Project Report – June 2015

Project: Chiral Terpenes - Quantitation, Threshold Determination and Sensory Impact on Aromatic White Wines

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Dr. Tomasino recently presented her work to date on this project in a seminar, which can be viewed online at the following link.

https://media.oregonstate.edu/media/t/0_dg700t97

Some brief statements about overall accomplishments to date.

A successful method to measure chiral terpenes in aromatic white wines has been successfully developed and published.

Both Pinot gris and Riesling wines have different chiral monoterpene composition based on place of origin.

Riesling wines also have different chiral monoterpene composition based on vintage and style. Possible interactions with place of origin, style and vintage are being investigated.

Further steps in project

Which chiral monoterpenes are impacting wine aroma?

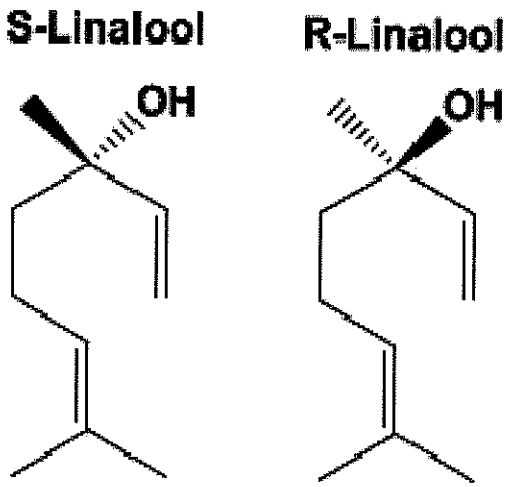
Chiral monoterepene composition of a variety of white wine varieties beyond Pinot gris and Riesling.

More details and results are found under each objective and sub-objective.

Below are a few definitions for frequently used terms.

Chiral – molecules that have identical composition but are arranged in non-super imposable mirror images. The presence of an asymmetric carbon creates the chirality.

Isomer – molecules that contain the same number of atoms of each element but have different arrangements in space. Therefore chiral compounds have several different isomers.
An example of chiral linalool with its 2 isomers.



Perception threshold – the lowest level at which a compound can be detected.

OBJECTIVES & RESULTS

Objective 1 – Development of methodology using multi-dimensional gas chromatography-mass spectrometery to measure chiral terpenes in aromatic white wines.

Method to measure chiral terpenes in aromatic white wine has been completed and been published. Please see Table 1 for the compounds included in the method, their known aroma descriptors and the currently known perception thresholds.

The methodology paper was publishedhttp://www.mdpi.com/1420-3049/20/4/7359in an open access journal and can be viewed at the following link.

http://www.mdpi.com/1420-3049/20/4/7359

Table 1 – Chiral monoterpenes included in the HS-SPME-MDGC-MS method with their aroma descriptors and known perception thresholds

Compound	**Aroma descriptor**	**Perception threshold (µg/L)**
(S)-(-)-Limonene	Lemon, turpentine	500
(R)-(+)-Limonene	Orange	200
(-)-(2S,4R)-cis-rose oxide	Herbal, green, hay	50
(+)-(2R,4S)-cis-rose oxide	Floral, green, clean	0.5
(+)-(2R,4R)-trans-rose oxide	Floral, green, minty	160
(+)-(2S,4S)-trans-rose oxide	Herbal, bitter peel	80
(2R,5R)-(+)-trans-linalool oxide	Earthy, leafy	3,000-4,000*
(2R,5S)-(-)-cis-linalool oxide	Stronger earthy, leafy	3,000-4,000*
(2S,5S)-(-) trans-linalool oxide	Sweet, floral	3,000-4,000*
(2S,5R)-(+)-cis-linalool oxide	Sweet, floral	3,000-4,000*
(R)-(-)-Linalool	Woody, lavender	0.8
(S)-(+)-Linalool	Sweet, petigrain	7.4
(-)-α-terpineol	Coniferous, tar	300,000*
(+)-α-terpineol	Heavy floral, lilac	300,000*
(R)-(+)-β-citronellol	Rose-leafy, petal-like	50

*perception thresholds determined in racemic (mix of all isomers) solutions.

Objective 1a - Does place of origin influence chiral monoterpene content?

PINOT GRIS RESULTS

50 Pinot gris wines were collected/donated in total.

5 from New York
21 from Oregon
3 from Washington
7 from Australia
12 from New Zealand
3 from Italy

Yes, the wines can be separated based on place of origin!

The following compounds were not found in the analyzed Pinot gris wines
(+)-(2R,4S) – cis-rose oxide
(-)-(2S,4S)-trans rose oxide

Not all wines contained all of the measured chiral monoterpenes. Complete data for each compound can be provided upon request.

<u>In summary</u>
Linalool oxides and α-terpineol isomers were present in all Pinot gris wines.
Both Linalool isomers were found in half of the New Zealand and Australian wines
Both Limonene isomers were found in half of the Australian and 1/3 of the Oregon wines.

Disciminant anlaysis graphs (Figure 1) show that there is some separation based on place of origin. Specifically the circles (representing the 95% confidence intervals) that are not overlapping or touching are considered significantly different.

Oregon Pinot gris is different from NZ, NY and Italian wines.
NZ wines are different from OR, Australian, NY and Italian wines.
NY wines are different from AU, NZ and OR wines etc.

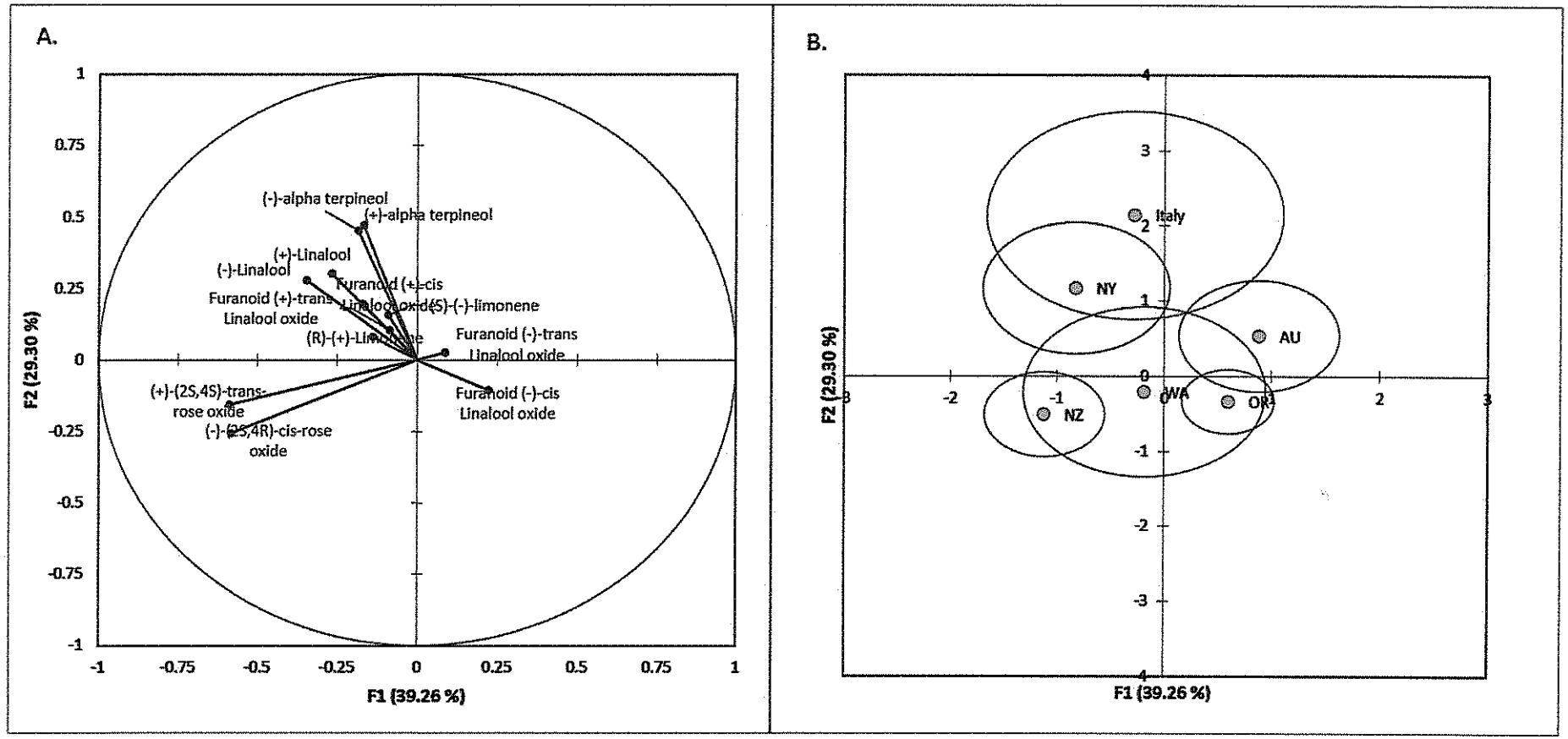


Figure 1 – Separation of Pinot gris wines by place of origin (AU-Australia, NY-New York, USA, NZ –New Zealand, OR – Oregon, USA, WA – Washington, USA) using discriminant analysis. Places are positioned using centroids for the wines and circles represent 95% confidence intervals surrounding the centroid means. Loadings for the chiral monoterpenes are to the left (A) and scores are plotted to the right (B). Dimensions for F1 and F2 represent 69% of the variance.

In summary from Figure 1.

OR Pinot gris wines characterized by higher levels of (2R,5S)-(-)-cis-linalool oxide.

NZ Pinot gris characterized by higher levels of (+)-(2R,4S)-trans-rose oxide and (-)-(2S,4R)-cis-rose oxide.

WA Pinot gris is fairly balanced and not characterized by any one specific chiral monoterpene.

AU Pinot gris is characterized by high levels of (2S,5S)-(-)- trans linalool oxide

Italian Pinot grigio is characterized by high levels of both α-terpineol isomers.

Italian and NY Pinot gris wines also contain the greater variety of chiral monoterpenes.

- We are getting in some additional Pinot gris wines that will be analyzed this September to ensure that place of origin differences are due to the place of origin and not because of the sample size for each place.

RIESLING RESULTS

138 Riesling wines were collected/donated and run through the same chiral terpene analysis as Pinot gris wines.

12 Australian wines
3 Californian wines
6 Canadian wines (since this analysis we have received about 18 more Canadian wines, to be analyzed this September)
23 German wines
31 Wines from the Fingerlakes, New York
12 wines from New Zealand
30 wines from Oregon
21 Wines from Washington
(in the second round of analysis we also have numerous Riesling samples from Michigan, to be analyzed in September)

Riesling wines also were from a number of vintages

4 wines from 2008
3 wines from 2009
11 wines from 2010
18 wines from 2011
73 wines from 2012
32 wines from 2013

The following compounds were not found in the analyzed Riesling wines.
(+)-(2R,4S)-cis-rose oxide

Very few wines contained
(-)-(2S,4R)-cis-rose oxide
(-)-(2R,4R)-trans-rose oxide
(+)-(2S,4S)-trans-rose oxide

Complete data for each compound can be found in Table 5-7 at the end of this report.

In summary

Unlike Pinot gris wines, the majority of the Riesling wines contained all of the measured chiral monoterpenes, except those mentioned above.

About ½ of all of the3 dry style Riesling wines did not contain any of the Linalool isomers.

Due to the number of Riesling wines analyzed we investigated 3 different factors

1. Place of origin (or region) (Figure 2)
2. Vintage (Figure 3)
3. Style (based on EU regulation 743/2002) (Figure 4)

There is separation based on place of origin but what is interesting is that 2 large groups appear in Figure 2, B. To the right all the wines are from regions considered cold climate and on the left the wines are from regions considered hot climates.

Specifically cooler climates produced wines with higher levels of all linalool oxide isomers and warmer climates produced wines with higher levels of linalool isomers, α-terpineol isomers and Limonene isomers.

Younger wines from 2013 and 2012 are characterized by more linalool isomers, α-terpineol isomers and Limonene.

Wines from 2010 are characterized by (+)-(2R,4S)-cis-rose oxide and (+)-(2S,4S)-trans rose oxide

Wines from 2009 and 2008 are characterized by all linalool oxide isomers and (-)-(2R,4R)-trans-rose oxide

Wine styles have been differentiated by EU standards of residual sugar.

sweet	≥45g/L
medium sweet	12>--≤45g/L
Medium dry	4>--≤12g/L
Dry	≤4g/L

Sweet wines are characterized by Linalool and limonene isomers.

Medium sweet wines are characterized by α-terpineol isomers and (-)-(2S,4R)-cis-rose oxide and (-)-(2R,4S)-cis-rose oxide

Medium dry wines are characterized by linalool oxide isomers.

Dry wines were not characterized by any of the chiral monoterpenes measured.

*We are currently investigating any interactions between place of origin, vintage and style for Reisling wines. Results are pending at this time.

Due to difficulties reading the labels in the following figures we have assigned numbers to each terpene isomer. The key is as follows;

2. (S)-(-)-Limonene
4. (R)-(+)-Limonene
5. (-)-(2S,4R)-cis-rose oxide
6. (+)-(2R,4S)-cis-rose oxide
7. (2R,5R)-(+)-trans-linalool oxide
8. (2R,5S)-(-)-cis-linalool oxide
9. (-)-(2R,4R)-trans-rose oxide
10. (+)-(2S,4S)-trans-rose oxide
11. (2S,5S)-(-)-trans-linlool oxide
12. (2S,5R)-(+)-cis-linalool oxide
14. R-(-)-Linalool
16. (S)-(+)-Linalool
18. (-)-α-Terpineol
20. (+)-α-Terpineol
21. (R)-(+)-β-citronellol

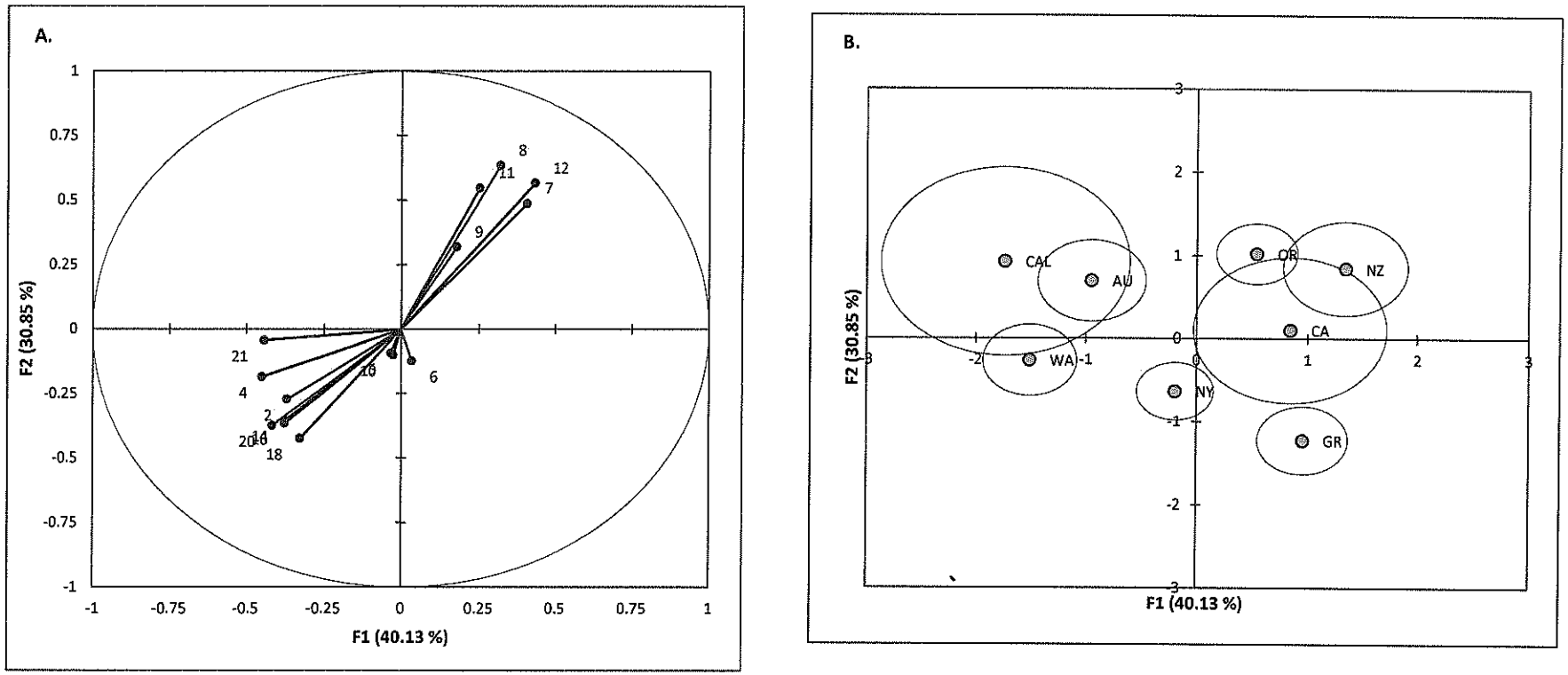


Figure 2 – Separation of Riesling wines by place of origin (AU-Australia, CA-Canada, CAL-California, GR – Germany, NY-New York, USA, NZ –New Zealand, OR – Oregon, USA, WA – Washington, USA) using discriminant analysis. Places are positioned using centroids for the wines and circles represent 95% confidence intervals surrounding the centroid means. Loadings for the chiral monoterpenes are to the left (A) and scores are plotted to the right (B). Dimensions for F1 and F2 represent 71% of the variance.

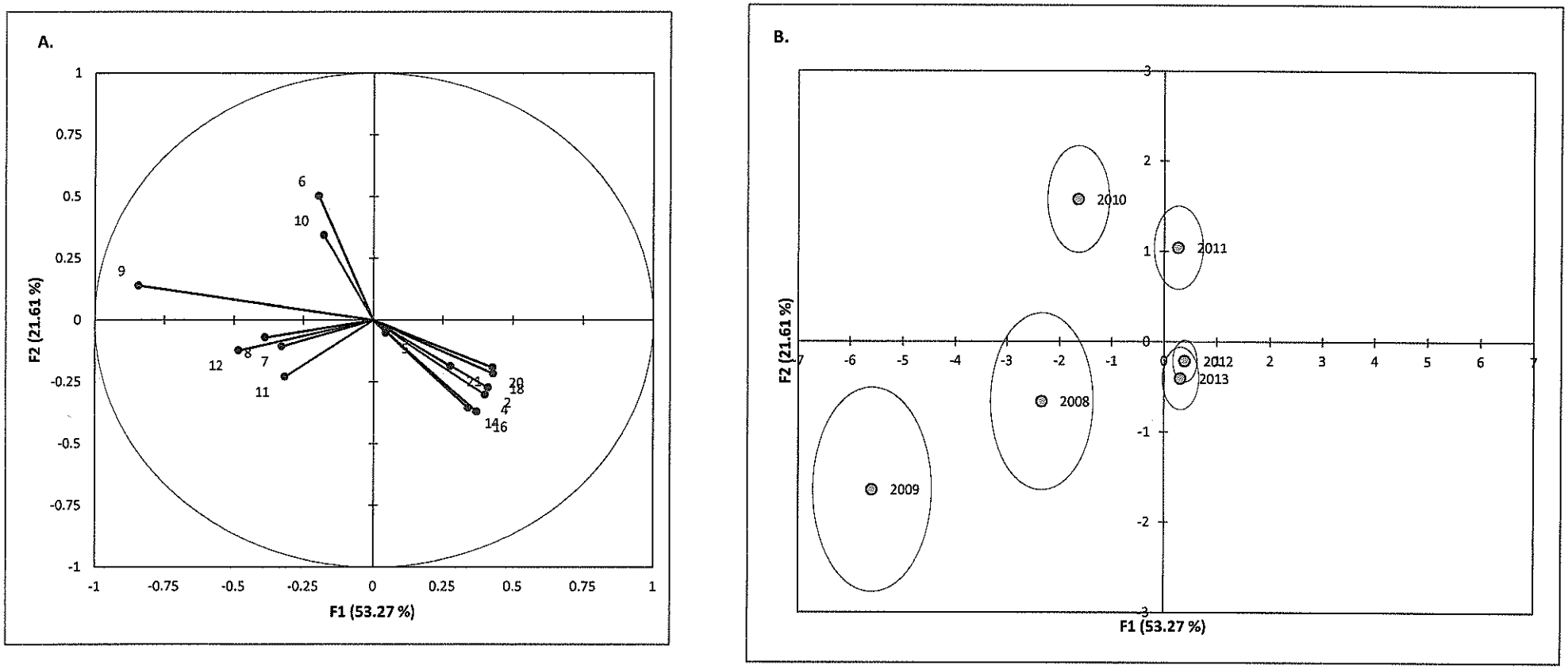


Figure 3 – Separation of Riesling wines vintage using discriminant analysis. Places are positioned using centroids for the wines and circles represent 95% confidence intervals surrounding the centroid means. Loadings for the chiral monoterpenes are to the left (A) and scores are plotted to the right (B). Dimensions for F1 and F2 represent 75% of the variance.

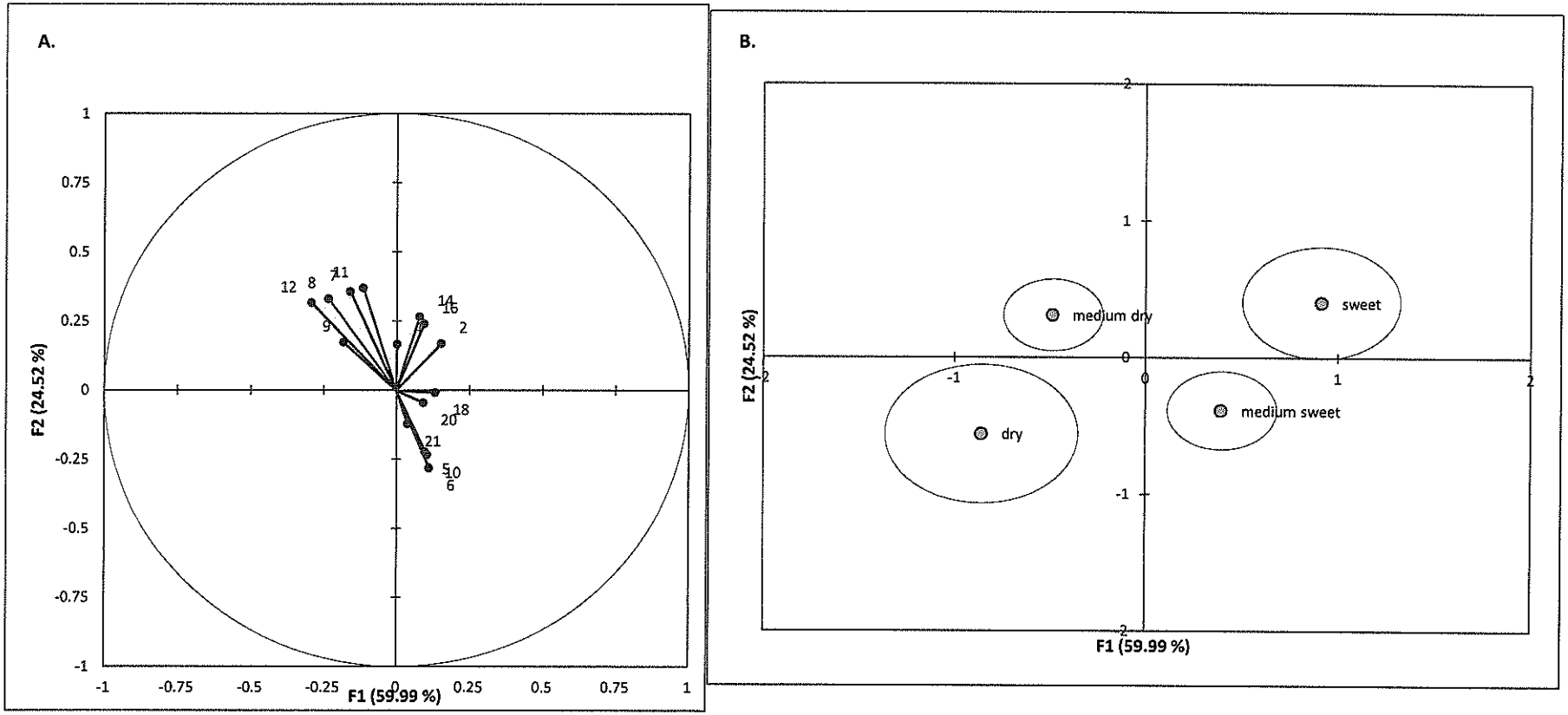


Figure 4 – Separation of Riesling wines based on style (sweet = ≥45 g/L residual sugar, medium sweet = 12> - ≤45 g/L residual sugar, medium dry = 4> - ≤12 g/L residual sugar, and dry = ≤4 g/L residual sugar) using discriminant analysis. Places are positioned using centroids for the wines and circles represent 95% confidence intervals surrounding the centroid means. Loadings for the chiral monoterpenes are to the left (A) and scores are plotted to the right (B). Dimensions for F1 and F2 represent 75% of the variance.

Table 2 – Basic wine parameters for Pinot gris wines

Wine	Country	vintage	ALC	RS
AU1	AU	2013	12.50%	1.86
AU2	AU	2013	12.50%	2.66
AU3	AU	2013	12.50%	5.49
AU4	AU	2013	14.00%	3.82
AU5	AU	2013	10.70%	3.91
AU6	AU	2013	13.00%	4.81
AU7	AU	2013	13.00%	3.34
NY1	NY	2012	12.50%	7.86
NY2	NY	2012	12.70%	1.50
NY3	NY	2013	11.80%	16.43
NY4	NY	2013	13.50%	4.06
NZ1	NZ	2012	13.50%	0.79
NZ2	NZ	2012	13.00%	4.31
NZ3	NZ	2013	13%	17.06
NZ4	NZ	2013	13.50%	7.41
NZ5	NZ	2013	14.00%	5.74
NZ6	NZ	2013	13.50%	6.31
NZ7	NZ	2013	13.00%	4.98
NZ8	NZ	2013	14.0%	5.84
NZ9	NZ	2013	14.00%	12.05
NZ10	NZ	2013	13.50%	5.90
NZ11	NZ	2013	14.50%	6.73
OR1	OR	2010	13.00%	5.47
OR2	OR	2011	12.60%	4.47/L
OR3	OR	2011	12.50%	0.99
OR4	OR	2011	12.60%	8.75
OR5	OR	2012	13.90%	3.95
OR6	OR	2012	14.00%	5.82
OR6a	OR	2012	14.00%	6.10
OR7	OR	2012	13.20%	2.40
OR8	OR	2012	13.00%	6.11
OR9	OR	2012	14.10%	4.15
OR10	OR	2012	14.20%	8.91
OR11	OR	2012	15.00%	5.43
OR12	OR	2013	11.90%	10.05
OR13	OR	2013	13.30%	3.12
OR14	OR	2013	13.20%	4.23
OR15	OR	2013	12.00%	3.98

OR16	OR	2013	13.50%	7.19
OR17	OR	2013	13.20%	2.15
OR18	OR	2013	13.15%	2.68
OR19	OR	2013	13.00%	6.96
OR20	OR	2013	13.50%	1.19
WA1	WA	2012	13.50%	6.36
WA2	WA	2012	13.80%	4.26
WA3	WA	2013	13.30%	4.09
IT1	Italy	2011	12.50%	0.86
IT2	Italy	2012		0.71
NY5	NY	2010	12.00%	3.55
NZ1	NZ	2009	13.00%	3.03
NZ2	NZ	2011	12.60%	3.13