

# Key Odorants of Jura Flor-Sherry Wines: Strong Analogy with Gueuze Beers

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## 62.1 INTRODUCTION

“Yellow Wines” are produced in the famous Château-Chalon area or in one of three other recognized French AOCs (appellation d’origine contrôlée): Côtes du Jura, Arbois/Arbois-Pupillin, and Etoile [1]. Savagnin is the sole grape used to produce this dry white wine (maturation with *S. cerevisia* in a 228-liter oak barrel for 6 years and 3 months). Collin et al. [2] recently described the main odorants of yellow wines. As expected, many oak-related odorants were found in the flavor extracts. The key role of sotolon, the well-known spicy/curry/nut compound, was confirmed. This work also enabled evidence, for the first time, of its ethyl analogue, abhexon. Most probably issuing from oxidation of the grape constituent thespirane, 4-hydroxy-7,8-dihydro- $\beta$ -ionone (with a very nice grenadine aroma) and dihydrodehydro- $\beta$ -ionone (with a pleasant Sauternes descriptor) emerged as two other main odorants at the sniffing port (identified by RI on two columns and by GC-HRMS).

Gueuze, the traditional Belgian sour beer, is a mixture of young and old lambics that have been mixed before bottle refermentation. At least 30% of unmalted wheat is added to the grist. Only aged hops (stored for 1 year or more) can be added to the kettle, where boiling occurs for a very long time, strongly reinforcing oxidation. Lambics will be kept in oak barrels for 1–3 years. Several microorganisms [3], mainly *Enterobacteria*, *Saccharomyces* yeasts, lactic acid bacteria, and *Brettanomyces*, slowly modify the product, leading to very distinctive dry, cidery, and musty flavors, with strong acetic acid and lactic acid aftertastes.

In sensorial analyses, some Gueuze samples evoked the typical aroma of yellow wine [4]. The goal of the present work was therefore to quantify the above described oxidation-derived compounds, in Gueuze. Two different extraction procedures (XAD 2 to investigate all odorants, and specific extraction for hydrophilic flavors like sotolon) were applied to two beers. GC-olfactometry (the AEDA method) and GC-MS were used to compare them with three yellow wines.

## 62.2 MATERIALS AND METHODS

### 62.2.1 Wine Samples

Two wines of 2002 vintage and one wine of 2003 vintage were investigated: Château-Chalon AOC (2002) from Domaine Jean-Claude Credo (JCC-2002), and Stéphane Tissot from Arbois AOC (ST-2002, ST-2003). Two different Gueuze beers were also analyzed: GB-1/Jacobins and GB-2/Mort Subite Oude Gueuze, from local supermarkets. They were selected for their characteristic oxidation aromas similar to those found in yellow wines [4].

### 62.2.2 Global Extraction Procedures

Beer samples were extracted in duplicate with an XAD 2 resin. This procedure is described by Lermusieau et al. [5] (2 g of XAD 2 resin was added to 50 mL of beer, followed by elution with  $2 \times 20$  mL diethyl ether). The extract was dried with anhydrous sodium sulfate; 0.5 mL of dodecane (20 mg/L) was added as an external standard (EST), and the mixture was concentrated to 0.5 mL in a Kuderna-Danish at 39°C (total concentration factor = 100, final EST concentration = 20 mg/L).

### 62.2.3 Sotolon and Abhexon Extraction Procedure

The procedure derived from Blank et al. [6] and Bailly et al. [7] was recently described by Collin et al. (pH sample brought to 11.5; the XAD 2 unretained fraction and 50 mL of resin washing water mixed before adjusting the pH to 3; final extraction three times with 40 mL

dichloromethane [2]). The thus obtained 120 mL fraction was centrifuged either for 10 minutes at 1000 rpm (wine) or for 15 minutes at 2500 rpm (beer). All organic phases were dried with anhydrous sodium sulfate and concentrated, in the presence of hexadecane (EST; spiking with 0.25 mL of 10-mg/L stock solution), to 0.5 mL in a Kuderna-Danish at 45°C (total concentration factor = 100, final EST concentration = 5 mg/L).

## 62.3 RESULTS

Specific extraction dedicated to hydrophilic compounds allowed us to evidence, for the first time, sotolon in Gueuze (6–8 µg/L, FD = 16) (Table 62.1). These concentrations and dilution factors are, of course, much lower than those found in yellow wines (up to 112 µg/L), but close to the threshold (15 µg/L in wine) [2]. Only traces of abhexon were found (0.3–0.8 µg/L).

Another strong analogy with yellow wines was the presence of two very pleasant sweet aromas, identified as 4-hydroxy-7,8-dihydro-β-ionone and dihydrodehydro-β-ionone. The concentrations of 4-hydroxy-7,8-dihydro-β-ionone were very close to those found in yellow wines (Table 62.1). Collin et al. [2] showed that these molecules issue from theaspirane oxidation. Theaspirane was described for the first time in hops by Daenen et al. [8], who found theaspirane A and B glycosides. Theaspirane or its glycosylated precursors are suspected to be oxidized and hydrolyzed during hop storage, wort boiling, and oak-ageing, allowing the occurrence of these unreduced carbonyles in Gueuzes.

Because of the long barrel ageing, many oak-related odorants previously evidenced in yellow wines were found, at least by GC-O, in the XAD 2 flavor extracts from Gueuzes (Furaneol<sup>®</sup>, homofuraneol, guaiacol, eugenol, vanillin ...; Table 62.2).

Also to be emphasized is the key role of 4-ethylguaiacol (>400 µg/kg in Gueuze beers; threshold value around 20 µg/kg). It is most probably generated in Gueuze beers via metabolism of *Brettanomyces* (reduction of 4-vinylguaiacol derived from malt and wheat ferulic acid decarboxylation). Isovaleric acid is another compound shared by Gueuzes and yellow wines. It is usually described as oak-derived in the wine literature, but in Gueuzes it might also arise from the degradation of hop bitter acids.

**Table 62.1** Main Oxidation-Derived Compounds in “Yellow Wines” and Gueuzes

RI	RI	Compound	GB-1		GB-2		JCC-2002		ST-2002		ST-2003		Odor
CPSIL5	FFAP		FD	µg/kg	FD	µg/kg	FD	µg/kg	FD	µg/kg	FD	µg/kg	
1068	2213	Sotolon	16	6	16	6	512	387	256	112	1024	255	Curry
1150	2304	Abhexon	0	0.3	0	0.5	64	74	64	31	32	256	Curry
1373	1698	4-Hydroxy-7, 8-dihydro- β-ionone	256	7	1024	10	1024	8	256	2	64	0.6	Grenadine
1419	1783	Dihydrodehydro- β-ionone	4	0.2	64	4	4	2	1	0.5	1	0.5	Sauternes

Data from GC-O (AEDA) and GC-MS, applied on both types of extracts (XAD 2 for all compounds except sotolon and abhexon quantified in the hydrophilic extracts).

**Table 62.2** Compounds Possibly Derived from Oak in "Yellow Wines" and in Gueuzes

RI	RI	Compound	GB-1		GB-2		JCC-2002		ST-2002		ST-2003		Odor
CPSIL5	FFAP		FD	µg/kg	FD	µg/kg	FD	µg/kg	FD	µg/kg	FD	µg/kg	
808	1659	Isovaleric acid	≤256	1000	≤256	1300	128	1247	32	117	64	112	Cheese
1025	1992	Furaneol®	≤256	ud	≤256	ud	64	ud	2	ud	4	ud	Cotton candy
1063	1873	Guaiacol	≤256	ud	≤256	ud	16	ud	32	ud	64	ud	Wood, phenolic
1104	2083	Homofuraneol	≤256	ud	≤256	ud	256	ud	64	ud	16	ud	Cotton candy
1257	2032	4-Ethylguaiacol	256	413	1024	1072	128	157	32	54	64	52	Clove
1281	1968	<i>cis</i> -β-Methyl- octalactone	≤256	ud	≤256	90	256	118	256	114	256	112	Sweet, coconut
1286	2192	4-Vinylguaiacol	≤256	192	≤256	39	2	27	64	591	64	87	Dentist
1337	1835	Eugenol	≤256	ud	≤256	ud	2	63	2	84	4	83	Clove, dentist
1360	2555	Vanillin	≤256	ud	≤256	ud	32	ud	64	56	64	17	Vanilla

Data from GC-O (AEDA) and GC-MS, applied on global XAD 2 extract. ud-undetected.

## 62.4 CONCLUSIONS

Sotolon, abhexon, dihydrodehydro- $\beta$ -ionone, and 4-hydroxy-7,8-dihydro- $\beta$ -ionone coexist in Gueuze beers and yellow wines, thus justifying some sensorial analogies mentioned in the literature [4]. Isovaleric acid, 4-ethylguaicol, and several oak-derived odorants were also evidenced in both matrixes.

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