Identification of Volatile and Powerful Odorous Thiols in Bordeaux Red Wine Varieties

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The use of a new technique combining low-temperature vacuum distillation with a specific chemical capture with an organomercuric compound enabled the extraction of volatile odorous thiols present at very low concentrations in the Bordeaux red wine varieties Merlot and Cabernet Sauvignon. The analysis of wine extracts by gas chromatography coupled with detection by olfactometry, flame photometry, and mass spectrometry led to the identification of three aromatic thiols: 3-mercapto-2-methylpropanol, identified for the first time in wine; 3-mercaptohexanol; and 3-mercaptohexyl acetate, already described in Sauvignon Blanc wines.

Keywords: *Vacuum distillation; p-hydroxymercuribenzoate; aroma; 3-mercapto-2-methylpropanol; 3-mercaptohexanol; 3-mercaptohexyl acetate; Bordeaux red wines; Cabernet Sauvignon; Merlot*

INTRODUCTION

Cabernet Sauvignon and Merlot, which are very widespread varieties all over the world and notably in the region of Bordeaux, give wines with many varied aromatic characteristics matching fruity or floral registers (blackcurrant, cherry, violet) with roasted notes, liquorice odors, and even cooked meat or woodsmoke nuances (Peynaud et al., 1980). Cabernet Sauvignon wines may also have herbaceous odors, the intensities of which vary depending on the conditions of grape maturation. Some methoxypyrazines, such as 2-methoxy-3-isobutylmethoxypyrazine, present in Cabernet Sauvignon grapes (Bayonove et al., 1975) and wines (Boison et al., 1990; Allen et al., 1989, 1994), may contribute to their green-pepper-like character. Numerous volatile compounds belonging to other chemical families have been identified in red wine varieties, in particular Cabernet Sauvignon and Merlot (Webb et al., 1964; Shimoda et al., 1993; Baumes et al., 1986). Some of these compounds possess odors reminiscent of nuances perceived during the tasting of wines. They are notably derivatives of C13-norisoprenoids, including β-damascenone, characterized by fruity and floral notes, that may greatly exceed the olfactive perception threshold of this substance in water (Baumes et al., 1986). Several monoterpenes may also contribute to the floral nuances of some Cabernet Sauvignon and Merlot wines (Ribéreau-Gayon et al., 1975; Baumes et al., 1986; Bertrand et al., 1995).

Other compounds, with a thiol functional group and often characterized by a strong odorous power, have been described in numerous foods. The study of Sauvignon Blanc wine varietal aroma has led to the identification of highly odorous thiols, 4-mercapto-4-methylpentan-2-one (4MMP) (Darriet et al., 1995), 3-mercaptohexyl acetate, 3-mercaptohexanol, 4-mercapto-4-methylpentan-2-ol, and 3-mercapto-3-methylbutan-1-ol (Tominaga et al., 1998a), the quantification of which has made it possible to show the dominating role of this chemical family in the aroma of these wines (Bouchilloux et al., 1996; Tominaga et al., 1998b). 4MMP, which has a characteristic box tree odor, has also been detected in Scheurebe wines (Guth et al., 1997). Two other mercaptans identified in Sauvignon wines (Lavigne-Cruège et al., 1998), 2-mercaptoethyl acetate and 3-mercaptopropyl acetate, may participate in the toasted and roasted-meat-like nuances of this wine aroma. These two compounds have also been detected in Cabernet Sauvignon and Merlot wines.

We noted that a simple addition of copper sulfate in a Cabernet Sauvignon or Merlot wine led to a significant decrease in the aromatic complexity, which may suggest the contribution of odorous thiols in the varietal aroma of the wines from red cultivars.

This paper reports the results of our experiments using an extractive method based on a vacuum distillation and a specific chemical trap to demonstrate the presence of odorous volatile thiols in Cabernet Sauvignon and Merlot wines.

MATERIALS AND METHODS

Wine. Cabernet Sauvignon and Merlot wines from different appellations of Bordeaux (Pessac-Léognan, Pauillac, Pomerol, and Bordeaux) and from the 1995 and 1996 vintages were studied.

Chemicals and Reference Compounds. *p*-Hydroxymercuribenzoic acid (p-HMB) and sodium chloride were provided by Sigma Chemical Co. (St. Louis, MO). L-Cysteine hydrochloride was provided by Aldrich-Chemie (Steinheim, Germany) and dichloromethane (Atrasol quality) by SDS (Peypin, France). The reference compounds of 3-mercaptohexyl acetate, 3-mercaptohexanol, and 4-mercapto-4-methylpentan-2-one were purchased from Interchim (Montluçon France).

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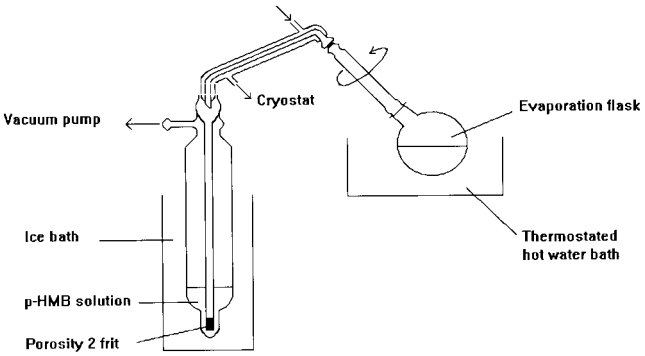
S0021-8561(97)01027-3 CCC: $15.00
Published on Web 07/18/1998

Scheme 1. System of Extraction by Vacuum Distillation and Selective Thiol Trap



Infrared (IR) and Nuclear Magnetic Resonance (NMR) Analyses. Infrared spectra of the synthesized compound were recorded on a Perkin-Elmer model 1310 spectrometer. ^{1}H NMR spectra were obtained in $CDCl_3$ on a Bruker AC 200 (200 MHz) spectrometer with tetramethylsilane [$Si(CH_3)_4$] as internal standard.

Gas Chromatography/Olfactometry (GC/O), Gas Chromatography/Flame Photometry (GC/FPD), and Gas Chromatography/Mass Spectrometry (GC/MS) Analyses. The wine extract analyses by gas chromatography coupled to an olfactometric or flame photometric mode of detection were performed with the same HP 5890 gas chromatograph (Hewlett-Packard, Avondale, PA). The samples were injected in splitless mode (injector port temperature, 230 °C; purge on time, 1 min) onto two types of capillaries, BPX35 and BPX5 (50 m × 0.22 mm i.d., 0.25 μm film thickness; SGE, Ringwood, Victoria, Australia). The carrier gas was hydrogen U (Air Liquide, France). The column head pressure was 20 psi and the flow rate 1.54 mL/min at 35 °C. The temperature program began with an isotherm at 35 °C for 1 min. The temperature of the oven was then raised by 3 °C/min to 230 °C and held for 15 min. The sensorial detection system was composed of an olfactometric installation ODO1 (Scientific Glass Engineering, SGE), as described previously (Darriet et al., 1991). The flame photometry detector was a type HP 19256A (Hewlett-Packard) fixed at the specific sulfur emission wavelength λ = 393 nm. Its temperature was 200 °C, and the gas flow rates were 90 mL/min for hydrogen, 76 mL/min for air, and 38 mL/min for nitrogen. Peak integration was performed with an HP 3365 (Hewlett-Packard) system. The samples analyzed by GC/MS were injected onto a STAR 3400 CX chromatograph (Varian, Harbor City, CA) coupled to a SATURN 2000 mass spectrometer (Varian) functioning under the following conditions: transfer line temperature, 250 °C; ionization by electronic impact generated at 70 eV; temperature of detector, 150 °C; analysis by ion capture (ion trap detector). The extracts were injected onto two capillaries, BPX5 and BPX35 (50 m × 0.22 mm i.d., 0.25 μm film thickness, SGE). The carrier gas was helium N60 (Air Liquide) with a 20 psi column head pressure.

Synthesis. *3-Mercapto-2-methylpropanol (3M2MP).* The preparation of the enantiomers of 3M2MP was done separately by decomposition of isothiourea salts synthesized from 3-bromo-2-methylpropanol according to the procedure described by Bogatskii et al. (1974). The mixture containing 3-bromo-2-methylpropanol (Aldrich-Chemie) (1 g), thiourea (0.5 g), and ethanol (1 mL) was heated under reflux for 5 min. After evaporation of ethanol, the residue was mixed with ethyl acetate (1 mL) while cold, then filtered and rinsed with the same solvent. A solution of the isothiourea salt obtained (1.25 g; mp = 98 °C) in sodium hydroxide 2 M (4 mL) was heated under reflux for 1 h. The reaction mixture was then cooled at room temperature and acidified to pH 1 with 1 N hydrochloric acid. The solution obtained was extracted with diethyl oxide (5 × 20 mL). The organic phases were collected, dried over Na_2SO_4, and then evaporated. The residue was purified on a silica (silica gel 60, 63−200 μm, Merck, Darmstadt, Germany) column. 3M2MP was eluted with the solvent mixture diethyl ether/pentane (80 + 20, v/v): yield, 0.40 g (63%). The purified product was characterized by IR and ^{1}H NMR measurements and by its mass spectral data: IR 3350, 2560, 1450, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.98 (d, 3H, CH_3), 1.32 (t, 1H, SH), 1.65 (s, 1H, OH), 1.85 (oct, 1H), 2.45−2.72 (m, 2H, CH_2−SH), 3.59 (d, 2H, CH_2−OH) ppm [downfield from $Si(CH_3)_4$]; MS/EI, *m/z* (intensity) 106 (M+) (12%), 89 (22%), 75 (15%), 72 (100%), 59 (14%), 57 (70%), 55 (72%), 47 (39%), 45 (43%), 41 (38%), 39 (53%).

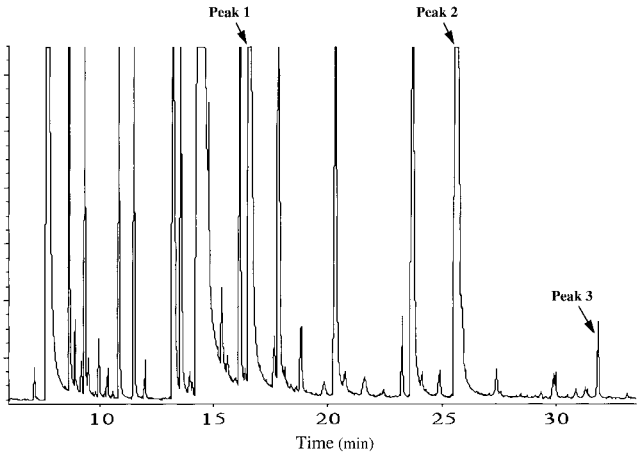


Figure 1. Typical chromatogram obtained by GC/FPD from a Cabernet Sauvignon wine extract injected onto a BPX5 capillary: peak 1, 3-mercapto-2-methylpropanol; peak 2, 3-mercaptohexanol; peak 3, 3-mercaptohexyl acetate.

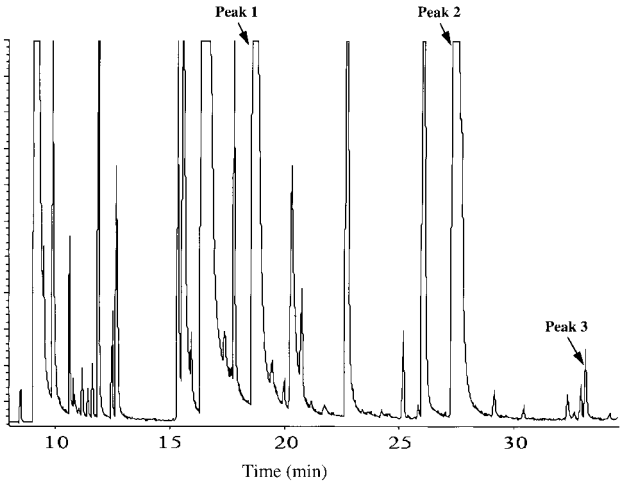


Figure 2. Typical chromatogram obtained by GC/FPD from a Cabernet Sauvignon wine extract injected onto a BPX35 capillary: peak 1, 3-mercapto-2-methylpropanol; peak 2, 3-mercaptohexanol; peak 3, 3-mercaptohexyl acetate.

Extraction of Volatile Thiols by Vacuum Distillation. Extraction System. The vacuum distillation system (Scheme 1) was composed of a 3 L evaporation flask immersed in a thermostated hot water bath and attached to a modified rotary evaporating apparatus (Rotavapor R-114, Büchi, Switzerland). The rotation shaft was connected to a cooler supplied with ethylene glycol cooled at 0 °C by a cryostat (Chrompack, Middleburg, Netherlands). The cooler was extended with a glass pipe, the end which, consisting of a porosity 2 frit, was plunged into a vessel connected to a vacuum pump (Trivac D25-B, Leybold) and immersed in an ice bath at 0 °C.

Isolation of Volatile Thiols. The volatile compounds contained in wine were extracted by distillation at 35−45 °C and carried, by the application of a high-level vacuum (pressure = 0.5−1.5 Pa), to the whole system toward a p-HMB solution, where molecules with a thiol functional group were specifically captured (Darriet et al., 1995; Bouchilloux et al.,

Table 1. Aromagrams of Bordeaux Red Wine Extracts Obtained after Analysis by GC/O

GC performed with a BPX35 capillary			GC performed with a BPX5 capillary		
RT[a] (min)	odorous zone	KI_{BPX35}[b]	RT[a] (min)	odorous zone	KI_{BPX5}[b]
12.75	nut/meaty		11.99	nut/meaty	
15.34	box tree/broom		13.14	boiled potatoes	
15.40	fungus		13.34	ivy	
15.54	roasted meat		13.47	box tree/broom	
17.30	mushroom soup		14.09	sulfury	
17.39	box tree/broom	1033	14.48	floral	
17.55	undergrowth		15.33	box tree/broom	
18.38	broth/sweat	1057	15.84	box tree/broom	899
21.55	sweat/leek		16.47	broth/sweat	914
22.50	fresh mushroom		18.46	stock	
23.68	grapefruit		18.52	earthy	
24.86	marmalade		19.58	sweat/leek	
25.51	burnt		20.20	mushroom soup	
26.07	eucalyptus		22.39	fruity	
27.20	grapefruit	1256	23.27	burnt	
28.95	caramel/roasted coffee		24.57	caramel/roasted coffee	
29.13	plum		25.63	grapefruit	1124
33.31	box tree/broom	1389	31.00	grapefruit	
			31.90	box tree/broom	1279

[a] Retention times obtained after analysis by GC/O and GC/FPD of the wine extracts on the same chromatograph. [b] Kovats index determined by GC/MS.

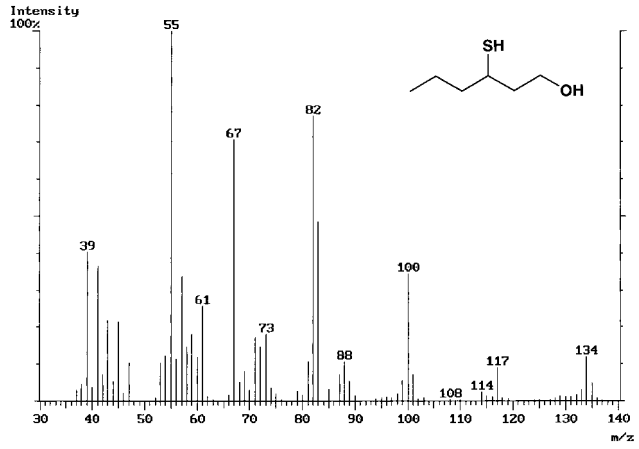


Figure 3. MS/EI of 3-mercaptohexanol obtained from a Cabernet Sauvignon wine extract injected onto a BPX5 capillary.

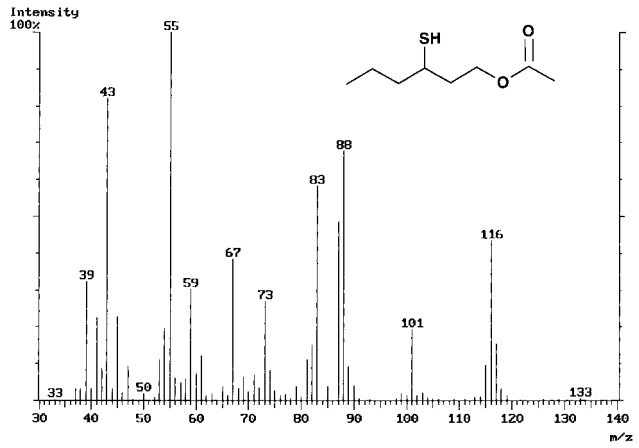


Figure 4. MS/EI of 3-mercaptohexyl acetate obtained from a Cabernet Sauvignon wine extract injected onto a BPX5 capillary.

1996). Three liters of the same wine were successively extracted according to the following procedure.

One liter of wine to which had first been added sodium chloride (100 g) was poured into an evaporation flask placed in the thermostated bath. The application of vacuum to the apparatus made it possible to carry the headspace toward a basic solution (100 mL), 0.1 mM p-HMB (36 mg of p-HMB in NaOH N/10, 15 mL) contained in a vessel kept at 0 °C.

Table 2. Odor Thresholds and Approximate Quantities of Thiols Recovered from Cabernet Sauvignon and Merlot Wines of Bordeaux

odorous compound	odor threshold (ng/L of water)	odor qualities	approx quantity[b] (ng/L of wine)
3-mercapto-2-methyl-propanol	3000	broth, sweat	250−10000
3-mercaptohexanol	12−15[a]	grapefruit[a]	10−5000
3-mercaptohexyl acetate	2−3[a]	box tree, broom, passion fruit[a]	1−200

[a] Odor thresholds determined by Tominaga et al. (1996, 1998a). [b] Approximate quantities determined by applying the method described by Bouchilloux et al. (1996).

After 90 min of distillation of 1 L of wine, the solution containing the thiols combined with p-HMB was acidified with hydrochloric acid (1 M) to pH 2 and then evaporated to dryness. The dry residues, corresponding to the extraction of 3 L of wine, were assembled and washed with dichloromethane. They were then diluted in ultrapure water (Millipore, Bedford, MA) (100 mL). The solution obtained was evaporated again to dryness and the residue diluted in ultrapure water (50 mL). The solution was basified with a concentrated sodium hydroxide solution (10 N NaOH) to pH 8. An L-cysteine hydrochloride solution in water, corresponding to 20 times the p-HMB molarity used during the previous distillation, was basified to pH 8 before addition to the solution containing the combined thiols. The reaction mixture was stirred for 20 min at room temperature. After decombination, the solution was extracted with dichloromethane (5:2.5:2.5 mL). The obtained organic extract was concentrated under a flow of nitrogen (100 mL/min) to 20 μL, before analysis by GC/O, GC/FPD, and GC/MS (injection volume = 3 μL).

Determination of Olfactive Perception Thresholds. The odor threshold of a substance was determined as the minimum concentration below which 50% of the tasters failed to taste the difference from the control by the triangle test at five increasing concentrations in distilled water. Tasting of the solutions placed in glasses corresponding to AFNOR (Association Française des Normes) standards was done by a 35-person jury in a climatized room at 11:00 a.m. (Boidron et al., 1988).

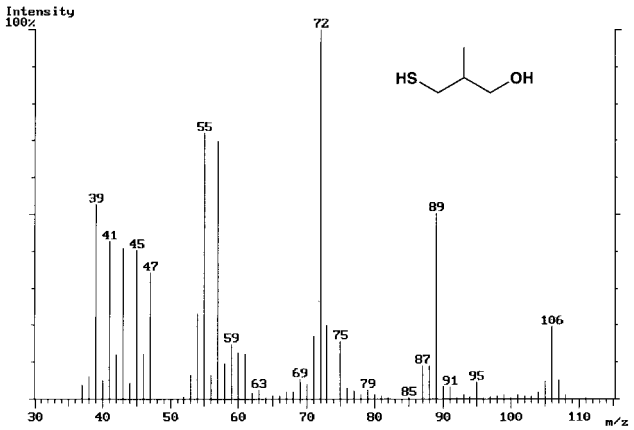


Figure 5. MS/EI of 3-mercapto-2-methylpropanol obtained from a Cabernet Sauvignon wine extract injected onto a BPX5 capillary.

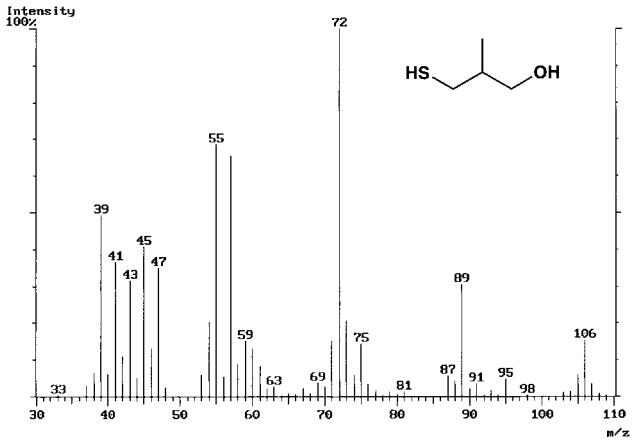


Figure 6. MS/EI of the pure compound of 3-mercapto-2-methylpropanol injected onto a BPX5 capillary.

RESULTS AND DISCUSSION

The use of a vacuum distillation process coupled to a specific reaction of mercaptans with an organomercuric compound made it possible to extract volatile thiols from Cabernet Sauvignon and Merlot wines without the polyphenols which greatly disturb the analysis of the wine extracts by GC/O, GC/FPD, and GC/MS. The injection of the samples onto a gas chromatograph coupled to a flame photometry detector displayed rather complex sulfur compound chromatograms (Figures 1 and 2), as shown in Sauvignon Blanc wines by Tominaga et al. (1996, 1998a). The aromagrams obtained from the same extracts using an olfactometric detection mode showed many odorous zones (Table 1). Some resembled odors already perceived during Sauvignon Blanc wine extract analysis, notably box tree/broom [retention time $(RT)_{BPX5} = 15.84$ and 31.90 min, $RT_{BPX35} = 17.39$ and 33.31 min), broth/sweat ($RT_{BPX5} = 16.47$ min, $RT_{BPX35} = 18.38$ min), and grapefruit ($RT_{BPX5} = 25.63$ min, $RT_{BPX35} = 27.20$ min] (Table 1). With flame photometry detection and after injection onto two capillaries, we noted, at the same retention times, the presence of sulfur compound peaks (peaks 1−3, Figures 1 and 2), except for the odorant zone of box tree/broom at $RT_{BPX5} = 15.84$ min and $RT_{BPX35} = 17.39$ min. Peaks 1 and 2 possessed the same retention times as those of 3-mercaptohexanol and 3-mercaptohexyl acetate standards analyzed with the same chromatographic conditions. The analysis by GC/MS of the same wine extracts, on two capillaries, made it possible to confirm the identification of these two compounds in red wines (Figures 3 and 4) by comparison of their mass spectral data at the same retention times and Kovats indices with those of the pure substances (Table 1). 3-Mercaptohexanol and 3-mercaptohexyl acetate are powerful odorous compounds (Table 2) already identified in passion fruit (Engel et al., 1991; Weber et al., 1995) and recently in Sauvignon Blanc wines (Tominaga et al., 1996, 1998a).

The odorous zone of box tree ($RT_{BPX5} = 15.84$ min, $RT_{BPX35} = 17.39$ min) we detected by GC/O in several Bordeaux red wines possessed a retention time coinciding with that of the 4-mercapto-4-methylpentan-2-one also identified in Sauvignon Blanc and Scheurebe wines (Darriet et al., 1995; Guth et al., 1997).

The coincidence, on two capillaries, of the retention time of 3-mercapto-2-methylpropanol synthesized and that of peak 3 obtained after analysis by GC/FPD of a wine extract allowed us to show the presence of this compound in wines (Figures 1 and 2). Its identification was confirmed by comparison of the mass spectral data of the compound present in the wine extracts and those of the pure substance (Figures 5 and 6). The presence of 3-mercapto-2-methylpropanol was shown for the first time in wine. The odor threshold of its racemic mixture was determined in water at 3000 ng/L.

These whole thiols were detected in many Bordeaux red wine varieties from recent or old vintages (Table 3). The approximate amounts of these compounds in wines were also estimated, by comparison to a standard curve, with a method used for the quantification of 4MMP in Sauvignon Blanc wines (Bouchilloux et al.,

Table 3. Detection[a] of 3-Mercapto-2-methylpropanol, 3-Mercaptohexanol, and 3-Mercaptohexyl Acetate in Bordeaux Red Wines

	3-mercapto-2-methylpropanol	3-mercaptohexanol	3-mercaptohexyl acetate
Pessac-Léognan 1996 (Cabernet Sauvignon)	a, b, c	a, b, c	a, b, c
Pessac-Léognan 1996 (Merlot)	a, b, c	a, b, c	a, b
Pauillac 1996 (Cabernet Sauvignon)	a, b, c	a, b, c	a, b, c
Pauillac 1996 (Merlot)	a, b, c	a, b, c	a, b
Pomerol 1996 (Merlot)	a, b, c	a, b, c	a, b, c
Bordeaux 1995 (Cabernet Sauvignon)	a, b	a, b	a, b
Bordeaux 1994 (Cabernet Sauvignon)	a, b	a, b	a
Pessac-Léognan 1994 (Cabernet Sauvignon, Merlot)	a, b	a, b	a, b
St. Julien 1989 (Cabernet Sauvignon, Merlot)[b]	a	a	a
St. Julien 1988 (Cabernet Sauvignon, Merlot)[b]	a	a	a
St. Julien 1986 (Cabernet Sauvignon, Merlot)[b]	a	a	a
St. Julien 1985 (Cabernet Sauvignon, Merlot)[b]	a	a	a

[a] a, detection by GC/O; b, detection by gas chromatography/flame photometry; c, detection by GC/MS. [b] Analysis made from 1 L of wine.

1996), combining a technique of dynamic headspace distillation with the specific trap of thiols with p-HMB. We noted that the approximate amounts of these compounds, notably in Merlot and Cabernet Sauvignon young wines, could stand clearly above their olfactive perception thresholds.

Moreover, it has been established that 3-mercaptohexanol was present in Cabernet Sauvignon grapes (Darriet et al., 1997) as well as in Sauvignon Blanc grapes (Tominaga et al., 1997) as S derivatives of cysteine precursor forms.

CONCLUSION

The method of extraction coupling vacuum distillation to the specific reaction of the thiols with an organomercuric compound has demonstrated the abundance of volatile thiols in Bordeaux Cabernet Sauvignon and Merlot wines. These initial studies have led to the identification of three very odorous mercaptans, which may contribute to their aromatic expression: 3-mercapto-2-methylpropanol, characterized by a broth/sweat odor; and 3-mercaptohexanol and 3-mercaptohexyl acetate, with grapefruit and box tree aromas.

ACKNOWLEDGMENT

We thank M. Pons for her contribution to this research study.

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Registry No. Supplied by the Author: 3-mercaptohexanol, 51755-83-0; 3-mercaptohexyl acetate, 136954-20-6; 4-mercapto-4-methylpentan-2-one, 19872-52-7.

Received for review December 3, 1997. Revised manuscript received April 23, 1998. Accepted April 30, 1998. We are grateful to the CIVB (Conseil Interprofessionnel des Vins de Bordeaux) and the Aquitaine Region Council for financial support.

JF971027D