Ph.D. THESIS

Research on the influence of the degree of toasting of oak barrels and chips and the ageing period on the quality of some red and white wines

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(SUMMARY OF Ph.D. THESIS)

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Introduction

Ageing red wines in barrels is a common practice for centuries. With regard to white wines, until now, only in the Burgundy region is practiced fermentation in barrels, but, in recent years, the maturation of white wines is becoming an increasingly widespread practice in obtaining wines with organoleptic and high quality properties.

In 2006, the OIV (International Organization for Wine and Wine) approved the use of chips (OENO Resolution 3/2005) and of staves as an alternative for aging in barrels (barrels).

Literature rewiew

1. Use of different woody essences in vinification

1.1. Evolution of the use of wine storage vessels

The oak barrels are fundamental to the production of wine (McGOVERN, 2013). Unlike *krevi* and amphoras that were made of clay, the wooden barrels are porous and allow a slight oxidation of the wine. The Romans noticed that the wood left a mark on the wine, changing the aroma and the content in the tannin and keeping the wine for a longer time, during the long trips by sea, it tasted much better when it reached its destination.

1.2. Woody essences used in winemaking

Quercus alba or white oak represents 45% of the oak species in the United States (BAINBRIDGE, 1986.

Quercus robur s native to the European continent to the west of the Caucasus. It is found in the temperate climate, but also in different parts of China and North America (DUCOUSSO, 2004).

1.3. The chemical composition of wood essences

Oak wood has a varied composition, it is composed of cellulose (49-52%), lignin (31-33%), hemicellulose (22%) and a fraction volatile oils, volatile and non-volatile acids , sugars, steroids, tannin compounds, pigments and inorganic compounds (7-11%) (HORNSEY, 2016).

1.4. Technology for the production of chips and barrels

1.4.1. Technology for the production of chips

The pieces of wood are marketed in different forms (del ALAMON SANZA, 2006). Wood chips can be toasted by different methods (fire, hot air, infrared radiation). The toasted can have different stages (light, medium and intense frying) at specific temperatures.

1.4.2. Technology for the production of barrels

The wood used to make barrels is naturally dry to a humidity of 14% to 18%. The methods of drying the staves are natural drying outdoors, under the action of natural conditions, for 18 or 36 months and artificial drying in the oven. The toasting of wood has the most significant influence on the chemical composition, modifying, both the quantity and the quality of the extractable substances (CUTZACH et al., 1997; CHATONNET et al., 1999).

1.4.3. The process of toasting of barrels

The heat applied to the wood during the toasting process, by pyrolysis and thermolysis, breaks the chemical bonds inside the biopolymers such as cellulose, hemicellulose, lignin, polysaccharides, polyphenols and lipids (FERNÁNDEZ DE SIMÓN și colab., 2009).

2. Aromatic profile of ageing wines

2.1. Volatile compounds in wine

2.1.1 Alcohols are the largest group of volatile compounds in wine, both in terms of number and concentration, followed by esters and fatty acids. Alcohol results from the degradation of amino acids, carbohydrates and lipids (ANTONELLI et al., 1999).

2.1.2 Esters are onether large group of volatile compounds in wine, being produced during alcoholic, malolactic and acetic fermentation through enzymatic reactions (biological esterification) and during wine storage / aging (chemical esterification) (ȚÂRDEA, 2007).

2.1.3 Fatty acids are the main chemical compounds that ensure the quality and preservation of the wine. Acids give the wine acidity, a refreshing taste, brightens the color and maintains the physico-chemical balance of substances dissolved in wine (ȚÂRDEA, 2007).

2.2. Volatile compounds extracted from oak

2.2.1. Compounds derived from polysaccharides. Furanic compounds are derived from polysaccharides, furfural being produced by heating the pentoses (xyloses) contained in hemicellulose. In the combustion process, from the degradation of the hexoses (rhamnoses) present in the cellulose, 5-hydroxymethylfurfural and 5-methylfurfural are obtained (HERRERO et al., 2016).

2.2.2. Compounds derived from polyphenols and lignin. Thermal degradation of lignin results in the formation of volatile phenols (guaiacol and eugenol) and phenolic aldehydes (vanillin and syringaldehyde).

2.3. Maturing white and red wines in barrels and chips

Volatile phenols and benzoic aldehydes are important compounds, they impart the most important sensory characteristics to wine (CANAS et al., 2004; PUECH et al., 1999; PEREZ-COELLO et al., 1999; MASSON et al,. 1996; IBERN-GOMEZ et al., 2001).

2.4. Correlation between volatile compounds and sensory properties of wines

Gas chromatography is an important technique for analyzing volatile components in wine (JĂNTSCHI and NAȘCU, 2009), although the aromatic impact of the identified volatile compounds is evaluated, generally by determining the perception thresholds. The value of odor activity (OAV) is a useful parameter to evaluate the relative importance of the individual chemical components present in a wine (PEINADO et al., 2004).

Personal contribution

3. The research objectives.

In order to evaluate the oenological parameters and aroma compounds in the wine assortments (red and white) aged by different methods and periods, two major research directions were addressed: determining the oenological parameters and quantifying and identifying the volatile compounds.

4. Particularities of the natural environment of samples provenance

Red wine-making took place at the Dobra and Rătești Wineries (Crișanei and Maramuresului Hills) and at the Alira Winery (Dobrogea Hills). The white vinification took place at the Teaca Winery, Lechința Vineyard.

5. Materials and methods

5.1. The grape varieties used for vinification were Cabernet Sauvignon, Fetească neagră, Merlot, Pinot noir, Fetească albă, Fetească regală. The grapes were harvested manually, at full maturity.

5.2. Biological materials. Oak chips (*Querqus robur*) - untoasted and light toasted were provided by Sodinal, Romania and oak barrels with a capacity of 225 l (untoasted and medium toasted) were provided by Transilvania Bois, Sighetu Marmației (Maramureș).

5.3. Research methods

5.3.1. Determination of the main oenological parameters in wine

The main oenological parameters of the wines were determined according to the methods approved by the OIV (Bora et al., 2015).

5.3.2. Identification and quantification of volatile compounds in wine

Detection and quantification of volatile compounds in red and white wines was done with Shimadzu QP 2010 PLUS mass spectrometer coupled with gas chromatography, the apparatus being presented in sub-chapter **5.3.3.** The reagents and chemicals used are presented in subchapter **5.3.4.**

5.3.5. Liquid-liquid extraction. The protocol used by ANDUJAR-ORTIZ et al., 2009, was adapted and used to isolate volatile compounds from wine samples.

5.3.6. Analysis of volatile compounds of wine with gas chromatograph coupled to mass spectrometer

The calibration curves were at three points for the standard compounds: isoamyl alcohol, butyrolactone, ethyl decanoate, ethanol, containing the internal standard (1-octanol).

5.3.7. Calculation of the value of the odorant activity of the wines (OAV) and the elaboration of the aromatic profile. OAV was calculated by dividing the concentration of each compound at the respective perception threshold. Only compounds with VAO> 1 contribute in particular to the aroma of wine (JIANG and ZHANG, 2010). The total intensities for each aromatic series were calculated as the

OAV sum of each of the compounds assigned to this series, and on their basis the aromatic profile was prepared.

5.3.7. Organoleptic assessment was done by the method of quantitative descriptive analysis.

5.4. Methods of executing experiences. This sub-chapter describes how to organize experiences I and II.

5.5. The statistical-mathematical methods used were the Duncan test and the MANOVA test (multiple variance analysis).

6. Results and discussions

6.1. Oenological parameters determined in red wines

The ethanol content of the wine was significantly influenced by the barrel ageing only in the case of the wines from Fetească neagră and Merlot.

Following the MANOVA analysis it can be noticed that the alcoholic degree was highly influenced by the area of experimentation and variety (wine), and the ripening period significantly influenced. Volatile acidity increased significantly during the aging period.

6.2. Volatile compounds identified and quantified in barricaded red wine samples

6.2.1. Alcohols. 10 alcohols were identified, the most representative being isopentyl, isobutyric, 1-hexanol, 2,3-butanediol and 2 phenylethanol.

6.2.2. Esters. 9 different quantitative and qualitative esters were quantified.

6.2.3. Fatty acids. Five fatty acids were identified in wine samples.

6.2.4. Lactone and other compounds. The ageing period significantly influenced the accumulation of butyrolactone.

According to the multivariate analysis, the ageing period significantly influenced the evolution of isopentyl alcohol, isobutyl alcohol, ethyl succinate, diethyl succinate, ethyl caprate, butyric acid and hexanoic acid.

6.3. The odor activity value of the red wines

Isopentyl alcohol, isobutyl alcohol, 2,3-butanediol phenyl 2-ethanol, ethyl lactate, ethyl caproate, 3 ethyl hydroxybutanoate, ethyl succinate, diethyl succinate, 4-hydroxymethyl butanoate and butyrolactone exhibited a OAV>1 in most variants of the studied samples.

6.4. The aromatic profile of red wines

The ageing period has significantly and very significantly influenced the fruity character ,the fatty character, influences were also on the characters of wood and sweet.

6.5 The influence of the method and the ageing period on the oeological parameters in Fetească albă and Fetească regală wines

The alcohol content decreased with the ageing period, in all ageing methods, for both wines. The volatile acidity varied very little between the samples with the same ageing period, with a minimum of 0.22 g/l acetic acid, for both wines.

6.6 Influence of ageing mode and ageing period on volatile compounds in Fetească albă wines

6.6.1. Alcohols. 18 alcohols were quantified, in the initial wine and according to different methods and ageing periods.

6.6.2. Fatty acids. 12 fatty acids were quantified, with different concentrations, both in the initial wine, as well as in the methods and ageing periods.

6.6.3. Esters and other volatile compounds. 13 esters were quantified, in the initial wine samples, the highest amounts of volatile esters were found, which determine the pleasant aromas. Butirolactone was in greater quantities after 30 days of ageing, in variants with untoasted chips (576 μg/l) and untoasted barrels (307 μg/l).

Furanic compounds (3,4-dimethyl-2 (5H) -furanone and 2,3-dihydrobenzofuran) and guaiacoli (p-vinyl guaiacol), compounds that come from the thermal degradation of wood, are found in the highest quantities when matured with lightly fried chips, compared to those with unpeeled chips and unpeeled barrels.

6.7 Influence of ageing mode and ageing period on volatile compounds in Fetească regală wines

6.7.1 Alcohols. 18 alcohols were quantified, in the initial wine, which subsequently had very different trends depending on the method and the ageing period. The most important compounds in the aromatic profile are alcohols 2 phenylethanol, 1-hexanol, isopentyl alcohol and isobutanol. Higher alcohols were present in the largest quantities of the volatile compounds. Terpenic compounds (linalool - 303.4 μg/l, terpineol - 132.1 μg/l and transgeraniol - 59.4 μg/l) after ageing are hydrolyzed to much smaller amounts.

6.7.2. Fatty acids. 12 fatty acids were quantified, with different concentrations both in the initial wine, as well as in the variants and ageing periods.

6.7.3. Esters and other volatile compounds. The esters identified in the highest amounts in the initial wine were ethyl caproat (42.6 μg/l), ethyl lactate (322 μg/l), ethyl hydrogen succinate (4415 μg/l), diethyl succinate (195 μg/l), ethyl octanoate (198 μg/l). Butirolactone in the initial wine had values of 40 μl, after which it increased significantly in variants with untoasted chips (279-387 μl/l) and barrels (312-294 μl/l). After ageing with light toasted chips, the amount of butyrolactone was between 216-203 μl/l. Wooden compounds extracted such as p-vinyl guaiacol, 2,3-dihydrobenzofuran, butyrolactone and 3,4-dimethyl-2(5H)-furanone were most influenced by the ageing method and less by the ageing period.

6.8 Odor activity value (OAV) for white wines

In Fetească albă, the OAV was 21 (initial wine), following an important increase up to 48 (untoasted chips - 30 days), following a decrease after 60 days (15) and 90 days (13).

In Fetească regală, in the initial wine, the OAV was 76. After a 30-day ageing with light toasted chips, the OAV decreases slightly to 70, followed by a continuous decrease to 51 (60 days) and 45 (90 days).

6.9. The aromatic profile of white wines

Volatile compounds have been classified into aromatic series (1-chemical; 2-floral; 3-sweet, 4-green, 5-spice; 6-fruity; 7-alcohol; 8-fatty; 9-toast; 10-woody), depending on the odorant descriptors.

6.9.1 The aromatic profile of Fetească albă wines

The wines obtained from Fetească albă are characterized by a floral character. The ageing in untoasted barrels and the use of chips after 30 days highlight the floral profile. After 60 and 90 days of ageing, the floral profile is filled with sweet, fruity aromas or, on the contrary, covered by other aromas (greasy, burnt).

6.9.2. The aromatic profile of Fetească regală wines

After 30 and 60 days of ageing, the floral and sweet character were most influenced by the ageing method. After 60 days of ageing, the variant in which the light toasted chips were used, it accentuates the burned and fat character. At 90 days of ageing, the burnt character is emphasized in addition to the fruity one.

6.10. Organoleptic assessment through quantitative descriptive analysis

The floral character was perceived more intensely after 6 months of ageing in the barrel, but after 12 months, it was covered by other flavors in the case of Merlot and Fetească neagră (Alimanu), Cabernet Sauvginon (Dobra) and Fetească neagrra (Rătești) wines.

In the white wines (Fetască alba and Feteasca regala), when aged with light toasted chips, the tasters perceived the smell of toasted bread, from 30 days after maturation, the maximum intensity after 90 days.

It should be noted that, after different ageing periods, the floral and fruity character is kept close to the intensity perceived in the original wine to the Feteasca albă wine.

7. Conclusions and recomandation

7.1. Conclusions regarding the influence of the barrels and the ripening period on the quality of red wines

7.1.1. Oenological parameters

The ethanol content was significantly influenced by the barrel ageing, decreasing by 0.3-0.5% after 12 months of ageing. The volatile acidity was very significantly influenced by the experimentation area, variety (wine), ageing period, but also by the interaction between these factors.

7.1.2. Volatile compounds

The composition of the alcohols was different, both quantitatively and qualitatively, in all the samples analyzed. The total quantity of alcohols changed significantly during the ageing period, noting an increase in concentration of these compounds.

The total ester content was significantly influenced by the barrel period, increasing after 12 months, intensifying the fruity aroma with the maturation period in barrels with medium combustion. In all the variants, the increase of the ripening time has led to an increase in the quantity of fatty acids.

7.1.3. Odor activity value

Isopentyl alcohol, isobutyl alcohol, 2,3-butanediol phenyl 2-ethanol, ethyl lactate, ethyl caproate, 3 ethyl hydroxybutanoate, ethyl succinate, diethyl succinate, 4-hydroxymethyl butanoate and butyrolactone exhibited a OAV>1 in most variants of the studied samples.

7.1.4 The aromatic profile of red wines

The ageing period significantly and very significantly influenced the fruity character of Cabernet Sauvignon (Dobra), Fetească neagră and Merlot (Aliman), Pinot noir and Fetească neagră (Rătești).

7.2. Conclusions regarding the influence of the method and the ageing period on the quality of Fetească albă wines

7.2.1. Oneological parameters

The alcohol content in the initial sample was 13.77% vol., with decreases with the ageing period of 0.5-0.9%. The volatile acidity was 0.22 g/l acetic acid, increasing significantly with the ageing period. The limits of variability were quite small between samples with the same ageing period, but significant between methods.

7.2.2. Volatile compounds

Compounds that play a major role in the aromatic profile of Fetească regală wines were 2-phenylethanol, 1-hexanol, isopentyl alcohol and isobutanol.

The terpenic compounds quantified in Fetească regală wines were linalool, terpeniol and transgeraniol, which decreased at the end of the ageing period with light toasted chips and even no longer detected, in the case of ageing with untoasted chips and untoasted barrels.

The compounds extracted from wood quantified in the wine samples differed, depending on the ageing method, but also on the ageing period.

As the aging period increased, the amount of some fatty acids decreased, but did not reach the value of the initial wine (hexanoic acid) or, for other compounds, it decreased to below the value of the initial wine (octanoic and decanoic acid).

7.2.3. Odor activity value and aromatic profile of Fetească albă wines

1-heptanol, linalool and 2-phenylethanol, octanoic acid, n-amyl acetate had VAO values> 1 and were sensory sensed.

The floral profile, after 60 and 90 days of ageing, is complemented by the sweet, fruity aromas or, on the contrary, covered by other aromas (greasy, burnt). The floral and fruity descriptors were most significantly influenced by the ageing method, after 30 and 60 days of ageing. After 90 days of ageing, the fatty and burnt character intensify, these being also influenced by the ageing method.

7.3. Conclusions regarding the influence of the method and the aging period on the quality of Fetească regală wines

7.3.1. Oenological parameters

The content of 12.62% vol. alcohol decreased significantly after ageing, the biggest losses being in the case of barrels. Between the variants aged with untoasted chips (12.59-12.54% vol.alc,) and light toasted chips (12.58-12.53% vol.alc.) the differences were insignificant, only the ageing period having a significant influence.

The limits of volatile acidity variability were quite small between samples with the same ripening period, this parameter increasing significantly with the ageing period.

7.3.2. Volatile compounds

18 alcohols were quantified, in the initial wine, which subsequently had very different trends depending on the method and the ageing period.

Compared with the other volatile compounds determined, in the wine samples analyzed, the higher alcohols were present in the highest quantities.

Fatty acids had different concentrations in the initial wine as well as in the variants and ageing periods. The acids determined in the largest quantities in the initial wine samples were hexanoic acid, octanoic acid, malic acid and decanoic acid.

The esters were determined in higher quantities after different ageing periods. The accumulation of the compounds extracted from wood have an increasing tendency as the ageing period increases.

7.3.3. Odor activity value and aromatic profile of Fetească regală wines

For Fetească regală wines, it is recommended to use the ageing with light taosted chips for 30 and 60 days. Untoasted chips and untoasted barrels improve the aromatic profile after a 30-day ageing period.

The profile of Fetească regală wines was floral, sweet and green, with a slight decrease after 30 days of ageing by different methods. After 60 days of ageing, the variant with light toasted chips emphasizes the burnt, fatty and fruity character. After 90 days of ageing with light toasted chips, the burnt character is accentuated in addition to the fruity one.

7.4. Recomandations

1. The oenological parameters of the red wines change according to the ripening period. It is recommended to take the necessary measures to ensure constant temperature, required humidity, lack of light and trepidation, full of vessels and periodic verification, in the laboratory, of the variable parameters of wine (volatile acidity, free sulfur). Depending on the volatile composition and the desired aromatic profile, certain ripening periods are used.Parametrii oenologici și compușii volatili din vinurile albe se modifică semnificativ în funcție de perioada de maturare, se recomandă perioade de maturare de scurtă durată, 30-90 zile, în condiții propice de temperatură, umiditate etc.
2. The value of the odorant activity (VAO) of the volatile compounds in the white and red wines is significantly influenced by the aging period and method. Depending on the odorant activity, the maturation period and method can be chosen.
3. The aromatic profile of red wines aged for 6 and 12 months is different, depending on the variety, so it is recommended to age for a period of 6 months the red wines obtained from Fetească neagră and Pinot noir and aged for a period of 12 months wines from Merlot and Cabernet Sauvignon.
4. For white wines it is recommended to age for a short period, as it loses its specific characteristics, as the agein period increases. We recommend untoasted barrels. Also, the untoasted chips are recommended for 30 days and light toasted chips for 30 and 60 days.