IMPACT OF CLIMATE CHANGE ON THE AROMA OF RED WINES: A FOCUS ON DRIED FRUIT AROMAS

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INTRODUCTION

One of the main characteristics of great red wines is their aromatic complexity, with nuances such as herbaceous, green pepper, blackcurrant, blackberry, or figs and prunes. It is generally recognized that grape intrinsic composition, in terms of flavor and flavor precursors gives wine specific volatile compounds composition. The wine varietal aromatic component, which is specific to each variety, is modulated by human choices implicating the parameters of vine growing and grapes vinification and is also much impacted by natural factors (climatic conditions, nature of the soil). Among agronomical parameters affecting grapes composition and wine quality we can find: maturity level at harvest [1], water status [2], and the intensity of sun exposure.[3]

The aroma of must and red wines made with unripe grapes is systematically marked by grassy, green, or capsicum flavors, irrespective of the grape variety, *i.e.* the grapes release these flavors directly into the wine. This phenomenon is particularly well-described for non-aromatic wine grape cultivars. Today, it is recognized that 3-isobutyl-2-methoxypyrazine (IBMP) is responsible for the green pepper odor of Cabernet Sauvignon grapes and wines.[4]
On the contrary, red wines made with overripe or dried grapes share dried fruit nuances, as reported in several grape cultivars, including Garnacha Tintirera[5], Merlot, Cabernet Sauvignon [6], and Rondinella.[7]

The prospects of climate change over the next decade raise questions about the potential impact of an average rise in temperatures on the aromatic potential of grapes and wine quality.[8-10] Indeed, the projected rise in temperature will deeply alter grape composition and the wine styles produced and, along with predicted changes in precipitation amounts and seasonal timing, will challenge grape growing and wine making in the future.

Rarely detected in Bordeaux red wines until the early 2000s, dried-fruit flavors (dried figs, dried apricots, and prunes) are found in musts and young red wines, especially Merlot, with increasing frequency. This reflects a significant increase in the average maturity level of the grapes, associated with a modification of the climate on a local scale, as well as changes in viticultural practices. Indeed, these nuances used to be more specifically associated with red wines made from grapes grown in warmer, more southerly regions or produced by traditional wine making procedures involving dehydration of the grapes (Amarone, Recioto) or fortification of the wine (Port and VDN).[5, 11] Moreover, as also observed in other vineyards around the world, these flavor modifications reflect the biological consequences of global warming.[10, 12]

Few studies have focused on identifying the molecular markers of dried-fruit nuances (reminiscent of dried figs or prunes), found in Merlot and Cabernet Sauvignon grapes and wines. This work investigated the occurrence of specific compounds associated with dried-fruit flavors in musts and wines, as well as presenting new data on the effect of over-ripening (or late harvest) on the formation of these aroma compounds.

So, this manuscript proposes to summarize the results coming from a project began in 2012 aimed at evaluating the impact of climatic change in connection with the maturation of the grapes, on varietal aroma compounds and the sensory perception of Merlot and Cabernet Sauvignon musts and wines.

Identification of key molecular markers.

To begin, must and red wines marked or not by dried fruit aromas were extracted with dichloromethane. After concentration, the extracts were analyzed by GC–O–MS. The aromagram obtained revealed odorous zones reminiscent of the must and wine flavors. Several odorant zone (OZ) were found in musts and wines both marked by prune and fig flavors. The odorant was structurally assigned by comparing its retention index and odor quality with the NIST and FFNSC databases. To confirm the structural assignments, the wine volatile fractions were also analyzed by gas chromatography coupled with olfactometry and mass spectrometry (GC–O–MS) or multidimensional GC-GC-O-MS in case of coelution, and assignment issues, with the corresponding reference compound. Thanks to this approach, six molecules corresponding to the dried fig OZs were identified (Figure 1). We also determined their detection threshold in must and wine model solutions.

Two OZ corresponding to caramel notes were identified as furaneol (Fur, 2,5-dimethyl-4-hydroxy-3(2H)-furanone) and homofuraneol (Hfur). These compounds are both well-known for their contribution to the caramel notes of Merlot red,[13] Grenache rosé,[14] and the overall aroma of Botrytized wines.[15] Furaneol has been detected at high concentrations in hybrid grapes (non *Vitis vinifera*), with aromas distinctly reminiscent of cooked strawberries,[16] as well as in red wines made with dried grapes, such as Primitivo (900 µg/L).[17]

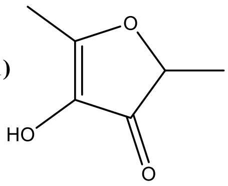
Two lactones were also identified: γ-nonalactone and (-)-massoia lactone. The first one with peach and dried-fruit aromas, had already been reported in red [18] and botrytized wines.[15] Pons *et al.* [19] demonstrated that high concentrations of γ-nonalactone were related to oxidative aging. (-)-Massoia lactone, with coconut and fig flavors, has already been described in Merlot and Cabernet Sauvignon musts and wines,[20] where it contributed directly to dried-fruit aromas in must.

Two ketones, with very low detection threshold, were also reported in these samples. 3-methyl-2,4-nonanedione (MND), a key compound in prune and figs flavors in prematurely aged red wines [21], was reported for the first time in musts and young wines marked with theses nuances. (*Z*)-1,5-octadien-3-one, a very powerful aroma compound with a geranium aroma, was identified as a key compound in dried-fig aromas in Merlot and Cabernet Sauvignon musts.[22] In grapes, its presence has been demonstrated by GC-O, and it is associated with the development of pathogens such as *Uncinula necator*, also called powdery mildew. To our knowledge, its presence in musts and wines marked by dried fruit nuances is reported for the first time.

Analytical strategies for the quantitation of volatile compounds

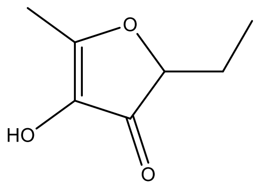
Quantitation of furanones and lactones did not deserve particular method development or validation as they were already well described in literature.[23] Extraction was performed with dichloromethane for furanones and massoia lactone whereas SPME was used for γ-nonalactone. Detection and quantitation in musts and wines were conducted with GC-MS in EI mode.

(1)



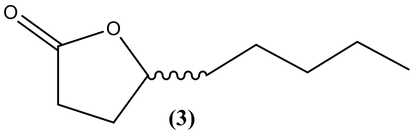
caramel, jammy strawberry
$Dthd_{must}$ 10,5 µg/L
Dth_{wine} 49 µg/L

(2)



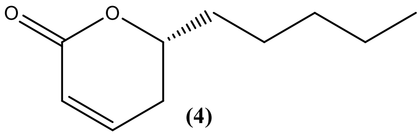
caramel
Dth_{must} 5,5 µg/L
Dth_{wine} 26,5 µg/L

(3)



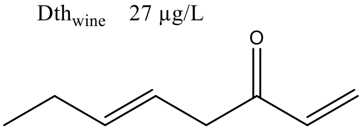
coconut, cooked peach
Dth_{must} 0,9 µg/L
Dth_{wine} 27 µg/L

(4)



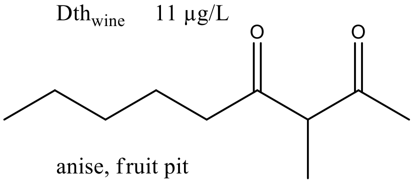
coconut, dried fig
Dth_{must} 10 µg/L
Dth_{wine} 11 µg/L

(5)



geranium
Dth_{must} 0,002 ng/L

(6)



anise, fruit pit
Dth_{must} 62 ng/L
Dth_{wine} 16 ng/L

Figure 1 : Chemical structures, descriptors and detection thresholds (D_{th}) of compounds identified in musts and wines marked by dried fruits aromas. (1) furaneol, (2) homofuraneol, (3) (R/S)- γ-nonalactone, (4) (-)-massoia lactone, (5) (Z)-1,5-octadien-3-one, (6) 3-methyl-2,4-nonanedione (MND).

On the contrary, for MND and (*Z*)-1,5-octadien-3-one specific analytical development were undertaken. Therefore, we validated a methodology to quantify them in musts and red wines before determining their concentration in several samples. Indeed, the mass spectrum obtained in electronic impact mode was highly fragmented with a low *m/z* ion at high intensity, making their quantitation in a complex matrix tricky by this ionization technique. Furthermore, the ability of chemical ionization (CI) with methanol was evaluated as non-conventional reactant gas to detect and quantify these compounds. In addition, SPME parameters were tested in an experimental design to determine the best conditions for the extraction experiment including incubation temperature, extraction time, salt concentrations, volume of sample. The methodology was validated in terms of linearity, sensitivity (LOD, LOQ), repeatability and accuracy for MND [24] and (*Z*)-1,5-octadien-3-one.[22]

Distribution in musts and wines marked or not by dried fruits aromas

Chemical markers were quantified in many musts marked (DF) or not (control) by dried fruit nuances. The samples were classified by the jury (expert) according to the intensity of their dried fig and prune flavors (0−10 scale) and characterized as either being marked (>5) or not (0−≤5) by them (Table 1).

The results for furaneol and homofuraneol indicated significantly higher concentrations in DF samples. Average concentrations released during alcoholic fermentation, reached 125.2 µg/L and 29.4 µg/L, respectively. Average concentrations of both compounds in must and wine exceeded their Dth. Finally, these results highlighted the contribution of furaneol and homofuraneol to the dried-fruit aromas of red musts and wines.

Table 1 : Average concentrations of volatiles compounds in musts and wines (Merlot and Cabernet Sauvignon) marked or not by dried fruits aromas.

Composés	**Must**			**Wine**		
	Control	**Dried Fruit**	***p*** [b]	**Control**	**Dried Fruit**	***p*** [b]
Furaneol® [c]	4.5 (1.6)	**25.4 (6.2)**	***	16.9 (5.1)	**125.2 (25.2)**	***
Homofuraneol® [c]	2.9 (0.9)	**5.4 (1.5)**	***	5.2 (1.1)	**29.4 (23.7)**	***
(*R/S*)-γ-nonalactone [c]	**1.5 (0.5)**	**3.2 (2.3)**	ns	12.8 (2.7)	**34.2 (7.2)**	***
(-)-Massoia lactone [c]	5.9 (3.1)	**19.6 (5.6)**	***	1.4 (0.9)	6.6 (3.5)	*
(*Z*)-1,5-Octadien-3-one [d]	**8.9 (3.6)**	**92.6 (7.5)**	***	*nd*	*nd*	-
MND [d]	33.4 (8.6)	**68.1 (12.1)**	***	**18.6 (4.5)**	**34.5 (6.2)**	**

[a] in parentheses standard deviation. [b] *p*-value*:* $p < 0.001$ (***), $p < 0.01$ (**), $p < 0.05$ (*), ns (non significant). [c] µg/L. [d] ng/L. In bold : average concentration with OAV > 1. nd: non detected.

Massoia lactone was detected at high levels in musts marked by DF aromas (> Dth), but at lower concentrations in wines, irrespective of their aromatic profile. This result was consistent with our previous study describing the evolution of this lactone during off-vine over-ripening of grapes, as well as during alcoholic fermentation.[20]
γ-nonalactone concentrations were slightly higher in must samples with marked DF aromas compared to controls. On the contrary, the difference was much greater for wines with marked DF aromas. In these samples, average concentrations were 12.8 and 34.2 µg/L in C and DF samples, respectively.

Significant differences were also detected in MND levels between control and DF samples. Musts and wines marked by dried-fruit aromas contained higher MND concentrations than those without these aromas. These results, showing a high average content in must (68.1 ng/L) and wine (34.5 ng/L), suggested that this compound contributed to the dried-fruit aromas perceived in wines. Moreover, the MND concentrations in wine were lower than those in must. (*Z*)-1,5-octadien-3-one was present at significantly higher concentrations in DF musts (92 ng/L) than controls, well above its detection threshold (0.0022 ng/L). Although the formation mechanisms of this compound in musts are unknown to date, it has been described as a product of the oxidative degradation of eicosapentaenoic acid. This ketone was not detected in red wines. So, for both compounds, these results reflected the effect of yeast metabolism on these ketones, probably via biochemical reduction.

Sensory impact study

To study the sensory impact of (Z)-1,5-octadien-3-one in musts, a control must (Merlot, Pessac-Leognan) was supplemented with increasing concentrations of (Z)-1,5-octadien-3-one: 0, 32, 64, 96, 128, and 240 ng/L.[22] Beforehand, the must was analyzed by GC-MS to verify its absence. The jury was asked to evaluate the intensity of several descriptors including “dried fig” and “geranium”, on a 0 to 7 scale (Figure 2). An ANOVA showed that increasing the concentration of (Z)-1,5- octadien-3-one modify the intensity of dried fig, and geranium descriptors. Indeed, the must spiked with 96 ng/L (Z)-1,5-octadien-3-one developed fig aromas ($p = 1.98 \times 10^{-8}$), whereas beyond 96 ng/L, the fig aromas decreased significantly and geranium nuances increased ($p = 4.35 \times 10^{-9}$). At high concentrations, (*Z*)-1,5-octadien-3-one gave the must its geranium nuances. Finally, we demonstrated that (*Z*)-1,5-octadien-3-one has a very strong impact on the flavor of the must according to its concentration and especially according to its concentration in musts marked by dried fruit aromas (Table 1).

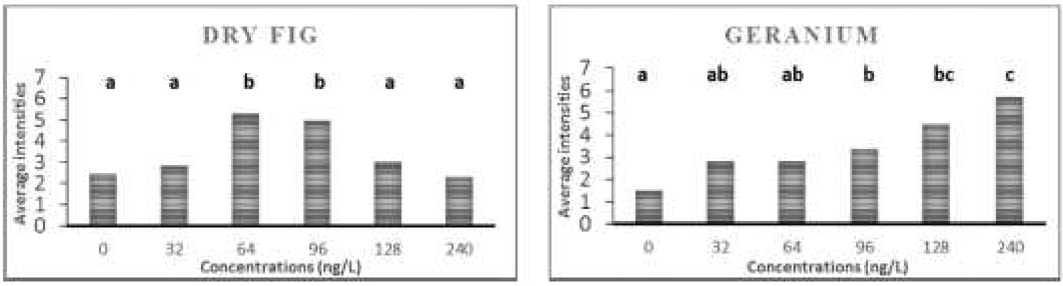


Figure 2 : Evolution of odor intensity mean of dry fig and geranium descriptors at increasing (Z)-1,5-octadien-3-one concentrations in Merlot musts. Different letters indicate significant values at p<0.05.

In red wines where furanones (Fur, Hfur) reminiscent of caramel, γ-nonalactone (cooked peach) and MND (fruit pit) were detected individually at high level (OAV>1), we hypothesized that they were able to give their aroma to the wine. But, to throw light on the contribution of these aroma compounds to the flavor of the red wine, the following aroma reconstitution experiment was conducted.

Five red Merlot wines samples were presented to a trained panel to evaluate the intensity of their dried-fruit aromas. The control wine had no marked dried-fruit aromas and contained low concentrations of lactone, furanones, and MND. The same wine was spiked with these aroma compounds, individually or in mixtures, at the concentrations found in a red wine with marked dried-fruit aromas. The concentration of aroma compounds in this wine was in close agreement with those found in red wines marked by dried fruit aromas reported in Table 1.
As shown in Figure 3, significant differences in the intensity of the dried fruit aromas of the various wine samples were perceived by the panel. Adding MND at subthreshold level to the red wine did not change the intensity of the dried fruit character. However, the addition of furanones or γ-nonalactone significantly modified the perception of dried-fruit aroma intensity. Finally, adding a mixture of MND, γ-nonalactone, furaneol, and homofuraneol mimicked this aromatic character in the red wine, thus validating the contribution of these compounds to dried-fruit aromas.

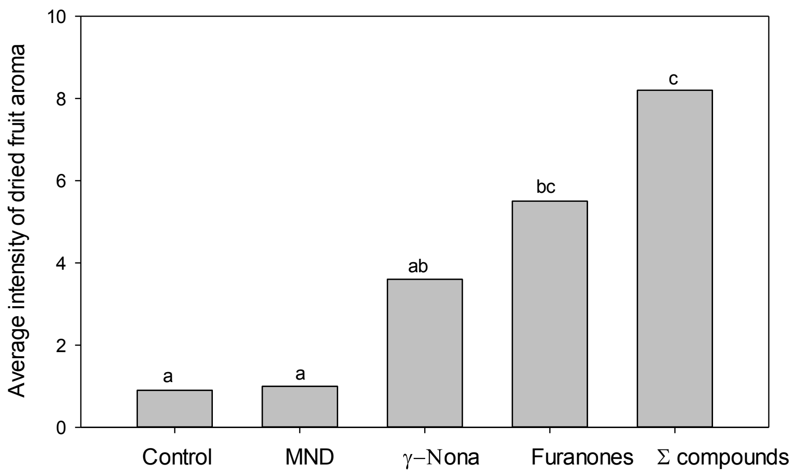


Figure 3 : Evolution of the average intensity of «dried fruit » descriptor according to the compounds spiked to a Merlot wine (Control) non marked by these nuances. Concentrations of volatile compounds in the control wine were (MND 26,8 ng/L, (R/S)-γ-nonalactone 4,3 µg/L, Fur 35,0 µg/L ; Hfur 0,7 µg/L) and were modified to reach those found in a red wine marked by these "dried fruits" aromas (MND 52,3 ng/L ; (R/S)-γ-nona 27,9 µg/L, Fur 179,1 µg/L ; Hfur 85 µg/L). Anova (p < 0,05).

In another experiment we also evaluated the sensory impact of (-)-massoia lactone in must and wine.[20] According to its distribution, this lactone contribute directly to the dried fruit and fig aroma of must. On the contrary, according to its detection threshold reported in Figure 1, its direct organoleptic contribution to this characteristic flavor detected in red wines remains uncertain.

Application to the evaluation of the impact of harvest date on the aroma and chemical composition of must and wine (*var.* Merlot)

A same Merlot plot (2014 vintage) was harvested at several dates, based on harvest date (HD) defined by the technical staff of the winery. Each batch was fermented in a 25 HL stainless steel tank. Basic enological analysis as well as sensorial analysis by a trained panel (0-10 scale) were conducted on must and wine. Evolution of specific descriptor intensities according to the harvest date was reported in Figure 4. We can observe a clear decrease in vegetal character and an increase in dried fruit intensity. We demonstrate that 13 days delay has a strong and deep impact on the aroma of the wine.

Fine chemical analysis was also performed on the must and the wine. As an example we report in Figure 5, the evolution of furaneol and γ-nonalactone concentration during the last stage of maturation. Whereas their concentrations were not modified in must we can observe a strong “harvest date” effect in the wine, evidencing once again the role of alcoholic fermentation on their formation in wine. We conducted the same experiments with Cabernet Sauvignon grapes and similar observation were obtained, strengthening at the end our conclusions concerning the sensory impact of chemical markers identified in this work as well as their enological interest.

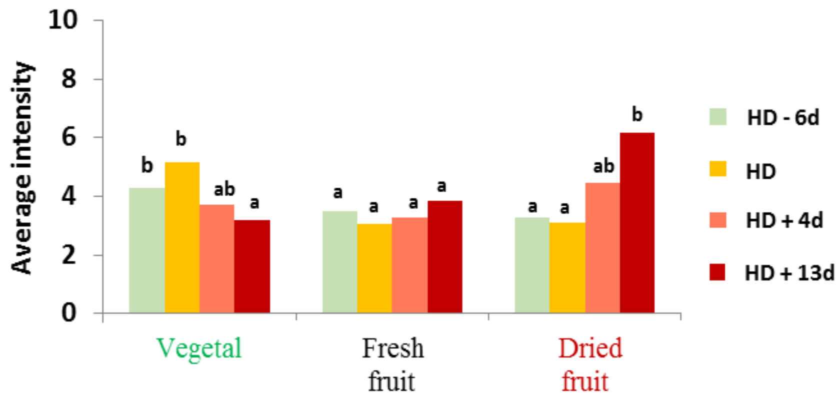


Figure 4: Average intensity of vegetal, fresh fruit and dried fruit descriptors detected in wine according to the harvest date (HD). HD corresponds to the optimum maturity evaluated by the technical staff of the winery. (ANOVA, p<0.05)

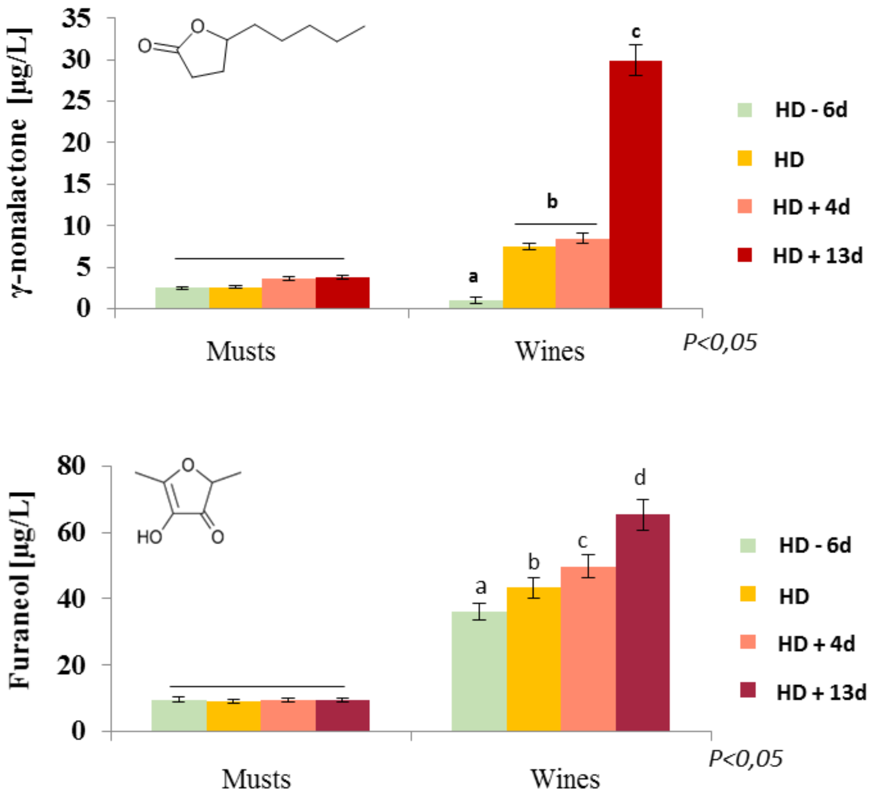


Figure 5: γ-nonalactone and furaneol concentration in Merlot musts and wines according to the harvest date (HD). HD corresponds to the optimum maturity evaluated by the technical staff of the winery. n=3. ANOVA p<0.05

CONCLUSION

Finally, overall results suggested that several impact chemical species associated with the dried fruit nuances were produced in berries of Merlot and Cabernet Sauvignon grapes and modulated in wines thanks to alcoholic fermentation. Off course, biosynthesis and accumulation study of secondary metabolites, potentially conferring a chemical and sensory identity on young red wines, might deserve additional works.

This first identification of chemical markers associated with dried fruits aromas could contribute in the future to build new tool box to help wine growers to define, in an analytical point of view, the right time to harvest based on their objectives. In addition, knowledge of these markers might be used to study more precisely the impact of constraints such as water supply, light (UV) and temperature at the vineyard on the sensorial quality of the grapes and wines. Finally, these aroma markers might be also used as new indicators of drought et temperature resistance, to select new varieties more adapted to these new stress conditions at local level, in order to fight indirectly, against climate change and global warming impact on the overall quality of red wines.

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