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CONTRIBUTION OF VITICULTURAL FACTORS TO ENHANCE AN AROMATIC PRECURSOR FOR AGED RED WINE OF *VITIS VINIFERA* CV MALBEC N

CONTRIBUTION DE FACTEURS VITICOLES A LA PRESENCE D'UN PRECURSEUR AROMATIQUE POUR UN VIN ROUGE DE GARDE DE *VITIS VINIFERA* CV MALBEC N

DUFOURCQ, Thierry[1*]; BESNARD, Elisabeth[2]; MILLE, Brigitte[3]; DAGAN, Laurent[4]; YOBREGAT, Olivier[3]

[1]*Institut Français de Vigne et du vin, Pôle Sud-ouest, Château de Mons, 32100 Caussens, France*
[2]*Ferme Expérimentale d'Anglars-Juillac, 46140 Anglars-Juillac, France*
[3]*Institut Français de Vigne et du vin, Pôle Sud-ouest, V'Innopole, 81310 Lisle/Tarn, France*
[4]*Nyseos, 53 rue Claude François 34080 Montpellier, France*

[*]**Corresponding author**: *thierry.dufourcq@vignevin.com*

Abstract

This study seeks to assess viticultural factors having an effect on the dimethyl sulfide precursor concentration in grapes of *Vitis vinifera L.* cv. Malbec N. This odorless precursor, remaining in young wines after fermentation, releases dimethyl sulfide in wine during aging and contributes to a reductive and complex aromatic bouquet, with reminiscent of truffle. During three vintages, from 2012 to 2014, we generated a data base with 45 variables – climatic, agronomic, grape analysis data – registered from 25 vine plots representing the diversity of "terroirs" in a south western France vineyard, PDO (protected designation of origin) Cahors. Multi-criteria data analysis tried to select main variables that could explain the status of dimethyl sulfide precursor in grape berries. The first results showed a repartition of plots by vintages due to a strong climatic effect. Partial Least Square regression led to the determination of influent variables that occurred. Altitude and longitude were significant in relation with terroir. Cool temperature and thermal amplitude during grape maturation were also influent as well as associated variables of summer rainfalls. The main influent variables from grape analysis were berry size, potassium, amino-acids ratio and carbon isotope discrimination. This work completes on the vineyard level the knowledge to manage the potential of dimethyl sulfide to produce particular aged red wine. It is possible to promote a set of variables in order to select grapevine parcels with optimal potential regarding terroir and vintage.

Keywords: Malbec N, dimethyl sulfide precursor, aged red wine, terroir, multi-criteria analysis

Résumé

Ce travail cherche à évaluer les facteurs qui, au niveau du vignoble, influencent la présence dans les raisins du précurseur aromatique du sulfure de diméthyle qui s'exprimera dans les vins de *Vitis vinifera L.* cv. Malbec N. Ce précurseur, non odorant, est retrouvé dans les vins jeunes. Il sera libéré au cours du vieillissement du vin et produira un bouquet réducteur complexe à odeur de truffe. Au cours de trois années, 2012 à 2014, nous avons constitué une base de données de 45 variables climatiques, agronomiques et analytiques sur raisins, à partir d'un réseau de 25 parcelles représentant la variabilité des terroirs de l'Appellation d'Origine Protégée Cahors. L'analyse multicritère des données a cherché à mettre en avant les variables qui ont contribué à expliquer la présence du précurseur dans les raisins. En premier, on observe un effet millésime lié au climat. Également, l'altitude et la longitude sont deux variables explicatives significatives. Pour le climat, les températures fraiches en septembre et l'amplitude thermique sont identifiées, ainsi que les variables associées aux précipitations estivales. On retrouve enfin dans les analyses sur raisins la contribution des variables liées au potassium, à la taille des baies, à la proportion d'acides aminés dans l'azote du moût ainsi qu'au $\delta^{13}C$. Ce travail vient compléter les connaissances, dès le vignoble, pour la maitrise du potentiel en DMS dans un objectif de production d'un vin rouge de garde. Il semble possible de proposer un ensemble de critères simples pour sélectionner des parcelles à potentiel optimal en fonction du terroir et du millésime.

Mots clés: Malbec N, précurseur du sulfure de diméthyle, vin rouge de garde, terroir, analyse multi-critères

Introduction

Cot N or Malbec N was considered as one of the most widespread grapevine cultivars in France before the end of the nineteenth century. A hundred synonyms or spelling variants exist for this variety, and Galet (2015) stated that it was grown in 30 French departments. Its origin is probably the southwest of France, the region of Cahors. Today world-wide known as Malbec N, derived from the name of a merchant who popularized it in the Bordeaux area, it was introduced in Chile and Argentina probably in the 1850s. For a long time considered as the ancestor of an important ampelographic family in South-west France (Bisson, 1995), genetic analysis based on the use of SSR markers established its complete kinship (Boursiquot *et al.*, 2009). Cot N is the offspring of Magdeleine noire des Charentes N, a poorly documented cultivar found for the first time in 1996, and Prunelard N, an old grape variety from the southwestern vineyards of France.

The vineyard of Cahors is situated in the department of the Lot, 100 km to the North of Toulouse. The climate is oceanic with mediterranean influences at the end of vegetative cycle. The annual average temperature is of 12,6 °C and the annual precipitation is about 750 mm. The Cahors Appellation Vineyard extends around 5000 ha actually planted, mainly by following the meanders of the Lot river. The Appellation accounts 9 types of soils or terroirs, classified in two different families: the terroirs of « valleys », former alluvial terraces of the Lot (Würm, Riss and Mindel) from the riverside to the slope, and the terroirs of plateau, above the valley: calcareous or marno-calcareous plateau or red plateau from siderolithic formation. Two third of the vineyard are established on the terroirs of valleys, on relatively deep soils, with more or less sloping and rocky grounds and argilo-muddy texture. Locally, the terroirs of plateau can present very superficial grounds (40-50cm).
Dimethyl sulfide (DMS) is an aroma compound that is described with a large range of odors in wine, truffle, garbage, olive, undergrowth, and with a perception threshold in wine from 10 to 160 µg/l (Dagan and Schneider, 2012; Spedding and Rahut, 1982). In association with others compounds, it could intensify the fruity perception of the wine and then, is considered as a flavor enhancer. This has been reported in wines from different origins, French Rhône valley, Spain, Australia. The DMS precursor (PDMS) corresponds to all compounds able to release DMS during wine aging. The S-methylmethionine has been identified in grape must and represents the main form of DMS precursor (Loscos *et al.*, 2008). This DMS precursor is odorless and remains in young wines after fermentation.

During aging, the released DMS contributes to a reductive and complex aromatic bouquet (Picard *et al.*, 2015). Obviously, wine making process, fermentation conditions and yeast material are key factors to optimize the concentration of PDMS in young wine. Nevertheless, accumulation of precursor in grape during maturity and previous studies on this compound at the vineyard (De Royer Dupré *et al.*, 2014) let us think that it could be interesting to look at differences due to terroir variability.

In a previous study we confirmed the presence of DMS in several Malbec wines, from 3 to 33 years old, elaborated in the Cahors region by the Ferme Expérimentale d'Anglars-Juillac. During the tasting trials, the "truffle" word was often used to describe Malbec wines with DMS concentration over than 0,8 µmol/l. With concentration around 1,5 à 2 µmol/l in young wines, the release of DMS during aging led to the development of wine aromatic complexity (Dufourcq *et al.*, 2012).

This study seeks to assess viticultural factors having an effect on the dimethyl sulfide precursor concentration in grapes of *Vitis vinifera L.* cv. Malbec N at terroir scale. Our approach is based on a multi-criteria analysis of data generated by a network of plots representing the variability of viticultural conditions in the Cahors region.

Materials and methods

25 parcels of Malbec N were selected. This network of plots was located in the different terroirs of the Cahors region, including the Lot riverside, the valley slope and the plateau above the valley.

Meteorological data, minimal, maximal and mean daily temperatures, daily rainfall and Penman potential evapotranspiration are generated by virtual weather stations created on each plot and supplied by Meteo France models for the Institut Français de la Vigne et du Vin (IFV). These allow us to calculate a set of climatic indices, sum of growing degree days, cool night index, thermal amplitude, periodical sum of rainfall.

Plot diagnosis and measurements give us agronomical data for geographical location, soil management practices, planting geometry, canopy management practice like height, width or discontinuity of the foliage and crop yield. On each plot, berries are sampled at harvest time for composition analysis. Classical grape maturity analysis were done at IFV laboratory: sugar content by refractometry, total acidity by titrimetry, malic and tartaric acides, ammonium and amino acid nitrogen by KonéLab sequential analyzer, polyphenols index by DO280 sepctrometry and anthocyanin extraction by ITV methods (Cayla *et al.*, 2002) and Puissant Léon analysis method, HCl 1% w/w and DO520 nm spectrometry. Carbon isotope discrimination ($\delta^{13}C$) to determine the post veraison vine water status was realized by OEA Labs Callington (Corwall, UK) using standard international procedure for isotope analysis.

For PDMS analysis, labelled dimethylsulfonium propanoic acid (DMSPA-d_6, internal standard, 200 µg/l), NaCl (875 mg) and sodium hydroxide (300 mg of pellets) were successively added to the sample (8 ml) in a glass vial (22 ml). PDMS was released by performing a thermal treatment under alkaline conditions at 80 °C for 1h. After cooling, samples were analyzed by GC-MS/MS. A synthetic grape juice was used to build the calibration curves for PDMS quantification in grape juices. DMSPA-d6 was added at the same concentration as the one used in the samples as internal standard. S-Methylmethionine (SMM) was added at 6 different concentrations 0 à 3 mg/l in juice). Analyses were carried out using a GC-MS Varian MS 4000 fitted with a DBWax Column (30 m x 0.25 µm x 0.25 µm). Extraction was performed with an automatic SPME sample with a CAR/PDMS SPME fiber.

The data set is made with 45 variables from 25 parcels during 3 vintages 2012-2014. Statistical analyses including Principal Component Analysis (PCA), Partial Least Square Regression (PLS-Regression), variance analysis, were conducted with Xlstat software (Addinsoft, Paris, France).

Results and discussion

PDMS concentration in berries is our main variable to explain. In this study, we got concentrations from 1,4 to 13,1 µmol/l of PDMS in grapes which is above the concentrations found in French Côtes du Rhone for Grenache in a previous study (De Royer Dupré *et al.*, 2014). PDMS in berries is accumulating during the maturity period especially when registered in late harvested white wine (Dagan, 2006). In our case, sampling occurs relatively at the same time on each vintage and limits this effect. Then, we consider that the presence of PDMS in berry results as a consequence of “terroir” influence (soil, climate, vineyard management).

PCA analysis (figure 1) shows projections of variables and observations (vintage x plot) on 2 components. As often, observations are grouped by vintages, supposing a main climatic influence. PDMS variable is also projected close to the component F2. This component is positively correlated with the altitude variable and negatively with the sum of degree days in September (maturity period).

In order to go further in the analysis of the link between PDMS and the data set, we ran partial least square regression (PLS-Regression) as it might have strong collinearity between the variables. This regression allows us to establish and rank the weight of the different variables. The normalized coefficients (figure 2) indicate the variables relative weight. When the absolute value is high, the weight of the variable is important and when the confident interval (error bar in figure 2) doesn’t cross the value 0 it is significant in the regression model. 17 variables among the 45 contribute significantly. Elevated altitude (ALT) and longitude west (LONG) were positively significant in relation with terroir location. 64% (7/11) of climatic variables contribute also, summarized by cool temperature (DD09) and thermal amplitude (ATH68) during grape maturation as well as weak summer rainfalls (RAIN68) and evapotranspiration (ETP69). Influent agronomical variables are in relation with low yield (PR), aged vineyard (AGE), small berry size (B) and deficit hydric status ($\delta^{13}C$). The main influent variables from grape analysis were potassium (K+) and tartaric acid (TH2) content, amino-acids ratio (AA/YAN). These results are consistent with (De Royer Dupré, 2014) who showed that hydric deficit and amino acid under Mediterranean climatic conditions are correlated with PDMS in berry.

The 2014 vintage is not favorable for PDMS accumulation in grape comparing to 2012 and 2013, around two fold less (figure 3). 7 plots are located on the plateau terroir that is actually cooler in September due to the altitude and continental influence. Despite the 2014 vintage effect, the plateau terroir led to produce higher level of PDMS in berries than the others in the Valley during the 3 years’ study (figure 3). This result should remain an important information to promote the selection of plots able to produce, in the end, aged red wine with DMS aromatic contribution.

Conclusion

These results need to be evaluated in their context and the interval of variability of the data set (table 1). This work completes, on the vineyard level, the knowledge to manage the potential of dimethyl sulfide to produce particular aged red wine especially the link with cool temperature during maturation and location of plots on the plateau terroir. It is possible to promote a set of variables in order to select grapevine parcels with optimal potential regarding terroir and vintage. Due to the concentrations observed in grapes, it is obvious that part of the PDMS should be transferred to the wine and would enhance the aromatic bouquet after the aging period.

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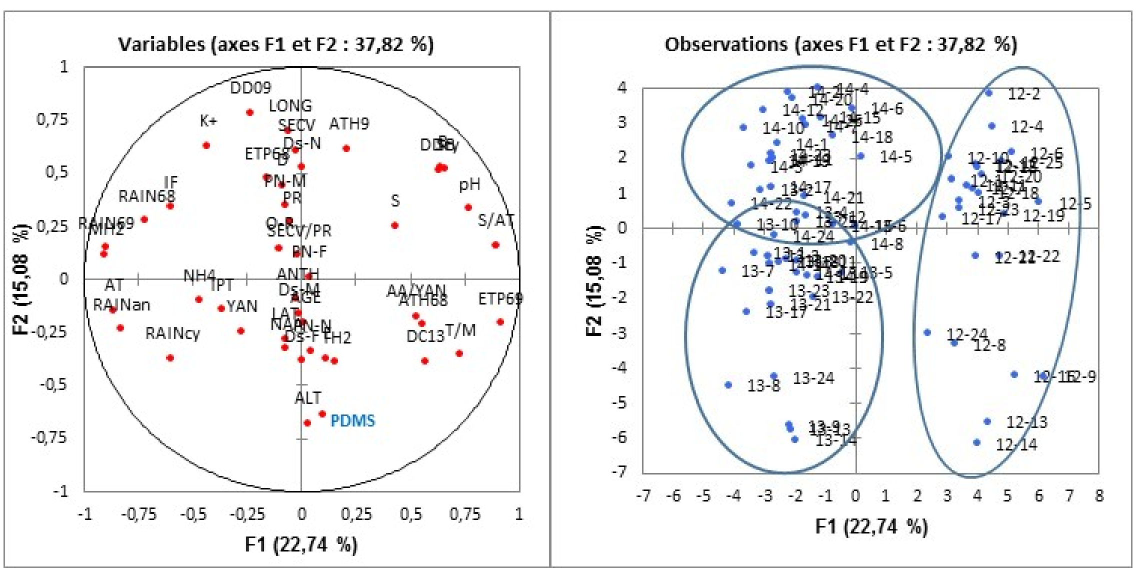

Figure 1. Principal component analysis; 45 variables and 74 observations (plot x vintage); cv Malbec N ; vintage 2012 to 2014.

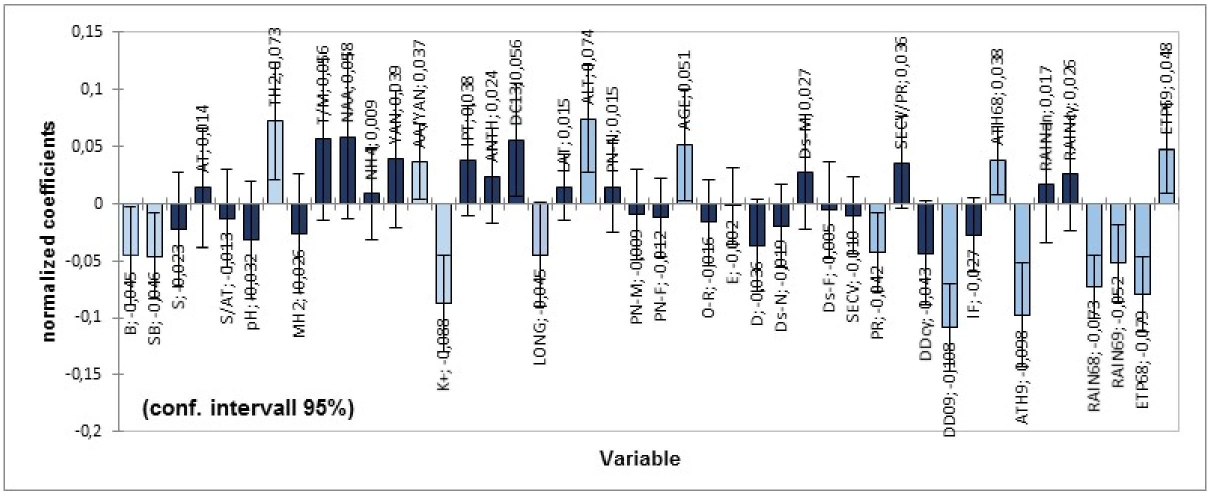

Figure 2. Influent variables (B coefficients) to explain PDMS in Malbec wines; light blue bars: significant variables; dark blue bars: no significant variables; error bar: confident interval 95%; Partial Least Square Regression, 74 observations (plot x vintage), 44 variables X, and 1 variable Y = PDMS (µmol/l); cv Malbec N; vintage 2012 to 2014.

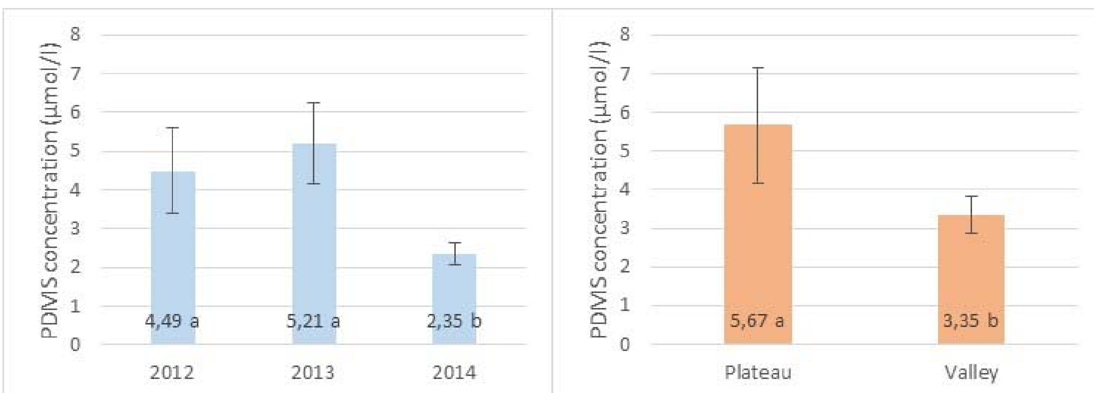

Figure 3. Grape concentration of PDMS in relation with vintages and terroir location; error bars: confident interval 95%; a, b: significant groups at 5%, Newman-Keuls test; cv Malbec N; vintage 2012 to 2014.

Table 1. Data set of the study; 45 variables and 73 observations (plot x vintage); cv Malbec N; vintage 2012 to 2014.

Variable name	code	sample	Min	Max	Mean	SD
Dimethyl sulfide precursor (µmol/l)	PDMS	73	1,4	13,1	4,0	2,5
Berry weight (g)	B	73	1,31	3,01	2,05	0,39
Sugar per berry (mg)	SB	73	243	654	417	95
Sugar (g/l)	S	73	162	226	203	14
Total acidity (g/l H_2SO_4)	AT	73	2,2	6,1	3,9	0,9
Sugar/acidity ratio	S/AT	73	31	97	55	15
pH	pH	73	2,94	3,63	3,26	0,15
Tartaric acid (g/l)	TH2	73	3,0	5,0	3,9	0,5
Malic acid (g/l)	MH2	73	1,1	6,1	3,6	1,2
Tartaric/malic ratio	T/M	73	0,55	3,90	1,17	0,66
Amino acid nitrogen (mg/l)	NAA	73	33	135	66	21
Ammonium nitrogen (mg/l)	NH4	73	11	88	48	17
Yeast assimilable nitrogen (mg/l)	YAN	73	52	201	114	35
Amino acid ratio	AA/YAN	73	0,45	0,78	0,59	0,07

Potassium (g/l)	K+	73	0,78	1,86	1,31	0,23
Total Polyphenols Index	IPT	73	61	135	99	16
Anthocyanins (mg/l)	ANTH	73	905	2391	1596	291
Carbon isotope $\delta^{13}C$	DC13	73	-28,8	-21,7	-26,1	1,5
Longitude	LONG	73	44,381	44,525	44,466	0,038
Latitude	LAT	73	1,017	1,495	1,231	0,103
Altitude	ALT	73	104	286	164	70
Slope null	PN-N	73	0,0	1,0	0,55	0,50
Slope medium	PN-M	73	0,0	1,0	0,37	0,49
Slope steep	PN-F	73	0,0	1,0	0,08	0,28
Year of plantation	AGE	73	1972	2006	1986	11
Row orientation (°)	O-R	73	0	135	76	48
Row width (m)	E	73	2,00	2,50	2,10	0,19
Vine distance (m)	D	73	1,00	1,25	1,11	0,10
Foliage discontinuity null	Ds-N	73	0,0	1,0	0,40	0,49
Foliage discontinuity medium	Ds-M	73	0,0	1,0	0,25	0,43
Foliage discontinuity high	Ds-F	73	0,0	1,0	0,36	0,48
Leaf area (m^2/m^2)	SECV	73	0,6	1,6	1,1	0,3
Yield (kg/m^2)	PR	73	0,21	1,73	0,74	0,26
Leaf fruit ratio (m^2/kg)	SECV/PR	73	0,38	4,33	1,66	0,69
Sum degree.days 04/01 to 09/30	DDcy	73	1321	1602	1476	69
Sum degree.days 09/01 to 09/30	DD09	73	237	299	268	15
Cool night index (°C)	IF	73	12,3	14,0	13,2	0,4
Day/night temperature 06/01 to 08/31 (°C)	ATH68	73	9,9	12,8	11,3	0,7
Day/night temperature 09/01 to 09/30 (°C)	ATH9	73	9,7	13,2	11,5	1,0
Annual rainfall	RAINan	73	650	1148	878	140
Rainfall 04/01 to 09/30 (mm)	RAINcy	73	373	558	446	40
Rainfall 06/01 to 08/31 (mm)	RAIN68	73	88	287	174	50
Rainfall 06/01 to 09/30 (mm)	RAIN69	73	120	346	236	63
Evapotranspiration 06/01 to 08/31 (mm)	ETP68	73	445	548	487	34
Evapotranspiration 06/01 to 09/30 (mm)	ETP69	73	527	605	555	28

AROMA RESPONSE TO GENETIC VARIATIONS AND LIGHT INTENSITY IN CABERNET SAUVIGNON GRAPE BERRIES IN A PRACTICAL CANOPY MANAGEMENT APPLICATION

RESPUESTA DE AROMAS A LAS VARICIONES GENETICAS E INTENSIDAD DE LUZ SOLAR EN CABERNET SAUVIGNON CON UNA PRACTICA DE MANEJO DE CANOPIA

KOCH, Alfredo[1*]; EBELER, Susan E.[2]; MATTHEWS, Mark A.[2]; WILLIAMS, Larry E.[2]

[1]Allan Hancock College, Santa Maria, California 93454, USA. [2]University of California at Davis, Davis, California 95616, USA

***Corresponding author:** akoch@hancockcollege.edu

Abstract

The light sensitivity of several aroma compounds and in particular grassy/bell pepper aromas in Cabernet Sauvignon berries was tested for three seasons in Rutherford, California. The aim of this study was to determine how changes in grape composition brought about by artificial shading (sunlight exclusion) influence Cabernet Sauvignon berries aroma profile. Right after fruit set, clusters of Cabernet Sauvignon berries were enclosed in three different shading treatment cloth prepared to eliminate light without altering cluster