purchased from Tianli Chemical Company (Tianjin, China). UV/VIS spectrophotometer was purchased from Unico Instrument Company (Unico UV/VIS 2802S, Shanghai, China).

Wine samples

All five regional Cabernet Sauvignon vines were grown in commercial vineyards, and grafted onto SO4 rootstock. Vines were Dulong-trained and aged five years. The vineyards were irrigated by drip irrigation system and the row spacing of vine was 2.5 × 1.0 m. Soil was managed with cover grass, and grape yield per hectare was limited to 22.5 tons. The ecological conditions in the five terroirs are displayed in Table 1.

All wines were produced with Cabernet Sauvignon variety. Grape harvesting took place in September to October 2016 at optimum technological maturity, as judged by ratio of sugar and acid content. The grape was destemmed and crushed, 50-80 mg/L (as needed) of SO_2 and 30 mg/L of pectinase (Lallzyme Ex) were added, and the must was left overnight for skin contact. Then, the must was inoculated with selected yeast (*Saccharomyces cerevisiae* strain EC-1118, Lallemand, Danstar Ferment AG, Switzerland) at 200 mg/L. Alcoholic fermentation was carried out in 60 L stainless steel at 20 to 25°C, and racking was performed at a residual sugar level of less 4 g/L. Then, the new wines were transferred to another tank at 4°C, followed by stabilisation. Before bottling, each wine sample was determined for physicochemical parameters, such as alcohol, residual sugar, titratable acidity, pH, dry extract, total SO_2, and free SO_2 following the OIV methods (OIV, 2018).

All wine samples were bottled six months after winemaking. Coloured bottles had a capacity of 750 mL, and were sealed with cork stoppers. The bottles were stored in an upright position in the dark at a

Table 1. Regional meteorological parameters and soil types from five different wine grape growing-regions.

Wine samples	Climate types	Annual accumulated temperature (°C)	Precipitation (mm)	Sunshine hours	Regional soil types	Average altitude (m above sea level)
NW1	Cold-cool, arid and semi-arid climate	2800-3000	166	2730-3030	Sandy soil	1400
NW2	Cool and semi-arid climate	3298-3351	150-200	2800-3000	Gravelly soil	1036
NW3	Warm temperature zone	3850-4010	550-600	2852	Clay loamy soil	480
OW1	Cool-warm, semi-humid climate	3840-3990	700	2600-2800	Clay and sandy soil	214
OW2	Warm and semi-humid climate	3800-4200	750-800	2550-2800	Sandy soil	40

controlled temperature of 14°C, and sampled after 0, 6, and 18 months of bottle ageing. The wines from GSWW, NXYQY, and SXJY terroirs were labelled as NW1, NW2, and NW3, respectively; while those from HBCL and SDYT terroirs were labelled as OW1 and OW2, respectively.

Analyses of phenolics by spectrophotometry

The total phenolic (TP) content was measured by the Folin-Ciocalteau (Rapisarda *et al.,* 1999) method. Absorbance of sample solutions was measured against a blank at 765 nm. The TP content in wines was expressed as milligrams of gallic acid equivalents per litre (mg GAE/L).

The total flavonoid (TFO) and total flavanol (TFA) contents were measured by the colorimetric assay following Kim *et al.* (2003) and the DMACA method of Li *et al.* (1996), respectively. Both TFO and TFA were expressed as milligrams of catechin equivalents per litre (mg CTE/L).

The total anthocyanin (TA) content was assessed by the pH differential method (Orak, 2007). The TA content was calculated from the difference in absorbance values between both solutions, and the result was expressed as milligrams of malvidin-3-*O*-glucoside equivalents per litre (mg ME/L).

Analyses of antioxidant capacity by spectrophotometry

The ability to scavenge DPPH•free radicals was assessed following the method of Merouane *et al.* (2019). The absorbance of the reaction mixture was determined at 515 nm. The antioxidant effectiveness was expressed as micromole of Trolox equivalents per litre (μmol TE/L).

The cupric reducing antioxidant capacity was determined following the method of Apak *et al.* (2004). The antioxidant effectiveness was also expressed as micromole of Trolox equivalents per litre (μmol TE/L).

Analyses of individual phenolic compounds by HPLC

Ten mL of wine samples were filtered through a 0.22 μm cellulose acetate filters prior to the HPLC analysis, and injected directly into a liquid chromatography (Thermo Corporation, USA) coupled with a Waters 2998 diode array detector. The column used was a Waters Sun Fire C18 (250 mm × 4.6 mm, 5 μ m) with 10 mL automatic sampler (Waters 2707). The mobile phases were (A) acetonitrile and (B) water/formic acid (1:100, v/v). The samples were analysed by gradient elution at a flow rate of 1.0 mL/min. The elution conditions were: 0 - 25 min at 5% A; 25 - 45 min from 14 to 25%; 45 - 55 min from 25 to 40% A; 55 - 65 min from 40 to 60% A; 66 - 80 min at 5% A. The column temperature was set at 30°C. The individual phenolic compounds were monitored at four different wavelengths: 260 nm for hydroxybenzoic acids, 280 nm for flavan-3-ols, 320 nm for hydroxycinnamic acids, and 360 nm for flavonols. A standard solution in methanol, containing standard substances of all individual phenolic compounds, was used to identify and quantify the analysis. Calibration curves were obtained by three injections of five different concentrations ranging from 31.25 to 500 mg/L.

Statistical analysis

All the experiments were performed in triplicate, and the data were expressed as means ± standard deviations (SD). The analyses of variance were carried out by SPSS 16.0 for Windows (SPSS Inc., Chicago IL, USA). The probability of $p < 0.05$ (Tukey's Test) was considered statistically significant between means. A two-tailed Pearson's correlation test was conducted to determine the correlations between the phenolic compound contents and antioxidant capacities of the wines.

Results and discussion

Ecological conditions and physicochemical parameters

The terroir includes mainly climate, soil, and geomorphology properties; which are important factors affecting wine quality and style. Each of the five terroirs selected in the present work displayed unique ecological conditions from northwest (cold-cool, arid, and semi-arid climate) to east (warm and semi-humid climate) of China (Table 1). The annual accumulated temperature (from 4200 to 2800°C) and precipitation (from 150 to 800 mm) decreased with increasing altitude (from 40 to 1400 m), while sunshine hours (from 2550 to 3030 h) increased with increasing altitude. The soil types of the sampling terroirs at different altitudes are shown in Table 1. All terroirs' soils were classified as "sandy soil, gravelly soil, clay loamy soil, clay and sandy soil". Gravelly soil and sandy soil are more helpful to improve the root permeability of grape trees.

In order to minimise the potential impact of the brewing factor, all the five terroirs applied the same procedure, and had no added sugar during winemaking. All wine samples were dry red wines according to the National Standard of the P.R.China (GB, 15037-2006) (Standards China, 2006). Several important physicochemical parameters of the five regional wines are shown in Table 2.

Polyphenol changes during bottle storage

To investigate the effect of bottle storage on the four phenolic classes of five regional Cabernet Sauvignon red wines, the young Cabernet Sauvignon red wines were studied by spectrophotometric analysis after 0, 6, and 18 months of bottle ageing.

As can been seen from Figure 2(A), the TP content ranged from 943.36 to 2244.23 mg GAE/L. The highest mean TP content was found in NW1, mg GAE/L) which was by about 58% lower than in NW1. (2273.78 mg GAE/L), followed by NW3, OW1, and NW2 at 1564.81, 1304.43 and 1128.90 mg GAE/L, respectively, while the lowest was found in OW2 (966.16

After 6- and 18-month of bottle ageing, there were no significant ($p > 0.05$) changes in the TP contents as compared to the beginning of bottling (0-month) for NW3 and OW2, respectively. However, both NW2 and OW1 showed significant ($p < 0.05$) decrease after 18-month of bottle ageing. The TP content of NW1 showed a significant ($p < 0.05$) increase after 18-month of bottle ageing as compared to 0- and 6-month. Therefore, it can be concluded that the TP contents continuously varied during wine ageing, and the changes in TP contents were irregular before 6- and 18-month of ageing, which was also confirmed by Del Caro *et al.* (2014) and Mezey *et al.* (2016). As to whether the change trend is reversible, in the present work, it is unknown. The decrease or increase is generally ascribed to polymerisation, oxidation and polysaccharide interaction reactions occurring during bottle storage (Gómez-Plaza *et al.,* 2002; Kallithraka *et al.,* 2009), but also to the enzymatic activity from residual microorganisms in wine (Monagas *et al.,* 2006).

The values of TFO varied in the present work in the range of 2238.19 to 7005.55 mg CTE/L in the five regional wines (Figure 2(B)). The highest average TFO content was found in NW1 during bottle storage (6534.32 mg CTE/L), whereas the lowest was found in OW2 (2412.57 mg CTE/L). The TFO contents in the five regional wines increased in the following order: OW2 < NW2 < NW3 < OW1 < NW1. After 6-month bottle storage, significant decrease in TFO contents were observed in NW1, OW1, and OW2, except for NW2 and NW3. Overall, among the five regional wines, NW2 had the highest TFO content at any storage time assessed in the present work.

The contents of TFA varied from 169.86 to 1104.43 mg CTE/L; a very significant change in the

Table 2. Physicochemical parameters of Cabernet Sauvignon wines from five different wine grape growing-regions at the beginning of bottle storage.

Wine samples	Alcohol (v/v %)	Residual sugar (g/L)	Titratable acidity (g/L)	pH	Dry extract (g/L)	Total SO_2 (mg/L)	Free SO_2 (mg/L)
NW1	11.9 ± 0.4^{a}	1.8 ± 0.0^{a}	6.5 ± 0.2^{b}	3.3 ± 0.1^{a}	20.3 ± 0.5^{c}	96.8 ± 4.1^{cd}	25.6 ± 2.4^{b}
NW2	12.0 ± 0.3^{a}	2.1 ± 0.1^{a}	6.7 ± 0.1^{b}	3.1 ± 0.0^{ab}	22.0 ± 0.4^{b}	107.5 ± 4.3^{b}	19.2 ± 2.7^{c}
NW3	11.9 ± 0.6^{a}	1.9 ± 0.2^{a}	7.3 ± 0.2^{a}	3.2 ± 0.2^{a}	21.4 ± 0.3^{b}	119.4 ± 6.7^{a}	30.8 ± 2.4^{a}
OW1	12.2 ± 0.5^{a}	2.0 ± 0.0^{a}	7.0 ± 0.0^{a}	3.0 ± 0.1^{b}	20.5 ± 0.5^{c}	127.1 ± 5.2^{a}	25.9 ± 2.4^{b}
OW2	11.8 ± 0.1^{a}	1.3 ± 0.1^{b}	6.7 ± 0.3^{b}	3.1 ± 0.2^{ab}	23.0 ± 0.4^{a}	99.7 ± 4.5^{bc}	20.1 ± 2.3^{c}

TFA contents were found in all five regional wines after 18-month bottle storage (Figure 2(C)). Like TP and TFO, the TFA content in NW1 showed the highest value among the five regional wines at any storage time. After 6- and 18-month bottle storage, the TFA contents of all these regional wines decreased significantly. This is not in accordance with the result in the literature, which reported increases in TFA contents with ageing (Fang *et al.,* 2008). The possible polymerisation and precipitation of these TFA may occur at a faster rate if the contents are high enough (Revilla and Gonzalez-Sanjosé, 2003). This might explain why the levels in NW1 with the highest contents seemed to decrease greatly after 6- and 18-month bottle storage, while the other regional wines with lower contents decreased slightly.

Anthocyanins are pigmented compounds; they are mainly derived from grape skin. As anthocyanins directly relate to the red wine colour, it is considered as an important quality parameter of red wine. In the present work, the Cabernet Sauvignon wines' TA contents ranged from 153.58 to 654.97 mg ME/L (Figure 2(D)), which were comparable with the value of previous reports (Li *et al.,* 2009; Balga *et al.,* 2014). After 6- and 18-month bottle ageing, the TA contents of all regional red wines exhibited decreasing trend. During ageing, NW1 had a significant higher value of TA content than those in the other four regional wines, whereas the lowest amount was detected in OW2. The TA contents in the five regional wines increased in the following order: OW2 < NW3 < OW1 < NW2 < NW1. During ageing, the level of anthocyanins has the tendency to decrease, which could be due to polymerisation, as well as to the increased oxidation and precipitation of anthocyanins that take place in this process. So, the wines would have a rather brownish red colour, which could be detected using a spectrophotometer by hue augmentation (Balga *et al.,* 2014). In addition, as shown in (Figure 2(D)), the present work also indicated that the wines made from grape grown at higher altitude yielded higher content of TA, especially NW1 and NW2. This could be explained by the fact that the increase in vineyard altitude resulted in the increased grape skin thickness. It is well known that the interaction of strong sunlight, especially UV radiation, low temperature and significant diurnal temperature difference at high altitude affect anthocyanins accumulation in grape skins (Yamane *et al.,* 2006).

Most of wines are consumed after a period of ageing. In the present work, we found that the four phenolic classes' contents of the five regional Cabernet Sauvignon red wines had decreasing trend to different extent during bottle ageing except for TP content in NW1, the result of which is in accordance with Balga

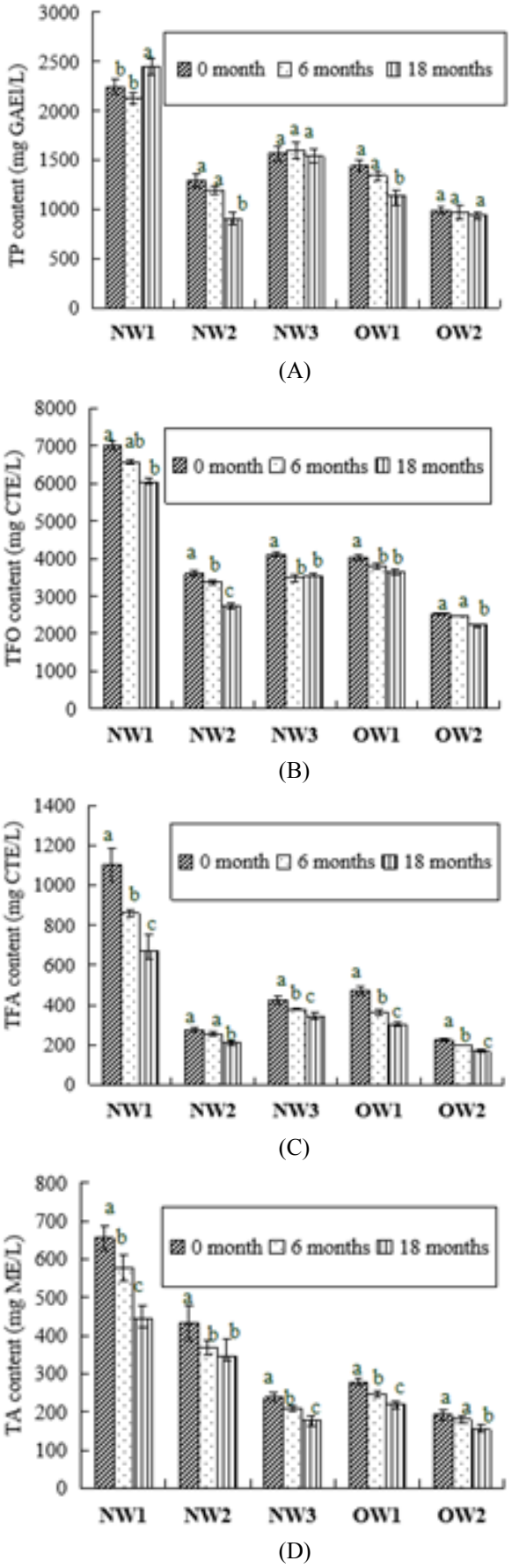

Figure 2. Changes in the TP, TFO, TFA, and TA contents in Cabernet Sauvignon wines from five different wine grape growing-regions during bottle ageing.

et al. (2014) and Galanakis *et al.* (2015). This phenomenon is mainly due to the reason that during ageing some chemical reactions modify chemical composition in wines, making some of them more and the others less intense, consequently changing the wine quality. In addition, among the five regional wines, NW2 had the second highest amount of TA, and NW1 had significantly the highest amounts of TP, TFO, TFA, and TA than the other four regional wines, whereas the lowest concentrations of these phenolic compounds were detected in OW2. These phenolic compounds' contents in NW3 changed significantly during storage, in contrast to what was observed in OW1, but both regions were much higher than OW2. It can be confirmed that NW1, NW2, and NW3 were outstanding during bottle ageing in terms of phenolic compounds content, in particular, NW1. It was also found that regional meteorological condition plays a key role in the regulation of biosynthesis of polyphenols in grapes, resulting in significantly higher levels in polyphenol contents of grapes grown in vineyards with higher average altitude and less precipitation. Moreover, infertile soil usually provides with more composite and content of inorganic ions, activating the flavonoid synthesis (Reeve *et al.,* 2005). In the present work, the vineyards in GSWW and NXYQY are in Gobi Desert zones with the texture of sandy soil and gravelly soil, both of which are more likely to have infertile soil.

Antioxidant capacity changes during bottle storage

In order to assess the changes in antioxidant capacities in Cabernet Sauvignon red wines from five terroirs during bottle ageing, two *in vitro* assays (DPPH and CUPRAC) were conducted. Both assays measured the ability of antioxidants in wines to capture free radicals via electron-transfer and electron donors, respectively. Because multiple reactions and mechanisms are involved in antioxidant capacity of the biological body, the different assays will accurately reflect all antioxidants in a mixed or complex system. Figure 3 shows the variation of antioxidant capacity in the assessed wines. As shown, all wine samples exhibited potent antioxidant capacity, which decreased during bottle ageing. Our results, which ranged from 3965.42 to 12333.04 μmol/L (Figure 3(A)), are quite consistent with those of Li *et al.* (2009) and Alén-Ruiz *et al.* (2009). Among all wine samples, the highest antioxidant capacity value was detected in NW1 at any storage time, whereas the lowest antioxidant capacity value was detected in OW2. After 6-month bottle storage, no significant differences ($p > 0.05$) were observed for all samples except for OW2. After 18-month, a significant ($p < 0.05$) decrease in DPPH values was found for all wines. This indicated that aged wines exhibited lower antioxidant capacity than even very young wines (Mezey *et al.,* 2016; Lombardi *et al.,* 2017). The correlation coefficients of phenolic compounds (including TP, TFO, TFA, and TA) and antioxidant capacity were calculated. The contents of TP ($r^2 = 0.943$ and 0.734, $P = 0.01$), TFO ($r^2 = 0.947$ and 0.793, $P = 0.01$), TFA ($r^2 = 0.894$ and 0.701, $P = 0.01$), TA ($r^2 = 0.968$ and 0.846, $P = 0.01$) exhibited significant correlation to DPPH and CUPRAC assays, respectively. This results again confirmed that the correlations between phenolic compounds and antioxidant capacity, in which the higher the content of phenolic content in wine, the stronger its antioxidant capacity, are in line with previous report (Ma *et al.,* 2014).

The results obtained for the CUPRAC assay slightly differed from those provided by the DPPH assay (Figure 3(B)), where unlike DPPH, after 6-month bottle storage, a significant ($p < 0.05$) difference in the ageing impact on antioxidant capacity changes was observed for all samples except for OW2. Therefore, the magnitude of the difference depends on the assay employed. Ma *et al.* (2014) have also reported this occurrence.

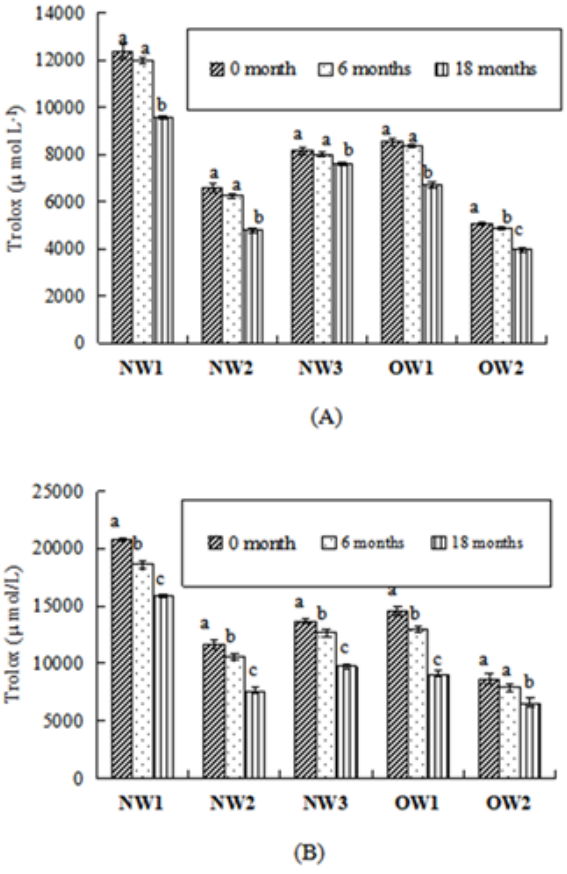

Figure 3. Changes in the antioxidant capacities in Cabernet Sauvignon red wines from five different wine-producing regions during bottle ageing as determined using the DPPH method (A) and the CUPRAC method (B).

Individual phenolic compounds changes during bottle storage

In order to determine the polyphenol composition of three "new terroirs" and two "old terroirs" Cabernet Sauvignon red wines during bottle storage, the analysis was performed by HPLC-MS, and the results are listed in Table 3. According to their chemical structures, these 17 compounds were classified into seven flavan-3-ols, five flavonols, three hydroxybenzoic acids and two hydroxycinnamic acids. Most of these polyphenol compounds were usually found in red wines at varying levels. Moreover, catechin, (-)-epicatechin, procyanidin B1, gallic acid, and procyanidin B2 were the main compounds in terms of concentration in wine samples, as reported in two previous papers (Alén-Ruiz *et al.,* 2009; Lombardi *et al.,* 2017). However, (-)-gallocatechin gallate, cyanidin chloride and coumarin were detected in only some wine samples, at very low levels.

Based on Table 3, nearly all individual phenols evolved in five regional Cabernet Sauvignon wines after 6- and 18-month bottle storage. At the beginning of bottle storage, NW1 and NW2 were rich in flavan-3-ols (263.56 mg/L in NW1 and 189.01 mg/L in NW2), flavonols (32.98 mg/L in NW1 and 19.70 mg/L in NW2) and hydroxybenzoic acids (66.64 mg/L in NW1 and 33.38 mg/L in NW2), whereas NW3 was rich in hydroxycinnamic acids (5.44 mg/L). As shown in Table 3, except for procyanidin B1, procyanidin B2, gallic acid, caffeic acid, and ferulic acid, the concentrations of other 12 individual compounds in wine samples showed decreasing trends during bottle storage. As regards the comparison with two "old terroirs" wines, NW1 and NW2 always had much higher concentrations for flavan-3-ols and flavonols during bottle storage. Generally, the results obtained in the present work showed high variability in polyphenolic composition during bottle storage. After 18-month bottle storage, most individual polyphenols' concentrations from three "new terroirs" wines were still significantly ($p < 0.05$) higher than two "old terroir" wines.

In order to determine the contribution of individual phenolic compounds to antioxidant capacity, the correlation between concentrations of 17 individual phenolic compounds and antioxidant capacity was also estimated (Table 4). As shown in Table 4, the concentrations of 14 individual phenolic compounds correlated significantly with antioxidant capacity except for kaempferol, coumarin, and caffeic acid. This means the contribution of kaempferol, coumarin, and caffeic acid to the antioxidant capacity of wines was very low. It is important to determine which group of phenolic compounds is most significant in antioxidant of wines. In the present work, the results obtained suggest that most of individual phenolic compounds (including flavan-3-ols, flavonols and hydroxybenzoic acids) can make a major contribution to the overall antioxidant capacity of wines, which is in agreement with previous published reports (De Quirós *et al.,* 2009; Vrček *et al.,* 2011). But Zhu *et al.* (2012) concluded that the antioxidant activity (FRAP assay) was poorly correlated to the flavanols and most of the phenolic acids, the opposite conclusion could be due to the different antioxidant assays used in their studies.

Table 4. Pearson's correlation coefficient between antioxidant capacity (DPPH and CUPRAC methods) and individual phenolic compounds in Cabernet Sauvignon wines from five different wine grape growing-regions.

Phenolic compounds	**DPPH**	**CUPRAC**	**Phenolic compounds**	**DPPH**	**CUPRAC**
Catechin	0.743 **	0.813 **	Kaempferol	0.295	0.416
(-)-Epicatechin	0.774 **	0.827 **	Rutin	0.788 **	0.840 **
(-)-Gallocatechin gallate	0.698 *	0.745 *	Coumarin	0.247	0.296
Procyanidin B1(P1)	0.483	0.519 *	Gallic acid	0.849 **	0.819 **
Procyanidin B2 (P2)	0.729 **	0.816 **	Salicylic acid	0.750 **	0.801 **
Cyanidin chloride	0.856 **	0.897 **	Syringic acid	0.807 **	0.889 **
Cyanidin-3-galactoside	0.656 **	0.689 **	Caffeic acid	- 0.288	-0.384
Myricetin	0.808 **	0.861 **	Ferulic acid	0.495	0.516 *
Quercetin	0.688 **	0.748 **			

**Correlation significant at the 0.01 level (2-tailed); *Correlation significant at the 0.05 level (2-tailed).

Table 3. Changes in the phenolic composition in Cabernet Sauvignon wines from five different wine grape growing-regions during bottle ageing (mg/L).

Phenolic compound	Different ageing time (0, 6, 18 months)														
	NW1			NW2			NW3			OW1			OW2		
	0	6	18	0	6	18	0	6	18	0	6	18	0	6	18
Flavonoids															
Flavan-3-ols															
Catechin	87.63 ± 2.53^{a}	80.01 ± 1.24^{b}	64.10 ± 1.39^{c}	67.45 ± 1.51^{a}	63.71 ± 0.77^{b}	45.58 ± 1.24^{c}	41.27 ± 0.95^{a}	36.24 ± 0.75^{b}	29.06 ± 2.04^{c}	45.02 ± 0.98^{a}	42.81 ± 1.25^{a}	29.62 ± 1.31^{b}	31.95 ± 1.18^{a}	26.38 ± 1.69^{b}	17.46 ± 0.89^{c}
(-)-Epicatechin	82.49 ± 1.36^{a}	76.04 ± 1.31^{b}	56.38 ± 1.49^{c}	57.35 ± 1.33^{a}	56.05 ± 1.14^{a}	33.76 ± 1.12^{b}	40.25 ± 2.11^{a}	34.16 ± 0.99^{b}	29.72 ± 1.27^{c}	30.38 ± 1.00^{a}	27.93 ± 1.21^{a}	16.51 ± 1.11^{b}	19.08 ± 0.96^{a}	18.45 ± 1.49^{a}	12.03 ± 1.41^{b}
(-)-Gallocatechin gallate	3.56 ± 0.49^{a}	3.19 ± 0.54^{a}	1.27 ± 0.35^{b}	1.95 ± 0.31^{a}	1.04 ± 0.12^{b}	0.76 ± 0.09^{b}	1.13 ± 0.19^{a}	0.92 ± 0.81^{a}	trace^{b}	trace	nd	nd	nd	nd	nd
Procyanidin B1(P1)	67.75 ± 2.94^{ab}	69.39 ± 2.04^{a}	62.37 ± 1.69^{b}	50.38 ± 2.97^{b}	56.34 ± 2.35^{ab}	59.17 ± 2.70^{a}	20.34 ± 2.88^{b}	22.25 ± 1.82^{ab}	26.59 ± 1.35^{a}	7.36 ± 0.88^{b}	8.15 ± 0.66^{b}	14.66 ± 1.70^{a}	14.93 ± 1.10^{a}	15.02 ± 1.17^{a}	9.15 ± 0.47^{b}
Procyanidin B2 (P2)	18.52 ± 0.90^{a}	16.31 ± 1.82^{ab}	14.67 ± 1.11^{b}	10.65 ± 0.90^{a}	8.97 ± 0.54^{b}	7.75 ± 0.45^{b}	7.03 ± 0.30^{a}	5.34 ± 0.35^{b}	3.61 ± 0.46^{c}	14.15 ± 1.12^{a}	13.26 ± 1.26^{a}	4.67 ± 0.81^{b}	5.38 ± 0.73^{b}	7.61 ± 0.59^{a}	7.99 ± 0.53^{a}
Cyanidin chloride	1.27 ± 0.17^{a}	0.78 ± 0.10^{b}	0.55 ± 0.07^{b}	0.56 ± 0.08^{a}	trace^{b}	trace^{b}	nd	nd	nd	0.43 ± 0.04^{a}	trace^{b}	nd	trace	trace	nd
Cyanidin-3-Galactoside	2.34 ± 0.30^{a}	1.85 ± 0.29^{a}	0.39 ± 0.07^{b}	0.67 ± 0.08^{a}	0.41 ± 0.04^{b}	0.31 ± 0.05^{b}	1.06 ± 0.25^{a}	0.89 ± 0.04^{a}	0.47 ± 0.04^{b}	0.58 ± 0.07^{a}	0.52 ± 0.05^{ab}	0.42 ± 0.05^{b}	1.12 ± 0.19^{a}	0.96 ± 0.15^{a}	0.46 ± 0.05^{b}
Total	263.56	247.57	199.73	189.01	186.52	147.33	111.08	99.80	89.45	97.92	92.67	65.88	72.46	68.42	47.09
Flavonols															
Myricetin	7.68 ± 0.56^{a}	6.14 ± 0.30^{b}	5.53 ± 0.41^{b}	5.45 ± 0.33^{a}	4.64 ± 0.25^{b}	4.05 ± 0.25^{b}	5.60 ± 0.16^{a}	4.07 ± 0.26^{b}	3.17 ± 0.33^{c}	7.17 ± 0.27^{a}	6.75 ± 0.26^{a}	4.13 ± 0.31^{b}	3.15 ± 0.09^{a}	2.53 ± 0.30^{b}	1.58 ± 0.17^{c}
Quercetin	8.35 ± 0.25^{a}	6.73 ± 0.71^{b}	1.36 ± 0.19^{c}	4.92 ± 0.49^{a}	4.35 ± 0.26^{a}	2.78 ± 0.31^{b}	5.61 ± 0.45^{a}	4.24 ± 0.36^{b}	2.68 ± 0.30^{c}	3.82 ± 0.43^{a}	2.67 ± 0.31^{b}	0.97 ± 0.09^{c}	3.35 ± 0.36^{a}	1.06 ± 0.23^{b}	0.89 ± 0.12^{b}
Kaempferol	2.56 ± 0.19^{a}	1.83 ± 0.35^{b}	1.11 ± 0.24^{c}	3.76 ± 0.34^{a}	2.35 ± 0.17^{b}	0.89 ± 0.02^{c}	1.73 ± 0.12^{a}	1.05 ± 0.25^{b}	0.86 ± 0.09^{b}	4.33 ± 0.43^{a}	2.61 ± 0.33^{b}	0.84 ± 0.09^{c}	1.59 ± 0.21^{a}	1.15 ± 0.23^{ab}	0.94 ± 0.19^{b}
Rutin	12.36 ± 2.13^{a}	8.49 ± 0.73^{b}	6.78 ± 0.66^{b}	3.71 ± 0.35^{a}	3.11 ± 0.36^{a}	2.07 ± 0.19^{b}	3.12 ± 0.32^{a}	2.53 ± 0.21^{a}	1.44 ± 0.22^{b}	1.49 ± 0.23^{a}	0.74 ± 0.09^{b}	0.60 ± 0.10^{b}	2.46 ± 0.51^{a}	1.28 ± 0.15^{b}	0.76 ± 0.07^{b}
Coumarin	2.03 ± 0.13^{a}	1.67 ± 0.08^{b}	1.55 ± 0.08^{b}	1.86 ± 0.12^{a}	1.46 ± 0.11^{b}	1.45 ± 0.06^{b}	0.45 ± 0.05^{a}	trace^{b}	nd	nd	nd	nd	nd	nd	nd
Total	32.98	24.86	16.33	19.70	15.91	11.24	16.51	11.89	8.15	16.81	12.77	5.70	10.55	6.02	4.17
Non-flavonoids															
Hydroxybenzoic acids															
Gallic acid	46.37 ± 2.56^{a}	36.18 ± 1.87^{b}	25.67 ± 0.84^{c}	27.06 ± 0.92^{a}	13.64 ± 1.37^{b}	8.04 ± 0.49^{c}	14.28 ± 1.23^{b}	16.34 ± 1.05^{b}	23.54 ± 1.22^{a}	14.26 ± 1.04^{b}	15.37 ± 1.26^{b}	20.60 ± 1.50^{a}	16.39 ± 1.12^{a}	7.75 ± 0.53^{b}	1.36 ± 0.09^{c}
Salicylic acid	11.74 ± 0.62^{a}	5.26 ± 0.66^{b}	1.76 ± 0.10^{c}	2.63 ± 0.26^{a}	1.55 ± 0.19^{b}	0.61 ± 0.09^{c}	1.37 ± 0.05^{a}	0.89 ± 0.06^{b}	0.63 ± 0.07^{c}	2.58 ± 0.23^{a}	1.24 ± 0.11^{b}	0.61 ± 0.04^{c}	1.06 ± 0.08^{a}	0.63 ± 0.05^{b}	0.59 ± 0.04^{b}
Syringic acid	8.53 ± 0.52^{a}	5.37 ± 0.39^{b}	4.15 ± 0.25^{c}	3.69 ± 0.73^{a}	2.18 ± 0.78^{b}	1.92 ± 0.13^{b}	3.69 ± 0.41^{a}	3.07 ± 0.35^{a}	1.56 ± 0.12^{b}	4.26 ± 0.31^{a}	1.97 ± 0.19^{b}	1.77 ± 0.17^{b}	2.48 ± 0.16^{a}	2.25 ± 0.07^{ab}	1.96 ± 0.16^{b}
Total	66.64	46.81	31.58	33.38	17.37	10.57	19.34	20.30	25.73	21.10	18.58	22.98	19.93	10.63	3.91
Hydroxycinnamic acids															
Caffeic acid	0.79 ± 0.07^{c}	1.26 ± 0.15^{b}	3.42 ± 0.22^{a}	3.53 ± 0.15^{b}	1.69 ± 0.11^{c}	4.96 ± 0.60^{a}	5.34 ± 0.37^{b}	5.88 ± 0.53^{b}	7.96 ± 0.40^{a}	4.63 ± 0.55^{a}	4.07 ± 0.19^{a}	2.95 ± 0.37^{b}	2.58 ± 0.09^{c}	3.21 ± 0.06^{b}	3.95 ± 0.24^{a}
Ferulic acid	0.42 ± 0.04^{c}	0.53 ±	0.79 ± 0.06^{a}	0.21 ±	0.33 ±	0.36 ± 0.04^{a}	0.10 ±	0.13 ±	0.14 ±	0.21 ±	0.25 ±	0.23 ±	0.11 ±	0.18 ±	0.24 ±

nd: not detected.

Conclusion

In the present work, the effect of bottle storage on changes in phenolics and antioxidant capacity of Cabernet Sauvignon red wines from three "new terroirs" (NW1, NW2, and NW3) and two "old terroirs" (OW1 and OW2) were analysed. Findings indicate that the phenolics and antioxidant capacity of all wines continuously changed as storage progressed. Moreover, most phenolic contents and their antioxidant capacity of five regional wines showed a decreasing trend as the storage time progressed, and this variation did not occur at the same rate during bottle ageing, but generally seemed to be faster after 6-month bottle storage. Following 6- and 18-month storage, the wine's phenolic contents and antioxidant capacity of NW1 was significantly ($p < 0.05$) higher than OW1 and OW2. As a conclusion, these three "new terroirs" have a big potential for producing high quality Cabernet Sauvignon wine. The obtained results can be used in the optimisation process of wine ageing which would allow producers to time the optimal date of wine release onto the market, depending on the desired content parameters. Since the magnitude of the effect was different among the five regional wines, further studies are required to document the changes in other monovarietal wines under different ageing periods to better understand the changes in wines.

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