JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Identification of Trace Volatile Compounds in Freshly Distilled Calvados and Cognac Using Preparative Separations Coupled with Gas Chromatography−Mass Spectrometry

JÉRÔME LEDAUPHIN,† JEAN-FRANÇOIS SAINT-CLAIR,† ODILE LABLANQUIE,‡ HUGUES GUICHARD,§ NICOLE FOUNIER,# ELISABETH GUICHARD,# AND DANIEL BARILLIER*,†

ERPCB, IUT-UFR Sciences, 6 Boulevard du Maréchal Juin, F-14032 Caen Cedex, France; BNIC, Station Viticole, 69 Rue de Bellefonds, B.P. 18, F-16101 Cognac, France; ADRIA Normandie, Boulevard du 13 Juin 1944, B.P. 2, F-14310 Villers-Bocage, France; and UMRA-INRA-ENESAD, 17 Rue Sully, B.P. 86510, F-21065 Dijon Cedex, France

Gas chromatography coupled with mass spectrometry (GC-MS) using both electron impact and chemical ionization detection modes led to the determination of the volatile composition of two samples of freshly distilled Cognac and two samples of freshly distilled Calvados. A total of 169 volatile compounds were directly identified in dichloromethane extracts obtained by liquid−liquid extraction. Trace compounds present in both spirits were characterized with the help of preparative separations. In a first step, groups of compounds were separated by preparative GC, and the fractions were analyzed on a polar stationary phase by GC-MS. In a second step, silica gel fractionation was used to separate them by polarity. In this study, 331 compounds, of which 162 can be considered as trace compounds, were characterized in both freshly distilled Cognac and Calvados. Of these, 39 are common to both spirits; 30 are specific to Cognac with numerous hexenyl esters and norisoprenoidic derivatives, whereas 93 are specific to Calvados with compounds such as unsaturated alcohols, phenolic derivatives, and unsaturated aldehydes.

KEYWORDS: Calvados; Cognac; volatiles; gas chromatography−mass spectrometry; preparative separations

INTRODUCTION

Cognac and Calvados are two of the most prestigious French spirits.

Calvados. Calvados is a typical spirit produced in Normandy. Distillation of cider yields freshly distilled Calvados. The French label "AOC" (Appellation d'Origine Controlée) is given just after this step. Only a few works (*1*, *2*) have appeared to advance the knowledge of the chemical composition of freshly distilled Calvados. In a previous study (*3*, *4*), this was more largely investigated, leading to the identification of >120 molecules. Compounds were extracted from Calvados samples of various qualities using pentane, and separations were realized by gas chromatography−mass spectrometry (GC-MS) analysis on medium polar and apolar stationary phases. Results were correlated with those obtained by olfactometric analysis, and although a majority of the odors detected could be characterized, some important ones remained unidentified.

Cognac. Cognac is produced in the French area of Charentes. Double distillation of wine is necessary for the production of freshly distilled Cognac. The volatile composition of aged products has been largely studied and discussed. In the early 1970s Schaefer et al. (*5*) identified 81 flavor compounds in Cognac with the help of GC-MS and fractionation on preparative gas chromatography. Carbonyl compounds were isolated in the form of their 2,4-dinitrophenylhydrazones and analyzed by thin-layer chromatography. Schreier et al. (*6*) fractionated extracts of grape brandies on silica gel, and 139 volatile compounds were determined by gas chromatography. They showed the presence of numerous esters, alcohols, and carboxylic acids.

Analysis of freshly distilled beverages traditionally includes quantification of compounds revealing a deviation in the fabrication process and/or in the quality of the raw material (*1*, *7*−*9*). Moreover, the previous studies (*4*, *10*) showed that trace or ultratrace compounds could be present and could have a real olfactive impact on both of the two young spirits. These compounds are hardly or even not detectable with common and simple chromatographic procedures. Spirit analyses are tradi-

* Author to whom correspondence should be addressed [telephone +33-(0)-2-31-56-70-29; fax +33-(0)-2-31-56-73-03; e-mail Barillier@iutcaen.unicaen.fr].
† ERPCB, IUT-UFR Sciences.
‡ BNIC, Station Viticole.
§ ADRIA Normandie.
# UMRA-INRA-ENESAD.

10.1021/jf040052y CCC: $27.50
Published on Web 07/16/2004

tionally performed using either headspace techniques such as solid-phase microextraction (SPME) (*11*, *12*) or liquid−liquid extraction with dichloromethane (*13*, *14*). Separation of volatile compounds by GC or GC-MS is then commonly performed on polar stationary phases. Preparative separations have been largely used in the past in order to identify trace compounds. HPLC fractionation was already used for analysis of distilled beverages (*15*) and gave rather concentrated extracts. However, this avoids a further step of concentration of fractions. Separations on preparative GC allow very concentrated extracts to be obtained, which can be dissolved in a small volume of solvent prior to analysis by GC-MS. This was notably employed for the characterization of two olfactive markers of Portuguese wines (*16*). Silica gel fractionation is commonly employed for the purification of compounds present in mixtures, and it was already used for the separation of volatile compounds in foods (*17*, *18*) according to their polarity.

This work was carried out in the framework of a national program realized in a common way by different research teams. It was aimed at the control of spirit technology, which is why freshly distilled samples of good quality were specifically selected. Our goal was to identify trace and ultratrace compounds that are likely to have an olfactive impact in Calvados and Cognac and then to compare qualitatively these two products. This was led by means of preparative separations prior to analysis by GC-MS. Olfactometric analyses were also realized on both products and will be soon published. In this paper we present successively the extractive, preparative, and analytical tools used for the identification of trace compounds in the samples. Thereafter, the synthetic results obtained in terms of major/minor levels in two samples of Calvados and two samples of Cognac are discussed followed by a comparison of the chemical compositions of these two products.

MATERIALS AND METHODS

Materials. Two freshly distilled Calvados and two freshly distilled Cognac samples were provided by industrial producers. Produced in their respective limited regions of AOC in 2000 and 2001, they were first selected in-house by producers themselves as "good quality" spirits. Solvents were as follows: dichloromethane and *n*-pentane, HPLC grade from Acros Organics (Fair Lawn, NJ). Authentic chemical compounds (3- and 4-methylpentanol) and GC retention index (RI) standards (straight-chain hydrocarbons) were from Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France).

Extraction and Concentration of Volatile Constituents. Two hundred milliliters of either Calvados or Cognac was mixed with 200 mL of ultrapure water and then extracted with 32 mL of dichloromethane. NaCl (20.4 g) was added, and the mixture was stirred magnetically during 3 min. Layers were separated in a separatory funnel, and the organic layer was kept then dried on magnesium sulfate. After filtration on deactivated glass wool, extracts were reduced to 2 mL using a Kuderna−Danish column and then stored at −18 °C prior to analysis. The extract was then directly analyzed on GC-MS before being submitted to preparative fractionations.

Silica Gel Fractionation. Final extracts were separated on 10 g of silica gel ($60F_{254}$ from Merck) placed in a 10 mm diameter buret plugged with deactivated glass wool. Elutions were first carried out with 20 mL of pentane and then successively with 10 mL of various *n*-pentane/dichloromethane mixtures (80/20, 60/40, 40/60, 20/80) and finally 20 mL of pure dichloromethane. Sixteen fractions (labeled in order of elution from 1A to 16A) each containing 5 mL were successively recovered and then reduced to 200 μL using a Kuderna−Danish column. Each fraction was analyzed by GC-MS.

Preparative Gas Chromatography. Preparative GC was carried out on a Varian 3400 gas chromatograph equipped with a thermal conductivity detector. Separations were performed using a 4 m × 5.2 mm (i.d.) "homemade" column filled with a 5% SE-30 (100% dimethylpolysiloxane supported on Chromosorb PWA 100 mesh) stationary phase. Hydrogen was used as a carrier gas with a 50 mL/min flow rate. The injector port and the detector temperatures were 240 °C. The oven program temperature used was 40−220 °C at a rate of 10 °C/min, with an initial temperature hold for 5 min and a final temperature hold for 10 min. In a first stage, 10 μL of final extracts was injected to control separation of volatile compounds. In a second stage, five successive injections of 80 μL were realized and, for each injection, eight different fractions were collected from 40 to 60 °C (labeled 1B), from 60 to 80 °C (2B), from 80 to 100 °C (3B), ..., and finally from 160 to 180 °C (7B). These fractions were recovered manually in collector-connected glass tubes immersed in liquid nitrogen at the end of the chromatographic system. Twenty-five microliters of dichloromethane was then added in each tube, and each fraction was analyzed by GC-MS.

GC-MS. GC-MS analyses were carried out on a Varian 3800 gas chromatograph interfaced with a Saturn 2000 mass spectrometer. Separations were performed using a 30 m × 0.25 mm (i.d.) capillary column, coated with a 0.15 μm film of ZB-Wax stationary phase (100% polyethylene glycol from Phenomenex, Torrance, CA) equivalent to DB-Wax or Carbowax 20M. Helium was used as a carrier gas with a 1 mL/min flow rate. For the analysis of the dichloromethane extracts the oven program temperature used was 35−220 °C at a rate of 1.8 °C/min, with an initial temperature hold for 10 min and a final temperature hold for 10 min resulting in a total run of ∼120 min. Two chromatograms of dichloromethane extracts of Calvados and Cognac are presented as an illustration in **Figure 1** including peak numbers corresponding to **Tables 1−5**. For the analysis of the extract fractions the oven program temperature used was 35−220 °C at a rate of 5 °C/min, with an initial temperature hold for 5 min and a final temperature hold for 10 min, resulting in a total run of 52 min. Extracts (1.5 μL) were injected in both splitless and split modes (ratio 100:1), and injection port temperature was fixed at 250 °C.

For each extract investigation, the mass spectrometer, equipped with an ion trap analyzer, was operated both in electronic impact mode and in chemical ionization mode. Ionization voltage was 70 eV, ion source temperature was 150 °C, and electron multiplier voltage was 1350 V. Scanning was performed from *m*/*z* 35 to 400 in electronic impact mode (EI-MS) and from *m*/*z* 65 to 400 in chemical ionization mode (CI-MS) at 2 scans/s. Acetonitrile was used for the chemical ionization.

For each detected peak, a linear retention index (RI) was calculated using GC retention index standards (hydrocarbons from C7 to C31 used as internal standards) according to the method of Van den Dool and Kratz (*19*).

Identification of volatile compounds was principally performed by comparison of recorded mass spectra with those of the NIST 98 MS database or of a "homemade" database. Theoretical linear indices were also calculated for compounds belonging to the same chemical classes and compared to indices of unknown chromatographic peaks. Diluted pure 3-methylpentanol and 4-methylpentanol were also injected to verify their presence in samples. Compounds identified in Calvados and Cognac extracts and fractions are listed in **Tables 1−8**. They are labeled from **1** to **331** according to their retention time on a ZB-Wax stationary phase. The mode of characterization is given for compounds that could not be identified by a direct comparison of mass spectra.

Synthesis of Acetals. The chemical structures of two acetals derived from methylbutanals could not be clearly determined. Acetals can be easily formed from reaction of aldehydes with an excess of alcohol in an acidic medium (*20*). As a consequence, synthesis of 1,1-diethoxy-2-methylbutane, 1,1-diethoxy-3-methylbutane, and 1,1-diethoxypentane was carried out by mixing 600 μL of 2-methylbutanal (from Aldrich), 300 μL of 3-methylbutanal (from Merck, Schuchart, Germany), and 100 μL of pentanal (from Aldrich) in 20 mL of pure ethanol. Two milliliters of HCl (1 M) was added, and the mixture was stirred at 60 °C for 1 h. After cooling, 10 mL of pentane was added, and the organic layer was recovered after decantation in a separatory funnel. One microliter of this solution was injected in the split mode (ratio 1:100) in GC-MS for identification.

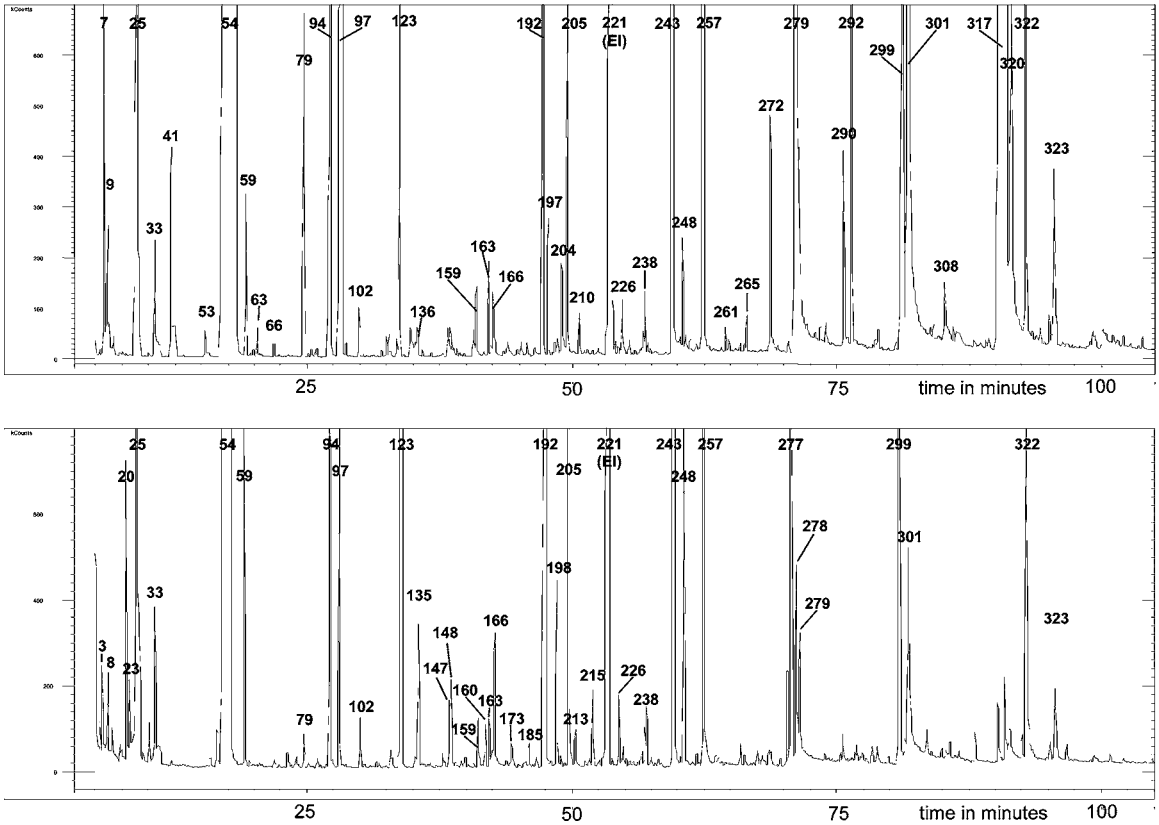

Figure 1. GC-MS chromatograms in EI detection mode of dichloromethane extracts of Calvados (**a**, top) and Cognac (**b**, bottom) on ZB-Wax stationary phase with principal peaks labeled (see **Tables 1**–**5**).

RESULTS AND DISCUSSION

Preparative GC. Separations of the same extract injected five times were realized by preparative GC on an apolar dimethylpolysiloxane (SE-30) stationary phase after detection on a nondestructive detector (TCD). Cumulative fractions thus contained highly concentrated volatile compounds presenting similar molecular weights (or volatility) for each fraction. Further analytical separation on a polar polyethylene glycol stationary phase (ZB-Wax in GC-MS) was performed resulting in a fractionation of the compounds according to their polarity. As a consequence, many coelutions could be resolved by the cumulative effect of these two separation processes. Fractions labeled from 1B to 2B contained only highly volatile compounds with molecular masses of <156 g·mol^{-1}. Numerous alcohols were present in them because of their poor affinity for the stationary phase in preparative GC. In contrast, the heaviest fractions contained principally aromatic compounds (phenols, esters, ketones, etc.) and high molecular weight aliphatic esters. Intermediate fractions contain lots of compounds, and some of them can be found in three or four successive fractions due to either high volumes injected in preparative GC (resulting in overloading of the stationary phase and tailing peaks) or pollution of the collector for the less volatile compounds. Nevertheless, this method enables identification of compounds with very low detection thresholds. For example, oct-1-en-3-one (**75**) and methional (**127**) are rarely identified in GC-MS analysis, and they were found in the preparative fractions. In the same way, aldehydes are often present with low concentrations in Calvados or Cognac samples, and some of them could be identified with support of this technique.

Silica Gel Fractionation. Separation of extracts of Calvados and Cognac was also realized by preparative adsorption chromatography on silica gel. This enabled volatile compounds to be grouped according to their polarity. Compounds separated with this technique were examined by chemical classes and by preparative fractions as can be seen in **Tables 4**−**8**. In fractions 5A and 6A, esters and acetals are in a large majority (>80 for a total of 110 identified compounds in each fraction), whereas alcohols are more present in fractions 8A and 9A (40 for a total of ∼90 identified compounds in each fraction). Carboxylic acids were mostly detected in fractions 9A and 10A. Terpenoic or norisoprenoidic derivatives and phenolic derivatives can have various functionalities and as a consequence were principally identified in "intermediate" fractions (6A−8A) but were also observed in lots of other preparative fractions (4A−12A). Ketones were located in fractions 5A−7A, whereas lactones were mostly found in fraction 9A. Only a few aldehydes and sulfur compounds were identified in preparative fractions, and because of their various functionalities and chain lengths they could be detected in both polar and apolar fractions. Results show that Calvados or Cognac is mainly composed of compounds with medium polarity detected in fractions 5A and 6A and polar (or very polar) compounds located in fractions 8A and 9A.

Identification Tools: Use of CI Detection Mode. EI-MS was systematically used for the determination of volatile compounds present in the extracts. A majority of compounds were identified by comparison of their spectra with those recorded in a database. Unknown spectra can be resolved by employing other identification tools. In this study, we systematically chose to confirm each identification by duplicating the injection with the same chromatographic conditions carried out in CI-MS detection mode. Indeed, spectra of distinct compounds can be very similar in EI-MS detection mode, which can undergo wrong interpretations when using databank comparison. CI-MS was already used for the characterization of volatile

Table 1. Volatile Compounds Identified in Dichloromethane Extracts of Cognac and Calvados

no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments	no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments
3	2-methylpropyl acetate	ester	<1000			**172**	methyl decanoate	ester	1586		
7	butan-2-ol	alcohol	1019			**192**	ethyl decanoate	ester	1634		
8	ethyl butanoate	ester	1023			**193**	butanoic acid	carbox[e]	1637		
9	propanol	alcohol	1030			**194**	furfural ethyl isoamyl acetal	acetal	1652	*b*	125, 167, 213
18	butyl acetate	ester	1057			**196**	nonanol	alcohol	1658		
20	1,1-diethoxy-3-methylbutane	acetal	1062			**197**	ethyl benzoate	aromatic[f]	1658		
21	hexanal	aldehyde	1064			**198**	3-methylbutyl octanoate	ester	1658		
23	1,1-diethoxy-2-methylbutane	acetal	1067			**204**	2- and 3-methylbutanoic acid	carbox	1675		
25	2-methylpropanol	alcohol	1089			**205**	diethyl succinate	ester	1677		
28	1-(1-ethoxyethoxy)-3-methylbutane	acetal	1107			**207**	ethyl dec-9-enoate	ester	1689		
32	2-methylbutyl acetate	ester	1116			**209**	α-terpineol	terp[g]	1694		
33	3-methylbutyl acetate	ester	1117			**214**	1,1-diethoxy-2-phenylethane	acetal	1711		
41	butanol	alcohol	1147			**216**	3-(methylthio)propanol (methionol)	sulfur[h]	1720		
42	ethyl but-2-enoate	ester	1156								
53	3-ethoxypropanal	aldehyde	1185	*b*	103	**221**	ethyl undecanoate	ester	1737		
54	3-methylbutanol	alcohol	1208			**223**	pentanoic acid	carbox	1746		
59	ethyl hexanoate	ester	1226			**225**	methyl salicylate	aromatic	1762		
62	3-methylbut-3-en-1-ol	alcohol	1245			**226**	decanol	alcohol	1764		
63	pentanol	alcohol	1249			**229**	β-citronellol	terp	1768		
66	hexyl acetate	ester	1265			**231**	ethyl phenylacetate	aromatic	1783		
79	1,1,3-triethoxypropane	acetal	1299			**238**	2-phenylethyl acetate	aromatic	1811		
81	4-methylpentanol	alcohol	1312	*c*		**239**	β-damascenone	terp	1811		
85	heptan-2-ol	alcohol	1318			**243**	ethyl dodecanoate	ester	1840		
86	3-methylpentanol	alcohol	1323	*c*		**247**	2-methylbutyl decanoate	ester	1858		
94	ethyl 2-hydroxypropanoate	ester	1342			**248**	3-methylbutyl decanoate	ester	1859		
97	hexanol	alcohol	1352			**249**	hexanoic acid	carbox	1862		
98	(*E*)-hex-3-en-1-ol	alcohol	1362			**252**	ethyl dihydrocinnamate	aromatic	1879		
102	(*Z*)-hex-3-en-1-ol	alcohol	1381			**253**	benzyl alcohol	aromatic	1881		
109	hex-2-en-1-ol	alcohol	1390			**254**	ethyl 3-hydroxyoctanoate	ester	1892	*b*	189, 171
111	octan-3-ol	alcohol	1392			**256**	ethyl 3-methylbutyl succinate	ester	1901	*b*	129, 217, 71
120	ethyl 2-hydroxy-3-methylbutanoate	ester	1422			**257**	2-phenylethanol	aromatic	1914		
122	(*E*)-linalool oxide (furanoid)	terp	1427			**263**	2-methylpropyl dodecanoate	ester	1964		
123	ethyl octanoate	ester	1428			**270**	γ-nonalactone	lactone	2020	*b*	157, 85, 139
124	acetic acid	carbox	1434			**277**	ethyl tetradecanoate	ester	2046		
129	oct-1-en-3-ol	alcohol	1450			**278**	3-methylbutyl dodecanoate	ester	2064		
131	3-methylbutyl hexanoate	ester	1452			**279**	octanoic acid	carbox	2069	*b*	127, 145
134	furfural diethyl acetal	furan[i]	1456			**281**	ethyl 3-hydroxydecanoate	ester	2102	*b*	217, 199
135	furfural	furan	1462			**287**	ethyl pentadecanoate	ester	2148		
136	(*Z*)-linalool oxide (furanoid)	terp	1463			**291**	tetradecanol	alcohol	2188		
137	6-methylhept-5-en-2-ol	alcohol	1464			**295**	methyl hexadecanoate	ester	2213		
141	2-ethylhexanol	alcohol	1491			**299**	ethyl hexadecanoate	ester	2252		
144	2-acetylfurane	ester	1500			**301**	decanoic acid	carbox	2270	*b*	155, 173
147	vitispirane-1	terp	1507			**308**	farnesol	terp	2354		
148	vitispirane-2	terp	1510			**312**	2-phenylethyl octanoate	aromatic	2376	*d*	
149	benzaldehyde	aldehyde	1513			**317**	ethyl octadecanoate	ester	2458		
157	propanoic acid	carbox	1527			**318**	ethyl elaidate	ester	2476		
159	ethyl 2-hydroxyhexanoate	ester	1544			**320**	ethyl oleate	ester	2484		
160	linalool	terp	1550			**321**	dodecanoic acid	carbox	2485	*b*	201, 183
163	octanol	alcohol	1559			**322**	ethyl linoleate	ester	2524		
164	ethyl 3-(methylthio)propanoate	sulfur	1562			**323**	ethyl linolenate	ester	2591		
166	3-methylbutyl 2-hydroxypropanoate	ester	1570	*b*	71, 161, 91	**324**	tetradecanoic acid	carbox	>2600	*b*	211, 229
168	2-methylpropanoic acid	carbox	1572			**326**	2-phenylethyl dodecanoate	aromatic	>2600	*d*	

[a] Identification remarks. [b] Identification based on examination of electron impact and chemical ionization mass spectrum. [c] Identification based on retention index and electron impact mass spectrum of authentic pure sample. [d] Identification based on theoretical retention index calculation. [e] Carboxylic acid. [f] Aromatic compound. [g] Terpenic derivative. [h] Sulfur compound. [i] Furan derivative.

compounds in numerous matrices (*21*, *22*) and notably in cider in the early 1980s (*23*). It gives complementary information to spectra obtained from EI-MS as CI mass spectra are actually much simpler with a predominant $[M + 1]^+$ ion (or $[(M + 1) - 18]^+$) for alcohols). This detection mode was, for example, particularly useful for the identification of succinic esters, which present very similar EI mass spectra. The $[M + 1]^+$ peak was always detectable in CI-MS for ethyl propyl succinate (**228**), ethyl 3-methylbutyl succinate (**256**), and two succinic esters (**232** and **245**) having a molecular mass of 202 g·mol^{-1}. As a consequence these four compounds were characterized in Calvados and Cognac.

Moreover, CI spectra of 2- or 3-hydroxy esters exhibit a $[(M + 1) - 18]^+$ peak. In fact, 3-hydroxy esters all present a *m*/*z* base peak of 117 in EI-MS mode, and it is rather difficult to differentiate them. CI spectra of these compounds exhibit two

Table 2. Volatile Compounds Identified in Dichloromethane Extracts of Cognac but Not in Extracts and Preparative Fractions of Calvados

no.	compound	chem class	RI ZB-Wax	ID[a]
13	3-methylbutyl formate	aldehyde	1042	
72	2-pentylfuran	furan[i]	1275	
73	octanal	aldehyde	1282	
83	hex-3-enyl acetate	ester	1314	
165	5-methylfurfural	furan	1566	
173	undecan-2-one	ketone	1593	
184	myrcenol	terp[g]	1618	
186	hex-3-enyl butanoate	ester	1621	
189	β-terpineol	terp	1625	
211	γ-terpineol	terp	1696	
215	1,1,6-trimethyl-1,2-dihydronaphthalene (TDN)	norisoprenoidic derivative	1714	
303	3-methylbutyltetradecanoate	ester	2279	
309	ethyl heptadecanoate	ester	2355	

[a,g,i] Same as in **Table 1**.

Table 3. Volatile Compounds Identified in Dichloromethane Extracts of Calvados but Not in Extracts and Preparative Fractions of Cognac

no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments
31	prop-2-en-1-ol	alcohol	1116		
35	pentan-2-ol	alcohol	1119		
36	ethyl pentanoate	ester	1127		
68	3-hydroxybutan-2-one (acetoin)	ketone	1269		
84	3-methylbut-2-en-1-ol	alcohol	1316		
110	2-butoxyethanol	alcohol	1391		
112	ethyl 2-hydroxybutanoate	ester	1396	*b*	133, 105
143	ethyl 2-hydroxypentanoate	ester	1495		
155	butyl 2-hydroxypropanoate	ester	1520	*b*	147, 91
175	4-terpineol	terp[g]	1595		
180	3,3-diethoxypropanol	alcohol	1611		
203	4-vinylanisole	aromatic[f]	1670		
210	methyl undecanoate	ester	1694		
244	geraniol	terp	1845		
261	4-methylguaiacol	aromatic	1960		
268	methyleugenol	aromatic	2014		
272	4-ethylguaiacol	aromatic	2034		
283	ethyl cinnamate	aromatic	2126		
289	2-phenylethyl hexanoate	aromatic	2164		
290	eugenol	aromatic	2171		
292	4-ethylphenol	aromatic	2190		
293	4-vinylguaiacol	aromatic	2200		

[a,f,g] Same as in **Table 1**.

significant fragments corresponding to the detection of $[M + 1]^+$ and $[(M + 1) - 18]^+$ peaks, which enables the chemical structure to be determined rapidly. As a consequence, numerous 3-hydroxy esters (**154**, **213**, **254**, and **281**) could be identified. 2-Hydroxy esters detected in Calvados and Cognac can be separated in two chemical classes: ethyl esters and various ones deriving from lactic (2-methylpropanoic) acid. In both cases, spectra present a significant $[M + 1]^+$ peak but the $[(M + 1) - 18]^+$ peak cannot be observed. Lactic esters can be differentiated from the others by a specific *m*/*z* peak of 91 in their spectra issued from the protonated lactic acid resulting from a MacLafferty rearrangement of the corresponding basic ion. With the help of CI-MS, various 2-hydroxy esters (**112**, **151**, **155**, and **166**), lactones (**208**, **259**, **270**, **286**, and **310**), furfuryl acetals (**161** and **194**), and carboxylic acids (**279**, **301**, **321**, **324**, and **325**) could also be integrated in the chemical composition of the two investigated spirits.

Aliphatic alcohols submitted to chemical ionization using acetonitrile undergo a rapid decomposition of the $[M + 1]^+$ ion with first a loss of water and then successive losses of ethylene molecules. As a consequence, the information given by CI-MS for this chemical class was not of interest. An alternative way to identify unknown spectra was to calculate theoretical retention indices using linear equations. Thus, retention indices of heavier compounds can be evaluated from retention indices of low-weight ones. Identification of these heavier compounds can be then confirmed by examination of EI spectra, which are usually presenting the same fragmentations

Table 4. Volatile Compounds Identified in Dichloromethane Extracts of Cognac but Detected in Only Preparative Fractions of Calvados

						label of preparative fraction	
no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments	silica gel	GC
92	ethyl hex-2-enoate	ester	1336			5A-6A	
93	rose oxide	terp[g]	1338			5A-6A	
99	3-ethoxypropanol	alcohol	1370	*b*	87, 105		4B
104	nonan-2-one	ketone	1382			5A-6A	5B
108	methyl octanoate	ester	1386			5A-6A	5B-6B
156	nonan-2-ol	alcohol	1521	*d*		8A-9A	5B
171	diethyl propanedioate	ester	1580			7A-8A	5B
185	ethyl 2-furoate	furan[i]	1621				5B
217	propyl decanoate	ester	1720			4A-5A	
218	undecan-2-ol	alcohol	1723	*d*		8A-9A	6B
227	5-methyl-2-thiophenecarboxaldehyde	sulfur[h]	1767				5B
228	ethyl propyl succinate	ester	1767	*b*	101, 129, 189	7A	
230	diethyl pentanedioate	ester	1780			7A	
232	*succinic ester*[j]	ester	1793	*b*	101, 129, 203	6A-7A	7B
235	methyl dodecanoate	ester	1800			5A-6A	
241	dec-4-en-1-ol	alcohol	1816			8A-9A	
267	hexyl decanoate	ester	2011			5A	

[a–d,g–i] Same as in **Table 1**. [j] Compounds only partially identified are given in italic type.

Table 5. Volatile Compounds Identified in Dichloromethane Extracts of Calvados but Detected in Only Preparative Fractions of Cognac

						label of preparative fraction	
no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments	silica gel	GC
10	1,1-diethoxybutane	acetal	1031			4A-6A	
11	ethyl 2-methylbutanoate	ester	1036			5A-6A	3B
17	ethyl 3-methylbutanoate	ester	1053			5A-6A	3B
132	heptanol	alcohol	1454				4B
146	3-ethyl-4-methylpentanol	alcohol	1507			9A	
154	ethyl 3-hydroxybutanoate	ester	1518	*b*	133, 115		4B
158	ethyl nonanoate	ester	1530			5A-6A	7B
191	methyl ethyl succinate	ester	1632				5B-6B
222	α-farnesene	terp[g]	1744			4A-6A	
224	2-methylpropyl decanoate	ester	1751			5A-6A	
258	propyl dodecanoate	ester	1927			4A-5A	
265	dodecanol	alcohol	1970			8A	
266	methyl tetradecanoate	ester	2006			5A-6A	
302	ethyl hexadec-9-enoate	ester	2277			6A-7A	

[a,b,g] Same as in **Table 1**.

Table 6. Volatile Compounds Identified in Only Both Preparative Fractions of Calvados and Cognac

						label of preparative fraction	
no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments	silica gel	GC
34	4-methylpent-3-en-2-one	ketone	1118				2B
38	1,1-diethoxypentane	acetal	1135			5A-6A	5B
45	pentyl acetate	ester	1169			6A	4B
46	heptan-2-one	ketone	1173			5A-7A	3B
48	limonene	terp[g]	1175				4B
49	methyl hexanoate	ester	1176			4A-6A	4B
60	1,1-diethoxyhexane	acetal	1235			5A-6A	4B-5B
65	3-methylbutyl butanoate	ester	1259			5A	
69	ethyl (*E*)-hex-3-enoate	ester	1270			6A-7A	
75	oct-1-en-3-one	ketone	1289				4B-5B
76	ethyl (*Z*)-hex-3-enoate	ester	1291			6A	4B
77	4-methylpentan-2-ol	alcohol	1292				3B-4B
88	ethyl heptanoate	ester	1328			5A-6A	5B
90	1,1-diethoxyheptane	acetal	1332	*d*		5A-6A	
106	4-methylpent-3-en-1-ol	alcohol	1385			9A-10A	3B
114	hex-4-en-1-ol	alcohol	1408			8A-9A	3B
119	4-methyl-2-oxopentanoic acid	carb[e]	1421			8A-10A	4B-5B
133	2-methylpropyl 2-hydroxypropanoate	ester	1455			8A-9A	4B
138	ethyl oct-4-enoate	ester	1470			6A	6B
150	propyl octanoate	ester	1514			4A-5A	7B
151	ethyl 2-hydroxy-4-methylpentanoate	ester	1515	*b*	161	7A-8A	
152	dihydro-2-methyl-3(2*H*)-thiophenone	sulfur[h]	1518			7A-8A	4B-5B
153	5-ethenyl-4-methylthiazole	sulfur	1518			8A	5B
177	β-cyclocitral	terp	1606			7A	5B
188	3-methylthiopropyl acetate	sulfur	1625	*b*	137	8A	5B-6B
190	2-phenylethanal	aldehyde	1631			9A	4B
199	2-hydroxymethylfurane	furan[i]	1662			8A	3B
206	2-thiophenecarboxaldehyde	sulfur	1684			7A-8A	4B-5B
220	1,1-diethoxyundecane	acetal	1726	*d*		5A	
233	nerol	terp	1798			7A-8A	6B
240	butyl decanoate	ester	1812			4A-5A	
260	ethyl tridecanoate	ester	1943			5A	
275	nerolidol	terp	2039			6A-7A	
282	ethyl 2-methyltetradecanoate	ester	2119			5A	
300	2,3-dihydrofarnesol	terp	2262			7A	
315	methyl linoleate	ester	2420			6A	
327	2-phenylethyl tetradecanoate	aromatic[f]	>2600			6A-7A	
328	2-phenylethyl hexadecanoate	aromatic	>2600			7A	

[a–i] Same as in **Table 1**.

Table 7. Volatile Compounds Identified in Only Preparative Fractions of Cognac

						label of preparative fraction	
no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments	silica gel	GC
1	ethyl 2-methylpropanoate	ester	< 1000			5A	
27	2,6,6-trimethyl-2-ethenyltetrahydro-2*H*-pyran	terp[g]	1096			4A	
74	2,2,6-trimethylcyclohexanone	terp	1284			5A-7A	4B
91	hex-2-enyl acetate	ester	1334				4B
96	2-methylpropyl hexanoate	ester	1347			5A-6A	
103	3,5,5-trimethylcyclohex-2-en-1-one (isophorone)	terp	1381			6A-7A	4B
107	nonanal	aldehyde	1385			6A	
118	hex-3-enyl propanoate	ester	1418			6A	
130	2-methylbutyl hexanoate	ester	1451			5A	
162	2-methylpropyl octanoate	ester	1550			5A-6A	
167	terpin-3-en-1-ol	terp	1571				5B
169	methyl furoate	furan[i]	1572			6A-7A	
170	methylthiobenzene	sulfur[h]	1574				3B-4B
187	acetophenone	aromatic[f]	1624			7A-8A	
195	2-methylbutyl octanoate	ester	1657			5A-6A	
201	β-farnesene	terp	1664			5A-6A	
202	2,2,6-trimethylcyclohex-2-en-1,4-dione (4-oxo-isophorone)	terp	1668			7A-8A	6B
236	hexyl octanoate	ester	1804			5A	
259	δ–nonalactone	ketone	1937	*b*	157, 99		7B
284	1,1-diethoxypentadecane	acetal	2132			5A	
288	2-methylpropyl tetradecanoate	ester	2160			4A-5A	
296	heptadecan-2-one	ketone	2220			6A	
305	propyl hexadecanoate	ester	2335			5A	
311	2-methylpropyl hexadecanoate	ester	2367			5A-6A	
314	methyl octadecanoate	ester	2417			6A	
316	benzophenone	aromatic	2427			7A	
319	3-methylbutyl hexadecanoate	ester	2479			6A	
329	ethyl eicosanoate	ester	>2600			6A	
330	3-methylbutyl octadecanoate	ester	>2600			6A	
331	3-methylbutyl linoleate	ester	>2600			6A	

[a–d,f–i] Same as in **Table 1**.

in the series of homologous compounds. This has confirmed the presence of primary alcohols [nonanol (**196**), decanol (**226**), ...] from retention indices of butanol (**41**), pentanol (**63**), and hexanol (**97**). Secondary alcohols [nonan-2-ol (**156**), undecan-

Table 8. Volatile Compounds Identified in Only Preparative Fractions of Calvados

						label of preparative fraction	
no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments	silica gel	GC
2	methyl 2-methylbutanoate	ester	<1000			5A	
4	3,3-diethoxypropene	acetal	<1000			5A	
5	1-(1-ethoxyethoxy)-2-methylpropane	acetal	<1000			4A-5A	
6	toluene	aromatic[f]	1014			5A	
12	4-methyl-1,3-dioxane	acetal	1041				2B
14	2-methyl-1,3-dioxane	acetal	1044			7A	2B
15	1-(1-ethoxyethoxy)butane	acetal	1049			5A-6A	3B
16	dimethyl disulfide	sulfur[h]	1050				2B-3B
19	4-methylpentan-2-one	ketone	1059			7A	
22	2-methylpropyl propanoate	ester	1065				3B
24	pent-2-enal	aldehyde	1073				2B
26	methyl but-2-enoate	ester	1095			6A-7A	
29	pentan-3-ol	alcohol	1111			8A-9A	2B
30	pent-3-en-2-one	ketone	1114			8A	
37	butyl propanoate	ester	1135			5A-6A	3B
39	propyl 2-methylbutanoate	ester	1136				4B
40	heptan-3-one	ketone	1141			6A	
43	pent-1-en-3-ol	alcohol	1157			9A	
44	but-2-enyl propanoate	ester	1158				3B
47	methyl 2-methylbut-2-enoate	ester	1175				3B
50	pent-3-en-2-ol	alcohol	1177			9A	
51	eucalyptol	terp[g]	1179				4B
52	3-methylbutyl propanoate	ester	1183			5A	4B
55	4-methylhept-3-en-2-one	ketone	1210			6A	
56	butyl butanoate	ester	1213			6A	
57	hexan-2-ol	alcohol	1216			8A	
58	ethyl 2-methylbut-2-enoate	ester	1223			6A-7A	4B-5B
61	octan-3-one	ketone	1239			6A	
64	1-(1-ethoxyethoxy)hexane	acetal	1258			4A-5A	5B
67	1,3-diethoxypropan-1-ol	acetal	1268				4B
70	2-methylbutyl 2-methylbutanoate	ester	1274				5B
71	3-methylbutyl 2-methylbutanoate	ester	1274				5B
78	pent-4-en-1-ol	alcohol	1295				3B
80	methyl 2-hydroxypropanoate	ester	1309			9A	3B
82	propyl hexanoate	ester	1312			4A	
87	6-methylhept-5-en-2-one	ketone	1327				4B
89	ethyl 3-ethoxypropanoate	ester	1332			8A	4B-5B
95	diacetone	ketone	1344				3B-4B
100	non-3-en-5-one	ketone	1372			5A	5B
101	ethyl hept-4-enoate	ester	1374				5B
105	butyl 2-methylbutanoate	ester	1384				5B
113	oct-2-enal	aldehyde	1402				4B
115	tetrahydrolinalool	terp	1414			6A	
116	octan-2-ol	alcohol	1416	*d*		8A	
117	2,3-butanediol	alcohol	1417			9A	
121	propyl 2-hydroxypropanoate	ester	1424			8A-9A	4B
121	dimethyl pentanedioate	ester	1699				5B-6B
125	ethyl methylthio acetate	sulfur	1436				4B
126	ethyl 2-(1-ethoxyethoxy)propanoate	ester	1442				5B
127	3-methylthiopropanal (methional)	sulfur	1443				3B
128	1-(ethoxyethoxy)octane	acetal	1449			5A-6A	
139	ethyl 6-oxononanoate	ester	1488			6A	
140	methyl 2-hydroxy-3-methylpentanoate	ester	1489				5B
142	camphor	terp	1491			7A	
145	hept-4-en-1-ol	alcohol	1502			9A	4B
161	furfural ethyl propyl acetal	furan[i]	1550	*b*	97, 125, 189	5A	
174	dimethyl succinate	ester	1595				5B
176	methyl citronellate	terp	1596			4A	
178	ethyl 4-oxopentanoate	ester	1607			8A-9A	
179	butyl octanoate	ester	1610			4A-5A	
181	oct-4-en-1-ol	alcohol	1612			7A-8A	5B
182	methyl benzoate	aromatic	1614			6A	5B
183	oct-5-en-1-ol	alcohol	1616			8A-10A	
200	furfural acetal[e]	furan	1663			5A	
208	γ-hexalactone	ketone	1690	*b*	115, 85	9A-10A	5B-6B
213	butyl 3-hydroxybutanoate	ester	1707	*b*	161, 143	8A-9A	
219	benzyl acetate	aromatic	1726				5B
24	ethyl salicylate	aromatic	1798			6A	6B-7B
237	2,3-dimethoxytoluene	aromatic	1806			7A	
242	dimethyl hexanedioate	ester	1817				7B
245	*succinic ester*[e]	ester	1851	*b*	129, 101, 203	7A-8A	
246	guaiacol	aromatic	1855				5B
250	tridec-2-enal	aldehyde	1868			5A	
251	4-ethyl-2-methoxyanisole	aromatic	1875			6A-7A	
255	diethyl hexanedioate	ester	1897			7A-8A	
262	2-phenylethyl 2-methylpropanoate	aromatic	1963			6A	
264	2-phenylethyl butanoate	aromatic	1968			6A	
269	pentadecan-2-one	ketone	2019			6A	
271	butyl dodecanoate	ester	2024			5A	
273	1,1-diethoxytetradecane	acetal	2035	*d*		4A	
274	isoeugenol	aromatic	2036			7A	
276	3,4-dimethoxystyrene	aromatic	2040				7B
285	propyl tetradecanoate	ester	2134			4A-5A	

Table 8. (Continued)

no.	compound	chem class	RI ZB-Wax	ID[a]	CI major fragments	label of preparative fraction: silica gel	label of preparative fraction: GC
286	γ-decalactone	ketone	2138	*b*	171, 85	9A	
294	hexyl salicylate	aromatic	2203			6A	
297	1,1-diethoxyhexadecane	acetal	2231	*d*		6A	
298	methyl hexadec-9-enoate	ester	2238			8A	
304	ethyl 3-hydroxydodecanoate	ester	2306	*d*		9A	
306	chavicol	aromatic	2339			7A	
307	1,1-diethoxyheptadecane	acetal	2347	*d*		6A	
310	γ-dodecalactone	ketone	2367	*b*	199, 85	9A	
313	hexadecanol	alcohol	2382			8A-9A	

[a–i] Same as in **Table 1**. [j] Compounds only partially identified are given in italic type.

2-ol (**218**), ...] were also identified from retention indices of butan-2-ol (**7**) and heptan-2-ol (**85**). The presence of heavy diethyl acetals (**220**, **273**, **297**, and **307**) was also verified using theoretical retention indices. At this point, it is important to note that calculation of theoretical retention indices was also widely used to confirm the presence of compounds already identified by direct comparison of EI spectra.

Injection of authentic pure compounds was used to verify the presence of 3-methyl- (**86**, RI = 1323) and 4-methylpentanol (**81**, RI = 1312) in both extracts of Calvados and Cognac. Three acetals [1,1-diethoxy-2-methylbutane (**23**), 1,1-diethoxy-3-methylbutane (**20**), and 1,1-diethoxypentane (**38**)] were not present in our laboratory as authentic pure compounds. They were injected in their synthesized form in an ethanolic medium. The two methyl-branched acetals with RI = 1062 and 1067 were identified in the extracts, but the presence of 1,1-diethoxypentane (RI = 1135) was determined in only preparative fractions.

Comparison of Volatile Compounds Present in Extracts of Calvados and Cognac. One hundred and sixty-nine compounds listed in **Tables 1**−**5** were identified in dichloromethane extracts of Calvados or Cognac. They are reported according to their chemical classes and can be considered as the most concentrated volatile compounds present in both spirits. This includes 65 esters, 34 alcohols, 9 acetals, 12 carboxylic acids, 7 aldehydes, 4 ketones or lactones, 3 sulfur compounds, 17 terpenoic or norisoprenoidic derivatives, and finally 18 aromatic compounds or phenolic derivatives. In these extracts 103 compounds (listed in **Table 1**) are common to both spirits, whereas 13 compounds (listed in **Table 2**) are specific to Cognac and 22 compounds (listed in **Table 3**) are specific to Calvados. Compounds reported in **Tables 2** and **3** were thus identified in only dichloromethane extracts of either Cognac or Calvados, but they were not further detected in preparative fractions of the other spirit. Seventeen major compounds of Cognac are also reported in **Table 4**, but they were also detected as minor ones in preparative fractions of Calvados. On the contrary, **Table 5** shows 14 major compounds of Calvados that were also identified as minor in preparative fractions of Cognac. These compounds listed in **Tables 4** and **5** can be considered as less specific, but they are undoubtedly more concentrated in one of the two spirits. At that point the most important differences in terms of volatile composition will be discussed. They concern mainly three chemical classes: aromatic compounds, furan derivatives, and terpenic or norisoprenoidic derivatives.

Aromatic Compounds and Phenolic Derivatives. Major differences between Calvados and Cognac are recorded for this chemical class. Nine aromatic compounds or phenolic derivatives were identified in Cognac extracts. They are all common to both spirits, but Calvados extracts contain eight more aromatic compounds (see **Table 3**), which seem to be specific of that distillate. 4-Ethylphenol (**292**) and 4-ethylguaiacol (**272**), which have relatively high concentrations in Calvados, are missing in Cognac extracts and were even not identified in preparative fractions. They are known to give heavy or undesirable odors at high levels (*24*) in red wine. As a consequence, these compounds traditionally described as defects in Cognac possibly do not affect the quality of Calvados. 4-Vinylguaiacol (**293**) was also identified in only Calvados extracts. In these phenolic derivatives, highly odorous compounds such as eugenol (**290**), methyleugenol (**268**), or 4-vinylanisole (**203**) already found as key odorants of Calvados (*4*) were not detected in Cognac.

Furan Derivatives. Furan derivatives seem to be more specific to Cognac. For instance, the peak area of furfural (**135**) in Cognac extracts is really important (see **Figure 1**), whereas only small peaks were recorded in the two Calvados extracts. As a consequence, derivatives such as ethyl 2-furoate (**185**) were detected as major compounds in Cognac samples. 5-Methylfurfural (**165**), which results like furfural from dehydration of rhamnose (*25*), was already identified in Cognac samples in 1970 (*6*) but was not present in Calvados. 2-Pentylfuran (**72**) can also be considered as specific to Cognac.

Terpenic and Norisoprenoidic Derivatives. β-Damascenone (**239**) identified in various types of wines (*26*−*28*) can also be detected in Cognac samples. Distillation enables concentrates this compound, and that is why it generally belongs to the aromatic map of Calvados (*4*) and probably to that of Cognac. α-Terpineol (**209**), linalool (**160**), and its oxidation derivatives (**122** and **136**) are commonly identified in distilled spirits, but the presence of β-citronellol (**229**) and farnesol (**309**) is more marginal. It is interesting to note that terpenic derivatives found in Cognac are generally different from that detected in Calvados. Thus, geraniol (**244**) and 4-terpineol (**175**) were present in Calvados extracts, whereas rose oxide (**93**), myrcenol (**184**), β-terpineol (**189**), and γ-terpineol (**211**) were specific to Cognac. Mateo et al. (*29*) showed that vitispiranes (**147** and **148**) and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) (**215**) were produced from the chemical hydrolysis of glycosides. The first ones were detected in both products, but TDN, totally missing in Calvados, was detected as an important peak in the Cognac extracts chromatograms (see **Figure 1**).

Miscellaneous. Differences in terms of volatile composition that are obvious between Calvados and Cognac for the three chemical classes mentioned above are less important for other ones, notably for alcohols and esters. Nevertheless, some particular compounds seem to be specific. Allylic alcohol (**31**), detected in only Calvados, is generally considered as an acrolein marker produced by reduction. As a consequence, the level of acrolein, which cannot be evaluated in our conditions because it is coeluted with the solvent (dichloromethane), could be higher in Calvados samples than in Cognac ones. 3-Methylbut-2-en-1-ol (**84**), which was found at high concentration as an important "herbaceous" defect in Calvados (*6*), seems to be specific to

that product as it could not be detected in Cognac extracts. A good relationship appears between the presence of alcohols and their corresponding ketones. For example, nonan-2-one (**104**) and undecan-2-one (**173**) are highly concentrated in Cognac extracts as well as nonan-2-ol (**156**) and undecan-2-ol (**218**). The presence of 5-methylthiophenecarboxaldehyde (**227**) in Cognac is surprising because it was never identified in wine to our knowledge. It is also present in Calvados in a less important amount.

Trace Compounds. Numerous compounds were identified in only preparative fractions of Calvados and Cognac. They could not be detected in dichloromethane extracts of Cognac and Calvados and can be considered as trace compounds due to their extremely low concentration. In this study, a total of 331 compounds was identified including 162 trace compounds. Thirty-nine trace compounds listed in **Table 6** are common to Calvados and Cognac, whereas 30 listed in **Table 7** are specific to Cognac and 93 listed in **Table 8** are specific to Calvados.

Esters. Ethyl and 3-methylbutyl esters are generally highly concentrated because of the presence of corresponding alcohols and acids. On the contrary, methyl, propyl, butyl, 2-methylpropyl, or 2-methylbutyl esters are generally found as trace levels because of the small amount of corresponding alcohols in samples compared to that of ethanol and 3-methylbutanol. Only a few of them can be considered as specific of one or the other spirit. Tiglic (2-methylbut-2-enoic) esters such as methyl tiglate (**47**) and ethyl tiglate (**58**) were identified in only Calvados fractions. On the contrary, hexen-3-yl derivatives such as hex-3-enyl acetate (**83**), hex-3-enyl propanoate (**118**), and hex-3-enyl butanoate (**186**) seem to be specific to Cognac.

Alcohols. Low concentrated alcohols identified in Calvados or Cognac are quite similar. Only low-weight secondary alcohols such as pentan-3-ol (**29**), hexan-2-ol (**57**), and octan-2-ol (**116**) seems to be specific to Calvados. Very small peaks of unsaturated alcohols such as pent-4-en-1-ol (**78**), hept-4-en-1-ol (**145**), oct-4-en-1-ol (**181**), pent-1-en-3-ol (**43**), pent-3-en-2-ol (**50**), and oct-5-en-1-ol (**183**) were recorded in preparative fractions of one of the two samples of Calvados.

Acetals, Hemiacetals, and Ethers. Both trace and highly concentrated acetals present in freshly distilled beverages are usually formed by the reaction of "common" aldehydes with ethanol. It is rather complicated to discriminate the two products by observing their composition in acetals because, depending on the shift of equilibrium, several parameters such as medium acidity or ethanol content are involved. Note that 4-methyl-1,3-dioxane (**12**) and 2-methyl-1,3-dioxane (**14**) were identified in only preparative fractions of Calvados. The first one could be formed by reaction between formaldehyde and butane-1,3-diol, whereas 2-methyl-1,3-dioxane was probably produced from acetaldehyde and propane-1,3-diol.

Carboxylic Acids. Except for 4-methyl-2-oxopentanoic and hexadecanoic acids, all carboxylic acids were identified in dichloromethane extracts. Calvados and Cognac are very poor in these compounds, which can be due to the shift esterification−hydrolysis equilibrium during fermentation and/or distillation.

Aldehydes. Study of the preparative fractions confirms the presence in a high concentration of furfuryl derivatives in that chemical class. 5-Methylfurfural (**165**) was notably found in several fractions of Cognac in preparative GC as well as on silica gel. Other aldehydes were also detected in fractions. Nonanal (**107**), already found in a first study in the aromatic map of Calvados, was detected in only one fraction of Cognac. Due to its very low detection threshold, it could have a real olfactive impact in that sample. Unsaturated aldehydes such as pent-2-enal (**24**), oct-2-enal (**113**), and tridec-2-enal (**250**) can also be cited as trace compounds. They were identified only in Calvados fractions. As a consequence, they can be regarded as specific of that spirit.

Ketones and Lactones. Ketones and lactones are generally present in weak concentrations in freshly distilled spirit, but this does not mean that they have no aromatic impact. Oct-1-en-3-one (**75**) is a trace compound identified in both spirits. Usually found as an important olfactive marker in numerous beverages, its presence is generally determined by comparison of retention indices. Preparative separations allow a peak corresponding to this compound to be recorded. Except for some methyl ketones such as nonan-2-one (**104**) or heptan-2-one (**46**), ketones and lactones are detected as very small peaks in fraction chromatograms, but it can be noted that numerous unsaturated ketones were identified as ultratrace compounds, especially in Calvados.

Sulfur Compounds. In the sulfur compounds group, methional (**127**) and 3-(methylthio)propyl acetate (**188**) seem to follow the same process of formation as methionol (**216**), which was already present in dichloromethane extracts. Methional is known to have a very low detection threshold and was already identified as a key odorant of Calvados (*6*). 3-(Methylthio)propyl acetate identified with the help of CI-MS already plays a significant role in the "grilled" aroma of wines (*30*). 2-Thiophenecarboxaldehyde (**206**), which was also identified in the past (*6*), was not detected in dichloromethane extracts. This compound, present in several preparative fractions of Calvados and Cognac, was coeluted with the highly concentrated diethyl succinate (**205**) in dichloromethane extracts.

Terpenic and Norisoprenoidic Derivatives. Eighteen terpenic or norisoprenoidic derivatives were identified as trace compounds in both spirits. They are highly functionalized, and many of them were characterized in either Calvados or Cognac fractions. Thus, compounds such as eucalyptol (**51**) or camphor (**142**) seem to be specific to Calvados, whereas 2,6,6-trimethyl-2-ethenyltetrahydro-2*H*-pyran (**27**) and β-farnesene (**201**) are probably more specific to Cognac. 2,2,6-Trimethylcyclohex-2-ene-1,4-dione (**202**, RI = 1668) was identified only in preparative fractions of Cognac. This compound develops according to Rogerson et al. (*16*) a "sweet honey" aroma and was already identified in preparative GC fractions of Portuguese wines with a very closed retention index (RI = 1676). Its sensory threshold limit of 25 $\mu g \cdot L^{-1}$ calculated in model port wine solutions shows that this compound is likely to be a contributor to the overall aroma of freshly distilled Cognac. Among this class of compounds, 2,2,6-trimethylcyclohexanone (**74**) and isophorone (**103**), also identified in fractions of Portuguese wine (*31*), were found in only Cognac, which can be explained by the fact that these norisoprenoid compounds are already included at low concentrations in grapes.

Aromatic Compounds and Phenolic Derivatives. Study of the preparative fractions confirmed the fact that aromatic or phenolic compounds seem to be more specific to Calvados despite only a few of them being detected in Cognac. The chemical composition of Calvados includes notably salicylic esters (**234** and **294**), guaiacol (**246**), and isoeugenol (**274**), whereas some phenylethyl esters were identified in both spirits.

Conclusion. Three hundred and thirty-one compounds were identified in freshly distilled Calvados and Cognac. This represents a significant base of retention indices and mass spectra, which can be devoted to the development of the knowledge of the volatile composition of freshly distilled spirits.

With a large majority of esters and alcohols, >100 volatile compounds are common to freshly distilled Calvados and Cognac. Besides, numerous aromatic compounds such as guaiacols or phenolic derivatives were detected in only Calvados extracts. The presence of that type of compound seems not to depreciate the overall aroma of Calvados because all samples were chosen for their "good quality". On the contrary, lots of terpenic derivatives are specific to Cognac samples. This study showed that separations according to polarity and volatility can be complementary. This resulted in the identification of trace compounds such as oct-1-en-3-one, methional, or 4-oxoisophorone, which are usually difficult to characterize in beverages. This type of compound can be of great interest because many of them present very low detection thresholds. Systematic detection in EI- and CI-MS modes enables many unidentified compounds to be characterized. The volatile composition of Calvados was previously characterized by liquid−liquid extraction using pentane. This paper shows that information recovered using dichloromethane extracts is complementary. Dichloromethane can easily extract highly polar compounds, whereas pentane is more adequate for recovering apolar compounds. Preparative separations investigated are very selective, and 162 trace compounds were identified in both spirits. Some of these compounds are likely to have an organoleptic impact, and this will be soon completed by olfactometric analysis to determine aromatic markers of "good quality" of both freshly distilled Cognac and Calvados.

ABBREVIATIONS USED

GC, gas chromatography; EI, electron impact; CI, chemical ionization; HPLC, high-performance liquid chromatography; MS, mass spectrometry; MW, molecular weight; RI, retention index; SPME, solid-phase microextraction.

LITERATURE CITED

(1) Deschamps, S. Informations Techniques sur la Composition Chimique des Calvados. In *La Bonne Chauffe*; Lebrun, R., Ed.; Bulletin No. 13, Caen, 1970; pp 26−34.

(2) Schreier, P.; Drawert, F.; Schmid, M. Changes in the Composition of Neutral Volatile Components During the Production of Apple Brandy. *J. Sci. Food Agric.* **1978**, *29*, 728−736.

(3) 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.

(4) Ledauphin, J.; Guichard, H.; Saint-Clair, J.-F.; Picoche, B.; Barillier, D. Chemical and Sensorial Aroma Characterization of Freshly Distilled Calvados. 2. Identification of Volatile Compounds and Key Odorants. *J. Agri. Food Chem.* **2003**, *51*, 433−442.

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

(6) Schreier, P.; Drawert, F.; Winkler, F. Composition of Neutral Volatile Constituents in Grape Brandies. *J. Agric. Food Chem.* **1979**, *27*, 365−372.

(7) Villallon Mir, M.; Lopez Garcia de la Serrana, H.; Lopez Martinez, M. C. Etude des Constituants des Rhums par Chromatographie en Phase Gazeuse: Contrôle de Qualité. *Analusis* **1988**, *16*, 341−345.

(8) Tourlière, S. Commentaires sur la Présence d'un Certain Nombre de Composés Accompagnant l'Alcool dans les Distillats Spiritueux Rectifiés et Eaux-de-Vie. *Ind. Aliment. Agric.* **1977**, 565−574.

(9) Cantagrel, R.; Vidal, J. P.; Mazerolles, G. Comparaison de Méthodes de Dosage de Quelques Eléments du Non Alcool dans les Spiritueux: Aldéhydes, Esters et Furfural. *Bull. O. I. V.* **1990**, *869*, 1−12.

(10) Lablanquié, O.; Snakkers, G.; Cantagrel, R.; Ferrari, G. Characterisation of Young Cognac Spirit Aromatic Quality. *Anal. Chim. Acta* **2002**, *458*, 191−196.

(11) Fitzgerald, G.; James, K.; MacNamara, K.; Stack, M. Characterisation of whiskeys using solid-phase microextraction with gas chromatography−mass spectrometry. *J. Chromatogr. A* **2000**, *896*, 351−359.

(12) Ebeler, S.; Terrien, M.; Butzke, C. Analysis of Brandy Aroma by Solid-Phase Microextraction and Liquid−Liquid Extraction. *J. Sci. Food Agric.* **2000**, *80*, 625−630.

(13) Wanikawa, A.; Hosoi, K.; Kato, T.; Nakagawa, K.-I. Identification of Green Note Compounds in Malt Whisky using Multidimensional Gas Chromatography. *Flavour Fragrance J.* **2002**, *17*, 207−211.

(14) Benn, S.; Peppard, T. Characterisation of Tequila Flavor by Instrumental and Sensory Analysis. *J. Agric. Food Chem.* **1996**, *44*, 557−566.

(15) Piggott, J. R.; Clyne, J.; Paterson, A.; Conner, J. M. Preparative HPLC as a tool for concentrating flavour compounds from distilled beverages. In *Elaboration et Connaissance des Spiritueux*; BNIC, Ed.; Lavoisier-Tech and Doc: Cognac, France, 1992; pp 464−467.

(16) Rogerson, F.; Castro, H.; Fortunato, N.; Azevedo, Z.; Macedo, A.; De Freitas, V. Chemicals with Sweet Aroma Descriptors Found in Portuguese Wines from the Douro Region: 2,6,6-Trimethylcyclohex-2-ene-1,4-dione and Diacetyl. *J. Agric. Food Chem.* **2001**, *49*, 263−269.

(17) Shimoda, M.; Yoshimura, Y.; Yoshimura, T.; Noda, K.; Osajima, Y. Volatile flavor compounds of sweetened condensed milk. *J. Food Sci.* **2001**, *66*, 804−807.

(18) Choi, H.; Sawamura, M.; Kondo, Y. Characterisation of the Key Aroma Compounds of *Citrus flaviculpus* Hort. ex Tanaka by Aroma Extract Dilution Analysis. *J. Food Sci.* **2002**, *67*, 1713−1718.

(19) 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.

(20) Vollhardt, K. Chapter Aldehydes and ketones. In *Organic Chemistry*, 2nd ed.; Vollhardt, K., Schore, N., Eds.; Freeman: New York, 1994; pp 645−647.

(21) Fortes, I.; Baugh, P. Study of Analytical On-line Pyrolysis of Oils from Macauba Fruit. *J. Braz. Chem. Soc.* **1999**, *10*, 469−477.

(22) Abalos, M.; Bayona, J. Application of Gas Chromatography coupled to Chemical Ionisation Mass Spectrometry Following Headspace Solid-Phase Microextraction for the Determination of Free Volatile Fatty Acids in Aqueous Samples. *J. Chromatogr. A* **2000**, *891*, 287−294.

(23) Williams, A.; May, H. Examination of an Extract of Cider Volatiles Using Both Electron Impact and Chemical Ionization Gas Chromatography−Mass Spectrometry. *J. Inst. Brew.* **1981**, *87*, 372−375.

(24) Monje, M. C.; Privat, C.; Gactine, V.; Nepveu, F. Determination of Ethylphenol Compounds in Wine by Headspace Solid-Phase Microextraction in Conjunction with Gas Chromatography and Flame Ionization Detection. *Anal. Chim. Acta* **2002**, *458*, 111−117.

(25) Mangas, J.; Rodriguez, R.; Moreno, J.; Suarez, B.; Blanco, D. Furanic and Phenolic Composition of Cider Brandy. A Chemometric Study. *J. Agric. Food Chem.* **1997**, *45*, 4076−4079.

(26) Kotseridis, Y.; Baumes, R. Identification of impact odorants in Bordeaux red grape juice, in the commercial yeast used for its fermentation, and in the produced wine. *J. Agric. Food Chem.* **2000**, *48*, 400−406.

(27) Acree, T.; Braell, P.; Butts, R. The Presence of Damascenone in Cultivars of *Vitis vinifera* (Linneaus), *rotundifolia* (Michaux), and *labruscana* (Baily). *J. Agric. Food Chem.* **1981**, *29*, 688−690.

(28) Lopez, R.; Ortin, N.; Perez-Trujillo, J.; Cacho, J.; Ferreira, V. Impact Odorants of Different Young White Wines from the Canary Islands. *J. Agric. Food Chem.* **2003**, *51*, 3419−3425.

(29) Mateo, J.; Gentilini, N.; Huerta, T.; Jimenez, M.; Di Stefano, R. Fractionation of Glycoside Precursors of Aroma in Grapes and Wine. *J. Chromatogr. A* **1997**, *778*, 219−224.

(30) Lavigne, V.; Henry, R.; Dubourdieu, D. Identification et Dosage de Composés Soufrés Intervenant dans l'Arôme "Grillé" des Vins. *Sci. Aliments* **1998**, *18*, 175−191.

(31) De Freitas, V.; Ramalho, P.; Azevedo, Z.; Macedo, A. Identification of some volatile descriptors of the rock-rose- like aroma of fortified red wines from Douro demarcated region. *J. Agric. Food Chem.* **1999**, *47*, 4327−4331.

Received for review February 4, 2004. Revised manuscript received May 5, 2004. Accepted May 8, 2004. This study was a part of J.L.'s Ph.D. work and was carried out within the framework of the Association de Coordination Technique pour l'Industrie Agro-alimentaire (ACTIA).

JF040052Y