Fate of Key Odorants in Sauternes Wines through Aging

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Recent work has revealed the importance of polyfunctional thiols in young Sauternes wines, but very little is yet known about the fate of such compounds during aging in the bottle. In this study, two Sauternes wines were investigated by gas chromatography–olfactometry (GC–O) aroma extract dilution analysis (AEDA), gas chromatography–mass spectrometry (GC–MS), and gas chromatography–pulsed flame photometric detector (GC–PFPD) after XAD 2 and thiol-specific extractions. Most polyfunctional thiols (3-sulfanylpropyl acetate, 2-sulfanyl ethyl acetate, 3-methyl-3-sulfanylethylbutanal, etc.) proved to be completely degraded after 2 years of 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 odorants found in the young noble rot wine were still detected 5–6 years after harvest: varietal aroma (α-terpineol), sotolon, fermentation aldehydes (3-methylbutan-1-ol and 2-phenylethanol) and esters (ethyl butyrate, isobutyrate, hexanoate, and isoamylate), and oak maturation-related compounds (guaiacol, vanillin, eugenol, β-damascenone, trans-non-2-enal, β-methyl-γ-octalactone, γ-nonalactone, and furanone), as well as three newly identified aromas exhibiting interesting cake, honey-like, and dried apricot odors: homofuraneol, theaspirane, and γ-decalactone. Interestingly, abhexon, never mentioned in sweet wines before, was found to be synthesized during bottle aging. An optimized extraction method allowed us to quantify this honey/spicy compound at levels close to its threshold value (up to 7 μg/L after 5–6 years), thus suggesting a key role of this strong odorant in old Sauternes wines.

KEYWORDS: Abhexon; polyfunctional thiols; aging; Sauternes wines; aroma; noble rot

INTRODUCTION

Sauternes wines are characterized by an exceptional range of aromas, evoking not only citrus but also crystalized and dried fruit as well as honey. Recent works have revealed the importance of polyfunctional thiols in these botrytized wines, especially sulfanylaldehydes, sulfanylalcohols, and sulfanyl esters (1,2). A synergistic effect was highlighted between 2-methylfuran-3-thiol and 3-methyl-3-sulfanylethylbutanal, exhalating bacon–petroleum odors (1), and between three grapefruit-like alcohols: 3-sulfanylhexan-1-ol, 3-sulfanylethylpentan-1-ol, and 3-sulfanylethylbutan-1-ol (2). 2-Methylbut-2-ene-1-thiol, 3-sulfanylpropyl acetate, 3-sulfanylethylpentanal (1), and 2-methyl-3-sulfanylethylbutan-1-ol (2) were found as other potent aromas in this kind of wine. The presence of aldehydes in a fermented beverage was surprising, because Saccharomyces cerevisiae can reduce them to sulfanylalcohols. Release of sulfanylaldehydes at the end of fermentation from S-cysteinylated conjugates was therefore suspected (1).

A few studies have focused on the fate of wine flavors in the bottle. In Spanish red wines, phenol aldehydes [vanillin (4-hydroxy-3-methoxybenzaldehyde) and syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde)], volatile phenols (2-methoxyphenol, 2-methoxy-4-methylphenol, and 4-allyl-2-methoxyphenol), and some furanic compounds revealed to decrease during the first years of storage in the bottle, while 4-ethylphenol, 2-methoxy-4-ethylphenol, 2-furaldehyde, and whisky lactone [5-butyl-4-methyl-2-dihydrofuran-3(2H)-one] were generated (3,4). Garde-Cerdán and Acién-Azpilicueta (5) showed that sulfur dioxide in the bottle lead to higher contents of esters and alcohols in experimental white wines. In rosé Bordeaux wines, Murat et al. (6) measured the loss of half of 3-sulfanylhexan-1-ol during the first year of storage and anthocyanin addition was shown to limit the decrease of this compound. Sulfur dioxide is reported to have the same effect in red Bordeaux wines (7). In Sauvignon wines, 4-methyl-4-sulfanylethylpentan-2-one, 3-sulfanylethanol-1-ol, and its acetate have been shown to decrease during storage (8). The instability of the two latter, likely related to ester hydrolysis and alcohol oxidation (9), has also been observed in Malborough Sauvignon Blanc wines, whereas an increase of 2-furylethanol has been reported in red Bordeaux wines (10) and Champagne stored on lee before disgorging (11). In the latter case, phenylethanol and ethyl 3-sulfanylpropionate were also found to increase.

To highlight the compounds responsible for the aroma of an aged Sauternes wine, the present paper reports the fate of polyfunctional thiols and other key aromas of two vintages through bottle aging in a cellar.

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MATERIALS AND METHODS

**Wine Samples.** Sauternes wine samples were a kind gift from Château Guiraud, Sauternes, France. Two vintages (W-2002 and W-2003) were analyzed from September 2004 or 2005 (bottling 2 years after grape harvest) to March 2009. Bottles were stored in their original wood box, in a wine cellar maintained at 14 ± 2 °C.

**Chemicals.** Diethyl ether (99.9%), p-hydroxymercuribenzoic acid (pHMB), and dodecane (99.9%) were purchased from Sigma-Aldrich (Bornem, Belgium). Methanol (99.9%) and dichloromethane were obtained from Romil (Cambridge, U.K.), and ethyl acetate (99%) was obtained from Fisher Scientific (Leicestershire, U.K.). 4-Methoxy-2-methylbutan-2-thiol was obtained from Omega Chemicals (Oxford, U.K.). Amberlite XAD 2 resin (Supelco, Bellefonte, PA) (pore size, 9 nm; specific area, 330 m²/g) was sequentially washed with methanol and diethyl ether (each for 4 h) in a Soxhlet and kept in methanol at 4 °C. Milli-Q water was used (Millipore, Bedford, MA). A strongly basic Dowex resin 1 × 2, C - form (Sigma-Aldrich, Bornem, Belgium) was stored in hydrogen chloride (0.1 M). Anhydrous sodium sulfate was obtained from Merck (Darmstadt, Germany), and tris(hydroxymethyl)aminomethane (TRIS) was obtained from USB (Cleveland, OH). As numbered in Table 1, compounds 1, 2, 4, 6, 9, 11, 15, 17, 19, 20, 22, 23, and 25 were obtained from Sigma-Aldrich (Bornem, Belgium), compounds 7 and 10 were obtained from Fluka (Bornem, Belgium), compounds 3 and 12 were obtained from Janssen Chimica (Koln, Belgium), compounds 18, 24, 26 were obtained from Acros Organics (Geel, Belgium), and compound 14 was obtained from Alkemi (Lokeren, Belgium). Compound 21 was a kind gift from Haarmann and Reimer GmbH (Nanterre, France). Compounds 8 and 16 were produced by combinatorial synthesis (12, 13), and compound 5 was produced according to Bailly et al. (1).

**Polynuclear Thiols Analysis.** pHMB Extraction Procedure. Thiols were selectively extracted according to the protocol of Tominaga et al. (14, 15). A total of 250 mL of wine spiked with 6.7 μg/L 4-methoxy-2-methylbutan-2-thiol [used as an internal standard (IST)] was extracted twice with 50 mL of ethyl acetate. A 10 min centrifugation at 2000 rpm was necessary before collecting the organic layer. The organic layer was extracted with 2 × 20 mL of pHMB solution (360 mg of pHMB and 24.6 g of TRIS in 1 L of Milli-Q water). The aqueous layers were loaded on a strongly basic anion-exchange column (Dowex resin), washed sequentially beforehand with 50 mL of 0.1 M sodium hydroxide, 150 mL of Milli-Q water, 50 mL of 2 M hydrogen chloride, and 150 mL of Milli-Q water. After loading, the resin was washed with 50 mL of sodium acetate buffer (pH 6) and thiols were eluted with 60 mL of cysteine solution [640 mg of L-cysteine monohydrate hydrochloride (Alkemi, Lokeren, Belgium) in 50 mL Milli-Q water at pH 7.5]. The eluate was extracted first with 4 mL and then with 3 mL of dichloromethane. The extract was then dried with anhydrous sodium sulfate and concentrated to 0.25 mL (expected concentration factor = 1000) in a Kuderna-Danish [dodecane as an external standard (EST); spiking before concentration with 0.5 mL of the 20 mg/L stock solution], and the mixture was concentrated to 0.5 mL in a Kuderna-Danish—Danish (concentration factor = 100, final EST concentration = 20 mg/L). The final extract was stored at −80 °C for further analyses. All extractions have been performed in duplicate from two different bottles. Except for small lactones, such as 2,3-dimethylbutane, this aroma extraction procedure gives a recovery factor > 75% (1).

**Gas Chromatography Hyphenated to Olfactometric Detection (GC–O).** A total of 1 mL of the XAD 2 extract was analyzed by 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 analyzed with a WCOT apolar CP-Sil-5 CB (50 m × 0.32 mm inner diameter, 1.2 μm film thickness) and a polar FFAP (25 m × 0.32 mm inner diameter, 0.3 μm film thickness) capillary column. The carrier gas was nitrogen, and the pressure was set at 50 kPa (CP-Sil-5 CB) or 30 kPa (FFAP). The oven temperature was programmed to rise from 36 to 85 °C at 2 °C/min, then to 145 °C at 1 °C/min, and finally to 250 °C at 3 °C/min for the CP-Sil-5 CB column or to 220 °C at 3 °C/min for the FFAP column. To assess the olfactory potential of the extract, the column was connected to a GC–O port (Chrompack) maintained at 250 °C. The effluent was diluted with a large volume of air (20 mL/min) prehumidified with an aqueous copper(II) sulfate solution. All extracts were analyzed by three trained panelists. Complete AEDA was performed on XAD 2 extract by only two of them (the same panelists all along the study), with the CP-Sil-5 CB column. The wine extracts were diluted stepwise with diethyl ether (1 + 2 by volume). The dilution factor (FD) is defined as the highest dilution at which the compound could still be detected (FD = 3ⁿ, with n = number of dilutions applied on the XAD 2 extract before no detection by GC–O). The precision of this AEDA is n ± 1 (factor 3 between FD values). The constant sensibility of our trained panelists during a so long period of time (4.5 years for W-2002) was confirmed every 6 months by analyzing two standard solutions (compound numbers 2, 6, 8, 11, 12, 15, 16, 18, 21, 22, and 26) prepared at concentrations of 1 and 2 times the BE-GC-LOADS (17). To control the stability of the chromatographic system with an alcaline standard solution, the column was also connected every week to a FID (250 °C) equipped with a Shimadzu CR6-A integrator.

**Gas Chromatography Hyphenated to Mass Spectrometry (GC–MS).** A total of 1 mL of the XAD 2 extract was analyzed by GC–MS as described above for thiols analysis. Concentrations of key odorants in the XAD 2 extract were assessed for some compounds after MS calibrations with commercial standards (recovery factor approximated to 100%).

**Optimized Likens–Nickerson Extraction (I8) and Analysis of Dried Apricots and Canned Peaches.** To remove sugars, 100 g of fruit was cut into small pieces and extraction was performed for 60 min under nitrogen with 200 mL of dichloromethane (1000 rpm). The organic layer was collected (with peaches, a 10 min longer centrifugation at 2000 rpm was required) and concentrated into 1 mL in a Kudernar–Danish kept at 45 °C in a water bath. Optimized Likens–Nickerson dichloromethane extraction was then applied according to Bouseta et al. (18). The extracts were analyzed by GC–O and GC–MS as described above for the XAD 2 wine extracts.

**Abhoxen Extraction.** Because small lactones are poorly retained on XAD 2 resin, a specific extraction procedure derived from Bailly et al. (19)
### Table 1. Evolution of Identified Odorants in W-2002 and W-2003 through Aging [Samples Were Investigated after Bottling (around 2 Years after Grape Harvest)] by GC−O AEDA on XAD 2 Extract

<table>
<thead>
<tr>
<th>RI</th>
<th>CPSi5</th>
<th>FFAP</th>
<th>substance</th>
<th>odor</th>
<th>2 years</th>
<th>3.5 years</th>
<th>5 years</th>
<th>6 years</th>
<th>6.5 years</th>
<th>identification reliability</th>
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<td></td>
<td>707</td>
<td>1217</td>
<td>3-methylbutan-1-ol 1</td>
<td>alcohol, chocolate</td>
<td>243</td>
<td>81/243</td>
<td>729</td>
<td>729</td>
<td>729</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>730</td>
<td>1572</td>
<td>ethyl isobutyrate (ethyl 2-methylpropanoate) 2</td>
<td>crystalized fruit, acid drops</td>
<td>729</td>
<td>243</td>
<td>243</td>
<td>729</td>
<td>729</td>
<td>b</td>
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<tr>
<td></td>
<td>770</td>
<td>969</td>
<td>ethyl butyrate (ethyl butanoate) 3</td>
<td>acid fruit, liquor</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>243</td>
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<tr>
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<td>1114</td>
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<td>243</td>
<td>81</td>
<td>243</td>
<td>243</td>
<td>243</td>
<td>b</td>
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<td>842</td>
<td>1653</td>
<td>3-methyl-3-sulfanylbutanal 5</td>
<td>petroleum, bacon</td>
<td>27</td>
<td>ud</td>
<td>ud</td>
<td>ud</td>
<td>ud</td>
<td>d</td>
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<td></td>
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<td>1306</td>
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<td>243</td>
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<td></td>
<td>989</td>
<td>1565</td>
<td>3-sulfanylpropiol acetate 8</td>
<td>roasted, burned</td>
<td>81</td>
<td>9</td>
<td>3</td>
<td>9</td>
<td>ud</td>
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<td></td>
<td>1025</td>
<td>1992</td>
<td>furanole (4-hydroxy-2,5-dimethylfuran-3(2H)-one) 9</td>
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<td>81</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>243</td>
<td>f</td>
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<td></td>
<td>1063</td>
<td>1873</td>
<td>guaiacol (2-methoxyphenol) 10</td>
<td>wood, phenolic, spicy</td>
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<td>243</td>
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<td>27</td>
<td>81</td>
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<tr>
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<td>sotolon (3-hydroxy-4,5-dimethylfuran-2(5H)-one) 11</td>
<td>caramel, praline, curry</td>
<td>243</td>
<td>243</td>
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<td>243</td>
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<td></td>
<td>1090</td>
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<td>2-phenylthetan-1-ol 12</td>
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<tr>
<td></td>
<td>1556</td>
<td>1570</td>
<td>linool (3,7-dimethylocta-1,6-dien-3-ol) 13</td>
<td>floral, musty orange</td>
<td>243</td>
<td>81</td>
<td>243</td>
<td>81</td>
<td>243</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>1096</td>
<td>1835</td>
<td>3-sulfanylhexan-1-ol 14</td>
<td>fruity, rhubarb</td>
<td>243</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>243</td>
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<td></td>
<td>1104</td>
<td>2083</td>
<td>homofuranole [unknown in Bailly et al. (1) = U1] (2-ethyl-4-hydroxy-5-methylfuran-3(2H)-one) 15</td>
<td>cotton candy, cake, sweet</td>
<td>2187</td>
<td>729</td>
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<td>1659</td>
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<td>1497</td>
<td>trans-non-2-enal 17</td>
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<td>9</td>
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<td>27</td>
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<tr>
<td></td>
<td>1150</td>
<td>2304</td>
<td>abhexon (5-ethyl-3-hydroxy-4-methylfuran-2(5H)-one) 18</td>
<td>curry, spicy, honey</td>
<td>3</td>
<td>27</td>
<td>243</td>
<td>729</td>
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<td></td>
<td>1179</td>
<td>1706</td>
<td>α-terpineol (2-(4-methylcyclohex-3-en-1-yl)propan-2-0) 19</td>
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<td>243</td>
<td>81</td>
<td>243</td>
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<td></td>
<td>1281</td>
<td>1968</td>
<td>β-methyl-γ-yoctlaceton (5-buty-4-methylhydrofuran-2(3H)-one) 20</td>
<td>sweet, cocoa, butter</td>
<td>243</td>
<td>243</td>
<td>729</td>
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<td>1305</td>
<td>1498</td>
<td>theaspirane [unknown in Bailly et al. (1) = U2] (2,10,10-trimethyl-1-oxaspiro[4,5]dec-6-ene) 21</td>
<td>honey, acid drops</td>
<td>243</td>
<td>81</td>
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<td>81</td>
<td>243</td>
<td>f</td>
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<tr>
<td></td>
<td>1322</td>
<td>2032</td>
<td>γ-nonalactone (4-methyl-5-pentylhydrofuran-2(3H)-one) 22</td>
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<td>27</td>
<td>27</td>
<td>27</td>
<td>81</td>
<td>27</td>
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<td>1835</td>
<td>eugenol (4-allyl-2-methoxyphenol) 23</td>
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<td>81</td>
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<td>81</td>
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<td>1360</td>
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<td></td>
<td>1368</td>
<td>1818</td>
<td>β-damascenone [(2E)-1(2,6,6-trimethylocyclohexan-1,3-dien-1-yl)-but-2-ene-1] 25</td>
<td>stewed fruit, peach</td>
<td>81</td>
<td>81</td>
<td>243</td>
<td>243</td>
<td>243</td>
<td>f</td>
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<tr>
<td></td>
<td>1430</td>
<td>2139</td>
<td>γ-decalactone [Unknown in Bailly et al. (1) = U3] (5-hexylidihydrofuran-2(3H)-one) 26</td>
<td>peach, dried apricot</td>
<td>27</td>
<td>27</td>
<td>27</td>
<td>81</td>
<td>81</td>
<td>f</td>
</tr>
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</table>

*Only the compounds with a FD value ≥ 27 in both vintages have been listed (FD = 3^n−1, with n = number of dilutions of the extract before no detection — precision: n ± 1 or a factor 3 between FD). Two compounds resistant to aging with a FD value ≥ 27 in both wines are still unidentified: RICP-Sil5-CB = 1270 and RICP-Sil5-CB = 1419. Compound identified by coincidence of GC retention indexes, odors on two capillary columns (CP-Si5-CB and FFAP) with pure compound available and mass spectrum data with those of pure standard available on CP-Si5-CB (full-scan monitoring). ud = undetected. Compound tentatively identified by coincidence of GC retention indexes, odors on two capillary columns (CP-Si5-CB and FFAP) with pure compound available. Compound tentatively identified by coincidence of GC retention indexes, odors on two capillary columns (CP-Si5-CB and FFAP) with pure compound available and mass spectrum data with those of pure standard available on CP-Si5-CB (single-ion monitoring selection).
was used. Aqueous eluate from the XAD 2 resin and the first 50 mL of resin washing water were extracted twice with 40 mL of dichloromethane (10 min, 1000 rpm). To improve the concentration step, the combined extracts were washed twice with 10 mL of water (10 min, 1000 rpm), then dried with anhydrous sodium sulfate, and concentrated in the presence of dodecane (EST; spiking with 0.25 mL of the 20 mg/L stock solution) to 0.25 mL in a Kuderna−Danish (concentration factor = 200, final EST concentration = 20 mg/L). A recovery factor of 89% was calculated by the standard addition procedure for this optimized procedure, while only 11% was recovered by the usual XAD 2 procedure. For quantification of abhexon in aged W-2002 and W-2003 (6.5 and 5.5 years after harvest, respectively), the complete standard addition method was applied (additions of 0, 5, 10, 25, and 50 μg/L) on each wine in triplicate, before single-ion monitoring (SIM) (m/z 97) GC−MS analyses.

Most thiols were found to have disappeared by the end of 1−2 years of bottle aging (3−4 years after harvest; Figure 1). The FD value of 3-sulfanylpentylacetate (roasted/burned flavor) dropped from 81 to 27 (W-2002 and W-2003, respectively) to 1, while the GC−PFPD signal for W-2002 indicated a drop from 0.8 μg/L (IST equivalents) to below 0.1 μg/L (Figure 1a). Similarly, 2-sulfanylethyl acetate was detectable in the W-2002 sample only before aging (FD = 9; 0.35 μg/L IST equivalents; Figure 1a). Hydrolysis of sulfanylalcohol acetates was suspected; however, 3-sulfanylpropyl alcohol was detected in neither young nor aged wines, and 2-sulfanylethanol was only detected in fresh W-2002 wine (1 μg/L IST equivalent). Sulfanylaldehydes also completely disappeared (3−3.5 years after harvest, panels b and c of Figure 1). Oxidation is most likely responsible for this disappearance, despite the high sulfite level found in such wines. Figure 1d shows that the 3-sulfanylexan-1-ol concentration also decreased through storage in both vintages, but a concentration (IST equivalents) 50 times above its threshold value [60 ng/L (14)] was still measured after more than 4 years in the bottle. Tominaga et al. (8) reported the hydrolysis of 3-sulfanylexanoylacetate to its corresponding alcohol during bottle aging of dry white wines, but this ester is undetectable in our Sauternes wines. The apparent higher stability of 3-sulfanylexan-1-ol compared to other polyfunctional thiols might be explained by the reduction of 3,3′-disulfanyldihexan-1-ol or 3-propyl-1,2-oxathiolane, both recently identified in Sauternes wines (21).

**RESULTS AND DISCUSSION**

The key role of polyfunctional thiols in young Sauternes wines has been established (1, 2). In the present study, two vintages of Sauternes wines (W-2002 and W-2003) were followed from September 2004/2005 (bottling 2 years after harvest) until March 2009.
Table 2. Concentrations of Four Fermentation and One Oak Maturation-Related Compounds, before and after Aging in the Bottle\(^a\)

<table>
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<tr>
<th>RI</th>
<th>CPSi5</th>
<th>FFAP</th>
<th>substance</th>
<th>W-2002 2 years</th>
<th>W-2002 6.5 years</th>
<th>W-2002 5.5 years</th>
<th>W-2003 2 years</th>
<th>W-2003 5.5 years</th>
<th>threshold (μg/L)</th>
</tr>
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<tbody>
<tr>
<td>770</td>
<td>969</td>
<td></td>
<td>ethyl butyrate (ethyl butanoate) 3</td>
<td>56</td>
<td>50</td>
<td>103</td>
<td>109</td>
<td>20(^b)</td>
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</tr>
<tr>
<td>828</td>
<td>1114</td>
<td></td>
<td>ethyl isovalerate (ethyl 3-methylbutanoate) 4</td>
<td>38</td>
<td>23</td>
<td>42</td>
<td>39</td>
<td>3(^b)</td>
<td></td>
</tr>
<tr>
<td>975</td>
<td>1241</td>
<td></td>
<td>ethyl hexanoate 7</td>
<td>268</td>
<td>186</td>
<td>472</td>
<td>419</td>
<td>5(^b)</td>
<td></td>
</tr>
<tr>
<td>1090</td>
<td>1921</td>
<td></td>
<td>2-phenylethan-1-ol 12</td>
<td>6696</td>
<td>5410</td>
<td>8380</td>
<td>7987</td>
<td>10000(^c)</td>
<td></td>
</tr>
<tr>
<td>1281</td>
<td>1968</td>
<td></td>
<td>(\beta)-methyl-(\gamma)-octalactone (5-butyl-4-methylhydrofuran-2-(3H)-one) 20</td>
<td>348</td>
<td>193</td>
<td>202</td>
<td>220</td>
<td>&gt;10(^c)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Quantification in XAD 2 extract by GC—MS (variation coefficient < 5%). \(^b\) Guth (30). \(^c\) Ribereau-Gayon et al. (31).

Figure 2. Structure of (a) homofuraneol, (b) theaspirane, and (c) \(\gamma\)-decalactone.

Among all polyfunctional thiols, only 2-methylfuran-3-thiol (RI\(_{CP-Si5-CB} = 844\)) revealed to be synthesized in the bottle (FD = 243/729 5–6 years after harvest; Table 1).

AEDAs of XAD 2 extracts showed that most other key compounds of young Sauternes wines (I) were still detected 5.5–6.5 years after harvest (Table 1): varietal aroma (\(\alpha\)-terpineol), sotolon, fermentation alcohols (3-methylbutan-1-ol and 2-phenylethan-1-ol), and esters (ethyl butyrate, hexanoate, isobutyrate, and isovalerate), and oak maturation-related compounds (guaiaacol, vanillin, eugenol, \(\beta\)-damascone, \(\alpha\),\(\beta\)-non-2-enal, \(\beta\)-methyl-\(\gamma\)-octalactone, \(\gamma\)-nonalactone, and furaneol). As depicted in Table 2, the MS quantification of three esters, 2-phenylethan-1-ol, and \(\beta\)-methyl-\(\gamma\)-octalactone confirmed the relative stability of those compounds, with most of them still found above their threshold value after 5.5–6.5 years.

Three interesting compounds with typical cake, honey-like, and dried apricot—peach descriptors remained unidentified in our previous work (I) (U1 at RI\(_{CP-Si5-CB} = 1104\), U2 at RI\(_{CP-Si5-CB} = 1305\), and U3 at RI\(_{CP-Si5-CB} = 1430\)). The former, relatively stable through aging, was identified as homofuraneol (Figure 2a), an ethyl analogue of furaneol, by co-injection of the commercial standard [odor at the sniffing port and retention indexes on the CP-Sil5-CB (RI = 1104) and FFAP (RI = 2083) columns] and MS data. Its odor impact is very high, especially in the W-2002 extract (FD = 729–2187). Sarrazin et al. (22) recently confirmed the contribution of this compound in botrytized wines.

In an attempt to identify the two other compounds, XAD 2 extraction was applied to a dry wine from the same vineyard, also made with Semillon and Sauvignon grapes. Only U2 was detectable at the sniffing port (FD = 27 versus 243 in young Sauternes wines), without a corresponding MS peak. Likens—Nickerson extraction was then applied to dried apricots and canned peaches. The two unknowns were easily detected by GC—O in both fruit extracts at RI\(_{CP-Si5-CB} = 1305\) and 1430, and GC—MS yielded well-resolved peaks. U2 in the apricot extract was identified as theaspirane (Figure 2b). This identification was confirmed in the Sauternes wine XAD 2 extract by a comparison to the commercial standard [odor at the sniffing port and retention indexes on the CP-Sil5-CB (RI = 1305) and FFAP (RI = 1498) columns]. In the SIM mode (ions selected = 82, 138), it was even possible to resolve its peak in the Sauternes wine extract. Its FD value (81/243) revealed quite stable through aging in both vintages. This C-13 norisoprenoid was previously found in Albariño (23), Mencia (24), and Fernão-Pires (25) wines, where it may contribute to a honey-like flavor.

Finally, U3 was identified as \(\gamma\)-decalactone (Figure 2c) in the peach extract on the basis of the mass spectrum. Identification was confirmed in wine XAD 2 extracts by co-injection of the commercial standard on two columns (odor at the sniffing port and retention indexes of 1430 and 2139 on CP-Sil5-CB and FFAP, respectively) and by SIM analysis (ions selected = 85 and 128). Sarrazin et al. (22) have recently mentioned \(\gamma\)-decalactone as an odorant of botrytized wine.

The follow-up of our two Sauternes wines also enabled us to identify abhexon [5-ethyl-3-hydroxy-4-methyl-2(SH)furanone] as an indicator of a long storage. This ethyl analogue of sotolon was identified by a comparison to the commercial standard on the basis of odor (spicy/honey) and retention indexes on two capillary columns (RI\(_{CP-Si5-CB} = 1150\) and RI\(_{FFAP} = 2304\), respectively), as well as GC—MS (SIM mode, \(m/z\ = 97\); Figure 3). Abhexon has never before been mentioned in sweet wines. It has been detected in Chardonnay wines, but its concentration could not be determined (26). Along with sotolon, furaneol, and homofuraneol, abhexon is reported to be responsible for the sweet-caramel note of coffee beverages (27, 28). It was just barely detectable in our young Sauternes wines (FD = 3 in both W-2002 and W-2003), but its FD value (XAD 2 extraction) reached 729 5–6 years after harvest in both vintages (Figure 4). Most likely, our AEDA data still underestimate its impact. Indeed, the XAD 2 extraction procedure does not allow very efficient recovery of hydrophilic molecules, such as sotolon (I) and abhexon (recovery factor assessed by standard addition = 11%). Therefore, a modified procedure was optimized before starting MS quantification in the aged samples (dichloromethane extraction of the XAD 2 unretained fraction and ethanol washing with water before concentration). A recovery factor of 89% was calculated for abhexon from the ratio of the standard addition and calibration slopes. The SIM quantification (\(m/z\ = 97\); complete standard addition method applied in triplicate on both samples) indicated concentrations of 3.8 ± 0.5 and 6.8 ± 1.0 μg/L in aged W-2002 and W-2003 (6.5 and 5.5 years after harvest, respectively). These abhexon levels are very close to its flavor threshold value of 4.5 μg/L that has been assessed in an 88:12 ethanol/water (v/v) solution by triangular tests. The organoleptic impact of abhexon could depend upon the distribution of the \(R\) and \(S\) forms. In comparison to the \(R\) form, (S)-sotolon (methyl analogue of abhexon) was recently found to possess, by far, more intense organoleptic properties (29). Similar investigations are needed for abhexon. Racemization could occur during bottle aging, therefore modifying the wine flavor.

In conclusion, while thiols can explain the distinctive citrus nuances of young botrytized wines (2), other chemicals clearly influence the aroma of aged samples. Most thiols are lost during the first year in the bottle, with only 3-sulfanylhexan-1-ol and 2-methylfuran-3-thiol still being found in aged samples. On the
other hand, most fermentation and oak maturation-related flavors and three newly identified compounds characterized by sweet-honey-like descriptors proved relatively resistant to aging. Abhexon, never mentioned in sweet wines before, emerged as a very interesting compound to investigate in aged Sauternes wines.

**ABBREVIATIONS USED**

- pHMB: p-hydroxymercuribenzoic acid
- IST: internal standard
- EST: external standard
- GC: gas chromatography
- GC–O: gas chromatography–olfactometry
- AEDA: aroma extract dilution analysis
- GC–MS: gas chromatography–mass spectrometry
- SIM: single-ion monitoring
- GC–PFPD: gas chromatography–pulsed flame photometric detector
- W: 2002, Sauternes wine, 2002 vintage
- W: 2003, Sauternes wine, 2003 vintage
- FD: factor dilution
- RI: retention index

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**NOTE ADDED AFTER ASAP PUBLICATION**

The original posting of August 24, 2009, contained an incorrect structure in Figure 2a. This has been corrected with the posting of September 16, 2009.

**LITERATURE CITED**


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