Hydroxycinnamic acids management in winemaking

– role played by malolactic bacteria and consequences on strain selection for winemakers

What exactly are these ''hydroxycinnamic acids''?

Hydroxycinnamic acids are organic acids, naturally present in grapes and wines, predominantly in their tartaric acid bound form – cinnamate esters. These cinnamate esters (ρ-coutaric acid, fertaric acid, caftaric acid) are water soluble and have a bitter taste (Nagel et al. 1979; Waterhouse 2002). The hydroxycinnamic acid and the cinnamate ester content of grapes, musts or wines and its distribution depends on grape variety and growth conditions (Nagel et al. 1979; Waterhouse 2002).

Why hydroxycinnamic acids management may be of interest in winemaking?

This family of organic acids has features reportedly impacting the colour, taste and flavour the profile of wines:

- *Colour stabilizer*: hydroxycinnamic acids may act as a co-pigment binding to anthocyanins, and thereby stabilising the colour (Hernandez et al. 2006). This is the primary axis of research regarding hydroxycinnamic acids in wines.
- *Antioxidant*: hydroxycinnamic acids may act as an antioxidant and radical scavenger (Kikuzaki et al. 2002) as well as an antioxidants together with glutathione (Bouzanquet et al. 2012).
- *Flavour precursors in some specific conditions*: hydroxycinnamic acids can be converted by *Brettanomyces/Dekkera spp.* into volatile phenols: 4-ethylphenol (4-EP), 4-ethylguaiacol (4-EG), 4-ethylcatechol (4-EC). These volatile phenols are associated with the so-called ''Brett.'' aroma's.

How does hydroxycinnamic acids concentration evolve over time in wines?

Hydroxycinnamic acids are hydrolysed from tartaric acid during the winemaking process, via different paths:

- Chemical hydrolysis due to the acidity of the wine – a slow process that gradually proceeds through the winemaking and the wine storage (Waterhouse 2002; Hixon et al. 2012)
- Enzymatic hydrolysis – via added enzymes (Hixon et al. 2012) or via microorganisms having a specific enzyme named **cinnamoyl esterase**. Some lactic acid bacteria strains of *Oenococcus ssp.and Lactobacillus ssp.* have been shown to be cinnamoyl esterase 'positive' while some others are 'negative' and scientists have demonstrated that the cinnamoyl esterase can also be present in different Fungi (Hernandez et al. 2006; Hernandez et al. 2007; Cabrita et al. 2008; Ginjom et al 2011; Burns and Osborne 2013).

Cinnamoyl esterase positive strains can hydrolyze hydroxycinnamic acids from the tartrate bound and therefore increase their concentration in wines. This may be seen as a positive feature to stabilize colour or impact the red-ox potential of white, rosé and red wines. It may be considered as a risk for wines made in barrels or aged in barrels, conditions where *Brettanomyces* risk of infection is higher.

How to practically use this information in my winery to avoid volatile phenols production?

Volatile phenols can be produced by different yeasts and lactic acid bacteria. However, only *Brettanomyces* yeasts are able to produce high concentrations of these compounds under oenological conditions (Hixon et al. 2012). Therefore, to avoid the production of volatile phenols the primary aim should be to avoid *Brettanomyces* contaminations. These contaminations generally occur during barrel ageing (Benito et al 2008) and wines with low SO_2, high pH, temperatures over 15°C are more susceptible (Benito et al. 2008). Maturation in old barrels and poor disinfection of barrels also creates a higher risk of *Brettanomyces* contamination.

Hydroxycinnamic acids are only seen as an issue in situations of spoilage with specific *Brettanomyces* strains that can produce volatile phenols from hydroxycinnamic acids. Therefore, cinnamoyl esterase activity by lactic acid bacteria does not represent a risk by itself of higher volatile phenol concentration in wines but only a potential risk in case of a *Brettanomyces* infection which can potentially lead to the increase these volatile phenols production.

In the light of these new findings, wineries that have previously experienced problems with *Brettanomyces* contaminations and wineries producing barrel aged wines may consider using strains of malolactic cultures that are cinnamoyl esterase negative in order to minimize the impact of a potential *Brettanomyces* spoilage. Furthermore, it would be particularly risky to have the malolactic fermentation managed by spontaneous lactic acid flora, the probability being high to have at least one strain being cinnamoyl esterase positive.

Chr. Hansen recommends using cinnamoyl negative strains for barrel aged wines; inoculating with Viniflora® CH16, CH11, CH35, 'Oenos 2.0' or NoVA™ is the solution of choice for this application.

How to know if the strain of malolactic bacteria used is cinnamoyl esterase positive or negative?

Following the latest findings from James Osborne from Oregon State University (USA), Chr. Hansen now delivers the 'cinnamoyl esterase' profile for each and every strain commercialized. This information may help winemakers to select the strain of malolactic culture they want to use in regards to the type of wine to produce. 'Cinnamoyl esterase' is now a common trait used in selecting malolactic cultures within Chr. Hansen.

For instance, the strains linked to the products Oenos and CiNe™ are cinnamoyl esterase positive and therefore their use is recommended in wines that do not mature in barrels: white wines (to avoid oxidation) and red or rosé wines (to stabilize the colour) while NoVA™, CH16, CH11, CH35 or Oenos 2.0 are cinnamoyl esterase negative and are recommended for barrel aged wines would they be white or red wines.

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What are the remaining questions regarding hydroxycinnamic acids in wine?

Hydroxycinnamic acids and their decarboxylation by *Brettanomyces* in wine is a research theme with a lot of pending questions. Research shows for instance that hydroxycinnamic acids are not stable during maturation and storage of wine (Hernandez et al. 2006) raising the question of their fate in wines aged in barrels. Aside from these acids, not all strains of *Brettanomyces* yeasts are capable of metabolising hydroxycinnamic acids into ethylphenols (Schopp et al. 2013) and it is not yet understood why some *Brettanomyces* strains produce ethylphenols (Lucy Joseph et al. 2013). Finally, *Brettanomyces* can also produce 4-ethylphenol via another pathway, where ethyl coumarate is the initial precursor (Hixon et al 2012) making this topic even more complicated than originally anticipated.

Conclusions:

New findings from the Oregon State University (J. Osborne) and Chr. Hansen show some strains of *Oenococcus oeni* are able to hydrolyze cinnamate esters, naturally present in wines, into hydroxycinnamic acids when they possess a cinnamoyl esterase activity. These hydroxycinnamic acids may be of interest in white wines (as antioxidant) or red wines (to stabilize the colour) that are not matured in barrels. However, they may be unwanted in barrel aged wines as they can be converted in volatile phenols by *Brettanomyces* in case of contamination. It is therefore recommended to avoid spontaneous malolactic fermentation in barrel aged wines (wild strains may have the cinnamoyl esterase activity) and to manage malolactic fermentations with commercial strains that are known to be cinnamoyl esterase negative such as Viniflora® NoVA™, Viniflora®CH16, Viniflora® CH11, Viniflora® CH35 or Viniflora® 'Oenos 2.0' to be on the safe side in case of spoilage.