STUDY OF QUERCOTRITERPENOSIDES EXTRACTION IN WINES AGED IN CONTACT WITH OAK: INFLUENCE OF THE SHAPE OF THE PIECES OF WOOD ON EXTRACTION KINETICS

By Andrei Prida[(a)], Thomas Oui[(b)], Benoît Verdier[(a)], Delphine Winstel[(c)], Axel Marchal[(c)]

(a) Tonnellerie Seguin Moreau, Avenue de Gimeux, CS 10225 Merpins.
(b) Groupe ICV Centre œnologique, 6, route de Carpentras, 84190, Beaumes-de-Venise
(c) University of Bordeaux, Bordeaux INP, INRAE, OENO, UMR 1366, ISVV, F-33140 Villenave d'Ornon, France

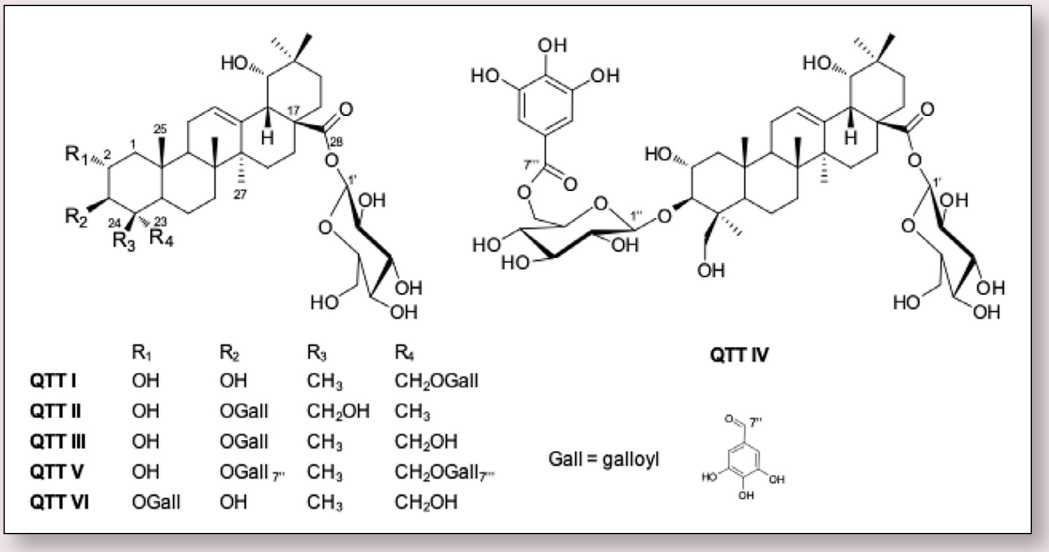
INTRODUCTION

*Quercotriterpenosides (QTT) are a family of sweet compounds (**fig. 1**) that were first identified in oak wood (Marchal 2011). One characteristic of these molecules is that they have a very low gustatory detection threshold (590 µg/L for QTT I). They contribute to an impression of "sweetness" and an effect of "volume" and "viscosity" in wines matured in contact with oak (in barrels or in contact with pieces of oakwood). The first results obtained about QTT (Marchal et al. 2011) demonstrated that these molecules are stable over time. The compounds were detected in wines aged in oak barrels after having been kept in bottles for several years. However, little is known about the extraction kinetics of these compounds. To fill this gap, we studied the release of these compounds from various pieces of oakwood, compared to other, better-known, wood compounds.*

For our study, we chose the following reference molecules:

• Cis-whisky-lactone: a wood volatile compound that brings wine sweet notes, and at high levels, marked coconut flavors.

• Furfural: this compound is produced with heat; therefore, it is virtually non-existent in non-heated oak wood. On its own, the molecule has no sensory effect, but it is a precursor of furfuryl thiol, a compound that gives wine an intense coffee/roasted aroma (Tominaga et al. 2000). A more recent study demonstrated that the presence of furfural in wine is a major analytical marker of the intensity of a wine's "toasted" and "woody" attributes (Prida et al. 2010).



	R_1	R_2	R_3	R_4
QTT I	OH	OH	CH_3	CH_2OGall
QTT II	OH	OGall	CH_2OH	CH_3
QTT III	OH	OGall	CH_3	CH_2OH
QTT V	OH	OGall 7'''	CH_3	$CH_2OGall_{7'''}$
QTT VI	OGall	OH	CH_3	CH_2OH

Figure 1 : *Quercotriterpenoside structures.*

MATERIALS AND METHODS

Preparation of the oakwood samples

It has been demonstrated that QTT levels vary widely in oakwood, as do most compounds. The better part of this variability is associated with the variability between individual trees. So to resolve this variability issue and be able to compare the different modalities, we had use a specific set-up for our sampling.

For this experimentation, our raw material was non-heated wine staves (pieces of wood measuring 900 mm x 50 mm x 18 mm).

They were cut into 3 pieces of identical mass. Then each was fractioned into pieces the following sizes:

• A – staves measuring 300 mm x 50 mm x 18 mm (i.e. a third of the initial piece);

• B – this part was chopped into blocks measuring 50 mm x 50 mm x 18 mm (such blocks of oak are frequently used for winemaking);

• C – this part was ground into wood chips of irregular dimensions, measuring approximately 5mm.

Figure 2 shows how the samples were prepared. Parts A, B and C of different staves were mixed to form batches of non-heated wood containing identical initial amounts of QTT, but with different grain sizes.

Because non-heated pieces of wood contain very little furfural, we followed the same methodology for heated pieces of wood. We carried out both in parallel to dose this molecule.

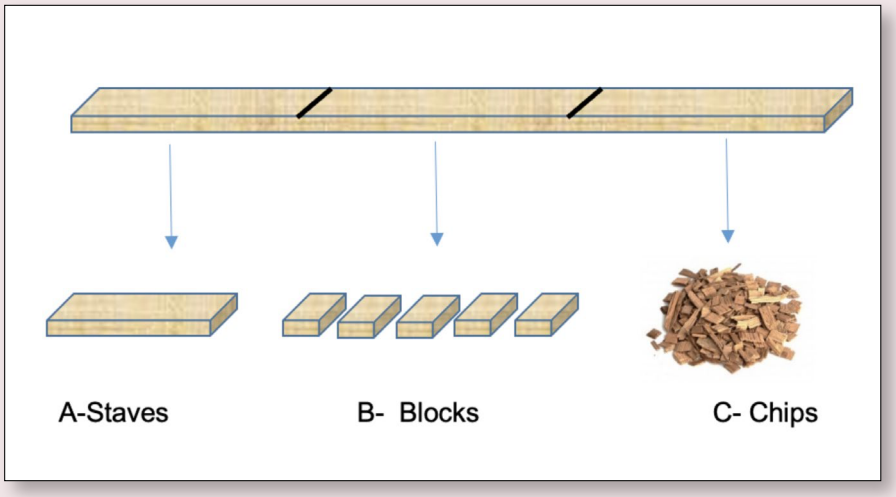


Figure 2 : Diagram of the preparation of the samples.

Maceration and modalities

The wood samples comprising chips, blocks and mini-staves were macerated in a Syrah wine (Rhône valley, 2020 vintage; ABV: 14,53% vol.; pH: 3,81; total acidity: 3,38 g/L sulfuric acid equivalent) in six 200L-vats, at doses of 5 g/L, the common dose for treating wine with pieces of oakwood, from 01/02/2021 to 30/08/2021.

We thus obtained:

• modality A: vat with non-heated staves

• modality B: vat with non-heated blocks

• modality C: vat with non-heated wood chips

• modality AC: vat with heated staves

• modality BC: vat with heated blocks

• modality CC: vat with heated wood chips.

During the 7 months the maceration lasted, we took 100ml samples of wine at the following time intervals: after 2 weeks of extraction, after 1 month, 2 months, 3 months and 7 months of extraction.

Chemical analysis

We analyzed three quercotriterpenosides (QTT I, QTT II, QTT III) with ultra high performance liquid chromatography combined with Fourier transform mass spectrometry (LC-FTMS) according to the method developed by Marchal (Marchal et al 2016).

The volatile compounds (whisky-lactones and furfural) were dosed using gas chromatography coupled with mass spectrometry; the solid-phase headspace microextraction technique was used for preparation and then followed by gas chromatography coupled with mass spectrometry (HS-SPME-GCMS) according to the method described by Diaz-Maroto (Diaz-Maroto et al. 2004).

RESULTS AND DISCUSSION

QTT extraction kinetics

*The extraction curves for the sum of the three QTT (QTT I, QTT II and QTT III) are presented in **figure 3**. QTT levels in the wines vary depending on the size of the pieces of wood used. At a dose of 5g/L, QTT levels reach the detection threshold after 15 days of maceration for modality C ("wood chips"), at the end of the maturation stage for modality B ("blocks") but do not reach it for modality A ("staves") after the 7-month maceration time.*

When examining kinetics, QTT levels reach a plateau after 3 months for wood chips. But extraction is slower for staves and blocks, and levels are still increasing towards the end of the maturation. This result suggests that for both of these formats, maximum extraction still hasn't been reached after 7 months of contact.

If we compare the different grain sizes (size of the pieces) used in this experiment, we notice that the QTT extraction ratio staves/blocks/chips is approximately 1/2/8 at the beginning of maturation and 1/2/3.5 towards the end. We may draw the conclusion that extraction is much stronger with chips in the early stages of maturation, which is logical and explained by the wine/wood exchange surface.

The gap narrows towards the end of the aging, but QTT levels remain higher with wood chips than with staves and even with blocks.

In practice, that means that the transfer of QTT with blocks and staves becomes effective only after sufficient contact time, lasting longer than 3 months. However with the chips, the result is visible after only 1 month, and extraction peaks around 3 months.

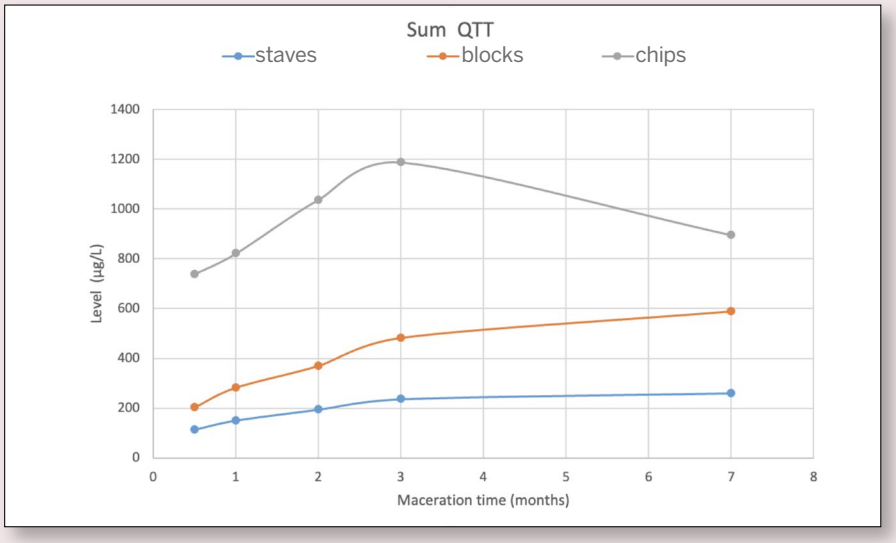


Figure 3 : *Evolution of QTT levels in the wine as a function of maceration time.*

Extraction kinetics of whisky-lactone

*We compared QTT extraction with that of whisky-lactone, in its cis form, which is predominant in oakwood (**figure 4**). Extraction kinetics for this molecule are similar to those of QTT: the curves and extraction rates are similar for all three grain sizes. Between 3 and 7 months, the level of this compound remains stable for chips but rises for blocks and staves.*

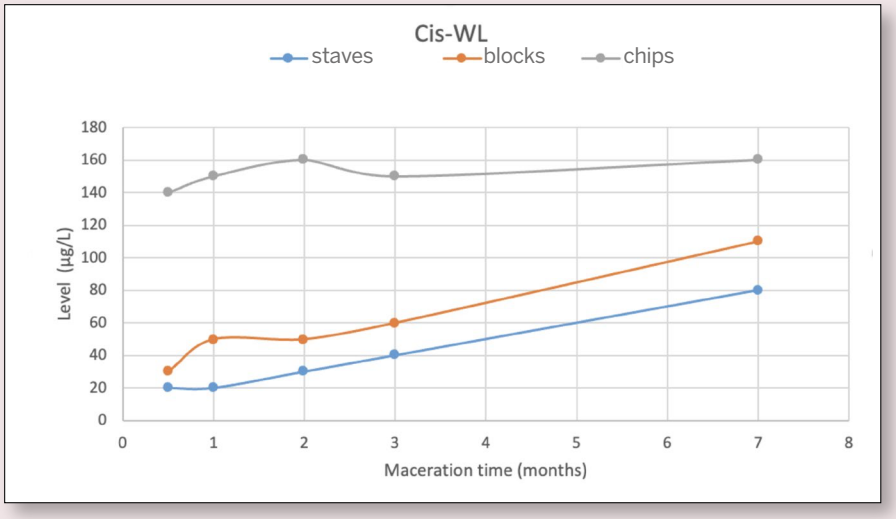


Figure 4 : *Evolution of cis whisky-lactone levels in the wine as a function of maceration time.*

RESULTS AND DISCUSSION (CONT.)

Extraction kinetics of furfural

Figure 5 shows furfural extraction kinetics in the AC (heated staves), BC (heated blocks) and CC (heated chips) modalities.
For this molecule, all three curves are bell shaped, with relative differences in the time needed to reach an extraction peak: 1 month in the case of chips, 3 months for blocks and 5 months for staves. After that, levels decrease to reach similar levels at the end of aging. These results show faster extraction rates compared to QTT and cis-whisky-lactone, but also suggest that this molecule is transformed in the wine environment. When comparing the behavior of the various compounds described above, major differences can be noted regarding the first extraction phase. Furfural is rapidly extracted, whereas extraction is gradual for QTT and cis-whisky-lactone. This could be explained by the fact that the latter are native wood molecules and therefore naturally "linked" with the wood matrix. In contrast, furfural is a molecule created by heat and can easily be "dissociated" from wood.
During the second extraction phase, furfural levels decrease, due to reactions in the wine matrix. In comparison, lactones and QTT remain more stable during the experiment:
• QTT: slight decrease for chips for 7 months of extraction and slower accumulation for the staves and blocks.
• Cis-whisky-lactone: stable values for chips and gradual extraction for the staves and blocks.

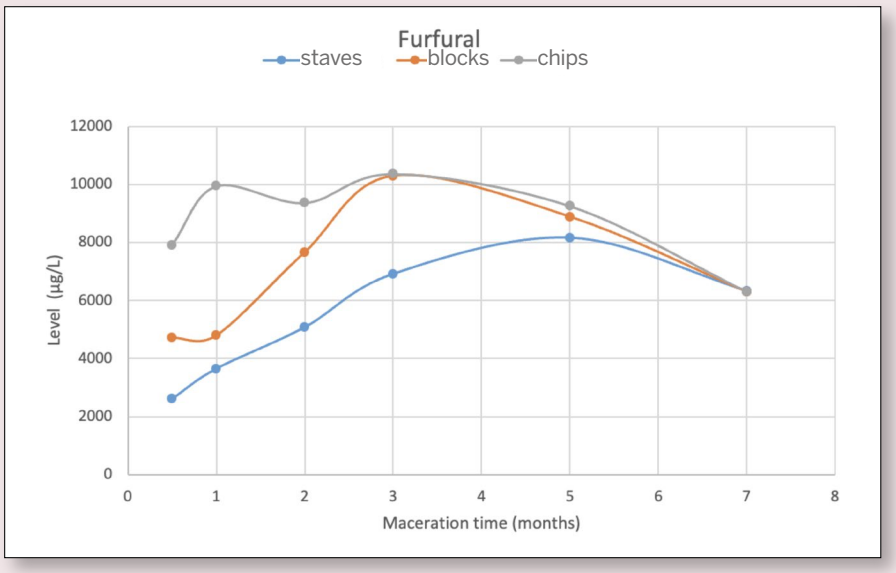


Figure 5 : Evolution of furfural levels in the wine as a function of maceration time.

CONCLUSION

This experimental work demonstrates that extraction kinetics for QTT, non-volatile compounds that contribute to the sweet taste of wines aged in contact with oakwood, vary widely depending on the shape of the pieces of wood used in wine cellars. The extraction kinetics of these compounds can be compared with that the cis-whisky-lactone, another compound present in non-heated wood. We were able to show how important it is to take into account grain size to make the best of the woods used and reach extraction targets for taste compounds within a time span often limited by the need to bring to market wines grown with winemaking woods.
It must be noted that not all oakwoods contain similar amounts of these key compounds and that it is crucial to first select them carefully in order to reap the benefits of QTT in wines aged in barrels or with winemaking woods.

REFERENCES

- Marchal, A.; Waffo-Téguo, P.; Génin, E.; Mérillon, J. M.; Dubourdieu, D. 2011 Identification of new natural sweet compounds in wine using centrifugal partition chromatography-gustatometry and Fourier transform mass spectrometry. Anal. Chem. 83 (24), 9629–9637.
- Prida A., Chatonnet, P., 2010 Impact of chemical composition of oak extractives on the olfactory perception of barrel aged wines. Am. J. Enol. Vitic., 61 (3), 408-413.
- Marchal, A., Génin; E., Waffo-Téguo, P., Bibès, A., Da Costa, G., Mérillon, J.M., Dubourdieu, D. 2015 Development of an analytical methodology using Fourier transform mass spectrometry to discover new structural analogs of wine natural sweeteners Anal. Chim. Acta, 853 (1), 425–434.
- M. Diaz-Maroto, Eva Sánchez-Palomo, M Soledad Pérez-Coello, 2004, Fast Screening Method for Volatile Compounds of Oak Wood Used for Aging Wines by Headspace SPME-GC-MS (SIM), J. Agric. Food Chem. 52, 6857-6861.
- Tominaga, T., Blanchard, L., Darriet, P., Dubourdieu, D., 2000. A Powerful Aromatic Volatile Thiol, 2-Furanmethanethiol, Exhibiting Roast Coffee Aroma in Wines Made from Several Vitis vinifera Grape Varieties. J. Agric. Food Chem. 48, 1799–1802.