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EFFECT OF AGEING SYSTEM AND TIME ON THE QUALITY OF WINE BRANDY AGED AT INDUSTRIAL-SCALE

EFEITO DO SISTEMA DE ENVELHECIMENTO E DO TEMPO NA QUALIDADE DA AGUARDENTE VÍNICA ENVELHECIDA À ESCALA INDUSTRIAL

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SUMMARY

During the first six months of ageing it was performed the analysis of dissolved oxygen, dry extract, total polyphenol index, chromatic characteristics and low molecular weight compounds of Lourinhã brandies aged in different systems: 650 L wooden barrels (traditional system) and stainless steel tanks of 3000 L with wood staves (alternative system). In each system two kinds of wood were used simultaneously and arranged alternately: Portuguese chestnut (*Castanea sativa* Mill.) and Limousin French oak (*Quercus robur* L.) with medium plus toasting level. The quantity of staves was calculated in order to reproduce the surface/volume ratio of a 650 L wooden barrel. The results obtained show that the ageing system has a very significant effect on the chemical composition and colour of the aged brandies. The alternative system promotes further evolution of colour and lower oxygen consumption, while the traditional system yields higher dry extract, total phenolic and low molecular weight compounds contents. These outcomes, which have been proven by an essay based on the dry extract method, indicate that the changes observed in the brandy during the ageing process are closely related to the ageing system, suggesting that the constituents and the phenomena that occur in each one are different. Regarding the ageing time, there is a highly significant effect on the characteristics of the aged brandies, even though the observations are made in a short period of time (minimum requested by the European legislation for the ageing of the wine brandy), with higher extraction of the wood compounds up to 90 days.

RESUMO

Durante os primeiros seis meses de envelhecimento, procedeu-se à análise do oxigénio dissolvido, extracto seco, índice de polifenóis totais, características cromáticas e compostos de massa molecular baixa de aguardentes vínicas Lourinhã envelhecidas em diferentes sistemas: vasilhas de madeira de 650 L (sistema tradicional) e depósitos de aço inoxidável de 3000 L com aduelas de madeira (sistema alternativo). Em cada sistema foram utilizadas duas madeiras em simultâneo e dispostas alternadamente: castanheiro português (*Castanea sativa* Mill.) e carvalho francês Limousin (*Quercus robur* L.) com queima média mais. A quantidade de aduelas foi calculada de modo a reproduzir a relação superfície/volume de uma vasilha de 650 L. Os resultados obtidos revelam que a forma da madeira exerce um efeito muito significativo na composição química e na cor das aguardentes envelhecidas. O sistema alternativo promove maior evolução da cor e menor consumo de oxigénio, enquanto o sistema tradicional origina maior extracto seco, bem como maior teor de polifenóis totais e de compostos de massa molecular baixa. Estes resultados, comprovados através de um ensaio baseado no método de determinação do extracto seco, indicam que as modificações observadas na aguardente durante o processo de envelhecimento se encontram estreitamente relacionadas com o sistema de envelhecimento, sugerindo que os constituintes e os fenómenos que ocorrem em cada um são diferentes. Relativamente ao tempo de envelhecimento, existe um efeito altamente significativo nas características das aguardentes envelhecidas, mesmo num período curto de tempo (o mínimo requerido pela legislação europeia para o envelhecimento de aguardente vínica), verificando-se maior extracção dos compostos da madeira até aos 90 dias.

Key words: aged wine brandy, ageing system, ageing time, physicochemical characteristics, low molecular weight compounds.
Palavras-chave: aguardente vínica envelhecida, sistema de envelhecimento, tempo de envelhecimento, características fisico-químicas, compostos de massa molecular baixa.

INTRODUCTION

The quality of the aged wine brandy is determined by the distillate characteristics and the transformations that occur during the ageing process (Puech *et al*., 1998; Canas *et al*., 1999; Canas *et al*., 2000a; Belchior *et al*., 2001; Canas *et al*., 2002; Belchior *et al*., 2003; Patrício *et al*., 2005; Caldeira *et al*., 2006). According to the Regulation CE No 110/2008, six months is the minimum period of ageing in wooden barrels without which the wine brandy cannot be sold for consumption.

During the ageing process in wooden barrels, complex changes such as reactions between distillate compounds, reactions among extractable wood compounds, impregnation of brandy in the wood, as well as release of extractable compounds from the wood into the brandy (Puech, 1984; Singleton, 1995; Canas *et al*., 2002) that occur in the presence of oxygen (Belchior and San-Romão, 1982; Moutounet *et al*., 1998), along with the evaporation and concentration phenomena (Puech *et al*., 1998; Canas *et al*., 2002; Patrício *et al*., 2005). These transformations are influenced by the wood chemical composition, which is mainly dependent on the botanical species (Fengel and Wegener, 1989; Mosedale, 1995; Canas *et al*., 1999; Canas *et al*., 2000a; Jordão *et al*., 2005; Prida and Puech, 2006), the geographical origin (Canas *et al*., 2000b; Doussout *et al*., 2002), the seasoning and the heat treatment during barrel making (Sarni *et al*., 1990; Belchior *et al*., 2001; Canas *et al*., 2007), the barrel size (Belchior *et al*., 2005; Canas *et al*., 2008), as well as the cellar environment (Mosedale, 1995; Singleton, 1995).

The oak species that stand out are: *Quercus robur* L., predominantly from the Limousin region (France), *Quercus sessiliflora* Salisb., especially from the Allier region (France) and *Quercus alba* L. (USA). However, the research that has been performed on chestnut wood (*Castanea sativa* Mill.) proved its suitability for this purpose (Canas *et al*., 1999; Canas *et al*., 2000a; Belchior *et al*., 2001; Caldeira *et al*., 2006; Canas *et al*., 2011).

Nevertheless, the need to optimize and reduce the costs of the brandy's ageing in the traditional system in wooden barrels, such as the invested capital in brandy and wooden barrels for a long period, and the sustainable utilization of wood, encourage the search for alternative ageing systems.

Several studies were conducted using alternative systems for the ageing of wine (Araptisas *et al*., 2004; Eiriz, 2007; Nevares and Del Álamo., 2008; Nevares *et al.*, 2009; Del Álamo *et al*., 2010; Cabrita *et al*., 2011), as well as for the ageing of its derivatives: vinegar (Morales *et al*., 2004; Tesfaye *et al*., 2004) and wine brandy (Belchior *et al*., 2003; Madrera *et al*., 2003; Canas *et al*., 2009a,b; Caldeira *et al*., 2010). Alternative systems for ageing other drinks such as cider, rum, whiskey and sake have also been target of research (Martinez *et al*., 2001; Chang., 2004; Fan *et al*., 2006). It was showed that the quality of the final product in alternative ageing systems depends on the shape and size of the wood used, the dosage, the heat treatment and the botanical species, since these factors influence the kinetics of extraction/oxidation and diffusion of the wood extractable compounds (Afonso., 2002, Fan *et al*., 2006), along with the contact time between the wood and wine, and the possibility of using micro-oxygenation (Piracci *et al*., 2001). In the attempt to simulate similar conditions to those of the wooden barrels using stainless steel tanks, promising results were obtained in red wine namely the colour stabilization, and the decrease of astringency and herbaceous notes (Kelly Wollan and, 2003).

In this context, Belchior *et al*. (2003) performed a first approach, at laboratorial-scale, of Lourinhã wine brandy ageing with small logs and chips of Limousin oak and chestnut wood. Recently, in a project on a pilot scale, studies were conducted to evaluate the effects of different ageing systems – wooden barrels, staves and tablets with equal surface/volume ratio - along with the botanical species (Limousin oak and chestnut) and oxygenation, in the physicochemical characteristics and sensory properties of a Lourinhã brandy over two years and a half of ageing (Canas *et al*., 2009a,b; Caldeira *et al*., 2010). The results showed that alternative systems seem to accelerate the ageing process and originate wine brandy with different physicochemical characteristics and sensory properties. Moreover, the close relationship found between the ageing systems and the characteristics of wine brandies led to conclude that many constituents and phenomena governed by several ageing factors should be involved. It was also verified that chestnut wood has great interest to brandy ageing, whatever the ageing system. These results indicate that modifications observed in the brandies are closely related to the kind of ageing system.

The present work aims to deepen the technical and scientific knowledge about the two kinds of ageing systems in order to obtain reliable results on their potential for the ageing of wine brandy, based on the evaluation of dry extract, total phenolic content, chromatic characteristics, low molecular weight compounds and dissolved oxygen of a Lourinhã brandy aged in 650 L wooden barrels and in stainless steel tanks of 3000 L with wood staves.

MATERIAL AND METHODS

Experimental design and brandy sampling

The same Lourinhã wine distillate (77.2 % v/v) was aged in two different ageing systems: 650 L new barrels and 3000 L stainless steel tanks with wood staves, in duplicate. In each system two different kinds of wood were used simultaneously and arranged alternately: Portuguese chestnut (*Castanea sativa* Mill.) and Limousin oak (*Quercus robur L.*). The barrels and the wood staves were manufactured by J. M. Gonçalves cooperage (Palaçoulo, Portugal) with medium plus toasting level. The barrels were heated over a fire of wood offcuts and the staves were heated in an oven. The quantity of staves (91 cm length x 5 cm width x 1.8 cm thickness) was calculated in order to reproduce the surface area to volume ratio of a 650 L barrel. The wooden barrels and the stainless steel tanks were placed at Adega Cooperativa de Lourinhã in similar cellar conditions. The brandies were sampled and analysed after 8, 15, 90 and 180 days of ageing; a total of 16 samples were taken.

Determination of dry extract

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

Determination of total polyphenol index

The total phenolic content of the brandies was determined by the absorbance at 280 nm (Ribéreau-Gayon, 1970). Brandies were diluted with ethanol/water 75:25.

Determination of chromatic characteristics

The chromatic characteristics (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 D65 illuminant and a 10º standard observer. The parameters measured were: lightness (L*); saturation (C*); chromaticity coordinates (a* and b*). Coordinate a* takes positive values for reddish colours and negative values for greenish

ones, whereas coordinate b* takes positive values for yellowish colours and negative values for bluish ones. In addition, the brown colour of the brandies was measured by the absorbance at 470 nm (Martins and Van Boekel, 2003), which was calculated from the value of transmittance at 470 nm provided by CIELab output.

Analysis of low molecular weight phenolic compounds and furanic derivatives by High Performance Liquid Chromatography

Samples of brandies were added with an internal standard (4-hydroxybenzaldehyde, 20 mg/L), filtered through 0.45 µm membrane (Titan) and analysed by direct injection of 20 µL. Chromatography was performed as described by Canas *et al*. (2003), with a HPLC Lachrom Merck Hitachi system 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) management, acquisition and treatment data. The identification of chromatographic peaks was made both by retention time and UV-Vis spectra matching with standards. 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 dissolved oxygen

Dissolved oxygen in brandies was determine 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).

Statistical analysis

The two-way analysis of variance (ANOVA) was performed to evaluate the effects of ageing system and ageing time on the characteristics of the aged brandies, as well as on the essay based on the dry extract method. Fisher's least significant difference (LSD) test was applied to compare the different averages. All the calculations were carried out using Statistica vs '98 edition (Statsoft Inc., Tulsa, USA). The correlation analysis was performed using Statgraphic v.5 (STSC Inc., Rocksville, USA).

RESULTS AND DISCUSSION

Effect of the ageing system

The ageing system has a highly significant effect on the dry extract, total polyphenol index, luminosity and dissolved oxygen of the aged brandies (Table I), and a significant effect on the coordinate a*. The absorbance at 470 nm that is a reliable indicator of the melanoidins content (Martins and Van Boeckel, 2003) is very significantly influenced by this factor.

Brandies aged in wooden barrels present higher dry extract and higher total polyphenol index, but lower colour intensity (inversely proportional to luminosity), lower red hue (a*) and brown hue (A 470) than those aged in stainless steel tanks with wood staves. Therefore, the greatest enrichment of the chemical composition of the brandies does not correspond to a greater colour evolution, contradicting the results obtained in several essays performed on the ageing of brandies in the traditional system (Canas *et al*. 2000a; Belchior *et al*. 2001; Canas, 2003).

During ageing the brandy is enriched in wood extractable compounds, which contribute to its dry extract. The contents of such compounds depend both on the wood botanical species and the heat treatment of the barrel (Câmpeanu *et al*., 1992). The heat treatment of the wood used in the two ageing systems is theoretically the same, although it has a greater effect on the extraction of compounds from the barrels than from the staves. This variability should be partially attributed to the different kind of heat processes applied together with the wood shape.

Concerning the total phenolic content, given that the distillate has no phenolic compounds (Canas, 2003) the difference found can be due to the influence of the ageing system. The highest total polyphenol index of brandies aged in wooden barrels may be related to the higher extraction/diffusion rate of phenolic compounds.

According to Belchior and San-Romão (1982), the extraction of compounds from wood already involves some oxidation, therefore the lowest dissolved oxygen content (corresponding to higher consumption) and the highest content of phenolics detected in the brandies aged in wooden barrels seem to be linked.

It should be noted that the values of dry extract and total polyphenol index show high correlation (r=0.98), which is in agreement with the results obtained by Canas *et al*. (2009b).

As for the chromatic characteristics, there is a faster evolution of colour in the brandies aged in stainless steel tanks, shown by greater colour intensity and red hue. Although not significant, saturation and yellow hue behave similarly. It is verified that the colour of the brandy aged in tanks results from a more intense red-yellow combination.

Belchior and Carvalho (1983) found a direct relationship between the total phenolic content and the colour of the aged brandy, and Bakker *et al*. (1986) report that the luminosity is inversely related to the content of phenolic compounds. Similar results were obtained in brandies aged in wooden barrels (Canas *et al*., 2000a; Belchior *et al*., 2001; Canas, 2003). In the present study, the correlations between the total polyphenol index and the chromatic characteristics, namely the brightness (r=-0.69) and the coordinate a* (r=0.51), are in accordance with the results obtained

TABLE I

Ageing system effect on the chemical composition and chromatic characteristics of the wine aged brandies

Efeito do sistema de envelhecimento na composição química e nas características cromáticas das aguardentes vínicas envelhecidas

	Effect	Wood shape	
		Staves	Barrels
DE	***	0.37 ± 0.24 a	0.53 ± 0.33 b
TPI	***	11.57 ± 6.29 a	15.13 ± 7.25 b
L*	***	91.91 ± 4.88 a	94.91 ± 3.87 b
C*	ns	29.43 ± 18.61	28.77 ± 15.03
a*	*	1.41 ± 1.26 b	0.73 ± 0.57 a
b*	ns	29.39 ± 18.57	28.76 ± 15.03
A 470	**	0.13 ± 0.09 b	0.10 ± 0.07 a
DO	***	19.53 ± 2.11 b	14.35 ± 2.77 a

x ± SD (average ± standard deviation) of 16 values; Mean values in the same row with different letters are significant (*P=95%), very significant (**P=99%) or highly significant different (***P=99.9%); ns – not significant; DE – dry extract (g/L); TPI – total polyphenol index; L*- lightness; C* - saturation; a* and b* - chromaticity coordinates; A 470 – absorbance at 470 nm; DO – dissolved oxygen (mg/L).

in the mentioned works. Therefore, the lowest total phenolic content and lightness of the brandies aged in stainless steel tanks with staves may arise from unknown reactions that can be associated with the use of two different wood species simultaneously and/or the presence of non-phenolic compounds, which have a great influence on colour, as observed by Canas *et al*. (2009b). On the other hand, the heat treatment can also be responsible for the observed effect, once the kind of heat intensity and the staves dimension can promote higher degradation of phenolic compounds (Sarni *et al*., 1990; Rabier and Moutounet, 1991; Canas *et al*. 2000c; Canas *et al*, 2007), as well as a more intense alteration of the wood structure (Hale *et al*., 1999). In addition, the Maillard reactions occurring during the heat treatment origin many volatile (Cutzach *et al*., 1997) and non-volatile compounds (Alañón *et al*., 2010) in the wood. Avakians (1992) indicated that these reactions have great influence on the colour of the aged brandy. It is also known that among the non-volatile compounds resulting from the Maillard reactions, there are some key-chromophores (compounds with high impact on colour) which cause the yellow, red and brown hues (Hofmann., 1998; Gokmen and Senyuva., 2006). The melanoidins belong to this group of chromophores and are closely related to the brown colour in foods (Gokmen and Senyuva., 2006). In the case of wood, melanoidins are formed during the heat treatment (Borrelli *et al*., 2002).

It is important to point out that the relationship between the chemical composition and the colour of the brandy is different from that observed in red wines aged in different systems (Del Álamo *et al*., 2008, De Beer *et al*., 2009). This suggests that other compounds not quantified in the dry extract and in the total polyphenol index determine the colour of brandies. Addict to these factors, the acetaldehyde resulting from the oxidation of ethanol during ageing (Reazin, 1981; Nishimura *et al*., 1983), as well as some phenolic aldehydes such as vanillin (Es-Safi *et al*., 2000) and furanic aldehydes such as 5-hydroxymethylfurfural and 5-methylfurfural (Es-Safi *et al*., 2000) may also act in condensation reactions between phenolic compounds present in the brandy, particularly tannins, and influence the chromatic characteristics.

Comparing the absorbance at 470 nm of the brandies from the two ageing systems, there is a higher concentration of melanoidins in the brandies aged in stainless steel tanks with staves than in those aged in wooden barrels. Thus, the results of this study are in accordance with the hypothesis raised by Canas *et al*. (2009b), who consider melanoidins as another type of colouring compounds formed by the Maillard reactions, which are also present in toasted wood and are likely to be released into the brandy during the ageing process. On this basis, the highest intensity of toasting (Gokmen and Senyuva., 2006) may have favoured the formation and accumulation of these compounds in the corresponding staves and brandy, whose concentration did not affect the dry extract but considerably contributed to the colour.

Moreover, oxygen is a key element in the chemical changes of brandy during ageing (Avakiants, 1992; Puech and Mosedale, 1998), and it is analyzed in order to obtain more information on the phenomena involved in the evolution of the brandy's composition during this process. Since there is a continuous and slow diffusion of oxygen through the bung and the wood in the barrels (Moutounet *et al*., 1998; Kelly and Wollan, 2003), which does not occur in stainless steel tanks during ageing, the lowest level of dissolved oxygen found in the brandies aged in wooden barrels seems to indicate a high consump-

tion in this situation (Nevares and Del Álamo., 2008; Canas *et al*., 2009a,b). Despite the surface/volume ratio was equal and the same botanical species were used in both systems, the differences observed in the brandies are possibly related with the extraction rate of compounds from the wood and their subsequent transformation in the brandy. Such transformation is associated with the reactions that occur during ageing - oxidations, esterifications, Maillard reactions, polymerizations and polycondensations. Puech and Mosedale (1998) state that oxidation is the most important, involving both the compounds of the distillate and from the wood. The oxidation may be specific to each ageing system and have contributed to the differentiation of brandies.

Concerning the low molecular weight compounds, the results of the analysis of variance (Table II) show a highly significant effect on the contents of 5-hydroxymethylfurfural, gallic acid, coniferaldehyde and sinapaldehyde, a very significant effect on the contents of ellagic acid and furfural, and a significant effect for syringaldehyde and the total content of compounds analysed. It should be noted that the total content of compounds is higher in brandies aged in wooden barrels, which can be distinguished particularly by the content of 5-hydroxymethylfurfural, gallic acid, coniferaldehyde and sinapaldehyde.

The contents of furanic aldehydes are higher in the brandies aged in barrels than in those aged in stainless steel tanks with staves (Table II). The furfural is quantitatively the most important compound of the aged brandies in both systems, not only due to its presence in the distillate (Jeuring and Kuppers, 1980; Canas *et al*., 2004; Caldeira *et al*., 2010), but also because it exhibits the highest extraction/diffusion rate in the aged brandy (Canas *et al*., 2004; Patrício *et al*., 2005). Moreover, furfural results from the degradation of hemicelluloses of the wood during the heat treatment. These polymers are those with lower thermal resistance (Fengel and Wegener, 1989) and hence are preferentially degraded, contributing to make furfural the main furanic derivative of the toasted wood (Rabier and Moutounet, 1991; Chatonnet , 1995; Canas *et al*., 2007) and of the corresponding brandies (Canas, 2003).

It is found that the content of phenolic acids is higher in brandies aged in wooden barrels (Table II). For gallic acid, the great difference between the ageing systems probably derives from the kind of heat treatment performed owing to the thermal sensitivity of this compound (Rabier and Moutounet, 1991; Canas *et al*., 2000c, 2007), which content usually tends to decrease from medium toast. Given that the melting point of the gallic acid is 249.9 °C, that is similar to

TABLE II

Content of low molecular weight compounds in wine brandies aged in wooden barrels and in stainless steel tanks with staves (mg/L)

Teores de compostos de massa molecular baixa das aguardentes vínicas envelhecidas em vasilhas de madeira e em depósitos de inoxidável com aduelas (mg/L)

		Wood Shape	
	Effect	Staves	Barrels
HMF	***	1.80 ± 1.09 a	9.42 ± 5.19 b
furf	*	29.26 ± 7.04 a	32.44 ± 7.33 b
5mfurf	--	nd	(0.08 ± 0.09) b
gall	***	4.17 ± 3.55 a	21.74 ± 16.44 b
van	ns	(0.92 ± 0.83)	1.17±0.95
syrg	***	(0.30 ± 0.28) a	1.69 ± 0.68 b
ellag	**	3.09 ± 1.96 a	3.97 ± 2.45 b
vanil	ns	0.83 ± 0.57	1.01 ± 0.79
syrde	*	3.31 ± 2.22 b	2.85 ± 1.91 a
cofde	***	3.62 ± 2.36 a	6.81 ± 3.60 b
sypde	***	5.57 ± 3.66 a	10.51 ± 5.59 b
Total	*	52.92 ± 5.24 a	91.69 ± 8.30 b

x ± SD (average ± standard deviation) of 16 values; Mean values in the same row with different letters are significant (*P=95%), very significant (**P=99%) or highly significant different (***P=99.9%); ns – not significant; nd – not detected; () value below limit of quantification; HMF – 5-hydroxymethylfurfural; furf - furfural; 5mfurf – 5-methylfurfural; gall – gallic acid; van – vanillic acid; syrg – syringic acid; ellag – ellagic acid; vanil - vanillin; syrde - syringaldehyde; cofde - coniferaldehyde; sypde – synapaldehyde.

the toasting temperature that the wood used in both ageing systems underwent, the results obtained suggest that the wood from barrels suffered the greatest accumulation of gallic acid. Indeed, since the surface/volume ratio is the same in both systems and therefore did not promote differences in the extraction process, the lowest content of gallic acid in the brandies aged in stainless steel tanks may be associated with a more intense degradation of this compound during the toasting of the staves due to their smaller thickness. The ellagic acid proceeds from the degradation of ellagitannins (Chatonnet, 1995). The high melting point of this acid (around 450 °C) allowing to its accumulation in the wood in the free form that can be release into the wine brandy during ageing.

Regarding the phenolic aldehydes, despite the observed variability in the brandies aged in each system, there is a higher concentration in those aged in wooden barrels, except for syringaldehyde (Table II). This fact may be related to the type of chemical reactions that occur in each system and the probability of triggering differently. However, syringaldehyde and vanillin have a complex profile extraction and may result from: i) very intense toasting; ii) more pronounced oxidative process in the wood and/or brandies, according to Puech (1984).

To better understand the results of this study, such as the fact that the brandies aged in wooden barrels present higher dry extract and higher total polyphenol index but less evolved chromatic characteristics than the brandies aged in stainless steel tanks with staves, it was performed an essay based on the dry extract method (OIV, 1994). For this purpose, it was used samples of the brandy with 90 and 180 days of ageing in one wooden barrel and in one stainless steel tank (four modalities), with three replications. In each modality the comparison was made between an aliquot of control brandy (C) with an aliquot of the same brandy subjected to the dry extract method and redissolved with an hydroalcoholic solution having the same pH and alcohol content of the control brandy (ES), in order to obtain relevant information about the possible modification of brandy's compounds during the application of the method and its impact on the total polyphenol index and the chromatic characteristics.

The temperature of 100 °C (method conditions) does not affect significantly the majority of the extractable compounds of the brandy (Table III), although it is registered a highly significant decrease of furfural in the brandies aged in both systems, a significant increase in syringic acid in the brandies aged in stainless steel tanks with staves and a highly significant decrease of syringic acid in the brandies aged in wooden barrels (Table III). Since the furanic aldehydes are quantified in the dry extract but also in the total polyphenol index (Canas and Belchior, 2012), the detected alteration implies that the concentration of volatile compounds in the free form (more susceptible to evaporation, oxidation and/or involvement in other chemical reactions) decreases and thus leads to a decrease of its contribution to the total polyphenol index. Regarding the phenolic acids, their behaviour can be justified by oxidation and/or degradation during the essay, and appears to contribute to the decrease of the total polyphenol index. The difference of these acids behaviour in the hydroalcoholic solutions corresponding to each ageing system after applying the dry extract method, points out once again that the chemical reactions are likely specific in each ageing system. The concentration of phenolic aldehydes is lower in the hydroalcoholic solution than in the brandy after applying the dry extract method, except for sinapaldehyde. This outcome contributes to the decrease in total polyphenol index. The decrease of the content of vanillin results from its evaporation, as well as from some degradation phenomena, such as oxidation, that also affect the decrease of concentration of syringaldehyde and coniferaldehyde.

The results also demonstrate that the total polyphenol index is consistent with that obtained previously (Table I), being higher in the brandies aged in wooden barrels. After applying the dry extract method, it is verified that the total polyphenol index decreased, in which phenolic compounds and furanic derivatives are quantified (Canas and Belchior, 2012).

For the chromatic characteristics, the results obtained confirm what was previously reported (Table I). The increase of colour intensity after the application of the dry extract method in the brandies can be caused by a great contribution of the non-phenolic compounds. It is known that the combination of high values of coordinates a* and b* are associated with the topaz hue. In this assay the coordinates a* and b* do not undergo significant changes. However, despite the slight increase in the coordinate a* and A 470 after application of the method, it may have contributed to the evolution of the brandy's colour towards topaz hue. This combined effect can result from the formation of non-phenolic pigments by temperature action and possibly by oxidation, supporting the hypothesis that the colour of aged brandies in different systems depends on the non-phenolic and/or volatile compounds.

Effect of the ageing time

The Figure 1 shows that the dry extract and the total polyphenol index of the aged wine brandies present a gradual increase, minor in the first 15 days of ageing, followed by a marked evolution between 15 and 90 days. The kinetics displayed are in accordance with the findings of Belchior *et al*. (2001), Canas *et al*. (2002) and Patrício *et al*. (2005). The dissolved oxygen decreases up to 90 days, followed by an increase up to 180 days of ageing. Similar results were reported by Canas *et al*. (2009a). This behaviour can result from a higher consumption of oxygen at the

TABLE III

Average values of the analytical parameters of the samples before and after applying the dry extract method
Valores médios dos parâmetros analíticos das amostras antes e após aplicação do método do extrato seco

System		Staves				Barrels		
Essay	Effect	C	ES	ES-C (%)	Effect	C	ES	ES-C (%)
TPI	ns	16.78	12.27	-27	ns	23.70	17.01	-28
L*	ns	90.28	84.44	-6	ns	89.83	85.07	-5
C*	ns	47.56	47.65	0	ns	45.00	46.29	3
a*	ns	2.06	3.51	70	ns	1.18	2.72	130
b*	ns	47.51	47.51	0	ns	44.98	46.20	3
A 470	ns	0.19	0.24	26	ns	0.18	0.23	24
HMF	ns	2.79	2.17	-22	ns	15.08	12.79	-15
furf	***	35.20 b	(0.06) a	-99.8	***	41.67 b	0.24 a	-99
5mfurf	ns	(0.09)	nd	-55	*	(0.18) b	nd a	-68
gall	ns	7.68	7.42	-3	ns	41.96	43.16	3
van	ns	1.57	1.85	18	ns	2.46	1.63	-34
syrg	*	0.53 a	1.13 b	113	***	2.48 b	0.06 a	-97
ellag	ns	4.46	4.27	-4	ns	6.71	5.60	-17
vanil	ns	1.35	1.02	-24	ns	1.99	1.36	-32
syrde	ns	5.27	5.10	-3	ns	5.05	4.50	-11
cofde	ns	2.07	1.96	-5	ns	5.75	5.39	-6
sypde	ns	8.73	9.10	4	ns	17.23	17.13	-1

x (average) of 16 values, means followed by different letters in the row indicate a significant difference (* P = 95%) and highly significant (P*** = 99.9%) ns - no significant difference; nd = not detected ; () value indicates <quantification limit. C = control (brandy before applying the dry extract method); ES = hydroalcoholic solution used for dissolving the dry extract after application of the method. TPI – total polyphenol index; L*- lightness; C* - saturation; a* and b* - chromaticity coordinates; A 470 – absorbance at 470 nm; HMF – 5-hydroxymethylfurfural; furf - furfural; 5mfurf – 5-methylfurfural; gall – gallic acid; van – vanillic acid; syrg – syringic acid; ellag – ellagic acid; vanil - vanillin; syrde - syringaldehyde; cofde - coniferaldehyde; sypde – synapaldehyde.

beginning of ageing owing to several reactions in which oxygen participates, particularly in the extraction of wood compounds (Belchior and San-Romão, 1982). At 180 days there is a further increase in the availability of dissolved oxygen, which can be associated with the predominance of extraction regard to oxidation.

Concerning the evolution of the chromatic characteristics, it is observed a continuous increase of saturation and a decrease of lightness, thereby being consistent with that described by Canas *et al*. (2009a).

It is inferred that these kinetic may arise from the increase of phenolic and non-phenolic compounds in the brandy, and found a very strong correlation with the content of melanoidins. As can be seen in Figure 1, the value of A 470 nm presents a gradual increase even after 90 days of ageing, and between 90 and 180 days the increase becomes not significant, which may be partly explained by the high standard deviation associated with the sampling carried out at 180 days. The largest standard deviation at this ageing stage possibly reflects the influence of several

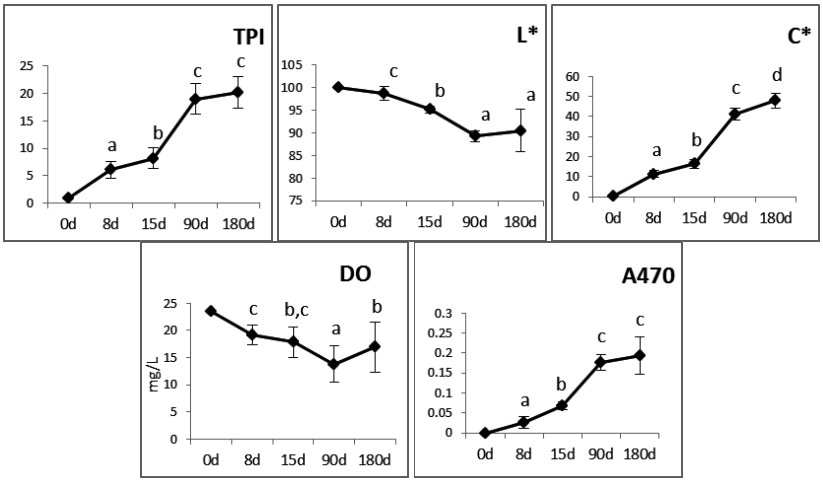

Figure 1 - Kinetics of dry extract (DE), total polyphenol index (TPI), dissolved oxygen (DO), lightness (L*), saturation (C*) and absorbance at 470 nm (A 470) of the wine brandies during the first six months of ageing. Mean values with different letters indicate highly significant (P=99.9%).

Cinéticas do extrato seco (DE), índice de polifenóis totais (TPI), oxigénio dissolvido (DO), luminosidade (L), saturação (C*) e absorvência a 470 nm (A 470) da aguardente vínica durantes os primeiros seis meses de envelhecimento. Valores médios assinalados com letras diferentes indicam diferença altamente significativa (P=99.9%).*

factors: the wood intra-specific variability; the shape of the wood; the variability associated with the heat treatment to which the wood was subjected.

Evaluating the kinetics of the chromaticity coordinates (Figure 2), it is found that the raw distillate has a green colour (corresponding to a negative value of a*), while the colour exhibit by the aged brandies result from the combination of red (positive values of coordinate a*) and yellow (positive values of coordinate b*) hues. In the first 15 days of ageing, the evolution of red (a*) and yellow (b*) hues is higher than those of the brandies aged in wooden barrels. But after 90 days, in the brandies aged in stainless steel tanks with staves both hues progressively increase. In the brandies aged in wooden barrels, it is observed a gradual evolution of the coordinates a* and b* up to 15 days, but after 90 days the yellow hue becomes predominant since the b* coordinate increase and a* coordinate has a slight variation.

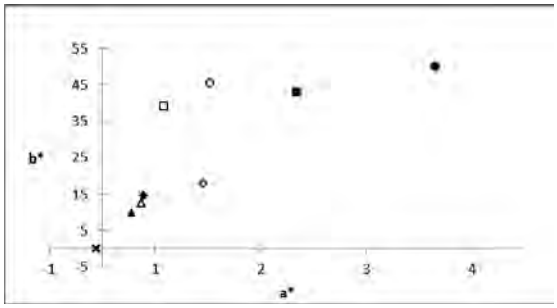

Figure 2 - Projection of the mean values of chromaticity coordinates of the wine brandies in the first six months of ageing. x 0 days; ▲ 8 days; ♦ 15 days; ■ 90 days; ● 180 days; Tanks – filled symbol; Barrels – unfilled symbol.

Projeção dos valores médios das coordenadas retangulares das aguardentes vínicas durante os primeiros seis meses de envelhecimento. x 0 dias; ▲ 8 dias; ♦ 15 dias; ■ 90 dias; ● 180 dias; Depósitos – símbolo com preenchimento; Vasilhas - símbolo sem preenchimento.

There are relevant changes in the furanic and phenolic composition of the brandies over the time, shown by the steady increase in the contents of all of the studied low molecular weight compounds (Figure 3). The 5-hydroxymethylfurfural, and especially the 5-methylfurfural, have a slow increase in the initial phase of ageing (first 15 days), whereas the furfural increase significantly in the same period of time. When comparing the first 15 days with 90 days of ageing, it is clear that the three furanic aldehydes have a significant increase. From 90 to 180 days the concentrations of furfural and 5-hydroxymethylfurfural not vary significantly. This behaviour may be related to the occurrence of condensation reactions between these compounds and phenolic compounds present in the brandy (Es-Safi *et al*., 2002). Distinctly the 5-methylfurfural continues to increase significantly from 90 to 180 days.

In the case of phenolic acids, the evolution between 8 and 15 days is only significant for syringic acid. After this phase vanillic and ellagic acids increase progressively up to 180 days. The kinetics of these acids may reveal the effect of the heat treatment of the wood in the brandy's chemical composition (Nishimura et al., 1983; Rabier and Moutounet, 1991). Gallic and syringic acids do not show a significant increase between 90 days and 180 days, probably due to the high standard deviation, as mentioned before.

The phenolic aldehydes show similar kinetics, except for syringaldehyde. The contents of vanillin, coniferaldehyde and sinapaldehyde have only a significant increase from 15 to 90 days, which is consistent with the results of Belchior *et al*. (2001) and Canas *et al*. (2004), suggesting that the extraction kinetics is more pronounced in this period of time. The kinetics of syringaldehyde distinguishes itself by a significant increase throughout the ageing period studied. Recalling that the benzoic aldehydes (vanillin and syringaldehyde) mainly result from the oxidation of cinnamic aldehydes (coniferaldehyde and sinapaldehyde) proceeding from the lignin degradation during the heat treatment of the wood and/or its hydroalcoholysis during ageing (Puech, 1984), Quaresma (2000) states that the kinetics of vanillin and coniferaldehyde and those of syringaldehyde and sinapaldehyde appear to be related, since the slower increase of coniferaldehyde and sinapaldehyde corresponds to a continuous increase in the concentration of vanillin and syringaldehyde, respectively.

The analysis of interactions indicates that the kinetics of lightness and 5-hydroxymethylfurfural (highly significant), gallic acid (very significant), and coordinate a *, dissolved oxygen, A 470, syringic acid and 5-methylfurfural (significant) depend on the ageing system.

CONCLUSIONS

This study provides, for the first time, specific information about the physicochemical characterization of wine brandies aged in alternative systems at industrial-scale.

Under these experimental conditions, it is found that after six months of ageing the alternative system comprising stainless steel tanks with staves in contact with the wine brandy did not allow the acquisition of the physicochemical characteristics achieved by the same wine brandy aged in wooden barrels. However, the colour evolution is greater in the brandies aged in the alternative system, which raises issues regarding the relationship between the chemical composition and the chromatic characteristics of the wine brandy aged in different systems.

The brandies aged in barrels present higher dry extract, higher total polyphenol index and higher concentration of phenolic and furanic compounds, i.e., have the richest chemical composition, but lower chromatic evolution than the brandies aged in stainless steel tanks with staves. This negative correlation

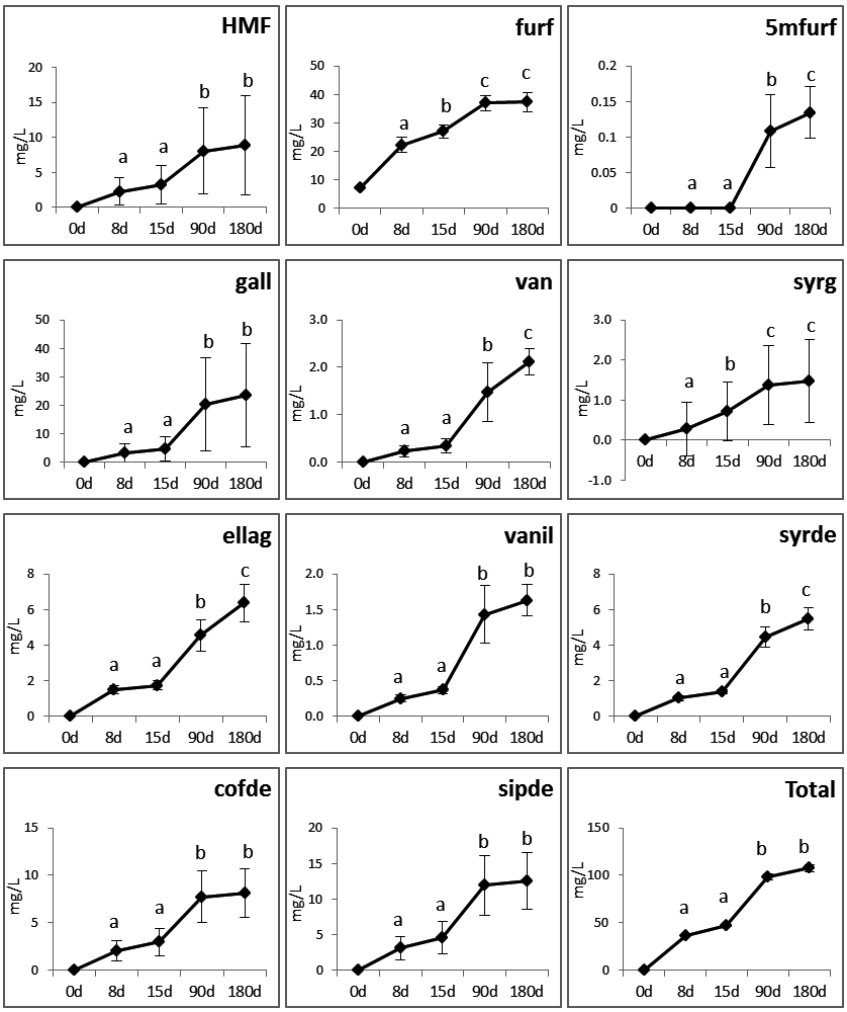

Figure 3 - Kinetics of the low molecular weight compounds of the wine brandies in the first six months of ageing. Different letters indicate highly significant difference (P=99.9%). HMF – 5-hidroxymethylfurfural; furf - furfural; 5mfurf - 5-methylfurfural; gall – gallic acid; van – vanillic acid; syrg – syringic acid; ellag – ellagic acid; vanil – vanillin; syrde – syringaldehyde; cofde – coniferaldehyde; sipde – sinapaldehyde; Total – total of the low molecular weight compounds.

Cinéticas dos compostos de massa molecular baixa na aguardente vínica nos primeiros seis meses de envelhecimento. Letras diferentes indicam diferença altamente significativa (P=99.9%). HMF – 5-hidroximetilfurfural; furf - furfural; 5mfurf - 5-metilfurfural; gall – ácido gálhico; van – ácido vanílico; syrg – ácido siríngico; elag – ácido elágico; vanil – vanilina; syrde – siringaldeido; cofde – coniferaldeido; sipde – sinapaldeido; Total – total dos compostos de massa molecular baixa.

between chemical composition and the chromatic characteristics suggests the existence of unknown reactions that may have been caused by the use of two kinds of wood simultaneously, by specific phenomena in each ageing system, and/or the presence of non-phenolic compounds that influence the colour of the aged brandies.

The results obtained for the absorbance at 470 nm and from the dry extract essay reinforce the hypothesis of the crucial role of some non-phenolic compounds to the colour of the aged brandies, that may explains the apparent inconsistency between the chemical composition and the chromatic characteristics, as well as the difference to the positive correlations found in previous studies on the traditional ageing of wine brandies.

Among the low molecular weight compounds of the studied brandies, the 5-hydroxymethylfurfural, gallic acid, coniferaldehyde and sinapaldehyde seem to be chemical markers of the ageing system.

Regarding the ageing time, there is a significant increase of furanic and phenolic compounds release from the wood into the brandy, which indicates that extraction was preponderant to oxidation in both ageing systems during the first six months of ageing.

The ongoing research of wine brandy ageing until the second year will provide information that may contribute to clarify the doubts about the role of phenolic and non-phenolic compounds on the chromatic characteristics, and also about the main related phenomena.

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