Freshness of red wines finally revealed !

Wine aromas are the result of a superposition of aromatic volatile molecules that draw a unique pattern according to their nature and concentration. Recent studies have shown that many volatile compounds, altough dosed below their detection thresolds, participate in the aromatic complexity of a wine via perceptual interactions.

Among the great diversity of wine aromas, and descriptors related to them, the term « vegetal » is widely used in oenology to describe red wines aroma, and is therefore an integral part of the tasting lexicon. Its use is commonly negative. However, this sensory notion covers many aromatic nuances. Negatively correlated vegetal notes like « green pepper », with especially IBMP, govern and dominate the overall aromatic notes, with a mask effect on the fruity perception. On the other hand, there are vegetal aromatic notes that are positively correlated, with minty and mentholated nuances, that contribute to the aromatic identity of famous wines. Thus, instead of masking the fruity character, these notes reinforce the complexity of the aromatic bouquet by bringing them both freshness and elegance.

Different research thesis have been recently done at the ISVV of Bordeaux, especially by Magali Picard and Xavier Poitou, through sensory and analytical approaches with the use of advanced chromatographic techniques, in order to better understand the nature of the volatile compounds associated in red wines with markers of freshness. These markers are at the origine of very complex aromatic sensations.

D,L- piperitone and other markers of menthol nuances

Magali Picard's research at ISVV has highlighted a link between piperitone and the smell of mint that is sometimes found in old red wines from Bordeaux. Indeed, studies have shown that wines with a bouquet of aging, and especially the peppermint scent, which is one of the characteristics of mature wines, have significantly higher levels of D, L-piperitone compared to intermediate wines or those which don't have any. Magali Picard's work suggests a detection limit of 30.2 µg / L in water. However, she insists that it is important to consider this threshold with great precaution, given the great complexity of the integration at the cerebral level of the perception of mentholiness. In addition to the multimodal sensory process that will govern this perception, there are specific anosmia for the various aromatic compounds responsible for the smell of mint, which will lead to inter-individual differences in the perception of these nuances of freshness.

Significant differences in intensity for the "mint" descriptor were observed according to the main grape variety present in the blends tasted during sensory tests. These differences could then be correlated with the D, L piperitone contents, which are significantly lower in the "right bank" wines of Bordeaux, where the main grape variety is the Merlot, as in the "left bank" wines, where we found mainly Cabernet Sauvignon. These results suggest a varietal origin for this compound. (See **Fig. 1** below).

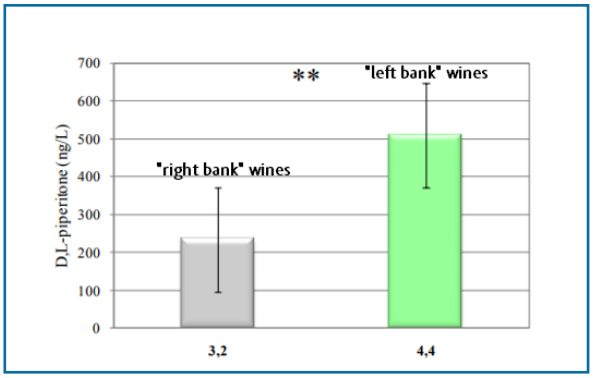

Fig. 1 (from Magali Picard thesis : Research on the aging bouquet of Bordeaux red wines: sensory and molecular studies of a complex olfactory concept)
Average concentration of D, L-piperitone as a function of the mean intensity of the "mint" descriptor in red wines of left and right bank

Piperitone is a cyclic monoterpene ketone, which would result from the limonene transformation pathway, following several enzymatic reactions. It has an odor described in the literature as "herbaceous", "minty" and "camphorated".
It is very important to take into account the positive dimension of piperitone. Indeed, it has not only been identified as an aromatic compound responsible for the aroma of mint, but mostly as an aromatic compound contributing to the positive nuances of mint perceived in wines, and more particularly in the old red wines of the Bordeaux vineyard.

The p-menthane lactones are also part of the expression of these minty shades perceived in red wines as well as other monoterpenes ketones such as menthone and carvone. Furthermore, eucalyptol (= 1,8-cineole) has been recognized as responsible for an increase in menthol nuances when present at levels above 0.7 µg / L. The quantitative analysis of 1,8-cineole in Bordeaux Cabernet Sauvignon has confirmed the varietal origin of this compound, as opposed to the exogenous origin linked to the presence of eucalyptus in the vineyards of California or Australia. It has also confirmed the parentage of eucalyptol contents with the level of maturity of the grapes. Xavier Poitou's works show indeed a significant decrease, from 57 to 90% of this molecule during the last month of maturation berries.

Methyl salicylate

Methyl salicylate is an aromatic substance found in all varieties of grapes. It is responsible for a flavor described as camphorated and fresh. It is generally under the effect of a parasite pressure that this compound will be produced by the vine as shown in the figure below extracted from Xavier's thesis.

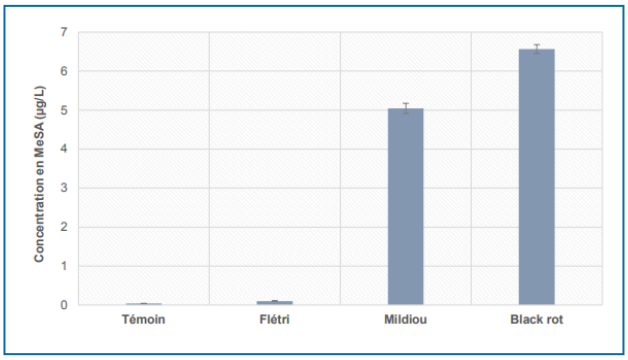

Fig. 2 : (From Xavier Poitou thesis: Contribution to the aromatic knowledge of red wines: sensory and molecular approach of the "vegetal, green" nuances in relation to their origin)
Concentration (µg / L) in methyl salicylate (MeSA) in model fermentation media in the presence of healthy berries (control), withered naturally, withered under the action of late blight or withered under the action of Black rot

These works are promising. The dosage of this compound could represent an excellent marker of the physiological state of the vine and its cryptogamic environment, and this before the grapes are reached.

But these links of cause and effect should not divert from the interest of this compound regarding to the balances of freshness, today highly sought after by consumers. Unlike IBMP or some C6 alcohols as hexenal responsible for green pepper or herbaceous flavors, methyl salicylate is at the origin of vegetative flavors with a positive connotation, that contribute to aromatic freshness of red wines. Its structural analogue, ethyl salicylate, was also quantified in red wines but at much lower levels of concentration. The odor released by this compound is similar to that identified for methyl salicylate.

The trials in the laboratory of metered additions in different wines corroborate the concentration of perceptions mentioned by Xavier Poitou. From about 60 µg/L, methyl salicylate becomes very strongly expressive. Its perception can then be judged negative. But between 5 and 20 µg/L, all the tasting tests conducted internally or with partner customers suggest that the compound would then have a real interest to support a perception of freshness unanimously appreciated by the tasters. The goal could therefore be to control the routes in order to guarantee the presence of these compounds at these concentration levels, in order to favor their positive contribution without falling into excessive and dominant perceptions. Interestingly, it is mainly in the stalks that methyl salicylate is found. The dosage of these compounds could therefore also be a tool for controlling winemaking in "whole harvest".

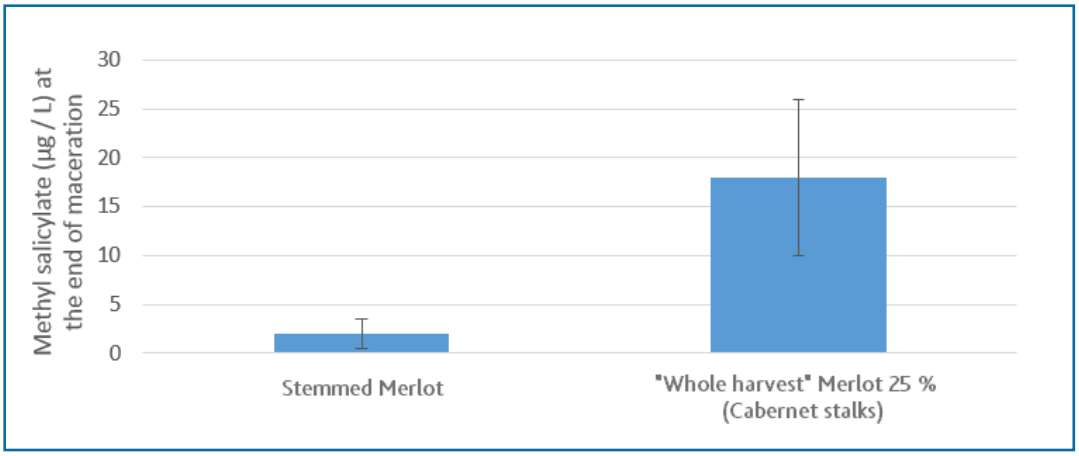

Fig. 3 : Methyl salicylate concentration (µg/L) during trial of stalks addition performed with a partner

These analytical developments must also be related to the development of the 4-MND determination method in the laboratory. The MND is responsible for the prune aroma. With some partners, we started to work on aromatic indices based on ratios between methyl salicylate concentrations and MND concentrations, in order to evaluate the balance between freshness and jammy notes on a batch of grapes, must or wine.

Conclusions and applications

SARCO & EXCELL laboratory has recently developped new analyzes allowing to measure these markers.

The first analysis, by **SPME-GCMS** doses methyl salicylate and ethyl salicylate. The methyl salicylate assay has a double interest: in addition of being a marker of freshness, this molecule could also be an indicator of parasitic attack on the vineyard. The aim of the analytical monitoring is therefore both to assess the health of the vine and to estimate the potential of freshness. These data can also be correlated with those of MND (prune aroma). The ratio of these two concentrations would be the slider between freshness and jammy notes for the management of harvest dates, maceration times but also the choice of certain oeno-technical practices such as the winemaking in presence of stalks, the types of extraction, the pressing and the re-incorporation of the different presses ...

The second is an analysis by **SBSE-GCMSMS** which doses different molecules responsible for the mint flavors in the wines: piperitone, menthol, menthone, mintlactone, eucalyptol, limonene, carvone and pulegone.

We have therefore put in place three analytical proposals:

	Proposal	Applications
1	Methyl salicylate and ethyl salicylate	- Cryptogamic pressure - Stalks potential - Fresh perception or even "resinous"
2	(Methyl salicylate and ethyl salicylate) / MND	- Maturity and potentiality of the grapes - Indicator of fresh notes vs. jammy
3	- Methyl salicylate and ethyl salicylate - Molecules with mint flavors (piperitone, menthol, menthone, mint lactone, eucalyptol, limonene, carvone, pulegone)	- Menthol or varietal flavors of a vintage, a must or a wine - Testing and validation of oenotechnical operations favoring these expressions

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