



Short communication

Rapid fingerprinting of grape volatile composition using secondary electrospray ionization orbitrap mass spectrometry: A preliminary study of grape ripening



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ABSTRACT

We present a rapid and sensitive method based on secondary electrospray ionization mass spectrometry (SESI-MS) for profiling volatile emissions from the intact berries of non-Muscat grape cultivars (Pinot Noir, Chardonnay and Sauvignon Blanc). The method does not require sample preparation or concentration steps. Grape volatiles were tentatively identified based on accurate mass, the related elemental composition and literature. Approximately 300 peaks were detected in positive ion mode, and fewer (70–100) in negative ion mode. We monitored changes in grape berry volatile composition during ripening to screen for potential ripeness markers and observed ten $[M+H]^+$ peaks and two $[M-H]^-$ peaks that evolved in a significant linear trend ($R^2 \geq 0.80$, $p < 0.05$) for the combined data across all cultivars either increasing or decreasing in the final four weeks of ripening. Peaks assigned to C_{13} -norisoprenoids and benzenoid derivatives have shown similar trends in previous studies using offline gas chromatography (GC) approaches. Principal components analysis showed that negative ion mode clearly separated each stage of grape ripeness, whilst positive ion mode only separated berries in the final stage, pre-harvest. From this preliminary study, we conclude that SESI-MS holds promise as a tool for rapid screening of grape volatiles. Some marker ions had no interfering peaks within a 1-Da window, such that they could be monitored with simple unit-resolution instruments in future studies. This implies that SESI-MS in combination with portable MS instrumentation has potential for field analysis where real-time analysis is key.

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1. Introduction

Grape maturity is an important issue in winemaking because the grape chemical composition at harvest time is a key determinant of the resultant wine quality (Alexandre et al., 2015; Coelho, Rocha, Barros, Delgadoillo, & Coimbra, 2007; Giovenzana, Civelli, Beghi, Oberti, & Guidetti, 2015; Vilanova, Genisheva, Bescansa, Masa, & Oliveira, 2012). The grape ripening period from post-véraison (i.e. color change) to harvest is the most critical stage

(Geffroy et al., 2014) because many compounds of oenological importance (free and bound aroma compounds, phenolics, sugar and organic acids) undergo complex changes in this growth phase reaching an “optimal” quality (for a given style of wine) at a certain point in time (Bisson 2001).

Even though sugar and acidity measurements are the most common indices of grape maturity, it is well recognized that they provide only basic information related to wine quality (González-Barreiro, Rial-Otero, Cancho-Grande, & Simal-Gándara, 2013) and no information on the aromatic quality of the grapes. Furthermore, as there is no physiological basis for the general inverse correlation between sugar and acidity during ripening (Jackson, 2008) many exceptions have been observed (Moreno & Peinado, 2012). Accordingly, there is a need to complement sugar and acidity indices with other measures to better reflect the multifaceted

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nature of grape quality (Šuklje et al., 2014).

Grape-related wine aromas are derived from volatile organic compounds (VOCs) present in grapes as “free” aroma compounds and indirectly from non-volatile “bound” aroma precursors that are released during the winemaking process. Volatile emissions play a key role in fruit ripening (Goff & Klee, 2006) and therefore, VOC emissions from grape berries (whether directly related to wine aroma quality or not) may provide indicators of grape maturity and ripeness (Aleixandre et al., 2015). Previous studies regarding the evolution of free grape berry VOCs have focused on aromatic Muscat grape varieties in part because of the low concentration of VOCs in neutral non-Muscat grape cultivars (Ferrandino, Carlomagno, Baldassarre, & Schubert, 2012; Kalua & Boss, 2010; Salinas, Zalacain, Pardo, & Alonso, 2004). Furthermore, most studies analyzed grape must (crushed grapes) rather than the intact berries. Sensitive analysis of VOCs directly from intact grapes could ultimately facilitate the deployment of miniature mass spectrometer systems on all-terrain autonomous mobile robots in precision viticulture applications (Lopes et al., 2016).

In this preliminary study we use a numerically optimized Secondary Electrospray ionization Mass Spectrometry (SESI-MS) ion-source (Barrios-Collado, Vidal-De-Miguel, & Martinez-Lozano Sinues, 2016), (SEADM, Spain) to analyze VOCs directly from intact grapes without sample concentration steps. SESI-MS has already demonstrated promise in the real-time analysis of VOCs (Sinues et al., 2012; Wu, Siems, & Hill, 2000), including monitoring VOC emissions from plants (Barrios-Collado et al., 2016). Furthermore, a similar technique was previously shown to discriminate different stages of ripeness in a variety of fruits including table grapes (Chen, Sun, Wortmann, Gu, & Zenobi, 2007).

Grape berry volatiles from three non-Muscat cultivars (Pinot Noir, Chardonnay and Sauvignon Blanc) were monitored over a four-week period in the lead-up to harvest date. Our aims were to determine: (i) the VOC signals (i.e. high resolution m/z and elemental composition) that can be detected directly from intact grapes in real-time (ii) whether clear trends in the evolution of specific ion signals can be identified as potential candidates for grape ripeness markers. We utilize a high resolution Orbitrap™ MS (Thermo Fisher, Bremen) in this preliminary study to maximize the chemical information collected. We note however, that a SESI source can be readily interfaced to a mini-MS for portable applications (Lee, Misharin, Novoselov, Laiko, & Doroshenko, 2013).

2. Materials and methods

2.1. Chemicals

Triethylamine (99.5% purity) and chromatography grade water (Sigma-Aldrich, Buchs, Switzerland). A standard solution was prepared 10 $\mu\text{g}/\text{mL}$ in water for the MS sensitivity checks and stored at 4 °C. External mass calibration was performed using the standard positive and negative ion calibration solutions from Thermo-Fisher (Bremen, Germany).

2.2. Grape berry sampling and pre-measurement handling procedures

The volatile composition of intact berries from three non-Muscat grape cultivars was measured weekly, over a four-week period in the lead-up to harvest. The Pinot Noir, Sauvignon Blanc and Chardonnay grape samples were collected from a research vineyard located at Au, Wädenswil, Zurich canton, Switzerland (8°38'43.272"E, 47°14'56.136"N) in the 2015 vintage. *Véraison* was August 5th for all cultivars and harvest dates were September 25th (Chardonnay), September 29th (Sauvignon Blanc) and October 5th

(Pinot Noir). Grape samples were collected weekly from September 4th to September 25th. Approximately, 200 grape berries were collected for each cultivar, randomly sampled from different grapevines (both shadowed and sun exposed bunch positions) from the same rows of vines each week. Picked grapes (pedicel removed) were immediately placed in food-grade plastic bags, stored in a cooler and delivered to the lab for analysis within 3 h of picking. Approximately 50 berries were used for classical ripeness assessment conducted by Vinalytik (Seewen, Schwyz, Switzerland); pH and total acidity were measured by a potentiometer whilst glucose, fructose, tartaric and malic acid were measured using high-performance liquid chromatography (HPLC).

2.3. SESI-orbitrap-mass spectrometry

Grapes were counted, weighed and equilibrated to room temperature (21 °C) prior to SESI-MS analysis. The assessment of grape volatiles was conducted on the same day as sample collection avoiding freezing and storage steps. A random sample of the collected grapes (~80 berries) was measured per cultivar over a 2 min period. Grapes were placed in a 500 ml Schott bottle, closed using a modified cap that enabled the headspace of the bottle to be continuously swept (1 L/min, air) into the SESI source (SEADM, S.L.). The SESI source was interfaced to a Thermo-Fisher LTQ-Orbitrap XL mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). The ion source, and MS settings were as previously described (Barrios-Collado et al., 2016). Grapes were also measured in negative mode in the final three weeks prior to harvest (September 11th, 18th and 24th, 2015) to explore a wider range of VOCs. In negative mode, lock masses were m/z 61.98837 and m/z 115.07645, corresponding to NO_3^- and $\text{C}_6\text{H}_{11}\text{O}_2^-$ respectively. External mass calibration was performed weekly prior to grape VOC analysis. MS sensitivity was checked weekly (post-measurement) using triethylamine as a standard.

After a 2 min blank measurement the bottle was opened, filled with sample grapes and closed. Grape berry VOCs were swept from the sample bottle headspace into the ion source. The headspace was measured continuously (3 micro-scans per scan, maximum injection time of 0.2 s) for 2 min, after which the bottle was removed and replaced with an empty, clean bottle. The ion source was flushed with clean air for 10 min between samples to avoid carryover. Negative-ion mode measurements were conducted on the same grape berry samples, following a 15 min equilibrium period.

2.4. Data processing and analysis

MS acquisition files (.raw format) were converted to .mzml files via ProteoWizard software (Kessner, Chambers, Burke, Agus, & Mallick, 2008). Subsequent data processing was performed using python modules based on pymzML (Bald et al., 2012). Data processing steps included; peak picking (measured precision 1 ppm, minimum counts 5000), averaging spectra, m/z binning (2 ppm tolerance), removal of contaminants (Keller, Sui, Young, & Whittal, 2008) and inter-quartile range normalization. Average spectra were calculated over a 1 min period in the 2nd min of measurement. The first minute was discarded due to unstable signals from pressure changes in the ion source when opening and closing the sample bottle. Peak intensities were adjusted according to number of grape berries providing results on a per berry basis. Finally, peak intensities over the four weekly measurements were z-score standardized to facilitate comparison of the evolution profiles for the different m/z peaks. Principal components analysis was performed using XLstat (Addinsoft, Paris, France, version 2015.2.01.16529).

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