



***Mass Spectrometry &
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Distribution of atypical ageing defect precursors in berry fractions (skin, pulp and seeds) by high resolution mass spectrometry

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Atypical ageing (ATA), also known as untypical ageing (UTA), is an aroma defect first reported in *Vitis vinifera* Riesling wines from Germany at the end of the 1980s, and then recognised in other growing areas around the world. The presence of reasonable amount of 2-aminoacetophenone (AAP) in wines is regarded as the main cause of this distinct sensory deviation with a smell similar to acacia blossom and mothballs.^{1,2} The principal precursors of this molecule responsible of the aroma defect were identified in L-tryptophan (Trp) and indole-3-acetic acid (IAA).

The study was conceived to develop and validate an analytical method for AAP precursors identification and quantification using high performance liquid chromatography coupled with high resolution mass spectrometry. The high resolution hybrid spectrometer allowed the rapid detection and quantification of four AAP precursors: IAA, skatole (Ska), tryptophol (Trh), and Trp. Moreover, in order to extend our investigation, a suspect screening approach was performed permitting the tentatively identification of indole-3-acetaldehyde (IAAld), indole-3-acetonitrile (IAN), indole-3-acetadoxime (IAOx), indole-3-acetamide (IAM), indole-3-lactic acid (ILA), indole-3-pyruvate (IPA), N-hydroxyl tryptamine (NHT) and tryptamine (TAM), reported as possible precursors of IAA.³

Chromatographic separation was performed using a Raptor Byphenyl 3 x 150 mm column at a flow rate of 0.3 mL/min and a ternary mobile phase. Mass spectra were acquired in profile mode through full MS-data dependent MS/MS analysis (full MS–dd MS/MS). Full mass spectra were recorded at a resolution of 70,000 full width at half-maximum (FWHM, calculated for m/z 200, 12 Hz). The automatic gain control (AGC) target was set at $3 \cdot 10^6$ ions, the maximum inject time (IT) at 200 ms, while data-dependent mass spectra were recorded at a resolution of 17,500 FWHM (defined for m/z 200, 12 Hz; AGC target of $1 \cdot 10^5$ ions, IT of 50 ms).

The range of quantitation went from the quantification limits to 3000 $\mu\text{g/L}$ and the LOD ranged from 1 $\mu\text{g/L}$ for IAA and Trh, to 5 $\mu\text{g/L}$ for Ska. Within-run precision (RSD %), had median values ranging from 5% (low and medium concentration levels) to 11% (high).

The study permitted to describe in detail the AAP precursors profiles of the three berry fractions (skin, pulp and seeds) in two *V. vinifera* grapes (Chardonnay, Merlot)

and two hybrids (Solaris, white; Cabernet cortis, red). Regarding the relative distribution among the three fractions, IAA (100%), Trp (71 %), Trh (60 %) and Ska (54 %) were predominantly present in skins.

References

1. Rapp, A., Versini, G., and Ullemeyer, H. 1993. 2-Aminoacetophenone: Causal component of 'untypical ageing flavour,' 'naphthalene note,' 'hybrid note' of wine. *Vitis* **32**, 61-62.
2. Schneider, V. 2014. Atypical ageing defect: sensory discrimination, viticultural causes, and enological consequences. A review. *Am. J. Enol. Vitic.* **65**, 277-284.
3. Pieck M., Yuan Y., Godfrey J., Fischer C., Zolj S., Vaughan D., Thomas N., Wu C., Ramos J., and Celeza, J.L. 2015. Auxin and Tryptophan Homeostasis Are Facilitated by the ISS1/VAS1 Aromatic Aminotransferase in Arabidopsis. *Genetics* **201**, 1185-1190.