FATE OF POLYFUNCTIONAL THIOLS IN SAUTERNES WINES THROUGH AGEING

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Abstract

Recent papers have revealed the importance of polyfunctional thiols in fresh Sauternes wines (1, 2), but very little is yet known about the fate of such compounds during aging in the bottle. Here it is shown that most polyfunctional thiols with roasted or citrus notes (3-sulfanylpropyl acetate, 2-sulfanylethyl acetate, 3-methyl-3-sulfanylbutanal, and 3-sulfanylheptanal) are degraded within a year upon bottle aging in a cellar. Only 3-sulfanylhexan-1-ol was still found in aged samples at concentrations above its threshold value. Most other key aromas previously found in the fresh noble rot wine are still present in aged samples: varietal aroma (α-terpineol), sotolon, fermentation alcohols (3-methylbutan-1-ol and 2-phenylethanol) and esters (ethyl butyrate, ethyl hexanoate and ethyl isovalerate), carbonyls (*trans*-non-2-enal and β-damascenone), and wood flavours (guaiacol, vanillin, eugenol, β-methyl-γ-octalactone and furaneol).

Introduction

Sauternes wines are traditional AOC French wines made from cv Sauvignon Blanc, Semillon, or Muscadelle grapes contaminated by noble rot (*Botrytis cinerea*). Recent papers have revealed the importance of polyfunctional thiols in fresh Sauternes wines (1,2). A few studies were dedicated to the fate of polyfunctional thiols during ageing in the bottle (3,4,5). In the present work, polyfunctional thiols were monitored through cellar aging of Sauternes wines.

Experimental

Wine samples. Sauternes wines samples were a kind gift from Château Guiraud, Sauternes, France. W-2002 sample was taken just after bottling (18 months of maturation in oak barrels, vintage 2002) and analysed after 1,5 and 3 years of storage in a wine cellar (14°C ± 2°C).

XAD 2 and pHMB extraction procedures were used, according to Bailly *et al.* (1) and Lermusieau *et al.* (6).

Gas chromatography analyses with Olfactometric Detection (GC-O). 1 µL extract was analysed with a Chrompack CP9001 gas chromatograph equipped with a splitless injector maintained at 250°C; the split vent was opened 0.5 min post-injection. Compounds were analysed using wall-coated open tubular apolar CP-Sil 5-CB (50m x 0.32 mm i.d., 1.2 µm film thickness) and polar FFAP (25m x 0.32 mm i.d., 0.3 µm film thickness) capillary columns. The carrier gas was nitrogen and pressure was fixed to 50 kPa (CP-Sil 5-CB) or 30 kPa (FFAP). The oven temperature was programmed to raise from 36°C to 85°C at 20°C/min, then to 145°C at 1°C/min, and finally to 250°C at 3°C/min. Extracts were analysed by three panellists and complete AEDA was performed by two of them on CP-Sil 5-CB column. The extracts were diluted stepwise with diethyl ether (1+2 by volume). The dilution factor (FD) is defined as the dilution where the compound can still be detected.

Gas chromatography analyses with PFPD (GC-PFPD). 2 µL of pHMB extract was analysed on a ThermoFinnignan Trace GC 2000 gas chromatograph connected to a ThermoFinnigan Trace PFPD detector and equipped with a splitless injector maintained at 250°C; the split vent was opened 1 min post-injection. The carrier gas was helium at a flow rate of 1.7 mL/min. Compounds were analysed using an apolar CP-Sil5-CB capillary column as described above. The oven temperature was programmed to stay for 4 min at 40°C, and then raised from 40°C to 132°C at 2°C/min, then to 250°C at 10°C/min.

Results

In a previous work (1), we determined key odorants of two Sauternes wines by GC-O AEDA (7) applied to Amberlite XAD 2 resin extracts. This extraction method allowed recovery yields above 75%, except for small hydrophilic lactones such as sotolon. Various complementary techniques have been used to identify the odorants: co-injection of commercial standards or combinatorial synthesis products (8,9) on one or two capillary columns, GC-MS, GC-PFPD on pHMB extract, and odour description at the sniffing port (especially when no peak was available with the usual detectors).

Among the key odorants, α-terpineol (floral, musty orange with FD= 81-243) is a well-known grape constituent present in free or glycoside form. Fermentation modifies the aroma profile, with production of many alcohols, esters, and acids. Fusel alcohols such as 3-methylbutan-1-ol (alcohol, chocolate with FD= 243-729) and 2-phenylethanol (co-eluting with linalool ; rose, wine with FD= 243-729) are present in considerable amount. Fermentation ethyl esters are also produced (ethyl butyrate, acid fruit, liquor with FD= 81; ethyl hexanoate, syrup, acid fruit, green apple with FD= 27-243 ; ethyl isovalerate, red fruit with FD= 81-243), bringing some fruity aromas to the wine. A few unreduced carbonyls such as β-damascenone (stewed fruit, peach with FD= 81-243) and *trans*-non-2-enal (cardboard, rubber with FD= 9-243) show high dilution factor values. Among the key odorants, oak-derived flavours are also of prime importance. Guaiacol (wood, phenolic with FD= 81-243), eugenol (hay tree, dental with FD= 27-81), vanillin (vanilla, cake with FD= 9-81), β-methyl-γ-octalactone (sweet, coconut, butter with FD= 243) and γ-nonalactone (sweet, coconut with FD= 27-81) are genuine wood-extractable compounds (10). Furaneol (cotton candy with FD= 27-81) is one of the compounds responsible for the "toasty caramel" aroma. Finally, sotolon (caramel, curry with FD= 81-243) brings the sweetened aroma to botrytized wines. Also worth mentioning is the presence of many polyfunctional thiols: 3-sulfanylpropyl acetate (olive, bacon, plastic with FD= 27-81), 3-sulfanylhexan-1-ol (fruity, rhubarb with FD= 81-729), 3-sulfanylheptanal (fruity, lemon with FD= 81-2187), 2-(sulfanylmethyl)hexan-1-ol (unpleasant, floral with FD= 9-81), 3-methyl-3-sulfanylbutanal (petroleum-like with FD= 0-27), and 2-methylfuran-3-thiol (bacon-like with FD = 27-81). A synergistic effect is suspected between the two latter thiols.

As shown in Table 1, most varietal aromas, fermentation esters, and wood flavours previously found in fresh noble rot wines are still present in aged samples. On the other hand, most polyfunctional thiols with roasted or citrus notes (3-sulfanylpropyl acetate, 2-sulfanylethyl acetate, 3-methyl-3-sulfanylbutanal, 3-sulfanylheptanal) (Table 2) proved to be degraded within a year, upon of bottle aging in a cellar. Oxidation (thiol and/or aldehyde) and ester hydrolysis are most probably

Table 2. *Evolution of thiols during the ageing in bottle of a 2002 Sauternes vintage. GC-O AEDA (FD= 3^{n-1} with n = number of dilutions before no detection) in XAD2 extracts or IST equivalents (µg/L) from GC-PFPD on pHMB extracts.*

RI CPSil5	RI FFAP	Substance	Odour	FD-factor fresh	FD-factor 1.5 year	FD-factor 3 years	IST equivalents (µg/L) fresh	IST equivalents (µg/L) 1.5 year	IST equivalents (µg/L) 3 years
845	1653	3-Methyl-3-sulfanylbutanal [b]	Petroleum, bacon	27	0	0			
845	1306	2-Methylfuran-3-thiol [a]	Petroleum, bacon	81	27	27			
884		2-Sulfanylethyl acetate [a]	Roasted	9	0	0	0.3	0	0
989	1565	3-Sulfanylpropyl acetate [a]	Olive, bacon, plastic	81	3	3	0.8	0	0
1096	1853	3-Sulfanylhexan-1-ol [a]	Fruity, rhubarb, grapefruit	81	81	729	4.5	3	3
1118	1659	3-Sulfanylheptanal [b]	Fruity, lemon	2187	0	0			
1217	1985	2-(Sulfanylmethyl)-hexan-1-ol [b]	Unpleasant, floral	81	n.d.	n.d.			

a: Coincidence of GC retention indices, odours on two capillary columns (CP-Sil5-CB and FFAP-CB), and mass spectrometric data with those of pure compounds available;
b: Coincidence of GC retention indices and odours on two capillary columns (CP-Sil5-CB and FFAP-CB) with those of pure standards.

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the main phenomena responsible for this disappearance. The same profile has been observed in vintage 2003 still under investigation (data not shown).

Table 1. *Evolution of varietal, fermentation, oak and noble rot key-odorants during the ageing in bottle of a 2002 Sauternes vintage. GC-O AEDA (FD= 3^{n-1} with n = number of dilutions before no detection) in XAD 2 extracts.*

RI CPSil5	RI FFAP	Substance [a]	Odour	FD-factor fresh	FD-factor 1.5 year	FD-factor 3 years
		Varietal aroma				
1179	1706	α-Terpineol (2-(4-methylcyclohex-3-en-1-yl)propan-2-ol)	Floral, musty orange	243	81	243
		Fermentation compounds				
707	1217	3-Methylbutan-1-ol	Alcohol, chocolate	243	81/243	729
770	969	Ethyl butyrate (ethyl butanoate)	Acid fruit, liquor	81	81	81
828	1114	Ethyl isovalerate (ethyl 3-methylbutanoate)	Red fruit	243	81	243
975	1241	Ethyl hexanoate	Syrup, acid fruit, green apple	243	81	81
1090	1921	2-Phenylethan-1-ol and	Rose, wine	243	243	243
	1556	Linalool (3,7-dimethylocta-1,6-dien-3-ol)*				
		Influence of oak maturation				
1025	1992	Furaneol (4-hydroxy-2,5-dimethylfuran-3(2*H*)-one)	Cotton candy	81	81	27
1063	1873	Guaiacol (2-methoxyphenol)	Wood, phenolic, spicy	81	243	27/81
1130	1497	*trans*-non-2-enal	Cardboard, rubber	9	27	27
1281	1968	β-Methyl-γ-octalactone	Sweet, cocoa, butter	243	243	729
1322	2032	γ-Nonalactone	Sweet, cocoa, butter	27	27	27
1337	1835	Eugenol (4-allyl-2-methoxyphenol)	Hay tree, dental	81	81	81
1360	2555	Vanillin (4-hydroxy-3-methoxybenzaldehyde)	Vanilla, cake	81	81	27
1368	1818	*β*-Damascenone	Stewed fruit, peach	81	81	243
		Botrytis cinerea **or oxidation compound**				
1068	2213	Sotolon (3-hydroxy-4,5-dimethylfuran-2(5*H*)-one)	Caramel, praline, curry	243	243	243

*: Co-elution of both compounds;
[a]: Coincidence of GC retention indices, odours on two capillary columns (CP-Sil5-CB and FFAP-CB), and mass spectrometric data with those of pure compounds available.

Only 3-sulfanylhexan-1-ol (grapefruit) proved to survive, suggesting the existence of a pool protected against oxidation. A concentration 50 times above its threshold value (60 ng/L (11)) is still measured in vintage 2002 after 3 years.

This work has also revealed two very interesting compounds which are generated through aging: abhexon (ethyl analogue of sotolon), never mentioned before in sweet wines, and raspberry ketone. Unfortunately, as previously shown for sotolon, the usual XAD-2 extraction does not allow very efficient recovery of hydrophilic molecules like abhexon. A modified protocol is therefore required to improve quantification of this spicy aroma in aged wine.