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JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Chemical and Sensorial Aroma Characterization of Freshly Distilled Calvados. 2. Identification of Volatile Compounds and Key Odorants

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Eight samples of freshly distilled Calvados were extracted using pentane. Gas chromatography with either a mass spectrometer or flame ionization detector was used to determine the volatile compounds composition of the extracts. More than 120 molecules were identified in Calvados and then correlated with results obtained by olfactometric analysis in our earlier work [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.* **2002**, *50*, 424−432 (preceding paper in this issue)]. Of these, 16 of the 19 molecules that constitute the "aroma skeleton" were identified, including 5 esters, 2 ketones, 5 phenolic derivatives, 2 alcohols, and 2 carboxylic acids. Numerous compounds were also associated with odors found in part 1. These molecules can be considered as being responsible for the good quality of Calvados or, in contrast, for defects. Relative levels of some major olfactive compounds were also estimated and tentatively compared with olfactometric indices found in part 1. A good correlation was found in many cases. Two important markers of defects in Calvados were also identified. 3-Methylbut-2-en-1-ol leads to an "herbaceous" defect, and 1,1,3-triethoxypropane seems to give an "acrolein" defect in the product. "Floral" notes of the aroma of freshly distilled Calvados seem to be due to the presence of phenolic derivatives such as 2-phenylethanol and 2-phenylethyl acetate. Low-molecular-weight esters such as ethyl 2-methylpropanoate, ethyl 2-methylbutanoate, and 3-methylbutyl acetate give, in general, the "fruity" notes. However, the overall aroma of Calvados seems likely to be a subtle balance of various functionalized compounds.

KEYWORDS: Calvados aroma; gas chromatography/mass spectrometry; key odorants

INTRODUCTION

In our previous paper (*1*), we reported the characterization of freshly distilled Calvados by sensorial and olfactometric investigations. The aim of the present work was to advance our knowledge of the chemical composition of Calvados as well as to relate the identified molecules to sensory characteristics of the product.

Calvados is an alcoholic "labeled" beverage made from cider by processes that date back more than five centuries. A number of studies have been carried out to determine the volatile compounds composition of aged spirits, but characterization of freshly distilled spirits is still marginal. The composition of unaged distillates depends on the nature of the raw material or the distillation technology employed, or both.

Moreover, investigations on the chemical composition of Calvados are not well developed in the literature, and only one report can be cited (*2*). The majority of these papers deal with methods that measure compounds that can lower the quality of the product. Thus, these works were essentially aimed at evaluating low-molecular-weight ethyl esters, methanol, furfural, acrolein, higher alcohols, and also acidic volatility (*3*, *4*).

Different works on the basic source from which Calvados is derived, apples, reveal the predominance, in their aroma, of methyl-branched flavor compounds, especially 2-methylbutanoic acid and the corresponding esters and alcohols (*5*). 3-Methyl-branched derivatives were also cited in the literature as apple constituents (*6*). However, they were generally found to be produced during fermentation.

In the production of Calvados, first, apples are mashed and then stored in oak barrels. During the first step of this process,

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the amount of acetates decreases due to the presence of a carboxylesterase (*7*). There is also production of C6-aldehydes and derivatives (*8*), which possess a characteristic green-grass-like odor. During the second step, apple juice is transformed into cider by fermentation. The decrease of sugar results in production of high-molecular-weight esters. Fermentation also causes numerous aroma components to appear, formed as byproducts of the metabolism of amino acids and fatty acids by yeasts (*9*). 2-Phenylethanol becomes one of the major compounds (*10*), and hexanol is formed by reduction of hexanal and (*E*)-hex-2-en-1-al (*8*).

Distillation of cider leads to production of unaged Calvados. At this point in the process, the amount of esters increases due to reactions between acids and alcohols or aromatic compounds. As a consequence, 2-phenylethanol derivatives are generated. Apple brandy contains β-damascenone (rose-like odor), methyl heptanones, and β-cyclocitral (minty), products of thermal degradation of carotenoids (*8, 11*).

The composition of aged spirits is quite different than that of freshly distilled ones. One of the major changes that occurs during aging is the formation of acetals by combination of alcohols with aldehydes under acidic conditions. Numerous compounds are formed during maturation in casks, due to extraction of wood tannins, chemical reactions such as oxidation and hydrolysis, and evaporation of small molecules (*12*). The aromas of most alcoholic beverages consist of more than 100 chemical compounds. A total of 175 constituents were identified in tequila (*13*). Spirits such as rum (*14*) and whiskey (*15*) contain as major compounds aliphatic esters, alcohols, aldehydes, and acids. Cider brandies (*16*) contain also an important amount of furanic and phenolic derivates. Changes occur during the maturation step, but the composition of aged spirits is directly dependent on the quality of the distillates.

In the first part of this study (*1*), the aroma of freshly distilled Calvados was characterized by sensory analysis and olfactometry. Seventy-one odors were detected in eight different samples. This revealed 19 odors that are common to all Calvados, constituting the skeleton of the aroma. Twenty-eight odors were specific to a quality class (good, neutral, or defect). Thus, results obtained by olfactometry, giving a retention index for each odor, can be related to compounds identified by gas chromatography/mass spectrometry (GC/MS) to determine the key odorants of Calvados.

In this paper, we present the chemical composition of freshly distilled Calvados, as well as the identification of the odor-active compounds in that spirit. Injections of samples on GC/MS enable separation and identification of compounds. Levels found in GC/FID of some olfactive markers were also compared to olfactometric indices determined previously (*1*).

MATERIALS AND METHODS

Extraction and Concentration of Volatile Constituents of Calvados. For physicochemical analysis, the same eight samples used in part 1 (*1*) were used: two "good-quality" freshly distilled Calvados (samples 1 and 2), two "neutral" Calvados (samples 3 and 4), and four others with "defects" (samples 5−8).

Extraction and concentration of volatile compounds from Calvados were carried out by liquid−liquid extraction according to the procedure previously described (*1*).

Gas Chromatography/Mass Spectrometry. GC/MS analyses were carried out on a Varian 3800 gas chromatograph interfaced with a Varian Saturn 2000 mass spectrometer. Separations were performed using either a 30-m × 0.32-mm-i.d. capillary column, coated with a 0.25-μm film of SPB-5 stationary phase [(5% diphenyl/95% dimethyl)-polysiloxane from Supelco, Bellefonte, PA], or a 25-m × 0.22-mm-i.d. capillary column, coated with a 0.25-μm film of BP-10 stationary phase [14% cyanopropylphenyl/86% dimethylpolysiloxane from SGE, Milton Keynes, UK]. Helium was used as the carrier gas at 1 mL/min flow. For analysis of the extracts on either a nonpolar stationary phase (SPB-5) or a medium-polarity stationary phase (BP-10), the oven temperature program used was 40−220 °C at a rate of 5 °C/min, with an initial temperature hold for 1 min and a final temperature hold for 20 min, resulting in a total run time of 57 min. Injections were made in split mode with a split ratio of 1:100. Injection volumes ranged from 1.0 to 2.0 μL. The injection port temperature was 250 °C. The mass spectrometer, equipped with an ion trap, was operated with an ionization voltage of 70 eV, ion source temperature of 150 °C, and electron multiplier voltage of 1350 V. Scanning was performed from *m*/*z* 35 to 400 at 1 scan/s.

Analyses were performed using the software Saturn WS version 5.3. The mass spectra obtained were compared using the NIST 98 MS Library Database or a database created by making injections of pure authentic compounds.

Linear retention indices were calculated for each peak, using as internal reference a series of hydrocarbons, C7−C31, according to the method of Van den Dool and Kratz (*17*). Identification was performed using either linear retention indices found in the literature on SPB-5 or comparison with pure authentic substances analyzed on the same stationary phase under the same conditions. As little information was available about linear retention indices relative to BP-10 (or analogous data), comparison with linear retention indices was not pursued on this stationary phase.

At this point, it is important to note that a medium-polarity stationary phase (such as BP-10) exhibits a good selectivity for separation of medium-polarity compounds in gas−liquid partition chromatography. It can separate either nonpolar or polar compounds. Its selectivity for separation is poorer for more polar compounds such as alcohols and carboxylic acids. As a consequence, some compounds may coelute. Moreover, there is a lack of literature references for retention indices on this stationary phase, because in past work, three or four "popular" phases were used exclusively (Carbowax 20M, FFAP, DB-5, etc.). Our study offers a new compilation of data on BP-10 which can be a good basis for the determination of key odorants in other foods or alcoholic beverages. We then had to carry out a cross analysis with a more commonly used stationary phase (analogous to SPB-5 and DB-5). Its characteristics are not too different from those of the initial BP-10 phase, and its use enabled us to find numerous retention indices in the literature.

For further identification of more polar compounds, it would be reasonable to carry out a study using a more polar stationary phase such as Carbowax 20M, which is commonly used in analysis of brandies. This kind of stationary phase was not used in the present work because BP-10 stationary phase presents a good compromise in terms of selectivity versus run time for the olfactometric study. According to that, the longer the run time, the more extensive will be the olfactometric procedure.

Gas Chromatography/FID. Some investigations, allowing the determination of the relative level of some compounds in Calvados, were carried out using GC with flame ionization detection on a Varian 3400 gas chromatograph. Separations were performed using the same capillary column (SPB-5 and BP-10), and the same temperature program. The flow rate of the carrier gas (nitrogen) was adjusted to 1 mL/min. Split-mode injections were made with a split ratio of 1:100. The injection volume ranged from 0.5 to 1.0 μL, depending on the sample. The injection port temperature was 230 °C, and the detector temperature was 230 °C.

Liquid−liquid extraction was carried out on 50-mL Calvados samples, as described in part 1 (*1*). Ethyl undecanoate (200 ppm) was added as an internal standard to control extraction at the beginning of the procedure. Ethyl oleate (130 ppm) was added to the 1-mL extract to control injection at the end of the procedure. A semiquantitative evaluation of the level of some olfactive markers was made according to the following calculation, based on area data recorded by FID detection: (area of compound to evaluate/area of ethyl undecanoate) × 1000 (in order to obtain readable values). Levels calculated in this manner are given in **Table 2**.

Table 1. Results of GC/MS Analysis of Calvados Samples

peak no.	compound	odor descriptor[a]	n[b]	retention indices: SPB-5 ref[c,d]	SPB-5 top[e]	BP-10 beginning[f]	BP-10 top[g]	BP-10 end[h]	ID type[i]
		Esters							
1	ethyl acetate		8			700	704	708	EI
5	ethyl propanoate		8		712	774	774	775	EI
7	propyl acetate		8			783	784	785	EI
8	methyl butanoate		2	720[d]	722	786	786	786	EI
13	**ethyl 2-methylpropanoate**[j]	fruity (3)	8			811	812	815	EI
14	methyl 2-methylbutanoate		4			830	830	830	EI
18	ethyl butanoate[k]	fruity, alcohol (7)	8	804[c]	804	855	857	860	EI
20	butyl acetate		8			874	875	881	EI
24	**ethyl 2-methylbutanoate**	fermented apple (12)	8	849[c]	850	903	904	908	EI
26	ethyl 3-methylbutanoate		6		904	909	910	910	EI
27	ethyl lactate		8			915	916	923	EI
28	**3-methylbutyl acetate**	banana (17)	8	880[c]	878	936	937	944	EI
29	2-methylbutyl acetate		7			939	940	943	EI
	methyl hexanoate		6	942[d]	927				EI
43	3-methylbutyl propanoate		8		972	1028	1028	1030	EI
46	ethyl hexanoate		4	1000[c]	1001	1056	1058	1061	EI
47	ethyl 2-hydroxy-3-methylbutanoate		8		968	1060	1062	1063	EI
49	hexyl acetate	sweat, floral (31)	7		1015	1075	1077	1080	EI
56	3-methylbutyl butanoate		8	1061[d]	1062	1114	1114	1114	EI
57	ethyl hex-2-enoate		1			1118	1118	1118	EI
	methyl octanoate		6	1138[d]	1127				EI
63	ethyl 2-hydroxyhexanoate	floor cloth, animal, vegetal (38)	8			1154	1155	1161	EI
78	ethyl octanoate		8	1200[c]	1199	1254	1258	1261	EI
87	diethyl succinate		3		1182	1295	1296	1299	EI
89	3-methylbutyl 3-methylbutanoate		5		1252	1309	1309	1310	EI
	methyl decanoate		6		1327				EI
104	butyl hexanoate		2			1450	1450	1450	EI
106	**ethyl decanoate**	cinnamon, woody (68)	8	1397[d]	1397	1457	1459	1462	EI
109	decyl acetate		1			1478	1478	1478	EI
	methyl undecanoate		1		1427	1490	1490	1490	EI
114	3-methylbutyl octanoate		8		1449	1506	1508	1511	EI
120	*ethyl undecanoate (internal standard)*					*1553*	*1555*	*1557*	*EI*
123	butyl octanoate		2			1647	1648	1649	RI, EI
124	ethyl dodecanoate		8	1591[d]	1596	1658	1660	1662	RI, EI
126	3-methylbutyl decanoate		8		1647	1708	1709	1710	RI, EI
129	butyl decanoate		4		1548	1848	1848	1848	RI, EI
130	ethyl tetradecanoate		8	1790[d]	1796	1859	1861	1863	EI
131	3-methylbutyl dodecanoate		8		1847	1909	1910	1911	EI
132	methyl hexadecanoate		3		1928	1997	1997	1997	EI
133	ethyl hexadec-9-enoate		8			2051	2053	2054	EI
134	ethyl hexadecanoate		8			2061	2063	2065	EI
136	3-methylbutyl tetradecanoate		3			2112	2112	2112	EI
138	*ethyl oleate (internal standard)*					*2243*	*2245*	*2247*	*EI*
139	ethyl linoleate		6			2249	2250	2251	EI
140	ethyl octadecanoate		4			2261	2262	2264	EI
141	3-methylbutyl hexadecanoate		4			2313	2313	2313	EI
		Acetals							
4	**1,1-diethoxyethane**	fruity (2)	8	730[c]	726	771	773	774	EI
	1,1-diethoxypropane		8		813				EI
22	1,1-diethoxybutane	fruity (11)	8			889	891	894	EI
40	1,1-diethoxy-3-methylbutane	fruity (19)	2		952	986	986	987	EI
42	1-(1-ethoxyethoxy)pentane		4			1007	1007	1007	EI
58	1,1,3-triethoxypropane	floral, vegetal (36)	8		1075	1129	1130	1132	EI
		Alcohols							
2	butan-2-ol		8			715	721	725	EI
6	butanol		8			780	782	784	DI
16	**3-methylbutanol**	plastic (5)	8		773	837	844	896	EI
17	2-methylbutanol		8			848	848	848	EI
21	3-methylbut-2-en-1-ol	herbaceous (9)	8			875	876	876	EI
32	(*E*)-hex-3-en-1-ol		8			958	958	958	EI
34	(*Z*)-hex-3-en-1-ol		8		858	967	968	969	EI
37	**hexanol**	green grass (20)	8	870[c]	873	973	979	999	DI, EI
39	hex-5-en-1-ol		1			981	981	981	EI
41	heptan-2-ol		1	901[d]	906	997	997	997	EI
52	octan-3-ol		2			1086	1086	1086	EI
	heptanol		2		973				EI
	oct-1-en-3-ol		1	982[d]	982				EI
53	**6-methylhept-5-en-2-ol**	sweat, sponge (33)	7		997	1092	1093	1094	EI
59	3-ethyl-5-methylpentanol		3		1025	1134	1135	1137	EI
67	octanol		8		1077	1175	1178	1180	RI, EI
82	nonanol		1			1277	1277	1277	RI, EI

Table 1 (Continued)

peak no.	compound	odor descriptor[a]	n^b	retention indices SPB-5 ref[c,d]	SPB-5 top[e]	BP-10 beginning[f]	BP-10 top[g]	BP-10 end[h]	ID type[i]
98	decanol	bind cider, floral (62)	6			1375	1376	1377	RI, EI
	dodecanol		6		1479				RI, EI
	tetradecanol		6		1682				RI, EI
	hexadecanol		6		1886				RI, EI
		Terpenes and Derivates							
62	(*E*)-linalool oxide		8		1091	1151	1152	1154	EI
65	(*Z*)-linalool oxide		8			1170	1171	1172	EI
71	linalool	fruity, spicy (42)	8	1103[c]	1103	1190	1191	1191	EI
79	4-terpineol	floral (jasmine) (52)	8		1188	1263	1264	1265	EI
95	verbenone		2			1364	1364	1364	EI
113	eugenol	clove, medicinal, phenolic (71)	8	1355[c]	1359	1500	1502	1506	EI
115	methyl eugenol		4		1405	1527	1527	1527	EI
	farnesol		7		1725				EI
		Aldehydes							
3	3-methylbutanal		2			738	738	738	EI
33	furfural		5		837	965	965	965	EI
38	heptanal		2			979	979	979	EI
48	benzaldehyde		8		968	1076	1076	1076	EI
51	octanal		1			1083	1083	1083	EI
64	salicylaldehyde		1			1161	1161	1161	EI
70	nonanal		3			1184	1184	1184	EI
86	decanal		1			1285	1285	1285	EI
		Acids							
44	3-methylbutanoic acid		8			1056	1057	1057	EI
45	**2-methylbutanoic acid**	sweat, yeast (30)	8			1059	1060	1074	EI
68	**hexanoic acid**	yeast-like, cider, mushroom (43)	8		980	1180	1182	1195	EI
96	octanoic acid		8		1199	1363	1365	1367	EI
119	decanoic acid		8		1379	1553	1554	1555	EI
128	dodecanoic acid		2		1565	1746	1747	1748	EI
		Ketones							
35	heptan-3-one		2			969	969	969	EI
36	heptan-2-one		2	891[d]	891	977	977	977	EI
47	**oct-1-en-3-one**	mushroom (28)	1			1059	1059	1059	DI, EI
50	6-methylhept-5-en-2-one		2			1081	1081	1081	EI
69	nonan-2-one		2	1093[d]	1093	1182	1182	1182	EI
84	decan-2-one		2			1283	1283	1283	RI, EI
99	undecan-2-one		2	1295[d]	1293	1387	1387	1387	EI
111	***β*-damascenone**	fruity, floral (70)	8	1395[c]	1386	1496	1497	1499	EI
116	2-acetylcyclopentanone		1			1530	1530	1530	EI
		Sulfur Compounds							
11	dimethyl disulfide		8			805	805	807	EI
	3-methylthiopropanal	potato (25)					1031		DI
55	dihydro-2-methyl-3(2*H*)-thiophenone	sweat, earthy, animal (34)	3			1106	1106	1108	EI
61	2-thiophenecarboxaldehyde	vinous, mushroom (37)	1			1144	1145	1145	EI
73	ethyl 3-methylthiopropanoate	meaty, vinous, acid (45)	7		1105	1204	1204	1204	EI
		Aromatic Compounds and Phenolic Derivatives							
12	toluene		3			809	810	811	EI
25	ethyl benzene		6			908	908	908	EI
30	styrene		8	893[d]	895	951	952	952	EI
72	benzyl alcohol	old sponge, mold (44)	1		1040	1202	1202	1202	EI
77	**4-vinylanisole**	perspiration, delicatessen (49)	8		1159	1248	1249	1252	EI
80	ethyl benzoate		8		1176	1269	1270	1272	EI
81	**2-phenylethanol**	rose, mushroom (51)	8	1116[c]	1119	1270	1270	1306	EI
88	methyl salicylate		3			1299	1300	1300	EI
94	ethyl phenylacetate		8		1248	1357	1358	1359	EI
97	**2-phenylethyl acetate**	floral, underwood (61)	8	1260[c]	1260	1370	1371	1375	EI
100	**4-ethylphenol**	animal (64)	8		1169	1389	1390	1396	EI
102	**4-ethylguaiacol**	floral (hyacinth) (65)	7		1194	1417	1418	1419	EI
103	butyl benzoate		2			1432	1432	1432	EI
107	ethyl 3-phenylpropanoate		4		1354	1461	1461	1461	EI
108	2-phenylethyl propanaote		5		1356	1464	1464	1464	EI
	ethyl anisate		1		1457				EI
121	ethyl cinnamate		6	1460[c]	1475	1597	1598	1599	EI

[a] The odor number from ref *1* is given in parentheses. Odors 1, 4, 6, 10, 21, 27, 29, 35, 39, 46, 50, 53, 55, 57, 58, 59, 60, 66, 67, and 69 could not be identified. [b] Occurrence of identification in the eight samples in GC/MS chromatograms on BP-10. [c,d] Retention indices on SPB-5 according to (*c*) Guth (*23*) and (*d*) Moio et al. (*32*). [e] Retention indices on SPB-5 corresponding to top of peaks in GC/MS. [f] Retention indices on BP-10 corresponding to beginning of peaks in GC/MS. [g] Retention indices on BP-10 corresponding to top of peaks in GC/MS. [h] Retention indices on BP-10 corresponding to end of peaks in GC/MS. [i] Type of identification (EI, electronic impact; RI, retention indices; DI, direct injection). [j] Boldface and underlined: compound belonging to the "aroma skeleton" of Calvados. [k] Underlined: compound detected by olfactometry specific to some of the eight Calvados samples studied.

Table 2. Levels of Aroma-Active Compounds in Calvados Samples Detected by GC/FID[a]

compound	BP10[b]	odor descriptor[c]	levels[d] (bold) and olfactometric indices[e] (italic) in Calvados samples							
			1	2	3	4	5	6	7	8
1,1-diethoxyethane	773	fruity (4)	**586**	**2532**	**661**	**1530**	**907**	**3699**	**3143**	**1080**
			203	*243*	*243*	*95*	*203*	*243*	*189*	*203*
isopentanols	844	plastic (5)	**148457**	**385911**	**142772**	**96232**	**273580**	**286247**	**225169**	**41104**
			5	*9*	*34*	*126*	*7*	*82*	*29*	*102*
ethyl butanoate	857	fruity, alcohol (7)	**234**	**82**	**116**	**216**	**164**	**132**	**302**	**250**
			10	*28*		*3*		*16*		
1,1-diethoxybutane	891	fruity (11)	**276**	**100**	**80**	**76**	**41**	**31**	**78**	**48**
			142	*20*	*29*	*14*				
ethyl 2-methyl butanoate	904	fermented apple (12)	**76**	**100**	**111**	**90**	**109**	**131**	**78**	**128**
			125	*144*	*183*	*135*	*203*	*243*	*189*	*203*
3-methylbutyl acetate	937	banana (17)	**2038**	**502**	**608**	**517**	**2031**	**893**	**471**	**886**
			89	*29*	*44*	*41*	*90*	*54*	*21*	*54*
hexanol	979	green grass (20)	**4828**	**8351**	**4852**	**2336**	**4560**	**4719**	**2056**	**5968**
			24	*26*	*5*	*14*	*9*	*11*	*9*	*18*
1,1-diethoxy-3-methylbutane	986	fruity (19)	nd[f]	nd	nd	nd	nd	nd	**22**	**122**
										29
2-methylbutanoic acid	1060	sweat, yeast (30)	**155**	**183**	**319**	**53**	**255**	**354**	**134**	**216**
			11	*45*	*149*	*5*	*95*	*162*	*8*	*89*
hexyl acetate	1077	sweat, floral (31)	nd	**36**	**34**	**59**	**48**	**52**	**68**	**110**
						8			*41*	*62*
6-methylhept-5-en-2-ol	1093	sweat, sponge (33)	nd	**24**	**30**	**40**	**26**	**33**	**45**	**34**
				2		*17*	*2*		*21*	*2*
1,1,3-triethoxypropane	1130	floral, vegetal (36)	**101**	**203**	**434**	**108**	**64**	**3757**	**6446**	**174**
								28	*90*	
ethyl 2-hydroxyhexanoate	1155	floor cloth, animal, vegetal (38)	**264**	**298**	**314**	**62**	**69**	**321**	**216**	**224**
			3	*24*	*30*			*28*	*22*	*2*
hexanoic acid	1182	yeast-like, cider, mushroom (43)	**1174**	**622**	**700**	**425**	**830**	**8710**	**495**	**508**
			125	*69*	*75*	*5*	*89*	*84*	*32*	*36*
4-vinylanisole	1249	perspiration, delicatessen (49)	**122**	**83**	**30**	**100**	**32**	**97**	**34**	**114**
			162	*71*	*14*	*90*	*18*	*95*	*50*	*162*
2-phenylethanol	1270	rose, mushroom (51)	**924**	**1236**	**1777**	**719**	**3665**	**4492**	**666**	**740**
			124	*35*	*70*	*26*	*109*	*14*	*101*	*71*
2-phenylethyl acetate	1371	floral, underwood (61)	**164**	**120**	**154**	**340**	**140**	**96**	**101**	**292**
			27	*11*	*28*	*77*	*10*	*7*	*17*	*108*
decanol	1376	bind cider, floral (62)	**223**	nd	**51**	**128**	nd	**176**	**107**	**22**
			30							*3*
4-ethylphenol	1390	animal (64)	**243**	**1018**	**478**	**434**	**265**	**552**	**916**	**1380**
			32	*203*	*162*	*30*	*108*	*189*	*89*	*203*
4-ethylguaiacol	1418	floral (hyacinth) (65)	nd	**72**	**342**	nd	**50**	**232**	**185**	**80**
			11	*74*	*182*	*10*	*27*	*108*	*95*	*83*
ethyl decanoate	1459	cinnamon, woody (68)	**1437**	**1565**	**1195**	**782**	**1401**	**983**	**1666**	**1408**
			128	*149*	*88*	*71*	*129*	*86*	*124*	*102*
β-damascenone	1497	fruity, floral (70)	**201**	**121**	**342**	**124**	**50**	**140**	**105**	**160**
			185	*88*	*243*	*101*	*6*	*122*	*68*	*142*
eugenol	1502	clove, medicinal, phenolic (71)	**158**	**68**	**20**	**88**	**47**	**34**	**29**	**92**
			104	*8*		*70*	*3*			*83*

[a] Ethyl 2-methylpropanoate, 3-methylbut-2-en-1-ol, linalool, 4-terpineol, oct-1-en-3-one, 3-methylthiopropanal, dihydro-2-methyl-3(2*H*)-thiophenone, 2-thiophenecarboxaldehyde, ethyl 3-methylthiopropanoate, and benzyl alcohol could not be detected by GC/FID. [b] Retention indices on BP10 stationary phase. [c] The odor number from ref *1* is given in parentheses. [d] Level = (peak area of compound/peak area of ethyl undecanoate) × 1000. [e] Olfactometric indices reported in ref *1*. [f] Weak peak areas do not allow level determination.

RESULTS AND DISCUSSION

This analysis of eight Calvados extracts led to the identification of 120 compounds. Identification was made by examination of mass spectra and (i) comparison with the NIST databank; (ii) comparison of experimental GC retention indices on SPB-5 stationary phase and those reported in the literature; or (iii) examination of both mass spectra and retention indices from direct injection of authentic samples if necessary.

The compounds identified are listed in **Table 1**, including peak numbers corresponding to **Figure 1**, which represents a typical chromatogram of Calvados sample 8. In **Table 2** are given levels of compounds detected as olfactive markers in Calvados (*1*). Exact concentrations of each aroma-active compound were not given, since a complete quantitative analysis of about 30 sophisticated compounds would be rather extensive, expensive, and time-consuming. It should be based on calibration with standards of each pure compound. Data are expressed as relative FID area of the compound versus the surface of an internal standard (ethyl undecanoate) added to the pure sample prior to extraction. The resulting semiquantitative data (see **Table 2**) represent not the concentration of the product but an estimated level which is, in our opinion, sufficient to be related to the measured olfactive impact of the product.

Identification by Compound Class. Among the volatile compounds identified are present chemical functionalities usually cited in alcoholic beverages: alcohols, acids, esters, acetals, carbonyl compounds, sulfur compounds, and aromatic hydrocarbons.

Esters. The ester functionality represents the larger group, with more than 50 compounds identified in the extracts. In this group, ethyl esters are numerously and quantitatively preponderant. These ethyl esters could be produced during distillation by esterification of fatty acids with a large excess of ethanol. However, a lot of methyl, butyl, 3-methylbutyl (isoamyl), and

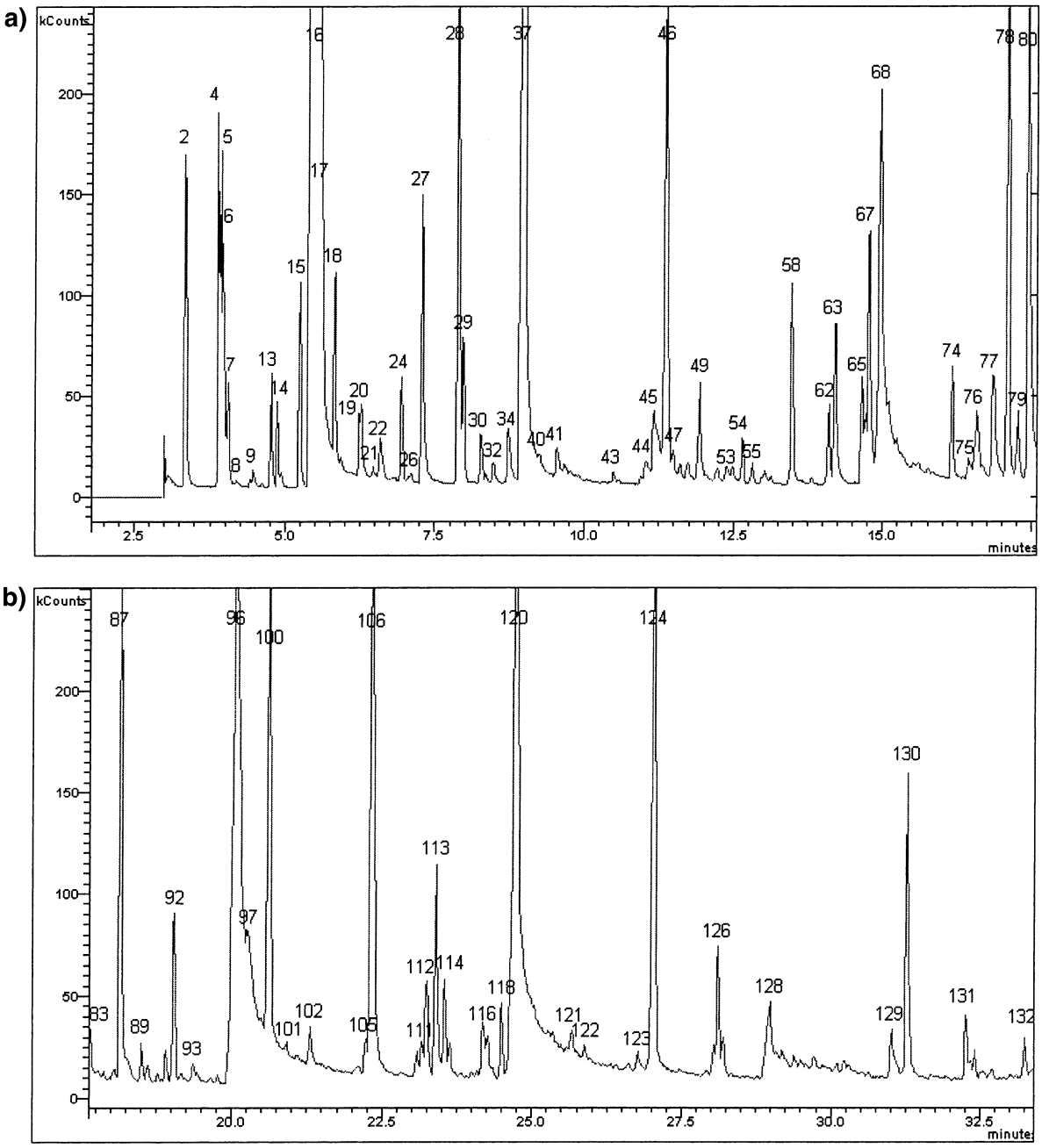

Figure 1. Chromatogram of Calvados sample 8 on BP-10 stationary phase with compounds labeled (see **Table 1**). (a) Retention times from 2.5 to 17.5 min. (b) Retention times from 17.5 to 33 min.

phenylethyl esters were also detected. Some hydroxy and unsaturated esters could be noted along with aromatic ones. Evidently, most of the esters were produced either from the apples themselves or from the fermentation process by yeast, particularly *Saccharomyces cerevisiae* (*18*).

Alcohols and Acids. The alcohol group is quantitatively the second main group, with some 30 compounds detected. Aliphatic primary alcohols are present in large amounts, especially low-molecular-weight alcohols. For instance, isopentanols were found to be the major components in our products, as previously noted for cognac spirits (*19*, *20*) and brandies (*8*). It should be noted that 2-methylbutanol and 3-methylbutanol coelute under our experimental conditions. These low-molecular-weight alcohols are generally produced during glucose fermentation in the presence of asparagic, glutaric, and malic acids (*21*). In addition to high-molecular-weight aliphatic alcohols, unsaturated ones such as 3-methylbut-2-en-1-ol and 6-methylhept-5-en-2-ol were detected as minor products in GC/MS but have a high olfactive impact. Six short fatty acids were also identified in Calvados. They were undoubtedly formed during the fermentation process.

Acetals. Although eight aldehydes have been identified, the lack of corresponding acetals which could result from combination with corresponding alcohols, of which a lot were present in large amounts, was noteworthy. It seems likely that these acetals, being predominantly formed during aging, are present at too low a level to be detected in freshly distilled Calvados, except the ones deriving from the major aldehydes and/or alcohol moieties.

Carbonyl Compounds. Along with the eight ketones that could be detected, some aldehydes, including furan (furfural) and thiophene (2-thiophenecarboxaldehyde) derivatives, could be

formed during thermal and distillation processes, mostly via Maillard reactions between saccharides and peptides containing lysine or other amino residues.

Miscellaneous. Included among the various chemical functionalities detected were also some terpenoids and a lot of phenolic and aromatic acid derivatives, which presumably came from the apple fruit. Phenolic residues, for example, result from hydrolysis and/or biodegradation of polyphenolic compounds contained in fruit fibers. Noteworthy also is the lack of detectable levels in derivatives of vanillic and syringic acids, which are well known as markers of wood chemistry and aging processes (*22*).

Identification of Olfactive Markers. Of the 58 odors, 33 could be correlated with compounds identified in the eight Calvados extracts. Correlations were carried out in three different ways. The first involved comparison of the retention indices found by olfactometry and by GC/MS on the BP-10 phase. The second involved examination of notes given in olfactometry, which enabled us to propose a hypothesis for the identification of some compounds; either they were well known or they were largely investigated in the literature. Finally, in some cases, odors were also correlated with compounds by checking, when the chemical identity was obvious, a possible shift of the retention indices resulting from GC/olfactometry. Indeed, the recorded retention times could differ slightly between a GC/MS and an olfactometric run. In the first case, indices correspond to the top of the chromatographic peak, while in olfactometry they were calculated at the beginning of the odor perceived by the judges. To minimize this problem, retention indices were also calculated at the beginning and end of each peak identified in GC/MS, as noted in **Table 1**.

A lot of odors could not be related to a specific chemical compound. This is mainly due to mixed contributions of compounds which coeluted under our experimental conditions. Odor 53, with a "spicy, mushroom" descriptor, could not be identified because of its coelution with the peak for odor 81, corresponding to 2-phenylethanol (rose-like odor), which is one of he major aromatic compounds found in Calvados. In other cases, some odorant compounds could not be identified because either no response or too low a signal was recorded at that retention index. This corresponds to compounds having low detection thresholds by nose and high detection thresholds in chromatography. For example, odor 46 could not be identified because no response was recorded on the GC/MS chromatograms.

Olfactometric analysis in part 1 (*1*) revealed that 19 odors are common to the eight Calvados samples studied. These odors form the "aroma skeleton" of Calvados. Unfortunately, three of them could not be identified (odors 4, 46, and 53). Identification of the 16 others will be discussed in detail below.

Acetals. 1,1-Diethoxyethane (odor 2, "fruity") is the only acetal present in the aroma skeleton of Calvados. It is well known that this acetal is formed by association of ethanal with ethanol under acidic conditions. 1,1,3-Triethoxypropane (odor 36, "floral, vegetal") was detected only in Calvados samples with defects. Very high levels of this compound (about 10-fold more, see **Table 2**) were detected in Calvados samples 6 and 7. Undoubtedly, it could result from acetalization and Michael-type addition of acrolein in the presence of an excess of ethanol. This acetal is formed only when acrolein has a high concentration in Calvados, but a high level of acrolein does not lead necessarily to formation of 1,1,3-triethoxypropane. In fact, the presence of acrolein in Calvados can lead to formation of either allylic alcohol by reduction or 1,1,3-triethoxypropane by acetalization.

Esters. Four esters are identified as key odorants in the aroma skeleton. They have a real positive impact on the quality of Calvados, giving in general the fruity note of the aroma. These compounds are mostly low-molecular-weight esters identified in numerous food products and alcoholic beverages. Ethyl 2-methylpropanoate (odor 3, "fruity") has been identified on an analogous stationary phase (OV-1701) in white wines (*23*) and is one of the most potant odorants in Rambutan fruit (*24*). Odor 12 has been identified as ethyl 2-methylbutanoate. This compound typically comes from apples (*5*) and is supposed to be their key odorant. It is not surprising that this molecule is associated with the descriptor "fermented apple". The next ester found in the skeleton, 3-methylbutyl acetate (odor 17, "banana") is a typical key odorant of distillated beverages. It is formed during fermentation (*4*) and is part of the aromatic map of cognac (*19*) and whiskey (*25*). This compound is rather important in Calvados because of its low detection threshold [30 mg/L in water/ethanol (90/10, w/w)] (*26*). In contrast to the fruity note recorded to the previous esters, ethyl decanoate (odor 68) has a "cinnamon, woody" note, which can be explained by its heavier chemical structure. It can be formed during distillation by association between decanoic acid and ethanol.

Phenolic Derivatives. The aroma of Calvados is generally described as fruity and floral. The floral note in the "body" is given by different aromatic compounds. 2-Phenylethanol (odor 51, "rose, mushroom") and its acetate derivative 2-phenylethyl acetate (odor 61, "floral, underwood") are usually described in the literature as rosy. 2-Phenylethanol is produced by *S. cerevisiae*, which is found to be the most dominant species during fermentation (*27*). Its association with acetic acid during distillation leads to the production of 2-phenylethyl acetate.

4-Vinylanisole (odor 49, "sweat, delicatessen") seems to be a characteristic compound of Calvados. The highest levels of this molecule were found in Calvados samples 1, 4, and 8 (see **Table 2**). As a consequence, we conclude that the concentration of 4-vinylanisole does not influence the quality of Calvados.

4-Ethylphenol (odor 64, "animal") and 4-ethylguaiacol (odor 65, "floral (hyacinth)") were also detected in the aromatic skeleton of Calvados. These compounds were previously identified in red wines and in spirits such as Armagnac (*28*) and were found to be responsible for organoleptic defects. In Armagnac, they were described as "horse sweat", and their presence was attributed to *Brettanomyces* yeasts. Apparently, no such defect is present in our samples, as no "horse sweat" note was found by the judges in sensory evaluation (*1*). In some Armagnac, the ratio of 4-ethylphenol to 4-ethylguaiacol was found to be constant and equal to 0.8. In our case, no clear correlation can be found between the levels of these two compounds.

Alcohols. Alcohols are present in large amounts in Calvados. These compounds generally have very high detection thresholds, but their high concentration in Calvados give them a real olfactive impact. Isopentanols coelute under our experimental conditions. They develop a rather negative descriptor (odor 5, "plastic"), even though they contribute to the overall aroma of Calvados. They are really characteristic of beverages due to their formation during fermentation (*5*). A large amount of isopentanols is usually present in brandies (*10*), as is also confirmed by routine analysis (*1*). Hexanol (odor 20), a product of linoleic acid transformation during enzymatic oxidation (*29*), has a high concentration (from 4.53 to 22.89 g/hl of pure alcohol; see part

1) and gives a green-grass-like odor. However, this compound, present in every Calvados sample studied, is not responsible for the "herbaceous" defect in Calvados sample 7.

The presence of two alkenols seems to reflect a poorer quality of Calvados. 6-Methylhept-5-en-2-ol (odor 33, "sweat, sponge") and 3-methylbut-2-en-1-ol (odor 9, "herbaceous") are mainly present in Calvados sample 7. The concentrations of hexanol and (*Z*)-hex-3-en-1-ol are not high enough in that Calvados to cause the herbaceous defect. Therefore, 3-methylbut-2-en-1-ol is undoubtedly responsible for this herbaceous defect. Because it coeluted with butyl acetate, this compound could not be quantified. A retention index of 876 (see **Table 1**) was calculated for this compound on the BP-10 stationary phase. This value was compared to the retention index on OV-17 (870) estimated by Acree and Arn (*30*), who associated the same descriptor, "herbaceous", with this molecule.

Ketones. The presence of odor 28, corresponding to oct-1-en-3-one, in Calvados is not surprising. This key odorant of mushrooms was previously found in numerous beverages, but its extremely low detection threshold often prevents its identification by GC/MS in complex mixtures. We succeeded in identifying it in one Calvados (sample 8), but it is evidently present in all of them. Along with oct-1-en-3-one, β-damascenone (odor 70), smelling "fruity, floral", is the second ketone present among the 19 common odors common to all Calvados samples studied. It was commonly identified in distillated beverages and was also found in red wines (*31*).

Acids. 2-Methylbutanoic acid (odor 30, "sweat, yeast") has previously been identified in food products, but except in cheeses (*32*), it is not generally considered as a key odorant. In fact, this compound, like its derivative, ethyl 2-methylbutanoate, comes from the apples themselves (*5*). The concentration of this acid seems to influence the quality of Calvados, because products of good quality have rather low concentrations of 2-methylbutanoic acid (see **Table 2**). Hexanoic acid (odor 43, "yeast-like, cider, mushroom") is also important in the aroma composition of Calvados. Like numerous acids, it was forming during fermentation of apples or came directly from the fruit (*33*). Acids usually give rather negative descriptors, and the judges, in part 1 (*1*), qualified them as "yeast-like". They are still present in Calvados, even though distillation of cider facilitates transformation of acids into ethyl esters.

Sulfur Compounds. Sulfur compounds often possess a very low detection threshold, and it is usually difficult to identify them. Five of them were identified in Calvados, and except for dimethyl disulfide, they were all detected in at least three of the Calvados samples studied. 2-Thiophenecarboxaldehyde (odor 37, "vinous, mushroom") was detected only in Calvados of good quality. This compound could not be quantified due to its apparently too low concentration in the different Calvados. It was only detected by GC/MS in Calvados sample 2. A characteristic potato-like odor was detected only in Calvados with defects. In numerous studies, methional (3-methylthiopropanal) could not be detected, because of its extremely low detection threshold. This sulfur compound has a potato-like odor. Thus, an authentic sample was directly injected in GC/MS to compare its retention index with that of odor 25 ("potato"). The same retention index was found, and after injection in GC/O, the same descriptor was also recorded, confirming our hypothesis.

Terpenoids. Odors present mainly in Calvados of good quality are in general fruity or floral. Linalool (odor 42, "fruity, spicy"), a key component of numerous essential oils, was also detected in our samples. It actually gives a floral note, but under our experimental conditions it coeluted with hexanoic acid. This coelution can slightly transform the perception of this terpene derivative in olfactometry. Two other terpenoids have an important olfactive impact: 4-terpineol (odor 52, "floral (jasmine)") and eugenol (odor 71, "clove, medicinal, phenolic"). As the olfactometric index of 4-terpineol seems abnormally high in Calvados sample 5 [126, see **Table 3** of part 1 (*1*)], we think that a high concentration of the coeluted 2-phenylethanol (7.82 g/hl of PA) could enhance the odor of this compound. Eugenol has no evident specificity; it was detected in good-quality, neutral, and defective Calvados. It is found in numerous spicy products.

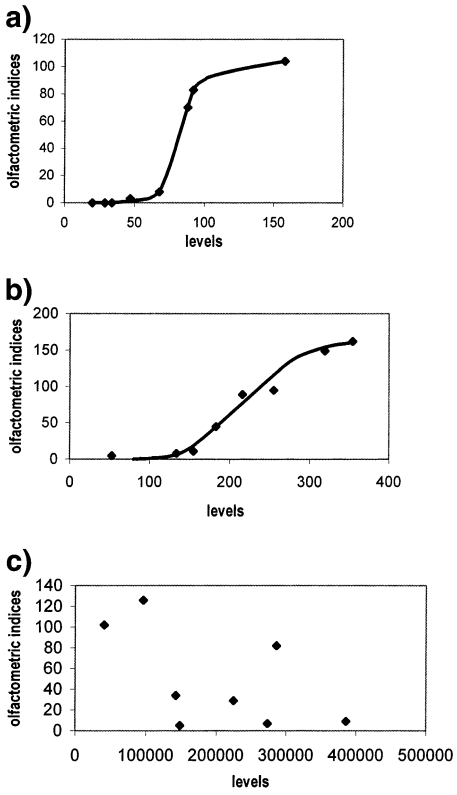

Figure 2. Correlation between olfactometric indices and levels obtained in **Table 2**. (a) Eugenol; (b) 2-methylbutananoic acid; (c) isopentanols.

Some odors are not present in all brandies. They can be present mainly either in good-quality brandies, in neutral brandies, or in brandies with defects. Not all odors have been identified, but this study gives a good representation of molecules responsible for quality or defects in Calvados.

Levels of Olfactometric Markers. The relative levels of some olfactometric markers are recorded in **Table 2**. They are not all given in this table, because they could not always be detected by GC/FID. The first interest of this semiquantification, then, is to determine the lowest detection thresholds of the compounds identified in this study. For example, the relative level of 3-methylbut-2-en-1-ol could not be given and the peak areas of 6-methylhept-5-en-2-ol (from 0 to 45 level units) were just over the detection limit, but these alkenols have a significant olfactive impact. In the same way, the levels of oct-1-en-3-one, sulfur compounds, and terpenoids (like linalool and 4-terpineol) could not be evaluated. In contrast, esters and some other alcohols identified as aroma-active compounds with high concentrations in Calvados do not have important olfactometric indices (the level of 3-methylbutanol is more than 50 000 units and the level of hexanol is more than 2000 units in all samples).

Olfactometric indices are also reported in **Table 2**. A direct correlation was investigated by plotting quantified levels versus olfactometric indices for each compound (**Figure 2**). This correlation was not appropriate for four compounds in two particular situations. In the first one [isopentanols (**Figure 2c**) and hexanol], too high concentration prevented a good semiquantification due to saturation. In the second situation, ethyl butanoate and 2-phenylethanol respectively coeluted with isopentanols and ethyl benzoate, preventing accurate semiquantification. The correlation works rather well in all other cases. Eugenol (presented in **Figure 2a**) is a good example of the observed model: it cannot be detected by olfactometry if its level is less than a threshold value (50 units). Above this value, the olfactometric index increases rapidly and quite linearly with eugenol concentration until it reaches a plateau (about 100 units). The odor intensity then increases slowly due to saturation of perception. As shown in **Figure 2b**, the detection threshold of 2-methylbutanoic acid seems to be greater than that of eugenol. The model is suitable for other compounds, even if some aberrant points are recorded. In the past, such correlation was usually studied on odorant compounds taken alone. Our experiments show that the model could also be applied to olfactive markers in a complex flavored matrix.

Conclusion. Over 120 compounds were characterized in freshly distilled Calvados. These results, compared with those obtained by olfactometry, advance our knowledge of the aromatic composition of Calvados. Numerous potent odorants responsible for the overall flavor of this spirit were found, allowing identification of the chemical composition of the "aroma skeleton". Other molecules identified were found to reflect the organoleptic quality of the samples.

It seems that the aroma of Calvados depends on a subtle balance of various functionalized compounds. Low-molecular-weight esters (with high concentrations in Calvados) and low-molecular-weight acetals actually give the fruity aroma of the product. Numerous phenolic derivatives were detected by olfactometry and were supposed to be responsible of the floral flavor. Although the aroma is described as fruity and floral, some compounds, such as alcohols and acids, give rather negative descriptors. Nevertheless, they are presumed to be important for the overall aroma. The presence of some compounds makes it possible to discriminate different Calvados and classify them according to their quality. A high amount of 3-methylbut-2-en-1-ol leads to an "herbaceous" defect, and a high concentration of 1,1,3-triethoxypropane gives Calvados an "acrolein" defect.

The correlation between relative levels and olfactometric indices makes it possible to determine detection thresholds, expressed as internal standard concentration equivalents. This could be convenient in the further study of Calvados samples without using the olfactometric method.

More efforts will be aimed at the characterization of unidentified compounds by using a more polar stationary phase (like Carbowax20M) and preparative separations to improve their ability to be detected by GC/MS. This could lead to identification of compounds with extremely low detection thresholds that could not be detected in this study.

ABBREVIATIONS USED

GC, gas chromatography; GC/MS, gas chromatography/mass spectrometry; FID, flame ionization detector; PA, pure alcohol; GC/O, gas chromatography/olfactometry.

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