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STUDY OF THE INFLUENCE OF AGING IN DIFFERENT BARRELS ON SHIRAZ WINES

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Abstract

The Syrah/Shiraz grape variety is rather newly introduced in Romania and the producers are still working on establishing optimum winemaking technologies for it. Aging in oak barrels is an important technological step for this high tannic wine, therefore, the selection of the appropriate barrel to improve the structure, colour and flavour of this wine is of great importance. This study aims to compare the influences on the colour and sensory parameters induced on Shiraz wine by aging it for 1 year in barrels made of oak with various origins (French, Romanian, Russian and Hungarian oak) and various toasting levels. Wine kept in stainless steel tank was also used as control. It was observed that the French oak tends to differ compared to Russian and Hungarian oak as regards the colour differences induced in the wines, while the influence of Romanian oak is rather similar to that of French oak. Concerning the sensory quality of the wine aged in barrels, preliminary results point out that barrels from the provider "Transilvania bois" (Romanian and Russian oak) offer constant sensory quality, but some French oak barrels may ensure outstanding sensory quality. Regarding the toasting degree, for Shiraz wines the medium plus toasting offered the best results for structure and aromatic profile after 1 year of aging. These findings need to be confirmed with more precise aromatic profile analyses.

Key words*: oak barrel, Shiraz, flavor, maturation, wine.*

INTRODUCTION

Aging wine in oak barrels is a well known technique used to improve the quality of red wine by reducing the tannin astringency, increase the intensity of colour through tannin-anthocyians condensation and to improve the structure and taste under the influence of the substances extracted from the wood. The earliest literature on the use of oak containers for wine can be traced back to the Roman Empire (Zhang *et al*., 2015).

The topic is important for many wineries, therefore plenty of studies have been performed in order to determine the various effects that wood contact and aging in oak barrels induce in the wines. However, selecting the oak type and toasting degree for the oak to match the structure and complexity of a certain varietal wine is a difficult task, and not many studies are found on this subject.

The present study focuses on several oak barrel types destined for the aging of red wine from the Shiraz grape variety grown in Dealu Mare region of Romania.

The barrels selected for comparison are produced from wood of various origins (French, Russian, Hungarian and Romanian), with various levels of toasting (heavy, medium plus and medium).

The oak wood used in winemaking is mainly from two sources: American oak (Quercus alba - the white oak) and French oak (Quercus robur – the pedunculate oak or sometimes the less common Quercus petraea - sessile oak). American oak induces intense vanilla and coconut flavours, while the French oak induces a more subtle favour. The Eastern European Oak is actually Quercus robur too, as the French oak, but the flavour it imparts is considered in-between American and French Oak, due to a higher content of volatile phenols and phenolic aldehydes than the French oak, even though they belong to the same species (De Simon *et al*., 2003).

Studies dating back as far as 1974 (Singleton, 1974, Singleton 1995) showed that the

chemical composition of oak with various types is quantitatively different, but more recent studies are also available (Alanon *et al.*, 2011). Beside the botanical species, the geographic origin is also important regarding the proportions of various compounds found in the wood (Prida and Puech, 2006; Guchu *et al.*, 2006).

The aging of wines in oak wood barrels leads to the extraction of numerous compounds that have an impact on wine colour, astringency and bitterness, either directly or indirectly. The ellagitannins extracted from wood and the presence of oxygen have a major impact on taste and colour through the process of co-pigmentation of anthocyanins and tannins during red wine aging (Asen *et al*, 1972; Mateus *et al.*, 2001, 2002).

New types of compounds, such as oaklins, have been reported to contribute to changes in the colour and astringency of wines during aging (Sousa *et al.,* 2005).

The grape variety of the wine kept in barrels is also important, as the wine composition too influences the way in which the wine is aging. In this study Shiraz was selected as the grape variety, a rather rare variety for Romania, but for which the interest has been growing steadily during past 10 years.

The wines of Shiraz have a good structure, being quite tannic and requiring aging.

For these reasons, the aim of this work was to study the influences of oak barrels on the Shiraz wine sensory and colour characteristics, in order to determine the most appropriate type of wood in accordance to its origin.

MATERIALS AND METHODS

Raw material

To carry out the study regarding the influence of barrels on the aging of red wines, different types of barrels and Shiraz wines were used.

The Shiraz wine was produced in 2013, from grapes harvested in Dealu Mare Vineyard. The grapes were harvested in plastic boxes of 10 kg each, on October 3, 2013, when they reached the sugar concentration of 260 g/l, which corresponded too with the phenolic maturation phase and a moderate level of total acidity (5.48 g/l tartaric acid). Grapes harvested in this way allowed for both quality and high yield in the resulted wine. Shiraz is a grape variety that does not benefit from over-maturation, not only because it does not accumulate more sugar as in the case of other varieties, but also loses aroma and acidity.

Winemaking process

The harvested grapes were brought directly to the wine cellar and crushed within maximum four hours after harvesting. For antioxidant protection a dose of 40 mg/l of sulfur dioxide (SO_2) was applied during the crushing process.

The winemaking was based on classic red wine maceration fermentation process.

To accomplish the maceration-fermentation phase, 8000 kg of the crushed grapes were introduced in a 10,000 l stainless steel tank. To extract more color from the skins, 1 g/100 kg of enzyme Lallzyme EX-V was added during maceration. The fermentation was started by inoculation of 20 g/hl 15 RP selected yeast from Lallemand. A dose of 20 g/hl OptiRed (yeast membranes) was also added (from Lallemand products catalog).

Maceration-fermentation for this red wine took place at a temperature of 25-29°C, for 15 days. During all this period the homogenisation of the crushed berries was performed 3-4 times a day, by punching down the cap formed at the upper part of the tank.

After the alcoholic fermentation the wine was separated from the solid parts. Malolactic fermentation (MLF) began at the end of alcoholic fermentation, when the wine was still warm (18-20°C) and yeast population was decreasing. To facilitate MLF the wine was slightly aerated and inoculated with 0.5 g/hL malolactic bacteria. The MLF was slow and accomplished in 20-40 days. In the end the wine was again slightly aerated. After the completion of MLF the wine was separated from the lees by racking and then sent to maturation in oak barrels of 225 l volume.

The wine cellar where winemaking was performed is built on the principle of gravity, which prevents excessive pumping and oxidation, allowing for the production of wines with increased quality.

Types of barrels

For the wine maturation different types of barrels were used, obtained from various manufacturers. The oak used for barrels was of different origins and processed to have different

toasting levels. Furthermore, the barrels were either new or in their second or third year of use. For this experiment, the types of barrels available were as follows: barrels of Russian and Romanian oak from the Romanian producer Transilvania Bois; barrels of French oak from the French producers – Radoux, Boutes and Francois Freres; barrels of Hungarian oak from a Hungarian producer - Trust Hungary.
Toasting levels varied from medium, medium plus to heavy toast.

Analyses

The main grape and wine parameters were determined in accordance to the usual methods: the sugar content by refractometry, total acidity by automatic titration by using a Mettler Toledo titrator, alcohol concentration by ebuliometry and sulphur dioxide by Ripper method.
The evolution of wines from different barrels was monitored every 3 months over a period of 1 year, by tasting with an in-house panel of wine experts. Organoleptic analyses of the wines were done by examining and recording the visual, smell and taste traits on a special evaluation sheet. An OIV score sheet for the evaluation in international contests was used to score the wine on a scale of 100 points (OIV, 2008).
The determination of total polyphenol was performed with an UV-VIS – spectrophotometer, by diluting the wine 100 times and measuring the absorbance at 280 nm in cuvettes of 1 mm path length. The value of the absorbance measured at 280 nm was reported after multiplying it with 100.
The determination of color intensity, hue and chromatic characteristics of wine was also performed with an UV-VIS – spectrophotometer. The absorbance of wine was measured at three wavelengths, 620, 520, 420 nm, representative for the description of wine colour. Young red wines have a maximum absorbance at 520 nm, while for aged wines color absorbance shifts, their maximum getting closer to 420 nm.
The reference method for reporting the color parameters was a spectrophotometric method by which tristimulus values and chromaticity coordinates X, Y, Z, are determined according to the standards of International Commission on Illumination (CIE, 2015).

RESULTS AND DISCUSSIONS

The wines of Shiraz were introduced in barrels and aged for 1 year and then their parameters determined. As control, the Shiraz wine aged in stainless steel tank was used.
In Table 1 the main wine parameters are included. It can be seen that the barrel, irrespective of type of oak or year of production (and usage) does not influence much the main wine parameters. The only noticeable exception is the volatile acidity, which is clearly higher in all barrels (around 1 g/l acetic acid) as compared to the volatile acidity determined from wine kept in the stainless steel tank (0.75 g/l acetic acid).

Table 1. Main physico-chemical parameters of Shiraz wines aged in barrels and in stainless steel tank

Barrel type	Free SO_2 mg/l	Total SO_2 mg/l	pH	Alcohol % v./v.	Total acidity g/l tartaric acid	Volatile acidity g/l acetic acid
Control (Stainless steel tank)	53	54	3.68	14.8	5.05	**0.75**
Radoux R TGS H TH – French oak	48	93	3.51	15.5	5.78	0.99
Radoux R TGS M TH – French oak	32	43	3.52	15.4	5.63	0.97
Radoux R TGS Rev TH – French oak	39	74	3.53	15.4	5.93	0.98
Radoux Evol R TGS M+ TH – French oak	31	81	3.52	15.3	5.63	1.08
Francois Freres 2011 TG M TH – French oak	27	65	3.53	15.5	5.66	0.95
Boutes Tradition M – French oak	49	71	3.53	15.3	5.73	1.00
Transilvania bois - Romanian oak	39	55	3.52	15.4	5.76	0.98
Transilvania bois 2013 M – Russian oak	23	52	3.53	15.4	5.78	0.98
Transilvania bois M+ 2013 – Russian oak	30	43	3.52	15.3	5.78	0.99
Transilvania bois M 2011 – Russian oak	33	74	3.53	15.3	5.70	0.92
Transilvania bois M+ 2011 – Russian oak	39	77	3.53	15.3	5.70	0.92
Trust M+ – Hungarian oak	26	61	3.53	15.3	5.76	0.97

The organoleptic analyses revealed that the barrels induced significant differences in the aspect, smell and taste of the wines, and also that these characteristics evolved during the maturation.

In Table 2 the sensory evolution of wines during their maturation is presented, while Table 3 presents the sensory descriptions and scores obtained by the wines evaluated after 1 year of aging in barrels.

Table 2. Average scores awarded to Shiraz wines matured in barrels, evaluated at various time intervals during 4 wine tasting sessions

Barrel type and year of usage	Score March 2014	Score July 2014	Score October 2014	Score March 2015
FrFreres M - II	79.0	81.8	76.8	78.0
Trans B Rus M - I	82.2 Silver	80.0	84.2 Silver	78.0
Radoux H - I	78.5	81.0	82.2 Silver	82.0 Silver
Trust Hung M+ - III	76.6	79.4	76.2	83.0 Silver
Trans B Rus M - II	76.6	79.6	78.6	83.0 Silver
Trans B Rus M+ - I	85.0 Gold	80.2	81.4	83.0 Silver
Trans B Rom M -III	76.6	81.4	76.6	84.0 Silver
Radoux Rev M - I	81.8	82.4 Silver	77.4	84.0 Silver
Radoux Evol M+ - I	82.8 Silver	78.6	76	85.0 Gold
Radoux M - I	77.6	82.8 Silver	81.8	86.0 Gold
Trans B Rus M+ - I	76.6	77.8	77.6	86.0 Gold
Boutes Trad M - I	76.4	73.2	78.0	86.0 Gold

As it can be seen in Table 2, most of the wines aged in new barrels (first year of usage) were highly appreciated by the winetasters after 1 year of maturation. Among the them, those aged in Transilvania Bois – Russian oak, Radoux (both classic and evolution style of toasting) – French oak and Boutes – French oak received top marks, irrespective of the toasting level.

The scores for all the wines ranged from 78-86, which, in accordance to the OIV rules for wine contests signify: good wines (78-81.9 points), silver medal wines (82-84.9), gold medal wines (85-91.9), and great gold medal wines (92-100). Generally, keeping the wines in contact with oak for 1 year improved the perceived quality, but in some cases the quality was not much improved, remaining around 78-82 during all the evaluated period. The Romanian oak only improved the wine up to a silver medal level, but this should be interpreted with caution as the barrel employed was in its third year of usage. It can be noticed that the greatest improvement is generally achieved in new barrels, followed by barrels used in their second and third year.

Aside of the effect on wines' aroma, the barrels are expected to influence the polyphenolic composition of wines (Table 4).

The total polyphenol index of the wine stored in barrels for a year was, on average 37.95 ± 3.46, with only one wine exceeding the range 35.5-38.0 and reaching TPI = 48.57.

This higher polyphenol wine was kept in a French oak new barrel from Radoux, obtained with a special toasting technique called "Evolution" (Radoux, 2009), in which the maximum toasting temperature was lowered compared to the classical toasting process, while the length of the toasting operation extended through a "re-cooking" phase.

Colour has also undergone some changes during barrel aging. The samples were analyzed after one year of storage in tank or in barrel and the CIE*Lab* colour parameters determined are included in Table 4.

Table 3. Wine sensory description and average scores awarded to Shiraz wines matured in barrels after 1 year of aging

Type barrel	Score	Description
FrFreres M - II	78	The medium toast induces less structure and complexity in the taste, a volatile acidity covering the wine fragrance
Trans B Rus M - I	78	Intensely colored, pigments remaining on the tasting glass surfaces, due to a perceptible volatile acidity, which, through acetaldehyde favors copolymerisation
Radoux H - I	82	Intensely colored, with a dominant aroma of vanilla, but still with harsh tannins which dry the mouth; some sweetness is also perceivable
Trust Hung M+ - III	83	Fruity aroma of cherry and sour cherry, quince and fig jam, with a slight hint of volatile acidity, still aggressive tannins
Trans B Rus M - II	83	Powerful, astringent, with aggressive tannins in taste, but with a well balanced acidity
Trans B Rus M+ - I	83	Floral aroma and vanilla notes, still rough, but long, with a burning aftertaste due to alcohol and tannins
Trans B Rom M -III	84	Fine olfactory quality, well integrated medium toast oak and long taste
Radoux Rev M - I	84	More classic style wine, giving the feeling of a shorter term contact with wood, with notes of vanilla and spices, complex in taste, yet harsh, but ready for the market
Radoux Evol M+ - I	85	Long, lingering, peppery aftertaste with persistent, complex flavour of vanilla, tobacco, toast, coffee and caramel
Radoux M - I	86	Fruity aroma of cherries and bitter- sweet cherries, vanilla and truffles notes, long, complex, drinkable, but still a bit harsh in aftertaste
Trans B Rus M+ - I	86	Very well balanced wine, round, lingering, complex, elegant, with notes of over-ripen fruits and spices
Boutes Trad M - I	86	Elegant wine, intense and round in the same time, well balanced acidity and bitterness, well integrated oak flavor

Table 4. Total polyphenolic index and CIE*Lab* parameters of Shiraz wines aged in barrels and in stainless steel tank

Barrel type	TPI	a	b	c	h	L	ΔE*
Control (Stainless steel tank)	46.14	49.38	6.11	49.76	0.12	52.86	0
Radoux R TGS H TH – French oak	36.51	49.56	15.78	52.01	0.31	46.07	11.82
Radoux R TGS M TH – French oak	37.86	54.22	11.87	55.50	0.22	41.39	13.72
Radoux R TGS Rev TH – French oak	37.91	51.35	13.12	53.00	0.25	44.40	11.16
Radoux Evol R TGS M+ TH – French oak	48.57	52.57	13.89	54.37	0.26	40.78	14.72
Francois Freres 2011 TG M TH – French oak	36.91	55.56	13.22	57.11	0.23	40.66	15.41
Boutes Tradition M – French oak	37.86	48.78	11.83	50.20	0.24	50.68	6.15
Transilvania bois - Romanian oak	35.54	52.67	11.06	53.82	0.21	47.23	8.19
Transilvania bois 2013 M – Russian oak	36.28	51.72	14.13	53.62	0.27	34.87	19.83
Transilvania bois M+ 2013 – Russian oak	37.28	54.63	12.11	55.96	0.22	39.58	15.49
Transilvania bois M 2011 – Russian oak	37.76	54.85	13.85	56.57	0.25	42.07	14.36
Transilvania bois M+ 2011 – Russian oak	37.43	52.95	10.86	54.05	0.21	46.92	8.41
Trust M+ – Hungarian oak	35.49	54.55	15.03	56.58	0.27	40.83	15.85

* ΔE is the colour difference calculated against the colour of wine in tank

All the wines have an intensely red colour, with some differences in the colour tone. Some samples aged in barrels, in accordance to parameter *a*, have their colour shifted on thee green-red axis toward more red tones (*a*=50-55), as compared to the wine stored in stainless steel tank (*a*=49.4). Not all the wines kept in barrels evolved toward a higher value of parameter *a*, showing that the type of barrel and the amount of oxygen which enters through it is important, although no clear tendency regarding the origin of oak or type of toasting was identified. As regards the parameter *b*, the position on the blue-yellow axis, this one was clearly influenced by the barrel. The values of parameter *b* are more or less double (*b*=10.9-15.8) for the wines in barrels than the value of the wine kept in tank (*b*=6.1), clearly showing a shift toward yellow components, which means that they lost their blue-violet tones and acquired more yellow-brown tones, typical for wine oxidative maturation. This tendency is easier to observe when we place the samples in the *ab* colour space (Fig. 1).

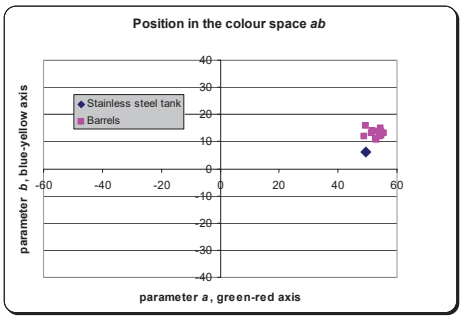

Figure 1. The position of wine the tank (blue) and in barrels (magenta) in the *ab* colour space

As expected, the evolution of wine in barrels is faster than in tank, the hue increasing in all the wines kept in barrels, irrespective of the oak origin and type of toasting (Fig. 2).

However, although for the separate colour parameters changes related to a certain type of oak could no be clearly demonstrated, the overall colour difference, ΔE, which takes into account the variations of a, b and L parameters ($\Delta E = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{(1/2)}$) seems to show that some types of oak induce more colour changes than others (Fig. 3).

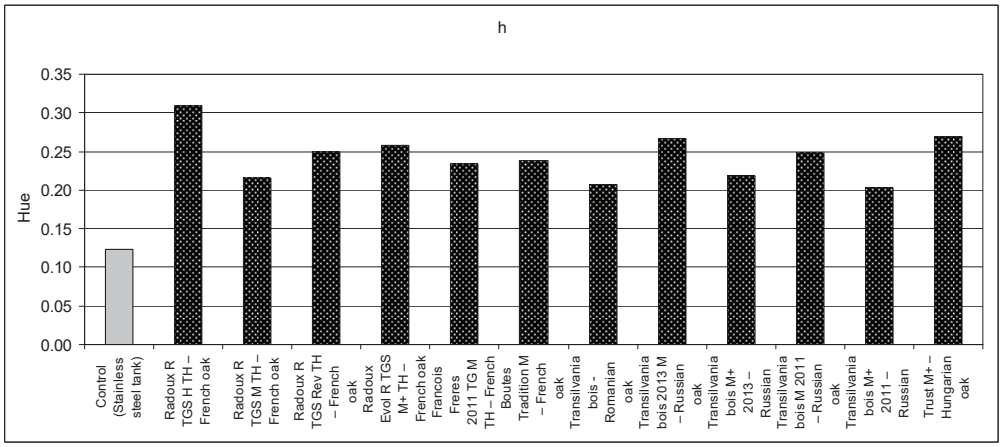

Figure 2. The wine hue in the tank (left sample) and in barrels

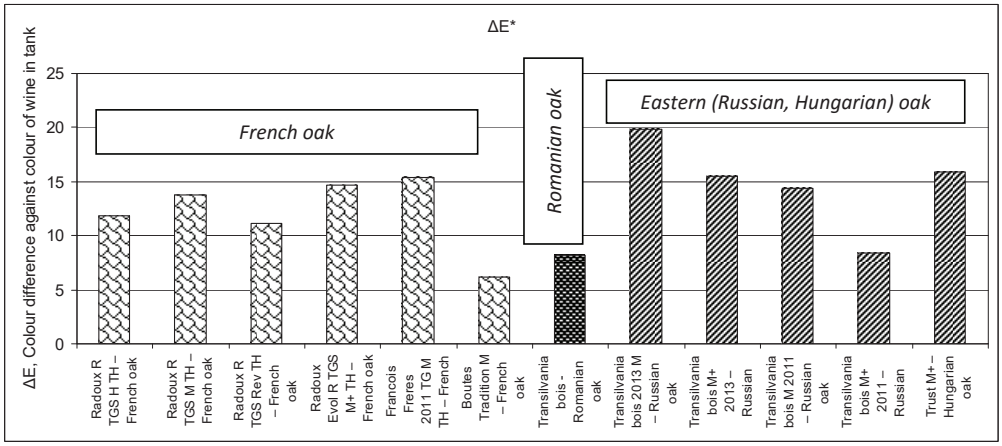

Figure 3. The difference in color ΔE wines depending on the type of barrel compared with the control sample kept in tank (groups of barrels made of French oak, Romanian Oak and Russian or Hungarian oak were outlined with different patterns)

It was observed that Eastern oak (Russian and Hungarian oak) tends to induce more colour differences in the wines (Fig 3 – the right group, average ΔE=14.8±1.8) as compared to French oak (Fig 3 – the left group, average ΔE=12.2±1.4). In this respect, the Romanian oak (Fig. 3, the middle sample, ΔE=8.19) tends to behave more like the French oak, although, by applying statistical analysis for the three groups, due to the small number of barrels analyzed and the inherent barrel-to-barrel variation (Towey and Waterhouse, 1996), no statistically significant difference was found at the 0.05 level of certainty. Moreover, it must be reminded that the barrel made of Romanian oak is in its 3rd year of usage and that the colour is not only influenced by the porosity and oxygen allowed to dissolve in wine, but also by the tannins transferred by the barrel to wine and their condensation with the existing polyphenols of wine. However, also in the third year of usage are the barrel Boutes Tradition-French oak (ΔE=6.68) and barrel Trust M+ – Hungarian oak (ΔE=15.85), showing that the Romanian oak behaves rather like the French oak than the others, suggesting that the Eastern oak is allowing more oxygen in the wine than the French oak.

CONCLUSIONS

In order to determine the evolution of Shiraz wine in barrels and select the most appropriate barrels for the wine style the simplest analyses to perform are colour determination by CIE*Lab* method and sensory analysis.

Some colour differences were induced by aging in barrels, and based on these changes we observed that the French oak effects tend to differ compared to Russian and Hungarian oak, while the Romanian oak places itself closer to the French oak in this respect.

Transilvanian bois barrels (Romanian and Russian oak) offer constant sensory quality (silver and gold medal scores), but some French oak barrels led to outstanding sensory qualities in wines (gold medal scores).

Among the tested barrels, the Radoux Evolution barrel, produced by a special toasting technique, stood out by producing the wine with highest total polyphenol index, one of the highest colour differences compared to the control wine and the gold medal score obtained in sensory evaluation.

Based on the studied parameters, no clear correlations were found regarding the colour of the final wine and the toasting degree and the barrel year of usage. Apparently, the medium plus toasting degree is more suitable for the structure and aromatic profile of Shiraz wine, thus they were described as being more complex and round in the same time, with the classical notes of coffee and spices. However, more precise analyses are needed to draw accurate conclusions regarding the changes in aromatic profile induced by certain types of barrels or toasting levels.

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