Food Chemistry 243 (2018) 103–117

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Sensory, olfactometry and comprehensive two-dimensional gas chromatography analyses as appropriate tools to characterize the effects of vine management on wine aroma

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ARTICLE INFO

Keywords:
Canopy
Volatile compounds
HS-SPME-GC × GC/TOFMS
GC-O
QDA
Wine aroma
Vine management

ABSTRACT

For the first time, the influence of different vine management was evaluated in relation to volatile profile and sensory perception through GC × GC/TOFMS, QDA, GC-FID, GC/MS, and GC-O. GC × GC/TOFMS analyses and QDA have shown that a larger spacing between vine rows (2 rather than 1 m), attachment of shoots upwards, and irrigation did not result in wine improvement. Conversely, wines elaborated with grapes from a vine with a lower bud load (20 per plant; sample M1) stood out among the other procedures, rendering the most promising wine aroma. GC × GC/TOFMS allowed identification of 220 compounds including 26 aroma active compounds also distinguished by GC-O. Among them, eight volatiles were important to differentiate M1 from other wines, and five out of those eight compounds could only be correctly identified and quantified after separation in second dimension. Higher levels of three volatiles may explain the relation of M1 wine with red and dry fruits.

1. Introduction

Vine management encompasses viticulture practices aimed at improving the enological quality of grapes. The canopy of the vine, namely the aboveground portion of the vine, consisting of leaves, flowers, fruits, branches, buds, shoots, arms, and trunks, is well known to play a key role in both the light energy capture *via* photosynthesis, and in the microclimate around grapes (Keller, 2010). Indeed, vine vigor has been related to the characteristics of its canopy, and in particular to the balance between vegetative (number of leaves) and reproductive (number of grape bunches) growth, which may be achieved through adequate bud load. In the beginning of each growth cycle, buds generate new shoots, onto which leaves and grapes will later develop. Increase in bud load results in a higher number of shoots and bunches per plant. Accordingly, it can also increase the canopy density and shading of the vine. Under such conditions, the proportion of infertile buds increases, favoring shoots without bunches, and leading to greater vegetative and lower reproductive growth in the next cycle. Contrariwise, lower vegetative growth or lower canopy density allows for greater air circulation, which aids in controlling air humidity, and promoting the exposure of grapes to greater light incidence. Therefore, a reduction in fungal growth and improvement in the uniformity of grape maturation may occur (Smart, 1985).

Canopy management, as part of vine management, is categorized as a set of viticulture practices widely used to avoid excessive foliage density that would shade the fruit zone and turn it more humid. Leaf removal (defoliation) in the fruiting zone is the most applied canopy management strategy, to enhance air circulation and light penetration into the canopy. This practice may occur from the flowering stage until *véraison*, and has been shown to affect various parameters that influence wine quality. For instance, this practice has been shown to increase the phenolic content of Istrian Malvasia (Rescic, Mikulic-Petkovsek, & Rusjan, 2016), Pinot Noir (Feng, Skinkis, & Qian, 2017), Nero di Troia (Baiano et al., 2015) and Tempranillo (Vilanova, Diago, Genisheva, Oliveira, & Tardaguila, 2012) wines. Furthermore, defoliation has also been associated with increased sugar concentration and decreased volatile acidity in Nero di Troia (Baiano et al., 2015) and Tempranillo (Moreno et al., 2017; Vilanova et al., 2012) wines. Despite

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http://dx.doi.org/10.1016/j.foodchem.2017.09.078
Received 25 June 2017; Received in revised form 10 September 2017; Accepted 14 September 2017
Available online 21 September 2017
0308-8146/

the advantages of defoliation, it is important to note that leaf removal in the fruit zone or the apical shoot trimming is not excessive. In general, the grapevine needs 1.2 square meters of leaf surface to maintain the ripening of 1 kg of grapes (Keller, 2010). However, this ratio can vary between cultivars and cultivation conditions.

Aroma, an important parameter in wine quality, may be evaluated through sensorial and chromatographic techniques. Quantitative descriptive analysis (QDA) is one of the most informative tools used in the sensory evaluation of a product. In QDA a comprehensive description of the characteristics of aroma, appearance and flavor of a given wine is performed by a panel of selected and trained judges using an intensity scale (Stone, Sidel, Oliver, Woolsey, & Singleton, 1974). Data obtained by sensory evaluation may be linked to findings gathered using the olfactometric technique, in order to find the aroma-active compounds of a wine. Gas chromatography–olfactometry (GC-O) has been used to study odoriferous compounds that were previously identified mainly with one-dimensional GC (1D-GC) (Gürbüz, Rouseff, & Rouseff, 2006). However, previous studies have shown that wine is a complex matrix, and that co-elutions of volatile compounds may occur in 1D-GC, leading to problematic identification/quantification of co-eluted peaks, which might be resolved with the use of comprehensive two-dimensional chromatography with a time-of-flight mass spectrometric detector (GC × GC/TOFMS) (Nicolli et al., 2015; Welke, Manfroi, Zanus, Lazarotto, & Alcaraz Zini, 2012a; Welke, Zanus, Lazzarotto, & Alcaraz Zini, 2014a).

Association of GC-O and GC × GC/TOFMS data may help to resolve co-elutions and consequently, may also help the identification of compounds in regions indicated by sensory judges, as odor-active, in GC-O analyses (Chin, Eyres, & Marriott, 2011; Villire et al., 2012). In a former study, 334 volatile compounds were found in commercial Merlot wines from the Serra Gaúcha region (Brazil) through analysis with GC×GC/TOFMS (Welke et al., 2012a). Among these compounds, 17 aroma-active compounds, previously appointed by GC-O analysis as important to Merlot aroma, were only correctly identified and quantified by means of GC × GC/TOFMS, due to co-elutions with other sample compounds (Welke, Nicolli, Barbará, Marques, & Zini, 2017).

The combined use of GC × GC/TOFMS and GC-O was also adopted by Chin et al. (2011) to analyze Shiraz wine from Australia. In that work, eleven aroma-active compounds were identified after the heart-cutting of some regions of the chromatogram (acetic acid, 1-octen-3-ol, ethyl octanoate, methyl-2-oxo-nonanoate, butanoic acid, 2-methylbutanoic acid, 3-methylbutanoic acid, 3-(methylthio)-1-propanol, hexanoic acid, β-damascenone, and ethyl-3-phenylpropanoate). The combined use of QDA and 1D-GC with detection by mass spectrometry and olfactometry towards the study of wine aroma has also already been reported in the literature (Escudero, Campo, Fariña, Cacho, & Ferreira, 2007; Raposo et al., 2016). Escudero et al. (2007) used QDA to understand the role of some groups of odorants on aroma perception of Spanish assemblage aged red wines. The authors identified volatile compounds by gas chromatography with mass spectrometric detector (GC/MS) and GC-O; furthermore, the fruity character of these wines was found to result from the interactions among esters, norisoprenoids, dimethyl sulfide, and ethanol. Raposo et al. (2016) combined QDA, GC/MS, and GC-O to evaluate the influence of replacing SO_2 by a natural extract, named Vineatrol®, on wine aroma. Wines treated with Vineatrol® showed in QDA higher savory intensity, bitterness, astringency and persistence compared to wines treated with SO_2.

To date, only a few studies have evaluated the influence of canopy management on volatile profile, using GC/MS and odor-activity value calculations. Indeed, previous studies have been focused only on leaf removal and volatile profiling (Feng et al., 2017; Moreno et al., 2017; Vilanova et al., 2012). For instance, Feng et al. (2017) highlighted greater concentrations of linalool (floral odor), α-terpineol (floral odor) and β-damascenone (sweet/fruity) in Pinot Noir wine in addition to the highest levels of fruity esters (ethyl octanoate, isoamyl acetate and 2-phenethyl acetate) as compared to Tempranillo wines reported by Vilanova et al. (2012). Moreno et al. (2017) reported an increased concentration of two fruity esters (ethyl butanoate and ethyl hexanoate) in Tempranillo wines. The authors also reported enhancements in 3-methyl-1-butanol (odor described as alcohol/solvent), 2-methylbutanoic acid, and hexanoic acid (both acids, with cheesy odor), as negatively influencing the aroma of wines.

The main objective of the present study was the combined evaluation of three different parameters related to vine canopy management (bud load in single and double space between vines in the planting row; leaf area reduction by apical trimming in different number of leaves per shoot; and trained canopy with and without vertical attached shoots) on the volatile composition and aroma of Merlot wines through sensory, olfactometry, GC, and GC × GC analyses. This is the first report relating information gathered from various platforms (QDA, GC/MS, gas chromatography with flame ionization detector (GC-FID), GC-O and GC × GC/TOFMS) to comprehensively elucidate the volatile profiles of Merlot wines and their associated sensory perception as a result of the influence of different canopy management practices.

2. Materials and methods

2.1. Reagents and chemical standards

Standard compounds purchased from Aldrich (Steinheim, Germany) included isobutanoic acid (2-methylpropanoic acid), isovaleric acid (3-methylbutanoic acid), valeric acid (pentanoic acid), hexanoic acid, octanoic acid, nonanoic acid, dodecanoic acid, 1-hexanol, (*Z*)-2-hexen-1-ol, 1-nonanol, benzyl alcohol, 1-dodecanol, ethyl 3-methylbutanoate, hexyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, diethyl succinate (diethyl butanedioate), 2-phenylethyl acetate, ethyl dodecanoate, furfural, 2-furanmethanol, 2-heptanone, 2(5*H*)-furanone, 4-ethylphenol, eucalyptol, α-terpineol, citronellol, β-damascenone, geraniol, guaiacol, 3-mercaptohexanol. The purity of all listed compounds was higher than 98%.

Model wine was prepared as previously reported (Welke et al., 2012a). Standard solutions were prepared in ethanol and diluted in a wine model solution, in order to obtain a matrix similar to wine with regards to percentage of ethanol and acidity. Wine samples possessed a density of 1.1 g mL^{-1}, pH ranging from 3.4 to 3.5, and ethanol content ranging from 11.5 to 13.2% (*v*/*v*) (Table S1).

The solid-phase microextraction (SPME) fiber, 2-cm 50/30 μm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS) StableFlex, was purchased from Supelco (Bellefonte, PA) and conditioned according to the manufacturer's recommendations prior to its first use. Sodium chloride of analytical grade was purchased from Nuclear (São Paulo, Brazil) and oven dried at 150 °C for two hours before use. Twenty-milliliter headspace vials with Teflon septa were purchased from Supelco.

2.2. Vineyard experimental design

Ten different vine treatments involving distinct parameters of vine management (M) were conducted in a vineyard (30° 44′ 52,591″ S and 55° 23′ 49,637″ W) located in Santana do Livramento, Campanha Gaúcha region, Brazil. According to Table 1, treatments were named as M1 to M10, and they were conducted in the same vertical trellis system vineyard of 'Merlot' (*Vitis vinifera* L.) grafted onto SO4 rootstock, during the 2013/14 growth cycle. The experiments were conducted without irrigation and with attachment of shoots upward. Furthermore, two different spaces between vines (1 m and 2 m) were evaluated and two additional treatments were performed, without shoot attaching in a support wire (M6) and using drip irrigation (M10).

Management experiments (M1-M10) were conducted in the vineyard following a randomized block design formed by three areas (in a direction of less slope and almost without influence of the relief, Areas 1, 2 and 3 of Fig. S1) and five blocks (in the direction of greater slope