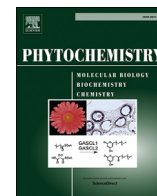




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Diel rhythms in the volatile emission of apple and grape foliage

Valentino Giacomuzzi^a, Luca Cappellin^{b,c}, Iuliia Khomenko^b, Franco Biasioli^b, Alan L. Knight^d, Sergio Angeli^{a,*}^a Faculty of Science and Technology, Free University of Bozen-Bolzano, Piazza Università 5, 39100 Bolzano, Italy^b Research and Innovation Centre, Fondazione Edmund Mach (FEM), Via E. Mach 1, 38010 San Michele all'Adige, Italy^c School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, 02138 Cambridge, Massachusetts, USA^d USDA, Agricultural Research Service, 5230 Konnowac Pass Rd, 98951 Wapato, Washington, USA

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(E)-4,8-dimethyl-1,3,7-nonatriene

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(E)-β-ocimene (PubChem CID: 5281553)

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ABSTRACT

This study investigated the diel emission of volatile organic compounds (VOCs) from intact apple (*Malus x domestica* Borkh., cv. Golden Delicious) and grape (*Vitis vinifera* L., cv. Pinot Noir) foliage. Volatiles were monitored continuously for 48 h by proton transfer reaction - time of flight - mass spectrometry (PTR-ToF-MS). In addition, volatiles were collected by closed-loop-stripping-analysis (CLSA) and characterized by gas chromatography-mass spectrometry (GC-MS) after 1 h and again 24 and 48 h later. Fourteen and ten volatiles were characterized by GC-MS in apple and grape, respectively. The majority of these were terpenes, followed by green leaf volatiles, and aromatic compounds. The PTR-ToF-MS identified 10 additional compounds and established their diel emission rhythms. The most abundant volatiles displaying a diel rhythm included methanol and dimethyl sulfide in both plants, acetone in grape, and mono-, homo- and sesquiterpenes in apple. The majority of volatiles were released from both plants during the photophase; whereas methanol, CO₂, methyl-butenol and benzeneacetaldehyde were released at significantly higher levels during the scotophase. Acetaldehyde, ethanol, and some green leaf volatiles showed distinct emission bursts in both plants following the daily light switch-off. These new results obtained with a combined analytical approach broaden our understanding of the rhythms of constitutive volatile release from two important horticultural crops. In particular, diel emission of sulfur and nitrogen-containing volatiles are reported here for the first time in these two crops.

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1. Introduction

Volatile organic compounds (VOCs) play a key role in the myriad of intra- and interspecific ecological interactions that occur among plants, as well as plants with other trophic levels, e.g. insects. Most studies have reported the significant qualitative changes and/or increases in the volatile emissions from plants following sustained

injury by insect pests or pathogens (Arimura et al., 2008; Chalal et al., 2015; Schaub et al., 2010; Turlings et al., 1990). In comparison with damaged plant foliage, volatile emissions from intact plants are relatively low with both herbaceous and woody species (Gouinguéné et al., 2003; Paré and Tumlinson, 1998; Tollsten and Müller, 1996). Low-weight volatiles represent a significant portion of the constitutive volatile emissions in many species, e.g. isoprene is the major contributor to the VOC emissions from intact foliage of Grey poplar (*Populus x canadensis*), willow (*Salix* spp.) and oil palm (*Elaeis guineensis* Jacq.) (Müller et al., 2015; Rosenkranz and Schnitzler, 2013).

* Corresponding author.

E-mail address: sergio.angeli@unibz.it (S. Angeli).

Rhythmic emissions of volatiles across the daily light and dark periods are a typical occurrence for plants, and have been compared for a number of plants, including poplar (*Populus* spp.) (Arimura et al., 2004; McCormick et al., 2014), maize (*Zea mays* L.) (Christensen et al., 2013), Stone pine (*Pinus pinea* L.) and Norway spruce (*Picea abies* Karst) (Martin, 2003), and cotton (*Gossypium hirsutum* L.) (Loughrin et al., 1994). Photosynthesis is the main driver of the biosynthesis of major classes of volatile secondary metabolites, such as terpenoids and phenylpropanoids/benzenoids (Dudareva et al., 2013; Vogt, 2010). This explains the diurnal peak in volatile emissions that is usually observed in both coniferous and deciduous species (e.g. Chalal et al., 2015; Grabmer et al., 2006; Hüve et al., 2007; Misztal et al., 2015). Diel rhythms of volatile emissions likely match plant specific needs, such as the attraction of pollinators (Balao et al., 2011; Pichersky and Gershenzon, 2002) or the repulsion of pest insects (De Moraes et al., 2001). Indeed, plants do have a certain degree of control over the volatile release, due to stomatal control (Hüve et al., 2007) and to specific storage glands (Fürstenberg-Hägg et al., 2013), which allow previously biosynthesised volatiles to be released on plant's demand. In addition, the growth of plant tissue can account for the biosynthesis and emission of several volatiles, such as methanol and acetaldehyde (e.g. Brilli et al., 2011; Harren and Cristescu, 2013) according to an endogenously-controlled rhythm that is independent from photosynthesis (Ruts et al., 2012). To date, the characterization of diel rhythms of volatiles is missing for the majority of agricultural crops, including apple (*Malus domestica* Borkh.) and grape, (*Vitis vinifera* L.), with whom both pollination and pests are key factors affecting their productivity and management.

The relatively recent development of proton transfer reaction – mass spectrometry (PTR-MS), a direct-injection mass-spectrometric method characterized by high sensitivity and low detection limits (Lindinger et al., 1998) improves our ability to detect and measure real-time volatile plant emissions. PTR-MS is particularly suitable for the continuous monitoring of several hundred different VOCs at the same time, including for volatiles with a low-mass range (20–60 a.m.u.), and it has been used in a number of applications, including environmental sciences, medical sciences, food technology, and bioprocess monitoring (Cappellin et al., 2013). First generation PTR-MS systems were equipped with a quadrupole mass spectrometer providing unit mass resolution and therefore a limited analytical power, but recent versions of PTR-MS are coupled to a time-of-flight (ToF) mass spectrometer (PTR-ToF-MS) reaching mass resolutions around 5000 (m/Δm) (Jordan et al., 2009). Although this instrument cannot discriminate isomers, its use complemented with GC-MS provides a powerful binary analytical tool, as described by Danner et al. (2012) and verified in our previous work (Giacomuzzi et al., 2016).

To date, only a few studies have investigated the volatile emission patterns from higher plants using a PTR-MS-based approach. Several studies analysed the VOCs released from coniferous and deciduous forest canopies in order to understand the role of biogenic VOCs, such as sesquiterpenes, in the atmospheric chemistry and aerosol formation (Holzinger et al., 2005; Karl, 2004; Kim et al., 2009). In other studies, leaves or branches attached to the plant were enclosed or clamped in gas exchange cuvettes for analysing VOC emissions in response to wounding or to brief exposure to abiotic stresses, such as elevated ozone or temperature (e.g. Beauchamp et al., 2005; Brilli et al., 2011). This technique has also been used to characterize the circadian rhythms of isoprene emission from intact poplar (Loivamaki et al., 2007).

The sensory qualities of apple and grape fruits are key attributes associated with their production and value as fresh and processed commodities (Slegers et al., 2015; Ting et al., 2016). Thus, it is not surprising that the majority of the studies with these crops have

focused on the aroma composition of fruits and wine/cider (Campbell-Sills et al., 2016; Song et al., 2012; Ting et al., 2015). However, a few studies have also characterized the volatiles released by foliage of apple and grape under controlled conditions of air temperature, relative humidity, light-dark cycle and non-limiting soil water conditions. For example, Bengtsson et al. (2001) collected the VOCs from detached apple branches at different developmental stages, thus identifying the mix of volatiles from leaves, from leaves and flowers, from leaves and unripe fruits, and from mature fruits. Eleven VOCs were identified from leaves only, and the most abundant were (Z)-3-hexenyl acetate, (E,E)- α -farnesene, (Z)-3-hexenol, and (E)- β -farnesene. Other studies collected undifferentiated volatiles from attached apple branches bearing both leaves and fruits, thus identifying 34 (Casado et al., 2006) and 62 volatiles (Vallat et al., 2005) respectively, which included all the volatiles already found by Bengtsson et al. (2001). Chalal et al., 2015 collected the volatiles from grape (cv. Marselan) foliage that were either intact or treated with sulfated laminarin, an elicitor of induced resistance. Forty-seven compounds were identified, including 24 sesquiterpenes, 18 monoterpenes, one unidentified sesquiterpene alcohol, linalool, (Z)-3-hexenyl acetate, methyl salicylate and methyl jasmonate. A second study with grape used Porapak Q cartridges to collect the volatiles from freshly cut branches or grape clusters, cv. Chardonnay, and identified 23 compounds being emitted (Tasin et al., 2005). None of the studies reported above measured low-mass volatiles (<60 a.m.u.), because of the collection techniques used, nor examined the diel release of volatiles from intact grape foliage.

Here, we employed PTR-ToF-MS in combination with GC-MS to track and quantify the diel VOC emissions from apple and grape. This study provides evidence that several VOCs emitted by intact foliage of both crops follow a diel rhythm that is linked to the light-dark cycle, including sulfur- and nitrogen-containing compounds that were detected for the first time in these plants. Furthermore, we show that both apple and grape emit bursts of acetaldehyde, ethanol, and green-leaf-volatiles (GLVs) following a light switch-off.

2. Results

2.1. CLSA-GC-MS

Fourteen and ten VOCs were detected in volatile collections from intact foliage of apple (Table 1) and grape (Table 2) foliage, respectively. Thirteen compounds were quantified using analytical standards, whereas the monoterpene (E,E)-cosmene and the sesquiterpenes α -curcumene and germacrene D could not be quantified because the respective analytical standards were not available. The highest emission rates were with (Z)-3-hexenyl acetate and benzaldehyde in apple, and (E)- β -ocimene and (E,E)- α -farnesene in grape. Eight compounds were found to be emitted by both plants (Tables 1 and 2). In addition, apple released six volatiles that were not detected in grape: benzaldehyde, phenylacetonitrile, 2-phenylethanol, linalool, (Z)-3-hexenyl butyrate, and germacrene D. Conversely, only grape emitted the monoterpene (E,E)-cosmene and the sesquiterpene (E)- β -farnesene.

2.2. PTR-ToF-MS

Twenty-one different mass peaks showing a significant diel rhythm were detected from both intact foliage of apple and grape. Eighteen compounds were found in both plant species. Benzaldehyde, phenylacetonitrile, and the unidentified compound of m/z 115.039 were found uniquely in apple, whereas pyridine, methylbutenol and phenylacetaldehyde were found uniquely in grape.

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