

Impact of the Diamant® process on the organoleptic characteristics of cork powder

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TECHNICAL

Introduction

Cork has been used for many years as a closure for wines and spirits. Thanks to its exceptional and as-yet unmatched physical properties, cork remains an essential solution for the optimal preservation of wines.

However, consumers are increasingly seeking out products with “zero defects”, and this is forcing the entire cork industry to develop technical solutions in order to propose completely homogenous closures, both in terms of their physical properties and the guarantee that they are free of any organoleptic deviations. A great number of research studies have focused on eradicating «moldy tastes and odors» associated with the presence of molecules of the chloro-

anisole family, in particular 2,4,6-trichloroanisole. A certain number of cork closure suppliers now offer innovative processes aimed at providing a solution to this “moldy taste” taint.

In conjunction with the Supercritical Fluids and Membranes Laboratory of Pierrelatte (CEA – French Atomic Energy Commission), Oeneo Bouchage has thus developed a supercritical CO₂ extraction process (Diamant® process), which eliminates the targeted undesirable organic compounds with the greatest possible extraction efficiency: the chloroanisoles and their precursors (chlorophenols).

The principle of supercritical fluid extraction is described in the article “Supercritical fluids: An innovation for cork closures – Part 1/2” (1). The steps for validating the Diamant® process are presented in the article: “Supercritical fluids: An innovation for cork closures – Part 2/2” (2).

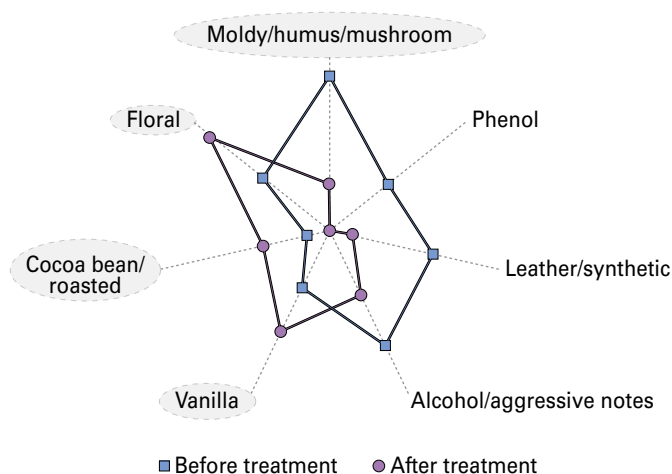
These articles confirm that residual releasable 2,4,6-TCA results for cork treated on an industrial scale are systematically below the limit of quantification of the analytical me-

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(1) Lumia Guy and Perre Christian, Les fluides supercritiques – une innovation au service du bouchon de liège – partie 1/2. Revue des Œnologues n° 117 spécial, 2005.

(2) Lumia Guy and Aracil Jean-Marie, Les fluides supercritiques – une innovation au service du bouchon de liège – partie 2/2. Revue des Œnologues n° 118, 2006.

■ Figure 1: Sensory profiles of cork powder macerates before and after treatment using the Diamant® process. The circled descriptors indicate a significant difference (95%) using the chi-square test.



■ Figure 2: Results of quantitative descriptive sensory analysis (on a scale of 10) on a wine with different enrichments from the liquid (2a) and solid (2b) fractions of the Diamant® process extract.

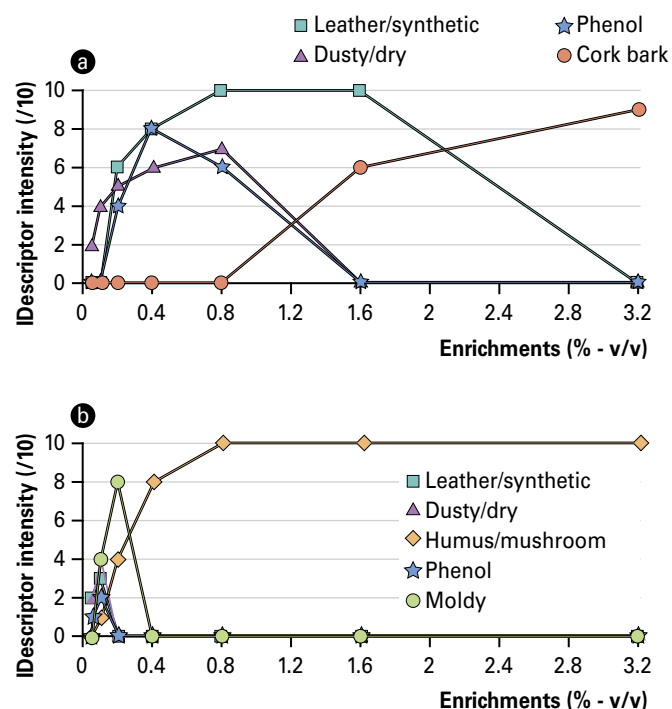


Table 1: Inventory of compounds identified in the liquid and solid fractions of the Diamant® process.

Compounds	Method	m/z	Extract	
			Liquid fraction	Solid fraction
2-propanone	MS	43-58	D	
2-butenal	MS	41-69-70	D	
3-buten-2-one,3-methyl	MS	43-69-84	D	
pentanal	MS	41-44-57-58	D	
butanal,3-methyl-	MS	44-58-71-86	D	
acetic acid	MS	43-45-60	D	
furan,tetrahydro-2,5-dimethyl	MS	41-43-56-85	D	
2-propanone-1-hydroxy	MS	43-74	D	
1-pentanol	MS	42-55-70	D	
2-buten-1-ol,3-methyl or 3-buten-2-ol,2-methyl	MS	41-53-71-86	D	
2-butenal-3-methyl	MS	41-55-84	D	D
2-hexanone or 3-hexanone	MS	43-58	D	D
hexanal	MS, GC	44-56-57	D	D
2-butanone, 4-hydroxy	MS	43-70-88	D	D
furfural	MS	39-95-96	D	
2-furanmethanol or 3-furanmethanol	MS	53-81-97-98	D	D
2-hexanone,3,4-dimethyl	MS	43-72	D	D
cyclohexene,1-acetyl	MS	81-43-109	D	D
cyclopentene, 1,2-dimethyl-4methylene	MS	77-91-93-108	D	D
2-heptanone	MS	43-58	D	D
heptanal	MS, GC	44-55-70	D	D
cyclopentene, 1-ethenyl-3-methylene	MS	91-106	D	
2-acetylfuran	MS	95-110	D	
2(5H)-furanone	MS	55-84	D	
phenol, dimethyl (2,5 or 2,4 ou 3,4)	MS	107-122	D	D
2,5-hexanedione	MS	43-99	D	D
2-heptenal	MS, GC	41-55-83-70		D
benzaldehyde	MS	77-105-106	D	D
6-hepten-1-ol	MS	54-67-81	D	
cycloheptanol	MS	57-68-81-96	D	
1-heptanol	MS	43-56-70	D	D
1-octen-3-ol	MS, GC	43-57-72	D	D
5-hepten-2-one-6-methyl	MS	43-55-69-108	D	
beta-myrcene	MS	41-69-93		D
5-hetpen-2-ol, 6-methyl	MS	41-69-95-110	D	
decane	MS	43-57-71-85		D
octanal	MS, GC	41-57-84-69	D	D
benzene,1,4-dichloro	MS	111-146-148	D	
1H-pyrrole-2-carboxaldehyde	MS	66-94-95	D	
benzene,1- methyl-3-(1-methylethyl)	MS	91-119-134		D
limonene	MS, GC	68-93-107-136	D	D
1-hexanol,2-ethyl	MS,GC	41-57-70-83	D	
2,5 furandione,3,4-dimethyl	MS	54-82-126		D
benzyl alcohol	MS	77-79-107-108	D	D
benzene alkyl (ethyl,dimethyl)	MS	91-119		D
2-octenal	MS,GC	41-55-70-83		D
benzaldehyde,4-methyl or (2-methyl)	MS	91-119-120	D	D
benzene alkyl (ethyl,dimethyl)	MS	91-119		D
p-cresol (phenol-4-methyl)	MS,GC	77-107-108	D	T
benzene alkyl (ethyl,dimethyl)	MS	91-119		D
guaïacol (phenol, 2-methoxy-)	MS,GC	81-109-124	D	T
benzene,1-methyl-4-(1-methylethyl)	MS	91-119-134	D	D
furan,3-[4-methyl-3-pentenyl]	MS	41-69-81-150		D
undecane	MS	43-57-71-85		D
linalool	MS,GC	55-71-93-121	D	
6-methyl-3,5 heptadiene-2-one	MS	43-79-81-109	D	D

thod (< 0.5 ng/L) and that the organoleptic performance of the Diamant® closure is excellent (AWRI – 36 months).

Throughout the validation phase of this process and during the comparative tasting tests conducted by dozens of actual and prospective customers worldwide, Oeneo Bouchage has found that the wines capped with the Diamant® closure are characterized by greater organoleptic cleanness, better fruitiness and greater crispness (Wine Estate, special edition 2005).

Following these results, Oeneo Bouchage launched a research program in early 2005, with the goal of verifying whether the organoleptic cleanness of wines corked with Diamant® closures is solely correlated with the eradication of 2,4,6-trichloroanisole or with the extraction of other aroma compounds present in the cork material.

The work presented in this article summarizes the initial results from this study.

Materials and Methods

Materials analyzed

To accentuate any differences in terms of sensory descriptors and analytical results, we made the choice to work directly on cork powder and on the corresponding extracts (recovered at the separator outfeed after CO₂ release).

Over a duration of 2 months, 5 production batches of cork powder (before and after treatment with the Diamant® process) were sampled randomly in order to work on the most diverse sampling of cork powder possible. The releasable 2,4,6-TCA contents are between 10 and 15 ng/L for the untreated powder and are less than the limit of quantification for the treated powder.

Since the Diamant® process is now industrialized, we had the opportunity to acquire extracts resulting from the extraction of compounds using supercritical CO₂ on several batches of cork (6 metric tons total). These extracts are highly concentrated, which enabled us to have access to compounds which are naturally present in the cork material at very low concentrations or in trace amounts. The collected extracts are present in the form of a liquid emulsion with a slight supernatant layer. The liquid and solid fractions are separated by membrane filtration and then analyzed individually.

Analysis of cork powders

Sensory approach

Comparative sensory analyses were conducted on cork powder macerates before and after treatment:

- By two independent tasting panels,
- In different media (wine, aqueous ethanol solution, 12.5% v/v, acidified to pH 3.5),
- Under different storage conditions in terms of time and temperature (10 days at 40°C – 15 days at ambient temperature).

The objectives are as follows:

1. Compare the sensory profiles before and after treatment,
2. Reveal the most characteristic organoleptic descriptors,
3. Measure the intensity of those descriptors on a scale of 0 (no defect) to 3 (saturation threshold during tasting).

Analytical approach

The cork powders were analyzed by different complementary sample preparation techniques (headspace-solid phase micro-extraction, liquid-liquid extraction, solid phase extraction, etc.).

The samples were analyzed (qualitative approach) by gas

■ **Table 1 (cont.): Inventory of compounds identified in the liquid and solid fractions of the Diamant® process.**

Compounds	Method	m/z	Extract	
			Liquid fraction	Solid fraction
nonanal	MS,GC	57-82-95-98		D
maltol	MS	55-71-126	D	
phenyl ethyl alcohol	MS	65-91-92-122	D	
hexanoic acid	MS	41-60-73-87	D	
benzene alkyl	MS	91-119		D
benzene alkyl	MS	91-119		D
benzyl alcohol, o-methyl	MS	91-104-107-122	D	D
benzene, 1,2-dimethoxy	MS	77-95-123-138	D	
2-nonenal	MS,GC	43-55-70-83		D
phenol,alkyl	MS	107-121-150	D	
benzoic acid	MS	51-77-105-122	D	
1-nonanol	MS	43-56-70		D
p-cresol (phenol-2-methoxy-4-methyl)	MS	95-123-138	D	
octanoic acid	MS, GC	43-60-73-85-101	D	T
4-methyl-acetophenone	MS	91-119-134	D	
alpha terpineol	MS	59-93-121-136	D	D
octanoic acid, ethyl ester	MS	41-57-88-101-127	D	
dodecane	MS	43-57-71-85		D
decanal	MS,GC	43-57-70-82	D	D
2,5-cyclohexadiene-1,4-dione,2,3,5-trimethyl	MS	79-107-122-150	D	
ethanol,2-phenoxy	MS	77-94-138	D	
2,6 octadien-1-ol,3,7-dimethyl	MS	41-69-154	D	D
benzothiazole	MS	69-82-108-135	D	
bicyclo [2,2,1] hept-2-ene,1,7,7-trimethyl (bornylene)	MS	93-108-121-136	D	
anisole, isopropyl,methyl (isomer)	MS	149-164	D	D
anisole,isopropyl,methyl (isomer)	MS	149-164	D	D
2-oxabicyclo[2,2,2] octan-6-ol,1,3,3-trimethyl	MS	43-71-108-126	D	
bicyclo[2,2,1]heptane-2,5-dione,1,7,7-triméthyl	MS	83-109-123-166	D	
2,6 octadienal,3,7-dimethyl	MS	41-69-84-152	D	D
1-dodecene	MS	41-55-69-83	D	
nonanoic acid	MS	60-73-115-129	D	T
2-undecanone	MS	43-58-71		D
benzene methanol,4-(1-methylethenyl) (p-cymene-7-ol)	MS	105-119-135-150	D	
nonanoic acid, ethyl ester	MS	88-101-141	D	
4-decenoic acid,methyl ester	MS	55-69-74-110		D
phenol-2-methoxy-4-vinyl	MS	77-107-135-150	D	
p-benzoquinone,2,3,5,6-tetramethyl	MS	93-121-136-164	D	D
benzene,1,3,5-trichloro-2-methoxy (2,4,6-trichloroanisole)	MS, GC	195-210-212	T	D
2(3H)-furanone,dihydro-5-pentyl	MS	85-	D	D
2-undecenal	MS	41-55-70-83		D
unknown sesquiterpene	MS	105-119		D
5-tetradecene	MS	55-69-83-97		D
2-dodecanone	MS	43-58-71		D
decanoic acid, ethyl ester	MS	43-73-88-101	D	
tetradecane	MS	43-57-71-85		D
2-undecanone,6,10-dimethyl	MS	43-58-71-180		D
vanillin (benzaldehyde-2-hydroxy-3-methoxy)	MS	106-109-152	D	
dodecanal	MS	43-57-82	D	
caryophyllene	MS	63-69-93-105		D
1,2-dimethoxy-3,5-dichloro-benzene	MS	128-163-191-206		D
naphthalene, 2,7-dimethyl	MS	115-128-141-156	D	
5,9-undecadien-2-one-6,10-dimethyl (geranyl acetone)	MS	41-43-69	D	D
vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol)	MS	93-125-137-154	D	
1H cycloprop[e]azulene, decahydro1,1,7- trimethyl-4-methylene	MS	105-119-161-204		D
2,5-cyclohexadiene-1,4-dione,2,6-bis(1,1-diméthylethyl)-	MS	135-177-205-220	D	

Table 1 (cont.): Inventory of compounds identified in the liquid and solid fractions of the Diamant® process.

Compounds	Method	m/z	Extract	
			Liquid fraction	Solid fraction
azulene,1,2,3,4,4a,5,6,8a-octahydro-1,4-dimethyl-7-(1-methylethenyl)	MS	105-119-204		D
unknown sesquiterpene	MS	105-119		D
cyclododecane	MS	41-55-69-83-97		D
cis[-]-2,4a,5,6,9a hexahydro-3,5,5,9-tetramethyl (1H)-benzocycloheptene	MS	105-119-133-204		D
unknown sesquiterpene	MS	105-119		D
benzene alkyl	MS	91-119	D	D
acetovallinone (phenol-2-methoxy-4-acetyl)	MS	108-123-151-166	D	
longifolene	MS	105-119-161-204		D
2H-pyran-2-one,tetrahydro-6-pentyl	MS	55-77-99-114	D	
naphtalene,1,2,4a,5,6,8a,hexahydro-4,7-dimethyl-1-(methylethyl)	MS	105-119-161-204		D
benzene,1-methyl-4-(1,2,2-trimethylcyclopentyl) (cuparene)	MS	105-119-132-202		D
naphtalene,1,2,3,4,4a,5,6,8a,octahydro-7-methyl-4-methyle-1-(methylethyl) (mururolene)	MS	105-119-161-204		D
3,5,9-undecatrien-2-one-6,10-dimethyl	MS	41-69-81-109-124	D	
1H-2-benzopyran-1-one,3,4-dihydro-8-hydroxy-3-methyl	MS	134-149-160-178	D	
1,6,10-dodecatrien-3-ol,3,7,11-trimethyl	MS	41-69-93-107		D
vanillic acid	MS	97-125-153-168	D	
unknown sesquiterpene	MS	105-119		D
dodecanoic acid	MS	60-73-129-200	D	
2,6,10-dodecatrien-3-ol,3,7,11-trimethyl	MS	41-69-93-107		D
hexadecane	MS	43-57-71-85		D
unknown sesquiterpene	MS	105-119		D
naphthalene,2,3,4,4a,5,6-hexahydro-1,4a-dimethyl-7(1-methylethyl)	MS	105-119-161-204	D	
unknown sesquiterpene	MS	105-119		D
unknown sesquiterpene	MS	105-119		D
unknown sesquiterpene	MS	105-119		D
copaene or cucubene	MS	105-119-161-204		D
unknown sesquiterpene	MS	105-119		D
syringaldehyde (benzaldehyde, 4-hydroxy-3,5-dimethoxy)	MS	139-167-181-182	D	
unknown sesquiterpene	MS	105-119		D
naphtalene,1,6,dimethyl-4-(1-methylethyl)	MS	153-168-183-198		D
heptadecane	MS	43-57-71-85		D
4-hydroxy-2-methoxycinnamaldehyde	MS	135-147-161-178	D	
2,6,10-dodecatrienal,3,7,11-trimethyl	MS	41-69-84		D
3,5-di-tert-butyl-4-hydroxybenzaldehyde	MS	191-203-219-234	D	
tetradecanoic acid	MS	43-55-60-73	D	
octadecane	MS	43-57-71-85		D
benzophenone,2,4,6-trimethyl	MS	77-147-209-223	D	
phenol,2,3,5,6-tetrachloro-4-methoxy	MS	246-247-260-262	D	
longifolenaldehyde	MS	109-135-205-220	D	
2-pentadecanone,6,10,14-trimethyl	MS	43-58-71-109		D
1-hexadecene	MS	55-69-83-97-111	D	
nonadecane	MS	43-57-71-85		D
unknown sesquiterpene	MS	105-119		D
hexadecanoic acid	MS	43-60-73-129	D	
hexadecanoic acid, ethyl ester	MS	43-88-101-157	D	
heptadecanoic acid	MS	60-73-129-270		D
1-heptadecene	MS	55-69-83-97-111		D
9,12-octadecadienoic acid	MS	55-67-81-95-110		D
9-octadecenoic acid	MS	41-55-69-83-97		D
octadecanoic acid	MS	43-57-60-73	D	
15-heptadecenal	MS	55-69-83-97		D
1-octadecene	MS	55-69-83-97-111		D
2-nonadecanone	MS	43-58-71-85-96		D
octadecanal	MS	57-69-82-96-109		D
eicosanoic acid	MS	57-73-129-312		D

chromatography coupled with mass spectrometry (internal methodologies developed by GAEA Analytic). The compounds are identified by comparison of their mass spectrum with the mass spectra in the Nist and Wiley databases, or for certain compounds, by their retention times and the mass spectra of chemical standards.

Analysis of Diamant® extracts

Sensory approach

The organoleptic impact of the extract is evaluated by enrichment of a white wine (Chardonnay) with the liquid or solid fractions (dissolved in ethanol) at different percentages (0.05 - 0.1 - 0.2 - 0.4 - 0.8 - 1.5 and 3.2% v/v). The sensory analyses were conducted by two independent tasting panels. The objectives were as follows:

1. Compare the sensory profiles of the control and overloaded white wines,
2. Reveal the most characteristic organoleptic descriptors,
3. Measure the intensity of those descriptors on a scale of 0 (no defect) to 10 (saturation threshold during tasting).

Analytical approach

The same analytical approach as above was followed on the liquid and solid fractions of the collected extracts in order to verify whether the Diamant® process can be used to extract aroma compounds other than 2,4,6-TCA.

Results and discussion

Cork powder

The results from the first tasting panel (4 enologists) on a white wine showed that the cork powder macerates had different aroma profiles before and after treatment. Before treatment, the cork macerate

has a strong aroma intensity characterized by the presence of pre-dominant corky and moldy notes.

After Diamant® treatment, the cork macerate is characterized by a much lower aroma intensity and a remarkable crispness related to the absence of corky and moldy notes, and a “much rounder and silkier mouthfeel”.

A second tasting panel (8 trained subjects) showed that in a model wine, the Diamant®-treated cork powder undergoes a complete change of its aroma profile, with:

- Greater organoleptic neutrality of the treated cork powder,
- Elimination of the moldy descriptor as well as a clear decrease in humus/mushroom – leather/synthetic – phenol and alcohol/aggressive notes.
- Better expression of floral and vanilla notes (*figure 1*).

Table 1 (cont.): Inventory of compounds identified in the liquid and solid fractions of the Diamant® process.

Compounds	Method	m/z	Extract	
			Liquid fraction	Solid fraction
5-nonadecene	MS	69-83-97-111-266		D
1,19-eicosadiene	MS	55-69-82-96		D
1-eicosanol	MS	57-69-83-97-111		D
3-eicosene	MS	57-69-83-97-111		D
docosanoic acid	MS	57-73-129-140		D
1-docosene	MS	55-97-111-308		D
1-docosanol	MS	55-97-111-308		D
1-tricosene	MS	57-83-97-111-322		D
1-tetracosanol	MS	55-97-111-336		D
squalene	MS	81-121-137-149		D

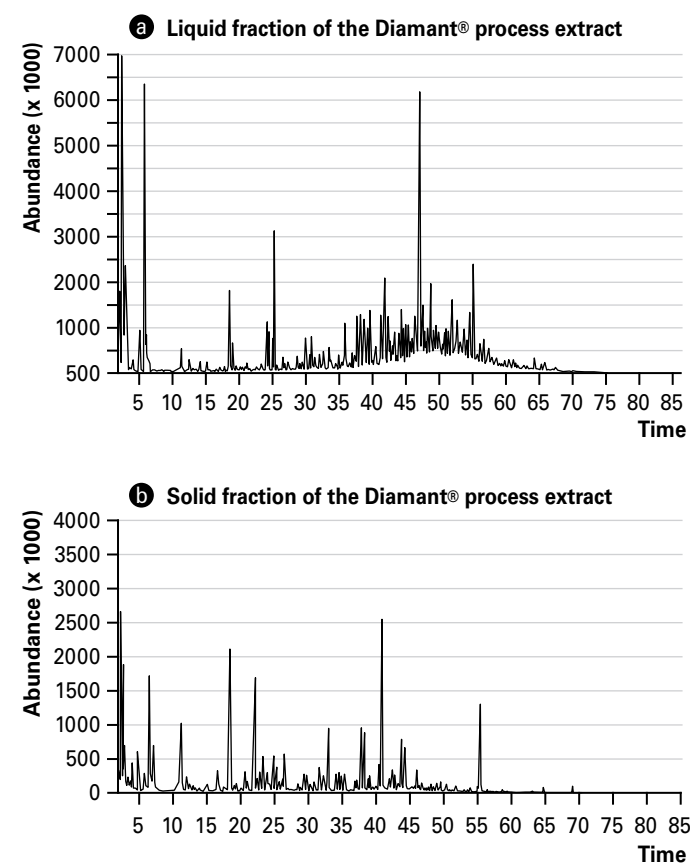
MS: identification based on the Nist, Wiley database. D: detected /T: trace.
GC: identification confirmed by the retention time and mass spectrum of the chemical standard.

The results from these two independent tasting panels are similar. They confirm the better organoleptic neutrality of the treated powder. They show that elimination of certain negative notes of the moldy, mushroom and humus type enables better expression

of other positive aroma notes that are naturally present in the cork material.

The presence of vanilla and cocoa bean/roasted notes for the Diamant®-treated cork powder is not related to heat degradation. The treatment with supercritical CO₂ occurs at low temperature (close to 50°C) and is routinely used in the food and perfume industries in order to preserve temperature-sensitive volatile compounds.

Figure 3: Examples of chromatograms (total ion current mass spectrometry) of the liquid (2a) and solid (2b) fractions of the Diamant® process extract (preparation technique: headspace – solid-phase micro-extraction).



Diamant® extracts

The results from the two independent tasting panels show a very significant change of the organoleptic profile of wines enriched with extracts, as compared with the control wine.

For the wines enriched with the liquid fraction of the extract, leather/synthetic – phenol – dusty/dry notes appear, starting with low concentrations, and their intensity increases as the percentages of enrichment increase. Nevertheless, at the highest level of enrichment, the phenol, dusty and dry descriptors are masked by the corky note, which is pre-dominant, with a very high intensity of 10/10. An aggressive note is then perceived in the mouth (*figure 2a*).

For wines enriched with the solid fraction, the dusty/dry notes evolve progressively towards a medium- to high-intensity moldy descriptor and then humus, undergrowth and mushroom notes, as the percentage of enrichment increases.

At the higher enrichment levels, the humus, undergrowth and mushroom descriptor is pre-dominant at a very high intensity (10/10) (*figure 2b*).

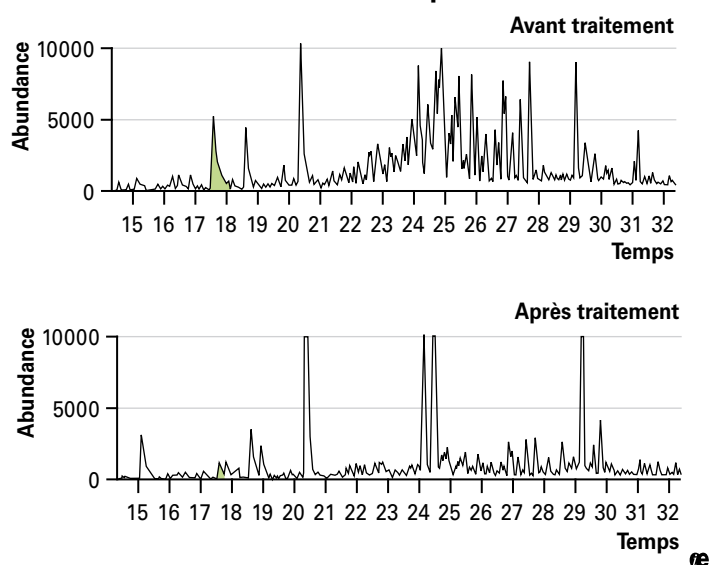
The aroma notes described during this enrichment study (synthetic/leather – dusty/dry – cork bark – moldy – humus/mushroom) are identical to those cited by the tasting panels during the organoleptic analyses conducted with non-treated cork powder macerates.

The chromatographic analyses conducted on the solid and liquid fractions of the Diamant® extract reveal the presence of more than 150 compounds, a very large number of which can be identified (*figures 3a, 3b et table 1*).

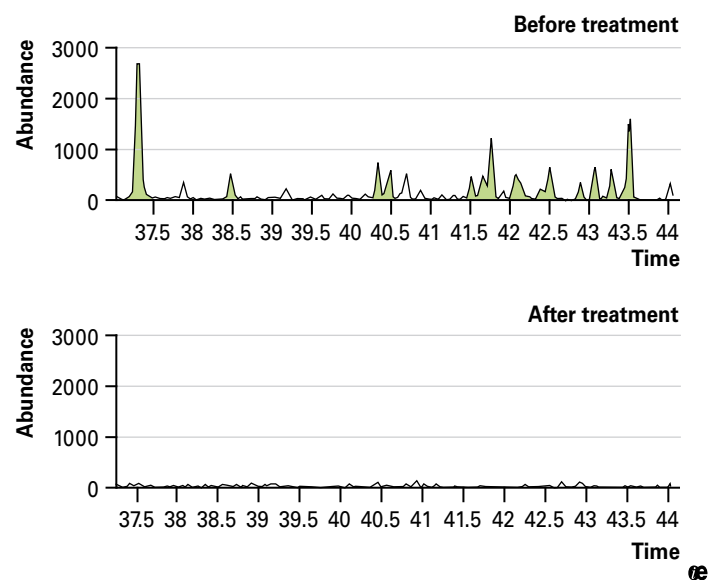
These compounds belong to various chemical families: alcohols, ketones, aldehydes, acids, esters, phenolics, anisoles, furans, furanones, pyranones; alkylbenzenes, hydrocarbons; terpenes, sesquiterpenes...

The chromatographic analyses conducted on the cork before and after treatment show differences in profiles for the chemical families cited above. As examples, the impact of the process on sesquiterpenes, methyl isopropyl anisoles (isomers) and 1-octen-3-ol is illustrated in *figures 4, 5 et 6*.

■ **Figure 4: Examples of chromatograms of 1-octen-3-ol (extracted ion mass spectrometry 57) of cork powder before and after treatment with the Diamant® process.**



■ **Figure 5: Examples of chromatograms of sesquiterpene structures (extracted ion mass spectrometry 119) of cork powder before and after treatment with the Diamant® process.**



Some of the compounds identified previously by GC-MS can be associated with the aroma notes found during this study:

- 1-octen-3-ol is associated with the humus/mushroom descriptor,
 - p-cresol; guaiacol and octanoic acid are associated with the phenol – leather – synthetic descriptors,
 - vanillin (and other derivatives) is associated with the vanilla descriptor,
 - furans are associated with the cocoa bean/roasted descriptors.
- These correlations are confirmed via GC-Sniff analyses (not described in this article).

This study clearly reveals that the Diamant® process developed for the eradication of 2,4,6-TCA from cork powder can be used to extract a very great number of other aroma compounds belonging to diverse chemical families (alcohols, ketones, aldehydes, etc.).

This extraction induces a very significant change of the sensory profile of the cork powder after treatment. The cork powder treated by supercritical CO₂ is characterized by much greater organoleptic neutrality as well as by the expression of certain positive aroma notes of the floral, vanilla and cocoa bean (roasted) type, which are naturally present in the cork material, but which are masked normally by other, less positive aroma notes (humus/mushroom, phenol – leather/synthetic, etc.).

These results offer an initial explanation for the comments from the tasting panels during comparative tests, in particular as concerns the fruitier, crisper and cleaner characters of wines corked with Diam® closures.

This study is currently being continued in order to quantify the compounds present in the cork and to evaluate their real organoleptic impact. ■

■ **Figure 6: Examples of chromatograms of methyl isopropyl anisole isomers (extracted ion mass spectrometry 149) of cork powder before and after treatment with the Diamant® process.**

