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Determination of Key Odorant Compounds in Freshly Distilled Cognac Using GC-O, GC-MS, and Sensory Evaluation

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This aim of this work was to identify the odorant compounds responsible for the typical sensory descriptors attributed to freshly distilled Cognac spirits, not matured in barrels. Panelists were first selected and trained for gas chromatography−olfactometry. Among the 150 volatile compounds identified by gas chromatography−mass spectrometry analysis, only 34 are mainly responsible for the odors detected in the spirits. The "butter" descriptor is explained by the presence of diacetyl, the "hay" descriptor by nerolidol, the "grass" descriptor mainly by *Z*-3-hexen-1-ol, but also by other compounds, the "pear" and "banana" descriptors by 2- and 3-methylbutyl acetates, the "rose" descriptor by 2-phenylethyl acetate, and the "lime tree" descriptor by linalool. This study demonstrated that many odorant molecules are already present in freshly distilled Cognac, thereby giving the spirit its specific aroma.

KEYWORDS: Distilled beverage; key odorant; gas chromatography−olfactometry; mass spectrometry; sensory analysis

INTRODUCTION

The quality of Cognac spirits is recognized worldwide. The geographic area concerned with Cognac production in France includes nearly all of Charente Maritime, a very large part of Charente, and some neighboring communities. The wine distilled to obtain Cognac spirits is made from specific vine varieties (mainly Ugni blanc nowadays). On tasting, the spirits of the different vine varieties and different areas present specific characteristics. Moreover, the quality of the final product mainly depends first on viticultural and enological expertise and then on blending and aging (*1*). However, until now little has been known about the volatile compounds mainly responsible for the organoleptic quality of this specific spirit.

The flavor of distilled beverages has been reviewed by various authors (*2*, *3*). Volatile compounds responsible for the overall odor perception belong to various chemical classes such as hydrocarbons, alcohols, esters, carboxylic acids, ketones, aldehydes, and nitrogen- and sulfur-containing compounds. Raw materials and the original process supply the ingredients that give the distilled spirit its specific character. Hydrocarbons do not actively participate in the overall aroma perception, due to their high detection thresholds. The most abundant alcohols are fusel alcohols, which are formed in fermentation from amino acids through decarboxylation and deamination. They have a strong influence on the perceived flavor of distilled beverages (*3*). Esters constitute the most abundant chemical class of aroma compounds in brandies. Most of them are formed during fermentation, from carboxylic acids. Their formation and quantification in brandies have been the subject of numerous studies. Low-boiling esters from acetic and butanoic acids have rather low sensory odor thresholds and thus contribute to the global odor evaluation of the spirit, together with ethyl esters from other acids and also carbonyl compounds (*4*). The level of nitrogen compounds depends on the grape variety. Even if the sulfur-containing compounds are present only in low amounts, they contribute considerably to the odor specificity of brandies. Changes in the distillation system, oak wood type, and aging time induce considerable modifications to the volatile composition of cider brandies (*5*). For example, alcohols of higher molecular weight were better recovered in the rectification column than in the double-distillation system (Charente type with pot still), whereas the opposite was observed for esters. These changes in the relative amounts of aroma compounds in the brandy induce noticeable differences in overall odor and aroma perception.

Among the different types of brandies, French Cognac has been the subject of specific studies dealing with its composition in aroma compounds. Cognac and whiskey contain almost the

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same volatile compounds, but they differ in the quantified amounts (*3*). However, the incidence of these differences on overall perception has not yet been established. Among the identified compounds in Cognac, some directly originate from the vine, for example, alcohols, which give to the brandy its specificity, independent of the vintage (*6*). The quality of the brandy also depends on that of the wine. The different phases of the grape crop, the composition of the must, the activity of the yeasts, and fermentation conditions all have a strong influence on the level of flavor compounds (*7*). Fatty acids and their corresponding esters are mainly formed by the yeast during fermentation (*8*). Fatty acid esters form the largest group of flavor compounds, with typical fruity and flowery odor notes. The date of distillation is also of importance for the organoleptic quality of the brandy. Lengthening the distillation period induces an increase in the amount of ethyl acetate and acetals in the wine and thus produces undesirable aromas. The distillation technique therefore has to be improved in order to produce a spirit of the desired sensory quality (*9*). During maturation in oak barrels some reactions leading to the formation of new aroma compounds in the spirit may occur by direct extraction of molecules from the wood, degradation of wood macromolecules into aroma compounds, or oxidation of tannins and the formation of quinones, which produce flavor compounds such as vanillin and phenolic compounds (*10*). For example, the type of oak used to make barrels and the heating of staves influence the formation of lactones responsible for the typical woody aroma, such as β-methyl-γ-octalactone stereoisomers, leading to different proportions of the isomers and thus to different organoleptic properties (*11*, *12*). Finally, a commercial product with the desired organoleptic properties may be obtained only if blending is correctly performed (*1*). A specific premium quality brandy, such as Cognac, thus results from a subtle blend of different contributions of the vine, the terroir, distillation, and wood aging.

Despite previous data on the physicochemical composition of Cognac (*13*, *22*), there has been no recent study on the identification of the key aroma compounds in Cognac or on freshly distilled spirit, which is the "raw material" for Cognac aging and blending. Every year Cognac merchants buy freshly distilled spirits from many winegrowers (know as "bouilleurs de cru") and from distilleries. In their search for high-quality brandies (each merchant aims to find his own specific aroma) they select the most aromatic ones by nose testing. For this reason, they require specific knowledge regarding the component of white spirits quality to be able to make their selection.

Not all volatile compounds are responsible for the characteristic odor of a given beverage. Consequently, there is a need to identify those that have a real olfactive impact on this very specific French spirit. Therefore, the aim of the present work was first to select representative samples from freshly distilled Cognac, to find a representative method of extraction, and to determine the volatile compounds mostly responsible for the typical odor notes by using gas chromatography−olfactometry (GC-O). GC-O is a valuable tool for the selection of aroma-active components from a complex mixture (*14*, *15*) and has been successfully applied for the identifying key odorants of freshly distilled Calvados and for determining the compounds responsible for either defects in or quality of different typical samples (*16*, *17*). We thus decided to apply GC-O analysis on representative extracts to determine the typical odor notes detected by a trained sensory panel. These odors were then compared with volatile compounds identified by gas chromatography−mass spectrometry (GC-MS) in order to determine key odorants from selected freshly distilled Cognac.

Table 1. Synthetic Aroma Solution for the GC-O Panelist Evaluation

compound	odor	mean RT[a]	RI[b]	concn (mg/L)
3-methylbutyl acetate	fruity, banana	6.43	1121	125
3-methylbutanol	chocolate	7.40	1203	1030
ethyl hexanoate	fruity, ripe fruits	7.85	1233	146
Z-3-hexen-1-ol	herbaceous, grass	10.01	1377	159
linalool	orange flower	12.43	1537	180
butanoic acid	putrid	13.59	1617	150
benzyl acetate	jasmine	15.12	1733	180
2-phenylethyl acetate	rose	16.23	1820	184

[a] Retention time. [b] Retention index.

MATERIALS AND METHODS

Spirit Material. Freshly distilled Cognac samples from the 2000 vintage were supplied and selected by Cognac merchants to provide premium quality spirits. We analyzed successively three years, but we report here only the 2000 vintage results, as they were consistent with others.

Sensory Studies. The panelists (14 judges) were used to taste freshly distilled spirits (Cognac merchants' tasters, spirits brokers, BNIC laboratory technicians) and worked with a vocabulary reduced to 10 pertinent descriptors (*18*, *19*). They evaluated the spirits' quality only by nose smelling in order to establish aromatic profiles. Tests were performed in tulip glasses containing 20 mL of spirit. Each sample was tasted first crude (70% v/v of pure alcohol) and then after a dilution with water to reduce its alcoholic strength to ~40%. From 20 first spirits selected by merchants, we kept only 3 characteristic ones for analysis by GC-O. These were representative of specific aromatic types found in the 2000 vintage and with previous ones.

Gas Chromatography Quantitative Analysis. Quantification of volatile compounds in the spirits was done by GC, either by direct injection or after iso-octane extraction according to OIV methods (*20*). Particular conditions were the following: a Hewlett-Packard 6890 gas chromatograph (Agilent) equipped with a split/splitless injector (220 °C with autosampler) and a flame ionization detector (220 °C; H_2, 30 mL/min; air, 320 mL/min; makeup gas, N_2 at 25 mL/min); the carrier gas was hydrogen at 1.4 mL/min.

For direct injection a CP-Wax 57CB fused silica WCOT column (50 m × 0.25 mm, 0.2 μm from Chrompack) was used: split ratio, 1/14; sample volume injected, 0.2 μL; oven temperature, 5 min at 35 °C, raised at 4 °C/min to 220 °C and then held for 10 min at 220 °C. Internal standard was methyl-4-pentanol-2.

For iso-octane extract injection a DB-Wax fused silica WCOT column (60 m × 0.25 mm, 0.25 μm from J&W Scientific) was used: splitless injection of 1 μL sample; oven temperature, 0.7 min at 35 °C, raised at 20 °C/min to 60 °C, held for 3.4 min at 60 °C, raised at 4 °C/min to 220 °C, and held for 20 min at 220 °C. Internal standards were ethyl nonanoate and ethyl tridecanoate.

Most pure chemicals were purchased from Sigma-Aldrich-Fluka (St. Quentin Fallavier, France) and the others from Interchim (Montluçon, France), ACROS Organics (Noisy-Le-Grand, France), Merck-Eurolab (VWR International S.A.S, Fontenay-sous-Bois, France), except 1,2-dihydro-1,1,6-trimethylnaphthalene (TDN), which was synthesized. Acetals were synthesized by J. Ledauphin (23).

The chromatographic data were obtained by H-P Chemstation software (Agilent). The volatile compounds of interest were quantified with reference to a calibration table established with pure standard compounds. Check samples were used periodically to ensure permanent quality control of those analyses accredited by COFRAC (with reference to ISO 17025 standard), the French laboratories accreditation committee. The BNIC laboratory also participated in the proficiency scheme on spirits.

Organic Aromatic Extract for GC-O and GC-MS. A mixture of 100 mL of spirit with 200 mL of water and 15 g of NaCl was shaken with 16 mL of dichloromethane. The organic layer was recovered after decantation in a separating funnel and was concentrated to 2 mL with a Kuderna−Danish apparatus. We checked that this concentration did not produce artifacts, using blank samples and standard solution.

Table 2. Total Time of Olfaction and Missing and Ghost Odor Numbers for Each Judge Sniffing the Test Solution

	total olfaction time					missing odors no.					ghost odors no.				
judge	R1[a]	R2[a]	R3[a]	mean	SD	R1	R2	R3	mean	SD	R1	R2	R3	mean	SD
1	2.91	3.95	2.74	3.20	0.66	1	1	1	1	0	4	3	1	2.7	1.5
2	3.63	2.67	2.70	3.00	0.55	0	0	1	0.3	0.6	4	0	1	1.7	2.1
3	3.04	2.72	2.61	2.79	0.22	0	0	0	0	0	1	1	0	0.7	0.6
4	1.17	0.83	1.24	1.08	0.22	0	1	0	0.3	0.6	0	0	0	0.0	0.0
5	4.07	4.76	4.02	4.28	0.41	0	1	1	0.7	0.6	3	3	2	2.7	0.6
6	2.85	2.54	2.23	2.54	0.31	0	1	0	0.3	0.6	0	0	0	0.0	0.0
7	2.85	2.61	2.65	2.70	0.13	0	0	0	0	0	0	0	0	0.0	0.0
8	1.64	1.74	2.01	1.80	0.19	0	0	0	0	0	0	0	0	0.0	0.0
9	4.96	2.24	3.84	3.68	1.37	0	2	2	1.3	1.2	2	2	4	2.7	1.2
ref[b]	4.98	4.76	5.04	4.93	0.15	0	0	0	0	0	0	0	0	0.0	0.0

[a] R1, R2, R3 = three replicates. [b] Expert judge taken as reference.

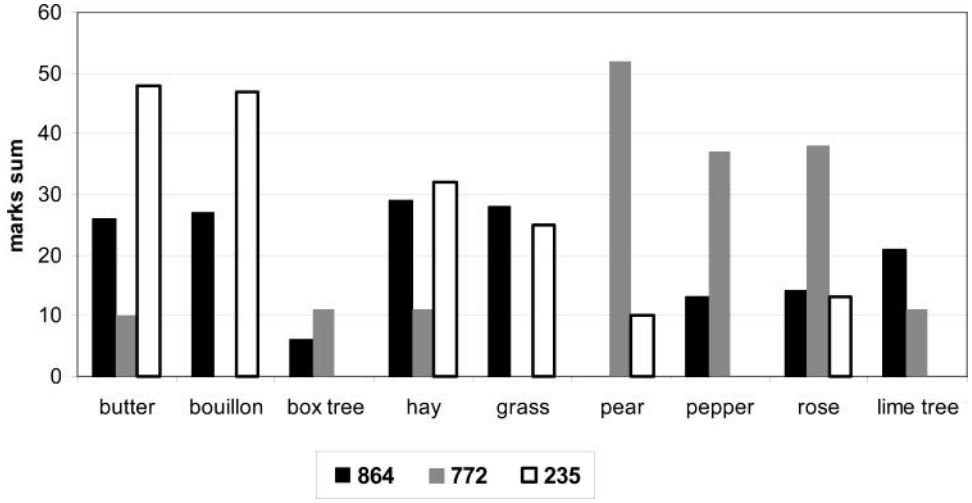

Figure 1. Sensory profiles of the three selected spirits presented by descriptor (14 judges).

GC-O. GC analysis were performed using a Hewlett-Packard HP 5890 series 2^+ gas chromatograph equipped with an on-column injector (T = 80 °C), a flame ionization detector (T = 250 °C), and an SGE-ODO 1 (Scientific Glass Engineering) sniffing port. The column effluent was split equally between the detector and the sniffing port, and humid air (20 mL/min) was added as makeup gas to prevent nasal dryness. The separations were carried out with a CP-Wax 52 CB capillary column (50 m × 0.25 mm i.d. × 0.2 μm) connected with a deactivated precolumn (1 m × 0.53 mm i.d.). The oven temperature was set at 80 °C for 4 min and then increased stepwise to 240 °C at a rate of 10 °C/min. The carrier gas flow (helium) was set at 2.55 mL/min, so the sniffing time was reduced to 20 min, to prevent tiredness in the judges.

For each sniffing run, 1 μL of the CH_2Cl_2 extract was injected in order to obtain ~20 main odors.

GC-O was done with seven panelists and two replicates for each spirit. Panelists were selected first after specific training with a solution of synthetic odors and then with a Cognac spirit extract.

The olfactograms were obtained by the HP Chemstation, in parallel with the FID chromatograms, from the acquisition of the signal generated by a switch pressed by the judge when detecting an odor. Thus, we could check those chromatograms with the quantitative ones.

Results from all of the panelists were collected in a file where retention times were reported in seconds. Every second during acquisition time, the mark "0" was attributed if nothing was smelt and the mark "1" was given if an odor was detected. The nasal impact frequency (NIF) value (NIF = 1 if all of the panelists detected the odor and NIF = 0 if nobody smelled it) was calculated for each odorant zone. For each descriptor and in each extract, the sum of NIF values was calculated and then divided by the number of "sniffing" runs performed.

GC-O Panelist Training and Evaluation. The performances of our panel were improved with a training program and a performance test. Running tests were performed with a 21 aromatic compound synthetic solution, representative of Cognac. Each panelist undertook several sniffing sessions of this solution to recognize the odors before testing a new solution (three replicates). The new solution contained a selection of 7 odorant compounds (presented in **Table 1**) from the 21 of the synthetic solution and an "unknown" odor (butanoic acid) that was to be detected. Concentrations of volatiles were close to those found in Cognac, but linalool was slightly greater. The results of GC-O on test solutions are presented in **Table 2**. Among the 10 judges, 1 was taken as a reference expert (no error, no ghost odor). After training, the judges' performances were close (except one, judge 9) for the number of odors detected. There was a larger difference with total olfaction time in comparison with the reference judge, who was more sensitive. Judges 1 and 9 were not selected for further sessions on the spirits. Indeed, these two judges missed at least one odor and added almost three ghost odors per run on the test solution.

The eight remaining panelists were trained with a spirit extract before beginning the study.

GC-MS. GC-MS analyses were conducted to detect new volatile compounds or to confirm the presence of others identified in previous investigations on the chemical composition of the same extracts (*19*) and Cognac samples from various origins (*22*). A Hewlett-Packard 6890 gas chromatograph was coupled with an MSD 5973 quadrupolar mass detector. The split/splitless injector (T = 240 °C) was used in splitless mode for 0.70 min and then in split mode at 70 mL/min. The column was a DB-Wax (60 m × 0.25 mm i.d. × 0.25 μm from J&W Scientific). Helium was the carrier gas at 1 mL/min. Oven temperature was 35 °C for 0.7 min, then increased stepwise to 70 °C at a rate of 20 °C/min and then to 240 °C at 4 °C/min. The mass detector was used in scan mode (m/z 40−400 uma) with an ion source temperature of 230 °C. Electron multiplicator voltage was set at 400 V with a solvent delay of 7 min. Identification was done by comparing the MS spectra with those of the NIST 98 MS database, the Wiley database, and the Inramass database and with those obtained with pure standard compounds. A ratio of not less than 90−95% was taken to mean that a compound

Table 3. Identification of Volatile Compounds in Freshly Distilled Spirits, by GC-MS Analysis (RI on a DB-Wax Column)

RI	compound[a]	RI	compound[a]	RI	compound[a]
<900	acetaldehyde (a,c)[1]	1378	methyl octanoate (a)[1]	1725	propyl decanoate[1]
<900	2-methylpropanal (a)[2]	1379	nonanal (a)[1]	1729	pentanoic acid (a,c)[1]
<900	3,3-dimethoxybutan-2-one[2]	1385	octan-3-ol (a)[1]	1730	1,3-dimethoxybenzene[1]
<900	ethyl acetate (a,c)[1]	1402	*E*-hex-2-en-1-ol (a)[1]	1732	ethyl undecanoate[1]
<900	1,1-diethoxyethane (a,b)[1]	1411	ethyl 2-hydroxy-3-methylbutanoate[2]	1737	α-farnesene[1]
<900	2-methylbutanal (a)[1]	1424	ethyl octanoate (a,b,c)[1]	1752	decan-1-ol (a)[1]
915	ethyl propanoate (a,c)[1]	1443	oct-1-en-3-ol[1]	1756	methyl salicylate (a)[1]
935	propyl acetate (a,c)[1]	1444	heptan-1-ol (a)[1]	1758	β-citronellol (a)[1]
943	diacetyl (2,3-butanedione) (a)[1]	1445	acetic acid (a,c)[1]	1768	diethyl pentanedioate[2]
955	ethyl 2-methylpropanoate (a,c)[2]	1450	3-methylbutyl hexanoate (a,c)[1]	1785	ethyl 2-phenylacetate[1]
975	1-(1-ethoxyethoxy)butane[2]	1453	2-furaldehyde (a,b,c)[1]	1785	ethyl 2-methylpropyl succinate (b)[2]
985	2-methylpropyl acetate (a,c)[1]	1453	linalool oxide (b)[1]	1793	methyl dodecanoate[1]
1012	butan-2-ol (a,c)[1]	1485	decanal (a)[1]	1802	β-damascenone (b)[1]
1022	ethyl butanoate (b,c)[1]	1489	2-acetylfuran (b)[1]	1805	2-phenylethyl acetate (b)[1]
1029	propan-1-ol (a,c)[1]	1502	benzaldehyde (b,c)[1]	1835	ethyl dodecanoate (b,c)[1]
1035	ethyl 2-methylbutanoate (a,b)[1]	1501	2,10,10-trimethyl-6-oxaspiro[4,5]dec-7-ene[2]	1840	hexanoic acid (a,c)[1]
1051	ethyl 3-methylbutanoate (a,b)[1]	1504	methylidene-1-oxaspiro[4,5]dec-7-ene[2]	1854	2-methylbutyl decanoate (b,c)[1]
1062	1,1-diethoxy-3-methylbutane (b,c)	1506	dihydro-2-methyl-3(2*H*)-thiophenone[2]	1863	3-methylbutyl decanoate (b)[1]
1068	1,1-diethoxy-2-methylbutane (b,c)	1509	nonan-2-ol (a)[1]	1868	benzyl alcohol (a)[1]
1076	isobutanol (a)[1]	1526	ethyl nonanoate (a,c)[1]	1884	ethyl 3-hydroxyoctanoate[2]
1104	1-(1-ethoxyethoxy)pentane[1]	1528	propanoic acid (a,c)[1]	1892	ethyl 3-methylbutyl succinate[2]
1112	2-methylbutyl acetate (a,b)[1]	1533	ethyl 2-hydroxyhexanoate (b)[2]	1896	2-phenylethanol (a,b,c)[1]
1113	3-methylbutyl acetate (a,b)[1]	1540	linalool (a)[1]	1936	heptanoic acid (a)[1]
1136	butan-1-ol (a,c)[1]	1547	octan-1-ol (a,b,c)[1]	1956	butyl dodecanoate [1]
1153	ethyl but-2-enoate[1]	1556	2-methylpropanoic acid[1]	1957	dodecan-1-ol[1]
1153	3-ethoxypropanal[2]	1558	3-methylbutyl lactate (a)[1]	1993	γ-nonalactone[1]
1169	limonene[1]	1559	5-methylfurfural (c)[1]	2025	*E*-nerolidol[1]
1193	3-methylbutanol (a,c)[1]	1570	undecan-2-one (a)[1]	2040	ethyl tetradecanoate (b,c)[1]
1223	ethyl hexanoate (b,c)[1]	1572	diethyl propanedioate[2]	2051	octanoic acid (a,c)[1]
1230	1,1-diethoxyhexane[1]	1585	methyl decanoate[1]	2059	3-methylbutyl dodecanoate (b)[1]
1235	3-methylbut-3-en-1-ol[2]	1602	hex-3-en-1-yl butanoate[1]	2102	ethyl 3-hydroxydecanoate[2]
1240	pentanol (a)[1]	1604	myrcenol[2]	2135	ethyl pentadecanoate[1]
1256	3-methylbutyl butanoate (a)[2]	1611	ethyl furoate (b)[1]	2145	tetradecan-1-ol (b)[1]
1263	hexyl acetate (b)[1]	1620	butanoic acid (a,c)[1]	2213	methyl hexadecanoate[1]
1282	2,2,6-trimethyl cyclohexanone[2]	1619	acetophenone[2]	2246	ethyl hexadecanoate (b)[1]
1290	ethyl hex-3-enoate[1]	1629	ethyl decanoate (a,b,c)[1]	2264	decanoic acid (a,c)[1]
1297	1,1,3-triethoxypropane[1]	1649	ethyl benzoate[1]	2267	ethyl hexadec-9-enoate (b)[2]
1302	4-methyl pentan-1-ol[1]	1651	3-methylbutyl octanoate (b,c)[1]	2271	3-methylbutyl tetradecanoate[1]
1304	hex-3-en-1-yl acetate[1]	1653	nonan-1-ol (a)[1]	2365	undecanoic acid (a)[1]
1310	heptan-2-ol (a)[1]	1656	2-[ethoxy-(3-methylbutoxy)methyl]furan[2]	2340	ethyl heptadecanoate[1]
1314	3-methyl pentan-1-ol[1]	1660	3-methylbutanoic acid (a)[1]	2350	farnesol[1]
1316	oct-1-en-3-one[1]	1662	2-methylbutanoic acid[1]	2400	hexadecan-1-ol[1]
1323	hex-2-en-1-yl acetate[2]	1667	diethyl succinate[1]	2455	ethyl octadecanoate[1]
1329	ethyl hex-2-enoate[2]	1678	2 and 3-thiophencarboxaldehyde[1]	2469	ethyl octadec-9-enoate (b)[1]
1331	ethyl 2-hydroxypropanoate (b)[2]	1681	α-terpineol (a,c)[1]	2469	dodecanoic acid (a,c)[1]
1342	hexan-1-ol (a,b,c)[1]	1683	γ-terpineol[1]	2515	ethyl octadec-9,12-dienoate[1]
1352	e-hex-3-en-1-ol (a,c)[1]	1685	ethyl dec-9-enoate[2]	2545	ethyl octadec-9,12,15-trienoate[1]
1359	3-ethoxypropanol[1]	1702	3-methylthiopropanol[1]	2550	vanillin (a)[1]
1369	3,5,5-trimethyl-2-cyclohexen-1-one[2]	1710	undecan-2-ol (a)[1]	>2550	tretradecanoic acid (a,c)[1]
1371	*Z*-hex-3-en-1-ol (a)[1]	1722	1,2-dihydro-1,1,6-trimethylnaph-		
1374	nonan-2-one (a,b,c)[1]		thalene[1] (TDN)		

[a] (a) Marché et al. (*13*); (b) Nykänen and Nykänen (*3*); (c) Schaefer and Timmer (*22*); [1] = verified with reference compound; [2] = tentatively identified.

was identified, providing the other information about it was consistent [retention index (RI), odors].

For each peak detected, a linear retention index was calculated using GC retention index standards (hydrocarbons from C7 to C31) according to the method of Van den Dool and Kratz (*21*). To identify key odorants, retention indices of volatile compounds were compared with those of odors detected during GC-O analyses.

RESULTS

Sensory Analysis. Figure 1 shows the sensory profile of the three selected spirits from the 2000 vintage. Spirit 864 was described as having a medium sensory perception of all the descriptors except "pear", which was absent, so it can be considered as a neutral spirit. Spirit 772 obtained its maximum mark for "pear". Consequently, it was perceived as fruitier but also as peppery and flowery. On the contrary, the panelists did not find any "bouillon" or "grass" descriptor in this sample. Sensory analysis of spirit 235 showed a real difference with that of spirit 772. The most perceived odors here were "butter" and "bouillon", whereas "pepper" and "lime tree" were completely absent. Moreover, the mark of the fruity descriptor "pear" was 5-fold less than in spirit 772.

Identification by GC-MS. The volatile compounds identified in the three spirits are presented in **Table 3**.

A total of 150 compounds were identified in the three spirits, most of which have already been identified by previous authors (*3*, *13*, *22*). It is noted that unlike previous ones, the present study concerned freshly distilled spirits not matured in oak barrels.

Besides the fatty acids, esters, and fusel alcohols originating from the wine and already identified in many types of spirits, other volatile compounds were identified. Some terpenic compounds, such as limonene, myrcenol, α-terpineol, α-farnesene,

Table 4. Identification and Quantification of Compounds Responsible for the Main Odorant Zones (NIF= Nasal Impact Frequency)

olfac zone	odor descriptors	RI min	RI max	identified compound[c]	content[a] (mg/L) 235	content[a] (mg/L) 772	content[a] (mg/L) 864	NIF[b] 235	NIF[b] 772	NIF[b] 864
1	solvent, alcohol	900	940	ethyl acetate (1)	194 (1)	302 (1)	213 (1)	0.93	0.71	0.93
2	butter, pastry	932	953	2,3-butanedione (1)				0.93	0.64	0.93
3	solvent, alcohol	959	984	ethyl alcohol				0.64	0.57	0.50
4	green,	971	1039	2-methylpropyl acetate (2)				0.93	0.86	1
	fruity,			ethyl butyrate (1)	0.97 (1)	1.92 (1)	0.64 (1)			
	kiwi			ethyl 2-methylbutanoate (2)						
5	banana, pear	1041	1136	2- and 3-methylbutyl acetate (1)	4.738 (2)	15.66 (2)	2.196 (2)	0.79	0.86	0.79
6	fruity, cacao, sweat	1165	1200	2- and 3-methylbutan-1-ol (1)	2586 (1)	1683 (1)	2571 (1)	1	0.93	1
7	strawberry, anise	1210	1260	ethyl hexanoate (1)	3.7 (2)	5.7 (2)	2.5 (2)	1	1	0.93
8	mushrooms	1297	1330	oct-1-en-3-one (2)				0.79	0.71	0.93
9	flowery, green	1339	1363	*n*-hexan-1-ol (1)	5.8 (1)	11.5 (1)	12.2 (1)	0.57	0.64	0.43
10	green,	1364	1400	*Z*-hex-3-en-1-ol (1)	1.47 (1)	1.46 (1)	2.32 (1)	0.64	0.71	0.86
	bug			nonanal (2)						
11	flowery, undergrowth	1393	1445	oct-1-en-3-ol (2)				0.57	0.29	0.50
12	potato	1450	1480	3-methylthiopropanal (3)	39 (3)	0 (3)	5 (3)	0.86	0.64	0.71
13	flowery	1490	1586	vitispiranes 1 and 2[d] (1)	0.174 (2)	0.180 (2)	0.235 (2)	0.64	0.50	0.71
	lemony			linalool (1)	0.370 (2)	0.380 (2)	0.649 (2)			
	dust			2-methylpropanoic acid (2)						
14	green, cucumber	1587	1640	2,6-nonadienal (2)				0.79	0.71	0.93
15	cheese,	1650	1746	2- and 3-methylbutanoic acid (2)				1	1	1
	stock-bouillon			2-thiophencarboxaldehyde (2)						
16	hay, tea, dry, spicy	1728	1800	β-citronellol (1)				0.93	0.86	0.71
	cooked fruit			methyl salicylate (2)						
				β-damascenone (1)	0.191 (2)	0.218 (2)	0.222 (2)			
17	rose	1802	1880	2-phenylethyl acetate (1)	0.814 (2)	1.705 (2)	0.364 (2)	0.93	0.93	1
18	rose	1890	2005	2-phenylalcohol (1)	18.5 (1)	7.2 (1)	16.4 (1)	0.86	0.79	0.86
	wine			butyl dodecanoate (2)						
				dodecanol (2)						
19	dry wood, hay	2020	>	nerolidol (1)	0.469 (2)	0.170 (2)	0.511 (2)	0.29	0.57	0.29

[a] Means of quantification: (1) = direct injection, (2) = iso-octane extraction, (3) = specific method (*23*). [b] Nasal impact frequency. [c] Means of identification: (1) = routine GC-MS, (2) = CH_2Cl_2 extract GC-MS, (3) = preparative GC (*23*). [d] Vitispirane 1 = 2,10,10-trimethyl-6-oxaspiro[4,5]dec-7-ene; vitispirane 2 = methylidene-1-oxaspiro[4,5]dec-7-ene.

nerolidol, and farnesol, were identified for the first time in this type of spirit. These compounds may originate from the grapes. Oct-1-en-3-one was also identified for the first time in freshly distilled Cognac. Note that vanillin, which was previously identified in spirits matured in oak barrels (*10*), was also found in freshly distilled spirits.

GC-O Analysis of the Selected Spirits. Table 4 presents the 19 main odorant zones with their olfactometric indexes (NIF values). They were selected from the olfactograms obtained with the three spirits and were previously described as mainly responsible for the basic structure of the spirit's aromatic profile (*19*). In each zone, the odor was attributed to one or more aroma compounds, taking into account the retention index and the odor description. These compounds were also quantified in parallel by classical methods (direct injection or iso-octane injection), and results are presented in **Table 4**.

DISCUSSION

Olfactive Zones (Table 4). The first odorant zone (zone 1) was defined by judges as "solvent, alcohol", which is the characteristic descriptor of ethyl acetate, a major ester in distilled spirits. Possessing a retention index of <900 (see **Table 3**) on a DB-Wax stationary phase, its chromatographic peak can be shifted due to high ethanol content in dichloromethane extracts. The "butter" sensory descriptor is due to the presence of diacetyl, the butter odor of which is detected in zone 2. Its detection threshold was found between 2.3 and 6.5 ppb in water (*24*), and it was quantified in a higher amount in spirits 864 and 235. The third zone (zone 3) corresponds to the end of the perception of the saturated tailing peak of ethanol. In zone 4, the "fruity" note was attributed to ethyl butanoate, with a threshold in water of 1 ppb (*25*, *26*), and the "kiwi" note to both ethyl methylbutanoates, which have sensory thresholds near 0.3 ppb in water (*27*). A descriptor of "banana, pear" was given by the judges for the fifth zone (zone 5). This odor can be attributed to 2- and 3-methylbutyl acetates, which present very low sensory detection thresholds of ~2 ppb in water (*28*). With methylbutyl acetates, methylbutanols are well-known key aroma compounds of distilled spirits and are responsible for the "cacao, sweat" descriptor found for zone 6. Moreover, these higher alcohols were described as cacao by our panelists in the test solution. The "strawberry" odor in zone 7 may be explained by the presence of ethyl hexanoate, which is usually described as "fruity" and has an odor threshold of 0.3 ppb in water (*29*). The typical "mushroom" note due to oct-1-en-3-one (*30*), with a threshold of 0.005−4 ppb (*31*), was found in zone 8, whereas oct-1-en-3-ol, with a threshold of 1 ppb (*32*), was perceived in zone 11 with an "undergrowth" note. Zones 9 and 10 both presented a strong "green" note. The first olfactive note can be attributed to hexan-1-ol, which presents high amounts in distilled beverages, whereas *Z*-hex-3-en-1-ol is responsible for this odor in zone 10. The "potato" aroma of zone 12 is characteristic of the presence of methional (3-methylthiopropanal) (*33*). With an extremely low detection threshold of 0.2 ppb in water (*31*, *34*), it was identified only by its retention index but was further identified in fractions obtained by preparative GC analysis (*23*). Owing to various coelutions, the olfactives notes reported for zone 13 cannot be attributed to only one volatile compound. The overall aroma of that zone is constituted by the odors of vitispiranes, linalool, and 2-methylpropanoic acid. Strong "green" notes in spirits often reveal the presence of unsaturated aldehydes. 2,6-Nonadienal has notably been characterized not

only in whiskies (*35*) but also in wine spirits (*36*). The retention index of this powerful "green, cucumber" odorant, with a perception threshold of 0.01 ppb (*37*), corresponds to that of zone 14. Consequently, 2,6-nonadienal may have an important olfactive impact in freshly distilled Cognac. In zone 15, the principal odors recorded were "cheese" and "stock-bouillon". The first is due to the presence of 2- and 3-methylbutanoic acids (*38*) and the second to 2-thiophenecarboxaldehyde. The descriptor of the sulfur compounds was verified to confirm its identification as a key odorant. Various odors (hay, tea, dry, spicy) were perceived in zone 16 and may be due to the combined contribution of volatile compounds such as β-citronellol and methyl salicylate, which are usually described with such odors. β-Damascenone, with a threshold of 0.002 ppb (*31*, *39*), was detected in zone 17 by its typical "cooked, fruity" odor with also a contribution of 2-phenylethyl acetate, which has a sensory threshold of 1.8 ppm in wine (*40*) and an odor described as "fruity, rose". 2-Phenylethanol, with its "rose" descriptor, should be the major contributor to the odor detected in zone 18. Finally, zone 19 presents a "dry wood, hay" descriptor due to the presence of nerolidol.

Association between Olfactometry and Sensory Analyses. The "butter" sensory descriptor is obviously ascribable to the presence of diacetyl. This was confirmed by NIF values. Indeed, the lowest mark for this descriptor (**Figure 1**) was found for spirit 772, which also has the lowest NIF value (0.64 versus 0.93 for the other samples). In GC-O the "stock-bouillon" descriptor was detected in only zone 15. Consequently, 2- and 3-methylbutanoic acids may have been responsible for this odor in the samples. NIF values recorded in olfactometry (1 for each sample) could not discriminate the three spirits, but sensory analyses seemed to reveal the lowest concentration of "stock-bouillon" in spirit 772. "Box tree" was not found by olfactometry, so it may be due to a mixture of different odors. "Hay" was found in both sensory evaluations and olfactometry (zones 16 and 19). It was perceived more in spirits 864 and 235 and could not be clearly associated with β-citronellol present in zone 16. On the contrary, marks of that descriptor were well correlated with nerolidol (zone 19) concentrations obtained after iso-octane extractions, the odor of which had already been described as "dry grass" (*41*). "Grass" is usually attributed to (*Z*)-hex-3-en-1-ol in distilled beverages, due to its low detection threshold of 0.07 ppm in water (*42*), but hexanol and 2,6-nonadienal can also contribute to the perception of this "green" note. "Pear", characteristic of spirit 772, is directly associated with a concentration of 2- and 3-methylbutyl acetates, which has sensory detection thresholds of 2 ppb in water (*28*). A high concentration of these esters was found in spirit 772 (15.7 mg/L), whereas its concentrations in spirits 864 and 235 were 4−6-fold lower. The presence of ethyl hexanoate and ethyl butanoate at higher concentrations in spirit 772 (respectively, 5.7 and 1.92 mg/L) may also have enhanced this "fruity" note. "Pepper" was not found by olfactometry. Only a "spicy" odor was perceived in zone 16, but no aroma compound in this area was found that might have been responsible for this odor. 2-Phenylethanol is usually considered to be responsible for "rose" in spirits, but in this study in cognac, 2-phenylethyl acetate played a more significant role. Indeed, a close association was found between marks obtained by sensory analyses for the "rose" descriptor with concentrations of 2-phenylethyl acetate in all three spirits. On the contrary, the intensity of "rose" is completely independent of the amount of 2-phenylethanol. The last descriptor given was "lime tree", which could be associated with the typical lemony note of linalool in zone 13, the sensory threshold of which is ~6 ppb in water (*34*). Its greater perception in spirit 864 was certainly due to a higher amount (0.65 versus 0.37 and 0.38 mg/L for the others) of this molecule in that sample.

Among the numerous volatile compounds identified in the three spirits, only some of them were distinctive in the samples according to their specific odors. The "rose" and "pear" in spirit 772 were mainly due to the presence of 2-phenylethyl acetate and 2- and 3-methylbutyl acetates, respectively. The "hay" found in spirits 864 and 235 was attributed to nerolidol and the "lime tree" in spirit 864 to the presence of linalool.

Conclusion. This study shows that GC-O can identify odorous compounds responsible for the specific aroma descriptors of freshly distilled Cognac spirits. Freshly distilled Cognac spirits already present specific odor notes that could be assigned to aroma compounds present in grapes and wines or formed during the distillation process. Their aromatic quality depends on the subtle association of these specific odorous compounds.

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LITERATURE CITED

(1) Cantagrel, R.; Lurton, L.; Vidal, J. P.; Galy, B. From vine to Cognac. In *Fermented Beverage Production*; A. G. H., L., Piggott, J. R., Eds.; Blackie Academic and Professional: London, U.K., 1994; pp 208−228.

(2) Ter Heide, R. The flavour of distilled beverages. In *Developments in Food Science 3B, Food Flavours*; Morton, I. D., MacLeod, A. J., Eds.; Elsevier Science: Amsterdam, The Netherlands, 1986; pp 239−312.

(3) Nykänen, L.; Nykänen, I. Distilled beverages. In *Volatile Compounds in Foods and Beverages*; Maarse, H., Ed.; Dekker: New York, 1991; pp 547−579.

(4) Salo, P.; Nykaenen, L.; Suomalainen, H. Odor threshold and relative intensities of volatile aroma components in an artificial beverage imitating whisky. *J. Food Sci.* **1972**, *37*, 394−398.

(5) Madrera, R. R.; Gomis, D. B.; Alonso, J. J. M. Influence of distillation system, oak wood type, and aging time on volatile compounds of cider brandy. *J. Agric. Food Chem.* **2003**, *51*, 5709−5714.

(6) Galy, B.; Desache, F.; Cantagrel, R.; Lurton, L.; Courlit, Y.; Menard, E.; Gaschet, J. Comparaison de différents cépages aptes à la production d'eaux de vie de cognac: aspects analytiques et organoleptiques. In *Elaboration et Connaissance des Spiritueux*; BNIC, Ed.; Tec & Doc, Lavoisier: Paris, France, 1993; pp 62−66.

(7) Galy, B.; Roulland, C.; Lurton, L.; Cantagrel, R., Connaissance des paramètres influant sur la conservation des vins destinés à l'élaboration des eaux-de-vie de Cognac. In *Elaboration et Connaissance des Spiritueux*; BNIC, Ed.; Tec & Doc, Lavoisier: Paris, France, 1993; pp 218−224.

(8) Nykänen, L.; Nykänen, I. Distribution of esters produced during sugar fermentation between the yeast cell and the medium. *J. Inst. Brew.* **1977**, *83*, 32−34.

(9) Cantagrel, R.; Galy, B.; Jouret, C., Eaux-de-vie d'origine viticole. In *Oenologie. Fondements Scientifiques et Technologiques*; Flanzy, C., Ed.; Tec & Doc: Paris, France, 1998; pp 1083−1107.

(10) Puech, J. L.; Le Poutre, J. P.; Baumes, R.; Bayonove, C.; Moutounet, M., Influence de thermotraitement des barriques sur l'évolution de quelques composants issus du bois de chêne dans les eaux de vie. In *Elaboration et Connaissance des Spiritueux*; Cantagrel, R., Ed.; Tec & Doc, Lavoisier: Paris, France, 1992; pp 583−588.

(11) Guichard, E.; Fournier, N.; Masson, G.; Puech, J. L. Stereoisomers of β-methyl-γ-octalactone. I. Quantification in brandies as a function of wood origin and treatment of the barrels. *Am. J. Enol. Vitic.* **1995**, *46*, 419−423.

(12) Masson, G.; Guichard, E.; Fournier, N.; Puech, J. L. Stereoisomers of β-methyl-γ-octalactone. II. Contents in the wood of French (*Quercus robur* and *Quercus petraea*) and American (*Quercus alba*) oaks. *Am. J. Enol. Vitic.* **1995**, *46*, 424−428.

(13) Marché, M.; Joseph, E.; Goizet, A.; Audebert, J. Etude théorique sur le Cognac, sa composition et son vieillissement naturel en fûts de chêne. *Rev. Fr. Oenol.* **1976**, *57*, 1−108.

(14) Acree, T. E.; Barnard, J.; Cunningham, D. G. A procedure for the sensory analysis of gas chromatographic effluents. *Food Chem.* **1984**, *14*, 273−286.

(15) Grosch, W. Detection of potent odorants in foods by aroma extract dilution analysis. *Trends Food Sci. Technol.* **1993**, *4*, 68−73.

(16) Guichard, H.; Lemesle, S.; Ledauphin, J.; Barillier, D.; Picoche, B. Chemical and sensorial aroma characterization of freshly distilled calvados. 1. Evaluation of quality and defects on the basis of key odorants by olfactometry and sensory analysis. *J. Agric. Food Chem.* **2003**, *51*, 424−432.

(17) Ledauphin, J.; Guichard, H.; Saint-Clair, J. F.; Picoche, B.; Barillier, D. Chemical and sensorial aroma characterization of freshly distilled cavados. 2. Identification of volatile compounds and key odorants. *J. Agric. Food Chem.* **2003**, *51*, 433−442.

(18) Leclaire, E.; Cantagrel, R.; Maignial, R.; Snakkers, G.; Ferrari, G. Essai de caractérisation aromatique d'eaux de vie nouvelles de Cognac. *J. Int. Sci. Vigne Vin* **1999**, *33*, 133−141.

(19) Lablanquie, O.; Snakkers, G.; Cantagrel, R.; Ferrari, G. Characterisation of young Cognac spirit aromatic quality. *Anal. Chim. Acta* **2002**, *458*, 191−196.

(20) Bertrand, A. *Recueil des Méthodes d'Analyse des Boissons Spiritueuses, des Alcools, de la Fraction Aromatique des Boissons*; OIV: Paris, France, 1994.

(21) Van Den Dool, H.; Kratz, P. A. Generalization of the retention index system including linear temperature programmed gas−liquid partition chromatography. *J. Chromatogr.* **1963**, *11*, 463−471.

(22) Schaefer, J.; Timmer, R. Flavor components in Cognac. *J. Food Sci.* **1970**, *35*, 10−12.

(23) Ledauphin, J.; Saint-Clair, J. F.; Lablanquie, O.; Guichard, H.; Fournier, N.; Guichard, E.; Barillier, D. Identification of trace volatile compounds in freshly-distilled Calvados and Cognac using preparative separations coupled with GC/MS. *J. Agric. Food Chem.* **2004**, *52*, 5124−5134.

(24) Leffingwell, J. C.; Leffingwell, D. GRAS Flavor chemicals detection thresholds. *Perfum. Flavor.* **1991**, *16*, 2−19.

(25) Flath, R. A.; Black, D. R.; Guadagni, D. G.; McFadden, W. H.; Schultz, T. H. Apple volatiles. *J. Agric. Food Chem.* **1967**, *15*, 29−35.

(26) Takeoka, G. R.; Flath, R. A.; Mon, T. R.; Teranishi, R.; Guentert, M. Volatile constituents of apricot. *J. Agric. Food Chem.* **1990**, *38*, 471−477.

(27) Buettner, A.; Schieberle, P. Characterization of the most odor-active volatiles in fresh, hand-squeezed juice of grapefruit (*Citrus paradisi* Macfayden). *J. Agric. Food Chem.* **1999**, *47*, 5189−5193.

(28) Takeoka, G.; Buttery, R. G.; Flath, R. A.; Teranishi, R.; Wheeler, E. L.; Wieczorek, R. L.; Guentert, M. Volatile constituents of pineapple. In *Flavor Chemistry: Trends and Developments*; Teranishi, R., Buttery, R. G., Shahidi, F., Eds.; American Chemical Society: Washington, DC, 1989; pp 221−237.

(29) Pyysalo, T.; Suiko, M.; Honkanen, E. Odour Thresholds of the Major Volatiles Identified in Cloudberry (*Rubus chamaemorus* L.) and Arctic Bramble (*Rubus arcticus* L.). *Lebensm. Wiss. Technol.* **1977**, *10*, 36−39.

(30) Kubickova, J.; Grosch, W. Evaluation of potent odorants of Camembert cheese by dilution and concentration techniques. *Int. Dairy J.* **1997**, *7*, 65−70.

(31) Buttery, R. G.; Teranishi, R.; Ling, L. C.; Turnbaugh, J. G. Quantitative and sensory studies on tomato paste volatiles. *J. Agric. Food Chem.* **1990**, *38*, 336−340.

(32) Buttery, R. G.; Turnbaugh, J. G.; Ling, L. C. Contribution of volatiles to rice aroma. *J. Agric. Food Chem.* **1988**, *36*, 1006−1009.

(33) Aznar, M.; Lopez, R.; Cacho, J. F.; Ferreira, V. Identification and quantification of impact odorants of aged red wines from Rioja. GC-olfactometry, quantitative GC-MS, and odor evaluation of HPLC fractions. *J. Agric. Food Chem.* **2001**, *49*, 2924−2929.

(34) Fazzalari, F. A., Ed. *Compilation of Odor and Taste Threshold Values Data*; ASTM: Philadelphia, PA, 1978.

(35) Wanikawa, A.; Hosoi, K.; Nakagawa, K. I. Identification of green note compounds in malt whisky using multidimensional gas chromatography. *Flavour Fragrance J.* **2002**, *17*, 207−211.

(36) Rogerson, F. S.; De Freitas, V. A. Fortification spirit, a contributor to the aroma complexity of Port. *J. Food Sci.* **2002**, *67*, 1564−1569.

(37) Boehlens, M. H.; Van Gemert, J. Odor and taste threshold values. *Perfum. Flavor.* **1987**, *12*, 31−43.

(38) Guerra, R. L.; Guth, H.; Lopez, M. G. Identification of the most potent odorants in Huitlacoche (*Ustilago maydis*) and Austern Pilzen (*Pleurotus* ssp.). *J. Agric. Food Chem.* **1997**, *45*, 1329−1332.

(39) Buttery, R. G.; Teranishi, R.; Flath, R. A.; Ling, L. C. Fresh tomato volatiles—composition and sensory studies. In *Flavor Chemistry: Trends and Developments*; Teranishi, R., Buttery, R. G., Shahidi, F., Eds.; American Chemical Society: Washington, DC, 1989; pp 213−222.

(40) Etiévant, P. Wine. In *Volatile Compounds in Food*; Maarse, H., Ed.; Dekker: New York, 1991; pp 483−546.

(41) Tu, N. T. M.; Onishi, Y.; Choi, H. S.; Kondo, Y.; Bassore, S. M.; Ukeda, H.; Sawamura, M. Characteristic odor components of *Citrus sphaerocarpa* Tanaka (Kabosu) cold-pressed peel oil. *J. Agric. Food Chem.* **2002**, *50*, 2908−2913.

(42) Ulrich, D.; Hoberg, E.; Rapp, A.; Kecke, S. Analysis of strawberry flavour-discrimination of aroma types by quantification of volatile compounds. *Z. Lebensm. Unters. Forsch.* **1997**, *205*, 218−223.

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