COMPREHENSIVE STUDY OF AUSTRALIAN ROSÉ WINES: CHARACTERISATION OF CHEMICAL AND SENSORY PROFILES

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A thesis submitted for the degree of Doctor of Philosophy

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Table of Contents

Thesis Summary

Rosé wine is a versatile and diverse style which is increasing in popularity in Australia and elsewhere, and the development of new markets such as China offers great potential to the Australian wine industry. In terms of consumer appeal, aroma and flavour attributes make a wine attractive, however, there is an absence of research related to the volatile compounds that are important to rosé wines produced in Australia. This thesis comprises a number of studies involving rosé wine that have been drafted as manuscripts and published. After an introduction chapter, manuscripts are presented in chapters as outlined in the following summary.

Firstly, insight into the sensory attributes and volatile profiles of Australian rosé wines was obtained. An HS-SPME–GC–MS method was developed and used in conjunction with a new application of a recently developed HPLC–MS/MS method to quantify 51 volatile compounds, including 4 potent sulfur compounds, in more than 2 dozen commercial rosé wines. Sensory descriptive analysis (DA) was undertaken and the corresponding results were correlated with quantitative chemical data to explore relationships between wine composition and sensory profiles. Based on the results, esters were prominent aroma volatiles, and β-damascenone, 3-methylbutyl acetate, ethyl hexanoate and 3-MHA were deemed to be important, in accord with other studies. Wines were described into three different styles with terms ranging from developed, spicy and savoury to fresh green, citrus, tropical fruit, floral and confectionery. This work has been published in Food Chemistry (Wang, J.; Capone, D. L.; Wilkinson, K. L.; Jeffery, D. W. Chemical and Sensory Profiles of Rosé Wines from Australia. Food Chem., 2016, 196, 682-693.)

Secondly, Australian rosé wines characterised in the previous study were selected and shipped to China for a blind tasting, which included several wines from China and France. Rosé wine tends to match well with a range of Asian cuisines, yet little was known about the factors driving the desirability of rosé wines in emerging markets such as China. To gain the first insight, rosé wine blind tastings were conducted in three major cities of China by 62 Chinese wine professionals. In total, 23 rosé wines that originated from Australia, China and France were evaluated by judges. Basic wine chemical parameters and 47 volatile compounds (included 5 potent thiols) were determined for the wines, and a novel use of network analysis (NA) provided good visualisation of the correlations between chemical and sensory components. The levels of residual sugar or developed characters were not related with preference, quality or expected price and acetate esters were related to red fruit characters and preferences. This work has been published in Food Chemistry (Wang, J.; Capone, D. L.; Wilkinson, K. L.; Jeffery, D. W. Rosé Wine Volatile Composition and the Preferences of Chinese Wine Professionals. Food Chem., 2016, 202, 507–517).

Thirdly, two representative rosé wines (tropical sample and fruity/floral sample) were selected for a gas chromatography-olfactometry (GC-O) study and volatiles were also quantified in order to evaluate in detail the compounds that were important to these particular styles. Two volatile extraction methods were compared to obtain extracts for aroma extraction dilution analysis (AEDA): liquid-liquid extraction (LLE) followed by solvent assisted flavor evaporation (SAFE), and a recently developed headspace (HS) sampling method. A HS-SPME-GC-MS with method selected ion monitoring (SIM) was developed, which enabled the quantification of 35 volatile compounds. In total, 51 odourants were detected by AEDA with FD factors ≥ 3, and 92 volatiles were quantified.

For the different samples, compounds like 2-phenylethanol, β-damascenone and a range of esters were more correlated with fruity and floral characters, while some volatile acids and 3-SHA were more associated with the tropical rosé wine. The HS method was as efficient as LLE to extract volatiles with lower boiling point and polarity, which were mostly esters and higher alcohols associated with fruity and floral characters. On the other hand, LLE was better able to capture compounds that were not very volatile. It was suggested that the application of both HS and LLE extraction methods would be necessary to obtain the most representative extracts of wine for AEDA when evaluating the impact of different volatiles on sensory profiles. This work has been published in Journal of Agricultural and Food Chemistry (Wang, J.; Gambetta J. M.; Jeffery, D. W., Comprehensive study of volatile compounds in two Australian rosé wines: Aroma extract dilution analysis (AEDA) of extracts prepared using solvent-assisted flavor evaporation (SAFE) or headspace solid-phase extraction (HS-SPE). J. Agric. Food Chem., 2016, 64 (19), 3838–3848).

In conclusion, this work has contributed new knowledge regarding the chemical and sensory compositions of Australian rosé wines, and important aroma volatiles have been determined. It has also greatly enhanced understanding of the preferences towards rosé wine from industry professionals in China, which is an important market for the Australian wine industry. Ultimately, this body of work can assist rosé wine producers to create their desired wine styles through greater knowledge of compositional and sensory characteristics, and preferences in a target market.

Declaration

I declare that this thesis is a record of original work and contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference has been made in the text. The publications included in this thesis have not been previously submitted for the award of any degree at the University of Adelaide or other University.

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Jiaming Wang	Date

Publications

This thesis is a collection of manuscripts that were published in Food Chemistry and Journal of Agricultural Food Chemistry (JAFC) during candidature. Two of three manuscripts were published in Food Chemistry, which in 2014 had an impact factor of Food Chemistry according to Thomson Reuters Journal Citation Reports of 3.391, and a 5-year impact factor of 3.901. The impact factor of JAFC was 2.912 in 2014 and the 5-year impact factor was 3.27.

The text and figures in Chapter 2 to 4 appear in different formats due to each journal's specific requirements. A statement of authorship, signed by all of the authors and listing individual contributions to the work, is included at the beginning of each chapter.

The thesis is based on the following refereed publications.

Chapter 2	Wang, J., Capone, D. L., Wilkinson, K. L., & Jeffery, D. W. (2016). Chemical and sensory profiles of rosé wines from Australia. Food Chemistry, 196, 682-693.
Chapter 3	Wang, J., Capone, D. L., Wilkinson, K. L., & Jeffery, D. W. (2016). Rosé Wine Volatile Composition and the Preferences of Chinese Wine Professionals. Food Chemistry, 202, 507–517.
Chapter 4	Wang, J., Gambetta, J. M., & Jeffery, D. W. (2016). Comprehensive study of volatile compounds in two Australian rosé wines: Aroma extract dilution analysis (AEDA) of extracts prepared using solvent-assisted flavor evaporation (SAFE) or headspace solid-phase extraction (HS-SPE). Journal of Agricultural and Food Chemistry, 64 (19), 3838–3848.

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Also, I thank my co-supervisor, Associate Professor Kerry Wilkinson for her support, advice and encouragement along my PhD and it has been a pleasure to work with her. I would also like to thank my external advisor Dr Mark Sefton for his priceless advice and Dr Dimitra Capone from The Australian Wine Research Institute (AWRI) for her valuable time, advice and help on my project and I did learn a lot from her.

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Chapter 1

LITERATURE REVIEW

This literature review was mostly prepared within the first 6 months of candidature and updated in March 2016. It mainly covers the literature up to April 2013 and also contains some latest references. The relevant literature beyond this review has been included in the introduction sections of the publications covered in Chapters 2 to 4.

1.1 Wine aroma

1.1.1 Grape-derived aroma compounds

Grape-derived aroma compounds that accumulate as secondary metabolites during grape ripening are largely responsible for the varietal differences of wines – especially varietal aromas. Their formation naturally depends on grape variety but environmental factors, such as soil nutrient, water stress, climate, and balance of vegetative and fruit growth, also influence secondary metabolite production (Rapp 1990; Reynolds & Vanden Heuvel 2009). Generally, these so-called varietal aroma compounds can be classified into four groups: isoprenoids (monoterpenoids and sesquiterpenoids), C_{13}-norisoprenoids, methoxypyrazines (MPs), and varietal (polyfunctional) thiols. These compounds are mainly located in grape skin whereas sugars and acids are found in the pulp (Table 1). Their structures, odour descriptions, perception thresholds and concentrations in wines were summarised in Table 2.

Table 1. Main grape-derived compounds are located in exocarp (skin) or mesocarp (flesh) tissues. Modified from Lund and Bohlmann (2006).

exocarp	isoprenoids	geraniol
		linalool
		terpineol
		nerolidol
		rotundone
	C_{13}-norisoprenoids	β-damascenone
		β-ionone
	thiols	*S*-3-(hexan-1-ol-L-cysteine)
	MPs	2-methoxy-3-isobutyl (IBMP)
		2-methoxy-3-isopropyl (IPMP)
		2-methoxy-3-sec-butyl (SBMP)
mesocarp	organic acids	malate
		tartrate
	sugar	glucose
		fructose

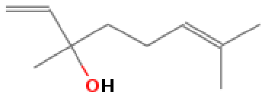
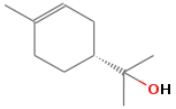
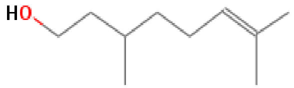
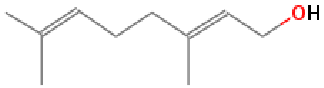
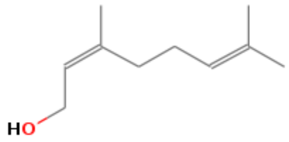
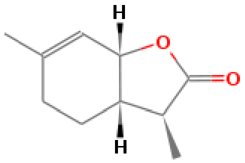
Isoprenoids are one important group of compounds contributing varietal aromas to wine (Black et al. 2015). Monoterpenoids, found in free and bound (glycosylated) forms and particularly abundant in Muscat grape varieties, are closely linked with floral characters such as rose and lilac (Clarke & Bakker 2011). In contrast to monoterpenoids, which have been studied for decades, sesquiterpenoids had gained little attention in wine research until the peppery compound, rotundone, was identified in Shiraz wines (Siebert et al. 2008; Wood et al. 2008). Investigations have since focussed on environmental and winemaking factors that influence grape and wine rotundone concentrations, as well as the biosynthesis of sesquiterpenoids (Black et al. 2015).

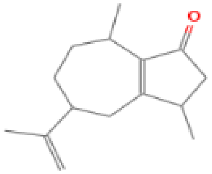
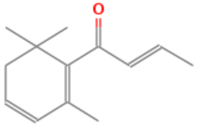
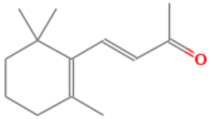
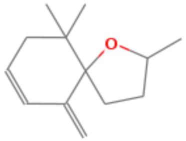
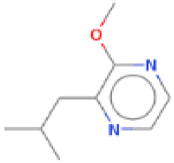
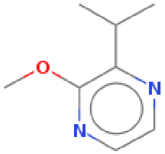
C_{13}-Norisoprenoids derived from carotenoids in grapes are ubiquitous aroma compounds in both neutral and “aromatic” cultivars (Black et al. 2015; Schneider et al. 2001). These volatiles impart floral or fruit characters to wine and can be found as odourants in many other food and perfumes (Winterhalter & Rouseff 2001). The unsaturated ketone β-damascenone (Table 2) imparts ‘cooked apple’ and ‘quince’ aromas and can be regarded as an aroma enhancer that heightens the fruity aromas of other volatiles (Pineau et al. 2007). Another C_{13}-norisoprenoid, β-ionone, which has violet and raspberry aroma (Black et al. 2015) and has been suggested that it has no impact on white wine aroma (Ribéreau-Gayon et al. 2006).

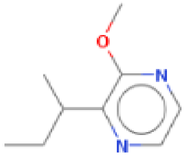
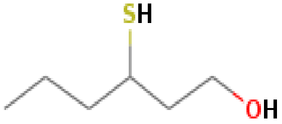
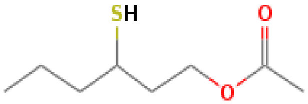
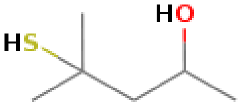
Methoxypyrazines (MPs) have received a good deal of attention in recent years. Having extremely low aroma detection thresholds, MPs are impact compounds responsible for varietal characters such as a green capsicum and herbaceous aromas (Allen & Lacey 1998) in some red (e.g., Cabernet sauvignon) and white (e.g., Sauvignon blanc) wines (Sala et al. 2004). There are three important MPs in wine in the form of 3-alkyl-2-methoxypyrazines: they are isopropyl (IPMP), *sec*-butyl (SBMP), and isobutyl (IBMP) (Cai, Koziel & O'Neal 2007; Cudjoe, Wiederkehr & Brindle 2005). IBMP, which contributed green and capsicum notes, was usually a dominant MP with concentrations several times higher than other MPs (Allen & Lacey 1998). SBMP and IPMP can be found at low ng/L in wine where they impart earthy, asparagus and vegetal aromas (Allen & Lacey 1998). When MPs reached a high level, their sensory impact was defined as an off-flavour, which was unpleasant and overcoming (de Boubée et al. 2002; Rapp 1990). Certain MPs can be found due to a phenomenon known as ladybeetle taint, caused by IPMP in particular, as a result of multi-coloured Asian ladybeetles (MALB) infesting grapevines (Botezatu et al. 2012). Light exposure was demonstrated to have opposite effects on MPs (Sala et al. 2004) as on one hand the concentration of MPs was higher with more light exposure. On the other hand, MPs was sensitive to light and could be decomposed with light exposure. Also, skin contact could increase the MP level in must and wine (Maggu et al. 2007).

Varietal thiols are another important group of grape-derived volatiles that act as impact compounds. There are three main varietal thiols in wine: 4-mercapto-4-methylpentan-2-one (4MMP), 3-mercaptohexan-1-ol (3MH) and 3-mercaptohexyl acetate (3MHA), which can be related to 'boxtree', 'passionfruit', 'grapefruit', 'gooseberry', and 'guava' odour in wines. However, high concentrations can lead to 'cat pee' or 'sulfur-like' aromas (Dubourdieu et al. 2006; Howell et al. 2006), thus the odour of these compounds could be positive or negative. Varietal thiols have been determined in a number of different varieties and different geographic regions with varying concentrations (Benkwitz et al. 2012b) (Table 2). In general, wines from Australia tend to have low concentrations of the three thiols, and New Zealand Sauvignon blanc has the highest. Therefore, it could be possible to use varietal thiols concentration as a marker to differentiate wines from differ regions, although the reason for these differences needs to be investigated further.

Table 2. The structure, odour description and perception threshold, concentrations in wines of varietal aroma compounds.

compound	**structure**^{a}	**CAS number**	**odour description**	**odour perception threshold**^{b}	**concentration**^{b} **white wines**	**red wines**
Isoprenoids						
linalool		78-70-6	citrus, floral, lavender^{c}	25.2^{c}	nd^{d}-230^{c}	nd-170^{c}
α-terpineol		98-55-5	floral, lilac, pine^{c}	250^{c}	nd-181^{c}	nd-49.2^{c}
citronellol		106-22-9	citronella, rose, green^{c}	100^{c}	nd-60^{c}	nd-22^{c}
geraniol		106-24-1	rose, geranium^{c}	30^{c}	nd-221^{c}	nd-25.8^{c}
nerol		106-25-2	rose, fruity, floral^{c}	680-2200^{e}	nd-48^{c}	nd-100.3^{c}
wine lactone		182699-77-0	coconut, woody, sweet^{c}	0.01^{c}	nd-0.2^{c}	nd-0.09^{c}

rotundone		18374-76-0	black pepper[c]	0.016[f]	0.009[c]	nd-0.232[c]
β-damascenone		23726-93-4	fruity, rose, cooked apple[c]	0.05, 0.14, 0.85, 2.1	nd-190[c]	nd-164[c]
β-ionone		79-77-6	violet, raspberry, rose[c]	0.09[c]	nd-29[c]	nd-5.61[c]
vitispirane		65416-59-3	eucalyptus, camphor, vegetable[c]	800[g]	nd-81[c]	nd-9[c]
Methoxypyrazines						
2-methoxy-3-isobutyl (IBMP)		24683-00-9	musty, green pepper[h]	2, 6 (ng/L)[h]	<0.2-307 (ng/L)[h]	0.5-227.3 (ng/L)[h]
2-methoxy-3-isopropyl (IPMP)		25773-40-4	musty, earthy, leafy[h]	2 (ng/L)[h]	<0.2-48.7(ng/L)[h]	0.2-18.1(ng/L)[h]

2-methoxy-3-sec-butyl (SBMP)		24168-70-5	green, ivy leaves, bell pepper[h]	1, 2 (ng/L)[h]	0-2 (ng/L)[h]	0-18.2(ng/L)[h]
polyfunctional thiols						
3-mercaptohexan-1-ol (3MH)		51755-83-0	grapefruit, passionfruit[i]	60[i]	0.0258-18.7[j]	0.678-11.5[j]
3-mercaptohexyl acetate (3MHA)		136954-20-6	passionfruit, box tree[i]	4[i]	ND-2.51[j]	0.005-0.154[j]
4-mercapto-4-methylpentan-2-one (4MMP)		19872-52-7	box tree, guava[i]	0.8[i]	ND-0.088[j]	0.005-0.05[j]
4-mercapto-4-methyl-2-pentanol (4MMPOH)		255391-65-2	citrus zest[i]	55[i]	0-45[k]	na[l]

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[a] Structures were obtained from National Institute of Standards and Technology (NIST) Chemistry WebBook (http://webbook.nist.gov/chemistry/). [b] In µg/L except where specified otherwise. [c] Black et al. (2015) and citations therein. Odour perception thresholds were determined in model wine. [d] Not detected. [e] Burdock (2009). [f] Wood et al. (2008) and determined in red wine. [g] Eggers, Bohna and Dooley (2006) and determined in model wine. [h] Sala et al. (2004) and citations therein. Odour perception thresholds were determined in model wine. [i] Tominaga, Murat and Dubourdieu (1998) and odour perception thresholds were determined in model wine. [j] Lund et al. (2009b); Mateo-Vivaracho et al. (2010); Rigou, Triay and Razungles (2014); Sarrazin et al. (2007); Tominaga et al. (2000). [k] Tominaga et al. (2000) and Mestres, Busto and Guasch (2000) and citation therein. [l] Not available.

1.1.2 Aroma compounds derived from pre-fermentation processes

Volatiles can appear in this period before winemaking due to physical treatments, such as harvesting, destemming, crushing and pressing. These processes destroy grape berry structures, releasing free varietal compounds contained within grape tissues. There is also the release of nonvolatile aroma precursors, but these do not contribute to aroma at this stage unless released enzymatically. One notable occurrence is the enzymatic formation of C_6 alcohols and aldehydes, such as *cis*-3-hexen-1-ol and *trans*-2-hexenal, which can confer a 'green' character to Grenache, Sauvignon blanc wines (Benkwitz et al. 2012b; Ferreira, López & Cacho 2000).

1.1.3 Volatiles derived from fermentation

The fermentation process is very important for producing volatiles that impact wine aroma. Compounds arising in this period are mostly produced by metabolic activity of yeast (alcoholic fermentation) and bacteria (malolactic fermentation, MLF) and form the largest pool of volatiles in terms of wine aroma composition. However, these volatiles are often produced at concentrations below their aroma detection threshold, thus having little impact on wine aroma (Ebeler 2001). In addition, most volatiles generated during fermentation are more or less the same regarding different grape varieties, so they do not necessarily help to differentiate wines. The metabolic pathways and types of volatile compounds produced by yeast and malolactic bacteria can be seen in Figures 1 and 2.

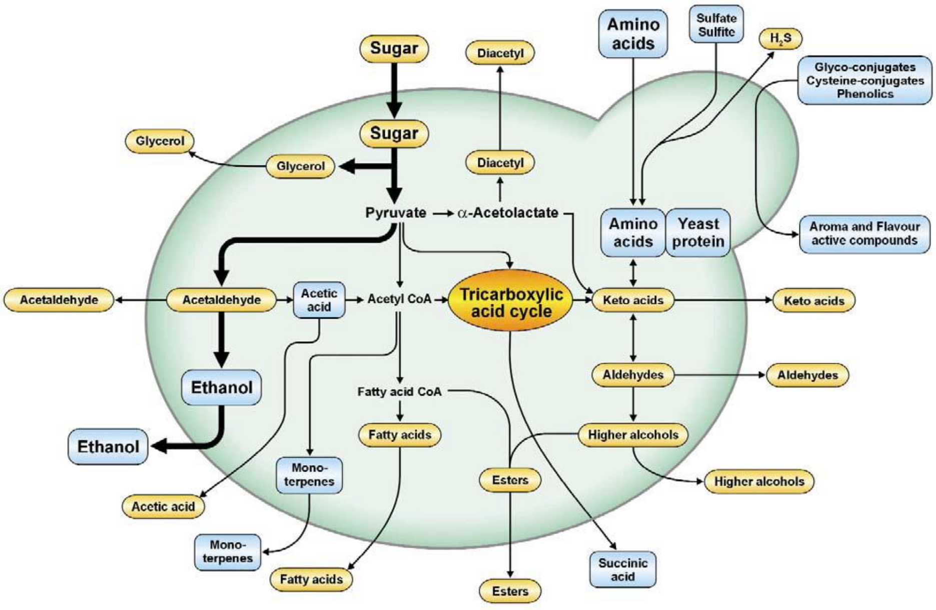

Figure 1. A schematic representation of the metabolic pathways of odourous and non-odourous compounds produced by wine yeast (Swiegers et al. 2005).

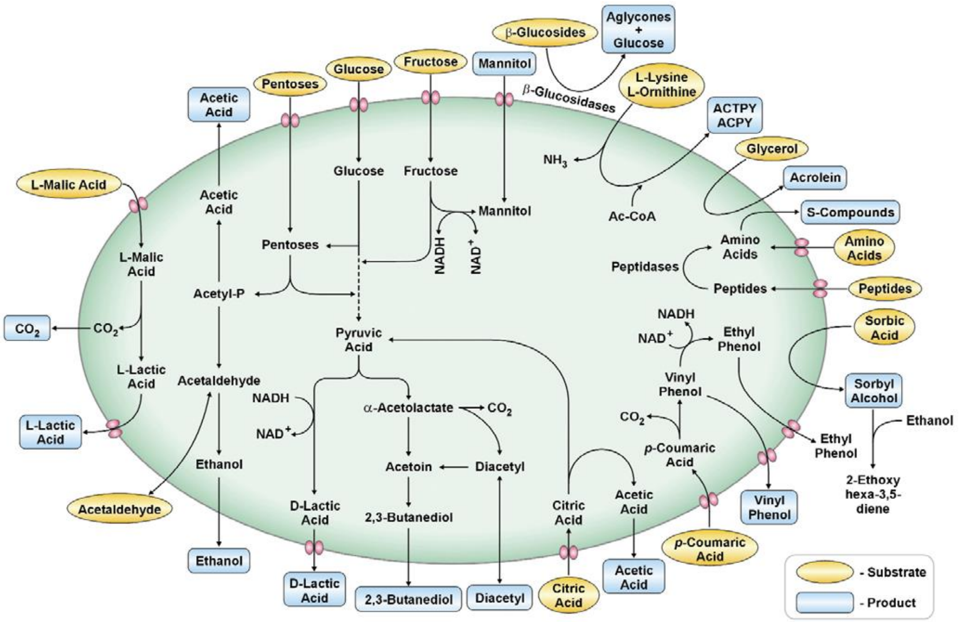

Figure 2. A schematic representation of the biosynthesis of wine volatile compounds by malolactic bacteria (Swiegers et al. 2005).

Qualitatively, the most important volatiles arising during fermentation are esters that impart fruity characters to wines in general (Styger, Prior & Bauer 2011). Fatty acid ethyl esters and acetate esters are two main ester classes produced during fermentation. Acetate esters often contribute to a fruity and floral aroma and shorter chain acetates introduced strong fruity odour, which is more significant in young wines. As a rule, the aroma of esters gradually progresses from fruity and floral to soap and lard as the length of the hydrocarbon chain increases (Swiegers et al. 2005).

Alcohols are also produced during alcoholic fermentation. Ethanol formed via the catabolism of hexoses is by far the main alcohol generated during fermentation. It has been determined that ethanol could suppress the fruity aromas of wine (Escudero et al. 2007; Robinson et al. 2009); high ethanol concentrations can also result in the bitterness in wine, while imparting a sweet aroma with a ‘hot’ feeling (Noble 1994). Other than ethanol, a range of higher (fusel) alcohols are produced during fermentation, including 1-propanol, 1-butanol, 3-methyl-1-butanol and so on; these can add complexity to wine but generally have undesirable aromas at high concentrations (above 300 mg/L) (Rapp & Mandery 1986).

Yeasts also produce volatile fatty acids during fermentation, which normally have unpleasant characters in wine, such as sweaty, cheesy and rancid characters. They are generally present at concentrations lower than their odour detection thresholds. Acetic acid accounts for up to 90% of volatile fatty acids produced during fermentation, and contributes a vinegar or sour aroma to wine (Swiegers et al. 2005). Excessive levels of acetic acid may impart an undesirable character to wine, such as rancid and cheesy smells(Bakker & Clarke 2011). Also, ethyl esters can be formed by volatile fatty acids, so they are aroma precursors of esters (Swiegers et al. 2005).

A range of carbonyl compounds are produced during fermentation. The most common of these in wine is acetaldehyde, which has a nutty character and is important to some wine styles. However, high levels could contribute grassy or apple-like off-odours to wine (Liu & Pilone 2000). Another important carbonyl compound, diacetyl, is produced during MLF by lactic acid bacteria. It has a butter-like aroma and its impact on wine aroma depends on various factors, such as grape variety, age, and origin of the wine (Bartowsky & Henschke 2004; Martineau, Acree & Henick-Kling 1995).

Volatile sulfur compounds are produced by both yeast and bacteria. Their odour detection thresholds are usually in the low µg/L range and they have a negative impact on wine aroma (Pripis-Nicolau et al. 2004). Compounds such as hydrogen sulfide and dimethyl sulfide were produced during fermentation. The former has an unpleasant 'rotten egg' odour (Siebert et al. 2010), while the latter contributes an asparagus-like aroma to wine (at concentration ≥27 µg/L in red wine) (Segurel et al. 2004) and can enhance the fruity aroma at low concentrations (Siebert et al. 2010). Grape-derived varietal thiols, which are potent compounds with tropical characters, can be differentiated at this point as they could be released by wine yeast from nonvolatile cysteine bound conjugates (Swiegers et al. 2005) and depending on various yeast strains, the ability of releasing thiols can be hugely different (Swiegers et al. 2005).

A range of other compounds can be produced during MLF or as a results of spoilage by both wine yeasts and bacteria. Depending on the strain and fermentation conditions, lactic acid bacteria can produce volatiles which had impact on wine aroma, beyond diacetyl mentioned above (Ebeler 2001; Liu 2002; Lerm, Engelbrecht & du Toit 2010). There are several other compounds including acetoin, acetic acid, and γ-butyrolactone, which have been associated with the change of fruity aromas that occur after MLF (Lytra et al. 2012). Compared with MLF, microbial spoilage could contribute some negative aromas to wine, due to volatile phenols for example, which have leathery and medicinal aromas (Chatonnet, Dubourdieu & Boidron 1995).

1.1.4 Ageing-related volatiles

The concentrations of wine volatiles, such as esters, higher alcohols, oak derived compounds and volatile sulfur compounds, can change during ageing and are effected by different factors such as whether storage involves oak (Cerdán & Ancín-Azpilicueta 2006), oxygen contact (Ferreira et al. 2014), temperature (Hopfer et al. 2013) and the length of storage time (Recamales et al. 2011). Most volatiles mentioned above can be modified during maturation and ageing periods through reactions such as the hydrolysis of esters, dehydration of carbohydrates, and acid-catalysed rearrangement of monoterpenes, and new aroma compounds are also produced (Pérez-Coello & Díaz-Maroto 2009). Also, oak barrels are used frequently to mature wine (especially red) and different volatiles, such as oak lactones, phenolic aldehydes, isoprenoids can be extracted by wine (Figure 3) and introduce different impacts on wine aroma characters (Pérez-Coello & Díaz-Maroto 2009), together with those reactions, they contribute to an aged bouquet in general and make wines transition away from their primary fruit characters over time (Pérez-Coello & Díaz-Maroto 2009) as shown in Figure 4.

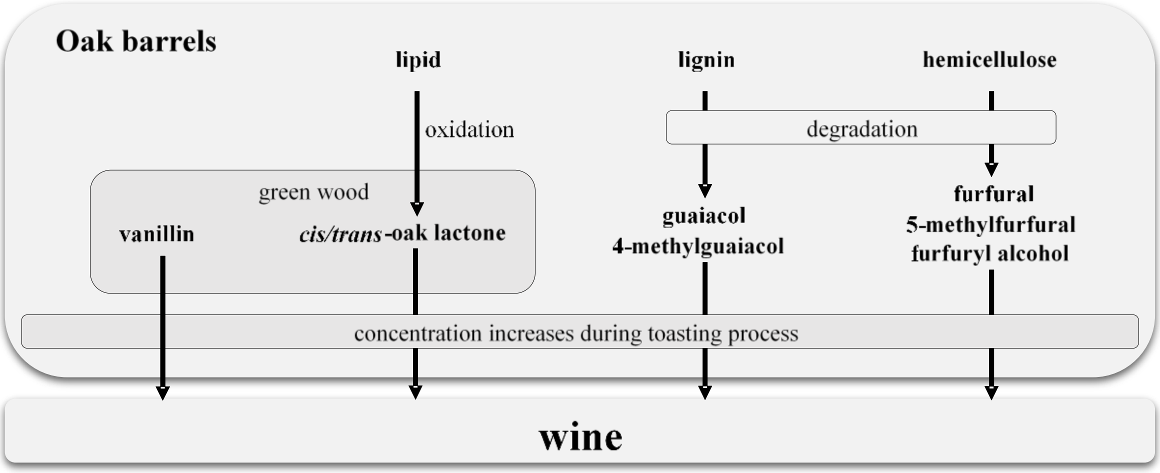

Figure 3. Origins of volatiles extracted during wine maturing in oak barrels (Cutzach et al. 1999; Garde-Cerdán & Ancín-Azpilicueta 2006; Mosedale & Puech 1998; Pérez-Prieto et al. 2002).

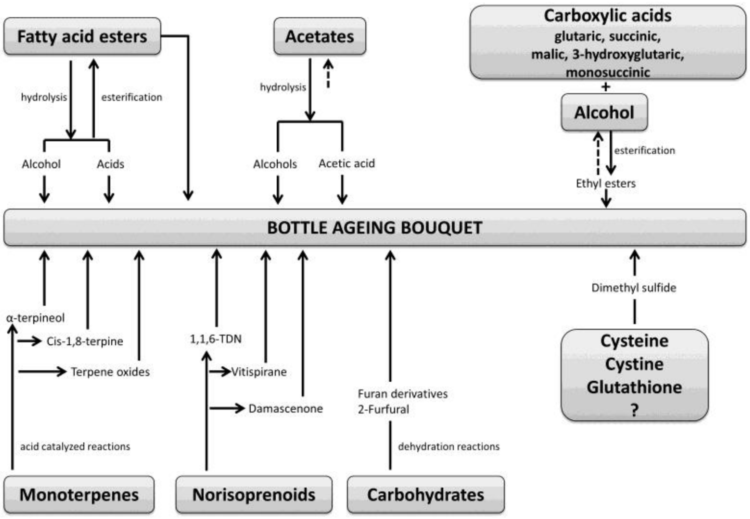

Figure 4. Volatiles produced during bottle ageing (Adapted from Aldave et al. 1993).

For grape-derived volatile compounds during ageing, the level of C_{13}-norisoprenoids such as β-damascenone, (*E*)-1-(2,3,6-trimethylphenyl)buta-1,3-diene (TPB), and 1,1,6-trimethyl-1,2-dihyrdonapthalene (TDN) can be changed differently over time. The level of β-damascenone can increase in oak barrels but decrease during tank storage or bottle ageing (Sefton et al. 2011). The concentration of TDN and TPB usually increase during ageing and are closely related to grape variety and closure type of the wine (Black et al. 2015). TDN can contribute noticeable kerosene and petrol-like odours in aged wine, especially Riesling (Sacks et al. 2012) where it contributes to the character of the wine. However, excessive TDN is considered as a sensory defect (Winterhalter 1991). The same situation is evident for TPB, which imparted pungent and chemical odours to some white wines (Cox et al. 2005). Varietal thiols are also affected during ageing, with acetate ester 3MHA undergoing hydrolysis to produce 3MH, especially at higher temperatures (Makhotkina, Pineau & Kilmartin 2012). In contrast, 4MMP and 3MH were relatively stable in maturation process (Culleré et al. 2004; Tominaga et al. 2000). Hydrolysis of the more potent 3SHA to 3SH, with its higher aroma detection threshold, can have an important impact on the changes in wine aroma through ageing.

Yeast-derived volatiles also show complex changes during the maturation and ageing period. The concentration of acetate esters generally decrease during ageing (Blake et al. 2009; D'Auria, Emanuele & Racioppi 2009), which leads to a loss of fruity characters. Branched-chain fatty acid ethyl esters are stable and their levels could increase during ageing time, while the concentration of straight-chain fatty acid ethyl esters decreases (Díaz-Maroto, Schneider & Baumes 2005). Higher alcohols were also stable during this period (Blake et al. 2009).

Oak barrels have been widely used for wine ageing and storage, and contact with the oak wood introduces some volatiles to wine. At the same time nonvolatile components are released, some aroma compounds are absorbed from wine and different chemical reactions are facilitated (some due to the slow ingress of oxygen) (Garde-Cerdán & Ancín-Azpilicueta 2006; Tao, García & Sun 2014). Oak woods impart *cis*- and *trans*-oak lactones, which contribute oaky and coconut-like aromas to wine (Jarauta, Cacho & Ferreira 2005; Spillman, Sefton & Gawel 2004) and vanillin, which imparted vanilla odour to wine (Jarauta, Cacho & Ferreira 2005). Some aldehydes from oak, like 2-furfural and 4-methylfurfural, contribute sweet and woody aroma to wine (Campo, Cacho & Ferreira 2008). Toasting of oak barrels produces compounds like guaiacol and 4-methylguaiacol, which are then extracted into wine and contribute smoky or tobacco-like characters to wine (Jarauta, Cacho & Ferreira 2005). Benzylmercaptan could also contribute smoky aroma to wine and 2-furanmethanethiol can impart roasted coffee aroma (Dubourdieu & Tominaga 2009)

During the maturation, some off-flavour volatiles can also be produced. *Brettanomyces* spoilage yeasts produce volatile phenols that lead to bretty and metallic aromas in wine (Jarauta, Cacho & Ferreira 2005). Suboptimal packaging materials or conditions may result in off-flavours or taints, with one of the most common being a sensory defect known as cork taint, caused by 2,4,6-trichloroanisole (TCA) (and other haloanisoles), geosmin, 1-octen-3-one and 2-methoxy-3,5-dimethylpyrazine (MDMP) (Sefton & Simpson 2005).

1.2 Wine aroma analysis

1.2.1 The importance and outcome

The aroma of wine, attributable to the presence of a range of volatile compounds, can vary as a result of different grape varieties, diverse wine styles, the age of the wine and even the volume of wine in a glass (Ebeler & Thorngate 2009). Aroma is a very important sensory property that combines with taste, flavour and chemosensory sensations to contribute to the perception of quality of wine as a whole during consumption (Lukić et al. 2008). Evaluating volatile compounds could therefore provide critical information about the nature of wine aroma and can be reflective of quality of wine. Until now, there have been more than 1000 volatile compounds detected in wine (Polášková, Herszage & Ebeler 2008), although wine aroma quality may be determined by hundreds of volatile compounds in general (Alves, Nascimento & Nogueira 2005). However, it was also suggested that only a small number of volatiles had remarkable impact on the final sensory quality of wines (Ebeler & Thorngate 2009; Villamor & Ross 2013).

Volatile compounds in wine can have individual impacts on wine aroma and positive or negative influences on others components, with effects such as masking, synergism or counteraction (Lytra et al. 2012; Lytra et al. 2013) in the perception of other volatiles (Rocha et al. 2010; Vilanova et al. 2010), and as a whole contribute to wine aroma. Some aroma compounds have been defined as characteristic of certain wines from different regions or made by different varieties. For different regions, thiols are defined as one of the most important characteristics in Sauvignon blanc wine from New Zealand (Benkwitz et al.

2012a) and rotundone is found as a key aroma compound in Shiraz wines produced in Australia (Siebert et al. 2008; Wood et al. 2008). Also, speaking of different varieties, polyfunctional thiols are especially important for Sauvignon blanc (Dubourdieu & Tominaga 2009) and methoxypyrazines are significant in Cabernet Sauvignon (Sidhu et al. 2015). Also, it was shown that the content of ethyl esters of medium chain fatty acids, along with ethyl tetradecanoate, methyl octanoate, 3-methylbutanoic acid, 1,4-butanediol, 6-methyl-1-octanol 1-hexanol, and dihydro-2-methyl-3(2H)thiophenone, could be different in Merlot wines comparing to wines made by other grape varieties (Welke et al. 2012).

In summary, the importance to identify and quantify volatile compounds is without doubt when trying to understand wine quality (and consumer preference, as the ultimate test). However, attention should be paid to evaluating how many volatiles are important and how strongly each could impact wine aroma. In the end, the aroma of different wines is often related to only a small proportion of wine volatiles that have a large sensory effect.

1.2.2 Instrumentation

The research on wine aroma is mainly the application of chromatography considering the nature of aroma compounds in this matrix. However, till now, developing a universal method that is suitable for evaluating all volatile compounds with varying physicochemical properties and hugely different concentration in a matrix such as wine is still a big challenge (Weldegergis et al. 2011b).

Gas chromatography (GC) is a useful tool for wine aroma analysis. It separates volatile components based on different boiling points and polarities using different column phases and an increasing temperature program. GC is coupled to different detectors, such as flame ionisation detector (FID) or more often a mass spectrometer (MS), so quantification (and identification in the case of MS) can be accomplished. Conventional one dimensional

(1D) GC, which was first introduced in the1950s (James & Martin 1952), has been applied in wine research for years since then (Ebeler & Thorngate 2009). Relying on its sensitivity and robustness, much fundamental knowledge has been gained and a wide range of volatiles discovered (Ebeler 2001; Ebeler & Thorngate 2009; Polášková, Herszage & Ebeler 2008). In terms of quantification, with the right sampling technique GC methods can quantify compounds with concentrations as low as several ng/L, such as polyfunctional thiols (Dubourdieu & Tominaga 2009) and MPs (Allen, Lacey & Boyd 1994). Therefore, it has become one of the standard procedures in wine aroma analysis.

Better resolution with GC was achieved by adding extra separation capability (2D separation) with the advent of multidimensional GC (MDGC) or with more powerful detectors, such as time-of-flight MS (TOFMS) and quadrupole-time-of-flight (QTOF) MS. In the case of analytes having the same vapour pressure or polarity, co-elution may occur on a certain column and this is where MDGC techniques have a place. MDGC, also known as heart-cutting GC, takes the flow of analytes separated on the first column and transfers it into the second column, which is usually shorter and with a different phase to the first one. Analytes then have the chance to be separated further in the second phase before going to the detector. It has been applied in wine research since around a decade ago (Table 3) and has been used to identify new compounds or lower the limit of detection (LOD) of various analytes. Moreover, the flow from the first column could be concentrated and refocused using liquid nitrogen or liquid carbon dioxide through a cryogenic trap (Figure 5), which would provide a better resolution and capability of separation in the second column. However, it has serious limitations because each second-dimension analysis would easily add 30 to 45 minutes to the whole run time, making it time consuming for the general monitoring and/or the search for unknowns. To solve these problems, a truly comprehensive approach was required, which was able to provide second-dimension analysis based on the entire first-dimension chromatography. With the modulator problem (insufficient speed and discontinuous operation to produce peaks on the second column to match with the first dimension) solved by Phillips and his colleagues (Liu & Phillips 1991), a new powerful instrument – comprehensive two dimensional gas chromatography (2D-GC or GC×GC) started to be applied in research.

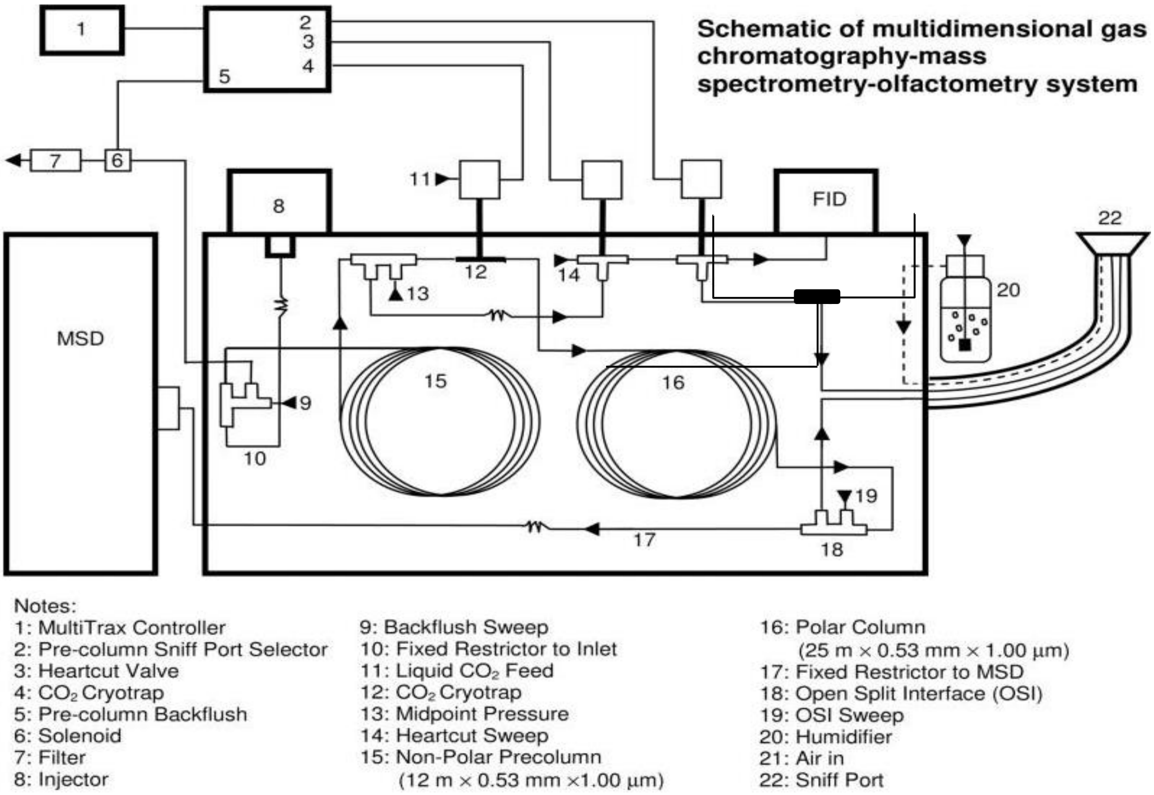

Figure 5. Schematic of multidimensional gas chromatography-mass spectrometry system (MDGC–MS) (Lo et al. 2008).

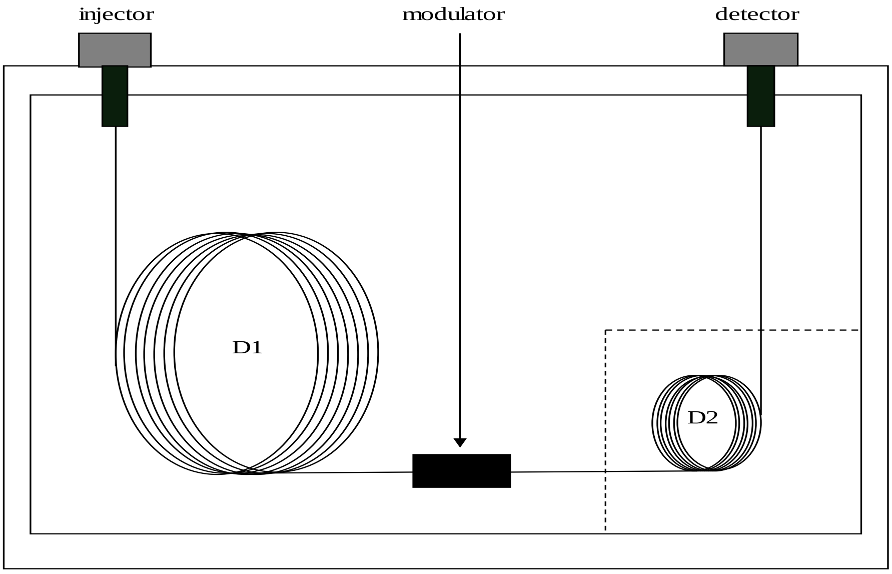

Figure 6. Schematic of the basic setup for GC×GC (Ramos & Brinkman 2009). Dotted line: optional secondary oven, placed inside the main over, for independent temperature control of the second column.

GC×GC typically consists of a long non-polar column for the 1st dimension (D1) and a relatively short polar column for the 2nd (D2) (Figure 6). The dimensions are connected through a special modulator and only one detector is required, which is enough for general scanning. With a properly selected orthogonal separation principle, GC×GC could separate hundreds of compounds in a single run because of the additional selectivity of the second column and corresponding higher peak capacity.

GC×GC has been successfully applied in wine area. It has been used for determination of MPs, *trans*-resveratrol, monoterpenoids, aldehydes, ethyl carbamate (EC), hydroxypyrazines, furans, lactones, volatile phenols, acetals, pesticides, and other volatiles in grapes and corresponding wines (Table 4).

Table 3. The application of multidimensional GC to grape and wine research.

reference[a]	sample matrix	target	extract methods[b]	column set[c]	detectors[d]
1	cork soaks, white wines	corky off-flavour compounds	HS-SPME	D1: DB-XLB (30*0.25*0.25) D2: TG-1301MS (15*0.25*0.25)	D1: FID D2: ECD
2	Shiraz wine	-[e]	SPME	D1: DB-FFAP (30*0.25*0.25) D2: DB-5 (30*0.25*0.25)	D1:MS D2:Olfactory
3	grape juice and wine	fresh mushroom odour 1-nonen-3-one and 1-octen-3-one	LLE	D1: BP20 (30*0.25*0.22) D2: VF-5ms: (50*0.25*0.25)	D1: FID D2: MS
4	12 different varieties of white wine	aliphatic aldehydes	SPE	D1: DB-WAX (30*0.32*0.50) D2: VF-5MS (30*0.32*1)	D1: FID D2: MS
5	Riesling juice, Sauvignon Blanc wine, Riesling wine and a red wine	3-alkyl-2-methoxypyrazines	SPE	D1: ZB-WAX (20*0.25*0.5) D2: ZB-35 (15*0.25*0.5)	D1: FID D2: MS
6	Cabernet Sauvignon red wine, different white wines 17 Cabernet Sauvignon must sample	3-alkyl-2-methoxypyrazines	HS–SPE SPE	D1: DB-WAX (30*0.32*0.50) D2: VF-5MS (30*0.32*1)	D1: FID D2: MS
7	prematurely aged red wines	volatile compounds responsible for prune aroma	LLE	D1: SPB1 (30*0.25*0.25) D2: BP20 (50*0.25*0.25)	D1: - D2: O–MS
8	five single varietal red wines	2-methyl-3-(methyldithio)furan	SPE	D1: DB-WAX 9 (30*0.32*0.50) D2: VF-5MS (30*0.32*1)	D1: FID D2: MS
9	white wine	2-aminoacetophenone	SPE	D1: ZB-WAX (20*0.25*0.50) D2: ZB-5 (15*0.25*0.5)	D1: FID D2: MS
10	fortified Porto wines, botrytised wine, aged red wines, young red and white wines, sparkling wine, sherry brandies and whiskeys	ethyl 2-, 3- and 4-methylpentanoate; ethyl cyclohexanoate	SPE	D1: DB-WAX (30*0.32*0.50) D2: VF-5MS (30*0.32*1)	D1: FID D2: MS
11	sherry white wine	ethyl cyclohexanoate, ethyl, 2-hydroxy-3-methyl butanoate and ethyl 2-hydroxy-4-methylpentanoate	SPE	D1: DB-WAX (30*0.32*0.50) D2: VF-5MS (30*0.32*1)	D1: FID D2: MS
12	ripening grape berries	linalool oxides, hotrienol and rose oxide	SPE SBSE	D1: SE-52 (30*0.25*0.23) D2: DiMe-β in SE-52 (30*0.25*0.25) D1: SE-52 (30*0.25*0.23) D2: DiMe-β in SE-52 (30*0.25*0.23)	D1: FID D2: MS D1: FID D2: ITD 800

[a] The corresponding references are: 1, Slabizki and Schmarr (2013); 2, Chin, Eyres and Marriott (2012); 3, Pons, M et al. (2011); 4, Culleré, Ferreira and Cacho (2011); 5, Schmarr et al. (2010b); 6, Culleré et al. (2009); 7, Pons, A et al. (2008); 8, Culleré et al. (2008); 9, Schmarr et al. (2007); 10, Campo, Cacho and Ferreira (2007); 11, Campo, Cacho and Ferreira (2006); 12, Luan et al. (2006). [b] HS, headspace; SPME, solid-phase microextraction; LLE, liquid-liquid extraction; SPE, solid phase extraction; SBSE, stir bar sorptive extraction. [c] Dimension was in length * internal diameter * film thickness. [d] ECD, electron capture detector; O–MS, olfactory-mass spectrum; ITD, ion trap detector. [e] Not available.

Table 4. The application of comprehensive GC×GC on grape and wine research.

reference[a]	sample matrix	target	extract methods[b]	column set[c]	detection[d]
1	Merlot, Shiraz, Cabernet Sauvignon	*trans*-resveratrol	SPME	BPX5 (30×0.25×0.25) BPX50 (1.2×0.1×0.3)	FID
2	model wine & Sauvignon Blanc wine	IBMP	HS-SPME	BPX5 (30×0.25×0.25) BP20 (1×0.1×0.1)	NPD, TOFMS
3	grape	monoterpenoids	HS-SPME	Equity-5 (60×0.25×1) Supelcowax-10 (2.5×0.1×0.1)	TOFMS
4	grape	pesticides	DSPE	RTX-5MS (10×0.18×0.2) TR-50MS (1×0.1×0.1)	TOFMS
5	Brunello di Motalciano and Pinot noir wine, grape seed oil samples	aldehydes	HS-SPME	SolGel-Wax (30×0.25×0.25) OV-1701-vi (0.15×0.15×0.15) BPX-5 (2×0.15×0.25)	qMS
6	Chardonnay, Riesling, Sauvignon Blanc, Merlot, Cabernet Sauvignon and Syrah wines	-[e]	SPME	Set 1: CP-Sil8 (25×0.25×0.25) BGB-1701 (0.5×0.1×0.1) Set 2: CP-Sil8 (25×0.25×0.25) TR-50MS (0.6×0.1×0.1) Set 3: HP-1701 (10×0.25×0.25) HP-1 (1×0.1×0.12) Set 4: HP-50+ (24×0.2×0.31) HP-1 (0.6×0.1×0.12)	FID
7	Fernão Pires (white) and Baga (red) grapes	-	HS-SPME	Equity-5 (60×0.25×1) Supelcowax-10 (2.5×0.1×0.1)	TOFMS
8	Cabernet Franc grape	IBMP	HS-SPME	RTX5 (30×0.25×0.5) VF-WAXms (2.5×0.1×0.1)	TOFMS
9	grape	selected OPPs, triazines and pyrethroids	SPE, MSPD	Three first column: ZB-5, HT-8, DB-17 (30×0.25×0.25) Two Second column: HT-8, BPX-50 (0.8×0.1×0.1)	µECD
10	grape	pesticides	-	VF-5 (30×0.25×0.25) VB-50 (0.4×0.1×0.1)	FID µECD
11	Cabernet Franc grapes, corresponding juice and wine	IBMP, IPMP	HS-SPME	RTX5 (30×0.25×0.5) VF-WAXms (2.5×0.1×0.1)	TOFMS
12	Thompson seedless grapes, Cabernet Sauvignon wine	-	DSPE	DB-5MS (30×0.25×0.25) V-17 (1×0.1×0.1)	TOFMS
13	Madeira wines, model wine	ethyl carbamate (EC)	HS-SPME	HP-5 (30×0.32×0.25) DB-FFAP (0.79×0.25×0.25)	TOFMS

14	Cabernet Franc, Riesling and Pinot Noir grapes	IBMP, IBHP	HS-SPME, SPE	CP Wax 52CB (30×0.25×0.25) VF-17ms (2×0.1×0.2)	TOFMS
15	Pinot Noir, Dornfelder, Cabernet Sauvignon red wine	-	HS-SPME	ZB-Wax (30×0.25×0.5) BPX-5 (2×0.15×0.25)	qMS
16	Sauvignon Blanc grapes and corresponding wine	IBMPs	HS-SPME	SolGel-Wax (30×0.25×0.25), OV-1701-vi (0.15×0.15×0.15)/BPX-5 (2×0.15×0.25)	MS
17	Merlot, Sauvignon Blanc, Semillon wine	-	SPE	DB-FFAP (15×0.25×0.25) DB-5 (1.1×0.1×0.1)	FPD/FID TOFMS
18	Cabernet Sauvignon wine	-	HS-SPME	VF-5MS (30×0.25×0.25) VF-17MS (1.44×0.1×0.2)	TOFMS
19	Madeira wines	furans, lactones, volatile phenols, and acetals	HS-SPME	HP-5 (30×0.32×0.25) DB-FFAP (0.79×0.25×0.25)	TOFMS
20	Cabernet Sauvignon wine	-	HS-SPME	VF-5MS (30×0.25×0.25) VF-17MS (1.65×0.1×0.2)	TOFMS
21	Pinotage and Cabernet Sauvignon wine	-	HS-SPME, SPE	Rxi-5Sil MS (30×0.25×0.25) Rtx-PCB (0.8×0.18×0.18)	TOFMS
22	Pinotage wine	-	HS-SPME	VF-1 (30×0.25×1) SolGel-Wax (1.5×0.25×0.25)	TOFMS
23	Merlot, Chardonnay and Pinot Noir, Sauvignon Blanc, Cabernet Sauvignon wine	-	HS-SPME	Set 1: DB5 (30×0.25×0.25) DB-Wax (1×0.1×0.1) Set 2: DB-WAX (30×0.25×0.25) DB1ms (1.7×0.1×0.1) Set 3: DB-WAX (30×0.25×0.25) DB17ms (1.7×0.18×0.18)	TOFMS

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[a] The corresponding references are: 1, Shao, Marriott and Hügel (2003); 2, Ryan et al. (2005); 3, Rocha et al. (2007); 4, Banerjee et al. (2008). 5, Schmarr et al. (2008); 6, Kallio et al. (2008); 7, LECO Corporation and Joseph (2008); 8, Ryona et al. (2008); 9, Ramos, Gonzalez and Ramos (2009); 10, Pizzutti et al. (2009); 11, Ryona, Pan and Sacks (2009); 12, Dasgupta et al. (2010); 13, Perestrelo et al. (2010); 14, Ryona, Leclerc and Sacks (2010); 15, Schmarr et al. (2010a); 16, Schmarr et al. (2010b); 17, Chin, Eyres and Marriott (2011); 18, Robinson et al. (2011a); 19, Perestrelo et al. (2011); 20, Robinson et al. (2011b); 21, Weldegergis et al. (2011a); 22, Weldegergis et al. (2011b); 23, Welke et al. (2012). [b] DSPE, dispersive solid-phase extraction; MSPD, matrix solid phase dispersion; the rest please refer to footnote b in Table 3. [c] Please refer to footnote C in Table 3. [d] NPD, nitrogen–phosphorus detector; qMS, quadrupole mass analyser; µECD, microcell electron capture detector; FPD, flame photometric detector; the rest please refer to footnote d in Table 3. [e] Not available.

All papers mentioned in Table 2 were pioneering in some aspects. It was the first time to report HS-SPME with GC×GC–TOFMS, together with the specific detection system GC×GC–NPD, for the quantification of IBMP in wines in Ryan's research (Ryan et al. 2005). Also, Welke et al. (2012) first used GC×GC–TOFMS, this specific experimental setting, to analyse volatiles in Merlot wines and suggested this methodology could also be a significant tool for differentiating Merlot wines from other wines. A new method of extracting volatiles based on MSPD (matrix-solid-phase dispersion) plus GC×GC–μECD was also developed and can be used to achieve a better sensitivity (Ramos, Gonzalez & Ramos 2009). What's more, it was the first time that ethyl carbamate in alcoholic beverages was determined thanks to GC×GC–TOFMS (Perestrelo et al. 2010). Also with the help of this powerful instrument, numerous volatile compounds in Pinotage wines were reported for the first time (Weldegergis et al. 2011a). In a word, GC×GC, especially coupled with TOFMS detection, provides a unique capability in wine chemistry research (Bojko et al. 2012).

In 2012, a new and highly functional separation method incorporating 1D-GC, heart-cut MDGC, and GC × GC coupled to simultaneous O/FID and O/MS detection in one integrated instrument was developed (Chin, Eyres & Marriott 2012). Quantification of potent odourants in Shiraz wine and separation overlapping compounds in a mixture of suspected allergens were achieved with this application. It was suggested that this novel setup showed significantly improved separating ability and very strong detection capability, which could potentially be applied in different fields, not only in flavour chemistry, but also in determination of different environmental and biological samples.

1.2.3 Sample preparation

Sample preparation is a very important part of undertaking wine aroma analysis. It became even more important and productive than the instrumentation development, as the sensitivity of instruments was in general high enough, and whether a compound could be detected and quantified mostly depended on how the sample was prepared.

The choice of extraction procedure is a critical issue and has a major influence on the final results. For volatile aroma compounds, common procedures involve direct and indirect contact between wines (liquid) and extract media. The direct contact consists of liquid-liquid extraction (LLE) of wine with organic solvent such as dichloromethane (Komes, Ulrich & Lovric 2006; Silva Ferreira, Barbe & Bertrand 2003), or solid phase extraction (SPE) (Escudero et al. 2007) by passing wine through cartridges filled with resin and eluting the volatile components with organic solvent. In each case the extraction is followed by concentrating the extract and injecting a liquid sample. The indirect ways comprise static and dynamic headspace (HS) and headspace solid-phase microextraction (SPME) approaches (Bojko et al. 2012; Zhang et al. 2011), followed by introducing analytes directly into the GC injector port. Specifically, static HS utilises a large volume syringe, dynamic HS uses gas to sweep volatiles from a sample and trap them with sorbent, and SPME involves adsorbing volatiles from a sample with a sorbent-coated fibre.

Except LLE and SPE, which have been widely applied for a long time and are not discussed here, headspace and SPME sampling methods were developed rapidly in the past 20 years (Bojko et al. 2012). There are few studies performed with a static HS technique, as it not only requires a large volume of headspace to be injected into the GC, but also the injection contains ethanol and water, which could cause problems, such as degradation of the stationary phase, increasing the bleeding, in the column. Static HS methods are usually conducted on wines instead of extracts, which necessitates a long time to extract and thus the consistency would become a potential problem. Comparing with static HS sampling, dynamic HS offers a better option in general. Combining with new types of sorbents, such as Tenax TA, LiChrolut EN resin, this technique exhibited great ability to extract aroma volatiles and has been widely applied in evaluating different types of wine (Campo et al. 2005; Gomez-Miguez et al. 2007; Ortega-Heras, González-SanJosé & Beltrán 2002; Zapata et al. 2012). As another sampling method, SPME has been popular in recent years as it is simple to use and there are different fibre coatings for targeting different analytes (Bojko et al. 2012; Jeleń, Majcher & Dziadas 2012). With these two benefits, SPME has been applied in many recent studies (Nguyen, Nicolau & Kilmartin 2012; Risticevic, DeEll & Pawliszyn 2012; Villière et al. 2012; Weldegergis et al. 2011b; Welke et al. 2012; Xi et al. 2011). However, it still does not provide a universal technique that is adequate to all tasks. As it was not an exhaustive extraction method and there can be manufacturing differences in every single fibre, the accuracy and repeatability have proven problematic (Boyacı et al. 2015). Also, quantitative work using SPME was based on the equilibrium it reached, being the time when the sensitivity was highest and the calibration was the most linear.

It is vital for researchers to be clear about what aim they have for their study and what target compounds they want to look when choosing the most appropriate extraction methods. There were two directions where wine chemists' devoted attention: the first was trying to identify and quantify every single volatile compound in wine, which apparently involved a lot of analytical chemistry work and instrumentation development; the second one was trying to build up an extractant that could represent the preliminary aroma of the wine most, with the consideration of sensory impact of different volatiles and interactions among them. In another word, the idea was to be as close as to what and how much human's pituitary received from the wine glass. In most cases, these two aims could be the same as the more volatiles extracted and the more accurate concentration of volatiles obtained, the closer is the extract to the real sample. However, no matter what kind of technique was chosen, it could not achieve complete extraction of target analytes or an entire range of compounds that wine might contain. Also, it would be time consuming and uneconomical in order to extract everything from a wine matrix. Aroma compounds were all different in regard of chemistry (polarity, boiling point, volatility and so on) and sensory (odour characters, threshold and so on) properties, so there was no perfect single extraction method. For instance, the recovery ability of HS extraction could be different when the target compounds have higher boiling points. Some higher alcohols, such as 2-phenylethyl alcohol, can have a very high concentration, but because of their higher aroma threshold values, even though most of them would be extracted out with LLE, their impact on sensory were still little (Guth 1997). Also, some volatiles, especially the most volatile and non-polar compounds, were transferred very efficiently for final perception, while others, which were most polar and least volatile, were often neglected during the olfaction process (Escudero et al. 2014) (Figure 7).

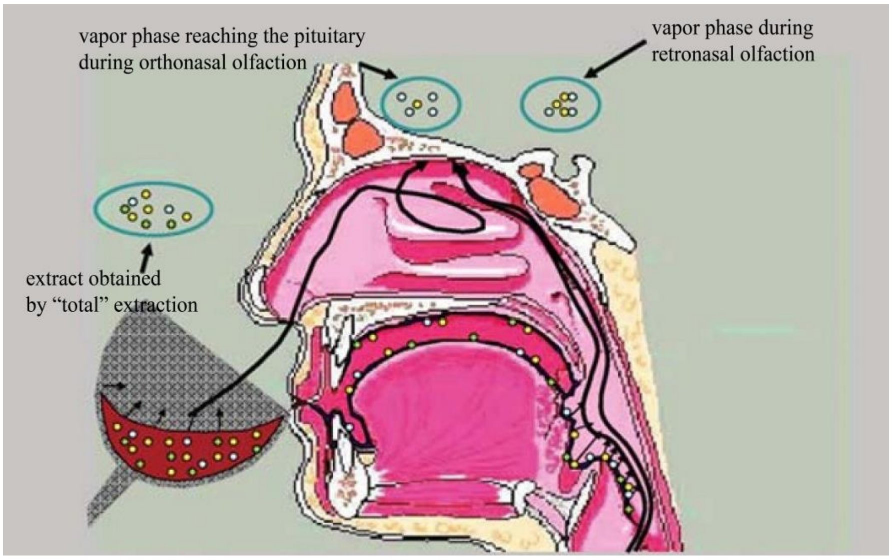

Figure 7. The schematic drawing showed that the vapour phase could reach to pituitary either by ortho or retronasal olfaction, but the polar compounds could not be transported to the pituitary with any of these two pathways (Ferreira & Cacho 2009).

1.2.4 Procedures for analysis of wine aroma

With the knowledge of volatiles in grape and wine, instrumentation and sample preparation, wine aroma analysis could be effectively carried out. In general, there are three aspects of work involving in wine aroma analysis – identification, quantification and characterisation. These three steps could be applied in a row on a single volatile compound or a complete wine product. The first two steps are usually relate to analytical chemistry using a lot of instrument-based analysis. With the incorporation of sensory studies, the final characterisation of either a particular compound or a wine product can be achieved.

1.2.4.1 Identification of components

The first step was to identify the volatiles with the help of GC coupled to detectors. Sample or sample extracts are injected in GC and separated through a capillary column before going to detectors which record a signal, so the chemical property of compounds can be obtained, such as mass spectrum from MS.

The linear retention index, LRI, is calculated using the retention times (RT) of the alkanes and aroma compounds under the same GC conditions (column, temperature program, etc.). Alkanes are the simplest organic molecules that only consist of carbon and hydrogen with a general formula C_nH_{n+2}. A mixture of alkanes (e.g. C8-C20) is commonly used in GC analysis for determining LRI values.

$$LRI = 100 \times \left[\frac{t_{Ri}-t_{Rn}}{t_{R(n+1)}-t_{Rn}} + n\right] \text{ (Nic et al. 2006)}$$

LRI: retention time of the odour zone i; $t_{R(n)}$: the retention time of the *n*-alkane eluting before the odour zone; $t_{R(n+1)}$: the retention time of the *n*-alkane eluting after; *n*: the number of carbon atoms in such *n*-alkane. The odour zone R was eluted between the *n*-alkane and (*n+1)*-alkane.

LRI may not always be consistent regarding different labs, instrument settings, or processing (Molyneux & Schieberle 2007), so it was suggested that LRI provided some information, but alone it was not very convincing to identify compounds. LRI should also be obtained on an opposite polarity column (Molyneux & Schieberle 2007) and even two columns are used, it was still hard to detect and identify some volatiles, such as 4-hydroxy-2,5-dimethyl-3(2H)-furanone (furaneol), aldehydes, mercaptans and some polyfunctional thiols. Thus it was necessary to contemplate other ways to capture them as identification could not be made solely depending on a comparison to commercial databases and LRI information. This is where GC–O analysis becomes important, as it should be used to compare with reference data and odour descriptions to help verify identity (Molyneux & Schieberle 2007).

The compounds identities are fully confirmed only when the information from the three aspects, mass spectrum, olfactory description, and LRI on opposite polarity columns, are matched with literature and authentic compounds, where the latter point is especially important. Matching with authentic compounds may occur by obtaining commercially available reference standards or through chemical synthesis. In addition, more detailed chemical structure…and high-resolution MS (HRMS) (Salih & Çelikbıçak 2012), especially for new compounds. Obtaining enough analyte for nuclear magnetic resonance spectroscopy (NMR) in particular could prove to be very tedious, however, and proper characterisation of new compounds is a complex task.

1.2.4.2 Quantification

After identities of compounds were confirmed, the next step was to find out how much they were in wine, which was quantification. The major volatiles were usually evaluated by GC–FID and the minor volatiles could be quantified directly by GC–MS. The accuracy of quantification data were depended on sample preparation to a large extent (Clarke & Bakker 2011) and it was clear that there was no method could determine 100% of the target compounds (Schieberle & Molyneux 2012) All techniques had some limitations which have been discussed before.

Also, in order to quantify the compounds at ultratrace level, it was necessary to include internal standards. Stable isotope dilution assay (SIDA) was developed so as to have a quantification method which was definitive and the closest to the real concentration of a certain compound (Boyd 1993; Giovannini, Pieraccini & Moneti 1991). The target compounds were isotopically labelled and added as internal standards, which were closely same as the authentic compounds in regard to the chemical properties, the compensation for losses, such as extraction variation, differences in injection volumes and responses to detectors. The labelled compounds were through the whole process of isolation, extraction, concentration, exactly same as what analytes went through. Also, it was suggested that SIDA was beneficial to eliminate the effect of matrix where for example ethanol level and pH could make differences in different wine matrices, not to mention the interactions among volatiles (Siebert et al. 2005). This technique has been used to quantify MPs (Allen, Lacey & Boyd 1994) and C_{13}-norisoprenoids (Petrozziello et al. 2012) in red wines, polyfunctional thiols compounds in Muscat wines (Schneider et al. 2003), smoke-derived phenols in Merlot juice (Kennison et al. 2008) and different volatile precursors in grape juice and wines (Capone et al. 2010; Dungey, Hayasaka & Wilkinson 2011; Fudge et al. 2008; Hayasaka et al. 2010).

With the development of separation science and more sensitive instruments, measuring some compounds at trace levels (ng/L) became substantially easier. For example, volatile sulfur compounds in wine could be measured readily and the limit of detections

(LOD) were as low as ng/L, which were mostly below their corresponding aroma detection thresholds with the help of SIDA using gas chromatography with NCI–MS (Roland et al. 2011). The off-flavour compounds in wine, such as 2,4,6-trichloroanisole (TCA), 2,3,4,6-tetrachloroanisole (TeCA) and 2,4,6-tribromoanisole (TBA) were determined by SIDA with LODs as low as 0.1 ng/L after applying MDGC coupled with halogen-sensitive electron capture detector (ECD) (Slabizki & Schmarr 2013).

1.2.4.3 Evaluating the importance of different odourants to wine aroma

With the quantification data obtained above, the sensory impacts of different volatiles could be evaluated next. Two aspects to this and depend on whether volatiles are studied individually or together in a matrix are discussed below.

Assessing individual volatiles:

a) Odour activity values (OAVs)

Odour activity values are calculated as the concentration of a compound divided by its corresponding aroma detection threshold, as firstly introduced by Grosch (1993). If the OAV of a compound is larger than one, that is, the concentration is larger than its threshold, this compound could be considered as an active odourant. In reality, individual compound’s thresholds have often been measured in model wine (or neutral white or red base wine) by increasing its concentration with an exact factor. A series of triangle tests are then conducted with a trained tasting panel on samples with compound concentration from low to high. The lowest concentration level with the correct answer when no further mistakes at higher levels is considered as the odour threshold of this compound for an individual sniffer. In the end, the average of all geometric means of individual thresholds are calculated and then the odour threshold of this volatile component is the normal number transformed by the log values (ASTM E679-04 2011). Many studies have been undertaken based on OAVs (Benkwitz et al. 2012a; Losada et al. 2011; Pino et al. 2012; Vilanova et al. 2012a; Vilanova et al. 2012b). However, it can be tricky to decide which threshold should be applied to calculate the OAV, as ideally, the appropriate threshold should be determined under the same condition as the real wine sample, where the matrix effect can be considered. The matrix could make a huge difference on some volatiles' OAV, for example β-damascenone, which has an OAV in water of 2 ng/L (Buttery et al. 1990) and approximately 50 ng/L in model wine solution (Lopez et al. 2003). Furthermore, wine is a complex matrix and an individual compound's role is also complex and may not be solely determined by its OAV due to interactions such as synergistic and suppression effects (Ferreira & Cacho 2009). For instance, similar compounds could be considered together to make a contribution to final aroma as one homogeneous group instead of as individuals (Shepherd 2006). MPs, volatile phenols and some aldehydes could suppress the fruit aroma intensity of red wines (Ferreira et al. 2009).

b) GC–O

Gas Chromatography-olfactometry (GC–O) was introduced in 1960s by Fuller, Steltenkamp and Tisserand (1964), which was able to separate hundreds of volatiles through a chromatographic column and then elute them to the "detector"--the human nose using an olfactory detection port (ODP). With this technique, judges could connect the sensory profile of a compound with its chemical property and also rank its perceived intensity on an action panel.

There were different ways to collect data generated by GC–O and AEDA was the most common procedure applied now, with the evaluations based on the threshold concentration. It was a simple method established by Ullrich and Grosch (1987) and the normal process of it is shown in Figure 7 (Etievant et al. 1994). During the procedure, an extract containing volatiles is consecutively diluted at a fixed rate R that is usually set as 2, 3, 5, 10, or even more (Frank et al. 2011; Steinhaus et al. 2008). Then each dilution is analysed with GC–O by panellists, with dilution factors from low to high. When the highest dilution of an odourant that could be detected by the majority of the judges was P (P=0, 1, 2, 3, …, n), the R^P value of this dilution was determined as the flavour dilution (FD) of the compound (Steinhaus et al. 2008). Although the FD factors in many studies were obtained from the maximum FD factor of only one judge or the majority, a more reasonable FD should be the geometric mean value of FD from each judge (Ferreira, Pet'ka & Aznar 2002). Now, with the help of specific software such as GERSTEL ODP-Recorder and other accessories such as odour action panel, the AEDA process has become easier as panellist could press button on the action panel when they sniffed something and the software could record what they said simultaneously and convert it to a word based on a vocabulary developed beforehand.

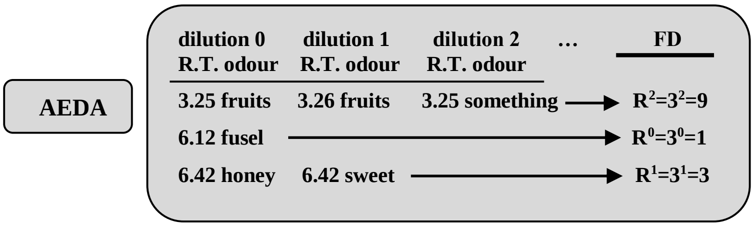

Figure 7. Theoretical procedure of AEDA (Modified from Ferreira & Cacho 2009).

There were some other techniques applied with GC–O analysis as well, such as Charm analysis also based on threshold concentration, the nasal impact frequency (NIF) based on the frequency of citations, and Osme (derived from the Greek word meaning odour) or olfactometry global analysis (OGA) based on odour zones' different intensity. It has been proposed that AEDA, Osme and OGA had similarity and could be correlated well to each other (Le Guen, Prost & Demaimay 2000).

Assessing volatiles in a matrix:

a) Descriptive analysis

This is a traditional sensory analysis method that has been used for many years. It is usually conducted on real samples containing the different volatiles in their normal matrix. Sensory characters of the samples are evaluated by trained panellists chosen to form a tasting group. An unstructured line scale can be used to represent the intensity of one aroma/flavour. The reference standards of aroma attributes are selected based on the consensus concluded in panel training period, wine lexicon or references by others. The process usually follows a procedure such as that described in Lawless and Heymann (2010). The samples provided to judges in random order are evaluated in duplicate or triplicate. Then variance analysis or PCA can be applied to evaluate the data and characterize different wine samples by their aroma profiles.

b) Reconstitution and omission

Recently, more attention has been paid to reconstitution and omission tests when the key volatile compounds have been determined in different samples (by GC–O and quantitative analysis). These two approaches offered new insight into details of individual volatile's impact on the wine aroma. However, it was shown that there was no obvious difference in odour quality between the one model and another with one or two compounds absent (Grosch 2001). The maximum number of volatiles for humans to differentiate at the same time was three or four (Laing 1994), which means if one mixture contained more than four odourants, it would show an overall aroma instead of every single compound's odour. After all, the aroma reconstitution was the only method now to confirm whether one single volatile could have impact on sensory characters in the matrix (Steinhaus et al. 2009). One thing to note is for some particular wines, a large number of low OAV compounds might also contribute to the aroma, but they were often ignored when a reconstitution and omission model was built (Francis & Newton 2005).

The basic procedure of reconstitution and omission test starts with the preparation of aroma reconstitution models which could be evaluated in different non-volatiles matrices. Synthetic (model) wine was the one that has been used most as it has controlled variables and is easy to prepare. However, as it is simply a water-ethanol solution and does not contain all non-volatile substances originally in wine. Therefore, the impact of non-volatiles, such as polyphenols, proteins and polysaccharides, which all have some effect on perception of aroma compounds (Kang et al. 2010; Lund et al. 2009a; Mitropoulou, Hatzidimitriou & Paraskevopoulou 2011), are not taken into account. For instance, the physicochemical properties of volatiles, such as volatility and K_{aw} value (air-water partition coefficient), could be influenced by non-volatiles (Rodríguez-Bencomo et al. 2011b).

Deodorised wine could be used to solve the problem to a certain extent. There are different strategies to prepare deodorized wine, such as collecting the non-volatile matrix left after undergoing LLE, elution from a resin or freeze drying. Solvent assisted flavour evaporation (SAFE), which can be used to purify LLE extracts by separating volatiles from non-volatile matrix compounds (Engel, Bahr & Schieberle 1999), can be proposed as a new way to build up the non-volatile matrix. Usually GC–MS is applied later to check the purity of the matrix. Then different aroma compounds can be mixed and added into matrix to build reconstituted models based on different principles, like the quantification results, corresponding thresholds and OAVs. These models would be compared against the original wines to check they were significantly different, usually by using a triangle test. Omission models are prepared by leaving one or several compounds out and checking with reconstituted models and also original wines through triangle testing in order to study the impacts of one or several particular compounds on the sensory properties of a sample.

Not long ago, a new technique based on GC, which was called gas chromatography recomposition–olfactometry (GC–R) (Figure 8), was developed (Johnson, Hirson & Ebeler

2012). The compounds eluting from a GC column could be easily reconstituted in a mixture for sensory analysis (in this case for flowering lavender volatiles). The mixture in a reconstitution test could be prepared based on peaks, sections according to the retention time or even particular compounds according to their MS information. A Deans switch was installed directly in-line with the column, so compounds were controlled to run to waste or to a cryotrap. The technique could bring all compounds, consisting of those which were undetectable and whose concentrations were below their odour detection threshold, to build a complete aroma reconstitution of all aroma compounds in samples in order to avoid the "reconstitution discrepancy" in sensory analysis, where the reconstitution model smells different from the original sample (Bult et al. 2001). Also, this application could replace a large number of steps, including preparing reconstitution with chemical standards, deodorising wine, and determining OAVs through quantitative analysis. However, it still does not consider the non-volatiles in the matrix, which could potentially have a strong impact on volatiles.

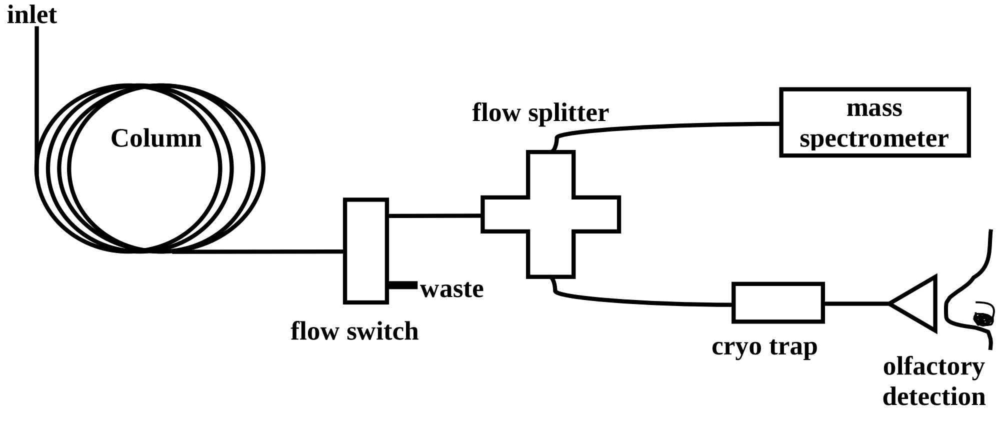

Figure 8. Theoretical schematic of the basic setup for GC–R (Johnson, Hirson & Ebeler 2012).

1.3 Perspective

A great deal of information on wine aroma and flavour have been obtained through the years, but only more recently has research been conducted to show how these individual components worked together as a matrix. As wine tasting involves different aspects, such as image, aroma, and mouthfeel, consumers could not judge wine only depending on one factor. Comprehensive methodology should be developed (Shepherd 2006) to have an overall consideration. For instance, there are several adventurous attempts undertaken in this area, such as the impact of different environmental factors, music (North 2012), colour (Morrot, Brochet & Dubourdieu 2001), label (Mueller et al. 2010), and brand (Lockshin et al. 2006), on wine tasting and how they influence the final purchasing behaviour.

Also, more specific market segmentation led academics and industry to try to develop customized products to satisfy the needs of different groups, such as rosé wine, which is a more specific category in between red and white wine according to the colour differences. Rosé wine is becoming more popular and matches well with Asian cuisine. Therefore, more attention has been paid to rosé wine in recent years, and it was also the focus here, more particularly, rosé wines made in Australia.

1.4 Rosé wine

1.4.1 Definition and winemaking techniques

Rosé wine is a type of wine which had a general pink colour in between red and white wines. More specifically, the colour can range from “onion skin” orange to vivid near-purple, depending on the varietals and also wine making methods. Rosé wines can be made in still, semi-sparkling or sparkling styles and the sugar content may vary from dry to sweet.

In general there are three ways to make rosé wine (Grainger & Tattersall 2007). The first one involves bleeding off, which is used most commonly. After a short period of skin contact, part of the juice in a red grape must is removed in order to leave more concentrated tannins, colour and flavour in the must for red wine making. The juice is moved to another vessel and fermented separately as rosé wine, which obviously had less colour and phenolics, but usually had more lifted aromas, such as floral and fruity characters (Grainger & Tattersall 2007). With the second method, instead of having a short period of skin contact, the juice is immediately transferred to start the fermentation after pressing the grapes, which usually ends with a much lighter coloured rosé wine. The last one, which was not used very often, involves decolourization. Red wine can be decoloured by treating with activated carbon, which could absorbed a lot of colour compounds. However, during the decolourization process, some aroma and flavour compounds also have the potential to be stripped out of wine, which is not ideal for the final product. In addition, this engineering process was not economic either and seldom applied in industry now (Robinson 2006).

Different wine regions use different varieties to make rosé wine. For instance in Bordeaux area, Merlot, Cabernet Sauvignon, and Cabernet Franc grapes are often used to make rosé wine (Murat 2005). In Australia, Grenache, Cabernet Sauvignon, or Pinot Noir are commonly used varieties (Wang et al. 2016). Grenache is also commonly used to make rosé wine in Spain (Ferreira et al. 2002; Fraile, Garrido & Ancín 2000).

1.4.2 Aroma in rosé wine

Different volatile compounds have been detected and quantified in rosé wines as summarised in Table 5.

Table 5. Summary of volatiles that have been evaluated in rosé wines.

compounds	concentration (µg/L)[a]	OAV[a]	descriptors[a]	extraction method	GC detectors
linear esters					
ethyl propanoate	63-211 (1)	< 1 (7)	sweet fruity (6)	LLE	FID
ethyl butanoate	196-439 (1, 2, 3)	9.8 (2)	fruity (2)	LLE	FID, Ion trap–MS
ethyl hexanoate	542-890 (1, 2, 3, 4)	39 (2)	fruity (2), raspberry, strawberry (4)	LLE	FID, MS, Ion trap–MS
ethyl octanoate	206-1100 (1, 2, 3, 4, 5)	41 (2)	fruity, fresh (2)	LLE	FID, MS, Ion trap–MS
ethyl decanoate	270-500 (2, 3, 4, 5)	0.2 (2)	smoky, cheese (7)	LLE	FID, MS, Ion trap–MS
other esters					
ethyl 2-methyl butanoate	1.2-9.7 (1, 2)	<0.1 (2)	candy, apple (7)	LLE	FID, Ion trap–MS
ethyl 2-methylpropanoate	17.9-75 (1, 2)	1.2 (2)	Strawberry (2)	LLE	FID, Ion trap–MS
ethyl 3-methyl butanoate	3.1-20 (1, 2)	1.0 (2)	fruity (2)	LLE	FID, Ion trap–MS
ethyl lactate	1500-47800 (1, 2, 3, 4, 5)	0.1 (2)	solvent (7)	LLE	FID, MS, Ion trap–MS
ethyl furoate	9.9-20 (1)	0 (8)	fruity, floral (6)	LLE	FID
diethyl succinate	503-6600 (1, 3, 4, 5)	0.8 (9)	wine (9)	LLE	FID, MS, Ion trap–MS
ethyl dodecanoate	5 (4)	0.01 (9)	sweet, waxy, floral, soapy (9)	LLE	FID
acetates					
butyl acetate	13.7-29 (1)	0 (8)	solvent, fruity, banana (6)	LLE	FID
ethyl acetate	27709-84419 (1, 2, 3, 4, 5)	3.2 (2)	fruity (7)	LLE	FID
hexyl acetate	32-106 (1, 4)	<1 (7)	red berry (7)	LLE	FID
isoamyl acetate	500-5433 (1, 2, 3, 4, 5)	42 (2)	banana (2)	LLE	FID, MS, Ion trap–MS
isobutyl acetate	40-347 (1, 2, 3)	<0.1 (2)	sweet (10)	LLE	FID, MS, Ion trap–MS
2-phenylethyl acetate	81-4000 (1, 2, 3, 4, 5)	0.3 (2)	jammy, plum, floral (7)	LLE	FID, MS, Ion trap–MS
methyl anthranilate	< 0.3 (2)	< 0.1 (2)	peach (2)	LLE	Ion trap–MS
acids					
butanoic acid	730-5020 (1, 2, 3, 5)	11 (2)	cheese (2)	LLE	FID, MS, Ion trap–MS
decanoic acid	457-1250 (1, 2, 3, 5)	0.6 (2)	earthy, caramel (7)	LLE	FID, MS, Ion trap–MS
hexanoic acid	1260-5989 (1, 2, 3, 5)	4.9 (2)	green (2)	LLE	FID, MS, Ion trap–MS
isobutyric acid	616-1399 (1, 2)	5.8 (2)	fatty (2)	LLE	FID, Ion trap–MS
isovaleric acid	510-1780 (1, 2, 3, 5)	21 (2)	fatty, rancid (2)	LLE	FID, MS, Ion trap–MS
octanoic acid	2560-6481 (1, 2, 5)	5.1 (2)	fatty, unpleasant (2)	LLE	FID, MS, Ion trap–MS
acetic acid	80000 (2)	0.4 (2)	acid, fatty (2)	LLE	Ion trap–MS
phenylacetic acid	40 (2)	< 0.1 (2)	honey, pollen (2)	LLE	Ion trap–MS
alcohols					
1-pentanol	15789 (4)	< 0.1 (12)	fuel, oil (6)	LLE	FID
1-propanol	26500 (3, 5)	< 0.1 (12)	alcohol (6)	LLE	FID
2-methyl-1-propanol	23058-49800 (1, 2, 3, 4, 5)	1.3 (2)	bitter (13)	LLE	FID
butanol	1031-1307 (1, 4)	< 1 (7)	fuel, oil (6)	LLE	FID
isoamyl alcohol	171200-265404 (1, 2, 3, 5)	5.7 (2)	cheese (2)	LLE	FID
1-hexanol	863-2230 (1, 2, 3, 4, 5)	0.3 (2)	floral, green, spice (7)	LLE	FID, MS, Ion trap–MS

cis(Z)-3-hexenol	60-1396 (1, 2, 4)	0.4 (2)	grass (10)	LLE	FID, Ion trap–MS
benzyl alcohol	193-295 (1)	< 0.1 (12)	citrusy, sweet (12)	LLE	FID
2-phenylethanol	21600-48309 (1, 2, 3, 4, 5)	1.5 (2)	roses (2)	LLE	FID, MS, Ion trap–MS
methionol	500-3855 (1, 5)	1.8 (2)	baked cabbage (2)	LLE	FID, MS
2/3-methylbutanol	31279 (4)/193575 (4)	1000 (7)	earthy, solvent (7)	LLE	FID
2,3-butanediol	520-70739 (4, 5)	1 (7)	berry, sweet (7)	LLE	FID, MS
carbonyl compounds					
acetaldehyde	35.6-3128 (1, 2, 3, 4, 5)	0.1 (2)	pungent, alcoholic (6)	LLE	FID
acetoin (3-hydroxy-2-butanone)	220-13713 (1, 2, 3, 4, 5)	< 0.1 (2)	flowery, wet (2)	LLE	FID, MS, Ion trap–MS
diacetyl (2,3-butanedione)	60-1071 (1, 2)	0.6 (2)	fruity, buttery (2)	LLE	FID, Ion trap–MS
phenylacetaldehyde	119-181 (1)	1.5 (8)	fresh, flowery (8)	SPE	Ion trap–MS
terpenes					
linalool	3.1-29.6 (1, 2)	0.1 (2)	fruity, citric (2)	LLE, SPE	Ion trap–MS
α-terpineol	7.7-26.7 (1)	1 (7)	spicy (7)	SPE	Ion trap–MS
citronellol	7.0-9.1 (1)	1, 4 (14)	fruity, rosy (14)	SPE	Ion trap–MS
geraniol	7.3-10.1 (1)	128, 256 (14)	floral (14)	SPE	Ion trap–MS
C$_{13}$-norisoprenoids					
β-damascenone	3-8.8 (1, 2, 4)	61 (2)	sweet, apple (2)	LLE, SPE	MS (SIM),Ion trap–MS
β-ionone	0.1-14 (1, 2, 4)	1.1 (2)	violet (8)	LLE, SPE	MS (SIM),Ion trap–MS
volatile phenols					
guaiacol	0.9-1.6 (1, 2)	0.1 (2)	phenolic, chemical (2)	LLE, SPE	Ion trap–MS
m-cresol	0.35-0.53 (1)	1, 4 (14)	animal, leather, phenolic (10)	SPE	Ion trap–MS
o-cresol	1.3-1.5 (1)	32 (14)	musty, sweat (10)	SPE	Ion trap–MS
4-ethylguaiacol	n.q.^{b} (1)	4 (14)	phenolic, spicy (14)	SPE	Ion trap–MS
eugenol	0.4-8.3 (1, 2)	<0.1 (2)	clove (2)	LLE, SPE	Ion trap–MS
4-ethylphenol	0.41-42 (1, 2)	<0.1 (2)	leather (2)	LLE,SPE	Ion trap–MS
4-vinylguaiacol	9.7-14 (1)	2 (16)	spices, curry (17)	SPE	Ion trap–MS
2,6-dimethoxyphenol	5.2-35 (1, 2)	<0.1 (2)	phenolic, chemical (2)	LLE,SPE	Ion trap–MS
4-allyl-2,6-dimethoxyphenol	4.4 (1)	< 0.1 (18)	roasted, burnt, meaty (6)	SPE	Ion trap–MS
4-vinylphenol	7-22 (1, 2, 3)	0.1 (2)	sweet, pleasant, phenolic (2)	LLE, SPE	MS, Ion trap–MS
vanillin derivatives					
methyl vanillate	23.1-25.5 (1)	0 (8)	vanilla, spicy (6)	SPE	Ion trap–MS
ethyl vanillate	47.7-165 (1)	0.2 (18)	pollen, flowery (13)	SPE	Ion trap–MS
acetovanillone	138-153 (1)	< 0.1 (8)	vanilla, sweet (6)	SPE	Ion trap–MS
benzene derivatives					
benzaldehyde	3.2 (1)	64, 128 (14)	nutty, cherry (14)	SPE	Ion trap–MS
ethyl dihydrocinnamate	0.1-1.8 (1, 2)	<0.1 (2)	sweet, pleasant (2)	LLE, SPE	Ion trap–MS
ethyl cinnamate	0.01-0.46 (1, 2)	<0.1 (2)	cinnamate, sweet (2)	LLE, SPE	Ion trap–MS
ketone					
4-methoxyacetophenone	0.4±0.1 (5)	n.a.^{c}	anisic, hawthorn (6)	LLE	GC–MS
furaneol	36-94 (2, 4)	7.2 (2)	candy cotton, caramel (2)	LLE, SPE	Ion trap–MS, Ion trap–MS/MS
homofuraneol	4-78 (2, 4)	0.6 (2)	candy cotton (2)	LLE, SPE	Ion trap–MS, Ion trap–MS/MS

lactones					
ɣ-nonalactone	7.6-70.6 (1, 2)	2.4 (2)	peach (18)	LLE, SPE	Ion trap–MS
ɣ-decalactone	0.4-2.5 (1, 2)	< 0.1 (2)	sweet, lactone-like (2)	LLE, SPE	Ion trap–MS
δ-decalactone	32-33 (1)	< 0.1 (8)	sweet, oily, coconut (6)	SPE	Ion trap–MS
ɣ-butyrolactone	9238-10,168 (1, 5)	0.9 (18)	creamy, oily, fatty, caramel (6)	LLE	GC–FID
cis-whiskylactone	6.1 (1)	5.4 (18)	coconut (18)	SPE	Ion trap–MS
trans-whiskylactone	3.2 (1)	0.2 (18)	coconut (18)	SPE	Ion trap–MS
sotolon	< 9 (2)	<1.8 (2)	burnt, curry (2)	SPE	Ion trap–MS
thiols					
4-mercapto-4-methyl-2-pentanone	22-24 ng/L (1)	8.9 (18)	box tree (13)	SPE	NCI[d]–MS
3-mercaptohexyl acetate	26-89 ng/L (1, 4)	13.2 (18)	box tree (18)	LLE, SPE	MS (SIM), NCI–MS
3-Mercapto-1-hexanol	211-4000 ng/L (1, 2, 4)	67 (2)	green, unpleasant (2)	LLE, SPE	MS (SIM), Ion trap–MS, NCI–MS
furfurylthiol	2.4-3.7 ng/L (1)	< 0.1 (8)	coffee, toasty (18)	SPE	NCI–MS
benzylmercaptan	4.2-4.4 ng/L (1)	< 2-437 (19)	toasty, burnt, empyreumatic (19)	SPE	NCI–MS
2-methyl-3-furanthiol	< 0.02 (2)	< 4 (2)	fried (2)	SPME	Ion trap–MS

[a] The corresponding references are in brackets: the first 5 references were measured in rosé wines, the rest were in other type of wines. 1, Álvarez-Pérez et al. (2012); 2, Ferreira et al. (2002); 3, Gil et al. (2006); 4, Masson and Schneider (2009); 5, Fraile, Garrido and Ancín (2000). 6, The Good Scents Company (http://www.thegoodscentscompany.com/); 7, Mayr et al. (2014); 8, Gomez-Miguez et al. (2007); 9, Noguerol-Pato et al. (2009); 10, Ferreira et al. (2009); 11, Rodríguez-Bencomo et al. (2011a); 12, Jiang and Zhang (2010); 13, Ferreira et al. (2001); 14, Fang and Qian (2005); 15, Yuan and Qian (2016); 16, Sánchez-Palomo et al. (2010); 17, Guth (1997); 18, Culleré et al. (2004); 19, Mateo-Vivaracho et al. (2010). [b] Not quantified. [c] not available. [d] Negative chemical ionization.

1) Polyfunctional thiols

The importance of varietal thiols in wine has been well demonstrated, especially for Sauvignon Blanc wines (Murat, Tominaga & Dubourdieu 2001; Tominaga, Guimbertau & Dubourdieu 2003; Tominaga et al. 2006). Although varietal thiols are difficult to detect and quantify, there were still some developments regarding their quantification (Capone, Sefton & Jeffery 2012; Tominaga & Dubourdieu 2006), identification and analysis of precursors (Capone, Black & Jeffery 2012; Capone et al. 2011; Fedrizzi et al. 2009; Kobayashi et al. 2011; Roland et al. 2010; Winter et al. 2011) and the impact on wine aroma (Benkwitz et al. 2012a; Coetzee & du Toit 2012; Escudero et al. 2004; King et al. 2011).

More specifically, the group of compounds, including 4MMP, 3MH and 3MHA, was also one of the most important groups of odourants in rosé wine. It was suggested that 3MH, 3MHA, along with phenylethyl acetate (rose aroma, mentioned further below), were very important to the aroma of 30 rosé wines made from 6 different varieties from Bordeaux (Murat 2005). The highest 3MH, 3MHA and phenylethyl acetate concentrations were found in the fruitiest samples from sensory descriptive analysis. 3MHA was also detected in 14 out of 30 wines and the level was generally higher than its perception threshold. Also, 3MH and 3MHA have been justified with significant contributions to the aroma of Provence rosé wines using reconstitution and omission tests, with triangle testing of initial, deodorized and reconstituted wines (Masson & Schneider 2009). This was consistent with a study on Grenache rosé wine from Calatayud (Zaragoza, Spain), where 3MH proved to have a deep impact on fruity and citrus notes in wines through omission tests (Ferreira et al. 2002). The same result was obtained when the rosé wines made of Merlot, Cabernet Sauvignon and Cabernet Franc were studied (Murat, Tominaga & Dubourdieu 2001). Also, omission tests revealed that other compounds, such as β-damascenone, were suggested to work together with 3MH or 3MHA to make an obvious difference to the original aroma of rosé wines

(Benkwitz et al. 2012a). However, the concentration of 3MHA was different in rosé wine from Provence and Bordeaux, which was probably caused by the grape varieties or different yeast strains used in each region (Masson & Schneider 2009). 4MMP, which has a boxtree-like odour, was suggested as a possible reason why some rosé wines exhibited "exotic fruits" aroma in a previous study (Álvarez-Pérez et al. 2012).

2) 2-Phenylethanol

2-Phenylethanol is produced via the shikimate pathway and induces positive spice/honey/rose/lilac aromas to wine (Francis & Newton 2005). The detection threshold of 2-phenylethanol was determined to be 14 mg/L (Ferreira, López & Cacho 2000). It was important to the aroma of white wine when at suprathreshold concentrations (Guth 1997; Lopez et al. 2003). In rosé wines, 2-phenylethanol was proposed as the principle higher alcohol when 53 rosé wines from DO "Vinos de Madrid" of Spain were analysed (Gil et al. 2006), However, together with β-damascenone (apple compote), isoamyl acetate (banana) and β-ionone (violet), 2-phenylethanol was suggested as a negligible element in regards to the aroma of Provence rosé wine (Masson & Schneider 2009). Its corresponding ester, phenylethyl acetate, which was also an important volatile in wines, has been detected with concentration higher than its threshold in rosé wines as well (Álvarez-Pérez et al. 2012).

3) Esters

Some fermentation esters also had impacts on rosé wine aroma. It was shown that the concentrations of ethyl hexanoate (OAV = 63.6), ethyl butanoate (OAV = 13.5) and ethyl octanoate (OAV = 220) were higher in all white and rosé wines compared to the red wines studied (Gil et al. 2006), thus being very important to aroma characters. Moreover, some esters in rosé wines – ethyl octanoate, ethyl hexanoate, isoamyl acetate, ethyl butanoate, ethyl decanoate, ethyl acetate – along with other compounds including isovaleric acid, butanoic acid, hexanoic acid, octanoic acid, isoamyl alcohols, 2-phenylethanol and decanoic acid, were justified as a group which had a major impact on overall wine aroma. Some have been defined as key aroma compounds in rosé wines from DO “Vinos de Madrid” of Spain (Gil et al. 2006). In addition, some esters with low OAV could be used to differentiate rosé wine styles (Gil et al. 2006).

4) C_{13}-Norisoprenoids

β-Damascenone and β-ionone (C9) were identified as the most important C_{13}-nrisoprenoids in white and red wines (Bordiga et al. 2013; Pineau et al. 2007; Rutan et al. 2014). It was also revealed that β-damascenone was an important volatile in Grenache rosé wine as it had the second highest OAV (Ferreira et al. 2002). It has been suggested that β-damascenone might act as an enhancer of red fruit aromas in red wines (Pineau et al. 2007), which might be the same case in rosé wines. In contrast, β-ionone was found at very low concentration and had little impact on the aroma of Provence rosé wines (Masson & Schneider 2009).

5) The influence of yeast strain on rosé wine aroma

Yeast strains have a determined influence on fruity aromas in rosé wines (Murat & Dumeau 2005), as for instance, terpene compounds associated with fruity and floral aromas in wine (Ribéreau-Gayon et al. 2006) had a close relationship with yeast strain (Loscos et al. 2007). Synthesis of 2-phenylethanol can also be related to yeast genera based on their different glycosidase activity (Hernández-Orte et al. 2008). It was suggested that different strains had varied ability to produce 3MH and phenylethyl acetate, so picking a suitable yeast strain is very important to make a fruity rosé wine. It was demonstrated that isolated yeast strains had particular effects on the concentrations of linear and branched ethyl esters, fatty acids, phenylethyl acetate and some varietal compounds, which were all important to rosé wine (Álvarez-Pérez et al. 2012).

6) Other factors influencing rosé wine aroma

Rosé wine aroma could also be affected by the maceration process. It was shown that musts with longer maceration had higher C_6 compounds and monoterpenoids than the control, and more alcohols and C_6 compounds but lower levels of esters, terpenols, and acids were obtained from rosé wines without a pre-fermentative maceration processing (Salinas et al. 2003). Also, longer maceration might be preferable in order to protect thiols in rosé wine, as the stability of 3MH in model media was increased compared to a control sample by adding anthocyanins extracted from wine (Murat & Dumeau 2005); anthocyanin concentration is positively related to the length of maceration (hence the colour differences for rosé wines mentioned above). Moreover, it was suggested that ageing on lees was beneficial, affording higher concentrations of 3MH and 3MHA, which might then have a positive impact on sensory characters (Murat & Dumeau 2005).

Summary of research aims

The first aim of this project was to evaluate aroma compounds in Australian rosé wines and to identify the characteristic aroma profiles of these wines using sensorial and chemical studies. Another aim was to investigate the preference of rosé wine in target markets and reveal the linkage between rosé wine composition and quality. To achieve this, the project has the following objectives:

1. Establish a HS-SPME-GC–MS method to identify and quantify volatile compounds in Australian rosé wines by GC–MS and correlate the results with sensory analysis, such as quantitative descriptive analysis.

2. Explore the preference of Chinese market towards rosé wine and demonstrate the relationships between rosé wine volatile compounds, taster preferences and quality.

3. Compare methods to obtain representative odourant extract from rosé wine and evaluate in detail the impact of aroma compounds on rosé wine sensory characters by applying GC–MS–O and AEDA, and quantitatively and qualitatively determine the impact aroma compounds present in Australian rosé wines.

Objective 1: Chemical and sensory profiles of Australian rosé wine

Sensory characters and aroma profiles of Australian rosé wines were evaluated to obtain the first insight on this specific category. An HS-SPME-GC–MS method was developed which enabled the identification of 47 volatile compounds, present in 26 commercial rosé wines, and quantitative descriptive analysis was conducted in order to ascertain the different sensory characters of the wines. Relationships were revealed between sensory results and quantitative wine compositional data, linking chemical and sensory profiles. Samples were compared regarding to their chemical and sensorial details, some important aroma compounds were proposed and different rosé wine styles were suggested. Details of this study can be found in the publication presented in Chapter 2.

Objective 2: The preferences of Chinese wine professionals for rosé wine

A selection of rosé wines was chosen based on the chemical and sensorial information obtained in the first study, and together with other rosé wines from China and France (23 rosé wines in total), blind rosé wine tastings were conducted in three major cities of China with Chinese wine professionals. Sensory characters, preference, quality and expected price were gained from the tastings and volatiles in wines were measured. Correlations between chemical composition, sensory characters and preference/quality/expected price were evaluated and visualised by a novel approach using network analysis. Details of this study can be found in the publication presented in Chapter 3.

Objective 3: GC–O analysis of rosé wines using two extraction strategies.

In order to look into detail at the impact of different aroma compounds on sensory characteristics of rosé wine, two representative rosé wines (tropical sample and fruity/floral sample) were chosen to conduct GC–O analysis. Volatile extracts were prepared using liquid-liquid extraction (LLE) followed by solvent assisted flavour evaporation (SAFE), or a recently developed headspace (HS) sampling method to undertake AEDA. In conjunction, a HS-SPME-GC–MS method with selected ion monitoring (SIM) was developed, and a total of 92 volatile compounds were quantified in the two samples. The sensory impact of different volatiles was rationalised based on FD and OAV values. The performance of different extraction methods was compared and a strategy for preparing a representative volatile extract was proposed. Details of this study can be found in the publication presented in Chapter 4.

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Chapter 2

Chemical and sensory profiles of rosé wines from Australia

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By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);

ii. permission is granted for the candidate in include the publication in the thesis; and

iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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Chemical and sensory profiles of rosé wines from Australia

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ABSTRACT

The appeal of rosé wine is attributable to its sensory profiles and underlying chemical composition, which are determined by viticultural and oenological inputs. This study provided the first insight into the sensory attributes and volatile profiles of Australian rosé wines. An HS-SPME–GC–MS method and a recently developed HPLC–MS/MS method were used to quantify 51 volatile compounds, including 4 potent sulfur compounds, in 26 commercial rosé wines. Descriptive analysis on all wines was undertaken and the sensory results were correlated with quantitative chemical data to explore relationships between wine composition and sensory profiles. Based on odour activity values, esters were prominent aroma volatiles, and β-damascenone, 3-methylbutyl acetate, ethyl hexanoate and 3-MHA were deemed to be important, in accord with other studies. Wines were described with terms ranging from developed, spicy and savoury to fresh green, citrus, tropical fruit, floral and confectionery.

1. Introduction

Rosé wine is a diverse style which is increasing in popularity internationally, especially with young consumers. Global consumption of rosé wine increased by about 17% in the decade to 2012, which mirrors the 19% increase as a proportion of wine sold from French supermarkets over 23 years since 1990 (Conseil des vins de provence, 2015). In 2013 alone, the value of rosé wines exported from the renowned Provence region of France to the USA increased by 40%, while total export value from this region grew by 390% over the previous decade (Conseil des vins de provence, 2015). In Australia, off-trade sales of bottled rosé wine

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Abbreviations: DA, descriptive analysis; 3-MH, 3-mercapto-1-hexanol; 3-MHA, 3-mercaptohexyl acetate; FT, furfurylthiol; BM, benzyl mercaptan; GC–MS, gas chromatography–mass spectrometry; HPLC–MS/MS, high-performance liquid chromatography–tandem mass spectrometry; TA, titratable acidity; HS-SPME, headspace-solid-phase microextraction; DVB/CAR/PDMS, divinylbenzene/carboxen/polydimethylsiloxane; DTDP, 4,4′-dithiodipyridine; SPE, solid-phase extraction; LOD, limit of detection; LOQ, limit of quantitation; PCA, principal component analysis; PLS, partial least squares; RT, retention time; RI, retention index; CRI, calculated retention index; VA, volatile acidity; ND, not detected; OAV, odour activity value; PC, principal component; VIP, variable importance in the projection.

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increased by 5% to about AU$35 million between 2013 and 2014, with the strongest growth over the past few years being in the higher price segments, i.e., >AU$20/bottle (Rowley, 2014). This growth may be attributable to an emphasis on marketing, which has become more evident with the *Rosé Revolution* initiative (Rosé revolution, 2014), where events are held during the summer months in Australia to raise awareness of dry rosé wines.

As with all wine styles, aroma is necessarily a determining factor for consumer preference, but little is known about what constitutes an Australian rosé wine. In contrast, aroma compounds of rosé wines have been determined for some wine regions, such as those in Spain, Turkey, and France (Bordeaux and Provence) (Darici, Cabaroglu, Ferreira, & Lopez, 2014; Ferreira, Ortin, Escudero, Lopez, & Cacho, 2002; Masson & Schneider, 2009; Murat, 2005; Álvarez-Pérez et al., 2012). Previous research has demonstrated that aroma compounds which contribute fruity characters are important for rosé wines; these include ethyl esters, higher alcohol acetates (particularly 3-methylbutyl (isoamyl) acetate and 2-phenylethyl acetate), furaneol and especially the polyfunctional thiols 3-mercapto-1-hexanol (3-MH) and 3-mercaptohexyl acetate (3-MHA)[1] (Álvarez-Pérez et al., 2012; Darici et al., 2014; Ferreira et al., 2002; Masson & Schneider, 2009; Murat, 2005). Analysis of Bordeaux rosé wines prepared from blends of different red grape varieties highlighted the importance of 3-MH, 3-MHA and 2-phenylethyl acetate, with the fruitiest wines from descriptive analysis (DA) containing the highest concentrations of these compounds (Murat, 2005). The impact of 3-MH, which has an aroma detection threshold of 60 ng/L in model matrix and confers passionfruit and grapefruit notes in wine (Dubourdieu & Tominaga, 2009 and citations therein), was verified with omission tests as the most important odorant of a Grenache rosé wine from Spain (Ferreira et al., 2002). Besides these important compounds, the C_{13}-norisoprenoid β-damascenone has also been found to be a key contributor to the aroma of rosé wines in a number of studies (Álvarez-Pérez et al., 2012; Darici et al., 2014; Ferreira et al., 2002; Masson & Schneider, 2009; Murat, 2005). Overall, these compounds are closely related to grape-derived aroma precursors (for compounds such as 3-MH and β-damascenone) and yeast strains used for fermentation (for ethyl and acetate esters) (Dubourdieu & Tominaga, 2009 and citations therein; Swiegers, Bartowsky, Henschke, & Pretorius, 2005); therefore, differences among grape varietals, viticulture, and winemaking processes provide the diverse aroma and flavour profiles of rosé wines.

Considering the increasing popularity of rosé wines, it was important from both industry and scientific perspectives to understand the aroma and flavour attributes of such wines produced in Australia. Gas chromatography–mass spectrometry (GC–MS) and high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) analyses of volatiles, and sensory DA were undertaken and their relationships explored to provide the first insight into the chemical and sensory profiles of a range of commercial Australian rosé wines.

2. Materials and methods

2.1. Chemicals

Compounds used for identification and calibration (⩾97% purity) were supplied by Sigma–Aldrich (Castle Hill, NSW, Australia), except for ethyl butanoate, ethyl 2-methylbutanoate, methyl octanoate, ethyl 2-phenylacetate, and nonanoic acid, which were supplied by Alfa Aesar (Ward Hill, MA, USA). Sodium chloride was supplied by JT Baker (Phillipsburg, NJ, USA) and analytical grade solvents were obtained from Merck (Kilsyth, Victoria, Australia). Deuterium-labelled internal standards (Supporting information, Table S1) were supplied by CDN Isotopes (Pointe-Claire, QC, CA), or synthesised as previously reported for d_5-ethyl nonanoate (Boss et al., 2015) and polyfunctional thiols (Capone, Ristic, Pardon, & Jeffery, 2015). Stock solutions of standards were prepared volumetrically in absolute ethanol and stored at −20 °C and working solutions were stored at 4 °C until required. All chemicals were analytical reagent grade unless otherwise stated, and water was obtained from a Milli-Q purification system (Millipore, North Ryde, NSW, Australia).

2.2. Wine samples

Wines included in this study, comprising different grape varieties, were commercially produced in Australia ($n = 26$) and were sourced from a variety of producers. Wines were selected based on being dry styles of rosé (i.e., 9 g/L residual sugar or less), and ranged in vintage from 2012 to 2013, and in alcohol content from 11.1% to 13.5% (v/v) (Supporting information, Table S2). Wines were all bottled under screw cap closures and were coded 1–26. A 2012 commercial rosé wine (bag-in-box, 13.5% v/v ethanol, pH 3.56, titratable acidity (TA) = 6.2 g/L, SO_2 (free) = 26 mg/L, SO_2 (total) = 127 mg/L) was used as a base wine for qualitative/quantitative analysis of major volatiles and to prepare sensory aroma reference standards.

2.3. Basic wine composition

Ethanol content (% v/v) was determined using an Alcolyzer Wine ME/DMA 4500 M (Anton Paar, Austria). Titratable acidity (TA, expressed as g/L of tartaric acid) and pH were measured with a combined pH meter and autotitrator (CompacT Titrator, Crison Instruments, S.A., Allela, Spain) and residual sugar (glucose + fructose) was determined using an enzymatic test kit (Megazyme, Wicklow, Ireland). All measurements were performed in duplicate (Supporting information, Table S2).

2.4. Headspace-solid-phase microextraction (HS-SPME)–GC–MS analytical method

Procedures and conditions were based on standard techniques reported for HS-SPME analysis of wine by GC–MS (Mendes, Gonçalves, & Câmara, 2012; Paula Barros et al., 2012).

2.4.1. GC–MS instrumentation

Samples were analysed with a Gerstel selectable 1D/2D-GC–MS system (Lasersan Australasia Pty Ltd., Robina, QLD, Australia) using an Agilent 7890 GC equipped with a Gerstel MPS autosampler and low thermal mass (LTM) series II external column modules coupled to a 5897 mass selective detector. A deactivated SPME inlet liner (0.75 mm i.d., Supelco) and DB-Wax LTM column module (30 m, 0.25 mm i.d., 0.25 μm film thickness, Agilent J&W, Folsom, CA) were used for 1D separations. Ultrapure helium (Coregas, Cavan, SA, Australia) was used as the carrier gas at a constant flow of 1 mL/min. The LTM module temperature program began at 40 °C for 1 min, increased to 135 °C at 2 °C/min, then to 212 °C at 5 °C/min, and finally to 250 °C at 15 °C/min, then remained at 250 °C for 10 min, giving a total run time of 76 min. The transfer line was set at 200 °C and positive ion electron impact spectra at 70 eV were recorded in the range m/z 35–350 for scan runs. Instrument control and data analysis were performed with Agilent ChemStation software (E.02.02.1431).

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[1] The correct IUPAC prefix for thiol has been changed from “mercapto” to “sulfanyl” as in 3-sulfanylhexan-1-ol (3-SH) and 3-sulfanylhexyl acetate (3-SHA); both terms (and abbreviations) are still used and “mercapto” is more common in the older literature.

2.4.2. Qualitative and quantitative analysis of major volatiles

In duplicate, wine samples were spiked with 10 μL of an internal standard mixture (Supporting information, Table S1) in 10 mL volumetric flasks and a 0.5 mL aliquot was transferred to a 20 mL SPME headspace vial (Supelco) and diluted with 4.5 mL of Milli-Q water. After mixing, 2 g of NaCl was added, the contents were shaken by hand and the vial was sealed prior to GC–MS analysis. Samples were incubated for 10 min and extracted with a DVB/CAR/PDMS SPME fibre (50/30 μm, 1 cm, 23 gauge) for 45 min; incubation and extraction temperatures were both 50 °C and agitation speed was 500 rpm. Desorption temperature was set at 240 °C and injection mode was splitless with a desorption time of 10 min. New fibres were conditioned in the injection port for 1 h at 270 °C before use and then pre-baked for 10 min before every sample to avoid carryover. Blank runs were routinely undertaken after the assessment of every set of five samples. Compound identity was verified by determining retention indices for the DB-Wax column using a series of alkanes (C7-C40, Sigma–Aldrich), and through mass spectral library matches (NBS 75 K). The retention index (RI) of each compound used for comparison purposes was obtained from Aroma Office 2D, Version 2.01.00 (Gerstel KK, Tokyo, Japan). Analyte CAS number, retention time, reference RI, calculated RI, and quantifier/qualifier ions are shown in Table 1.

GC–MS analysis provided quantitative data for 35 volatiles that had readily available reference standards, while the remaining 12 compounds were semi-quantified based on their equivalence to other calibrated compounds or an internal standard (Table 1). Calibration and validation were undertaken (Thompson, Ellison, & Wood, 2002) with a series of duplicate standard additions of authentic standards to the 2012 commercial rosé bag-in-box wine spiked with internal standard mixture. Each calibration function had at least 6 points which were evenly spaced to cover 0–150% of the estimated analyte concentration in wine samples. The internal standard used for calibration of each analyte was chosen based on retention time, chemical similarity and coefficient of determination (R^2). Linearity of calibrations was determined from an inspection of residuals plots, and from R^2 values (Ellison, 2006). Precision and recovery for each compound were determined from seven replicate determinations at low and high analyte concentrations (i.e., 10% and 90% of maximum concentrations, respectively). The limit of detection (LOD) was determined based on visual evaluation of the chromatograms, by establishing the minimum level at which the analytes could be reliably detected from the analysis of samples with known concentrations of analyte (i.e., signal/noise ratio of 3). The limit of quantitation (LOQ) was determined by multiplying LOD by 3.3 (i.e., signal/noise ratio of 10).

2.5. Quantitative analysis of polyfunctional thiols

3-Mercapto-1-hexanol (3-MH), 3-mercaptohexyl acetate (3-MHA), 4-mercapto-4-methylpentan-2-one (4-MMP), furfurylthiol (FT) and benzyl mercaptan (BM) were analysed by HPLC–MS/MS, after thiol derivatization with 4,4′-dithiodipyridine (DTDP) and isolation of derivatives by solid-phase extraction (SPE) (Capone et al., 2015). Briefly, 20 mL of wine was spiked with labelled internal standard mixture, followed by the addition of EDTA 2Na (20 mg), 50% acetaldehyde (80 μL), and freshly thawed DTDP reagent (10 mM, 200 μL). After 30 min, the sample was loaded onto a pre-conditioned Bond Elut C18 cartridge, washed with 12 mL of 50% methanol, dried for 5 min, and eluted with 3 mL of methanol. The eluate was concentrated to dryness and reconstituted with 10% aqueous ethanol (200 μL) for analysis with an Agilent 1200 HPLC connected to an Applied Biosystems 4000 QTrap hybrid tandem mass spectrometer that was configured with electrospray ionisation in positive ion mode.

2.6. Descriptive analysis

Sensory profiles of the 26 rosé wines were determined by DA in a purpose-built sensory laboratory. Panellists ranging in age from 25 to 45 were recruited from a pool of wine science researchers at The University of Adelaide. A total of 12 panellists (5 females, 7 males) participated, with the majority having previous wine DA experience. This sensory study was approved by the Human Research Ethics Committee of The University of Adelaide (Project No. H-2013-019).

Training of panellists included four two-hour sessions held over two weeks and involved attribute generation, discussion and consensus, scale use and agreement on reference standards. Subsequently, four training sessions were conducted in sensory booths over another two weeks to familiarise panellists with the tasting environment and sensory software. Sensory booths were illuminated with red lights throughout evaluations to eliminate biases attributable to wine colour differences. Standard black Institut National des Appellations d'Origine (INAO) approved tasting glasses were used and wine samples were always covered with plastic lids.

DA panellists rated 25 attributes (13 aroma and 12 flavour, including an attribute of overall intensity in both) on a 15 cm unstructured line scale anchored by wordings of "low", "moderate" and "intense" at 10%, 50% and 90% of the scale, respectively. Table S3 (Supporting information) provides details of the attributes and reference standards used in DA. During the training period all samples were presented to the panellists at least twice, without disclosing the number of samples to be evaluated. In the booth training sessions, data were collected using FIZZ software (version 2.47b, Biosystemes, Couternon, France). The panel commenced formal evaluation of the samples once there were no significant assessor–sample interactions.

During formal sessions, panellists evaluated wines in four sessions over two weeks. Wine samples (30 mL) were presented (in duplicate) using a randomised and balanced presentation order for each panellist determined using Design Express (Qi Statistics). Data were collected using FIZZ software and each sample was assigned a random three-digit code generated by FIZZ. Timers were set in FIZZ, forcing panellists to have a 1 min break after each sample and 5 min after every five samples, to avoid sensory fatigue. Filtered water and unsalted water crackers were provided for assessors to cleanse their palates.

2.7. Statistical analysis

Basic chemical data were processed with Microsoft Excel 2010. All chemical data are presented as mean values with standard deviation from replicate determinations. Sensory data were evaluated by two-way analysis of variance (ANOVA, judge and sample) using SENPAQ software, version 5.01 (Qi Statistics, Reading, England). Chemical data were analysed by one-way ANOVA (sample) using the statistical package XLSTAT (version 2012.2.02, Addinsoft SARL, Paris, France). The significantly different attribute means were subjected to Pearson's type principal component analysis (PCA) using XLSTAT and partial least squares (PLS) regression using The Unscrambler (version 9.7, CAMO Software AS, Oslo, Norway) with chemical parameters (x-variables) and DA data (y-variables). All variables were standardised before analysis. The number of principal components used for PCA was determined from scree plots. The PLS model was cross-validated using an uncertainty test (leave-one-out cross-validation). The optimal number of components for the PLS models were determined by inspection of the variable importance in the projection (VIP) values (only components with VIP > 0.8 were included) (Eriksson, Johansson, Kettaneh-Wold, & Wold, 2001).

Table 1
Qualitative information and method characteristics for volatile compounds determined by HS-SPME–GC–MS in rosé wines.

Compound	CAS number	RT (min)	RI[a]	CRI[b]	Ions[c] (*m/z*)	R^2	Range[d] (μg/L)	Internal standard	Aroma detection threshold[e] (μg/L)	Odour quality[f]
Ethyl acetate	141-78-6	5.053	881	882	**61**, 88	0.9938	16816–300000	d_4-3-Methyl-1-butanol	15000 (Moyano, Zea, Moreno, & Medina, 2002)	VA, nail polish[g]
Ethyl butanoate	105-54-4	9.320	1030	1041	29, **71**, 88	0.9935	4.9–900	d_4-3-Methyl-1-butanol	20 (Guth, 1997)	Strawberry, lactic[h]
1-Propanol	71-23-8	9.603	1049	1048	**31**, 42, 59	0.9948	1149–25000	d_{13}-1-Hexanol	500 (Swiegers et al., 2005)	Alcohol, pungent
Ethyl 2-methylbutanoate	7452-79-1	9.997	1047	1059	**57**, 85, 115	0.9995	0.23–250	d_3-Hexyl acetate	1 (Guth, 1997)	Fruity, anise, strawberry[h]
Ethyl 3-methylbutanoate	108-64-5	10.676	1070	1078	57, **88**, 130	Equivalent to ethyl 2-methylbutanoate		d_3-Hexyl acetate	3 (Guth, 1997)	Fruit
2-Methyl-1-propanol	78-83-1	12.549	1100	1119	**31**, 55, 47	0.9985	638–15000	d_{13}-1-Hexanol	40000 (Ferreira et al., 2000)	Wine, solvent, bitter
3-Methylbutyl acetate	123-92-2	13.088	1123	1128	55, **70**, 87	0.9941	120.5–9000	d_4-3-Methyl-1-butanol	30 (Guth, 1997)	Banana
Ethyl 2-butenoate	10544-63-5	15.378	1158	1168	**69**, 99, 114	Equivalent to ethyl 2-methylbutanoate		d_3-Hexyl acetate	unknown	Compost[i]
Limonene	138-86-3	16.817	1193	1193	**68**, 79, 107	0.9958	0.38–12.0	d_{13}-1-Hexanol	15 (Zalacain, Marín, Alonso, & Salinas, 2007)	Lemon, orange
3-Methyl-1-butanol	123-51-3	19.072	1215	1228	42, **55**, 70	0.9925	2359–240000	d_4-3-Methyl-1-butanol	30000 (Guth, 1997)	Harsh, nail polish[g], fusel[h]
Ethyl hexanoate	123-66-0	19.850	1236	1240	**88**, 99, 60	0.9931	0.36–9000	d_4-3-Methyl-1-butanol	14 (Ferreira et al., 2000)	Apple peel, fruit
Hexyl acetate	142-92-7	22.189	1275	1276	**43**, 56, 69	0.9919	5.5–9000	d_3-Hexyl acetate	670 (Peinado, Moreno, Bueno, Moreno, & Mauricio, 2004)	Fruity, floral[j]
Ethyl 2-hexenoate	1552-67-6	26.943	1345	1348	55, **97**, 142	Equivalent to 3-methylbutyl hexanoate		d_5-Ethyl nonanoate	0.02 (Berger, Drawert, Kollmannsberger, Nitz, & Schraufstetter, 1985)	Spicy, candy, earthy[i]
Ethyl lactate	97-64-3	27.160	1341	1351	29, **45**, 75	0.9925	385–250000	d_{13}-1-Hexanol	146000 (Moyano et al., 2002)	Solvent[i]
1-Hexanol	111-27-3	28.165	1357	1366	**56**, 69, 84	0.9996	225–15000	d_{13}-1-Hexanol	8000 (Guth, 1997)	Green, grass[h]
Methyl octanoate	111-11-5	29.990	1392	1394	**74**, 127, 158	Equivalent to 3-methylbutyl hexanoate		d_5-Ethyl nonanoate	4 (Clarke & Bakker, 2011)	Orange
Nonanal	124-19-6	30.111	1390	1396	41, **70**, 82	0.9932	10.5–75.0	d_4-3-Methyl-1-butanol	2.5 (Clarke & Bakker, 2011)	Fat, citrus, green
1-Methyl-4-(prop-1-en-2-yl)benzene	1195-32-0	32.695	1434	1436	91, 117, **132**	Equivalent to 3-methylbutyl hexanoate		d_5-Ethyl nonanoate	unknown	Phenolic, spicy, clove, guaiacol[k]
Ethyl octanoate	106-32-1	33.318	1450	1465	**88**, 101, 127	0.9949	9.4–7500	d_4-3-Methyl-1-butanol	20 (Swiegers et al., 2005)	Melon, wood[i]
Acetic acid	64-19-7	34.276	1462	1464	15, **43**, 60	0.9995	19535–600000	d_{19}-Decanoic acid	200000 (Guth, 1997)	Sour, vinegar[h,i]
3-Methylbutyl hexanoate	2198-61-0	34.554	1475	1474	**70**, 99, 117	0.9962	0.72–37.5	d_5-Ethyl nonanoate	unknown	Cooked meat, mushroom[i]
Furfural	98-01-1	34. 626	1480	1480	95, **96**, 39	0.9917	12.2–2500	d_5-Phenylethanol	14100 (Ferreira et al., 2000)	Earthy, wood[i]
2-Ethyl-1-hexanol	104-76-7	36.978	1491	1501	**57**, 70, 98	0.9952	8.8–2400	d_{13}-1-Hexanol	8000 (Buttery, Turnbaugh, & Ling, 1988)	Citrus, green
Benzaldehyde	100-52-7	38.053	1519	1519	51, **77**, 106	0.9966	2.4–250	d_{13}-1-Hexanol	350 (Clarke & Bakker, 2011)	Almond, burnt sugar
Vitispirane	65416-59-3	38.670	1526	1529	**93**, 121, 192[l]	Equivalent to linalool		d_{13}-1-Hexanol	800 (Eggers, Bohna, & Dooley, 2006)	Vanilla, quince fruit[m]
Ethyl nonanoate	123-29-5	39.461	1541	1541	**88**, 101, 141	Equivalent to d_5-ethyl nonanoate		d_5-Ethyl nonanoate	1200 (Burdock, 2009)	Fruity, rose, waxy, rum, tropical
Linalool	78-70-6	40.410	1544	1557	**71**, 121, 136	0.9905	2.2–750	d_{13}-1-Hexanol	15 (Guth, 1997)	Flower, lavender
1-Octanol	111-87-5	41.168	1569	1569	**56**, 70, 84	0.9916	3.2–300	d_{13}-1-Hexanol	0.7 (Clarke & Bakker, 2011)	Chemical, metal, burnt
Methyl decanoate	110-42-9	42.999	1588	1598	**74**, 101, 143	Equivalent to ethyl decanoate		d_4-3-Methyl-1-butanol	unknown	Wine
Ethyl furoate	614-99-3	44.460	1622	1624	**95**, 122, 140	0.9927	0.89–75.0	d_5-Phenylethanol	16000 (Ferreira et al., 2000)	Fruity, floral[k]
Ethyl decanoate	110-38-3	45.885	1643	1648	**88**, 101, 155	0.9956	34.8–8750	d_4-3-Methyl-1-butanol	200 (Ferreira et al., 2000)	Floral, soap[g]
3-Methylbutyl octanoate	2035-99-6	46.961	1651	1667	70, **127**, 145	0.9915	9.8–500	d_5-Ethyl nonanoate	125 (Ferreira et al., 2000)	Sweet, fruity, pineapple, coconut[k]

(*continued on next page*)

Table 1 (*continued*)

Compound	CAS number	RT (min)	RI[a]	CRI[b]	Ions[c] (m/z)	R^2	Range[d] (μg/L)	Internal standard	Aroma detection threshold[e] (μg/L)	Odour quality[f]
Diethyl succinate	123-25-1	47.990	1675	1685	101, **129**, 147	0.9915	3.9–10000	d$_4$-3-Methyl-1-butanol	1250000 (Moyano et al., 2002)	Wine, fruit
Ethyl 9-decenoate	67233-91-4	48.521	1685	1694	55, **88**, 110	Equivalent to ethyl decanoate		d$_4$-3-Methyl-1-butanol	unknown	Fruity, fatty[k]
α-Terpineol	98-55-5	48.940	1701	1702	**59**, 93, 136	0.9913	19.6–250	d$_{13}$-1-Hexanol	250 (Ferreira et al., 2000)	Oil, anise, spicy[i]
1-Decanol	112-30-1	51.902	1764	1774	**55**, 83, 112	Equivalent to 1-octanol		d$_{13}$-1-Hexanol	500 (Moyano et al., 2002)	Fat
β-Citronellol	106-22-9	51.952	1775	1775	**69**, 95, 123	0.9940	2.7–180	d$_{13}$-1-Hexanol	100 (Guth, 1997)	Citrus
Ethyl 2-phenylacetate	101-97-3	52.388	1785	1785	65, **91**, 164	0.9930	0.20–45.0	d$_{13}$-1-Hexanol	650 (Burdock, 2009)	Fruit, sweet
2-Phenylethyl acetate	103-45-7	53.470	1811	1815	65, 91, **104**	0.9946	3.2–750	d$_5$-Phenylethanol	250 (Guth, 1997)	Jammy, plum, floral, fruity[g,i]
β-Damascenone	23726-93-4	53.689	1813	1821	**69**, 121, 190	0.9943	0.42–30.0	d$_5$-Ethyl nonanoate	0.05 (Guth, 1997)	Apple, rose, honey
Ethyl dodecanoate	106-33-2	54.619	1847	1850	88, 101, **183**	0.9914	13.2–450	d$_5$-Phenylethanol	500 (Moyano et al., 2002)	Fruity, floral[n]
Hexanoic acid	142-62-1	54.672	1861	1851	**60**, 73, 87	0.9914	84.7–9000	d$_{13}$-1-Hexanol	420 (Ferreira et al., 2000)	Leafy, wood, varnish[i]
2-Phenylethanol	60-12-8	56.695	1915	1915	65, **91**, 122	0.9965	270–50000	d$_5$-Phenylethanol	14000 (Ferreira et al., 2000)	Floral, rose[g,i]
Octanoic acid	124-07-2	60.719	2065	2066	**60**, 73, 101	0.9910	613.4–7500	d$_5$-Phenylethanol	500 (Ferreira et al., 2000)	Butter, almond[i]
Nonanoic acid	112-05-0	63.138	2167	2173	**60**, 115, 129	0.9963	38.5–1000	d$_{19}$-Decanoic acid	3000 (Burdock, 2009)	Green, fat
Decanoic acid	334-48-5	64.978	2285	2277	60, **129**, 172	0.9923	12.4–3500	d$_{19}$-Decanoic acid	1000 (Ferreira et al., 2000)	Rancid, fat
Dodecanoic acid	143-07-7	68.432	2482	2479	**73**, 129, 157	Equivalent to decanoic acid		d$_{19}$-Decanoic acid	6100 (Meilgaard, 1975)	Metal

[a] RI values were obtained from Aroma Office 2D.

[b] Calculated retention index (CRI) based on alkanes (C7–C40) analysed in this study.

[c] The bolded ion was used as the quantifier.

[d] Spans from the LOQ to the highest calibrant used.

[e] Reference given in parentheses. Thresholds are reported for aqueous ethanol except for Swiegers et al. (2005) and Ferreira et al. (2000), which were in a wine matrix.

[f] Obtained from flavornet (http://www.flavornet.org) by Terry Acree and Heinrich Arn, except where specified.

[g] Refers to Swiegers et al. (2005).

[h] Refers to Ferreira et al. (2009).

[i] Refers to Mayr et al. (2014).

[j] Refers to Peinado et al. (2004).

[k] Obtained from the Good Scents Company, http://www.thegoodscentscompany.com.

[l] Ions from Eggers et al. (2006).

[m] Refers to Schulte-Elte et al. (1978), and Umano, Shoji, Hagi, and Shibamoto (1986).

[n] Refers to Moyano et al. (2002).

3. Results and discussion

3.1. Descriptive sensory analysis of 26 rosé wines

Panellists identified 13 aroma attributes and 12 flavour attributes that defined the sensory properties of the various rosé wines. Significant differences among the 26 wines were established for 23 of those 25 attributes (Table 2 and Supporting information, Table S4). Aromas associated with tropical fruit, citrus, spicy and reduced, and overall aroma intensity, were highly significantly different ($p < 0.001$) among the wines, as were most flavour attributes, whereas fresh green and reduced were not significantly different.

Fig. 1 displays the scores and loadings from the PCA of sensory data for each wine sample, showing the first two principal components, which accounted for 53% of variation in the data (although modest, this level of explained variance is reasonable for a diverse set of commercial wines). As expected, the majority of the aroma attributes were positioned closely to their corresponding flavour terms (Fig. 1a) (Aubry, Schlich, Issanchou, & Etiévant, 1999). The first principal component separated samples which were fruity, floral and confectionery from those that exhibited reduced, savoury, and spicy characters. Samples with tropical and citrus attributes were differentiated along PC2 from those that were spicy, savoury or had other fruit characters. A positive correlation between red fruit and overall intensity was observed for aroma and flavour, which indicated the large contribution of red fruit characters to the overall sensory expression of all wines. Citrus flavour was clearly separated from other descriptors, including citrus aroma. This suggested that the general perception of citrus on the nose and palate was not solely driven by simple orthonasal/retronasal perceptions of the citrus character, and wine acidity may have contributed to the panel's rating of citrus flavour intensity.

Wines were relatively dispersed within the PCA score plot (Fig. 1b), indicating variation in terms of both the sensory profiles and wine styles covered within this sample set, although some clustering could also be observed. Wines 1, 6, 7–11, 16, 21, 23 and 24 were perceived to be higher in red/dark fruit, stone fruit, honey, floral and confectionery characters, and overall intensity. These samples comprised several different varieties (Supporting information, Table S2), indicating those sensory attributes were not variety driven. In comparison, wines 5, 12 and 22 displayed spicy, savoury and oaky characters and less intense tropical and citrus fruits. Wine 5, which was more savoury and smoky, and 22, which was more spicy, primarily consisted of Pinot Noir (Supporting information, Table S2), but neither exhibited characteristic red fruit and stone fruit attributes associated with this varietal (Fang & Qian, 2006), in contrast to 10 (also a Pinot Noir wine). Overall, variation in olfactory profiles among the wines did not appear to reflect differences in grape variety or vintage. Wines 3, 4, 14, 18, and 20 were differentiated but displayed fresh green, yeasty and reduced aromas with less fruity, floral and confectionery attributes, and wines 2, 13, 15, 17, 19, and 26 tended to be less fruit-driven but exhibited citrus flavour. Wine 25 had more intense citrus aroma and tropical fruit aroma and flavour, whereas wines situated closest to the x-axis (e.g. 3, 4, 7, 11, 16, and 20) had attributes associated with PC2 that were either not prominent or were rated relatively highly in the characters loaded in both positive and negative directions (Supporting information, Table S4).

On the basis of descriptions above and the results shown in Fig. 1, the sensory profiles of these rosé wines related broadly to characters consisting of tropical fruit and citrus; reduced, yeasty and fresh green; savoury, oaky and spicy; red/dark fruits, floral and confectionery.

3.2. Analysis of aroma volatiles by GC–MS and HPLC–MS/MS

Although one sample preparation technique cannot be thought of as universal for analysis of analytes in complex matrices (Boyaci et al., 2015), based on its simplicity an HS-SPME–GC–MS method with full scan MS was applied using standard extraction techniques (Mendes et al., 2012; Paula Barros et al., 2012). A recently developed HPLC–MS/MS method was used specifically for determination of polyfunctional thiols in wine (Capone et al., 2015). This

Table 2
Results of sensory descriptive analysis (DA) for 26 rosé wines[a].

Attribute	Minimum	Maximum	Median	Mean	SD[b]	Significance[c]
Tropical fruit	2.89	8.16	6.13	6.00	1.40	***
Red/dark fruit	3.21	6.61	4.74	4.80	0.86	*
Floral	1.73	4.83	3.06	3.09	0.88	*
Citrus	2.71	5.52	4.00	3.91	0.79	**
Stone fruit	1.60	4.18	2.68	2.76	0.69	*
Fresh green	0.83	3.91	1.52	1.60	0.65	*
Spicy	1.05	5.18	2.21	2.58	1.06	***
Confectionery	2.01	5.67	3.10	3.14	0.79	*
Honey	0.98	3.98	1.58	1.76	0.66	*
Yeasty	0.73	2.64	1.33	1.47	0.47	*
Oaky/smoky	1.48	4.36	2.56	2.63	0.83	*
Reduced	0.89	3.99	2.14	2.16	0.93	**
Overall intensity	6.33	9.84	8.28	8.20	1.02	***
f-Tropical fruit[d]	3.05	8.45	6.12	5.90	1.13	***
f-Red fruit	4.10	7.90	5.55	5.82	1.16	***
f-Floral	1.21	3.45	2.03	2.13	0.58	**
f-Citrus	3.79	8.84	5.85	5.93	1.11	***
f-Stone fruit	1.88	5.01	2.88	3.10	0.98	***
f-Fresh green	0.96	3.27	1.85	1.88	0.48	ns
f-Spicy	0.69	4.01	1.67	1.82	0.81	***
f-Confectionery	1.48	4.11	2.67	2.59	0.74	***
f-Honey	0.72	3.30	1.25	1.38	0.61	**
f-Savoury	0.81	2.59	1.44	1.49	0.42	*
f-Reduced	1.02	2.73	1.79	1.68	0.48	ns
f-Overall intensity	7.05	10.33	8.83	8.73	0.89	***

[a] Evaluated on a 0–15 scale.

[b] SD, standard deviation.

[c] Significant differences among wines: $^{*}p < 0.05$; $^{**}p < 0.001$; $^{***}p < 0.0001$; ns, not significant.

[d] The suffix f- is used to differentiate flavour attributes.

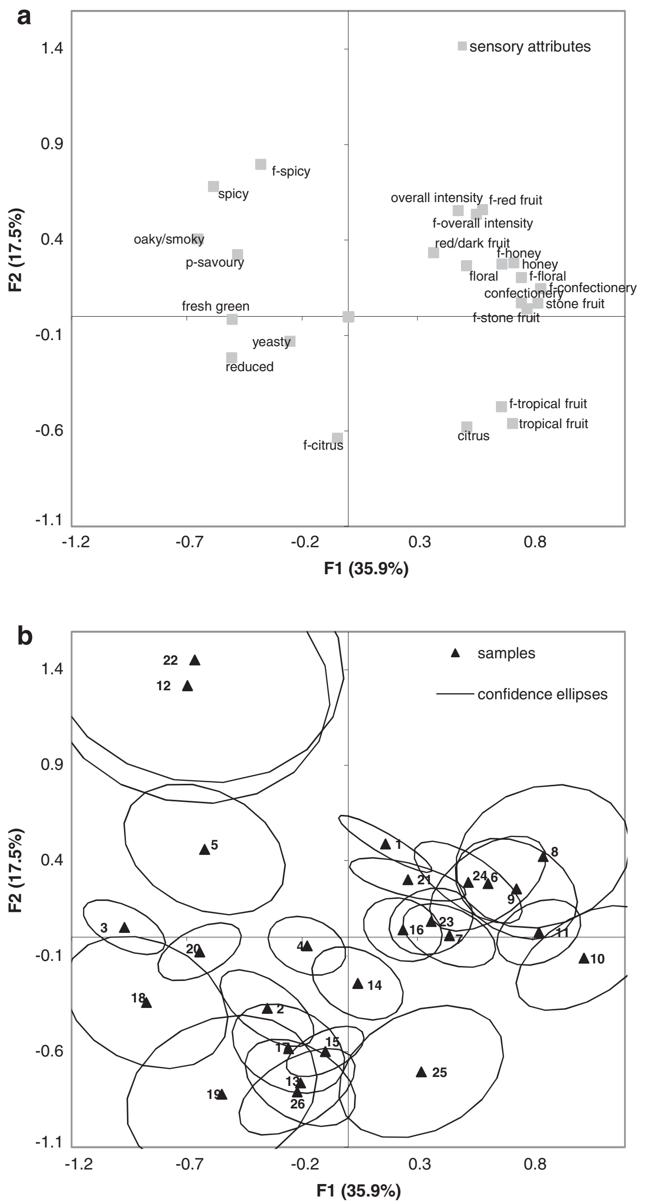

Fig. 1. PCA plots generated from DA data (mean values of significantly different sensory attributes) for 26 rosé wines showing (a) loadings and (b) scores with 95% confidence ellipses. Sample labels relate to the different wines described in the text. The letter f in front on an attribute designates it as a flavour term.

method involved derivatisation of thiols with DTDP directly in wine and recovery of the derivatives by SPE followed by concentration and analysis by HPLC–MS/MS with multiple reaction monitoring. A total of 51 compounds were quantified across 26 rosé wine samples and analyte concentrations are summarised with a number of descriptive statistics in Table 3 (comprehensive data for the individual wines appear in Supporting information, Tables S5 and S6). The HS-SPME–GC–MS method was calibrated and validated for 35 volatile compounds in rosé wine and the remaining 12 were semi-quantified by expressing them as equivalent to either another calibrated analyte or a labelled internal standard (Table 1). Calibrations were linear throughout the concentration range with R^2 values of 0.99 or greater. Precision at low and high concentrations ranged from 8% to 21% and recoveries generally varied between 90% and 110%. LOQ values were frequently below the reported aroma detection thresholds for the analytes.

Of the compounds determined, almost half comprised ethyl and acetate esters, which are typically associated with fruity and floral aromas (Darici et al., 2014; Ferreira et al., 2002; Masson & Schneider, 2009) (Table 1). A number of alcohols were identified, in particular 2-phenylethanol, which was deemed responsible for rose notes in both Grenache (Ferreira et al., 2002) and Çalkarası (Darici et al., 2014) rosé wines. Limonene, linalool, α-terpineol, β-citronellol and β-damascenone were also detected. Apart from limonene, which imparts a lemon or orange aroma, in general these compounds are responsible for floral characters in wine (Clarke & Bakker, 2011) (Table 1). Specifically, β-damascenone was found to be one of the key aroma compounds associated with fruity characters in Provence rosé wine (Masson & Schneider, 2009), and it might also act as a fruity aroma enhancer in Prieto Picudo (Álvarez-Pérez et al., 2012) and Grenache (Ferreira et al., 2002) rosé wines. Several volatile fatty acids were also present (Table 3) and these compounds tend to have a negative effect on wine aroma, contributing green and fatty/rancid aromas (Table 1) (Clarke & Bakker, 2011). Four polyfunctional thiols were quantified (Table 3), particularly 3-MH and 3-MHA, which have been considered as key aroma compounds with fruity and citrus notes in several rosé wine studies (Darici et al., 2014; Masson & Schneider, 2009).

Except for linalool, nonanal, 3-methylbutyl octanoate, and 3-methylbutyl hexanoate (4-MMP was not detected), the concentrations of the other 47 compounds were significantly different among the wines (Table 3). For major volatiles, the concentrations of ethyl acetate, 1-propanol, 3-methyl-1-butanol and 1-octanol were above their aroma detection thresholds in all samples, indicating a direct impact on the aroma characters of these wines. On the other hand, compounds such as 2-methyl-1-propanol, limonene, furfural, 2-ethyl-1-hexanol, benzaldehyde, vitispirane, ethyl nonanoate, ethyl furoate, 3-methylbutyl octanoate, diethyl succinate, α-terpineol, 1-decanol, ethyl 2-phenylacetate, ethyl dodecanoate, nonanoic acid and dodecanoic acid were present below their corresponding aroma detection thresholds, implying little contribution to the sensory profiles on an individual compound basis. The remaining volatiles were often determined at suprathreshold concentrations so were very likely to influence the aroma of the wines. For instance, the concentration of hexyl acetate, which has a fruity and floral aroma (Table 1), was above its aroma detection threshold in the majority of samples (Supporting information, Table S5) with a mean value of 2603 μg/L (Table 3), and β-citronellol, which imparts citrus characters (Table 1), was close to or above its threshold in about half the wines (Supporting information, Table S5) with a mean value of 62 μg/L (Table 3). Other than highlighting these examples, which point to the relevance of additional compounds being of importance to rosé wine aroma, the discussion below focuses on the compounds that have previously been reported to be of greatest significance to rosé wine.

The concentration of β-damascenone ranged from not detected (i.e., <0.13 μg/L) to 29.7 μg/L (Table 3), in agreement with previous rosé wine studies (Darici et al., 2014; Ferreira et al., 2002; Masson & Schneider, 2009). Generally the concentration of β-damascenone in the wines studied (mean of 4.6 μg/L) was much larger than its aroma detection threshold of 0.05 μg/L (in 10% aqueous ethanol (Guth, 1997)). 3-Methylbutyl acetate, which had the largest odour activity value (OAV, i.e., concentration ÷ aroma detection threshold) in a Çalkarası rosé wine (Darici et al., 2014) with a concentration of 3509 μg/L (OAV = 117), was found in our work at a maximum concentration of 8523 μg/L (mean of 3005 μg/L, Table 3). This suggested a positive contribution from 3-methylbutyl acetate to the fruity sensory profiles of the majority of the wines, based on its aroma detection threshold of 30 μg/L (in 10% aqueous ethanol (Guth, 1997)). The concentration of ethyl hexanoate, which had

Table 3
Concentrations (µg/L)[a] of volatile compounds determined in 26 rosé wines.

Compound	Minimum	Maximum	Median	Mean (OAV)	SD[b]	Significance[c]
Ethyl esters						
Ethyl butanoate	ND[d]	560	257	255 (13)	172	***
Ethyl 2-methylbutanoate	ND	178	0	30.3 (30)	51.7	***
Ethyl 3-methylbutanoate	ND	395	67.5	89 (30)	88	***
Ethyl 2-butenoate	ND	220	127	130 (-)	55.5	***
Ethyl hexanoate	ND	1885	843	875 (62)	587	***
Ethyl 2-hexenoate	ND	29.9	1.5	4.4 (–)	7	***
Ethyl lactate	ND	203080	9979	24611 (0.2)	41491	***
Ethyl octanoate	ND	6787	2492	2704 (135)	1620	***
Ethyl nonanoate	0.57	67.4	2.4	7.3 (<0.01)	14.5	***
Ethyl furoate	ND	69.4	0	4.5 (<0.01)	13.7	***
Ethyl decanoate	153	5618	3249	2979 (15)	1431	***
Diethyl succinate	ND	9039	0	1334 (<0.01)	2510	***
Ethyl 9-decenoate	ND	162	0	9.6 (–)	32	***
Ethyl 2-phenylacetate	ND	35.8	3.1	5.5 (<0.01)	7.3	***
Ethyl dodecanoate	ND	326	114	134 (0.3)	86.9	***
Acetate esters						
Ethyl acetate	74639	265274	192966	185440 (12)	47452	***
3-Methylbutyl acetate	ND	8523	2380	3005 (100)	2830	***
Hexyl acetate	49.7	8429	1930	2603 (4)	2501	***
2-Phenylethyl acetate	ND	675	110	173 (0.7)	177	***
Other esters						
Methyl octanoate	ND	13	6.2	5.9 (1.5)	4.5	***
3-Methylbutyl hexanoate	ND	14.8	2.4	3.4 (–)	3.8	ns
Methyl decanoate	ND	7.6	0.039	1.4 (–)	2	***
3-Methylbutyl octanoate	ND	81.4	1145	16.7 (0.1)	20.8	ns
Alcohols						
1-Propanol	7279	24754	12614	13362 (27)	5065	***
2-Methyl-1-propanol	1039	12471	2804	3620 (0.1)	2565	***
3-Methyl-1-butanol	65685	206723	101708	109343 (4)	29098	***
1-Hexanol	641	12269	4324	4982 (0.6)	2670	***
2-Ethyl-1-hexanol	16.9	104	55.1	57.9 (<0.01)	19	*
1-Octanol	4.5	95.2	27.6	28.7 (41)	18.4	***
1-Decanol	ND	108	0	4.9 (<0.01)	21.1	***
2-Phenylethanol	2972	22479	7298	7609 (0.5)	3871	***
Isoprenoids						
Limonene	ND	1.8	0	0.55 (0.04)	0.70	**
Linalool	ND	248	56.7	66.6 (4)	58.1	ns
α-Terpineol	8.1	68.4	33.3	34.6 (0.1)	14	***
β-Citronellol	7.7	147	58.5	62.2 (0.6)	34.7	***
Vitispirane (sum of isomers)	0.17	3.8	0.84	1.4 (<0.01)	1.1	***
β-Damascenone	ND	29.7	1.3	4.8 (96)	8.6	***
Acids						
Acetic acid	99387	348820	150477	165323 (0.8)	59923	***
Hexanoic acid	ND	6570	2533	2894 (7)	2054	***
Octanoic acid	ND	5101	2019	1974 (4)	1623	***
Nonanoic acid	ND	893	502	430 (0.1)	279	*
Decanoic acid	38	3178	1975	1883 (2)	846	***
Dodecanoic acid	ND	143	50.3	54.9 (<0.01)	34.3	***
Carbonyls						
Nonanal	ND	43.9	18.4	19.8 (8)	10.7	ns
Furfural	ND	1414	80.3	149 (0.01)	280	***
Benzaldehyde	ND	160	2	25.1 (0.1)	44.6	***
Thiols						
3-MH (ng/L)	215	3250	502	713 (12)	656	***
3-MHA (ng/L)	ND	8.4	-	1.2 (0.3)	2.3	***
FT (ng/L)	ND	21.1	2.7	3.2 (8)	4.0	***
BM (ng/L)	1.3	5.3	2.5	2.7 (9)	1.1	***
Other						
1-Methyl-4-(prop-1-en-2-yl)benzene	ND	14.6	1.8	3.2	3.6	***

[a] In µg/L except where specified otherwise. Results are derived from the mean of duplicate determinations (Supporting information, Tables S5 and S6).
[b] Standard deviation.
[c] Significant differences among wines: $^{*}p < 0.05$; $^{**}p < 0.001$; $^{***}p < 0.0001$; ns, not significant.
[d] ND, not detected (below LOD).

an OAV around 40 in both Çalkarası (638 µg/L) (Darici et al., 2014) and Grenache (542 µg/L) (Ferreira et al., 2002) rosé wines, ranged from not detected (i.e., <0.11 µg/L) to 1885 µg/L in our wines, with the mean value of 875 µg/L (Table 3) easily exceeding its aroma detection threshold of 14 µg/L (in model wine matrix (Ferreira, López, & Cacho, 2000)). On the other hand, 2-phenylethyl acetate (aroma detection threshold of 250 µg/L in 10% aqueous ethanol (Guth, 1997)) ranged from not detected (i.e., <0.97 µg/L) to

675 μg/L (mean of 173 μg/L, Table 3) and was found at suprathreshold concentrations in only a small number of wines (Supporting information, Table S5). This contrasted with the potential importance of 2-phenylethyl acetate to rosé wine aroma, although our results were within the range of concentrations reported for Çalkarası (1926 μg/L) (Darici et al., 2014) and Grenache (81 μg/L) (Ferreira et al., 2002) rosé wines.

Regarding polyfunctional thiols, 3-MH and 3-MHA (along with FT and BM) were detected and quantified in a range of wines (Table 3). Whereas 3-MH featured routinely, 3-MHA was often not detected and 4-MMP was absent from this set of wines, yet this was not too surprising considering thiols can decrease rapidly during rosé wine storage (Murat, 2005). The typical concentrations of these compounds in wine are extremely low (several ng/L to around 20 μg/L) (Dubourdieu & Tominaga, 2009 and citations therein; Swiegers et al., 2005), but given their correspondingly low aroma detection thresholds, tropical characters are usually apparent in wines where these thiols are present (Dubourdieu & Tominaga, 2009 and citations therein). Using a simple and unique HPLC–MS/MS method, these thiols were quantified at ng/L levels, and the concentration of 3-MH in all samples (mean of 710 ng/L) was above its aroma detection threshold (60 ng/L (Dubourdieu & Tominaga, 2009)); wines 1 (OAV = 35), 5 (OAV = 20) and 15 (OAV = 53) had higher concentrations (Supporting information, Table S5) than reported in previous studies of rosé wines (Darici et al., 2014; Masson & Schneider, 2009). FT and BM, which have descriptors of roasted coffee and smoke, respectively, were detected in most samples at concentrations above their aroma detection thresholds (0.4 ng/L for FT and 0.3 ng/L for BM (Dubourdieu & Tominaga, 2009)), with an extreme example, wine 1, having the largest OAV for FT of 53.

Overall, the results for volatiles analysis indicated that a range of wines had considerable concentrations of a number of compounds that contribute floral and fruity characters. PCA of the volatile composition of the 26 wines explained 70% of the variance with the first four principal components retained. Fig. 2 shows the first two components, which explained 43% of the variance. As with the PCA of sensory data, samples were spread across the bi-plot but some wines clustered together. According to the loading data, the first PC was mainly driven by ethyl decanoate, and octanoic and decanoic acids in the positive direction and by ethyl 2-methylbutanoate, diethyl succinate, and ethyl 3-methylbutanoate in the negative direction. The second PC was mainly driven by vitispirane, α-terpineol and β-citronellol in the positive direction, and by ethyl 2-hexenoate, ethyl nonanoate and dodecanoic acid in the negative direction. Also, positive loadings for 3-MH and 3-MHA were observed in PC1 and PC2 separately, which suggested there was no correlation between these two thiols among the samples.

Wines 2, 4 and 8 were relatively high in ethyl esters of butanoic, hexanoic, and octanoic acids, along with methyl decanoate and octanoic acid but lower in alcohols such as 2-methyl-1-propanol and 2-phenylethanol. Wines 3, 5, 12, 20 and 22 (the most distinct) were higher in ethyl lactate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl phenylacetate and diethyl succinate, having less acetate esters. Wines 6, 7, 9, 10, 11, 13 and 26 were located together, being higher in ethyl decanoate, decanoic acid and 3-MHA, and having less diethyl succinate and 2-methyl-1-propanol, among other volatiles. Wine 1 was characterised as having higher amounts of vitispirane, α-terpineol, β-citronellol, FT and 3-MH, whereas in the opposite direction wines 14 and 23 had higher amounts of β-damascenone, benzaldehyde and some

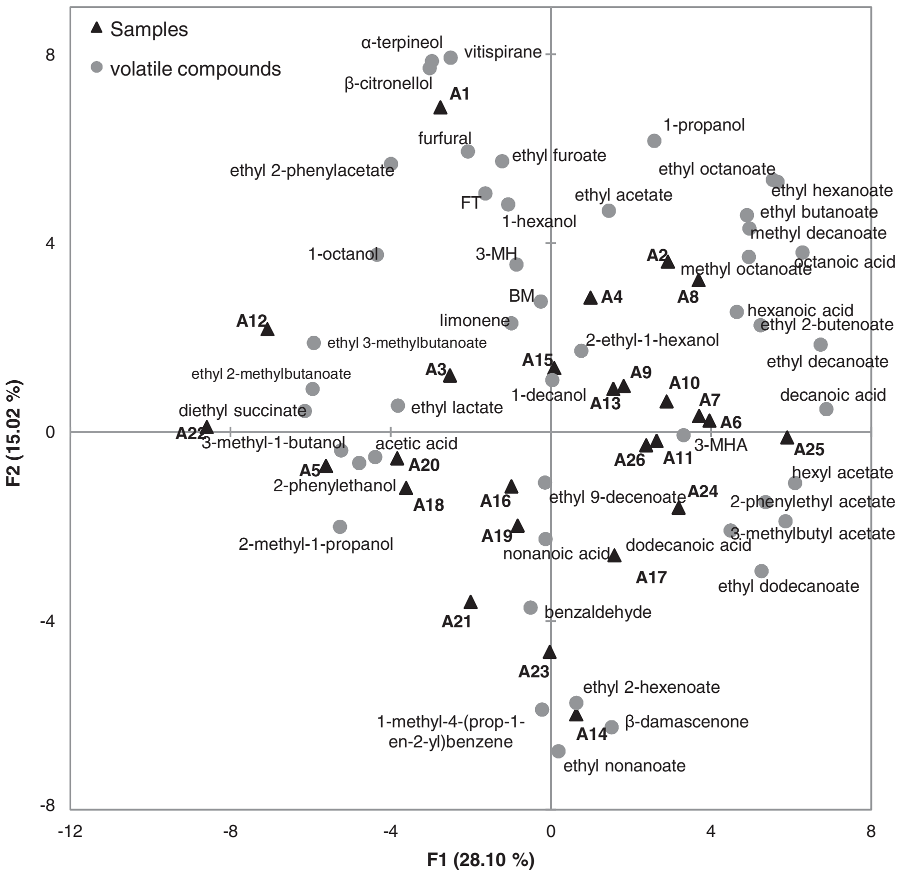

Fig. 2. PCA bi-plot generated from the volatile composition for 26 rosé wines.

ethyl esters. Wines 15, 16, 18, 19, and 21 were characterised by several higher alcohols and volatile acids, whereas the remaining samples on the right (e.g., 17, 24, 25) had greater concentrations of ethyl and acetate esters.

Referring briefly to PC1 vs. PC3 (not shown, 10.9% of the variance explained), only sample 1 was separated from other samples along PC3 in the positive direction, with higher amounts of ethyl furoate, furfural, benzaldehyde, FT and BM. Interestingly, furfural and benzaldehyde may be related to FT and BM, respectively, through putative formation pathways; FT may arise from addition of H_2S to furfural (Blanchard, Tominaga, & Dubourdieu, 2001), and although inconclusive, BM may similarly occur from H_2S and benzaldehyde. Some other samples, such as 2, 11, 12, and 22, which had more 3-methyl-1-butanol, 2-phenylethanol and ethyl butanoate, were separated in the negative direction on PC3 to a small extent.

Focusing only on the most extreme samples, 5 and 15 clearly stood out when assessing PC1 vs. PC4 (not shown, 7.6% of the variance explained), and were characterised mostly by higher amounts of benzaldehyde, acetic acid, 3-MH, BM, ethyl lactate, 2-ethyl-1-hexanol, limonene and nonanoic acid. The negative direction of PC4 was associated with dodecanoic acid, 1-hexanol, methyl octanoate and β-damascenone, where wines 7, 12, 17 and 24 were located, whereas in general other samples were separated along PC1.

Some compounds, such as 2-methyl-1-propanol, ethyl decanoate, α-terpineol and vitispirane, were detected in most samples, but at concentrations below their respective aroma detection thresholds. However, they had a relatively large loading on PC1 or PC2 and were determined to be compounds which could differentiate samples on the basis of volatile composition. Furthermore, these compounds may influence the perception of other aromas, for example through additive effects, as in the case of various esters (Ferreira, López, Escudero, & Cacho, 1998), thereby impacting the overall aroma profile of the wines.

3.3. Relating wine composition and sensory data by PLS regression

Volatile composition, basic chemical parameters and DA data determined for 26 rosé wines were analysed through PLS regression to explore their underlying relationships, rather than to construct a predictive model. This approach with PLS has been used as a useful tool to evaluate mixed sensory and chemical data sets, for example in Sauvignon blanc wines (Benkwitz et al., 2012). Two components were chosen to build the PLS model, and based on the VIP scores (data not shown), 33 of the 51 significantly different wine compositional parameters made good contributions to the PLS model (VIP > 0.8) (Eriksson et al., 2001) and were reanalysed by PLS regression. The first two principal components explained 48% of the variation in wine composition (*x*-variables,) and 38% of the variation in sensory properties (*y*-variables).

Wines clustered together based on their chemical and sensory profiles (Fig. 3). PLS component 1 contributed to the spread of samples (score plot, Fig. 3a) on the left side of the plot mainly based on the intensity of fresh green, spicy, oaky, savoury and reduced attributes (correlation loadings plot, Fig. 3b), as opposed to samples on the right which generally had more citrus, stone fruit, tropical fruit, floral and confectionery characters for both aroma and flavour. PLS component 2 separated samples vertically, primarily based on citrus, fresh green, tropical fruit and reduced attributes in the lower section, and spicy, red/dark fruits, floral and confectionery characters, and overall intensity in the upper section.

Two wines located in the top left quadrant (Fig. 3a) mostly exhibited more developed aromas and flavours such as spicy and savoury (Fig. 3b), and wines in the bottom left quadrant had fresh green, reduced, yeasty and oaky characters. Those in the bottom right quadrant were mostly perceived as having citrus and tropical fruit characters, whereas wines appearing in the top right quadrant (Fig. 3a) displayed stone fruit, confectionery, floral, honey and red/dark fruit attributes (Fig. 3b).

Aroma attributes on the left of the plot were mainly developed characters such as savoury, oaky/smoky, and spicy in particular, which was strongly positively correlated with diethyl succinate, ethyl 2- and 3-methylbutanoate and a number of alcohols, such as 3-methyl-1-butanol, 2-methyl-1-propanol, and 2-phenylethanol (Fig. 3b). These developed characters were negatively correlated with decanoic and octanoic acids, and most esters, including medium chain fatty acid ethyl esters and acetates. For those sensory attributes on the right of the plot, citrus aroma and tropical fruit aroma/flavour were positively correlated (strongly in the case of tropical descriptors) with medium chain fatty acids and ethyl esters, and in general the compounds on the right contribute fruity and floral characters to wines (Darici et al., 2014; Ferreira et al., 2002; Masson & Schneider, 2009).

Red/dark fruits, stone fruit, floral and confectionery attributes were dominant in the upper right quadrant of the plot. Red/dark fruit and floral did not correlate with compounds that can be associated with these types of traits. Monoterpenoids such as α-terpineol and β-citronellol derived from the grapes can contribute to the floral character of wines (Swiegers et al., 2005), while red/dark fruit aromas can be related to ethyl and acetate esters arising from fermentation (Lytra, Tempere, Revel, & Barbe, 2012). In contrast, confectionery aroma was positively related to ethyl and acetate esters, with a strong correlation with 3-methylbutyl acetate, which accords with the relationship determined between esters and confectionery aroma using a PLS model for Sauvignon blanc wine (King, Osidacz, Curtin, Bastian, & Francis, 2011). Similarly, stone fruit was positively correlated with 3-methylbutyl acetate and to a lesser extent with other esters.

Two volatile sulfur compounds, BM and 3-MHA, were projected in the PLS model. BM had the largest loading on the vertical axis and was negatively correlated with fruit and floral characters, but positively related to reduced and yeasty aromas, with the latter potentially relating to the evolution of this compound (Fig. 3b). 3-MHA was positively correlated with stone fruit attribute, in agreement with a study of Sauvignon blanc wine, although it was not related to its usual role of contributing tropical characters (Lund et al., 2009). A fair proportion (35%) of the chemical components quantified were not well modelled by PLS (based on VIP values), possibly due to their high aroma detection thresholds and relatively low concentrations; for example, 1-hexanol and 1-propanol were frequently encountered at concentrations far below their respective aroma detection thresholds of 8000 μg/L (in 10% aqueous ethanol (Guth, 1997)) and 500,000 μg/L (in wine (Swiegers et al., 2005)) (Supporting information, Table S5). In contrast, 3-MH was not well modelled despite having a very low aroma detection threshold, presumably because the concentration in most samples was relatively high so as not to differentiate much among them. Furthermore, some compounds which were not well modelled may not have an individual sensory contribution but could mask or enhance other aroma compounds. Alternatively, these compounds might be perceived in certain wines as the result of synergistic effects or other interactions (Ferreira et al., 2002; Lytra et al., 2012), and could not be discounted in terms of potential importance to rosé wine aroma.

4. Conclusions

In summary, this was the first detailed study of rosé wines from Australia, a new world winemaking country with an absence of chemical and sensory data on rosé wines. Specifically, this work

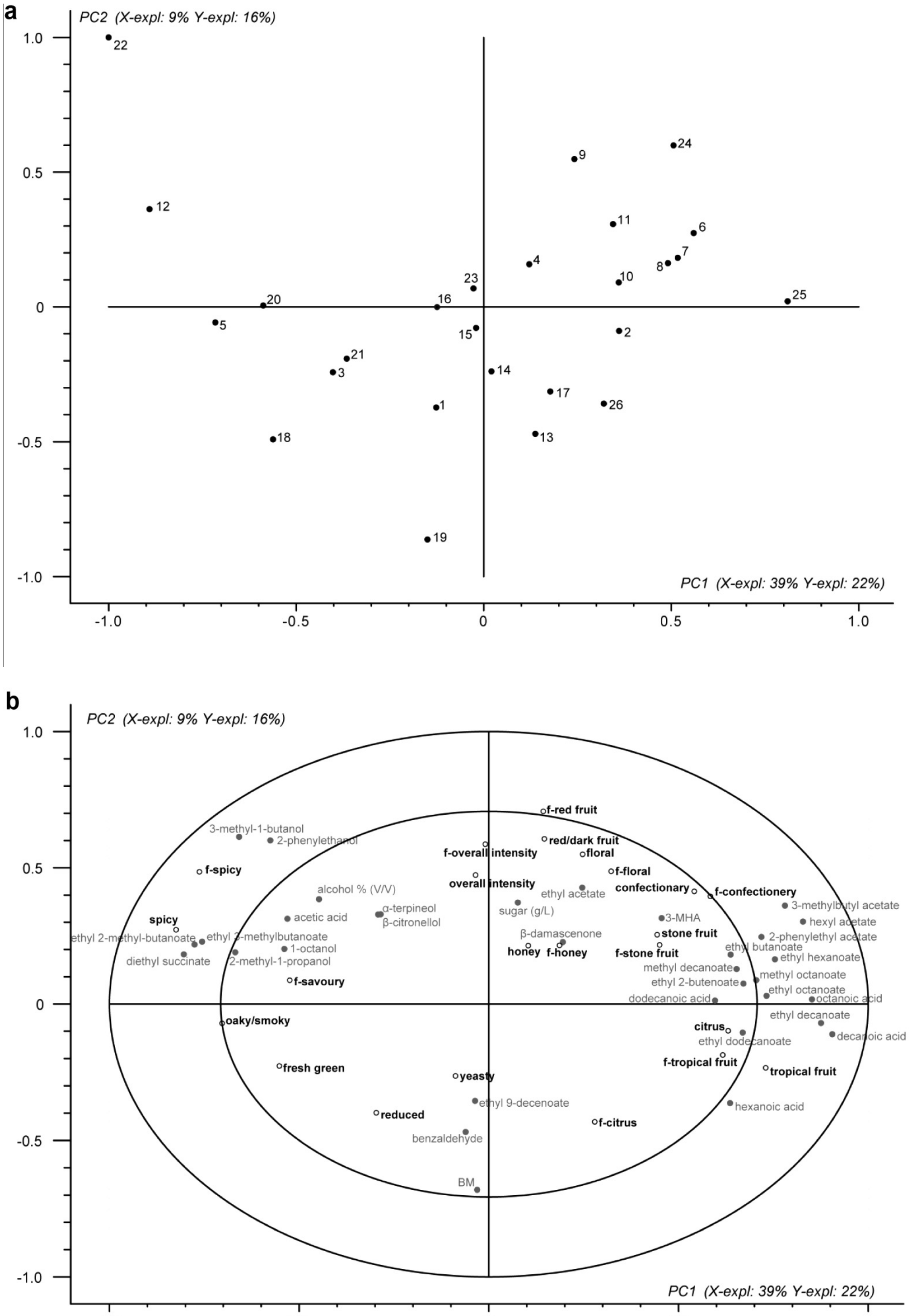

Fig. 3. PLS regression plots of standardised volatile aroma compounds ($p < 0.05$) as x-variables and standardised sensory attributes ($p < 0.05$) as y-variables showing (a) scores for wine samples, and (b) correlation loadings between chemical and sensory data showing the 50% (inner) and 100% (outer) explained variance limits.

involved comprehensive evaluation of 26 commercial rosé wines, which underwent descriptive sensory analysis and determination of 51 volatile compounds, including 4 potent sulfur compounds. Among the range of aroma compounds reported, of which almost half were fruity and floral acetate and ethyl esters, and based on OAV, components such as β-damascenone, 3-methylbutyl acetate and ethyl hexanoate were deemed to be important, in accord with other studies. 3-MHA seemed to be more significant than 3-MH in terms of characterising wine styles, yet 3-MH was found with a high OAV in a number of wines, and together the results were consistent with the reported contribution of these thiols to rosé wine aroma. As a result of the composition of aroma volatiles (a range of which are described in this work), some rosé wines tended to show developed, green and citrus characters with some tropical fruit, a selection were floral and fruit-driven, others displayed tropical and citrus notes, and the remainder were oaky and spicy but with fruity and floral characters.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2015.09.111.

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Chapter 3

Rosé wine volatile composition and the preferences of Chinese wine professionals

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iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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Name of Co-Author	Kerry L. Wilkinson		
Contribution to the Paper	Supervised the work, contributed to the research idea and sensory analysis design, and editing of the manuscript.		
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Rosé wine volatile composition and the preferences of Chinese wine professionals

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ABSTRACT

Rosé wine aromas range from fruity and floral, to more developed, savoury characters. Lighter than red wines, rosé wines tend to match well with Asian cuisines, yet little is known about the factors driving desirability of rosé wines in emerging markets such as China. This study involved Chinese wine professionals participating in blind rosé wine tastings comprising 23 rosé wines from Australia, China and France in three major cities in China. According to the sensory results, a link between the preference, quality and expected retail price of the wines was observed, and assessors preferred wines with prominent red fruit, floral, confectionery and honey characters, and without developed attributes or too much sweetness. Basic wine chemical parameters and 47 volatile compounds, including 5 potent thiols, were determined. Correlations between chemical components, sensory attributes and preference/quality/expected price were visualised by network analysis, revealing relationships that are worthy of further investigation.

1. Introduction

Rosé wine is produced from red grape varieties such as Cabernet Sauvignon, Grenache and Pinot Noir, but without the extensive maceration on grape solids that is usually associated with red winemaking. This produces "blush" coloured wines of different styles, with vibrant fruit and floral characters, or more spicy and savoury notes, and varying levels of residual sugar (sweetness), balanced by the acidity of the wine. These sensory aspects are important to wine quality and are underpinned by the chemical constituents arising from the grapes, fermentation and maturation. In particular, volatile compounds impacting on wine aroma can be related to quality judgements of wine (Sáenz-Navajas et al., 2015).

Rosé wine, which accounted for about 9% of the world's wine production (24.1 million hectolitres in 2011) (FranceAgriMer, 2013), is becoming more popular around the world, with global consumption increasing by about 17% in the decade to 2012. France is the leading producer of rosé wine, followed by Italy, the United States of America and Spain, which together account for almost three quarters of global production (FranceAgriMer, 2013). Furthermore, Europeans are the largest consumers of rosé

Abbreviations: DA, descriptive analysis; TA, titratable acidity; PCA, principal component analysis; PC, principal component; NA, network analysis.

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wine (with France accounting for about half this volume), but interest has grown significantly in New World wine countries as well; e.g. in 2011, 12.9% of world rosé consumption was attributed to the United States of America (FranceAgriMer, 2013). Rosé wine has even grown to about 60% of all wine consumption in smaller countries like Tunisia or Uruguay (FranceAgriMer, 2013). In keeping with the global popularity of rosé wines, events have been held during the summer months in Australia to promote chilled rosé wine as an alternative to white wine. Although aimed at local consumers, emerging global markets also need to be better understood and targeted further.

Over the past ten years Asia has become one of the main focal points for wine producers because of the great potential it offers in terms of the sheer volume of consumers. Being a relatively new market requires effective promotional strategies, which may be regarded as a wine producer's top priority, but this requires knowledge of consumer preferences and expectations (Lockshin, 2014). Within Asia, China is an obvious choice for producers seeking to expand their consumer base. From 2000 to 2012, wine consumption in China grew 67% (International Organisation of Vine and Wine (OIV), 2013) and 16.8 million hectolitres of wine was consumed in 2013 (International Organisation of Vine and Wine (OIV), 2014). Despite this volume being slightly lower (around 4%) than the figure for 2012, China was still the fifth largest wine importer in 2013 (International Organisation of Vine and Wine (OIV), 2014).

Undoubtedly the Chinese wine market has entered a period of slower progression after the initial dramatic growth. Nonetheless, sales of imported bottled wines are still increasing, likely as a result of a burgeoning middle class and deeper understanding of wine (Lockshin, 2014), thereby suggesting this young market is gradually maturing. For the Australian wine industry, establishing new segments in emerging markets is always important and China is no exception, becoming Australia's third largest market for bottled wine exports (by value) since 2012 (Wine Australia, 2014). As such, developing the exports of Australian rosé wine, which can be characterised by sensory traits (Wang, Capone, Wilkinson, & Jeffery, 2016) likely to be desired by Chinese consumers, should be a focus for the Australian industry. As a starting point, the opinions of Chinese wine professionals, from winemakers and educators, to retailers and journalists, will be influential in understanding this market, but to the best of our knowledge there had been no reports on the impressions of such experts towards rosé wine from Australia or elsewhere to date.

The purpose of this study was therefore to gain the first insight into the preferences of Chinese wine experts towards different rosé wines, through wine tastings conducted in three cities in mainland China. Wines were predominantly from Australia, but several from China and France were included for comparison, and chemical compositions were investigated to correlate the volatile components and basic wine chemistry with sensory outcomes determined by the experts. Results from the study were visualised using a novel application of network analysis to the field of wine science.

2. Materials and methods

2.1. Chemicals

All chemicals, standards and solutions used in this study were the same as specified in a previous study (Wang et al., 2016).

2.2. Wine selection

Twenty-three rosé wines were studied, comprising different grape varieties from vintage 2013 and 2014 (Supporting Information, Table S1). Eighteen Australian rosé wines (provided by producers) were selected as they represented different rosé styles based on the results from previous sensory descriptive analysis (DA) (Wang et al., 2016). Two traditional rosé wines produced in Provence, France were purchased from a bottle shop in Australia and encompassed different price points (AU$9 and AU$45). Three rosé wines originating from two Chinese wine regions were donated by producers and selected based on input from Chinese wine professionals. All wine samples were stored at 15 °C before sensory and chemical analyses. Except for the three Chinese wines, all wines were shipped from Australia with each wine checked for faults before every tasting.

2.3. Basic wine composition

All measurements were performed in duplicate (Supporting Information, Table S1). Ethanol content, titratable acid (TA), pH and residual sugar (glucose + fructose) were determined as described previously (Wang et al., 2016). Malic and lactic acids were measured with an Agilent Series 1100 HPLC (Agilent Technologies, Forest Hill, VIC, Australia) equipped with a vacuum degasser, quaternary pump, thermostated column oven, refractive index detector and diode array detector. Separation was achieved using an Aminex HPX-87H column (300 mm × 7.8 mm; Bio-Rad, Gladesville, New South Wales, Australia) at an operating temperature of 60 °C. The injection volume was 20 μL and the isocratic mobile phase was 2.5 mM aqueous H_2SO_4 at a flow rate of 0.5 mL/min. Data acquisition and processing were conducted with Agilent ChemStation software (Version # 3.0.1 B) and analyte quantitation was performed at 210 nm using external standards.

2.4. Quantitative analysis of aroma volatiles

2.4.1. GC–MS analysis of major volatiles

Solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) was used to identify and quantify major volatiles. Sample preparation, extraction conditions and GC–MS method were the same as previously reported in Wang et al. (2016) and samples were analysed in duplicate. Overall, 42 aroma volatiles were identified based on their retention index (RI) and mass spectral library match; quantitative data was obtained for 36 calibrated compounds, whereas the remainder were semi-quantified and expressed as equivalent to other calibrated compounds.

2.4.2. HPLC–MS/MS analysis of polyfunctional thiols

3-Mercaptohexan-1-ol (3-MH),[1] 3-mercaptohexyl acetate (3-MHA), 4-mercapto-4-methylpentan-2-one (4-MMP), furfurylthiol (FFT) and benzyl mercaptan (BM) were quantified by high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) in duplicate as previously described (Capone, Ristic, Pardon, & Jeffery, 2015).

2.5. Chinese wine professional panel tasting

Sixty-two Chinese wine professionals, who met one or more criteria that defined them as wine experts (Parr, White, & Heatherbell, 2004), were recruited to take part in one of three blind rosé wine tastings conducted in three major cities of China – Beijing

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[1] The correct IUPAC prefix for thiol is now "sulfanyl" as in 3-sulfanylhexan-1-ol (3-SH), 3-sulfanylhexyl acetate (3-SHA) and 4-methyl-4-sulfanylpentan-2-one (4-MSP). "Mercapto" was the previous prefix and is more common in the literature. Both prefixes (and respective abbreviations) are used in current literature when referring to these specific compounds and we have chosen to use the more common terms in this case.

Table 1
Demographics of Chinese wine professionals ($n = 62$) involved in the study.

Age (years)	Under 30 46.8%	30–40 38.7%	41–50 9.7%	51–60 4.8%	
Gender	Male 62.9%	Female 37.1%			
Years of industry experience	Less than 1 4.8%	1–5 51.6%	6–10 37.1%	Over 10 4.8%	Over 30 1.7%
Current job title	Oenologist 17.7%	(Assistant) Winemaker 21.0%	Production 1.6%	Marketing & sales 53.2%	Other[a] 6.5%
Frequency of wine tasting	Daily 16.1%	1–3/wk 56.5%	1–3/mo 25.8%	1–3/yr 1.6%	
Is wine tasting part of your job title	Yes 77.4%	No 22.6%			
Years of professional tasting experience	Less than 1 8.1%	1–5 50.0%	6–10 35.5%	Over 10 4.8%	Over 30 1.6%

[a] Such as viticulturists, sommeliers, trainers.

($n = 20$), Shanghai ($n = 22$) and Xi'an ($n = 20$) – over three consecutive days. Participants were asked to complete a demographics questionnaire as well as to answer wine industry related questions proposed by Hopfer and Heymann (2014). Participants worked in different aspects of the wine industry, either as winemakers, oenologists, wine consultants, wine retailers, wine journalists, viticulture and oenology teachers, and so on (Table 1). An open-ended question was also asked after the demographic details about their impression of Australian wines available in the Chinese market.

An open discussion was conducted before formal evaluation to ascertain the quality and expected characters of rosé wine. Five levels of wine quality (Supporting Information, Table S2) were defined based on the UC Davis 20 points wine judging system, with which participants were familiar. As a consensus, the expected characters of rosé wine were generated (Supporting Information, Table S3). After discussion, tasters were given a reference page that included aroma and flavour attributes summarised from a previous study (Wang et al., 2016). After a brief induction on how to complete the tasting sheet, formal evaluation was conducted. The 23 wines were divided into 6 brackets, comprising 5 brackets of 4 samples and one bracket of 3 samples. Filtered water and unsalted crackers were provided for assessors to cleanse their palate flavour and a short rest followed each group to avoid sensory fatigue. Samples (25 mL) served at 20 °C, with glasses coded with a random three-digit number and presented in a random order within a session determined using Design Express (Qi Statistics, UK). For every sample, participants were asked firstly to refer to a reference page and to select one colour description, and the three most appropriate descriptors for both aroma and flavour. Participants were then asked to assign the sample to one of 5 defined quality categories (Supporting Information, Table S2). Lastly, overall liking using a 9-point hedonic scale (labelled from left to middle to right: "dislike extremely" to "neither like nor dislike" to "like extremely") and expected retail price using a multiple choice question (A. less than 100 Chinese yuan (CNY); B. 100-200 CNY; C. 200-300 CNY; D. more than 300 CNY) were also recorded. All materials in sensory analysis were written in both English and Chinese.

2.6. Statistical analysis

All data were preliminarily processed with Microsoft Excel 2010. For sensory data, the number of times each attribute was selected for a given sample was recorded as the intensity of that attribute. Five quality brackets assigned as A, B, C, D and E during sensory assessment were recoded with points worth 5, 4, 3, 2, and 1, respectively. Overall liking from "dislike extremely" to "like extremely" was recorded from 1 to 9. The A to D options in the expected retail price question were assigned a value of 1–4 in order. All data (basic wine chemistry, volatiles, sensory and others) were analysed by one way analysis of variance (ANOVA) using the statistical package XLSTAT (version 2012.2.02, Addinsoft SARL, Paris, France). The significantly different ($p < 0.05$) means were subjected to Pearson's type principal component analysis (PCA) for sensory and volatiles analysis with preferences, quality and expected retail price data as supplementary variables. The number of principal components retained for PCA was determined from scree plots. Network analysis was conducted on all significantly different variables which had strong positive ($r \geqslant 0.6$) or negative ($\leqslant -0.6$) correlations with each other. Every node was defined as one variable and every edge represented a positive relationship between pairs of variables. The size of each node was proportional to the number of connections (that is, degree) and the thickness of each edge increased following the correlation coefficient value (r) from small to large. The arrow in the end of each edge does not represent any form of directionality. All nodes were processed by modularity function, first based on the algorithm from Blondel, Guillaume, Lambiotte, and Lefebvre (2008), and colourised according to different modularity class. All nodes were distributed in figures using the Fore Atlas 2 layout. The position of each node and the length of each edge were modified in order to achieve a better visualisation and do not represent any information. Network analysis and visualisation was performed using the interactive platform Gephi (Bastian, Heymann, & Jacomy, 2009). All variables were standardised before analysis.

3. Results

3.1. Chinese wine professional panel tasting

3.1.1. Preference, quality and expected retail price

The expert mean ratings for preference, quality and expected retail price (Fig. 1) were significantly different ($p < 0.0001$) according to one way ANOVA. Preference scores differed among the 23 samples, ranging from 5.1 (A6) to 6.5 (A17), which showed that judge preferences for all samples were categorised from "neither like nor dislike" to "like moderately". The mean preference values for Australian ($n = 18$), French ($n = 2$) and Chinese ($n = 3$) rosé wines were 5.7, 5.8 and 6.1, respectively. The mean quality scores ranged from 3.2 to 4.0, and showed a similar trend to the preference scores, with a strong positive relationship of $r = 0.74$. The mean expected price varied between 160 and 240 CNY (approximately AU$30 to AU$50) and also had a strong positive correlation

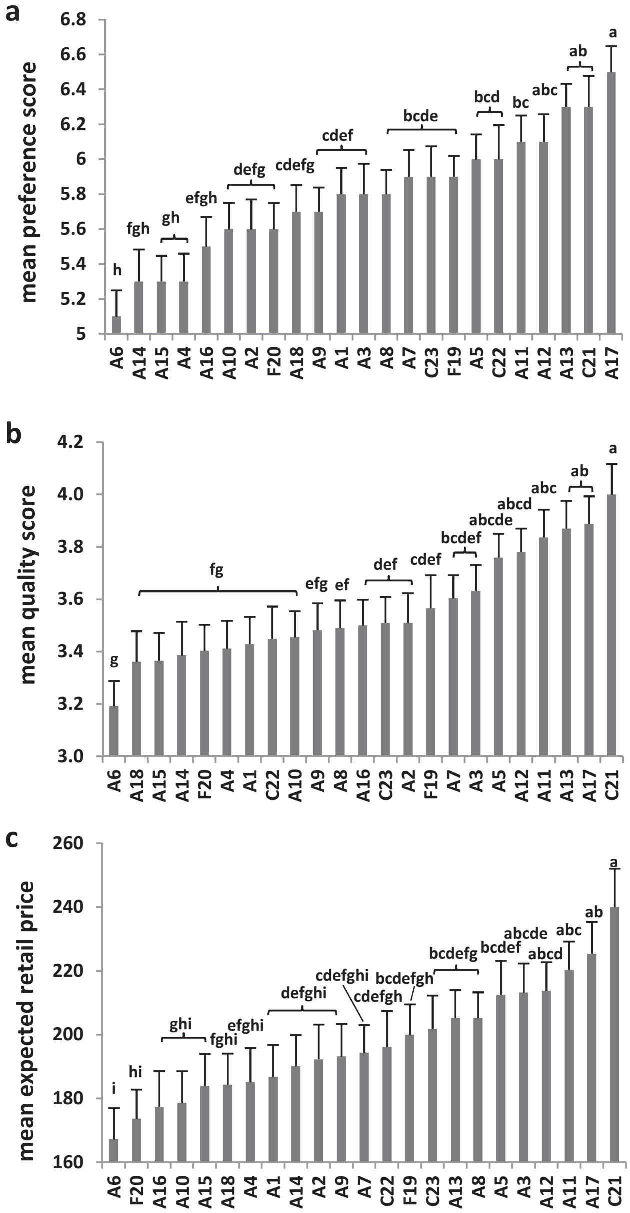

Fig. 1. (a) Mean preference score, (b) mean quality score, and (c) mean expected retail price (units are CNY) for 23 rosé wines. The order of wines is based on increasing scores. Error bars represent the standard error of the mean. Different lowercase letters indicate significant differences ($p < 0.05$) in mean scores according to one way ANOVA ($n = 62$ judges). A = Australia; C = China; F = France.

with mean preference score ($r = 0.69$). Interestingly, the average preference score of male panellists was slightly higher than that of female panellists (5.3 vs. 4.9).

3.1.2. Aroma and flavour sensory attributes

Of the 28 aroma and flavour attributes ascribed by the experts, 19 attributes were rated as significantly different ($p < 0.05$). PCA was conducted on these attributes, with preference, quality and expected retail price data used as supplementary variables (Fig. 2). The first three principal components (PCs) retained could explain 67% of the variance, with the first two PCs explaining 57% of the variation in the data (Fig. 2). The first PC separated wines that had fruity, floral, honey and confectionery attributes (which were positively associated with preference, expected price and quality scores) from those with more citrus, yeasty and developed characters such as savoury, spicy, oaky, earthy and leather. Wines which had developed characters were also differentiated along PC2 from those that were floral, citrus and savoury. In general, variation among the wines did not appear to reflect differences in grape variety or vintage in terms of olfactory profiles. Samples A12, A17 and C22 exhibited more intense red/dark fruit, tropical fruit, honey and confectionery characters; this gave an indication of the rosé style preferred by the judges. Samples A3, A5, A7, A11, A13 and F19 were perceived to be higher in floral characters, whereas A1, A6, A15, A18, F20 and C21, which were all produced in 2013, displayed citrus and savoury attributes. The remaining samples A2, A4, A8-A10, A16, and A14 and C23 in particular, were primarily characterised by developed notes.

A further 10% of variance between samples could be explained by PC3 (Supporting Information, Fig. S1). A11, A14 and C21 had large positive scores along PC3 as a result of spicy and red fruit aromas, and citrus, savory and red fruit flavours. Chinese sample C23, together with A2, A15 and A16, had more intense herbal aroma, and A3 had higher honey flavour, in the negative direction on PC3.

3.2. Volatile compound analysis

Among the 51 volatile compounds determined in a previous study of Australian rosé wines (Wang et al., 2016), 47 were again quantified in the present research (Table 2 and Supporting Information, Table S4). Apart from ethyl acetate, ethyl butanoate, nonanal, isoamyl hexanoate, isoamyl octanoate and nonanoic acid, the remaining 41 compounds were significantly different for the 23 rosé wines (Table 2) and were therefore subjected to PCA. The first 5 PCs retained could explain 67% of the variance observed between the wines. Samples were differentiated based on ester and alcohol concentrations in the first two PCs, which explained around 40% of the variance (Fig. 3). The first PC was driven by esters (hexyl acetate, isoamyl acetate, methyl octanoate and ethyl dodecanoate), some fatty acids (octanoic acid and decanoic acid) and 3-MHA in the positive direction, and by diethyl succinate, 2-methyl-1-propanol, ethyl 2-phenylacetate and 4-MMP in the negative direction on PC1. Ethyl esters of hexanoic, octanoic and decanoic acids had a large loading on PC2 in the positive direction, whereas the negative direction of PC2 was mainly driven by limonene, linalool, furfural and ethyl lactate.

The wines were situated across the four quadrants, except wine C22, which was isolated in the bottom left quadrant, well separated from the other wines (Fig. 3). Wines A5 and A7 had high scores on both PC1 and PC2, due to the presence of ethyl esters, and some fatty acids, such as octanoic and decanoic. Samples A3, A8 and A18 were in the same quadrant and were higher in 1-hexanol, ethyl dodecanoate, ethyl 2-hexenoate, BM and 3-MH. A1, A4, F20 and C21, which were in the top left quadrant, were characterised by higher alcohols (3-methyl-1-butanol, 1-octanol, 1-decanol and 2-phenylethanol), ethyl 2- and ethyl 3-methylbutanoate, diethyl succinate and ethyl 2-phenylacetate. Wines A2, A15 and A16, which were in the same quadrant but closer to the origin, were relatively high in 4-MMP. In the bottom left quadrant, wines A6, A9, A14 and F19 tended to have greater concentrations of two alcohols (2-methyl-1-propanol, 2-ethyl-1-hexanol), monoterpenoids (linalool and limonene), furfural and acetic acid. Samples A10–A13, A17, C23, which incorporated 4 of the top 5 most preferred rosé wines among the 23, were in the bottom right corner, having greater amounts of acetate esters (hexyl, isoamyl and 2-phenylethyl), methyl octanoate, β-damascenone and 3-MHA.

According to the PCA on PC1 vs. PC3 (Supporting Information, Fig. S2), PC3 explained 10% of the variance. A9, A14 and C21 had higher scores in the positive direction of PC3 due to three polyfunctional thiols (3-MH, FFT and BM), whereas A5 and A16 had higher

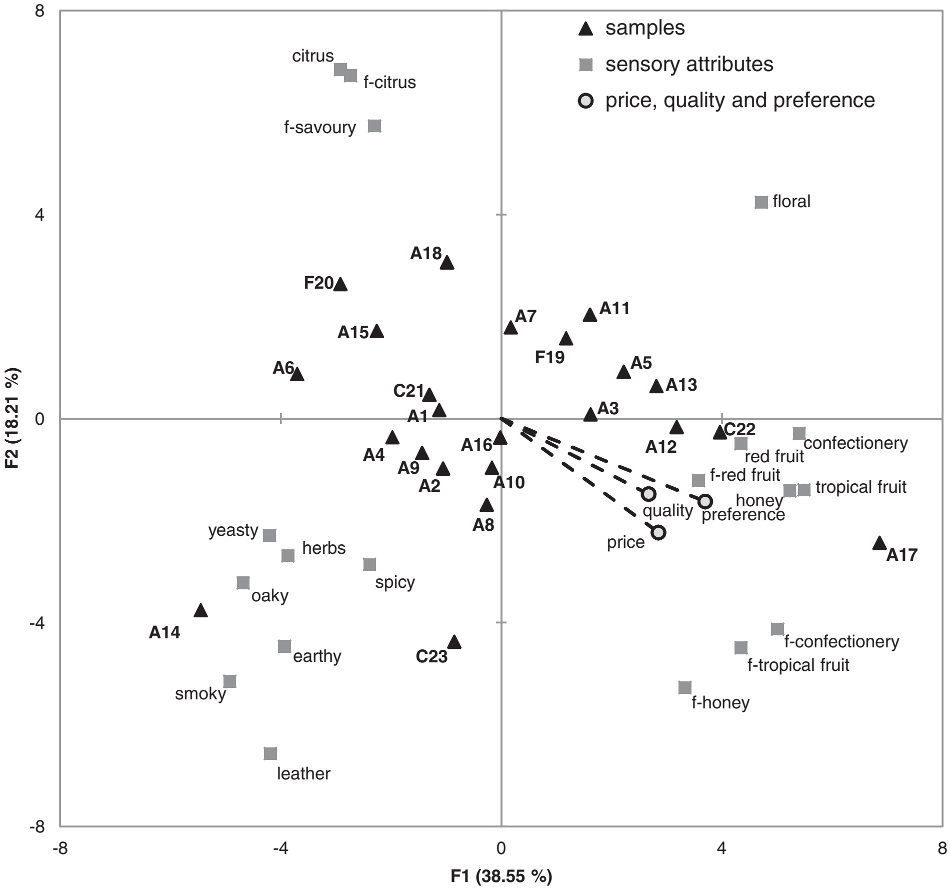

Fig. 2. Bi-plot generated from PCA of blind tasting data for 23 rosé wines. The descriptor prefix 'f' refers to flavour.

scores in the negative direction along PC3 as a result of their concentrations of ethyl furoate, some higher alcohols and 4-MMP. Samples were not separated very clearly along PC4 and PC5, which could explain 9% and 8% of the variance, respectively (data not shown). C22 scored highest in the positive direction along PC4 and as a result of ethyl lactate, hexanoic acid, limonene, furfural and linalool concentrations. Both French samples (F19, F20) as well as A16 and C21 stood out along the positive direction of PC5 because of their contents of isoamyl acetate, acetic acid, 3-methy-1-butanol and 2-ethyl-1-hexanol.

3.3. Network analysis (NA) of volatile and sensory data for 23 rosé wines

In total, 83 strong positive correlations ($r \geqslant 0.6$) (edges) were found between pairs for 54 of 69 significantly different variables including basic chemical parameters, aroma volatiles, and sensory, preference, quality and expected retail price data (nodes), giving 8 different modules (indicated with different colours in Fig. 4). The majority of the volatiles were separated on the left within 3 modules, except linalool, acetic acid, polyfunctional thiols, and a module containing β-damascenone and several esters, which correlated with sensory attributes and other variables. All sensory attributes appeared on the right side within 4 different modules, two of which were closely associated with preference, quality and expected retail price.

Focusing on the sensory attributes, tropical fruit, honey, confectionery and sugar content were closely related in one module (orange) and all except sugar showed correlations to preference in a separate module. Floral character was also part of this module but did not correlate with other sensory attributes, only correlating with linalool and preference. Red fruit and TA were in a module consisting of correlations with preference, quality and expected price. 3-MH (correlating with price) and 3-MHA (correlating with red fruit aroma and flavour) were also located in this module. The developed characters, such as oaky, smoky, earthy and leather were correlated with each other, whereas citrus was correlated with savoury taste. Sugar content, though it correlated with confectionery (which had a positive relationship with preference), was not correlated with preference, quality or expected price. On the contrary, TA was positively associated with quality and expected price in the 23 rosé wines. Only red fruit sensory attributes were positively related to quality and red fruit flavour correlated directly with expected price. On the other hand, dark fruit did not have any positive correlations with other variables.

Volatile compounds were mainly on the left side of the network (Fig. 4) within three modules. The red and yellow classes on the left were mainly volatiles that are introduced through yeast metabolic activity during alcoholic fermentation. The fatty acids, hexanoic, octanoic and decanoic, were associated with their corresponding esters, especially ethyl hexanoate and octanoate in the red module. Malic acid was also in this module and acted as a connector by correlating with hexanoic acid in red module and TA in the purple module. 2-Phenylethanol was correlated in the yellow module with ethyl hexanoate and octanoate, ethyl 2-phenylacetate, 1-decanol and 3-methyl-1-butanol. In the dark blue module on the top left, limonene was found to be associated with ethyl lactate, diethyl succinate, several alcohols as well as furfural.

It was noted that only 7 of the 47 volatile compounds quantified, including all sulfur compounds except 4-MMP, had direct positive

Table 2
Concentrations (μg/L)[a] of volatile compounds determined in 23 rosé wines.

Compound	Minimum	Maximum	Mean (OAV)	SD[b]	Significance[c]
Ethyl esters					
Ethyl butanoate	143	666	391 (20)	129	ns
Ethyl 2-methylbutanoate	6.9	101	29.5 (30)	23.4	**
Ethyl 3-methylbutanoate[d]	7.9	149	46.2 (15)	36	***
Ethyl 2-butenoate[d]	3.8	15	9.3 (–)	3.2	*
Ethyl hexanoate	567	1843	1211 (87)	327	*
Ethyl 2-hexenoate[e]	ND[f]	17.7	7.3 (365)	5.2	**
Ethyl lactate	ND	305370	21,186 (0.2)	63,185	***
Ethyl octanoate	1535	5009	3228 (161)	838	*
Ethyl furoate	ND	51.1	16 (<0.01)	16	***
Ethyl decanoate	ND	4258	2013 (10)	1161	***
Diethyl succinate	ND	3627	1502 (<0.01)	1411	***
Ethyl 9-decenoate[g]	ND	27.8	6.6 (–)	6.6	***
Ethyl 2-phenylacetate	2.1	21.6	8.6 (0.01)	6	***
Ethyl dodecanoate	38.6	270	149 (0.3)	69.1	***
Acetate esters					
Ethyl acetate	49,594	213,360	118,800 (8)	37,313	ns
Isoamyl acetate	ND	12,134	5003 (167)	3316	***
Hexyl acetate	54	2696	718 (1.1)	689	***
2-Phenylethyl acetate	ND	311	128 (0.5)	90.8	***
Other esters					
Methyl octanoate[e]	ND	15	4.4 (1.1)	4.1	***
Isoamyl hexanoate	ND	10.9	3.1 (–)	2.5	ns
Isoamyl octanoate	ND	33.7	19.8 (0.2)	8.4	ns
Alcohols					
1-Propanol	5612	26,593	12,568 (25)	4859	*
2-Methyl-1-propanol	36.9	12,533	3743 (0.1)	3089	**
3-Methyl-1-butanol	26,738	112,550	55,199 (1.8)	23,939	*
1-Hexanol	ND	8932	3752 (0.5)	3099	***
2-Ethyl-1-hexanol	25	187	52.1 (<0.01)	37	***
1-Octanol	7.2	45.4	21.6 (31)	9.6	***
1-Decanol[h]	14.8	126	62.1 (0.1)	32	***
2-Phenylethanol	2955	20,589	9384 (0.7)	4770	***
Isoprenoids					
Limonene	5.4	18.5	8.3 (0.6)	2.8	***
Linalool	ND	57.3	18.5 (1.2)	17.1	***
α-Terpineol	ND	52.7	19.4 (0.1)	11	***
β-Citronellol	ND	67.1	19.9 (0.2)	22.1	**
β-Damascenone	ND	31.5	6.7 (134)	9.6	***
Acids					
Acetic acid	78,414	420,830	180,630 (0.9)	81,272	***
Hexanoic acid	1846	4702	3174 (7.6)	863	***
Octanoic acid	ND	5569	1893 (3.8)	1503	**
Nonanoic acid	456	3297	1963 (0.7)	868	ns
Decanoic acid	38	369	211 (0.2)	83.3	***
Carbonyls					
Nonanal	60.7	127	95.2 (38)	18.8	ns
Furfural	ND	961	192 (0.01)	220	***
Benzaldehyde	37.2	132	102 (0.3)	25.5	***
Thiols					
4-MMP (ng/L)	ND	2.4	0.45 (0.6)	0.74	***
3-MH (ng/L)	22.9	1730	597 (10)	358	***
3-MHA (ng/L)	ND	35.6	5.1 (1.3)	7.8	***
FFT (ng/L)	ND	4.6	1.3 (3.3)	1.5	***
BM (ng/L)	ND	4.4	2.2 (7.3)	0.87	***

[a] In μg/L except where specified. Results are derived from the mean of duplicate determinations (Supporting Information, Table S4).
[b] Standard deviation.
[c] Significant differences among wines: $^{*}p < 0.05$; $^{**}p < 0.001$; $^{***}p < 0.0001$; ns, not significant.
[d] Equivalent to ethyl 2-methylbutanoate.
[e] Equivalent to isoamyl hexanoate.
[f] ND, not detected.
[g] Equivalent to ethyl decanoate.
[h] Equivalent to 1-octanol.

correlations with sensory properties and other attributes (Fig. 4). Linalool was correlated with floral and honey characters in the orange module (as well as with lactic acid, which was itself related to pH). Isoamyl acetate was the only volatile directly associated with preference, and linked with the tropical fruit and confectionery characters in the adjacent module, which were also associated with preference. Hexyl acetate was related to red fruit and β-damascenone was correlated with confectionery. For the polyfunctional thiols, FFT and BM were related to developed sensory attributes such as smoky and oaky in the green module, 3-MHA was correlated with red fruit character for both aroma and flavour, and 3-MH had a positive correlation with expected retail price.

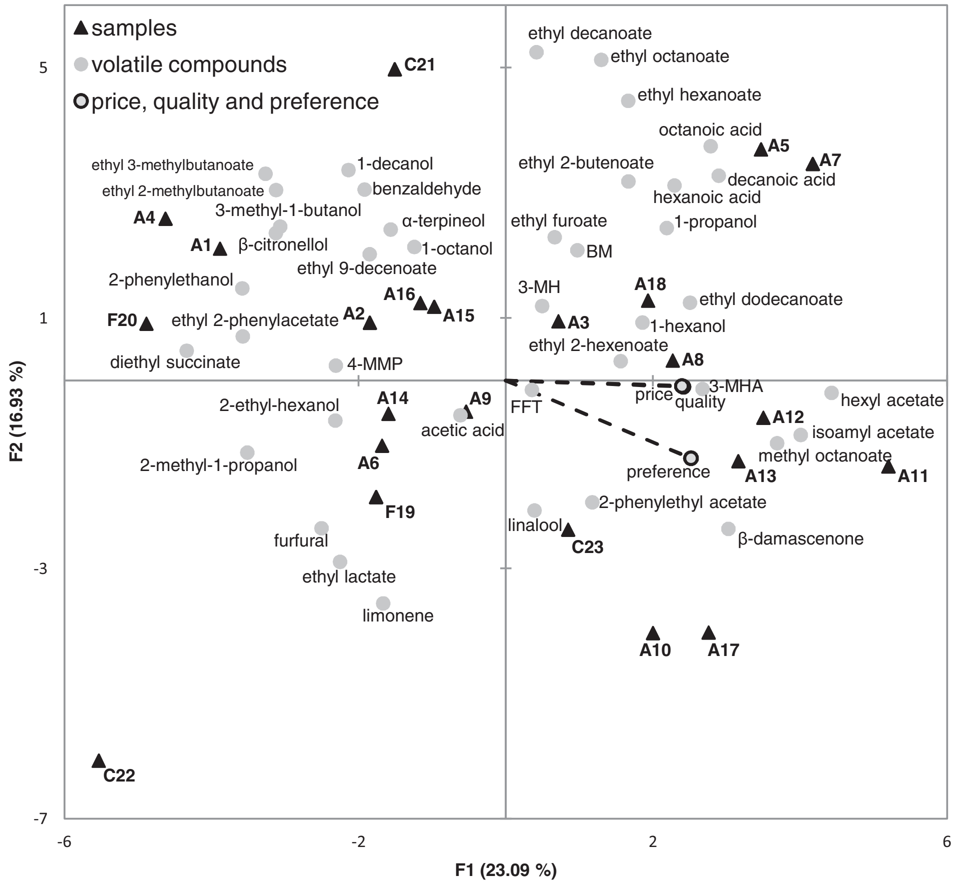

Fig. 3. Bi-plot generated from PCA of volatiles in 23 rosé wines.

For the negative relationships, 18 strong correlations ($r \leqslant -0.6$) were observed between pairs for 23 significantly different variables, which were displayed within 7 modules (Supporting Information, Fig. S3). Diethyl succinate, which was central within a module, had 7 nodes consisting of negative correlations to sensory attributes (red fruit and honey aromas, red fruit flavour), volatile compounds (isoamyl and hexyl acetates, methyl octanoate) and preference. Of these 7 nodes, 3 were negatively correlated with another compound: isoamyl acetate with β-citronellol, hexyl acetate with ethyl 2-methylbutanoate, and red fruit flavour with 2-phenylethanol. Smoky and leather aromas were negatively related to floral notes, and sugar content and honey flavour were negatively associated with citrus flavour. The remaining nodes involved volatile compounds that were correlated negatively within two modules.

4. Discussion

This study focused on wine experts, because unlike consumers, experts can more precisely evaluate wine quality (D'Alessandro & Pecotich, 2013) and have a perceptual advantage in recognising wine-relevant attributes (Parr, Heatherbell, & White, 2002). Furthermore, expert liking and quality ratings are based on objective, descriptive attributes such that their ratings can be adequately modelled by descriptors arising from a trained panel (Hopfer & Heymann, 2014).

Tastings of commercial rosé wine were undertaken in Xi'an, Beijing and Shanghai. Xi'an is a smaller city than the other two, but was included because it is the most important city in the northwest of China and is located close to wine regions like Ningxia and Gansu. Also, Northwest Agricultural and Forestry University, which has the first college of oenology in Asia, is situated in Xi'an, so it was considered reasonable to include winemakers, oenologists and wine-related academics in this location.

4.1. Chinese wine professional panel tasting

4.1.1. Preference, quality and expected retail price

The mean quality scores of all samples (Fig. 1) showed similar trends to preference scores, with a strong positive relationship demonstrating that judges associated greater preference for wines with higher quality. The mean expected price also had a strong positive correlation with mean preference scores. Compared with the general retail price of imported wines in the Chinese market (Insel, 2014), the expected retail price of rosé wines as judged in the current study by Chinese wine experts was in the low price segment (i.e., less than CNY300, which accounts for the bulk of wine sales in China). This result may demonstrate that the perception of quality for rosé wines is still low, even among Chinese wine industry stakeholders, although it might not account for the substantial margins that can be added to imported wine in China (Insel, 2014).

4.1.2. Aroma and flavour sensory attributes

Based on the results generated for sensory composition (Fig. 2), the samples were reasonably dispersed in the plot, indicating a range of rosé wine profiles was covered by this sample set. Australian rosé wines (A1–A18) were situated across all four quadrants, demonstrating a diversity of Australian rosé wine styles. Despite this being a limited study, a similar observation could be made for the three Chinese rosé wines (C21–C23), which were either fruit driven, developed, or dominated by citrus and savory characters. One French rosé wine (F20) also had citrus and savoury

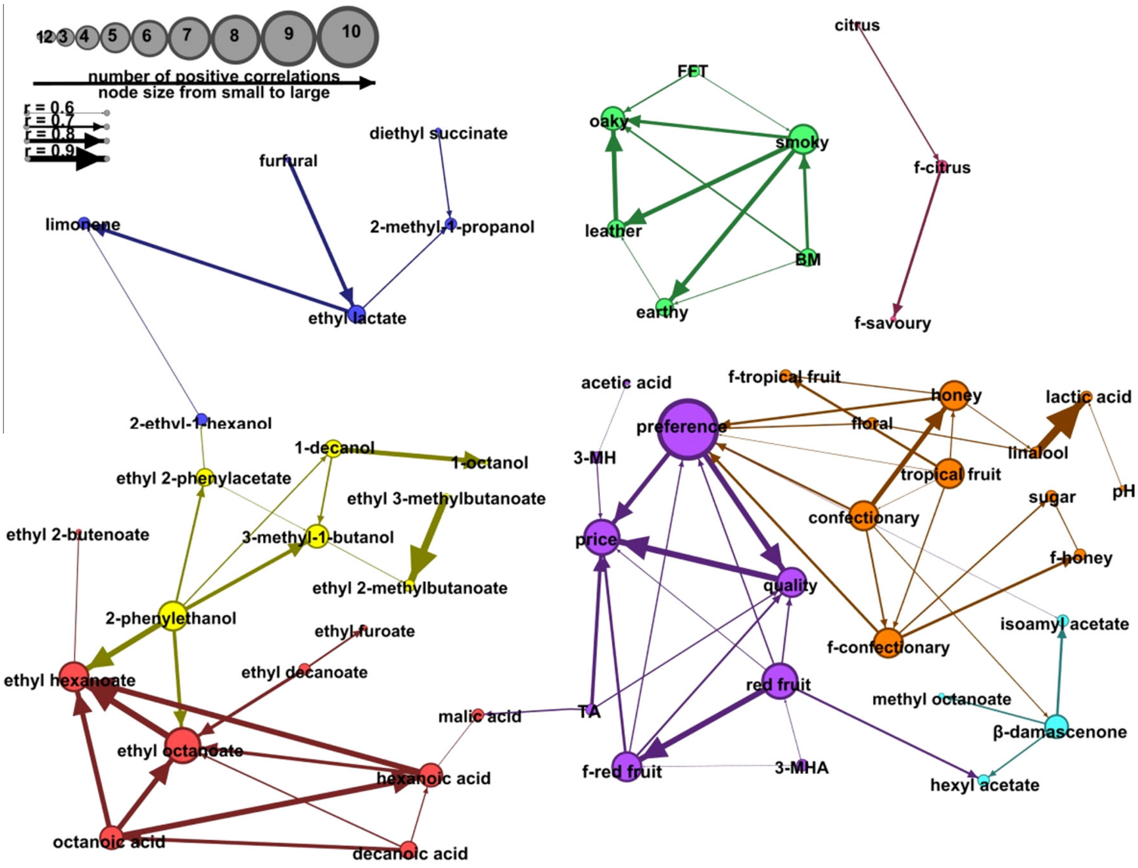

Fig. 4. Network analysis of variables which had positive relationships with each other in 23 rosé samples.

characters, whereas the other (F19) had floral characters, and was considered to be quite different from F20. In general, rosé wines from these three geographical regions showed some similarities in sensory properties, as well as some differences in characters within a country of origin.

4.2. Volatile compound analysis

Wine volatile composition can be related to quality judgments made by both consumers and experts (Sáenz-Navajas et al., 2015), reinforcing the importance of evaluating aroma volatiles in wines. Consistent with our previous work (Wang et al., 2016), almost half the compounds determined here were ethyl and acetate esters (Table 2), which are usually related to floral, strawberry and fruity aromas in rosé wine (Darici, Cabaroglu, Ferreira, & Lopez, 2014; Masson & Schneider, 2009). 2-Phenylethanol, which imparts a floral aroma to rosé wines (Darici et al., 2014), was also quantified, as well as a number of other alcohols (Table 2). In addition, the monoterpenoids linalool, α-terpineol and β-citronellol (responsible for citrus and floral attributes) were identified, and compounds related to developed and savoury characters (Mayr et al., 2014) were detected, including furfural and some fatty acids (e.g., hexanoic, octanoic, nonanoic and decanoic acid). Of the 47 compounds detected here, 24 had an odour activity value (OAV, i.e., concentration ÷ aroma detection threshold) > 1 according to their mean concentrations, and some compounds had substantial OAVs, in particular β-damascenone (mean OAV = 134).

4.3. Network analysis of volatile and sensory data for 23 rosé wines

As a state-of-the-art statistical method and visualisation tool, NA has become more frequently used not only in the mainstream media but also in peer-reviewed journals. It was first recorded as a formal method within the social science community in 1978 (Prell, 2011). It has been applied in many different disciplines since. The *nodes* in NA are different entities that depend on the specific purpose of the research, and every *edge* between two nodes represents a connection between them, which could be a strong correlation, a certain social relationship, a conditional probability, a communication pathway or a neurologic connectivity (Salter-Townshend, White, Gollini, & Murphy, 2012). Connected nodes give the diagram modularity, which shows the interconnection between different classes (modules) of the network. NA can be regarded as a very clear and direct way, in terms of visualisation, to examine the connections among variables. Besides research conducted on wine and health (Aleixandre, Aleixandre-Tudo, Bolanos-Pizzaro, & Aleixandre-Benavent, 2013) and a recent study on kinetics of port wine ageing (Monforte, Jacobson, & Ferreira, 2015), this appears to be the first time that relationships among different wine sensory attributes and compositional data have been evaluated using NA. Furthermore, the complex relationships between preference, sensory properties and compositional parameters were suited to evaluation by NA.

With the positive relationships, aromas were generally correlated with their corresponding flavours (Fig. 4), which suggested interactions between the judges' retronasal and orthonasal olfactory functions (Aubry, Schlich, Issanchou, & Etiévant, 1999). Residual sugar concentrations were not correlated with preference, quality or expected price, which appeared to align with French consumers who preferred dry rosé (Velikova et al., 2014). This was noticeably different compared with other studies involving Chinese wine consumers (Lockshin, 2014; Williamson, Robichaud, & Francis, 2012) and US rosé drinkers (Velikova et al., 2014) who always preferred sweeter styles. In contrast, despite acidity in red wine being considered low in acceptability in a study of Chinese consumers (Williamson et al., 2012), a positive relationship was observed between TA and quality and expected price. Nonetheless, as a balanced acidity is an important criteria for wine of high quality, this present result was consistent with previous research involving evaluation of red wines by experts (Sáenz-Navajas, Martin-Lopez, Ferreira, & Fernández-Zurbano, 2011).

The red fruit aroma attribute, which was the only node directly correlated with quality, was previously deemed as a preferable character in a study on red wines involving Chinese wine consumers (Williamson et al., 2012), and gave a similar result to studies involving Australian (Lattey, Bramley, & Francis, 2010) and French/Spanish experts (Sáenz-Navajas et al., 2015). The correlation between red fruit flavour and expected price indicated this character may have been a marker of price and quality for these judges. Developed characters, which are often associated with high quality wine (Ferreira et al., 2009), were not correlated with either preference or quality, which suggests that the experts in our study were not seeking such characters in the rosé wines evaluated.

In terms of volatiles, the associations of fatty acids with their corresponding esters were sensible given they are produced from yeast saturated fatty acid metabolism. 2-Phenylethanol, which arises from phenylalanine during fermentation, was correlated with other alcohols which are also introduced during alcoholic fermentation. It was noticeable that limonene, a grape-derived compound (Swiegers, Bartowsky, Henschke, & Pretorius, 2005), was related to several alcohols derived from alcoholic and malolactic fermentations (Swiegers et al., 2005) as well as furfural, a Maillard reaction product (Ferreira, Escudero, Fernández, & Cacho, 1997). In the case of linalool, which had a mean concentration (18.5 μg/L) just below its aroma detection threshold (25 μg/L in wine) (Darici et al., 2014), the relationships with sensory and other attributes were in line with observations for Australian Shiraz (Mayr et al., 2014) and some premium Spanish red wines (Ferreira et al., 2009). Isoamyl acetate, the only volatile directly associated with preference, can be responsible for fruity (banana) character (Ferreira et al., 2009), and the correlation between hexyl acetate and red fruit was reasonable, as it provides red berry characters to wine (Mayr et al., 2014). β-Damascenone, deemed to be an important aroma compound in several rosé studies (Darici et al., 2014; Ferreira et al., 2009; Masson & Schneider, 2009; Wang et al., 2016; Álvarez-Pérez et al., 2012), was a feature of desirable rosé wines in this study. Furthermore, β-damascenone has been suggested as a fruity character enhancer (Pineau, Barbe, Van Leeuwen, & Dubourdieu, 2007; Álvarez-Pérez et al., 2012) that positively relates to wine quality as measured by wine experts (Sáenz-Navajas et al., 2015), so its correlation with isoamyl acetate and hexyl acetate suggests an indirect contribution to aroma and preference. In regard to polyfunctional thiols, the correlations of FFT and BM (thresholds of 0.4 ng/L and 0.3 ng/L, respectively) with smoke and oak characters were in complete accord with previous research (Dubourdieu & Tominaga, 2009). Additionally, the correlation of 3-MHA (aroma detection threshold of 4 ng/L) with red fruit seems rational as it has been observed as a contributor to fruity characters in previous studies on rosé wine (Darici et al., 2014; Álvarez-Pérez et al., 2012). Related to this, 3-MH (aroma detection threshold of 60 ng/L), which imparts passionfruit and grapefruit notes (Tominaga, Furrer, Henry, & Dubourdieu, 1998), was considered one of the most important odorants in rosé wine (Darici et al., 2014; Masson & Schneider, 2009; Álvarez-Pérez et al., 2012), and our findings indicate rosé wines with higher 3-MH content were preferred by Chinese wine experts.

With respect to the acids involved with malolactic fermentation, a microbial process that can influence both the aroma and flavour of wine, malic acid was positively related to TA, which was reasonable given it is one of the main contributors to this parameter in wine. In addition, the positive correlation between lactic acid and pH made sense on the basis that wine acidity decreases (pH increases) as the level of lactic acid increases during malolactic fermentation due to metabolism of malic acid.

Visualisation of negative correlations by NA (Supporting Information, Fig. S3) showed that diethyl succinate, which can be associated with wine age (Francioli, Torrens, Riu-Aumatell, López-Tamames, & Buxaderas, 2003; Marais & Pool, 1980), was negatively correlated with hexyl and isoamyl acetates (fruity notes); this is a unique finding for rosé wine but is in accord with previous studies of white and sparkling wines (Francioli et al., 2003; Marais & Pool, 1980). Diethyl succinate was also negatively correlated with red fruit aroma and flavour, honey aroma, and preference, which indicated that samples potentially showing aged characters were not appreciated by judges in this study. Additionally, the developed sensory attributes, smoky and leather, were negatively related with floral aroma, and citrus flavour was negatively associated with residual sugar and honey flavour. Ethyl dodecanoate, which contributes fruity/floral characters typical of ethyl esters, was negatively correlated with another age related compound, furfural (San Juan, Cacho, Ferreira, & Escudero, 2012). Wine pH was negatively related to benzaldehyde and ethyl decanoate, and although higher pH may result in lower formation of aldehydes (Ferreira, Bueno, Franco-Luesma, Cullere, & Fernandez-Zurbano, 2014), the explanation for ethyl decanoate was not as apparent, but oxidation as a result of higher pH may be a factor (Patrianakou & Roussis, 2014). Benzaldehyde, a potential oxidation marker related to grape variety (Ferreira et al., 1997), was also negatively correlated to a fruity marker compound, β-damascenone (Pineau et al., 2007).

5. Conclusions

The study provided the first insight into the preferences of Chinese wine experts towards rosé wines determined by blind wine tastings in three large cities in mainland China. The sensory results revealed links between preference, quality and expected retail price of the wines. Overall, experts preferred rosé wines with lower residual sugar, which exhibited red fruit, floral, confectionery and honey characters and lacked apparent developed characters. The acidity level and intensity of red fruit character were related to higher quality, while β-damascenone, 3-MH and 3-MHA were important volatiles associated with preference, quality and expected price.

A diverse set of Australian rosé wines were evaluated, together with a number of wines from France and China for comparison. Despite only three Chinese rosé wines being assessed, this was the first attempt at understanding the sensory and chemical profiles of such wines produced in China. According to the sensory properties, the Chinese wines represented three different styles, with similarities to some of the Australian styles. C21 was driven by red fruit, confectionery and honey characters; C22 was more tropical fruit and floral; C23 had more developed characters, such as smoky, leather, oaky and spicy. In the opinions of Chinese wine experts, sample C21 was the third most popular rosé of the 23 samples, which partly indicated that along with their Australian and French counterparts, Chinese rosé wines have the potential to develop interest in the local market.

Regarding to the composition of volatiles, 47 compounds were quantified, including 5 polyfunctional thiols. Isoamyl acetate, hexyl acetate, β-damascenone, 3-MH, 3-MHA, FFT and BM appeared to be most important to the aroma of these wines, and were all related to either sensory properties or preference, quality and expected retail price.

Network analysis was applied to readily visualise the positive and negative relationships among these different wine variables for the first time. On the whole this helped explain correlations between sensory and chemical data, and the findings were consistent with other research. Some interesting relationships between aroma volatiles, sensory descriptors and preference/quality/expected price were observed and these can now be investigated further. For example, studies on the relationship between diethyl succinate and rosé wine age, in conjunction with acetate esters, red fruit characters and consumer preference, could be pursued. Finally, large scale studies involving Chinese wine consumers should also be conducted to verify the styles of rosé wine preferred by the public and to identify the drivers behind purchasing behaviour.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2016.02.042.

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Chapter 4

Comprehensive study of volatile compounds in two Australian rosé wines: aroma extract dilution analysis (AEDA) of extracts prepared using solvent-assisted flavor evaporation (SAFE) or headspace solid-phase extraction (HS-SPE)

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Contribution to the Paper	Designed experiments, performed experimental work, conducted sensory work in China, analysed and interpreted data, drafted/constructed manuscript.
Overall percentage (%)	85%
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.

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Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

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Comprehensive Study of Volatile Compounds in Two Australian Rosé Wines: Aroma Extract Dilution Analysis (AEDA) of Extracts Prepared Using Solvent-Assisted Flavor Evaporation (SAFE) or Headspace Solid-Phase Extraction (HS-SPE)

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S *Supporting Information*

ABSTRACT: Two rosé wines, representing a tropical and a fruity/floral style, were chosen from a previous study for further exploration by aroma extract dilution analysis (AEDA) and quantitative analysis. Volatiles were extracted using either liquid–liquid extraction (LLE) followed by solvent-assisted flavor evaporation (SAFE) or a recently developed dynamic headspace (HS) sampling method utilizing solid-phase extraction (SPE) cartridges. AEDA was conducted using gas chromatography–mass spectrometry/olfactometry (GC-MS/O) and a total of 51 aroma compounds with a flavor dilution (FD) factor ≥3 were detected. Quantitative analysis of 92 volatiles was undertaken in both wines for calculation of odor activity values. The fruity and floral wine style was mostly driven by 2-phenylethanol, *β*-damascenone, and a range of esters, whereas 3-SHA and several volatile acids were seen as essential for the tropical style. When extraction methods were compared, HS-SPE was as efficient as SAFE for extracting most esters and higher alcohols, which were associated with fruity and floral characters, but it was difficult to capture volatiles with greater polarity or higher boiling point that may still be important to perceived wine aroma.

KEYWORDS: *rosé wine, volatile composition, liquid–liquid extraction, headspace sampling, GC-O, flavor dilution factor, odor activity value*

■ INTRODUCTION

Aroma is one of the most important sensory components that contributes to wine quality, varietal characters, and consumer acceptance, but the study of wine aroma is not a straightforward undertaking. Aside from the inherent genetic differences in individuals that can influence perception of aromas, consideration needs to be given to the biological and chemical origins of wine aroma volatiles, the concentration ranges spanning many orders of magnitude, and the influences of grape variety and matrix interactions. Fortunately, continuous advances in analytical technology, such as in gas chromatography instrumentation and sample preparation techniques, and decades of research in flavor chemistry have contributed to current methodologies and understanding.

One very useful technology that has arisen is gas chromatography–olfactometry (GC-O), often performed in conjunction with detection by mass spectrometry (MS). Quite uniquely for an analytical instrument, GC-O utilizes human olfaction (sense of smell) in combination with a conventional instrument detector to simultaneously evaluate odor characteristics and chemical identity (at least in the case of MS) for chromatographically separated volatile components. GC-O can be conducted in a number of ways to evaluate the potential sensory importance of odorants,[1] with one of the most common, aroma extract dilution analysis (AEDA), being based on threshold concentrations in air. This relatively simple (albeit time-consuming) approach provides quantitative information on odorants (intensity) and is used to assess their relative importance to wine aroma. This is achieved by calculating a flavor dilution (FD) factor for each odorant, being the highest dilution level at which an odor is still detected, which can be plotted against retention index (RI) to produce an aromagram (olfactogram). An aroma model can be proposed upon the identification and quantification of significant odorants and the calculation of odor activity values (OAV) from threshold data.[2] Evidently, a GC-O strategy does not model the enhancing or suppressive effects of odorant mixtures, which could occur in a real matrix,[3] and reconstitution/omission sensory studies are often undertaken to account for any perceptual interactions and verify an aroma model.[1,2,4] In general, however, odorants with high OAVs and/or with aromas that are readily distinguishable are likely to have an impact on wine aroma.[1,5]

Besides different GC-O strategies to assess the importance of various odorants to overall wine aroma, preparation of a representative sample of the original wine is always a fundamental issue.[1,5,6] Different methodologies have been developed to obtain samples for study by GC-O more generally and can be applied to wine, but none offer a universal approach to extracting relevant odorants. Liquid–liquid extraction (LLE) using various organic solvents provides for a simple and exhaustive extraction but without selectivity; virtually all volatiles and some nonvolatiles are recovered from the

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wine.[5,7] LLE is accompanied by concentration of the solvent by distillation or with a stream of nitrogen in a sample concentrator. Distillation can be rapidly and conveniently carried out under high vacuum using solvent-assisted flavor evaporation (SAFE), with a SAFE apparatus allowing careful isolation of volatile compounds from a solvent extract.[7] Solid-phase extraction (SPE) is extensively used for isolation of volatiles and gives a result similar to that of LLE,[8] albeit with more selectivity and efficiency and using lower quantities of organic solvent.

Extracts obtained by LLE followed by SAFE or from SPE are unlikely to reflect the profile of volatiles released from the original matrix that end up being perceived during olfactory evaluation.[9] Furthermore, the concentration step to remove solvent can lead to loss of highly volatile components, and injected solvent can mask the detection of compounds during GC analysis.[2] Headspace (HS) methods fill a gap in the extraction technique repertoire, as they can more closely approximate the volatile aroma fraction of a wine. In particular, dynamic HS extraction using a purge and trap system seems to be more representative of the original sample and has been successfully applied in wine research.[6,10] Recent efforts toward obtaining a representative HS extract (from model wine) have involved the development and refinement of a purge and trap system utilizing a specific flask and commercial SPE cartridge containing polymeric sorbent.[6,9] An alternative HS method involves solid-phase microextraction (SPME), which is much less time-consuming than other methods because it allows for direct AEDA of a wine sample, either following successive dilution[5] or by altering the split ratio of the GC injector port.[11] In terms of being able to obtain a representative SPME method, however, there are many parameters requiring careful optimization (e.g., different fiber coating, fiber length, extraction time and temperature, volume of the sample), making HS-SPME approaches challenging to optimize[1,5] and not widely adopted for wine aroma characterization using AEDA compared to the other techniques.

Characterization of rosé wine aroma is of interest due to the somewhat peculiar nature of the production technique, which uses red grape varieties such as Pinot noir, Grenache, and Cabernet Sauvignon, among others, in conjunction with white winemaking practices. Although there is some extraction of grape skin components such as red pigments, unlike red winemaking the grape juice does not macerate with the grape solids during fermentation to produce rosé wine. Despite the limited skin contact, different grape varietals can still play a role in the aroma profile of the corresponding wines. Researchers have studied aroma compounds of rosé wines from Turkey, Spain, and France.[12−14] More recently, different styles of commercial Australian rosé wine have been proposed, with sensory analysis of a range of wines revealing characters such as oaky/spicy, tropical/citrus, fruit-driven, and floral.[15] Fruity aroma attributes have often been found to be important to rosé wine aroma and can be associated with a number of ethyl esters and higher alcohol acetates and also with grape-derived aroma compounds such as polyfunctional thiols including 3-sulfanyl-1-hexanol (3-SH) and its corresponding ester 3-sulfanylhexyl acetate (3-SHA),[10,12−17] and the C_{13}-norisoprenoid *β*-damascenone.

A previous study on rosé wine from Australia identified, among other sensory characters, fruity and confectionery notes in a number of wines and tropical and citrus attributes in others.[15] On the basis of these differences, two rosé wines representing fruity/floral versus tropical were selected for GC-MS/O analysis to evaluate the volatile compounds driving the particular sensory styles. A recent headspace sampling method,[6] refined by Escudero et al.[9] but so far used only for synthetic wine spiked with a selection of volatiles, was modified and compared with LLE and SAFE to evaluate the differences in the AEDA results for the two wines. Quantitative analysis of a wide range of volatiles was also undertaken to calculate OAVs. This study provides understanding of the important aroma compounds in two different Australian rosé wines and also offers guidance in obtaining a representative volatile extract for wine aroma research.

■ MATERIALS AND METHODS

Chemicals. Volatile compounds (≥97% purity) used in quantitative analysis and as reference standards during GC-O (ethyl 2-methylpropanoate, 2,3-butanedione, 2-methyl-2-butanol, ethyl 3-methylbutanoate, butyl acetate, 2-methyl-1-propanol, 3-methylbutyl acetate, 1-butanol, 3-methyl-1-butanol, ethyl hexanoate, hexyl acetate, 3-hydroxybutan-2-one, 3-methyl-1-pentanol, ethyl lactate, 1-hexanol, (*Z*)-3-hexenol, ethyl octanoate, acetic acid, 3-methylbutyl hexanoate, furfural, octyl acetate, 3-isobutyl-2-methoxypyrazine (IBMP), 2,3-butanediol, linalool, 2-methylpropanoic acid, butanoic acid, ethyl decanoate, *γ*-butyrolactone, furfuryl alcohol, 3-methylbutanoic acid, diethyl succinate, methionol, 3-sulfanylhexyl acetate (3-SHA), benzyl acetate, *δ*-valerolactone, 2-phenylethyl acetate, *β*-damascenone, hexanoic acid, guaiacol, benzyl alcohol, 2-phenylethanol, anisaldehyde, octanoic acid, *γ*-decalactone, decanoic acid, diethyl tartrate, 2-furoic acid, benzoic acid, dodecanoic acid) were supplied by Sigma-Aldrich (Castle Hill, NSW, Australia), except for ethyl butanoate and ethyl 2-methylbutanoate, which were supplied by Alfa Aesar (Ward Hill, MA, USA). Sodium chloride was supplied by J. T. Baker (Phillipsburg, NJ, USA), and analytical grade solvents were obtained from Merck (Kilsyth, VIC, Australia). GC grade solvents were supplied by VWR International (Tingalpa, QLD, Australia). Deuterium-labeled compounds were supplied by CDN Isotopes (Pointe-Claire, QC, Canada). Stock solutions of standards were prepared volumetrically in absolute ethanol and stored at −20 °C, and working solutions were stored at 4 °C until required. All chemicals were of analytical reagent grade unless otherwise stated, and water was obtained from a Milli-Q purification system (Millipore, North Ryde, NSW, Australia).

Wine Samples. One fruity and floral (Cabernet Sauvignon) and one tropical (Shiraz) rosé wine (Supporting Information, Table S1) were selected on the basis of the results of a previous study[15] and following an informal tasting of a selection of rosé wines conducted with wine researchers at The University of Adelaide (UA). To accomplish this, two candidates for each style were chosen, and 10 experienced assessors were asked to select the most representative sample for each style. The wines were bottled under screw cap and donated by local wineries. A 2014 commercial rosé wine (bag-in-box, 12.5% v/v ethanol, pH 3.40, titratable acidity (TA) = 6.8 g/L, SO_2 (free) = 29 mg/L, SO_2 (total) = 134 mg/L) was used as a base wine for calibration of the quantitation methods and also for training purposes during the GC-O study to allow sniffers to become familiar with the GC-O process.

Basic Wine Composition. Alcohol, TA, pH, and residual sugar (glucose + fructose) were measured as previously described.[15] Free and total SO_2 were determined by the aspiration method. All measurements were performed in duplicate (Supporting Information, Table S1).

Isolation of Volatiles for AEDA. Both samples were extracted in duplicate, but no differences were detected between replicates by GC-MS analysis. Only one extract from each replicate was chosen to conduct AEDA.

LLE-SAFE Extract. Wine (100 mL) was extracted with CH_2Cl_2 (3 × 50 mL) using a separating funnel and vigorous shaking for 10 min. The combined organic phases were spiked with a 2-octanol solution (0.75 mL of 500 mg/L in ethanol) as internal standard and washed with a saturated sodium chloride solution (150 mL) and dried over anhydrous sodium sulfate. After filtration and concentration to approximately 100 mL by distillation on a water bath at 40 °C with a Vigreux column (50 × 1 cm), the volatiles were isolated by means of SAFE. The apparatus was thermostated at 40 °C and kept under high vacuum (10^{-3} Pa), and the sample was added dropwise into the evaporation flask over 30 min. After an additional 5 min, the vacuum was released and the distillate was thawed at room temperature. The SAFE extract was concentrated to 100 μL by distillation, again using a Vigreux column as described above, and aliquots of extract were stored at −20 °C until required for GC-O analysis. These samples arising from LLE and SAFE were designated T-SAFE and F-SAFE for tropical and fruity/floral wines, respectively.

HS-SPE Extract. The procedure was adopted from a previous study[9] with modifications. Different extraction conditions including different cartridge size (1, 3, and 20 mL), mass of sorbent (300, 400, and 500 mg), and length of extraction (60, 100, 180, 360, and 720 min) were evaluated by GC-MS to obtain the optimal parameters using the bag-in-box rosé wine. On the basis of the total peak area and peak heights, the combination of 500 mg of resin in a 20 mL cartridge with 360 min extraction time was chosen. Wine (100 mL) was added to a customized flask (Supporting Information, Figure S1) and purged without agitation at room temperature. Volatiles were trapped with 500 mg of LiChrolut EN sorbent (Merck, Kilsyth, VIC, Australia) packed into 20 mL polypropylene SPE tubes (fitted with PTFE frits), which had been previously washed with CH_2Cl_2 (25 mL) and dried. A controlled stream of nitrogen (500 mL/min), which did not disturb the liquid surface, was applied to the headspace of the wine for 6 h. The cartridge was removed and dried using a stream of nitrogen (0.6 bar, 10 min). Analytes were subsequently recovered with CH_2Cl_2/MeOH (95:5 v/v, 4 mL) using a dropwise elution rate. The extract was spiked with 2-octanol solution (0.02 mL of 500 mg/L in ethanol, to keep the same concentration as LLE) as internal standard and concentrated under a stream of nitrogen (0.6 bar, 10 min) to a final volume of 100 μL. Extracts were stored as described above until required. These samples arising from HS extraction were designated T-HS and F-HS for tropical and fruity/floral wines, respectively.

Gas Chromatography−Mass Spectrometry/Olfactometry (GC-MS/O). *GC-MS Conditions.* Analyses were performed using an Agilent 7890 GC equipped with a Gerstel MPS autosampler (Lasersan Australasia Pty Ltd., Robina, QLD, Australia) and coupled to a 5897 mass selective detector (Agilent, Palo Alto, CA, USA). The GC was also fitted with a Gerstel olfactory detection port (ODP series 1). A DB-Wax column (60 m × 0.25 mm, 0.25 μm film thickness Agilent J&W, Folsom, CA, USA) was used with helium as carrier gas (Coregas, Cavan, SA, Australia) in constant pressure mode (263.9 kPa, nominal initial flow = 2.6 mL/min). The oven was held at 40 °C for 5 min and then heated at 3 °C/min to 240 °C and held at this temperature for 5 min. Splitless injection mode was used for liquid injections (2 μL), and the split vent was opened after 3 min. A single taper, ultrainert liner with glass wool was used (splitless, deactivated, 4 mm i.d., 900 μL, Agilent). The MS transfer line was set at 250 °C, and electron impact spectra at 70 eV were recorded in the range m/z 35−350. The MS quadrupole was set at 150 °C, and the source was set at 230 °C. The transfer line to the ODP and the humidifier mixing chamber were set at 250 and 200 °C, respectively. The humidified gas and makeup gas in the ODP system were nitrogen (Coregas) with preset rates at 12 and 50 mL/min, respectively. The capillary column lengths from splitter to ODP and MS were set using an Agilent pressure flow calculator to achieve a 2:1 split ratio. Simultaneous detection of MS signal and odorant by olfaction was verified by injecting a CH_2Cl_2 solution containing several volatiles that have distinguishing odors. Instrument control and data analysis were performed with Agilent ChemStation software (E.02.02.1431), and the Gerstel autosampler was controlled with Maestro software integrated version 1.3.3.51/3.3.

Identification of Volatiles. Compound identity was verified by comparing the following: mass spectra with library matches (NBS 75K) and authentic reference compounds; calculated RI (using C7−C40 alkanes, Sigma-Aldrich) with those obtained from AromaOffice 1D (version 2.01.00 (2012/03/09, Gerstel K.K., Tokyo, Japan) for a DB-Wax column; odor quality with those of reference compounds or literature reports.

Aroma Extract Dilution Analysis (AEDA). GC-O analysis was conducted on volatile extracts prepared by SAFE and HS-SPE. Five sniffers (four males, one female, average age of 32 years) were involved for the AEDA study. Four sniffers had previous GC-O experience and participated in an earlier rosé wine sensory descriptive analysis (DA) panel.[15] The total sniff time for each assessor was up to 50 min (consisting of two separate 25 min sessions), and assessors conducted up to five runs per day with at least a 25 min break between sessions. Assessors evaluated the undiluted base wine extracts three times for training purposes before the formal analysis, to eliminate potential gaps in detecting odor active regions and to ensure consistency of detection. A recorder system (ODP-Recorder, Gerstel GmbH & Co. KG, version 3.0.2.2) was used, and the comments of panelists were saved and simultaneously recognized by the software while the button was being held down on the recorder. The sensory vocabulary for the recorder system was developed from attributes generated in the previous rosé wine DA panel[15] and from terms used during GC-O test runs. Extracts were stepwise diluted with CH_2Cl_2 (1:2 (v/v) to yield dilutions of 3, 9, 27, 81, etc., and up to 177147 relative to the original extracts (i.e., 3^n where $n = 1, 2, 3$, etc.)). After analysis by GC-O, FD factors of each odor-active compound in the four samples (T-SAFE, T-HS, F-SAFE, and F-HS) were determined. FD was defined as the maximum dilution at which three of five sniffers could still perceive the odorant. Compounds that had FD factors ≥3 in at least one sample were studied further.

Quantitation of Volatiles. *HS-SPME-GC-MS Analysis.* A total of 28 compounds (one of which was tentatively identified) were quantified using a previous method for rosé wine.[15] Standards at three concentrations (covering the concentration range and evenly spaced) in base wine were analyzed in duplicate to develop calibration functions for quantitation.

HS-SPME-GC-MS Analysis with Selected Ion Monitoring (SIM). A SIM method was established to quantify a further 34 compounds (10 of which were tentatively identified) using the SPME parameters and sample preparation as reported in a previous study.[15] Samples were analyzed on an Agilent 6890 GC equipped with a 5973N MS. A deactivated SPME inlet liner (0.75 mm i.d., Supelco) and DB-Wax column (60 m, 0.25 mm i.d., 0.25 μm film thickness, Agilent J&W) were used with a constant flow rate of 1.5 mL/min and an average velocity of 31 cm/s. The inlet temperature was set to 240 °C, with the pressure set at 157.8 kPa, and splitless injection mode was used. The split vent was opened after 3 min. The oven was held at 40 °C for 5 min, then heated at 2 °C/min to 240 °C, and held at this temperature for 10 min. The MS transfer line was set to 240 °C, the MS source was 230 °C, the quadrupole was 150 °C, and electron impact spectra were recorded at 70 eV. Ultrapure helium (Coregas) was used as the carrier gas. Authentic compounds were first analyzed in scan mode to select the SIM ions for each analyte. On the basis of retention time, 15 SIM groups with dwell times ranging from 20 to 100 ms were established. Instrument control and data analysis were performed with Agilent ChemStation software (E.02.02.1431). Calibration, validation, and calculation of the limit of detection (LOD) and limit of quantitation (LOQ) for each analyte were undertaken as described previously.[15] The retention index (RI), SIM ions, regression coefficient (R^2), and calibrated concentration range for each compound are given in the Supporting Information (Table S2).

Analysis for Other Volatiles. C_6 compounds were quantified by HS-SPME-GC-MS,[18] and polyfunctional thiols (3-sulfanyl-1-hexanol (3-SH), 3-sulfanylhexyl acetate (3-SHA), 4-methyl-4-sulfanylpentan-2-one (4-MSP), furfurylthiol (FT), and benzenemethanethiol (BMT)) were determined by HPLC-MS/MS after derivatization.[19] Analyses of methoxypyrazines,[20] oak volatiles,[21] and oxidation volatiles[22] were performed by the Australian Wine Research Institute (AWRI) Commercial Services Laboratory (Adelaide, Australia) using published methods. A further 11 tentatively identified compounds that were important according to AEDA were semiquantified on the basis of

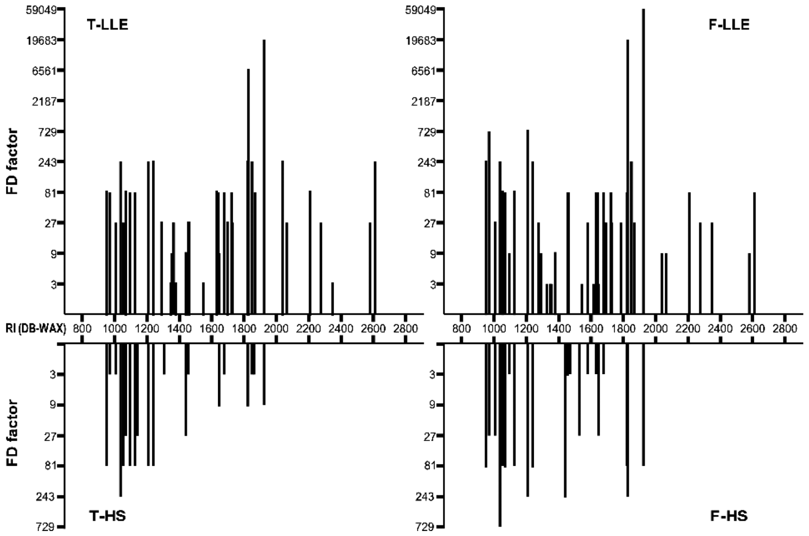

Figure 1. Flavor dilution (FD) aromagrams of volatile fractions (FD ≥ 3) isolated from two representatives rosé wines (tropical, T; and fruity/floral, F) with two extraction techniques (LLE-SAFE and HS).

their equivalence to other calibrated compounds. In total, 92 volatile compounds were quantified.

Data Analysis. Quantitative chemical data are presented as mean values with standard deviation from replicate determinations (Microsoft Excel 2010). Flavor dilution (FD) aromagrams were created in SPSS-20 (SPSS Inc., Chicago, IL, USA) and refined in Adobe Illustrator CS6 (Adobe Systems, Palo Alto, CA, USA).

■ RESULTS AND DISCUSSION

GC-O and AEDA. Extracts from two commercial rosé wines, with one being tropical in style and the other fruity and floral, were obtained using LLE followed by SAFE, as well as with HS-SPE. Using AEDA, a total of 51 odorants were determined with an FD factor ≥3; the highest FD factors obtained were 59049 (i.e., 3^{10}) for 2-phenylethanol and 729 (i.e., 3^6) for ethyl butanoate in SAFE and HS samples, respectively (Figure 1 and Table 1). According to the AEDA results, the most important aroma compounds in these two wines were a number of fermentation compounds, especially 3-methyl-1-butanol, ethyl 2-methylpropanoate, ethyl butanoate, ethyl hexanoate, ethyl octanoate, 2-phenylethyl acetate, hexanoic acid, and 2-phenylethanol, along with β-damascenone, a grape-derived compound, which was similar to the AEDA results reported for Çalkarası[12] and Grenache[13] rosé wines.

Comparison of Extraction Methods and Identity of Important Odorants. It was not surprising that a greater number of odor-active compounds were detected in samples obtained by SAFE and, especially, those compounds with larger RIs (Figure 1). Heavier volatiles and those with greater polarity are not as easily extracted with the HS-SPE process,[6,9] whereas SAFE is an exhaustive extraction procedure. In contrast, light volatiles may be lost during extraction using SAFE, and a dynamic HS method might better represent the aroma compounds that are perceived during olfactory assessment of wine.[9] Whereas the HS-SPE purge and trap technique might come closest to being an ideal extraction method, as pointed out earlier, there is no universal approach to chemically assessing wine aroma. Highly volatile compounds such as dimethyl sulfide (DMS) would be better captured with static HS sampling,[23] so for the most complete assessment of wine aroma a combination of extraction techniques would be necessary to prepare samples for GC-O.

The FD factors for both SAFE and HS samples were similar and relatively high at the beginning of the aromagrams (Figure 1), which indicated not only the sensory importance of the more volatile compounds (such as fermentation esters and alcohols) but also that the SAFE and HS-SPE techniques performed similarly in the extraction of such compounds. As the volatility of compounds decreased and their polarity increased, FD factors for HS samples gradually tapered off compared with SAFE samples until odorants were barely perceptible around the middle part of a GC-O run (RI ≈ 1900). On the contrary, SAFE samples contained odorants with the highest FD factors at around this time and odorants could still be detected for some time afterward.

The highest FD factor for SAFE samples was determined for 2-phenylethanol (59049 and 19683 for F-SAFE and T-SAFE, respectively, Table 1), a compound responsible for rose aroma that has been identified in previous rosé wine studies.[12,13] The second highest FD was observed for β-damascenone (19683 and 6561 for F-SAFE and T-SAFE, respectively), a ubiquitous odorant with fruity-floral aroma[33] found to be a key aroma compound related to fruity aroma in Provencal[14] and Australian[15] rosé wines. Guaiacol (smoky and bacon) and δ-decalactone (caramel and coconut), which both eluted relatively late, were principally detected in SAFE samples. Also, FD factors of volatile acids and isoprenoids were higher in SAFE samples, which suggested that they were not easily volatilized to be trapped in the HS extraction process. For HS samples, ethyl butanoate had the highest FD factor for both tropical (FD = 243) and fruity (FD = 729) samples; this fatty acid ethyl ester was described as having red fruit and confectionery notes by the sniffers (Table 1) and contributes strawberry notes in red wines.[34] Ethyl octanoate, a related ester with fruity characters, which has been reported as an important odorant in Grenache rosé wine,[13] had an FD factor that was higher in both HS samples compared with SAFE, particularly for the fruity/floral sample (Table 1). For most other early-eluting volatiles, such as branched-chain ethyl esters, fusel alcohols, and 3-methylbutyl (isoamyl) acetate (Table 1), the FD factors were around the same as for the SAFE samples, which suggested that the HS-SPE extraction method could be as efficient as SAFE for the majority of the more highly volatile

Table 1. Details of Odorants Detected by AEDA (with FD ≥ 3) of Rosé Wine Extracts Prepared by Two Different Extraction Techniques

				FD factor					OAV	
RI[a]	odorant description[b]	identity[c] determined by	identity[d]	T-SAFE	T-HS	F-SAFE	F-HS	threshold[e]	tropical	fruit/ floral
952	fruity, tropical fruit	MS, O, RI	ethyl 2-methylpropanoate	81	81	243	81	15[24]	2.7	3.0
969	butter, yogurt	MS, O, RI	2,3-butanedione	81	3	729	27	100[25]	6.3	13.0
1009	plastic, solvent, fly spray	MS, O, RI	2-methyl-2-butanol	27	3	27	27	n/a[f]	–[g]	–
1036	red fruit, confectionery	MS, O, RI	ethyl butanoate	243	243	243	729	20[24]	20.5	22.4
1052	strawberry, bubble gum	MS, O, RI	ethyl 2-methylbutanoate	27	81	81	81	18[24]	<0.1	<0.1
1060	caramel, yogurt	MS, *O*, RI	2,3-pentanedione	1	0	9	3	900[26]	–	–
1070	citrus, tropical fruit, artificial fruit	MS, O, RI	ethyl 3-methylbutanoate	81	27	81	81	3[24]	3.7	7.0
1094	fusel, amyl alcohol	MS, O, RI	2-methyl-1-propanol	81	81	9	3	40000[24]	0.2	0.3
1126	banana	MS, O, RI	3-methylbutyl acetate	81	81	81	81	30[24]	108	87
1142	fruity, alcoholic	MS, O, RI	1-butanol	0	27	0	0	150000[27]	<0.1	<0.1
1210	solvent, sweaty feet	MS, O, RI	3-methyl-1-butanol	243	81	729	243	30000[25]	4.6	5.6
1239	confectionery, strawberry, green apple, Chinese white spirit	MS, O, RI	ethyl hexanoate	243	81	243	81	14[24]	139	50
1276	confectionery, fruity	MS, O, RI	hexyl acetate	1	1	27	1	1500[27]	0.2	0.1
1289	wet, sweaty	MS, O, RI	3-hydroxybutan-2-one	27	1	9	1	150000[27]	<0.1	<0.1
1305	solvent	MS, *O*, RI	1-hydroxy-2-propanone	0	3	1	1	50000[28]	–	–
1327	green, solvent	MS, O, RI	3-methyl-1-pentanol	1	1	3	1	830[29]	0.1	0.1
1348	yeasty, creamy	MS, O, RI	ethyl lactate	3	1	3	0	154000[27]	0.1	0.06
1355	spicy, green	MS, O, RI	1-hexanol	9	1	3	1	8000[24]	0.3	0.3
1362	burning, alcohol	MS, *O*, RI	2-hydroxy-3-pentanone	27	1	1	0	n/a	–	–
1365	green	MS, O, RI	(*Z*)-3-hexenol	27	0	0	0	400[24]	0.5	0.2
1378	solvent, earthy	MS, *O*, RI	3-ethoxy-1-propanol	3	0	9	0	100[26]	–	–
1439	green, fruity	MS, O, RI	ethyl octanoate	9	27	1	243	20[27]	279	145
1456	vinegar	MS, O, RI	acetic acid	27	3	81	3	200000[25]	0.9	0.5
1461	caramel, yeasty	MS, O, RI	3-methylbutyl hexanoate	27	0	81	0	900[28]	<0.01	<0.01
1472	floral, candy, fruity	MS, O, RI	furfural	1	0	1	3	14100[24]	0.01	<0.01
1530	capsicum	MS, O, RI	IBMP	1	0	0	27	0.002[27]	–	–
1542	floral, creamy	MS, O, RI	2,3-butanediol	1	1	3	0	100000[29]	0.3	0.2
1549	floral	MS, O, RI	linalool	3	0	0	1	25[24]	0.7	0.2
1616	moldy	MS, *O*, RI	dehydrolinalool	0	0	3	0	n/a	–	–
1632	sweaty, cheesy	MS, O, RI	butanoic acid	81	1	81	3	173[24]	10.3	4.9
1641	burnt, floral	MS, O, RI	ethyl decanoate	81	1	81	3	200[24]	17.0	6.0
1647	sweaty	MS, O, RI	*γ*-butyrolactone	9	9	3	27	35000[30]	0.5	0.3
1677	cheesy, sweaty	MS, O, RI	3-methylbutanoic acid	81	3	81	3	33[24]	2.8	3.5
1679	onion	*MS*, *O*, RI	2-methyl-3-(methyldithio)furan	27	0	0	1	0.3[31]	–	–
1681	creamy	MS, O, RI	diethyl succinate	0	1	27	0	200000[27]	<0.01	<0.01
1693	fruity	MS, *O*, RI	ethyl 9-decenoate	0	0	27	0	n/a	–	–
1722	caramel, yeasty, burnt milk, bready	MS, O, RI	methionol	81	1	81	0	1000[24]	0.3	0.4
1727	passionfruit, tropical, thiols	MS, O, RI	3-SHA	27	0	27	1	0.004[32]	5.1	3.1
1784	green, woody	MS, *O*, RI	diethyl glutarate	1	0	27	0	5000[28]	–	–
1824	honey, floral	MS, O, RI	2-phenylethyl acetate	243	9	81	81	250[25]	0.6	0.2
1828	fruity, tobacco, woody, floral	MS, O, RI	*β*-damascenone	6561	0	19683	243	0.05[25]	62	74
1850	sweaty, acid	MS, O, RI	hexanoic acid	243	3	243	1	420[24]	10.1	4.2
1864	smoky, burnt plastic	MS, *O*, RI	*N*-(3-methylbutyl)acetamide	0	3	1	0	n/a	–	–
1870	smoky, bacon	MS, O, RI	guaiacol	81	1	27	1	9.5[24]	0.6	0.2
1923	roses, perfume	MS, O, RI	2-phenylethanol	19683	9	59049	81	10000[25]	1.3	1.3
2039	aniseed, caramel, popcorn	MS, O, RI	anisaldehyde	243	1	9	1	20[28]	3.6	1.5
2066	leesy, acidic	MS, O, RI	octanoic acid	27	0	9	0	500[24]	14.8	6.0
2207	caramel, coconut	MS, *O*, RI	*δ*-decalactone	81	0	81	1	386[24]	–	–
2277	sweaty	MS, O, RI	decanoic acid	27	1	27	1	1000[24]	3.3	2.1
2347	hospital, cheesy	MS, O, RI	diethyl tartrate	3	0	27	0	n/a	–	–
2578	pungent, coconut, acidic, sweet	MS, *O*, RI	phenylacetic acid	27	0	9	0	2500[13]	–	–

[a]RI, retention index calculated using a series of alkanes (C7–C40). [b]Summarized based on the comments from sniffers. [c]MS, mass spectrum matches with authentic compound and/or library; *MS* (italicized), mass spectrum matches with literature; O, odor matches with authentic compound; *O* (italicized), odor matches with literature; RI, retention index matches with literature and/or authentic compound. [d]Underlined

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Table 1. continued

compounds were tentatively identified. [e]Concentration in μg/L and literature reference as superscript number. In refs 13 and 31 the matrix was 10% water/ethanol solution at pH 3.2; in ref 24 the matrix was an 11% water/ethanol solution containing 7 g/L glycerol and 5 g/L tartaric acid, pH adjusted to 3.4 with 1 M NaOH; in ref 25 the matrix was 10% water/ethanol solution; in ref 26 the matrix was 10% water/ethanol solution, adjusted to pH 3.5 with tartaric acid; in ref 27 thresholds were calculated using a 12% water/ethanol mixture; in ref 28 the thresholds of 1-hydroxy-2-propanone and 3-methylbutyl hexanoate were determined in beer, and the threshold of diethyl glutarate was determined in 18% water/alcohol solution with 100g/L sugar at pH 3.5 and the threshold of anisaldehyde was determined in water; in ref 29 as specified in Fenaroli's Handbook; in refs 30 and 32 the matrix was water/ethanol solution. [f]Not available. [g]"—" indicates the OAV of the compound was not determined either because its threshold was not available, its concentration was under the LOQ, or it was semiquantified.

compounds in wine. The FD factors of 2-phenylethanol and β-damascenone in the F-HS sample, in particular, showed them to be important odorants, but the values were much lower than the corresponding SAFE sample values due to the decrease in volatility of these odorants. Around the time these compounds eluted marked the point where odorants were no longer detectable in HS samples, and it may also indicate the stage at which odorants start to become overemphasized (in terms of sensory importance) in the SAFE samples.

Odorants in Fruity and Tropical Wine Styles. With regard to the different volatile compounds in the two rosé wines, there were several more odorants with an FD factor ≥3 in the fruity/floral sample compared to the tropical one (Table 1), such as 2,3-pentanedione and hexyl acetate. Ethyl and acetate esters related to fruity characters in rosé wines,[10,12−17] such as ethyl 2-methylpropanoate, ethyl 2-methylbutanoate, ethyl butanoate, ethyl hexanoate, and 3-methylbutyl acetate, also had FD factors that were quite often higher in the fruity/floral sample. Whereas 3-methylbutyl acetate has been determined as an impact odorant in its own right if the concentration is high enough, individual ethyl esters arising during fermentation via the same pathways (i.e., esterification of branched versus straight chain fatty acids) do not have such a role, but can be considered as impact families.[1] Perceptual interaction of esters in the wine matrix can lead to additive and enhancing effects that modulate fruity notes, particularly the berry aromas of red wines.[30] Although not captured with the two extraction techniques employed here, the common sulfur volatile DMS can also interact with esters to enhance the perception of fruity aromas.[35] Esters such as ethyl 2-methylpropanoate and ethyl hexanoate have been deemed to be important in Pinot noir wine[36,37] and red wines made from either Merlot, Cabernet Sauvignon, or Grenache.[38] Ethyl 2-methylbutanoate was suggested as a key aroma compound in Dornfelder red wine[39] and was one of the volatiles with the highest FD factor in red wine made from Merlot or Cabernet Sauvignon.[38] For acetate esters, 3-methylbutyl acetate, responsible for confectionery and fruity notes in wine[25] and one of the key odorants in a Çalkarası rosé wine[12] and a selection of Australian rosé wines,[15] had an FD factor of 81 across the four samples, which was similar to the observation in Pinot noir wines.[36] 2-Phenylethyl acetate (honey, floral) also had high FD factors and was important in Çalkarası rosé wine.[12] Hexyl acetate, which has fruity characters,[36,40] was not very strong in samples except for F-SAFE, with a moderate FD factor at 27. Despite these esters being ubiquitous fermentation volatiles, grape variety and composition may play a role in their formation,[41] and given that rosé wines are made from different red grape varieties, it is interesting to observe parallels in the importance of these esters. The scarcely reported ester 3-methylbutyl hexanoate, which was detected only in SAFE samples with FD = 27 and 81 for tropical and fruity/floral samples, respectively, had caramel and yeast aromas. Diethyl esters of succinic, glutaric and tartaric acids, which arise during aging, were detected by sniffers with an FD of 27 in the F-SAFE sample. Diethyl succinate can be negatively associated with fruity aromas,[17] as can diethyl tartrate, although it has been suggested there was no direct effect on the fruitiness of wines.[42] Beside these compounds, ethyl lactate (yeasty) and ethyl 9-decenoate (fruity) were detected mainly with low FD factors in SAFE samples, indicating little contribution to aroma profile of these wines.

A group of higher alcohols were perceived and identified in extracts of the two wines. 2-Phenylethanol had the highest FD factor of all odorants in both SAFE samples, with a higher FD factor in fruity/floral extracts compared to tropical ones for both SAFE and HS extraction methods. These results parallel those for 2-phenylethanol having the highest FD factor in Pinot noir wine from New Zealand[36] and the United States,[37] Dornfelder red wine from Germany,[39] and aged red wine from Spain.[43] 3-Methyl-1-butanol, a commonly abundant higher alcohol, was one of the most powerful odorants (solvent and sweaty) in this study and received higher FDs in the fruity/floral sample, which in concert with other higher alcohols can induce perceptual changes to fruity aromas in wine.[44] 2-Methyl-1-propanol, another common higher alcohol, was observed with moderate FD factors and was more perceivable in tropical extracts (81 in T-SAFE and T-HS, 9 in F-SAFE, and 3 in F-HS). (Z)-3-hexenol, a grape-derived alcohol with green and grassy notes,[34] was detected only in the tropical SAFE sample with an FD value of 27. Methionol (meaty, bready, and yeasty), related to methionine content in grapes[45] and responsible for negative aromas potentially affecting red wine quality,[34] had FD = 81 in both SAFE samples. 2,3-Butanediol (floral, vanilla), which is a malolactic fermentation (MLF) product, apparently contributed more to the fruity/floral sample with FD = 3 for the extract obtained by SAFE. Aside from these higher alcohols, 2-methyl-2-butanol (plastic, solvent), 1-butanol (fruity, alcoholic), 3-methyl-1-pentanol (green, solvent), 1-hexanol (spicy, green), and 3-ethoxy-1-propanol (solvent, earthy) were all identified by AEDA, but none had an FD factor >27.

Volatile acids such as 3-methylbutanoic acid, acetic acid, and other even-numbered medium-chain fatty acids (C_4−C_{10}) and phenylacetic acid were detected by AEDA. Acetic acid (vinegar), the main volatile acid in wine,[4] had FD = 3 in both HS samples, but its FD for the fruity/floral sample was larger than the tropical sample using SAFE; this was reasonable given acetic acid may have a positive impact on the overall fruity aroma expression.[46] 3-Methylbutanoic acid, which had cheesy and sweaty aromas, had the same FD factors in both samples (81 for SAFE and 3 for HS) and was not differentiated according to the aroma styles of the two wines. Butanoic acid, which had similar sweaty notes in wine,[39] had the same FD factors as 3-methylbutanoic acid in both samples obtained by SAFE, and only slightly higher FD in fruity/floral sample with HS sampling. Hexanoic acid, with FD = 243 in both tropical and fruity/floral SAFE samples, was found to be a key odorant

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Table 2. Volatile Compound Concentrations (μg/L) Determined for Two Rosé Wines[a]

compound	tropical	fruity/floral	compound	tropical	fruity/floral
ethyl esters			**acids**		
ethyl butanoate	410.3 ± 35.6[b]	448.4 ± 34.4	acetic acid	189115 ± 2033	95969 ± 4035
ethyl hexanoate	1940 ± 93	699 ± 13	butanoic acid	1780 ± 57	850.6 ± 34.8
ethyl octanoate	5587 ± 404	2903 ± 163	hexanoic acid	4236 ± 62	1777 ± 103
ethyl decanoate	3407 ± 22	1194 ± 10	octanoic acid	7412 ± 70	3001 ± 43
ethyl dodecanoate	61.9 ± 0.6	46.4 ± 0.4	decanoic acid	3372 ± 166	2099 ± 83
ethyl lactate	15685 ± 234	9750 ± 582	dodecanoic acid	6546 ± 453	3189 ± 58
ethyl furoate	22.5 ± 0.5	28.3 ± 0.5	2-methylpropanoic acid	516.9 ± 24.2	437.3 ± 30.8
ethyl 2-methylbutanoate	0.66 ± 0.01	1.39 ± 0.12	3-methylbutanoic acid	93.7 ± 0.9	114.2 ± 6.5
ethyl 3-methylbutanoate	11.1 ± 0.2	21.1 ± 1.1	benzoic acid	1283 ± 70	1166 ± 8
ethyl 2-methylpropanoate	39.8 ± 3.9	45.6 ± 2.1	2-furoic acid	253.7 ± 14.4	121.7 ± 2.6
ethyl 9-decenoate[c]	2.01 ± 0.07	39.50 ± 0.70	phenylacetic acid[h]	1538 ± 36	4536 ± 74
diethyl succinate	1324 ± 38	1571 ± 122	**phenols**		
diethyl tartrate	641.6 ± 36	462 ± 31	guaiacol	6.00 ± 1.00	2.00 ± 1.00
diethyl glutarate[d]	68.4 ± 1.8	117.4 ± 6.6	4-ethylguaiacol	<10.0	<10.0
acetate esters			4-ethylphenol	<10.0	<10.0
butyl acetate	2.46 ± 0.13	1.31 ± 0.07	4-methylguaiacol	<1.00	<1.00
hexyl acetate	291.6 ± 0.2	108.0 ± 8.4	eugenol	<10.0	<10.0
octyl acetate	3.04 ± 0.05	7.55 ± 0.29	**aldehydes**		
2-phenylethyl acetate	143.8 ± 0.7	53.8 ± 0.8	hexanal	10.0 ± 0.5	11.0 ± 0.6
3-methylbutyl acetate	3235 ± 263	2623 ± 148	(*E*)-2-hexenal	0.50 ± 0.025	0.55 ± 0.028
benzyl acetate	7.77 ± 0.06	2.52	(*E*)-2-heptenal	<0.01	<0.01
other esters			(*E*)-2-octenal	0.02 ± 0.001	0.03 ± 0.002
3-methylbutyl hexanoate	5.93 ± 0.58	6.39 ± 0.43	(*E*)-2-nonenal	0.08 ± 0.004	0.53 ± 0.027
alcohols			2-methylpropanal	12.0 ± 0.6	16.0 ± 0.8
1-butanol	619 ± 55	531 ± 12	3-methylbutanal	5.8 ± 0.3	11.0 ± 0.6
1-hexanol	2754 ± 33	2191 ± 22	furfural	200.0 ± 20.0	105.0 ± 10.5
2-methyl-2-butanol	132.1 ± 11.0	130.7 ± 10.3	5-methylfurfural	<10.0	<10.0
3-methyl-1-butanol	136977 ± 949	168369 ± 2882	benzaldehyde	105.0 ± 5.3	81.0 ± 4.1
2-methyl-1-propanol	6800 ± 169	11540 ± 763	anisaldehyde	71.22 ± 3.37	29.25 ± 0.83
3-methyl-1-pentanol	85.9 ± 0.5	117.4 ± 2.3	phenylacetaldehyde	10.00 ± 0.50	8.40 ± 0.42
2-ethyl-1-hexanol	26.5 ± 0.3	31.9 ± 1.6	vanillin	<10	<10
3-ethoxy-1-propanol[e]	123.0 ± 5.0	57.6 ± 0.9	methional	<0.01	0.43 ± 0.02
benzyl alcohol	128.0 ± 2.1	91.2 ± 6.3	**ketones**		
2-phenylethanol	12653 ± 214	12520 ± 38	1-hydroxy-2-propanone[i]	240.0 ± 7.6	150.1 ± 39.2
(*Z*)-3-hexen-1-ol	193.5 ± 0.7	66.5 ± 0.7	2-hydroxy-3-pentanone[i]	166.5 ± 1.6	67.3 ± 7.8
(*E*)-2-hexenol	≤0.20[f]	≤0.20	3-hydroxybutan-2-one	646.0 ± 42.9	322.1 ± 1.3
methionol	311 ± 16	424 ± 21	2,3-butanedione	626.4 ± 27.5	1297 ± 31
furfuryl alcohol	123.4 ± 4.1	108.3 ± 7.3	2,3-pentanedione[j]	279.6 ± 6.7	363.0 ± 4.3
2,3-butanediol	31630 ± 1471	19457 ± 1535	**lactones**		
isoprenoids			γ-butyrolactone	17004 ± 1659	12075 ± 874
linalool	17.1 ± 1.4	5.9 ± 0.1	δ-valerolactone	42.5 ± 0.5	36.2 ± 1.2
α-terpineol	21.5 ± 0.1	31.9 ± 0.3	γ-decalactone	2.61 ± 0.01	2.07 ± 0.09
β-ionone	7.25 ± 0.03	7.23 ± 0.01	δ-decalactone[k]	1.03 ± 0.08	2.06 ± 0.21
β-damascenone	3.12 ± 0.16	3.70 ± 0.25	*cis*-oak lactone	<10	<10
dehydrolinalool[g]	0.99 ± 0.01	1.90 ± 0.34	*trans*-oak lactone	<10	<10
thiols			sotolon	0.75 ± 0.004	<0.01
4-MSP (ng/L)	≤1.1	≤1.1	**others**		
3-SH (ng/L)	532 ± 2	539 ± 1	mesityl oxide	≤0.5	≤0.5
3-SHA (ng/L)	20.2 ± 0.3	12.5 ± 0.1	2-methyl-3-(methyldithio)furan[i]	31.9 ± 0.2	23.9 ± 1.6
FT (ng/L)	≤1	≤1	*N*-(3-methylbutyl)acetamide[l]	8.8 ± 0.7	23.0 ± 1.6
BMT (ng/L)	1.90 ± 3.72	10.50 ± 0.07	homofuraneol	312.0 ± 15.6	132.0 ± 6.6

[a] Concentrations in μg/L unless specified otherwise. The aroma descriptors, thresholds, and OAVs of compounds can be found in Table 1 and in the Supporting Information (Table S3). [b] Values are shown as the mean ± SD (standard deviation) of duplicate analyses. [c] Equivalent to ethyl decanoate. [d] Equivalent to diethyl tartrate. [e] Equivalent to 1-butanol. [f] "≤" or "<" indicates the content was below the limit of quantitation (LOQ). [g] Equivalent to linalool. [h] Equivalent to dodecanoic acid. [i] Equivalent to 3-hydroxybutan-2-one. [j] Equivalent to 2,3-butanedione. [k] Equivalent to γ-decalactone. [l] Equivalent to 3-methylbutyl acetate.

in a Pinot noir study[37] and had a sweaty and acid smell. Decanoic acid (sweaty) and phenylacetic acid (pungent, acidic) had the same FD factors in both samples under each extraction technique and did not seemingly contribute to differences in tropical and fruity/floral wines. Contrarily, octanoic acid (leesy, acidic) had a larger FD factor in the tropical SAFE sample (FD

= 27) compared with the fruity/floral extract (FD = 9), indicating that it might contribute more to the aroma characteristics of the tropical wine style.

Isoprenoids contributed markedly according to the AEDA results. Altogether, linalool, β-damascenone, and dehydrolinalool were detected with FD factors ≥3 in at least one sample. Most notably, β-damascenone had higher FD factors irrespective of extraction technique in fruity/floral extracts (F-SAFE = 19683 and F-HS = 6561) compared to tropical extracts (T-SAFE = 6561, T-HS = 0), which was in agreement with its fruity and floral aroma nuances. β-Damascenone has also been reported with the highest FD factor in Pinot noir wines[36] and aged red wine,[43] and may play a role in enhancing fruity characters in rosé wines.[10,13] Besides β-damascenone, the FD factors of the other isoprenoids were not above 27, indicating their limited contribution to overall wine aroma profiles.

Several ketones were identified by AEDA, with three of them being related to MLF. The first was 2,3-butanedione (butter, yogurt), also known as diacetyl, which had larger FD factors in fruity/floral samples (FD = 729/27) compared to the tropical samples (FD = 81/3) for each extraction method. This appears to be consistent with a GC-O study of premium Spanish red wines, in which it was described as having a strawberry aroma (as well as the usual lactic descriptor).[34] 2,3-Butanedione was generally higher in FD factor when the current results were compared with different white wines[47] (which do not necessarily go through MLF), but similar to that reported for a Barossa Valley Shiraz wine that had been through MLF.[40] The other two MLF products, 3-hydroxybutan-2-one (wet, sweaty) and 2,3-pentanedione (caramel, yogurt), behaved differently; 3-hydroxybutan-2-one was more important in the T-SAFE sample with FD = 27 compared to F-SAFE with FD = 9, whereas 2,3-pentanedione was higher in fruity/floral samples (FD = 9/3) with either extraction technique. Additionally, 1-hydroxy-2-propanone and 2-hydroxy-3-pentanone were detected, and both were associated with solvent aromas. 2-Hydroxy-3-pentanone seemed to be more important in the tropical sample with FD = 27 in T-SAFE, whereas 1-hydroxy-2-propanone had less contribution, with lower FD factors that did not seem to relate to the wine styles. Apart from the (hydroxy)ketones, two aldehydes were detected during AEDA. Anisaldehyde, which has been detected in sherry musts[48] and oak wood,[49] had aniseed, caramel, and popcorn nuances and was determined to have a large FD factor of 243 in the T-SAFE sample. Furfural (floral, candy, fruity), a Maillard-related volatile that can be released by contact with toasted oak,[33] contributed little to either sample with FD ≤ 3 in accord with its general unimportance as an aroma volatile, although indirect effects on aroma (increased oak intensity, decreased fruit intensity) have been noted previously.[50]

Two varietal impact compounds were identified by AEDA, namely, the polyfunctional thiol 3-SHA and the methoxypyrazine 3-isobutyl-2-methoxypyrazine (IBMP). 3-SHA, synonymous with Sauvignon blanc aroma and closely associated with tropical aroma in wines,[32] was detected with the same FD factor of 27 in both SAFE samples. On this basis it was not distinctly responsible for the tropical nuances of the Shiraz wine that was designated a tropical style. Unlike the somewhat special case of Sauvignon blanc wines,[20] the tropical style of this rosé wine was not solely driven by varietal thiols acting as character impact compounds, although they have been found in other studies to be important odorants in rosé wines.[12,13,15,17] On the other hand, IBMP is often found to be an impact compound in Sauvignon varietal wines, where it can be responsible for green bell pepper characters at very low levels (several ng/L).[51] Only the F-HS sample (obtained from the Cabernet Sauvignon wine) had FD = 27 for IBMP, and despite not being detected during quantitative analysis, it was clearly perceived by the sniffers.

Other compounds identified in this study were of mixed (including ill-defined) origins and included γ-butyrolactone (sweaty), δ-decalactone (caramel, coconut), and guaiacol (smoky, bacon), which were all determined in rosé wines previously.[12,13] 2-Methyl-3-(methyldithio)furan, which had a distinguishing onion aroma, was detected only in the T-SAFE sample with FD = 27. It has previously been found in red wines and could potentially arise via Maillard reaction of ribose and cysteine, followed by mixed disulfide formation with methanethiol.[31] *N*-(3-Methylbutyl)acetamide, which had smoky and burnt plastic characters, has formerly been determined in Amarone[52] and fortified wines,[53] and its concentration was found to increase with a longer skin-contact time.[54] This latter observation suggested that it could be a marker of the extent of maceration on skins during rosé wine production.

Volatile Compound Quantitation and Calculation of OAVs. In one of the most comprehensive assessments of volatiles accomplished on rosé wine to date, a total of 92 compounds were quantified for two different wine styles (Table 2). Among these, esters, alcohols, and volatile acids, mainly arising during fermentation, together accounted for more than half of the total, with the remaining compounds detected and quantified comprising phenols, carbonyls, lactones, isoprenoids, thiols, and furans.

Along with using an existing SPME scan method[15] to quantify 27 volatiles and several other published methods[18−22] for a number of specific compounds, an SPME-GC-MS SIM method was developed to quantify a further 34 compounds. The R^2 values of each calibrated analyte were ≥0.99, and calibrations were linear across the concentration range (Supporting Information, Table S2). Precision at low and high concentrations ranged from 1 to 17%, and recoveries varied between 91 and 118%. LOQ values were below the reported aroma detection thresholds for the analytes.

Most compounds were detected and quantified in both tropical and fruity/floral wine samples at concentrations that were consistent with other rosé wine studies.[10,12−15] The largest OAVs (Table 1) were obtained for ethyl octanoate (green, fruity) in both tropical (OAV = 279) and fruity/floral (OAV = 145) samples, which suggested it had a large contribution to both aroma styles, but perhaps more so for the tropical style wine. Ethyl octanoate was similarly found with a large mean OAV (135) in a study of 26 Australian rosé wines[15] and had the fourth largest OAV in Grenache rosé.[13] Ethyl hexanoate (confectionery and strawberry) had the second largest OAV in the tropical style wine (OAV = 139) as did 3-methylbutyl acetate (banana) in the fruity/floral wine (OAV = 87), with these high OAV results being consistent with previous studies on rosé wines;[12,15] both esters had substantially higher OAVs in the tropical wine in contrast to the fruity/floral one. The C_{13}-norisoprenoid β-damascenone had OAVs ≥ 50 for both samples, which was entirely consistent with the large FD factor obtained for this compound by AEDA. These results accord well with other research, in which ethyl hexanoate, 3-methylbutyl acetate, and β-damascenone were determined as the top three odorants with the largest OAVs in Çalkarası rosé[12] and were among the top five most important odorants in

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Grenache rosé[13] and a set of Australian rosé wines.[15] Other esters, such as ethyl decanoate, along with butanoic, hexanoic, and octanoic acids, had larger OAVs (at least double) in the tropical wine compared to the fruity/floral one. Tropical odorant 3-SHA had a 1.6-fold larger OAV in the tropical wine (OAV = 5.1), which could potentially help to further differentiate the two styles being studied. In contrast, 2,3-butanedione, ethyl butanoate, ethyl 3-methylbutanoate, and 3-methyl-1-butanol had larger OAVs in the fruity/floral sample, with the two esters in particular likely to be driving the fruity characters. On the other hand, 3-methyl-1-butanol can attenuate fruity characters in model solution[44] but has also been described as intensifying berry notes when added to dearomatized red wine,[14] which implies a variable effect depending on the matrix. It was interesting to note that although 2-phenylethanol was suggested as an important volatile from the AEDA results, on the basis of calculated OAVs it was seemingly not the case and only just reached values above its threshold (OAV = 1.3).

Compounds not detected by AEDA were quantified at levels (Table 2) mostly below or around their corresponding aroma detection thresholds (i.e., OAV < 1, Supporting Information, Table S3), except for four compounds, β-ionone, 3-SH, BMT, and phenylacetaldehyde. β-Ionone, which has descriptors such as violet and fruity aroma,[36] was determined with an OAV of around 80 in both wines. This is a substantially greater value than previously found for other rosé wines, in which β-ionone had an OAV of 3−6.[10,12] 3-SH contributes grapefruit aroma to wine[32] and had OAV around 9 for both samples, which accords well with other rosé wine studies[10,12] but contrasts with 3-SH having the largest OAV among odorants in Grenache rosé (OAV = 67).[13] BMT, which seems not to have been reported previously in AEDA studies on wine, was determined to have OAV = 35 in the fruity/floral sample, with this magnitude being consistent with previous rosé wine studies.[10,12] Phenylacetaldehyde, which induces honey and floral notes,[22] had OAV = 10 in the tropical wine and OAV = 8.4 in the fruity and floral one. Despite the relatively large OAVs, the lack of any sizable difference between the two rosé wines for these particular compounds, aside from BMT, indicated that in isolation they did not differentiate the different sensory styles.

To summarize the outcomes of this work, when the AEDA results for the two isolation methods are compared, HS was as good as SAFE for odorants eluting at the beginning of a GC run with a DB-Wax column. These compounds were primarily esters and higher alcohols associated with floral and fruity characters. As the RI of analytes increased, the exhaustive extraction ability of LLE became more evident; the compounds with higher boiling points and lower K_{aw} (air−water partition coefficient) were difficult to sample by the dynamic HS-SPE technique. However, for wine that was mostly fruity and floral driven, HS was sufficient to extract aroma compounds that were reflective of the sensory characters of the wine. From another perspective, HS was environmentally friendly compared with SAFE as the former was almost solvent free. Despite this advantage, light volatiles such as DMS were not captured by either extraction method, and it seems that AEDA information from at least two sample preparation strategies (i.e., static and dynamic HS methods or static HS and SAFE) is needed to determine a representative aroma model for olfactory analysis.

From the AEDA study and quantitative analysis, 2-phenylethyl acetate, ethyl butanoate, ethyl hexanoate, ethyl octanoate, ethyl 2-methylpropanoate, 3-methyl-1-butanol, 2-phenylethanol, hexanoic acid, and one grape-derived compound, β-damascenone, were deemed to have an important impact on sensory profiles in both samples. In particular, compounds such as 2-phenylethanol, β-damascenone, and a range of esters more associated with fruity and floral characters were apparently important to the fruity/floral rosé wine, whereas 3-SHA and several volatile acids were more related to the tropical style wine. The study was also explained in terms of OAVs calculated from quantitative results and published thresholds; ethyl octanoate, 3-methylbutyl acetate, ethyl hexanoate, β-damascenone, and β-ionone all had relatively large OAVs, along with BMT to a lesser extent. Within these compounds, the three esters were more associated with the tropical wine, whereas β-damascenone and BMT apparently contributed more to the fruity/floral wine. The concentration of β-ionone was not different between the two samples.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.6b01030.

> Wine basic chemical composition; method characteristics for volatile compounds determined by HS-SPME-GC-MS SIM; aroma properties for volatile compounds quantified; customized flask for conducting HS-SPE analysis (PDF)

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Notes

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■ ABBREVIATIONS USED

AEDA, aroma extract dilution analysis; LLE, liquid−liquid extraction; SAFE, solvent-assisted flavor evaporation; HS-SPE, headspace-solid phase extraction; FD, flavor dilution; 3-SHA, 3-sulfanylhexyl acetate; GC-O, gas chromatography−olfactometry; GC-MS, gas chromatography−mass spectrometry; RI, retention index; OAV, odor activity value; HS-SPME, headspace-solid phase microextraction; 3-SH, 3-sulfanyl-1-hexanol; TA, titratable acidity; ODP, olfactory detection port; DA, descriptive analysis; SIM, selected ion monitoring; LOD, limit of detection; LOQ, limit of quantitation; 4-MSP, 4-methyl-4-sulfanylpentan-2-one; FT, furfurylthiol; BMT, benzenemethanethiol; IBMP, 3-isobutyl-2-methoxypyrazine; DMS, dimethyl sulfide; K_{aw}, air−water partition coefficient

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Chapter 5

Concluding remarks and future perspectives

It was important to understand the sensory attributes of Australian rosé wines, particularly aroma and flavour attributes, as well as the preferences of consumers in a target market, in order to gain scientific knowledge that could ultimately lead to further development of this style in the future. Researchers have previously conducted several studies on rosé wine produced from a certain region (such as Provence, France) or from a specific variety (such as Grenache), but until now, no studies none have been undertaken on Australian rosé wines produced from different varieties. Therefore, it was essential to address gaps concerning rosé wine from Australia, a region in which the wine industry is closely involved in research. Being a style situated between white and red wine styles, rosé wine differs with respect to aspects including sugar content, volatile composition, tannin profiles and other non-volatile components, and investigations were necessary to establish a more detailed and comprehensive understanding of Australian rosé wines. Also, determining links between wine composition and wine quality/preference in a target market would help industry to tailor their products to meet specific consumer expectations.

5.1 Conclusions

Rosé wine is more or less intermediate between white and red wines. It is made from different red grape varieties, but differs from the normal red winemaking process due to substantially less skin contact time, which yields wine colours ranging from red onion skin to deep purple due to limited extraction of the grapes. In general, rosé wine has fruity and floral aroma characters, although some wines show developed attributes, such as savoury and oaky notes. It is a versatile and diverse style that is becoming more popular around the world, especially with younger consumers. Also, it is a burgeoning style in Asian countries as it tends to match well with eastern cuisines.

5.1.1 Chemical and sensorial profiles of Australian rosé wines

This work constituted the first study on volatiles and aroma/flavour profiles of Australian rosé wines, which led to the first aim stated in Chapter 1 being accomplished. During this phase, 47 volatiles were quantified using an HS-SPME–GC–MS method in scan mode that was developed and validated within the study. This quantitative method was linear across the required concentration ranges, with an $R^2 \geq 0.99$. Recoveries were between 90 % and 110 % and the precision varied from 8 % to 21 %, at low and high concentrations. Limit of quantitation values were frequently below the reported aroma detection thresholds of the analytes. Sensory descriptive analysis with 12 trained panellists (5 females, 7 males) was also undertaken in order to correlate sensory data with compositional data, so as to explore relationships between chemical and sensory profiles. Panellists were firstly trained to generate sensory attributes, reach consensus on scale use, and to refine reference standards before being familiarised with the tasting environment of the sensory booths. In total, 13 aroma and 12 flavour attributes were selected for evaluation during formal descriptive analysis. 26 samples were sourced from different wine regions (Barossa Valley, Adelaide Hills etc.) and different varieties (Grenache, Pinot Noir, Shiraz, etc.), and 47 out of 51 volatiles measured were found to be significantly different; almost half were fruity and floral acetate and ethyl esters. Compounds such as hexyl acetate (fruity, floral), β-damascenone (floral, fruity), 3-methylbutyl acetate (fruity), ethyl hexanoate (apple peel) and 3-sulfanyl-1-hexanol (3-SH) (tropical, passion fruit) were considered to be important based on odour activity value (OAV), in accord with earlier studies on different rosé wines (Prieto Picudo, Çalkarası or Grenache) from France, Spain or Turkey. Additionally, compounds like 2-phenylethyl acetate, β-citronellol, furfurylthiol and benzyl mercaptan contributed to the differentiation of samples as they all had large OAVs in some rosé wines. According to principal component analysis, samples were separated along PC1 based on ethyl decanoate, and octanoic and decanoic acids in the positive direction and ethyl 2-methylbutanoate, diethyl succinate, and ethyl 3-methylbutanoate in the negative direction. Vitispirane, α-terpineol and β-citronellol separated samples along PC2 in the positive direction and ethyl 2-hexenoate, ethyl nonanoate and dodecanoic acid in the negative direction. In the end, different aroma/flavour profiles were described using 23 sensory descriptors. In general, aroma attributes related to tropical fruit, citrus, spicy and overall intensity were all significantly different and only the fresh green and reduced were not different in flavour among the wines. Some wines exhibited more red/dark fruit, stone fruit, honey, floral and confectionery characters; three wines were more associated with developed characters, four displayed more green, yeasty and reduced aromas but less fruit and floral, and the remainder tended to be more related to citrus flavour. Various sensory characters were broadly covered by all rosé wines in this study and generated four distinct styles: tropical and citrus; reduced, yeasty and fresh green; savoury, oaky and spicy; red/dark fruits, floral and confectionery.

5.1.2 Chinese wine professionals' preferences for rosé wines and links between wine composition and quality

In order to achieve the second aim of this project, a preliminary study of the opinions of Chinese wine industry professionals towards Australian rosé wines was undertaken. This was completed in conjunction with a first comparison of the sensory and chemical profiles of rosé wines from three geographic regions, Australia (n = 18), China (n = 3) and France (n = 2). Altogether, 62 Chinese wine professionals took part in blind tastings of rosé wines, in three major cities of China. The panellists in each tasting were asked to have a discussion on the quality and expected characters of rosé wines in order to generate consensus before the formal evaluation, during which they tasted 23 rosé wines in 6 brackets. Basic wine chemical parameters and 47 volatile compounds (including 5 potent thiols) were determined for the wines, and a novel use of network analysis provided good visualisation of the correlations between chemical and sensory components. Overall, panellists preferred rosé wines with red fruit, floral, confectionery and honey characters and lower residual sugar. Better wine quality had a positive correlation with acidity and red fruit character, and preference, quality and expected retail price were closely related to β-damascenone and 3-MHA levels. 3-Methylbutyl acetate, hexyl acetate, β-damascenone, and some polyfunctional thiols appeared to be most important to the aroma of these wines, and were all related to either sensory properties or preference, quality and expected retail price. The links between wine volatiles, sensory characters and preference/quality/expected retail price were identified by network analysis and were consistent with earlier research, although some interesting relationships between the variables are worthy of further investigation. In particular, studies on the relationship between diethyl succinate and rosé wine age, in conjunction with acetate esters, red fruit characters and consumer preference, could be pursued.

5.1.3 AEDA study on rosé wines and strategies to produce a representative extract for GC-O analysis

Based on the preliminary study in Chapter 2, two rosé wine styles (one tropical and one fruity/floral) were chosen for further exploration by aroma extract dilution analysis (AEDA) and quantitative analysis of volatile compounds. The third aim established in Chapter 1 was achieved during this stage. Two extraction methods, being an often utilised liquid-liquid extraction (LLE) followed by solvent assisted flavour evaporation (SAFE), and a recently developed dynamic headspace (HS) solid–phase extraction (SPE) sampling method, were applied to obtain odourant extracts from the two wines. The HS-SPE approach was applied to wine for the first time. AEDA was conducted using gas chromatography−mass spectrometry/olfactometry (GC−MS/O) (split ratio = 1:2 between MS and olfactometry) with liquid injection. The extracts were stepwise diluted to obtain 3, 9, 27, …, 177147 dilutions and were evaluated by 5 sensory panellists. The flavour dilution (FD) factors for each odourant in four extracts were recorded and defined as the maximum dilution when more than half (n ≥ 3) of the sniffers could still detect the aroma. A newly developed and validated HS-SPME–GC–MS method with Selected Ion Monitoring (SIM), together with several other methods, were applied to quantitate volatiles in both wines. In total, according to the AEDA results, 51 aroma compounds with a FD factor ≥ 3 were detected and 92 volatiles were quantified in both samples. Compounds including 2-phenylethyl acetate, ethyl butanoate, ethyl hexanoate, ethyl octanoate, ethyl 2-methylpropanoate, 3-methyl-1-butanol, 2-phenylethanol, hexanoic acid, and one grape-derived compound, β-damascenone, were important to the aroma profiles of both samples. Specifically, the fruity and floral sample was more related to a range of esters, together with 2-phenylethanol (rose, perfume) and β-damascenone (fruity, floral). Compounds such as 3-SHA (passion fruit, tropical) and several volatile acids were considered to be more important for the tropical sample. Moreover, based on quantitative data, large OAVs were observed for ethyl octanoate (green, fruity), 3-methylbutyl acetate (banana), ethyl hexanoate (confectionery, strawberry), 3-methylbutyl hexanoate (caramel, yeasty) and β-damascenone. The concentrations of the first four volatiles were higher in the tropical sample, whereas β-damascenone contributed more to the fruity and floral sample, consistent with AEDA results. For different extraction methods, HS was sufficient to extract aroma compounds which had lower boiling points/polarity, which usually involved higher alcohols and esters. Based on retention index increases for later eluting compound (on a polar column), it became difficult to capture volatiles using the HS-SPE technique, but this also indicates the time that compounds extracted by LLE would be overestimated. In summary, when assessing the impact of different volatiles on wine sensory profiles by AEDA, both LLE and a HS method could be considered simultaneously to build the most representative volatile extract of wine.

5.2 Future directions

1). Based on the quantitation method developed and sensory descriptive analysis outcomes described in Chapter 2, a similar procedure should be undertaken on a larger set of rosé wines collected across different regions and grape varieties in order to explore the links between rosé wine composition and sensory characters as a function of region and variety. Also, the impact of different seasons on rosé wine sensory characters and preference could be explored. Moreover, the effect of viticultural and/or winemaking practices on rosé wine aroma needs to be investigated further. Ultimately, the differences or similarities in wine flavour and sensory characters between Australian rosé wine and rosé wine from old world or emerging wine countries could be examined.

2). In total, 23 rosé wines, chosen based on the outcomes from the initial study or sourced from Chinese and French wine regions, were assessed by Chinese wine professionals in blind tastings in three major cities of China. Links between wine composition, sensory attributes, quality/preference/expected price were evaluated. A greater number and range of rosé wines should be included in the sensory evaluation and large scale consumer testing is needed with more regular wine drinkers from different parts of China. Brand recognition, various wine drinking vessels and occasions, and particularly food pairing with rosé wine, could be explored further in order to understand the preferences of Chinese wine consumers for rosé wine, the driving force behind their purchasing behaviour and how aroma/flavour profiles interact or match with different foods. Significant economic gains through increased market share in emerging Asian markets could be possible with a better understanding of the desirable aroma profiles of Australian rosé wines.

3). More detailed studies were accomplished on two different rosé wine styles by applying AEDA in Chapter 4. In conjunction with the approach taken, more volatiles could be evaluated in future, and reconstitution and omission tests conducted with different aroma compounds to confirm the AEDA results and investigate the sensory impact of aroma compounds in a matrix that is closer to a real wine environment. Also, different non-volatile components, such as polyphenols, polysaccharides, acids, residual sugar, proteins and nitrogenous compounds, could be studied to examine their impact on aroma profiles. Two extraction methods have been tested in Chapter 4 where the traditional LLE-SAFE method and recent dynamic HS-SPE method exhibited different performance characteristics according to GC-O results. The effect of different parameters on extraction performance using the HS-SPE method could be further investigated, such as the shape of the glassware, in order to better imitate the sniffing process when a glass of wine is evaluated during consumption. The most representative odourant extract for sensory analysis, which is non-discriminatory towards different volatiles with various properties, could then be determined. Also, the HS-SPE method could be creatively used for studying the change of volatiles in the headspace of sparkling wine during normal consumption, as it has been observed by others that the general aroma of sparkling wines changes markedly while carbon dioxide is being released.

In summary, this research provided the first insight into the chemical and sensory characteristics of Australian rosé wines. The impact of different volatiles on rosé aroma profiles was studied and the desirability of aroma profiles of Australian rosé wines was investigated with professionals from an emerging wine market. This project has contributed comprehensive knowledge of Australian rosé wine composition, sensory styles and impact of different volatiles on aroma profiles. The studies presented in this thesis may assist the wine industry to modify and customise rosé wines to meet specific consumer appeal through an increased understanding of rosé wine composition and preferences of the target market. In addition, the research accomplished on different volatile extraction strategies could assist other researchers to construct the most objective and representative extract from a natural product for GC-O experiments. In the end, the new knowledge generated in this thesis can help drive competitiveness, innovation, control of quality and ultimately local and global market share of rosé wine.

List of abbreviations

µECD	microcell electron capture detector
1D−GC	one dimensional gas chromatography
2D−GC or GC×GC	two dimensional gas chromatography
3MH	3-mercaptohexan-1-ol
3MHA	3-mercaptohexyl acetate
3-SH	3-sulfanyl-1-hexanol
3-SHA	3-sulfanylhexyl acetate
4MMP	4-mercapto-4-methylpentan-2-one
4MMPOH	4-mercapto-4-methyl-2-pentanol
4MSP	4-methyl-4-sulfanylpentan-2-one
AEDA	aroma extract dilution analysis
AWRI	The Australian Wine Research Institute
BMT	benzenemethanethiol
CRI	calculated retention index
CSC	China Scholarship Council
DA	descriptive analysis
DMS	dimethyl sulfide
DSPE	dispersive solid-phase extraction
DTDP	4,4′-dithiodipyridine
DVB/CAR/PDMS	divinylbenzene/carboxen/polydimethylsiloxane
EC	ethyl carbamate
ECD	electron capture detector
FD	flavour dilution
FID	flame ionisation detector
FPD	flame photometric detector
FT	furfurylthiol
GC	gas chromatography
GC−MS/O	gas chromatography−mass spectrometry/olfactometry
GC−O	gas chromatography−olfactometry
GC−R	gas chromatography recomposition
HPLC–MS/MS	high-performance liquid chromatography–tandem mass spectrometry

HRMS	high-resolution mass spectrometer
HS	headspace
IBMP	2-methoxy-3-isobutyl
IPMP	2-methoxy-3-isopropyl
ITD	ion trap detector
K_{aw}	air-water partition coefficient
LLE	liquid-liquid extraction
LOD	limit of detection
LOQ	limit of quantification
LRI	linear retention index
LTM	low thermal mass
MALB	multi-coloured Asian ladybeetles
MDGC	multidimensional gas chromatography
MDMP	2-methoxy-3,5-dimethylpyrazine
MLF	malolactic fermentation
MPs	methoxypyrazines
MS	mass spectrometer
MSPD	matrix solid phase dispersion
NA	network analysis
NCI	negative chemical ionization
ND	not detected
NIF	nasal impact frequency
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
NPD	nitrogen phosphorus detector
NQ	not quantified
OAVs	odour activity values
ODP	olfactory detection port
OGA	olfactometry global analysis
O−MS	olfactory−mass spectrum
PCA	principal component analysis
PC	principal component
PLS	partial least squares
qMS	quadrupole mass analyser

QTOFMS	quadrupole–time-of-flight mass spectrometer
RT	retention time
SAFE	solvent assisted flavour evaporation
SBMP	2-methoxy-3-sec-butyl
SBSE	stir bar sorptive extraction
SIDA	stable isotope dilution assay
SIM	selected ion monitoring
SPE	solid phase extraction
SPME	solid-phase microextraction
TA	titratable acidity
TBA	2,4,6-tribromoanisole
TCA	2,4,6-trichloroanisole
TDN	1,1,6-trimethyl-1,2-dihyrdonapthalene
TeCA	2,3,4,6-tetrachloroanisole
TOFMS	time-of-flight mass spectrometer
TPB	(*E*)-1-(2,3,6-trimethylphenyl)buta-1,3-diene
UA	The University of Adelaide
VA	volatile acidity
VIP	variable importance in the projection

Appendices

These are additional data generated during candidature, corresponding to content from Chapters 2 to 4, and submitted with the publications as supplementary information.

Appendix 1. Details of Deuterium-Labelled Internal Standards (corresponding to Table S1 in Chapter 2).

compound name	CAS no.	concentration (mg/L)	RI (DB-Wax)	ions[a]
d_4-3-methyl-1-butanol	1219795-21-7	23.8	1224	42, 59, **74**
d_3-hexyl acetate	1219805-39-6	0.250	1276	**46**, 56, 84
d_{13}-1-hexanol	204244-84-8	0.500	1354	**64**, 78, 96
d_5-ethyl nonanoate	–	0.012	1534	74, **93**, 106
d_5-2-phenylethanol	35845-63-7	5.00	1899	**96**, 127, 205
d_{19}-decanoic acid	88170-22-3	0.502	2244	63, **141**, 191

[a] Qualifier and quantifier (bold) ions used.

Appendix 2. Basic Wine Composition for 26 Australian Rosé Wines[a] (corresponding to Table S2 in Chapter 2).

sample no.	variety	vintage	region	alcohol (% v/v)	pH	TA (g/L)	glucose+fructose (g/L)
1	Shiraz, Cabernet Sauvignon, Grenache	2012	Blackwood Valley	12.4 l	3.41 de	7.2 ±0.1 e	3.1 ±0.2 f
2	Sangiovese	2012	Barossa Valley	13.1 ±0.1 fg	3.15 lm	6.4 ±0.2 hi	1.3 jklm
3	Grenache	2012	Barossa Valley	12.5 k	3.37 fg	5.6 ±0.1 n	0.6 m
4	Grenache, Shiraz, Cabernet Sauvignon, Dolcetto	2012	Barossa Valley	13.3 d	3.37 fg	6.1 jk	5.1 e
5	Pinot Noir	2012	Yarra Valley	13.5 bc	3.64 b	5.2 ±0.1 o	0.8 ±0.1 lm
6	Shiraz	2012	Barossa Valley	11.3 q	3.33 h	6.6 ±0.1 g	7.7 ±1.4 bc
7	Shiraz	2012	Barossa Valley	12.5 k	3.37 fg	7.0 f	4.8 ±0.2 e
8	Grenache, Shiraz	2012	South Australia	13.2 e	3.36 fg	6.5 ghi	1.8 ±0.1 hij
9	Shiraz, Cabernet Sauvignon, Grenache, Merlot	2013	Barossa Valley	13.1 g	3.21 l	6.6 gh	2.6 ±0.2 fg
10	Pinot Noir	2012	Adelaide Hills	13.1 g	3.43 d	6.4 ±0.1 i	2.1 ±0.1 ghi
11	Sangiovese	2013	Big Rivers	12.7 j	3.37 fg	6.4 hi	7.5 ±0.1 c
12	Grenache, Mourvèdre, Shiraz.	2012	Barossa Valley	13.1 g	3.23 ±0.1 l	6.4 ±0.1 hi	2.2 gh
13	Sangiovese, Pinot Noir	2012	Adelaide Hills	11.7 n	3.23 k	7.6 c	6.0 ±0.8 d
14	Shiraz, Merlot	2013	Mudgee	13.5 bc	3.65 b	5.7 mn	2.1 ghi
15	Mourvèdre, Grenache, Sangiovese	2012	Clare Valley	13.5 b	3.41 de	5.9 ±0.1 lm	2.2 ghi
16	Cabernet Sauvignon, Merlot, Shiraz	2012	Margaret River	13.0 ±0.1 h	3.29 i	7.1 ef	5.0 e
17	Shiraz, Cabernet Sauvignon	2012	Yarra Valley	12.9 i	3.52 c	5.8 mn	1.5 ±0.1 ijk
18	Cabernet Franc	2012	Hunter Valley	13.2 ef	3.39 ef	7.5 ±0.1 d	0.9 klm
19	Pinot Noir	2012	Lake George	11.5 p	3.25 jk	9.1 a	4.8 ±0.2 e
20	Sangiovese, Cabernet Franc	2012	Padthaway	13.4 c	3.14 lm	6.2 ±0.1 j	1.3 jkl
21	Cabernet Sauvignon	2012	Margaret River	12.4 l	3.05 n	6.5 ghi	9.3 ±0.4 a
22	Pinot Noir, Cinsaut, Mourvèdre	2012	McLaren vale	13.7 a	3.35 gh	8.6 b	7.9 ±0.3 bce
23	Cabernet Franc, Shiraz, Pinot Noir	2013	Orange	13.3 d	3.70 a	5.9 ±0.2 kl	2.2 ±0.1 gh
24	Cabernet Sauvignon	2013	Barossa Valley	12.7 j	3.13 m	7.2 e	8.3 b
25	Sangiovese	2013	King Valley	11.7 o	3.27 ij	7.2 e	1.7 hij
26	Sangiovese	2012	King Valley	11.8 ±0.1 m	3.42 de	7.0 f	0.8 klm

[a] All data are expressed as the mean ± standard deviation (n = 2). Where SD is not shown the value was 0. Different lowercase letters indicate significant differences ($p < 0.05$) between sample means within a column according to Tukey's HSD test.

Appendix 3. Attributes Used during Descriptive Analysis (DA) to Determine the Sensory Profiles of Rosé Wines (corresponding to Table S3 in Chapter 2).

aroma attribute	descriptors	recipes used for standards[a]
tropical fruit	passionfruit, pineapple, melon, lychee, papaya	rock melon 5.91 g (flesh+seeds) + lychee 2 g + lychee juice 2 mL + pineapple 6.45 g + passionfruit 2.3 g
red/dark fruit	raspberry, strawberry, also dark fruits	high intensity (raspberry 3 g + strawberry 8 g) medium intensity (raspberry 1 g + strawberry 3 g) low intensity (raspberry 0.3 g + strawberry 1.2 g)
floral	rose, violet, perfumed, blossom	rose water 20 drops[b] + jasmine flower 0.17 g + rose flower petal 0.53 g + rose flower stamen 0.33 g
citrus[c]	grapefruit, lemon, lime, orange, mandarin	grapefruit 6.5 g + lemon 5.27 g + lime 3 g + mandarin 3.5 g + orange 3 g
stone fruit[c]	peach, apricot	dried peach and apricot mixture 8.35 g + nectarine 4.95 g + peach 3.95 g + fresh apricot 6.88 g
fresh green	grassy, green capsicum, tomato leaf, mint, apple	grass 2 g + green capsicum 0.4 g + tomato leaves 1 g + green apple peel 3.48 g
spicy	mixed spice, sweet spice, cinnamon, clove	a mixture of mixed spice, sweet spice, cinnamon and clove 0.1 g
confectionery	lolly, banana, estery, musk lolly, Turkish delight	fruit lollies 3.5 g (yellow, green and red ones half each)
honey	honey	low intensity (honey 0.6 g) high intensity (honey 2.69 g)
yeasty	creamy, cheesy, leesy	dried yeast 0.2 g
oaky/smoky[d]	oaky, toasty, caramel, coconut, nutty, vanilla, woody	vanilla extract 1 drop + coconut extract 1 drop + oak extract 5 drops + smoke extract 5 drops
reduced	rubbery, burnt rubber, struck flint, onion, asparagus, sulfurous	base wine 30 mL + onion 1 g
savoury	gamey, meat broth, soy sauce, cooked bacon	one smoked almond + 10 mL cask rosé wine
overall intensity	overall aroma intensity	low intensity (1:5)[e] high intensity (5:3)[e]

[a] Apart from the additional descriptions, all aroma standards were prepared in 25 mL of base wine. [b] Each drop was equal to approximately 0.05 g. [c] All components were used, i.e. both flesh and peel. [d] All ingredients were natural extracts. [e] Ratio of raspberry cordial/water.

Appendix 4. Mean Scores for Each Attribute Rated during DA for 26 Australian Rosé Wines[a] (corresponding to Table S4 in Chapter 2).

sample no.	tropical fruit	red/dark fruit	floral	citrus	stone fruit	fresh green	spicy	confectionery	honey	yeasty	oaky/smoky	reduced	overall intensity
1	7.26	3.21	2.11	2.91	4.18	1.38	2.67	2.74	2.34	1.29	3.74	1.48	9.84
2	5.42	5.13	3.22	4.03	2.36	1.07	2.34	3.03	1.03	2.19	2.20	2.22	6.33
3	3.61	3.84	3.78	2.71	2.26	1.81	3.86	2.04	1.30	1.38	3.09	3.66	6.65
4	5.48	5.39	2.69	3.63	1.80	1.07	2.11	3.50	1.28	2.31	2.77	2.21	7.33
5	3.43	4.65	2.65	2.83	2.50	1.83	4.10	2.76	1.52	1.19	2.65	2.59	7.91
6	5.97	5.34	2.31	4.08	3.08	0.98	2.04	3.40	1.72	1.14	2.68	1.08	8.13
7	7.65	4.94	3.32	4.01	2.96	1.31	2.18	3.38	1.65	1.86	2.47	1.65	9.23
8	6.88	6.48	4.31	4.29	2.93	0.83	2.20	5.67	2.47	1.22	2.05	1.21	9.14
9	7.09	6.61	3.58	4.45	3.83	1.46	1.43	3.74	2.73	1.03	1.53	1.41	8.83
10	7.32	4.35	4.07	5.19	3.65	1.35	1.05	3.79	2.20	0.73	1.80	1.88	9.13
11	7.37	4.94	4.29	4.50	3.99	0.94	2.15	4.33	2.21	1.85	1.64	1.63	8.69
12	3.46	4.63	3.64	2.79	2.24	1.58	5.18	2.44	2.18	1.91	4.03	2.15	9.63
13	6.95	4.83	3.07	5.39	2.33	1.34	2.21	2.39	1.41	1.91	2.87	3.39	8.42
14	6.37	4.24	2.41	4.00	2.56	0.88	2.71	3.57	2.06	0.99	2.14	1.32	7.14
15	8.16	4.00	2.34	4.60	2.73	2.13	1.96	2.28	1.06	1.50	2.45	2.87	7.89
16	5.97	4.52	3.77	4.58	2.64	1.78	3.51	2.89	1.65	0.97	1.73	1.19	8.13
17	6.06	4.41	1.73	4.03	2.91	1.59	1.95	2.47	1.23	1.35	2.33	2.16	7.93
18	5.47	3.90	1.93	3.18	1.83	3.91	2.57	2.25	0.98	1.23	3.68	3.82	8.58
19	6.19	4.84	2.07	3.74	1.60	2.23	1.51	2.01	1.32	2.64	2.67	3.99	6.68
20	5.06	3.83	2.53	3.94	2.59	1.71	4.03	3.17	1.19	1.49	3.79	0.89	7.23
21	5.50	4.33	2.29	3.51	3.19	2.51	2.45	2.88	3.98	1.89	3.66	3.13	9.14
22	2.89	6.61	3.11	3.10	1.77	2.21	4.91	2.91	1.51	1.32	4.36	2.14	9.36
23	7.10	5.71	4.64	3.59	3.31	1.46	2.84	3.59	1.41	1.25	1.59	1.41	7.47
24	5.61	5.08	4.83	2.91	3.47	1.63	1.86	3.19	1.83	1.09	1.48	3.43	9.22
25	6.97	4.05	3.06	5.52	2.84	1.71	1.61	3.70	2.12	1.36	2.66	1.15	8.58
26	6.82	4.85	2.64	4.28	2.32	1.01	1.77	3.58	1.46	1.08	2.26	2.14	6.66

[a] Evaluated on a 0-15 scale.

Appendix 4. continued

sample no.	f-tropical fruit	f-red fruit	f-floral	f-citrus	f-stone fruit	f-fresh green	f-spicy	f-confectionery	f-honey	f-savoury	f-reduced	f-overall intensity
1	6.99	5.59	2.03	5.03	4.64	2.02	2.44	2.74	2.29	1.88	1.78	9.34
2	5.05	5.46	1.49	6.72	1.97	2.00	1.65	2.26	0.96	1.58	1.86	7.67
3	4.39	4.10	1.69	5.16	1.88	2.39	2.41	2.61	0.99	2.06	1.62	7.36
4	6.12	6.31	1.96	6.07	2.95	1.83	1.29	3.06	1.32	2.14	1.96	8.18
5	5.00	5.33	2.28	3.79	2.86	1.78	2.78	1.83	0.85	1.86	2.04	8.36
6	6.00	7.90	2.56	4.36	4.96	0.96	1.23	3.37	1.63	1.44	1.04	9.51
7	7.46	6.29	2.61	6.16	3.64	1.78	1.79	3.68	2.06	1.09	1.22	9.32
8	6.36	7.86	2.48	5.52	3.22	2.02	1.28	4.11	1.72	1.36	1.07	9.54
9	6.19	7.81	2.15	5.33	5.01	1.44	2.08	3.26	2.10	1.15	1.35	10.03
10	6.02	6.19	3.08	5.58	4.36	1.15	1.28	3.70	2.03	0.81	1.52	9.28
11	6.88	6.11	2.99	5.60	3.98	1.84	1.71	3.54	1.48	0.94	1.26	8.86
12	3.79	6.06	2.19	5.13	1.94	1.47	4.01	1.62	1.56	2.59	2.18	8.78
13	6.61	5.51	1.62	6.57	2.70	1.43	0.90	2.11	1.16	1.33	1.80	8.34
14	6.13	4.74	2.15	4.45	2.89	1.55	1.41	2.24	1.24	1.76	1.99	7.34
15	8.45	5.36	2.04	5.73	2.99	1.92	1.56	1.84	0.72	1.49	1.90	9.08
16	6.06	6.76	2.67	7.42	2.51	2.05	2.33	2.88	1.27	0.83	1.09	8.89
17	5.09	4.86	1.36	6.21	4.17	2.07	1.44	1.84	0.79	1.45	2.31	7.54
18	4.99	4.75	1.21	6.83	2.21	3.27	1.75	1.48	0.86	1.13	2.49	8.79
19	5.24	4.56	1.36	8.84	2.46	2.42	0.96	1.88	0.93	1.39	1.94	8.66
20	5.43	4.92	1.38	6.27	2.21	1.86	2.59	1.66	0.83	1.54	1.02	7.94
21	6.52	6.46	2.01	5.40	3.81	2.19	1.49	3.13	3.30	1.28	2.73	9.63
22	3.05	7.59	1.88	4.84	2.12	2.50	3.74	2.21	0.98	1.96	1.90	10.33
23	6.68	4.61	3.45	5.96	2.86	2.15	2.04	2.84	1.09	1.49	1.19	8.91
24	6.14	7.04	2.88	6.41	3.83	1.56	1.68	2.83	1.71	1.26	1.92	9.98
25	6.38	4.36	1.84	7.60	2.51	1.30	0.91	2.73	1.25	1.40	1.20	8.33
26	6.44	4.66	1.98	7.22	1.90	1.85	0.69	1.84	0.73	1.45	1.31	7.05

Appendix 5. Mean Concentrations of Volatile Compounds with Standard Deviations (n = 2) in 26 Australian Commercial Rosé Wines[a] (corresponding to Table S5 in Chapter 2)

Compounds/Wine No.	1	2	3	4	5	6	7	8	9	10	11
ethyl acetate	222336±37746	165703±37011	191277±18345	225800±7961	207697±14325	228966±2148	202084±8430	194655±12874	228361±21397	241265±2740	236165±376
ethyl butanoate	147±101	560±175	527±79.3	442±33.1	N.D.[b]	448±5.1	369±34.2	431±90.0	503±84.6	282±20.8	357±21.3
1-propanol	17946±1385	16553±121	15434±1568	22049±847	8650±53.4	9764±610	12732±393	23607±235	24754±1111	12495±1216	12793±1070
ethyl 2-methylbutanoate	17.9±0.9	N.D.	33.1±4.9	53.1±2.6	29.7±3.7	7.8±1.3	12.5±0.21	N.D.	N.D.	N.D.	N.D.
2-methyl-1-propanol	2296±27.3	1983±362	4753±508	2948±47.6	12471±635	2089±70.4	2429±145	2423±346	2660±376	1864±57.5	2136±41.6
3-methylbutyl acetate	N.D.	1987±746	N.D.	2773±254	131±51.0	6366±69.6	4751±506	3716±667	8131±1294	4007±234	8523±167
limonene	0.88±0.04	1.8±0.019	N.D.	N.D.	1.4±0.15	N.D.	N.D.	1.7±0.27	N.D.	N.D.	0.99±0.01
3-methyl-1-butanol	77901±2144	100580±16674	135207±5974	125713±7098	141238±4158	89678±1428	99575±857	99541±1717	124773±4718	93668±4060	90976±811
ethyl hexanoate	728±263	1885±784	1347±101	1666±105	121±40.6	1592±18.6	1221±112	1714±330	957±128	1396±125	1083±112
hexyl acetate	779±139	2191±253	258±3.5	1575±118	340±41.6	8429±72.3	5802±245	3007±608	3463±173	4737±212	3592±22.4
ethyl lactate	22576±178	4578±579	80663±6213	N.D.	203080±21435	N.D.	7317±3.7	41301±15.7	N.D.	2830±223	4655±480
1-hexanol	9296±271	4599±880	12269±504	5819±390	4249±270	8408±109	8208±57.1	4562±8.0	3904±250	4807±216	641±35.6
nonanal	35.7±15.2	28.3±16.8	18.1±8.8	25.8±3.6	N.Q.[c]	43.9±6.3	33.6±3.8	N.Q.	14.8±1.7	11.1±0.42	40.6±7.8
furfural	1414±32.2	37.1±52.5	100±5.1	60.5±85.5	164±13.7	258±5.7	334±3.2	180±11.2	N.D.	183±0.41	N.D.
3-methylbutyl hexanoate	N.D.	5.4±0.15	4.4±0.28	14.8±0.74	1.4±0.54	N.D.	5.4±1.2	4.9±0.43	6.8±0.0.058	3.1±0.2	1.5±0.030
acetic acid	188030±14201	141728±34690	113475±5738	143275±21961	300041±891	108772±3747	99387±1485	184611±9712	134907±2966	221622±9743	111887±6014
ethyl octanoate	2493±553	6787±1935	1870±28.7	4796±216	1652±119	3787±190	3798±416	5676±376	2492±10.1	4793±189	3407±97.5
2-ethyl-1-hexanol	54.8±11.8	69.2±35.9	62.1±16.4	43.6±7.8	56±15.4	50.4±9.5	25.4±8.2	52±6.4	72.4±4.5	54.3±12.4	104±7.8
benzaldehyde	74.0±5.0	N.D.	N.Q.	N.Q.	27.7±2.8	N.D.	N.Q.	11.3±1.4	N.D.	N.Q.	N.Q.
linalool	38.2±11.3	114±36.1	86.6±2.9	54.4±43.6	115±90.6	37.9±23.3	8.5±0.14	66.2±26.7	N.Q.	14.2±1.5	19.8±1.3
1-octanol	38.5±3.0	43.6±20.9	42.1±1.8	46.6±4.8	36.6±0.45	9.6±0.79	18.0±1.4	31.8±1.9	29.7±1.3	16.2±5.8	21.8±4.5
ethyl furoate	69.4±2.8	7.0±1.2	N.D.	6.0±0.85	N.D.	N.D.	3.4±0.15	2.3±1.2	N.D.	N.D.	N.D.
ethyl decanoate	2298±232	5106±1039	610±16.0	3931±237	1512±50.9	3867±293	4111±393	5618±33.9	2899±84.7	4777±317	3292±129
3-methylbutyl octanoate	N.D.	21.7±2.1	26.4±0.51	81.4. ±1.4	N.Q.	N.D.	21.5±1.7	25.4±1.4	31.8±0.19	12.2±1.2	N.Q.
diethyl succinate	72.6±9.1	N.D.	1954±77.9	916±23.8	7607±490	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
α-terpineol	68.2±8.4	47.2±8.9	29.4±4.0	35.0±0.79	39.3±2.8	27.6±2.1	27.6±0.46	44.4±0.15	47.9±1.1	38.5±7.3	26.8±1
β-citronellol	147±21.3	93.7±22.6	48.7±10.1	62.8±2.0	73.7±7.1	44.0±5.4	44.0±1.2	86.7±0.38	95.6±2.9	71.8±18.4	42.2±2.6
ethyl phenylacetate	35.8±2.8	4.7±0.73	1.9±0.19	5.7±0.24	4.3±0.37	0.56±0.033	2.9±0.068	5.1±0.024	N.D.	2.4±0.15	0.67±0.05
2-phenylethyl acetate	28.6±1.0	240±17.9	N.D.	113±3.2	8.2±4.9	199±4.3	481±7	152±16.8	107±2.6	210±1.4	675±1.6
β-damascenone	N.D.	N.D.	N.D.	1.0±0.045	N.D.	4.8±3.6	5.6±0.098	N.D.	15.3±0.52	2.0±0.18	1.3±0.098
ethyl dodecanoate	31.4±44.4	55.5±4.2	N.D.	89.3±5.5	96.5±39.2	119±2.2	243±3.9	241±6.8	158±6.7	215±59.7	50.9±1.2
hexanoic acid	6570±563	5505±462	143±202	1781±397	N.D.	2429±8.1	2571±115	5362±208	802±221	5207±1152	2494±225
2-phenylethanol	5583±143	7361±997	6075±292	7856±266	9244±538	4584±0.059	9380±221	4753±0.84	4362±65.2	5480±105	7255±79.6
octanoic acid	2134±215	5094±515	N.D.	3241±66.5	N.D.	3679±48.6	3672±232	4266±591	800±214	3588±278	2137±175
nonanoic acid	668±1.9	574±326	N.Q.	N.D.	594±223	506±86.7	229±323	471±665	119±168	475±671	497±112
decanoic acid	1858±39.1	2246±575	76.7±3.7	1965±15.5	698±7.8	3049±22.4	3027±58.3	2744±169	2007±119	2676±118	1802±47.2
3-mercapto-1-hexanol (ng/L)	2132±6.3	339±2.1	303±0.25	1007±3.4	1214±0.66	490±2	734±3.1	401±3.8	534±0.85	478±0.73	330±3.4

3-mercaptohexyl acetate (ng/L)	N.D.	2±0.025	N.D.	N.D.	N.D.	1.4±0.078	N.D.	N.D.	N.D.	2.6±0.13	8.4±0.38
2-furfurylthiol (ng/L)	21.1±0.047	N.D.	4.4±0.045	6.3±0.075	4.1±0.29	1.9±0.13	3.2±0.013	1.3±0.025	0.94±0.041	2.8±0.16	2.5±0.048
benzyl mercaptan (ng/L)	5.1±0.021	3.2±0.089	3.1±0.056	3.5±0.0053	4.1±0.038	2.0±0.094	2.5±0.13	1.6±0.071	1.6±0.035	2.2±0.083	3.1±0.056

[a] Concentrations in µg/L unless specified otherwise. [b] Not detected (below LOD). [c] Not quantified (below LOQ).

Appendix 5. continued

Compounds/Wine No.	12	13	14	15	16	17	18	19	20	21	22
ethyl acetate	185071±9642	139539±7069	160838±4209	209868±1927	133760±341	175743±7747	74639±2783	129241±9437	265274±4932	74978±33536	190758±984
ethyl butanoate	233±19.7	243±38.9	242±33.9	272±8.2	73.4±4.8	161±61.9	129±33	87.7±29.6	60.4±8.4	9.9±13.9	N.D.
1-propanol	10788±619	20808±1577	11443±1075	16654±378	7402±293	13860±211	13392±278	7758±127	9802±197	7279±551	8342±317
ethyl 2-methylbutanoate	178±11.8	N.D.	N.D.	N.D.	N.D.	N.D.	117±2.8	25.9±0.53	117±12.4	41.8±10.1	155±1.2
2-methyl-1-propanol	4217±207	1235±132	4244±59.8	3602±175	4014±290	3664±96.2	3624±89.5	4458±11.7	4428±13.2	1039±3.8	9952±155
3-methylbutyl acetate	N.D.	1632±253	5907±622	1791±69.9	1243±42.8	3036±514	N.D.	1045±195	N.D.	N.D.	411±106
limonene	N.D.	0.48±0.02	0.29±0.0.04	1.3±0.25	1.6±0.0.34	N.D.	N.D.	0.71±0.0.09	N.D.	N.D.	1.7±0.38
3-methyl-1-butanol	156560±3464	65685±1179	111889±16688	100901±334	115507±2009	102515±2189	114513±4232	79523±934	123811±5036	83625±1062	206723±3143
ethyl hexanoate	276±50.7	693±76.9	318±4.1	1127±41.4	563±16.2	435±257	375±107	366±88.9	543±7.5	13.1±0.63	N.D.
hexyl acetate	77.6±7	1669±98.4	3290±0.11	1628±64.1	1030±15.8	2403±679	138±52.1	1017±56.9	333±14.5	85.8±121	49.7±9.3
ethyl lactate	20115±48	31475±125	3400±213	41583±221	31574±120	14053±91	10544±172	6043±138	19451±213	4796±145	58073±145
1-hexanol	9292±150	2884±11.4	3986±20.6	7344±82.4	2927±39.7	5552±71.6	2608±18.7	3849±154	2764±90.0	2055±43.9	4399±30.4
nonanal	18.4±2.6	25.7±8.5	19.0±26.8	23.1±1.3	12.6±4.1	16.6±12.0	13.3±4.9	N.Q.	22.0±2.0	18.3±2.1	N.D.
furfural	333±7.0	N.D.	N.D.	N.D.	N.D.	39.3±55.6	263±7.6	114±1.0	115±163	124±2.1	159±3.0
3-methylbutyl hexanoate	N.D.	N.D.	5.7±0.42	N.D.	N.D.	N.D.	N.D.	1.7±0.23	2.3±0.23	N.D.	10.0±0.41
acetic acid	173441±10357	115305±3551	210659±73790	159339±8683	114571±13136	139010±25384	115197±12844	157679±7264	235282±14427	129655±11723	348820±2294
ethyl octanoate	936±148	2773±22.4	1734±470	3261±90.6	1698±163	1549±164	1322±161	1971±197	1901±172	216±305	N.D.
2-ethyl-1-hexanol	59.4±5.1	83.4±11	54.5±14.0	80.7±2.3	58.8±7.2	49.1±12.9	53.2±16.1	51.7±6.7	82.7±0.42	36.1±16.5	33.1±4.6
benzaldehyde	34.4±1.7	N.D.	160±21.7	N.D.	N.D.	27.2±3.5	N.D.	139±17.9	N.Q.	N.D.	N.D.
linalool	40±40.1	33.5±2.2	59.1±7.6	117±46.4	248±310	107±83.9	151±37.9	133±9.6	96.5±80.3	69.4±34.1	27.4±12.1
1-octanol	95.2±6.9	9.9±2.0	34.3±6.2	29.4±2.0	25.9±2.6	32.5±3.3	40.5±3.2	11.5±0.85	19.6±0.13	4.5±3.4	44.1±1.0
ethyl furoate	4.1±0.69	9.0±1.0	N.D.	N.D.	N.D.	N.D.	3.3±0.18	N.D.	N.D.	12.9±0.12	N.D.
ethyl decanoate	1084±103	3338±27.4	3265±731	3374±96.7	2188±100	3407±631	1674±229	2419±131	1986±191	1157±209	153±5.1
3-methylbutyl octanoate	N.D.	N.D.	25.4±3.1	N.D.	N.D.	N.D.	N.D.	N.Q.	14.5±2.3	N.D.	54.9±2.6
diethyl succinate	9039±397	N.D.	N.D.	435±103	N.D.	N.D.	3583±408	N.D.	5132±467	1843±201	4106±60.1
α-terpineol	52.3±1.6	34.7±1.8	N.Q.	35.0±0.2	35.8±0.88	N.Q.	21.4±0.74	36.7±0.32	27.2±2.2	21.1±0.84	68.4±2.9
β-citronellol	107±4.0	62.1±4.6	7.7±10.9	62.8±0.5	65.0±2.2	18.6±0.46	28.3±1.9	67.1±0.81	43.2±5.6	27.6±2.1	147±7.4
ethyl phenylacetate	15.6±0.65	2.5±0.15	1.8±0.33	3.2±0.35	4.3±0.54	7.6±0.0005	8.3±0.013	3.6±0.46	7.9±0.29	2.9±0.16	14.6±0.073
2-phenylethyl acetate	N.D.	97.7±2.7	262±144	77.5±1.9	96.3±10.6	234±28.6	N.D.	74.1±6.3	69.9±5.2	N.D.	42.2±0.36
β-damascenone	0.84±0.098	N.D.	29.7±2.5	1.3±0.39	3.3±0.71	4.4±1.8	N.D.	0.54±0.051	N.D.	2.5±1.3	1.9±0.075
ethyl dodecanoate	51±7.8	231±23.7	176±69.9	110±4.5	109±10.5	279±14.3	103±5.9	144±14.2	38.4±0.62	109±19.3	N.D.
hexanoic acid	N.D.	2981±308	3841±1299	3802±263	3458±250	5528±472	2722±327	2370±128	970±41.5	1004±166	N.D.
2-phenylethanol	12984±496	2972±30.3	8000±1.4	6534±56	8183±43.4	7340±20.4	9652±98.2	3751±210	10472±92.3	4140±16.2	22479±508
octanoic acid	N.D.	2083±293	803±4.3	1623±119	1955±503	2125±1024	980±324	1360±75.3	N.D.	N.D.	N.D.
nonanoic acid	N.Q.	427±176	893±132	515±202	N.D.	N.D.	821±100	538±123	624±18.4	755±47.8	411±51.8
decanoic acid	696±71.7	2160±5.5	1796±20.2	2057±13.4	1845±6.9	2523±11.4	1337±1.5	1620±59.5	1191±40.4	1446±27.7	38±18.1
3-mercapto-1-hexanol (ng/L)	700±9	627±3.5	347±1.4	3250±17.2	827±0.95	902±5.4	326±1.5	906±3.2	349±5.8	515±1.8	215±4.4

3-mercaptohexyl acetate (ng/L)	N.D.	N.D.	N.D.	3.4±0.25	1.4±0.27	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2-furfurylthiol (ng/L)	1.5±0.039	N.D.	N.D.	2.9±0.071	2.8±0.18	3.3±0.15	4.9±0.032	4.6±0.091	2.5±0.11	4.1±0.088	1.1±0.17
benzyl mercaptan (ng/L)	1.6±0.037	5.1±0.23	2.5±0.066	2.5±0.091	1.6±0.08	2.6±0.066	3.3±0.084	5.3±0.073	2.4±0.096	2.3±0.0075	1.3±0.0052

[a] Concentrations in μg/L unless specified otherwise. [b] Not detected (below LOD). [c] Not quantified (below LOQ).

Appendix 5. continued

Compounds/Wine No.	23	24	25	26
ethyl acetate	145920±2163	178886±1525	208000±4331	204609±3264
ethyl butanoate	62.8±13.7	318±8.4	376±29.9	292±12.9
1-propanol	9901±658	8656±119	13667±455	10878±215
ethyl 2-methylbutanoate	N.D.	N.D.	N.D.	N.D.
2-methyl-1-propanol	5858±585	1783±11.4	2136±75.6	1803±136
3-methylbutyl acetate	3718±25.7	6769±380	7664±638	4536±63.2
limonene	N.Q.	N.D.	N.D.	1.5±0.23
3-methyl-1-butanol	121317±8067	106439±1303	93744±419	81321±92.9
ethyl hexanoate	268±118	1429±86.1	1672±97.6	965±36.5
hexyl acetate	3170±123	7567±230	7851±343	3197±49.1
ethyl lactate	19241±256	3145±130	N.D.	9415±146
1-hexanol	3616±85.9	4971±56.0	3035±51.7	3497±15.0
nonanal	17.2±4.7	21.5±9.8	N.Q.	24.7±0.15
furfural	N.D.	N.D.	N.D.	N.D.
3-methylbutyl hexanoate	4.6±0.51	9.2±1.1	4.9±0.82	2.5±0.23
acetic acid	187409±5522	160843±3700	126319±242	177142±13683
ethyl octanoate	1384±260	3015±302	3797±45.9	3188±198
2-ethyl-1-hexanol	55.4±5.8	16.9±3.2	69.1±0.69	76.8±10.3
benzaldehyde	67.7±4.2	7.9±0.3	2.7±0.72	89.8±1.8
linalool	82.2±45.3	11.7±9.4	N.D.	N.D.
1-octanol	23.6±1.1	11.1±2.4	11.2±0.28	19.5±1.5
ethyl furoate	N.D.	N.D.	N.D.	N.D.
ethyl decanoate	3233±15.8	2821±157	5060±3.4	4271±300
3-methylbutyl octanoate	41.1±2.1	39.4±4.1	28.1±1.3	10.9±0.56
diethyl succinate	N.D.	N.D.	N.D.	N.D.
α-terpineol	21.2±0.42	26.2±0.021	29.3±0.85	31.8±2.5
β-citronellol	27.9±1.1	40.6±0.052	48.4±2.1	54.8±6.3
ethyl phenylacetate	1.2±0.29	2.5±0.14	0.37±0.52	1.7±0.22
2-phenylethyl acetate	168±15.2	426±4.7	516±36.3	220±13.3
β-damascenone	27.2±0.88	21.7±0.74	2.1±0.2	N.D.
ethyl dodecanoate	157±3.6	220±3.7	326±43.0	118±3.2
hexanoic acid	1797±545	2349±109	6079±17.1	5482±183
2-phenylethanol	8293±23.3	10234±506	5873±106	4998±68.3
octanoic acid	753±265	2949±171	5101±555	2969±404
nonanoic acid	579±43.9	82.3±79.8	566±265	779±206
decanoic acid	1985±77.4	2111±110	3178±36.1	2834±145
3-mercapto-1-hexanol (ng/L)	372±2.8	681±4.2	289±5.1	263±0.56
3-mercaptohexyl acetate (ng/L)	N.D.	7±0.073	4.6±0.14	N.D.

2-furfurylthiol (ng/L)	1.2 ±0.038	2.8 ±0.065	2.1 ±0.031	1.9 ±0.0076
benzyl mercaptan (ng/L)	1.4 ±0.06	2.2 ±0.046	2.5 ±0.074	2.4 ±0.059

[a] Concentrations in μg/L unless specified otherwise. [b] Not detected (below LOD). [c] Not quantified (below LOQ).

Appendix 6. Mean Concentrations (μg/L) of Semi-Quantified Volatile Compounds with Standard Deviations (n = 2) in 26 Australian Rosé Wines (corresponding to Table S6 in Chapter 2).

Compounds/Wine No.	1	2	3	4	5	6	7	8	9	10	11
ethyl 3-methylbutanoate	91.3±2.7	68.0±12.2	61.8±0.21	105±7.5	68.5±9.1	27.6±2.5	39.1±2.8	64.3±4.6	38.2±8.3	42.9±4.2	28.6±2.5
ethyl 2-butanoate	74.7±14.5	204±9.3	216±17.7	178±3	107±18.1	220±1.8	214±9.5	191±2.3	154±12.6	144±15.4	110±6.9
ethyl 2-hexenoate	7.7±0.73	N.D.	0.95±1.3	2.1±0.3	N.D.	4.9±5.7	6.8±0.37	N.D.	3.0±0.35	0.91±0.12	N.D.
methyl octanoate	10.2±1.7	6.3±1.1	1.5±0.49	13.0±0.19	N.D.	7.0±6.7	12.7±0.99	8.3±0.75	12.3±0.34	3.6±0.37	4.8±0.24
1-methyl-4-(prop-1-en-2-yl)benzene	3.1±0.49	N.D.	N.D.	0.71±0.26	0.3±0.42	0.88±1.2	1.5±0.24	N.D.	2.4±0.14	0.35±0.49	0.25±0.034
vitispirane	3.8±0.46	2.6±0.51	1.7±0.039	2±0.01	0.42±0.04	0.59±0.0011	0.8±0.018	2.5±0.049	2.5±0.21	0.63±0.043	0.81±0.042
ethyl nonanoate	2.6±0.029	0.81±0.098	0.57±0.8	1.1±0.064	1.4±0.9	1.8±1.2	3.1±2.5	1.3±0.71	2.6±1.1	1.7±1.9	1.4±0.066
methyl decanoate	N.D.	5.4±2.0	N.D.	1.9±0.5	N.D.	2.5±0.68	2.7±0.71	7.6±0.31	2.8±0.057	1.1±0.75	2.1±0.072
ethyl 9-decenoate	N.D.	18.4±4.8	N.D.	N.D.	N.D.	N.D.	N.D.	4±0.007	36.2±0.7	N.D.	8.6±0.48
1-decanol	N.D.	0.057±0.08	N.D.	2.3±2.2	N.D.	N.D.	N.D.	3.7±0.0082	N.D.	N.D.	N.D.
dodecanoic acid	48±5.3	43.7±47.8	N.D.	39.2±8.8	28.4±4.4	75.9±12.2	95.7±3	96.1±20.2	75.9±35.9	85±24.3	11.9±1.9

Appendix 6. continued

Compounds/Wine No.	12	13	14	15	16	17	18	19	20	21	22
ethyl 3-methylbutanoate	395±5.6	74.5±2.2	7.7±10.9	67.0±2.7	91.7±4.6	83.2±1.1	192±10.0	87.7±2.3	143±3.7	151±24.0	286±2.2
ethyl 2-butanoate	85.2±2.7	142±11.9	121±14.3	139±3.3	103±1.5	158±17.3	N.D.	89.9±6.0	56.2±0.6	116±49.2	37.9±1.9
ethyl 2-hexenoate	1.2±0.22	N.D.	29.9±9.5	1.7±0.4	5.1±0.95	19±10.2	N.D.	14.0±5.2	N.D.	7.1±0.26	N.D.
methyl octanoate	3.3±0.63	7.3±0.37	N.D.	2.8±0.46	5.0±0.86	6.8±4.1	N.D.	7.5±3.3	N.D.	N.D.	N.D.
1-methyl-4-(prop-1-en-2-yl)benzene	2.1±0.27	1.0±0.54	4.9±6.9	1.6±0.69	6.3±0.44	14.6±5.8	3.5±1.4	3.4±2.2	1.4±0.066	10.7±5.0	3.3±0.3
vitispirane	3.8±0.12	2.6±0.1	0.17±0.07	0.87±0.005	0.94±0.086	0.4±0.058	2.2±0.028	0.77±0.032	2.2±0.0018	0.47±0.27	1.6±0.081
ethyl nonanoate	2.1±0.15	3.0±0.17	67.4±4.4	6.7±0.34	0.97±0.018	3.1±1.0	9.5±1.6	12.9±7.6	1.5±0.022	8.3±1.5	1.4±0.0004
methyl decanoate	N.D.	2.8±0.11	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
ethyl 9-decenoate	4.5±1.1	N.D.	0.78±1.1	4.2±0.17	N.D.	N.D.	N.D.	162±17.2	N.D.	N.D.	5.7±0.54
1-decanol	N.D.	N.D.	0.64±0.9	108±0.085	10.2±0.086	N.D.	2.0±0.79	N.D.	N.D.	N.D.	N.D.
dodecanoic acid	8.8±12.4	55.8±7.1	37.2±13.6	20.9±0.41	52.6±4.5	143±0.034	32.3±6.7	60±22.8	19.2±13.4	79.4±21.1	24.0±14.2

Appendix 6. continued

Compounds/No.	23	24	25	26
ethyl 3-methylbutanoate	N.D.	55.0±0.36	N.D.	43.2±0.12
ethyl 2-butanoate	106±18.1	129±6.4	163±6.5	124±0.87
ethyl 2-hexenoate	7.2±0.34	3.8±0.44	N.D.	N.D.
methyl octanoate	6.1±0.42	11.9±1.1	10.1±0.19	11.6±0.31
1-methyl-4-(prop-1-en-2-yl)benzene	8.8±0.75	1.1±0.092	6.0±0.15	4.4±0.39
vitispirane	0.21±0.026	0.4±0.022	0.77±0.0019	0.69±0.034
ethyl nonanoate	39.1±2.3	2.1±0.082	4.1±1.2	9.2±1.4
methyl decanoate	N.D.	0.43±0.6	4.6±0.46	2.7±0.52
ethyl 9-decenoate	4.5±0.11	N.D.	N.D.	N.D.
1-decanol	N.D.	N.D.	N.D.	N.D.
dodecanoic acid	71.8±6.1	99.0±8.9	84.8±6.7	37.5±19.1

Appendix 7. Details of the 23 Rosé Wines included in the Study (corresponding to Table S1 in Chapter 3).

Sample No.	vintage	variety	region	alcohol % (v/v)	pH	TA (g/L)	glucose+fructose (g/L)	malic acid (g/L)	lactic acid (g/L)
A1	2013	Shiraz, Cabernet Sauvignon, Merlot	South Australia	12.8[a] f[b]	3.10 n	12.9±1.0 cde	4.3±0.1 efgh	1.0 m	0.5 hi
A2	2013	Mourvèdre, Grenache, Sangiovese, Dolcetto	Clare Valley	12.4 k	3.26 j	11.5±0.2 gh	2.9±0.1 fghij	1.4 jk	0.3 lmn
A3	2013	Grenache, Shiraz	South Eastern Australia	13.2 d	3.31 h	13.3±0.1 bcd	5.9±0.1de	1.8 h	0.4 ij
A4	2013	Shiraz, Cabernet Sauvignon, Merlot	Western Australia	12.4 l	3.11 n	13.7±0.1 bc	4.6±0.1 efg	1.2 kl	0.7 g
A5	2014	Grenache, Shiraz	South Australia	12.7 i	3.16 l	12.3±0.2 defg	3.2±1.0 fghij	1.4 j	0.5 h
A6	2013	Grenache	Barossa Valley	13.4 b	3.29 i	10.1±0.1 i	0.8±0.4 ij	0.8 n	0.8 g
A7	2013	Sangiovese	South Australia	12.6 j	3.18 k	11.7±0.2 fgh	2.9±0.1 fghij	2.4 d	0.1 p
A8	2013	Mourvèdre, Grenache, Sangiovese	South Australia	13.2 c	3.46 c	12.5±0.1 defg	2.3±0.1 ghij	2.6 c	0.3 mno
A9	2014	Sangiovese	South Australia	12.7 h	3.40 e	11.0±0.1 hi	6.7±0.1 de	1.1 ±0.1 lm	0.4 jk
A10	2014	Pinot noir	Yarra Valley	12.4 m	3.69 a	10.1 i	0.9±0.2 ij	1.0 ±0.1 m	4.0 a
A11	2014	Pinot noir	Adelaide Hills	11.9 p	3.39 e	13.2 bcd	4.0 efghi	2.3 de	0.7 g
A12	2013	Shiraz	Barossa Valley	11.7 r	3.26 j	12.6 cdefg	8.4±0.2 d	2.0 g	0.4 kl
A13	2013	Shiraz	Barossa Valley	11.3 s	3.24 j	13.6±0.1 bc	15.5±0.1 c	1.8 ±0.1 h	0.4 jkl
A14	2013	Sangiovese, Cabernet Franc	Padthaway	12.9 e	3.29 i	12.2±0.1 defg	1.2±0.5 ghij	1.6 i	0.3 klm
A15	2013	Cabernet Sauvignon, Shiraz	Yarra Valley	14.0 a	3.39 e	10.4±0.1 i	0.4±0.3 j	1.3 jk	0.2 ±0.1 o
A16	2013	Shiraz, Merlot	New South Wales	13.4 b	3.70 a	10.1 i	1.8±0.4 ghij	2.2 ±0.1 ef	3.0 c
A17	2014	Grenache	McLaren Vale	12.9 e	3.51 b	13.0 bcde	20.1±1.1 b	2.1 fg	2.3 d
A18	2013	Sangiovese	King Valley	11.7 q	3.35 fg	12.7±1.3 cdef	1.0±0.2 hij	3.2 b	0.3 no
F19	2013	Grenache, Shiraz, Cinsaut, Mourvèdre	Provence, France	12.7 gh	3.44 d	12.0±0.1 efgh	1.3±0.1 ghij	2.2 ef	1.7 e
F20	2013	Grenache, Shiraz, Mourvèdre	Provence, France	12.7 g	3.36 f	11.0±0.1 hi	1.0±0.1 hij	1.4 j	1.5 f
C21	2013	Cabernet Sauvignon	Linfen, Shanxi, China	12.2 o	3.13 m	16.7 a	6.9±1.4 de	4.0 ±0.1 a	0.3 o
C22	2013	Muscat	Huaizhuo Basin, China	12.2 n	3.52 b	11.1±0.1 hi	2.7±0.6 fghij	1.1 lm	3.6 b
C23	2013	Merlot	Huaizhuo Basin, China	10.8 t	3.33 g	14.1 b	40.7±3.3 a	2.7 c	0.3 lm

[a] All data are expressed as the mean ± standard deviation (n = 2). Where SD is not shown the value was 0. [b] Different letters indicate significant differences ($p < 0.05$) between samples according to Tukey's HSD test.

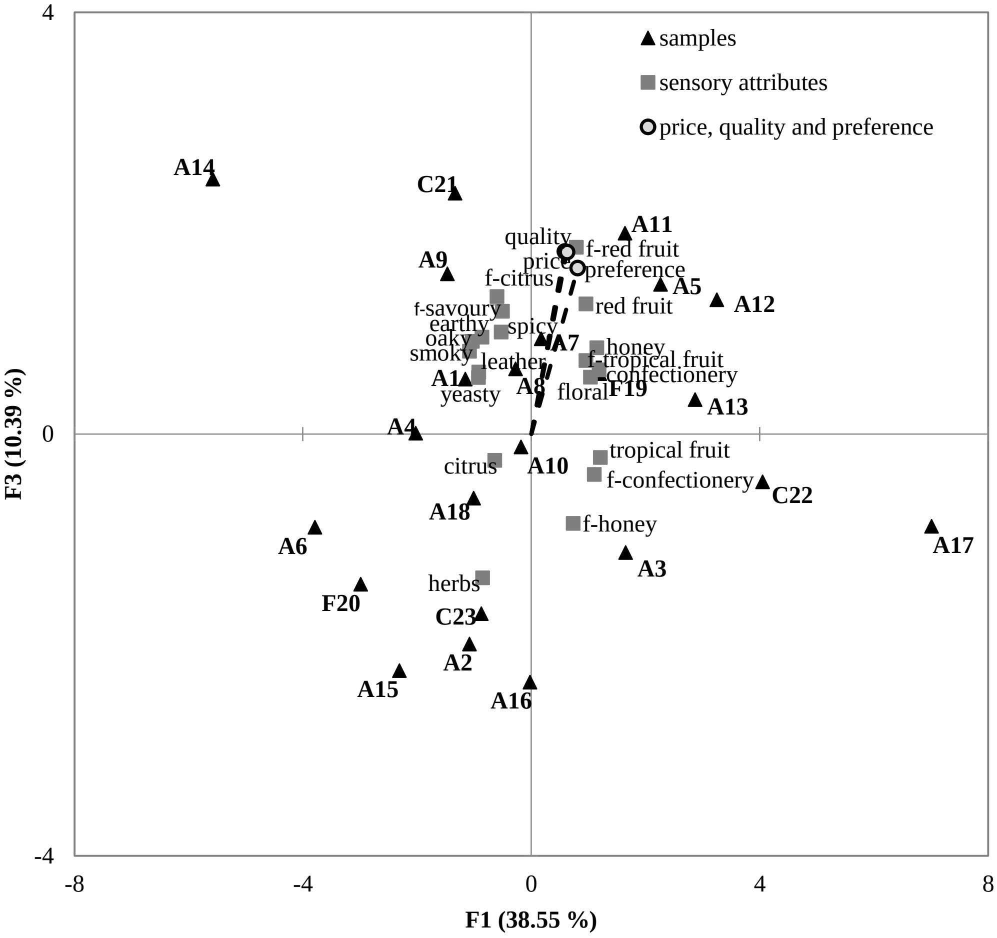
Appendix 8. Quality Classification of Wines[1] (corresponding to Table S2 in Chapter 3).

	A	**B**	**C**	**D**	**E**
quality bracket out of 20	wines of outstanding characteristics having no defects	standard wines with neither outstanding character or defect	wines of commercial acceptability with noticeable defects	wines below commercial acceptability	completely spoiled wines

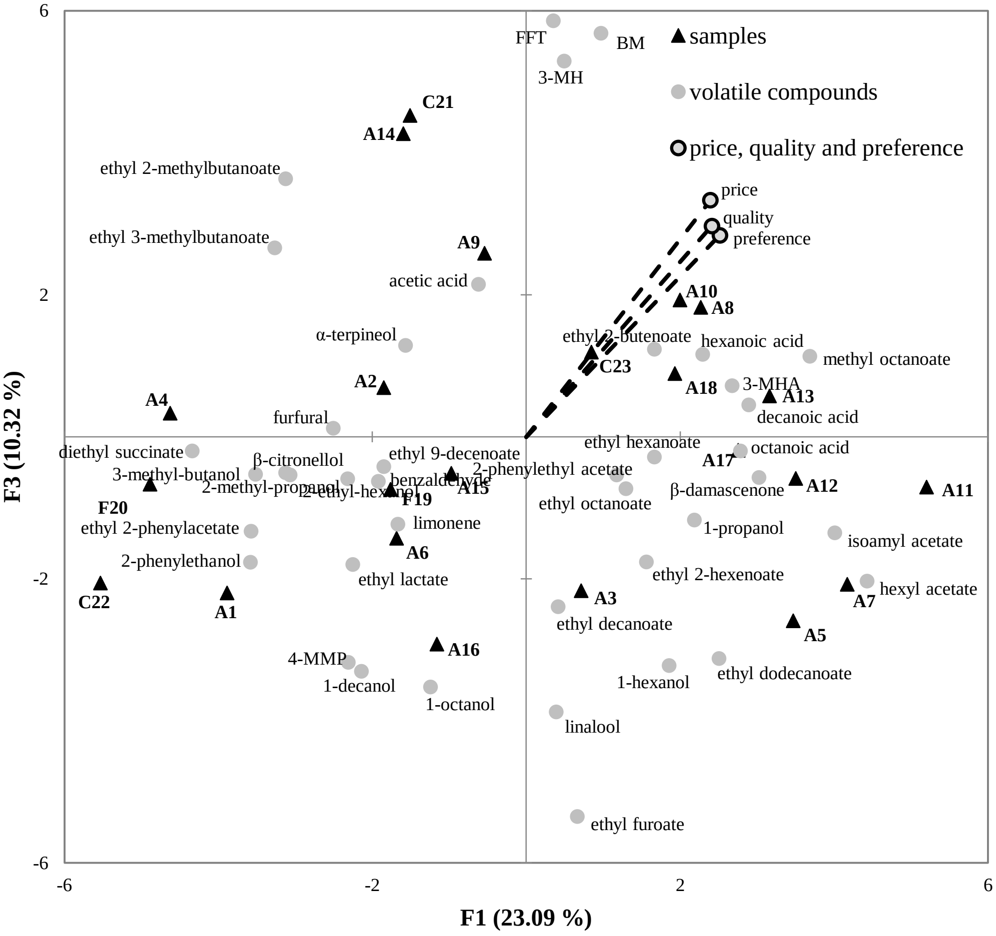
Appendix 9. Expected Sensory Characters generated during three Tastings of Ros é Wines (corresponding to Table S3 in Chapter 3).

Sensory character	Description
appearance	brilliantly clear with a bright colour
aroma	clean, good aroma intensity comprising red/dark fruit, tropical fruit, floral and confectionery aromas, some developed characters may also be detected
flavour	higher amounts of acid (i.e. crisp finish), low sugar content, moderate astringency and good intensity of flavours which correspond to aroma terms
general impression	balanced and elegant, light body

Appendix 10. Bi-plot generated from PCA of Blind Tasting Data for 23 Rosé Wines (PC1 vs. PC3) (corresponding to Figure S1 in Chapter 3).



Appendix 11. Bi-plot generated from PCA of Volatiles in 23 Rosé Wines (PC1 vs. PC3) (corresponding to Figure S2 in Chapter 3).



Appendix 12. Mean Concentrations (μg/L)[a] of Volatile Compounds with Standard Deviations (n = 2) in 23 Rosé Wines (corresponding to Table S4 in Chapter 3).

compounds/wine no.	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11
ethyl acetate	73698±165	49594±362	139200±767	126050±5904	112120±17504	101760±13243	116710±2135	131070±39219	113380±4045	164620±3705	148590±12794
ethyl butanoate	207±4.5	373±5.9	410±9.5	339±16.1	456±90.4	362±34.7	618±2.3	534±148	425±20.6	143±10.3	287±26.8
1-propanol	15400±307	10383±1613	15964±332	9917±860	26593±3812	11257±593	11745±1223	6139±3730	12863±607	15505±1283	16759±7131
ethyl 2-methylbutanoate	53.8±1.4	30.9±2.5	20.2±0.23	70.5±3	8.2±1.3	20.4±0.8	16.5±1.3	15.5±4.3	40±0.2	10.3±0.61	6.9±0.77
ethyl 3-methylbutanoate	83.8±3.8	45.2±1.2	35.1±0.45	135±8.2	18.1±4	30.7±0.46	30±1.4	31.3±7	55.9±1.5	13.2±3.3	7.9±3.7
2-methyl-1-propanol	8090±253	1369±66	2081±569	7922±145	1508±260	4631±87	1509±15	ND[b]	2687±125	7165±591	976±163
isoamyl acetate	ND	968±29.7	4832±170	574±50.7	10035±1892	1204±146	6502±43.7	4409±1132	4385±626	5819±333	10730±855
ethyl 2-butenoate	8.7±0.9	7.5±0.17	9.5±0.69	7.9±0.66	12.4±0.5	12.4±1.2	14.6±0.018	12.5±0.85	8.7±0.1	8.4±0.2	6.1±0.89
limonene	6.3±0.74	6.1±1.3	8.1±0.4	5.4±0.22	5.6±0.31	6.5±1.5	5.8±0.13	5.8±1.4	6.2±0.062	6.4±0.55	8.8±3.6
3-methyl-1-butanol	78981±1330	35148±1363	48156±7754	74018±529	61748±3434	68921±7830	30183±18.1	33812±321	42252±4202	41670±439	39321±1408
ethyl hexanoate	934±63.2	1466±4.2	1322±54.9	1277±88.8	1776±222	1037±142	1676±19.9	1403±354	1119±92.4	567±17.2	1372±93
hexyl acetate	77.6±2.8	204±4.3	662±16.2	54±17.5	1745±271	135±2.7	1785±119	869±162	239±16.6	705±47.9	2696±491
ethyl 2-hexenoate	8±5	ND	10.9±0.19	ND	7.9±0.43	9±5.5	6.1±3.1	13.2±3.5	ND	ND	7.9±9.8
ethyl lactate	9989±110	2624±135	2821±4.5	1703±191	3775±1611	51649±9762	ND	2428±330	17373±148	2322±47.5	3194±89.8
1-hexanol	8932±442	4714±681	2116±497	ND	3702±639	7606±1367	8554±170	3234±648	ND	3126±151	8619±626
methyl octanoate	ND	1.5±0.37	3.4±0.75	0.46±0.72	7.1±1.2	0.88±0.19	4.5±0.31	5±2.8	5.8±1	15±2.4	9.6±5.9
nonanal	70.4±55.8	68±28.4	84.1±2.8	84.1±4.5	89.3±6.3	88.7±9.6	60.7±5.2	72.1±0.71	79.4±5.9	80.7±14.1	104±33.9
ethyl octanoate	2721±199	3273±131	3659±115	3743±296	4333±722	2614±509	5009±71.1	3484±934	2986±117	1535±63.6	3392±20.6
acetic acid	123290±1473	133000±19048	154140±2631	220280±7731	105390±6958	128110±14434	127810±4500	146370±34026	78414±61390	282020±31727	280650±5442
isoamyl hexanoate	1.3±0.17	1.8±0.01	3.4±0.37	4.5±1.8	4.9±1.7	4.7±1.9	4.2±0.6	2.4±0.9	NQ	3.6±0.95	3.7±3.4
furfural	135±5.1	313±39.2	44.7±46	150±21.1	ND	184±20	NQ	183±15.8	551±81	ND	ND
2-ethyl-1-hexanol	30.3±0.88	26.9±0.5	29±1.1	40.7±0.86	40.9±18.6	25±0.53	27.8±0.37	34.5±12.9	26.3±2.3	45.5±16.6	35.8±2.3
benzaldehyde	125±8.3	125±7.6	124±2.4	122±1	132±12.6	83±14	107±1.9	104±6.4	107±7.2	37.2±3	85.9±22.8
linalool	ND	5±0.16	30.5±0.75	ND	33.6±5	NQ	23.7±0.68	15.3±0.88	8.1±0.44	26.7±1.9	6.9±1
1-octanol	27.1±0.24	36.7±2	26.5±0.98	32.1±0.14	30.2±2.3	31.1±3.3	17.1±0.61	22.4±0.93	10.5±0.95	23±0.81	12.8±1.5
ethyl furoate	51.1±4.2	2.9±0.32	38.8±0.86	2.5±0.21	41.4±4.1	16.1±3	49.6±1.3	2.6±0.01	2.8±0.37	11±0.63	18.1±2.1
ethyl decanoate	4067±420	1987±219	3131±17.6	2799±347	4258±921	791±497	4133±181	1623±646	1890±129	544±28.1	1519±353
isoamyl octanoate	14.5±0.68	10.2±1.7	33.7±3.3	30.5±7.9	30.1±9.9	29.1±8	16.5±0.36	24.4±3.7	28.1±4.1	28.5±8.4	19.5±5.1
diethyl succinate	3627±9.9	2484±64.2	548±3.1	3380±87.7	ND	3143±404	65.5±15.8	712±163	1576±142	609±51.5	ND
ethyl 9-decenoate	5.6±0.89	ND	4.9±0.019	6.3±0.065	12.5±1.6	1.8±0.67	7.8±0.86	3.4±0.6	17.6±0.099	0.55±0.33	3.3±0.24
α-terpineol	NQ	34.2±4	NQ	28.7±0.69	NQ	ND	20±1.6	24.4±3.5	27.3±2.7	NQ	NQ
1-decanol	118±26	85.3±4.1	94.1±1.4	90.9±6.8	88.7±14.1	91.3±11.6	66.9±2.5	46.7±7.8	22.9±5.7	60.8±5.3	14.8±7
β-citronellol	67.1±3.4	57.3±12.1	ND	54.8±4.7	31.4±2.8	50±5	ND	32.1±2.8	10.4±1.1	ND	ND
ethyl 2-phenylacetate	8.4±0.011	5.8±0.2	5.4±0.098	20.4±0.44	3.4±0.9	5±0.52	5.5±0.3	7.9±0.44	5.2±0.91	4.4±0.32	2.1±0.051
2-phenylethyl acetate	20.6±3.5	119±10	15.3±1	217±1.4	15.4±3.3	233±9.1	184±9.7	187±21.3	138±16	193±7.3	177±21
β-damascenone	0.74±0.3	0.87±0.11	4.7±0.12	ND	13.1±0.22	1.2±0.34	1.8±0.16	3.9±0.26	ND	31.5±4.2	28.4±8.4
ethyl dodecanoate	109±9.8	44±11.6	234±1.8	112±10.8	232±5.2	164±37.3	230±0.95	184±6.1	83.3±30.8	184±37	220±4.6
hexanoic acid	2073±64.8	3890±189	2722±46.5	3107±138	3969±349	1922±351	4352±86.8	3768±447	2850±171	1846±292	3923±2.5
2-phenylethanol	14122±345	8993±501	9032±204	15347±327	6316±287	11574±731	6035±136	6394±259	8954±471	6978±44.3	4086±211
octanoic acid	ND	1925±386	1323±102	2709±129	4005±130	ND	5569±977	2879±50.4	1873±319	ND	3070±525
nonanoic acid	3170±426	2747±373	2795±6.6	2860±5.2	2688±310	3235±186	1617±214	671±12.9	1861±151	1607±190	1513±446
decanoic acid	143±30.6	98.5±11.4	144±6.4	181±7.8	285±12.9	133±15.9	369±22.4	156±0.29	218±7.3	166±1.2	253±4.8
4-MMP (ng/L)	1.2±0.012	1.1±0.025	1.3±0.041	1.7±0.014	1.6±0.037	ND	ND	ND	ND	ND	ND
3-MH (ng/L)	384±6.7	594±14.9	572±6.4	598±19.7	420±1	22.9±0.83	252±2.1	972±4.2	336±0.24	1147±41.5	668±5.7
3-MHA (ng/L)	ND	1±0.088	10.1±0.15	ND	8.6±0.5	ND	7.7±0.26	35.6±0.3	4.9±0.16	4.9±0.025	4.7±0.31
FFT (ng/L)	ND	2.9±0.087	ND	ND	2.1±0.067	ND	ND	3±0.077	4±0.053	4±0.034	ND
BM (ng/L)	1.8±0.14	1.7±0.056	1.9±0.061	1.7±0.076	2.4±0.0047	2±0.025	2.2±0.014	2.9±0.081	2.7±0.021	3±0.076	1.8±0.07

[a] All in μg/L except where specified. [b] ND, not detected. [c] NQ, not quantified.

Appendix 12. continued

compounds/wine no.	A12	A13	A14	A15	A16	A17	A18	F19	F20	C21	C22
ethyl acetate	99496 ±11488	91455 ±4541	109570 ±9683	92050 ±17386	187440 ±85246	143880 ±12170	77370 ±5848	109090 ±2500	111150 ±3451	213360 ±163000	81962 ±27658
ethyl butanoate	432 ±44.4	402 ±4.1	280 ±27	341 ±38.8	666 ±338	503 ±44.8	452 ±10.4	258 ±18.8	285 ±9.4	560 ±478	293 ±89.3
1-propanol	19604 ±650	14930 ±1688	8770 ±438	12855 ±2099	9945 ±477	7001 ±606	14188 ±428	5612 ±391	9185 ±1764	17115 ±10030	8293 ±253
ethyl 2-methylbutanoate	8.6 ±0.98	8.7 ±0.36	58.6 ±7.4	35.4 ±2.5	37 ±15.6	8.5 ±1.8	18.6 ±0.66	17.1 ±1.2	40.7 ±2.7	101 ±77.6	19.4 ±4.6
ethyl 3-methylbutanoate	17 ±0.61	17.1 ±0.12	54.3 ±6.1	53.5 ±3.5	48.3 ±14	15.4 ±3.4	29.7 ±0.31	36.3 ±0.076	77.5 ±3.1	149 ±110	30.9 ±8.8
2-methyl-1-propanol	NQ[c]	1017 ±532	5457 ±858	3747 ±270	6261 ±28	1081 ±125	5258 ±520	2395 ±757	2942 ±529	4748 ±54	12530 ±3065
isoamyl acetate	7345 ±508	6812 ±17.3	2462 ±207	2679 ±142	8090 ±3694	12134 ±1016	5569 ±158	6623 ±371	3554 ±101	3554 ±42	1009 ±329
ethyl 2-butenoate	11.1 ±2.8	13.9 ±0.057	11.7 ±0.47	7.6 ±0.56	10.5 ±6	6.3 ±0.31	10 ±0.43	3.8 ±0.098	5.7 ±0.49	15 ±0.8	6.3 ±0.86
limonene	8.4 ±2	8.3 ±0.9	8.1 ±1.5	8.5 ±2.2	9.5 ±0.06	11.6 ±0.091	7.8 ±1.6	10.1 ±0.23	10.6 ±0.93	9.2 ±1.4	18.5 ±2.1
3-methyl-1-butanol	26738 ±12074	35990 ±228	75692 ±1940	60934 ±5579	112550 ±1128	29331 ±287	46258 ±3306	78979 ±1769	82555 ±6505	93322 ±1430	46062 ±2155
ethyl hexanoate	1339 ±107	1197 ±17.6	1068 ±75	1217 ±101	1504 ±71	863 ±68.8	1359 ±28.8	771 ±71.7	828 ±4.4	1843 ±25	953 ±14
hexyl acetate	1198 ±83.6	988 ±3.9	188 ±4.9	335 ±31.6	629 ±280	1645 ±140	704 ±5.1	466 ±54.1	232 ±13.5	164 ±123	54.3 ±16
ethyl 2-hexenoate	16.5 ±3.7	17.7 ±3.5	11.8 ±4.5	4 ±0.65	13.7 ±8.4	3.9 ±3.3	7.7 ±1.3	9 ±0.014	9.1 ±0.15	3.2 ±0.12	3.4 ±0.095
ethyl lactate	2397 ±165	2567 ±319	3652 ±227	2272 ±101	34291 ±157	2866 ±517	1193 ±192	3026 ±613	3572 ±584	22672 ±174	305370 ±2145
1-hexanol	6499 ±62	6363 ±180	1488 ±259	2047 ±254	7275 ±47	ND	1448 ±498	1058 ±579	2206 ±264	1033 ±24	NQ
methyl octanoate	10.7 ±0.67	7.1 ±0.33	ND	ND	4.7 ±0.2	5.2 ±0.83	10.8 ±0.4	ND	ND	5.2 ±0.4	2 ±0.2
nonanal	109 ±8.2	98 ±15.9	102 ±10.1	117 ±10	104 ±25	117 ±4.1	101 ±6.4	121 ±4.9	127 ±5	85.5 ±32.1	121 ±18.8
ethyl octanoate	3365 ±235	2834 ±178	2682 ±209	3728 ±658	3826 ±1131	2548 ±136	3703 ±199	2676 ±242	2775 ±93.6	4874 ±2857	2135 ±418
acetic acid	132010 ±20631	93273 ±12705	178110 ±39697	150910 ±12248	232920 ±65433	292140 ±6188	92180 ±15275	195550 ±13706	199290 ±36875	420830 ±17210	224520 ±44503
isoamyl hexanoate	3.7 ±1.4	2.3 ±0.37	6.9 ±0.073	3.7 ±0.073	10.9 ±1.4	NQ	2.7 ±0.83	NQ	0.82 ±0.03	4.9 ±0.9	NQ
furfural	324 ±31.3	334 ±21	259 ±0.48	24 ±1.4	263 ±15.4	ND	117 ±8.3	72.9 ±0.83	297 ±6	110 ±81.2	961 ±11
2-ethyl-1-hexanol	30.5 ±14.9	51.5 ±8.5	25.5 ±8.2	41.3 ±7	77.7 ±10.8	62.4 ±21.7	56 ±3.2	48 ±1.3	187 ±3.6	88.2 ±36	115 ±52.1
benzaldehyde	82.8 ±1.2	74.5 ±5	92.3 ±6.3	117 ±26.8	50.5 ±1.4	76.1 ±2.7	114 ±7.5	124 ±1.6	131 ±12.9	119 ±17.2	107 ±11.6
linalool	45.2 ±3.1	21.2 ±1.8	ND	3.8 ±0.11	44.4 ±3.2	30.5 ±5.4	6.2 ±0.034	31.7 ±1.1	29 ±2.3	5.5 ±11.2	57.3 ±0.78
1-octanol	19.9 ±0.36	14.4 ±0.35	7.2 ±0.96	28.6 ±2.3	45.4 ±19	19.4 ±0.47	11.4 ±0.27	14.1 ±0.027	18.3 ±0.33	21.7 ±15.2	17.1 ±0.33
ethyl furoate	10.6 ±14.1	0.99 ±0.11	2.1 ±0.094	19.8 ±1.1	26.3 ±2.2	14.7 ±0.83	1.1 ±0.057	21.1 ±1.7	23.1 ±2	2.5 ±2.3	ND
ethyl decanoate	1589 ±43.8	1367 ±78.8	982 ±11.3	2749 ±1082	2100 ±582	920 ±47.9	2544 ±326	1418 ±271	2138 ±179	2825 ±2007	ND
isoamyl octanoate	14.4 ±3.2	13 ±0.026	16.4 ±0.43	20.4 ±0.6	28.4 ±1.7	NQ	15.7 ±0.33	11.3 ±1.2	9.9 ±1.5	24.8 ±2.7	NQ
diethyl succinate	ND	NQ	3618 ±335	3226 ±181	2871 ±901	ND	863 ±8.9	448 ±21.2	2780 ±99.2	1011 ±737	3116 ±249
ethyl 9-decenoate	3.3 ±0.55	2.3 ±0.21	4 ±0.2	5.2 ±1.6	11.3 ±2.6	ND	ND	12.8 ±1.1	27.8 ±1.5	12.3 ±1.7	4.3 ±0.65
α-terpineol	26.3 ±2.7	NQ	NQ	NQ	NQ	NQ	32.6 ±2.8	NQ	52.7 ±1.7	21.7 ±13.5	NQ
1-decanol	36.7 ±8.5	29.1 ±7.3	37 ±2.4	71.2 ±0.83	126 ±4.1	35.7 ±5	31 ±1.1	67 ±3.4	83.2 ±7.7	78.3 ±5.4	25.2 ±2.2
β-citronellol	ND	ND	8 ±1.6	6.1 ±0.3	11.4 ±0.8	ND	19.9 ±1.3	ND	49.8 ±9.1	30.2 ±1.4	19.3 ±2.4
ethyl 2-phenylacetate	12 ±12.2	3.3 ±0.28	7.2 ±0.21	7.3 ±0.93	19.9 ±6.4	3.6 ±0.5	4.7 ±0.084	12.1 ±0.61	21.6 ±0.83	11.8 ±5.4	17.3 ±0.027
2-phenylethyl acetate	194 ±31.5	55.8 ±7.9	88.4 ±4.4	117 ±10	250 ±12.2	311 ±17.1	ND	184 ±5.1	41.1 ±4.3	7.9 ±4.4	28.7 ±0.19
β-damascenone	8.1 ±0.88	12.9 ±1.7	ND	1.3 ±0.65	11.4 ±1.3	25.2 ±4.8	ND	3 ±0.087	ND	2.2 ±0.4	1.3 ±0.4
ethyl dodecanoate	127 ±59.1	92.5 ±34.3	43.8 ±2.1	270 ±50.1	150 ±78.7	208 ±5.3	191 ±60.1	91.2 ±0.92	211 ±7.1	84.2 ±11.5	38.6 ±4.5
hexanoic acid	4046 ±115	3754 ±480	2862 ±157	3038 ±117	3347 ±873	2392 ±70.5	4443 ±13.8	2059 ±57.5	2295 ±146	4702 ±2385	2936 ±299
2-phenylethanol	4844 ±44.3	4990 ±48.7	8451 ±524	11091 ±44	16741 ±7605	6411 ±27.5	7470 ±231	18818 ±883	20589 ±376	8978 ±169	6663 ±81.9
octanoic acid	2813 ±189	1872 ±21	1003 ±41	1649 ±122	2514 ±54	800 ±28	4244 ±37.7	NQ	NQ	3090 ±23	NQ
nonanoic acid	1030 ±390	2154 ±12	3297 ±11	718 ±16.7	1195 ±13	2114 ±14	1759 ±25	456 ±34.8	1210 ±44	2923 ±19	1748 ±38
decanoic acid	248 ±84.3	288 ±11.9	181 ±2.9	250 ±5.3	303 ±15	181 ±20.6	360 ±19.1	146 ±3.6	180 ±30.3	312 ±18.1	38 ±4.3
4-MMP (ng/L)	ND	ND	ND	1 ±0.0008	ND	ND	ND	ND	ND	ND	2.4 ±0.0017
3-MH (ng/L)	637 ±3.2	709 ±0.43	904 ±10.1	805 ±2.7	322 ±2.1	525 ±5	401 ±7.8	361 ±20.2	656 ±7.2	504 ±12.8	1730 ±27.5
3-MHA (ng/L)	9.9 ±0.05	8.5 ±0.033	2.3 ±0.23	1.9 ±0.29	ND	12.5 ±0.37	ND	3.3 ±0.028	1.1 ±0.0099	ND	ND
FFT (ng/L)	ND	1.2 ±0.2	4.6 ±0.014	1.7 ±0.077	ND	1.3 ±0.051	1.1 ±0.019	1.1 ±0.11	ND	1.1 ±0.088	2.4 ±0.022
BM (ng/L)	2.3 ±0.11	1.9 ±0.056	4.4 ±0.087	1.5 ±0.027	1.9 ±0.024	1.7 ±0.033	2.7 ±0.064	2.2 ±0.13	1.8 ±0.014	2.5 ±0.022	4 ±0.11

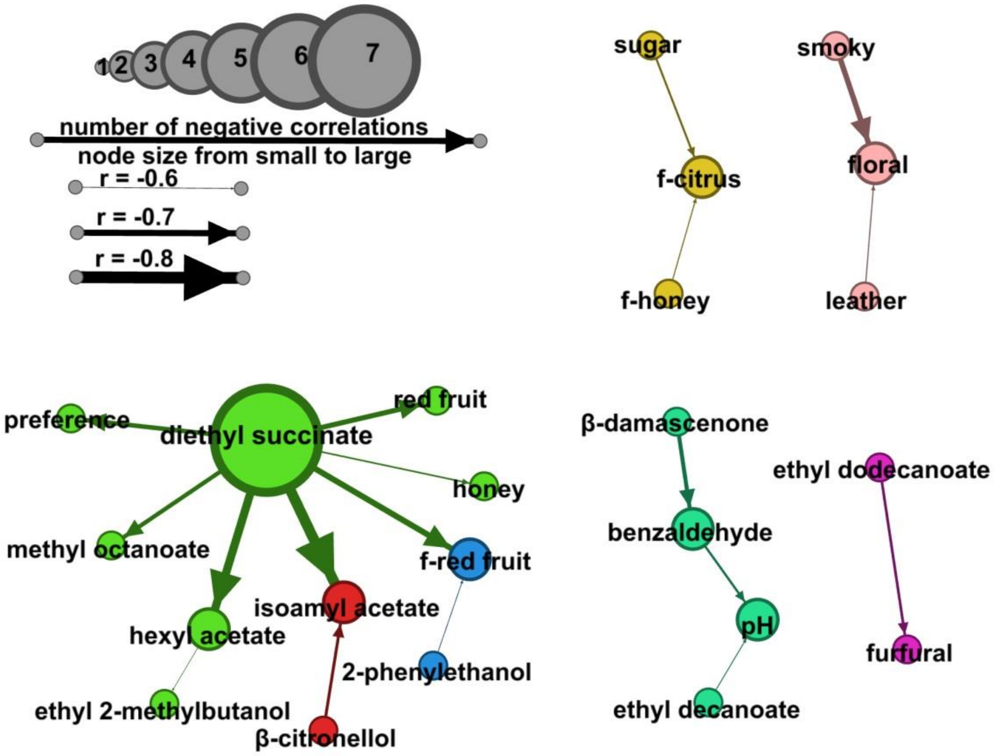
[a] All in µg/L except where specified. [b] ND, not detected. [c] NQ, not quantified.

Appendix 12. continued

compounds/wine no.	C23
ethyl acetate	138840±8091
ethyl butanoate	355±6.1
1-propanol	9036±1814
ethyl 2-methylbutanoate	32.6±0.93
ethyl 3-methylbutanoate	46.9±1.5
2-methyl-1-propanol	2252±17
isoamyl acetate	5788±112
ethyl 2-butenoate	4.3±0.37
limonene	9.4±0.67
3-methyl-1-butanol	26946±1064
ethyl hexanoate	959±10.7
hexyl acetate	736±0.15
ethyl 2-hexenoate	4.5±0.2
ethyl lactate	5517±723
1-hexanol	6172±874
methyl octanoate	3.5±0.62
nonanal	106±0.54
ethyl octanoate	2344±89.3
acetic acid	163350±15087
isoamyl hexanoate	ND
furfural	81.1±26.7
2-ethyl-1-hexanol	52.1±9.7
benzaldehyde	98.1±9.8
linalool	ND
1-octanol	9.1±0.92
ethyl furoate	9.6±0.2
ethyl decanoate	919±160
isoamyl octanoate	23±1.2
diethyl succinate	460±97.5
ethyl 9-decenoate	4.9±0.076
α-terpineol	ND
1-decanol	28±1.9
β-citronellol	10.3±0.5
ethyl 2-phenylacetate	3.1±0.41
2-phenylethyl acetate	157±6.4
β-damascenone	1.5±0.69
ethyl dodecanoate	133±1.3
hexanoic acid	2697±200
2-phenylethanol	2955±144
octanoic acid	891±50.6
nonanoic acid	1772±24
decanoic acid	212±4.1
4-MMP (ng/L)	ND
3-MH (ng/L)	207±0.5
3-MHA (ng/L)	ND
FFT (ng/L)	ND
BM (ng/L)	ND

[a] All in μg/L except where specified. [b] ND, not detected. [c] NQ, not quantified.

Appendix 13.



Network Analysis of Variables which had Negative Relationships with Each Other in 23 Rosé Wines (corresponding to Figure S3 in Chapter 3).

Appendix 14. Basic Wine Composition for Tropical and Fruity/Floral Rosé Wine Samples (corresponding to Table S1 in Chapter 4).

sample	tropical	fruity/floral
variety	Shiraz	Cabernet Sauvignon
vintage	2014	2014
region	Barossa Valley	Barossa Valley
alcohol % (v/v)	11.7	11.7
pH	3.10 ± 0.01	3.17 ± 0.01
TA (g/L)	6.4 ± 0.1	5.4
glucose + fructose (g/L)	5.9 ± 0.3	5.4 ± 0.1
free SO_2 (mg/L)	24.8 ± 1.1	17.2 ± 0.6
total SO_2 (mg/L)	100.8	112.4 ± 0.6

Appendix 15.

Customized Flask for HS-SPE of Wines for AEDA (corresponding to Figure S1 in Chapter 4).

Appendix 16. Method Characteristics for 34 Volatile Compounds Determined in Rosé Wine by HS-SPME-GC-MS with Selected Ion Monitoring (SIM) (corresponding to Table S2 in Chapter 4).

compound	CAS no.	RI[a]	CRI[b]	ions[c] (*m/z*)	R^2	range[d] (µg/L)	internal standard
ethyl 2-methylpropanoate	97-62-1	955	952	**71**, 88, 116	0.9975	1.3 - 600	d$_{13}$-1-hexanol
2,3-butanedione	431-03-8	970	969	**43**, 50, 86	0.9966	30 - 2000	d$_4$-3-methyl-1-butanol
2-methyl-2-butanol	75-85-4	1011	1009	55, **59**, 73	0.9986	1.7 - 150	d$_{13}$-1-hexanol
2,3-pentanedione	600-14-6	1058	1060	**43**, 57, 100	equivalent to 2,3-butanedione		d$_4$-3-methyl-1-butanol
butyl acetate	123-86-4	1075	1078	**43**, 56, 73	0.9964	0.02 - 1800	d$_3$-hexyl acetate
1-butanol	71-36-3	1148	1142	41, 43, **56**	0.9990	6.8 - 1200	d$_4$-3-methyl-1-butanol
3-hydroxybutan-2-one	513-86-0	1289	1289	43, **45**, 88	0.9910	5.0 - 2700	d$_4$-3-methyl-1-butanol
1-hydroxy-2-propanone	116-09-6	1306	1305	**43**, 58, 74	equivalent to 3-hydroxybutan-2-one		d$_4$-3-methyl-1-butanol
3-methyl-1-pentanol	589-35-5	1327	1327	41, **56**, 69	0.9967	1.3 - 180	d$_4$-3-methyl-1-butanol
2-hydroxy-3-pentanone	5704-201-1	1368	1362	**45**, 57, 102	equivalent to 3-hydroxybutan-2-one		d$_4$-3-methyl-1-butanol
3-ethoxy-1-propanol	111-35-3	1375	1378	**45**, 59, 86	equivalent to 1-butanol		d$_4$-3-methyl-1-butanol
octyl acetate	112-14-1	1479	1480	56, **70**, 84	0.9996	0.05 - 6000	d$_5$-ethyl dodecanoate
2,3-butanediol	513-85-9	1542	1542	45, 57, **75**	0.9931	257 - 36000	d$_{13}$-1-hexanol
2-methylpropanoic acid	79-31-2	1574	1573	55, 60, **73**	0.9971	134 - 2700	d$_5$-phenylethanol
dehydrolinalool	29957-43-5	1621	1616	**69**, 119, 137	equivalent to linalool		d$_{13}$-1-hexanol
butanoic acid	107-92-6	1631	1632	42, **60**, 73	0.9918	14.2 - 6000	d$_5$-ethyl nonanoate
γ-butyrolactone	96-48-0	1643	1647	42, 56, **86**	0.9921	124 - 21000	d$_{13}$-1-hexanol
furfuryl alcohol	98-00-0	1667	1667	53, 81, **98**	0.9916	1.1 - 180	d$_{13}$-1-hexanol
3-methylbutanoic acid	503-74-2	1678	1677	43, **60**, 87	0.9965	0.8 - 600	d$_{13}$-1-hexanol
2-methyl 3-(methyldithio)furan	65505-17-1	1675	1679	45, **112**, 160	equivalent to 3-hydroxybutan-2-one		d$_4$-3-methyl-1-butanol
benzyl acetate	140-11-4	1738	1738	91, **108**, 150	0.9942	0.03 - 90	d$_5$-phenylethanol
diethyl glutarate	818-38-2	1780	1784	114, 115, **143**	equivalent to diethyl tartrate		d$_{13}$-1-hexanol
δ-valerolactone	542-28-9	1786	1817	42, 56, **100**	0.9971	16.1 - 120	d$_{13}$-1-hexanol
N-(3-methylbutyl)acetamide	13434-12-3	1866	1864	73, 114, **129**	equivalent to 3-methylbutyl acetate		d$_4$-3-methyl-1-butanol
benzyl alcohol	100-51-6	1884	1884	51, **79**, 108	0.9983	0.9 - 1200	d$_{13}$-1-hexanol
β-ionone	79-77-6	1958	1958	91, 135, **177**	0.996	1.7 - 120	d$_{13}$-1-hexanol
anisaldehyde	123-11-5	2030	2039	77, 92, **135**	0.9925	0.60 - 1500	d$_5$-ethyl dodecanoate
γ-decalactone	706-14-9	2152	2154	**85**, 100, 128	0.9941	0.02 - 60	d$_5$-phenylethanol
δ-decalactone	705-86-2	2209	2207	**99**, 114, 152	equivalent to γ-decalactone		d$_5$-phenylethanol
diethyl tartrate	87-91-2	2358	2347	76, 104, **206**	0.9923	10.3 - 600	d$_{13}$-1-hexanol
2-furoic acid	88-14-2	2440	2442	39, 95, **112**	0.9947	1.3 - 1200	d$_5$-ethyl dodecanoate
benzoic acid	65-85-0	2449	2444	77, **105**, 122	0.9904	5.6 - 1500	d$_5$-ethyl dodecanoate
dodecanoic acid	143-07-7	2493	2492	60, **73**, 129	0.9955	21.9 - 30000	d$_5$-ethyl dodecanoate
phenylacetic acid	103-82-2	2585	2578	65, **91**, 136	equivalent to dodecanoic acid		d$_5$-ethyl dodecanoate

[a] RI values were obtained from Aroma Office 2D. [b] Calculated retention index (CRI) based on a series of alkanes (C7-C40). [c] Qualifier and quantifier (bold) ions. [d] Spans from the LOQ to the highest calibrant used.

Appendix 17. Aroma Descriptors, Thresholds and Odour Activity Values (OAVs) for Volatile Compounds Quantified in two Rosé Wines (corresponding to Table S3 in Chapter 4).

compounds	odour descriptors	threshold (µg/L)	OAV tropical	OAV fruity/floral
ethyl esters				
ethyl butanoate	refer to Table 1 in Chapter 4			
ethyl hexanoate	refer to Table 1 in Chapter 4			
ethyl octanoate	refer to Table 1 in Chapter 4			
ethyl decanoate	refer to Table 1 in Chapter 4			
ethyl dodecanoate	fruity, floral[2]	500[2,a]	0.1	0.1
ethyl lactate	refer to Table 1 in Chapter 4			
ethyl furoate	fruity, floral[2]	16000[2,b]	<0.1	<0.1
ethyl 2-methylbutanoate	refer to Table 1 in Chapter 4			
ethyl 3-methylbutanoate	refer to Table 1 in Chapter 4			
ethyl 2-methylpropanoate	refer to Table 1 in Chapter 4			
ethyl 9-decenoate	refer to Table 1 in Chapter 4			
diethyl succinate	refer to Table 1 in Chapter 4			
diethyl tartrate	refer to Table 1 in Chapter 4			
diethyl glutarate	refer to Table 1 in Chapter 4			
acetate esters				
butyl acetate	fruity[9]	1800[9,c]	<0.01	<0.01
hexyl acetate	refer to Table 1 in Chapter 4			
octyl acetate	waxy, fruity[12]	800[12,d]	<0.01	<0.01
2-phenylethyl acetate	refer to Table 1 in Chapter 4			
3-methylbutyl acetate	refer to Table 1 in Chapter 4			
benzyl acetate	floral, herbal[3]	2[13,e]	3.9	1.3
other esters				
3-methylbutyl hexanoate	refer to Table 1 in Chapter 4			
alcohols				
1-butanol	refer to Table 1 in Chapter 4			
1-hexanol	refer to Table 1 in Chapter 4			
2-methyl-2-butanol	refer to Table 1 in Chapter 4			
3-methyl-1-butanol	refer to Table 1 in Chapter 4			
2-methyl-1-propanol	refer to Table 1 in Chapter 4			
3-methyl-1-pentanol	refer to Table 1 in Chapter 4			
2-ethyl-1-hexanol	green, flowery, green cucumber[14]	270[15,b]	0.1	0.1
3-ethoxy-1-propanol	refer to Table 1 in Chapter 4			
benzyl alcohol	floral, dried fruit[3]	10000[17,e]	<0.1	<0.1
2-phenylethanol	refer to Table 1 in Chapter 4			
(*Z*)-3-hexen-1-ol	refer to Table 1 in Chapter 4			
(E)-2-hexenol	green, fruity[7]	17[17,e]	<0.1	<0.1
methionol	refer to Table 1 in Chapter 4			
furfuryl alcohol	floral, lavender, candy, sweet[18]	45000[8,f]	<0.01	<0.01
2,3-butanediol	refer to Table 1 in Chapter 4			
acids				
acetic acid	refer to Table 1 in Chapter 4			
butanoic acid	refer to Table 1 in Chapter 4			
hexanoic acid	refer to Table 1 in Chapter 4			
octanoic acid	refer to Table 1 in Chapter 4			
decanoic acid	refer to Table 1 in Chapter 4			
dodecanoic acid	metal[2]	6100[2,h]	1.1	0.5
2-methylpropanoic acid	rancid[3]	2300[4,g]	0.2	0.2
3-methylbutanoic acid	refer to Table 1 in Chapter 4			
benzoic acid	floral[3]	85000[5,e]	<0.1	<0.1
2-furoic acid	acidic[6]	n/a	n/a	n/a
phenylacetic acid	refer to Table 1 in Chapter 4			
phenols				
guaiacol	refer to Table 1 in Chapter 4			
4-ethylguaiacol	medicine, clove[7]	140[8,f]	<0.1	<0.1
4-ethylphenol	rubber, medicine[7]	620[8,f]	<0.1	<0.1
4-methylguaiacol	smoky[10]	65[10,i]	<0.1	<0.1
eugenol	clove-like[11]	6[4,g]	<2	<2
aldehydes				
hexanal	grassy, green[11]	20[11,e]	0.5	0.6
(*E*)-2-hexenal	green apple[11]	4[11,e]	0.1	0.1
(*E*)-2-heptenal	soapy fatty[11]	4.6[11,e]	<0.01	<0.01
(*E*)-2-octenal	fatty, nutty[11]	3[11,e]	<0.01	0.01
(*E*)-2-nonenal	green, fatty, sawdust[11]	0.17[11,e]	0.5	3.1
2-methylpropanal	malty[11]	6[11,j]	2.0	2.7
3-methylbutanal	malty[11]	4.6[4,g]	1.3	2.4
furfural	refer to Table 1 in Chapter 4			
5-methylfurfural	sweet, bitter almond[11]	2000[11,j]	<0.01	<0.01
benzaldehyde	bitter almond-like[11]	20000[11,e]	<0.01	<0.01
anisaldehyde	refer to Table 1 in Chapter 4			
phenylacetaldehyde	honey, floral[11]	1[11,j]	10.0	8.4
vanillin	vanilla[3]	200[16,k]	<0.1	<0.1
methional	cooked potato-like[11]	0.5[4,g]	<0.1	0.9
ketones				
1-hydroxy-2-propanone	refer to Table 1 in Chapter 4			
2-hydroxy-3-pentanone	refer to Table 1 in Chapter 4			
3-hydroxybutan-2-one	refer to Table 1 in Chapter 4			
2,3-butanedione	refer to Table 1 in Chapter 4			
2,3-pentanedione	refer to Table 1 in Chapter 4			
lactones				

isoprenoids				
linalool	refer to Table 1 in Chapter 4			
α-terpineol	floral[3]	250[4,g]	0.1	0.1
β-ionone	phenolic, pleasant[21]	0.09[4,g]	80.6	80.3
β-damascenone	refer to Table 1 in Chapter 4			
dehydrolinalool	refer to Table 1 in Chapter 4			
thiols				
4-MSP (ng/L)	boxwood[25]	0.8[25,h]	≤1.4	≤1.4
3-SH (ng/L)	grapefruit[25]	60[25,h]	8.9	9.0
3-SHA (ng/L)	refer to Table 1 in Chapter 4			
FT (ng/L)	roasted coffee[25]	0.4[25,h]	≤3	≤3
BMT (ng/L)	smoke[25]	0.3[25,h]	6.3	35.0
γ-butyrolactone	refer to Table 1 in Chapter 4			
δ-valerolactone	freshly cut hay[19]	10[19,h]		
γ-decalactone	caramel, fatty-sweet[20]	10[20,h]	0.3	0.2
δ-decalactone	refer to Table 1 in Chapter 4			
cis-oak lactone	coconut, raspberry[22]	24[22,l]	<0.4	<0.4
trans-oak lactone	coconut, green, wood[22]	172[22,l]	<0.1	<0.1
sotolon	curry[23]	5[24,m]	0.2	0
others				
mesityl oxide	sweet, flowery, sickening [26]	n/a		
2-methyl 3-(methyldithio)furan	refer to Table 1 in Chapter 4			
N-(3-methylbutyl)acetamide	refer to Table 1 in Chapter 4			
homofuraneol	caramel[23]	125[23,n]	2.5	1.1

[a] Citations therein and determined in 14% water/ethanol solution adjusted to pH 3.5 with tartaric acid. [b] Citations therein and determined in an 11% water/ethanol solution containing 7 g/L glycerol and 5 g/L tartaric acid at pH 3.2. [c] Determined in 10% water/ethanol solution adjusted to pH 3.5 with tartaric acid. [d] Citations therein and determined in dearomatized red wine [e] Citations therein and determined in water. [f] Determined in red wine. [g] Determined in 11% water/ethanol solution with 7 g/L glycerol and 5 g/L tartaric acid and the pH was adjusted to 3.4 with 1M NaOH. [h] Citations therein and determined in water/ethanol or model solutions. [i] Determined in Ugni-blanc and Merlot wines. [j] Determined in 10% water/ethanol solution with 7 g/L glycerol at pH = 3.2. [k] Determined in 10% (w/w) water/ethanol solution. [l] Determined in white wine. [m] Determined in 12% water/ethanol solution. [n] Determined in 11% water/ethanol solution with 4 g/L of tartaric acid and adjusted to pH 3.5 with K_2CO_3.

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