Comparison of Volatile Compounds in Two Brandies Using HS-SPME Coupled with GC-O, GC-MS and Sensory Evaluation

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The aim of this study was to compare the volatile compounds between Changyu XO and Hennessy XO. Sensory evaluation was performed by a panel of tasters. Qualitative and semi-quantitative analysis was achieved by headspace solid phase micro-extraction (HS-SPME), coupled with gas chromatography-mass spectrometry (GC-MS) and gas chromatography-olfactometry (GC-O). A total of 160 volatile compounds were identified in the two brands of brandy. Of these, 118 compounds were common to both Changyu XO and Hennessy XO; 18 compounds were specific to Changyu XO and 24 were specific to Hennessy XO. A total of 85 aroma compounds responsible for brandy flavour were identified by GC-O, of which 68 were common to both brands, while seven and ten were specific to Changyu XO and Hennessy XO, respectively. The study provided detailed information about the compounds responsible for the characteristic flavour of specific brandies. According to statistical analysis, significant differences were recorded between Changyu XO and Hennessy XO. Most volatile compounds in Changyu XO occurred at lower concentrations than those in Hennessy XO. Based on sensory evaluation analysis, the floral, alcohol and rancid aroma descriptors achieved higher scores in Changyu XO and Hennessy XO, while the lime aroma seemed specific to Hennessy XO. Herb and almond aromas were specific to Changyu XO.

INTRODUCTION

Hennessy XO, a typical French spirit liquor, is famous for its premium quality and Changyu XO, a well-known Chinese brandy, is produced in Yantai (China). Yantai is located at the same latitude as Bordeaux (France) and is one of the largest grape growing regions in Asia. With brandy having become more popular in China over recent decades, its characteristic and distinct flavour began to receive closer scrutiny from the consumer.

In general, brandy is a distilled product of fermented grapes matured in oak barrels, with hundreds of volatile compounds developing over a period. Several authors (Onishi et al., 1978; Pérez-Coello et al., 1995; Caldeira et al., 2002; Ledauphin et al., 2004; Caldeira et al., 2006; Go'mez-Mı'guez et al., 2007) have studied the chemical modifications in different brandies. The volatile compounds include various chemical classes, such as hydrocarbons, alcohols, esters, acids, ketones, aldehydes, and nitrogen- and sulphur-containing compounds. These are all volatile compounds derived from each successive stage of the production process and contribute to the aroma of brandies. Ledauphin et al. (2004) identified more than 300 volatile compounds in freshly distilled Cognac and Calvados by preparative separations coupled with GC-MS. Ferrari et al. (2004) identified 150 volatile compounds in freshly distilled Cognac by GC-MS. Of these, 34 are responsible for the odours. Zhao et al. (2009b) identified 144 volatile compounds in Changyu and Hennessy brandies by HS-SPME coupled with GC-MS.

Volatile compounds are produced by grapes and in wines during fermentation, distillation and ageing in oak barrels (Milicevic et al., 2002; Ferrari et al., 2004; Go'mez-Mı'guez et al., 2007; Van Jaarsveld et al., 2009a,b,c). Hydrocarbons are formed by the raw materials and the original process (Ferrari et al., 2004; Fan & Qian, 2006). Fusel alcohols, the most abundant alcohols, are formed during fermentation from amino acids through decarboxylation and deamination (Ferrari et al., 2004; Fan & Qian, 2006). Esters, mainly formed during fermentation, constitute the most abundant chemical class of aroma compounds in brandies (Ferrari et al., 2004; Fan & Qian, 2006). Ketones and aldehydes are derived from the fermentation and distillation processes (Fan & Qian, 2006). Some aroma compounds may form by direct extraction of molecules from the oak and by degradation of oak macromolecules into aroma compounds (Ferrari et al., 2004; Fan & Qian, 2006).

The aim of this study was to compare the volatile compounds of Changyu XO and Hennessy XO by GC-MS coupled with GC-O and sensorial analysis to explore the key components resulting in the volatile difference between the two brands.

MATERIALS AND METHODS Brandy samples

Three Changyu XO samples were provided by the Changyu

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Pioneer Wine Co. Ltd. (Yantai, China), which included CXO1 (bottledin2000,730mL,40%v/vethanol),CXO2(bottledin2008, 730 mL, 40% v/v ethanol) and CXO3 (bottled in 2004,730 mL, 40% v/v ethanol). Three Hennessy XO samples were purchased from a local store; these included HXO1 (bottled in 1998, 700 mL, 40% v/v ethanol), HXO2 (bottled in 2005, 700mL, 40% v/v ethanol) and HXO3 (bottled in 2006, 700 mL, 40% v/v ethanol).

Reagents

Sodium chloride was purchased from China National Pharmaceutical Ground Corporation (Shanghai, China). Methanol was purchased from Merck Chemical Co. Inc. (Shanghai, China). All standards, including 3-octanol (inner standard) and the C7 to C30 alkanes were obtained from Aldrich-Sigma Chemical Co. (Shanghai, China).

Sensory analysis

Sensory evaluation was performed by a panel of 12 members (six males and six females), trained for primary sensory analyses. The aroma descriptors previously selected by the panel were e.g. floral, woody, rancid, caramel, burned/toasted, rose, butter, fruity, green, tails and glue/varnish. Brandy quality was assessed according to odour and aroma balance. The panel scored the samples according to a structured scale (0, no perception, 5 to 10, 10 to 15, 15 to 20, and above 20).

HS-SPME parameters

The operating factors for GC-MS analysis (Howard *et al.*, 2005), including extraction time (10 min, 20 min, 30 min and 40 min), extraction temperature (30°C, 40°C, 50°C and 60°C), ethanol concentration (5%, 10%, 15% and 35%, v/v), and salt added (0.5 g, 1.0 g, 1.5 g and 2.0 g), were optimised by the 4⁵ four-level full-factorial design (FFD). The best condition was at 50°C for 30 min, with 2.0 g salt added and the alcohol content adjusted to 10% (v/v).

HS-SPME analysis

A 50/30 μ m DVB/CAR/PDMS fibre (Supelco, Inc., Bellefonte, PA) was used for aroma extraction. Each liquor sample was diluted with deionised water to a final concentration of 10% (v/v) ethanol. The total volume [5 mL solution and 5 μ L inner standard (3-octanol, 640.56 mg/L)], was transferred into a 20 mL vial. The diluted sample was saturated with sodium chloride and the vial tightly capped with a silicon septum. The sample was equilibrated at 50°C in a thermostatic bath for 10 min and extracted at the same temperature for 30 min, under stirring. After extraction, the fibre was inserted into the injection port of the GC (250°C).

GC-MS analysis

GC-MS analysis was performed using a Shimadzu GC 2010 mass selective detector. Samples were analysed on a DB-Wax column. The carrier gas was helium at a constant flow rate of 1.2 mL/min (39 cm/s). The oven temperature was kept at 50°C for two min, followed by an increase of 4°C/min to a final temperature of 250°C and kept at the final temperature for three min. The splitless injector port was set to 250°C. The mass spectrometer was operated with the electron impact (EI) at 70 eV as ionisation potential. The injector temperature was kept constant at 250°C. The transfer line was kept at 250°C. A mass range from m/z 32-500 (2 scan/s) was recorded in full

scan mode, without solvent delay.

Qualitative and quantitative analysis *Qualitative analysis*

Mass spectra of unknown compounds were compared with those in the National Institute of Standards and Technology (NIST) 98 MS database or a "private" database. Retention indices (RI) were calculated in accordance with a modified Kovats method (Ledauphin *et al.*, 2004). A standard mixture of paraffin homologues C_7 to C_{30} was prepared. The sample and the hydrocarbon standard mixture were co-injected into the GC, and the retention times were used to calculate the RI. Identification of unknown compounds was achieved by comparing the mass spectra and RI of the standards or retention indices from literature (RIL) (Fan and Qian, 2006).

Semi-quantitative analysis

Semi-quantitative analysis was used to analyse the volatiles in brandy. An internal standard solution (3-octanol, 640.56 mg/L) was individually prepared in ethanol prior to dilution. Selective ion monitoring (SIM) was used for the integrations of all chromatogram peaks. And the semi-quantitative concentrations of volatiles in brandies were calculated according to the method proposed by Zhao *et al.* (2009b), as follows:

Semiquantitative	concentrations	=	peak area	\times	IS
concentration			I S peak area		

Statistics analysis

Mean peak areas and standard deviations from replicate analyses were calculated and treatment variables were compared using the Student T test (Steel & Torrie, 1980).

RESULTS AND DISCUSSION

Sensory analysis

The tasting panel provided an assessment of brandy samples. The observed relative standard deviations (RSD) from the mean aroma descriptor intensities varied within the range of 2.0 to 4.0%. The aroma profiles (Fig. 1) are characteristic for each brandy sample. The three Hennessy XO samples showed similar profiles in which the floral, alcohol and rancid aroma descriptors had higher scores, followed by fruity, grass, hay, lime, tails, and roast aromas. As for three Changyu samples, their higher scores were the floral, alcohol and rancid aromas, followed by fruity, grass, hay, tails, herb, almond, and roast aromas. The lime aroma seemed specific to Hennessy XO samples, whereas the herb and almond aromas were specific to Changyu XO samples. In addition, the greater differences were found in the aroma profiles of the three Changyu samples.

Identification of aroma volatile compounds

The GC-MS analysis was performed to identify the volatile compounds in the six brandies. The total chromatograms of volatiles in Changyu XO and Hennessy XO are shown in Fig. 2. The common volatiles in Changyu XO and Hennessy XO are listed in Table 1, whereas, the specific compounds in these samples are presented in Tables 2 and 3, respectively. A total of 184 compounds were identified in the six brandies,

TABLE 1

Common volatile compounds in th	ree Changyu samples and three	Hennessy samples by	y GC-MS on a DB-Wax column.

ים	Compound	Descriptor	Idontificatio-?		concenti (mg/L) ³	ration	CV	Mear	1 concenti (mg/L)	ation	CV	Inda-4
RI	Compound ¹	Descriptor	Identification ²	CXO1	<u>, , ,</u>	CXO2	CV	HXO1	HXO2	НХОЗ	CV	Judge ⁴
	Esters											
>900	ethyl acetate	pineapple	MS,A,RI	2.346	2.889	2.880	0.11	1.481	1.640	1.246	0.14	**
1022	ethyl butanoate	fruity	MS,A,RI	0.026	0.028	0.021	0.14	0.060	n.i.	0.076	0.17	***
1040	ethyl 2-methylbutanoate		MS,RIL ^a	n.i.	0.060	0.059	0.02	0.122	0.148	0.190	0.22	***
1051		apple	MS,A,RI	0.010	0.020	0.014	0.31	0.059	0.045	0.050	0.14	***
1127		banana	MS,A,RI	0.286	n.i.	0.446	0.31	0.139	0.701	0.820	0.66	n.s.
1230		fruity, wine	MS,A,RI	0.340	0.262	0.331	0.14	1.569	1.181	1.232	0.16	***
1240	ethyl orthoformate ^T	57	MS	0.063	0.084	0.076	0.14	0.180	0.159	0.210	0.14	***
1261	hexyl acetate	fruity, sweet	MS,A,RI	0.038	0.035	0.013	0.47	0.007	0.005	n.i.	0.16	***
1301	methyl 2-hydroxypropanoate ^T	57	MS	0.003	0.007	0.004	0.46	0.007	0.010	0.016	0.42	***
1321	ethyl heptanoate	fruity	MS,A,RI	0.154	0.025	0.039	0.97	0.018	0.018	0.015	0.11	***
1329	ethyl 3-ethoxypropanoate ^T		MS	n.i.	0.025	0.018	0.21	0.026	0.063	0.045	0.41	***
1341	ethyl 2-hydroxypropanoate	fruity	MS,A,RI	0.126	0.109	0.129	0.09	0.123	0.126	0.115	0.04	***
1411	ethyl 2-hydroxy-3-methylbutanoate	floral	MS,A,RI	0.005	0.009	0.010	0.33	0.009	0.022	0.012	0.48	***
1414	ethyl octanoate	cooked fruity	MS,A,RI	26.725	28.339	27.985	0.03	29.336	27.237	28.313	0.04	n.s.
1442	-	cooked multy	MS	0.003	0.003	0.003	0.00	0.052	0.041	0.050	0.13	***
1470		floral	MS,A,RI	0.003	0.007	0.005	0.00	0.010	0.010	0.009	0.08	***
1533	ethyl nonanoate	fruity	MS,A,RI	0.004	0.007	0.007	0.27	0.052	0.062	0.009	0.08	***
	5	nuny	MS,A,KI MS,RIL ^b	0.028	0.031	0.031	0.08		0.030	0.038	0.08	***
1550	ethyl 2-hydroxyhexanoate		MS,RIL ^b		0.023	0.028		0.014	0.030 n.i.			
1567	3-methylbutyl 2-hydroxypropanoate		-	0.058			0.32	0.021		n.i.		n.s. ***
1577	diethyl propanedioate		MS,RIL ^a	0.008	0.016	0.014	0.33	0.008	0.026	0.016	0.55	***
1584	5		MS,RIL ^a	0.013	0.010	0.010	0.13	0.037	0.030	0.029	0.13	
1610	ethyl 4-oxopentanoate	grape	MS,A,RIL ^b	0.009	0.007	n.i.	0.24	0.013	0.033	0.020	0.46	***
1648	ethyl decanoate	fruity	MS,A,RI	10.247	10.155	9.892	0.02	11.506	12.005	11.821	0.02	***
1649	2-methylbutyl octanoate	fruity	MS,A,RIL ^a	0.136	0.110	0.134	0.11	0.355	0.338	0.361	0.03	***
1680	diethyl succinate	fruity	MS,A,RI	0.289	0.282	0.327	0.08	0.472	0.345	0.475	0.17	***
1685	ethyl dec-9-enoate	fruity	MS,A,RI	0.062	0.118	0.112	0.32	0.255	0.206	0.201	0.13	***
1705	5		MS	0.005	n.i.	0.003	0.47	0.016	0.025	0.059	0.69	***
1747	propyl decanoate	fruity	MS,A,RIL ^a	0.020	0.018	0.026	0.20	0.142	0.138	0.131	0.04	***
1771	5 5	pine	MS,A,RI	0.024	0.017	0.017	0.20	0.062	0.063	0.081	0.16	***
1775	diethyl pentanedioate		MS,RIL ^a	n.i.	0.004	n.i.		0.030	0.029	0.032	0.05	n.s.
1800	ethyl 2-methylpropyl succinate	fruity	MS,A,RIL ^a	0.009	0.013	0.010	0.18	n.i.	0.091	0.080	0.09	***
1831	ethyl 2,3-diethoxypropanoate		MS,RIL ^c	n.i.	n.i.	0.005		0.025	0.032	0.039	0.22	n.s.
1843	ethyl dodecanoate	sweet, fruity	MS,A,RIL ^a	14.235	15.849	15.167	0.05	17.332	15.731	15.967	0.05	n.s.
1862	isopentyl decanoate		MS,RIL ^a	0.089	0.085	0.094	0.05	0.135	0.445	0.231	0.59	**
1890	diethyl hexanedioate ^T		MS	n.i.	0.012	0.013	0.07	0.020	0.025	0.023	0.12	***
2005	diethyl pentanedioate		MS,RIL ^c	0.024	0.014	0.020	0.24	0.022	0.076	0.075	0.53	***
2060	ethyl tetradecanoate		MS,RIL ^a	0.167	0.181	0.127	0.18	0.272	0.702	0.496	0.44	**
2078	isopentyl dadecanoate		MS,RIL ^a	0.018	0.013	n.i.	0.24	0.018	0.092	n.i.	0.94	***
2107	ethyl 3-hydroxydecanoate ^T		MS	0.013	0.020	n.i.	0.28	0.045	0.048	0.052	0.08	***
2112	diethyl octanedioate	fruity	MS,A,RIL ^c	0.009	0.014	0.007	0.40	0.026	0.031	0.022	0.18	***
2139	ethyl pentadecanoate		MS,RIL ^b	0.028	0.020	0.017	0.25	0.014	0.025	n.i.	0.38	***
2224	isopropyl palmitate ^T		MS	0.105	0.146	0.083	0.29	0.135	0.154	0.109	0.17	***
2241	ethyl hexadecanoate	fatty	MS,A,RIL ^a	0.119	0.136	0.093	0.19	0.105	0.417	0.346	0.57	*
2251	ethyl hexadec-9-enoate	fatty	MS,A,RIL ^a	0.033	0.009	n.i.	0.80	0.041	0.037	0.034	0.09	***
2477	ethyl octadecanoate	-	MS,RIL ^a	0.004	0.003	n.i.	0.28	0.007	0.022	0.004	0.91	***
2479	ethyl oleate		MS,RIL ^a	0.009	0.009	n.i.	0.00	0.013	0.013	0.015	0.09	***
2531	ethyl linoleate		MS,RIL ^a	0.013	0.010	n.i.	0.16	0.022	0.029	n.i.	0.18	***
	Total		,	55.944	59.262	58.302	0.03	64.413	62.706	63.194	0.01	n.s.

TABLE 1 (CONTINUED)

1094 2 1162 1 1214 2 1214 2 1254 1 1254 1 1296 2 1319 1 1350 1 1360 (1371 2 1381 (1409 1 1451 1 1478 2 1649 1 1759 0 2171 1 2369 1 1441 2 1668 2 2066 0 2154 1	Compound ¹ Alcohols propan-1-ol 2-methylpropanol butan-1-ol 3-methylbutanol 1-pentanol 4-methylpentanol heptan-2-ol hexan-1-ol (E)-hex-3-en-1-ol 3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol hex-1-ol	Descriptor alcohol, fruity fusel alcohol, fruity fusel fruity floral, green grass, leaf green	Identification ² MS,A,RI MS,A,RI MS,A,RI MS,A,RI MS,RIL ^b MS,RIL ^b MS,A,RI MS,A,RI	CXO1 0.157 1.729 0.018 15.796 n.i. 0.004 0.018	(mg/L) ³ CXO3 0.134 2.822 0.018 15.390 0.005 0.005	CXO2 0.081 2.879 0.016 15.692 0.005	CV 0.31 0.26 0.09 0.01	HXO1 0.125 2.569 0.023 24.338	(mg/L) HXO2 0.173 2.682 0.020 23.524	HXO3 0.169 2.971 0.021 23.367	CV 0.17 0.08 0.08	Judge ⁴ *** n.s.
1094 2 1162 1 1214 2 1214 2 1254 1 1254 1 1296 2 1319 1 1350 1 1360 (1371 3 1381 (14451 1 1478 2 1561 (1649 1 1759 (1869 (2171 1 2369 1 1441 2 1627 1 1668 2 2066 (2154 1	propan-1-ol 2-methylpropanol butan-1-ol 3-methylbutanol 1-pentanol 4-methylpentanol heptan-2-ol hexan-1-ol (E)-hex-3-en-1-ol 3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol	fusel alcohol, fruity fusel fruity floral, green grass, leaf	MS,A,RI MS,A,RI MS,A,RI MS,A,RI MS,RIL ^b MS,RIL ^b	0.157 1.729 0.018 15.796 n.i. 0.004	0.134 2.822 0.018 15.390 0.005	0.081 2.879 0.016 15.692	0.26 0.09 0.01	0.125 2.569 0.023	0.173 2.682 0.020	0.169 2.971 0.021	0.08	n.s.
094 2 1162 1 214 2 2254 1 296 2 319 1 350 1 360 (371 3 381 (4478 2 561 0 649 1 759 0 869 1 973 0 2171 1 2369 1 4441 2 668 2 2066 0 2154 1	2-methylpropanol butan-1-ol 3-methylbutanol 1-pentanol 4-methylpentanol heptan-2-ol hexan-1-ol (E)-hex-3-en-1-ol 3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol	fusel alcohol, fruity fusel fruity floral, green grass, leaf	MS,A,RI MS,A,RI MS,A,RI MS,A,RI MS,RIL ^b MS,RIL ^b	1.729 0.018 15.796 n.i. 0.004	2.822 0.018 15.390 0.005	2.879 0.016 15.692	0.26 0.09 0.01	2.569 0.023	2.682 0.020	2.971 0.021	0.08	n.s.
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1214 2 1254 1 1254 1 1296 2 1319 1 1350 1 1350 1 1350 1 1350 1 1350 1 1350 1 1350 1 1371 3 1381 (1409 1 1451 1 1478 2 1561 (1649 1 1759 (1869 (1973 (2369 1 1441 (1627 1 1668 2 2066 (2154 1	3-methylbutanol 1-pentanol 4-methylpentanol heptan-2-ol hexan-1-ol (E)-hex-3-en-1-ol 3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol	fusel fruity floral, green grass, leaf	MS,A,RI MS,A,RI MS,RIL ^b MS,RIL ^b MS,A,RI	15.796 n.i. 0.004	15.390 0.005	15.692	0.01				0.08	والد والو مالو
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1296 2 1319 1 1350 1 1350 1 1360 (1371 3 1381 (1409 1 1451 1 1478 2 1561 (1649 1 1759 (1869 (2171 1 2369 1 1441 2 1668 2 2066 (2154 1	4-methylpentanol heptan-2-ol hexan-1-ol (E)-hex-3-en-1-ol 3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol	floral, green grass, leaf	MS,RIL ^b MS,RIL ^b MS,A,RI	0.004		0.005				23.30/	0.02	***
1319 1 1350 1 1350 1 1360 (1371 2 1381 (1409 1 1441 2 1561 (1759 (1869 (2171 (2369 1 1441 2 1668 2 2066 (2154 1	heptan-2-ol hexan-1-ol (E)-hex-3-en-1-ol 3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol	grass, leaf	MS,RIL ^b MS,A,RI		0.005		0.00	0.009	0.008	0.009	0.09	***
1350 1 1360 (1371 2 1381 (1409 1 1451 1 1478 2 1561 (1649 1 1759 (1869 1 1973 (2369 1 1441 2 1668 2 2066 (2154 1	hexan-1-ol (E)-hex-3-en-1-ol 3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol	grass, leaf	MS,A,RI	0.018	0.005	0.005	0.16	0.008	0.011	0.009	0.16	***
1360 (1371 3 1381 (1409 1 1451 1 1478 2 1561 (1649 1 1759 (1869 (1973 (2171 (1441 (1667 (1649 (1973 (2171 (1441 (1668 (2066 (2154 ((E)-hex-3-en-1-ol 3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol	grass, leaf			0.030	0.025	0.24	0.035	0.046	0.050	0.17	***
1371 3 1381 (1409 1 1451 1 1478 2 1561 (1649 1 1759 (1869 (2171 1 2369 1 1441 2 1668 2 2066 (2154 1	3-ethoxypropanol (Z)-hex-3-en-1-ol hex-2-en-1-ol		MS,A,RI	0.783	0.761	0.727	0.04	0.908	1.140	1.025	0.11	***
1381 (1409 1 1451 1 1451 1 1478 2 1561 (1649 1 1759 (1869 (1973 (2171 (2369 1 1441 (1627 1 1668 2 2066 (2154 1	(Z)-hex-3-en-1-ol hex-2-en-1-ol	green		0.004	0.003	0.004	0.22	0.003	0.004	0.076	1.53	***
1409 H 1451 H 1478 2 1561 0 1649 H 1759 0 1869 1 1973 0 2171 t 2369 H 1441 a 1627 H 1668 2 2066 0 2154 H	hex-2-en-1-ol	green	MS,RIL ^b	n.i.	0.001	n.i.		n.i.	0.003	0.005	0.47	n.s.
1451 1 1478 2 1561 0 1649 1 1759 0 1869 1 1973 0 2171 1 2369 1 1441 2 1668 2 2066 0 2154 1			MS,A,RI ^b	0.080	0.100	0.110	0.16	0.138	0.146	0.168	0.10	***
1478 2 1561 0 1649 1 1759 0 1869 1 1973 0 2171 t 2369 1 1441 a 1627 t 1668 2 2066 0 2154 1	heptan-1-ol		MS,RIL ^a	0.003	0.004	0.004	0.22	0.003	0.008	0.012	0.62	***
1561 c 1649 r 1759 c 1869 u 1973 c 2171 t 2369 l 1441 a 1627 t 1668 2 2066 c 2154 r			MS,RI	0.007	n.i.	n.i.		0.013	0.018	n.i.	0.22	n.s.
1649 1 1759 0 1869 1 1973 0 2171 t 2369 1 1441 a 1627 t 1668 2 2066 0 2154 t	2-ethylhexanol	floral	MS,A,RI	0.009	0.055	0.029	0.74	0.059	0.077	0.077	0.15	***
1759 c 1869 t 1973 c 2171 t 2369 l 1441 a 1627 t 1668 2 2066 c 2154 r	octan-1-ol	floral, green	MS,A,RI	0.091	0.174	0.140	0.31	0.234	0.289	0.239	0.12	***
1869 1 1973 0 2171 t 2369 1 1441 a 1627 t 1668 2 2066 0 2154 t	nonan-1-ol	floral	MS,A,RI	0.025	0.034	0.034	0.17	0.050	0.067	0.077	0.21	***
1973 c 2171 t 2369 l 1441 a 1627 t 1668 2 2066 c 2154 r	decan-1-ol	fatty	MS,A,RI	0.140	0.236	0.228	0.26	0.324	0.416	0.294	0.18	***
2171 t 2369 l 1441 a 1627 t 1668 2 2066 c 2154 r	undecan-1-ol		MS,RIL ^a	0.001	0.001	0.005	0.87	n.i.	0.005	n.i.		***
2369 1 1441 a 1627 b 1668 2 2066 c 2154 r	dodecan-1-ol	rancid	MS,A,RIL ^a	0.052	0.091	0.059	0.30	0.035	0.101	0.114	0.50	**
1441 a 1627 t 1668 2 2066 c 2154 r	tetradecan-1-ol		MS,RIL ^a	0.087	0.096	0.071	0.15	0.094	0.144	0.810	1.14	n.s.
1441 a 1627 b 1668 2 2066 c 2154 r	hexadecan-1-ol		MS,RIL ^a	0.029	0.047	0.030	0.29	0.055	0.033	0.073	0.38	***
1627 b 1668 2 2066 c 2154 r	Total			19.033	20.007	20.144	0.03	29.023	28.915	29.566	0.01	***
1627 b 1668 2 2066 c 2154 r	Acids											
1668 2 2066 c 2154 r	acetic acid	vinegar	MS,A,RI	0.178	0.257	0.287	0.23	0.332	0.384	0.300	0.13	***
2066 o 2154 r	butanoic acid	rancid	MS,A,RI	n.i.	n.i.	0.017		0.024	0.025	0.031	0.14	n.s.
2154 r	2/3-methylbutanoic acid	rancid	MS,A,RI	0.009	0.016	n.i.	0.37	0.046	0.056	0.067	0.19	***
	octanoic acid	fatty	MS,A,RI	7.570	9.250	7.675	0.12	10.706	11.401	10.312	0.05	n.s.
2248 c	nonanoic acid	rancid	MS,A,RIL	0.024	0.025	0.029	0.11	0.063	0.070	0.073	0.07	***
	decanoic acid	rancid	MS,A,RIL ^a	13.015	12.700	12.530	0.02	13.658	13.828	13.369	0.02	**
2358 9	9-decenoic acid ^T		MS	0.003	0.010	0.008	0.57	0.029	0.014	0.022	0.33	***
2493 d	dodecanoic acid		MS,RIL ^a	0.649	0.907	0.783	0.16	1.331	1.628	1.758	0.14	***
2680 t	tetradecanoic acid		MS,RIL ^a	0.129	0.104	0.109	0.12	0.252	0.117	0.310	0.44	***
2931 p	pentadecanoic acid		MS,RI	0.024	0.007	0.016	0.56	0.043	n.i.	n.i.		n.s.
2975 l	hexadecanoic acid ^T		MS	0.130	0.101	0.105	0.14	0.210	0.224	0.250	0.09	***
	Total			21.731	23.376	21.559	0.05	26.693	27.749	26.493	0.03	*
	Benzene derivatives											
	3,4,4a,5,6,7-hexahydro-1,1,4a- trimethyl-2(1H)-naphthalenone ^T		MS	0.047	0.063	0.058	0.14	0.101	0.206	0.091	0.48	***
1664 6	ethyl benzoate	floral	MS,A,RI	0.038	0.018	0.042	0.39	0.048	0.054	0.060	0.11	***
1784 e	ethyl 2-phenylacetate	honey	MS,A,RI	0.014	0.020	0.016	0.16	0.094	0.072	0.105	0.18	***
1805 2	2-phenylethyl acetate	floral	MS,A,RI	0.093	0.050	0.075	0.30	0.092	0.091	0.101	0.06	***
1879 ł	benzyl alcohol	floral	MS,A,RI	n.i.	0.026	0.026	0.00	n.i.	0.022	0.028	0.15	***
1883		floral, fruity	MS,A,RIL ^d	0.018	0.064	0.064	0.54	0.179	0.207	0.198	0.07	***
1929 2	ethyl benzenepropanoate	rosy	MS,A,RI	0.433	0.034	0.155	0.99	0.158	0.155	0.141	0.06	n.s.
2030 2	ethyl benzenepropanoate 2-phenylethanol		MS,RIL ^a	0.051	0.037	0.034	0.23	0.052	0.066	0.053	0.13	***
2117	• • • •		MS	0.072	0.112	0.126	0.30	0.120	0.291	0.266	0.35	***
2183 4	2-phenylethanol			0.072	0.112	0.136	0.30	0.139	0.271	0.200		
2445 t	2-phenylethanol 2-methoxy-4-ethylphenol 1-(2,3,6-trimethylphenyl)-3-buten-	leather	MS,A,RIL ^a	0.045	0.112	n.i.	0.30	0.139	0.291	0.266	0.11	***
2512 B	2-phenylethanol 2-methoxy-4-ethylphenol 1-(2,3,6-trimethylphenyl)-3-buten- 2-one ^T	leather fruity									0.11	*** ***

TABLE 1 (CONTINUED)

DI	Compound ¹	Descriptor	Identification ²	Mean concentration (mg/L) ³			CV	Mean concentration (mg/L)			CV	T., 1 4
RI				CX01	CXO3	CXO2	CV	HX01	HXO2	НХО3	CV	Judge
2540	diisopropyl phthalate ^T	plastic	MS,A	0.278	0.660	0.164	0.71	0.158	0.129	0.136	0.11	*
2549	vanillin	vanilla	MS,A,RI	0.008	0.010	0.012	0.20	n.i.	0.061	0.058	0.04	***
2906	dibutyl phthalate	plastic	MS,A,RIL°	0.589	0.142	0.129	0.92	0.223	0.218	0.215	0.02	n.s.
	Total	*		1.704	1.336	0.938	0.29	1.433	1.848	1.620	0.13	n.s.
	Terpenes and norisoprenoids							0				
1422	(E)-linalool oxide	floral	MS,A,RIL ^b	0.021	0.020	0.035	0.34	0.054	0.064	0.069	0.12	***
1462	(Z)-linalool oxide	woody, floral	MS,A,RI	0.021	0.018	0.020	0.07	0.030	0.031	0.031	0.03	***
1506	nerol	floral, sweet	MS,A,RI	0.026	0.012	0.017	0.40	0.027	0.033	0.029	0.09	***
1689	α-terpineol		MS,RIL ^a	0.114	0.105	n.i.	0.06	0.197	0.207	0.245	0.12	***
1742	1,1,6-trimethyl-1,2-dihydrona phthalene	asphalt	MS,A,RI	0.231	0.265	0.353	0.22	0.043	0.046	0.060	0.18	***
1763	β-citronellol	tea, spicy	MS,A,RI	0.066	0.035	0.045	0.32	0.026	0.070	0.097	0.56	***
1818	β-damascenone	floral, sweet	MS,A,RI	0.093	0.108	0.110	0.09	0.331	0.299	0.276	0.09	***
1856	(E)-geranyl acetone		MS,RIL ^c	0.042	0.054	0.052	0.13	0.097	0.118	0.079	0.20	***
2037	nerolidol	floral	MS,RIL ^c	0.105	0.161	0.157	0.22	0.363	0.340	0.256	0.18	***
2197	cadinol ^T		MS	0.004	0.017	n.i.	0.88	0.007	0.037	n.i.	0.99	***
2361	farnesol	floral	MS,A,RI	0.012	0.010	0.012	0.07	0.018	0.013	0.017	0.17	***
	Total			0.735	0.805	0.801	0.15	1.193	1.258	1.159	0.05	***
	Aldehydes and ketones											n.s.
10	acetaldehyde	fruity	MS,A,RI	0.049	0.031	0.037	0.22	0.039	n.i.	n.i.		n.s.
1082	hexanal	green	MS,A,RI	n.i.	n.i.	0.001		n.i.	n.i.	0.007		n.s.
1195	heptan-2-one	floral, green	MS,A,RIL ^b	n.i.	0.007	0.004	0.35	n.i.	0.007	0.005	0.16	***
1482	decanal		MS,RI	0.033	0.018	0.016	0.41	n.i.	0.102	0.058	0.39	***
1598	undecan-2-one		MS,RIL ^a	n.i.	0.007	0.007	0.00	0.014	0.018	0.017	0.12	***
	Total			0.081	0.063	0.064	0.15	0.054	0.127	0.087	0.41	***
	Furans											
1452	furfural	toasty	MS,A,RI	0.577	0.584	0.602	0.02	1.458	1.120	1.697	0.20	***
1571	5-methylfurfural	roasted	MS,A,RI	0.050	0.049	0.045	0.06	0.095	0.115	0.079	0.19	***
1622	ethyl 2-furoate	balsamic	MS,A,RIL ^b	0.007	0.055	0.059	0.73	0.147	0.337	0.419	0.46	***
2093	2,5-dihydro-2,2-dimethyl-5-(1- methylethenyl)-3-(1-methylethyl)- furan ^T		MS	0.211	0.105	0.177	0.33	0.071	0.156	0.147	0.38	**
	Total			0.845	0.792	0.883	0.05	1.770	1.729	2.341	0.18	**
	Lactones											
1888	δ -nonalactone ^T		MS	0.025	0.037	0.038	0.22	0.025	0.037	0.038	0.22	n.s.
1961	γ-nonalactone	cream, coconut	MS,A,RI	0.003	0.010	n.i.	0.85	0.074	0.075	0.089	0.11	***
2120	γ-decalactone		MS,RIL ^d	0.007	0.007	0.007	0.00	0.010	0.024	0.029	0.45	***
	Total			0.034	0.054	0.045	0.22	0.110	0.135	0.156	0.17	***
	Acetals											
1294	1,1,3-triethoxypropane	fruity, vegetal	MS,A,RIL ^d	0.013	0.007	0.010	0.33	n.i.	0.008	0.007	0.13	***
	Total			0.013	0.007	0.010	0.33	n.i.	0.008	0.007	0.13	***

RI: Retention index

¹Tentatively identified by mass spectra

² Identified by MS (mass spectra), A (aroma descriptors), RI (retention index), and RIL (retention indices from literature).

^a Ferrari et al. (2004);^bLedauphin et al. (2004); ^c Zhao et al. (2009b); ^dFan and Qian (2005)

³ n.i.: Not identified; CV: Coefficient of variation of concentrations in three Changyu and Hennessy XO samples

⁴ Judge: Difference between mean concentration of three Changyu samples and that of three Hennessy samples

*Difference at 0.05; **Difference at 0.01; ***Difference at 0.001; n.sNo significant difference

most of which have already been identified by other authors (Ferrari *et al.*, 2004; Ledauphin *et al.*, 2004; Janacova *et al.*, 2008). Among these volatiles, 118 compounds were found to be common to both Changyu XO and Hennessy XO, and 21 and 36 volatiles were specific to Changyu XO and Hennessy XO, respectively.

GC-O analysis

The aroma compounds obtained in the six brandies by GC-O are shown in Tables 1, 2 and 3. A total of 92 aroma compounds were identified in the six brandies. The most abundant perceived aromas were descriptors such as fruity, floral, alcohol, grass and green, and rancid, for Changyu XO samples. Besides grass and green, the majority of these descriptors have been found in three Hennessy XO samples. Among the 92 aroma compounds, 71 aromas were common to both Changyu XO and Hennessy XO, and nine and twelve compounds were specific to Changyu XO and Hennessy XO, respectively.

Comparison of volatile compounds in Changyu and Hennessy XO

Esters

Esters were the most abundant volatile compounds in both Changyu XO and Hennessy XO, with ethyl esters dominating this class. As seen in Table 1, 47 esters were common compounds, and the whole average concentration (abbreviated to AC_w) of esters in Changyu XO (57.836 mg/L) was lower than that in Hennessy XO (63.438 mg/L). According to the T-test, no significant difference was found in AC_w of esters in Changyu XO and Hennessy XO. However, there were significant differences in average concentrations (abbreviated to AC) of each ester, excepting 3-methylbutyl acetate, ethyl octanoate, 3-methylbutyl 2-hydroxypropanoate, diethyl pentanedioate, ethyl 2,3-diethoxypropanoate, and ethyl dodecanoate. Three esters, i.e. ethyl octanoate, ethyl decanoate and ethyl dodecanoate, were the most concentrated compounds and covered up to 80% of the whole of the ester concentrations in both Changyu XO and Hennessy XO. These esters were the most important skeleton compounds in the brandy samples and revealed a low coefficient of variation (CV $\leq 20\%$).

Esters are mostly formed through the esterification of alcohols with fatty acids during fermentation, distillation and the ageing processes (Ledauphin *et al.*, 2003; Fan and Qian, 2005; Zhao *et al.*, 2009a). Of these volatile esters, 22 aroma compounds were identified by GC-O. Esters mainly contribute fruity, floral, pineapple, apple-like and banana-like aromas (Fan and Qian, 2006). For example, ethyl butanoate, ethyl heptanoate and ethyl 2-hydroxypropanoate generated fruity aroma; pineapple aroma was explained by the presence of ethyl acetate; ethyl 3-methylbutanoate was responsible for apple aroma. According to statistical analysis, there were significant differences in these aroma esters in both Changyu XO and Hennessy XO, except for 3-methylbutyl acetate and ethyl octanoate.

As seen in Table 1, ethyl pentanoate, isopentyl isopentanoate and 2-ethylhexyl acetate were specific to Changyu XO. Of these, ethyl pentanoate and isopentyl isopentanoate imparted apple and fruity odours to the global aroma. Table 2 shows that eight esters, including ethyl hex-2-enoate, 2-methylpropyl acetate, isobutyl hexanoate, propyl octanoate, isobutyl octanoate, methyl dodecanoate, isobutyl dodecanoate, and decyl decanoate, were specific to Hennessy XO, and 2-Methylpropyl acetate, ethyl hex-2-enoate, isobutyl hexanoate, propyl octanoate, and isobutyl octanoate were detected with floral and fruity odours.

Alcohols

Alcohols formed the second group of concentrated compounds in these samples. As seen in Table 1, 21 alcohols were common to both Changyu XO and Hennessy XO. Similar to esters, the AC_w of alcohols in Changyu XO (19.728 mg/L) were lower than those in Hennessy XO (29.168 mg/L). According to the T-test, a significant difference between the AC_w of alcohols in Changyu XO and Hennessy XO was identified. Moreover, significant differences were also found in the AC of most alcohols, excepting 2-methylpropanol, 3-ethoxypropanol, heptan-1-ol and tetradecan-1-ol. The most concentrated of the compounds, covering up to 80% of the whole alcohol concentrations in both Changyu XO and Hennessy XO, was 3-methylbutanol. The CV levels of 3-methylbutanol in Changyu XO and Hennessy XO were 1% and 2%, respectively. Based on these results, 3-methylbutanol was the most important skeleton compound in the brandies. Four alcohols, i.e., 2,3-butanediol, nonan-2-ol, undecan-2-ol and 2-tetradecen-1-ol, were only found in Hennessy XO. Butan-2-ol was specific to Changyu XO.

Among these alcohols, 13 were identified as aroma compounds. Most alcohols have high sensory thresholds and impart fruity, fusel, floral, grass, and alcohol-like aromas (Fan and Qian, 2006). Propan-1-ol and butan-1-ol generated alcohol and fruity odours; fusel aroma was explained by the presence of 2-methylpropanol and 3-methylbutanol; (E)-hex-3-en-1-ol and (Z)-hex-3-en-1-ol were responsible for grass, leaf and green aromas; decan-1-ol contributed to fatty aroma and dodecan-1-ol imparted a rancid aroma. Significant differences in the concentrations of the 12 aroma alcohols, except for 2-methylpropanol, were recorded (Table 1).

Acids

Acids are mainly derived from the grapes. Small amounts of acids were formed from amino acids catalysed by yeast under anaerobic conditions (Watts et al., 2003). In the current analysis, a total of 18 acids were identified in Changyu XO and Hennessy XO. Eleven of these acids were common to both brands, whereas five acids, including isobutanoic, 4-methylhexanoic, 2-ethyl hexanoic, 3-ethylhepatanoic, and tridecanoic acid, were specific to Hennessy XO. Two acids involving hexanoic and heptanoic acid were found specific to Changyu XO. The AC_w of acids in Changyu XO (22.222 mg/L) was lower than in Hennessy XO (26.978 mg/L). According to the T test, there was a significant difference in the total concentration of acids between Changyu XO and Hennessy XO. Moreover, there were significant differences in the AC of most acids, except for butanoic acid, octanoic acid and pentadecanoic acid. Decanoic acid and octanoic acid were the most important acid compounds, comprising up to 90% of the total acid concentrations in both Changyu XO and Hennessy XO. Of these acids, six aroma-active acids, including acetic acid, butanoic acid, 2/3-methylbutanoic acid, octanoic acid, nonanoic acid and decanoic acid, were identified by GC-O. These acids mainly contribute to rancid and vinegar odours for the global aroma of both brand brandies.

Benzene derivatives

Benzene derivatives were identified as the fourth largest volatile group in the brandies, followed by esters, alcohols and acids. The AC_w of benzene derivatives in Changyu XO (1.326 mg/L) was slightly lower than those in Hennessy XO (1.634 mg/L). No significant differences between Changyu XO and Hennessy XOwere observed in the ACw of benzene derivatives by T-test analysis. Fifteen benzene derivatives were common to both Changyu XO and Hennessy XO. In Changyu XO samples, 2-phenylethanol, 1-(2,3,6-trimethylphenyl)-3-buten-2-one, diisopropyl phthalate, and dibutyl phthalate were the higher concentrated compounds. Six compounds were specific to Changyu XO, including benzaldehyde, butyl benzoate, eugenol, 2,4-(1,1-dimethylethyl) phenol, 2-phenylethyl octanoate, and benyl benzoate. As for Hennessy XO, the number of benzene derivatives were less than that contained in Changyu XO; and ethyl benzenepropanoate, 1-(2,3,6-trimethylphenyl)-3-buten-2-one, 4-ethylphenol, and dibutyl phthalate were the important compounds. Of these, dibutyl phthalate, 4-ethylphenol and ethyl benzenepropanoate (CV $\leq 20\%$) were considered as the skeleton compounds in Hennessy XO.

Among these benzene derivatives, 11 aroma compounds were identified by GC-O. Ethyl benzoate, 2-phenylethyl acetate, benzyl alcohol and ethyl benzenepropanoate contributed to floral aromas; the honey aroma was explained by the presence of ethyl phenylacetate; 2-phenylethanol imparts a rosy aroma; and vanillin aromas are explained by vanillin. 4-Ethylphenol, with an undesirable leather odour, was produced by the contaminant yeasts *Brettanomyces/Dekkera* from grape-derived phenolic acids (Bautista-ortín *et al.*, 2008; Garde-Cerdan & Ancin-Azpilicueta, 2006; Martorell *et al.*, 2002). Plastic aroma, as an off-flavour, mainly explained by diisopropyl phthalate and dibutyl phthalate, has been identified by Zhao *et al.* (2009b). This aroma in brandy may be introduced during wine-making through exposing wine to plastic equipment.

Terpenes and norisoprenoids

Compared to the volatile compounds discussed above, all other volatiles, including terpenes, norisoprenoids, aldehydes, ketones, furans, lactones and acetals, had relatively lower concentrations and lower numbers, but they also played an important role in the development of brandy flavour due to their special and unique characteristics.

A total of twelve terpenes and three norisoprenoids were detected in Changyu XO and Hennessy XO. Among them, three compounds, namely linalool, geraniol and β -ionone, were specific to Changyu XO, whereas γ -terpineol was uniquely detected in Hennessy XO. The AC_w of terpenes in Changyu XO (0.780 mg/L) was nearly half of that in Hennessy XO (1.203 mg/L). According to the T-test, significant difference was found in the AC of all the terpenes. Of these, nerolidol, α -terpineol and β -damascenone occurred in a comparatively higher concentration than the other compounds in both Changyu XO and Hennessy XO.

Terpenes largely originate from grapes (Ferrari et al., 2004). β-Damascenone, a sweet odorant, mainly comes from the degradation of carotenoids in grapes (Strauss et al., 1987; Buttery et al., 1990). Though present in a low content, the terpenes and norisoprenoids were important due to their low aroma threshold values. Among these volatiles, a total of 10 terpenes and norisoprenoids were identified by GC-O; these were (E)-linalool oxide and farnesol (floral aroma), (Z)linalool oxide (woody, floral aroma), nerol (floral aroma), β -damascenone (sweet aroma), and β -citronellol (tea, spicy odour). Geraniol and β -ionone, with sweet, floral odour, were specific to Changyu XO samples, whereas, γ -terpineol gave a lime odour to Hennessy XO samples. The 1,1,6-trimethyl-1,2dihydronaphthalene (TDN) content was lower in Hennessy XO than in Changyu XO; it imparts asphalt tones and has been reported as an off-flavour in wine.

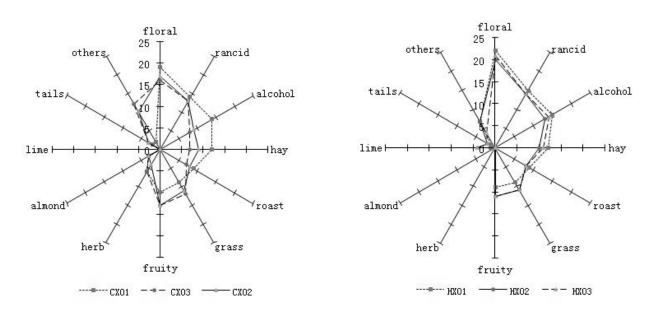
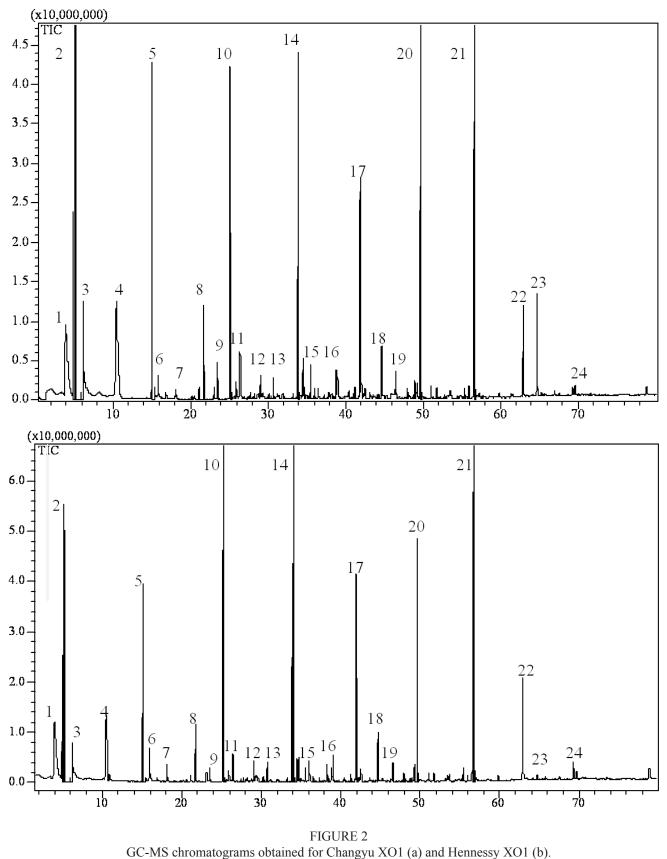


FIGURE 1 The aroma profiles obtained for Hennessy XO and Changyu XO.



Note: 1, ethyl acetate; 2, ethanol; 3, ethyl butanoate; 4, 2-methylpropanol; 5, 3-methylbutanol; 6, ethyl hexanoate; 7, ethyl orthoformate; 8, hexan-1-ol; 9, octan-3-ol; 10, ethyl octanoate; 11, furfural; 12, ethyl nonanoate; 13, octan-1-ol; 14, ethyl decanoate; 15, diethyl succinate; 16, decan-1-ol; 17, ethyl dodecanoate; 18, 2-phenylethanol; 19, dodecan-1-ol; 20, octanoic acid; 21, decanoic acid; 22, dodecanoic acid; 23, diisopropyl phthalate; 24, dibutyl phthalate.

 TABLE 2

 Special volatile compounds in Changyu XO samples by GC-MS on a DB-Wax column.

RI	Compound ¹	Descriptor	Identification ²]	CV ⁴		
	Compound	p		CXO1	CXO2	CXO3	
	Esters						
1137	ethyl pentanoate	apple	MS,A,RI	0.016	n.i.	n.i.	
1275	isopentyl isopentanoate	fruity	MS,A,RIL ^b	0.043	0.005	0.046	0.730
1374	2-ethylhexyl acetate		MS,RIL ^b	n.i.	0.003	n.i.	
	Total			0.059	0.008	0.046	0.70
	Alcohols						
1016	butan-2-ol		MS,RIL ^b	0.002	n.i.	n.i.	
	Total			0.002	n.i.	n.i.	
	Acids						
1849	hexanoic acid		MS,RI	n.i.	0.126	0.131	0.030
1951	heptanoic acid		MS,RI	0.030	0.036	0.023	0.220
	Total			0.030	0.162	0.154	0.640
	Benzenes and derivatives						
1510	benzaldehyde	almond	MS,A,RI	0.132	0.185	n.i.	0.240
1788	butyl benzoate ^T		MS	n.i.	0.017	n.i.	
2156	eugenol		MS,RI	0.011	n.i.	0.010	0.070
2351	2,4-(1,1-dimethylethyl)phenol ^T	herb	MS,A	0.016	0.014	0.017	0.100
2377	2-phenylethyl octanoate ^T		MS	n.i.	0.008	0.006	0.200
2639	benzyl benzoate		MS,RIL ^c	0.026	0.015	0.022	0.270
	Total			0.185	0.239	0.055	0.59
	Terpenes and norisoprenoids						
1555	linalool		MS,RI	0.111	n.i.	0.067	0.350
1851	Geraniol	sweet, rosy	MS,A,RI	n.i.	0.018	0.026	0.260
1924	β-ionone	floral	MS,A,RI	0.035	0.043	0.046	0.140
	Total			0.146	0.061	0.139	0.41
	Aldehydes and ketones						
1202	3-ethoxypropanal	fusel	MS,A,RIL ^b	0.007	0.007	n.i.	0.000
1235	octan-3-one		MS,RIL ^b	0.008	0.004	0.006	0.330
	Total			0.015	0.011	0.006	0.420
	Acetals						
978	1,1-diethoxy-2-methylpropane		MS,RIL ^d	0.003	0.003	n.i.	0.000
	Total			0.003	0.003	n.i.	0.000

RI: Retention index.

¹Tentatively identified by mass spectra

² Identified by MS (mass spectra), A (aroma descriptors), RI (retention index), and RIL (retention indices from literature).

^a Ferrari et al. (2004); ^bLedauphin et al. (2004); ^cZhao et al. (2009b); ^dFan & Qian (2005)

³ n.i.: Not identified.

⁴CV: Coefficient of variation of concentrations in three Changyu and Hennessy XO samples.

Aldehydes and ketones

Only five aldehydes and ketones were common to both Changyu XO and Hennessy XO. The AC_w of aldehydes and ketones were 0.070 mg/L and 0.089 mg/L in Changyu XO and Hennessy XO, respectively. According to the T-test, there were no significant differences in the AC of acetaldehyde and hexanal, whereas a significant difference was found in the other three compounds; 3-ethoxypropanal and octan-3-one were specific in Changyu XO, and nonanal and 11-dodecen-2-one were specific to Hennessy XO. Of these, five aroma compounds, acetaldehyde, hexanal, 3-ethoxypropanal, nonanal and heptan-2-one included, were identified. These compounds contributed green and fruity aromas to the global aroma of brandies.

Furans

Four furans common to both brands of brandy were identified. The AC_w of furans in Changyu XO (0.84 mg/L) was markedly lower than that in Hennessy XO (1.947 mg/L). According to the T-test, there were significant differences between Changyu XO and Hennessy XO in the whole concentrations of furans and in the AC of all furans. Of these furans, furfural was the most concentrated compound, with concentrations of up to 70% of the whole concentrations of furans. Furans are primarily oak derived, but also form in the hot conditions of distillation (Van Jaarsveld *et al.*, 2009a,b,c). Among these furans, three were aroma compounds. Toasty, roasted and balsamic aromas were explained by furfural, 5-methylfurfural and ethyl 2-furoate, respectively.

RI	Compound ¹	Descriptor	Identification ²	Me	CV ⁴		
				HXO1	HXO2	НХОЗ	
	Esters						
985	2-methylpropyl acetate	floral	MS,A,RI	n.i.	n.i.	0.013	
1333	ethyl hex-2-enoate	fruity	MS,A,RIL ^a	n.i.	0.004	0.002	0.47
1345	isobutyl hexanoate ^T	fruity	MS,A	n.i.	0.003	n.i.	
1509	propyl octanoate ^T	fruity	MS,A	0.016	n.i.	n.i.	
1558	isobutyl octanoate ^T	fruity	MS,A	0.079	n.i.	n.i.	
1801	methyl dodecanoate ^T		MS	0.034	0.061	0.049	0.28
1957	isobutyl dodecanoate ^T		MS	0.003	0.024	0.005	1.05
2658	decyl decanoate ^T		MS	0.026	0.017	0.026	0.23
	Total			0.158	0.102	0.08	0.35
	Alcohols						
1410	2,3-butanediol		MS,RIL ^a	n.i.	0.01	0.002	0.94
1513	nonan-2-ol		MS,RIL ^b	0.221	0.305	n.i.	0.23
1721	undecan-2-ol		MS,RIL ^b	0.041	0.051	0.053	0.13
2029	2-tetradecen-1-ol ^T		MS	n.i.	n.i.	0.002	
	Total			0.262	0.356	0.055	0.69
	Acids						
1563	isobutanoic acid	rancid	MS,A,RI	0.0180	n.i.	n.i.	
1932	4-methylhexanoic acid ^T		MS	n.i.	0.023	0.028	0.14
1948	2-ethylhexanoic acid ^T		MS	0.0140	0.051	0.057	0.57
2073	3-ethylheptanoic acid ^T		MS	0.0180	0.06	0.06	0.53
2659	tridecanoic acid ^T		MS	0.0080	n.i.	0.014	0.39
	Total			0.058	0.134	0.159	0.45
	Terpenics						
1602	γ-terpineol	lime	MS,A,RI	n.i.	0.025	n.i.	
	Total			n.i.	0.025	n.i.	
	Aldehydes and ketones						
1384	nonanal	fruity	MS,A,RI	n.i.	0.017	0.030	0.400
1802	11-dodecen-2-one ^T	2	MS	0.009	n.i.	0.005	0.400
	Total			0.009	0.017	0.035	0.800
	Acetals						
885	1,1-diethoxyethane	fruity	MS,RIL ^d	0.082	n.i.	0.096	0.120
1084	1,1-diethoxy-2-methylbutane	2	MS,A,RIL ^d	n.i.	0.006	n.i.	
1237	1,1-diethoxyhexane	floral	MS,A,RIL ^d	0.010	0.029	n.i.	0.670
	Total			0.092	0.035	0.696	1.340
	Others						
1686	3-ethoxy-p-menth-1-en-8-ol ^T		MS	0.012	0.020	0.040	0.60
	Total			0.012	0.020	0.040	0.60

RI: Retention index

¹ Tentatively identified by mass spectra

² Identified by MS (mass spectra), A (aroma descriptors), RI (retention index), and RIL (retention indices from literature).

^a Ferrari et al. (2004); ^bLedauphin et al. (2004); ^cZhao et al. (2009b); ^dFan & Qian (2005)

³ n.i.: Not identified.

⁴ CV: Coefficient of variation of concentrations in three Changyu and Hennessy XO samples.

Lactones

Three lactones, including δ -nonalactone, γ -nonalactone and γ -decalactone, were identified as compounds common to both Changyu XO and Hennessy XO. AC_w of lactones in Changyu XO (0.044 mg/L) was clearly lower than these in Hennessy XO (0.134 mg/L). Lactones are mostly derived from oak barrels, and the condition of barrels (wood type, manufacturing, prior use, etc.) greatly influence the extraction of lactones (Caldeira *et al.*, 2002; Watts *et al.*, 2003). In these lactones, only γ -nonalactone, with cream and coconut aromas, was identified by GC-O. According to the T test, the concentration of γ -nonalactone showed a significant difference between Changyu XO and Hennessy XO.

Acetals

Acetals are largely formed from the condensation of aldehydes with alcohols (Wondra and Berovic, 2001; Zhao *et al.*, 2009a). While 1,1,3-triethoxypropane, with a fruity and vegetal aroma, was found as a unique acetal compound common to both Changyu XO and Hennessy XO, 1,1-diethoxymethane, 1,1-diethoxy-2-methylbutane, and 1,1-diethoxyhexane were specific to Hennessy XO and 1,1-diethoxy-2-methylpropane was specific to Changyu XO.

CONCLUSIONS

The current study compared the differences related to volatile compounds in Changyu XO and Hennessy XO. Three different batches of brandy selected from each brand were analysed by GC-MS coupled with HS-SPME, GC-O and sensory evaluation. A total of 160 volatile compounds were identified in the two brand samples. Among these volatiles, 85 aroma compounds responsible for brandy flavour were identified by GC-O, of which, 68 were found common to both brandies, and seven and ten were separately specific to Changyu XO and Hennessy XO. Most volatile compounds in Changyu XO had lower concentrations than those in Hennessy XO. This could be ascribed to the development of knowledge of the aroma compositions of both brandies. Judging from the results of statistical and sensory analyses, the differences found between Changyu XO and Hennessy XO are significant.

LITERATURE CITED

Bautista-ortín, A.B., Lencina, A.G., Cano-lópez, M., Pardo-mínguez, F., Lópezroca, J.M. & Gómez-plaza, E., 2008. The use of oak chips during the ageing of a red wine in stainless steel tanks or used barrels: Effect of the contact time and size of the oak chips on aroma compounds. Aust. J. Grape Wine Res. 14, 63-70.

Buttery, R.G., Teranishi, R., Ling, L.C. & Turnbaugh, J.G.J., 1990. Quantitative induced by heat treatment. J. Food Eng. 76, 202-211.

Caldeira, I., Belchior, A.P., Climaco, M.C. & De Sousa, R.B., 2002. Aroma profile of Portuguese brandies aged in chestnut and oak woods. Anal. Chim. Acta 458, 55-62.

Caldeira, I., Climaco, M.C., De Sousa, R.B. & Belchior, A.P., 2006. Volatile composition of oak and chestnut woods used in brandy ageing: Modification induced by heat treatment. J. Food Eng. 76, 202-211.

Fan, W.L. & Qian, M.C., 2005. Headspace solid phase microextraction and gas chromatography-olfactometry dilution analysis of young and aged Chinese "Yanghe Daqu" liquors. J. Agr. Food Chem. 53, 7931-7938.

Fan, W.L. & Qian, M.C., 2006. Characterization of aroma compounds of Chinese "Wuliangye" and "Jiannanchun" liquors by aroma extract dilution analysis. J. Agr. Food Chem. 54, 2695-2704.

Ferrari, G., Lablanquie, O., Cantagrel, R., Ledauphin, H., Payot, T., Fournier, N. & Guichard, E., 2004. Determination of key odorant compounds in freshly distilled Cognac using GC-O, GC-MS, and sensory evaluation. J. Agr. Food Chem. 52, 5670-5676.

Garde-Cerdan, T. & Ancin-Azpilicueta, C., 2006. Review of quality factors on wine ageing in oak barrels. Trends Food Sci. Technol. 17, 438-447.

Go'mez-Mı'guez, M.J., Go'mez-Mı'guez, M., Vicario, I.M. & Heredia, F.J., 2007. Assessment of colour and aroma in white wines vinifications: Effects of grape maturity and soil type. J. Food Eng. 79, 758-764.

Howard, K.L., Mike, J.H. & Riesen, R., 2005. Validation of a solid-phase microextraction method for headspace analysis of wine aroma components. Am. J. Enol. Vitic. 56, 37-45.

Janacova, A., Sadecka, J., Kohajdova, Z. & Spanik, I., 2008. The identification of aroma-active compounds in Slovak brandies using GC-sniffing, GC-MS and sensory evaluation. Chromatographia 67, 113-121.

Ledauphin, J., Guichard, H., Saint-Clair, J.F., Picoche, B. & Barillier, D., 2003. Chemical and sensorial aroma characterization of freshly distilled Calvados. 2. Identification of volatile compounds and key odorants. J. Agr. Food Chem. 51, 433-442.

Ledauphin, J., Saint-Clair, J.F., Lablanquie, O., Guichard, H., Founier, N., Guichard, E. & Barillier, D., 2004. Identification of trace volatile compounds in freshly distilled calvados and cognac using preparative separations coupled with gas chromatography-mass spectrometry. J. Agr. Food Chem. 52, 5124-5134.

Martorell, N., Marti, M.P., Mestres, M., Busto, O. & Guasch, J., 2002. Determination of 4-ethylguaiacol and 4-ethylphenol in red wines using headspace-solid-phase microextraction-gas chromatography. J. Chromatogr. A 95, 349-354.

Milicevic, B., Banovic, M., Kovacevic-Ganic, K. & Gracin, L., 2002. Impact of grape varieties on wine distillates flavour. Food Technol. Biotechnol. 40, 227-232.

Onishi, M., Crowell, E.A. & Guymon, J.F., 1978. Comparative Composition of brandies from Thompson Seedless and three white-wine grape varieties. Am. J. Enol. Vitic. 29, 54-59.

Pérez-Coello, M.S., Sanz, J. & Cabezudo, M.D., 1995. Gas chromatographicmass spectrometric analysis of volatile compounds in oak wood used for ageing of wines and spirits. Chromatographia 47, 427-432.

Steel, R.G.D. & Torrie, J.H., 1980. Principles and Procedures of Statistics. McGraw-Hill , New York.

Strauss, C.R., Wilson, B., Anderson, R. & Williams, P.J., 1987. Development of precursors of C_{13} nor-isoprenoid flavorants in Riesling grapes. Am. J. Enol. Vitic. 38, 23-27.

Van Jaarsveld, F.P., Hattingh, S. & Minnaar, P., 2009a. Rapid induction of ageing character in brandy products – Part II. Influence of type of oak. S. Afr. J. Enol. Vitic. 30, 16-23.

Van Jaarsveld, F.P., Hattingh, S. & Minnaar, P., 2009b. Rapid induction of ageing character in brandy products – Part III. Influence of toasting. S. Afr. J. Enol. Vitic. 30, 24-37.

Van Jaarsveld, F.P., Minnaar, P., Blom, M. & Hattingh, S., 2009. Rapid induction of ageing character in brandy products – Part I. Effects of extraction media and preparation conditions. S. Afr. J. Enol. Vitic. 30, 1-15.

Watts, V.A., Butzke, C.E. & Boulton, R.B., 2003. Study of aged cognac using solid-phase microextraction and partial least-squares regression. J. Agr. Food Chem. 51, 7738-7742.

Wondra, M. & Berovic, M., 2001. Analyses of aroma components of chardonnay wine fermented by different yeast strains. Food Technol. Biotechnol. 39, 141-148.

Zhao, Y.P., Li, J.M., Xu, Y., Fan, W.L. & Jiang, W.G., 2009a. Characterization of aroma compounds of four brandies by aroma extract dilution analysis. Am. J. Enol. Vitic. 60, 269-277.

Zhao, Y.P., Xu, Y., Li, J.M., Fan, W.L. & Jiang, W.G., 2009b. Profile of volatile compounds in 11 brandies by headspace solid-phase microextraction followed by gas chromatography-mass spectrometry. J. Food Sci. 74, C90–C99.