

## COMPARISON OF ALTERNATIVE SYSTEMS FOR THE AGEING OF WINE BRANDY. OXYGENATION AND WOOD SHAPE EFFECT

### COMPARAÇÃO DE SISTEMAS ALTERNATIVOS PARA O ENVELHECIMENTO DE AGUARDENTE VÍNICA. EFEITO DA OXIGENAÇÃO E DA FORMA DA MADEIRA

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#### SUMMARY

During the first year of ageing, the dissolved oxygen, dry extract, total polyphenol index, low molecular weight compounds, colour parameters and sensory properties of wine brandies were analysed with regard to the kind of ageing system: 650-L wooden barrels (traditional system) and 40-L stainless-steel tanks with wood tablets, with and without oxygenation (alternative systems). The barrels and wood pieces were manufactured from Portuguese chestnut wood (*Castanea sativa* Mill.) with heavy toasting level. The quantity of tablets was calculated in order to reproduce the surface/volume ratio of a 650-L barrel. The oxygenation was made by the application of air with a specific device in the middle height of the tanks, after 60, 90, 120, 180 and 360 days of ageing. In the experimental conditions, the results obtained demonstrated that the chemical composition and the colour evolution of the wine aged brandies are closely dependent on the ageing system. The oxygen effect on the total polyphenol index and on the low molecular weight phenolic compounds found in the brandies aged in traditional and alternative systems is quite different. This aspect is of great importance since it is strongly related with the chemical changes that occur during the ageing process and determine the quality of the brandies. Contrary to what have been observed in the ageing of red wines, the oxygen consumption in the brandies aged in wooden barrels did not induced colour stabilization, suggesting that the chemical mechanisms and the compounds responsible for the colour changes of the brandy should be different from those identified in red wine.

#### RESUMO

Durante o primeiro ano de envelhecimento, procedeu-se à análise do oxigénio dissolvido, extracto seco, índice de polifenóis totais, compostos de massa molecular baixa, características cromáticas e sensoriais de aguardentes vínicas envelhecidas em diferentes sistemas: vasilhas de madeira de 650 L (sistema tradicional) e depósitos de aço inoxidável de 40 L com dominós de madeira, com e sem oxigenação (sistemas alternativos). As vasilhas e os dominós foram produzidos a partir de madeira de castanheiro português (*Castanea sativa* Mill.) com queima forte. A quantidade de dominós foi calculada de modo a reproduzir a relação superfície/volume de uma vasilha de 650 L. A oxigenação consistiu na aplicação de ar, através de equipamento específico, a meia altura dos depósitos, após 60, 90, 120, 180 e 360 dias de envelhecimento. Nas condições do ensaio, os resultados obtidos demonstram que a composição química e a evolução da cor das aguardentes vínicas envelhecidas são fortemente condicionadas pelo sistema de envelhecimento. O efeito do oxigénio no índice de polifenóis totais e nos compostos de massa molecular baixa das aguardentes envelhecidas nos sistemas tradicional e alternativos é consideravelmente diferente. Este aspecto assume considerável importância, na medida em que se encontra estreitamente relacionado com as alterações químicas que ocorrem durante o processo de envelhecimento e que determinam a qualidade da aguardente. Contrariamente ao que tem sido observado no envelhecimento de vinhos tintos, o consumo de oxigénio não induziu a estabilização da cor nas aguardentes envelhecidas durante um ano em vasilhas de madeira. Este facto sugere que os mecanismos químicos e os compostos envolvidos nas alterações cromáticas da aguardente devem ser diferentes dos que têm sido identificados no vinho tinto.

**Key words:** wine aged brandy, oxygenation, wood shape, physical and chemical characteristics.

**Palavras-chave:** aguardente vínica envelhecida, oxigenação, forma da madeira, características físico-químicas.

#### INTRODUCTION

During the traditional ageing process brandy undergoes important chemical modifications so that its sensory properties improve. These changes are the consequence of several phenomena, such as slow and continuous diffusion of oxygen through the wood (Belchior and San-Romão, 1982; Moutounet *et al.*, 1998) and the release of wood extractable compounds into the brandy (Joseph and Marché, 1972; Puech *et al.*, 1985; Canas *et al.*, 1999). Among the wood compounds, those of low molecular weight and hydrolysable tannins are of great importance due to their influence on the colour, astringency, bitterness, flavour and aroma of the aged brandy (Herve du

Penhoat *et al.*, 1991; Viriot *et al.*, 1993; Canas *et al.*, 1998; Canas *et al.*, 2000a; Belchior *et al.*, 2001; Caldeira *et al.*, 2002; Caldeira *et al.*, 2006a).

The diffusion rate of oxygen and the release of wood compounds are mainly determined by the wood botanical species (Marco *et al.*, 1994; Canas *et al.*, 1999; Canas *et al.*, 2000b; Snnakers *et al.*, 2000; Belchior *et al.*, 2001; Belchior *et al.*, 2003; Prida and Puech, 2006), the cooperage technology (Sarni *et al.*, 1990; Rabier and Moutounet, 1991; Canas *et al.*, 2000c; Caldeira *et al.*, 2006b; Canas *et al.*, 2006; Canas *et al.*, 2007), the barrel size (Belchior *et al.*, 2005; Canas *et al.*, 2008) and the cellar conditions (Cantagrel *et al.*, 1991). So, in the last decades these

ageing factors have been investigated in order to improve the traditional ageing process in conditions that sustain the economic viability of this practice. However, this ageing system presents high costs owing to the detention of capital in brandy and wooden barrels during a long period. Moreover, the ever-growing demand for wooden barrels and the limited availability of raw materials contribute to increase the costs.

Studies made in wine have shown that the use of oak wood pieces in stainless-steel tanks seems to be the available solution to solve this problem (Arapitsas *et al.*, 2004; Sanza *et al.*, 2004; Eiriz *et al.*, 2007; Frangipane *et al.*, 2007). There are several wood products that make possible these alternative ageing systems. These products differ in shape, size, toasting level and kind of wood. Considering the shape and size, there are “tablets” or “dominoes” with the shape of domino counters, “blocks” or “segments”, “cubes” or “beans”, “pencil shavings”, “chips”, “granulates” and “powder”. Furthermore, the quality of the final product is dependent on the dosage used, the ageing period, and the possible oxygenation.

Giving that oxygen is essential for the evolution of red wines during their ageing period, and wines stored in non-permeable tanks, such as stainless-steel ones, need of a slight oxidation to improve their quality, a new alternative system combining oxygenation with wood pieces has been applied to red wines (Kelly and Wollan, 2003). The results obtained show that the oxygenation dosage must be carefully managed to obtain the desired effect: colour stabilization, decrease of astringency and disappearance of excess vegetative notes (Moutounet *et al.*, 1998; Kelly and Wollan, 2003). It means that to operate the main chemical mechanisms responsible for these beneficial changes in wine quality requires small amounts of oxygen for lengthy periods. Delivery of more oxygen than is necessary for these reactions results in the oxidation of several other wine substrates, a process detrimental to resultant wine quality (Parish *et al.*, 2000).

Therefore micro-oxygenation has been proposed for reproducing, and even accelerating, the transformations that take place during the ageing in wooden barrels, bringing about desirable changes which cannot readily be obtained in that traditional ageing system (Parish *et al.*, 2000; Kelly and Wollan, 2003). According to Parish *et al.* (2000) and Nikfardjam and Dykes (2003) this new technology has proved highly successful for red wines, being now used in wineries all over the world as a cheaper alternative to barrel ageing. Despite the widespread application of micro-oxygenation in the ageing of red wines, the results of some recent studies do not correspond to the expected ones (Cano-López *et al.*, 2006; Llaudy *et al.*, 2006; Sartini *et al.*, 2007), leading to question the applicability of this alternative system.

Concerning the ageing of wine brandies, there is only

a first approach to the study of alternative systems (Belchior *et al.*, 2003) performed in our laboratory using chips and small blocks of oak and chestnut wood. So, the aim of the present work was to compare alternative ageing systems (stainless-steel tanks with wood tablets, with and without oxygenation) with the traditional ageing system of wine brandies (wooden barrels) based on their effects on the dissolved oxygen, dry extract, total polyphenol index, low molecular weight compounds, colour parameters and sensory properties of the brandies during the first year of ageing.

## MATERIALS AND METHODS

### Chemicals

Ellagic acid dihydrate (ellag), gallic acid monohydrate (gall), vanillic acid (van), syringic acid (syrg), vanillin (vanil), 5-hydroxymethylfurfural (HMF), 5-methylfurfural (5mfurf) and furfural (furf) were purchased from Fluka (Buchs, Switzerland); syringaldehyde (syrd), coniferaldehyde (cofde), sinapaldehyde (sipde), and 4-hydroxibenzaldehyde were purchased from Aldrich (Steinheim, Germany). All of them were used as standards (purity > 97%) without further purification. The solutions were prepared fresh prior to use with ethanol/water (75:25 v/v).

All solvents used were HPLC gradient grade purchased from Merck (Darmstadt, Germany).

### Experimental design and brandy sampling

The same Lourinhã wine brandy was aged into three different ageing systems: 650-L new barrels (B); 40-L stainless-steel tanks with wood tablets (T); 40-L stainless-steel tanks with wood tablets and oxygenation – (TOx). Every ageing system was used in duplicate.

The barrels and wood pieces were manufactured from Portuguese chestnut wood (*Castanea sativa* Mill.) with heavy toasting level, by JM Gonçalves cooperage (Palaçoulo).

The quantity of tablets (7 cm length x 3 cm width x 0.8 cm thickness) was calculated in order to reproduce the surface/volume ratio of a 650-L barrel.

The oxygenation was made by the application of air with a specific device in the middle height of the tanks: 150 mL of air immediately at 60, 90 and 120 days, and 200 mL of air immediately at 180 and 360 days.

The brandies were sampled and analysed after 6, 30, 90, 180 and 360 days of ageing (total of 10 samples for each ageing system).

### Determination of dry extract

Dry extract of brandies was analyzed according to the usual method of OIV (OIV, 1994).

### Determination of total polyphenols

Total polyphenols content of brandies was determined

by the absorbance at 280 nm (Ribéreau-Gayon, 1970). Brandies were diluted with ethanol/water 75:25.

### Determination of colour parameters

Colour parameters (CIELab) were determined with a Varian Cary 100 Bio spectrophotometer (Palo Alto, USA) and a 10-mm glass cell, by measuring the transmittance of the brandy every 10 nm from 380 to 770 nm, using a D<sub>65</sub> illuminant and a 10° standard observer.

The colour parameters measured were: lightness (L\*); chromaticity or saturation (c\*); rectangular coordinates (a\* and b\*). Coordinate a\* takes positive values for reddish colours and negative values for greenish ones, where as coordinate b\* takes positive values for yellowish colours and negative values for bluish ones.

### Determination of extractable compounds

The extractable compounds of brandies were quantified as described by Canas *et al.* (2003), with a HPLC Lachrom Merck Hitachi system (Merck, Darmstadt, Germany) equipped with a quaternary pump L-7100, a column oven L-7350, a UV-Vis detector L-7400, and an autosampler L-7250, coupled to a HSM D-7000 software (Merck, Darmstadt, Germany) for management, acquisition and treatment of data. A 250 mm × 4 mm i.d. Lichrospher RP 18 (5µm) column (Merck, Darmstadt, Germany), was used. UV detection was made at 280 nm for phenolic acids and furanic derivatives, and 320 nm for phenolic aldehydes. Samples of brandies were added with an internal standard (20 mg/L of 4-hydroxybenzaldehyde), filtered through 0.45 µm membrane (Titan, Scientific Resources Ltd., Gloucester, UK) and analyzed by direct injection of 20 µL. The identification of chromatographic peaks was made by comparison of their relative retention times with those of external standards, as well as by their UV-Vis spectra. The chromatographic purity of

the peaks and the UV-Vis spectra (200-400 nm) were performed using a Waters system equipped with a photodiode-array detector (Waters 996), with the same chromatographic conditions, managed by ?Millennium 2010? software (Waters, Milford, USA).

### Determination of soluble oxygen

Dissolved oxygen in brandies was determined with an Oximeter Oxi 340-B (WTW, Weilheim, Germany). Corrections for the temperature, dry extract and alcohol content of the brandies were made according to Mourges *et al.* (1973).

### Sensory analysis

The brandies sensorial analysis was made after 180 and 360 days of ageing by a panel of seven tasters, previously selected and trained (Caldeira *et al.*, 1999). The tasters were asked to scoring the colour, aroma and flavour descriptors with a structured scale (from 0, no perception to 5, highest perception), and the general balance (from 0 to 20) of the brandies.

### Statistical analysis

The analysis of variance and the calculation of least significant difference (LSD) were performed using Statistica vs '98 edition (Statsoft Inc., Tulsa, USA).

## RESULTS AND DISCUSSION

During the first year of ageing 4.5 mg oxygen/L were applied to the brandies aged in stainless-steel tanks with oxygenation (TOx). If a similar consumption of oxygen had occurred in the brandies aged in stainless-steel tanks with oxygenation (TOx) and without oxygenation (T), the dissolved oxygen should be much higher in TOx (Table I). Comparing the concentration of dissolved oxygen in the brandies aged in TOx and in T, it seems that the consumed oxygen was higher in TOx due to the higher

TABLE I

Analytical parameters of brandies aged in stainless-steel tanks with wood tablets, with and without oxygenation  
Parâmetros analíticos das aguardentes envelhecidas em depósitos de inox com dominós de madeira, com e sem oxigenação

	<i>Effect</i>	Without oxygenation (T)	With Oxygenation (TOx)
DO	*	18,27 ± 2,76 <i>a</i>	20,59 ± 1,91 <i>b</i>
DE	<i>ns</i>	0,79 ± 0,40	0,76 ± 0,39
Ipt	<i>ns</i>	16,51 ± 6,81	17,15 ± 8,54
L*	*	81,00 ± 8,62 <i>a</i>	82,20 ± 8,42 <i>b</i>
c*	*	53,82 ± 21,80 <i>b</i>	51,46 ± 21,95 <i>a</i>
a*	**	8,39 ± 5,97 <i>b</i>	7,37 ± 5,54 <i>a</i>
b*	*	53,08 ± 21,20 <i>b</i>	50,86 ± 21,44 <i>a</i>

x ± SD (average ± standard deviation) of 10 values; Mean values in the same row with different letters are significantly (\* p < 0.05) or very significantly (\*\* p < 0.01) different; ns - without significant difference; DO ? Dissolved oxygen (mg/L); DE ? Dry extract (g/L); Ipt ? Total polyphenol index; L\* - lightness; c\* - saturation; a\*, b\* - rectangular coordinates.

availability of dissolved oxygen in these brandies. Along with the increased consumption of oxygen, the brandies aged in TOx present a slightly lower dry extract and a slightly higher total polyphenol index than the brandies aged in T (Table I). Sartini *et al.* (2007) reported a similar behaviour of the total polyphenol index in red wines as a consequence of micro-oxygenation.

Since the oxygenated brandies (TOx) present the lowest content of low molecular weight extractable compounds (Table II), the highest total polyphenol index found in these brandies may be associated to

lower colour evolution than the brandies aged without oxygenation, that corresponds to a significantly higher lightness (lower colour intensity), significantly lower saturation and coordinate b\*, and very significantly higher coordinate a\* - Table I.

Accordingly, the sensory analysis allowed identifying the highest quality of the brandies aged in stainless-steel tanks without oxygenation. In fact, the scoring of these brandies' general balance was significantly higher than the scoring of the oxygenated brandies. The colour, aroma and flavour descriptors did not

TABLE II

Content of low molecular weight compounds in brandies aged in stainless-steel tanks with wood tablets, with and without oxygenation (mg/L of absolute ethanol)  
*Teores de compostos de massa molecular baixa das aguardentes envelhecidas em depósitos de inox com dominós de madeira, com e sem oxigenação (mg/L A.P.)*

	<i>Effect</i>	<b>Without oxygenation (T)</b>	<b>With Oxygenation (TOx)</b>
HMF	<i>ns</i>	2,37 ± 0,60	2,39 ± 0,67
furf	<i>ns</i>	20,40 ± 1,29	19,95 ± 1,35
5mfurf	<i>ns</i>	0,21 ± 0,18	0,19 ± 0,16
gall	**	12,77 ± 4,45 <b>b</b>	8,77 ± 3,55 <b>a</b>
van	**	3,54 ± 1,24 <b>b</b>	3,21 ± 1,09 <b>a</b>
syrge	<i>ns</i>	0,90 ± 0,48	0,90 ± 0,48
ellag	<i>ns</i>	11,12 ± 6,07	10,66 ± 5,92
vanil	<i>ns</i>	2,22 ± 0,49	2,17 ± 0,51
syrde	<i>ns</i>	9,66 ± 12,42	9,39 ± 11,89
cofde	<i>ns</i>	1,03 ± 0,35	0,95 ± 0,33
sipde	<i>ns</i>	3,93 ± 1,48	3,60 ± 1,40
Total	**	68,15 ± 25,75 <b>b</b>	62,18 ± 24,87 <b>a</b>

x ± SD (average ± standard deviation) of 10 values; Mean values in the same row with different letters are very significantly (\*\* p < 0.01) different; ns - without significant difference; HMF - 5-hydroxymethylfurfural; furf ? furfural; 5mfurf - 5-methyl-furfural; gall ? gallic acid; van ? vanillic acid; syrg ? syringic acid; ellag - ellagic acid; vanil ? vanillin; syrde ? syringaldehyde; cofde ? coniferaldehyde; sipde ? sinapaldehyde.

high molecular weight phenolic compounds extracted from the wood, such as the hydrolysable tannins (Canas *et al.*, 2004a; del Álamo *et al.*, 2008). Furthermore, the lowest content of low molecular weight extractable compounds (very significant for gallic acid and vanillic acid) can mean that even in the initial stage of ageing process the oxidative phenomena supplant the extractive phenomena (Canas *et al.*, 1999).

The higher consumption of oxygen observed in the oxygenated brandies should be related to the oxidation of brandy's compounds, namely those extracted from the wood, but also with the extraction process that already involves some oxidation (Belchior and San-Romão, 1982; Belchior *et al.*, 2003; Moutounet *et al.*, 1998).

The results also show that the increase of the total polyphenol index was not sufficient to balance the decrease of the dry extract and the content of low molecular weight extractable compounds, and to contribute positively to the colour evolution of the oxygenated brandies. In fact, these brandies present

permit to significantly distinguish the brandies.

So, the applied oxygen, although with a concentration lower than the natural rate of oxygen permeation into a new oak barrel (Moutounet *et al.*, 1998; Kelly and Wollan, 2003), had an undesirable effect on the brandies' evolution during the first year of ageing.

These results are in accordance with some other obtain in studies of oxygenation in brandies (Belchior *et al.*, 2003) and micro-oxygenation in red wines (Cano-López *et al.*, 2006; Llaudy *et al.*, 2006; Sartini *et al.*, 2007), but contradict those that have led to promote this technology as a successful alternative for a faster ageing process (Parish *et al.*, 2000; Nikfardjam and Dykes, 2002).

The wood shape effect (barrel *versus* tablets) and its relationship with the oxygen supply to the brandy is analysed in order to provide more information about the phenomena involved in the alteration of brandy's characteristics during the ageing process.

The analysis of variance shows a significant effect of the wood shape on the dissolved oxygen of the brandies (Table III). The brandies aged in wooden

TABLE III

Analytical parameters of brandies aged in wooden barrels and in stainless-steel tanks with wood tablets  
*Parâmetros analíticos das aguardentes envelhecidas em vasilhas de madeira e em depósitos de inox com dominós de madeira*

	<i>Effect</i>	<b>Wooden barrels (B)</b>	<b>Stainless-steel tanks with tablets (T)</b>
<b>DO</b>	*	12,37 ± 4,77 <sup>a</sup>	18,27 ± 2,76 <b>b</b>
<b>DE</b>	**	0,66 ± 0,45 <b>a</b>	0,79 ± 0,40 <b>b</b>
<b>Ipt</b>	**	20,38 ± 10,62 <b>b</b>	16,51 ± 6,81 <b>a</b>
<b>L*</b>	**	90,92 ± 5,42 <b>b</b>	81,00 ± 8,62 <b>a</b>
<b>c*</b>	**	33,81 ± 18,76 <b>a</b>	53,82 ± 21,80 <b>b</b>
<b>a*</b>	**	1,56 ± 2,16 <b>a</b>	8,39 ± 5,97 <b>b</b>
<b>b*</b>	**	33,74 ± 18,69 <b>a</b>	53,08 ± 21,20 <b>b</b>

x ± SD (average ± standard deviation) of 10 values; Mean values in the same row with different letters are significantly (\* p < 0.05) or very significantly (\*\* p < 0.01) different; DO ? Dissolved oxygen (mg/L); DE ? Dry extract (g/L); Ipt ? Total polyphenol index; L\* - lightness; c\* - saturation; a\*, b\* - rectangular coordinates.

barrels (B) present lower level of dissolved oxygen than the brandies aged in stainless-steel tanks with tablets (T).

Since there is a slow and continuous diffusion of oxygen in the wooden barrel, through the bunghole and the staves (Moutounet *et al.*, 1998; Kelly and Wollan, 2003) that does not exist in the stainless-steel tank, then the lower level of dissolved oxygen found in the brandies aged in wooden barrels seems to indicate higher consumption of oxygen in these situation. Nevares and del Álamo (2008) pointed out analogous results in a study with red wine aged in 225-L barrels and in alternative systems - stainless-steel tank with staves or chips, with micro-oxygenation.

The brandies aged in wooden barrels present lower dry extract (very significant), but higher total polyphenol index (very significant) than the brandies aged in stainless-steel tanks with wood tablets (Table

III). In this case, the total polyphenol index is well correlated with the content of low molecular weight extractable compounds, which the majority presents very significantly higher concentration in the brandies aged in barrels (Table IV).

As observed in the oxygenation experiment, the decrease of the dry extract was not balanced by the increase of total polyphenol index. Consequently, the brandies aged in wooden barrels present, with a very significant effect, higher lightness, lower saturation and coordinates a\* and b\* than the brandies aged in the alternative system, which means lower colour evolution of the former (Table III).

So, these results suggest the occurrence of a more extensive degradation of non-phenolic compounds (quantified as dry extract) and of some phenolic compounds (syringic acid, ellagic acid and syringaldehyde) in the brandies aged in wooden barrels, by the action of oxygen and other ageing

TABLE IV

Content of low molecular weight compounds in brandies aged in wooden barrels and in stainless-steel tanks with wood tablets (mg/L of absolute ethanol)  
*Teores de compostos de massa molecular baixa das aguardentes envelhecidas em vasilhas de madeira e em depósitos de inox com dominós de madeira (mg/L A.P.)*

	<i>Effect</i>	<b>Wooden barrels (B)</b>	<b>Stainless-steel tanks with tablets (T)</b>
HMF	**	18,40 ± 10,20 <b>b</b>	2,37 ± 0,60 <b>a</b>
furf	**	57,23 ± 19,08 <b>b</b>	20,40 ± 1,29 <b>a</b>
5mfurf	ns	0,17 ± 0,17	0,21 ± 0,18
gal	**	48,22 ± 38,36 <b>b</b>	12,77 ± 4,45 <b>a</b>
van	**	11,23 ± 5,24 <b>b</b>	3,54 ± 1,24 <b>a</b>
syr	**	0,65 ± 0,54 <b>a</b>	0,90 ± 0,48 <b>b</b>
ellag	**	6,91 ± 3,45 <b>a</b>	11,12 ± 6,07 <b>b</b>
vanil	**	2,65 ± 1,02 <b>b</b>	2,22 ± 0,49 <b>a</b>
syrde	**	6,98 ± 6,81 <b>a</b>	9,66 ± 12,42 <b>b</b>
cofde	**	4,34 ± 2,77 <b>b</b>	1,03 ± 0,35 <b>a</b>
sipde	**	14,63 ± 10,11 <b>b</b>	3,93 ± 1,48 <b>a</b>
Total	**	171,41 ± 90,63 <b>b</b>	68,15 ± 25,75 <b>a</b>

x ± SD (average ± standard deviation) of 10 values; Mean values in the same row with different letters are very significantly (\*\* p < 0.01) different; ns - without significant difference; HMF - 5-hydroxymethylfurfural; furf ? furfural; 5mfurf - 5-methyl-furfural; gall ? gallic acid; van ? vanillic acid; syrg ? syringic acid; ellag - ellagic acid; vanil ? vanillin; syrde ? syringaldehyde; cofde ? coniferaldehyde; sipde ? sinapaldehyde.

factors. Moreover, it may also have occurred the formation of polymeric pigments resulting from interaction between phenolic compounds (proceeding exclusively from the wood) or between phenolic and non-phenolic compounds, as verified in red wines (Es-Safi *et al.*, 2000; Asenstorfer *et al.*, 2001; Atanasova *et al.*, 2002; Alcalde-Eon *et al.*, 2006; Llaudy *et al.*, 2006; Sartini *et al.*, 2007; Sun *et al.*, 2007, 2008) and in Port wines (Mateus and Freitas, 2001; Mateus *et al.*, 2002, 2003a, 2003b). However, in wines the oxygen consumption during ageing induced colour stabilization owing to polymers formation (Timberlake and Bridle, 1976), while in brandies the opposite behaviour is observed. So, the lower colour evolution of the brandies aged in wooden barrels suggests that other chemical mechanisms and compounds are involved in the colour changes during their ageing.

On the other hand, the differences between the brandies aged in the traditional system and in alternative systems could also be induced by other ageing factors, such as the heat treatment of the wood and the compounds behaviour resulting from their chemical structure.

Concerning the heat treatment, theoretically the barrels and the tablets used have the same toasting level, but in the practice the tablets seem to have a stronger toasting throughout the thickness of the wood. Two aspects should be considered to explain this fact: i) the process of wood toasting was not the same; ii) the different shape of the wood should have conditioned the toasting effect in both the structure and chemical composition of the wood. The greater intensity of the toasting process applied to the tablets and their lower dimension should have favoured the degradation of phenolic compounds formed under toasting effect (Sarni *et al.*, 1990; Rabier and Moutounet, 1991; Canas *et al.*, 2000c; Canas *et al.*, 2007), as well as a more intense alteration of wood structure (Hale *et al.*, 1999), that could have contributed to the lower content of low molecular weight extractable compounds found in the brandies aged with wood tablets. The higher content of ellagic acid found in these brandies may derive from its high thermal resistance (Sarni *et al.*, 1990).

The compounds behaviour, namely their diffusibility (Canas *et al.*, 2004b; Arapitsas *et al.*, 2004; Patrício *et al.*, 2005), may also have determined the higher content of syringic acid, ellagic acid and syringaldehyde found in the brandies aged in stainless-steel tanks with wood tablets. Arapitsas *et al.* (2004) reported similar results for syringaldehyde when compared the ageing of red wine in oak barrels and in stainless-steel tanks with chips.

It is important to point out that the oxygen effect on the total polyphenol index and the low molecular weight phenolic compounds found in TOx and in B ageing systems is quite different, leading to the

conclusion that the correlation between the dissolved oxygen and the phenolic composition of the brandy is dependent on the ageing system.

## CONCLUSIONS

In the experimental conditions, the results obtained demonstrated that the chemical composition and the colour evolution of the wine aged brandies are closely dependent on the ageing system.

The oxygen effect on the total polyphenol index and on the low molecular weight phenolic compounds found in the brandies aged in traditional and alternative (stainless-steel tanks with wood tablets and oxygenation) systems is quite different. This aspect is of great importance since it is strongly related with the chemical changes that occur during the ageing process and determine the quality of the brandies.

Contrary to what have been observed in the ageing of red wines, the oxygen consumption in the brandies aged during one year in wooden barrels did not induced colour stabilization, suggesting that the chemical mechanisms and compounds responsible for the colour changes of the brandy should be different from those identified in red wine.

So, further experiments are required to elucidate the role of phenolic and non-phenolic compounds, and the involved mechanisms on the colour changes during the ageing of brandies. More detailed studies are also necessary to understand the role of oxygen on these phenomena, which may allow a deeper knowledge of the brandy's ageing process, as well as the optimisation of the oxygenation procedure in ageing alternative systems.

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