HOW CLIMATE CHANGE CAN MODIFY THE FLAVOR OF RED MERLOT AND CABERNET SAUVIGNON WINES FROM BORDEAUX

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Introduction

One of the main characteristics of great red Bordeaux wines is their aromatic complexity, whose connoisseurs recognize many nuances, herbaceous to fruity, reminiscent of green pepper, blackcurrant, blackberry, prune and figs. The aromatic expression of these wines is closely linked with grape maturity as well as grape variety, soil, climatic conditions, vinification and aging processes.

However, since 2000, overriding aromas of dried or cooked fruits, generally found in old oxidized wines such as port wine and VDN (Banyuls, Maury) and reminiscent of prune, fig or cooked peach, are being found more and more often in young Bordeaux red wines. This is especially the case in “extreme” vintages marked by very high temperatures such as 2003, when grapes were harvested overripe, and most of the time owing to a delay in the harvesting date as a result of a warm and dry late season. More generally, warmer temperatures due to climate change are resulting in earlier maturity and are impacting fruit quality and wine style. As a consequence, high sugar levels and acidity ratios reached before optimum color development often affect the aromatic composition of the wine leading to ‘unbalanced fruit’ (Mira de Orduña 2010,Sadras and Moran 2012).

Materials and methods

Wine Samples. Must and red wines used in this study were from Bordeaux vintages 2011 to 2014 produced by standard winemaking procedures (grapes were destemmed and crushed before being put into tanks, alcoholic fermentation was brought to dryness and followed by malolactic fermentation), without wood contact.

Must and wine extraction. *Organic solvent extraction*. Musts and red wines (100 mL) were extracted three times with dichloromethane (1/1, v/v; 3 x 10 mL). The organic layer was dried over Na_2SO_4, and then concentrated to 0.5 mL under nitrogen flow (approximately 100 mL/min).

SPME extraction. The methodology was adapted from different works reporting the assay of lactones in different matrices (Langen, et al. 2013,Mallia, et al. 2009). 1 mL of wine and 9 mL of MQ water were placed in a 20 mL vials containing 5 g ammonium sulfate and 10 µL internal standard (3-octanol, 100 mg/L, EtOH). The vial was sealed with a PTFE-lined cap (Chromoptic, France). Fiber was a 65 µm polydimethylsiloxane-divinylbenzene (PDMS/DVB, Supelco, Lyon, France). The fiber was conditioned as recommended by the manufacturer prior to use. Headspace-SPME parameters were set as follows: extraction temperature 50 °C, incubation time 5 min, extraction time 25 min, agitation speed 700 rpm. Desorption of volatile compounds was performed at 240 °C.

Gas chromatography-olfactometry (GC-O-MS). The Trace GC Ultra (Thermo Fisher, Waltham, MA, USA) was coupled with a DSQII (Thermo Fisher, Waltham, MA, USA) mass spectrometer and a sniffing port. At the outlet of the chromatographic column, the gas flow was split between the olfactometric port (ODP) and the mass spectrometer (MS). The columns used for the ODP and MS were deactivated silica columns connected together to the column capillary tube via a Y borosilicate glass. Two capillary columns identical to those used for the GC-O-MS analysis were used: a polar BP20 column (50 m - 0.22 mm - 0.25 µm) and an apolar BPX5 column (50 m - 0.22 mm - 0.25 µm).

The ions are detected within a range of *m/z* 40 – 250. Results were acquired with the Xcalibur software (Thermo Scientific, Ilkirch, France) associated with the NIST mass spectral library (National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA) and the Flavors and Fragrances database of Natural and Synthetic Compounds (2nd edition, Wiley). Volatiles were identified by comparison of mass spectra and IRL obtained on two chromatographic columns to those listed in the databases.

Incidence of harvest date on must and wine flavor: experiment in field. A plot of Cabernet Sauvignon (2012 vintage, Pauillac appellation) was harvested at three different dates 4 days apart. Part of the plot was harvested 4 days before the optimal harvest date set by the Technical Director (D-4d), a second part was collected the day corresponding to the optimal date (D) and a third part was harvested 4 days after the optimal date (D + 4d). These three lots were vinified in the same way according to the traditional winemaking process of the winery in order to study the incidence of the harvest date on the aroma and concentration of volatile compounds of interest assayed in musts and wines.

Results and discussion

This first step was to compare the flavors of organic extract prepared from musts and red wines marked by prune flavors to those detected by GC-O. After concentration, the extracts of must and red wines marked or not by prune and figs flavors were injected by GC–O. Wine is a very complex beverage with over 60 aroma-active compounds detected by GC–O, whereas only 30 have been reported in must extract.

Two odoriferous zones (OZ) perceived by GC-O as strongly reminiscent of prune and figs were: OZ 2, OZ 3. OZ1 had a strong geranium odor, but surprisingly, this odor was detected specifically in musts marked by these dried fruit flavors. OZ 2 and OZ 3 seemed to be specific to must and wines marked by these flavors. Indeed, OZ2 was detected only in must with dried fruit flavors. Consequently, these results showed a good agreement between the flavor of prematurely-aged red wines and fruit with the same odor. We can therefore postulate that the same compounds associated with the prune aroma of prematurely aged red wines are responsible for the flavor of prunes.

Using GC-MS with chemical standards, it was possible to identify the molecules corresponding to the following retention indices: OZ 1, 1,5-octadien-3-one (IRL_{polar}: 1376), OZ2, γ-nonalactone, (IRL_{polar}: 2041, $IRL_{nonpolar}$: 1363) and OZ3, furaneol (IRL_{polar}: 2050, $IRL_{nonpolar}$:1079).

Table 1: Distribution and identification of odoriferous zones (ZO) in musts and wines marked (DF) or not (Control) by dried fruit flavors – (nd: not detected; *: low intensity; **: high intensity)

ZO N°	IRL[a]	IRL[b]	Descriptors	Compounds	Musts		Wines	
					Control	DF	Control	DF
1	1376	/	Geranium	1,5-octadien-3-one	nd	**	nd	*
2	2050	1079	Caramel, strawberry	furaneol	nd	**	*	**
3	2041	1363	Cooked peach	γ-nonalactone	nd	**	nd	**

[a]: polar column BP20 - [b]: non-polar column BPX5

γ-nonalactone (Cutzach, et al. 1998,Fang and Qian 2005,Sarrazin, et al. 2007) and furaneol (Genovese, et al. 2005,Kotseridis, et al. 2000) have been identified in many different wines, but to our knowledge only rarely in grapes. Concerning *(Z)*-1,5-octadien-3-one, this ketone has already been described in moldy grapes (Uncinula necator) (Darriet, et al. 2002) but is reported for the first time in this work in healthy grapes. We determined their perception thresholds in wine model solution to be 28 µg/L, 49 µg/L, and 1,2 ng/L, respectively.

Quantification of lactone and furaneol has already been reported in the literature, but no quantitative data are available for the quantitation of 1,5-octadien-3-one in must and wines. We therefore developed an approach based on the extraction of this volatile thanks to SPME and separation and quantification with GC-MS in chemical ionization mode with methanol as reactant gas. Good results in terms of sensitivity, repeatability and linearity were obtained in must but unfortunately further optimization is required for its detection in wines. We analyzed many samples of must and red wines by these techniques. Before extraction (liquid/liquid and SPME), the prune flavor intensity of must and wines was assessed by a trained panel from the laboratory. Results are shown in Figures 1 and 2.

The must marked by prune flavor contained significantly high levels (higher than their perception threshold, respectively) of furaneol and 1,5-octadien-3-one, whereas red wines contained higher levels of γ-nonalactone and furaneol.

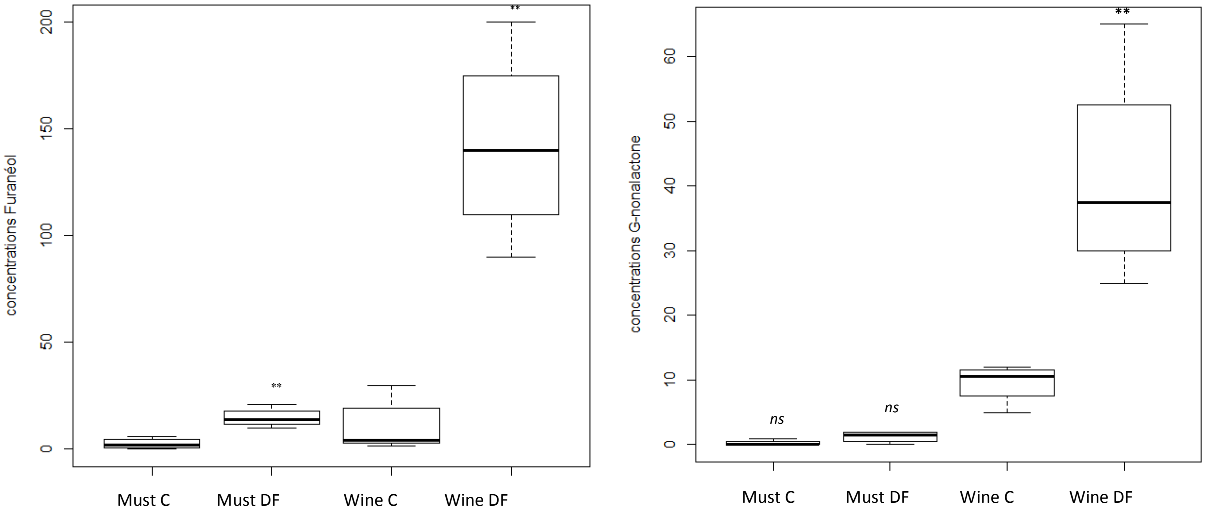

*Figure 1: Tukey boxplot of furaneol (A) and γ-nonalactone (B) concentrations in musts and wines marked (DF) or not (C) with dried fruit flavors (DF) (N=8). **Anova: p≤0.01*

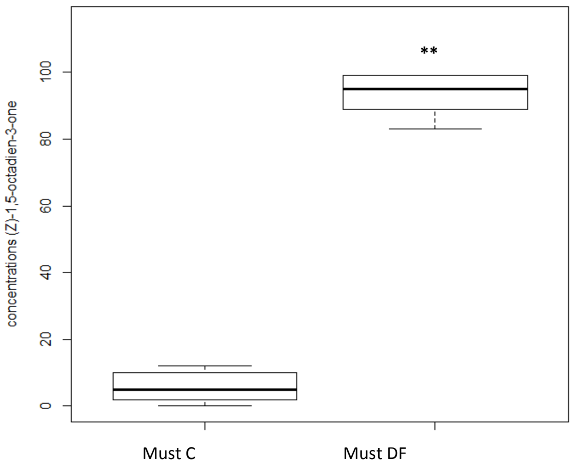

*Figure 2: Tukey boxplot of (Z)-1,5-octadien-3-one concentration in control musts and musts with dried fruit flavors (DF) (N=8). **Anova: p≤0.01*

Incidence of harvest date on flavor of musts and wines: analytical and sensorial approaches

In view of these first results, we studied the effect of grape maturity on the formation of these nuances and volatile compounds in musts and red wines. The following experiment was carried out during the 2012 vintage in a vineyard located in the Pauillac appellation (Cabernet Sauvignon grapes). Sensorial analysis was performed on wine after malolactic fermentation, whereas furaneol and γ-nonalactone where quantitated in must and wines.

As depicted in Figure 2, neither furaneol nor γ-nonalactone concentrations were modified between the first date and the last date 8 days apart in our experimental conditions. However, these compounds were produced during alcoholic fermentation by unidentified precursors found in grapes. In wine, a 4-day delay was sufficient to modify furaneol and γ-nonalactone concentrations significantly.

Finally, we asked a panel of 20 tasters to evaluate the intensity of dried fruit flavors, herbaceous and fresh fruit flavors of the three wines on a 0 to 10 scale. To determine whether significant differences could emerge from this experiment, variance analysis (ANOVA) was performed (Figure 3) on the results. Whereas the intensity of herbaceous aroma was not modified during the experiment, only a 4-day interval between two harvest dates modified the perception of the intensity of fresh fruit nuances and an 8-day interval sufficed to increase the dried fruit nuances significantly in wines.

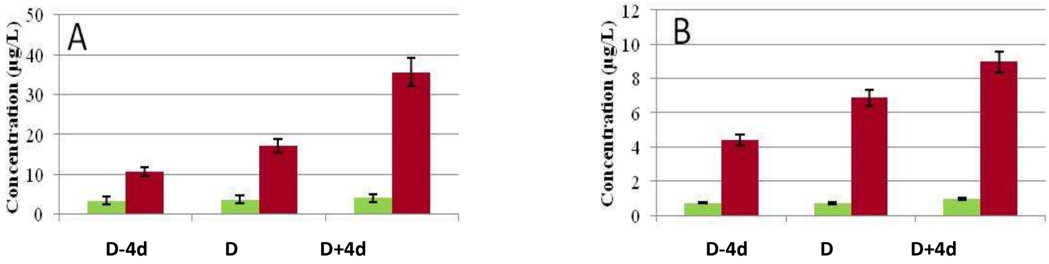

Figure 2: Incidence of harvest date on concentration of furaneol (A) and γ-nonalactone (B) in musts (green) and wines (red) from grapes harvested 4 days before optimal date (D-4d), on the optimal date (D) and 4 days after (D+4d)

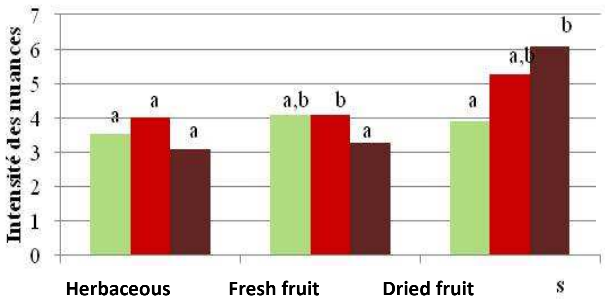

Figure 3: Incidence of harvest date on sensory analysis of wines from grapes harvested 4 days before the optimal date (D-4d, green), on the optimal date (D, red) and 4 days after (D+4d, brown). Letters correspond to ANOVA tests (α=0.05).

conclusions

In must and wine made from overripe grapes, three odorant zones were detected and identified thanks to GC-O-MS: furaneol, γ-nonalactone and *(Z)*-1,5-octadien-3-one. These compounds are reported for the first time in musts. We show that in controlled conditions in the laboratory, these compounds are produced in grapes during water loss and wilting. The contribution of γ-nonalactone and furaneol that are reminiscent of the flavor of red wine seems clear. However, the contribution of *(Z)*-1,5-octadien-3-one with a geranium flavor is still not clear. Further experiments are required to establish its contribution to the dried fruit flavors of red wines.

On the basis of these results, we performed an experiment in the field. We show that in must and wine a 4-day interval between two harvest dates is sufficient to increase the intensity of dried fruit flavor of wines. This observation is consistent with the increase in furaneol and γ-nonalactone in wines during the experiment.

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Abstract

The main goal of this research was to identify key aroma compounds linked with the maturity of grapes (ripe and overripe) and involved in grapes and wines with an intense dried fruits aroma. Odoriferous zones reminiscent of these aromas were detected by gas chromatography coupled with olfactometry (GC-O). Three odoriferous zones were identified (OZ1, OZ2, OZ3). Using GC-MS with chemical standards, they were identified as (Z)-1,5-octadien-3-one (geranium), furaneol (caramel) and γ-nonalactone (coconut, cooked peach), respectively. Studies of their sensory properties and quantitative assays by GC-MS (EI/CI) in musts and wines were performed. Furaneol and γ-nonalactone are well-known compounds in wines but have only rarely been reported in musts. On the contrary, the influence of (Z)-1,5-octadien-3-one on the aroma of must is reported for the first time. The perception threshold of this ketone in must is 1.2 ng/L and its concentration can exceed 200 ng/L in overripe merlot grapes. High concentrations of furaneol and γ-nonalactone were detected in musts and young red wines marked by dried fruit flavors. We also report the first results concerning the incidence of harvest date of Cabernet-Sauvignon grapes on the aromas and fine composition of musts and wines.