Ageing potential of selected rare native Greek cultivars

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ABSTRACT

The Hellenic vineyard embraces a large number of native cultivars, which are mostly unexploited for their ageing potential and hence ignored by the wine producers. Therefore, it was thought that analyzing some quality parameters of fifteen aged red wines (2003-2004 vintage) produced by rare native varieties would be of great importance in obtaining a general picture of their potential for commercial use. Various analytical methods, chemical (classical enological analyses, determinations of color characteristics, flavonoid composition and quality indexes) as well as sensorial, in conjunction with statistical analysis, were applied to the selected wines in an attempt to provide reliable answers to this issue and to evaluate their ageing potential. All wines examined were produced under identical winemaking protocol and all grape varieties originated from the National Collection of the Vine Institute of Athens. The results showed that some of the unexploited rare varieties (e.g. mavrotragano, limniona, mavrothiriko) would be worthy of further study and use for the production of quality wines.

INTRODUCTION

Wine is a complex system capable of undergoing many different compositional changes during storage. In general, high quality red wines require a period of time in the bottle, after which they are ready to be consumed. During this time, modifications of the sensory properties of the wine occur, such as decrease of astringency and the stabilization of color from purple red to tawny (Chira et al., 2011).

During wine maturation and aging in bottle, phenolic compounds participate in numerous chemical reactions. One of them is the gradual formation of condensed pigments between free anthocyanins and colorless phenols present in grapes. These compounds can be formed either in the presence or in the absence of oxygen (Gomez Plaza and Cano-Lopez, 2011). Different mechanisms have been proposed for the formation of these oligomeric and polymeric pigments such as direct and acetaldehyde mediated anthocyanin-flavanol condensation reactions, and other anthocyanin reactions leading to pyranoanthocyanins.

Viticulture and wine making in Greece have been widely practiced since antiquity. Continuous and intensive selection of grape varieties that favoured the production of desired wine styles led over the centuries to a plethora of native cultivars (Vitis vinifera sp.), which possess various distinct enological characteristics and

organoleptic properties. However, today, most of these native varieties are becoming rare since they are replaced by the well-known French ones due to their repute in producing quality wines. There exist a number of native red cultivars which have never been exploited for their ageing potential, therefore ignored by the wine producers. For that purpose, the national collection of the ‘‘Vine Institute of Athens’’ was used in order to provide the grapes for the experimental wines which were produced under identical enological practices within the premises of the Wine Institute of Athens. In this way, the variation due to environmental factors (soil type and climate) and enological techniques were eliminated.

MATERIALS AND METHODS

Wine samples: All varieties used were V. vinifera species. Fourteen varieties were chosen from the collection of the Vine Institute (Likovrisi, Athens). Details about the cultivars and their origin are given in Table 1. The grapes used for the production of the experimental wines were harvested at optimum technological maturity, as judged by indices of sugar and acid content, established by the Institute of Wine. All the wines tested were produced in the winery of the Wine Institute under similar oenological practices and stored under similar conditions. Crushed grapes stayed in contact with the must for six days at 15–18 °C. All samples were analyzed after eight years of their production.

Chemical analyses: The color characteristics of the wines were studied by measuring color intensity and hue (Glories, 1984), total anthocyanin concentration (Ribéreau-Gayon and Stonestreet, 1966), anthocyanin ionization index and anthocyanin polymerization index *(*Glories, 1978). In addition, for the determination of their tannin content two methods were employed (Ribéreau-Gayon and Stonestreet, 1966 and Haberstson et al., 2002).

Sensory analysis: The sensory assessment was done by a panel of 20 trained judges from the technological educational institute of Athens (dept. enology and beverage technology). The panelists were provided with 30 mL of wine in standard clear wine glasses, coded with random three-digit numbers. Wines were first observed then sniffed and tasted. In every session, the judges had to evaluate the color intensity and hue using scales 1-3 and 1-5 respectively. The following aroma parameters were evaluated using a 1-5 scale: Fresh fruits, dry fruits, chocolate, tobacco, spicy as well as the characteristic odor of oxidation. After a short break, they evaluated the taste (bitterness, sourness), the tactile sensation (astringency), the body and the overall quality.

RESULTS

1. Color parameters

Anthocyanin ionization index (AI) defines the percentage of free and combined anthocyanins producing color and it increases throughout aging from 10%-30% up to 80-90%. This value represents the optical density at 520 nm, including only those free and combined anthocyanins, colored at the pH of wine, that react with SO_2 (Glories, 1978). Figure 1 shows the AI of the experimental wines after eight years of their production. The wine from Thrapsa variety showed the highest AI value, followed by the wines from karvouniaris, kotselina and mpakouri cultivars. The lowest values were observed for the wines made by pardala and papadiko cultivars respectively.

Another parameter that is related with wine aging is anthocyanin polymerization index (AP) which defines the percentage of the polymerized anthocyanins and it is

related with wine “chemical age”. Karvouniaris and araklinos wines had the highest AP values followed by voidomatis. In contrast, wines from mavrotragano, kotselina and limniona varieties were characterized by the lowest AP values (Figure 1).
As wine ages, free anthocyanins disappear completely after a few years, although the wine remains red. Indeed, these molecules are unstable and combine with tannins to form stable pigments responsible for the color of older wine. The decrease in the anthocyanin concentration results from breakdown and stabilization reactions (Bakker et al., 1997). In breakdown reactions free anthocyanins are broken down into phenolic acids whereas in stabilization reactions they combine with tannins. All these reactions produce colors ranging from red mauve, to brick red and then to brown orange which depends relatively little on the SO_2 content of the wine. These molecules are not detected by chemical anthocyanin assays and are only partially taken account in the results.
The total anthocyanin content of the wines is presented in Figure 1. Limniona was the variety with the highest total anthocyanin concentration followed by mavrotragano, mavronikolas and mavrothirico, whereas karvouniaris, voidomatis and nerostafulo varieties resulted in wines poor in total anthocyanins.
The spectrum of red wine has a maximum at 520 nm, due to anthocyanins and their flavylium combinations, and a minimum in the region of 420 nm. As wine ages the absorption at 520 nm decreases while it simultaneously increases at 420 nm. The maximum color intensity (> 10) was observed in wines made by Limniona followed by mavrotragano and mavrothiriko (Figure 2) in agreement with their anthocyanin content (Figure 1). Moreover, high color intensities (higher that 8) were found for the wines from thrapsa and mpakouri cultivars. Mpakouri was characterized by high total anthocyanin concentration whereas the relatively intense color of thrapsa might be attributed to its high ionization degree (Figure 1). In contrast, voidomatis and karvouniaris varieties gave wines with the lowest color intensity values.
Color hue indicates the development of a color towards orange. Young wines have a value on the order of 0.5-0.7 which increases throughout aging, reaching an upper limit around 1.2-1.3. (Ribereaux-Cayon et al., 2000). The lowest hue value (0.85) was observed in thrapsa wine. Other wines with low hue values (1.06) were those made by limniona, mavrotragano and mavrothiriko varieties. The highest hue value (1.62) was found in the wine made by nerostafilo cultivar indicating shift of the color towards orange. Karvouniaris and voidomatis wines were also characterized by high hue values (1,51 and 1, 44 respectively).

2. Polyphenolic composition

If the composition of a wine is monitored regularly throughout aging, the results of the tannin assay decrease, or change little, during barrel aging and then increase regularly after bottling. At the same time, the content of tannins which react with proteins varies considerably, either increasing or decreasing, thereby indicating structural modifications (Ribereau-Gayon et al., 2000). The procyanidin molecules from the grapes tend to polymerize, condense with anthocyanins and combine with plant polymers, such as proteins and polysaccharides.
Throughout the time that the wine ages in an airtight bottle, it is initially subject to a slight oxidative reaction. It is then mainly affected by transformation reactions independent of oxidation. These reactions involve the carbocations formed from procyanidins, with condensation of anthocyanins (browning of color) and polymerization of homogenous tannins. Temperatures that are slightly too high promote these reactions and are responsible for accelerated aging (Gambuti et al.,

2013). A few years after bottling (1-3), however, a modification is observed in the flavor of certain wines, in particular their tannic character. These wines seem temporarily thinner, with less body, although their color is still strong. This phenomenon can be attributed to a structural rearrangement of tannins that takes place in a non oxidizing medium, leading to depolymerization reactions ((Ribereau-Gayon et al., 2000). Part of these polymers may be destroyed, prior to a later repolymerization. This is a feature of high-quality wines that from a wide range of tannin molecules during aging. These reactions add complexity to the color and flavor. These complicated tannin reactions do not occur during the development of more modest wines, which tend to evolve continuously and rapidly towards a 'mature' wine character.

In view of their influence on the character, flavor and development wine, there has been considerable interest in analyzing wine tannin content. Figure 3 presents tannin concentration of the aged wines. The first column corresponds to tannin concentration (g/L) measured after heating in acid medium and their conversion into cyanidin whereas the second to wine tannin content (mg catechin/L) measured after precipitation with bovine serum albumin (BSA). The first method although is highly reproducible and easy to implement, it tends to overestimate the wine tannin content. In general, it is not unusual to observe an increase in the results of this assay during barrel and bottle aging, which may not correspond to an increase in tannin since it doesn't take into account their degree of polymerization. The results of the second assay are strongly correlated with perceived astringency and therefore they can be used as a chemical estimation of wine astringency (Mercurio and Smith, 2008).

As it can be seen from Figure 3, kotselina wine was the richest in total tannins (3,86 g/L) followed by mavronikola (3.57 g/L) and mavrothiriko (3.47). In contrast, the lowest amounts were observed in voidomatis (1.39 g/L) and pardala (1.4 g/L) wines. As regards tannins precipitated with BSA, karvouniaris wine was the richest (1,47 mg catechin/L) followed by mpakouri (0.88 mg catechin/L) and nerostafilo (0.78 mg catechin/L). The lowest concentrations were observed in mavrothiriko, karvouniaris and mavronikolas wines (0.20, 0.36 and 0.47 mg catechin/L respectively). It can be observed that the results of the two methods are not in agreement, something that it was expected since the methods employed are based on different mechanisms for tannin determination and they make use of different chemical agents.

3. Sensory evaluation

Phenolic compounds play a vital role in the flavor of red wines. They are responsible for some positive tasting characteristics but also for some unpleasant, negative aspects.

Body, fullness and roundness are all organoleptic qualities which characterize great red wines. On the other hand, bitterness, roughness, harshness, astringency, thinness are faults that must be avoided as they are incompatible with quality. The overall organoleptic impression is based on a harmonious balance between these two types of sensations directly related to the type and concentration of various molecules such as anthocyanins and especially tannins (Preys et al., 2006).

According to the type and concentration of tannins they may produce a soft, balanced impression or, on the contrary, a certain aggressiveness that is either perceptible as bitterness on the end of palate or as astringency on the aftertaste. Although it is useful to measure tannin concentration in wine, it is not the only factor involved in the character, flavor and development of wine. Sensory analysis is required in order to provide such information.

PCA was applied to the sensory data of the aged wines in order to obtain any differentiation based on positive and negative for ageing organoleptic aspects (Figure 4). The first two factors retained 49% of the variance. According to the statistical analysis of the results of the sensory assessment, some grouping can be observed in the space formed by the two first components. The positive quality parameters formed a group on the left part of the vertical axe of the PCA graph while the negative on the right. The following parameters were considered as positive for high quality wines: high color intensity, low hue value, high scores for fresh, dried fruits, tobacco, spicy and chocolate aroma attributes, medium astringency, pleasant aroma, rich body and high overall quality. Exception is the high astringency attribute which is on the same part of the graph. However, wines that are characterized by high aging potential are also rich in tannins and therefore astringent. As they age, transformations such as polymerization reactions soften their flavor. On the contrary, the negative quality attributes were the following: low color intensity, high hue values, unpleasant aroma, oxidized flavor, sour and bitter taste, poor body and low scores for overall quality.

As far as wines are concerned, PCA resulted in three groups (Figure 5). The first group which consists of the wines made by limniona, mpakouri, thrapsa, mavrotragano and mavrothiriko varieties is situated on the left part of the graph indicating that these specific wines are characterized by high aging potential. The second group which includes wines from papadiko, araklino and kotselina varieties is situated in the middle part of the graph indicating that the specific varieties produce wines with lower aging potential. Finally, the rest wines are placed on the right part of the graph, meaning that they are not suitable for aging.

In conclusion, after eight years of vinification some of the unexploited rare native varieties were found to contain appreciable amounts of tannins as well as anthocyanins so that they would be worthy of further study and use for the production of quality wines. For example mavrotragano, mavrothiriko, limniona, thrapsa and kotselina varieties produced wines with the highest color intensities and simultaneously the lowest hue values. The wines with the best sensory characteristics were those made by limniona, mavrotragano, mpakouri, thraspa and mavrothiriko in accordance more or less with the results of the chemical analyses. In contrast, the lowest anthocyanin concentration and color intensity were observed in wines made by the varieties karvouniaris, voidomatis, nerostafilo and pardala, something that also agrees with the results of the sensory analysis since those wines are not suitable for aging. Finally, wines from papadiko, araklino and kotselina were characterized by a medium aging potential.

Table 1: Grape varieties used for the production of experimental wines

Variety	Origin
Araklinos	W.Pelopon/Kefalonia
Fidia	Corfu
Karvouniaris	Peloponnese
Kotselina	Preveza/Lefkada
Limniona	Thessaly
Mavrothiriko	Nisiros
Mavronikolas	Rhodes
Mavrotragano	Thira
Mpakouri	Peloponnese
Nerostafilo	Limnos
Papadiko	Kefalonia
Pardala	Preveza, Ionian Isl.
Thrapsa	Lakonia/Kithira
Voidomatis	Crete/Pelop./Ionian Isl.

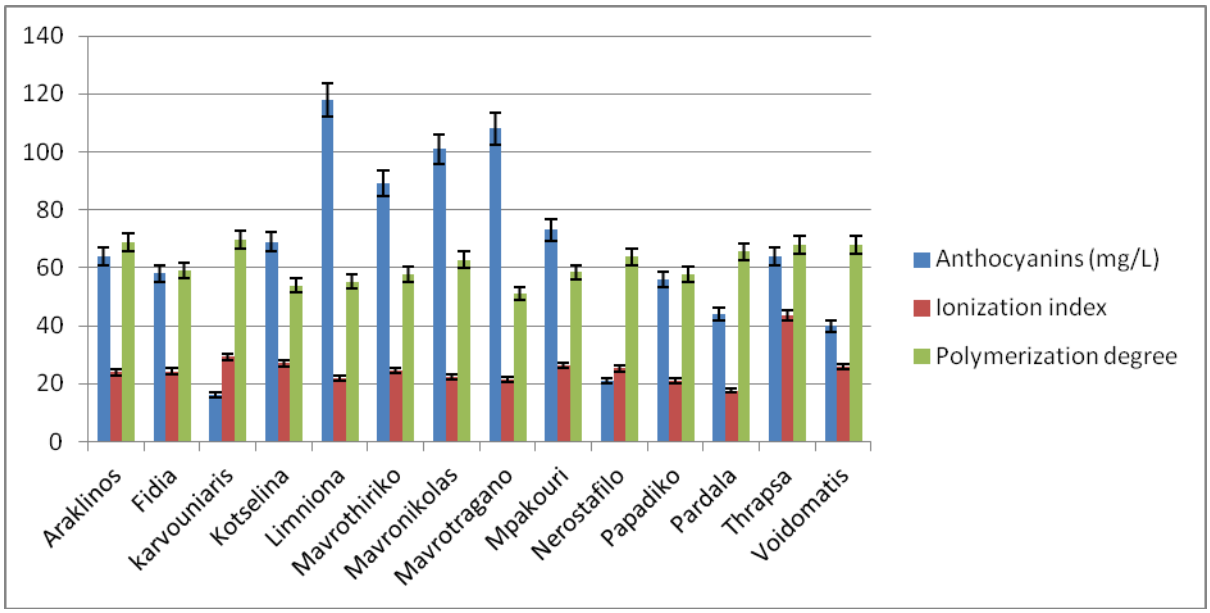

Figure 1: Anthocyanin concentration (mg/L), ionization and polymerization indices of the experimental wines after 8 years of their production.

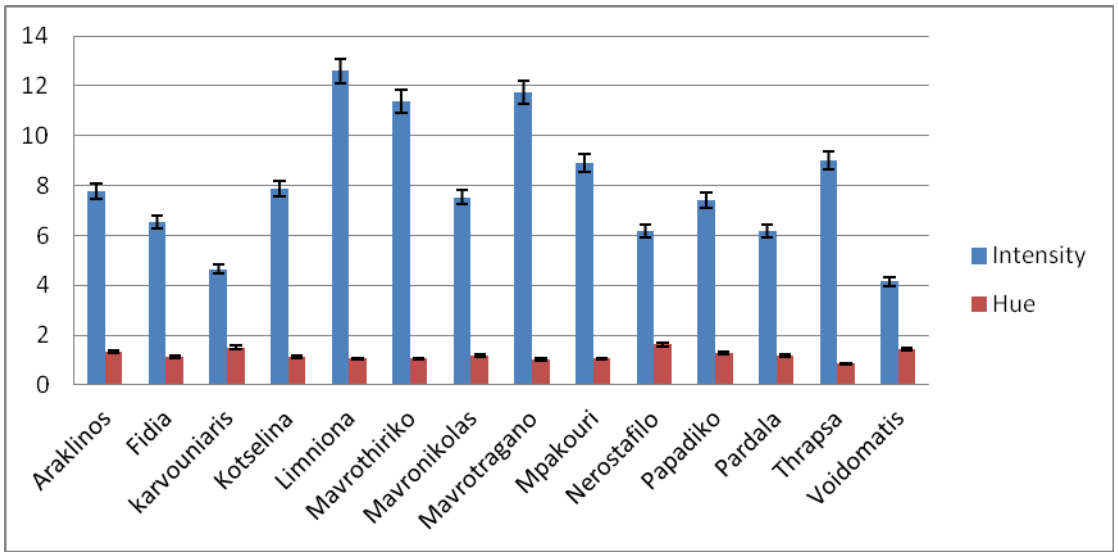

Figure 2: Color Intensity and Hue of the experimental wines after 8 years of their production.

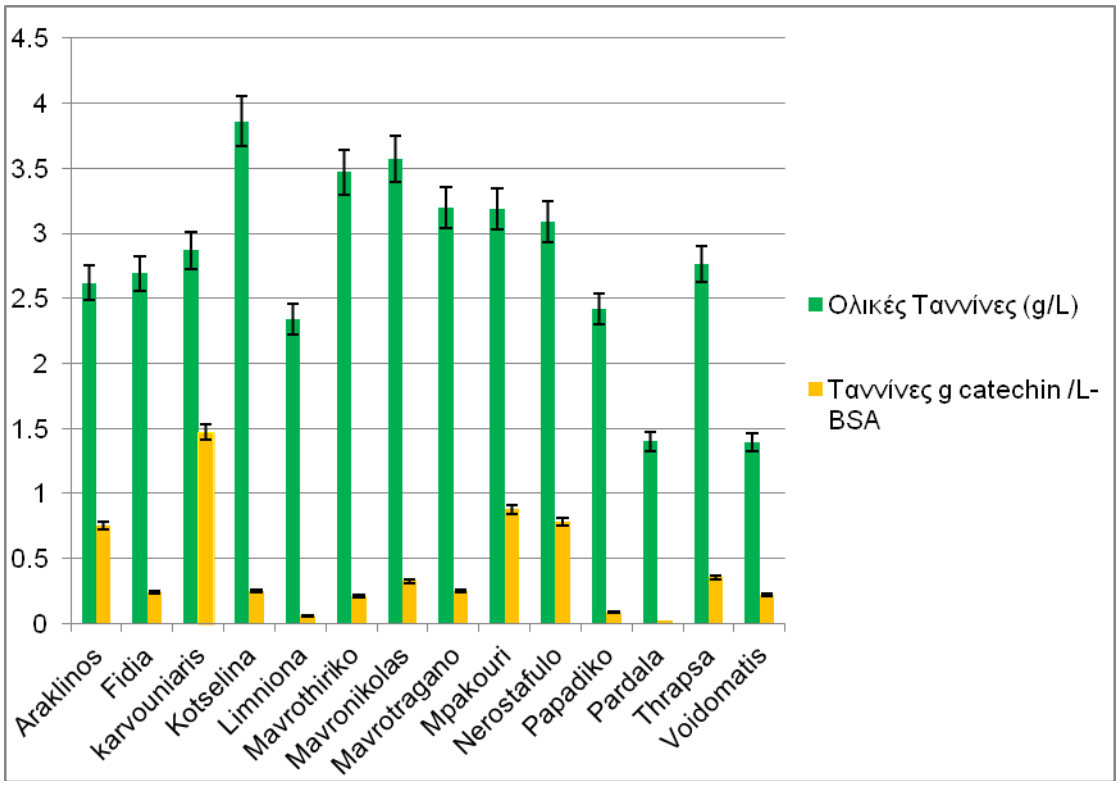

Figure 3: Tannin concentration of the aged wines

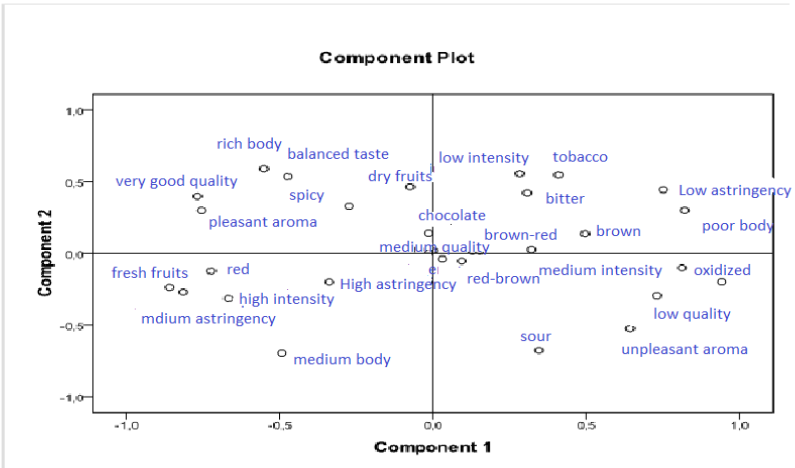

Figure 4: Principal Component Analysis of sensory analysis attributes

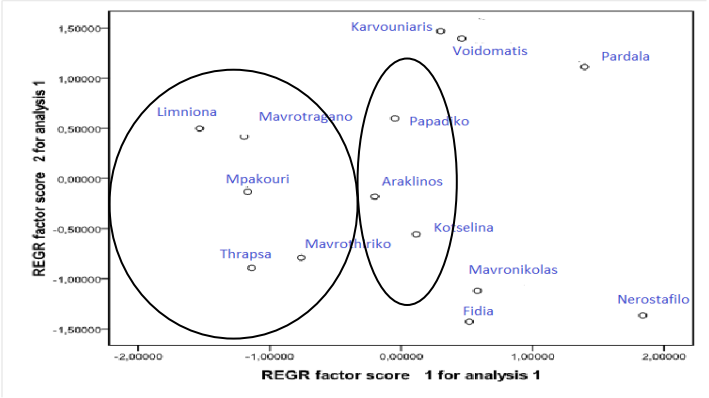

Figure 5: Principle component analysis of the aged wines

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