Volatile Compounds Involved in the Aroma of Sweet Fortified Wines (Vins Doux Naturels) from Grenache Noir

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A typical commercial sample of red Vins Doux Naturels (VDN), Maury 1991, was analyzed by liquid–liquid extraction with dichloromethane followed by chromatographic analysis by GC/FID, GC/MS, and GC/sniffing. GC/sniffing using a DB-Wax and a DB-5 fused silica capillary column revealed five substances having odors corresponding to the aromas of these sweet fortified wines: an enolic lactone, 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone or sotolon; an acetal, *trans*-2-methyl-5-hydroxy-1,3-dioxane; and three ethyl esters, 4-carbethoxy-γ-butyrolactone, ethyl 2-hydroxyglutarate, and ethyl pyroglutamate. The last four compounds have been synthesized and their olfactory characteristics checked under the same conditions, which confirmed the odors revealed for the natural compounds except for *trans*-2-methyl-5-hydroxy-1,3-dioxane, which exhibited no odor. Furthermore, five other sweet fortified wines subjected to different types of oxidative aging were analyzed to quantitatively determine the four identified aroma compounds. The three ethyl esters were found in these wines at different levels increasing with oxidative aging. However, sotolon could not be detected. In addition, other volatile compounds from the six wines were analyzed. The levels of polar ethyl esters and the related lactones, the carbonyl compounds, and their acetals increased in the wines after oxidative aging as well.

Keywords: *Sweet wine; aroma; oxidative aging; Grenache; Vins Doux Naturels*

INTRODUCTION

In enology, wines are aged in two ways, either in the classic way in bottles, the most common method, or by oxidative aging, used mainly for sweet fortified wines such as Vins Doux Naturels (VDN) from Roussillon (southern France). Red VDN are made from Grenache Noir grapes, and the oxidative aging gives them burnt notes of cocoa, chocolate, caramel, and coffee, and notes of dried fruits, prune, jam, cherries in brandy, and crystallized fruits (Brugirard et al., 1988; Torres, 1990). Our research concerns these volatile components involved in the aroma of these VDN. The vinification and aging methods used for Roussillon VDN are special. Alcohol is added to the must after initial fermentation to a density of ≈1.035–1.045. After this addition, the wine contains about 16% v/v ethanol and 50–100 g/L sugar. It is then subjected to frequent drastic oxidative aging (barrels not full in the cellar, demijohns or barrels exposed to the sun).

There have been few papers devoted to the aromas of oxidized wines (Dinsmoor Webb et al., 1967; Simpson, 1980; Criddle et al., 1983; Williams et al., 1983). Recently, De Revel et al. (1996) and Da Silva Ferreira and Bertrand (1996) demonstrated a correlation between the ethyl ester content of organic acids (ethyl lactate, diethyl succinate, etc.) and the age of various Douro Ports. Furthermore, Da Silva Ferreira and Bertrand (1996) showed the importance of carbonyl compounds in the aroma of old Port wines. However,

no precise sensorial data about the aromas of these wines were reported

The objective of this work was to identify the volatile compounds important to the aroma of the oxidized VDN from Roussillon using GC/olfactometric analysis.

MATERIALS AND METHODS

Materials Studied. Red VDN coming from three different wineries from Roussillon were sampled for this study: wine A, a typical commercial sample, Maury 1991 aged for 5 years in a 600 L old barrel, not full (headspace volume = 10 L, without any inert gas cover), in the cellar (Maury cooperative winery).

After vinification, another young Maury wine (1994) from the Mas Amiel winery was submitted to three aging modes: wine B0, stored for 5 months in a concrete full tank, then bottled and stored for 1 year at 4 °C; wine B1, stored for 5 months in a concrete full tank, then stored for 1 year in an old big barrel (200 hL), not full (headspace volume = 2 hL, without any inert gas cover), in the cellar (temperature = 16 °C); wine B2, stored for 5 months in a concrete full tank, then stored for 1 year in glass demijohns (50 L), not full (headspace volume = 1 L, without any inert gas cover), exposed to the sun, outside.

A VDN Rivesaltes 1991 from the Domaine des Chênes winery was submitted, after vinification, to two aging modes: wine C0, stored for 4 years in an old barrel (25 hL), not full (headspace volume = 1 hL, without any gas cover), in the cellar (temperature = 17 °C); wine C1, stored for 3 years in the same old barrel (25 hL), not full, in the cellar, then for 1 year in glass demijohns (50 L), not full (headspace volume = 1 L, without any inert gas cover) exposed to the sun, outside.

Extraction and Preparation of Extracts. Two hundred milliliters of wine with 110 μg of 4-nonanol added as an internal standard was stirred magnetically with 250 mL of dichloromethane at 0 °C for 1 h and 30 min (Moio et al., 1995).

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The magnetic stirrer was set at 750 rpm. The emulsion formed was destroyed by cold centrifugation (0−4 °C) (11600*g*). The organic phase was recovered, dried with Na_2SO_4, and then concentrated by distillation through a Vigreux and then a Dufton column at 47 °C to obtain a sample 200 times more concentrated than the initial wine. This procedure was performed in triplicate. The extracts were stored at −20 °C until analyzed.

Gas Chromatographic Techniques. Aroma compounds were analyzed by GC with detection alternatively by flame ionization and sniffing test (olfactive screening of chromatography effluents). A Hewlett-Packard 5890 Series II apparatus was used. The flow of hydrogen (Linde Gaz, Marseille) carrier gas was 2.1 mL/min. The oven was kept at 30 °C for 30 s and then programmed to 60 °C at 60 °C/min, kept at 60 °C for 3 min, and then programmed to 245 °C at 3 °C/min. It was then kept at 245 °C for 20 min. The injector was kept at 250 °C. Injection mode (1 μL) was split−splitless (1:10 split ratio). Two types of capillary columns were used: a DB-Wax (J&W Scientific, Folsom, CA) column, 30 m long, 0.32 mm i.d., 0.5 μm film thickness, and a DB-5 (J&W Scientific) column with the same characteristics.

The gas effluent was cooled and humidified before the sniff port (funnel-shaped).

The sniffing tests were performed by three testers trained to detect the specific VDN aromas (two per analysis, replaced at 15 min intervals) and only the odors corresponding to descriptors of the VDN from Roussillon and common to both separations were investigated. If the testers did not use the same attribute for an aroma eluted by GC, only the descriptors belonging to the same aroma class were retained.

Identification of the compounds was performed by GC/MS. A Hewlett-Packard 5890 Series II chromatograph was used with the DB-Wax and DB-5 columns specified as above (except that the DB-5 column was 60 m long). The flow of helium 6.0 (Linde Gaz, Marseille) carrier gas was 1.35 mL/min. Oven temperature programming was as above. Injection volume was 1 μL. The on-column injector temperature was programmed from 30 to 280 °C at 180 °C/min. It was held at 280 °C for 80 min. A Hewlett-Packard 5989A mass spectrometer with a quadrupole mass filter was coupled to the GC. Mass spectra were recorded in the electronic impact (EI) and positive chemical ionization (PCI) modes. The transfer line temperature was 250 °C. The source temperature was 250 °C in EIMS and 200 °C in PCIMS. Methane was used as the reactant gas. Mass spectra were scanned at 70 eV (EIMS) and 230 eV (PCIMS) in the range *m*/*e* 60−350 at 1 s intervals.

Chemical Syntheses. ^{1}H NMR spectra in $CDCl_3$ (TMS) of the synthetic compounds were obtained on a Varian INOVA 500 instrument. EIMS spectra were obtained by GC/MS as described above.

(5S)-Carbethoxy-2-pyrrolidone (ethyl ʟ-pyroglutamate) was obtained from Aldrich Chemical Co. (St. Quentin Fallavier, France).

Ethyl 2-Ketoglutarate. To a solution of 1.5 mL of *N,N*-dimethylformamide (19.5 mmol; 1.43 g) in 10 mL of acetonitrile stirred at −20 °C for 15 min was added dropwise a solution of oxalyl chloride (0.5 mL; i.e., 5.8 mmol, 0.74 g in 1 mL of acetonitrile) (Stadler, 1978). The precipitate formed was stirred at −20 °C for another 15 min. One gram of 2-ketoglutaric acid (6.9 mmol) was then added. A clear, orange-tinted solution formed that was stirred for 20 min. To this solution was added 1.2 g of ethanol (26 mmol) in 1.5 mL (18.6 mmol) of pyridine at low temperature (−20 °C). A brown solution that formed was left overnight and stirred at room temperature. The following day, 30 mL of dichloromethane was added to the solution. The mixture obtained was washed once with 30 mL of a 20% potassium carbonate solution and then twice with water (20 mL each time). The aqueous phases were then extracted again twice using 20 mL of dichloromethane. The organic phases were combined, dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated by evaporation under vacuum, yielding 0.8 g of a brown oily residue.

Ethyl (2R and 2S)-Hydroxyglutarate. Crude ethyl 2-ketoglutarate (0.5 g; 3.4 mmol) in 20 mL of absolute ethanol was stirred at 0 °C and 131 mg of sodium borohydride (2.85 mmol) was added gradually (Vogel, 1957). The mixture was kept at this temperature for 20 min, and then the reaction was quenched by addition of acetone. A phosphate−citrate buffer (5 mL, pH 6.5) and then 50 mL of water were added. The mixture was extracted with 25 mL of diethyl ether. The organic phase was separated, washed with 10 mL of water, dried over Na_2SO_4, and concentrated by evaporation under vacuum, giving 0.25 g of salmon-pink oily residue. The ^{1}H NMR and EIMS data were consistent with those reported by Ravid et al. (1978) and Cobb et al. (1978), respectively.

(4R and 4S)-Carbethoxy-γ-butyrolactone. Crude ethyl (2*R* and 2*S*)-hydroxyglutarate (0.1 g; 0.52 mmol) and 3 mg of *p*-toluenesulfonic acid (0.015 mmol) were dissolved in 10 mL of toluene in a Claisen flask. The mixture was heated to 45 °C in an oil bath under reduced pressure (300 mmHg). The elimination of the azeotrope toluene/ethanol could not be observed by monitoring the temperature because of the small amounts involved; for this reason, distillation was continued until the first drops of toluene came through. On completion of cyclization (after ≈40 min), the mixture was recovered, washed with water, dried over Na_2SO_4, and concentrated by evaporation under vacuum at 45 °C. An oily beige residue (0.06 g) was recovered. The ^{1}H NMR and EIMS data were consistent with those reported by Ravid et al. (1978) and Cobb et al. (1978), respectively.

cis- and trans-2-(Benzyloxy)-5-methyl-1,3-dioxane. 2-(Benzyloxy)-1,3-propanediol (0.5 g; 2.75 mmol) was stirred at 0 °C in 20 mL of dichloromethane with 18 mg of *p*-toluenesulfonic acid (2% by mole) and anhydrous calcium chloride ($CaCl_2$). Ethanal (250 mg; 5.5 mmol) was added slowly under intense cooling. The mixture was then stirred at room temperature. Once acetalization was complete, the mixture was filtered to remove the $CaCl_2$ suspension, washed with 20 mL of water, dried on Na_2SO_4, and concentrated by evaporation under vacuum at 30 °C. *cis-* and *trans-*5-benzyloxy-2-methyl-1,3-dioxane (0.51 g) were recovered.

cis- and trans-5-Hydroxy-2-methyl-1,3-dioxane. Crude *cis-* and *trans-*5-(benzyloxy)-2-methyl-1,3-dioxane (0.51 g) were dissolved in 50 mL of ethyl acetate. Hydrogenation was performed using 110 mg of palladium on activated carbon (10%). When the consumption of hydrogen had been stopped, the mixture was filtered on Celite and concentrated by evaporation under vacuum. An oily residue (0.21 g) was recovered. The ^{1}H NMR and EIMS data were consistent with those reported by Etievant (1979).

RESULTS AND DISCUSSION

The extraction method chosen was developed by Moio et al. (1995) to obtain representative extracts of wine aroma. As the wines studied were oxidized, the precautions used for classic wines to prevent oxidation phenomena were unnecessary.

1. Reproducibility of Extraction. The coefficients of variation (CV) of most compounds were between 0 and 19% (Table 1). Therefore, the extraction method appeared to be relatively reproducible. However, the CV was greater for sotolon in wine A (25.6%). The assay method used was poorly suited for this compound. As mentioned by Martin and Etievant (1991), sotolon could be degraded in solvents in particular and during injection in GC. This may explain the results observed for this compound. In addition, hexadecanoic acid and syringaldehyde were partially coeluted: this might explain the poor reproducibility of their quantification (CV = 22.2 and 36.5%, respectively).

2. Detection of Odor Compounds in a Maury Wine (A). The extract of wine A, a typical commercial wine of Maury 1991, was analyzed by GC with detection

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Table 1. Concentration of Volatile Compounds in Extracts from Maury Wine A

compound	mean concn (mg/L) ($n = 3$)	CV (%)
alcohols		
isobutyl alcohol	4.72	1.4
isoamyl alcohol	92.24	4.7
1-hexanol	1.51	1.8
3-(methylthio)-1-propanol	0.41	1.3
2-phenylethanol	46.28	3.8
tyrosol	1.43	11.4
total of alcohols	146.18	
esters		
ethyl lactate	34.23	1.4
methyl and ethyl succinate	0.12	18.5
diethyl succinate	13.59	2.4
ethyl 4-hydroxybutanoate	0.35	6.0
diethyl malate	2.54	6.1
2-phenylethyl lactate	0.50	1.3
ethyl 2-hydroxyglutarate	0.75	6.5
diethyl tartrate	0.86	2.8
monoethyl succinate	47.56	5.4
ethyl citrate	0.12	0.1
ethyl pyroglutamate	0.73	1.2
	0.06	2.9
total of esters	101.35	
acids		
acetic acid	10.22	1.6
3-methylbutanoic acid	0.50	0.3
hexanoic acid	0.59	3.2
octanoic acid	0.81	7.7
benzoic acid	0.08	5.4
hexadecanoic acid	0.16	22.2
total of acids	12.36	
carbonyl compounds		
acetoin	5.34	0.7
furfural	1.05	1.4
5-(hydroxymethyl)furfural	1.58	1.7
benzaldehyde + ethyl 3-hydroxybutyrate	0.28	13.6
total of carbonyl compounds	8.25	
lactones		
γ-butyrolactone	3.25	0.2
pantolactone	0.11	6.1
sotolon	0.01	25.6
4-carbethoxy-γ-butyrolactone	0.85	8.2
total of lactones	4.22	
acetals		
cis-2-methyl-5-hydroxy-1,3-dioxane	1.09	1.5
cis-2-methyl-4-(hydroxymethyl)-1,3-dioxolane	0.35	7.3
trans-2-methyl-5-hydroxy-1,3-dioxane	0.31	6.3
trans-2-methyl-4-(hydroxymethyl)-1,3-dioxolane	tr	
total of acetals	1.75	
phenols		
vanillin	tr	
ethyl vanillate	0.30	3.7
acetovanillone	0.06	7.8
syringaldehyde	0.01	36.5
4-hydroxybenzaldehyde	0.07	5.8
ethyl 4-hydroxybenzoate	0.14	4.4
ethyl syringoate + acetosyringone	0.23	1.2
total of phenols	0.81	
miscellaneous		
N-(3-methylbutyl)acetamide	1.93	4.3
2-phenylethylacetamide	0.75	0.2
vomifoliol	0.09	7.5

by flame ionization and sniffing test. After a first examination of the entire chromatogram, only the zones with odors corresponding to the descriptors of the red VDN from Roussillon (Brugirard et al., 1988; Torres,

1990) were examined in greater detail, and the corresponding compounds were identified using mass spectrometry. The sniffing test was carried out with separations on a DB-Wax column and on an apolar DB-5 column. The two separations enabled us to establish relations between substances and odors. However, only pairs common to both separations were investigated and revealed five substances having odors corresponding to the characteristic aromas of the Maury wine analyzed (Table 2). Only the odor of 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolon) was confirmed in the literature, its detection threshold being quite low (10 μg/L) (Martin et al., 1992). Despite quantification inaccuracy, the level of sotolon in wine A was 10 μg/L (Table 1). Thus, it was possible to conclude that it contributed to the aroma of the wine. *cis*- and *trans*-2-methyl-5-hydroxy-1,3-dioxanes were reported by Etievant (1979) to be odorless, but Guesdes de Pinho (1994) described them as having the odor of burnt sugar, coffee, and aniseed. According to Brock et al. (1984), the odor of 4-carbethoxy-γ-butyrolactone is similar to that of sherry, but its detection threshold in wine is unknown. No references were found concerning the odor of the other two ethyl esters (ethyl 2-hydroxyglutarate and ethyl pyroglutamate). Given this lack of information, we decided to check the sensorial characteristics of the four latter substances using synthetic compounds.

3. Synthesis and Sensorial Characteristics of the Compounds with Maury Wine Aromas. *Ethyl (R)-and (S)-2-Hydroxyglutarate.* This compound was prepared by esterification of 2-oxoglutaric acid and reduction of the keto group to alcohol. The synthetic substance obtained in a racemic form was injected in GC to verify the identification of the natural substance and for a sniffing test of the GC effluent under the same conditions as that of the natural extracts on the DB-WAX column. At the retention time of the substance, an intense milk chocolate odor was detected by the two testers, confirming the olfactory characteristics of ethyl 2-hydroxyglutarate. However, the configuration of the natural substance and thus its detection threshold have not yet been determined.

Ethyl L-*Pyroglutamate.* Injected in GC/olfactometry, this compound, commercially available, was synthesized by esterification of L-pyroglutamic acid and was described by the testers as being slightly aromatic with notes of honey or balsam. The synthetic compound thus possessed the odor notes reported during olfactory testing of the Maury extract. The configuration of the natural compound could be L, as its precursor was a natural amino acid, L-glutamic acid, but an epimerization during aging could not be excluded.

(4R) and (4S)-Carbethoxy-γ-butyrolactone. Synthesis was performed by acid-catalyzed trans-esterification of racemic ethyl 2-hydroxyglutarate with elimination of ethanol to shift the equilibrium toward the lactone. The product was obtained in a racemic form and appraised by olfactory testing as previously described. The olfactory sensations described by the testers were very close to the descriptions given during sensorial appraisal of the natural extract. At the retention time of the compound on DB-Wax, the testers observed a very sweet odor of coconut cake. This odor was strong and long lasting. Notes close to those described in Maury wine were found in the extract. The configuration of the natural substance and its olfactory characteristics have not yet been determined.

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Table 2. Identified Markers of the Aging Aroma of Maury Wine A

odor detected on DB-Wax	compound	odor detected on DB-5
prune, grape in rum[a]	*trans*-2-methyl-5-hydroxy-1,3-dioxane	concentrated sweet milk, dried fruits, caramel[a]
curry	sotolon	curry
chocolate	ethyl 2-hydroxyglutarate	chocolate, milk chocolate
coconut	4-carbethoxy-*γ*-butyrolactone	coconut, patisserie
bee's wax + burnt	ethyl pyroglutamate	burnt caramel, balsamic, honey

[a] No odor was detected with the synthetic compound.

trans-2-Methyl-5-hydroxy-1,3-dioxane. The synthesis was performed using 2-(benzyloxy)-1,3-propanediol to prevent dioxolane formation. Anhydrous calcium chloride shifted the acetalization equilibrium by trapping water. The benzyl group was removed by hydrogenation on completion of acetalization. The product of the reaction in the form of a mixture of cis and trans diastereoisomers was injected for olfactory appraisal to confirm or not the odors perceived in the wine extract. At the retention time expected on DB-Wax, for the *trans*-2-methyl-5-hydroxy-1,3-dioxane isomer, no odor for the corresponding peak was reported by either of the testers. This was somewhat surprising since the same odor−compound pair was found in both GC separations (DB-Wax and DB-5 columns) of the extract and the amounts of synthetic compounds injected were higher than those in the wine. However, the finding was in agreement with Etievant (1979), who reported that these compounds were odorless. It was also found that the cis diastereoisomer was odorless.

4. Volatiles of the Different Wines. Compounds were assayed in relation to 4-nonanol as the internal standard. Forty-four compounds were identified and classified into chemical families and arranged within each family in order of elution on the DB-WAX column (Tables 1, 3, and 4). The compounds that belong to several chemical families were entered in only one group. Among the 44 compounds assayed, two groups stood out in terms of quantity: alcohols and esters.

4.1. Presence of the Previous Four Aroma Compounds. *Ethyl 2-hydroxyglutarate* levels were higher in wines obtained by oxidative aging, especially in wines B1 and B2 from Mas Amiel (Table 3). The concentrations were close to those of the Maury A and Domaine des Chênes wines C0 and C1 (Table 4). The aging in demijohns under sunlight did not amplify the formation of this ester.

4-Carbethoxy-γ-butyrolactone present in all of the wines showed higher levels in those submitted to an oxidative aging.

Ethyl pyroglutamate was also present in all of the wines, and its levels were higher in the Maury wines submitted to an oxidative aging (A, B1, B2). The two wines from the Domaine des Chênes (C0, C1) showed lower concentrations, close to the level in wine B0, obtained without oxidative aging. It is interesting to note that the formation of the three previous compounds was related to the metabolism of glutamic acid by yeast or some species of lactic bacteria (Fagan et al., 1982; Radler and Bröhl, 1984). However, these compounds were reported in young wines at much lower levels (Baumes et al., 1986), suggesting that chemical esterification, lactonization, and lactamization or other unknown processes occurred to increase their level during their particular aging procedure. Thus, significant increase of esters of succinic, malic, lactic, and citric acids were reported in old port wines (De Revel et al., 1996). Furthermore, glutamine was shown to be readily converted into pyroglutamic acid, stable between pH 2.2 and 4.0 (Belitz and Grosch, 1987).

Sotolon. Its presence in only wine A could be indicative of an oxidative aging by flor yeast: indeed, it was found in large quantities in Vins Jaunes from Jura (France) and in Spanish flor sherries (Etievant, 1991). Sotolon was also reported recently to be formed by a pure chemical reaction in Vins Jaunes by aldolization of ethanal and 2-oxobutyric acid, mainly formed during aging by flor yeast (Charpentier et al., 1996). It would also be an indicator for *Botrytis cinerea* infection, although that was challenged (Sponholz and Hühn, 1993). This compound had not yet been shown in old VDN obtained without flor yeast. The yeast oxidative metabolism and the alcohol dehydrogenase (ADH2) necessary for ethanol metabolism are known to be suppressed in the presence of glucose or fructose (Vallari et al., 1992). The sotolon biosynthesis in high sugar concentrations requires further investigation.

4.2. Other Volatile Compounds. *Alcohols.* The main alcohols after ethanol were isoamyl alcohol and 2-phenylethanol (Etievant, 1991), the main volatiles of fermentation. However, their levels were lower than in classic red wines (Baumes et al., 1986). The likely explanation is that these VDN fermented only partially until they had an ethanol content of 6−7% by volume. Their levels were slightly influenced by aging.

Esters. The abundance of polar esters (hydroxy esters and diesters) and related lactones was in accordance with the results reported on Port wines by De Revel et al. (1996). Contrary to fatty acids esters detected in trace amounts, their levels increased with aging. Given their detection thresholds reviewed by Etievant (1991), their organoleptic impact was questionable.

Lactones. *γ*-Butyrolactone and pantolactone had the same behavior as the 4-carbethoxy-*γ*-butyrolactone. The levels were higher in the samples submitted to oxidation, but no difference was observed between the two modes of oxidative aging.

Carbonyl Compounds. Furfural and 4-(hydroxymethyl)furfural levels were much more important in the wines aged under oxidative conditions and particularly in demijohns (B2, C1) (Tables 3 and 4). These compounds were derived from sugars and could be considered as markers of the aging of sweet wines.

Acetals. The levels of acetals increased from reference wine B0 to wines aged in barrel or demijohn. The significant acetals detected in the present work were the acetals formed from glycerol and ethanal (dioxanes and dioxolanes) and were shown to be odorless (see above). They were reported in Australian flor sherries (Williams and Strauss, 1978; Simpson, 1980) and in Vins Jaunes (Etievant, 1979). On the other hand, acetals formed from ethanol and ethanal were present but not assayed with the method used.

Among the acetals, *cis*-2-methyl-5-hydroxy-1,3-dioxane, present in the six wines, showed higher levels in wines submitted to oxidation, especially in those con-

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Table 3. Concentration of Volatile Compounds in the Extracts from the Same Maury Wine (Mas Amiel Winery) Submitted to Three Aging Modes

compound	wine without oxidative aging (B0)		wine aged for 1 year in barrel (B1)		wine aged for 1 year in demijohns exposed to sun (B2)	
	mean concn (mg/L) ($n = 3$)	CV (%)	mean concn (mg/L) ($n = 3$)	CV (%)	mean concn (mg/L) ($n = 3$)	CV (%)
alcohols						
isobutyl alcohol	12.94	9.4	12.20	4.1	12.48	11.1
isoamyl alcohol	93.12	1.9	86.20	1.5	85.47	1.8
1-hexanol	1.44	2.1	1.35	0.3	1.74	0.6
2-phenylethanol	33.58	0.5	33.01	0.6	25.19	0.9
tyrosol	1.73	3.8	1.62	3.5	1.36	4.7
total of alcohols	142.8		134.38		126.24	
esters						
ethyl lactate	3.77	1.1	7.67	0.4	6.74	1.7
methyl and ethyl succinate	0.04	7.4	0.06	1.8	0.10	12.1
diethyl succinate	0.87	2.5	5.42	0.4	3.67	0.3
ethyl 4-hydroxybutanoate	0.55	0.4	0.31	1	0.29	2.3
diethyl malate	0.88	2.3	5.27	0.3	3.42	0.7
ethyl 2-oxoglutarate	0.05	7.9	0.09	2.8	0.07	15.0
2-phenylethyl lactate	0.67	1.4	0.48	24.1	0.65	2.5
ethyl 2-hydroxyglutarate	0.29	4.4	0.79	0.7	0.69	0.5
diethyl tartrate	0.10	8.2	0.46	8.0	1.04	32.6
monoethyl succinate	16.24	1.9	33.83	1.6	28.15	2.0
ethyl citrate	0.07	9.0	0.14	5.2	0.13	2.7
ethyl pyroglutamate	0.67	1.6	1.08	2.1	1.43	1.7
total of esters	24.20		55.60		46.38	
acids						
acetic acid	6.15	4.1	8.18	3.5	7.95	4.3
3-methylbutanoic acid	0.32	0.8	0.35	2.8	0.29	1.1
hexanoic acid	0.98	0.9	0.85	0.6	1.03	0.3
octanoic acid	1.34	0.4	0.96	0.6	1.37	0.7
benzoic acid	0.06	12.1	0.13	26.8	0.12	16.6
hexadecanoic acid	0.10	11.2	0.12	46.7	0.13	17.4
total of acids	8.95		10.59		10.89	
carbonyl compounds						
acetoin	2.20	0.6	2.58	1.8	2.41	2.8
furfural	0.12	6.8	0.40	1.1	0.69	1.2
5-(hydroxymethyl)furfural	0.03	16.2	0.34	18.0	0.44	6.1
benzaldehyde + ethyl 3-hydroxybutyrate	0.12	14.4	0.21	2.1	0.28	2.4
total of carbonyl compounds	2.47		3.53		3.82	
lactones						
γ-butyrolactone	2.14	0.6	2.68	0.4	2.40	1.1
pantolactone	0.11	1.0	0.16	5.0	0.16	6.7
sotolon	nd		nd		nd	
4-carbethoxy-γ-butyrolactone	0.38	2.6	0.63	2.5	0.57	1.3
total of lactones	2.63		3.47		3.13	
acetals						
cis-2-methyl-5-hydroxy-1,3-dioxane	0.10	5.4	0.36	0.9	0.53	2.3
cis-2-methyl-5-(hydroxymethyl)-1,3-dioxolane	0.05	4.6	0.24	1.6	0.17	2.5
trans-2-methyl-5-hydroxy-1,3-dioxane	0.04	11.4	0.12	5.1	0.18	3.9
trans-2-methyl-4-(hydroxymethyl)-1,3-dioxolane	tr		tr		tr	
total of acetals	0.19		0.72		0.88	
phenols						
ethyl vanillate	0.19	3.2	0.32	2.2	0.27	2.9
acetovanillone	0.07	6.4	0.07	5.2	0.08	2.8
syringaldehyde	0.02	31.8	0.02	3.7	0.02	5.9
4-hydroxybenzaldehyde	0.07	27.6	0.28	9.0	0.33	4.6
ethyl 4-hydroxybenzoate	0.19	6.0	0.23	4.8	0.14	1.1
ethyl syringoate	0.17	3.9	0.34	2.8	0.38	1.5
acetosyringone	0.01	42.1	0.02	3.7	0.01	17.1
total of phenols	0.72		1.28		1.23	
miscellaneous						
N-(3-methylbutyl)acetamide	0.64	1.2	3.30	0.2	0.52	0.4
2-phenylethylacetamide	0.07	2.9	0.41	5.4	0.11	10.8
vomifoliol	0.01	9.4	0.01	35.3	0.02	17.2

served in demijohns (B2 and C1). With demijohns stored outside, the coldness of the night improved oxygen levels in wine, whereas the higher temperature of the day favored oxidation reactions. This phenomenon was amplified by the smaller volume of demijohns compared to that of barrels. These conditions contrib-

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Table 4. Concentration of Volatile Compounds in the Extracts from the Same Rivesaltes Wine (Domaine des Chênes Winery) Submitted to Two Aging Modes

compound	wine aged for 4 years in barrel (C0)		wine aged for 3 years in barrel and then for 1 year in demijohn (C1)	
	mean concn (mg/L) ($n = 3$)	CV (%)	mean concn (mg/L) ($n = 3$)	CV (%)
alcohols				
isobutyl alcohol	12.35	12.5	11.26	7.1
isoamyl alcohol	109.61	2.2	91.58	1.4
hexanol	0.91	0.2	0.82	1.6
2-phenylethanol	49.58	0.4	42.54	2.7
tyrosol	2.06	0.9	1.66	0.1
total of alcohols	174.51		147.86	
esters				
ethyl lactate	4.87	0.2	4.56	0.9
ethyl hydroxyacetate	0.12	4.6	0.28	1.3
methyl and ethyl succinate	0.09	5.5	0.03	7.9
diethyl malate	9.03	0.6	9.13	2.0
ethyl 4-hydroxybutanoate	0.36	4.7	0.27	0.6
diethyl malate	4.52	0.2	5.62	1.8
ethyl 2-hydroxyglutarate	0.75	0.5	0.62	0.6
2-phenylethyl lactate	0.60	1.4	0.43	1.8
diethyl tartrate	0.31	14.1	0.34	4.2
monoethyl succinate	47.98	0.5	41.31	1.2
ethyl citrate	0.11	0.7	0.13	2.6
ethyl pyroglutamate	0.42	2.0	0.38	1.8
total of esters	69.04		63.10	
acids				
acetic acid	8.37	1.5	6.88	1.1
3-methylbutanoic acid	0.62	1.2	0.53	1.9
hexanoic acid	0.54	1.0	0.51	2.4
octanoic acid	0.73	1.1	0.52	4.6
benzoic acid	0.08	10.7	0.07	40.1
hexadecanoic acid	0.08	26.1	0.08	5.8
total of acids	10.42		8.59	
carbonyl compounds				
acetoin	0.57	1.5	0.87	0.7
furfural	0.47	6.1	1.26	3.5
benzaldehyde +	0.26	4.1	0.54	1.0
5-(hydroxymethyl)furfural	0.31	5.9	1.27	2.7
total of carbonyl compounds	1.61		3.94	
acetals				
cis-2-methyl-5-hydroxy-1,3-dioxane	0.48	1.6	1.69	1.0
cis-2-methyl-4-(hydroxymethyl)-1,3-dioxolane	0.22	1.8	1.16	0.8
trans-2-methyl-5-hydroxy-1,3-dioxane	0.16	3.50	0.57	0.8
trans-2-methyl-4-(hydroxymethyl)-1,3-dioxolane	tr		tr	
total of acetals	0.86		3.42	
lactones				
γ-butyrolactone	3.17	0.5	3.01	1.2
pantolactone	0.13	1.5	0.12	3.9
sotolon	nd		nd	
4-carbethoxy-γ-butyrolactone	0.50	3.2	0.42	1.6
total of lactones	3.80		3.55	
phenols				
ethyl vanillate	0.31	2.8	0.15	5.7
acetovanillone	0.08	15.5	0.17	2.3
syringaldehyde	0.05	21.3	0.07	50.8
4-hydroxybenzaldehyde	0.12	20.1	0.37	15.5
ethyl 4-hydroxybenzoate	0.08	15.2	0.07	3.2
ethyl syringoate	0.18	3.2	0.17	3.9
acetosyringone	0.03	22.3	0.04	11.2
total of phenols	0.85		1.04	
miscellaneous				
N-(3-methylbutyl)acetamide	1.47	0.7	2.99	1.1
2-phenylethylacetamide	0.84	2.3	1.93	1.5
vomifoliol	0.02	21.9	0.06	8.6

uted to the oxidation of ethanol to ethanal, the starting material of acetals. On the contrary, for the barrels stored inside the cellar, the range of temperatures between night and day was narrow.

Phenols. The amounts of phenols in these wines were relatively low. There was, however, an increase for some of them (ethyl vanillate, 4-hydroxybenzaldehyde, ethyl syringoate, and acetosyringone) between the reference young wine (B0) and the older ones, but there was no significant difference between the barrel-aged wine and the demijohn wine [except for acetovanillone and 4-hydroxybenzaldehyde, which increased in wines ex-

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posed to sun (B2 and C1)]. That observation suggested that volatile phenols were formed during aging from their glycosides (Bayonove et al., 1993). However, these phenols were not likely formed by degradation of lignin from barrels during aging as the barrels used were old (Boidron et al., 1988).

CONCLUSION

GC/olfactometry analysis of the synthesized compounds [racemic ethyl 2-hydroxyglutarate (chocolate), racemic 4-carbethoxy-γ-butyrolactarate (coconut), and ethyl L-pyroglutamate (honey)] suggests that they participate in the aroma of VDN from Roussillon. These volatile compounds were reported in young wines at much lower levels (Baumes et al., 1986), suggesting that chemical esterification, lactonization, and lactamization or other unknown processes occurred and increased their levels during the oxidative aging procedure. Similar trends were reported by De Revel et al. (1996) and Da Silva Ferreira and Bertrand (1996) in the aging of various Douro Ports.

trans-2-Methyl-5-hydroxy-1,3-dioxane, synthesized in the laboratory, was odorless. Even if it revealed interesting aromas by sniffing analyses of the wines extracts, we still do not assume that this compound could contribute to the particular aroma of such aged wines (Etievant, 1991).

All of these aroma compounds were detected and quantified in the six wines aged under different oxidative conditions. Their levels increased during aging with respect to a standard wine (B0) kept in a bottle without oxidation.

Sotolon was detected only in wine A. With its interesting aroma (green nut, curry), its presence could increase the flavor quality. However, further studies will be necessary to understand how it can be formed in these aged wines and to demonstrate the pathways of its biosynthesis.

Furthermore, other aroma compounds were quantitatively compared in the six wines. As previously reported by De Revel et al. (1996), there was an increase of polar ethyl esters and related lactones during aging. That trend was more pronounced in barrel-aged wine than in demijohn-aged wine. The formation of acetals in demijohns was more important; the wide range of temperatures induced by this aging process could explain such evolution. Furfural and 5-(hydroxymethyl)furfural increased in aged wines, especially in demijohns. They could be considered as aging markers of sweet wines.

This work opened up three lines of research. The detection thresholds of the three natural compounds (ethyl 2-hydroxyglutarate, 4-carbethoxy-γ-butyrolactone, and ethyl L-pyroglutamate) should be determined in wine for the evaluation of their contribution to the aroma. This will necessitate the determination of the structural configuration of the natural compounds and the preparation of the enantiomerically pure synthetic compounds. Second, the importance of aging conditions on the formation mechanisms should be established, particularly with regard to the formation of sotolon. Finally, a number of compound−odor combinations remain to be studied to complete the set of volatile compounds involved in aging aroma.

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