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(Article begins on next page)

**Isomer composition of aroma compounds as a promising approach for wine  
characterization and differentiation: A review**

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# **Isomer composition of aroma compounds as a promising approach for wine characterization and differentiation: A review**

## **ABSTRACT**

The perceived aroma is the result of the presence of volatile organic compounds (VOCs) as well as the interaction among them and with the non-volatile sample matrix. These compounds can derive from grape berries (varietal) and also be formed during winemaking and ageing processes. Varietal VOCs are strongly influenced by the grape variety, ripening, and geographical origin. Therefore, they were proposed as markers for wine discrimination. Nevertheless, recent studies highlighted the higher discriminating ability of VOC isomer forms. In this review the potential and importance of VOC isomers for terpenes, C<sub>13</sub>-norisoprenoids, C<sub>6</sub>-alcohols, thiols, lactones, and fatty acid esters, as well as isomeric relationships for wine characterization and differentiation have been described to get a full view of possible applications for the wine industry, highlighting potentialities and limitations. VOC isomers can be of paramount relevance to find reliable markers for wine authenticity and fraud prevention, regarding variety and geographical origin. Each isomer form owns a different olfactory threshold, influencing strongly wine sensory characteristics. Certain oenological treatments during winemaking and ageing were found to modify the isomeric profile, particularly yeasts, ageing, and wood in contact with wine. Nevertheless, this research field has potential and new research advances are expected in this field.

*Keywords:* volatile compounds; isomer forms; aroma; wines; discrimination; authenticity

## Introduction

Nowadays it is well recognized that the volatile composition of wines plays a fundamental role in the perceived aroma (Rapp 1995). Wines with a strong aroma imprint are undoubtedly of great relevance since the aroma strongly influences the quality and the acceptance by the consumer (Souza Gonzaga et al. 2020). This subject has stimulated scientific research to better understand the various molecules involved in the aroma perception. In the last decades, different categories of volatile organic compounds (VOCs) that impact the wine aroma have been identified, thus increasing the knowledge of how individual molecules affect sensory perception (Dunkel et al. 2014). Terpenes, C<sub>6</sub>-compounds, norisoprenoids, thiols, benzenoids, and pyrazines are some of the most relevant chemical classes deriving from grapes and, through extraction and possible transformations during winemaking, representing wine varietal aroma.

Terpenes are a large group of VOCs contributing to floral and fruity nuances. They are typical to aromatic wines made mainly from Muscat and Malvasia grape family, as well as Gewürztraminer and Riesling grape varieties (Pollon et al. 2019). Although the concentrations of these compounds are often below the perception threshold, their presence has been identified in almost all the wines (Black et al. 2015). Nearly 40,000 different chemical species have been detected in plants, thus demonstrating a considerable importance of terpenes from a physiological point of view. In fact, they are involved in the defense mechanisms as response against pathogens, as well as against biotic and abiotic stresses (Mele et al. 2021). The origin of these compounds starts from the condensation of two carbon skeletons with five carbon atoms (isopentenyl pyrophosphate or IPP and dimethylallyl pyrophosphate or DMAPP) through two different biosynthetic pathways: a cytoplasmic one through mevalonic acid (MAV) produced from acetyl-CoA and a vacuolar one through methylerythritol-4-phosphate (MEP) produced from pyruvic acid and glyceraldehyde-3-phosphate (Schwab and Wüst 2015). At a perception level, monoterpenes are the main aroma-related terpenes and they can occur in grape berries in the form of hydrocarbons, aldehydes, alcohols, acids, and esters. Moreover, terpenes can be present in grape musts and wines in free volatile form (olfactory active thanks to their hydrophobicity) and in potentially volatile glycosidically bound form with monosaccharides (no olfactory capacity due to the hydrophilic nature).

Terpene compounds are accumulated in grape berries from *véraison* to over-ripeness (Schwab and Wüst 2015). However, a decrease in the concentration of glycosylated forms has been reported before reaching the maximum sugar accumulation (Torchio et al. 2016). Numerous studies have

shown that there is a close correlation between the biosynthesis of terpenes and light radiation. In particular, UV-B radiation causes an increase in the production of terpenes probably as a response to light stress (Joubert et al. 2016; Loreto and Schnitzler 2010). Additionally, other authors have reported that the concentration of terpenes in shaded clusters is lower than in those exposed to the sunlight (Young et al. 2016), although it is not clear whether higher berry temperature is also directly correlated to the increased biosynthesis of terpenes (Luo et al. 2019). The extraction of terpenes from grape skins into must/wine can be enhanced by maceration, while endogenous or exogenous glycosidase enzymes facilitate the release and transformation of the aroma precursors into odor-active compounds (Black et al. 2015).

Another relevant class of grape-related aroma compounds is represented by C<sub>13</sub>-norisoprenoids, deriving from tetraterpenes (carotenoids) enzymatic breakdown. These compounds are present as glycosylated form in grapes, and then released in their odorant form, such as the floral nuanced  $\beta$ -damascenone and  $\beta$ -ionone, and yet increased by wine ageing such as the typical 'kerosene' Riesling note given by 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) (Ferreira and Lopez 2019). In fact, norisoprenoids are strongly connected with the bouquet of long-aged wines, where different powerful odorants, such as vitispirane or megastigmatrienone, may contribute to the tobacco and balsamic notes found in some Cabernet sauvignon, Amarone, and Merlot wines (Slaghenaufer et al. 2014, 2018).

Volatile thiols are grape-derived compounds particularly influencing wine sensory features given their low olfactory perception thresholds. Their contribution is particularly evident in some white wine varieties, such as Sauvignon blanc, Gewürztraminer, and Riesling where 3-mercapto-hexanol, 3-mercaptohexyl acetate, and 4-mercapto-4-methyl-pentan-2-one are conferring the typical passion fruit, grapefruit, and box tree scents. Several viticultural and enological practices, such as nitrogen fertilization, mechanical harvest, transportation, and juice treatments, influence their concentration, and selected yeasts promote both their release as free form from the corresponding nonvolatile precursors and esterification in wine (Capone and Jeffery 2011; Ruiz et al. 2019). In fact, in grapes they can be found as cysteinylated and glutathionylated precursors, being varietal volatile thiols released into the wine during alcoholic fermentation as a result of the  $\beta$ -lyase activity of yeasts.

The enzymatic oxidation leads to the formation of another class of grape-derived aromas, C<sub>6</sub>-alcohols and aldehydes, responsible for herbaceous and green notes of grape musts (Oliveira et al. 2006; Robinson et al. 2014). These compounds are particularly relevant in unripe grapes since their content decreases with maturity and post-harvest due to a reduction of lipoxygenase activity. The

increased alcohols over aldehydes ratio observed during ripening and the aldehydes enzymatic reduction to their respective alcohols during fermentation limit the herbaceous note in wines because C<sub>6</sub>-alcohols own a higher detection threshold than the corresponding aldehydes (Ferreira and Lopez 2019).

The complexity of wine aroma can be strongly influenced by fermentative volatile compounds, such as higher alcohols, esters, volatile fatty acids, and also by ageing aromas. Volatile compounds are released from wood in different extent depending on the origin, toasting, and barrel age. These other aroma compounds include mainly furanic compounds, volatile phenols, and lactones (Chira and Teissedre 2013).

Grape-derived secondary metabolites, in particular monoterpenes, have been used to differentiate wines made from different varieties and even wines from different geographical origin (Dziadas and Jeleń 2010; Skinkis, Bordelon, and Wood 2008; Vilanova et al. 2013; Zamuz and Vilanova 2006). However, the content of these compounds in the wine can be affected by the winemaking process. In this sense, various studies have been published and reviewed with the aim of determining the wine authenticity according to the volatile profile, based on the analysis of different chemical species (Versari et al. 2014). Nevertheless, these analytical methods are not still validated as certification tools for grape variety and/or geographic origin, and more research is required due to their discriminating limitations.

The evolution of instrumental analytical techniques (e.g., gas chromatography coupled to mass spectrometry, GC-MS) and extraction methodologies has permitted not only to lower the detection limits and to further characterize the volatile molecules, but also to determine the isomer forms of the single compounds. Terpenes, as well as norisoprenoids, thiols, C<sub>6</sub>-compounds, and other volatiles have different structures despite having the same structural formula. Isomerism can refer to the form (chain isomerism such as linear, branched, or cyclic structures), to the position of a specific substituent or type of bond along the main chain (position isomerism) or to the spatial arrangement of the atoms that make up the molecule (stereoisomerism). In turn, there are two kinds of stereoisomerism: geometric isomerism or diastereomerism (*cis/trans*, *E/Z*) and optical isomerism or enantiomerism (+/–, *R/S*). Regarding free volatile compounds, released in the must from the grape precursors or derived from the winemaking process, the main effect of the different isomers is the olfactory threshold and the aroma descriptors involved (Brenna, Fuganti, and Serra 2003). For instance, (*R*)-(–)-linalool is characterized by ‘wood’ or ‘lavender’ nuance whereas (*S*)-(+)-linalool has ‘sweet petitgrain-like’ notes and lower perception threshold (Song et al. 2018).

Although the isomer composition in wines has been little explored up to now, volatile compounds have numerous stereogenic centers, and therefore isomer forms can be significantly important for the wine quality, as well as for characterization and differentiation purposes (Song et al. 2018). This recent research field is of great economic interest, taking into account that wine is one of the most common beverages prone to fraud (Ruiz del Castillo, Caja, and Herraiz 2003). Adulterations and diverse winery malpractices (e.g., chemical addition to improve sensory characteristics of wines, dilution/replacement of expensive wine types with cheaper ones, and mislabeling regarding grape variety and geographical origin) are some of the most common fraud attempts (Holmberg 2010; Villano et al. 2017). In the European Union, most quality-labelled wines belong to the protected designation of origin/protected geographical indication (PDO/PGI) quality schemes [Regulation (EU) No 1308/2013], and they must comply with production rules, quality standards, as well as grape varieties and geographic origin.

The aim of this review is to summarize the significant recent advances and the current knowledge in the field of the characterization and differentiation of wines, based on VOC isomers, isomeric relationships, emphasizing factors affecting isomers in wine production and their impact on sensory characteristics (**Figure 1**). To date, there are no official methodologies to assess if a wine meets the legal requirements in terms of authenticity (winegrape variety and geographical origin) and ageing, as well as for fraud prevention and aroma adulteration. Therefore, an overview of the scientific literature published on this actual subject and the possible applications for the wine industry is provided, highlighting potentialities and limitations.

### **VOC isomer evolution during grape ripening**

Although this review is focused on wines, a brief section is dedicated to the evolution of terpenes during grape ripening because these compounds are responsible for the distinctive aroma of grape varieties belonging to Muscat group and of their respective wines. During grape ripening, enzyme-mediated oxidative transformations of monoterpenes can occur, which mainly influence the stereoisomeric ratios of various linalool-derived compounds. Regarding diastereoisomers *cis/trans*, significant differences were observed for free *trans*-furan linalool oxide, *cis*-rose oxide, and *trans*-rose oxide during berry ripening of Moscato bianco grapes, reaching their highest concentration at  $19.3 \pm 0.2$  °Brix (Torchio et al. 2016). Nevertheless, both diastereoisomers *cis/trans* for free rose oxide were much less affected by the sampling date than by the berry density (between 1.05 and 1.12 g/cm<sup>3</sup>), where a higher density effect was observed in the later stage of ripening. On the

contrary, the sampling date influenced strongly and negatively the concentration of bound *trans*-rose oxide whereas a combined effect of berry density and harvest date was observed for the *cis* isomer.

In another study, the accumulation of some terpene compounds during berry ripening for the Morio-Muskat variety has been evaluated by enantioselective multidimensional GC-MS using a chiral column consisting of a modified cyclodextrin as stationary phase (Luan et al. 2006). The accumulation of the various isomers of pyran and furan linalool oxides began at 14.6 °Oechsle (Oe) up to 78.7 °Oe (approx. 4 and 19 °Brix, respectively). Pyran linalool oxides were found mostly as a mixture of (2*S*)-configured *cis/trans* diastereoisomers, whereas (2*R*)-configured isomers occurred in small amounts. The high enantiomeric purity could be due to the preservation of the absolute configuration at C<sub>2</sub> from the linalyl 6,7-epoxide precursor derived from highly enantiomeric pure (3*S*)-linalool. The diastereoisomeric ratio was close to 1, being practically constant during berry ripening (Williams, Strauss, and Wilson 1980). This was not the case of furan linalool oxides because of the percentage of the *trans*-(2*S*,5*S*) isomer constantly increased at the expense of the *cis*-(2*S*,5*R*) isomer during maturation (from 1:9 to 1:1). A possible glycosylation of the *cis*-(2*S*,5*R*) isomer of furan linalool oxide could occur involving a discriminating glycosyl transferase. Moreover, the occurrence of (2*R*)-configured isomers of *cis*- and *trans*-furan linalool oxides can be explained by a different reaction mechanism from 3,7-dimethyloct-1-ene-3,6,7-triol involving partial racemization at C<sub>3</sub> (Williams, Strauss, and Wilson 1980). Although the dominant mechanism for the furanoid linalool oxides occurs in the berry through the epoxide pathway, they can be also formed via 3,7-dimethyloct-1-ene-3,6,7-triol.

Regarding other monoterpenes evaluated at berry ripeness in the same study (Luan et al. 2006), hotrienol was present at a high purity in all grape varieties investigated (Morio-Muskat, Muscat Ottonel, White Muscat, Muskat-Trollinger, Toli Muskotály, and Wuerzer) as the (3*S*)-configured enantiomer (higher than 92%) whereas (4*R*) enantiomer occurred mostly for *cis*- and *trans*-rose oxide (higher than 86%).

This information represents the starting point for a better understanding of the accumulation dynamics of metabolites in grape berries but also for the development of strategies aimed at authenticity control of unadulterated grape musts. In particular, another study provides valuable information on the potential of enantiomers to differentiate monoterpenes origin, including grape berries and yeasts (Luan et al. 2005). The high enantiomeric purity in grapes of (*S*)-configured free and glycosidically bound citronellol (higher than 95%) throughout the ripening process is a



consequence of the stereoselective enzymatic reduction of the C2/C3 double bond of geraniol. However, wine authenticity assessment requires the knowledge of which isomer distributions remain invariable during the technological process. So, the geraniol reduction during fermentation mediated by *Saccharomyces cerevisiae* yields is (*R*)-citronellol stereoselective. In addition, *cis*-(2*S*,4*R*)-rose oxide is stereoselectively biosynthesized from the reduction of (*S*)-citronellol.

A recent study has evidenced the effect of *Botrytis cinerea* infection on the enantiomer distribution of chiral terpenes (hoptrienol,  $\alpha$ -terpineol, and limonene) for Muscat yellow, Lipovina, and Furmint varieties. However, the effect was slightly variety dependent. A decreased enantiomer ratio was observed in Muscat yellow and Lipovina winegrape varieties for (*S*)-(-)- $\alpha$ -terpineol and (*S*)-(+)-hoptrienol (from -2% to -4% and from -10% to -17%, respectively) whereas (*S*)-(-)- $\alpha$ -terpineol increased for Furmint grapes (+5%). An opposite effect of botrytization was observed for limonene in Muscat yellow, where noble-rotten berries showed lower dominance of (*R*)-enantiomer with respect to healthy ones (-6%) (Machyňáková, Khvalbota, and Špánik 2021).

### **VOC isomers as markers of geographical origin**

The recent scientific literature evidences that the geographical differentiation of wines is one of the most important focus in fraud prevention (Holmberg 2010). In this sense, the isomers of volatile compounds have been used as markers of wine typicality and quality. Furthermore, the isomeric ratios of these compounds change for the same variety but growing in different regions, and they are related to geographic origin. Cabernet sauvignon, Syrah, and Pinot noir wines (a total of 104 samples analyzed) from four different geographic areas in Australia far from each other (Margaret River, Coonawarra, Barossa, and McLaren Vale) were analyzed for terpenes, in particular two positional isomers of cineole (1,4-cineole and 1,8-cineole) (Antalick et al. 2015). From the structural point of view, these isomers differ in the binding positions of the epoxy group, but they have also very different olfactory nuances. In fact, the first one is associated with 'mint' and 'camphor' descriptors, while the second gives very marked 'eucalyptus' notes. Analytes were extracted and enriched from wine by headspace solid-phase microextraction (HS-SPME) and determined by GC-MS technique. A growing zone effect was observed on the concentration of these compounds within the Cabernet Sauvignon and Syrah wines. For Cabernet sauvignon wines, the highest concentrations of 1,4-cineole were found in Margaret River region, whereas in the case of 1,8-cineole the richest Cabernet Sauvignon and Syrah wines corresponded to Coonawarra.

Barossa and McLaren Vale regions gave wines with the lowest concentrations of 1,4-cineole and 1,8-cineole. This variability found in wines from different geographical areas may be due to abiotic factors in which the terroir understood as the interaction between climate, soil, and grape variety plays an essential role (Deloire et al. 2005; Kalua and Boss, 2010). Thus, the 1,4-/1,8-cineole ratio was proposed as an aroma marker of regional typicality. Particularly, non-metric multidimensional scaling for the evaluation of dissimilarities between samples has shown that the wines from Coonawarra, having low 1,4-/1,8-cineole ratios, are associated with strong nuances of ‘eucalyptus’, ‘laurel’, and ‘licorice’, while wines from Margaret River with high 1,4-/1,8-cineole ratios are characterized by ‘herbaceous’ attributes (Antalick et al. 2015).

Another study, concerning the wine geographical characterization based on the distribution of terpene isomers, was carried out by Picard et al. (2016a). In this case, the molecule under investigation was piperitone, a monoterpene ketone (3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one) derived from limonene secondary transformation pathway in wine. This could have a varietal origin as already observed for 1,4-/1,8-cineol (Antalick et al. 2015). It has two enantiomeric forms: (6*S*)-(+)-piperitone and (6*R*)-(-)-piperitone, both characterized by ‘mint’ nuances. A wide range of 51 red wines from different vintages and Bordeaux appellations were sensory and chemically analyzed. GC-MS analyses were performed using an enantioselective cyclodextrin-based stationary phase to correlate these two enantiomers with the typicality of the wines produced in the Bordeaux wine-growing area (Picard et al. 2016a). The higher intensity of ‘mint’ notes related to wines with greater typicality corresponded to piperitone concentrations of 232–1091 ng/L and to an average 6*R* / 6*S* ratio of approximately 81:19 (**Table 1**). Those wines with lower typicality had piperitone concentrations of 203–470 ng/L and an average enantiomeric ratio of 97:3. In a previous study, similar enantiomeric distributions of 90:10 were reported for piperitone when only two young Bordeaux red wines were analyzed (Pons et al. 2016). Therefore, highly typical wines (Medoc appellation, most made from Cabernet sauvignon blends) had significantly higher piperitone concentrations with a higher proportion of the (6*S*)-(+) enantiomeric form showing a strong ageing bouquet characterized by more intense ‘mint’ nuances. The enantiomeric distribution of (6*R*)-(-)-piperitone and (6*S*)-(+)-piperitone is a potential molecular marker of geographical origin, which is related to the ‘minty’ ageing bouquet of Bordeaux red wines from the left bank of the Gironde estuary. Nevertheless, these findings may be due to the higher proportion of Cabernet Sauvignon over Merlot in these wine blends suggesting a possible varietal effect whose

confirmation requires additional studies on monovarietal Merlot and Cabernet Sauvignon wines from these Bordeaux areas.

It is important to evidence that the geographic origin of wines may influence not only terpenes but also other volatile compounds. Particularly, thiol compounds often have different isomer forms, which have also very different olfactory thresholds and characteristic scents. Studies carried out over 20 years ago (Bouchilloux et al. 2000) highlighted that only the (*R*)-(-) enantiomeric form of 3-mercapto-2-methylpropanol (characteristic thiol of Cabernet sauvignon) is detected in Bordeaux wines (**Table 1**). The (*R*)-(-)-3-mercapto-2-methylpropanol enantiomer with a ‘spicy’ nuance has a lower sensory threshold than (*S*)-(+) isomer having an exotic ‘fruity’ note. However, there was a considerable variability between different wine-growing areas (Pomerol, Margaux, St. Julien, and Pessac-Léognan). In this case, an enantioselective multidimensional GC based on the use of chiral stationary phase coupled to MS (enantio-MDGC-MS) was applied.

### **VOC isomers for variety characterization and differentiation**

An important application field of isomer forms and ratios for volatile compounds is the variety differentiation and similarity of wines. In fact, it is already possible to create similarity maps using techniques based on the genetic code. Nowadays, the most widely used method to establish the parentage degree among grape varieties is the genetic analysis through the study of microsatellites or simple sequence repeats (SSRs) (Emanuelli et al. 2013). Taking into account that this genetic association could be linked to a similarity at the level of the aromatic profile of the different cultivars, the isomer forms may become powerful variety markers. Particularly, terpene synthases are responsible for many terpene compounds in grapes, and therefore terpene isomers could be related to variety genetic information also in wines.

One of the first attempts to exploit the potential of volatile compounds for the characterization and differentiation of wines according to the grape variety have already been performed more than 20 years ago (Versini, Orriols, and Dalla Serra 1994). Twenty-three white Galician wines (Northwest Spain) were analyzed corresponding to three different winegrape varieties (14 Albariño, 2 Loureira, and 7 Godello, all from 1992 vintage). The concentration of both *cis* and *trans* isomers of 3-hexen-1-ol for Albariño and Godello wines was 3–4 fold higher than that corresponding to Loureira. In addition, Albariño wines were characterized by a higher abundance in the *cis* isomer conversely to Loureira and Godello wines, which were richer in the *trans* isomer. The isomers of C<sub>6</sub>-alcohols were also proposed as varietal markers of red wines from Valpolicella (Slaghenaufi et al. 2021a)

(**Table 1**). Particularly, Corvina wines were characterized by much higher average concentrations of *cis*-3-hexenol (197.0–215.0 µg/L) than other monovarietal red wines made from Corvina (13.3–34.5 µg/L), Rondinella (146.6 µg/L), Molinara (3.4 µg/L), Oseleta (21.6 µg/L), Raboso (59.9 µg/L), Croatina (15.9 µg/L), Sangiovese (33.7 µg/L), and Cabernet sauvignon (22.9 µg/L). In addition, Oseleta wines were the most abundant in *cis*-2-hexenol (20.3 µg/L) when compared to the other monovarietal wines studied (5.0–13.0 µg/L). In addition, the ratio between the *cis*-3-hexenol and *trans*-3-hexenol isomers was strongly influenced by the variety (ranging from around 11 for Corvina and Rondinella to 0.13 for Molinara), whereas *cis*-2-hexenol was prevalent on the *trans* isomer for all the varieties investigated. Tannat wines, obtained in 1999 and 2000 vintages from Uruguay, were characterized by a rather low content of free C<sub>6</sub>-alcohols with a prevalence of *cis*-3-hexen-1-ol over its *trans* form but only the *trans* isomer of 2-hexen-1-ol was detected (Boido et al. 2003) (**Table 1**). It is well known that the biosynthesis of C<sub>6</sub>-compounds is directly linked to grape enzymes, and therefore it is variety dependent.

Regarding terpene isomers, Albariño and Loureira wines showed a prevalence of free *trans*-pyran linalool oxide on the *cis* form and on furan linalool oxide isomers, whereas glycosidically bound *trans*-furan linalool oxide was more abundant than the *cis* form for Albariño and Loureira wines (Versini, Orriols, and Dalla Serra 1994). Finally, Godello wines had similar concentration of both bound 8-hydroxylinalool isomers, whereas Albariño was prevalent in the *cis* isomer. Similar results were reported for Alvarinho and Loureiro grapes growing in “Vinhos verdes” region in Portugal (Oliveira et al. 2004), confirming that the aromatic profile is able to characterize and discriminate wines made from different grape varieties (**Table 2**).

A total of 104 samples of Cabernet sauvignon, Syrah, and Pinot noir wines from four different geographic areas in Australia (Margaret River, Coonawarra, Barossa, and McLaren Vale) were analyzed for 1,4-cineole and 1,8-cineole (Antalick et al. 2015). An important varietal effect was reported: the highest mean concentrations of both isomers were found in Cabernet sauvignon (0.59 and 2.82 µg/L for 1,4-cineole and 1,8-cineole, respectively), followed by Syrah (0.07 and 1.75 µg/L) and Pinot noir (0.22 and 0.99 µg/L) (**Table 1**).

In a more recent study, Song et al. (2018) examined 148 commercial white wines, in two consecutive vintages (2012 and 2013), made from 8 winegrape cultivars (Chardonnay, Gewürztraminer, Muscat, Pinot gris, Riesling, Sauvignon blanc, Torrontés, and Viognier) from different countries and regions known for these varieties (**Table 2**). The concentration and the isomer profile of free monoterpenes were determined to establish the genetic parentage relationship

through the formation of homogeneous clusters. Seventeen monoterpene isomers were extracted and enriched by HS-SPME, and then determined with multidimensional gas chromatography mass spectrometry (MDGC-MS), including two hydrocarbons ((*S*)-(-)-limonene and (*R*)-(+)-limonene), ten oxides ((*2R,4S*)-(+)-*cis*-rose oxide, (*2S,4R*)-(-)-*cis*-rose oxide, (*2R,4R*)-(-)-*trans*-rose oxide, (*2S,4S*)-(+)-*trans*-rose oxide, (*2R,5R*)-(+)-*trans*-linalool oxide, (*2R,5S*)-(-)-*cis*-linalool oxide, (*2S,5S*)-(-)-*trans*-linalool oxide, (*2S,5R*)-(+)-*cis*-linalool oxide, (*S*)-(-)-nerol oxide, and (*R*)-(+)-nerol oxide) and five alcohols ((*R*)-(-)-linalool, (*S*)-(+)-linalool, (*S*)-(-)-terpineol, (*R*)-(+)-terpineol, and (*R*)-(+)-citronellol). Three variety groups were established according to the concentration of monoterpene isomers in the wines analyzed: the first one includes Muscat and Torrontés; the second group is formed only by Gewürztraminer; the last one contains Chardonnay, Viognier, Riesling, Sauvignon blanc, and Pinot gris. This classification agrees with the genetic analysis and parental information based on the use of microsatellites. Particularly, Muscat and Torrontés grapevines are associated because Muscat of Alexandria is one of the ancestors of the Torrontés variety (Aguero et al. 2003). Regarding the group formed by Chardonnay, Viognier, Riesling, Sauvignon blanc, and Pinot gris, a certain degree of genetic proximity was also found for Chardonnay and Pinot gris, which are progenies of Pinot noir, as well as Chardonnay is highly parentally linked to Riesling, Sauvignon blanc, and Viognier (Bowers and Meredith 1996). This correspondence between genetic footprint and terpene profile supports the possibility of using terpene isomers as varietal markers. Differences that cannot be explained genetically may be due to yeasts, bacteria, winemaking practices, and chemical rearrangement.

In the mentioned study (Song et al. 2018), the same 148 varietal wines were also grouped using the enantiomeric ratios calculated dividing the concentration of the earlier eluted enantiomer by that of the total enantiomers of each compound. For each of the 8 enantiomer pairs, enantiomeric ratios were calculated. Differently from what was observed with structural isomers, the enantiomeric ratios differentiated well the wines according to the variety aromatic character. The stereospecificity of grape monoterpene synthases strongly influences the relationship between two enantiomers for most aromatic wines, whereas the role of yeasts in the synthesis of monoterpenes may influence the relationship between enantiomers in neutral grape varieties, such as Chardonnay (Carrau et al. 2005). In particular, Muscat, Torrontés, and Riesling wines showed similar enantiomer profiles, where (*S*)-(-)-limonene and (*2R,4S*)-(+)-*cis*-rose oxide were the most important variables differentiating from other variety wines. Gewürztraminer and Viognier wines had been classified according to (*2R,5S*)-(-)-*cis*-linalool oxide. Chardonnay and Pinot gris wines

were differentiated on the basis of (2*R*,4*R*)-(-)-*trans*-rose oxide, (S)-(-)-nerol oxide, (S)-(-)- $\alpha$ -terpineol, and (R)-(-)-linalool. Sauvignon blanc wines were separated on the basis of (2*R*,5*R*)-(+)-*trans*-linalool oxide. Moreover, Song et al. (2018) highlighted that the relationship between enantiomer pair concentrations of wines obtained from the same variety does not change even though the geographical area, vintage, wineries, and winemaking process are different ( $R^2$  values were 0.8 or higher), confirming that the enantiomeric differences are strongly linked to the grape variety. Therefore, despite the significant sources of variability, the variety discrimination based on isomer profiles of monoterpenes is possible in wines.

Regarding Tokaj wines, Furdíková et al. (2021) have compared the volatile composition of 37 monovarietal wines produced from Furmint, Lipovina, and Muškát žltý grape varieties (**Table 3**). Muškát žltý wines showed the highest concentration of terpenoids whereas Furmint and Lipovina were similar to each other. In addition, the enantiomer analysis of dominant terpenoids (limonene, linalool, hotrienol, and  $\alpha$ -terpineol) was carried out by SPME-GC-MS using heart-cut two-dimensional GC with a  $\beta$ -cyclodextrin based analytical column after separation at a polar stationary phase. However, the reliable variety identification in wines based on enantiomer ratios was not possible in all cases. Using Linear Discriminant Analysis (LDA), it was possible to obtain satisfactory identification probabilities only for Muškát žltý wines (76.9% of correct identification), probably because they are produced from an aromatic grape variety. Nevertheless, the semi-quantification of dominant enantiomeric form of terpenoids has allowed to differentiate the winegrape varieties studied, being (R)-linalool the isomer responsible for this discrimination. The use of dominant enantiomer concentration as a sorting variable increased the reliability of the variety classification of wines, achieving a probability of 100% for Muškát žltý and higher than 80% for Furmint and Lipovina, even though the low discrimination of non-aromatic wines (Lipovina and Furmint) from each other. Therefore, the enantiomeric forms of terpenoids have a great potential for assessing varietal authenticity also for Tokaj wines.

### **Influence of winemaking and ageing processes on VOC isomers**

During winemaking and ageing, numerous transformations take place affecting the concentration and profile of volatile compounds when compared to the grape must. Alongside the chemical reactions (hydrolysis and oxide-reductions), yeasts and other microorganisms could modify the terpene composition through enzymatic processes hindering the differentiation based on the variety

and/or geographical origin, or on the contrary they could provide additional relevant information in relation to origin.

Yeasts can modify some monoterpenols present in grapes altering the enantiomeric purity. King and Dickinson (2000) have observed that approximately equal amounts of (+) and (–) enantiomers of linalool and  $\alpha$ -terpineol are produced by pure *Saccharomyces cerevisiae* cultures fed with geraniol, and by *Torulasporea delbrueckii* cultures fed with geraniol or nerol. Therefore, although there could potentially be some variability related to specific strains, the yeast-mediated formation of linalool and  $\alpha$ -terpineol seems to be not stereospecific.

### ***Dry and sweet white wines***

**Table 2** shows the studies published on the characterization of white wines according to isomer forms of different VOCs. An interesting study concerning the quantification of rose oxide in some white wines has highlighted how two enantiomers ((–)-*cis* and (+)-*cis*-rose oxide) are formed and how they evolve during winemaking of Gewürtztraminer wines (Koslitz et al. 2008). It is important to evidence that the *cis*-rose oxide forms are good markers of typicality for the Gewürtztraminer variety. Moreover, rose oxide is an important varietal volatile compound in the resulting wine showing high concentrations (Guth 1997). However, the enantiomer ratio changes during alcoholic fermentation (Koslitz et al. 2008). Particularly, it was observed a clear prevalence (97 to 88%) of the (2*S*,4*R*)-(–)-*cis* form on the (2*R*,4*S*)-(+)–*cis* form in grape musts whereas this enantiomeric ratio of *cis*-rose oxide was markedly lower in all wines analyzed (maximum 76% in favor of (2*S*,4*R*)-(–)-*cis* form), or even almost a racemic mixture of *cis*-rose oxide was found (**Table 2**). Fermentation studies carried out using a deuterated model must in combination with enantioselective HS-SPME stable isotope dilution assay (HS-SPME-SIDA) have evidenced at least two different yeast-mediated reduction biosynthetic pathways involved in the (+)-*cis*-rose oxide formation, in addition to hydrolytical processes by glycosidases. In this sense, yeasts play a decisive role through their stereoselective reductive yeast metabolism, explaining the lower enantiomeric purity of *cis*-rose oxide in wines when compared to the corresponding musts.

With the aim of wine authenticity, a comprehensive determination of both the enantiomeric forms and their ratios for the main chiral volatile organic compounds was performed on Slovak Tokaj wines obtained from noble-rotten grapes (Khvalbota et al. 2021). Fifty-three traditional Tokaj wines were analyzed, including 10 Tokaj selection 3-putňový (residual sugar concentration, RS  $\geq$  60 g/L), 9 Tokaj selection 4-putňový (RS  $\geq$  90 g/L), 13 Tokaj selection 5-putňový (RS  $\geq$  120 g/L),

15 Tokaj selection 6-putňový ( $RS \geq 150$  g/L), 4 Tokaj selection essence ( $RS \geq 180$  g/L), and 2 Tokaj essence from 1959–2015 vintages. Enantiomer separations were performed by heart-cut two-dimensional GC-MS system using a chiral cyclodextrin stationary phase after the compounds separation at a polar stationary phase. Regarding terpenes, linalool and limonene were detected only in younger wines. Linalool was present as racemic enantiomer mixture. The (*R*) form of limonene was slightly dominant (52–66%) whereas (*S*) enantiomer was prevalent for hotrienol (51–82%) and  $\alpha$ -terpineol (47–70%). Similar enantiomer distribution was reported by Furdíková et al. (2021) in 37 Tokaj varietal wines (63% for (*R*)-limonene, 67–78% for (*S*)-hotrienol, and 55–57% for (*S*)- $\alpha$ -terpineol), and also by Machyňáková, Khvalbota, and Špánik (2021) in 5 Tokaj selection essence wines (61–68% for (*S*)-hotrienol and 44–57% for (*S*)- $\alpha$ -terpineol), as shown in **Table 3**. Regarding volatile thiol compounds (**Table 2**), the enantiomeric distribution of 3-mercaptohexan-1-ol (3MH) and 3-mercaptohexyl acetate (3MHA) changed during fermentation, and also different enantiomeric ratios were reported for dry and sweet white wines produced from Sauvignon blanc and Semillon grapes in three different vintages (Tominaga et al. 2006). The enantiomer separation was carried out using GC on a cyclodextrin-based column. During alcoholic fermentation to produce dry wines, the ratio between (*R*) and (*S*) enantiomers changed approximately from 40:60 to 50:50 for 3MH whereas it remained constant at 30:70 for 3MHA enantiomers. At the beginning of alcoholic fermentation, some endogenous yeast  $\beta$ -lyases exhibit a certain chiral selectivity on the 3MH release. On the contrary, this enantiomeric ratio for 3MH was scarcely modified through fermentation and achieved values around 30:70 in sweet white wines made from botrytized grapes. This involves a higher concentration of the (*S*) enantiomer for 3MH when compared to dry wines, which could be due to a higher concentration of its precursor in overripe grapes. It is important to evidence that yeasts used for fermentation (three strains of *Saccharomyces cerevisiae* and one strain of *Saccharomyces bayanus*) had no influence on the enantiomer ratio of these compounds. The olfactory thresholds are similar for the (*R*) and (*S*) enantiomeric forms of 3MH (50 and 60 ng/L in hydroalcoholic model solution) but they are characterized by quite different aromatic traits, namely ‘grapefruit’ for the (*R*) form and ‘passion fruit’ for the (*S*) form. Regarding 3MHA, the (*S*) enantiomer has a lower perception threshold (2.5 ng/L) with ‘herbaceous’ notes than the (*R*) form (9 ng/L) giving ‘passion fruit’ nuances.

Among fermentation compounds, diethyl malate was identified only as (*S*)-enantiomer in Tokaj wines obtained from botrytized grapes by preserving the enantiospecificity of the malic acid present in grapevines as precursor (Khvalbota et al. 2021; Machyňáková, Khvalbota, and Špánik 2021).



The (2*R*,3*R*) enantiomer was the main form of 2,3-butanediol in all samples (**Table 3**), although it was found in unusual ratio for white wines (54–100%) as a result of non-*Saccharomyces* yeast activity and ageing that favor the formation of (2*S*,3*S*)-butanediol in Tokaj wines (Khvalbota et al. 2021; Machyňáková, Khvalbota, and Špánik 2021). In fact, *Kloeckera apiculata* and *Metschnikowia pulcherrima* are naturally present on winegrapes from Tokaj wine region, as well as *Candida stellata* and *Candida zemplinina* that are typically found in Tokajské samorodné, Tokaj selections, and Tokaj selection essence wines. All of these yeasts are particularly involved in spontaneous fermentation process. A decrease of (2*R*,3*R*)-2,3-butanediol was also observed with ageing time (Machyňáková, Khvalbota, and Špánik 2021).

### ***Sparkling wines***

**Table 3** also summarizes the studies published on the use of isomer forms of VOCs for the characterization of the different sparkling wine typologies. One study confirmed that the winemaking process can affect the aroma composition of wines, in particular terpenes. In this case, the traditional method (secondary fermentation in bottle with exogenous sugars), the Charmat-Martinotti method (secondary fermentation in autoclave with exogenous sugars), and its variant the Asti method (incomplete fermentation in autoclave by consuming endogenous grape sugars) were compared for the production of sparkling wines from Moscato giallo grapes (Caliari et al. 2015). With the same starting must, higher concentrations of both *cis*-furan linalool oxide and *trans*-furan linalool oxide were observed in sparkling wines obtained using the Asti method followed by the traditional and Charmat-Martinotti method. The sparkling wines produced by the Asti method were also the richest in *trans*-pyran linalool oxide whereas those obtained by the traditional method showed the highest concentration of *cis*-pyran linalool oxide. In fact, despite the lower concentration of total terpene compounds mainly due to a decrease in linalool, hotrienol, and  $\alpha$ -terpineol, linalool oxide forms represent 14% of average concentration of total terpenes in the sparkling wines obtained using the Asti method whereas only 7 and 4% for those obtained by the traditional and Charmat-Martinotti methods, respectively. Within the furanic forms, there was a certain stability in the relationship between the *cis* isomer and the *trans* isomer. However, regarding the pyranic forms, the wines produced with the Asti method had a much lower *cis/trans* ratio (1.4) than the other two methods (4.6 and 4.0). A possible explanation for these differences could be that the sparkling wine resulting from the Asti method contains reducing sugars at a concentration of

28.2 g/L and an alcohol content of 9.2% (v/v) whereas the other two ones are essentially dry wines with 1.1 g/L of residual sugars and alcohol content of 10.9% (v/v).

The isomeric ratio of linalool oxides was different for sweet red lightly (bottle pressure < 1.7 bar, “*Tappo raso*”) and fully (bottle pressure > 3.0 bar, “*Spumante*”) Brachetto d’Acqui sparkling wines. The wines were produced using the Charmat-Martinotti method in sealed tanks. This type of sparkling wines is characterized by residual sugar concentrations ranging 90–130 g/L and alcohol contents between 4.5 and 7.5% (v/v). Sweet lightly sparkling wines showed higher concentrations of both *cis* isomers of furan and pyran oxides whereas they had a significantly lower amount of *trans*-pyran linalool oxide when compared to fully sparkling wines (Torchio et al. 2012) (**Table 3**). These authors highlighted that the presence of linalool oxides is strongly related to the winemaking process used for producing sweet sparkling wines because these compounds were not detected in dry wines made from aromatic red Brachetto grapes. Therefore, linalool oxides may be used as markers of sweet sparkling wines, but more research is necessary. Furthermore, *cis*- and *trans*-furan linalool oxides increased significantly during ageing at different temperatures. This trend agreed with the significant increase observed in the *trans*-furan and *cis*-furanic forms of linalool oxide after ageing Muscat wines for one year (Usseglio Tomasset 1983).

### ***Red wines***

The different studies published on the potential of isomer forms of VOCs to characterize red wines are reported in **Table 1**. As already mentioned, piperitone is a molecular marker associated to aged Bordeaux red wines and is responsible for their typical ‘minty’ notes (Picard et al. 2016a, 2016b). The concentrations of piperitone varied between 170 and 1091 ng/L in 15 commercial red wines from different appellations (Margaux, Pomerol, Saint-Emilion, Saint-Estèphe, Saint-Julien, and Pauillac) and vintages (1996–2012). The highest typicality score corresponded to the most intense ‘mint’ nuance and also to the highest piperitone concentration (Picard et al. 2016b). Moreover, the continuous progress in the research field regarding the key role of isomers of volatile organic compounds in wines has led to the identification of new volatile substances and their relative isomers, as well as the direct impact on the sensory perception of some other red wines. As an example, lactones have a particular aptitude for the formation of enantiomers because of their structure. A recent study has reported, for the first time, the presence of three *p*-menthane lactone isomers (mintlactone, isomintlactone, and menthofurolactone) in a red wine from the Bordeaux region (Picard, De Revel, and Marchand 2017). The concentrations found ranged from 60 to 900

ng/L with a ratio of (–)-mintlactone to (+)-isomintlactone around 14:1 (**Table 1**), which was similar to this diastereoisomeric ratio reported in peppermint (10:1). These lactones derive from limonene secondary biotransformations, being menthofuran identified as their common precursor. All these compounds are powerful ‘mint-like’ odorants characterizing the freshness attributable to aged Boudeaux red wines.

Ethyl 2-hydroxy-4-methylpentanoate (ethyl *DL*-leucate) enantiomers were determined in 55 commercial wines (42 red wines from 1981 to 2010 and 13 white wines from 1989 to 2008) by chiral GC, showing different enantiomeric ratios for white wines with only the (*R*) form, and red wines having both enantiomers in various ratios according to ageing (**Tables 1 and 2**). An increased concentration of the (*S*) form was found in the most aged red wines (Lytra et al. 2012). The two enantiomeric forms were detected in wines at levels slightly above their perception threshold in hydroalcoholic solution (olfactory threshold was 126 µg/L for *R* isomer, 55 µg/L for the (*S*) form, and 51 µg/L for a *R* and *S* mixture with a 95:5 ratio) but they contributed synergistically to ‘fruity’ olfactory perception.

Bicyclic terpenes, such as 1,4-cineole and its isomer 1,8-cineole, were found in white and red wines. In Lugana and Verdicchio white wines from Italy, 1,4-cineole concentrations ranging from 0.28 to 1.06 µg/L have been detected (odor threshold of 0.54 µg/L), whereas 1,8-cineole was present at concentrations between 0.03 and 0.46 µg/L (all below the odor threshold of 1.1 µg/L) (Slaghenaufi et al. 2021b). That is, 1,8-cineole was found in significantly important amounts from the aromatic point of view only in red wines (up to 20 µg/L; Capone et al. 2011), probably due to its increased release during long maceration in contact with the berry skins. Furthermore, the concentration of these compounds, and their contribution to ‘minty’ and ‘balsamic’ nuances, increases progressively during ageing as a consequence of reactions involving limonene,  $\alpha$ -terpineol, and terpinolene precursors, as confirmed using model wine solutions (Farina et al. 2005; Slaghenaufi and Ugliano 2018).

### ***Wood-aged wines***

Some lactones, particularly whiskey lactones ( $\beta$ -methyl- $\gamma$ -octalactones), are important makers of wine ageing in contact with oak wood where they occur naturally as (*4S,5S*)-*cis* and (*4S,5R*)-*trans* enantiomers. When acacia, chestnut, cherry, and three oak wood species (*Quercus pyrenaica*, *Quercus alba*, and *Quercus petraea*) were compared, 3,4-dimethoxyphenol and 2,4-dihydroxybenzaldehyde were found to be chemical markers of acacia wood, *p*-anisaldehyde and

benzylsalicylate were detected only in cherry wood, whereas the *cis* and *trans* isomers of whiskey lactones and isobutyrovanillone were identified only in oak wood (Fernández de Simón et al. 2009). Monastrell red wines aged in American *Quercus alba* showed concentrations of *cis*-whiskey lactone between 4 and 16 times more than *trans*-whiskey lactone, whereas those ageing in French *Quercus petraea* achieved ratios ranging 1 and 4 times more (Pérez-Prieto et al. 2002) (**Table 1**). This is in agreement with the higher richness in *cis*-whiskey lactones for Fetească neagră red wines aged using oak chips, ranging between 190 and 618 µg/L for American oak chip-treated wines and from 93 to 172 µg/L for French oak chip-treated samples depending on dosage and contact time (Dumitriu et al. 2019) (**Table 1**). European oak woods have lower *cis*-/*trans*-whiskey lactone ratios and lower concentrations of the *cis* form than American oak species, these last showing higher isomeric ratios and higher concentrations of the *cis* form (Waterhouse and Towey 1994). Moreover, there were also differences between two European oak species. *Quercus petraea* contained 20 times more *cis*-whiskey lactone (6.90 vs. 0.34 µg/g of dry wood) and 12 times more *trans*-whiskey lactone (3.88 vs. 0.28 µg/g of dry wood) than *Quercus robur* (Prida et al. 2007). Therefore, the analysis of the enantiomeric distribution of whiskey lactone can provide relevant information regarding the origin of the wood used during wine ageing. An additional important aspect is the characteristic coconut-based olfactory nuance (*cis* form having additional ‘earthy’, ‘hay-like’ notes whereas *trans* form with ‘celery-like’ notes) and threshold associated with each isomer (Jelén and Gracka 2017).

Another study highlighted that not only the type of wood but also the length of time and temperature of toasting are two important factors affecting the isomeric ratio of whiskey lactone (Bosso et al. 2008). A Montepulciano d’Abruzzo D.O.C. Italian red wine was aged for 6 and 12 months in mixed French oak barrels of different wood grain (extra fine and fine, respectively <1.5 mm and 1.5-2.5 mm) and toasting (medium, light, short-time medium, and short-time pre-toasting at high temperature). For the same oak wood, differences were also reported in the concentration and ratio of *cis* and *trans* isomers of β-methyl-γ-octalactone in wines (**Table 1**). In fact, the highest concentration of *cis*-β-methyl-γ-octalactone was found when a short-time medium toasting was used in the production of the barrels, whereas the higher *cis*-/*trans*-β-methyl-γ-octalactone ratio corresponded to light toasting conditions. Taking into account the different olfactory threshold of the two diastereoisomers, the greater presence of *cis*-β-methyl-γ-octalactone was related to prevalence of ‘coconut’ notes.

In Bordeaux dessert white wines from 1966 to 2010 vintage, mostly from Sauternes region, the impact of chiral lactones on the wine sensory perception was investigated by multidimensional chiral GC-MS (Stamatopoulos et al. 2016). Two lactones associated with noble rot (2-nonen-4-olide and  $\gamma$ -nonalactone) and another related to ageing in contact with oak wood ( $\beta$ -methyl- $\gamma$ -octalactone or whiskey lactone) were determined. Regarding the first compound (2.3–13.2  $\mu\text{g/L}$ ), two enantiomer configurations are possible: the (*R*) form has an olfactory threshold of 1.9  $\mu\text{g/L}$  and ripe coconut nuances while the *S* isomer has an olfactory threshold of 6.3  $\mu\text{g/L}$  and a characteristic note of fresh citrus. During wine ageing, the dynamics of these two isomers were opposite: a longer ageing corresponded to a greater *R* isomer increase and a greater *S* isomer decrease. For  $\gamma$ -nonalactone (7.7–34.2  $\mu\text{g/L}$ ), the *R* configuration prevailed and no influence of the ageing factor was detected. Similarly, the evolution of the isomers of  $\beta$ -methyl- $\gamma$ -octalactone (2.4–1566  $\mu\text{g/L}$ ) was not significant with prevalence of the *cis* form (**Table 3**).

Recently, megastigmatrienone was also detected in 65 white and red wines, aged in oak barrels, at concentrations ranging from 2 to 41  $\mu\text{g/L}$ , where longer wine ageing led to a higher concentration (Slaghenaufi et al. 2014) (**Tables 1 and 2**). Five megastigmatrienone isomers were quantified, 4 diastereoisomers from two conjugated double bonds (megastigma-4,6*Z*,8*Z*-trien-3-one, megastigma-4,6*Z*,8*E*-trien-3-one, megastigma-4,6*E*,8*Z*-trien-3-one, megastigma-4,6*E*,8*E*-trien-3-one) and one position isomer (megastigma-4,7*E*,9-trien-3-one). Megastigmatrienone is characterized by ‘tobacco’ and ‘incense’ nuance, even though all five isomers have different sensory impact. Thus, the first two diastereoisomers and the position isomer are characterized by sweet scents attributable to ‘wood’, ‘tobacco’, and ‘honey’ while the remaining two give ‘burnt wood’ notes.

### **Wine matrix effect on VOC isomers**

Regarding the wine quality, one of the most important aspects of different isomer forms of volatile compounds is the significant sensory impact, particularly for monoterpenes as they are mainly linked to the sensory identity of some varietal wines of international relevance (Muscat and Malvasia variety groups, Riesling, Traminer, and Gewürztraminer varieties). However, knowledge on the impact of individual monoterpene isomers on the wine olfactory perception is very scarce, and even less on the possible interaction among them and with the non-volatile matrix. Nevertheless, those interactions affecting odorant molecules volatility or solubility in the wine could modify the olfactory perception. In a very interesting study, Tomasino, Song, and Fuentes

(2020) evaluated these physico-chemical interactions in 46 Pinot gris wines from Italy, Australia, New Zealand, and USA, in order to understand the possible effects among the various monoterpene isomers, as well as the matrix effect of non-volatile components. Instrumental HS-SPME coupled to multidimensional GC-MS and sensory olfactory analysis evidenced that synergistic or antagonistic phenomena between volatile compounds are possible. In fact, wines with linalool concentrations above the olfactory threshold did not show characteristic notes for this particular olfactory compound probably because limonene modified its olfactory threshold through a masking effect. Monoterpene isomers, such as linalool, linalool oxide, (–)-rose oxide, and (*R*)/(*S*)-limonene, play a reciprocal suppression role on odor perception while the non-volatile matrix strongly impacts the partitioning coefficient enhancing monoterpene isomers volatility with aroma exaltation. Therefore, although most monoterpene isomers are present in wines at concentrations below the olfactory thresholds, they could contribute significantly to wine aroma. This study highlighted that the interaction of the different isomers of the same volatile compound with the wine matrix strongly influences its sensory perception.

Furthermore, other studies have highlighted that some compounds can contribute to wine fruity aroma through a synergistic effect (Lytra et al. 2012). For this reason, ethyl 2-hydroxy-4-methylpentanoate isomers do not contribute directly to wine aroma but enhance the fruit perception ('black-berry' and 'fresh fruit' notes) in red wine.

### **Potential of VOC isomers for prevention of wine fraud**

The enantiomeric determination of terpenoids could play a key role in the identification of possible adulterations related to the addition of fragrances to enhance the wine natural aroma, especially in the case of aromatically-neutral wines. Commercially produced limonene, linalool, and  $\alpha$ -terpineol are isolated from citrus and citrus by-products, which are different to those present in grapes. Citrus-derived extracts are prevalent in (*R*)-limonene (99% dominancy), (*S*)-linalool (82–98%), and (*S*)- $\alpha$ -terpineol (84–95%) (Marsol-Vall et al. 2017) whereas (*R*)-limonene, (*S*)-hotrienol (93–97%), and (*S*)- $\alpha$ -terpineol isomers are dominant in grapes (Furdíková et al. 2021; Luan et al. 2006), even though the enantiomer ratio is grape variety-dependent. More research is needed in this field but the mentioned studies are promising. VOC isomer determination seems to have a great potential for the detection of possible aroma adulterations in the wine.

## Conclusions

The volatile component plays a key role in the wine quality and therefore it is subject to fraud attempts such as the addition of aromas or the false declaration of varieties or geographic origin, particularly detrimental for high standard quality wines. Recent scientific research is being addressed on the determination of isomer forms for volatile compounds and their isomeric relationships, particularly for chiral terpenes naturally occurring in grapes, to provide important information aimed at achieving more reliable wine characterization and differentiation according to variety and geographical origin. This review highlighted the current knowledge in this field, providing an overview of VOC isomer data gathered from scientific literature. Wine authenticity could be especially interesting for those varieties in which the aromatic fingerprint is strong and characteristic. For this, it is necessary to know the isomeric ratio of the target compounds in winegrapes and its consistency through handling or the technological process. Moreover, winemaking and subsequent wine ageing can play a key role in the prevalence of a certain isomer and in the isomeric ratios, which in turn affect the sensory characteristics. Minimal differences at molecular isomerism and optical activity level may affect the sensory perception of wines as a consequence of the different olfactory thresholds of the isomer forms of the same volatile compound. Nowadays, limited information on the isomer composition of volatile compounds in wines is available, and more research will be performed in next years in this field due to its great potential also in wine industry to manage the technological process according to established oenological objectives.

## Disclosure statement

The authors declare that they have not any financial interests or conflict of interest, which would affect this review.

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**Figure caption**

**Figure 1.** Schematic diagram of factors affecting VOC isomers during wine production and potentialities in wine industry.



**Table 1.** Concentration ( $\mu\text{g/L}$ ) of key VOC isomers in red wines.

Reference and grape variety	Origin	Samples	Chemical class	Compound	Isomer	Concentration <sup>c</sup>
<b>Amaral</b>						
Oliveira et al. 2004 <sup>a</sup>	Portugal (Amarante)	NA	Terpenes	Furan linalool oxide	<i>trans</i>	NA (0.4)
					<i>cis</i>	NA (0.8)
				Pyran linalool oxide	<i>trans</i>	NA (0.3)
					<i>cis</i>	NA (0.6)
				8-Hydroxy-linalool	<i>trans</i>	NA (0.2)
<i>cis</i>	NA (5.1)					
<b>Cabernet sauvignon</b>						
Capone et al. 2011 <sup>b</sup>	Australia	45	Terpene	Cineole	1,8-Cineole	$\leq 19.6$
Picard et al. 2016a <sup>b,*</sup>	France (Bordeaux)	51	Monoterpene ketone	Piperitone	(6 <i>S</i> )-(+)	0.08
					(6 <i>R</i> )-(-)	0.34
Bouchilloux et al. 2000 <sup>b</sup>	France (Bordeaux)	6	Thiol	3-Mercapto-2-methylpropanol	( <i>R</i> )-(-)	1.3-68.0
Slaghenaufi et al. 2021a <sup>a</sup>	Italy (San Pietro in Cariano)	1	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	54.30
					<i>cis</i>	22.90
			2-Hexenol	<i>cis</i>	12.63	
				<i>trans</i>	1.82	
			Terpene	Linalool oxide	<i>cis</i>	1.30
<i>trans</i>	1.80					
Antalick et al. 2015 <sup>b,†</sup>	Australia (Coonawarra, Margaret River, Barossa, McLaren Vale, South Australia, Victoria, New South Wales)	51	Terpene	Cineole	1,4-Cineole	0.59
					1,8-Cineole	2.82
<b>Cabernet sauvignon/Merlot/Cabernet franc blend</b>						
Picard, De Revel, and Marchand 2017 <sup>b,*</sup>	France (Bordeaux)	1	<i>p</i> -Menthane lactones	Mintlactone	(-)-Mintlactone	0.9
					(+)-Isomintlactone	0.1
<b>Corvina</b>						
Slaghenaufi et al. 2021a <sup>a,†</sup>	Italy (San Pietro in Cariano)	3	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	18.41-18.99
					<i>cis</i>	197.02-215.00
			2-Hexenol	<i>cis</i>	5.01-7.41	
				<i>trans</i>	< LOQ	
			Terpene	Linalool oxide	<i>cis</i>	1.34-1.47
<i>trans</i>	0.42-0.70					
<b>Corvinone</b>						
Slaghenaufi et al. 2021a <sup>a,†</sup>	Italy (San Pietro in Cariano)	4	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	52.05-67.11
					<i>cis</i>	13.32-34.54
			2-Hexenol	<i>cis</i>	9.48-11.58	
				<i>trans</i>	1.47-1.71	
			Terpene	Linalool oxide	<i>cis</i>	0.10-1.31
<i>trans</i>	0.01-0.13					
<b>Coratina</b>						
Slaghenaufi et al. 2021a <sup>a</sup>	Italy (San Pietro in Cariano)	1	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	69.70
					<i>cis</i>	15.90
			2-Hexenol	<i>cis</i>	12.99	
				<i>trans</i>	< LOQ	
			Terpene	Linalool oxide	<i>cis</i>	1.60
<i>trans</i>	0.00					
<b>Durif</b>						
Capone et al. 2011 <sup>b</sup>	Australia	6	Terpene	Cineole	1,8-Cineole	$\leq 19.6$
<b>Fetească neagră</b>						
Dumitriu et al. 2019 <sup>a,†</sup>	Romania (Șuletea Vaslui)	NA	Lactone	Whiskey lactone	<i>trans</i>	54-155 (American oak)
						91-178 (French oak)
					<i>cis</i>	190-618 (American oak)
						93-172 (French oak)

<b>Merlot</b>						
Pons et al. 2016 <sup>b,‡</sup>	France (Bordeaux)	2	Monoterpene ketone	Piperitone	(-)-4R	0.1-0.2
Capone et al. 2011 <sup>b</sup>	Australia	25	Terpene	Cineole	(+)-4S	0.01-0.02
<b>Merlot/Cabernet sauvignon blend</b>						
Capone et al. 2011 <sup>b</sup>	Australia	10	Terpene	Cineole	1,8-Cineole	≤ 19.6
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Bordeaux)	31	C <sub>13</sub> -Norisoprenoid	Megastigmatrienone	(6Z,8E)	0.4-7.2
					(7E)	< LOQ/LOD
					(6Z,8Z)	1.0-18.2
					(6E,8E)	0.2-4.2
					(6E,8Z)	0.6-11.5
<b>Molinara</b>						
Slaghenaufi et al. 2021a <sup>a</sup>	Italy (San Pietro in Cariano)	1	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	26.40
					<i>cis</i>	3.40
			Terpene	Linalool oxide	<i>cis</i>	9.40
					<i>trans</i>	< LOQ
					<i>cis</i>	1.40
			<i>trans</i>	0.80		
<b>Monastrell</b>						
Pérez-Prieto et al. 2002 <sup>a</sup>	Spain (Murcia)	NA	Lactone	Whiskey lactone	<i>trans</i>	12.2 (American)-20.6 (French oak)
					<i>cis</i>	54.2 (French)-203.2 (American oak)
<b>Montepulciano d'Abruzzo</b>						
Bosso et al. 2008a, <sup>†</sup>	Italy (Pescara)	NA	Lactone	Whiskey lactone	<i>trans</i>	4-122
					<i>cis</i>	2-185
<b>Oseleta</b>						
Slaghenaufi et al. 2021a <sup>a</sup>	Italy (San Pietro in Cariano)	1	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	108.40
					<i>cis</i>	21.60
			Terpene	Linalool oxide	<i>cis</i>	20.30
					<i>trans</i>	< LOQ
					<i>cis</i>	3.50
			<i>trans</i>	1.40		
<b>Pinot noir</b>						
Capone et al. 2011 <sup>b</sup>	Australia	17	Terpene	Cineole	1,8-Cineole	≤ 19.6
Antalick et al. 2015 <sup>b,†</sup>	Australia (Victoria, Orange, South Australia, Tasmania)	22	Terpene	Cineole	1,4-Cineole	0.22
					1,8-Cineole	0.99
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Burgundy)	2	C <sub>13</sub> -Norisoprenoid	Megastigmatrienone	(6Z,8E)	0.4-0.7
					(7E)	< LOQ/LOD
					(6Z,8Z)	< LOQ-1.4
					(6E,8E)	0.2
					(6E,8Z)	0.6-0.9
<b>Raboso</b>						
Slaghenaufi et al. 2021a <sup>a</sup>	Italy (San Pietro in Cariano)	1	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	27.40
					<i>cis</i>	59.90
			Terpene	Linalool oxide	<i>cis</i>	7.43
					<i>trans</i>	< LOQ
					<i>cis</i>	3.00
			<i>trans</i>	0.10		
<b>Rondinella</b>						
Slaghenaufi et al. 2021a <sup>a</sup>	Italy (San Pietro in Cariano)	1	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	13.20
					<i>cis</i>	146.60
			Terpene	Linalool oxide	<i>cis</i>	7.80
					<i>trans</i>	< LOQ
					<i>cis</i>	1.60
			<i>trans</i>	0.10		
<b>Sangiovese</b>						
Slaghenaufi et al. 2021a <sup>a</sup>	Italy (San Pietro in Cariano)	1	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	75.60
					<i>cis</i>	33.70
			Terpene	Linalool oxide	<i>cis</i>	10.42
					<i>trans</i>	2.97
					<i>cis</i>	2.50
			<i>trans</i>	0.00		

<b>Syrah</b>						
Antalick et al. 2015 <sup>b,†</sup>	Australia (Barossa, McLaren Vale, Coonwarra, Margaret River, South Australia, Victoria, New South Wales)	27	Terpene	Cineole	1,4-Cineole	0.07
					1,8-Cineole	1.75
Capone et al. 2011 <sup>b</sup>	Australia	43	Terpene	Cineole	1,8-Cineole	≤ 19.6
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Rhône)	2	C <sub>13</sub> -Norisoprenoid	Megastigmatrienone	(6Z,8E)	0.4-0.6
					(7E)	< LOD
					(6Z,8Z)	1.3
					(6E,8E)	0.3
					(6E,8Z)	0.9
<b>Tannat</b>						
Boido et al. 2003 <sup>a</sup>	Uruguay	10	C <sub>6</sub> -Alcohols	3-Hexenol	<i>trans</i>	24 (6.7)
					<i>cis</i>	49 (45.6)
				2-Hexenol	<i>trans</i>	76 (28.3)
<b>Vinhão</b>						
Oliveira et al. 2004 <sup>a</sup>	Portugal (Lima)	NA	Terpenes	Furan linalool oxide	<i>trans</i>	NA (0.5)
					<i>cis</i>	NA (2.2)
				Pyran linalool oxide	<i>trans</i>	0.3 (0.5)
					<i>cis</i>	NA (1.2)
				8-Hydroxy-linalool	<i>trans</i>	NA (1.0)
					<i>cis</i>	NA (4.6)
<b>NAs</b>						
Picard et al. 2016 <sup>b,‡</sup>	France (Bordeaux)	15	Monoterpene ketone	Piperitone	D,L	0.17-1.1
Lytra et al. 2012 <sup>b,†</sup>	France	42	Fatty acid esters	Ethyl 2-hydroxy-4-methylpentanoate	(R)	135.0-431.0
					(S)	0.0-32.0
Slaghenaufi et al. 2014 <sup>b,‡</sup>	Australia; France (Chinon, Rhône)	3	C <sub>13</sub> -Norisoprenoid	Megastigmatrienone	(6Z,8E)	0.7-2.3
					(7E)	< LOQ/LOD
					(6Z,8Z)	2.0-5.6
					(6E,8E)	0.5-1.3
					(6E,8Z)	1.3-3.6

<sup>a</sup> Samples were obtained after fermentation.

<sup>b</sup> Commercial wines.

<sup>c</sup> Values in round brackets represent the concentration of aglycons found in the glycosidically-bound fraction.

<sup>†</sup> The concentrations are presented as the mean values of respective samples.

<sup>‡</sup> Where possible, the concentrations were reported as minimum and maximum values of samples considered in the study.

\* The (range) concentrations reported are tentatively expressed, based on the isomer ratio calculation.

NA(s), information not available.

< LOQ/LOD, values were detected below the limit of quantitation/detection.

**Table 2.** Concentration ( $\mu\text{g/L}$ ) of key VOC isomers in white wines.

Reference and grape variety	Origin	Samples	Chemical class	Compound	Isomer	Concentration <sup>c</sup>
<b>Alvarinho</b>						
Oliveira et al. 2004 <sup>a</sup>	Portugal (Monção)	NA	Terpenes	Furan linalool oxide	<i>trans</i>	0.2 (21.5)
					<i>cis</i>	NA (7.2)
				Pyran linalool oxide	<i>trans</i>	6 (14.8)
					<i>cis</i>	0.4 (3.5)
8-Hydroxy-linalool	<i>trans</i>	NA (32.8)				
	<i>cis</i>	0.6 (183.3)				
<b>Avesso</b>						
Oliveira et al. 2004 <sup>a</sup>	Portugal (Baião)	NA	Terpenes	Furan linalool oxide	<i>trans</i>	NA (0.8)
					<i>cis</i>	NA (3.2)
				Pyran linalool oxide	<i>trans</i>	NA (1.2)
					<i>cis</i>	NA (1.1)
8-Hydroxy-linalool	<i>trans</i>	NA (6.1)				
	<i>cis</i>	NA (10.8)				
<b>Chardonnay</b>						
Song et al. 2018 <sup>b,†</sup>	Australia USA (Oregon, California)	21	Terpenes	Limonene	<i>S</i> -(-)	0.03
					<i>R</i> -(+)	0.04
				Rose oxide	(2 <i>R</i> , 4 <i>S</i> )-(+)- <i>cis</i>	0.02
					(2 <i>S</i> , 4 <i>R</i> )-(-)- <i>cis</i>	0.06
					(2 <i>R</i> , 4 <i>R</i> )-(-)- <i>trans</i>	0.00
					(2 <i>S</i> , 4 <i>S</i> )-(+)- <i>trans</i>	0.00
				Linalool oxide	(2 <i>R</i> ,5 <i>R</i> )-(+)- <i>trans</i>	8.53
					(2 <i>R</i> ,5 <i>S</i> )-(-)- <i>cis</i>	6.98
					(2 <i>S</i> ,5 <i>S</i> )-(-)- <i>trans</i>	3.14
					(2 <i>S</i> ,5 <i>R</i> )-(+)- <i>cis</i>	3.48
Nerol oxide	<i>S</i> -(-)	0.07				
	<i>R</i> -(+)	0.00				
Linalool	<i>R</i> -(-)	0.77				
	<i>S</i> -(+)	0.68				
$\alpha$ -Terpineol	<i>S</i> -(-)	1.80				
	<i>R</i> -(+)	0.45				
$\beta$ -citronellol	<i>R</i> -(+)	1.67				
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Burgundy) USA (Napa Valley)	8	$\text{C}_{13}$ -Norisoprenoid	Megastigmatrienone	(6 <i>Z</i> ,8 <i>E</i> )	0.2-1.3
					(7 <i>E</i> )	0.4-0.5
					(6 <i>Z</i> ,8 <i>Z</i> )	0.5-5.9
					(6 <i>E</i> ,8 <i>E</i> )	0.1-0.7
					(6 <i>E</i> ,8 <i>Z</i> )	0.3-2.8
Capone et al. 2011 <sup>b</sup>	Australia	12	Terpenes	Cineole	1,8-Cineole	$\leq 0.8$
<b>Chenin blanc</b>						
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Loire)	1	$\text{C}_{13}$ -Norisoprenoid	Megastigmatrienone	(6 <i>Z</i> ,8 <i>E</i> )	0.2
					(7 <i>E</i> )	< LOQ
					(6 <i>Z</i> ,8 <i>Z</i> )	< LOQ
					(6 <i>E</i> ,8 <i>E</i> )	< LOD
					(6 <i>E</i> ,8 <i>Z</i> )	< LOQ
<b>Gewürztraminer</b>						
Song et al. 2018 <sup>b,†</sup>	France USA (Oregon, New York, California)	21	Terpenes	Limonene	<i>S</i> -(-)	3.17
					<i>R</i> -(+)	1.69
				Rose oxide	(2 <i>R</i> , 4 <i>S</i> )-(+)- <i>cis</i>	0.20
					(2 <i>S</i> , 4 <i>R</i> )-(-)- <i>cis</i>	0.70
					(2 <i>R</i> , 4 <i>R</i> )-(-)- <i>trans</i>	0.25
					(2 <i>S</i> , 4 <i>S</i> )-(+)- <i>trans</i>	0.05
				Linalool oxide	(2 <i>R</i> ,5 <i>R</i> )-(+)- <i>trans</i>	9.70
					(2 <i>R</i> ,5 <i>S</i> )-(-)- <i>cis</i>	20.79
					(2 <i>S</i> ,5 <i>S</i> )-(-)- <i>trans</i>	7.93
					(2 <i>S</i> ,5 <i>R</i> )-(+)- <i>cis</i>	5.86
Nerol oxide	<i>S</i> -(-)	1.83				
	<i>R</i> -(+)	2.53				
Linalool	<i>R</i> -(-)	57.49				
	<i>S</i> -(+)	55.27				
$\alpha$ -Terpineol	<i>S</i> -(-)	56.35				
	<i>R</i> -(+)	58.89				
$\beta$ -citronellol	<i>R</i> -(+)	17.55				

Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	6	Terpenes	Rose oxide	(+)- <i>cis</i>	1.0-3.5
					(-)- <i>cis</i>	1.8-9.1
Guth et al. 1997 <sup>b</sup>	Germany	1	Terpenes	Rose oxide	(-)-(2 <i>S</i> ,4 <i>R</i> )- <i>cis</i>	7.0
					(+)-(2 <i>R</i> ,4 <i>S</i> )- <i>cis</i>	3.0
<b>Gwäss</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	1	Terpenes	Rose oxide	(+)- <i>cis</i>	0.1
					(-)- <i>cis</i>	0.1
<b>Himbertscha</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	1	Terpenes	Rose oxide	(+)- <i>cis</i>	0.3
					(-)- <i>cis</i>	0.4
<b>Humagne Blanc</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	1	Terpenes	Rose oxide	(+)- <i>cis</i>	0.1
					(-)- <i>cis</i>	0.2
<b>Lafnetscha</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	1	Terpenes	Rose oxide	(+)- <i>cis</i>	0.2
					(-)- <i>cis</i>	0.1
<b>Loureiro</b>						
Oliveira et al. 2004 <sup>a</sup>	Portugal (Lima)	NA	Terpenes	Furan linalool oxide	<i>trans</i>	4.6 (39.1)
					<i>cis</i>	3.2 (4.0)
				Pyran linalool oxide	<i>trans</i>	44.8 (11.6)
					<i>cis</i>	8.4 (1.9)
				8-Hydroxy-linalool	<i>trans</i>	NA (31.0)
					<i>cis</i>	NA (36.1)
<b>Moscato giallo</b>						
Carrau et al. 2005 <sup>a</sup>	Uruguay	NA	Terpenes	Furan linalool oxide	<i>trans</i>	< 0.5
					<i>cis</i>	
				Pyran linalool oxide	<i>trans</i>	< 0.5
					<i>cis</i>	
<b>Muscat<sup>#</sup></b>						
Song et al. 2018 <sup>b,†</sup>	France; USA (California); Italy	17	Terpenes	Limonene	<i>S</i> -(-)	11.96
					<i>R</i> -(+)	6.78
				Rose oxide	(2 <i>R</i> , 4 <i>S</i> )-(+)- <i>cis</i>	0.34
					(2 <i>S</i> , 4 <i>R</i> )-(-)- <i>cis</i>	0.50
					(2 <i>R</i> , 4 <i>R</i> )-(-)- <i>trans</i>	0.20
					(2 <i>S</i> , 4 <i>S</i> )-(+)- <i>trans</i>	0.11
				Linalool oxide	(2 <i>R</i> ,5 <i>R</i> )-(+)- <i>trans</i>	120.55
					(2 <i>R</i> ,5 <i>S</i> )-(-)- <i>cis</i>	136.21
					(2 <i>S</i> ,5 <i>S</i> )-(-)- <i>trans</i>	47.32
					(2 <i>S</i> ,5 <i>R</i> )-(+)- <i>cis</i>	67.42
				Nerol oxide	<i>S</i> -(-)	14.41
					<i>R</i> -(+)	19.30
Linalool	<i>R</i> -(-)	127.63				
	<i>S</i> -(+)	108.24				
$\alpha$ -Terpineol	<i>S</i> -(-)	276.36				
	<i>R</i> -(+)	252.72				
$\beta$ -citronellol	<i>R</i> -(+)	14.98				
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	8	Terpenes	Rose oxide	(+)- <i>cis</i>	0.3-4.6
					(-)- <i>cis</i>	0.4-5.4
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Alsace)	2	C <sub>13</sub> -Norisoprenoid	Megastigmatrienone	(6 <i>Z</i> ,8 <i>E</i> )-	0.2-0.3
					(7 <i>E</i> )-	< LOD
					(6 <i>Z</i> ,8 <i>Z</i> )-	0.9
					(6 <i>E</i> ,8 <i>E</i> )-	0.1
					(6 <i>E</i> ,8 <i>Z</i> )-	0.5
<b>Païen</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	1	Terpenes	Rose oxide	(+)- <i>cis</i>	0.28
					(-)- <i>cis</i>	0.32
<b>Petite Arvine</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	1	Terpenes	Rose oxide	(+)- <i>cis</i>	0.2
					(-)- <i>cis</i>	0.2
<b>Pinot gris</b>						
Song et al. 2018 <sup>b,†</sup>	USA (Oregon); France; Italy	21	Terpenes	Limonene	<i>S</i> -(-)	0.03
					<i>R</i> -(+)	0.04
				Rose oxide	(2 <i>R</i> , 4 <i>S</i> )-(+)- <i>cis</i>	0.04
					(2 <i>S</i> , 4 <i>R</i> )-(-)- <i>cis</i>	0.09
					(2 <i>R</i> , 4 <i>R</i> )-(-)- <i>trans</i>	0.01
					(2 <i>S</i> , 4 <i>S</i> )-(+)- <i>trans</i>	0.00

				Linalool oxide	(2 <i>R</i> ,5 <i>R</i> )-(+)- <i>trans</i>	7.11
					(2 <i>R</i> ,5 <i>S</i> )-(-)- <i>cis</i>	11.77
					(2 <i>S</i> ,5 <i>S</i> )-(-)- <i>trans</i>	4.48
					(2 <i>S</i> ,5 <i>R</i> )-(+)- <i>cis</i>	4.53
			Nerol oxide		<i>S</i> -(-)	0.80
						<i>R</i> -(+)
			Linalool		<i>R</i> -(-)	0.14
						<i>S</i> -(+)
			$\alpha$ -Terpineol	<i>S</i> -(-)	5.63	
					<i>R</i> -(+)	2.87
			$\beta$ -citronellol	<i>R</i> -(+)	1.21	
Tomasino, Song, and Fuentes 2020 <sup>b,†</sup>	Australia; Italy; New Zealand; USA (New York, Oregon, Washington)	46	Terpenes	Linalool oxide*	(2 <i>R</i> ,5 <i>R</i> )-(+)- <i>trans</i>	6.6
					(2 <i>R</i> ,5 <i>S</i> )-(-)- <i>cis</i>	9.7
					(2 <i>S</i> ,5 <i>S</i> )-(-)- <i>trans</i>	0.6
					(2 <i>S</i> ,5 <i>R</i> )-(+)- <i>cis</i>	4.7
				$\alpha$ -Terpineol*	<i>R</i> -(+)	8.4
					<i>S</i> -(-)	6.2
				$\beta$ -Citronellol*	<i>R</i> -(+)	5.1
				Rose oxide*	(2 <i>S</i> ,4 <i>R</i> )-(-)- <i>cis</i>	0.1
Limonene*	<i>R</i> -(+)	0.3				
	<i>S</i> -(-)	0.4				
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Alsace)	1	<sup>C</sup> <sub>13</sub> -Norisoprenoid	Megastigmatrienone	(6 <i>Z</i> ,8 <i>E</i> )	0.2
					(7 <i>E</i> )	< LOD
					(6 <i>Z</i> ,8 <i>Z</i> )	< LOQ
					(6 <i>E</i> ,8 <i>E</i> )	0.1
					(6 <i>E</i> ,8 <i>Z</i> )	< LOQ
<b>Plantscher</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	1	Terpenes	Rose oxide	(+)- <i>cis</i>	0.1
					(-)- <i>cis</i>	0.1
<b>Riesling</b>						
Song et al. 2018 <sup>b,†</sup>	USA (Oregon); France; Germany; Australia	19	Terpenes	Limonene	<i>S</i> -(-)	0.87
					<i>R</i> -(+)	0.32
				Rose oxide	(2 <i>R</i> , 4 <i>S</i> )-(+)- <i>cis</i>	0.07
					(2 <i>S</i> , 4 <i>R</i> )-(-)- <i>cis</i>	0.07
					(2 <i>R</i> , 4 <i>R</i> )-(-)- <i>trans</i>	0.04
					(2 <i>S</i> , 4 <i>S</i> )-(+)- <i>trans</i>	0.02
				Linalool oxide	(2 <i>R</i> ,5 <i>R</i> )-(+)- <i>trans</i>	32.22
					(2 <i>R</i> ,5 <i>S</i> )-(-)- <i>cis</i>	19.78
					(2 <i>S</i> ,5 <i>S</i> )-(-)- <i>trans</i>	7.78
					(2 <i>S</i> ,5 <i>R</i> )-(+)- <i>cis</i>	14.75
				Nerol oxide	<i>S</i> -(-)	12.27
					<i>R</i> -(+)	16.76
Linalool	<i>R</i> -(-)	2.96				
	<i>S</i> -(+)	2.90				
$\alpha$ -Terpineol	<i>S</i> -(-)	30.31				
	<i>R</i> -(+)	26.19				
$\beta$ -citronellol	<i>R</i> -(+)	0.44				
Capone et al. 2011 <sup>b</sup>	Australia	12	Terpene	Cineole	1,8-Cineole	≤ 0.8
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Alsace)	2	<sup>C</sup> <sub>13</sub> -Norisoprenoid	Megastigmatrienone	(6 <i>Z</i> ,8 <i>E</i> )-	0.3-0.5
					(7 <i>E</i> )-	< LOD
					(6 <i>Z</i> ,8 <i>Z</i> )-	0.6-1.2
					(6 <i>E</i> ,8 <i>E</i> )-	0.2-0.3
					(6 <i>E</i> ,8 <i>Z</i> )-	0.4-0.7
<b>Sauvignon blanc</b>						
Song et al. 2018 <sup>b,†</sup>	New Zealand; South Africa; France	19	Terpenes	Limonene	<i>S</i> -(-)	0.08
					<i>R</i> -(+)	0.05
				Rose oxide	(2 <i>R</i> , 4 <i>S</i> )-(+)- <i>cis</i>	0.04
					(2 <i>S</i> , 4 <i>R</i> )-(-)- <i>cis</i>	0.07
					(2 <i>R</i> , 4 <i>R</i> )-(-)- <i>trans</i>	0.02
					(2 <i>S</i> , 4 <i>S</i> )-(+)- <i>trans</i>	0.01
				Linalool oxide	(2 <i>R</i> ,5 <i>R</i> )-(+)- <i>trans</i>	23.63
					(2 <i>R</i> ,5 <i>S</i> )-(-)- <i>cis</i>	8.82
					(2 <i>S</i> ,5 <i>S</i> )-(-)- <i>trans</i>	2.02
					(2 <i>S</i> ,5 <i>R</i> )-(+)- <i>cis</i>	8.86
Nerol oxide	<i>S</i> -(-)	6.33				
	<i>R</i> -(+)	6.86				

				Linalool	<i>R</i> -(-)	0.54
					<i>S</i> -(+)	0.49
				$\alpha$ -Terpineol	<i>S</i> -(-)	10.13
					<i>R</i> -(+)	3.28
				$\beta$ -citronellol	<i>R</i> -(+)	0.70
Capone et al. 2011 <sup>b</sup>	Australia	10	Terpene	Cineole	1,8-Cineole	$\leq 0.8$
Bouchilloux et al. 2000 <sup>b</sup>	France (Bordeaux)	1	Thiol	3-Mercapto-2-methylpropanol	( <i>R</i> )	1.2-1.7
Slaghenaufi et al. 2014 <sup>b,†</sup>	France (Sancerre, Bordeaux); South Africa	8	$C_{13}$ -Norisoprenoid	Megastigmatrienone	( <i>6Z,8E</i> )	0.2-0.6
					( <i>7E</i> )	< <i>LOD/LOQ</i>
					( <i>6Z,8Z</i> )	0.5-1.4
					( <i>6E,8E</i> )	0.1-0.3
					( <i>6E,8Z</i> )	0.3-0.7
Tominaga et al. 2006 <sup>a</sup>	France (Bordeaux)	2	Thiols	3-Mercaptohexan-1-ol	( <i>R</i> )	0.7
					( <i>S</i> )	0.7
				3-mercaptohexyl acetate	( <i>R</i> )	0.2
					( <i>S</i> )	0.5
<b>Scheurebe</b>						
Guth et al. 1997 <sup>b</sup>	Germany	1	Terpenes	Rose oxide	(-)-(2 <i>S,4R</i> )- <i>cis</i>	< 1.0
					(+)-(2 <i>R,4S</i> )- <i>cis</i>	< 1.0
<b>Semillon</b>						
Capone et al. 2011 <sup>b</sup>	Australia	10	Terpene	Cineole	1,8-Cineole	$\leq 0.8$
Tominaga et al. 2006 <sup>a</sup>	France (Bordeaux)	2	Thiols	3-Mercaptohexan-1-ol	( <i>R</i> )	0.1
					( <i>S</i> )	0.1
				3-Mercaptohexyl acetate	( <i>R</i> )	0.0
					( <i>S</i> )	0.1
<b>Silvaner</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	3	Terpenes	Rose oxide	(+)- <i>cis</i>	1.2-2.4
					(-)- <i>cis</i>	0.8-1.6
<b>Torrontes</b>						
Song et al. 2018 <sup>b,†</sup>	Argentina	10	Terpenes	Limonene	<i>S</i> -(-)	9.70
					<i>R</i> -(+)	5.39
				Rose oxide	(2 <i>R,4S</i> )-(+)- <i>cis</i>	0.80
					(2 <i>S,4R</i> )-(-)- <i>cis</i>	0.85
					(2 <i>R,4R</i> )-(-)- <i>trans</i>	1.57
					(2 <i>S,4S</i> )-(+)- <i>trans</i>	0.74
				Linalool oxide	(2 <i>R,5R</i> )-(+)- <i>trans</i>	188.60
					(2 <i>R,5S</i> )-(-)- <i>cis</i>	139.63
					(2 <i>S,5S</i> )-(-)- <i>trans</i>	63.78
					(2 <i>S,5R</i> )-(+)- <i>cis</i>	82.39
				Nerol oxide	<i>S</i> -(-)	53.35
					<i>R</i> -(+)	77.12
				Linalool	<i>R</i> -(-)	63.35
<i>S</i> -(+)	48.26					
$\alpha$ -Terpineol	<i>S</i> -(-)	264.04				
	<i>R</i> -(+)	248.49				
$\beta$ -citronellol	<i>R</i> -(+)	12.51				
<b>Traminer</b>						
Koslitz et al. 2008 <sup>b,*</sup>	Switzerland	1	Terpenes	Rose oxide	(+)- <i>cis</i>	0.5
					(-)- <i>cis</i>	1.5
<b>Viognier</b>						
Song et al. 2018 <sup>b,†</sup>	France; USA (Oregon, California)	20	Terpenes	Limonene	<i>S</i> -(-)	1.53
					<i>R</i> -(+)	0.74
				Rose oxide	(2 <i>R,4S</i> )-(+)- <i>cis</i>	0.06
					(2 <i>S,4R</i> )-(-)- <i>cis</i>	0.06
					(2 <i>R,4R</i> )-(-)- <i>trans</i>	0.00
					(2 <i>S,4S</i> )-(+)- <i>trans</i>	0.00
				Linalool oxide	(2 <i>R,5R</i> )-(+)- <i>trans</i>	7.51
					(2 <i>R,5S</i> )-(-)- <i>cis</i>	19.32
					(2 <i>S,5S</i> )-(-)- <i>trans</i>	9.13
					(2 <i>S,5R</i> )-(+)- <i>cis</i>	9.80
				Nerol oxide	<i>S</i> -(-)	0.33
					<i>R</i> -(+)	0.43
				Linalool	<i>R</i> -(-)	29.85
<i>S</i> -(+)	24.90					
$\alpha$ -Terpineol	<i>S</i> -(-)	49.02				

					<i>R</i> -(+)	45.36
				$\beta$ -citronellol	<i>R</i> -(+)	2.70
Slaghenaufi et al. 2014 <sup>b,‡</sup>	France (Rhône)	1	<sup>C</sup> <sub>13</sub> - Norisoprenoid	Megastigmatrienone	(6 <i>Z</i> ,8 <i>E</i> )	< <i>LOQ</i>
					(7 <i>E</i> )	< <i>LOD</i>
					(6 <i>Z</i> ,8 <i>Z</i> )	< <i>LOQ</i>
					(6 <i>E</i> ,8 <i>E</i> )	0.1
					(6 <i>E</i> ,8 <i>Z</i> )	0.4
<i>NA</i>						
Lytra et al. 2012 <sup>b,†</sup>	France	13	Fatty acid esters	Ethyl 2-hydroxy-4- methylpentanoate	( <i>R</i> )	182.0-341.0
					( <i>S</i> )	0.0-2.0

<sup>a</sup> Samples were obtained after fermentation.

<sup>b</sup> Commercial wines.

<sup>c</sup> Values in round brackets represent the concentration of aglycons found in the glycosidically bound fraction.

<sup>†</sup> The concentrations are presented as the mean values of respective samples.

<sup>‡</sup> Where possible, the concentrations were reported as minimum and maximum values of samples considered in the study.

<sup>#</sup> Muscat-type variety is not specified in the cited studies.

<sup>\*</sup> The (range) concentrations reported are tentatively expressed, based on the isomer ratio calculation.

*NA(s)*, information not available.

< *LOQ/LOD*, values were detected below the limit of quantitation/detection.



**Table 3.** Concentration ( $\mu\text{g/L}$ ) of key VOC isomers in sweet and sparkling wines.

Reference and grape variety	Origin	Samples	Chemical class	Compound	Isomer	Concentration <sup>c</sup>
<i>Sweet white wines</i>						
<b>Furmint</b>						
Furdíková et al. 2021 <sup>b,†</sup>	Slovakia	11	Terpenes	Limonene	(R)	<i>nf</i>
				Linalool	(R)	16.0
				Hotrienol	(S)	37.7
				$\alpha$ -Terpineol	(S)	24.6
<b>Lipovina</b>						
Furdíková et al. 2021 <sup>b,†</sup>	Slovakia	13	Terpenes	Limonene	(R)	21.5
				Linalool	(R)	38.7
				Hotrienol	(S)	35.2
				$\alpha$ -Terpineol	(S)	30.9
<b>Muškat žltý</b>						
Furdíková et al. 2021 <sup>b,†</sup>	Slovakia	13	Terpenes	Limonene	(R)	420.2
				Linalool	(R)	190.7
				Hotrienol	(S)	272.0
				$\alpha$ -Terpineol	(S)	78.9
<b>NAs</b>						
Machyňáková, Khvalbota, and Špánik 2021 <sup>b,‡</sup>	Hungary	1	Alcohol	2,3-Butanediol	(R)	1198.0
					(S)	63.1
			Terpenes	$\alpha$ -Terpineol	(R)	330.4
					(S)	259.4
				Hotrienol	(R)	61.6
					(S)	96.4
	Lactone	Whiskey lactone	<i>trans</i>	218.0		
			<i>cis</i>	319.0		
	Slovakia	4	Alcohol	2,3-Butanediol	(R)	226.3-437.0
					(S)	2.4-83.7
			Terpenes	$\alpha$ -Terpineol	(R)	18.9-396.5
					(S)	25.1-484.6
				Hotrienol	(R)	36.2-74.5
					(S)	76.8-116.5
Limonene			(R)	32.8		
			(S)	30.2		
Lactone	Whiskey lactone	<i>trans</i>	71.0-258.0			
		<i>cis</i>	107.0-295.0			
Stamatopoulos et al. 2016 <sup>b,*</sup>	France (Bordeaux)	14	Lactones	2-Nonen-4-olide	(R)	0.7-9.8
					(S)	1.5-9.3
				$\gamma$ -Nonalactone	(R)	5.3-21.4
					(S)	2.3-15.4
				Whiskey lactone	<i>trans</i>	0.9-579.4
					<i>cis</i>	1.5-986.6
<i>Sparkling wines</i>						
<b>Moscato giallo</b>						
Caliari et al. 2015 <sup>a,‡</sup>	Brazil (Santa Catarina)	3	Terpenes	Furan linalool oxide	<i>trans</i>	35.6 (Charmat)-173.4 (Asti)
					<i>cis</i>	19.3 (Charmat)-74.7 (Asti)
				Pyran linalool oxide	<i>trans</i>	17.8 (Charmat)-51.1 (Asti)
					<i>cis</i>	72.0 (Charmat)-103.6 (Traditional)
			Alcohol	3-Hexenol	<i>trans</i>	19.6 (Asti)-24.2 (Traditional)
					<i>cis</i>	112.7 (Asti)-164.3 (Traditional)
<b>Brachetto d'Acqui</b>						
Torchio et al. 2012 <sup>a,#</sup>	Italy (Piedmont)	NA	Terpenes	Furan linalool oxide	<i>trans</i>	18.5 (38.0)
					<i>cis</i>	24.0 (88.0)
				Pyran linalool oxide	<i>trans</i>	30.0 (47.5)
					<i>cis</i>	29.0 (6.5)
Torchio et al. 2012 <sup>a</sup>	Italy (Piedmont)	NA	Terpenes	Furan linalool oxide	<i>trans</i>	18.0 (18.0)
					<i>cis</i>	12.5 (66.0)
					<i>trans</i>	49.0 (35.0)

				Pyran linalool oxide	<i>cis</i>	13.0 (19.5)
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<sup>a</sup> Samples were obtained after fermentation.

<sup>b</sup> Commercial wines.

<sup>c</sup> Values in round brackets represent the concentration of aglycons found in the glycosidically bound fraction.

<sup>†</sup> The concentrations are presented as the mean values of respective samples.

<sup>‡</sup> Where possible, the concentrations were reported as minimum and maximum values of samples considered in the study.

<sup>#</sup> Light sparkling wine

<sup>\*</sup> The (range) concentrations reported are tentatively expressed, based on the isomer ratio calculation.

*NA(s)*, information not available.

*nf*, not found.