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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

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Eight freshly distilled samples of Calvados, a fermented and distilled apple juice, were analyzed by sensory evaluation and direct injection GC to determine the composition of higher alcohols, esters, and aldehydes. The composition determined by direct injection was tentatively related to sensory descriptors. Esters have a probable maximum level around 500 g/hl of pure alcohol (PA). This level also corresponds to the threshold of the main ester constituent, ethyl acetate. A high ratio of esters to ethyl acetate seems to be of prime importance for good quality. Total aldehydes, with a maximum level between 8 and 11 g/hl of PA and mainly comprising acetal (maximum between 5 and 9 g/hl of PA), were related to a "green" descriptor. Higher alcohols do not have a direct impact on quality, but other volatile compounds with a positive impact on flavor should probably be present at a high level. As overall quality was not well related to sensory quality, it was necessary to perform more a precise analysis to determine the key odorants. The Calvados samples were thus extracted using pentane. Gas chromatography, employing both a flame ionization detector and an olfactometry port, was used to analyze the obtained extracts. Seventy-one odors were detected and distributed according to Calvados quality determined by sensory evaluation. Nineteen odors common to all Calvados samples constituted the "skeleton" of the aroma. Twenty-eight odors were specific to a quality class: 6 for good quality, 4 for neutral, and 18 for defective. Twenty-four other odors had either too low an odor impact or no evident specificity.

KEYWORDS: Calvados aroma; olfactometry; key odorants; sensory analysis; higher alcohols; esters; aldehyde

INTRODUCTION

Calvados is an apple brandy from a particular limited region in Normandy (France). This alcoholic beverage, with a label of controlled origin (AOC, appelation d'origine contrôlée), is made from fermented apple juice in which pear could be partially incorporated (*1*). Fruits of good sanitary quality are crushed or grated. The obtained pulp is then pressed and undergoes a slow fermentation without heating for a minimum period of 1 month. The cider can then be distilled twice or continuously in a copper still. To obtain the label of controlled origin, Calvados must then undergo a minimum of 2 years of aging in an oak barrel.

Unlike other brandies, Calvados is not well known, speaking in terms of composition and relationship with organoleptic quality. Major defects have been described, but the relationship with molecular occurrence is not yet established with certitude. On the other hand, there is no precise information, to our knowledge, on quality-related criteria. This in-depth knowledge of Calvados is necessary in order to follow factors affecting product quality.

In studies carried out in 1990−1992 (*2*, *3*), techniques of microdistillation and analyses by gas chromatography (GC) were developed in our laboratory. These techniques made it possible to study the consequences of technological tests on the physicochemical composition of brandies. This study was innovative due to its approach connecting the taste of Calvados samples with their physicochemical compositions. However, in the past few years, new techniques have been developed, allowing us to determine more precisely the composition of the volatile fraction.

For example, solid-phase microextraction (SPME) was used to determine the volatile compounds in various brandies (*4*−*7*). However, liquid−liquid extraction is the most commonly used method for flavor analysis of distilled alcoholic beverages. This method is easy to carry out and can reveal the presence of

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several hundred volatile compounds in such products. Knowledge of their identity is necessary. It appears, from examation of various studies carried out on distilled alcoholic beverages (whiskey, cognac, rum, apple brandies), that these products, by their nature, have a common aromatic base essentially composed of higher alcohols (alcohols of fusel oil), acids, and esters (*8*). The typicity of each of these drinks would be due either to the presence of compounds in small quantity, not easily detectable by conventional techniques, but having very low thresholds, or to a subtle balance between the various compounds involved in aroma (*9*). This remark would justify utilization of olfactometry to detect these kinds of differences. Another hypothesis, contrary to the first one, supposes a different biochemical flavor structure of various drinks (*10*); for instance, the flavor of brandies would resemble the flavors of the fruits used in their production. In this case, it seems that typicity is primarily due to raw material.

Distilled alcoholic beverages result from fermentation of sugar-rich raw material by microorganisms that convert it into ethanol. During this fermentation, the majority of significant molecules or flavor precursors are produced as higher alcohols and esters. The product then undergoes a stage of maturation, followed by distillation.

Distilled alcoholic beverages are stored in oak barrels for the aging step. During this process, phenolic compounds and lactones are generated (*11*). This stage is very complex and has already been studied to a great extent, in particular for apple brandies (*12, 13*). We did not include this step in this study because it tends to attenuate difference between brandies. Moreover, to obtain an AOC label, Calvados are all tasted freshly distilled. For these reasons, we decided to study freshly distilled brandies, which is one point that makes this work original.

Various olfactometric methods were proposed in the literature and were used in different food applications to give information on the organoleptic quality of products. These techniques are recognized to give satisfactory answers for evaluation of the aromatic profile, identifying the key odorants and the intensity of each one. In the literature, three techniques were used to quantify the data obtained by GC/olfactometry.

In the first approach, successive dilutions of the extract were carried out (*14*), which gave a dilution factor, which corresponded to the last dilution at which an odorous compound was detected: this is called aroma extract dilution analysis (AEDA), and its applications in various foods were recently reviewed (*15*). Another method involves determination of a value called "charm", calculated from the step of dilution and the duration of odor perception at the last dilution in which it was perceived, which makes it possible to construct an "aromagram" (*16*).

The second approach involved directly measuring the perceived intensity at the column exit. This made it possible to take into account the quantitative aspect of olfactometric detection on a single GC injection. This method was called "osme", which means "odor" in Greek (*17*). Comparable results for a model solution were obtained with this technique and the "charm" technique (*18*).

The third approach (*19*) involved calculating a frequency of odor detection by a trained panel of at least 10 different judges. This last method, called the citation index method, is faster to set up because it does not require the particular training that the "osme" method does.

In the first step of the work described herein, as direct injection analysis is the official method used to control spirits, the results of such analyses were tentatively related to sensory evaluation. Because poor correlations were found, it seemed interesting to determine the real olfactive impact of the different compounds on flavor. Olfactometry techniques are of great interest and have been rarely applied to brandies. The second step of the present study, then, involved characterizing freshly distilled Calvados with interesting sensory characteristics selected by professionals. Thus, the major goal of this study was to gain better knowledge of the physicochemical composition and organoleptic characteristics of Calvados. To achieve this goal, we decided to use an olfactometry method adapted from a combination of AEDA and frequency determination. This new method should give precise results with a smaller number of dilutions than AEDA and a smaller number of panelists than the citation index method. It will be possible, then, to discriminate classes of Calvados with specific odors. Identification and semiquantification will be the aim of our next paper (*20*).

MATERIALS AND METHODS

Materials. Calvados samples were provided voluntarily by six industrial producers located in the limited region of AOC. These apple brandies were first selected in-house by producers themselves. A uniform sampling procedure was determined. Four-liter samples of each batch were taken and then, later on, selected in-house by means of tasting. The goal of this selection was to keep the most interesting Calvados, those with defects or having particular qualities, and to limit the sampling of batches known as "neutral", not presenting much interest within the framework of this study.

Sensory Tasting. Twelve Calvados were retained among 32 batches on the basis of sensory and other criteria (quantities available, contact with wood, etc.) to be tasted in a more precise way by nine tasters. Porto glasses were used for all tasting. Panelists in individual boxes evaluated samples under white light. Calvados were first analyzed by nose in a monadic way with attribution of a total note from 0 to 10, based on the panelist's olfactive perception of the quality. Each taster had to indicate the presence or absence of 16 listed descriptors, with the option of making free comments on qualities or defects. This procedure was repeated in mouth on samples diluted to 50% (v/v) to confirm the panelists' impressions and to add the element of feeling in the mouth. Tasting both by nose and in mouth was repeated for each Calvados. From the 12 Calvados, the 8 most interesting samples in terms of sensory qualities were retained and numbered for additional physicochemical analyses. Results are given in **Table 1**.

Direct Injection Analysis. This official method (*21*), allowing quantitative evaluation of higher alcohols, aldehydes, esters, and methanol, was used as it is usually done for accreditation of Calvados. It involved measuring precisely 25 mL of Calvados at 20 °C and adding a precisely measured quantity of about 15 mg of 4-methylpentan-2-ol (Merck, Hohenbrunn, Munich, Germany) as an internal standard. Two injections per sample of 1-μL aliquots were made in a split mode (40/100) on a CP-Wax 57 CB column (50 m × 0.22 mm i.d.; film thickness 0.25 μm, from J&W Scientific, Folson, CA), with an injector temperature of 240 °C. This was performed on a Delsi DI 700 chromatograph. The carrier gas was helium, with a linear velocity of 50 cm/s. The oven temperature program was 35 °C (5 min hold); 35−220 °C at 4 °C/min; hold at 220 °C to the end of analysis. The detector temperature was fixed at 250 °C. Results are given in **Table 2**.

Extraction of Volatiles. The eight selected Calvados samples underwent a liquid−liquid extraction with pure pentane (Sigma-Aldrich Chimie SARL, St Quentin Fallavier, France). The alcohol content was brought to 15% (v/v) of pure alcohol (PA) by diluting 50 mL of sample with the calculated volume of ultrapure water (Lab Scan Ltd., Dublin, Ireland). One hundred grams of sodium chloride (Sigma-Aldrich Chimie SARL) was added to improve volatiles extraction. Two hundred micrograms of ethyl undecanoate (Sigma-Aldrich Chimie SARL) was added as an internal standard to control extraction. Volatile compounds were extracted twice with 24 mL of pentane in a closed conical flask under magnetic agitation for 30 min. The operation was then carried out one more time with 12 mL of pentane for 15 min. Between stages,

Table 1. Results of Sensory Evaluations of the Eight Calvados Samples Selected for the Physicochemical Analyses[a]

	good quality		neutral		defects				significance[b] of the difference between Calvados samples (sample no.)
quality	sample 1	sample 2	sample 3	sample 4	sample 5	sample 6	sample 7	sample 8	
quality by nose	5.67 (1.63)	4.90 (1.34)	4.58 (0.92)	4.29 (0.81)	3.64 (0.75)	3.08 (1.02)	3.00 (0.71)	2.08 (1.20)	*** (1)
quality in mouth	5.50 (1.38)	6.00 (1.67)	5.00 (0.89)	4.29 (1.11)	3.14 (0.90)	3.10 (1.67)	3.20 (1.30)	2.20 (1.30)	*** (2)
fruity	6	6							*** (1, 2)
acrolein			6	3	5	2	6		** (3, 7)
ethyl acetate								6	*** (8)
hot			6						*** (3)
rubber							6		*** (7)
straw				3					*** (4)
stagnant								6	** (8)
aggressive	1	2	2	4	5		2	4	
solvent	1		1	1	2	1		3	
acetic			2	1	2	1		1	
green apple				1	1	1	3		
herbaceous, green				1	1	1	4		** (7)
mold					1	1			
putrid				1			1	1	
heavy	2		1			2	1	1	
rancid	1			1	1	1	1	1	
yeast					1	1			
boiler				1					
milky, cheesy	1						1		

[a] Average of notes given by judges for the descriptors "quality by nose" and "quality in mouth"; the standard deviation is given in parentheses. Citation indices for the other descriptors. [b] *, significant; **, highly significant; ***, very highly significant.

Table 2. Analysis of Higher Alcohols, Aldehydes, and Esters in Calvados Samples by Gas Chromatography According to the Technique of Direct Injection[a]

	sample 1	sample 2	sample 3	sample 4	sample 5	sample 6	sample 7	sample 8
ethanal	0.86 (0.02)	3.31 (0.06)	1.11 (0.01)	1.71 (0.01)	0.90 (0.03)	2.73 (0.01)	2.19 (0.08)	1.51 (0.06)
ethyl formate	0.33 (0.05)	0.90 (0.12)	0.48 (0.00)	0.56 (0.00)	0.83 (0.02)	0.58 (0.01)	0.40 (0.00)	3.16 (0.04)
ethyl acetate	63.54 (3.57)	388.77 (4.87)	153.40 (0.91)	269.79 (0.94)	216.04 (1.42)	141.73 (0.21)	185.63 (1.15)	597.37 (17.76)
1,1-diethoxyethane (acetal)	1.30 (0.07)	4.05 (0.05)	2.45 (0.15)	2.84 (0.25)	1.32 (0.22)	5.54 (0.16)	9.02 (0.54)	2.70 (0.08)
butan-2-ol	138.49 (2.14)	379.16 (2.99)	90.22 (0.09)	173.23 (0.35)	109.52 (0.63)	44.97 (0.08)	17.69 (0.07)	250.85 (2.39)
ethyl butanoate	0.17 (0.00)	0	0	0	0.23 (0.09)	0.33 (0.01)	0.38 (0.00)	0.17 (0.02)
propan-1-ol	57.97 (0.70)	145.31 (0.87)	62.05 (0.18)	58.26 (0.02)	67.11 (0.60)	94.50 (0.19)	51.25 (0.08)	65.66 (0.51)
isobutan-1-ol	98.01 (1.19)	249.41 (1.15)	52.69 (0.16)	40.54 (0.02)	106.87 (0.29)	117.54 (0.02)	85.94 (0.16)	91.58 (0.40)
allylic alcohol	13.94 (0.19)	43.21 (0.28)	18.52 (0.17)	2.44 (0.05)	12.35 (0.03)	27.90 (0.01)	8.35 (0.33)	2.49 (0.05)
butan-1-ol	13.89 (0.15)	15.46 (0.05)	10.65 (0.08)	12.14 (0.00)	15.00 (0.15)	12.33 (0.13)	6.71 (0.01)	19.84 (0.18)
2-methylbutan-1-ol	50.05 (0.13)	132.61 (0.00)	45.02 (0.20)	48.57 (0.10)	71.39 (0.16)	66.92 (0.04)	61.18 (0.38)	42.49 (0.18)
3-methylbutan-1-ol	196.64 (1.20)	519.12 (1.15)	196.05 (0.69)	161.75 (0.19)	330.82 (0.32)	362.51 (1.23)	213.2 (0.37)	148.48 (0.34)
ethyl lactate	26.38 (0.58)	38.78 (0.34)	19.44 (0.08)	15.58 (0.01)	33.03 (0.04)	52.47 (0.06)	12.23 (0.28)	20.84 (0.14)
hexan-1-ol	7.61 (0.15)	22.89 (0.22)	7.39 (0.06)	4.53 (0.02)	7.67 (0.11)	7.33 (0.02)	6.17 (0.04)	11.62 (0.04)
(*Z*)-hex-3-en-1-ol	0.12 (0.01)	1.28 (0.02)	0.11 (0.00)	0.38 (0.02)	0.06 (0.01)	0.07 (0.01)	0.37 (0.00)	0.14 (0.00)
ethyl hexanoate	0.54 (0.01)	2.20 (0.08)	0.83 (0.01)	0.88 (0.00)	1.01 (0.00)	0.96 (0.01)	0.67 (0.01)	0.95 (0.01)
furfural	12.24 (0.35)	27.36 (0.22)	11.31 (0.06)	16.68 (0.06)	15.14 (0.04)	8.89 (0.03)	4.84 (0.05)	20.15 (0.01)
ethyl octanoate	0.44 (0.00)	2.45 (0.05)	1.23 (0.00)	0.58 (0.02)	0.68 (0.01)	0.60 (0.02)	0.93 (0.01)	1.26 (1.18)
diethyl succinate	0.45 (0.02)	1.59 (0.05)	1.14 (0.03)	0.60 (0.00)	1.02 (0.10)	1.35 (0.01)	0.66 (0.05)	2.30 (0.01)
ethyl dodecanoate	0.47 (0.01)	2.05 (0.04)	0.57 (0.01)	0.74 (0.02)	0.67 (0.02)	1.29 (0.08)	0.42 (0.05)	2.56 (0.03)
2-phenylethanol	3.34 (0.02)	4.40 (0.01)	3.04 (0.03)	1.92 (0.00)	7.82 (0.01)	9.27 (0.02)	1.59 (0.01)	1.64 (0.04)
higher acohols[b]	555.06	1,441.07	456.67	494.48	700.71	698.78	435.97	618.9
total aldehydes[c]	2.16	7.36	3.55	4.55	2.22	8.27	11.22	4.21
esters[d]	92.31	436.74	177.08	288.72	253.5	199.32	201.31	628.6
ratio esters[d]/ethyl acetate	1.45	1.23	1.16	1.07	1.18	1.40	1.08	1.05

[a] Levels given in grams per hectaliter of pure alcohol; the standard deviation is given in parentheses. [b] Higher alcohols = butan-2-ol + propan-1-ol + isobutan-1-ol + butan-1-ol + 2-methylbutan-1-ol + 3-methylbutan-1-ol. [c] Total aldehydes = ethanal + 1,1-diethoxyethane. [d] Esters = ethyl formate + ethyl acetate + ethyl butanoate + ethyl lactate + ethyl hexanoate + ethyl octanoate + diethyl succinate + ethyl dodecanoate.

the organic layer was recovered by decantation in a separatory funnel and was kept cold. The organic layers were then combined, dried over magnesium sulfate (Vel nv, Leuven, Belgium), and then filtered on deactivated glass wool (Touzard Matignon). This phase was then reduced by evaporation of solvent to a 1-mL final volume using a Kuderna-Danish column (Supelco, St Quentin Fallavier, France). The 1-mL extract obtained was stored at −20 °C prior to analysis; it was diluted four times successively with a 3-fold factor for olfactometry analysis. To control injection, 130 ppm of ethyl oleate (Sigma-Aldrich Chimie SARL) was added as a second internal standard.

Capillary Gas Chromatography/Olfactometry. *Chromatographic Conditions.* Olfactometry was performed on a Delsi DI 700 chromatograph using a BP 10 fused silica capillary column (12 m × 0.22 mm i.d.; film thickness 1 μm, from SGE, Villeneuve St Georges, France). Two systems for detection were used: a flame ionization detector (FID) and an olfactometry system (from SGE).

The carrier gas was helium with a linear velocity of 50 cm/s. The column effluent was split with a "Y"-type splitter at the capillary end (SGE). A 20% flow ratio was directed toward FID, while 80% was directed toward the "sniffing" port. To avoid condensation and mixing

Table 3. Olfactometric Indices and Descriptors of Odors Detected in Calvados Extracts

odor no.[a]	retention index	olfactometric index of Calvados sample: good quality 1	good quality 2	neutral 3	neutral 4	defective 5	defective 6	defective 7	defective 8	odor descriptors	significance[b] of the difference between Calvados samples (sample no.)	significance[b] of the difference between classes
						(a) Odors Common to the Eight Calvados Samples						
2	765	5	71	5	9	2	90	74	8	fruity		
3	805	17	101	122	15	90	82	70	185	fruity		
4	832	203	243	243	95	203	243	189	203	sweat, solvent	** (4)	
5	844	5	9	34	126	7	82	29	102	plastic		*, D
12	904	125	144	183	135	203	243	131	203	fermented apple		
17	947	89	29	44	41	90	54	21	54	banana		
20	989	24	26	5	14	9	11	9	18	green grass		*, G
28	1059	203	243	243	203	203	189	203	243	mushroom		
30	1074	11	45	149	5	95	162	8	89	sweat, yeast	*	
43	1194	125	69	75	5	89	84	32	36	yeast-like, cider, mushroom		
46	1218	4	10	8	2	2	5	5	30	woody	*** (8)	
49	1246	162	71	14	90	18	95	50	162	sweat, delicatessen		
51	1261	124	35	70	26	109	14	101	71	rose, mushroom		
53	1271	2	24	6	5	65	122	2	24	spicy, mushroom, floral	*** (6)	*, D
61	1362	27	11	28	77	10	7	17	108	floral, underwood	** (8)	
64	1392	32	203	162	30	108	189	89	203	animal	*	
65	1414	11	74	182	10	27	108	95	83	floral (hyacinth)	** (3)	
68	1457	124	149	88	71	129	86	124	102	cinnamon, woody		
70	1489	185	88	243	101	6	122	68	142	fruity, floral	* (3)	*, G
						(b) Compounds Specific to Some of the Eight Calvados Samples						
						(1) Odors mainly present in Calvados known as being of good quality						
7	856	10	28		3			16		fruity, alcohol	** (2)	**, G
11	898	142	20	29	14					fruity	*** (1)	***, G
37	1143	5	14	5	4	3				vinous, mushroom	*** (2)	**, G
42	1190		24		10					fruity, spicy	** (2)	*, G
62	1374	30							3	bind cider, floral	*** (1)	**, G
66	1429	27								floral, spicy	*** (1)	*, G
						(2) Odors mainly present in Calvados known as being neutral						
1	755			90	3					fruity, solvent	*** (3)	**, N
27	1053			62	41	4		5	2	leather, underwood		**, N
45	1206	5		122		11	75			meaty, vinous, acid	** (3)	
55	1289		27	82	86	29		18	17	phenolic, spicy, underwood		**, N
						(3) Odors mainly present in Calvados with defects						
6	844					21				pyrazin, hot	** (5)	
9	876					23	66	162		herbaceous	*** (7)	**, D
10	886			3	9	2		144		solvent, alcohol	*** (7)	
19	983								29	fruity	*** (8)	*, D
21	998	3	5	2		4		5	17	almond, floral	***** (8)	
25	1031		3	3			135	12	11	potato	*** (6)	*, D
29	1070					12			2	sweat	*** (5)	
31	1079				8			41	62	sweat, floral		
33	1097		2		17	2		21	2	sweat, sponge		
35	1112	4				10				old sponge, rotted	*** (5)	
36	1132						28	90		floral, vegetal	*** (7)	*, D
39	1164			9	3	3	14	4	11	vegetal, mushroom, fatty		**, D
44	1200					12		3	50	old sponge, mold	*** (8)	*, D
52	1266					126				floral (jasmine)	*** (5)	*, D
59	1328	3			9			34	47	mushroom, earthy, phenolic	*** (8)	*, D
60	1346		3		22				43	ham, mushroom, woody	*** (8)	
67	1440		5	70		64	29	63	14	phenolic, crackling		
69	1481		82			203	122	27	63	floral, fruity	*** (5)	**, D
						(4) Minor odors having no evident specificity						
34	1106	23					2	22	5	sweat, earthy, animal		
38	1154	3	24	30			28	22	2	floor cloth, animal, vegetal		
50	1253		128	144	23		125		83	floral, mushroom, acid		
57	1305	14	62		5	20	7	14	21	woody, mushroom, earthy		
58	1322	3	4	41		62	14	23		phenolic, spicy, thymol		
71	1506	104	8		70	3			83	clove, medicinal, phenolic		

[a] Odors 8, 13, 14, 15, 16, 18, 22, 23, 24, 26, 32, 40, 41, 47, 48, 54, 56, 63: results not shown for olfactometric indices under 10. [b] *, significant; **, highly significant; ***, very highly significant. G, good quality; N, neutral; D, defect.

of compounds in the pure silica column used for the "sniffing", an auxiliary gas, also helium, was flowed at the output of the divider at 15 mL/min. To avoid drying of nasal mucous membrane, humidified air was flowed at 60 mL/min.

The oven temperature program was 30 °C (1 min hold); 30−35 °C at 1 °C/min and then 35−240 °C at 10 °C/min; 240 °C (20 min hold). Injection of a 1-μL aliquot was done in a split−splitless mode (40:100) at a 240 °C injector temperature. The detector temperature was fixed at 250 °C.

Panel Conditions. Five assessors were selected and trained on a model solution of volatile compounds. After 1.5 min, the time necessary for solvent elution, they were asked to assign odor-active regions and

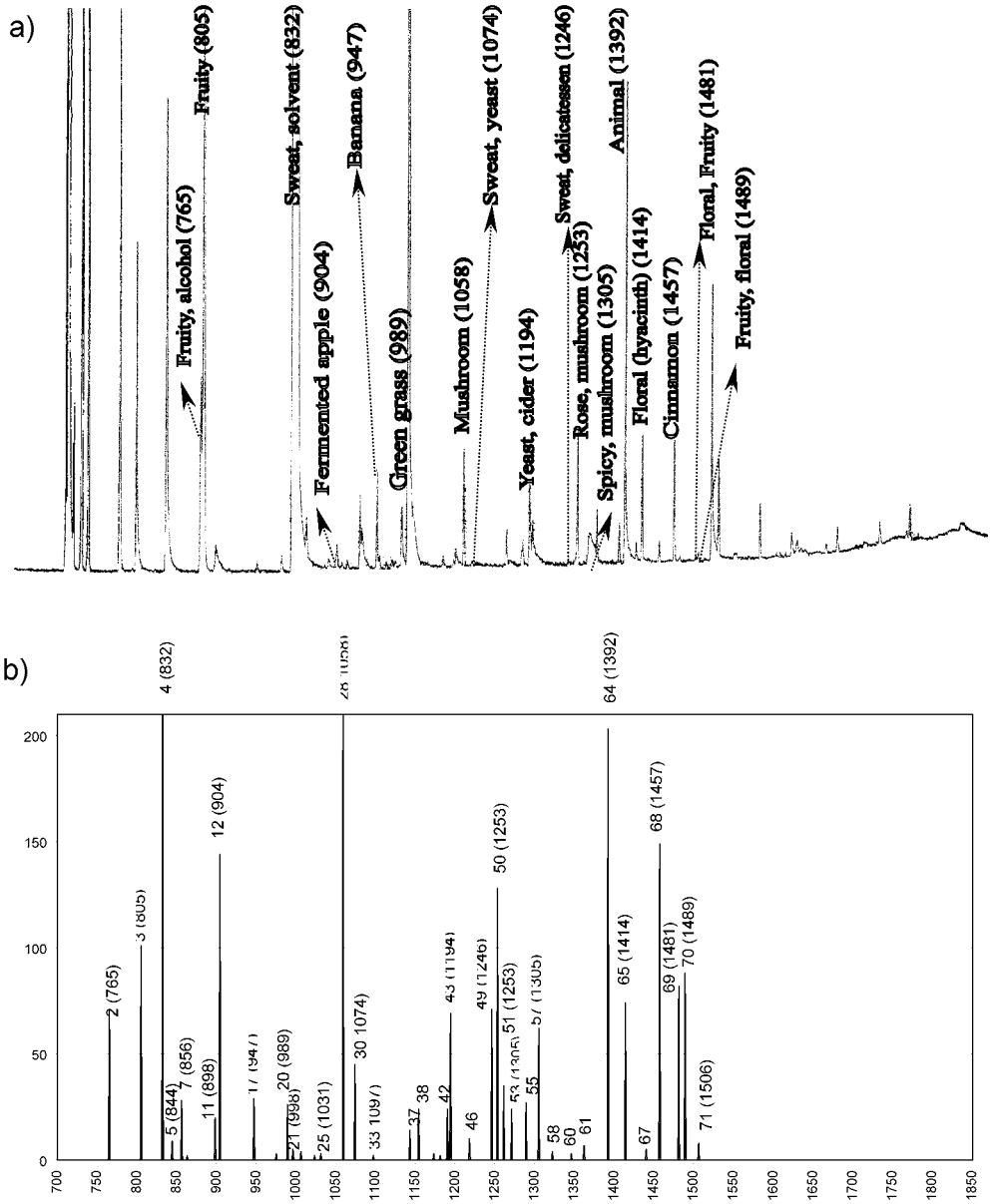

Figure 1. Analysis of Calvados sample 2 extract by (a) GC/FID and (b) GC/olfactometry. The *x*-axis is retention time, and the *y*-axis is (a) FID response or (b) olfactive index. Numbers on peaks in the aromagram are odor numbers (retention indices). Numbers on peaks in the gas chromatogram are retention indices.

odor descriptions at the beginning of each perception. Each run lasted for 20 min to avoid fatigue. All odor-active compounds were eluted during this time. Five dilutions of each extract were presented in a random order to each judge.

Aromagram Construction. At the beginning of each perceived odor, the retention index was calculated in comparison to a hydrocarbon series regularly injected (*22*). This made it possible to compensate for column evolution over time.

For each detected odor and each judge, an "olfactometric" index was calculated according to the formula $I = d^n$, where d is the dilution factor (3 in our case) and n is the number of dilutions for which the compound was detected. An odor detected only at the first dilution will have an index of 1, and an odor detected until the fifth dilution will have an index of 243. An index was obtained for each judge, and the average of the results of the five judges was then calculated to determine an average index for our panel. The higher this index, the higher the odor activity. Compounds detected only once were removed, assuming a very low odor impact. Results are given in **Table 3**. For each Calvados, it is thus possible to build a chart, called an "aromagram", giving an olfactive image of the product. A representative example is given in **Figure 1**.

Statistical Processing. Variance analysis processing was carried out using Statgraphics software (Statistical Graphics Corp. and Manugistics, Inc., Rockville, MD).

RESULTS AND DISCUSSION

Sensory Evaluation. The results of the sensory evaluations of the eight selected Calvados samples are given in **Table 1**. They correspond to average notes given by judges for the quality descriptors detected by nose and in mouth, and a frequency of quotation for other descriptors. Only noted descriptors are given.

Variance analysis was performed. Ten descriptors are significantly different from one Calvados to another. They might be the significant criteria for this specific series of products. The descriptor "fruity" seems to be a necessary criterion for a good-quality product, as only Calvados samples 1 and 2 had such a description. The highest qualities by nose and in mouth are specific respectively to Calvados samples 1 and 2, which justifies the classification into three subclasses. Five Calvados were described as "acrolein", which is the major defect in a

such product. However, Calvados samples 3 and 4 have quality notes between 4 and 5, and thus can be considered as nondefect or neutral products. Calvados samples 5, 6, and 7 have the "acrolein" defect and have quality notes under 4. Calvados sample 7 has two additional important defects: "rubber" and "herbaceous". Calvados sample 8 was noted as "ethyl acetate", which is another important defect. Those four products can be considered as Calvados with defects.

The Calvados samples were then classified in three categories:

Calvados of "good quality" (samples 1 and 2). These were described as "fruity", with a citation index of 6, and had an average note in mouth over 5.

"Neutral" Calvados (samples 3 and 4). These had average notes in mouth and by nose between 4 and 5.

Calvados with "defects" (samples 5−8). These were noted "acrolein", "ethyl acetate", "rubber", or "herbaceous" and had notes in mouth and by nose under 4.

Chromatographic Analyses. Analyses of higher alcohols, aldehydes, and esters, generally carried out by routine methods, were carried out on the eight Calvados of this study. Results are given in **Table 2**. All results are given in grams per hectaliter of pure alcohol (PA). From a legal point of view, the level of esters should be at minimum 100 ± 20. Calvados sample 1 barely reaches this minimum but was considered a good-quality product by the panel. This minimum level is then to be discussed. Ester composition is mainly represented by ethyl acetate and should not be too high. The maximum quantity is not presently fixed. However, regarding our results, we might establish a level around 500. Indeed, Calvados sample 2, which was a good-quality one, had an ester level of 436, compared to 628 for Calvados sample 8, with defect and, in particular, the sensory descriptor "ethyl acetate" with a frequency of quotation of 6. This might be confirmed by other experiments. It seems important to scrutinize the ratio of esters to ethyl acetate given in **Table 2**. Except for Calvados sample 6 (ratio 1.4), which had an important defect in mouth and then a penalizing particularity, this ratio is increases overall with good quality. We can note as well that extremes have opposite composition. Thus, Calvados sample 1 contains 63.54 g/hl AP of ethyl acetate, compared to 597.37 for Calvados sample 8, the more defective one. It seems, though, that the qualitative note of esters composition is a weighty factor to be considered, or at least gives a complementary information to quantitative analysis.

The level of higher alcohols was not related to any sensory descriptor. Calvados sample 2 had the higher alcohol level (1441). Regardless of the higher alcohol level, Calvados can either be of good quality or have defect. This is probably due to the presence of other compounds counterbalancing the negative impact. A good quality is probably reached when good composition balance is reached.

The total aldehydes (ethanal + acetal) level might be scrutinized as well. Calvados sample 7 is the richest in total aldehydes, with a quantity of 11.22. It is also the one with the highest "green apple" note. A high level of aldehydes is known to give this kind of defect. The maximum level is probably between 8 and 11 for aldehydes and between 5 and 9 for acetal, as we can see in **Table 2** for Calvados samples 6 and 7. However, it seems that ethanal has a lower impact. Calvados sample 2 has a level of 3.31, which is higher than those of Calvados samples 6 and 7, but does not bring out the defect.

The "herbaceous" defect is supposed to be related to hexan-1-ol and (*Z*)-hex-3-en-1-ol concentration, with respective upper limits of 20 and 3.5. Only Calvados sample 2 is over this limit for hexanol, but it does not seem to be defective. Only Calvados sample 7 was cited as such. Thus, this relationship does not seem so certain, and another compound might be responsible for the defect.

For Calvados sample 2, other compounds in high quantity might counterbalance the negative impact of different compounds. Indeed, as can be seen in **Table 2**, this Calvados is the most complex and richest product. It contains the largest quantities of butan-2-ol (379), propan-1-ol (145), isobutanol (249), 2-methylbutanol (132), 3-methylbutanol (519), and furfural (27). Some of these compounds might play a very significant role in determining Calvados quality (*1*, *2*).

These results show that no compound alone can explain Calvados quality, and an adequate composition balance must be reached, with minimum quantities of some compounds. It is, however, necessary to be careful in drawing conclusions for two reasons:

First, the number of data analyzed in this study limits the range of conclusions. It seems convenient to carry out analyses and to exploit results statistically in a more systematic way on Calvados tested by sensory analyses.

Second, current sensory evaluation has some limits, for the product is difficult to apprehend due to its alcoholic nature. A taster has six million olfactive cells, of which two million are saturated by only one glass of 50% (v/v) brandy; these two million cells become operational again only after a 6-h rest. This highlights the difficulty of tasting several samples well, especially if the samples are not diluted, in which case even more olfactive cells would be attacked (*23*).

These results are then to be considered with caution. Indeed, there is a significant judge's effect. The people on the jury do not all describe the defects with the same vocabulary. This introduced a bias into our results. For example, it seems that the descriptors "aggressive" and "acrolein" are associated with the same feeling. Further, sampling is of a reduced size, not sufficient for robust statistical analyses.

Olfactometry Analysis. As few correlations were made between composition as determined by direct injection and sensory evaluation, it seemed necessary to analyze other volatile compounds and to focus our research on key odorants. Olfactometry analyses were thus performed on pentane extracts. **Figure 1** shows a typical gas chromatogram, obtained by analysis of the whole Calvados sample 2 extract, together with the aromagram obtained by compilation of results from our five judges. Identification of key odorant compounds is presented and discussed in the following paper (*20*). First, it is necessary to recall, as can be seen on the chromatogram, that there is not necessarily a relationship between a compound's concentration and its odor impact in the product. Thus, a molecule in weak concentration can have a very significant odor impact, and vice versa. Seventy-one odors were detected. Eighteen odors with an olfactometric index of less than 10 are not presented and not discussed because their odor impact is too low. The remaining 53 odors are classified in two categories: odors present in all Calvados, and others specific to some of them. These are presented in **Table 3**. Identification of key odorants and semiquantification are reported in the following paper (*20*).

From a statistical point of view, and despite high standard deviation, probably due to the great difference in judges' sensory thresholds, significant differences between Calvados or classes are found.

(a) Odors Common to the Eight Calvados. Nineteen odors are present in all Calvados. The corresponding molecules form what we called the "aroma skeleton" of Calvados. It would seem that these compounds are necessary for aroma expression of

these Calvados because of their olfactive importance. As the descriptors associated with these molecules were not attributed to Calvados during sensory evaluations, it can be assumed that the mixture and balance between these compounds is determinant.

Odors 5 (plastic) and 53 (spicy, mushroom) have higher impacts for Calvados with defects, and the associated descriptors have negative connotations. Odors 46 and 61 are specific to Calvados sample 8, with defect. It seems that the concentrations of the corresponding compounds should not exceed a certain level in order to keep a good overall aroma. On another hand, odors 20 and 70 are important in good-quality products. It seems better to have a high concentration of the corresponding molecules.

Professionals gave a "yeast" note to Calvados samples 5 and 6. Two odors (30 and 43) were noted with such descriptors. However, these odors are present in other Calvados without this specific defect. A presumed association between the presence of compounds and the defect thus cannot be conclusive. Association of two or three compounds might be necessary for a defect to appear.

We can see in **Table 3** that odors 4 and 64 have a high impact in all Calvados, except respectively for Calvados sample 4 and Calvados samples 1 and 4, whereas their descriptors have negative connotations: "sweat", "solvent", and "animal:. "Fruity" and "floral" notes are commonly associated by experts with typicity of Calvados. Odors 2, 3, 12, 17, and 51 were noted with such descriptors in our study. Even if they are not significantly different from one Calvados to another, they seem to be necessary for the expression of product aroma. In the same way, due to their presence in all samples and despite their descriptors, odors 28, 49, 65, and 68 do not lower the quality of Calvados. This explains the complexity of good interpretation. It seems that an equilibrium between 19 compounds determines the "body" of Calvados.

(b) Odors Specific to Some of the Eight Calvados Studied. In addition to the 19 above-mentioned molecules, 34 other compounds were detected but only in a limited number of Calvados samples. It seems possible to associate some of them with a defect or a class of specific Calvados. However, six odors seem not to be specific to any class of Calvados. We distributed these various compounds in four subclasses.

(1) Odors mainly present in Calvados known as being of good quality. The descriptors used during olfactometry analyses are mainly "floral" and "fruity". It seems normal that such descriptors are prevalent for products of good quality, or even of average quality, as the descriptor "fruity" is given during sensory evaluation by the panel for this kind of products. Those six odors are statistically specific to either Calvados samples 1 or 2 and, by consequence, of good quality class. The presence of odor 7 in Calvados sample 7 with defects is to be noted. We can imagine that because of its low odor impact, it could be masked by another compound having a negative impact on aroma. This point needs to be clarified. We think that the presence of these different compounds allows expression of flavor quality. In any case, their presence cannot be related to a specific defect.

(2) Odors mainly present in Calvados known as being neutral. The four odors are statistically specific to Calvados sample 3 or to neutral class. Odor 1 is associated with the "fruity" descriptor. The presence of the corresponding molecule in the final mixture seems to have no effect on aroma. Other molecules, lowering its impact, probably mask this compound. For odors described as "underwood" and "meaty", interpretation is more difficult. Indeed, those are also present in Calvados with defects, although in lesser proportions, but not in Calvados of good quality. Thus, the presence of the corresponding compounds might have a negative impact on aroma. In any case, they do not seem to be of primary importance for good-quality aroma.

(3) Odors mainly present in Calvados with defects. Except for odors 31, 33, 39, and 67, all of these odors are specific either to Calvados with defect or to the defect class. The four above-cited odors are kept in this class because their indices are high in Calvados samples 5−8 and because their descriptors have negative connotations: "sweat", "vegetal", and "phenolic".

The majority of the descriptors given to these odors have negative connotations: "pyrazin, hot" for odor 6; "solvent" for odor 10; "sweat", "old sponge", "rotted", "mold" for odors 29, 31, 33, 35, and 44; "phenolic, crackling" for odor 67. It is not possible to connect these data with descriptors used in the sensory questionnaire. Indeed, Calvados were not described as "old sponge" and "sweat", despite having molecules evoking these notes. However, Calvados sample 5 was noted as "mold" in sensory evaluation. Olfactometry results emphasize that this Calvados was the only one to contain both odors 35 and 44 at the same time, whose given descriptors are respectively "old sponge, rotted" and "old sponge, mold". Is the simultaneous presence of these molecules necessary for the "mold" defect to appear? We cannot, for the time being, answer this question.

Odor 25 was described as "potato" by all judges who detected it. We cannot, however, associate it with a defect of Calvados with our current knowledge. It would be interesting to clarify this point in future studies.

Odor 9, whose descriptor was "herbaceous", was detected primarily in Calvados samples 5−7. Only Calvados sample 7 was described as having the "herbaceous" defect by one of the judges. It seems that the concentration of odor 9 in samples 5 and 6 is not sufficient for the defect to appear. A quantitative determination method should be developed to improve results on this point. It would be interesting to confirm this result on other Calvados having this defect. We are already sure that this compound is not (*Z*)-hex-3-en-1-ol or hexanol, commonly described as "green grass", both generally associated with the "herbaceous" defect. Indeed, the elution time of (*Z*)-hex-3-en-1-ol is 989, corresponding to odor 20, which was actually described as "green grass" by the "olfactometry" jury. As we mention above, we suspected a third molecule to be responsible. This odor, with a retention time of 876, is probably the molecule we were looking for.

Odors 19, 36, 52, and 69 were described as having "floral" or "fruity" notes and odors 39, 59, and 60 as "mushroom", "vegetal", or "phenolic". These descriptors are not unpleasant and negative notes. Their possible contribution to aroma quality might be counterbalanced by the presence of molecules with negative impact and lower detection threshold. It is possible, as well, that in a mixture, the impact of volatile compounds will not be the same.

(4) Minors odors having no evident specificity. We decided to classify these odors in a different category because they have similar olfactive indices for Calvados of different quality. The corresponding compounds do not seem to have an olfactive impact at the concentrations found in the Calvados studied. One can, however, modulate this remark for odors 50, 57, 58, and 71. Indeed, their indices reach significant values. It is probable that other volatile compounds counterbalance their presence. One can think that, because of their descriptors, these molecules have a rather positive impact on aroma. All this, however, remains to be confirmed.

Conclusions. Direct injection analyses of eight Calvados were carried out and the results related to sensory descriptors. Higher alcohols were not related to any sensory descriptor, but a high level should probably be compensated by other volatile compounds with positive flavor impact. Esters have a probable maximum level around 500 g/hl of PA. This level also corresponds to the threshold of the main esters constituent, ethyl acetate. A high ratio of esters to ethyl acetate seems to be of prime importance for good quality. Total aldehydes, with a maximum level between 8 and 11 g/hl of PA and mainly comprising acetal (maximum between 5 and 9 g/hl of PA), were related to a "green" descriptor. In addition, butan-2-ol (379), propan-1-ol (145), isobutanol (249), 2-methylbutanol (132), 3-methylbutanol (519), and furfural (27) might play very significant roles in Calvados quality.

In this study, analysis by GC/olfactometry made it possible to detect 71 odorous compounds, of which 19 constitute the "aroma skeleton" common to all the Calvados samples studied. It seems that a balance between these molecules is essential to the expression of aroma. The presence in too high levels of some compounds, i.e., those associated with odors 5 ("plastic"), 30 ("sweat"), 53 ("spicy", "mushroom"), 46 ("woody"), and 61 ("floral"), seems to notably decrease the quality of the product.

Some compounds, corresponding to olfactive odors, are present specifically in particular Calvados. Thus, compounds associated with odors 7, 11, 37, 42, 62, and 66 are mainly present in Calvados known as being of good quality. They generate fruity-type notes. Odors 1, 27, 45, and 55 are mainly present in Calvados known as being neutral. They can be regarded as minor impact odors at the concentrations found. Calvados with defects contain specifically 18 different compounds. It should be noted that no direct relationship with descriptors given in sensory evaluation has been made, except for odor 9. This odor appears in Calvados samples 5−7. The jury of professionals described only Calvados sample 7 as "herbaceous", a descriptor also given by the olfactometry jury for this odor. This suggests that a minimum quantity must be reached for this defect to appear. This compound is different from (*Z*)-hex-3-en-1-ol, generally described by the term "green grass", and whose retention time corresponds to odor 20.

The presence or differences in the composition balance of the different corresponding compounds will lead to a reduction or an increase in the quality of the products.

The originality of the olfactometry method used to obtain these results should be noted. We used in combination two types of data, i.e., AEDA and citation indices, which normally require two or three expert judges. The proposed method made it possible to reduce the number of dilutions required. As a consequence, and due to the fact that we needed fewer analyses, we were able to use more judges who needed a shorter training period. By determining an average of the results, we could calculate an index for each odor. This approach seemed to give more precise results than a single method, as it is quantitative, in contrast to the citation indices alone. As well, it requires less dilution than AEDA and gives an average for more people, lowering the potential for the problem of anosmia. The proposed method gives, on statistical bases, 31 significant criteria for classifying products. However, it is still time-consuming, which is the main fault of such methods.

The results presented in this paper need to be complemented. An "aroma skeleton" and specific defects were pointed out. It is essential to identify the corresponding molecules. This was pursued by mass spectrometry and is the subject of the following paper (*20*). Thus, the relationship between olfactometry indices and quantification of corresponding molecules will be determined.

ABBREVIATIONS USED

GC, gas chromatography; FID, flame ionization detector; AEDA, aroma extract dilution analysis; PA, pure alcohol; AOC, appellation d'origine contrôlée (label of controlled origin).

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