STUDY OF THE INFLUENCE CAUSE BY SOME MATURATION PROCESS (STAVES) ON THE PHENOLIC COMPOUNDS AND THE ANTHOCYANS FROM RED WINES

STUDII PRIVIND INFLUENȚA UNOR PROCEDEE DE MATURARE (MICRODOAGE) ASUPRA COMPUȘILOR FENOLICI ȘI ANTOCIANILOR DIN VINURILE ROȘII

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Abstract. *The demand for cost-effective and simpler techniques has encouraged the development of alternative ageing systems, such as the use of oak wood pieces (oak chips, stave), that accelerate ageing, shortening the time of contact, without decreasing the quality of the wine produced. The aim of this paper is to study the influence of various stave on the red wines physical-chemical parameters and phenolic compounds, because of their positive effects on human health. Experimental material used Feteasca neagră from the Şuletea area, Fălciului hill, harvested in 2013. The wines content of phenolic compounds varied, depending on the stave variant (V0-martor wine, V1-stave fruité, V2-stave vanillé and V3-stave épicé). Following the vinification, four technologic variants were obtained and analyzed at 1.5 and 3 months. For characterizing the phenolic compounds, a spectrophotometric measurement was used in order to evaluate the total polyphenolic index and the total quantity of anthocyans from wines. Photometric measurements were made using Analytik Jena S 200 spectrometer (at 280 nm, respectively 520 nm). The analyses show a small variation of phenolic compounds which means that stave types don't influence significantly their quantity. Although, we observed a quantitative decrease of phenolic compounds registrated at 3 months in comparison with samples at 1.5 months.*

Key words*: red wines, alternative products of maturation, phenolic compounds, anthocyans;*

Rezumat. *Cererea de tehnici rentabile şi simple au încurajat dezvoltarea unor sisteme alternative de maturare, precum utilizarea unor piese de lemn de stejar (aşchii de stejar, microdoage), care accelerează procesul de maturare, scurtează timpul de contact, fără diminuarea calității vinului produs. Obiectivul acestui studiu îl reprezintă influența diferitelor microdoage asupra caracteristilor fizico-chimice şi a compușilor fenolici din vinurile roșii, datorită beneficiilor asupra sănătății omului. Materialul experimental folosit a fost preluat din zona Şuletea, Vaslui-Fetească neagră, în anul de producție 2013. Vinurile au un conținut ridicat în compuși fenolici, funcție de tipul de produs alternativ (V0-proba martor, V1-microdoage de fructe, V2-microdoage de vanilie și V3-microdoage epice). În urma*

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vinificării s-au obţinut patru variante tehnologice, analizate la 1,5 şi 3 luni. Pentru a caracteriza compuşii fenolici, au fost utilizate măsuratori spectrofotometrice pentru a evalua indicele de polifenoli totali şi cantitatea totală de antociani. Măsurătorile fotometrice au fost realizate cu ajutorul spectrofotometrului Analitik Jena S 200 (la 280 nm, respectiv la 520 nm). În urma analizelor efectuate s-au observat mici variaţii ale compuşilor fenolici ceea ce semnifică că tipul de microdoagă nu influenţează semnificativ cantitatea acestora. Se observă însă o scădere a conţinutului de compuşi fenolici totali la 3 luni comparativ cu analizele efectuate la 1,5 luni.
***Cuvinte cheie**: vinul roşu, produse alternative de maturare, compuşi fenolici, antociani.*

INTRODUCTION

The phenolic composition of a wine is deeply influenced by grape variety, ripening, soil and climate, vinification procedures, and ageing (Zafrilla et al., 2003). The ageing process is a common technological procedure used in winemaking which seems to contribute to an increase in the antioxidant capacity of wines (Alonso et al., 2004; Canas et al., 2008; Larrauri et al., 1999). Phenolic compounds constitute one of the most important quality parameters of wines since they contribute to their organoleptic characteristics, particularly colour, astringency and bitterness (Santos-Buelga & de Freitas, 2009).

In recent years, several new techniques have been introduced in winemaking. One of these involves adding new pieces of wood (oak chips or inner staves) into inert containers (Arapitsas et al., 2004; Gomez Garcia-Carpintero et al., 2012; Alamo & Nevares, 2006). The use of stave is an alternative practice to barrels, which become widely used in the last years. Compared to traditional ageing, staves confer oak wood flavors to wines faster, easier and with a lower cost than barrels.

It is well-known that in both aging systems (alternative with oak fragments, or traditional in barrels), the characteristics of the final wines depend on the characteristics of the oak wood used (geographic origin, seasoning, toast, etc.) and on the factors that control the transfer processes of these compounds, such as contact surface between wine and wood, alcoholic degree, duration time, static or dynamic process, etc. In the traditional aging systems, the contact surface depends mainly on the size and shape of the oak barrels. However, in the "alternative systems", the contact surface depends on the size of the oak fragments (staves, chips, shavings, etc.) and on the amount used.

The aim of this paper is to evaluate the influence of stave on the physical chemical parameters, phenolic compounds and anthocyans quantity from Fetească neagră wines (local Romanian variety).

MATERIAL AND METHOD

The experiments used wines obtained from Fetească neagră grapes, from the Şuletea and Fălciului hills, Iasi region, in the vintage 2013.

The marc obtained was subjected to a maceration–fermentation process at temperature of 10-12˚C, for 7 days. In the next step, the marc was pressed and the wines obtained were transferred in fermentation tanks for the completing of alcoholic

and malolactic fermentation. At the end of the fermentation processes, we divided in four variants the wines: control wines (V0); wines with stave Medium Toast added (V1); wines with stave Medium Plus Toast added (V2) and wines with stave Heavy Toast added (V3) (Tab 1.). All the samples obtains used alternative products of maturation (4 g/L micro stave) that were immersed in 5L of wine and placed in glass vessels.

For characterizing the phenolic compounds, a spectrophotometric measurement was used in order to evaluate the total polyphenolic index and the total quantity of anthocyans from wines. The total phenolic content was determined by the enzymatic method described by Stevanato, Fabris, and Momo (2004) and total anthocyans by pH variation method. Photometric measurements were made using Analytik Jena S200 spectrometer (at 280 nm, respectively 520 nm).

The analytical methods used to characterize the above parameters are in accordance with European and OIV standards.

Wine samples, at 1.5 and 3 months, were analyzed for determining the basic physico-chemical parameters (alcohol strength (% vol.), total acidity (g/L $C_4H_6O_6$), volatile acidity (g/L $C_2H_4O_2$), relative density at 20 ˚C, reducing sugar (g/L), pH), but also the specific phenolic compounds parameters.

Analyses were done with the statistical software package Statgraphics Centurion XVI from StatPoint Technologies, Inc. (Warrenton, VI, USA). A cluster analysis, according to Ward's method, was carried out, which uses the total anthocyans as classifying variables (Fig. 3).

Table 1

Experimental design a Feteasca neagra wines

Sample code designation	Manufacturer	Produs type	Toasting level	Dose	Time
V0	-	Without products	-	-	3 months
V1	Amédée	Stave - fruité	French oak – Medium Toast	4 mini stave / 5L	3 months
V2	Amédée	Stave - vanillé	French oak – Medium plus Toast	4 mini stave / 5L	3 months
V3	Amédée	Stave - épicé	French oak – Heavy Toast	4 mini stave / 5L	3 months

RESULTS AND DISCUSSIONS

The general composition of Fetească neagră red wines (pH, alcoholic strength, total acidity, volatile acidity, relative density and reductive sugar) was analysed. We observed that the physical parameters were not affected by alternative process of maturation (Table 2).

During maturation occur many processes that modify the composition and organoleptic characteristics of the wine. Among these processes (physical, chemical and biological) we remember: the dissolution of wood components, condensation and deposition of phenolic compounds, modification of alcohol, aldehydes, acetals and esters contents and others.

Thermal process decomposes lignins in simple products and also can cause the formation of brown pigments by the effect of the Maillard reaction, favoured

by large amounts of sugars, the high temperature reached by grapes while raisining or the polymerization of phenol compounds (Moreno et al., 2007).

The pH of wine increased during the ageing process from 3.68 to 3.70 at V0 and V1, 3.64 to 3.69 at V2 and 3.65 to 3.68 at V3.

The alcohol strength doesn't present a significant variation between 1.5 and 3 months, which concludes that types of stave don't influence this parameter. Thought, we observed a decrease in alcohols during ageing caused by oxidation and esterification when ethanol is converted into other components. Acetaldehyde is the main organic by-product of ethanol metabolism, but other volatile compounds, notably acetic acid, butanediol, diacetyl, and acetoin, can also be formed.

Table 2

Physical-chemical characteristics of Feteasc㠠neagr㠠wines

Var.	pH	Alcohol strength %	Total acidity (g/L $C_4H_6O_6$)	Volatile acidity (g/L $C_2H_4O_2$)	Relative density (g/cm^3)	Reductive sugar (g/L)
Analysis of 1.5 months						
V0	3.68±0.01^c	14.96±0.17^c	5.80±0.04^b	0.56±0.01^c	0.9675±0.02^c	2.36±0.01^c
V1	3.68±0.01^c	14.94±0.24^a	5.90±0.04^c	0.57±0.01^d	0.9728±0.03^d	2.39±0.01^d
V2	3.64±0.01^a	14.95±0.14^b	5.95±0.05^d	0.55±0.02^b	0.9624±0.03^a	2.34±0.02^a
V3	3.65±0.00^b	14.95±0.09^b	5.67±0.04^a	0.53±0.02^a	0.9643±0.03^b	2.35±0.02^b
Analysis of 3 months						
V0	3.70±0.01^c	14.94±0.12^a	5.78±0.00^c	0.57±0.01^c	0.9675±0.01^c	2.36±0.00^c
V1	3.70±0.00^c	14.94±0.11^a	5.80±0.04^d	0.58±0.02^d	0.9675±0.02^c	2.36±0.01^c
V2	3.69±0.00^b	14.94±0.05^a	5.63±0.00^b	0.55±0.02^b	0.9624±0.03^a	2.34±0.01^a
V3	3.68±0.01^a	14.94±0.08^a	5.60±0.16^a	0.54±0.00^a	0.9643±0.01^b	2.35±0.02^b

Different letters indicate significant differences at 95% confidence level. Data expressed as mean ± standard deviation.

For the total acidity, we observed that the results at 1.5 months range from 5.67 g/L tartaric acid (V3) and 5.95 g/L tartaric acid (V2) and at 3 months the values decrease and range between 5.60 g/L tartaric acid (V3) and 5.8 g/L tartaric acid (V1) in accordance with Cotea et al., 2009.

The volatile acidity values increase proportionally with ageing, due to the non-enzymatic oxidation process, that converts a part of ethyl alcohol into acetaldehyde and then into acetic acid, the main component of volatile acidity. The maximum value is 0.57 g/L acetic acid (V1) at 1.5 months and 0.58 g/L acetic acid (V1) at 3 months.

In figure 1 is presented the content of total phenolic index (D_{280}) for the two time periods chosen, where it can be observed that the maximum values are for the samples at 1.5 months and values decrease for samples at 3 months. The small variation between samples concludes that the types and toasting process of stave don't influence significantly the total polyphenolic index.

In figure 2 we can notice that the total quantity of anthocyanins (mg/L) decrease significantly at 3 months. The decreases in the anthocyanin contents during wine ageing must have resulted from the gradual conversion of monomeric compounds into more stable oligomers or polymers (Monagas et al., 2006). Taken into account that anthocyanins are the major source of colour in red wines, we observed that the anthocyanin composition of the studied wines changed considerably during ageing.

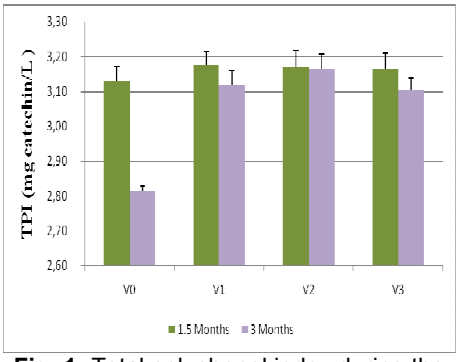

Fig. 1 -Total polyphenol index during the ageing Fetească neagră wines

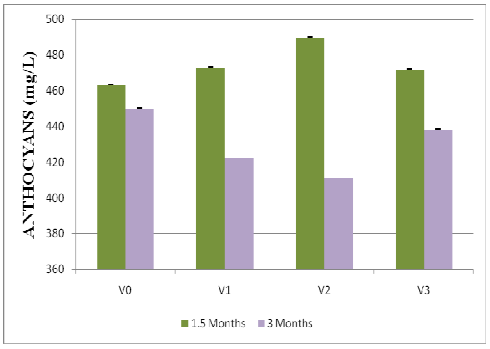

Fig. 2 - Total quantity of anthocyans during the ageing Fetească neagră wines

The maximum values recorded are 489,53 mg/L in variant V2 and 472.43 mg/L in variant V1, where V2 present the highest value for 1.5 months.

A cluster analysis according to Ward's method was carried out by using total anthocyans the as classifying variables (Fig. 3). In this work, cluster analysis was used to assess the similarity between variants analysed at 1.5 and 3 months. The distance at which the different groups were formed allowed us to differentiate sample analyzed at 1.5 and 3 months.

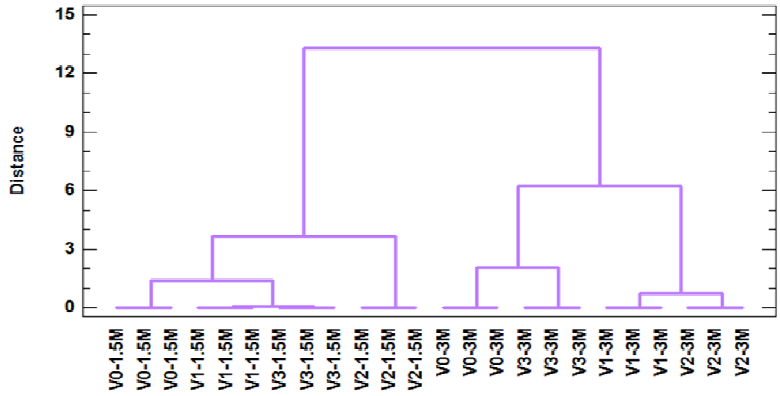

Fig. 3 - Cluster analysis performed with Ward's method and total anthocyans as classifying factors

CONCLUSIONS

1. According to the results obtained in this research, the trends of the phenolic compounds are very similar in the wines from all varieties at 1.5 months and 3 months. But the values at 3 months are slightly smaller then at 1.5 months.

2. The aging time decreased the total amount of anthocyans, as a cause of a series of mechanisms that can be related to these changes, such as adsorption by yeast, degradation and oxidation, precipitation with proteins and the progressive and irreversible formation of more complex and stable anthocyans derived pigments.

3. In conclusion the types and toasting stave don't influence significantly the physical chemical parameters, quantity of total polyphenolic index and anthocyans.

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