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ARTICLE

Differences in the Volatile Compositions of French Labeled Brandies (Armagnac, Calvados, Cognac, and Mirabelle) Using GC-MS and PLS-DA

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A total of 207 volatile compounds were identified in extracts of four French labeled brandies: Armagnac, Cognac, Calvados, and Mirabelle. Relative levels of all components were determined using GC-MS after integration of a selected peak of the mass spectrum of each. Each type of brandy could be clearly discriminated using PLS-DA statistical analyses based on these levels. French Mirabelle spirit, which was studied for the first time, was characterized by higher levels of many aldehydes and acetals and by the presence of compounds having an odd number of carbons together with benzaldehyde and some of its derivatives. Many possible derivatives of acrolein and high amounts of butan-2-ol were rather specific for the volatile composition of Calvados. The most important difference between the two wine-based samples seemed to be directly linked to the distillation system used. Many furanic compounds are specific to Cognac, whereas two or three compounds such as 1-(ethoxyethoxy)-2-methylbutane and γ-eudesmol were specific to Armagnac. These two brandies presented rather high distributions of isobutanol and isopentanols, whereas Mirabelle and Calvados compositions offer more concentrated aliphatic linear alcohols.

KEYWORDS: Volatile composition; GC-MS; brandies; discrimination; PLS-DA analysis

INTRODUCTION

Many brandies are produced in France, but the most renowned and consumed ones are Cognac, Armagnac, Calvados, and Mirabelle.

Cognac and Armagnac are protected by the French label "AOC" (Appelation d'Origine Contrôlée) for one century. In 1909, their respective areas of production were defined, but the rules governing their fabrication were more precisely given in 1936 (*1*, *2*). These two distilled wines present major differences in their geographic origins and in their distillation processes. Cognac is elaborated in the limited region of Charentes; wines with alcoholic degrees of about 9 are submitted to a double distillation in an "alambic charentais" (Cognac pot still). Armagnac is mainly produced in the Gers area and is resulting in a large majority of a single-step distillation in an "alambic armagnacais" (Armagnac column still) of wines with alcoholic degree between 7.5 and 12. Calvados is a cider brandy, which exclusively originates from Normandy. Single or double distillations of ciders containing about 5% ethanol are used to produce this spirit, and a label AOC was created for Calvados in 1942 (*3*). The production of Mirabelle De Lorraine has been regulated since 1953 by the French label "AOR" (Appellation d'Origine Réglementée) (*4*). It specifies that the plums (mirabelles) should be harvested in Lorraine and fermented before being distilled in stills. These four brandies are tasted after a few years of aging in casks.

The several steps leading to the elaboration of a brandy give rise to complex aromas and tastes, which result from specific volatile compositions. Schaefer and Timmer (*5*) determined the presence of 81 compounds in Cognac, whereas Schreier et al. (*6*) showed also the great complexity of the composition of grape brandies with 139 identified compounds in their samples. Two hundred and twenty-seven components were detected in Slovak grape brandies by Janacova et al. (*7*). Our previous works led to the characterization of 331 compounds in freshly distilled Cognac and Calvados of various qualities (*8*, *9*). Ninety-nine components were identified by Tesevic et al. (*10*) in old plum brandies.

The first studies on the volatile composition of distilled spirits (*11*−*14*) revealed high amounts of low molecular weight alcohols such as methanol, propanol, isobutanol, and isopentanols. In brandies, ethyl acetate is the major ester, with a concentration varying from 20 to 2000 mg/L (*14*−*18*). The volatile composition of brandies is also characterized by high contents of low molecular weight ethyl esters and some phenols, aldehydes, and acetals. However, these major components, due to their high concentrations in all brandies, may not be helpful in the discrimination of samples.

Various methods were used to discriminate brandies. Infrared spectra were used by Picque et al. to classify Cognacs (*19*) and also by Palma and Barroso to distinguish various wines and spirits (*20*). Atomic absorption and emission spectrometry was also used to

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differentiate Spanish brandies according to their metal content (*21*). Mangas et al. (*22*) showed that HPLC results and especially furfural content were sufficient for characterizing cider brandies according to their raw materials.

The volatile composition was widely used to characterize the origin or the methods employed during the process of production of spirits. Volatiles of brandies were mainly described using methods such as solid-phase microextraction (*7*, *23*, *24*) or liquid−liquid extractions with solvents (*6*−*10*, *25*, *26*) before separations in GC-MS. With the help of statistical analysis on that composition different types of gins (*27*), Cachaças (*28*), and cider brandies (*25*) were then differentiated. Recently, PLS-DA models were successfully applied to discriminate fermenting grape musts according to their volatile composition (*29*) but also to distinguish Cognacs of different ages (*24*).

The principal goal of the present work was to reveal the presence of specific volatile compounds of four different French labeled brandies using GC-MS and PLS-DA analyses. A relative area of each volatile compound was determined in each studied sample. These levels, without further quantification, were used to discriminate each class of brandy.

MATERIALS AND METHODS

Chemicals. Pentane (Aldrich, Steinheim, Germany) and diethyl ether (Carlo Erba, Val de Reuil, France) were used as solvents for extraction and syntheses. Ethyl undecanoate (Interchim, Montluçon, France) and 4-methylpentan-2-ol (Merck, Schuchardt, Germany) were used as internal standards.

Acetic acid, benzaldehyde, butanoic acid, decanoic acid, ethyl 2-hydroxypropanoate, furfural, hexanoic acid, hexanol, 2-methylbutanoic acid, 3-methylbutanoic acid, 2-methylpropanoic acid, nonanal, pentanoic acid, 2-phenylethanol, vanillin (Acros Organics, Geel, Belgium), acetoin, 2-acetylfuran, benzyl acetate, β-damascenone, ethyl but-2-enoate, ethyl cinnamate, ethyl 3-ethoxypropanoate, 4-ethylguaiacol, ethyl 3-hydroxybutanoate, ethyl 2-hydroxyhexanoate, heptanal, hexanal, 5-(hydroxymethyl)furfural, (*E*)- and (*Z*)-linalool oxide, maltol, 3-methylbut-3-en-1-ol, 5-methylfurfural, octanal, 1,1,3-triethoxypropane (Aldrich, Steinheim, Germany), 4-ethylphenol, 6-methylhept-5-en-2-ol (Aldrich, Milwaukee, WI), butanol, 3-methylbutanol, propanol (Carlo Erba, Val de Reuil, France), benzyl alcohol, decanol, ethyl 2-furoate, ethyl oleate, ethyl phenylacetate, eugenol, heptanol, 2-methylpropanol, oct-1-en-3-ol, 2-phenylethyl acetate, styrene, tetradecanol, 4-vinylanisole (Fluka, Buchs, Switzerland), butan-2-ol, 2-methylbutanol (Merck, Darmstadt, Germany), linalool, prop-2-en-1-ol (Merck, Schuchardt, Germany), pentanol (Prolabo, Paris, France), (*Z*)-hex-3-en-1-ol, geraniol, and octanoic acid (Sigma, St. Louis, MO) were used in mixtures diluted in pentane or diethyl ether and injected in GC-MS to be used as standards. They also could be used for the synthesis of volatiles.

Butanal, dodecanoic acid, heptanoic acid, heptan-2-one, (*E*)-hex-2-en-1-al, nonan-2-one, pentan-2-one, propanal, propanoic acid, sodium borohydride, sodium hydrogenocarbonate (Acros Organics, Geel, Belgium), tetradecanoic acid (Aldrich, Gillingham, Dorset, U.K.), 2-methylbutanal (Aldrich, Milwaukee, WI), benzoic acid, ethanol, salicylic acid (Carlo Erba, Val de Reuil, France), (*E*)-but-2-enoic acid, methanol, pentan-3-one (Fluka, Buchs, Switzerland), malonic acid (Janssen, Beerse, Belgium), 3-methylbutanal (Merck, Schuchardt, Germany), adipic acid, citric acid, succinic acid (Prolabo, Paris, France), malic acid (Riedel-De-Haën, Seelze, Germany), magnesium sulfate, nonanoic acid, pentanedioic acid (glutaric acid) (Sigma, St. Louis, MO), FAME 37 mix (Supelco, Bellefonte, PA), and sulfuric acid (VWR, Fontenay-sous-Bois, France) were used specifically for the synthesis of volatiles.

Syntheses of Volatile Compounds. 1,1-Diethoxybutane, 1,1-diethoxyheptane, 1,1-diethoxyhexane, 1,1-diethoxy-2-methylbutane, 1,1-diethoxy-3-methylbutane, 1,1-diethoxynonane, and 1,1-diethoxypropane were produced by adding to the corresponding aldehydes (100−500 μL) an excess of ethanol (20 mL) according to the method of Ledauphin et al. (*9*). Syntheses were widely adapted from these authors and Fan et al. (*30*).

Butyl acetate, ethyl butanoate, ethyl heptanoate, ethyl hexanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl 2-methylpropanoate, ethyl nonanoate, ethyl octanoate, ethyl pentanoate, ethyl propanoate, hexyl acetate, hexyl 2-methylbutanoate, hexyl 3-methylbutanoate, 2-methylbutyl acetate, 3-methylbutyl acetate, 3-methylbutyl hexanoate, 3-methylbutyl octanoate, 3-methylbutyl propanoate, methyl hexanoate, methyl nonanoate, methyl octanoate, 1-methylpropyl acetate, 2-methylpropyl acetate, and propyl acetate were prepared by mixing a microvolume (50−100 μL) of alcohol with an excess of carboxylic acid (1−2 mL) and 5 μL of concentrated sulfuric acid (98%) in a 15 mL closed test tube. The reaction was conducted for 3 h at 70 °C, and after cooling, 10 mL of pentane was added. The medium was then washed using a separatory funnel with 10 mL of ultrapure water and 10 mL of a saturated solution of sodium hydrogenocarbonate ($NaHCO_3$).

Ethyl benzoate, ethyl decanoate, ethyl dodecanoate, ethyl hexadecanoate, ethyl octadecanoate, ethyl salicylate, ethyl tetradecanoate, 3-methylbutyl decanoate, 3-methylbutyl dodecanoate, methyl benzoate, methyl decanoate, methyl dodecanoate, methyl hexadecanoate, methyl salicylate, 2-phenylethyl decanoate, 2-phenylethyl octanoate, and propyl decanoate were synthesized by mixing a small quantity of carboxylic acid (50−100 mg) with an excess of alcohol (1−2 mL) and 5 μL of concentrated sulfuric acid (98%) in a 15 mL closed test tube. The conditions of reaction and extraction were the same as above except that the solution of $NaHCO_3$ was replaced by ultrapure water.

2- and 3-methylbutyl 2-hydroxypropanoate were produced by transesterification of the corresponding ethyl esters. Fifty microliters of ethyl lactate was added to 1 mL of alcohol (2- or 3-methylbutanol) in the presence of 5 μL of concentrated sulfuric acid (98%) in a 15 mL closed test tube. The conditions of the reaction and purification were the same as above.

Ethyl hexadecanoate, ethyl hexadecenoate, ethyl linoleate, ethyl linolenate, ethyl octadecanoate, and ethyl pentadecanoate with 33 other ethyl esters were produced by ethylation following hydrolysis of the FAME 37 mixture. The reaction was performed in a 30 mL closed test tube with 250 μL of that mixture added with 5 mL of an ethanol/concentrated H_2SO_4 85:15 (v/v) solution and 5 mL of dichloromethane. It was heated for 3 h at 80 °C. After cooling, 2 mL of the lower organic layer was recovered.

Pentan-3-ol, pentan-2-ol, heptan-2-ol, (*E*)-hex-2-en-1-ol, nonan-2-ol, octanol, and nonanol were prepared by reduction of the corresponding carbonyl compounds: 100 μL of the aldehyde or ketone was dissolved in 10 mL of pure ethanol in a 250 mL Erlenmeyer flask placed in an ice bath. $NaBH_4$ (0.06 g) was added three times, and the mixture was magnetically stirred for 10 min. The mixture was then supplemented with 20 mL of ultrapure water and slowly acidified with 1.5 mL of HCl (37%) under stirring. The aqueous phase was extracted twice with 30 mL of diethyl ether. The organic phase was washed with 10 mL of a saturated solution of $NaHCO_3$ and then with 10 mL of ultrapure water.

Diethyl propanedioate, diethyl succinate, ethyl propyl succinate, diethyl pentanedioate, diethyl hexanedioate, ethyl 3-methylbutyl succinate, diethyl malate, and ethyl citrate were synthesized by adding to 500 mg of the corresponding acid an excess of alcohol. In the case of diethyl or triethyl esters, 4 mL of ethanol was used and for the mixed ones a mixture of two alcohols (2 mL each) was added. After heating for 3 h at 70 °C and then cooling to room temperature, the medium was extracted by addition of 20 mL of ultrapure water and 20 mL of pentane. Ten milliliters of a $NaHCO_3$ saturated solution was also used to wash and purify the organic phase. Only one residue was observed for diethyl or triethyl esters on GC-MS chromatograms. Three peaks were recorded in GC-MS for the other ones including the desired crossed ester.

3-Ethoxypropanal was produced by diluting 50 μL of 1,1,3-triethoxypropane in 2 mL of 0.1 M HCl. The mixture was heated for 3 h at 70 °C, and after cooling, the aldehyde was recovered in the organic layer after extraction with 10 mL of pentane and 10 mL of ultrapure water. Two components were then synthesized, a Diels−Alder adduct (major) and the 3-ethoxypropanal (minor).

Furfural diethyl acetal was prepared by mixing 200 μL of furfural, 7 mL of ethanol, and 5 μL of concentrated sulfuric acid (98%) in a 100 mL closed Erlenmeyer. The mixture was stirred magnetically for a week at room temperature. After filtration, the mixture was extracted with 10 mL of pentane.

The organic layers of all these preparations were dried on magnesium sulfate ($MgSO_4$) and filtered on deactivated glass wool. The extracts were stored at −18 °C prior to a 1 μL injection in GC-MS. Peak confirmations

were performed in electron impact and chemical ionization modes with separations on a BP-20 stationary phase (characteristics of the column and analytical conditions are given under Gas Chromatography−Mass Spectrometry). Retention times and mass spectra of peaks recorded for these preparations were examined and compared to those found in extracts of brandies.

Brandy Samples. Brandies used in this study were purchased in local markets. Each of these samples was produced according to standard procedures as they all possessed the French label AOC or AOR. Vintages were between 1995 and 2003 and were analyzed in 2007. Five Calvados were selected with three AOC Calvados and two AOC Calvados Pays d'Auge. Three Armagnac were studied with one AOC Armagnac, one AOC Bas-Armagnac, and one AOC Armagnac Tenareze. Six Cognac were also studied with three Fine Cognac and three Fine Champagne. Finally, three Mirabelle with two from Lorraine and one from Alsace were also selected. These brandies were from several origins in their respective delimited regions of production. Ethanolic content was 40% (v/v) for all brandies.

Brandy Extraction. In a 500 mL conical flask, 50 mL of each sample of the 17 selected brandies was diluted with 100 mL of ultrapure water and 40 g of NaCl. They were then amended with 100 μL of a 500 mg/L solution of ethyl undecanoate and 50 μL of a 1 g/L solution of 4-methylpentan-2-ol. Both solutions were of internal standard prepared in ethanol. The diluted brandies were then stirred magnetically during 20 min at 0 °C after the addition of a 20 mL mixture of pentane/diethyl ether 70:30. Layers were separated on a separatory funnel, and the organic layer was stored at −18 °C. The aqueous phase was also extracted with another 20 mL mixture of pentane/diethyl ether 70:30 and finally with 20 mL of pure diethyl ether. The organic layers were gathered, dried on magnesium sulfate, and filtered on deactivated glass wool. Thirty milliliters was taken to be reduced to 3 mL using a Kuderna-Danish column. The final extract was stored at −18 °C prior to analysis in GC-MS.

Gas Chromatography−Mass Spectrometry. Analyses of 1 μL extracts were conducted using a Varian 3800 gas chromatograph coupled with a Varian Saturn 2000R mass spectrometer. Volatiles were separated on a polar BP-20 capillary column (50 m × 0.25 mm i.d., film thickness = 0.25 μm, SGE, Courtaboeuf, France) and on a nonpolar DB-5 capillary column (60 m × 0.25 mm i.d., film thickness = 0.25 μm, J&W Scientific). The extracts were injected with a 40:1 split ratio in the split/splitless injector heated at 240 °C. Helium was used as a carrier gas with a 1 mL/min flow. The oven program temperature was from 35 to 240 °C at a rate of 5 °C/min with an initial temperature hold for 10 min and a final temperature hold for 9 min, resulting in a total run of 1 h for the polar stationary phase. The oven program temperature was from 35 to 250 °C at a rate of 4 °C/min with an initial temperature hold for 10 min and a final temperature hold for 10 min, resulting in a total run of 74 min for the less polar stationary phase. The transfer line temperature was fixed at 270 °C. The ion trap analyzer was operating in either electron impact (EI-MS) or chemical ionization (CI-MS) mode. EI-MS conditions were as follows: ionization voltage, 70 eV; ion source temperature, 250 °C; electron multiplier voltage, 1400 V; mass range, m/z 40−400; 1 scan/s. Acetonitrile was used in CI-MS mode, the mass range was from m/z 65 to 400; the other conditions were the same as for EI-MS mode. A retention index was calculated for each peak in each sample according to the Van Den Dool approach (*31*) using a standard of *n*-alkanes (C_8−C_{32} from Sigma, St. Louis, MO).

Identification of Volatile Compounds. Peak identifications of the volatile compounds were achieved by comparison of mass spectra with those of the NIST 98 MS database and of an in-house database created 10 years ago and containing about 300 EI and CI mass spectra of compounds previously recorded from injections of standards identified as key volatiles of foods and beverages. The presence of the components could be confirmed by comparison with retention indices found in the literature on both stationary phases, by observing the CI-MS spectra, and by comparing both retention times and mass spectra of pure or synthesized diluted standards using the same chromatographic and spectrometric conditions.

Level of Volatile Compounds. A specific ion was integrated for each peak, which was usually the most abundant. Values were only taken for a given compound in a given sample if the signal-to-noise ratio was reaching 10. A relative area was obtained after dividing that area by that of the m/z 88 ion of ethyl undecanoate (internal standard). For each extract the ratio of the area of the two internal standards (ethyl undecanoate and 4-methylpentan-2-ol) was calculated to check if it varied by >2% from the mean value.

Statistical Analyses. Partial least-squares discriminant analysis (PLS-DA) was used to develop models to discriminate samples according to their volatile composition. The objective of PLS-DA is to find a model that separates classes of observations on the basis of their X variables. The X matrix consists of the volatile composition data of the observations. The Y matrix contains dummy variables, which describe the class membership of each observation. Binary variables are used to encode a class identity. PLS-DA finds a discriminant plane in which the projected observations on the components are well separated according to class.

The PLS weight plot of composition variables enables an understanding of which variables contribute to the separation. Compounds that are close to the dummy variables of class membership contribute strongly to the separation of classes (*32*).

PLS-DA was carried out with SIMCA-P software (UMETRICS). SIMCA software uses the NIPALS algorithm (nonlinear iterative partial least squares) for the PLS regression. The number of components is determined by cross-validation. In this study, all composition variables were centered and scaled to unit variance (UV scaling).

RESULTS AND DISCUSSION

Volatile Composition of Brandies. Two hundred and seven compounds were detected in the extracts of the 17 selected brandies. They are all reported in **Table 1**, which summarizes all of the results obtained in this study. Major peaks obtained in GC-MS for four different extracts of brandies are presented in **Figure 1**. Volatiles were first tentatively identified using the comparison of their mass spectra with those of mass spectra databases and then by comparison with the retention indices found in the literature. CI-MS spectra were observed to confirm the identity of compounds via the determination of their molecular weight. Injections of diluted pure compounds were achieved, and for many of those that were not available in the laboratory, simple chemical reactions (esterifications, acetalizations or borohydride reductions) were conducted to produce the corresponding molecules. One hundred and thirty-three of them were clearly identified using pure or synthesized standards, and 51 were considered to be tentatively identified as (i) recorded EI mass spectra were similar to those present in the MS databases used and (ii) calculated retention indices were similar to those found for them in the literature. Twenty-three were unknown even if for some of them a chemical class could be proposed.

Forty-one compounds were common to all samples, whereas 54 others were characterized in at least one sample of each type of brandy. With 175 molecules found in the three extracts, Mirabelle seems to possess the richest volatile composition. Only 129 compounds were detected in the 3 extracts of Armagnac, 137 in Cognac (6 samples), and 167 in Calvados ones (5 samples). For all brandies, esters belonged to the most represented chemical class (between 41 and 58 esters for each type of brandy) followed by alcohols (between 26 and 37 alcohols). The composition in aromatic or phenolic compounds varies between these spirits. A few of them (16 for Cognac and 17 for Armagnac) were found in wine-based products, whereas Mirabelle and Calvados (25 for each) clearly contained the largest number. A dozen terpenic or norisoprenoic compounds were found in each beverage. Aldehydes and acetals were in their majority detected only in samples of Mirabelle. In this spirit, 13 acetals and 5 aldehydes were found, whereas only 8 or 9 acetals and 1 or 2 aldehydes were characterized in other brandies. The rest of the volatile composition of these brandies is organized with a few furanic compounds (between 6 and 8 for each type of brandy), acids (about 9 in each), and lactones (2 or 3 in each type of brandy).

Relative Levels of Volatiles. From 100 to 150 molecules could be detected in each extract, and their levels were evaluated using

Table 1. Volatile Composition of Brandies (Calvados, Cognac, Armagnac, and Mirabelle)

								Calvados[h]		Cognac[h]		Armagnac[h]		Mirabelle[h]		Cdos	Cog	Arm	Mir
entry	compound[a]	ID[b]	ID method[c]	CI major peaks[d]	RI BP-20[e]	RI DB-5[f]	ion[g]	low	high	low	high	low	high	low	high	nb[i]	nb[i]	nb[i]	nb[i]
1	**1,1-diethoxypropane**	S	CI, RI	87^{+1-46}	<1000	789	59							0.11	0.19				**3**
2	**ethyl propanoate**	S	CI, RI	103^{+1}	<1000	706	57	3.81	17.74	0.12	0.50	0.28	0.56	0.31	0.57	**5**	**6**	**3**	**3**
3	**ethyl 2-methylpropanoate**	S	CI, RI	117^{+1}	<1000	776	71	0.00	0.18	0.08	0.22	0.03	0.15	0.04	0.07	4	**6**	**3**	**3**
4	**propyl acetate**	S	CI, RI	103^{+1}	<1000	712	61	0.06	1.32			0.02	0.03	0.22	0.54	**5**		**3**	**3**
5	1,1-diethoxy-2-methylpropane	T	CI, RI	101^{+1-46}	<1000		75	0.00	0.09	0.35	1.53	0.13	0.42	0.07	0.28	1	**6**	**3**	**3**
6	**1-methylpropyl acetate**	S	CI	117^{+1}	<1000	783	43	0.00	1.65							3			
7	**2-methylpropyl acetate**	S	CI, RI	117^{+1}	1021	789	43	0.18	1.48	0.13	0.52	0.27	0.61	0.21	0.29	**5**	**6**	**3**	**3**
8	**butan-2-ol**	P	RI		1036		41	12.81	32.74	0.00	0.30	0.09	0.15	0.00	3.87	**5**	5	**3**	2
9	**ethyl butanoate**	S	CI, RI	117^{+1}	1045	804	71	0.36	0.97	0.28	0.63	0.32	0.53	0.61	1.28	**5**	**6**	**3**	**3**
10	**propanol**	P	RI		1050		42	6.61	22.88	4.10	7.26	4.19	4.72	9.64	14.70	**5**	**6**	**3**	**3**
11	2-methylbut-3-en-2-ol	T	CI, RI	69^{+1-18}	1051		71	0.07	0.14	0.14	0.22	0.12	0.20	0.28	0.66	**5**	**6**	**3**	**3**
12	**1,1-diethoxybutane**	S	CI	101^{+1-46}	1051	902	103							0.00	0.15				2
13	**ethyl 2-methylbutanoate**	S	CI, RI	131^{+1}	1060	863	102	0.31	0.98	0.00	0.15	0.00	0.16	0.12	0.18	**5**	4	1	**3**
14	2-ethoxytetrahydropyrane	T	CI	85^{+1-46}	1067		85	0.00	0.16	0.00	0.02					2	1		
15	**ethyl 3-methylbutanoate**	S	CI, RI	131^{+1}	1075	868	88	0.00	0.18	0.00	0.23	0.00	0.19	0.05	0.10	3	5	2	**3**
16	**butyl acetate**	S	CI, RI	117^{+1}	1079	817	43	0.05	0.39					0.00	0.11	**5**			2
17	**1,1-diethoxy-2-methylbutane**	S	CI, RI	115^{+1-46}	1080	945	103			0.03	0.18	0.00	0.05	0.00	0.19		**6**	2	2
18	**1,1-diethoxy-3-methylbutane**	S	CI, RI	115^{+1-46}	1084	945	103	0.00	0.02	0.00	0.15	0.04	0.06	0.27	1.01	1	5	**3**	**3**
19	**hexanal**	P	CI, RI	101^{+1}; 83^{+1-18}	1086	783	41							0.20	0.60				**3**
20	**2-methylpropanol**	P	RI		1099		41	38.45	51.71	50.80	90.04	53.08	76.37	18.01	25.94	**5**	**6**	**3**	**3**
21	1-(1-ethoxyethoxy)-2-methylbutane	T	CI	73; 115^{+1-46}	1103		73					0.04	0.06					**3**	
22	**pentan-3-ol**	S	CI	71^{+1-18}	1112	702	59	0.08	0.15					0.00	0.04	**5**			2
23	1-(1-ethoxyethoxy)-3-methylbutane	T	CI	73; 115^{+1-46}	1113	1015	71	0.03	0.21	0.10	0.34	0.10	0.34	0.00	0.05	**5**	**6**	**3**	1
24	**prop-2-en-1-ol (allylic alcohol)**	P	CI		1122		57	1.97	8.70	0.00	0.08			0.00	0.70	**5**	3		1
25	**pentan-2-ol**	S	CI, RI	71^{+1-18}; 83	1126	704	45	0.13	0.51	0.00	0.08	0.05	0.13	0.00	0.64	**5**	1	**3**	2
26a	**3-methylbutyl acetate**	S	RI	71	1127	885	43	1.71	4.91	0.46	2.04	1.24	1.65	0.79	1.08	**5**	**6**	**3**	**3**
26b	**2-methylbutyl acetate**	S	CI, RI	71; 131^{+1}	1127	884	43												
27	**ethyl pentanoate**	S	CI, RI	131^{+1}	1141	901	88							0.06	0.10				**3**
28	1,1-diethoxypentane	T	CI, LRI	115^{+1-46}	1143		103							0.00	0.22				2
29	**butanol**	P	RI		1151		41	8.65	14.46	0.53	0.83	0.80	0.92	4.83	12.04	**5**	**6**	**3**	**3**
30	pent-1-en-3-ol	T	CI, RI	69^{+1-18}	1167		57	0.08	0.26	0.05	0.11	0.04	0.04	0.04	0.07	**5**	**6**	**3**	**3**
31	**ethyl but-2-enoate**	P	CI, RI	115^{+1}	1169	841	99	0.00	0.04	0.00	0.05			0.07	0.52	2	1		**3**
32	**heptanal**	P	CI, RI	115^{+1}; 97^{+1-18}	1189	882	55							0.02	0.13				**3**
33	**methyl hexanoate**	S	CI, RI	131^{+1}	1191	916	74							0.03	0.06				**3**
34	**3-methylbutyl propanoate**	S	CI,RI	71; 145^{+1}	1192	976	57	0.00	0.12							2			
35	**3-ethoxypropanal**	S	CI	103^{+1}	1196	790	43	0.25	0.65	0.00	0.04	0.00	0.03			**5**	3	2	
36a	**2-methylbutanol**	P	CI, RI	71^{+1-18}	1214	715	41	77.58	101.61	90.44	140.73	81.00	117.64	44.87	49.36	**5**	**6**	**3**	**3**
36b	**3-methylbutanol**	P	CI, RI	71^{+1-18}	1214	718	41												
37	**1,1-diethoxyhexane**	S	CI, LRI	129^{+1-46}	1237	1120	103							0.23	1.16				**3**
38	**ethyl hexanoate**	S	CI, RI	145^{+1}	1239	995	88	0.68	1.61	0.87	2.36	0.97	1.16	0.57	1.42	**5**	**6**	**3**	**3**
39	**3-methylbut-3-en-1-ol**	P	CI, RI	69^{+1-18}; 83	1254	714	67	0.11	0.17	0.00	0.09	0.08	0.14	0.25	0.56	**5**	5	**3**	**3**
40	**pentanol**	P	CI, RI	71^{+1-18}	1255	778	41	0.43	0.64	0.08	0.14	0.11	0.15	0.44	0.80	**5**	**6**	**3**	**3**
41	unknown (acetal)	U		101; 142	1260		47	0.12	1.34	0.35	1.20	0.31	1.97	0.00	0.03	**5**	**6**	**3**	1
42	**styrene**	P	CI	105^{+1}	1263		78	0.00	0.04	0.00	0.02			0.00	0.10	3	1		2
43	**hexyl acetate**	S	CI, RI	145^{+1}	1278	1009	56	0.00	0.09	0.00	0.08	0.00	0.03	0.00	0.07	3	2	1	2
44	**acetoin**	P	CI, RI	89^{+1}	1292		45	0.00	0.21			0.04	0.14	0.00	0.18	2		**3**	1
45	**octanal**	P	CI, RI	129^{+1}; 111^{+1-18}	1294	982	67							0.00	0.04				2
46	furfuryl ethyl ether	T	CI, RI	81^{+1-46}; 127^{+1}	1294	874	81			0.04	0.08			0.00	0.48		**6**		2
47	**1,1,3-triethoxypropane**	P	CI, RI	131^{+1-46}; 87	1309	1115	47	1.02	3.69	0.08	0.26	0.12	0.16	0.08	0.19	**5**	**6**	**3**	**3**
48	4-methylpentanol	T	CI	85^{+1-18}	1317		56	0.00	0.04	0.07	0.16	0.04	0.11	0.00	0.02	2	**6**	**3**	1
49	**heptan-2-ol**	S	CI, RI	83; 99^{+1-18}	1322		45	0.00	0.45	0.00	0.11	0.05	0.09	0.00	0.40	4	5	**2**	2
50	pent-3-en-2-ol	T	CI	69^{+1-18}	1326		71	0.13	0.21			0.03	0.03	0.10	0.14	**5**		**2**	**3**
51	3-methylpentanol	T	CI, RI	85^{+1-18}	1330		56	0.12	0.19	0.08	0.18	0.05	0.13	0.06	0.06	**5**	**6**	**3**	**3**
52	**1,1-diethoxyheptane**	S	CI, LRI	143^{+1-46}	1334		103							0.07	0.29				**3**
53	**ethyl heptanoate**	S	CI, RI	159^{+1}	1339	1093	88	0.00	0.04					0.07	0.11	1			**3**
54	**ethyl 3-ethoxypropanoate**	P	CI	147^{+1}	1339	999	117	0.00	0.23	0.00	0.11	0.00	0.14			2	3	**3**	
55	hex-2-enyl acetate	T			1344		85							0.00	0.12				2
56	**ethyl 2-hydroxypropanoate**	P	CI, RI	119^{+1}	1351	816	45	13.58	40.27	8.98	20.50	7.32	13.70	8.14	50.99	**5**	**6**	**3**	**3**

Table 1. Continued

								Calvados[h]		Cognac[h]		Armagnac[h]		Mirabelle[h]		Cdos	Cog	Arm	Mir
entry	compound[a]	ID[b]	ID method[c]	CI major peaks[d]	RI BP-20[e]	RI DB-5[f]	ion[g]	low	high	low	high	low	high	low	high	nb[i]	nb[i]	nb[i]	nb[i]
57	**hexanol**	P	CI, RI	85^{+1-18}	1357	872	56	13.17	22.99	3.11	6.51	2.69	3.44	2.53	6.97	**5**	**6**	**3**	**3**
58	(*E*)-hex-3-en-1-ol	T	CI	83^{+1-18}	1368	864	67	0.09	0.22	0.04	0.14	0.08	0.09	0.00	0.03	**5**	**6**	**3**	1
59	3-ethoxypropanol	T	CI	105^{+1}; 87^{+1-18}	1380		57	0.00	0.04	0.00	0.02			0.00	0.23	1	1		2
60	**(*Z*)-hex-3-en-1-ol**	P	CI, RI	83^{+1-18}	1389	864	67	0.35	0.76	0.62	1.10	0.26	0.41	0.14	0.40	**5**	**6**	**3**	**3**
61	**methyl octanoate**	S	CI, RI	159^{+1}	1395	1110	74	0.00	0.03	0.00	0.02			0.04	0.12	3	3		**3**
62	octan-3-ol	T		71; 83	1396		83	0.00	0.07	0.00	0.02					3	1		
63	**nonanal**	P	CI, RI	143^{+1}; 125^{+1-18}	1399	1082	81							0.12	0.56				**3**
64	(***E*)-hex-2-en-1-ol**	S	CI, RI	83^{+1-18}	1410		57	0.00	0.02	0.00	0.05	0.00	0.05	0.00	0.07	1	2	2	1
65	unknown (hexenol)	U	CI	83^{+1-18}	1414		67	0.09	0.19							**5**			
66	butane-2,3-diol	T	CI	91^{+1}	1427		45	0.00	0.34					0.00	0.34	2			1
67	unknown (terpenic structure)	U		129; 173	1429	1166	111	0.00	0.44							4			
68	**1,1-diethoxyoctane**	S	CI, LRI	157^{+1-46}	1432		103							0.09	0.31				**3**
69	ethyl 2-hydroxy-3-methylbutanoate	T	CI, RI	147^{+1}	1434	980	73	0.71	1.37	0.07	0.37	0.09	0.11	0.06	0.46	**5**	**6**	**3**	**3**
70	**ethyl octanoate**	S	CI, RI	173^{+1}	1440	1190	88	2.26	4.95	3.58	8.48	3.07	3.79	1.30	3.58	**5**	**6**	**3**	**3**
71	**(*E*)-linalool oxide (furanoid)**	P	CI, RI	153^{+1-18}	1448	1107	59	0.07	0.30	0.03	0.41	0.04	0.07	0.06	0.45	**5**	**6**	**3**	**3**
72	**oct-1-en-3-ol**	P	CI, RI	111^{+1-18}	1454		57	0.00	0.08	0.00	0.07			0.00	0.03	2	3		2
73	α-ionene	T	CI	137; 175^{+1}	1454		159			0.00	0.01	0.01	0.01	0.02	0.14		2	**3**	**3**
74	**hexyl 3-methylbutanoate**	S			1455	1249	43	0.00	0.13					0.00	0.21	2			2
75	unknown (ester)	U			1456		57	0.04	0.12	0.05	0.14	0.06	0.17			**5**	**6**	**3**	
76	**heptanol**	P	CI, RI	99^{+1-18}	1459	971	55	0.09	0.12			0.02	0.05	0.16	0.36	**5**		**3**	**3**
77	**3-methylbutyl hexanoate**	S	RI		1464		70	0.00	0.07					0.00	0.04	2			1
78	2,2-diethoxyethanol	T	CI	89^{+1-46}	1465		47	0.06	0.47	0.00	0.34	0.20	0.73	0.00	0.02	**5**	5	**3**	1
79	**6-methylhept-5-en-2-ol**	P	CI, RI	111^{+1-18}	1467		95	0.08	0.17	0.00	0.03					**5**	1		
80	**furfural diethyl acetal**	S	CI, RI	125^{+1-46}	1471	1072	97	0.00	0.05	0.06	0.32	0.00	0.02	0.03	0.15	3	**6**	2	**3**
81	**acetic acid**	P	RI		1475		43	10.11	38.09	3.11	8.11	10.76	28.90	3.06	46.19	**5**	**6**	**3**	**3**
82	**furfural**	P	CI, RI	97^{+1}	1476	778	95	0.33	1.29	2.11	3.75	0.82	0.92	1.26	7.96	**5**	**6**	**3**	**3**
83	(***Z*)-linalool oxide (furanoid)**	P	CI, RI	153^{+1-18}	1477	1118	111	0.00	0.12	0.00	0.02	0.01	0.01	0.02	0.20	4	4	**3**	**3**
84	2-ethylhexanol	T	CI, RI	$71{,}113^{+1-18}$	1493		57	0.00	0.08	0.00	0.64	0.00	1.56	0.00	0.07	2	5	2	1
85	unknown (acetal)	U		103	1495		47	0.00	0.09	0.03	0.15	0.02	0.10			2	**6**	**3**	
86	**methyl nonanoate**	S	CI, LRI	173^{+1}	1498	1211	74							0.00	0.04				2
87	unknown (aldehyde)	U			1507		81	0.00	0.03					0.00	0.04	2			1
88	3-ethyl-4-methylpentanol	T	CI	71; 113^{+1-18}	1513		69	0.13	0.38					0.00	0.09	**5**			2
89	**2-acetylfurane**	P	CI, RI	111^{+1}	1517	874	95	0.00	0.18	0.07	0.16	0.03	0.03	0.00	0.06	3	**6**	**2**	2
90	γ-terpineol	T	CI	137^{+1-18}	1521		136					0.00	0.01	0.02	0.08			1	**3**
91	**nonan-2-ol**	S	CI, LRI	85; 127^{+1-18}	1521		45	0.00	0.28	0.00	0.11	0.00	0.11	0.00	0.06	3	3	2	1
92	ethyl 2-hydroxy-4-methylpentanoate	T	CI	161^{+1}	1524		69	0.13	0.22	0.00	0.06			0.00	0.14	**5**	3		1
93	**ethyl 3-hydroxybutanoate**	P	CI, RI	133^{+1}; 115^{+1-18}	1527		117	0.00	0.08	0.00	0.03	0.03	0.07	0.00	0.11	4	2	**3**	2
94	**1,1-diethoxynonane**	S	CI, RI	171^{+1-46}	1529		103							0.20	2.32				**3**
95	unknown (terpenic structure)	U		147	1532		93	0.00	0.03	0.00	0.02	0.00	0.01	0.02	0.04	3	2	1	**3**
96	**benzaldehyde**	P	CI, RI	107^{+1}	1538	884	105	0.00	0.23	0.23	0.50	0.13	0.22	3.37	22.60	4	**6**	**3**	**3**
97	vitispirane isomer 1	T	RI		1538	1267	177	0.00	0.26	0.06	0.13	0.06	0.08	0.00	0.04	4	**6**	**3**	1
98	vitispirane isomer 2	T	RI		1541	1273	177	0.00	0.23	0.07	0.13	0.05	0.06	0.00	0.02	4	**6**	**3**	1
99	**ethyl nonanoate**	S	CI, RI	187^{+1}	1541	1292	88							0.67	1.02				**3**
100	**ethyl 2-hydroxyhexanoate**	P	CI, RI	161^{+1}	1551	1084	87	0.12	0.22	0.00	0.08	0.00	0.03	0.06	0.27	**5**	4	1	**3**
101	**linalool**	P	CI, RI	137^{+1-18}; 81	1552		93	0.00	0.03	0.03	0.07	0.02	0.06	0.30	0.75	3	**6**	**3**	**3**
102	**octanol**	S	CI, RI	71; 113^{+1-18}	1561	1071	69	0.28	0.47	0.08	0.14	0.06	0.09	0.21	0.39	**5**	**6**	**3**	**3**
103	hexyl but-2-enoate	T	CI	171^{+1}	1564	1225	87							0.03	0.20				**3**
104a	**2-methylbutyl 2-hydroxypropanoate**	S	CI	71; 161^{+1}	1575	970	45	0.42	1.24	0.11	0.74	0.00	0.43	0.07	0.57	**5**	**6**	2	**3**
104b	**3-methylbutyl 2-hydroxypropanoate**	S	CI	71; 161^{+1}	1575	970	45	0.42	1.24	0.11	0.74	0.00	0.43	0.07	0.57	**5**	**6**	2	**3**
105	**diethyl propanedioate**	S	CI	161^{+1}	1586	1062	133	0.00	0.19	0.00	0.19	0.03	0.18	0.00	0.05	1	5	**3**	2
106	**5-methylfurfural**	P	CI, RI	111^{+1}	1587	907	109	0.00	0.09	0.12	0.23	0.04	0.06	0.02	0.17	3	**6**	**3**	**3**
107	**2-methylpropanoic acid**	P	CI, RI	71^{+1-18}	1590		41	0,29	0,47	0,17	0,64	0,24	0,42	0,00	0,53	**5**	**6**	**3**	2
108	**methyl decanoate**	S	CI, LRI	187^{+1}	1601	1312	74	0.00	0.04					0.06	0.17	1			**3**
109	4-terpineol	T	CI, RI	137^{+1-18}	1611	1151	93	0.00	0.08					0.03	0.05	4			**3**
110	3,3-diethoxypropanol	T	CI	103^{+1-46}	1615		103	0.07	0.41			0.00	0.02			**5**		1	
111	(*Z*)-oct-5-en-1-ol	T	CI	111^{+1-18}; 129^{+1}	1621		67	0.14	0.26					0.00	0.04	**5**			1
112	unknown (ester)	U		145; 99	1621		99	0.00	0.07	0.00	0.13	0.00	0.07			2	5	2	

Table 1. Continued

								Calvados[h]		Cognac[h]		Armagnac[h]		Mirabelle[h]		Cdos	Cog	Arm	Mir
entry	compound[a]	ID[b]	ID method[c]	CI major peaks[d]	RI BP-20[e]	RI DB-5[f]	ion[g]	low	high	low	high	low	high	low	high	nb[i]	nb[i]	nb[i]	nb[i]
113	**ethyl 2-furoate**	P	CI, RI	141^{+1}	1635	1002	95	0.00	0.10	0.12	0.26	0.07	0.15	0.17	0.28	3	**6**	**3**	**3**
114	**methyl benzoate**	S	CI, RI	137^{+1}	1637	1023	77							0.12	0.26				**3**
115	**ethyl decanoate**	S	CI, RI	201^{+1}	1644	1387	88	2.76	4.66	3.18	9.21	1.40	3.22	2.08	5.85	**5**	**6**	**3**	**3**
116	**butanoic acid**	P	CI, RI	71^{+1-18}	1651		60	0.35	0.96	0.25	0.45	0.45	0.60	0.23	0.97	**5**	**6**	**3**	**3**
117	**nonanol**	S	CI, RI	85; 71; 127^{+1-18}	1663	1172	55			0.00	0.07			1.07	1.48		3		**3**
118	**3-methylbutyl octanoate**	S	RI		1664	1458	70	0.06	0.10	0.09	0.18	0.05	0.11	0.03	0.15	**5**	**6**	**3**	**3**
119	citronellyl acetate	T	CI, RI	83; 139; 199^{+1}	1668		81							0.00	0.13				2
120	ethyl dec-4-enoate	T	CI	199^{+1}	1673	1375	152							0.05	0.64				**3**
121	**ethyl benzoate**	S	CI, RI	151^{+1}	1681	1107	105	0.74	1.87	0.00	0.03	0.00	0.03	7.48	18.64	**5**	3	1	**3**
122	**diethyl succinate**	S	CI, RI	129^{+1-46}; 175^{+1}	1684	1168	101	2.86	6.12	2.05	9.70	1.76	2.58	3.39	10.14	**5**	**6**	**3**	**3**
123	unknown (nonenol)	U	CI	143^{+1}; 125^{+1-18}	1689		67			0.00	0.02			0.08	0.13		1		**3**
124	**4-vinylanisole**	P	CI	135^{+1}	1691	1068	134							0.00	0.07				2
125	**2-methylbutanoic acid**	P	CI, RI	85^{+1-18}	1691	852	74	1.54	2.92	0.15	0.48	0.15	0.29	0.12	0.84	**5**	**6**	**3**	**3**
126	**3-methylbutanoic acid**	P	CI, RI	85^{+1-18}	1691	845	60	0.33	1.24	0.14	0.68	0.22	0.39	0.26	1.05	**5**	**6**	**3**	**3**
127	ethyl dec-9-enoate	T	CI	199^{+1}	1697	1382	152	0.00	0.01	0.00	0.01			0.00	0.06	2	1		1
128	α-terpineol	T	CI, RI	137^{+1-18}	1705		121	0.00	0.03	0.06	0.10	0.05	0.07	0.15	0.44	3	**6**	**3**	**3**
129	unknown	U			1705		79	0.00	0.04	0.00	0.04			0.07	0.18	2	1		**3**
130	**propyl decanoate**	S			1729	1490	155	0.00	0.01					0.00	0.02	1			2
131	**benzyl acetate**	P	RI	91; 132	1743	1108	108	0.00	0.01					0.10	0.53	2			**3**
132	1,1,6-trimethyl-1,2-dihydronaphthalene (TDN)	T	RI		1762	1291	157			0.13	0.41	0.07	0.10	0.00	0.10		**6**	**3**	2
133	**pentanoic acid**	P	CI, RI	85^{+1-18}	1763		60							0.03	0.19				**3**
134	**decanol**	P	CI, RI	85; 71; 141^{+1-18}	1765	1273	55	0.15	0.26	0.00	0.06	0.01	0.06	0.07	0.14	**5**	5	**3**	**3**
135	unknown	U			1769		67	0.00	0.18	0.00	0.05			0.31	3.60	1	2		**3**
136	**ethyl propyl succinate**	S	CI	129; 189^{+1}	1769	1265	101	0.00	0.06					0.04	0.06	1			**3**
137	β-citronellol	T	CI, RI	83; 157^{+1}	1770		81	0.00	0.05	0.00	0.04	0.00	0.02	0.21	2.65	2	2	1	**3**
138	**diethyl pentanedioate**	S		143	1787		143	0.00	0.02	0.00	0.03	0.00	0.02	0.00	0.03	1	2	1	2
139	unknown	U		143	1794		71	0.00	0.06							3			
140	**methyl salicylate**	S	CI, RI	153^{+1}	1795	1097	120	0.05	0.17	0.02	0.06	0.02	0.04	0.05	0.29	**5**	**6**	**3**	**3**
141	**ethylphenyl acetate**	P	CI, RI	165^{+1}	1799	1197	91	0.07	0.55	0.00	0.06	0.04	0.07	0.17	0.36	**5**	4	**3**	**3**
142	unknown (decenol)	U	CI	157^{+1}	1800		67	0.00	0.04					0.04	0.23	1			**3**
143	unknown (succinic ester)	U		129	1801	1332	101	0.00	0.07	0.00	0.16	0.00	0.06			3	4	1	
144	**methyl dodecanoate**	S	RI		1808	1516	74							0.00	0.08				2
145	unknown (acid)	U		133; 87; 115	1811		87			0.00	0.04	0.05	0.17	0.00	0.04		1	**3**	1
146	**ethyl salicylate**	S	CI	167^{+1}	1830	1185	120	0.00	0.02					0.51	0.66	2			**3**
147	**2-phenylethyl acetate**	P	RI	105; 146	1830	1210	104	0.29	1.48	0.00	0.34	0.04	0.29	0.18	0.44	**5**	5	**3**	**3**
148	**β-damascenone**	P	CI, RI	191^{+1}	1836	1377	121	0.06	0.10	0.07	0.14	0.00	0.04	0.08	0.14	**5**	**6**	2	**3**
149	ethyl 2,4-decadienoate	T			1838	1439	97							0.00	0.10				2
150	ethyl 3,3-diethoxypropanoate	T	CI	145^{+1-46}	1838		103	0.00	0.08	0.00	0.09	0.00	0.09			1	4	1	
151	**ethyl dodecanoate**	S	CI, RI	229^{+1}	1849	1590	88	0.86	2.29	0.82	2.41	0.39	1.36	1.23	2.24	**5**	**6**	**3**	**3**
152	**geraniol**	P	CI, RI	81; 137^{+1-18}	1853		69					0.00	0.04	0.16	2.40			2	**3**
153	*p*-cymen-8-ol	T	CI, RI	151^{+1}	1859		135	0.00	0.01	0.00	0.04			0.04	0.07	1	3		**3**
154	**hexanoic acid**	P	CI, RI	99^{+1-18}	1867	969	60	1.29	1.78	0.82	1.65	0.79	1.39	0.45	1.15	**5**	**6**	**3**	**3**
155	**3-methylbutyl decanoate**	S			1868	1658	70	0.00	0.18	0.16	0.34			0.00	0.17	3	**6**		1
156	4-ethyl-1,2-dimethoxybenzene	T	CI	167^{+1}	1889	1259	151	0.00	0.09			0.00	0.01			3		1	
157	**benzyl alcohol**	P	CI, RI	91^{+1-18}	1890	1071	79	0.14	0.22	0.07	0.53	0.12	0.22	3.23	22.09	**5**	**6**	**3**	**3**
158	ethyl 3-hydroxyoctanoate	T	CI	171^{+1-18}; 189^{+1}	1898		117	0.00	0.16	0.00	0.04			0.00	0.05	4	1		2
159	ethyl dihydrocinnamate	T	RI	105; 146	1899	1304	104	0.00	0.11	0.00	0.09	0.00	0.01	0.00	0.30	4	5	1	2
160	(*Z*)-whiskey lactone	T	CI, RI	157^{+1}	1904	1258	99	0.00	0.05	0.00	0.15	0.00	0.11			1	4	2	
161	**diethyl hexanedioate**	S			1905		111			0.00	0.05	0.00	0.36				2	1	
162	**ethyl 3-methylbutyl succinate**	S	CI	129; 217^{+1}	1909	1433	101	0.04	0.16	0.06	0.34	0.09	0.15	0.04	0.07	**5**	**6**	**3**	**3**
163	4-(methylthio)phenol	T	CI	169^{+1}	1918	1221	126	0.00	0.12							4			
164	**2-phenylethanol**	P	CI, RI	105^{+1-18}	1925		65	3.17	7.29	2.75	14.83	5.67	7.06	0.49	6.08	**5**	**6**	**3**	**3**
165	**maltol**	P			1938		126	0.00	0.06	0.00	0.01	0.00	0.04			4	1	1	
166	ethyl 3-hydroxyoctenoate	T	CI	169^{+1-18}; 187^{+1}	1953		117	0.00	0.11							4			
167	4-methylguaiacol	T	CI	139^{+1}	1972	1100	123	0.06	0.38					0.00	0.34	**5**			2

Table 1. Continued

								Calvados[h]		Cognac[h]		Armagnac[h]		Mirabelle[h]		Cdos	Cog	Arm	Mir
entry	compound[a]	ID[b]	ID method[c]	CI major peaks[d]	RI BP-20[e]	RI DB-5[f]	ion[g]	low	high	low	high	low	high	low	high	nb[i]	nb[i]	nb[i]	nb[i]
168	(*E*)-whiskey lactone	T	CI, RI	157^{+1}	1977	1284	99	0.00	0.10	0.04	0.20	0.00	0.12			1	**6**	2	
169	methyleugenol	T	CI	179^{+1}	2024	1342	178	0.00	0.04					0.02	0.07	4			**3**
170	**4-ethylguaiacol**	P	CI, RI	153^{+1}	2046	1196	137	2.00	3.24	0.04	0.72	0.06	0.25	0.00	0.26	**5**	**6**	**3**	2
171	**diethyl malate**	S	CI	117; 145^{+1-46}	2053		117	0.05	0.68	0.09	0.69	0.13	2.36			**5**	**6**	**3**	
172	**ethyl tetradecanoate**	S	CI, LRI	257^{+1}	2054	1794	88	0.13	0.82	0.07	0.35	0.21	0.38	0.15	0.46	**5**	**6**	**3**	**3**
173	**3-methylbutyl dodecanoate**	S	LRI		2072		70	0.00	0.16	0.00	0.11	0.00	0.11	0.00	0.03	4	3	1	1
174	**octanoic acid**	P	CI, RI	127^{+1-18}	2079	1160	60	2.75	3.48	1.71	5.07	1.34	3.52	0.41	0.77	**5**	**6**	**3**	**3**
175	4-propylguaiacol	T	CI	167^{+1}	2126		137	0.00	0.09	0.00	0.03			0.00	0.17	2	1		1
176	unknown	U			2134		173			0.12	0.25	0.03	0.07	0.00	0.04		**6**	**3**	1
177	**ethyl cinnamate**	P	CI, RI	177^{+1}; 131^{+1-46}	2149	1319	131	0.00	0.07					0.09	0.58	4			**3**
178	**ethyl pentadecanoate**	S	LRI		2157	1897	88	0.00	0.04					0.00	0.05	1			1
179	γ-decalactone	T	CI, RI	171^{+1}; 153^{+1-18}	2164	1423	85							0.15	0.62				**3**
180	unknown	U		155	2166		81	0.00	0.11							2			
181	**tetradecanol**	P	LRI		2175		83	0.00	0.04	0.00	0.22	0.00	0.02			1	1	1	
182	unknown	U		153	2175		85	0.00	0.05	0.00	0.06					2	1		
183	γ-eudesmol	T	RI		2182		161					0.05	0.09					**3**	
184	**eugenol**	P	CI, RI	165^{+1}	2184	1283	164	0.53	0.78	0.00	0.05	0.00	0.08	1.29	11.59	**5**	5	2	**3**
185	**4-ethylphenol**	P	CI, RI	123^{+1}	2191	1091	107	1.87	5.02	0.00	0.12	0.07	0.15	0.18	3.94	**5**	4	**3**	**3**
186	diethyl octanedioate	T			2220		152	0.00	0.05	0.00	0.03	0.00	0.05	0.03	0.08	2	2	2	**3**
187	**methyl hexadecanoate**	P	CI, LRI	271^{+1}	2223	1922	74	0.08	0.73	0.08	0.14	0.08	0.14	0.12	0.16	**5**	**6**	**3**	**3**
188	unknown	U			2247		181	0.00	0.06			0.00	0.01			3		1	
189	**ethyl hexadecanoate**	S	CI, LRI	285^{+1}	2259	1999	157	0.00	0.39	0.07	0.15	0.07	0.23	0.76	0.80	4	**5**	**3**	2
190	**ethyl hexadecenoate**	S	CI	283^{+1}	2287	1987	55	0.00	0.18	0.00	1.17	0.00	0.05	0.04	0.04	2	1	1	1
191	**decanoic acid**	P	CI, RI	155^{+1-18}	2292		60	0.50	1.51	0.22	1.26	0.27	0.72	0.08	0.22	**5**	**6**	**3**	**3**
192	farnesol	T	RI		2361		69	0.00	0.08			0.00	0.07	0.00	0.21	1		2	2
193	hexadecanol	T	LRI		2381		83	0.00	0.05	0.00	0.05			0.00	0.06	1	2		1
194	γ-dodecalactone	T	CI, RI	199^{+1}	2395	1640	85							0.07	0.37				**3**
195	**2-phenylethyl octanoate**	S			2398	1825	104	0,00	0.06	0.00	0.11	0.00	0.03	0.00	0.02	2	1	1	1
196	**ethyl octadecanoate**	S	CI, LRI	313^{+1}	2464	2202	157	0.00	0.04					0.00	0.06	1			1
197	**ethyl citrate**	S			2476	1695	157	0.00	0.16	0.00	0.22	0.00	0.21			3	3	2	
198	**ethyl oleate**	P	CI	311^{+1}	2487	2181	264	0.00	0.07			0.00	0.03	0.00	0.09	2		2	2
199	**5-(hydroxymethyl)furfural**	P	CI	127^{+1}; 109^{+1-18}	2518		97	0.00	0.73	0.11	1.19	0.07	0.58			2	**6**	**3**	
200	**ethyl linoleate**	S			2536	2177	67	0.00	0.12	0.00	0.14	0.00	0.16	0.04	0.74	2	1	2	**3**
201	**vanillin**	P	CI, RI	153^{+1}	2591	1306	151	0.00	0.63	0.11	0.62	0.26	0.69	0.00	0.18	4	**6**	**3**	2
202	**ethyl linolenate**	S			2605		79							0.00	0.17				2
203	**2-phenylethyl decanoate**	S			2613	2039	104	0.00	0.07			0.00	0.03	0.00	0.04	1		1	1
204	ethyl vanillate	T	RI		2650		151	0.00	0.14	0.00	0.08	0.00	0.04	0.00	0.03	1	2	1	1

[a] Underlined, compound detected in all samples of brandies; boldface, presence verified by injection of a pure or synthesized standard. [b] S, injection of synthesized compound; P, injection of pure commercial compound; T, tentatively identified; U, unknown. [c] CI, CI peaks confirming the proposed chemical structure; RI, retention index in BP-20 compared with those found in the literature for beverages or fruits; LRI, retention index confirmed by the calculation of linear retention indices using other compounds of the same chemical family. [d] Major peaks observed in chemical ionization using acetonitrile as liquid reactant with explanation of the obtained peaks in superscript ($^{+1}$, $^{+1-18}$ or $^{+1-46}$ for m/z M + 1, M + 1 − 18 (loss of water), or M + 1 − 46 (loss of ethanol) observed peaks). [e] Retention indices calculated on a 50 m × 0.25 mm × 0.25 μm BP-20 stationary phase. [f] Retention indices calculated on a 60 m × 0.25 mm × 0.25 μm DB-5 stationary phase. [g] Selected MS ion for the calculation of the relative level of each compound. [h] Lowest and highest values for each type of brandy; these values were calculated by dividing the area corresponding to the selected ion and that of the m/z 88 ion of the internal standard (ethyl undecanoate). [i] Number of samples in which the compound was detected (signal to noise ratio > 10). Boldface values correspond to brandies in which the compound was detected in every sample.

their relative area toward an internal standard (ethyl undecanoate). As mentioned before, our goal was not to determine the exact quantity of each compound in each type of brandy but to discriminate samples by using the most appropriate tool of evaluation for every component. From this point of view and to avoid any possible mistake in this evaluation, the most specific mass fragment of each molecule obtained in EI-MS mode (see **Table 1**) was chosen to be integrated. If the compound was never coeluted in our chromatographic conditions on the BP-20 stationary phase, then the MS ion with the highest signal-to-noise ratio was integrated. If the compound was coeluted in at least one analysis, we first eliminated from our selection all common mass fragments and, second, we integrated the remaining MS ion of each compound that possessed the highest signal-to-noise ratio. Peak integrations were realized only on BP-20 GC-MS chromatograms as resolutions of peaks were better than those obtained for DB-5 ones. Relative areas were calculated only for peaks having signal-to-noise ratios of >10; values of <10 indicate a doubtful-quantification. The lowest and highest values of relative areas for one class of brandy are given in **Table 1**; they can be compared with those of other types of brandies for the same compound. Nevertheless, as the detector response may be different from one compound to another, the values of relative area for two different compounds given in **Table 1** should not be compared.

Discrimination of Brandies. The number of values for each sample is very high, and a statistical analysis was then necessary.

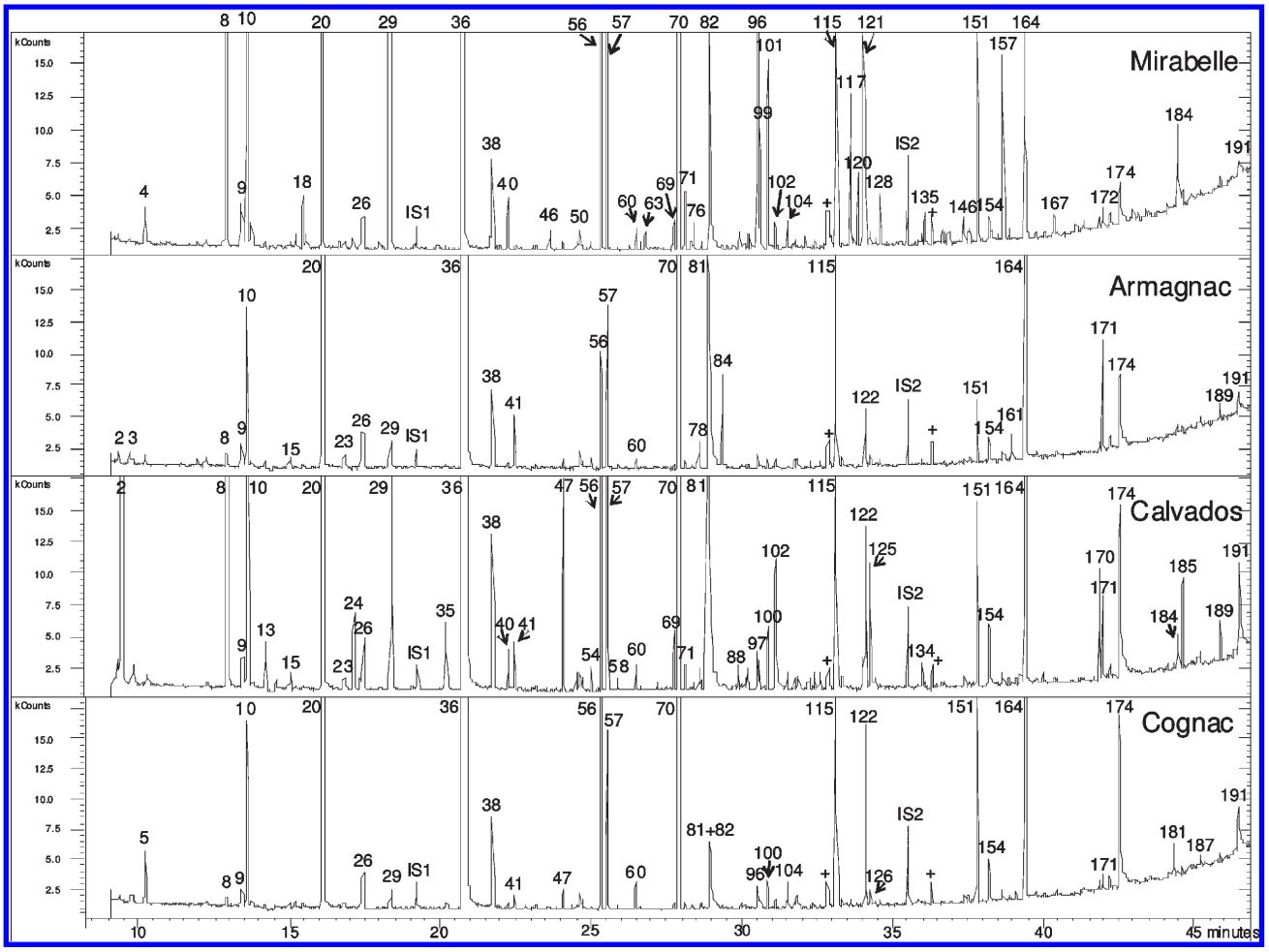

Figure 1. GC-MS chromatograms of four selected extracts of brandies (Mirabelle, Armagnac, Calvados, and Cognac) obtained on BP-20 stationary phase with peaks labeled as in **Table 1**. IS1, 4-methylpentan-2-ol; IS2, ethyl undecanoate, both internal standards used for quantification.

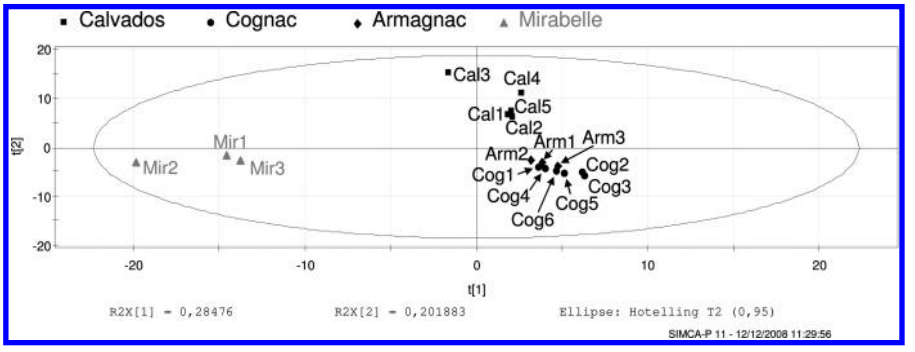

Figure 2. PLS-DA of the volatile composition of samples of all brandies (Calvados, Cognac, Armagnac, and Mirabelle) given as a two-dimensional representation of the scores (t[1] and t[2]) on the first [1] and second [2] PLS components. The first PLS component explains 28% (R2X [1]) and the second PLS component 20% (R2X [2]) of the variation of the *X* data.

PLS-DAs were performed on the values of relative area for each compound in each extract. The goal of the first analysis was to answer to this question: Is it possible to discriminate samples according to their volatile composition? The distribution of samples on the first and second components of this statistical analysis is presented in **Figure 2**. Three groups of samples can be clearly defined: a group for the samples of Mirabelle, and another one for the samples of Calvados; samples of Armagnac and Cognac, which were located close to each other, could not be clearly differentiated in two separate clusters with this first analysis. These last two kinds of brandies are issued from the distillation of wines, and it is not so surprising to observe a similar localization. The results concerning the nine samples of Armagnac and Cognac were exclusively selected for the second statistical analysis. The new map (**Figure 3**) showed a good discrimination of these two types of samples. PLS-DA was then used to highlight compounds that better represent one class of brandy.

Specific Volatile Markers of Mirabelle Brandies. Aside from the 41 volatile compounds that have been detected in all samples, some of the 166 others were particular to a few samples (**Table 1**). Seventeen compounds were exclusively found in the three samples of Mirabelle brandies. They can be considered as very specific of the product. In these, hexanal (**19**), heptanal (**32**), and nonanal (**63**) and their corresponding acetals, 1,1-diethoxyhexane (**37**),

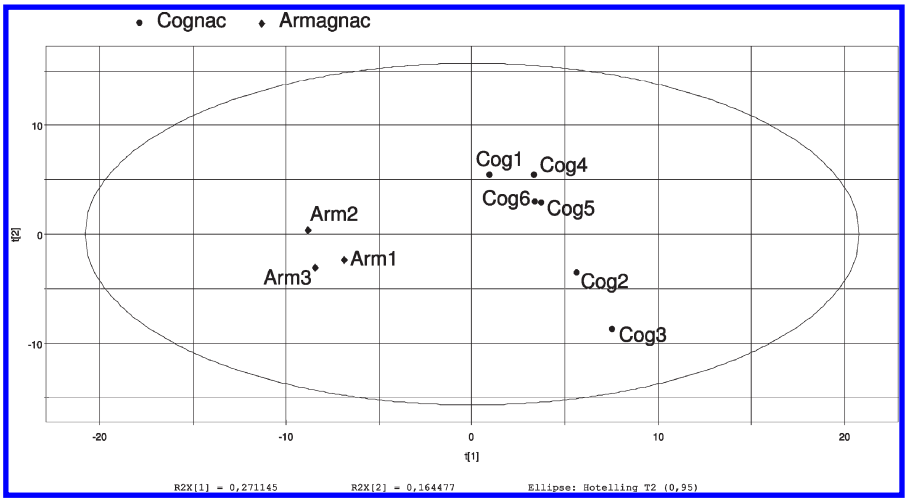

Figure 3. PLS-DA of the volatile composition of samples of Armagnac and Cognac given as a two-dimensional representation of the scores (t[1] and t[2]) on the first [1] and second [2] PLS components. The first PLS component explains 27% (R2X [1]) and the second PLS component 16% (R2X [2]) of the variation of the *X* data.

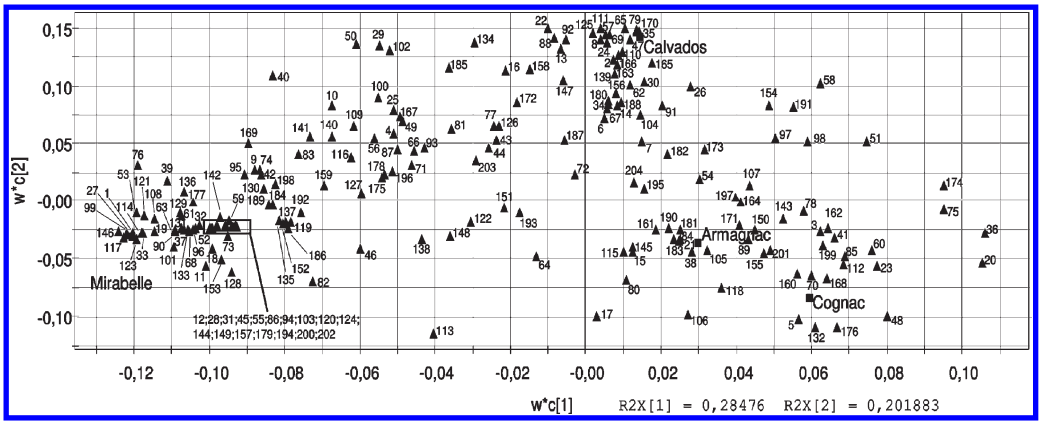

Figure 4. PLS-DA weight plot of composition variables, w*c[1] and w*c[2], for all studied samples of all brandies, respectively, on the first [1] and second [2] components. Compounds (listed in **Table 1**) are represented by numbers for vizualization purposes.

1,1-diethoxyheptane (**52**), and 1,1-diethoxynonane (**94**), were identified. This tends to confirm the fact that concentrations of aldehydes in that spirit are higher than in the other ones. It should be noted that a chemical equilibrium between acetals and aldehydes is effective in spirits due to the high content of ethanol. The presence of 1,1-diethoxypropane (**1**) was also determined only in Mirabelle samples, which indicates also a high concentration of propanal, which was eluted in our chromatographic conditions with the solvents used for the preparation. Pentanoic acid (**133**) and its corresponding ethyl ester (**27**) were also only found in the three samples of that plum brandy. This, with also the presence of ethyl nonanoate (**99**) and of some previously cited compounds, tends to indicate higher amounts of 3-, 5-, 7-, and 9-carbon derivatives in Mirabelle. Two methyl esters, methyl hexanoate (**33**) and methyl benzoate (**114**), were identified only in Mirabelle. It is not surprising to find two lactones in this list of specific compounds of the Mirabelle, γ-decalactone (**179**) and γ-dodecalactone (**194**), because, with their peach-like flavor, they play a key role in the aroma composition of various stone-fruits such as apricots (*33*, *34*) and nectarines (*35*). Hexyl 2-methylbutanoate (**68**), hexyl but-2-enoate (**103**), and ethyl dec-4-enoate (**120**) were also detected in only the three samples of Mirabelle.

However, a discussion on the presence or absence of compounds in extracts of any substances is directly linked to many factors such as the chromatographic or spectrometric conditions and the extraction method. A projection of the compound variables on the first and second component of the PLS-DA statistical analysis led to a complex two-dimensional representation (**Figure 4**). This model enables visualization of the volatiles that contribute the most to the discrimination of the four types of spirits.

Eight compounds on this representation (**Figure 4**) border the center of the class. In these, the presence of 1,1-diethoxypropane (**1**), ethyl pentanoate (**27**), methyl hexanoate (**33**), ethyl nonanoate (**99**), and methyl benzoate (**114**) was already discussed above. However, three other compounds contribute a lot to the specificity of Mirabelle: nonanol (**117**), an unknown compound with a mass spectrum similar to that of nonenol (**123**), and ethyl salicylate (**146**). These may also be present in other brandies, but their relative proportions in Mirabelle were much more important. In the 30 closest compounds we found 6 esters with an odd number of carbons: ethyl pentanoate (**27**), methyl hexanoate (**33**), ethyl heptanoate (**53**), methyl octanoate (**61**), ethyl nonanoate (**99**), and methyl decanoate (**108**). Heptanal (**32**), heptanol (**76**), nonanal (**63**), and nonanol (**117**) were also in these. In the same environment, benzaldehyde (**96**), which seems to be 15−20-fold more concentrated in Mirabelle than in other brandies, was present and accompanied by its derivatives or precursors benzyl acetate (**131**), benzyl alcohol (**157**), methyl benzoate (**114**), ethyl benzoate (**121**), and ethyl salicylate (**146**). Benzaldehyde and

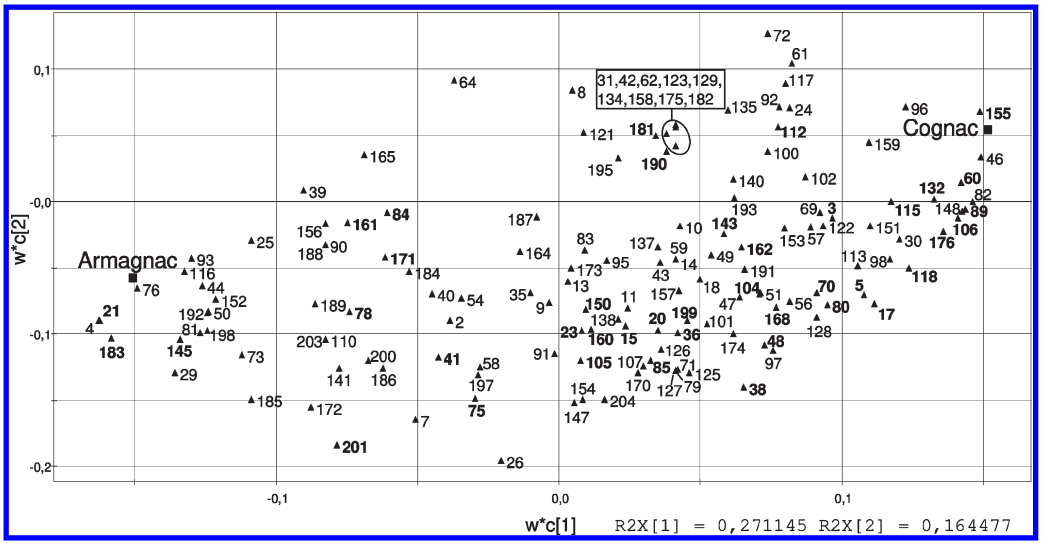

Figure 5. PLS-DA weight plot of composition variables, w*c[1] and w*c[2], for samples of Armagnac and Cognac, respectively, on the first [1] and second [2] components. Compounds (listed in **Table 1**) are represented by numbers for vizualization purposes. Boldface values correspond to compounds found in the lower right quarter of **Figure 4** (close to the center of the Armagnac and Cognac classes).

ethyl nonanoate were already regarded as key aroma compounds of plum juices by Ismail et al. (*36*). Moreover, these authors cited also linalool (**101**) as a contributor to the aroma of plum juices; it was detected in 15 of the 17 studied samples, but its concentration in Mirabelle is at least 5-fold higher than in other brandies. The proximity of 1,1-diethoxypropane (**1**), hexanal (**19**), 1,1-diethoxyhexane (**37**), heptanal (**32**), 1,1-diethoxyheptane (**52**), nonanal (**63**), and benzaldehyde (**96**) confirms that many aldehydes and acetals contribute also to the specificity of Mirabelle brandies. Some of them were thought to be at the origin of plum brandy flavor (*37*). Miscellaneous compounds such as 3-methylbut-3-en-1-ol (**39**), hexyl 2-methylbutanoate (**68**), and ethyl cinnamate (**177**) were particularly highly concentrated in Mirabelle spirits.

Specific Volatile Markers of Calvados. Among the 207 compounds detected in brandies, only 1 was found exclusively in the five samples of Calvados. That molecule (**65**) was unfortunately not clearly identified. Its EI mass spectrum seemed to be that of a hexenol, and such chemical structure could be confirmed by the presence of a m/z 83 ($MH^+ - 18$) peak in CI-MS and a retention index of 1414 on the polar BP-20 stationary phase.

These results show an important similarity in terms of volatile composition between brandies of various origins. In the statistical representation (**Figure 4**), the projection of five compounds covered the center, corresponding to Calvados samples. In addition to compound **65**, 6-methylhept-5-en-2-ol (**79**) and 4-ethylguaiacol (**170**) were there. 3-Ethoxypropanal (**35**) and 1,1,3-triethoxypropane (**47**) also contributed a lot to the discrimination of Calvados. These two compounds associated with allylic alcohol (**24**) and 3,3-diethoxypropanol (**110**), localized in the same environment, are thought to arise from the transformation of acrolein (*8*, *38*). The production of these derivatives seems to prove that the emergence of acrolein is a specific problem of apple juices through the presence of bacteria such as *Lactobacillus collinoides* (*39*, *40*). 2-Methyl-branched compounds such as ethyl 2-methylbutanoate (**13**) and 2-methylbutanoic acid (**125**) are important odorants of apples (*41*, *42*) and ciders (*43*). They were found close to the center of the class corresponding to Calvados like two 3-methyl-branched compounds, 3-methylbutyl acetate (**26**) and ethyl 2-hydroxy-3-methylbutanoate (**69**), which are thought to be more specific of fermentation products (*41*). We have shown in the past that butan-2-ol (**8**) can be highly concentrated in freshly distilled Calvados (*44*); it was found to highly discriminate Calvados from the other studied brandies. Other highly specific compounds of Calvados were from various chemical families. Ethyl propanoate (**2**) and hexanol (**57**) were detected in all extracts of brandies but were extremely more concentrated in Calvados samples than in Mirabelle, Cognac, and Armagnac ones. (*Z*)-Oct-5-en-1-ol (**111**) contributes also to the specificity of Calvados. The projections of 4-(methylthio)phenol (**163**), maltol (**165**), and an unknown compound (**166**) were also placed close to the center of the class corresponding to Calvados even if they were not detected in one sample of Calvados.

Specific Volatile Markers of Armagnac and Cognac. Two compounds were exclusively present in the three extracts of Armagnac: γ-eudesmol (**183**) and 1-(1-ethoxyethoxy)-2-methylbutane (**21**). The data collected for the samples of Cognac did not reveal any totally specific compound of this spirit. The model presented in **Figure 4** does not enable separation of the volatiles specific to Armagnac from those of Cognac. The projections of their center are definitely in the same direction from the center of the representation.

In a first step the differences of volatile composition of Armagnac and Cognac versus that of Calvados and Mirabelle can be illustrated using **Figure 4**. In this figure, these two compounds (**21** and **183**), specific to Armagnac samples, are located close to the center of the class, but some others are not very significant because, being located near the center of the diagram, their variables have small weights that contribute to the regression model. 1,1-Diethoxy-2-methylpropane (**5**), 4-methylpentanol (**48**), 1,1,6-trimethyl-1,2-dihydronaphthalene (**132**), and an unknown compound (**176**) are located far from this center and in opposition to Calvados and Mirabelle clusters. As a consequence, they contribute a lot to the characteristics of Armagnac and Cognac. The amount of ethyl octanoate (**70**) is generally more important in these two spirits. (*Z*)-Whiskey lactone (**160**) and (*E*)-whiskey lactone (**168**) are placed close together, and that reflects a potential identical origin. These two compounds exhibit a coconut-like flavor in alcoholic beverages such as whiskey (*45*) and wine (*46*−*49*). The (*E*)-whiskey lactone was encountered in this study in all wine-based brandies except in one sample of Armagnac (the youngest sample), whereas (*Z*)-whiskey lactone was also not detected in two samples of Cognac. They are known to be extracted from oak wood (*50*−*52*) and were present as well

in one sample of Calvados but not in samples of Mirabelle, which were aged in beech casks.

In a second step, another PLS-DA (**Figure 5**) based only on the results of Armagnac and Cognac was realized to show the differences between these two wine-based brandies. A dozen compounds seem to contribute a lot to the discrimination of Cognac from Armagnac. Among them, many furanic compounds were found such as furfuryl ethyl ether (**46**), furfural (**82**), 2-acetylfuran (**89**), and 5-methylfurfural (**106**). Their concentrations in beverages may vary according to the type of cask (*53*) or aging time (*54*). Our results corroborate those of Rodriguez Madrera et al. (*55*); the content of these components is highly influenced by the distillation system (*22*), which is rather different between these two wine-based spirits. The double distillation, which leads to the production of Cognac, enhances the amount of all furanic species such as the four previously cited compounds. However, a majority of these derivatives could not be considered as specific to Cognac because Calvados can be produced through a double distillation (labeled "Calvados Pays d'Auge") and high concentrations of furanic compounds are already present in the Mirabelle fruit. 5-Methylfurfural (**106**) and 2-acetylfuran (**89**) are, however, generally more concentrated in Cognac than in the three other brandies and can be considered as markers of this spirit with 3-methylbutyl decanoate (**155**), ethyl decanoate (**115**), (*Z*)-hex-3-en-1-ol (**60**), and 1,1,6-trimethyl-1,2-dihydronaphtalene (TDN; **132**). TDN was often recognized as a potent odorant of many wines (*56*). A highest level of heptanol (**76**) may be useful to distinguish samples of Armagnac from those of Cognac. However, its concentration is rather low concentration in wine-based spirits. 1-(Ethoxyethoxy)-2-methylbutane (**21**), γ-eudesmol (**183**), and the unknown compound (**145**) seem to be better markers to discriminate Armagnac from the three other brandies (**Figure 5**).

The statistical analysis of the volatile composition of these brandies tends also to show that higher alcohols are rather less present in Cognac and Armagnac than in Calvados and Mirabelle for the same ethanolic content. In **Figure 4**, aliphatic linear alcohols such as propanol (**10**), butanol (**29**), pentanol (**40**), octanol (**102**), and decanol (**134**) are placed on opposite directions from the center of the two wine-based spirit classes. They are gathered on the top left side of the representation, and this seems to confirm a common emergence during the fermentation process. It should be noted that hexanol (**57**) is located farther, which may signify a different origin for this component. 2-Methylpropanol (**20**) and isopentanol (**36**) are thought to be produced in the same time as linear aliphatic alcohols; however, our results show that the factors or mechanisms involved in their emergence in the products could be different.

Conclusion. The volatile compositions of brandies such as Mirabelle, Calvados, Cognac, and Armagnac are qualitatively rather similar. However, their organoleptic characteristics are really different. This is due to slight differences in the concentrations of volatiles. In this work, we showed that the determination of relative levels of about 200 components in GC-MS analysis followed by a PLS-DA was suitable for distinguishing these spirits. Compounds such as aldehydes (hexanal, heptanal, and nonanal) and acetals (1,1-diethoxypropane, 1,1-diethoxyhexane, 1,1-diethoxyheptane, and 1,1-diethoxynonane) have greater levels in Mirabelle and could be followed to discriminate that spirit from the three others. 3-Ethoxypropanal, 1,1,3-triethoxypropane, allylic alcohol, and 3,3-diethoxypropanol, which are thought to be produced from acrolein, are much more concentrated in Calvados together with butan-2-ol and ethyl 2-methylbutanoate. The highest concentrations of 1-(ethoxyethoxy)-2-methylbutane and γ-eudesmol are specific to Armagnac samples. No specific compound for Cognacs toward Armagnac, Calvados, and Mirabelle were found. However, wine brandies (Cognac and Armagnac) can be first distinguished from Calvados and Mirabelle because of their high quantities of 1,1-diethoxy-2-methylpropane, 1,1,6-trimethyl-1,2-dihydronaphthalene, 4-methylpentanol, and (*Z*)- and (*E*)-whiskey lactones. Cognac can then be differentiated second from Armagnac because this spirit contains highest contents of furan derivatives such as furfural, 5-methylfurfural, furfuryl ethyl ether, and 2-acetylfuran.

Supporting Information Available: GC-MS chromatograms used for identification purposes of four selected extracts of brandies (Mirabelle, Armagnac, Calvados, and Cognac) obtained on DB-5 stationary phase with peaks labeled as in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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