Ciência Téc. Vitiv. 23 (2) 97-110. 2008

A SENSORY AND CHEMICAL APPROACH TO THE AROMA OF WOODEN AGED *LOURINHÃ* WINE BRANDY

UMA ABORDAGEM SENSORIAL E QUÍMICA AO AROMA DE AGUARDENTES VÍNICAS ENVELHECIDAS DA LOURINHÃ

Ilda Caldeira*[1], R. Bruno de Sousa[2], A. Pedro Belchior[1] , M. Cristina Clímaco[1]

[1] INRB, INIA-Dois Portos, ex-Estação Vitivinícola Nacional. Quinta da Almoinha, 2565-191 Dois Portos, Portugal
[2] Departamento de Química Agrícola e Ambiental, Instituto Superior de Agronomia, Universidade Técnica de Lisboa (UTLisbon), Tapada da Ajuda, Portugal
*Corresponding author: Ilda Caldeira. Estação Vitivinícola Nacional, Quinta da Almoinha, 2565-191 Dois Portos, Portugal. Tel.:+351261712106, Fax:+351261712426, Email: evn.icaldeira@mail.net4b.pt

(Manuscrito recebido em 04.11.08 . Aceite para publicação em 12.12.08)

SUMMARY

The maturation of wine brandies in wooden barrels origin many sensory and physical-chemical changes in these alcoholic beverages.
This work studies the odorants in different aged brandies from Lourinhã. These brandies were analysed by gas chromatography coupled to olfactometry (GC-O). A panel taster profiled these brandies and the identified odorants were also quantified by gas chromatography coupled to a flame ionization detector (GC-FID).
The GC-O results showed 29 identified odorants (alcohols, esters, acids and phenols). Some of them are proceeding from the distillate while others are extracted from the wood. The analysis of correlation between the sensory profiles and the odorant quantification pointed out the relevance of several wood compounds for the brandy aroma, namely the vanillin, volatile phenols and furanic aldehydes. These compounds presented important correlations with several olfactory attributes like vanilla, smoke, toasted, dried fruits, woody, which influence positively the quality of the brandies.

RESUMO

O envelhecimento das aguardentes vínicas em vasilhas de madeira provoca alterações profundas na composição físico-química e sensorial destas bebidas.
Neste trabalho são estudados os odorantes em aguardentes vínicas da região da Lourinhã envelhecidas em diferentes condições. Para o efeito recorreu-se à avaliação dos compostos odorantes por cromatografia gasosa de alta resolução acoplada à olfactometria (GC-O), à quantificação de alguns dos compostos odorantes por cromatografia gasosa de alta resolução acoplada a um detector de ionização de chama (GC-FID) e à avaliação sensorial das aguardentes.
Os resultados de GC-O permitiram identificar 29 odorantes diferentes (álcoois, ésteres, ácidos e fenóis), uns originários do destilado e outros provenientes da madeira. A pesquisa de correlações entre a análise sensorial e a análise química confirmou a importância odorante de vários compostos com origem na madeira, designadamente a vanilina, os fenóis voláteis e os aldeídos furânicos. Estes compostos apresentaram importantes correlações com descritores sensoriais como a baunilha, fumo, torrado, frutos secos, madeira, os quais tem uma correlação positiva com a qualidade da aguardente.

Key words: odorants, wine brandies, maturation
Palavras-chave: odorantes, aguardentes vínicas envelhecidas, envelhecimento

INTRODUCTION

According to the regulatory requirements, the aged wine brandies must be matured in wooden barrels before sale and consumption. In the case of brandies produced in *Lourinhã,* a delimited Portuguese Region, they must stay in the wooden barrels for a minimum of two years (Dec. Lei nº 39 of 1992).

Many changes occur in the spirit during the maturation period, which can last up to 50 years. Therefore, the final product presents a very distinct flavour and aroma from the newly distilled spirit that is mainly due to the extended period of maturation (Leauté *et al*., 1998). The change in the flavour of the maturing brandies results from qualitative and quantitative modifications of brandy composition as a consequence of many reactions, which occur during the ageing processing. The extraction and subsequent transformation of wood compounds seem to be of the prime importance to the final aroma and final brandy composition, and these sensory differences have a significant effect on brandy consumers' preferences (Belchior *et al*., 2004). The kind of wood and the wood heat treatment are the most determining factors of sensory and physico-chemical modifications during the maturation period (Guymon and Crowell, 1970; Onishi *et al*., 1977; Artajona, 1991; Rabier and Moutonet, 1991; Puech *et al*., 1992; Viriot *et al*., 1993; Guichard *et al*., 1995, Canas *et al.*, 1999; Belchior *et al*., 2001; Canas, 2003; Caldeira, 2004).

The research on aged brandy aroma has been focused in the identification of many volatiles compounds. Several hundreds of volatile compounds, other than ethanol, have been identified in brandies (Marché *et*

al., 1975; Smedt e Liddle, 1978; ter Heide *et al.*, 1978; Rijke and Heide, 1983; Puech *et al.*, 1984; Nykänen and Nykänen, 1991; Vanderlinde *et al.*, 1992; Puech and Maga, 1993; Vidal *et al.* 1996; Caldeira *et al*., 2004; Ledauphin *et al*., 2006). Nykanen and Suomalainen (1983) and Caldeira (2004) presented an exhaustive review of volatile aroma compounds of brandies. However, the aroma research led to the conclusion that only 5 % of volatiles identified in foods contribute to aroma (Grosch, 2001). Thus, in the last years the researchers have been searched correlations between the sensory and the chemical results, by two approaches, in order to screen the most potent odorants or key odorants. The indirect approach pursuit mathematical correlations between the sensory and the chemical results, which were obtained separately. The direct approach is based on gas chromatography-olfactometry (GC-O) methodologies (van Ruth, 2001). These methodologies have been extensively applied for the screening of the key odorants for many food products. Nevertheless, there are few data about the most potent odorants of wine aged brandies (Janácová *et al.*, 2008), in spite of some interesting results of the odorants in freshly distilled Cognac, without wood maturation (Leclaire *et al*., 1999; Lablanquie *et al*., 2002; Ferrari *et al.* 2004).

Therefore, the aim of present work was to identify the odorants of aged wine brandies from *Lourinhã*, obtained in different ageing conditions.

MATERIAL AND METHODS

Brandies: 42 brandies sampled, after 4 four years of maturation, from 42 wood barrels, which were made according to a factorial experiment (7 woods x 3 toasting levels x 2 replicates). The seven different kinds of woods, botanically identified (Carvalho, 1998), were one Portuguese chestnut wood (*Castanea sativa* Mill.) CAST, one Portuguese oak wood (*Q. pyrenaica* Willd.) from three different sites (CNE, CNF, CNG), two French oak woods, one from Allier forest (*Quercus sessiliflora* Sallisb.) (CFA) and another from Limousin forest (*Quercus robur* L.) (CFL) and one American oak wood (*Quercus alba* L./*Quercus stellata*Wangenh. and (*Quercus lyrata* Walt./*Quercus bicolour* Willd.) (CAM). The barrels were then submitted to the heat treatment with 3 levels of toasting: light (QL), medium (QM) and strong (QF), with two replicates of each essay. The control of the heat treatment was based on the cooper's skill, being about 10 min (light toasting), 20 min (medium toasting) and 25 min (strong toasting) over a fire of wood chips.

The alcoholic strength, the acidity and the dry matter of brandies were evaluated according to the published methodologies (Belchior and Carvalho 1984, 1991; OIV, 1994).

Reagents: Dichloromethane, ethanol and sodium sulphate anhydrous, all analytical grade, were purchased from Merck (Darmstadt, Germany). Dichloromethane was redistilled in a Vigreux column. Distilled water was purified through a Seralpur Pro 90 CN from SERAL (Water Purification Systems, Ransbach–Baumbach, Germany).

GC-O and GC-MS standards: Acetic acid was purchased from Riedel-de-Haen (Seelze, Germany); ethyl isobutyrate, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate, 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol, ethyl hexanoate, ethyl L-lactate, 1-hexanol, ethyl octanoate, linalool, butanoic acid, 3-methyl butanoic acid, hexanoic acid, guaiacol, 2-phenylethanol, eugenol, 4-ethylphenol, 3,4-dimethylphenol (IS), syringol, dodecanoic acid, 4-hydroxy-3-methoxy-benzaldehyde (vanillin), 5-methyl-2-hexanol (IS) were purchased from Fluka (Buchs, Switzerland); isoamyl acetate, *trans*-2-hexen-1-ol, *cis, trans*-β-methyl-γ-octalactone, 4-propyl-guaiacol, 4-methyl-syringol, 4-allyl-syringol were purchased from Aldrich (Steinheim, Germany); 4-ethylguaiacol, DL-malic acid diethyl ester were purchased from TCI, ethyl butyrate was purchased from Merck (Darmstadt, Germany). Standards solutions were prepared with ethanol/purified water (20:80 v/v).

Isolation of volatiles from brandies: Volatiles were extracted using the procedure previously proposed by Caldeira *et al*. (2004). 100 cm^3 volume of brandy (diluted to 20% v/v) was extracted with dichloromethane, after addition of 1.6 cm^3 of 5-methyl-2-hexanol (IS 81 mg. dm^{-3} of 50% ethanol solution) and 0.5 cm^3 of 3,4-dimethylphenol (IS 100 $mg.dm^{-3}$ in ethanol) as internal standards (IS). Extraction was carried out with the successive addition of 30, 10 and 10 cm^3 of dichloromethane by ultrasonification (P Selecta model 3000515) for 10 min, for each volume. After separation, the organic phases were collected, dried over anhydrous sodium sulphate and concentrated on a rotary evaporator (Büchi rotavapor R114 at 42± 0.5 ?C, without vacuum), to a final volume of 200 mm^3. The extracts were stored at -20 ºC until analysis by GC-O, GC-FID and GC-MS.

Gas Chromatography-Mass Spectrometry Analysis (GC–MS): The GC-MS analysis of dichloromethane brandy extracts were performed in a gas chromatograph– mass spectrometer (Magnum, Finnigan MAT, SanJose, CA, USA). The chromatograph was equipped with a fused silica capillary column of polyethylene glycol (DB-WAX, JW Scientific, Folsom, CA, USA), 30 m length, 0.25 mm i.d., 0.25 μm film thickness. Operating conditions were as follows: injector and interface temperature, 250 ºC; carrier gas helium (inlet pressure 12 psi and split ratio 1:60); oven temperature program: 3.5 ºC min^{-1} from 45 ºC (10 min isothermal) until 180 ºC and held at this temperature for 30 min, volume injected of 0.2–0.4 mm^3. The MS was operated in the

electron impact mode at 70 eV, scanning the range *m/z* 40–340.

Gas chromatography-olfactometry analysis (GC-O): GC-O analysis was carried out using an Agilent Technologies 6890 Series gas chromatograph (Wilmington, DE, USA) equipped with a fused silica capillary column of polyethylene glycol (DB-WAX, JW Scientific, Folsom, CA, USA), 30 m length, 0.32 mm i.d., 0.50 µm film thickness. The carrier gas was hydrogen with an average velocity of 62 $cm.sec^{-1}$. The extract was injected (~2 mm^3) on the injector (250 ºC) in split mode (split ratio ½). The oven temperature program was 45 ºC (for 4 min), then increased at 3.5 ºC to 55 ºC (1 min), then increased at 10 $ºC.min^{-1}$ to 85 ºC, then increased at 7.5 $ºC.min^{-1}$ to 100 ºC, increased at 10 $ºC.min^{-1}$ to 130 ºC (1min) then increased at 5 $ºC.min^{-1}$ to 210 ºC and held for this temperature for a further 30 min. At the end of the capillary, the effluent was split into the flame ionization detector (FID) – 250 ºC and the olfactory detection port (ODP, Gerstel, Germany). The ODP was held at 220 ºC to prevent any condensation of volatile compounds. Humidified air (17 $cm^3.min^{-1}$) was added at sniffing cone to reduce fatigue and drying of the judge's nasal passage.

For determination of odour-active compounds, it was used a panel composed by eight judges. Sniffers were seated in front of the sniffing port and were asked to smell the effluent of the column. An "olfactometer button" (Gerstel, Germany) was depressed when an aroma was detected. The beginning and the end of detected odour were recorded by an HP Pascal workstation. Judges also gave verbal descriptions of the perceived odors, which were recorded. Each extract of the brandy (CNGQL, CNGQF, CFLQL, CFLQF, CASTQL, CASTQF) that has showed important differences in aroma by sensory descriptive analysis (Caldeira *et al*., 2006b) was evaluated once by GC-O by each of the eight judges. Peaks were identified as odour active using the detection frequency method (Linssen *et al*., 1993; Pollien *et al*., 1997). A peak was reported as odour-active compound, if was detected by three or more judges in the same brandy.

Odourant identification: Odour-active compounds screened by GC-O were tentatively identified by comparing GC retention data of the different odorants with those of pure standard compounds (when available). The identities were thoroughly confirmed by comparison of Kovats retention index (KI) and MS fragmentation pattern with those of reference compounds or with mass spectra in the NIST and Wiley libraries.

The Kovats retention indices (RI) of unknown compounds were determined by injection of the sample with a homologous series of alkanes (C9-C30) by linear interpolation (Philips, 1989).

Odourant quantification: The concentrations of some odour-active volatiles in all of the 42 brandies were determined by gas chromatography coupled to a flame ionization detector (GC-FID) according to the methodology proposed by Caldeira *et al*. (2004).

Sensory analysis: The panel taster was composed by a group of tasters previously selected and trained (Caldeira *et al*., 1999). The reliability of the panel was evaluated as previously described (Caldeira *et al*., 2002) by introduction of replicates in all sessions. The tasters previously generated the sensory attributes (Caldeira *et al*., 1999), which included olfactory and oral attributes. The reliability of the attributes was evaluated (Caldeira *et al*., 2002) and some of the reliable olfactory attributes (fruity, vanilla, woody, spicy, toasted, dried fruits, smoke, green, tails) were studied in this work. The tasters were asked to scoring these attributes with a structured scale (0-no perception to 5-highest perception) and they profiled the aroma of the 42 brandies.

Statistical analysis: The slope between the intensity of olfactory attributes and the concentration of odourants were calculated by log linear regression, and the Pearson correlation coefficient (r) was determined

RESULTS AND DISCUSSION

Some details about the brandies, concerning its alcoholic strength, acidity and dry matter are shown in the TABLE I.

The odourants detected in the GC-O analysis are shown in TABLE II with the corresponding odour descriptors.

The extracts of brandies exhibited numerous aroma compounds that derived from the distillate and from wood during the ageing process. In this study it were detected 59 odourant compounds from different chemical families. Figure 1 shows the register of a sniffer (at the bottom) *versus* the FID gas chromatogram (in the top). It is evident that the most of the minor compounds plays an important role in the aroma. Several of the major compounds, such as 2-methyl-1-propanol (peak 6), ethyl lactate (peak a), 1-hexanol (peak b) produced weak or no olfactory responses. On the other hand, some of the intense olfactory responses were found in regions with weak FID signals (ethyl isobutyrate-peak 2, ethyl 2-methylbutyrate-peak 4, ethyl 3-methylbutyrate-peak 5, unknown peak 11, unknown peak 15 guaiacol-peak 24 and many others). Low or inexistent FID response of many potent odourants makes their identification difficult. Thus, some compounds remain unknown, possibly because until now the human nose is the most powerful detector. However, further research on the odourant identification is intended.

The studied brandies had been profiled by sensory descriptive analysis over an ageing period of five years (Caldeira *et al*., 2006b). According to these

TABLE I

Alcoholic strength, acidity and dry matter of 4-year aged wine brandies.
Teor alcoólico, acidez e extracto seco das aguardentes vínicas com 4 anos de envelhecimento.

Wooden barrel	Barrel toasting level	Alcoholic strength (%v/v)	Total acidity (g acetic acid.dm^{-3})	Volatile acidity (g acetic acid.dm^{-3})	Dry matter (g.dm^{-3})
CNE	QL	65.9	1.07	0.84	2.4
CNE	QL	70.7	1.11	0.89	2.7
CNE	QM	66.5	1.07	0.86	2.5
CNE	QM	70.8	1.35	1.10	2.8
CNE	QF	69.7	1.24	0.90	4.7
CNE	QF	70.0	1.41	1.18	3.3
CNF	QL	69.4	1.26	1.18	2.5
CNF	QL	67.0	0.99	1.03	2.3
CNF	QM	68.9	1.52	0.89	3.4
CNF	QM	69.4	1.14	0.79	3.3
CNF	QF	64.7	1.59	1.28	4.1
CNF	QF	69.5	1.33	0.88	3.7
CNG	QL	52.5	1.23	1.34	2.3
CNG	QL	69.2	1.22	1.09	3.3
CNG	QM	65.8	1.30	1.00	3.4
CNG	QM	67.3	1.25	0.99	3.6
CNG	QF	69.0	1.52	0.99	5.7
CNG	QF	71.6	1.43	1.23	5.1
CAST	QL	64.4	1.29	1.17	2.7
CAST	QL	67.4	1.17	1.10	2.7
CAST	QM	66.9	1.47	0.81	4.1
CAST	QM	67.5	1.39	0.97	3.9
CAST	QF	67.8	1.50	1.10	4.6
CAST	QF	67.4	1.41	1.06	4.1
CFA	QL	72.8	0.87	0.74	1.5
CFA	QL	69.3	0.94	0.80	1.5
CFA	QM	70.1	0.91	0.79	1.6
CFA	QM	71.2	0.87	0.75	1.5
CFA	QF	71.2	1.04	0.89	2.1
CFA	QF	72.1	0.99	0.85	2.1
CFL	QL	68.3	0.93	0.79	1.6
CFL	QL	69.1	0.86	0.73	1.5
CFL	QM	69.6	1.04	0.88	2.1
CFL	QM	70.5	0.94	0.81	1.8
CFL	QF	69.7	1.01	0.86	2.3
CFL	QF	69.7	1.08	0.94	2.2
CAM	QL	70.0	0.85	0.75	1.1
CAM	QL	68.2	0.83	0.74	1.1
CAM	QM	69.8	0.89	0.79	2.7
CAM	QM	70.4	0.90	0.78	1.5
CAM	QF	69.9	0.96	0.82	1.8
CAM	QF	70.6	0.93	0.80	1.6

TABLE II

Odourant compounds detected in the 4-year aged wine brandy extracts analysed by GC-O.
Compostos odorantes detectados nos extractos de aguardentes vínicas com 4 anos de envelhecimento, analisadas por GC-O.

Peak number	Compound	Retention index (RI)	Detection frequency						Odour descriptor
			CNGQL	CNGQF	CASTQL	CASTQF	CFLQL	CFLQF	
1	Unknown	870	6	4	8	7	8	8	fruity
2	Ethyl isobutyrate	961	7	8	8	8	8	8	fruity
3	Ethyl butyrate	1042	6	8	7	8	6	8	fruity
4	Ethyl 2-methylbutyrate	1058	8	8	8	7	8	8	fruity
5	Ethyl 3-methylbutyrate	1076	8	7	8	7	8	7	fruity
6	2-Methyl-1-propanol	1109	0	0	5	3	0	0	smoke, herbaceous
7	Isoamyl acetate	1140	0	0	0	0	4	0	fruity, banana
8	Unknown	1206	4	0	0	0	0	0	burnt, sweet, fruity
9	Isoamylic alcohols	1229	8	8	7	8	8	8	stinky, unpleasant
10	Ethyl hexanoate	1251	4	6	7	6	6	4	fruity, floral
11	Unknown	1330	7	7	6	6	5	7	dried fruit, medicament-like
12	*trans*-2-Hexen-1-ol	1420	0	0	0	0	0	7	cabbage, flowery
13	Ethyl octanoate	1446	7	8	8	7	6	6	flowery, fruity
14	Acetic acid	1464	6	4	8	8	8	6	vinegar
15	Unknown	1529	8	8	8	8	8	7	plastic, greasy
16	Linalol	1561	5	6	5	5	3	0	flowery, violets
17	Butanoic acid	1646	7	7	7	7	8	8	butter, cheese
18	3-Methylbutanoic acid	1689	8	8	7	8	8	8	stinky, cheese
19	Unknown	1728	4	0	4	0	0	3	unctuous/greasy; olive oil
20	Unknown	1811	0	0	4	0	3	4	flowery. petroleum, sweet
21	Unknown	1851	7	8	8	8	8	8	fruity, flowery, sweet
22	Hexanoic acid	1867	3	5	6	4	0	5	smoke, flowery, pharmacy
23	Unknown	1874	5	0	0	4	4	5	petroleum
24	Guaiacol	1885	8	4	7	6	6	6	smoky, medicinal-like
25	*trans*-β-Methyl-γ–octalactone	1914	4	6	0	0	6	6	sweet, flowery
26	2-Phenyl ethanol	1941	7	7	7	7	7	7	roses, flowery
27	Unknown	1969	4	0	4	0	4	0	smoke, burnt
28	*cis*-β- Methyl-γ–octalactone	1991	4	5	0	0	5	6	coconut, sweet
29	Unknown	1995	0	0	4	0	0	0	flowery, fruity
30	Unknown	2027	0	4	0	0	0	0	sweet, woody
31	4-Ethylguaiacol	2057	3	6	8	8	8	8	carnation, flowery
32	Diethyl malate	2065	6	6	4	3	0	4	sweet, sweet cotton
33	Unknown	2113	0	0	0	0	0	4	greasy, almond
34	Unknown	2128	0	6	0	0	0	4	not defined
35	Unknown	2133	0	0	0	4	0	0	flowery
36	4-Propylguaiacol	2139	5	6	8	5	6	6	burnt, flowery, smoke
37	Unknown	2163	5	3	5	4	4	5	sweetened, dried fruit, fruity
38	Eugenol	2194	6	7	6	5	6	7	flowery, clove
39	4-Ethylphenol	2201	3	5	6	7	5	5	animal, horse stable
40	Unknown	2220	0	0	4	0	5	0	smoke, burnt
41	Unknown	2225	0	7	0	5	0	0	burnt
42	Unknown	2230	8	4	6	5	5	7	curry, burned wood
43	Unknown	2257	4	0	0	0	0	0	smoke, clove
44	Unknown	2274	0	0	5	0	0	0	coconut
45	Unknown	2281	0	0	0	0	4	0	not defined
46	Syringol	2295	8	6	7	6	8	8	burnt, smoke, burned wood
47	Unknown	2312	5	5	7	4	4	4	burned grass, flowery, herbaceous, spicy,
48	4-Methylsyringol	2374	6	7	5	7	4	5	smoke, burned, flowery
49	Unknown	2431	0	0	0	5	0	0	greasy
50	Unknown	2465	7	5	7	6	8	5	smoke, chimney, burned, burned wood
51	Unknown	2486	0	5	0	0	3	3	smoke
52	Dodecanoic acid	2504	3	0	0	3	4	0	soap
53	4-Allylsyringol	2561	0	0	0	3	4	0	flowery, carnation, smoke, burned
54	Vanillin	2588	8	8	8	8	8	8	vanilla
55	Unknown	2601	0	5	0	0	0	0	burned, burned sugar, sweet
56	Unknown	2633	4	0	0	0	4	0	toasted, smoke
57	Unknown	2640	6	4	4	4	3	5	dirty clothes, unpleasant
58	Unknown	2727	0	4	0	0	0	0	burned, spicy
59	Unknown	2739	4	4	5	5	3	3	toasted, smoke, flowery

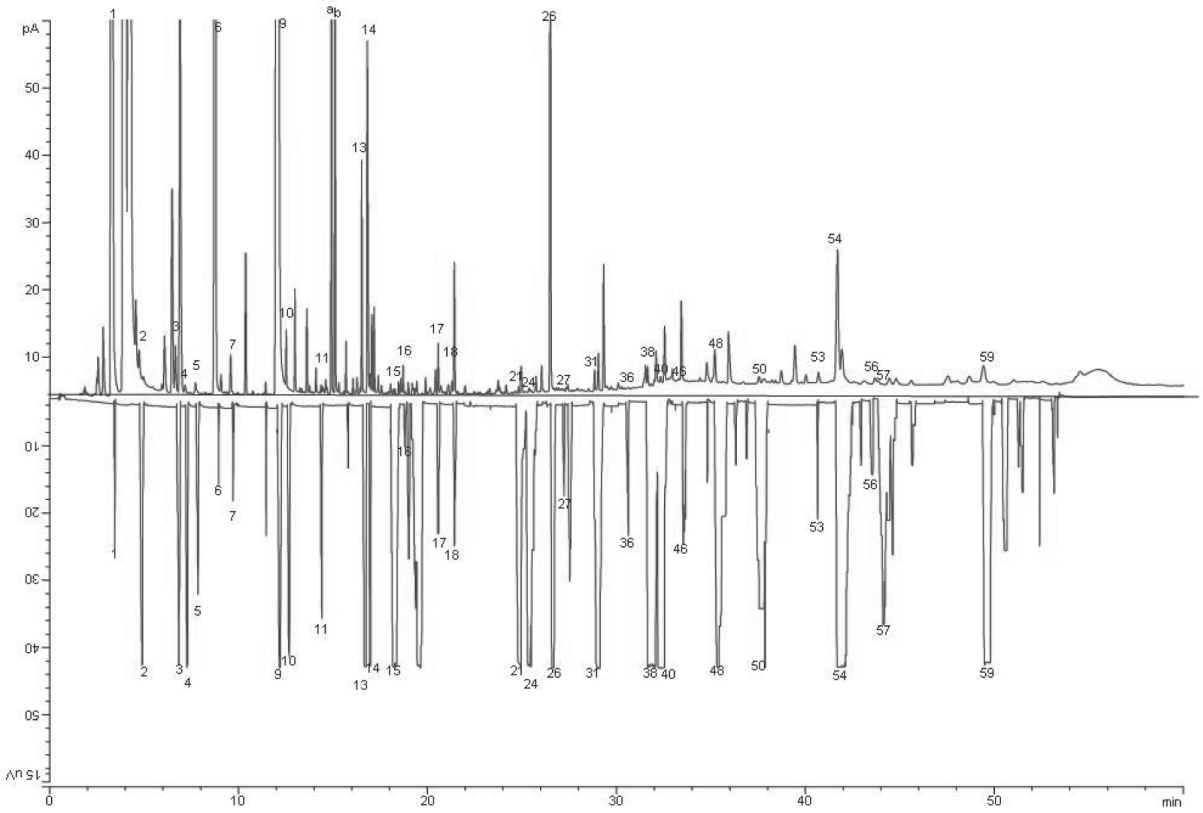

Fig. 1 – GC-FID chromatogram (in the top) *versus* a sniffer register (at the bottom) of a brandy extract (CASTQF), performed on DB-WAX column. Compounds numbers refer to TABLE II, however this sniffer did not detected the presence of all the peaks mentioned. Peaks a and b are not mention in the TABLE II because they don't present any odourant activity: a- ethyl L-lactate, b-1-hexanol.
Cromatograma GC-FID (na parte superior) versus um registo de um provador (na parte inferior) de um extracto de uma aguardente (CASTQF), obtidos numa coluna DB-WAX. Os números dos compostos referem-se ao QUADRO II, contudo este provador não detectou a presença de todos os compostos mencionados.Os picos a e b não são referidos no QUADRO II por não apresentarem qualquer actividade odorante: a- lactato de etilo, b-1-hexanol

results the most discriminating olfactory attributes were vanilla, woody, spicy, burned/toasted, dried fruits, smoke, fruity, green and tails. Nevertheless, the two last attributes were negatively correlated with the overall quality of the brandies while the first six are positively correlated with it (Caldeira *et al*., 2006b).

Thus, considering the profusion of odourants and the odour attributes of brandies (TABLE II) we have firstly focused the interest in the compounds that presented an odour attribute similar to those of high sensory discriminating power.

Vanilla attribute

Only the vanillin presented the descriptor vanilla (TABLE II). According to the GC-O results, this compound it is one of the most potent odourant of the analysed brandies. In fact, the levels found in the brandies (TABLE III) are higher than its threshold, which varies between 0.1 and 4 $mg.dm^{-3}$ (Maga, 1985; Boidron *et al*., 1988; Etievant, 1991) in water and alcoholic solutions. Moreover, it was found a linear relationship between the vanillin content and vanilla intensity of the 42 brandies analysed (TABLE IV).

Vanillin is extracted from oak and chestnut wood of the barrels, being its content dependent on the toasting levels of the barrels. During the ageing process, the vanillin level increased (Puech *et al.,* 1984; Quaresma, 2000; Canas, 2003) owing to the extraction process and the oxidation of coniferaldehyde (Puech *et al.,* 1984). This increment could explain the enhancement of vanilla attribute in older brandies (Leauté *et al.,* 1998; Caldeira *et al.*, 2006b).

Woody attribute

Several authors reported that the presence of β-metyl-γ-octalactone could be responsible for the woody and oak odourant notes in oak aged wines. The two isomers (*cis* and *trans*) of this compound also exist in the oak aged brandies at levels higher than their thresholds (0.064-0.79 $mg.dm^{-3}$ and 0.025-0.067 $mg.dm^{-3}$, respectively) determined by Otsuka *et al*. (1966) and Chatonnet (1995). In the chestnut wood aged brandies the two isomers are not present, in accordance with the chestnut wood composition (Clímaco and Borralho, 1996; Caldeira *et al*., 2006a). The GC-O results also pointed out the two isomers as potent odourants only in oak aged brandies (TABLE II). Nevertheless, the odour descriptors are coconut and sweet to the *cis* isomer and sweet and flowery to the *trans* isomer. There is no sniffer

TABLE III

Average levels of vanillin and syringol and average intensities of vanilla and woody attributes, in the 4-year aged wine brandies.
Teores médios de vanilina e siringol e valores médios da intensidade dos descritores baunilha e madeira, determinados nas aguardentes vínicas com 4 anos de envelhecimento.

Wooden barrel	Barrel toasting level	Vanillin ($mg.dm^{-3}$ EtOH 100%)	Intensity of vanilla attribute	Syringol levels ($mg.dm^{-3}$ EtOH 100%)	Intensity of woody attribute
CNE	QL	2.62	1.1	0.28	1.4
		4.83	1.1	0.31	1.9
	QM	6.43	1.5	0.26	1.7
		4.48	1.1	0.27	1.5
	QF	20.05	2.3	0.65	2.9
		15.53	2.2	0.43	2.9
CNF	QL	6.04	1.5	0.44	1.9
		4.88	1.4	0.35	1.9
	QM	9.45	2.1	0.38	2.6
		8.82	2.2	0.35	2.6
	QF	12.15	1.6	0.51	2.5
		15.42	2.2	0.67	2.6
CNG	QL	4.20	1.5	0.28	1.6
		6.74	1.7	0.25	2.0
	QM	7.88	1.8	0.28	1.4
		10.49	1.9	0.37	1.8
	QF	15.55	2.2	0.55	2.8
		15.07	2.3	0.37	2.4
CAST	QL	3.67	1.2	0.34	1.8
		2.52	1.3	0.26	1.6
	QM	17.48	2.0	0.28	2.8
		16.89	2.6	0.30	2.7
	QF	17.35	1.9	0.43	2.4
		12.70	2.6	0.39	2.9
CFA	QL	4.97	1.2	0.31	1.5
		4.89	0.7	0.38	1.2
	QM	11.23	0.4	0.36	1.5
		5.38	1.1	0.32	1.6
	QF	16.92	2.0	0.49	2.2
		13.75	2.3	0.43	2.3
CFL	QL	4.66	1.1	0.28	1.7
		4.09	0.6	0.23	1.4
	QM	10.92	1.5	0.43	2.2
		10.64	1.2	0.34	1.8
	QF	14.91	2.4	0.58	2.6
		12.63	0.8	0.45	1.8
CAM	QL	2.83	0.3	0.24	1.1
		4.40	1.4	0.37	1.3
	QM	9.09	0.7	0.45	1.1
		11.31	1.7	0.49	1.6
	QF	13.50	2.0	0.68	1.8
		11.62	2.1	0.68	2.2

TABLE IV

Relationships between vanillin and syringol levels and vanilla and woody intensities, in the forty-two 4-year aged wine brandies analysed.
Correlações entre os teores de vanilina e siringol e as intensidades dos descritores baunilha e madeira, determinadas nas 42 aguardentes vínicas com 4 anos de envelhecimento.

	Vanilla intensity (I) and vanillin level (S)	Woody intensity (I) and syringol level (S)	Woody intensity (I) and vanillin level (S)
Linear regression between logarithm of attribute intensity [Ln (I)] and the logarithm of the compound level [Ln (S)]	Ln(I)=0.48Ln(S)-0.65 [r=0.58]	Ln(I)=0.44Ln(S)+1.07 [r=0.46]	Ln(I) = 0.34Ln(S) - 0.09 [r=0.72]
Linear regression between the attribute intensity (I) and the logarithm of the compound level (Ln (S)	I=0.69Ln(S)+0.13 [r=0.67]	I=0.85Ln(S)+2.85 [r=0.46]	I = 0.68Ln(S) + 0.55 [r=0.73]
Linear regression between the attribute intensity (I) and the compound level (S)	I=0.08S+0.78 [r=0.69]	I=1.95S+1.21 [r=0.44]	I = 0.08S + 1.16 [r=0.77]

TABLE V

Average levels of eugenol and 4-allylsyringol and average intensities of spicy and smoke attributes, in the 4-years wine aged brandies.
Teores médios de eugenol e 4-alilsiringol e valores médios da intensidade dos descritores especiarias e fumo, determinados nas aguardentes vínicas com 4 anos de envelhecimento.

Wooden barrel	Barrel toasting level	Eugenol ($mg.dm^{-3}$ EtOH 100%)	Intensity of spicy attribute	4-Allylsyringol ($mg.dm^{-3}$ EtOH 100%)	Intensity of smoke attribute
CNE	QL	0.39	0.6	0.22	0.9
		0.94	0.4	0.52	0.9
	QM	0.54	0.1	0.31	0.6
		0.56	0.8	0.23	0.8
	QF	1.05	1.0	0.58	1.2
		0.62	1.5	0.46	1.6
CNF	QL	0.98	0.3	0.51	0.4
		0.52	0.3	0.31	0.9
	QM	0.90	1.1	0.37	1.1
		0.51	0.9	0.43	1.0
	QF	0.86	1.1	0.59	1.4
		0.90	1.4	0.60	1.3
CNG	QL	0.40	0.8	0.15	0.9
		0.52	1.2	0.19	0.6
	QM	0.63	0.7	0.34	0.9
		0.52	0.6	0.37	0.5
	QF	1.07	1.5	0.51	0.9
		0.85	0.8	0.51	0.7
CAST	QL	0.86	1.0	0.42	0.9
		0.63	0.3	0.29	0.6
	QM	1.18	1.1	0.66	1.0
		1.09	1.1	0.54	0.6
	QF	0.91	0.9	0.54	0.9
		0.70	0.9	0.41	0.9
CFA	QL	0.33	0.9	0.17	0.1
		0.38	0.4	0.18	1.0
	QM	0.50	0.3	0.24	0.6
		0.45	0.3	0.14	0.3
	QF	0.95	1.4	0.01	1.4
		0.71	0.6	0.42	0.9
CFL	QL	0.44	0.7	0.23	0.4
		0.39	0.4	0.20	0.9
	QM	0.52	0.9	0.37	1.3
		0.52	0.4	0.24	0.9
	QF	0.74	1.1	0.35	0.9
		0.59	0.3	0.34	0.9
CAM	QL	0.96	0.0	0.29	0.5
		1.14	0.6	0.27	0.4
	QM	1.31	0.0	0.34	1.1
		1.32	1.4	0.35	0.5
	QF	1.40	1.6	0.42	1.0
		1.24	1.0	0.41	1.3

TABLE VI

Relationships between eugenol, syringol and 4-allylsyringol levels and the spicy and smoke intensities, in the forty-two 4-year aged wine brandies analysed.
Correlações entre os teores de eugenol, siringol e 4-alilsiringol e as intensidades dos descritores especiarias e fumo, determinadas nas 42 aguardentes envelhecidas.

	Spicy intensity (I) and eugenol level (S)	Smoke intensity (I) and syringol level (S)	Smoke intensity (I) and 4-alylsyringol level (S)
Linear regression between logarithm of attribute intensity [Ln (I)] and the logarithm of the compound level [Ln (S)]	Ln (I)=0.74Ln(S)-0.09 [r=0.48]	Ln(I) = 0.65 Ln(S) + 0.40 [r=0.41]	Ln(I) = 0.07Ln(S) - 0.16 [r=0.10]
Linear regression between the attribute intensity (I) and the logarithm of the compound level (Ln (S)	I=0.40Ln(S)+0.92 [r=0.37]	I = 0.54Ln(S) + 1.38 [r=0.50]	y = 0.01Ln(x) + 0.8738 [r=0.03]
Linear regression between the attribute intensity (I) and the compound level (S)	I=0.55S+0.36 [r=0.37]	I = 1.27S + 0.36 [r=0.50]	I = 0.69S + 0.61 [r=0.32]

mention of woody or oak attribute for these isomers. Actually, it was not found any relationship between the levels of the two isomers and the woody intensity. So, it seems that other compound or compounds should be responsible for the woody note in the brandies. On the other hand, the results of TABLE II show that the woody descriptor is used for syringol and for three unknown compounds (RI 2027, RI 2230, RI 2465). Syringol is a wood derived compound resulting from the thermal decomposition of lignins (Fengel and Wegener, 1989) and the level of this volatile phenol also increases with heat treatment of the barrels (Maga, 1985; Dubois, 1989; Artajona, 1991; Chatonnet, 1995; Caldeira *et al*., 2006a).

The relationship found between syringol level and woody intensity (TABLE IV) presents a low correlation coefficient (r=0.46), that could indicate the contribution of other compounds to this descriptor. So, it was searched the correlation between the vanillin levels and the woody attribute (TABLE IV) and it was found a high linear correlation (r=0.77). Biau (1997) reported similar results with Armagnac brandies**.**

Spicy attribute

The spicy attribute is usually referred in the sensory analysis of brandies (Léauté *et al*., 1998; Caldeira *et al*., 2002; Bordeu *et al*., 2004; Caldeira *et al*., 2006b) and of other alcoholic beverages aged in wood, like wine (Genovese *et al*., 2007) and whisky (Piggot and Jardine, 1979).

The results presented in the TABLE II reveal that the spicy descriptor and the clove descriptor are used for three unknown compounds (RI 2257, RI 2312, RI 2727) and for eugenol. The levels of the eugenol in the brandies (TABLE V) are higher than its thresholds (0.007 – 0.015 mg.dm^{-3}) reported by Lehtonen (1982), Boidron *et al.*, (1988) and Etiévant (1991).

The eugenol is a wood derived compound proceeding from wood lignins´decomposition (Fengel and Wegener, 1989), which content increases along with the wood heat treatment intensity (Maga, 1985; Dubois, 1989; Artajona, 1991; Chatonnet, 1995; Caldeira *et al*., 2006a). Therefore, the highest contents of eugenol were found in brandies aged in barrels that were submitted to the strongest toasting level (Caldeira, 2004).

It was found a weak relationship between eugenol level and spicy intensity (TABLE VI), expressed by a correlation coefficient of 0.48, that suggests the possible contribution of other compounds to this attribute.

Smoke attribute

Smoke is another sensory attribute that permits the discrimination of the brandies resulting from different ageing conditions, namely the wood origin and the heat treatment of the barrels (Caldeira *et al*., 2002; Caldeira *et al*., 2006b). This attribute is positively correlated with the overall quality of the brandies (Caldeira *et al*., 2006b).

GC-O results (TABLE II) demonstrate that smoke attribute is associated with hexanoic acid, guaiacol, 4-propylguaiacol, syringol, 4-methylsyringol; 4-allylsiringol and with seven unknown compounds (RI 1969, RI 2220; RI 2257; RI 2465; RI 2486; RI 2633, RI 2739). Guaiacol, 4-propylguaiacol and 4-methylsyringol were identified by GC-MS but their levels were lower than the quantification limits. Regarding syringol, 4-allylsyringol and hexanoic acid it was found an interesting linear correlation (TABLE VI) between the syringol level and the smoke attribute (r=0.50), and both increased with the wood heat treatment intensity (Caldeira 2004; Caldeira *et al*., 2006a). The level of 4-allylsyringol has a low contribution (r=0.32) to the smoke attribute (TABLE VI).

Dried fruits attribute

Dried fruits attribute was mentioned in GC-O results for three unknown compounds (RI 1330, RI 2113, RI 2163). This attribute is also positively correlated with the overall quality of the brandies (Caldeira *et al.,* 2006b). So, further research is needed in order to identify these compounds related with dried fruits note.

Nevertheless, the furanic compounds were sometimes associated with dried fruits attribute, namely almond and toasted almond (Lee *et al.*, 2000), and with toasted and caramel attributes (Zea *et al*., 2007; Díaz-Maroto *et al.,* 2008). Moreover, in the analysis of toasted almonds some furanic compounds, such as furfural, 5-methylfurfural and HMF presented the major contribution to the aroma of this dried fruit (Vázquez-Araújo *et al.*, 2008). So, using the indirect approach it was found an important correlation (TABLE VIII) between the levels of furfural, 5-methylfurfural and HMF (TABLE VII) and the dried fruits attribute (r=0.58, r=0.58, r=0.69 respectively). These results are in accordance with those of Janácová *et al.* (2008) that pointed out these furanic compounds as key odourants of Slovak brandies.

The disagreement between the results obtained by the two approaches could be due to the fact, that in GC-O analysis the compounds are assessed separately and the behaviour of the compounds in mixture could be different (Laing and Panhuber, 1979).

Toasted attribute

Toasted or burned attribute are referred for many unknown compounds (RI 1206, RI 1969, RI 2220, RI 2225, RI 2295, RI 2465, RI 2601, RI 2633, RI 2727, RI 2739) and for 4-propylguaiacol, syringol, 4-methylsyringol and 4-allylsyringol. In the sensory analysis, it was found an important correlation between the syringol and 4-allylsyringol levels and the toasted attribute (r=0.44 and r=0.56, respectively).

TABLE VII

Average levels of furanic aldehydes and average intensities of dried fruits and toasted attributes, in the 4-year aged wine brandies.
Teores médios de aldeídos furâncios e valores médios da intensidade dos descritores frutos secos e torrado, determinados nas aguardentes vínicas com 4 anos de envelhecimento.

Wooden barrel	Barrel toasting level	Furfural ($mg.dm^{-3}$ EtOH 100%)	5-Methylfurfural ($mg.dm^{-3}$ EtOH 100%)	HMF ($mg.dm^{-3}$ EtOH 100%)	Intensity of dried fruits attribute	Intensity of toasted attribute
CNE	QL	9.36	0.47	4.81	0.1	0.7
		22.04	1.31	12.48	1.0	1.5
	QM	24.40	2.19	12.50	0.4	0.7
		15.65	1.22	9.64	0.6	1.3
	QF	118.04	10.33	37.88	1.0	2.6
		52.87	5.29	19.70	1.6	2.3
CNF	QL	20.64	1.34	18.19	0.4	0.9
		14.41	0.87	8.78	0.9	1.4
	QM	40.17	3.41	19.54	1.3	1.6
		36.23	4.55	16.40	1.3	2.3
	QF	79.54	7.46	34.46	1.5	1.9
		66.13	7.16	29.76	1.5	2.0
CNG	QL	14.91	0.63	9.01	0.6	1.1
		23.72	1.26	12.88	0.6	1.5
	QM	27.50	2.10	17.31	0.7	1.5
		40.90	3.00	25.35	0.6	1.3
	QF	130.96	11.80	40.95	1.8	2.6
		64.89	6.39	27.82	0.9	1.5
CAST	QL	3.55	0.28	7.59	0.3	1.5
		3.22	0.31	6.17	0.3	1.1
	QM	44.79	6.06	28.62	1.8	2.1
		9.62	3.24	18.28	1.1	1.9
	QF	43.32	4.25	19.71	0.5	1.9
		13.12	1.40	13.51	1.6	1.9
CFA	QL	16.26	0.89	8.55	0.6	0.5
		17.28	0.87	8.31	0.4	1.0
	QM	47.60	3.79	18.96	0.4	0.9
		11.38	1.08	7.96	0.3	0.8
	QF	66.34	6.43	26.73	1.4	2.0
		41.30	3.96	18.32	0.6	1.5
CFL	QL	10.67	0.70	5.44	0.9	0.6
		9.73	0.80	5.56	0.3	0.5
	QM	27.68	3.17	11.94	0.6	1.9
		31.72	3.30	13.51	0.4	1.4
	QF	53.64	6.23	18.95	1.0	1.7
		46.97	6.53	16.76	0.3	0.6
CAM	QL	4.20	0.42	3.06	0.1	0.0
		12.04	0.89	5.28	0.3	0.3
	QM	22.56	2.57	9.69	0.1	0.6
		32.06	3.68	14.41	1.2	1.4
	QF	52.30	6.47	18.21	0.5	0.9
		42.44	5.17	18.44	0.4	1.4

TABLE VIII

Relationships between furanic aldehydes levels and the dried fruits intensities, in the forty-two 4-year aged wine brandies analysed.
Correlações entre os teores de aldeídos furânicos e as intensidades do descritor frutos secos, determinadas nas 42 aguardentes vínicas com 4 anos de envelhecimento.

	Dried fruits (I) and furfural level (S)	Dried fruits (I) and 5-methylfurfural level (S)	Dried fruits (I) and HMF level (S)
Linear regression between logarithm of attribute intensity [Ln (I)] and the logarithm of the compound level [Ln (S)]	Ln (I)=0.49Ln(S)-2.10 [r=0.58]	Ln(I) = 0.42 Ln(S) - 0.85 [r=0.57]	Ln(I) = 0.85Ln(S) - 2.73 [r=0.69]
Linear regression between the attribute intensity (I) and the logarithm of the compound level (Ln (S)	I=0.30Ln(S)-0.21 [r=0.54]	I = 0.28Ln(S) + 0.54 [r=0.56]	I = 0.53Ln(S) + 0.62 [r=0.65]
Linear regression between the attribute intensity (I) and the compound level (S)	I=0.01S+0.42 [r=0.55]	I = 0.10S + 0.42 [r=0.58]	I = 0.04S + 0.18 [r=0.67]

TABLE IX

Relationships between furanic aldehydes levels and the toasted intensities, in the forty-two 4-year aged wine brandies analysed.
Correlações entre os teores de aldeídos furânicos e as intensidades do descritor torrado, determinadas nas 42 aguardentes vínicas com 4 anos de envelhecimento.

	Toasted (I) and furfural level (S)	Toasted (I) and 5-methylfurfural level (S)	Toasted (I) and HMF level (S)
Linear regression between logarithm of attribute intensity [Ln (I)] and the logarithm of the compound level [Ln (S)]	Ln (I)=0.27Ln(S)-0.69 [r=0.48]	Ln(I) = 0.27 Ln(S) - 0.01 [r=0.53]	Ln (I)=0.56Ln(S)-1.26 [r=0.67]
Linear regression between the attribute intensity (I) and the logarithm of the compound level (Ln (S)	I=0.42Ln(S)-0.00 [r=0.59]	I = 0.39Ln(S) + 1.04 [r=0.62]	I=0.78Ln(S)-0.69 [r=0.76]
Linear regression between the attribute intensity (I) and the compound level (S)	I=0.01S+0.86 [r=0.64]	I = 0.14S + 0.86 [r=0.65]	I=0.05S+0.55 [r=0.73]

TABLE X

Average level of *trans*-2-hexenol and average intensities of green and tail attributes, in the 4-year aged wine brandies.
Teores médios de trans-2-hexenol e valores médios da intensidade dos descritores herbáceo e caudas, determinados nas 42 aguardentes vínicas com 4 anos de envelhecimento

Wooden barrel	Barrel toasting level	*trans*- 2-Hexenol ($mg.dm^{-3}$ EtOH 100%)	Intensity of green attribute	Intensity of tails attribute
CNE	QL	0.66	0.6	0.1
		0.77	0.5	0.1
	QM	0.76	0.7	0.1
		0.59	0.8	0.4
	QF	0.74	0.6	0.2
		0.71	0.0	0.1
CNF	QL	0.88	0.9	0.2
		0.65	0.4	0.0
	QM	0.65	0.3	0.0
		0.66	0.3	0.0
	QF	0.63	0.4	0.3
		0.67	0.1	0.2
CNG	QL	0.55	0.4	0.1
		0.68	0.2	0.1
	QM	0.67	0.4	0.3
		0.75	0.0	0.1
	QF	0.69	0.0	0.0
		0.67	0.0	0.0
CAST	QL	0.67	0.1	0.6
		0.70	0.9	0.5
	QM	0.77	0.0	0.0
		0.81	0.1	0.0
	QF	0.64	0.0	0.0
		0.72	0.0	0.0
CFA	QL	0.62	0.7	0.3
		0.67	1.0	0.9
	QM	0.70	1.1	0.9
		0.59	1.0	1.0
	QF	0.63	0.3	0.0
		0.65	0.3	0.0
CFL	QL	0.70	0.9	0.7
		0.69	1.1	0.5
	QM	0.73	0.0	0.0
		0.62	0.7	0.3
	QF	0.63	0.0	0.2
		0.67	0.0	0.3
CAM	QL	0.61	0.8	0.9
		0.73	0.9	0.9
	QM	0.70	0.8	1.0
		0.68	0.8	0.0
	QF	0.62	0.9	0.4
		0.60	0.3	0.0

Hence, these results confirmed the sensory importance of volatile phenols in the aged brandies and are coherent with the GC-O results of oak wood extracts, which indicate several phenols as aroma-active compounds derived from oak woods (Díaz Maroto *et al.,* 2008).

The furanic aldehydes also presented high correlation coefficients with toasted attribute (TABLE IX). Therefore, further research must be done in order to study the behaviour of these compounds in the mixtures.

Fruity attribute

Fruity is an important sensory attribute for the younger brandies (Léauté *et al*.. 1998), which intensity decreases over the ageing time (Caldeira *et al*.. 2006b).

In the GC-O results (TABLE II) fruity is assigned to seven esters (ethyl isobutyrate, ethyl butyrate, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate, isoamyl acetate, ethyl hexanoate, ethyl octanoate) and to five unknown compounds (RI 870, RI 1206, RI 1851, RI 1995, RI2163). Some of these esters were identified as odour active compounds in brandies without ageing (Leclaire *et al*., 1999). However, it was not found any significant correlation between the levels of these esters and the fruity intensity. This discrepancy between the results from two approaches could be also due to the different behaviour of the compounds in mixtures (Laing and Panuber, 1979). Besides, it is known that the solubility of the esters is strongly influenced by the wood extractives (Piggot *et al*., 1992; Conner *et al*., 1996).

Green attribute

The green or herbaceous attribute was pointed out to 2-methyl-1-propanol and to the *trans*-2-hexenol (TABLE II). Nevertheless, there is no significant correlation between the levels of these alcohols (TABLE X) and the green attribute intensity in the analysed brandies.

Tails attribute

During the distillation of wine, the obtained distillate is split in three different fractions, the heads, the heart and the tails, that present a very different volatile composition (Onishi *et al.,* 1978; Léauté, 1990). The last one exhibit an unpleasant odour and it must not be included in the final brandy. Concerning the sensory evaluation of the brandy (Peña y Lillo *et al*., 2005) the detection of this odour contributes to the decrease of brandy' s overall quality (Caldeira *et al*., 2006b).

In the analysed brandies this attribute is very low or absent (TABLE X) and in the GC-O results (TABLE II) it was not found this descriptor for any compound. However, it was searched the relationship between the tails intensity and the levels of some acids (acetic, hexanoic, decanoic, dodecanoic), which also presented unpleasant odours, but it was not established any correlation.

CONCLUSIONS

29 odour active compounds were identified in the GC-O analysis of dichloromethane extracts of 4-years old Lourinhã brandies: ethyl isobutyrate, ethyl butyrate, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate, 2-methyl-1-propanol, isoamyl acetate, isoamylic alcohols (2+3-methyl-1-butanol), ethyl hexanoate, *trans*-2-hexen-1-ol, ethyl octanoate, acetic acid, linalool, butanoic acid, 3-methylbutanoic acid, hexanoic acid, guaiacol, *trans*-β–methyl–γ–octalactone, 2-phenyl ethanol, *cis*-β–methyl–γ–octalactone, 4-ethylguaiacol, diethyl malate, 4-propylguaiacol, eugenol, 4-ethylphenol, syringol, 4-methylsyringol, dodecanoic acid, 4-allylsyringol and vanillin. Some of these compounds proceed from the distillate and others are extracted from the wood.
The calculation of correlation coefficient between sensory and chemical data confirmed the sensory relevance of some compounds, which are extracted from the wood, namely vanillin and volatile phenols. Vanillin plays an important role in vanilla and woody attributes of the brandies. The volatile phenols are mainly related with smoke, spicy and also woody attributes of the aged brandies. This approach also pointed out the relevance of furanic aldehydes to dried fruits and toasted attributes of the brandies.

These results are encouraging for further research on the sensory properties of the identified odourants when they are mixed. Furthermore, a new task must be done in order to search the identity of the unknown odourants compounds.

ACKNOWLEDGMENT

The authors gratefully acknowledge the sniffers (Ana Mateus, Filomena Alemão, Filomena Duarte, Francisco Vicente, Luisa Avelar, Margarida Couto, Nilza Eiriz, Pedro Belchior), the tasting panel (Conceição Leandro, Estrela Carvalho, Francisco Carlos, Francisco Vicente, Hugo Quaresma, Isabel Pereira, João Braga, João Henriques, João Melícias, M.ª Lucinda Abrantes, Manuel Bento, Maria Dinis, Pedro Belchior, Pedro Corrêa, Rui Pereira, Sara Canas) and Francisco Vicente for their help in on GC-O analysis, sensory analysis and chromatographic analysis, respectively. The authors thank the financial support of PIDDAC 709/99 and PARIPI-Projecto A/2000 and the manuscript revision by Sara Canas.

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