EVOLUTION OF TOASTED AROMAS IN RED WINE DURING BARREL AGING

Denis DUBOURDIEU and Takatoshi TOMINAGA

Introduction

The woody aroma descriptors characterizing barrel-aged wines are well known: smoky, spicy, coconut, vanilla, roasted coffee, and toasted bread.

The main molecules responsible for the odors of spice, smoked and coconut have been well known for above ten years : volatile phenols, and in particular eugenol, produce the smoky, and/or spicy aromas; cis and trans methyl octalactone give the coconut note, and phenol aldehydes, in particular, confer the vanilla and vanillin notes. P. Chatonnet (1-3) in the 90's demonstrated the influence certain essential parameters of cooperage play on the formation of these compounds: oak botanic and geographic origin, wood drying and toasting intensity.

On the other hand, the nature of the odor components which are responsible for the roasted coffee notes has remained enigmatic for a long time; As a matter of fact, furanic aldehydes, in particular furfural, possess grilled odours but their sensory threshold is well below the levels at which they are present in wine. Their olfactory impact is negligible.

Recently, works by T.Tominaga et Blanchard (4) showed that key roasted aroma in barrel-aged wines is a volatile thiol, extremely odorous, 2-furanemethanethiol (2-FM). This molecule was identified for the first time in 1926 in roasted coffee (5); it is not surprising that tasters utilize this descriptor to qualify empyreumatic odor in barrel-aged wines. 2-FM was equally found in different cooked food, like meat juice, grilled meat, and popcorn where it forms by Maillard reaction between cystine and pentoses at high temperature.

The formation of 2-FM in wine is not totally elucidated. In white barrel-aged wines, its production occurs over the course of the alcoholic fermentation, by bio-transformation of furfural given by the wood, by yeast sulfur metabolism (6). In the red wines, 2-FM and the roasted character appear relatively quickly after being transferred in a new barrel. We will report on different observations on key parameters needed for 2-FM evolution over the course of red wine barrel aging.

Role of malolactic fermentation in new barrel on the content of 2-FM in red wines

Wines which undergo malolactic fermentation in new barrels develop faster, and more intense roasted aromas, than those which are barreled after malolactic in a tank. This character certainly explains why they are generally preferred by tasters during the spring tasting. This observation hasn't been verified on a molecular level so far.

Figure 1, the same Merlot (vintage 2000), in new barrels (French oak, full grown tree) barreled before malolactic fermentation, or just after completion in tank. Sampling was done after MLF, in March and June. Flocculated lees after MLF, in tank or in barrel, were removed; these deposits were re-incorporated at the moment of the other racking. Before racking in March, the concentration of 2-FM in the wine barreled after MLF was low 1ng/L; the wine barreled before MLF was 8ng/L of 2-FM; the roasted character is practically imperceptible in the first wine, and perceptible in the second wine. The sensory threshold of 2-FM is 5ng/L in red wine. The concentration of 2-FM increases over the course of aging for both treatments; they reach respectively 6 and 21 ng/L in

June. Both wines demonstrated a roasted character but it is more intense in the wine that underwent barrel MLF.

Figure 2 (Merlot 2001) shows that at the end of MLF of a red wine in barrel the 2-FM is already present in quantities above sensory threshold, and the roasted character is very noticeable. It seems that lactic acid bacteria can metabolize furfural from the wood by a route similar to which the yeast create 2-FM in white wines fermented in barrels. Laboratory experiments in model conditions of lactic acid bacteria supplemented with and without furfural confirm this hypothesis (results not shown). Over the course of aging similar to precedent experiment, 2-FM appear slowly, in the wine that was barrel aged after MLF and increases until June and then stabilizes. The concentration in 2-FM which underwent MLF in barrel is always higher, even though its evolution is irregular. In September, the concentration of 2-FM of the two wines was 7 and 16ng/L respectively.

It appears that 2-FM can form in red wines from wood furfural following two different ways: microbiologically from lactic acid bacteria during MLF in barrel, chemically after aging with H2S of the wine in a reductive state. Factors that can explain the decrease of 2-FM observed in wine which undergoes MLF in barrel are the oxidation from each racking and removal of the lees responsible for the oxidation protection 2-FM and H2S.

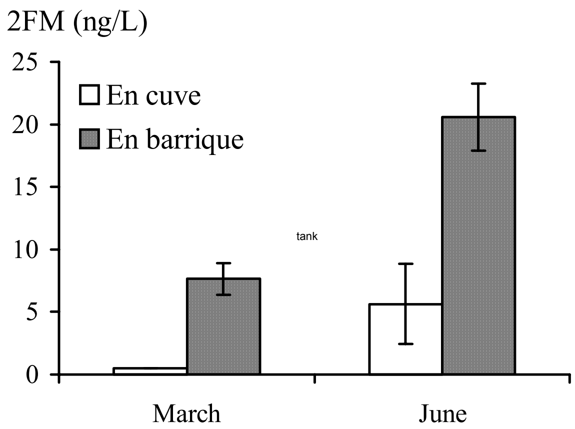

Figure 1. 2-FM evolution in barrel aged red wine (Merlot 2000) with malolactic fermentation in tank and barrel

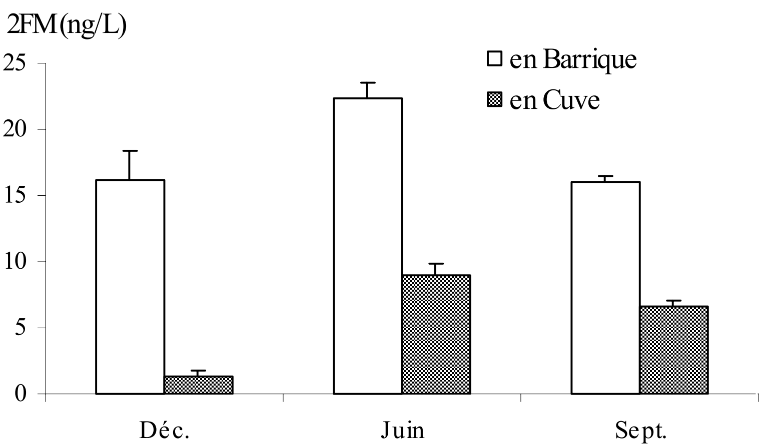

Figure 2. 2-FM evolution in barrel aged red wine (Merlot 2001) with malolactic fermentation in tank and barrel

Role of lees in the evolution of 2-FM during barrel aging of red wines

It is illustrated by the following experiment. The same Merlot 2001 from the precedent experiments, barrel aged in new barrels (French oak, full grown treeing) after MLF in tank or MLF in barrel

MLF in barrel

Three treatments of lees aging are compared; treatments were no lees (SL), after each racking (after MLF, March, June), lees were eliminated following classical method; total lees (LT), lees were re-incorporated after each racking yielding a turbidity of 500NTU; in fine lees (LF) lees were eliminated after MLF and lees from March and June were re-incorporated yielding a turbidity of 20 NTU

The concentration of 2-FM is measured before each racking; three rackings from December to September, in the presence of the fine lees or total modified little the concentration of 2-FM (figure 3).

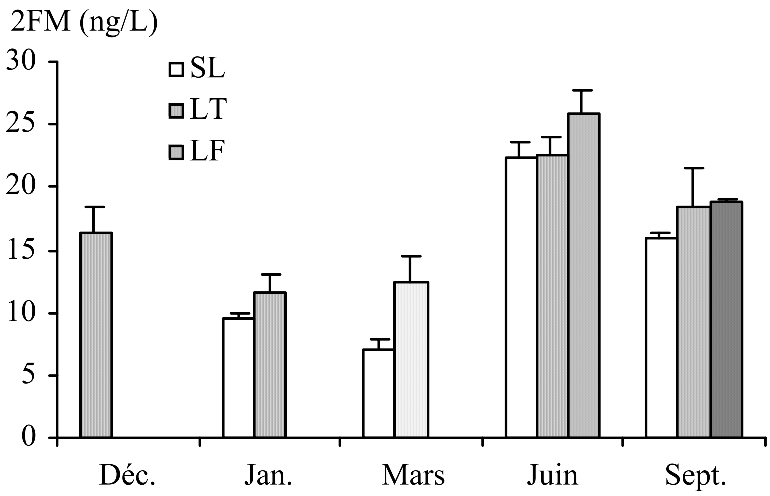

Figure 3. Influence of different lees treatments on the evolution of 2-FM in red wine (Merlot 2001) over the course of barrel aging.

(MLF was done in full grown tree barrels; treatment were no lees (SL), after each racking (after MLF, March, June), lees were eliminated following classical method; total lees (LT), lees were re-incorporated after each racking; in fine lees (LF) lees were eliminated after MLF and lees from March and June were re-incorporated

MLF in tank

In this case, racking after MLF removed the lees; the wines were barreled with a turbidity of 40 NTU; racked in March and June, the lees were removed or reincorporated corresponding to the treatments, no lees (SL) with fine lees (LF). Figure 4 shows the presences of fine lees influence little the concentration of 2-FM until June but eliminates the decrease afterwards.

The effect of lees on the formation of 2-FM over the course of red wine aging is not simple to interpret. Associated with racking, the reincorporation of the lees does not seem to favour the generation of 2-FM, except for fine aging; but this observation must be revisited; it is well know wine aeration in the presence of lees has a tendency to fix the thiols to the lees (7); If we reason by comparison with the evolution of other wine mercaptans, it is possible that the absence of racking favors more the augmentation of 2-FM than the reincorporation of lees during racking.

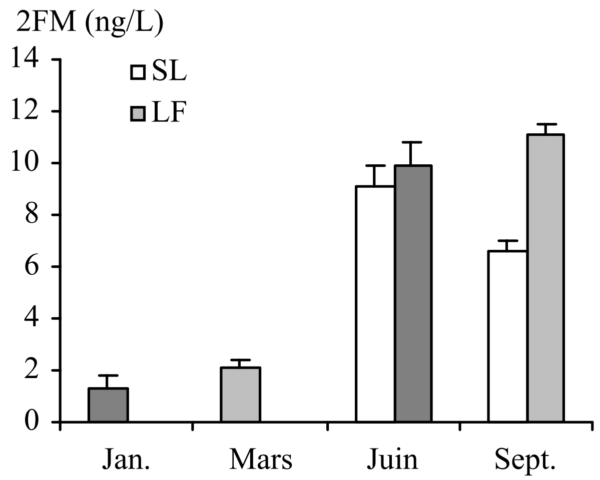

Figure 4. influence of different lees aging on the evolution of 2-FM in red wine (Merlot 2001) in barrel aging.
(Wine barrel aged after MLF in tank with a turbidity of 40 NTU; treatment no lees (SL): lees removed during racking in March and June; fine lees (LF): reincorporation during racking in March and June)

Role of wood origin and barrels mode of manufacturing on 2-FM formation in red wines.

In the following experiment, we compared, from June to November, 2-FM evolution in red wine (Merlot, 2000) barreled after MLF. Racking occurred in March and June with reincorporation of the lees at each racking. Comparison on the following barrels: French oak full grown trees (medium toast), Caucasus (medium toast), European blend (medium toast and medium plus toast) American oak and American oak “U-Stave”. U-Stave process corresponds to a longitudinal grooved surface of the stave of a ½ centimeter of depth and width, to create a toasting gradient during burning between the top of the groove (more toasted) and the bottom of the groove furthest from the fire (less toasted). This process is done to favor a degradation of lactone and production of furfural and vanillin during burning, in order to create an aromatic profile, toasted vanilla, coco, in other words, by combining the grooved surface and different toasting levels, to confer on the American oak, naturally rich in lactone, a wood more complex and less caricatured

Figures 5,6,7,8, and 9 report respectively the evolution of the following component in wine: 2-FM, furfural (FFA) and furfurylic alcohol (FFOH) cis-b-methly-g-octalactone (OC) and vanilla (VA)

2-FM concentration increases regularly from June to November (figure 5) 2-FM is particularly abundant in the wine aged in American oak “U-stave”

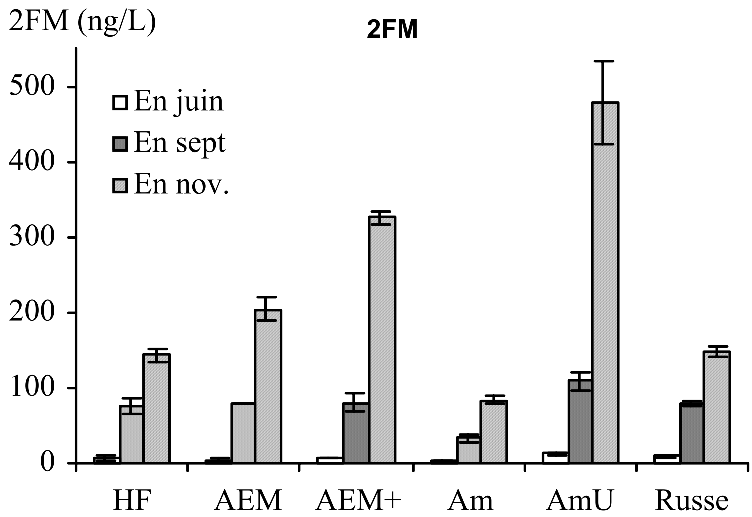

Figure 5. 2-FM evolution during barrel aging of red wine after MLF in tank (Merlot 2000) (HF: French oak full grown trees, medium toast; AEM: blended European, medium toast; AEM+: blended European, medium toast plus; Am: American oak, normal fabrication; AmU American oak, U-Stave fabrication; Caucasus: oak from Caucasus forest)

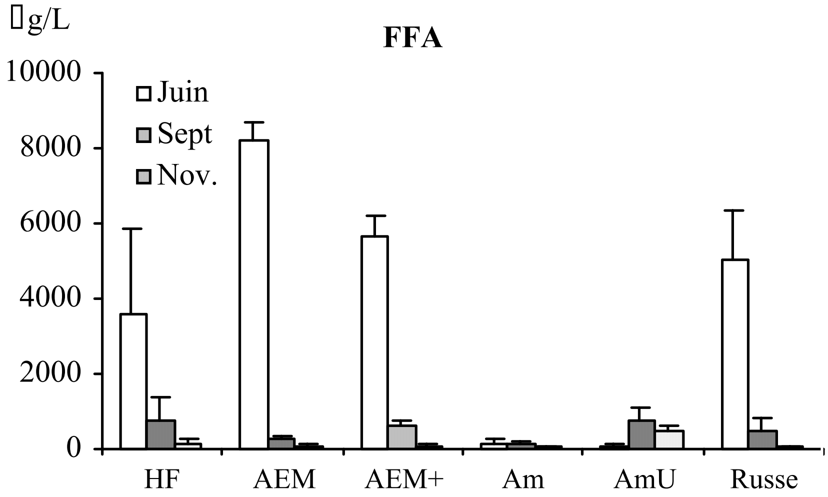

Figure 6.

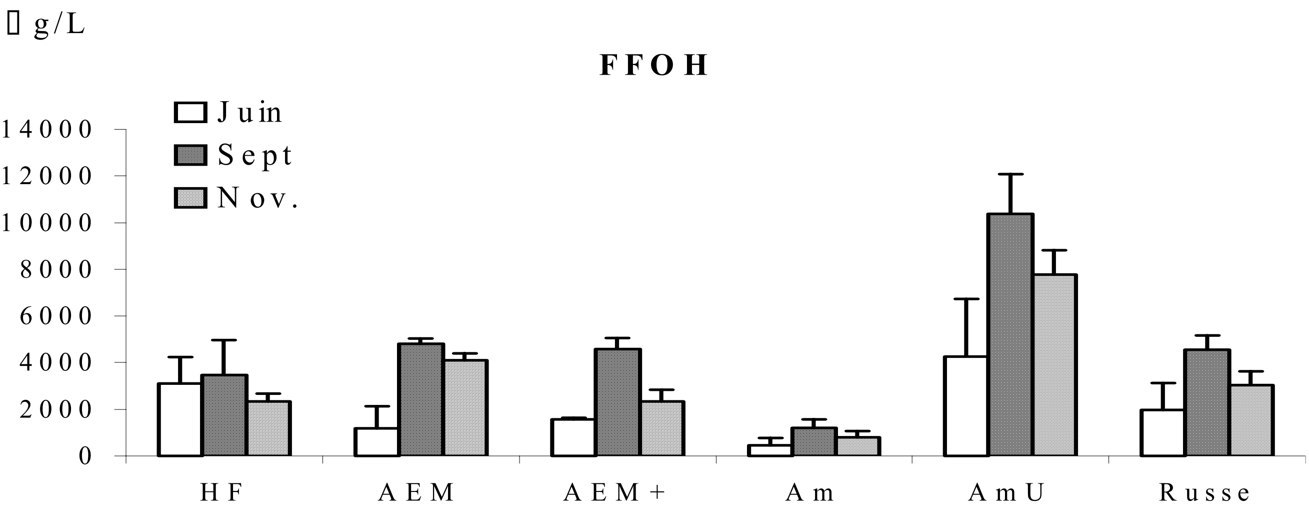

Figure 7.

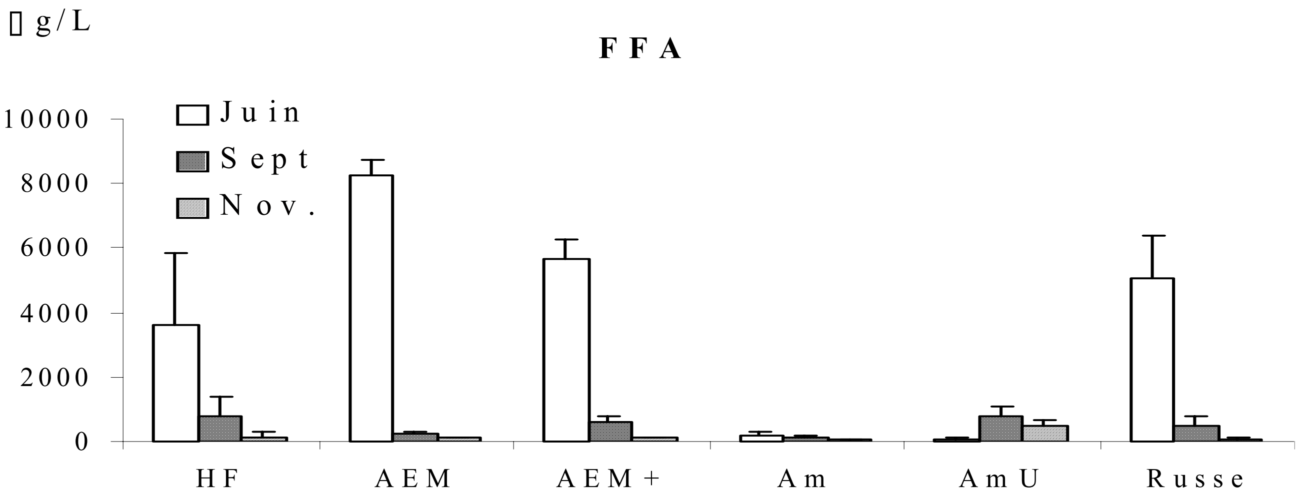

Figure 8

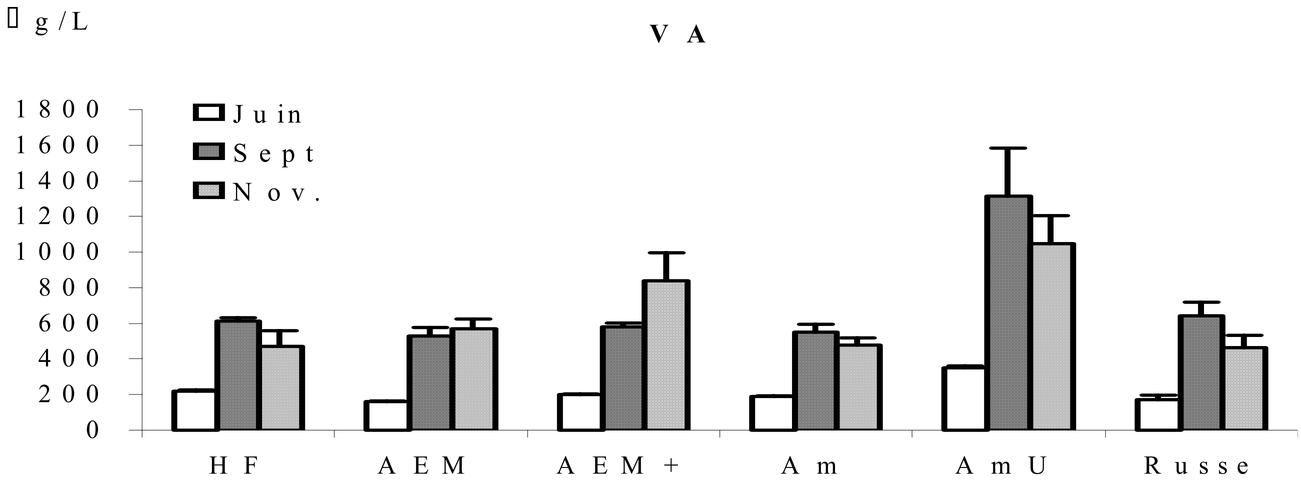

Figure 9

References:

1. Origines et traitements des bois en tonnellerie - Incidence de l'origine et du mode de séchage sur la composition et la qualité des bois de chênes en tonnellerie . P. Chatonnet. dans : Le Bois et la Qualité des Vins et Eaux-de vie. *Numéro spécial du Journal International des Sciences de la Vigne et du Vin,* **1992**, 39-50.

2. Les composés aromatiques du bois de chêne cédés aux vins.P. Chatonnet.
dans : Le Bois et la Qualite des Vins et Eaux-de vie. Numéro spécial du Journal International des Sciences de la Vigne et du Vin, **1992**, 81-92.

3. Evolution de certains composés volatils du bois de chêne au cours de son séchage, premiers résultats. P. Chatonnet, J.N. Boidron, D. Dubourdieu et Monique Pons. *Journal International des Sciences de la Vigne et du Vin,* **1994**, *28*, 4, 359-380.

4. A powerful aromatic volatile thiol, 2-furanmethanethiol, exhibiting roast coffee aroma in wines made from several *vitis vinifera* grape varieties. Tominaga , T.; Blanchard, L.; Darriet, Ph.; Dubourdieu, D. *J. Agric Food Chem.* **2000** , *48* (5),1799-1802.

5. Reichstein T., Staudinger H., 1926. British Patent 260 960.

6. Formation of furfurylthiol exhibiting a strong coffee aroma during oak barrel fermentation from furfural released by toasted staves. Blanchard, L.; Tominaga, T.; Dubourdieu, D. *J. Agric. Food Chem*. **2001**, *49* (10) 4833-4835.

7. Mise en évidence et interprétation de l'aptitude des lies à éliminer les thiols volatils du vin. Lavigne V., Dubourdieu D., *Journal International des Science de la Vigne et du Vin,* **1996**, *30* (4), 201-206.