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Chemo-diversity of chiral monoterpenes in different styles of Riesling wine from different regions

Mei Song¹, Claudio Fuentes² and Elizabeth Tomasino^{1,*}

¹ Food Science and Technology, Oregon State University, Corvallis, OR 97331, United States of America

² Statistics, Oregon State University, Corvallis, OR 97331, United States of America



*correspondence:
elizabeth.tomasino@oregonstate.edu

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ABSTRACT

Monoterpenes are important characteristic compounds for aromatic white wines, including Riesling, but their enantiomer composition has been little explored in wine. Enantiomers can differ depending on region and style, as they are sensitive to environmental factors, and thus could be used for wine authentication. Thirteen monoterpene isomers were quantified by HS-SPME-MDGC-MS in fifty-four commercial Riesling wines from three wine styles (dry, medium dry and medium sweet) and four well-established wine-growing regions in Germany, France (Alsace) and the USA (New York and Oregon). Significant differences were found for nine out of the 13 enantiomers among different regions and eight enantiomers among styles. X-Y scatterplots of enantiomer pair concentrations, with excellent fitted lines, implies low variation of enantiomeric ratios from each region. The study suggests that wines from different regions and styles were differentiated by chiral monoterpene profiles. Chiral monoterpene analyses could provide supporting information in Riesling wine authentication by offering an objective measure of flavour quality, as these compounds are key compounds for Riesling aroma and flavor.

KEYWORDS: SPME-MDGC-MS, enantiomer fraction, white wine, discriminant analysis



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INTRODUCTION

Riesling is one of the world's most widely-planted white grape varieties, with a total of more than 60,000 hectares worldwide since 2015 (German Wine Institute, 2019). The first documentation of Riesling cultivation was around 1350 AD in the Rhine Valley (Liu *et al.*, 2008; Sechrist, 2012). The Mosel and Rhine rivers of Germany and the Alsace region of France are considered to be the world's top Riesling regions (Jacobson, 2006). Riesling is also grown in new world regions, including New Zealand, Australia, and New York and Oregon in the United States, as well as other locations since 1955 (Sechrist, 2012).

Riesling is the result of a cross of *Heunisch* (the dominant cultivar) and *Vitis sylvestris* (wild cultivar) (Anhalt *et al.*, 2011). Riesling wines are very diverse, as the composition of grapes can be altered by environmental characteristics and viticultural practices (Kozina *et al.*, 2008; Myers *et al.*, 2013; Zanzotti *et al.*, 2021). The sensitivity of the grapes to environmental factors (e.g., the climate and soil in which the vines are grown) results in distinctly different flavours in the wines. It has been reported that Riesling wines from Ontario, Canada, showed distinctly different sensory profiles based on two terroirs: 'bench' and 'plains'. Wines from 'bench' had greater lemon/lime aroma than those from 'plains' (Douglas *et al.*, 2001). Riesling wines can also be characterised according to viticultural practices, specifically relating to residual sugar and ripeness at harvest; e.g. dry, medium dry, medium sweet or sweet wines, and the wines from the German Prädikatswein classifications (Sweet, 2009; Krebiehl, 2019).

There has been growing interest in monoterpene compounds due to the important impact of these compounds on varietal distinctiveness (Peña *et al.*, 2005). Additionally, understanding grape-derived wine aroma compounds (e.g., monoterpenes) has been a keystone in understanding research on wine flavour chemistry for many years (Ribéreau-Gayon *et al.*, 1975); for example, monoterpene alcohols can add subtle floral and citrus aromas to Riesling wines (Peña *et al.*, 2005). *Cis*-rose oxide, citronellol, linalool and α -terpineol have been reported to be important monoterpenes in Riesling wines that underwent more than three years of aging (Black *et al.*, 2015). Simpson and Miller (1983) found linalool, hotrienol and α -terpineol to be major monoterpenes in young Riesling wines, with concentrations decreasing with age (Simpson and Miller, 1983; Strauss *et al.*, 1986).

Enantiomer differentiation is of interest, because enantiomers display different aroma descriptors and sensory detection thresholds (Bentley, 2006). Enantiomeric composition has been used to assess information about foods by geographic origin (Ebeler *et al.*, 2001; Marchelli *et al.*, 1996) and the authenticity of fruit beverages (Ebeler, 2007; Ruiz del Castillo *et al.*, 2003). Region of origin is an important factor for many wine consumers. In Alsace, wine quality categories on the label are determined by a geographic classification system and are used to ensure wine quality (Fischer *et al.*, 1999).

As the adulteration of wine becomes more and more sophisticated, there is a need for accurate methods for wine characterisation to prevent this, and to ensure that wines are from the stated geographical origins or countries (Cordella *et al.*, 2002; González and Peña-Méndez, 2000; Kallio *et al.*, 1915; Liu *et al.*, 2008; Versari *et al.*, 2014).

Rapp *et al.* (1978) have shown that the ratios of the various monoterpenes can be used to not only distinguish one cultivar from another but also to differentiate cultivars according to region or origin. Such 'terpene profiles' are useful for the separation of Riesling wines from other so-called Riesling wines (e.g., Welsch Riesling, Kap Riesling and Emerald Riesling). Rapp (1998) reported a significant differentiation between Riesling and Welsch Riesling from different growing regions (Austria, Italy and Yugoslavia) based on an analysis of their terpene profiles; specifically, significantly higher concentrations of selected monoterpene compounds (e.g., linalool, *trans*-linalool oxide and α -terpineol) were present in true Riesling wines compared to Welsch Riesling. The objective of this study was to determine the effect of regions and styles on chiral monoterpene profiles and enantiomer fractions of Riesling wines to determine whether monoterpene enantiomers can be used for wine authentication.

MATERIALS AND METHODS

1. Chemicals

Standards of *S*-(-)-limonene ($\geq 99.0\%$), *R*-(+)-limonene ($\geq 99.0\%$), furanoid linalool oxide ($\geq 97.0\%$), and *R*-(-)-linalool ($\geq 98.0\%$) from Sigma Chemical Co. (St. Louis, MO, USA) were used to check the elution order of the isomers. Linalool ($\geq 97.0\%$), *R*-(+)- α -terpineol ($\geq 97.0\%$) and *R*-(+)- β -citronellol (98.0%) were obtained from Sigma Chemical Co. (St. Louis, MO, USA). *S*-(-)- α -Terpineol (96.0%) was obtained from BOC sciences (Ramsey Road, Shirley, NY, USA) and nerol oxide (99.0%) from ALFA chemistry (Waverly Avenue, Holtsville, NY, USA). The isotopic standards d_3 -(\pm)- α -terpineol and d_3 -(\pm)-linalool ($\geq 99.4\%$) were purchased from CDN Isotopes (Pointe-Claire, QC, Canada), while d_3 -(\pm)-limonene was synthesised as described in Song *et al.* (2015). Milli-Q water was obtained from a Millipore Continental water system (EMD-Millipore, Billerica, MA, USA). HPLC grade ethanol came from Pharmco-AAPER (Vancouver, WA, USA). Sodium chloride ($> 99\%$) was supplied by J.T. Baker (Avantor® Performance Materials, PA, USA).

2. Sample Preparation and Headspace Solid Phase MicroExtraction Multidimensional gas Chromatography Mass Spectrometry (HS-SPME-MDGC-MS)

The wine sample preparation and quantification method by HS-SPME-MDGC-MS for *S*-(-)-limonene, *R*-(+)-limonene, (2*R*, 5*R*)-(+)-*trans*-linalool oxide, (2*R*, 5*S*)-(-)-*cis*-linalool oxide, (2*S*, 5*S*)-(-)-*trans*-linalool oxide, (2*S*, 5*R*)-(+)-*cis*-linalool oxide, *R*-(-)-linalool, *S*-(+)-linalool, *S*-(-)- α -terpineol, *R*-(+)- α -terpineol and *R*-(+)- β -citronellol can be found in Song *et al.* (2015).

HS-SPME was conducted using a Shimadzu AOC-5000 plus autosampler fitted with a stack cooler. A three-phase StableFlex SPME fiberTM (50/30 µm DVB/CAR/PDMS, 2 cm, 24 Ga, Supelco®) was used for SPME. The heart cut-MDGC-MS analyses were performed using a Shimadzu GC-2000 plus coupled to a Shimadzu QP 2010 GCMS with a heart cutting dean switch (Shimadzu, USA). The first column was a Rtx-wax column (30m, 0.2 mm ID, 0.5 µm film thickness, Restek Corporation, Bellefonte, PA, USA) and the second GC contained two columns connected in sequence: an Rt®-βDEXsm and an Rt®βDEXse (60 m, 0.25 mm ID, 0.25µm film thickness, Restek Corporation). The isomers were quantified using the standard curves and the stable isotope dilution analysis method (Siebert *et al.*, 2005). All of the wines were run in three groups based on their styles (dry, medium dry and medium sweet) according to the wine label or available information for instrument analysis. Each wine was analysed in triplicate: three samples per bottle of wine. The standard curves for each wine style were run in the de-aromatized corresponding wine matrices respectively in order to minimise the matrix effects, and they were run in each batch to minimise any SPME fiber effects (Song *et al.*, 2015). Additional details of the method and analysis parameters can be found in Song *et al.* (2015).

3. Wines

Fifty-four commercial Riesling wines (2012 vintage) with three wine styles, dry, medium dry and medium sweet, were randomly selected from five well-established regions: old world producers from Germany (DE), France (FR; Alsace), and new world producers from the United States (NY; Finger lakes region and OR; Willamette valley AVA) (Table 1). Sample sizes were not well-balanced in terms of styles as differences were found between the style stated on the label and the actual style based on residual sugar measurements carried out using the revised Rebelein method (Rebelein, 1973). Moreover, medium sweet wine could not be obtained from Alsace during the course of this study. Alsace typically produces many dry style Rieslings and researchers had difficulty obtaining medium-sweet French wines in the USA. Wine style was categorised according to the Regulation of the European Community no 753/2002 (Commission Regulation, 2002), with revisions based on the measured residual sugar content. Wine can be considered as dry, medium dry or medium sweet when they have the following residual sugar contents: less than 4 g/L, between 7 g/L and 12 g/L and between 12 g/L and 45 g/L respectively. One bottle of each wine was purchased in April 2014. We chose to study as many different individual wines as the funding would allow, rather than multiple bottles of the same wine. Upon arrival, the wines were stored in the OSU wine cellar at 8 °C for 1 month. The bottles were then opened, and samples of the wine were poured into three 40 mL amber vials (Supelco®, Bellefonte, PA, USA) and three 50 mL centrifuge tubes (VWR International Corp. Visalia, CA, USA) and then stored at -20 °C until analysis.

TABLE 1. Distribution of Riesling wines across region of origin, vintage and wine style.

Region ^a	Vintage	Wine style (bottles)		
		Dry	Medium dry	Medium sweet
FR	2012	10	6	
DE	2012	2	5	5
NY, USA	2012	4	3	4
OR, USA	2012	3	8	4

^a FR: Alsace, GR: German, NY: New York, OR: Oregon.

4. Statistical Analysis

General linear models (GLM) were used to study the effect of region and wine style on chiral monoterpene profiles or enantiomer fraction of Riesling wines. Statistics were carried out using IBM® SPSS® statistic 20 (SPSS Inc., Chicago, IL). Linear discriminant analysis (DA) was carried out using XLSTAT 2014. 6. 01 software (Addinsoft, New York, USA).

RESULTS

1. Separation, Identification and Quantification of Chiral Monoterpenes in Riesling Wines

Thirteen chiral monoterpenes were investigated in 54 bottles of Riesling wines from four regions and three wine styles (Figure 1). Significant differences were found on chiral monoterpenes between regions and styles (Table 2). However, no interaction effect of region and style was found. (+)-Limonene, (-)-limonene, (+)-α-terpineol and (-)-α-terpineol were not found to be important for regional differentiation. German wines contained higher concentrations of (+)-linalool, (-)-linalool and *R*(+)-β-citronellol. The wines from New York and Alsace had very similar chiral monoterpene profiles composed primarily of linalool and nerol oxides and *R*(+)-β-citronellol. Oregon wines contained high concentrations of all oxide isomers.

The significant differences found between the three styles from all the regions were due to all monoterpene enantiomer concentrations, except (±)-limonene, (±)-α-terpineol and (2*S*, 5*R*)-(+)-*cis*-linalool oxide. In the considered wine from the 2012 vintage, medium dry wines contained the highest concentrations of isomers compared to the other two styles in Rieslings from France, Germany and New York. Medium sweet Riesling from Oregon had the highest concentrations of the three wine styles investigated. In addition, within the French wines from Alsace, the concentrations of linalool oxide enantiomers were significantly higher in the medium dry wines compared to the dry wines, and monoterpene alcohols had low concentrations in the medium dry wines. In the German wine samples from the 2012 vintage, there were no significant differences for any of the isomer concentrations among the three styles.

However, medium dry wines had the highest concentrations for most of the isomers, except for (2*R*, 5*S*)-(-)-*cis*-linalool oxide, (2*S*, 5*R*)-(+)-*cis*-linalool oxide and *R*(+)-β-citronellol.

TABLE 2. Mean of chiral monoterpenes (µg/L) and enantiomer fraction (EF) with standard deviations for Riesling wines by region and style determined by ANOVA and Tukey's HSD ($\alpha = 0.05$).

Isomers	FR			DE			NY			OR			F value (significance) [▲]	
	Dry	Medium dry	Style	Dry	Medium dry	Medium sweet	Dry	Medium dry	Medium sweet	Dry	Medium dry	Medium sweet		Region
S-(+)-limonene	1.42 ^a ± 0.32	1.50 ^a ± 0.51	1.72 ^a ± 0.07	2.58 ^b ± 0.64	0.92 ^a ± 0.11	1.74 ^a ± 0.23	2.77 ^a ± 0.77	1.86 ^a ± 0.32	1.54 ^a ± 0.49	1.39 ^a ± 0.07	1.25 ^a ± 0.32	1.25 ^a ± 0.32	1.88	3.01
R-(+)-limonene	0.78 ^a ± 0.50	0.74 ^a ± 0.28	0.81 ^a ± 0.19	1.55 ^a ± 0.04	0.37 ^a ± 0.10	1.11 ^a ± 0.00	1.71 ^a ± 0.63	1.21 ^a ± 0.25	0.90 ^a ± 0.09	0.60 ^a ± 0.11	1.25 ^a ± 0.32	1.25 ^a ± 0.32	2.28	1.73
Limonene EF [◆]	0.65 ^a ± 0.08	0.68 ^a ± 0.19	0.68 ^a ± 0.23	0.67 ^a ± 0.32	0.72 ^{ab} ± 0.29	0.61 ^a ± 0.08	0.63 ^a ± 0.21	0.61 ^a ± 0.19	0.63 ^a ± 0.12	0.71 ^{ab} ± 0.33	0.63 ^a ± 0.28	0.63 ^a ± 0.28	3.77 [*]	2.00
(2R,5R)(+)-trans-linalool oxide	35.26 ^a ± 3.55	62.93 ^b ± 5.09	28.91 ^a ± 2.64	38.89 ^a ± 5.51	28.56 ^a ± 3.11	32.49 ^a ± 4.82	50.26 ^a ± 3.96	35.79 ^a ± 3.48	24.19 ^a ± 6.23	73.10 ^b ± 10.37	76.65 ^b ± 15.88	76.65 ^b ± 15.88	3.35 [*]	6.21 ^{**}
(2S,5S)(-)-trans-linalool oxide	6.68 ^a ± 1.06	15.56 ^b ± 2.49	3.62 ^a ± 1.04	5.00 ^a ± 1.14	4.27 ^a ± 0.79	7.28 ^a ± 2.44	9.41 ^a ± 2.15	10.88 ^a ± 2.21	6.83 ^a ± 1.95	12.30 ^b ± 2.38	15.25 ^b ± 3.43	15.25 ^b ± 3.43	6.60 ^{***}	5.05 [*]
trans-linalool oxide EF [◆]	0.82 ^a ± 0.02	0.80 ^a ± 0.01	0.86 ^a ± 0.03	0.91 ^a ± 0.02	0.86 ^a ± 0.05	0.80 ^a ± 0.04	0.84 ^a ± 0.02	0.79 ^a ± 0.02	0.77 ^a ± 0.01	0.85 ^a ± 0.02	0.83 ^{ab} ± 0.07	0.83 ^{ab} ± 0.07	3.78 [*]	2.00
(2S,5R)(+)-cis-linalool oxide	10.06 ^a ± 2.11	23.55 ^b ± 4.56	19.37 ^a ± 6.35	9.75 ^a ± 1.01	9.08 ^a ± 2.59	11.52 ^a ± 2.71	12.52 ^a ± 1.89	14.63 ^a ± 2.50	12.60 ^a ± 1.40	23.34 ^b ± 6.85	32.43 ^c ± 7.43	32.43 ^c ± 7.43	5.538 [*]	2.18
(2R,5S)(-)-cis-linalool oxide	16.06 ^a ± 2.48	39.05 ^b ± 7.46	14.06 ^a ± 1.07	11.85 ^a ± 2.52	8.62 ^a ± 1.82	15.62 ^a ± 2.13	29.60 ^a ± 3.47	25.01 ^a ± 4.53	15.55 ^a ± 4.71	31.52 ^b ± 3.36	46.32 ^c ± 7.32	46.32 ^c ± 7.32	7.38 ^{***}	6.58 ^{**}
cis-linalool oxide EF [◆]	0.63 ^a ± 0.01	0.62 ^a ± 0.00	0.41 ^a ± 0.04	0.47 ^a ± 0.05	0.50 ^a ± 0.02	0.59 ^a ± 0.02	0.71 ^b ± 0.02	0.62 ^a ± 0.01	0.55 ^a ± 0.04	0.58 ^a ± 0.02	0.59 ^a ± 0.06	0.59 ^a ± 0.06	11.20 ^{***}	1.76
S-(+)-nerol oxide	20.85 ^a ± 4.55	32.41 ^a ± 2.64	11.96 ^a ± 2.20	16.31 ^a ± 1.71	11.33 ^a ± 1.45	19.11 ^a ± 2.83	30.65 ^a ± 4.66	29.39 ^a ± 6.51	12.07 ^a ± 2.16	32.63 ^b ± 7.40	33.92 ^b ± 4.46	33.92 ^b ± 4.46	4.41 ^{**}	5.54 ^{**}
R-(+)-nerol oxide	22.58 ^a ± 6.05	36.00 ^a ± 5.19	12.69 ^a ± 1.89	16.84 ^a ± 2.83	12.61 ^a ± 1.82	21.83 ^a ± 6.36	32.49 ^a ± 7.26	30.18 ^a ± 6.93	14.20 ^a ± 2.15	35.45 ^b ± 6.07	36.99 ^b ± 10.46	36.99 ^b ± 10.46	5.37 ^{**}	5.73 ^{**}
Nerol oxide EF [◆]	0.47 ^a ± 0.05	0.47 ^a ± 0.02	0.48 ^a ± 0.02	0.48 ^a ± 0.04	0.47 ^a ± 0.03	0.46 ^a ± 0.03	0.49 ^a ± 0.02	0.49 ^a ± 0.02	0.46 ^a ± 0.00	0.48 ^a ± 0.01	0.48 ^a ± 0.02	0.48 ^a ± 0.02	0.25	1.60
R-(+)-linalool	5.34 ^a ± 1.84	1.19 ^a ± 0.34	16.75 ^a ± 4.21	30.11 ^a ± 3.35	5.19 ^a ± 0.98	4.31 ^a ± 1.18	19.72 ^b ± 1.84	0.02 ^a ± 0.00	8.40 ^a ± 1.20	5.96 ^a ± 1.19	4.45 ^a ± 0.39	4.45 ^a ± 0.39	3.59 [*]	4.43 [*]
S-(+)-linalool	4.86 ^a ± 0.47	1.15 ^a ± 0.26	15.32 ^a ± 2.39	27.25 ^a ± 6.08	7.80 ^a ± 1.18	4.21 ^a ± 0.51	17.59 ^b ± 2.63	0.03 ^a ± 0.00	9.50 ^a ± 1.54	5.15 ^a ± 1.22	4.30 ^a ± 1.26	4.30 ^a ± 1.26	3.92 [*]	3.61 [*]
Linalool EF [◆]	0.44 ^a ± 0.04	0.39 ^a ± 0.03	0.52 ^a ± 0.01	0.46 ^a ± 0.00	0.50 ^a ± 0.02	0.44 ^{ab} ± 0.03	0.53 ^b ± 0.02	0.37 ^a ± 0.04	0.44 ^a ± 0.01	0.46 ^a ± 0.01	0.41 ^a ± 0.02	0.41 ^a ± 0.02	1.27	0.75
S-(+)-terpineol	26.98 ^a ± 4.70	24.69 ^a ± 4.29	34.30 ^a ± 6.41	45.61 ^a ± 6.84	20.91 ^a ± 2.30	36.48 ^a ± 2.79	42.77 ^a ± 4.04	44.57 ^a ± 8.41	27.31 ^a ± 3.65	19.98 ^a ± 3.98	26.97 ^a ± 4.15	26.97 ^a ± 4.15	2.41	0.26
R-(+)-terpineol	22.64 ^a ± 6.40	21.00 ^a ± 5.89	24.92 ^a ± 7.12	38.75 ^a ± 6.57	14.73 ^a ± 2.33	34.02 ^a ± 3.01	39.99 ^a ± 9.34	38.96 ^a ± 7.62	24.02 ^{ab} ± 5.54	12.00 ^a ± 1.40	25.13 ^b ± 5.07	25.13 ^b ± 5.07	2.22	0.13
α -terpineol EF [◆]	0.55 ^a ± 0.11	0.54 ^a ± 0.05	0.59 ^a ± 0.04	0.60 ^a ± 0.02	0.60 ^a ± 0.01	0.52 ^a ± 0.03	0.54 ^a ± 0.02	0.54 ^a ± 0.02	0.53 ^a ± 0.04	0.63 ^b ± 0.03	0.52 ^a ± 0.02	0.52 ^a ± 0.02	3.29 [*]	2.04
R-(+)- β -citronellol	0.39 ^a ± 0.08	0.42 ^a ± 0.12	2.02 ^a ± 0.29	1.46 ^a ± 0.31	0.01 ^a ± 0.00	0.44 ^a ± 0.10	0.78 ^a ± 0.26	0.01 ^a ± 0.00	0.43 ^a ± 0.16	0.23 ^a ± 0.09	0.01 ^a ± 0.00	0.01 ^a ± 0.00	3.70 [*]	5.01 [*]

Tukey HSD letters are compared across the row for each isomer.

▲ Significant difference level: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

◆ enantiomeric fractions are calculated as follows: S-(+)-limonene/total, [2R, 5R](+)-trans-linalool oxide/ total trans, [2R, 5S](+)-cis-linalool oxide/ total cis, S-(+)-nerol oxide/total, R-(+)-linalool/total, S-(+)-terpineol/total.

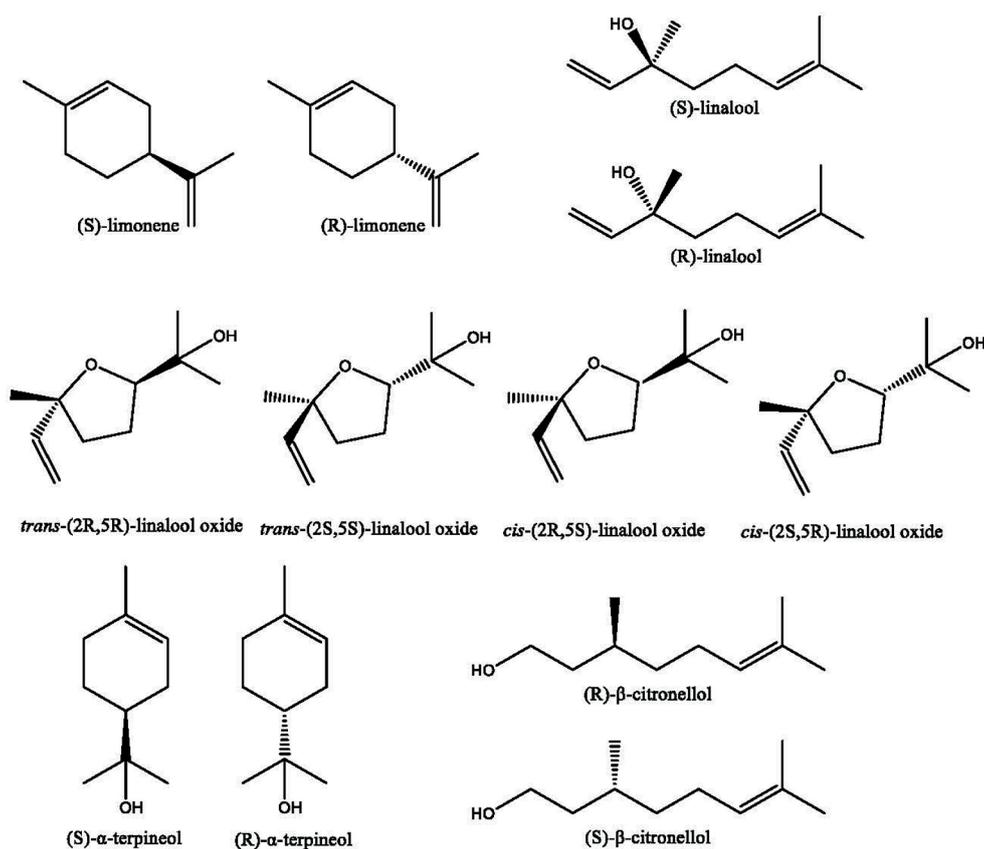


FIGURE 1. Molecular structure of the 13 monoterpene enantiomers measured in 2012 Riesling wines.

In terms of linalool enantiomers in New York wines, significant differences were found between the medium dry wines and the dry and medium sweet wines. All the different styles of wines from Oregon showed significant differences for all oxide isomers and *R*-(+)- α -terpineol in terms of their concentration. The medium sweet wines had the highest concentrations of oxide isomers and *R*-(+)- α -terpineol, while the dry wines had the highest concentration of the other isomers.

The distribution of chiral monoterpenes as affected by region and style can be visualised in a DA plot. DA was performed on isomer concentrations (mean of the three replicates) from all samples. Ninety-four percent of the variation was obtained in the first two discriminant functions for the regions, with F1 and F2 contributing 67 % and 27 % respectively (Figure 2). The Alsace and New York wines were separated from the other wines along the F1 axis. The New York wines were characterised by (+)-limonene, (-)-limonene, (+)- α -terpineol and (-)- α -terpineol compounds. The German wines had high negative scores along the F2 axis, characterised by (+)-linalool, (-)-linalool and *R*-(+)- β -citronellol isomers, whereas the Oregon wines on the opposite side of the F2 axis were characterised by all of the oxides, especially (+)-linalool oxides.

Likewise, two statistically significant discriminant functions were obtained for the styles, with F1 and F2 contributing 72 % and 28 % respectively (Figure 2). All three styles were

significantly separated from each other into three of the four quadrants of the DA. The medium dry wines were on the positive side of F1, separated from the other two styles and characterised by the majority of the isomers. The dry and medium sweet wines were separated by the F2 axis and characterised by lower *R*-(+)- β -citronellol concentration in the medium sweet wines. α -Terpineol enantiomers were not an important variable for differentiating wines by style.

2. Quantification of Enantiomer Fractions in Riesling Wines by Region and Style

Enantiomer fractions (EF) were calculated by dividing the concentration of the first eluting enantiomer in the chromatogram by the total enantiomer concentration of each monoterpene (Harner *et al.*, 2000). The effect of region, style and interaction of region \times style on enantiomer fractions was analysed by a general linear model. Significant differences were found between the regions, but not in terms of style and interaction effect (Table 2). For example in New York and Oregon wines, (2*R*, 5*S*)-(-)-*cis*-linalool oxide EF and *R*-(-)-linalool EF were significantly higher in the medium dry New York wines, (2*R*, 5*R*)-(+)-*trans*-linalool oxide EF and *S*-(-)- α -terpineol EF had the highest values in the medium dry Oregon wines. The *S*-(-)-nerol oxide and *R*-(-)-linalool concentrations observed from all regions and styles were lower or equal to the corresponding enantiomers (EFs \leq 0.50). Likewise, (2*R*, 5*S*)-(-)-*cis*-linalool oxide was lower or equal to the enantiomer pair in the German wines.

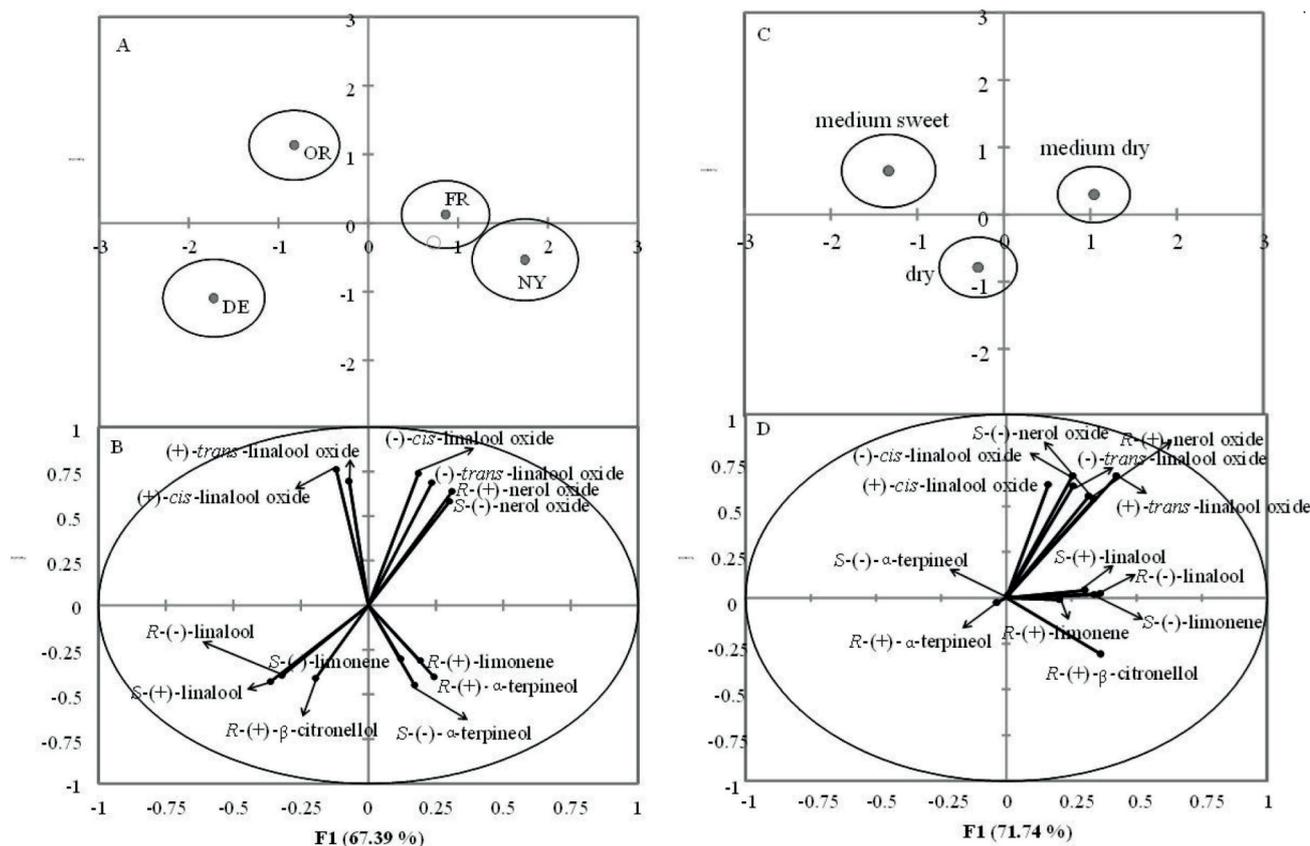


FIGURE 2. Linear discriminant plot on concentration of chiral monoterpene contents of Riesling wines in regions and styles.

Panel A, regions scores were represented by centroids surrounded by 95 % confidence regions (the solid circle). Panel B, all isomers vectors were shown based on regions. Panel C, wine styles scores were represented by centroids surrounded by 95 % confident regions. Panel D, all isomer vectors were shown based on wine style.

The differences in enantiomer fractions between regions can be seen vividly in the X-Y scatterplots of six enantiomer pairs (Figure 3). The fitted lines with slope and R² were plotted for all the wines from the same region. The slope was used to compare the similarity of enantiomer fractions in the different regions (there were no significant differences in styles). As can be seen in Figure 4.3, the slopes for the four regions in (2*R*, 5*R*)-(+)-*trans*-linalool oxide and (2*R*, 5*S*)-(-)-*cis*-linalool oxide pairs were quite different. The larger slope from Alsace wines compared to the German wines implied that the latter had greater (2*R*, 5*R*)-(+)-*trans*-linalool oxide EF. The results from the GLM analysis showed that there were significant differences for *S*-(-)-limonene EF and *S*-(-)- α -terpineol EF between regions. All of the regions contained similar *S*-(-)-nerol oxide and *R*-(-)-linalool EFs.

The coefficient of determination, R², indicates the variation of enantiomeric ratios in each region (higher R² values indicate less variations). Most of the regions showed high R² values in the enantiomer pairs, with R² values greater than 0.8, except for (2*R*, 5*R*)-(+)-*trans*-linalool oxide pair and (2*R*, 5*S*)-(-)-*cis*-linalool oxide pair. Low R² values were found for (2*R*, 5*R*)-(+)-*trans*-linalool oxide pair for the Alsace, New York and Oregon wines and (2*R*, 5*S*)-(-)-*cis*-linalool oxide pair for France, Germany and New York; this was due to one data point in the fitted line

that deviated from the others in each region. This implies that there was only one wine in each region that had significantly different EFs for these two pairs (data now shown). However, (2*R*, 5*R*)-(+)-*trans*-linalool oxide EF for the German wines did vary. The wines from New York and Germany showed lower R² values (lower than 0.68) in these two pairs, but higher R² values (greater than 0.97) in the other pairs. Less variation was found among regions and styles in terms of enantiomer fractions compared to differentiation in terms of chiral monoterpene content (Figure 2 & 4).

Two statistically significant discriminant functions were obtained for all the regions, with F1 and F2 contributing 87 % and 11 % respectively. The German wines were separated from the others along the F1 axis. *S*-(-)-limonene, *S*-(-)- α -terpineol, (2*R*, 5*R*)-(+)-*trans*-linalool oxide and *R*-(-)-linalool EFs had positive loadings along F1 (Figure 4.4), indicating greater amounts of these enantiomer fractions in the German wines. Alsace, New York and Oregon had similar EFs, characterised by (2*R*, 5*S*)-(-)-*cis*-linalool oxide EF. The opposite position of (2*R*, 5*R*)-(+)-*trans*-linalool oxide EF and (2*R*, 5*S*)-(-)-*cis*-linalool oxide EF on the plot indicated that these two EFs were important variables in the classification of regions. No significant differences were found in the three styles in terms of EFs.

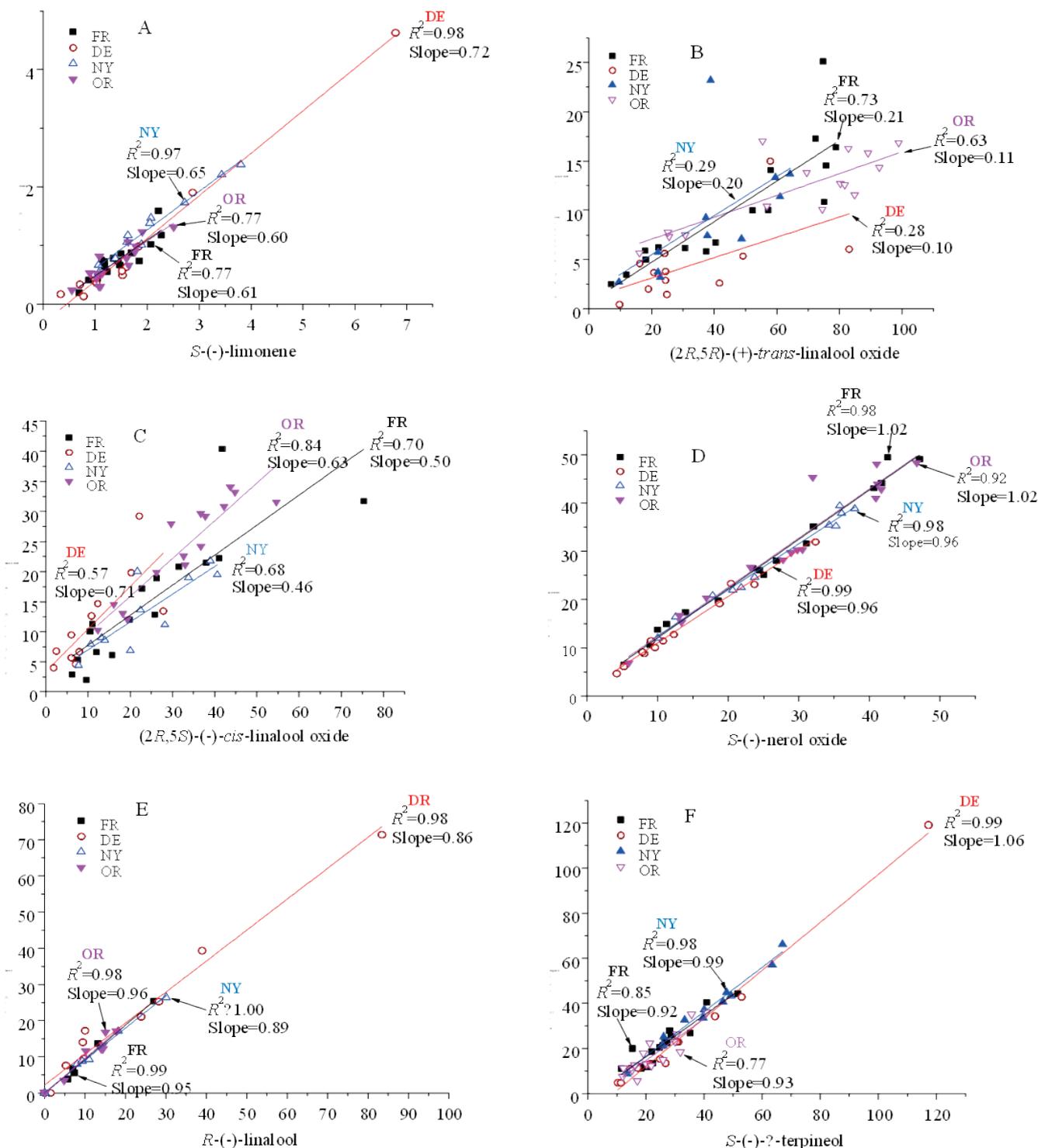


FIGURE 3. X-Y scatterplots of enantiomer pair concentrations ($\mu\text{g/L}$) in the 4 regions with fitted linear lines.

DISCUSSION

The amount of each chiral monoterpene across all Rieslings has been determined in previous work. Webster *et al.* (1993) reported that linalool oxides were the dominant monoterpenes in Riesling wines from 1986, 1987 and 1988. In the present study, (2*R*, 5*R*)-(+)-*trans*-linalool oxide had the highest mean concentration (46.54 $\mu\text{g/L}$). Our work also shows that *R*-(+)- β -citronellol concentrations in the analysed 2012 vintage wines were the lowest concentration (0.47 $\mu\text{g/L}$).

Dziadas and Jeleń (2010) reported α -terpineol to be one of the most dominant monoterpenes in 2006 and 2007 Riesling wines from Alsace, Germany and Hungary. Of the monoterpenes, this compound was not dominant in the wines of our study; this may be due to differences in vintage or region. The amount of *cis/trans*-linalool oxides was similar to those previously measured in other Riesling wines (Schüttler *et al.*, 2015). It is also important to note that all of the wines were from the same vintage. The content of the measured monoterpenes is known to change as wine ages,

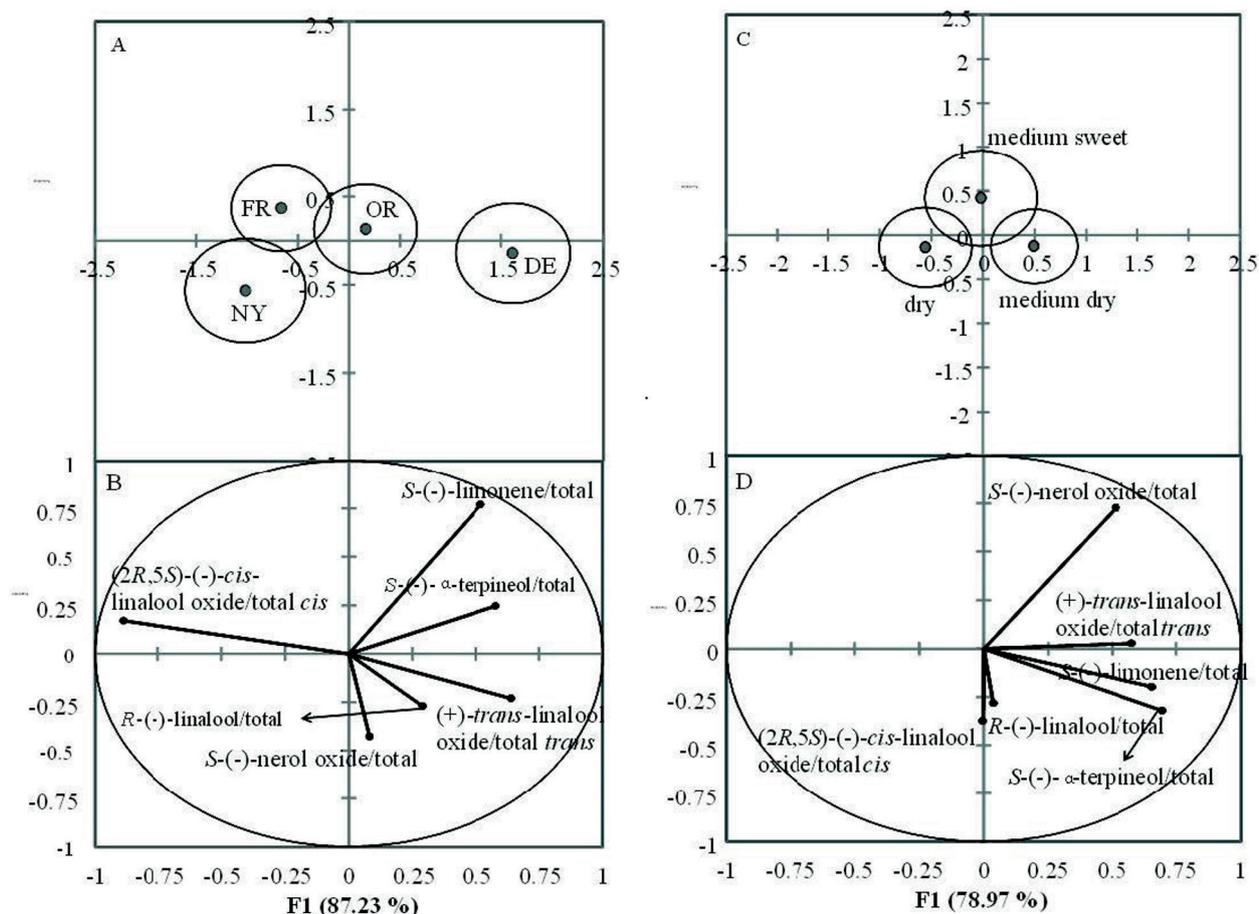


FIGURE 4. Linear discriminant plot on monoterpene enantiomer fractions of Riesling wines in regions and styles.

Panel A, regions scores were represented by centroids surrounded by 95 % confidence regions (the solid circle). Panel B, all enantiomer fractions vectors were shown based on varietal wines. Panel C, wine styles scores were represented by centroids surrounded by 95 % confident regions. Panel D, all enantiomer fractions vectors were shown based on wine style.

and therefore differences between our results and those of other work may be due to differences in wine age (Black *et al.*, 2015).

The sensitivity of Riesling grape to environmental factors results in the production of wines with distinctly different flavours. The differences in monoterpene enantiomers depending on region are most likely due to a combination of environmental factors and choice of Riesling clone. Monoterpene biosynthesis in Riesling has been shown to be very sensitive to a range of environmental factors, including soil, light and grape cultivar (Burbott and Loomis, 1967; Friedel *et al.*, 2016; Godshaw *et al.*, 2019; Marciniak *et al.*, 2017; Sweet, 2009). Grape genetics has also shown that different grape clones can result in different aroma composition of the same grape variety (Marais and Rapp, 2017; Versini *et al.*, 1990). Therefore, the differences between monoterpene isomers in wines from different regions are most likely due to the specific environment of a given location and choice of grape clone. Winemaking choices may also impact the monoterpene content of wines, as the choice of yeast strain, the application of maceration and the addition of enzymes can all alter, and in many cases increase, the monoterpene content of wines (Baron *et al.*, 2017;

Kim and Park, 2017; Rossouw and Bauer, 2016; Schmidt, 2016). While we cannot pinpoint the exact environmental or winemaking factor that contributes to the differences in monoterpene enantiomer in this study, the fact that we saw such clear regional separations suggests that general environmental factors may be the cause of differences between regional wines.

The differences in monoterpene enantiomers in terms of wine styles are most likely due to harvest decisions or winemaking practices. Harvest dates for Riesling in Germany for the different wine styles are based on grape sugar content (Cole, 2010); grapes left on the vine longer contain more sugar. Higher temperature and solar exposure increase the monoterpene contents of grapes (Marais *et al.*, 1999). Therefore, grapes used in sweeter wines will have higher monoterpene content than dryer wines. Additionally, some winemaking practices, such as choice of yeast strain, can alter the terpene content, which can differentiate the wines according to the desired wine style. Dessert Riesling fermentations have been found to contain a diverse array of both yeast and bacteria prior to alcoholic fermentation (Erasmus *et al.*, 2004; Spiczki *et al.*, 2010), which can alter the monoterpene content.

Therefore, the grapes used for sweeter wines would have different monoterpene content than those used for dryer wines. However, for winemaking practices to be the driver for regional differences, such practices would have to be used extensively in a given area. While this may be true for some regions, the winemaking practices of each wine were not known for the wines in this study. It is more likely that environmental factors are driving these differences, as they are more likely to be similar across a region. Although specific grapes are known to have optimal growing conditions, such as light and temperature, some environmental factors may not be that different between the regions. Further work is needed to determine which aspect contributes the most to the monoterpene differences from these regions.

The chiral monoterpenes of the regional Rieslings measured in this study were found at concentrations both above and below their known olfactory perception thresholds, thus potentially being able to affect aroma perception and wine quality. For example, the Oregon wines contained higher concentrations of all oxide isomers, which have high aroma threshold values (Garrido-Frenich *et al.*, 2006) and therefore may not contribute as much to aroma perception as other terpenes, such as (+)-linalool, (-)-linalool and *R*-(+)- β -citronellol isomers, which have low aroma perception thresholds (Garneau *et al.*, 2014; Gunata *et al.*, 1988). The dominant monoterpene groups in each region may contribute to specific aromas of these wines (Marais, 1983). Even those found at concentrations below their known thresholds may impact aroma, as combinations of different monoterpenes both at concentrations below and above their known perception thresholds in Pinot gris have been found to influence aroma perception (Tomasino *et al.*, 2020).

The enantiomeric ratios of key aroma compounds have been successfully used to distinguish between natural and synthetic food products, to define geographic area and to identify plant variety (Ebeler *et al.*, 2001; Weber *et al.*, 1995). Therefore, enantiomeric ratios could offer an interesting alternative to conventional flavour analysis methods for product authentication (Ebeler *et al.*, 2001; Marais and Rapp, 2017; Ruiz del Castillo *et al.*, 2003). Enantiomeric fractions have successfully been used to determine the age of Bordeaux dessert wines with the *R* enantiomer of 2-nonen-4-olide dominating in aged wines and the *S* form more dominant in younger wines (Stamatopoulos *et al.*, 2016). We attempted to determine whether region of origin is linked to EFs. Each measured monoterpene had similar enantiomeric fractions of linalool oxides. The low R₂ values for linalool oxide EFs may be due to racemisation or rearrangement at wine pH (Park and Noble, 1993; Strauss *et al.*, 1986). The sensitivity of some chiral monoterpenes to acidic conditions and to increases in temperature and storage time may cause the variation in linalool oxide concentrations (Whittaker, 1972). Linalool can easily be oxidized via an epoxide to form four linalool oxides (Ribéreau-Gayon *et al.*, 1975). Linalool oxide has been reported to increase in wine stored at room temperature compared to that stored at 10 °C (Strauss *et al.*, 1986). Similar reports in Riesling wines during aging have been observed in other research (Di Stefano, 1985; Strauss *et al.*, 1986).

The storage time and conditions prior to purchase of the wines in this study are unknown. Despite the low R₂ values for linalool oxide, the fact that the majority of EFs for the other monoterpenes had high R₂ values suggests that, despite this potential variation, Riesling wines can be authenticated using chiral monoterpene EF. However, regional and stylistic differentiation had more variation when using overall enantiomer content, suggesting that enantiomeric content could be a better measurement for region and wine style than EF.

CONCLUSIONS

The results of this study suggest that it is possible to classify Riesling wines according to their geographical origin and style on the basis of the chiral monoterpene profile and enantiomer fractions. The ANOVA and linear discriminant analysis showed a clear impact of region and style on the chiral monoterpene profiles in Riesling wines. The majority of the studied wines contained similar EFs regardless of region or style, except for German wines. However, monoterpenes are affected by confounding factors, such as light and temperature, representing additional challenges for researchers, winemakers and viticulturists. Hence, it is strongly recommended to carry out further studies on the effects of region and style over several vintages and using a bigger sample size (taking into account the different oenological treatments, as well as the bottling technique and the type of bottle closure), in order to gain a better understanding of the factors involved in these regional and stylistic chiral monoterpene differences.

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REFERENCES

- Anhalt, U.C., Martínez, S.C., Rühl, E., & Forneck, A. (2011). Dynamic grapevine clones—an AFLP-marker study of the *Vitis vinifera* cultivar Riesling comprising 86 clones. *Tree Genetics & Genomes*, 7, 739-746. <https://doi.org/10.1515/biol-2017-0005>
- Baron, M., Prusova, B., Tomaskova, L., Kumsta, M., & Sochor, J. (2017). Terpene content of wine from the aromatic grape variety 'Irsai Oliver' (*Vitis vinifera* L.) depends on maceration time. *Open Life Sciences*, 12, 42-50. <https://doi.org/10.1515/biol-2017-0005>
- Bentley, R. (2006). The nose as a stereochemist. Enantiomers and odor. *Chemical reviews*, 106, 4099-4112. <https://doi.org/10.1111/ajgw.12186>
- Black, C., Parker, M., Siebert, T., Capone, D., & Francis, I. (2015). Terpenoids and their role in wine flavour: recent advances. *Australian Journal of Grape & Wine Research*, 21, 582-600. <https://doi.org/10.1111/ajgw.12186>
- Burbott, A.J., & Loomis, W.D. (1967). Effects of light and temperature on the monoterpenes of peppermint. *Plant Physiology*, 42, 20-28. <https://doi.org/10.1104/pp.42.1.20>

- Cordella, C., Moussa, I., Martel, A.-C., Sbirrazzuoli, N., & Lizzani-Cuvelier, L. (2002). Recent developments in food characterization and adulteration detection: Technique-oriented perspectives. *Journal of Agriculture and Food Chemistry*, 50, 1751-174. <https://doi.org/10.1021/jf011096z>
- Cole, T. C. (2010). *Wörterbuch der Lebensmittel-Dictionary of Foods*. Springer-Verlag. <https://doi.org/10.1007/978-3-8274-2586-7>
- Commission Regulation (2002). Commission Regulation (EC) No 753/2002 of 29 April 2002 laying down certain rules for applying Council Regulation (EC) No 1493/1999 as regards the description, designation, presentation and protection of certain wine sector products (OJ L 118 04.05.2002, p. 1, CELEX: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32002R0753>)
- Di Stefano, R. (1985). Occurrence of favorable organoleptic properties of aged wines. Investigation about the composition of volatile aromatic compounds and about the chemical and physical properties of German Riesling wine. *Rivista di Viticoltura e di Enologia*, 38, 228-241
- Douglas, D., Cliff, M.A., & Reynolds, A.G. (2001). Canadian terroir: characterization of Riesling wines from the Niagara Peninsula. *Food Research International*, 34, 559-563. [https://doi.org/10.1016/S0963-9969\(01\)00071-0](https://doi.org/10.1016/S0963-9969(01)00071-0)
- Dziadas, M., & Jeleń, H.H. (2010). Analysis of terpenes in white wines using SPE–SPME–GC/MS approach. *Analytica Chimica Acta*, 677, 43-49. <https://doi.org/10.1016/j.aca.2010.06.035>
- Ebeler, S.E., Sun, G.M., Vickers, A.K., & Stremple, P. (2001). Gas chromatographic analysis of chiral aroma compounds in wine using modified cyclodextrin stationary phases and solid phase microextraction. In *Aroma Active Compounds in Foods*, ACS Publications, pp. 45-56. <https://doi.org/10.1021/bk-2001-0794.ch005>
- Ebeler, S.E. (2007). Enantiomeric analysis as a tool for authentication of foods and beverages. In: *Authentication of Food and Wine*, ACS Publications, pp. 39-49. <https://doi.org/10.1021/bk-2007-0952.ch003>
- Erasmus, D.J., Cliff, M., & van Vuuren, H. J. J. (2004). Impact of yeast strain on the production of acetic acid, glycerol and the sensory attributes of ice wines. *American Journal of Enology and Viticulture*, 55, 371-378
- Fischer, U., Roth, D., & Christmann, M. (1999). The impact of geographic origin, vintage and wine estate on sensory properties of *Vitis vinifera* cv. Riesling wines. *Food Quality and Preference*, 10, 281-288. [https://doi.org/10.1016/S0950-3293\(99\)00008-7](https://doi.org/10.1016/S0950-3293(99)00008-7)
- Friedel, M., Frotscher, J., Nitsch, M., Hofmann, M., Bogs, J., Stoll, M., & Dietrich, H. (2016). Light promotes expression of monoterpene and flavonol metabolic genes and enhances flavor of winegrape berries (*Vitis vinifera* L. cv. Riesling). *Australian Journal of Grape and Wine Research*, 22, 409-421. <https://doi.org/10.1111/ajgw.12229>
- Garneau, F.-X., Collin, G., & Gagnon, H. (2014). Chemical composition and stability of the hydrosols obtained during essential oil production. I. The case of *Melissa officinalis* L. and *Asarum canadense* L. *American Journal of Essential Oils and Natural Products*, 2, 54-62
- Garrido-Frenich, A., Romero-González, R., Martínez-Vidal, J., Plaza-Bolaños, P., Cuadros-Rodríguez, L., & Herrera-Abdo, M. (2006). Characterization of recovery profiles using gas chromatography-triple quadrupole mass spectrometry for the determination of pesticide residues in meat samples. *Journal of Chromatography A*, 1133, 315-321. <https://doi.org/10.1016/j.chroma.2006.08.039>
- German Wine Institute (2019). 2017 Wine Market. https://www.deutscheweine.de/fileadmin/user_upload/Website/Service/Downloads/Statistik_2018-2019.pdf
- Godshaw, J., Hjelmeland, A. K., Zweigenbaum, J., & Ebeler, S. E. (2019). Changes in glycosylation patterns of monoterpenes during grape berry maturation in six cultivars of *Vitis vinifera*. *Food Chemistry*, 297, 124921. <https://doi.org/10.1016/j.foodchem.2019.05.195>
- González, G., & Peña-Méndez, E. (2000). Multivariate data analysis in classification of must and wine from chemical measurements. *European Food Research and Technology*, 212, 100-107. <https://doi.org/10.1007/s002170000207>
- Gunata, Z., Bitteur, S., Brillouet, J.-M., Bayonove, C., & Cordonnier, R. (1988). Sequential enzymic hydrolysis of potentially aromatic glycosides from grape. *Carbohydrate Research*, 184, 139-149. [https://doi.org/10.1016/0008-6215\(88\)80012-0](https://doi.org/10.1016/0008-6215(88)80012-0)
- Harner, T., Wiberg, K., & Norstrom, R. (2000). Enantiomer fractions are preferred to enantiomer ratios for describing chiral signatures in environmental analysis. *Environmental Science & Technology*, 34, 218-220. <https://doi.org/10.1021/es9906958>
- Jacobson, J.L. (2006). Berry to Bottle. In *Introduction to Wine Laboratory Practices and Procedures*, Springer Science; pp. 83-117
- Kallio, M., Viikari, J., Kallonen, R., Lehtonen, P., Patrikainen, E., & Hyötyläinen, T. (1915). Characterisation of Wines by Comprehensive Two-Dimensional Gas Chromatography and Chemometric Methods. *Alcohol*, 358, 0252
- Kim, B. H., & Park, S. K. (2017). Enhancement of volatile aromatic compounds in black raspberry wines via enzymatic treatment. *Journal of the Institute of Brewing*, 123, 277-283. <https://doi.org/10.1002/jib.412>
- Kozina, B., Karoglan, M., Herjavec, S., Jeromel, A., & Orlic, S. (2008). Influence of basal leaf removal on the chemical composition of Sauvignon Blanc and Riesling wines. *Journal of food agriculture and environment*, 6, 28
- Kriebiel, A. (2019). *The Wines of Germany*. Infinite Ideas Ltd. Oxford, United Kingdom
- Liu, L., Cozzolino, D., Cynkar, W., Dambergs, R., Janik, L., O'Neill, B., Colby, C., & Gishen, M. (2008). Preliminary study on the application of visible–near infrared spectroscopy and chemometrics to classify Riesling wines from different countries. *Food Chemistry*, 106, 781-786. <https://doi.org/10.1016/j.foodchem.2007.06.015>
- Marais, J. (1983). Terpenes in the aroma of grapes and wines: a review. *South African Journal of Enology and Viticulture*, 4(2), 49-58. <https://doi.org/10.21548/4-2-2370>
- Marais, J., Hunter, J., & Haasbroek, P. (1999). Effect of canopy microclimate, season and region on Sauvignon blanc grape composition and wine quality. *South African Journal of Enology & Viticulture*, 20, 19-30. <https://doi.org/10.21548/20-1-2223>
- Marais, J., & Rapp, A. (2017). The Selection of Aroma-Rich Clones of *Vitis vinifera* L. cv. Gewürztraminer and Weisser Riesling by Means of Terpene Analyses. *South African Journal of Enology & Viticulture*, 12, 51-56. <https://doi.org/10.21548/12-1-2229>
- Marchelli, R., Dossena, A., & Palla, G. (1996). The potential of enantioselective analysis as a quality control tool. *Trends in Food Science & Technology*, 7, 113-119. [https://doi.org/10.1016/0924-2244\(96\)10011-X](https://doi.org/10.1016/0924-2244(96)10011-X)
- Marciniak, M., Reynolds, A. G., Brown, R., Jollineau, M., & Kotsaki, E. (2017). Application of Geospatial Technologies to understand Terroir Effects in an Ontario Riesling Vineyard. *American Journal of Enology and Viticulture*, 68, 169-187. <https://doi.org/10.5344/ajev.2016.16083>

- Myers, J.M., Sacks, G.L., & Heuvel, J.E.V. (2013). Glycosylated aroma compound responses in 'Riesling' wine grapes to cluster exposure and vine yield. *HortTechnology*, 23, 581-588. <https://doi.org/10.21273/HORTTECH.23.5.581>
- Park, S.K., & Noble, A.C. (1993). Monoterpenes and monoterpene glycosides in wine aromas. In: *Beer and Wine Production*, ACS Publications, pp. 98-109. <https://doi.org/10.1021/bk-1993-0536.ch006>
- Peña, R.M., Barciela, J., Herrero, C., & García-Martín, S. (2005). Optimization of solid-phase microextraction methods for GC-MS determination of terpenes in wine. *Journal of the Science of Food and Agriculture*, 85, 1227-1234. <https://doi.org/10.1002/jsfa.2121>
- Rapp, A., Hastrich, H., Engel, L., & Knipser, W. (1978). Possibilities of characterizing wine quality and vine varieties by means of capillary chromatography. In *Flavor of foods and beverages*, Charalambous, G.; Inglett, G.E., Eds.; pp 391. <https://doi.org/10.1016/B978-0-12-169060-1.50030-8>
- Rapp, A. (1998). Volatile flavour of wine: correlation between instrumental analysis and sensory perception. *Die Nahrung*, 42, 351-363. [https://doi.org/10.1002/\(SICI\)1521-3803\(199812\)42:06<351::AID-FOOD351>3.3.CO;2-U](https://doi.org/10.1002/(SICI)1521-3803(199812)42:06<351::AID-FOOD351>3.3.CO;2-U)
- Rebelein, H. (1973). Rapid method for the determination of the alcohol, sugar and total SO₂ contents (by distillation) in wine and fruit juices and also for determining blood alcohol. *Chemie Mikrobiologie. Technologie der Lebensmittel*, 2, 112-121.
- Ribéreau-Gayon, P., Boidron, J., & Terrier, A. (1975). Aroma of Muscat grape varieties. *Journal of Agricultural and Food Chemistry*, 23, 1042-1047. <https://doi.org/10.1021/jf60202a050>
- Rossouw, D., & Bauer, F. F. (2016). Exploring the phenotypic space of non-*Saccharomyces* wine yeast biodiversity. *Food Microbiology*, 55, 32-46. <https://doi.org/10.1016/j.fm.2015.11.017>
- Ruiz del Castillo, M.L., Caja, M.M., & Herraiz, M. (2003). Use of the enantiomeric composition for the assessment of the authenticity of fruit beverages. *Journal of Agriculture and Food Chemistry*, 51, 1284-1288. <https://doi.org/10.1021/jf025711q>
- Schmidt, D. M. (2016). Effect of pre-fermentation cold soak on the chemical and sensory qualities of aromatic white wines. *Dissertation, Cornell University*
- Schüttler, A., Friedel, M., Jung, R., Rauhut, D., & Darriet, P. (2015). Characterizing aromatic typicality of Riesling wines: merging volatile compositional and sensory aspects. *Food Research International* 2015, 69, 26-37. <https://doi.org/10.1016/j.foodres.2014.12.010>
- Sechrist, R. (2012). The Origin, Diffusion, and Globalization of Riesling. In *The Geography of Wine*, Springer, pp. 195-206. https://doi.org/10.1007/978-94-007-0464-0_11
- Siebert, T. E., Smyth, H. E., Capone, D. L., Neuwöhner, C., Pardon, K. H., Skouroumounis, G. K., Herderich, M. J., Sefton, M. A., & Pollnitz, A. P. (2005). Stable isotope dilution analysis of wine fermentation products by HS-SPME-GC-MS. *Analytical and Bioanalytical Chemistry*, 381, 937-947. <https://doi.org/10.1007/s00216-004-2992-4>
- Simpson, R., & Miller, G. (1983). Aroma composition of aged Riesling wine. *Vitis*, 22, 51-63.
- Sipiczki, M., Csoma, H., Antunovics, Z., & Pfliegler, W. P. (2010). Biodiversity in yeast populations associated with botrytised wine making. *Mitt Klosterneuberg*, 60, 387-394
- Song, M., Xia, Y., & Tomasino, E. (2015). Investigation of a quantitative method for the analysis of chiral monoterpenes in white wine by HS-SPME-MDGC-MS of different wine matrices. *Molecules*, 20, 7359-7378. <https://doi.org/10.3390/molecules20047359>
- Stamatopoulos, P., Brohan, E., Prevost, C., Siebert, T. E., Herderich, M., & Darriet, P. (2016). Influence of chirality of lactones in the perception of some typical fruity notes through perception interaction phenomena in Bordeaux dessert wines. *Journal of Agricultural and Food Chemistry*, 64, 8160-8167. <https://doi.org/10.1021/acs.jafc.6b03117>
- Strauss, C.R., Wilson, B., Gooley, P.R., & Williams, P.J. (1986). Role of monoterpenes in grape and wine flavor. In *Biogenesis of Aromas*, ACS Publications, pp. 222-242. <https://doi.org/10.1021/bk-1986-0317.ch018>
- Sweet, N. (2009). Riesling Selections. <http://iv.ucdavis.edu/files/121501.pdf>, accessed March 30, 2020
- Tomasino, E., Song, M., & Fuentes, C. (2020). Odor perception interactions between free monoterpene isomers and wine composition of Pinot gris wines. *Journal of Agricultural and Food Chemistry*, 69, 3220-3227. <https://doi.org/10.1021/acs.jafc.9b07505>
- Versari, A., Laurie, V. F., Ricci, A., Laghi, L., & Parpinello, G.P. (2014). Progress in: authentication, typification and traceability of grapes and wines by chemometric approaches. *Food Research International*, 60, 2-18. <https://doi.org/10.1016/j.foodres.2014.02.007>
- Versini, G., Rapp, A., Volkmann, C., & Scienza, A. (1990). Flavour compounds of clones from different grape varieties. In: *Proceedings of the 5th International Symposium on Grape Breeding*. Alleweldt, G., Eds. pp. 513-524
- Weber, B., Maas, B., & Mosandl, A. (1995). Stereoisomeric flavor compounds. LXXII: Stereoisomeric distribution of some chiral sulfur-containing trace components of yellow passion fruits. *Journal of Agricultural and Food Chemistry*, 43, 2438-2441. <https://doi.org/10.1021/jf00057a023>
- Webster, D.R., Edwards, C.G., Spayd, S.E., Peterson, J.C., & Seymour, B.J. (1993). Influence of vineyard nitrogen fertilization on the concentrations of monoterpenes, higher alcohols, and esters in aged Riesling wines. *American Journal of Enology and Viticulture*, 44, 275-284
- Whittaker, D. (1972). *The monoterpenes*: Academic Press: London, UK.
- Zanzotti, R., Roman Villegas, T., Paolini, M., Coller, E., Cappello, N., Moser, S., Malacarne, M., & Larcher, R. (2021). Influence of the agronomic management on the aroma of Riesling wines. In *Macrowine 2021*, <https://openpub.fmach.it/retrieve/handle/10449/70645/118655/2021%20IVAS%207874.pdf>