

CLIMATE AND HARVEST TIME IMPACT ON AROMATIC COMPOUNDS OF SAUVIGNON BLANC WINE

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ABSTRACT

Research was carried out in vineyard of King Peter I Karadjordjevic-Royal Winery at Oplenac-Topola municipality. Climate parameters included: mean monthly, vegetation and annual temperature and precipitation. Different compounds of aromatic complexes were detected by GC-MS and GC-FID analysis. Wine was made from grapes harvested in full maturity and fifteen days after full maturity. The relationship between measured attributes of aromatic wine complex were visualized using principal component analysis and presented graphically through dispersion diagram. In wine were detected following aromatic compounds: higher alcohols, lactones, organic acids, esters and amides. During the research it variation of the relative proportion of aromatic compounds was found in Sauvignon blanc wine influenced by different climate conditions, accordingly to temperature and precipitation distribution.

INTRODUCTION

The optimum harvesting time and grapes processing is often overlaps with the greatest concentration of most of phenolic compounds in berries. In this case talking about so-called "phenolic maturity." From fruitset through veraison and ending with grapes full maturity in berry comes drastic biochemical and physiological changes that can be expressed through varying and accumulation of individual chemical compounds. What is specific to each vine variety is to synthesis and its concentration varies from variety to variety (Kennedy et al., 2001).

The generally classification of aromas according to its origin implied four main groups: primary aroma (original grape flavor), secondary aroma resulting during primary processing (grapes pressing and enzyme activity), aroma that becomes during fermentation and aging aroma that occurs during wine storing and ageing. Total content of aromatic components in wine ranges from 0.8 to 1.2 g/l, where in 50% are higher alcohols. The detection threshold of smell different aromatic substances ranges between 10^{-4} and 10^{-12} g/l (Rusjan, 2010).

Wine aroma, physicochemical and sensory properties of wine can be affect under environmental site conditions-climate conditions (B duc -Cîmpeanu et al., 2010). According Ribereau-Gayon et al. (2006) in grapes and wine there are more than 800 aromatic compounds, but 30-40 of them are the most fragrant active. The most important aromatic compounds belongs to the following groups: terpenes, higher alcohols, benzene derivative, C13 norisoprenoids, esters, volatile organic acids and phenols (Jackson, 2008).

These compounds give a real grapes and wine aroma as single compounds or conjugated with sugars. Conjugated terpenes give a bitter taste, while during fermentation of geraniol under the influence of enzymatic reactions in presence of yeast turns into pink oxide. The other part of aromatic complex is non-volatile components which form the primary aroma (Kennison et al., 2008).

Floral tones of wines giving terpenes, fruitiness comes from esters and lactones, while herbal tones are related to aldehydes and higher alcohols. (Feel et al., 2007a, b; Castro-Vasquez et al., 2002; Schneider et al., 2001).

MATERIAL AND METHOD

Research was carried out in vineyard of King Peter I Karadjordjevic-Royal Winery at Oplenac-Topola municipality. Vineyard with Sauvignon blanc is planted in 2004 with row spacing of 2.70 m and 1.0 m spacing between vines in row. It is geographically positioned at GPS coordinates N 44° 14' 4" and E 20° 41' 15". Training system is characterized with height of 90 cm on which Guyot pruning is used. All experimental vines were uniformly pruned where one arc was left with eight buds and spur with two buds. Data for analysis of climatic site conditions is presented in multi-year series from 1982-2011 and separately for 2010 and 2011 year. Following parameters were analyzed: temperature (mean monthly, vegetation and annual temperature) and precipitation distribution: annual and vegetation.

Microvinification was performed in laboratory of Faculty of Agriculture, Belgrade University selected *Saccharomyces cerevisiae* yeasts strains-R2 Lalemand were used. Wine was made from grapes harvested in full maturity and fifteen days after full maturity.

For determination aromas, samples were prepared by liquid-liquid extraction, 25 ml of wine is measured in flask and 5 ml of methylene chloride was added. Extraction was done with magnetic stirring for 1 h in ice bath. After extraction resulting mixture is left in ultrasonic bath for 5 minutes to get "bust" obtained emulsion. The organic phase was separated and dried with anhydrous sodium sulfate. GC-MS and GC-FID analyzes were done on Agilent 7890A. Aromatic compounds were identified comparing their EI mass spectra with spectra from the library Wiley7 and Nist05 using software NIST MS Search 2.0. as well as comparing calculated retention index (RI) and retention indices of library Wiley7 and Nist05. Related concentrations were determined on the basis of peak areas in FID chromatogram. Chemical analysis of wine samples is carried out in laboratories of Department of Instrumental Analysis at the Department of Organic Chemistry, Faculty of Chemistry, University of Belgrade.

For data analysis software IBM SPSS Statistics 2.0, Chicago, IL, USA was used. The relationship between measured attributes of aromatic wine complex were visualized using principal component analysis (Principal Component Analysis, PCA) and presented graphically through dispersion diagram.

RESULTS AND DISCUSSIONS

1. Temperature

The average annual temperature for the period 1982-2011 to Oplenac was 11.3°C, while mean vegetation temperature was 16.8°C. During experimental years (2010-2011) observed variation of average monthly annual and vegetation temperature. During 2010, average monthly temperature varied in range of 0.0-21.9°C and in 2011 the variation ranged from 0.6-22.5°C.

Compared with period from the beginning of measurements in this climate station (1982-2011), June (21.5°C) and August (21.9°C) in 2010 can be considered as very hot months. Average annual temperature was in range of multi-year average for 1982-2011 period, while the average vegetation temperature was slightly lower (16.3°C).

In 2011 summer months (June with 20.0°C, July with 21.7°C and August with 22.5°C) were very warm and December (4.2°C) and November (3.8°C) were very cold compared to observations from 1965-2011 period (Figure 1). Average monthly temperature in September (20.6°C) was the highest ever measured for this month at this station. Also, in 2011 mean annual (11.6°C) and vegetation temperature (17.5°C) were higher than long-term average (11.3°C and 16.8°C, respectively).

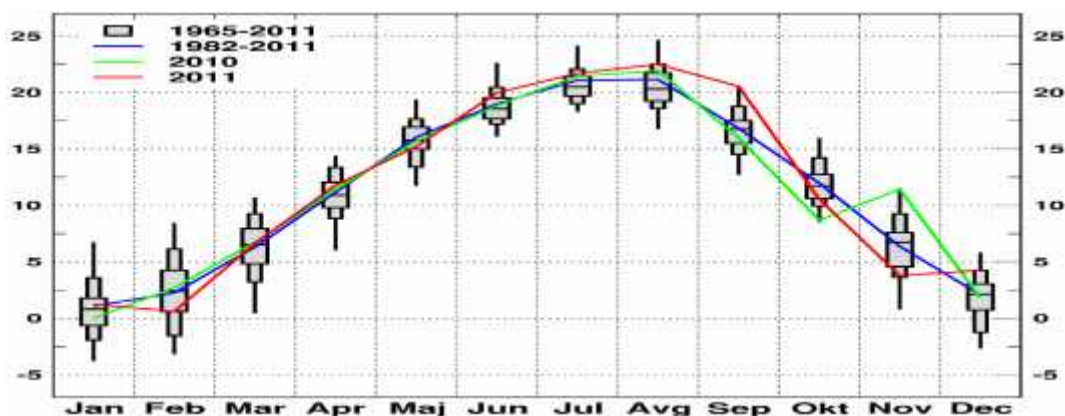


Figure 1. Average month temperature (°C) for 1982-2011 period 2010 and 2011 years

2. Precipitation

During the period from 1982-2011, average annual precipitation was 691.3 mm, whereby during growing season precipitation of 447.8 mm has been registered. On the basis of average precipitation for 2010, it can be said that this year is characterized by significantly rainy period. In 2010, average amount of precipitation per annum amounted to 832.1 mm, while during growing season precipitation was 546.8 mm. In 2011, during annual period but also during growing season, less precipitation was fallen (491.2 and 330.8 mm, respectively) compared to those in 2010 and period from 1982-2011 (Figure 2).

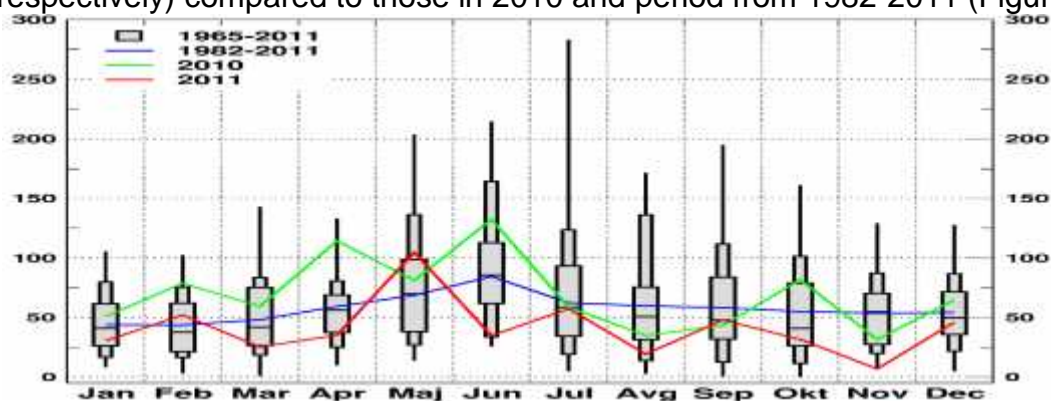


Figure 2. Monthly precipitation sum for period 1982-2011 (mm)

3. Aromatic complex of Sauvignon blanc wine

Of higher alcohols the biggest relative proportion in the period of later maturity in 2010, characterized 2-phenylethanol (65.4%). Among other higher alcohols with a higher relative proportion were detected p-hydroxyphenethyl and 3-methylthio-1-propanol, an alcohol which is the relative proportion was same in both terms of harvesting. Bigger relative share in the period of full maturity was recorded for 1-hexanol (0.6%) and benzyl alcohol. In the period of later harvest benzyl alcohol was detected in traces. Wines that are made from late harvest relative proportion of higher-alcohol 2-phenylethanol was higher compared to wines from the term of full maturity. The relative proportion of p-hydroxyphenethyl in this harvest period was the same as in the period of full maturity. The relative proportion of 1-hexanol was lower.

The same relative proportion in wines is determined for 3-hydroxy-4-phenylbutan-2-one in both harvest terms. Isoamyl acetate during a later harvest had more value (1.2%). Ethyl-3-hydroxy-butanoate in a later harvest was detected in traces. The relative proportion of -butyrolactone during term of later harvest was slightly higher (4.3%). Ethyl heksaonat in both terms of harvesting had similar values of relative proportion. Dihydro-5-(1-hydroxyethyl)-2 (3H)-furanone is detected during the full maturity in trace.

Table 1

Relative proportion (%) of aromatic complex in Sauvignon blanc wines

RT	RI	Aromatic compound	Maturity			
			2010		2011	
			Full	After 15 days	Full	After 15 days
4.35	868	1-hexanol	0.6	0.3	0.2	0.2
4.55	874	isoamylacetate	0.7	1.2	0.5	0.8
5.01	905	4-hydroxymethyl-2-methyl-1.3-dioxolane	/	/	0.1	/
5.37	917	-butyrolactone	3.5	4.3	3.3	4.1
5.85	937	ethyl-3-hydroxy butanoate	0.1	t	t	t
6.61	964	benzaldehyde	t	t	t	t
7.11	979	3-methylthio-1-propanol	0.2	0.2	0.3	0.3
7.13	980	hexanoic acid	0.8	1.2	0.6	0.3
7.70	1001	ethyl hexanoate	0.5	0.6	0.3	0.2
8.94	1035	benzyl alcohol	0.1	t	t	t
9.72	1057	ethyl-4-hydroxybutanoate	0.5	0.9	0.9	3.0
12.00	1117	2-phenylethanol	56.6	65.4	73.2	76.1
12.93	1138	N-(3-methylbutyl) acetamide	0.2	0.2	/	t
14.51	1177	ethyl hydrogen succinate	18.0	13.2	11.4	8.8
14.59	1178	octanoic acid	0.1	0.2	0.2	0.1
14.85	1182	diethyl succinate	6.6	3.9	2.5	1.2
15.51	1197	ethyl octanoate	0.8	1.0	0.5	0.3
16.37	1214	dihydro-5(1-hydroxyethyl)-2(3H)-furanone	t	0.1	0.1	t
18.15	1257	2-phenylethyl acetate	0.1	0.3	0.2	0.2
18.68	1269	diethyl 2-hydroxysuccinate	3.4	1.9	0.9	0.3
20.15	1303	5-oxotetrahydro-furan-2-carboxylic acid	2.1	1.1	1.0	0.7
21.02	1322	2,3-dihydroxi benzoic acid	0.2	0.1	/	/
22.14	1348	3-hydroxy-4-phenylbutan-2-one	0.1	0.1	0.4	0.2
22.82	1365	9-decanoic acid	0.4	0.3	0.1	0.1
23.15	1370	n-decanoic acid	0.4	0.7	0.6	0.5
23.59	1381	2-hydroxy-3-methyl-diethyl succinate	1.5	0.7	0.4	0.2
23.94	1389	Ethyl-9-decanoate	0.3	0.1	0.1	t
24.30	1397	Ethyl decanoate	0.2	0.2	0.4	0.1
25.59	1428	p-hydroxyphenethyl alcohol	0.3	0.3	0.4	0.4
25.78	1432	isoamyl ethyl succinate	0.1	0.1	t	t
26.19	1442	ethyl 2-hydroxy-3-phenylpropanoate	0.5	0.4	0.4	0.3
29.97	1531	2,5-dihydroxy benzoate	0.2	0.1	/	/
31.41	1567	3-hydroxy-4-methoxy benzoic acid	t	/	t	t

RT-retention time; RI-retention index; t-detected in traces

The ethyl ester 5-oxo-tetrahydrofuran-2-carboxylic acid had the highest values in terms of full maturity, in later harvesting relative proportion declined. From organic acids

were recorded the hexane and n-dacanoic acid in the period of later harvest. Relative proportion of butyl ester in all wines from both term harvest recorded minimal variation.

Esters such as ethyl decanoate, ethyl 2-hydroxy-3-phenylpropanoate and 2,5-dihydroxy methyl benzoate by their relative proportion in wines have been varied to a minimum in both terms of harvesting. Ethyl-4-hydroxybutanoate in wines harvested in the period of later harvesting had higher relative proportion. Same trend of variation was determined for ethyl octanoate.

Aldehyde compounds of the benzaldehyde was detected in trace amounts. Amides were not present except N-(3-methylbutyl) acetamide with the same relative proportion in two harvest terms.

In the wines from 2011 of higher alcohols the highest relative proportion is determined for 2-phenylethanol with same variation trend as in the previous year. The same trend was noted for p-hydroxyphenethyl alcohol. The benzyl alcohol was detected in trace amounts while the 1-hexanol and 3-methylthio-1-propanol had the same trend of variation.

For dihydro-5- (1-hydroxyethyl) -2 (3H) -furanone, 2-phenyl acetate and 3-hydroxy-4-phenylbutan-2-on are determined according in small variation in both terms of harvesting. Ethyl-3-hydroxybutanoate was detected in trace amounts.

Among the organic acids relative proportion of octanoic acid did not vary significantly by harvest time. Hexanoic acid and 5-oxotetrahydro-furan-2-carboxylic acid had same trend as in previous research year. The relative proportion of 9-butyl ester was not changed by harvest time.

During 2011 in wines were not detected esters of benzoic acid. Ester compounds have a higher relative proportion in period of full maturity.

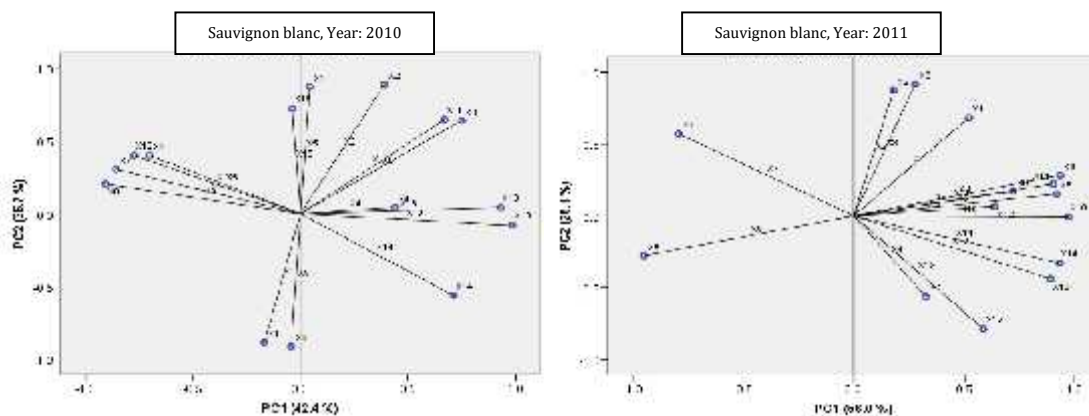
Aldehyde compounds had the same variation trend as in the previous year, while the presence of amide compounds in wines this year has not been determined. The results of chemical analysis for 2010 and 2011 are shown in Table 1.

For majority of determined aromatic complex compounds were higher in relative proportion as a result of meteorological conditions that prevailed (over the average daily temperature due to drought period and less rainfall). In dispersion diagrams 1 and 2 shown accumulation of aromatic complex compounds and correlation of all compounds. This results are according to Jones i Davis, 2000; Spayd et al., 2002 and Ruml et al., 2012.

Table 6

Used codes for aromatic complex compounds in PCA analysis

Cod	Compound	Cod	Compound
X1	1-hexanol	X14	dihydro-5(1-hydroxyethyl)-2(3H)-furanone
X2	isoamylacetate	X15	2-phenylethyl acetate
X3	-butyrolactone	X16	diethyl 2-hydroxysuccinate
X4	benzaldehyde	X17	5-oxotetrahydro-furan-2-carboxylic acid
X5	3-methylthio-1-propanol	X18	3-hydroxy-4-phenylbutan-2-one
X6	hexanoic acid	X19	2-hydroxy-3-methyl-diethyl succinate
X7	ethyl hexanoate	X20	p-hydroxyphenethyl alcohol
X8	benzyl alcohol	X21	ethyl 2-hydroxy-3-phenylpropanoate
X9	ethyl-4-hydroxybutanoate	X22	3-hydroxy-4-methoxy benzoic acid
X10	2-phenylethanol	X23	4-hydroxy-3-methoxy ethyl benzoate
X11	ethyl hydrogen succinate	X24	tryptophol
X12	diethyl succinate	X25	4-hydroxy-3.5-dimethoxy benzoic acid
X13	ethyl octanoate	X26	p-hydroxycinnamic acid



**Figure 4. Dispersion diagram 1 (2010) and 2 (2011).
Analyzed aromatic complex compounds**

Vectors X3 and X6 on dispersion diagram number 1 corresponding to following compounds: -butyrolactone and hexanoic acid, respectively, making an obtuse angle, which means that these two compounds are negatively correlated (in samples with more -butyrolactone will be in average less hexanoic acid). On the other hand, vectors which are related to X13 and X14 (ethyl octanoate and dihydro-5-(1-hydroxyethyl)-2(3H)-furanone, respectively) makes very sharp inclination angle that is compounds are positively correlated (in samples with more ethyl octanoate will be in average more dihydro-5-(1-hydroxyethyl)-2(3H)-furanone). Vectors X1 and X5 makes almost a right angle (orthogonal), which means that they represent compounds which have no correlation (1-hexanol and 3-methylthio-1-propanol, respectively).

CONCLUSIONS

In 2010 average annual temperature was in the range of multi-year average for 1982-2011 period, while the average vegetation temperature was slightly lower. In 2011, mean annual and vegetation temperature was higher than long-term average. It can be concluded that 2010 year was characterized by significantly rainy period compared to several years and since 2011. In wine were detected following groups of aromatic compounds: higher alcohols, lactones, organic acids, esters and amides. Accordingly to temperature and precipitation distribution during 2010, for most of compounds of aromatic wine complex was found higher values of the relative proportion especially in term of later harvest.

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BIBLIOGRAPHY

- B duc -Cîmpeanu, C., Beleniuc, G., Grigorica, L.** 2010- Climate Change Effect on Ripening Process and Wine Composition in Oltenia's Vineyard from Romania. *Acta Horticulturae*. No. 931: 47-54.
- Castro-Vasquez, L., erez Coello, M. S., Cabezudo, M. D.** 2002- Effects of enzyme treatments and skin extraction on varietal volatile in Spanish wines made from Chardonnay, Muscat, Airen and Macabeo grapes. *Anal. Chim. Acta*. 1:1-6.
- Kennedy, J. A., Hayasaka, Y., Vidal, S., Waters, E. J., Jones, G.** 2001- Composition of grape skin proanthocyanidins at different stages of berry development. *Journal of Agricultural and Food Chemistry*, 49, pp. 5348-5355.

- Kennison, K. R., Gibberd, M. R., Pollnitz, A. P., Wilkinson, K. L.** 2008- Smoke-derived taint in wine: the release of smoke-derived volatile phenols during fermentation of Merlot juice following grapevine exposure to smoke. *Journal of Agricultural and Food Chemistry*, 56, pp. 7379-7383.
- Jackson, R.** 2008- Wine science-principles and applications, third edition, Elsevier. 317-320.
- Jones, G., Davis, R.** 2000- Climate influences on grapevine phenology, grape composition, and wine production and quality for Bordeaux, France. *American Journal of Enology and Viticulture*, 51(3):249-261.
- Jones, G.V.** 2010- Climate, grape, and wine: Structure and suitability in a changing climate. *Acta Hort.* 931, 19-28
- Prosen, H., Janeš, L., Strli, M., Rusjan, D., and Koar, D.** 2007a- Analysis of free and bound aroma compounds in grape berries using headspace solid-phase microextraction with GC-MS and a preliminary study of solid-phase extraction with LC-MS. *Acta. Chim. Slov.* 54, 25-32.
- Prosen, H., Koar, D., Strli, M., Rusjan, D.,** 2007b- LC-MS in wine analysis. *LC GC Eur.* 12:617-621.
- Ribereau-Gayon, P., Glories, Y., Maujean, A., and Dubourdieu, D.** 2006- Handbook of enology vol. 2, The chemistry of Wine Stabilization and Treatments. John Wiley & Sons Ltd. England. 205-231.
- Ruml, M., Vukovi, A., Vujadinovi, M., urdjevi, V., Rankovi -Vasi, Z., Atana kovi, Z., Siv ev, B., Markovi, N., Matijaševi, S., and Petr vi, N.** 2012- On the use of regional climate models: Implications of climate change for viticulture in Serbia. *Agric. For. Meteorol.* 158, 53-62
- Rusjan Denis** 2010- Aromas in grape and wine. Methodologies and results in grapevine research. pp. 411-442
- Schneider, R., Razungles, A., Augier, C., Baumes, R.** 2001- Monoterpenic and norisoprenoidic glycoconjugates of *Vitis vinifera* L. cv MerlotB as precursors of odorant in Muscated wines. *J. Chromatogr. A.* 936:145-157.
- Spayd, S.E., Tarara, J.M., Mee, D.L., Ferguson, J.C.** 2002- Separation of sunlight and temperature effects on the composition of *Vitis vinifera* cv. Merlot berries. *American Journal of Enology and Viticulture*, 53:171-182.