EFFECTS OF CARAMEL ADDITION ON THE CHARACTERISTICS OF WINE BRANDIES

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SUMMARY

According to the European legislation, the wine brandies may only contain added caramel as a means to adapt colour. Nevertheless, there is no legal limit for the concentration of this additive, neither specifications for the product and the technological procedure. The present study was performed aiming at contribute to extend the knowledge on caramel’s composition and its effects on the chemical composition and chromatic characteristics of the wine brandies, for technological purposes and quality control. Thus, the physicochemical composition of three kinds of wine brandies (freshly distilled brandy, freshly distilled brandy diluted to 40 % v/v, and 13-years aged brandy) and two representative types of caramel (Royal® and E150d) were analysed. The results demonstrate that caramel has highly significant influence on the chromatic characteristics (lightness, saturation, chromaticity coordinates and absorbance at 470 nm), but also on the total phenolic index, furfural and HMF contents, and total reducing sugars content of the wine brandies. Among them, the caramel mainly affects coordinate a*, lightness, total phenolic index and HMF content according to the significant correlations found between the caramel concentration and the characteristics acquired by the brandies. In addition, the composition of the caramel has a determining role on its effect, although the result obtained is conditioned by the chemical composition of each kind of brandy. It is also shown the interest of the furfural/HMF ratio as discriminator for the caramel addition since it is higher than the unit only for the wine brandies produced without caramel, being a useful tool to assess the authenticity of the aged wine brandies.

INTRODUCTION

According to the Reg. EC nº 110/2008, which defines the “General rules concerning the categories of spirit drinks”, the wine brandies may only contain added caramel as a means to adapt colour. Nevertheless, there is no legal limit for the concentration of this additive, neither specifications for the product and the technological procedure, i.e., the type of caramel that can be used and the most appropriate moment for its application. On the other hand, the European legislation does not distinguish between the true wine brandies, resulting from the natural ageing process during at least six months in wooden barrels, and the brandies that are prepared (using caramel, vanillin and or other ageing agents), which can be easily obtained. All of them may have the designation of “brandy”, which can mislead the consumer.

The colour of the aged wine brandy may vary depending on the technological conditions of the ageing process, such as the wood botanical species and the toasting level of the barrel, the ageing time (Canas et al., 2002) that is specific for each commercial brand.
Besides, the caramel can be added to the wine brandy to intensify the colour acquired during the ageing process (Villalón-Mir et al., 1992), but there are other reasons leading to its employ: i) simulating the typical colour of the true aged wine brandies (golden/topaz); ii) making the brandy sweeter and smoother, in order to satisfy consumers preference (Belchior et al., 2004); iii) making the brandy looks older than it is, owing to its more evolved colour (Villalón-Mir et al., 1992; Canas and Belchior, 2007) and aroma. Indeed, the caramel is rich in furanic derivatives, mainly 5-hydroxymethylfurfural (HMF) and furfural (Pons et al., 1991; Villalón-Mir et al., 1992) that are key-odorant compounds of the aged wine brandies (Caldeira et al., 2008).

Concerning the technological procedure, normally the caramel is added to the wine brandy few weeks before bottling, when the brandy was already diluted with demineralised water to an ethanol concentration of 38–40% v/v in order to be commercialized.

In this context, a broader research on caramel’s composition and its effects on the chemical composition and chromatic characteristics of the wine brandies become indispensable for technological purposes and quality control. Thus, the present work was performed to study the mentioned topics, based on the assessment of total phenolic index, chromatic characteristics, furanic derivatives quantified by HPLC, and total reducing sugars content.

MATERIAL AND METHODS

Experimental design and sampling

The essay was based on a factorial design (three kinds of wine brandies x two types of caramel x three concentrations of caramel + three control groups) with three replications. The different kinds of wine brandies used were: B1 - freshly distilled brandy produced with a wine obtained from a mixture of white and red grape varieties, in an alambiq Charentais, at INIA–Dois Portos in 2009 (ethanol content - 74% v/v; pH – 5.7); B2 - brandy obtained by diluting the brandy B1 with distilled water (ethanol content - 40% v/v; pH – 4.8); B3 - 13-year-aged brandy produced with a wine obtained from a mixture of white and red grape varieties, in an alambiq Charentais, and aged in 250-L new barrels of Limousin oak wood at the cellar of INIA–Dois Portos (ethanol content – 38% v/v; pH – 3.7). The two distinct types of caramel used were: C1 – Royal® - syrup of gluco and fructose with sugar, and preservatives E-202 (potassium sorbate) and E-220 (sulphur dioxide), supplied by Kraft Foods Postres S.A.U. (Barcelona, Spain), representing a type of caramel that is commonly used in spirits companies. For each caramel, four concentrations were tested according to the information provided by wine brandy’s producers: 0.0 g/L (control group); 2.5 g/L; 5.0 g/L; 10.0 g/L.

The caramel was dissolved in the wine brandy, and the mixture was transferred to a centrifuge tube, which was weighted and centrifuged at 3,820 g for 10 min at 0 °C. The upper phase was removed and the centrifuge tube was weighted again. When there is a precipitate (weight registered), it was redissolved in the wine brandy and gathered with the upper phase (the resulting dilution was considered in the calculations made). Then the final mixture was analysed. A total of 63 samples were taken.

For the determination of caramel’s composition, the caramels were dissolved with distilled water prior to analysis. For each caramel three concentrations were tested, in triplicate: 2.5 g/L; 5.0 g/L; 10.0 g/L. Before analysis, the mixture was transferred to a centrifuge tube and centrifuged at 3,820 g for 10 min at 0 °C. A total of 18 samples were taken.

Chemicals

All HPLC solvents used were gradient grade purchased from Merck (Darmstadt, Germany). They were filtered through 0.45 µm membrane (Millipore, New Bedford, USA) and degasified in an ultrasonic bath. The standards of furanic derivatives (HMF and furfural) were purchased from Fluka (Buchs, Switzerland) and were used without further purification. The standard calibration and internal standard solutions were prepared fresh prior to use with ethanol/water (75% v/v). The solutions were prepared with ethanol gradient grade (Merck, Darmstadt, Germany) and water purified through a Seralpur Pro 90 CN from SERAL (Water Purification System in Ransbach-Baumbach).

Determination of total phenolic index

Total phenolic index (TPI) of wine brandies and caramels was determined by measuring the absorbance at 280 nm (Ribéreau-Gayon, 1970). Brandies were diluted with ethanol/water. Caramels were diluted with distilled water.

Determination of chromatic characteristics

The chromatic characteristics of wine brandies and caramels were assessed by the CIETLab method (Bakker et al., 1986), 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 10° standard observer. The colour 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 wine brandies and caramels was measured by the absorbance at 470
nm (A470), which was calculated from the value of transmittance at 470 nm provided by CIELab output. Indeed, research made with model solutions under food-relevant conditions (Hofmann, 1998a) and with different foods (Gokmen and Senyuva, 2006), including aged wine brandies (Avakiants, 1992) highlighted that Maillard reactions have great influence on colour development of foods and beverages. It is known that among the multiplicity of non-volatile Maillard reaction products there are some key chromophores (compounds with highest colour impact) that evoke the colours yellow, orange, red and brown (Hofmann, 1998a,b,c; Gokmen and Senyuva, 2006). The melanoidins belong to this group of chromophores and are closely related to the brown colour of foods (Gokmen and Senyuva, 2006). According to Martins and Van Boekel (2003) the absorbance at 470 nm is a reliable measure of the brown colour, which reflects the concentration of melanoidins.

Determination of furanic derivatives by HPLC

HMF, furfural and 5-methylfurfural are present in the aged wine brandies (Canas, 2003; Canas et al., 2004), but only furfural is found in the freshly distilled wine brandies (Onishi et al., 1977; Jeuring and Kuppers, 1980; Canas et al., 2004). On the other hand, the caramels only contain HMF and furfural. Therefore, 5-methylfurural is not a discriminant compound for brandies as result of caramel addition, and for this reason this compound was not quantified by HPLC. Among the furanic derivatives, HMF and furfural (Furf) were quantified in wine brandies and caramels as described by Canas et al. (2003), with an HPLC Lachrom Merck Hitachi system (Merck, Darmstadt, Germany) comprised of quaternary pump (Model L-7100), column oven (Model L-7350), UV-Vis detector (Model L-7400) and autosampler (Model L-7250), coupled to a HSM D-7000 software (Merck, Darmstadt, Germany) for management, acquisition and treatment of data. A Lichrospher RP 18 5µm 250 mm x 4 mm i.d. column (Merck, Darmstadt, Germany) was used. UV detection was made at 280 nm. Samples of wine brandies and caramels 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 analysed 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 (Model Waters 996), with the same chromatographic conditions, managed by “Millennium 2010” software (Waters, Milford, USA).

Determination of total reducing sugars

The total reducing sugars of wine brandies and caramels were analysed according to the usual method of OIV (1994).

Statistical analysis

The two-way analysis of variance was performed to evaluate the effects of the kind of wine brandy and the concentration of added caramel for each type of caramel. The one-way analysis of variance was performed to assess the caramel composition. Fisher’s least significant difference (LSD) test was applied to compare the different averages. All calculations were carried out using Statistica vs. ’98 edition (Statsoft Inc., Tulsa, USA).

A principal component analysis was carried out to compare the colour of the wine brandies B1 and B2 added with caramel with that of the wine brandy B3 without caramel (representing the true aged wine brandy), using NTSYSpc - vs 2.10q (Exeter Software, New York, USA).

It was also performed the correlation analysis between the concentration of caramel and the characteristics acquired by the wine brandies. Calculations were carried out using Statistica vs. ’98 edition (Statsoft Inc., Tulsa, USA).

RESULTS AND DISCUSSION

The results of the analysis of variance show that the caramel C1 originates a highly significant effect in the total phenolic index, chromatic characteristics and HMF content of all the analysed brandies (Table I). It also affects significantly the content of furfural in the brandies B1 and B2. The caramel C2 has a highly significant effect in all of the analysed parameters of the wine brandies (Table I).

The addition of C1 originates a gradual and differentiated increase of the total phenolic index of the brandies, in a concentration-dependent manner, which is in agreement with the results obtained for this caramel (Table II). The highest increment of this parameter is observed for 5.0 g/L in the brandy B1, 2.5 g/L in the brandy B2 and 10.0 g/L in the brandy B3. Furthermore, the increments are more pronounced in the brandies B1 and B2, probably due to the absence of wood extractable compounds in these non-aged brandies. The influence of C2 in the total phenolic index is similar to that of C1, but the highest augmentation is associated with the addition of 2.5 g/L at any studied brandy (Table I). The greatest effect of C2 can be ascribed to its higher total phenolic index (Table II). Moreover, this characteristic of the studied caramels may be related to the furanic derivatives contents (Table II). Indeed, according to Pons et al. (1991) the caramel does not have phenolic compounds, therefore the increase of brandies’ total phenolic index could be a consequence of the furanic derivatives release from the caramel added, which present a maximum of absorbance at 280 nm.
Table I
Physicochemical characteristics of the wine brandies

<table>
<thead>
<tr>
<th>Brandy</th>
<th>Caramel added (g/L)</th>
<th>TPI</th>
<th>L* (%)</th>
<th>C*</th>
<th>a*</th>
<th>b*</th>
<th>A470</th>
<th>HMF (mg/L)</th>
<th>Furf (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>0.0</td>
<td>0.71 ± 0.00a</td>
<td>100.00 ± 0.11d</td>
<td>0.25 ± 0.04d</td>
<td>0.05 ± 0.01d</td>
<td>0.24 ± 0.04d</td>
<td>0.00 ± 0.00d</td>
<td>0.00 ± 0.00d</td>
<td>10.62 ± 0.25b</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.95 ± 0.03b</td>
<td>98.55 ± 0.36c</td>
<td>5.10 ± 0.03b</td>
<td>-0.61 ± 0.08b</td>
<td>5.06 ± 0.03b</td>
<td>0.02 ± 0.00b</td>
<td>8.10 ± 0.19a</td>
<td>10.46 ± 0.95b</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>2.69 ± 0.19b</td>
<td>96.62 ± 0.35c</td>
<td>9.93 ± 0.38b</td>
<td>-0.94 ± 0.06b</td>
<td>9.88 ± 0.39b</td>
<td>0.04 ± 0.00b</td>
<td>15.88 ± 0.09b</td>
<td>11.17 ± 0.22b</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>4.98 ± 0.00c</td>
<td>94.03 ± 0.16c</td>
<td>18.69 ± 0.24d</td>
<td>-1.19 ± 0.07b</td>
<td>18.65 ± 0.24d</td>
<td>0.08 ± 0.00b</td>
<td>33.47 ± 0.31d</td>
<td>11.60 ± 0.03c</td>
<td></td>
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<tr>
<td>B2</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.46 ± 0.00c</td>
<td>98.85 ± 0.08c</td>
<td>0.99 ± 0.04c</td>
<td>0.12 ± 0.04d</td>
<td>0.99 ± 0.04c</td>
<td>0.01 ± 0.00b</td>
<td>0.00 ± 0.00b</td>
<td>6.07 ± 0.04c</td>
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</tr>
<tr>
<td>2.5</td>
<td>1.66 ± 0.01b</td>
<td>98.75 ± 0.22c</td>
<td>8.04 ± 0.11c</td>
<td>-0.80 ± 0.02c</td>
<td>8.00 ± 0.11c</td>
<td>0.02 ± 0.00b</td>
<td>13.24 ± 0.66c</td>
<td>5.39 ± 0.23b</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>2.71 ± 0.06c</td>
<td>97.20 ± 0.19c</td>
<td>15.16 ± 0.05c</td>
<td>-1.24 ± 0.05c</td>
<td>15.11 ± 0.05c</td>
<td>0.05 ± 0.00b</td>
<td>27.21 ± 0.26c</td>
<td>5.41 ± 0.28c</td>
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</tr>
<tr>
<td>10.0</td>
<td>5.27 ± 0.26c</td>
<td>94.29 ± 0.34c</td>
<td>27.22 ± 0.16d</td>
<td>-1.03 ± 0.17c</td>
<td>27.20 ± 0.16d</td>
<td>0.10 ± 0.00b</td>
<td>50.93 ± 0.73c</td>
<td>5.05 ± 0.09c</td>
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<tr>
<td>B3</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.0</td>
<td>52.80 ± 0.12c</td>
<td>71.73 ± 0.04c</td>
<td>84.84 ± 0.16a</td>
<td>18.42 ± 0.13a</td>
<td>81.38 ± 0.05a</td>
<td>0.60 ± 0.00b</td>
<td>28.17 ± 0.09b</td>
<td>38.66 ± 0.16c</td>
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</tr>
<tr>
<td>2.5</td>
<td>58.84 ± 0.73c</td>
<td>68.78 ± 0.26c</td>
<td>84.25 ± 0.25a</td>
<td>19.52 ± 0.21c</td>
<td>81.96 ± 0.22c</td>
<td>0.66 ± 0.00b</td>
<td>40.83 ± 2.01b</td>
<td>38.67 ± 0.41c</td>
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</tr>
<tr>
<td>5.0</td>
<td>59.31 ± 0.88c</td>
<td>68.06 ± 0.04c</td>
<td>85.06 ± 0.01b</td>
<td>20.21 ± 0.03c</td>
<td>82.62 ± 0.01c</td>
<td>0.71 ± 0.00b</td>
<td>51.19 ± 0.44c</td>
<td>38.04 ± 0.08c</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>62.22 ± 1.14d</td>
<td>68.80 ± 0.12b</td>
<td>86.80 ± 0.12b</td>
<td>21.89 ± 0.11d</td>
<td>84.00 ± 0.09d</td>
<td>0.71 ± 0.00b</td>
<td>68.60 ± 0.70d</td>
<td>39.28 ± 0.45c</td>
<td></td>
</tr>
</tbody>
</table>

Table II
Physicochemical characteristics of the caramels

<table>
<thead>
<tr>
<th>Caramel conc. (g/L)</th>
<th>TPI</th>
<th>L* (%)</th>
<th>C*</th>
<th>a*</th>
<th>b*</th>
<th>A470</th>
<th>HMF (mg/L)</th>
<th>Furf (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>1.25 ± 0.02a</td>
<td>98.97 ± 0.09a</td>
<td>7.37 ± 0.04b</td>
<td>-0.98 ± 0.01c</td>
<td>7.30 ± 0.04c</td>
<td>0.02 ± 0.00b</td>
<td>5.20 ± 0.29b</td>
<td>(0.05 ± 0.01b)</td>
</tr>
<tr>
<td>5.0</td>
<td>2.77 ± 0.01b</td>
<td>97.38 ± 0.10a</td>
<td>14.09 ± 0.22b</td>
<td>-1.49 ± 0.01b</td>
<td>14.03 ± 0.22b</td>
<td>0.05 ± 0.00b</td>
<td>12.05 ± 0.24b</td>
<td>(0.05 ± 0.00b)</td>
</tr>
<tr>
<td>10.0</td>
<td>4.36 ± 0.03c</td>
<td>94.60 ± 0.04a</td>
<td>25.74 ± 0.04d</td>
<td>-1.55 ± 0.09b</td>
<td>25.69 ± 0.04d</td>
<td>0.09 ± 0.00c</td>
<td>26.56 ± 1.02c</td>
<td>(0.10 ± 0.00b)</td>
</tr>
<tr>
<td>C2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>5.09 ± 0.00c</td>
<td>84.14 ± 0.01a</td>
<td>64.44 ± 0.01c</td>
<td>4.82 ± 0.01b</td>
<td>66.23 ± 0.07b</td>
<td>0.32 ± 0.00b</td>
<td>1.11 ± 0.03b</td>
<td>(0.09 ± 0.00b)</td>
</tr>
<tr>
<td>5.0</td>
<td>10.09 ± 0.03b</td>
<td>72.40 ± 0.10c</td>
<td>89.79 ± 0.14a</td>
<td>18.91 ± 0.11c</td>
<td>87.77 ± 0.12a</td>
<td>0.64 ± 0.00b</td>
<td>2.10 ± 0.06b</td>
<td>0.18 ± 0.00b</td>
</tr>
<tr>
<td>10.0</td>
<td>18.22 ± 0.03c</td>
<td>56.13 ± 0.07c</td>
<td>97.64 ± 0.05a</td>
<td>35.38 ± 0.06c</td>
<td>91.00 ± 0.07c</td>
<td>1.28 ± 0.00c</td>
<td>4.11 ± 0.01c</td>
<td>0.54 ± 0.02c</td>
</tr>
</tbody>
</table>

Values are mean ± standard deviation; a,b,c Values mean in the same column with different letters are highly significant different at *** α < 0.001 level of significance or very significant different at ** α < 0.01 level of significance; TPI – total phenolic index; L* – lightness; C* – saturation; a*, b* – chromaticity coordinates; A470 - absorbance at 470 nm; HMF – 5-hydroxymethylfurural; Furf – furfural; B1 – freshly distilled brandy produced at INIA-Dois Portos in 2009; B2 - brandy obtained by diluting the brandy B1 with distilled water to 40 % v/v; B3 - 13-years aged brandy produced at INIA-Dois Portos.

Concerning the furanic derivatives, results of the HPLC analysis show that HMF does not exist in the non-aged brandies (B1 and B2) without caramel, but it is present in the aged brandy (B3) without caramel (Table I). Actually, the HMF is released from the wood into the brandy during the ageing process (Canas, 2003). The HMF found in the wood derives from cellulose degradation during the heat treatment of the barrel (Hodge, 1967; Fengele and Wegener, 1989). The caramel promotes a continuous enrichment of the brandies in HMF according to the concentration added, being more evident with C1 in the
brandies B1 and B2 (Table I) owing to higher content of HMF in this caramel (Table II). The greatest increment on the content of this furanic derivative in the studied brandies is promoted by 2.5 g/L of either used caramels.

Furfural is already present in the freshly distilled wine brandy (Table I), as reported by Onishi et al. (1977) and by Jeuring and Kuppens (1980). In the aged wine brandies higher content of furfural is normally found as a result of its release from the wood, being mainly derived from the hemicelluloses (Hodge, 1967; Canas et al., 2004). The use of C1 originates an increase in the brandy B1 with 5.0 g/L and 10.0 g/L, while in the brandy B2 there is a continuous decrease, as also observed for C2 in all of the brandies (Table I). This last behaviour can be the consequence of several phenomena such as the interaction of furfural with other compounds of the caramel or of the brandy, namely those products of Maillard reactions (Severin and Kronig, 1972; Hofmann, 1998c).

Among the furanic derivatives, HMF is the most abundant compound in the caramel, varying between 1.1 mg/L and 26.6 mg/L (Table II). According to Pons et al. (1991) the caramel contains several degradation compounds, principally HMF. They have identified 33 compounds by solvent extraction, and also traces of coloured higher molecular weight species. Villalón-Mir et al. (1992) also indicate that caramels present high concentration of HMF (189.5 mg/L – 251.7 mg/L), which represents 99.9% of the total furanic aldehydes. Villalón-Mir et al. (1992) and Quesada-Granados et al. (1996) verified that caramel exerts a significant influence on the HMF content of the aged wine brandies, which becomes higher than the furfural content.

The results obtained for the aged brandy (B3) demonstrated the interest of furfural/HMF ratio as discriminator for the caramel addition since it is higher than the unit only for the wine brandies produced without caramel, as observed in a set of commercial wine brandies analysed in our previous work (Canas and Belchior, 2007). Therefore, this ratio is a useful tool regarding the authenticity of the wine brandies and should be considered in the routine methodology for their quality control.

Regarding the chromatic characteristics of the wine brandies (Table I), the lightness L* (negatively correlated with the colour intensity) decreases with increasing concentration of caramel, in a more pronounced way with C2. The saturation (C*) of the brandies B1 and B2 shows comparable variation (the highest at 2.5 g/L) as a consequence of caramel addition but there is more noticeable increase with C2. In the brandy B3 a significant difference is only achieved by the addition of 10.0 g/L of C1 or 2.5 g/L of C2.

The coordinate b* of the brandies tend to increase with the use of caramel, resulting in more intense yellow hue as the added concentration rises. A different behaviour is found in the brandy B3 added with C2, probably due to the interaction between compounds of this type of caramel and those of the aged wine brandy.

The effect in the coordinate a* seems to be strictly dependent on the type of caramel and brandy. For C1 the increase of caramel concentration causes a decrease of a* value (towards the green hue) in the brandies B1 and B2 that are colourless, and an increase of a* value in the brandy B3 (towards the red hue). Given that the coordinate a* of caramel C1 decreases in a concentration-dependent manner (Table II), a possible reason for a difference in behaviour at brandy B3 is the interaction between some compounds of caramel and wood extractable compounds present in the aged brandy. For C2, the positive variation induced in this chromaticity coordinate (towards the red hue) is similar in the brandies B2 and B3; the brandy B1 presents atypical behaviour.

The distinct influence of the two types of caramel on these chromatic characteristics of the brandies can be partly explained by lower lightness, higher saturation and higher values of the coordinates a* and b* of C2 (Table II).

The absorbance at 470 nm of the wine brandies has a gradual and highly significant increase with the rising of caramel concentration, independently of the type of caramel used (Table I). The highest values found in the brandies added with C2 can be related to the concentration of melanoids and other key chromophores present in this type of caramel (Hofmann, 1998a,b,c; Borrelli et al., 2002), which has higher A470 – Table II. There are also important differences between the aged brandy (B3) and the non-aged brandies (B1 and B2) that can result not only from the effect of caramel but also from the chemical composition of the brandies. Indeed, melanoids, and possibly other coloured compounds formed by the Maillard reactions, are also present in the toasted wood and can be released into the wine brandy during the ageing process, affecting its colour (Gokmen and Senyuva, 2006; Canas et al., 2009). On the basis of this hypothesis, the ageing of the brandy B3 may have favoured the formation and accumulation of such compounds, whose concentration contributed to its more evolved colour – higher values of brown hue.

In the principal component analysis performed to compare the colour of the wine brandies B1 and B2 added with caramel with that of the brandy B3 without caramel, the first component (PC1) and the second component (PC2) explain 84.6 % and 15.3% of the total variance, respectively (Figure 1). The first component (PC1) makes the splitting of the brandies according to the type of caramel used, showing the separation of two main clusters: one formed by the brandies added with C1 that are located at positive values of PC1, and another constituted by the
brandies added with C2 and the brandy B3 that are placed at negative values of PC1. The first component has strong positive vectors loading for lightness (L*) and A470, and strong negative vectors loading for saturation (C*) and coordinate b*, which are the most determining characteristics to distinguish these brandies. This global analysis demonstrates that the colour of the brandies B1_C2_10 and B2_C2_5 is that which is closest to the colour of B3 without caramel.

As regards the total reducing sugars, the results of the analysis of variance demonstrate their absence in the non-aged brandies B1 and B2 (Table III), and their presence in the brandy B3 that is assigned to its ageing in wooden barrels (Belchior and Carneiro, 1972; Marché et al., 1975). C1 is richer than C2 in total reducing sugars at any concentration. In addition, the total reducing sugars content increase gradually with the concentration of caramel (Table III). According to Pons et al. (1991) the caramel contains residual sucrose (mono- and oligosaccharides), fructose and glucose with a ratio of 3:4:3.

For quality control purposes, the results of the correlations between the caramel concentration (C1 and C2) and the characteristics of the brandies provide very important information, demonstrating that caramel mainly influences HMF content (rB1=0.81; rB2=0.75; rB3=0.95), total phenolic index (rB1=0.76; rB2=0.71; rB3=0.77), A470 (rB1=0.63; rB2=0.60; rB3=0.61) and coordinate a* (rB1=0.55; rB2=0.53; rB3=0.60), since the correlations are positive and significant for all of the brandies, as well as for the lightness (rB1=-0.66; rB2=-0.58; rB3=-0.65) which are negative and very significant for all of them.

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### Table III

<table>
<thead>
<tr>
<th>Teor de açúcares redutores totais (g/L) das aguardentes vínicas e dos caramelos</th>
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<tbody>
<tr>
<td>B1</td>
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<tr>
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<tr>
<td>2.5 g/L</td>
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<td>0.0 ± 0.0</td>
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<tr>
<td>0.1± 0.0</td>
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</tbody>
</table>

Values are mean ± standard deviation; B1 - freshly distilled brandy produced at INIA–Dois Portos in 2009; B2 - brandy obtained by diluting the brandy B1 with distilled water to 40 % v/v; B3 - 13-years aged brandy produced at INIA–Dois Portos; C1 – caramel 1; C2 – caramel 2.
CONCLUSIONS

To our knowledge, innovative information is provided about the effects of caramel on the composition of the wine brandies and the relationship with the caramel’s composition. It is demonstrated that caramel addition has highly significant influence in the chromatic characteristics (lightness, saturation, chromaticity coordinates and A470), but also in the chemical composition of the wine brandies (total phenolic index, furanic derivatives and total reducing sugars). As expected, higher variations induced by the caramel are found in the non-aged brandies with or without dilution, which seem to be older than they are due to their more evolved colour and chemical composition.

Moreover, the composition of the caramel has a determining role on its effect, although the result obtained is conditioned by the chemical composition of each kind of brandy. This finding is of great interest for technological purposes, since indicates that a preliminary essay should be performed in order to choose the most suitable type of caramel for a certain kind of wine brandy.

For quality control purposes, the correlation analysis between the caramel concentration and the characteristics of the brandies reveal that caramel mainly influences HMF content, total phenolic index and coordinate a*, since the correlations are positive and significant for all of the brandies, as well as for the lightness which are negative and very significant for all of them. It is also shown that the ratio furfural/HMF is a useful tool to detect the addition of caramel in aged wine brandies.

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