Perceptive interactions in red wines: How physico-chemical pre-sensorial effects may affect red wine fruity aromatic expression?

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Introduction

More than thousand volatiles have been identified in wine. To be perceived, these aroma compounds need to be first volatilized from the matrix to the headspace in order to reach the olfactory epithelium of the taster. From a physico-chemical point of view, compounds' release may be explained by their partition coefficient, which represents the ratio of aroma concentration between gas and liquid phase.

In red wine, a part of the fruity aroma is the consequence of perceptive interactions between various aromatic compounds, thanks to synergistic effects (Lytra et al., 2014, 2015), as well as masking effects, thus modulating the overall fruity expression (Cameleyre et al., 2015; Lytra et al., 2012). Even if these effects have been clearly described, the levels where they occur have been poorly investigated (Tempere et al., 2016).

This work proposes to explore the pre-sensorial level, where the release of flavour-active compounds from the matrix take place, using multiple partition coefficients determination.

Experimental

Sensory analysis

Sensory profiles were established for previously highlighted perceptive interactions. Impact on fruity perception of diacetyl, acetoin, acetic acid and γ-butyrolactone, but also dimethyl sulphide (DMS) at various concentrations and hydroxylated esters was studied.

Typical fruity aroma found in red wine was represented in the fruity aromatic reconstitution by 13 esters at concentrations listed in Table 1.

The panel consisted of 21 judges, 9 males and 11 females aged 28.7 ± 5.3 (mean ± SD) years. All panellists were research laboratory staff at ISVV, Bordeaux University, selected for their experience.

Partition coefficients calculation

Partition coefficient ($k_{g/m}$) represents, at the thermodynamic equilibrium, the ratio of concentrations between the gas phase (C_{gas}) and the liquid matrix (C_{liq}) of a volatile compound:

$$k_{g/m} = \frac{C_{gas}}{C_{liq}}$$

Partition coefficient determination was realized using Phase Ratio Variation (PRV) method developed by Ettre et al (1993), who established the following equation, where the concentration of volatiles in the headspace is proportional to the sample volume in the vial:

$$\frac{1}{A} = \frac{1}{f_i \times C_i^{liq} \times k_{g/m}} + \frac{1}{f_i \times C_i^{liq}} \times \beta$$

$k_{g/m}$ is the partition coefficient between the gas and the matrix, where A is the chromatographic peak area at the thermodynamic equilibrium, f_i is the detector response factor, C_i^{liq} is the initial compound concentration in the vial and β is the ratio between the headspace (V_g) and the liquid (V_l) volume (Ettre et al., 1993).

By plotting as 1/A against β, Equation 2 can be written as a linear relationship between 1/A and β, as follows:

$$\frac{1}{A} = a + b\beta$$

Where $a = \frac{1}{f_i \times c_i^{liq} \times k_{g/m}}$ and $b = \frac{1}{f_i \times c_i^{liq}}$.

The value of the partition coefficient $k_{g/m}$ is thus equal to the ratio between a and b, with $k_{g/m} = b/a$, expressed as a concentration ratio.

Partition coefficients were determined by plotting the inverse of the chromatographic areas against the phase ratio β, in order to obtain values for a and b. Glass vials (22.8 mL, Chromoptic, France) were filled with 6 amounts of volatiles solutions in dilute alcohol solution (0.05, 0.1, 0.5, 1, 1.5 and 2 mL), with phase ratios from 227 to 10.4 (according to the liquid samples volumes).

Table 1: Ethyl ester concentrations used for sensory analysis

Ethyl Esters and Acetates (µg/L)												
C_3C_2	C_4C_2	C_6C_2	C_8C_2	$2MeC_3C_2$	$(2S)$-$2MeC_4C_2$	$(2S)$- and $(2R)$-$2OH4MeC_5C_2$	C_2C_4	C_2C_6	C_2iC_4	C_2iC_5	$3OHC_4C_2$	$3MeC_4C_2$
150	200	200	200	250	50	400	10	2	50	250	300	50

C_3C_2, ethyl propanoate; C_4C_2, ethyl butanoate; C_6C_2, ethyl hexanoate; C_8C_2, ethyl octanoate; $2MeC_3C_2$, ethyl 2-methylpropanoate; S-$2MeC_4C_2$, S-ethyl 2-methylbutanoate; $2OH4MeC_5C_2$, ethyl 2-hydroxy-4-methylpentanoate; C_2C_4, butyl acetate; C_2C_6, hexyl acetate; C_2iC_4, 2-methylpropyl acetate; C_2iC_5, 3-methylbutyl acetate; $3OHC_4C_2$, ethyl 3-hydroxybutanoate; $3MeC_4C_2$, ethyl 3-methylbutanoate; 2MB, 2-methylbutan-1-ol; 3MB, 3-methylbutan-1-ol; 2MP, 2-methylpropan-1-ol; P, propan-1-ol; B, butan-1-ol.

Results and discussion

Sensory profiles establishment

Sensory analysis, and more precisely sensory profiles in dilute alcohol solution, showed modulation of fruity aroma perception in the presence of diacetyl, acetoin, acetic acid and γ-butyrolactone, but also with addition of dimethyl sulfide (DMS) at various concentrations (5, 10, 50 and 70 µg/L) or hydroxylated esters. Presence of these molecules led to masking and synergistic effects of fruity aromatic reconstitution, *via* some remarkable sensory interactions (results not shown).

Esters partition coefficients determination

SHS-LP-GC/MS method was applied, in order to research potential modifications of equilibrium release in headspace when compounds were mixed together.

Significant decrease in esters partition coefficients was observed demonstrating a masking effect when diacetyl, acetoin, acetic acid and γ-butyrolactone were added. This indicated a reduction in esters' presence in the headspace (Figure 1). This fact may explain, at least partially, that the taster was stimulated differently and was therefore possibly related to the masking effect observed for fruity notes, with an existence of pre-sensorial effects.
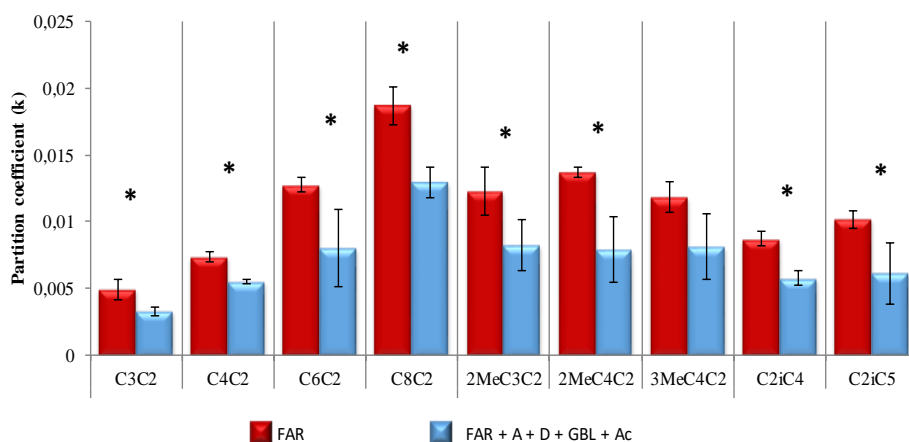

Figure 1: Impact of diacetyl, acetoin, acetic acid and γ-butyrolactone on partition coefficient of ethyl esters and acetates in dilute alcohol solution (12% v/v.). *, 5% significant level; error bars represent standard deviation; D, diacetyl; A, acetoin; Ac, acetic acid; GBL, γ-butyrolactone; FAR, fruity aromatic reconstitution.

DMS addition led to an increase in esters partition coefficients, especially as DMS concentration increased. Moreover, adding the 13 esters also led to an intensification of DMS partition coefficients (Figure 2). These observations suggested an intensification of these compounds release in the headspace when they were mixed together in dilute alcohol solution. These results may be correlated with the ones obtained using sensory analysis. Indeed, addition in fruity aromatic reconstitution of increasing concentrations of DMS led to a significant synergistic perception of black-fruit and blackcurrant notes.
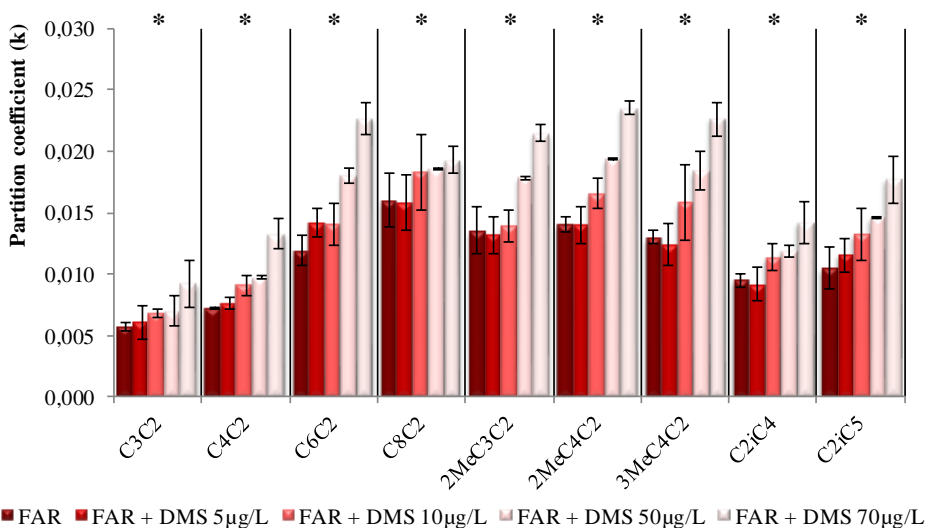
Figure 2: Impact of DMS at various levels on partition coefficient of esters in dilute alcohol solution (12% v/v.). *, 5% significant level; error bars represent standard deviation; FAR, fruity aromatic reconstitution.

The analytical tool application for hydroxylated esters highlighted that omission of ethyl 2-hydroxy-4-methylpentanoate or ethyl 3-hydroxybutanoate from fruity aromatic reconstitution did not change the partition coefficients of the other esters (results not shown). This fact was surprising, because omitting ethyl 2-hydroxy-4-methylpentanoate or ethyl 3-hydroxybutanoate from fruity aromatic reconstitution led to decrease of black- and fresh-fruit or red-, fresh- and jammy-fruit perception, respectively, even if these compounds were present at level below their olfactory thresholds. These data suggested that these synergistic effects related to hydroxylated esters were not the result of pre-sensorial interactions, but the consequence of interactions at sensorial level.

In general, our work highlighted the complexity of the mechanisms involved in perceptual interaction phenomena, whose origins can take place on several levels. They also contribute to the understanding of new perception modifications, especially between fruity and non-fruity compounds found in red wines.

References

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