

Differentiation of the Aromas of Merlot and Cabernet Sauvignon Wines Using Sensory and Instrumental Analysis[†]

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The aromas of six Merlot and three Cabernet Sauvignon wines of the 1996 vintage from the Bordeaux region were evaluated by sensory analysis. A panel of selected enology students was trained to assess 20 attributes previously generated for these wines by enologists of Bordeaux. Using statistical methods, this 20-attribute list was reduced to a 12-attribute list. The aroma profiles of the wines of Merlot and Cabernet Sauvignon were very close. Differentiation of the wines of these two varieties was significant only for the caramel descriptor, which was rated higher in the Merlot wines. Gas chromatography/olfactometry (GC/O) and GC/MS analyses were used to detect and identify the potent odorants with the caramel odor in the two most differentiated samples for this attribute, a Merlot wine and a Cabernet Sauvignon wine. Two odorant zones with this odor resulted in identification of 4-hydroxy-2,5-dimethylfuran-3(2H)-one (HDMF) and 4-hydroxy-2(or 5)-ethyl-5(or 2)-methylfuran-3(2H)-one (HEMF). Aroma extract dilution analysis (AEDA) method showed a higher dilution factor (*FD*) for HDMF in the Merlot wine extract than in the Cabernet Sauvignon extract. The HDMF levels determined in the wines studied using a stable isotope dilution assay (SIDA) method were consistent with the results found by sensory analysis and GC/O; i.e., higher HDMF levels were present in the Merlot wines than in the Cabernet Sauvignon wines.

Keywords: *Aroma; wine; descriptors; gas chromatography/olfactometry; sensory profiles; caramel*

INTRODUCTION

Merlot and Cabernet Sauvignon wines are among the most abundant in the Bordeaux region but also in vineyards all over the world. The aroma of these wines is often described as fruity or floral with roasted, wood-smoke, and cooked meat nuances (Peynaud et al., 1980) and often as herbaceous, especially for the wines of Cabernet Sauvignon (Allen et al., 1990, 1994).

Several authors have studied the aromatic profiles of wines of many varieties, using descriptive analysis (Noble and Shannon, 1987; Francis et al., 1992; Moio et al., 1993; Cliff and Dever, 1996). The descriptive analysis technique has been applied to Cabernet Sauvignon wines (Aiken and Noble, 1984; Noble et al., 1984), but the samples used were oak-aged and, thus, the aroma profiles were influenced by the oak-derived volatile compounds. Furthermore, no comprehensive sensory descriptive analysis study of Merlot wines has previously been attempted. Thus, the objectives of the present descriptive analysis study were to describe the aroma of nonaged Cabernet Sauvignon and Merlot wines. The first step was to establish the sensory profiles of the wines of Merlot and Cabernet Sauvignon using descriptive sensory analysis. The second step was to determine the sensorial differences among the wines

of these two varieties using the sensory profiles obtained in the first step. The third step was to identify the potent odorants determining the most important sensorial differences and, finally, to quantify these compounds.

MATERIALS AND METHODS

Wines. Nine wines of 1996 vintage (six Merlot and three Cabernet Sauvignon) from different appellations of Bordeaux (Pomerol, Saint Emilion, Pauillac, Moulis, and Pessac-Léognan) were chosen for their intense and representative aromas of the corresponding varieties (Kotseridis, 1999). The wines were prepared using the same vinification technique as reported elsewhere (Kotseridis et al., 1998). The wines were sampled after the malolactic fermentation was achieved, added with a mean quantity of 40 mg/L SO₂ at bottling and stored at 10 °C prior to analysis. The samples were one year old at the time of sensory and instrumental analysis. Characteristics of the wines are summarized in Table 1. **Sensory Analysis Protocol.** All the sensory evaluations were conducted in a sensory analysis laboratory where the panelists were seated in individual testing booths. The 40-mL samples were presented in a random order in coded (with a three-digit number) tulip-shaped glasses that were covered by plastic Petri dishes. At each session 3 or 4 samples were analyzed.

Panel Training and Selection. The panel of judges consisted of 17 enology students at ENSAM (Ecole Nationale Supérieure Agronomique de Montpellier) who had been selected from a group of 30 persons on the basis of their sensorial performances (Issanchou et al., 1995). All the participants had previous experience in wine tasting, and some panelists had experience in descriptive analysis studies. The judges were trained over two weeks (in 4 sessions) to identify natural aroma standards. The aroma reference standards were those defining the selected descriptors for the wines.

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Table 1. Merlot and Cabernet Sauvignon Wines Studied by Descriptive Sensory Analysis

samples	appellation	soil	code
<i>Merlot</i>	St Emilion	clayey–chalky	ME1
	Pomerol	clayey–gravely	MP2
	Pomerol	clayey	MP3
	St Emilion	clayey–chalky	ME4
	Graves	gravely	MG5
	Moulis	clayey–gravely	MM6
<i>Cabernet Sauvignon</i>	Moulis	clayey–gravely	CSM1
	Graves	gravely	CSG2
	Pauillac	gravely	CSP3

Table 2. Attributes Used for the Descriptive Analysis by the 17-Judge Panel

plum ^a	pear	box-tree	pepper	strawberry jam
orange	peach	bell pepper	smoky	caramel
black-currant	violet	eucalyptus	leather	cacao
cherry	rose	straw	licorice	coffee

^a Attributes in bold were selected after the second reduction step and used in the final score card.

Difference Tests. Difference tests were performed for aroma only using the triangular test method, and the significance of the tests was determined from statistical tables (Larmon, 1969).

Determination of the Odor Threshold of 4-Hydroxy-2,5-dimethylfuran-3(2H)-one (HDMF) and 4-Hydroxy-2(or 5)-ethyl-5(or 2)-methylfuran-3(2H)-one (HEMF) in a Model Base Wine. Five concentrations of HDMF (10, 20, 40, 80, and 160 $\mu\text{g/L}$) and five concentrations of HEMF (5, 10, 20, 40, and 80 $\mu\text{g/L}$) were prepared in a model base wine (water/ethanol mixture, 89:11, v/v; 1 L, tartaric acid (4 g), and pH adjusted to 3.5 with K_2CO_3), from initial solutions of HDMF and HEMF in ethanol. The olfactory perception thresholds were measured using successive triangle tests. The 17-judge trained jury tasted the five concentrations from the lowest to the highest. The three samples of the triangle tests contained about 40 mL of liquid. One sample contained the target compound dissolved in the model base wine, the other samples were the model base wine. For each comparison, samples were presented in a random order. The olfactory perception threshold corresponded to the minimum concentration under which 50% of the judges failed to find the single sample containing the target compound.

Descriptive Analysis. A list of 20 selected aroma attributes (Table 2) was provided by an experienced panel of Bordeaux enologists in order to describe Merlot and Cabernet Sauvignon wines, and was used for the first step of the descriptive analysis. A first score card was established with these 20 attributes. The 17 judges scored the magnitude of each attribute on a category scale (Edwards et al., 1985; Pages et al., 1987) from 0 (no perception) to 5 (highest perception). Subsequent reductions of this list were realized during the first descriptive sessions, resulting in a 12-descriptors inventory. Divers techniques were adopted in order to reach this listing: correlation matrix and comparison of geometrical means (GM). GM is the square root of the product of the frequency quotation (F) with the relative intensity (I): $\text{GM} = (F \times I)^{1/2}$ (Dravnieks, 1982).

The selected descriptors were presented to the panel on a ballot, and the panelists indicated their responses by checking the suitable box in such a way that it could be read by a scanner (ULISI, Serisud, Montpellier, France).

For all experiments and for the results of all descriptive analysis sessions a two-way analysis of variance (ANOVA), samples and judges, was performed on sensory means to test the significance of each attribute and to examine the panel homogeneity. Calculations of the least significant difference (LSD-test, t -method for multiple comparisons of means)-(Dagnelie, 1975) were applied for validation of the comparison of the different wines for each attribute. ANOVA and LSD-test were performed using ULISI, and the geometrical mean

and correlation matrix were performed using STATlab (Statistiques Logiciels Pédagogie, Ivry sur Seine, France).

Chemical and Reference Compounds. 4-Hydroxy-2,5-dimethylfuran-3(2H)-one (HDMF) was purchased from Aldrich Chemical Co. Inc. (St Quentin Fallavier, France). 4-Hydroxy-2(or 5)-ethyl-5(or 2)-methylfuran-3(2H)-one (HEMF) was purchased from International Express Service (Allauch, 13718, France). [$^2\text{H}_7$]4-Hydroxy-2,5-dimethylfuran-3(2H)-one (d_7 -HDMF) and [$^2\text{H}_6$]4-hydroxy-2(or 5)-ethyl-5(or 2)-methylfuran-3(2H)-one (d_6 -HEMF) were synthesized as reported previously (Kotseridis, 1999). Sodium chloride, sodium sulfate, potassium bicarbonate, tartaric acid, diethyl ether, and dichloromethane (ultrapure grade) were all obtained from Merck (64271 Darmstadt Germany).

Isolation of Volatiles from Wines for Gas Chromatography/Olfactometry Analysis. A 500-mL portion of wine was poured into a 1.5-L Erlenmeyer flask and cooled to 1 °C in an ice bath under nitrogen. Dichloromethane (200 mL) was added and the mixture was stirred at 700 rpm for 15 min (Moio et al., 1995). The wine–solvent mixture was supplemented with 200 mL of dichloromethane and stirring was continued for 15 min. The organic phase was separated in a separatory funnel, centrifuged (9000g, 5 min, 4 °C), dried over sodium sulfate, and then concentrated by distillation through a Vigreux distilling column and then a Dufton column at 47 °C to produce 1 mL. The final concentration factor was 500.

Extraction of HDMF and HEMF from Wines. In a 250-mL flask, 100 mL of a wine sample saturated with sodium chloride was spiked with 18.9 μg of d_7 -HDMF and 5.4 μg of d_6 -HEMF (by addition of 100 μL of a diethyl ether solution containing 189 and 54 $\mu\text{g/mL}$ of HDMF and HEMF respectively), then the flask was closed and the mixture was stirred for 10 min for equilibration of the media. The mixture was extracted with 3×10 mL of dichloromethane for 5 min while on a magnetic stirrer (1000 rpm). The organic phases were blended, centrifuged (9000g, 5 min, 4 °C), dried over sodium sulfate, and then filtered through glasswool and concentrated under vacuum (30 °C) down to 1 mL. The final concentration factor was 100.

Gas Chromatography/Olfactometry Analysis (GC/O). GC/O analysis was carried out using a Hewlett-Packard HP gas chromatograph 5890 series II fitted with a 30-m fused-silica column (0.32 mm i. d. and 0.5 μm film thickness), coated either with DB WAX (J&W Scientific), or with DB 5 (J&W Scientific, Folsom, CA). The injection (3 μL) of the extract was splitless/split (split ratio 1/10) in an injection port heated to 250 °C. The carrier gas was hydrogen (Linde Gaz, Marseille), with a flow-rate of 2 mL/min. The oven temperature program was 60 °C (for 3 min), then increased at 3 °C/min to 245 °C and held at this temperature for a further 20 min. The gas chromatography effluents were split to a sniffing port and a flame ionization detector (3/1). The dilution factors (FD) of the wine odorants with caramel odor were estimated, as recently reported by Guth (1997a). The extracts of the Cabernet Sauvignon CSM1 and Merlot MP3 wines were stepwise diluted with dichloromethane 1:2, 1:4, 1:8, 1:16, 1:32, 1:64, and 1:128, then 3 μL of each dilution was injected into the GC/O system and the sniffing tests were performed by two trained persons.

Gas Chromatography/Mass Spectrometry Analysis (GC/MS). GC/MS analysis was carried out using a Hewlett-Packard HP gas chromatograph 5890 series II fitted with a 30-m fused-silica column (0.32 mm i. d. and 0.5 μm film thickness) that had been coated with DB WAX (J&W Scientific). The injection of the extracts (3 μL) was on-column at 35 °C; then the temperature of the injector was increased at 180 °C/min to 250 °C. The carrier gas was helium 6.0 (Linde Gaz, Marseille), with a flow-rate of 1.35 mL/min. The oven temperature program was 35 °C (for 3 min), then increased at 3 °C/min to 245 °C and held at this temperature for a further 20 min. The GC instrument was coupled to a 5989A mass selective detector and an MS chemstation (HP-UX). The electron impact (EI) energy was 70 eV and the quadrupole temperature was set at 250 °C.

Quantification of HDMF and HEMF using GC/MS. Selective ion monitoring (SIM) of HDMF and HEMF used

various ions: for HDMF, $m/z = 85, 128$; for d_7 -HDMF, $m/z = 88, 134, 135$; the ions at $m/z = 128, 134, \text{ and } 135$ were used for quantification and the ions $m/z = 85$ and 88 were used as qualifiers; for HEMF, $m/z = 127, 142$; for d_6 -HEMF, $m/z = 132, 147, 148$; the ions at $m/z = 142, 147, \text{ and } 148$ were used for quantification and the ions at $m/z = 127$ and 132 were used as qualifiers.

Calibration curves were determined for the target compounds, HDMF and HEMF, using a dichloromethane solution containing 41.2 and $44.3 \mu\text{g mL}^{-1}$ of HDMF and HEMF, respectively. Subsequent serial dilutions were made from these solutions ($10, 50, 100, 300$ and $600 \mu\text{L}$ in 1 mL dichloromethane), followed by addition of the labeled internal standards ($100 \mu\text{L}$ of a diethyl ether solution, containing 188.5 and $53.6 \mu\text{g mL}^{-1}$ of d_7 -HDMF and d_6 -HEMF, respectively).

HDMF. The peak area ratios (peak area of the ion $m/z = 128$ /sum of peak areas of ions $m/z = 134$ and 135) were plotted against the mass ratios (μg of HDMF/ $18.85 \mu\text{g}$ of d_7 -HDMF) for the HDMF masses $0.41, 2.06, 4.12, 12.36, \text{ and } 24.72 \mu\text{g}$. The resultant curve was linear [response ratio = $(0.3846 \times \text{concentration ratio}) + 0.0012$; $R^2 = 0.999$].

HEMF. Peak area ratios (peak area of the ion $m/z = 142$ /sum of peak areas of ions $m/z = 147$ and 148) were plotted against the mass ratios (μg of HEMF/ $5.36 \mu\text{g}$ of d_6 -HEMF) for the HDMF masses $0.44, 2.22, 4.44, 13.36, \text{ and } 26.72 \mu\text{g}$. The resultant curve was linear [response ratio = $(1.129 \times \text{concentration ratio}) - 0.012$; $R^2 = 0.999$].

RESULTS AND DISCUSSION

The objective of using a sensory analysis procedure during this work was to obtain a guide for the forthcoming research on the odorants of the Cabernet Sauvignon and Merlot wines. The difference tests and descriptive analysis were performed by the trained panel of enology students of Montpellier.

Difference Tests. The existence of significant differences between the odors of Merlot and Cabernet Sauvignon wines was examined before sensorial profiling. For this test, two pairs of two wines from vicinal vineyards, produced using the same vinification procedure (MG5 vs CSG2 and MM6 vs CSM1, Table 1), were compared by triangular test (Larmon, 1969). The differences between the wines of Merlot and Cabernet Sauvignon were significant at the threshold of error of 0.1% . Consequently, further investigations using descriptive sensory analysis were performed on these wines.

Descriptive Analysis. The 17 selected judges were trained regarding the identification and quantification of the 20 attributes previously selected by the enologists of Bordeaux. Then, the first 3 tasting sessions were performed to familiarize the judges with the use of the descriptors list and their evaluation using a six-point scale. During these first sessions the olfactive evaluation of the wines of Merlot and Cabernet Sauvignon was performed by both direct and by-mouth olfaction. The ANOVA results, obtained on the data collected during the third session showed that the judges performances were not homogeneous. Thus, further training was necessary to determine the sources of the heterogeneity of the responses of the judges. Four samples, two Merlot and two Cabernet Sauvignon wines, were analyzed separately: the first analysis using direct olfaction of the samples and the second time using by-mouth olfaction. The ANOVA performed on the data obtained showed that the responses of the jury were homogeneous for only 7 of the 20 attributes ($p < 0.05$) when by-mouth olfaction was used. Inversely, direct olfaction gave more satisfactory results, as the responses of the

Table 3. Variance Analysis of Attribute Ratings

descriptors	samples means	samples F^a ratios	judges means	judges F^b ratios
plum	0.66	1.65	0.72	2.13*
cherry	2.92	0.25	2.86	3.04*
orange	1.63	0.96	1.63	2.24*
rose	1.47	2.40*	1.45	1.52
box-tree	0.78	0.82	0.92	3.91*
bell pepper	1.15	0.65	1.24	2.25*
straw	1.47	0.59	1.4	3.23*
pepper	1.41	0.97	1.41	2.21*
leather	1.23	2.06*	1.26	1.56
licorice	1.59	0.86	1.68	4.43*
coffee	0.9	0.96	0.91	1.61
caramel	1.37	4.43**	1.47	1.87*

^a F -value of Fisher-Snedecor for the samples; * ($F = 2.02, p < 0.05$); ** ($F = 2.65, p < 0.01$) ^b F -value of Fisher-Snedecor for the judges; * ($F = 1.73, p < 0.05$)

Table 4. Test of Multiple Comparisons (LSD-test) between the Wines and the Caramel Attribute

Sample	MP3	ME4	MP2	ME1	CSG2	MG5	CSP3	MM6	CSM1
Variety ^a	M	M	M	M	CS	M	CS	M	CS
Caramel ^b	2.82	2.41	1.49	1.41	1.23	1.06	1.00	0.94	0.88

^a Variety: M, Merlot; CS, Cabernet Sauvignon. ^b Mean intensity for caramel. The two wines on the left of Table 4 (MP3 and ME4) presented significantly higher intensities than the other wines (multiple comparisons t -test: least significant difference between means = $0.94, p < 0.05$).

judges were homogeneous for 13 of the 20 descriptors ($p < 0.05$). Thus, only direct olfaction was used for the following sessions.

Another potential source of variation of the judge's responses was the relatively high number of attributes (20) (Barthélémi, 1990). In the fifth and sixth sessions the attributes were sorted according to their geometrical mean (GM). Applying this method, the GM of the descriptors black-currant, peach, pear, and cacao were found to be low, and consequently they were discarded from the descriptors list.

A second reduction was obtained by gathering the descriptors displaying high correlation factors. Four pairs of descriptors were positively correlated: strawberry jam and caramel ($r^2 = 0.844, p < 0.05$), eucalyptus and box-tree ($r^2 = 0.941, p < 0.05$), rose and violet ($r^2 = 0.925, p < 0.05$), and smoky and leather ($r^2 = 0.838, p < 0.05$). Thus, it was decided with the judges, by consensus, that only the descriptors caramel, box-tree, rose, and leather would be used for the following session; the final list of descriptors is displayed in Table 3.

Final Session of Descriptive Analysis of the Wines. The sensorial profiling of six Merlot and three Cabernet Sauvignon wines was performed using the 12 remaining attributes. A two-way ANOVA showed that the descriptors significantly differentiating the wines were caramel, rose, and leather (Table 3). Conversely, the ANOVA showed that the performance of the judges ($F = 1.73, p < 0.05$) was homogeneous only for 2 descriptors: rose ($F = 1.52, p < 0.05$) and leather ($F = 1.56, p < 0.05$), but not for the caramel descriptor ($F = 1.87, p < 0.05$).

The LSD-test showed that only the caramel descriptor allowed separation of the samples. Thus, two Merlot samples (MP3 and ME4) displayed intensity means for this descriptor significantly higher than those for the Cabernet Sauvignon samples (Table 4). Furthermore, the classification of the wines by decreasing intensity means for the attribute caramel, sorted the majority of

Table 5. Contents ($\mu\text{g/L}$) and Odor Active Values (OAV) of HDMF and HEMF in the Merlot and Cabernet Sauvignon Wines

samples	origin	code	descriptor caramel ^a	HDMF	OAV ^b	HEMF	OAV ^c
Merlot	Pomerol	MP2	1.49	118	3.2	32	3.2
	Pomerol	MP3	2.82	156	4.2	75	7.5
	St Emilion	ME4	2.41	143	4.0	30	3.0
	Graves	MG5	1.06	90	2.4	50	5.0
	Moulis	MM6	0.94	71	2.0	38	3.8
Cabernet Sauvignon	Moulis	CSM1	0.88	20	0.5	25	2.5
	Graves	CSG2	1.23	63	1.7	50	5.0
	Pauillac	CSP3	1.00	30	0.8	38	3.8

^a Mean intensity attributed to the judges for the caramel descriptor. ^b Odor Active Value of HDMF in the wines, odor threshold of 37 $\mu\text{g/L}$. ^c Odor Active Value of HEMF in the wines, odor threshold of 10 $\mu\text{g/L}$.

the Merlot wines before the Cabernet Sauvignon wines. This separation, between the wines of the two varieties, was not observed for the attributes rose and leather. Consequently, caramel was a descriptor which differentiated the Merlot and the Cabernet Sauvignon wines of Bordeaux. However, this attribute differentiated also the two neighboring vineyards, Pomerol and Saint Emilion, which had the highest caramel intensities, whereas these intensities for the Merlot wines from Graves and Moulis were closer to those for the Cabernet Sauvignon wines. To ascertain this sensorial result, further work was carried out for the identification of compounds with caramel odor in these Merlot wines.

Research of the Potent Odorants Responsible for the Caramel Odor. Estimation of food impact aroma could be performed by various olfactometric techniques, as discussed recently by Pollien et al. (1997). The GC/O analysis for the identification of the compounds responsible for the caramel odors was performed using the aroma extract dilution analysis (AEDA) method (Ulrich and Grosch, 1987; Grosch, 1994). As representative extracts of the subject food or beverage were required for olfactometry analysis (Etievant et al., 1993), the extraction method previously reported by Moio et al. (1995) was used for the isolation of the volatiles of the wines. Two odorant zones corresponded to the caramel odor and the compounds exhibiting high FD-factors in the wine extracts were identified as HDMF and HEMF, as also previously reported in other Merlot and Cabernet Sauvignon samples (Kotseridis and Baumes, 2000). HDMF was identified in juice and wines from *Vitis labrusca* hybrid grapes (Rapp et al., 1980; Baek et al., 1997). However, its occurrence in *Vitis vinifera* wines was reported recently (Guth, 1997a and 1997b; Cutzach et al., 1998a and 1998b). HEMF was first reported in *Vitis vinifera* wines by Guth (1997a), then recently by Cutzach et al. (1998a). To compare the relative importance of these compounds in the Merlot and Cabernet Sauvignon extracts, AEDA was applied to the extract of Merlot MP3 (mean intensity = 2.82 as evaluated by the judges during the sensory analysis) and of Cabernet Sauvignon CSM1 (mean intensity = 0.88). In the Merlot extract, the FD values found for HDMF and HEMF were 128 and 64, respectively, whereas in the Cabernet Sauvignon they were 32 and 64. These values were indicative of a greater occurrence of HDMF in the Merlot wine and of similar levels of HEMF in both wines. To overcome the limitations of the AEDA method (Ferreira et al., 1998) and obtain conclusive results on the possible impact of these compounds on the caramel attribute of these wines, the determination of their odor thresholds in model wine and their comparison to the compound levels in wines were necessary.

Odor Threshold of HDMF and HEMF. As recently discussed by Buttery et al. (1995), the odor threshold values of HDMF reported in the literature were very different. As HDMF and HEMF were weak acids, their un-ionized fractions depended on the pH value of the medium, which could affect their odor threshold at the pH of wine. The odor thresholds of HDMF and of HEMF were reported to be 500 $\mu\text{g/L}$ in a water–alcohol mixture (89:11, v/v), evaluated by a “retronasal” process (Guth, 1997a). This assay was carried out at neutral pH which could explain the unusual high value found. Indeed, the determination of the odor threshold of these compounds in a model base wine, adjusted to pH 3.5, led to much lower values: 37 $\mu\text{g/L}$ for HDMF and 10 $\mu\text{g/L}$ for HEMF, which were similar to those reported by Buttery et al. (1995).

Quantification of HDMF and of HEMF. The wines of Merlot and Cabernet Sauvignon which were evaluated by sensory analysis were also analyzed by a stable isotope dilution assay method. Synthesis of the deuterated HDMF and HEMF and development of the method used for their quantification was reported elsewhere (Kotseridis, 1999). The ME1 sample was not quantified by instrumental analysis, as there was no more available after the sensory analysis sessions. Results of the analyses are reported in Table 5. The contents of these two molecules in six of the wines studied were higher than their odor thresholds (37 and 10 $\mu\text{g/L}$, respectively, for HDMF and HEMF), showing that both compounds were impact odorants of these wines. However, these contents were lower in two of the three Cabernet Sauvignon wines studied (20 and 30 $\mu\text{g/L}$, respectively, in CSM1 and CSP3). The contents found for HDMF in the wines of Merlot and Cabernet Sauvignon were significantly different ($F = 11.23$, $p < 0.02$). Conversely, the contents of HEMF did not significantly differentiate the wines. The relation between the logarithm of intensity (Ln I) attributed by the panelists to the caramel descriptor and the logarithm of HDMF level (Ln C) in the wines of the study was a significant linear regression (Stevens' law: $I = k C^n$) (MacLeod and Sauvageot, 1986) ($r = 0.8$, $F = 8.77$, $p < 0.03$) (Figure 1).

Consequently, the contents of HDMF differentiated significantly the wines of Merlot from the wines of Cabernet Sauvignon of the 1996 vintage.

CONCLUSION

Descriptive analysis of the samples showed that the aroma profiles of Merlot and Cabernet Sauvignon wines were very close. The explanation of this result could be that these wines were very young at the time of analysis, so that their aromas were mainly determined by common fermentation compounds. However the

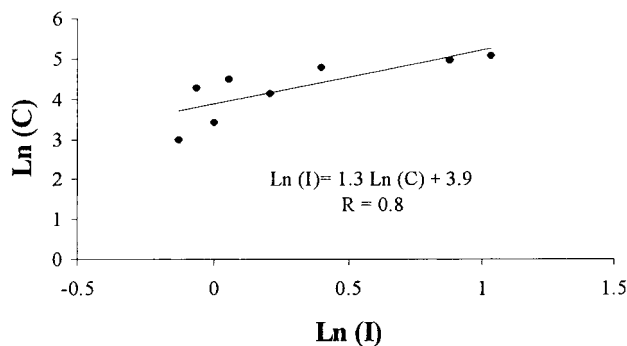


Figure 1. Linear regression between the logarithm of the mean intensity (Ln I) attributed by the panelists to the descriptor caramel and the logarithm of the level of HDMF ($\mu\text{g/L}$) (Ln C) in the corresponding wine.

target of this study was to characterize the aroma of these wines before generation of odorants due to the aging process, particularly in barrels, as usually carried out in the Bordeaux region. The only attribute that differentiated the Merlot wines from the Cabernet Sauvignon wines was the caramel descriptor, which could also differentiate the Pomerol and Saint Emilion neighboring vineyards from the other vineyards. GC/olfactometry analysis allowed this difference to be attributed to HDMF, a potent odorant with caramel odor. Its levels in the Merlot wines were higher than in the Cabernet Sauvignon wines and determined the intensity of the caramel attribute in the Merlot wines along with HEMF. Conversely, HEMF was found to produce the caramel perception in the Cabernet Sauvignon wines (as well as in the Merlot wines), but not to differentiate the Merlot from the Cabernet Sauvignon wines. Furthermore, the fact that FD-factors determined for HDMF as well as HEMF were much higher than their respective OAV must be emphasized. This statement confirmed that sensory evaluation results obtained by AEDA should always be completed by instrumental analysis and especially by SIDA quantification, as it was already underlined by Grosch (1994).

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LITERATURE CITED

- Aiken, J. W.; Noble, A. C. Comparison of the aromas of oak- and glass-aged wines. *Am. J. Enol. Vitic.* **1984**, *35*, 196–199.
- Allen, M. S.; Lacey, M. J.; Brown, W. V.; Harris, R. L. N. Occurrence of methoxypyrazines in grapes of *Vitis vinifera* cv. Cabernet Sauvignon and Sauvignon blanc. In *Actualités Œnologiques 89*; Ribèreau-Gayon, P., Lonvaud, A., Eds.; Dunod: Paris, France, 1990; pp. 25–30.
- Allen, M. S.; Lacey, M. J.; Boyd S. Determination of methoxypyrazine in red wine by stable isotope dilution gas chromatography–mass spectrometry. *J. Agric. Food Chem.* **1994**, *42*, 1734–1738.
- Baek, H. H.; Cadwallader, K. R.; Marroquin, E.; Silva, J. L. Identification of predominant aroma compounds in Muscadine grape juice. *J. Food Sci.* **1997**, *62*, 249–252.
- Barthélemy, J. Evaluation d'une grandeur sensorielle complexe: description quantifiée. In *Evaluation sensorielle: manuel méthodologique*; Société Scientifique d'Hygiène Alimentaire and Institut Scientifique d'Hygiène Alimentaire, Eds.; Technique et Documentation Lavoisier: Paris, 1990; pp 145–158.
- Buttery, R. G.; Takeoka, G. R.; Ling, L. C. Furanol: Odor threshold and importance to Tomato aroma. *J. Agric. Food Chem.* **1995**, *43*, 1638–1640.
- Cliff, M. A.; Dever, M. C. Sensory and compositional profiles of British Columbia Chardonnay and Pinot noir wines. *Food Res. Int.* **1996**, *29*, 317–323.
- Cutzach I.; Chatonnet, P.; Dubourdiou, D. Etude sur l'arôme des vins doux naturels non muscatés. 1^{ère} partie: analyse qualitative de l'arôme des Banyuls et Rivesaltes au cours de leur vieillissement. *J. Int. Sci. Vigne Vin* **1998a**, *32*, 99–110.
- Cutzach I.; Chatonnet, P.; Henry, R.; Pons M.; Dubourdiou, D. Etude sur l'arôme des vins doux naturels non muscatés. 2^e partie: dosages de certaines composés volatils intervenant dans l'arôme des vins doux naturels au cours de leur vieillissement. *J. Int. Sci. Vigne Vin* **1998b**, *32*, 211–221.
- Dagnelie, P. Les comparaisons multiples des moyennes. In *Théorie et Méthodes Statistiques*. Les Presses Agronomiques de Gembloux, Ed.; Gembloux, Belgium, 1975; Vol. 2.
- Dravniek, A. Odor quality: semantically generated multidimensional profiles are stable. *Science* **1982**, *218*, 799–801.
- Edwards, T. L.; Singleton V. L.; Boulton R. Formation of ethyl esters of tartaric acid during wine aging: chemical and sensory effects. *Am. J. Enol. Vitic.* **1985**, *36*, 118–124.
- Etievant, P. X.; Abbott, N.; Issanchou, S. N.; Langlois, D.; Lesschaeve, E. Représentativité olfactive des concentrés aromatiques. In: *Connaissance aromatique des cépages et qualité des vins*; Bayonove, C., Crouzet, J., Flanz, C., Martin, J. C., Sapis, J. C., Eds.; Revue Française d'Œnologie; Lattes, France, 1993; pp 352–359.
- Ferreira, V.; Lopez, R.; Escudero, A.; Cacho, J. F. The aroma of Grenache red wine: hierarchy and nature of its main odorants. *J. Sci. Food Agric.* **1998**, *77*, 259–267.
- Francis, I. L.; Sefton M. A.; Williams P. J. A study by sensory descriptive analysis of the effects of oak origin, seasoning, and heating on the aromas of oak model wine extracts. *Am. J. Enol. Vitic.* **1992**, *43*, 23–30.
- Grosch, W. Determination of potent odorants in foods by aroma extract dilution analysis (AEDA) and calculation of odour activity values (OAVs). *Flavour Fragrance J.* **1994**, *9*, 147–158.
- Guth, H. Identification of character impact odorants of different white wine varieties. *J. Agric. Food Chem.* **1997a**, *45*, 3022–3026.
- Guth, H. Quantitation and sensory studies of character impact odorants of different white wine varieties. *J. Agric. Food Chem.* **1997b**, *45*, 3027–3032.
- Issanchou, S.; Lesschaeve, I.; Köster E. P. Screening individual ability to perform descriptive analysis of food products: basic statements and application to a Camembert cheese descriptive panel. *J. Sens. Stud.* **1995**, *10*, 349–368.
- Kotseridis, Y. Etude de l'arôme des vins de Merlot et Cabernet Sauvignon de la région Bordelaise. Thèse doctorat de l'Université de Bordeaux II, Bordeaux, France, 1999, 268 pp.
- Kotseridis, Y.; Baumes, R. Identification of impact odorants in Bordeaux red grape juice, in the commercial yeast used for its fermentation, and in the produced wine. *J. Agric. Food Chem.* **2000**, *48*, 400–406.
- Kotseridis, Y.; Anocibar Belouqui, A.; Bertrand, A.; Doazan, J. P. An Analytical Method for Studying the Volatile Compounds of Merlot Noir Clone Wines. *Am. J. Enol. Vitic.* **1998**, *48*, 44–48.
- Larmond, E. *Méthodes d'appréciation sensorielle des aliments*. Ministère de l'Agriculture du Canada: Ottawa, Canada, 1969.
- MacLeod, P.; Sauvageot, F. Bases neurophysiologiques de l'évaluation sensorielle des produits alimentaires. In *Les Cahiers de IENS. BANA*; Ecole Nationale Supérieure de Biologie Appliquée à la Nutrition et à l'Alimentation, Eds.; Technique et Documentation Lavoisier: Paris, France, 1986.

- Moio, L.; Schlich, P.; Issanchou, S.; Etiévant, P. X.; Feuillat, M. Description de la typicité aromatique des vins de Bourgogne issus du cépage Chardonnay. *J. Int. Sci. Vigne Vin*, **1993**, *27*, 179–189.
- Moio, L.; Chambellaut, E.; Lesschaeve, I.; Issanchou, S.; Schlich, P.; Etiévant, P. X. Production of representative wine extracts for chemical and olfactory analysis. *Ital. J. Food Sci.* **1995**, *3*, 265–278.
- Noble, A. C.; Shannon, M. Profiling Zinfandel wines by sensory and chemical analysis. *Am. J. Enol. Vitic.* **1987**, *38*, 1–5.
- Noble, A. C.; Williams, A. A.; Langron, S. P. Descriptive analysis and quality ratings of 1976 wines from four Bordeaux communes. *J. Sci. Food Agric.* **1984**, *35*, 88–98.
- Pages, J.; Asselin, C.; Morlat, R.; Robichet, J. L'analyse factorielle multiple dans le traitement des données sensorielles. Application à des vins rouges de la vallée de la Loire. *Sci. Aliments* **1987**, *7*, 549–571.
- Peynaud, E. *Le Goût du Vin*. Dunod: Paris, France, 1980.
- Pollien, P.; Ott, A.; Montigon, F.; Baumgartner, M.; Munoz-Box, R.; Chaintreau, A. Hyphenated headspace-gas chromatography-sniffing technique: screening of impact odorants and quantitative aromagram comparisons. *J. Agric. Food Chem.* **1997**, *45*, 2630–2637.
- Rapp, A.; Knipser, W.; Engel, L.; Ullemeyer, H.; Heimann, W. Off-flavor compounds in the berry and wine aroma of grape vine hybrids. I. The strawberry-like aroma. *Vitis* **1980**, *19*, 13–23.
- Ullrich, F.; Grosch, W. Identification of most intense volatile flavor compounds formed during autoxidation of linoleic acid. *Z. Lebensm.-Unters.-Forsch.* **1987**, *184*, 277–282.

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