

EFFECT OF OAK WOOD HEATING ON COGNAC SPIRIT MATURED IN NEW BARREL: A PILOT STUDY

INCIDENCE DU NIVEAU DE CHAUFFE DU BOIS SUR UNE EAU-DE- VIE DE COGNAC LOGÉE EN FÛT NEUF : ÉTUDE PILOTE

G. SNAKKERS, J.-M. BOULESTEIX, Sylvie ESTRÉGUIL, Jacqueline GASCHET,
Odile LABLANQUIE, Annie FAURE et R. CANTAGREL

Station Viticole du Bureau National Interprofessionnel du Cognac,
69 rue de Bellefonds, 16100 Cognac, France

Abstract : This study investigates the influence of different levels of wood heat treatment on the quality of a Cognac spirit using a pilot barrel model. The pilot barrels were composed of a stainless steel cylinder closed at both ends by a piece of stave. The aim of the study was to analyze the impact of wood heat treatment on Cognac in both analytical and sensory terms and to confirm the validity of the pilot barrel model. The findings give a relatively wide view of the influence on the composition of Cognac of new wood heated at different temperatures. Heating gave notes of «vanilla» and «toasted» to the spirit while excessive heating led to lower quality with the appearance of «fungus» and «dusty». The good quality of the spirits obtained validates the pilot barrel as a model for the extraction of wood compounds by spirit.

Résumé : Cette étude porte sur l'influence de différents niveaux de chauffe du bois sur la qualité d'une eau-de-vie de Cognac en utilisant un modèle de fût pilote. Les fûts pilotes sont constitués d'un cylindre inox fermé aux deux extrémités par un morceau de douelle. L'objectif de cette étude est double : réaliser une synthèse sur l'incidence de la chauffe du bois sur les eaux-de-vie de Cognac, à la fois sur les aspects analytiques et sensoriels et confirmer la validité des fûts pilotes en tant que modèles.

La bonne qualité des eaux-de-vie obtenues valide les fûts pilotes comme modèle de la phase d'extraction des composés du bois des fûts par l'eau-de-vie.

Le bois non chauffé confère des notes «végétal», «lourd». La chauffe du bois se traduit par des eaux-de-vie plus appréciées avec des notes «vanillé». Une chauffe trop forte entraîne une nette dépréciation avec l'apparition de notes «champignon», «moisi», «terreux» ...

L'ensemble des résultats obtenus donne un aperçu assez large de l'influence du bois neuf plus ou moins chauffé sur la composition de l'eau-de-vie. Pour de nombreux composés les résultats obtenus avec le modèle pilote sont comparables à ceux obtenus sur des extraits de particules de bois : dérivés de la lignine, composés furaniques, méthyl octalactones... Pour d'autres composés, notamment les acides gras, les résultats diffèrent.

Keywords : Spirit, Cognac, wood, barrel, extraction, heating, pilot.

Mots clés : Spiritueux, Cognac, bois, fût, extraction, chauffe, pilote

INTRODUCTION

During the manufacture of barrels in which Cognac spirits are matured, the oak wood is heated. This process is essential for shaping the body since it decreases the mechanical resistance of the wood. Thereafter, the wood may be heated again in order to develop aromas, a process known as «bousinage». We studied the influence of various levels of wood heating on the quality of Cognac by using a pilot barrel model. Working with a pilot barrel closed at the extremities by pieces of stave constitutes a compromise between working with small pieces of wood such as sawdust and chips, which is a rapid and inexpensive method allowing the raw material wood to be controlled but which does not faithfully reproduce the transfer phenomena occurring

in barrel, and real barrels, in which it is difficult to control the raw material wood. The aim of the study was as follows: to gain insight into the impact of oak wood heat treatment on Cognac spirits from an analytical and sensory viewpoint; to confirm the validity of the pilot barrel as an experimental model for working with small volumes.

PILOT BARREL

WITHER *et al.* (1995) compared maturation of whisky spirit in normal barrels and miniature six-liter American white oak casks. The results demonstrated differences in analytical composition and sensory profile between the two types of maturation, the miniature casks giving a sweeter product than the normal-sized

barrels. The authors attributed the difference to a higher rate of oxidation in the miniature casks, a finding which may be partly explained by the very different surface/volume ratios for the two types of container. The spirit remained 24 months in the miniature casks and 60 months in normal barrels. The initial wood impregnation in the miniature cask was very high, leading to a large loss of volume and a considerable ullage above the liquid. There was no topping up in the protocol. FEUILLAT *et al.* (1994) tested a system composed of a PVC tube in which both extremities were blocked by wooden stoppers. This system, which gave a volume/wood surface ratio comparable to that of a real barrel, was used as a model by PUECH *et al.* (1996) and by FEUILLAT *et al.* (1997) to study the extraction of wood compounds.

WOOD HEATING

Many authors have examined the effect of heating wood. One strategy consists in heating wood chips in the laboratory in different heating conditions (temperature x time) (SARNI *et al.*, 1990 ; GIMENEZ MARTINEZ and LOPEZ GARCIA, 1996). The extracted compounds are measured on the macerated chip solution. Another strategy consists in first heating staves either in real conditions (NOMDEDEU and LÉAUTÉ, 1988a ; CHATONNET, 1995 ; CHATONNET *et al.*, 1996 ; CADAHIA *et al.*, 2001) or in the laboratory (CANAS *et al.*, 2000). It then becomes possible to sample wood particles on the heated staves and to perform maceration in order to assay the extractible compounds. This reveals a heat gradient in the thickness of the stave, from the face exposed to the heat to the unexposed face.

Oakwood heating may also be studied in full size by placing in barrels the product under study or a model solution such as wine and a hydro-alcoholic solution (12 % volume) (NOMDEDEU and LÉAUTÉ, 1988a and b), brandy (RABIER and MOUTOUNET, 1990 ; ARTAJONA *et al.*, 1990 ; PUECH and MAGA, 1993), Cognac spirit (LAVERGNE *et al.*, 1990 ; CALVO *et al.*, 1992 ; CANTAGREL *et al.*, 1992) or whisky spirit (PIGGOTT *et al.*, 1993). In the case of wine, inter-

actions occur between the extracted compounds of the wood and those of the wine, and the model solution makes it possible to measure the contribution of the wood more precisely (NOMDEDEU and LÉAUTÉ, 1988a). MOSEDALE and FORD (1996) used an intermediary protocol in which 14 x 1 x 1 cm wood bars were heated in an oven at 200 °C for 0, 30, 60 and 120 minutes. The extraction time was 6 months.

The compounds studied also differ, the lignin derivatives (vanillin, vanillic acid, coniferaldehyde, syringaldehyde, syringic acid, sinapaldehyde), the furanic aldehydes (furfural, 5-methyl furfural, 5 hydroxymethyl furfural), gallic acid and ellagic acid being the most frequently tested.

MATERIAL AND METHODS

I - PILOT BARREL

The protocol of FEUILLAT *et al.* (1994) was modified as follows. The tube was made of stainless steel, an inert material in relation to spirit. The pieces of wood were not embedded but were pressed against the tube, therefore allowing non-rounded pieces to be used (figure 1). Tightness was ensured with a wet flour paste as in cooperage, because plastic or similar washers do not remain inert during prolonged contact with spirit. The diameter of the tube was 10 cm and 27 cm long. This length was chosen to mimic the surface/volume ratio of a 350 l barrel.



Fig. 1 - Pilot barrel
Fût pilote

Table I - Heating parameters
Paramètres de la chauffe des bois

Type of heating	Abbreviation	Heating time (mn)	Thermostat	Heating temperature (°C)
Not heated	NH	-	-	-
Light	LH	7	8	304
Average	AH	10	8	304
Strong	SH	18	8	304
Very strong	VSH	22	10	340

II - OAK WOOD (NATURE AND HEATING)

The experimental material was composed of two pieces of cask wood having dried for more than three years in free air. Both pieces were cut into five sections, and five pairs were made including one section from each piece. Each pair underwent a different level of heating in the laboratory (table I) and then served as stoppers for a pilot cask. This ensured that the raw material was homogeneous between the five pilot barrels to be tested at the five different levels of heating. The temperatures were those measured in the empty oven without the wood (table I, figure 2).

III - COGNAC SPIRIT

The pilot barrels were filled with a new Cognac spirit (70 % vol.). After maturation for three months in the laboratory (25 °C), the pilot barrels were emptied and the samples were analyzed and tasted.

IV- CHEMICAL ANALYSES

Total phenols were determined using the procedure described by BLOUIN (1972) with Folin-Ciocalteu reagent.

Determination of ellagitannins was carried out by high-performance liquid chromatography according to the technique developed by PENG *et al.* (1991) and VIRIOT (1995). Results are expressed in milligrams of ellagic acid calculated by the difference between total ellagic acid (after acid hydrolysis) and the pre-existing free ellagic acid.

Phenolic acids, aromatic aldehydes, furanic aldehydes, aesculin and scopoletin were determined by high performance liquid chromatography. The column was a C18 silica type with spherical beads. Flow rate 1 ml/min. Eluant A (water: 95.5 %, acetic acid: 4 %, propanol-1: 0.5 %), eluant B: 100 % methanol. Gradient elution (A/B): 0 min. (100/0), 40 min. (60/40), 45 min. (10/90), 50 min. (100/0). Analysis was performed at room temperature. Analysis time was 50 min. and equilibration time was 15 min. Ultra-violet detection was performed at 295, 320, 272, 345 and 280 nm. Injected volume was 15 µl for the reference solution and the samples.

Other volatile phenols were converted into 2,4-dinitrophenyl ethers with the aid of 2,4-dinitro-1-fluorobenzene according to the technique of LEHTONEN (1980). After extraction, the derivatives were analyzed by gas chromatography with detection by electron capture.

Fatty acids were assayed according to the protocol described by VIDAL *et al.* (1994).

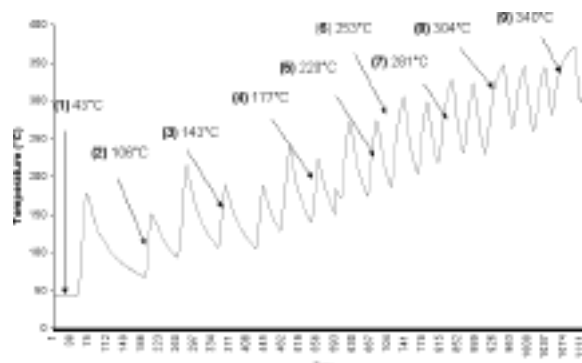


Fig. 2 - Oven temperature (thermostat)
Température du four pour la chauffe des bois (thermostat)

Volatile compounds were assayed by on-column injection gas chromatography or after iso-octane extraction (CANTAGREL, 1986).

Sugars were transformed into TMS-oxime derivatives and polyols and organic acids were transformed into TMS derivatives.

400 µl of sample or reference solution and 400 µl of internal standard solution were mixed in a 1.2 ml flask. 200 µl of the preceding mixture were placed in a flask for automatic injection with two drops of ammonia, and then were evaporated under nitrogen. Next, 100 µl of hydroxylamine hydrochloride solution in pyridine were added. The flask was stoppered and heated at 70 °C on a hot plate for 30 minutes. The sugars and acids were then transformed into silylated derivatives by adding 200 µl Sylon BFT for 20 minutes at 70 °C. A blank with different reagents was performed at the beginning of each series of analyses.

The gas chromatographic conditions were as follows: FID detector, split-splitless injection, silica glass capillary column type CPSIL 5 CB (50 m x 0.25 mm x 0.12µm), carrier gas hydrogen, injector 260 °C, detector 280 °C, 1 µl injection in split mode, temperature range: 45°C (0 min) increasing 4 °C/min up to 280 °C for 5 min.

The silylated derivatives of some sugars gave two or several chromatographic peaks, but only the highest peak was used for quantitative analysis. The solution of internal standards was a mixture of two compounds. Vanillic acid was used to quantify acids and phenyl-glucopyranoside to quantify sugars and polyols. Since quercitol is not available commercially, it was quantified by using the response factor of myo-inositol.

V – SENSORY ANALYSIS

An 11-person panel was composed of professionals working in the field of Cognac such as vintners, winebrokers and analysts. The Cognac spirits were pre-

Table II - Average tasting notes (/5)
Résultats d'analyse sensorielle, notes (/5)

Heating	Quality of wood aroma	Bitterness	Astringency	Acidity	Overall appreciation	Intention to buy
NH	1.64	2.64	1.82	1.64	1.73	56%
LH	2.55	1.45	1.77	1.86	3.09	78%
AH	3.45	2.09	1.91	2.00	3.55	100%
SH	3.00	2.27	2.50	1.73	2.73	78%
VSH	1.14	2.55	2.18	1.77	0.73	0%
Sign.	***	NS	NS	NS	***	***

NH: not heated ; LH : light heating ; AH: average heating ; SH : strong heating ; VSH : very strong heating ; Sign.: level of significance, heating effect ; NS : non-significant heating effect, $p > 0,05$; ***: very significant heating effect, $p < 0.001$

NH : non chauffé ; LH : chauffe légère ; AH : chauffe moyenne ; SH : chauffe forte ; VSH : chauffe très forte ; Sign.: niveau de signification, effet chauffe ; NS : effet chauffe non significatif, $p > 0,05$; ***: effet chauffe très significatif, $p < 0.001$

Table III - Polyphenols (mg gallic acid/l)
Polyphénols (mg acide gallique/l)

Compound/parameter	New spirit	NH	LH	AH	SH	VSH
Total polyphenols	0	31	79	125	187	100

Table IV - Tannins and derivatives assayed by HPLC (mg/l)
Tannins and derivatives assayed by HPLC (mg/l)

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
Ellagic tannins (1)	*	*	1.31	*	*	*	
Gallic acid	*	2.10	4.80	4.80	2.10	0.50	0.07
Ellagic acid	*	9.60	12.70	22.70	21.40	9.40	0.21

(1) ellagic acid released by hydrolysis ; (*) not detected

(1) acide ellagique libéré par hydrolyse (*) : non détecté

sented to the tasters undiluted (the level of dilution being chosen by each taster) and in blue glasses, in order that the tasters should not be influenced by the color.

The first part of the tasting sheet contained 5 descriptors to evaluate a scale of 0 to 5 : quality of wood aroma (nose), bitterness, astringency, acidity and overall appreciation. In the second part, tasters gave free descriptors of each sample. The last part was a purchasing question (yes/no), which was presented as follows: «Would you buy these spirits at a reasonable price?» The aim of this question was to validate the pilot model by showing that the spirits obtained were organoleptically similar to commercially available ones.

RESULTS

I - TASTING

The average notes obtained are presented in table II and figure 4. No taster appreciated the sample corresponding to very strong heating (table II), which was often attributed a note of «fungus», «dusty», «musty», «heavy» and «earthy». The sample matured in unheated wood was not highly appreciated, the wood aroma

being almost absent and described as «plant». The spirits corresponding to the three intermediary levels of heating were globally appreciated and judged «vanilla», but the optimal level of heating was different for each taster. The sample corresponding to the average level of heating received the best appreciations and therefore constituted the best compromise between the preferences of the various panel members.

II - CONCENTRATION FACTOR

The spirits matured in pilot barrels underwent a loss of volume that may largely be attributed to the impregnation of the wood. A phenomenon of concentration also occurred that was probably due to the evaporation of the most volatile substances, particularly ethanol. This concentration was evidenced by the levels of higher alcohols. While new spirit contained 3 736 mg/l, the mean higher alcohols level after maturation in pilot barrels was 3 863 mg/l (table XIII). The levels were homogeneous for all pilot barrels.

In order to assess the impact of wood on the compounds already present in new spirit, it is preferable to take this factor of concentration into account. Since higher alcohols undergo very little change during aging,

Table V - Lignin derivatives assayed by HPLC (mg/l)**Dérivés de la lignine dosés par HPLC (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
coniferaldehyde	*	*	2.60	7.44	11.52	5.93	0.02
vanillin	*	0.14	0.81	1.73	3.03	2.76	0.02
vanillic acid	*	0.30	0.30	0.60	1.50	1.90	0.02
sinapaldehyde	*	0.08	3.98	16.17	28.12	12.18	0.05
syringaldehyde	*	0.26	1.27	4.71	11.79	9.90	0.08
syringic acid	*	0.30	0.50	1.20	3.90	4.10	0.02
guaiacyls/syringyls		0.69	0.65	0.44	0.37	0.40	

(*) not detected ; SDr : Repeatability standard deviation estimated during single-laboratory validation, level for AH sample

(*) : non détecté ; SDr : Écart type de répétabilité estimé lors de la validation interne de la méthode, niveau de l'échantillon AH

Table VI - Other volatile phenols assayed by gas phase chromatography after derivatization (µg/l)**Autres phénols volatiles dosés par chromatographie gazeuse après dérivation (µg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
Phenol	2.90	3.20	3.20	3.50	7.20	13.30	0.29
o-cresol	0.72	0.50	0.50	0.60	1.10	2.00	0.24
m-cresol	0.83	0.70	0.60	0.60	1.10	1.90	0.29
p-cresol	0.62	0.50	0.50	0.70	1.20	1.70	0.15
Guaiacol	1.14	0.70	1.70	4.80	16.20	44.20	2.25
4-ethylphenol	2.27	2.10	2.20	2.10	2.00	2.10	0.22
4-ethylguaiacol	7.65	7.10	8.00	8.30	11.30	28.80	0.97
eugenol	1.03	9.30	24.90	39.40	55.50	51.30	4.33

SDr : Repeatability standard deviation, chemical analysis, 5 replications for SH sample

SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon SH

their concentrations were used to calculate the concentration factor. Thus, the levels in new spirit were multiplied by $3863 / 3736 = 1.034$.

III - COMPOSITION

1) Total polyphenols

The new Cognac spirit contained very few phenolic compounds (table III). Some volatile phenolic compounds were present but at only very low levels (cf. III.3.4., table VI). Most of the phenolic compounds came from the oak wood. The level of polyphenols increased in relation to the heating temperature and decreased at the highest temperatures. The level of polyphenols resulted from a balance between degraded compounds such as tannins and lignin, which is difficult to extract, the released molecules such as ellagic acid and the extractible derivatives of lignin, and the ability of the spirit to extract various molecules.

2) Tannins and derivatives

Irrespective of the temperature (table IV), the levels of ellagitannins, particularly combined ellagic acid, were low. Gallic and ellagic acid levels evolved similarly in relation to heating temperature. First, an increase

occurred probably due to the release of these molecules by thermal degradation of the more complex chemical forms, particularly the tannins. Thereafter, the levels decreased at the highest temperatures.

3) Lignin derivatives

Lignin derivatives are provided by the wood and their levels were strongly influenced by heating temperature (table V). The results may be summarized as follows:

- unheated wood released very few cinnamic compounds such as sinapaldehyde and coniferaldehyde;
- heating partly degraded the lignin and released derivatives which are easily extracted in the spirit;
- the forms released by heating were mainly:
 - syringylated forms compared to guaiacyl forms (ratio about 2/1);
 - cinnamic aldehydes such as sinapaldehyde and coniferaldehyde;
- the higher the temperature, the larger the amount of derivatives. At very high temperatures, the aroma-

Table VII - Furanic aldehydes assayed by HPLC (mg/l)**Aldéhydes furaniques doses par HPLC (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
5-(hydroxymethyl)-furfural	*	*	1.00	4.00	8.00	8.90	0.04
furfural	7.24	7.20	11.80	27.60	67.90	98.60	0.28
5-methyl furfural	0.11	0.11	0.37	1.47	4.01	5.34	0.02

(*) : not detected ; SDr : Repeatability standard deviation estimated during single-laboratory validation, level for AH sample

(*) : non détecté ; SDr : Écart type de répétabilité estimé lors de la validation interne de la méthode, niveau de l'échantillon AH

Table VIII - Coumarins and derivatives assayed by HPLC (mg/l)**Coumarines et dérivés dosés par HPLC (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
scopoletin	*	0.151	0.186	0.187	0.183	0.113	0.002
aesculin	*	*	*	*	*	*	*

(*) : not detected ; SDr : Repeatability standard deviation estimated during single-laboratory validation, level for AH sample

(*) : non détecté ; SDr : Écart type de répétabilité estimé lors de la validation interne de la méthode, niveau de l'échantillon AH

tic aldehydes were degraded in the following decreasing order of importance: coniferaldehyde, sinapaldehyde, vanillin and syringaldehyde;

- the higher the temperature, the lesser the guaiacyl/syringyl ratio, except at very high temperatures.

4) Other volatile phenols

The assay method used was not efficient to assay syringylated forms. These forms were present and in greater concentrations than the guaiacyl forms (CHATONNET, 1995 ; PUECH and MAGA, 1993), and their concentrations paralleled those of the lignin derivatives (cf. III.3.3.). The new spirit which we used already contained all of the volatile phenols assayed (table VI). Unheated wood mainly released eugenol. Whatever the heating temperature, the quantities of 4-ethylphenol released by the wood were very low. As the heating temperature increased, there was an increase in the levels of all the other volatile phenols. At the highest temperature, eugenol was partially degraded.

5) Furanic aldehydes

Unheated oak wood released hardly any furanic aldehydes. The levels in the unheated pilot barrel were identical to those in new spirit (table VII). Heating led to the formation of furanic aldehydes by thermal degradation of hemicelluloses.

6) Coumarins

Even the lowest heating temperatures led to an increase in the levels of scopoletin (table VIII), while the highest temperature led to partial degradation of this compound.

7) Sugars and polyols

Many sugars and polyols were released by the oak wood into the spirit (table IX). According to the temperature, there were two types of behavior: for D-xylose, arabinose, quercitol and L-rhamnose, there was an increase and then a decrease at higher temperatures; for 1,2,3-propanetriol, fructose, myo-inositol and saccharose, there was a decrease and then an increase.

8) Methyl octalactones

Levels of methyl octalactones increased as heating increased. However, at the highest temperature, degradation began to occur (table X).

9) Fatty acids

New wood released large quantities of acetic acid and appreciable quantities of propanoic acid, with levels continuously increasing as temperature increased (table XI). The long chain fatty acids released by the wood behaved very differently. On the one hand, for hexadecanoic acid and poly-unsaturated C18 acids such as linoleic and linolenic acid, there was first a decrease and then an increase at higher temperatures. On the other, oleic acid levels (C18 unsaturated in one step) increased and then decreased at very high temperatures. The levels of ethyl esters corresponding to the above-mentioned fatty acids did not follow the same pattern, probably because their balance was not yet reached. For example, there was no noticeable change in levels of ethyl acetate or ethyl hexadecanoate (table XII).

Table IX - Sugars and polyols assayed by silylation (mg/l)**Sucres et polyols dosés par silylation (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
lactic acid	5.79	6.50	6.90	6.70	7.70	8.50	0.26
1,2,3-propanetriol	*	20.49	15.48	12.76	18.03	16.06	0.23
erythritol	*	*	*	*	*	*	
arabinitol	*	1.30	0.94	0.75	1.02	0.63	0.05
D-xylose	*	3.67	3.48	6.37	9.30	8.30	0.76
arabinose	*	11.26	23.48	25.53	15.57	9.37	2.35
quercitol	*	41.80	47.00	51.50	48.50	33.80	1.79
L-rhamnose	*	0.80	0.95	1.42	1.49	1.41	0.24
fructose	*	42.00	11.00	9.00	38.00	84.00	1.78
galactose	*	3.62	1.92	3.77	6.00	7.81	0.45
glucose	*	71.00	19.00	18.00	75.00	170.00	3.22
myo-inositol	*	9.12	5.55	5.31	9.82	12.53	0.17
saccharose	*	32.00	18.00	16.00	37.00	53.00	0.30
sorbic acid	*	*	*	*	*	*	
ethylene diglycol	*	*	*	*	*	*	
D-glucitol	*	*	*	*	*	*	

(*) : not detected ; SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample

X(*) : non détecté ; SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH

Table X - Methyl octalactones (mg/l)**Méthyl octalactones (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
trans	*	*	0.069	0.079	0.114	0.116	0.006
cis	*	0.684	0.923	1.076	1.314	1.251	0.004

(*) : not detected ; SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample

(*) : non détecté ; SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH

10) Other compounds

Oakwood did not release any appreciable quantities of higher alcohols, esters of higher alcohols, terpenes or C13 norisoprenoids (tables XIII, XIV and XVII). On the other hand, there was a clear contribution of ethyl formate, probably in the form of methanoic acid then esterified with ethanol (table XV). As for acetic acid, the quantities increased continuously as heating increased.

New wood also released the following compounds:

- benzaldehyde (table XVI);
- ethyl furoate (table XV) and probably 2-furoic acid;
- diethyl butanedioate in the form of butanedioic acid;
- 1,1,3-triethoxypropane (table XVI).

DISCUSSION**I - VALIDITY OF PILOT BARREL AS MODEL**

The informal tasting session demonstrated similarity between Cognac spirits obtained in pilot barrels and commercial ones. For an identical maturation time, levels of oak wood compounds were higher in spirits obtained from pilot barrels than in those matured in real new barrels (CALVO *et al.*, 1992 ; PUECH and MAGA, 1993). These high levels are probably due to more rapid diffusion phenomena, since the distances in the pilot barrel are smaller than in real barrels. No oxidation phenomena were observed over a period of four months. Ethanal and 1,1-diethoxyethane levels were similar before and after aging in pilot barrels.

The first pilot barrel prototype to be designed had a wider diameter cylinder (BARBOTIN, 1997). The wood stoppers at the two ends were made out of two pieces of stave joined as the heading of a real barrel but without strips of reed. In that prototype, ethanal and 1,1-diethoxyethane levels had already evolved after three months. The joint between the two staves

Table XI - Fatty acids (mg/l)

Acides gras (mg/l)

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
acetic acid	54	91	130	143	207	285	1.4
propanoic acid	0.34	0.35	0.43	0.67	1.50	2.44	0.05
isobutyric acid	3.01	3.17	3.02	3.04	3.07	3.18	0.08
butanoic acid	0.43	0.37	0.36	0.35	0.47	0.49	0.02
isovaleric acid	1.78	1.83	1.83	1.82	1.84	1.76	0.02
pentanoic acid	*	*	*	*	*	*	
hexanoic acid	2.31	2.32	2.33	2.35	2.33	2.34	0.03
octanoic acid	8.48	8.30	8.30	8.60	8.20	7.90	0.09
decanoic acid	6.41	6.30	6.40	6.40	6.30	6.20	0.09
dodecanoic acid	2.30	2.24	2.34	2.31	2.28	2.21	0.02
tetradecanoic acid	0.41	0.44	0.45	0.43	0.44	0.49	0.02
hexadecanoic acid	1.38	5.11	4.05	3.60	6.54	9.06	0.09
octadecanoic acid	0.33	0.31	0.28	0.24	0.34	0.36	0.05
oleic acid	*	2.61	4.15	7.06	11.39	10.73	0.17
linoleic acid	0.30	8.70	5.07	3.80	15.12	29.99	0.10
linolenic acid	*	0.47	0.27	0.20	0.88	1.65	0.04

(*) : not detected ; SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample

(*) : non détecté ; SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH

Table XII - Ethyl esters of fatty acids (mg/l)

Esters d'éthyle des acides gras (mg/l)

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
ethyl acetate	235	214	218	220	225	210	2.0
ethyl butyrate	0.95	0.89	1.04	1.07	1.04	0.97	0.06
ethyl hexanoate	2.79	2.70	2.80	2.80	2.80	2.70	>0.01
ethyl octanoate	7.65	7.60	7.70	7.80	7.60	7.40	>0.01
ethyl decanoate	14.17	14.10	14.30	14.20	13.90	13.50	>0.01
ethyl dodecanoate	7.34	6.80	7.10	7.20	6.80	6.50	>0.01
ethyl tetradecanoate	0.90	0.84	0.91	0.91	0.83	0.79	>0.01
ethyl hexadecanoate	3.68	3.26	3.37	3.35	3.29	3.63	0.03
ethyl octadecanoate	0.47	0.30	0.38	0.38	0.31	0.33	0.01
ethyl oleate	0.67	0.78	0.72	0.70	0.79	0.97	0.01
ethyl linoleate	4.72	6.32	5.21	5.03	6.46	9.22	0.08
ethyl linolenate	1.21	1.27	1.25	1.22	1.29	1.48	0.02

SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample

SDr : Ecart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH

was probably not as tight as those of the body of a barrel because the staves are compressed during wood bending. Therefore, these findings suggest the following:

- the use of entire pieces of stave makes it possible to model only the extraction phase of the wood;

- if two jointed pieces of stave were to be used, it would be possible to model the aging of spirit in barrel more accurately by taking into consideration oxidation phenomena;

- the pilot barrels are a reliable tool for determining where the oxygen comes from, because it is possible to make the bung hole completely tight and to use whole wood or jointed wood.

II - COMPARISON OF PILOT BARRELS WITH WOOD PARTICLE EXTRACTS (SAWDUST, CHIPS)

This section deals with the advantages of pilot barrels in relation to sawdust and chip extracts.

Studies on the composition of wood consist in reducing the wood to different sized particles such as saw-

Table XIII - Alcohols (mg/l)**Alcools (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
methanol	292	264	271	276	281	273	2.4
butan-2-ol	*	*	*	*	*	*	
propanol	241	236	240	239	237	233	1.9
isobutanol	993	980	998	992	982	971	7.7
2-propenol	*	*	*	*	*	*	
butanol	2.7	2.6	2.7	2.5	2.6	2.5	0.03
2-methylbutanol	604	607	614	608	601	602	4.6
3-methylbutanol	2026	2039	2057	2041	2015	2022	15.3
hexanol	9.7	9.9	9.8	9.8	9.7	9.9	0.12
(Z)-3-hexenol	1.9	1.9	2.1	1.9	1.8	1.9	0.04
2-phenylethanol	15.2	15.7	14.6	14.3	13.6	15.6	0.21
heptan-2-ol	0.21	0.21	0.21	0.20	0.20	0.19	>0.01
octanol	0.24	0.24	0.24	0.24	0.25	0.25	>0.01
decanol	0.06	0.07	0.06	0.06	0.06	0.06	>0.01
dodecanol	0.03	0.04	0.04	0.04	0.04	0.04	>0.01
tetradecanol	0.21	0.20	0.21	0.22	0.22	0.21	>0.01
Total higher alcohols (1)	3863	3862	3909	3880	3835	3828	25.45

(*) : not detected ; SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample ; (1) : 2-methylbutanol +3- methylbutanol + isobutanol + propanol ; (*) : non détecté ; SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH ; (1) : 2-methylbutanol +3- methylbutanol + isobutanol + propanol

Table XIV - Esters of higher alcohols (mg/l)**Esters d'alcool supérieur (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
3-methylbutyl acetate	11.14	10.75	10.82	11.03	10.87	10.63	0.11
hexyl acetate	0.39	0.39	0.39	0.39	0.39	0.38	>0.01
(Z)-3-hexenyl acetate	0.05	0.05	0.05	0.05	0.05	0.05	>0.01
3-methylbutyl octanoate	0.38	0.38	0.38	0.38	0.37	0.37	>0.01
isobutyl decanoate	0.21	0.21	0.21	0.20	0.20	0.19	>0.01
2-phenylethyl acetate	1.51	1.42	1.44	1.46	1.44	1.42	>0.01
3-methylbutyl decanoate	1.05	1.03	1.04	1.04	1.02	1.00	>0.01
3-methylbutyl dodecanoate	0.47	0.48	0.51	0.51	0.49	0.47	>0.01
2-phenylethyl octanoate	0.04	0.04	0.04	0.04	0.04	0.04	>0.01

SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample

SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH

Table XV - Ethyl esters (mg/l)**Esters d'éthyle (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
ethyl formate	1.4	1.8	3.5	7.0	13.2	13.5	0.27
ethyl lactate	96	100	95	94	91	99	0.88
diethyl butanedioate	0.46	0.47	0.47	0.48	0.49	0.54	>0.01
ethyl furoate	0.23	0.23	0.23	0.26	0.28	0.29	>0.01

SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample

SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH

Table XVI - Aldehydes and acetals (mg/l)**Aldéhydes et acétals (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
ethanal	13	11	10	9	10	12	0.43
isobutanal	7.5	6.4	5.8	5.5	5.4	5.5	0.26
1,1-diethoxyethane	27	25	27	28	29	26	0.38
2-propenal	*	*	*	*	*	*	
1,1-diethoxyisobutane	9.90	9.14	8.91	8.95	8.92	8.60	0.09
1,1,3-triethoxypropane	0.43	0.49	0.70	0.73	0.58	0.47	0.02
benzaldehyde	0.47	0.48	0.47	0.49	0.52	0.52	>0.01

(*) : not detected ; SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample

(*) : non détecté ; SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH

Table XVII - Terpenes and C13 norisoprenoids (mg/l)**Terpènes et C13 norisoprenoïdes (mg/l)**

Compound	New spirit	NH	LH	AH	SH	VSH	SDr
(Z)-linalool oxide	0.11	0.11	0.12	0.12	0.13	0.12	>0.01
(E)-linalool oxide	0.10	0.09	0.10	0.09	0.09	0.09	>0.01
linalool	0.32	0.32	0.32	0.32	0.32	0.32	>0.01
alpha terpineol	0.14	0.14	0.14	0.14	0.14	0.14	>0.01
(S)-(+)-trans-nerolidol	0.69	0.68	0.68	0.68	0.67	0.66	>0.01
vitispiran 1	0.19	0.20	0.19	0.19	0.19	0.18	>0.01
vitispiran 2	0.18	0.18	0.18	0.19	0.18	0.18	>0.01
trimethylhydronaphthalene	0.11	0.11	0.11	0.11	0.11	0.11	>0.01
B-damascenone	0.26	0.25	0.26	0.26	0.25	0.24	>0.01

SDr : Repeatability standard deviation, chemical analysis, 5 replications for AH sample ;

SDr : Écart type de répétabilité du dosage, 5 répétitions sur l'échantillon AH

dust or chips, macerating them in a liquid such as hydroalcoholic solution or methanol, separating the liquid phase from the wood particles, and analyzing the chemical composition of the liquid solution containing wood extractives. Working with sawdust offers the following advantages. First, using the same quantity of wood, the results are more reproducible. For example, if a maceration test is reproduced, very similar results are obtained. Moreover, it is possible to work with very small quantities of wood. Finally, the maceration time may be reduced because the area of contact between the wood and the liquid is high. However, particle size has a direct impact on the sensory qualities of the extract and on the composition of the extractives. The smaller the particles, the lower the maximum sensory quality compared with that obtained with barrels. When sawdust is used, tasters detect "dusty" notes. The smaller the particles, the better some compounds are extracted, e.g. ellagitannins. This effect of particle size is due to the heterogeneity of the wood; the finer the particles, the greater the difference to the structure of real wood.

Maceration/extraction time also plays an important role mainly for the bound compounds that are extractible after hydrolysis. For example, with 10-day mace-

ration of chips (1 x 0.2 x 0.3), we observed a continuous decrease in levels of acetic acid and linoleic acid according to the temperature of treatment (different durations at thermostat 8). In pilot barrels, the opposite phenomenon was found for acetic acid, while linoleic acid behaved in a more complex manner. These discrepancies may be due to the following reasons:

- when small wood particles are used, the acetic acid released by heating becomes volatile, whereas with staves, the acid formed inside the wood is retained by the structure of the wood;

- the acetic acid and linoleic acid extracted during maceration are the most accessible forms, while the combined forms are much less extracted;

- the most accessible forms are probably more sensitive to the action of heat.

The pilot barrels in which pieces of stave were used produced spirits that were more similar to the spirits obtained in real barrels than those obtained by maceration with wood particles.

III - IMPACT OF HEATING

The impact of heating on the organoleptic characteristics and composition of wood extractives is discussed below.

1) Tasting

Our results are in agreement with those of ARTONAJA *et al.* (1990), i.e. low heating temperatures gave more flowery, fruity notes whereas higher temperatures led to vanilla notes which were highly appreciated by the tasters. LAVERGNE *et al.* (1990) also obtained comparable data, i.e. high temperature leading to toasted notes and low temperature providing finesse and lightness. Very high temperatures were detrimental, leading to the appearance of «fungus», «dusty».

2) Tannins and derivatives

In agreement with the findings of PUECH *et al.* (1996), ellagitannins were only slightly extracted in pilot barrels. Gallic acid levels decreased as heating temperatures increased, probably due to its partial degradation when heating (RABIER and MOUTOUNET, 1990 ; CHATONNET, 1995 ; GIMENEZ MARTINEZ and LOPEZ GARCIA, 1996). With regard to ellagic acid, the decrease we observed as temperature increased is in disagreement with previous findings (RABIER and MOUTOUNET, 1990 ; CHATONNET, 1995). It is unlikely that this decrease was due to degradation since ellagic acid is only slightly heat-sensitive (CHATONNET, 1995). MOSEDALE and FORD (1996) obtained higher ellagic acid levels after heating for 60 minutes and then a decrease after 120 minutes.

3) Lignin derivatives

Levels of lignin derivatives were similar to those previously published (NOMDEDEU and LÉAUTÉ, 1988b ; RABIER and MOUTOUNET, 1990 ; CHATONNET, 1995 ; GIMENEZ MARTINEZ and LOPEZ GARCIA, 1996 ; CADAHIA *et al.*, 2001).

4) Furanic aldehydes

For furanic aldehydes, levels increased continuously as heat increased, in agreement with previous findings (NOMDEDEU and LÉAUTÉ, 1988a and b ; RABIER and MOUTOUNET, 1990 ; CHATONNET, 1995 ; CHATONNET *et al.*, 1996).

5) Methyl octalactones

The increase in methyl octalactones is in agreement with previous findings (NOMDEDEU and LÉAUTÉ, 1988b ; MAGA, 1989 ; CHATONNET, 1995).

6) Coumarins

Unlike MOSEDALE and FORD (1996), we found an increased level of scopoletin at lower temperatures and then a decrease at higher temperatures. However, CADAHIA *et al.* (2001) found that aesculetin levels varied after heating according to the type of wood. These findings suggest that scopoletin exists in combined forms.

7) Fatty acids

First, glyceride forms of the wood were hydrolyzed; second, the fatty acids released were again esterified, usually with the ethanol of the spirit. The glyceride forms are probably not the only forms of combined fatty acids. In fact, compared to fatty acids, there were fewer moles of glycerol (1,2,3-propanetriol). For certain fatty acids and in relation to the heating temperature, levels decreased and then increased, a behavior probably due to two concomitant phenomena: thermal degradation of the most extractable forms at the lowest temperatures; thermal degradation of the less accessible non-extractable combined forms at higher temperatures.

8) Sugars and polyols

Certain sugars behaved like the fatty acids.

9) Other compounds

CADAHIA *et al.* (2001) assayed furoic acid in heated and unheated wood, and found that its levels increased after heating. Methanoic acid, acetic acid and propanoic acid are small molecules which are likely to be released during degradation of the more complex forms.

CONCLUSION

This study demonstrates the impact of the oak wood heating on the composition and sensory aspects of Cognac spirits. Although we studied several compounds, many of the volatile compounds having an impact on aroma were not assayed, particularly those providing the notes «fungus» and «dusty» that are found for oak wood heated at a high temperature. Olfactometry would be a useful tool to study these volatile aromatic compounds. Pilot barrels filled with a hydro-alcoholic solution would make it possible to differentiate the contribution of the wood from that of new spirit, and would facilitate the identification of compounds and olfactometric analysis. The results obtained by the tasting panel validated the relevance of the pilot barrel model. Therefore, we conclude that such barrels are a useful tool for studying certain fac-

tors associated with wood and for continuing pilot experimentation beyond the stage of new spirit.

BIBLIOGRAPHY

- ARTAJONA J., BARBERO E., LLOBET M., MARCO J. and PARENTE F., 1990. Influence du bousinage de la barrique sur les qualités organoleptiques des brandies vieillies en fûts de chêne. In : *Les eaux-de-vie traditionnelles d'origine viticole*. BERTRAND A., Lavoisier ed., Paris, p. 197-205.
- BARBOTIN A., 1997. Simulation expérimentale de «l'interface» fût. Rapport de stage, Institut National des Sciences Appliquées de Toulouse.
- BLOUIN J., 1972. Étude des conditions optimales pour la détermination des composés phénoliques totaux par le réactif de Folin-Ciocalteu. *Connaissance de la Vigne et du Vin*, **6**, 405-413.
- CADAHIA E., MUNOZ L., FERNANDEZ DE SIMON B. and GARCIA-VALLEJO M.-C., 2001. Changes in low molecular weight phenolic compounds in Spanish, French, and American oak woods during natural seasoning and toasting. *J. Agricultural Food Chemistry*, **49**, 1790-1798.
- CALVO A., CAUMEIL M. et PINEAU J., 1992. Extraction des polyphénols et des aldéhydes aromatiques pendant le vieillissement du Cognac, en fonction du titre alcoolique et du «degré d'épuisement» des fûts. In : *Elaboration et connaissance des spiritueux*. R. CANTAGREL, BNIC ed., Cognac ; Lavoisier ed., Paris, p. 562-566.
- CANAS S., GRAZINA N., BELCHIOR A.P., SPANGER M.I. and DE SOUSA R.B., 2000. Modelisation of heat treatment of Portuguese oak wood (*Quercus pyrenaica* L.). Analysis of the behaviour of low molecular weight phenolic compounds. *Ciencia Tec. Vitiv.*, **15**, 75-94.
- CANTAGREL R., 1986. Application de l'analyse multidimensionnelle à la caractérisation des Cognacs par rapport aux autres eaux-de-vie de vin et alcools de vin. In : *XIX Congrès International de la Vigne et du Vin*. 24-28 novembre 1986. Santiago, Chili.
- CANTAGREL R., MAZEROLLES G., VIDAL J.-P., GALY B., BOULESTEIX J.-M., LABLANQUIE O. et GASCHET J., 1992. Evolution analytique et organoleptique des eaux-de-vie de Cognac au cours du vieillissement. 1^{ère} partie : Incidence des techniques de tonnellerie. In : *Élaboration et connaissance des spiritueux*. R. CANTAGREL, BNIC ed., Cognac, Lavoisier ed., Paris, p. 567-572.
- CHATONNET P. 1995. Influence des procédés de tonnellerie et des conditions d'élevage sur la composition et la qualité des vins élevés en fûts de chêne. Thèse n° 338, U.F.R. Institut d'Oenologie, Bordeaux II, France.
- CHATONNET P., CUTZACH I., PONS M. et DUBOURDIEU D., 1996. Monitoring toasting intensity of barrels by chromatographic analysis of volatile compounds from toasted oak wood. *J. Agricultural Food Chemistry*, **47**, 4310-4318.
- FEUILLAT F., PERRIN J.R. et KELLER R., 1994. Simulation expérimentale de l'interface tonneau: mesure des cinétiques d'imprégnation du liquide dans le bois et d'évaporation de surface libre. *J. Int. Sci. Vigne et Vin*, **28**, 227-245.
- FEUILLAT F., MOIO L., GUICHARD E., MARINOV M., FOURNIER N. and PUECH J.-L., 1997. Variation in the concentration of ellagitannins and methyl octalactones extracted from oak wood (*robur*, *petraea*) under model wine cask conditions. *American J. Enology Viticulture*, **48**, 509-515.
- GIMENEZ MARTINEZ R. and LOPEZ GARCIA S.H., 1996. Influence of wood heat treatment, temperature and maceration time, on vanillin, syringaldehyde and gallic acid contents in oak wood and wine spirit mixtures. *American J. Enol. Vitic.*, **47**, 441-446.
- LAVERGNE J., OLIVIER J., THOMAS Y. et RAFFIER C., 1990. Origine géographique des grumes - bousinage et gestion des fûts neufs- incidence sur la composition des Cognacs. In : *Les eaux-de-vie traditionnelles d'origine viticole*. BERTRAND A., Lavoisier ed., Paris, p. 206-212.
- LEHTONEN M., 1980. Gas chromatographic determination of phenols as 2,4-dinitro phenyl ethers using glass capillary columns and ECD. *J. Chromatography*, **202**, 413-421.
- MAGA J., 1989. Formation and extraction of *cis*- and *trans*- β -méthyl- γ -octolactone from *Quercus alba*. In : *Distilled Beverage Flavour, recent developments*. PIGGOTT J.R. and PATERSON A., Ellis Horwood, Chichester ed., New York, p. 171-176.
- MOSEDALE J.R. and FORD A., 1996. Variation of the flavour and extractives of European oak wood from two French forests. *J. Science Food Agric.*, **70**, 273-287.
- NOMDEDEU L. et LEAUTE R., 1988a. Brûlage des barriques de chêne et qualité des vins de Médoc. *Le Progrès Agricole Viticole*, **21**, 505-514.
- NOMDEDEU L. et LEAUTE R., 1988b. Brûlage des barriques de chêne et qualité des vins de Médoc. *Le Progrès Agric. Vitic.*, **21**, 552-555.
- PENG S., SCALBERT A. and MONTIES B., 1991. Insoluble ellagitannins in *Castanea sativa* and *Quercus petraea* woods. *Phytochemistry*, **30**, 775-778.
- PIGGOTT J.R., CONNER J., PATERSON A. and CLYNE J., 1993. Effects on Scotch whisky composition and flavour of maturation in oak casks with varying histories. *Int. J. Food Sci... Technology*, **28**, 303-318.
- PUECH J.-L. and MAGA J., 1993. Influence du brûlage du fût sur la composition des substances volatiles et non volatiles d'une eau-de-vie. *Rev. CEnol.*, n°**70**, 13-16.

- PUECH J.-L., FEUILLAT F., MOSEDALE J.R. and PUECH C., 1996. Extraction of ellagitannins from oak wood of model casks. *Vitis*, **35**, 211 – 214.
- RABIER P. et MOUTOUNET M., 1990. Évolution d'extractibles de bois de chêne dans une eau-de-vie de vin. Incidence du thermotraitement des barriques. *In : Les eaux-de-vie traditionnelles d'origine viticole*. BERTRAND A., Lavoisier ed., Paris, p. 220-230.
- SARNI F., MOUTOUNET M. et PUECH J.-L., 1990. Composés phénoliques extractibles de copeaux de bois de chêne. *In : Les eaux-de-vie traditionnelles d'origine viticole*. BERTRAND A., Lavoisier ed., Paris, p. 231-239.
- VIDAL J.-P., LABLANQUIE O. et CANTAGREL R., 1994. Détermination des acides gras volatils dans les boissons spiritueuses. *FV OIV* n° 972.
- VIRIOT C., 1995. Polyphénols et polyosides du bois de chêne. Contribution au vieillissement des Cognacs en fût. *Thèse* Institut National Agronomique de Paris-Grignon, France.
- WITHER S.J., PIGGOTT J.R., CONNER J.M. and PATERSON A., 1995. Comparison of scotch malt whisky maturation in oak miniature casks and American standard barrels. *J. Inst. Brew.*, **101**, 359-364.

Manuscrit reçu le 7 avril 2003 ; accepté pour publication le 30 juin 2003