"TERROIR" AND GRAPE AND WINE QUALITY OF NATIVE GRAPE VARIETY ISTRIAN MALVASIA

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Abstract

Viticulture and wine production have a historical tradition in Istria. First written document of vine cultivation in this area date since antiquity. The most wide spread vine variety in Istria is Istrian Malvasia (white variety), and it capture about 60% of total vineyard surface in Istria today. The Istrian Malvasia is a native grape variety in Istria, and it is one of the best varieties in a huge family of Malvasian varieties from Mediterranean basin. The Istrian Malvasia gives quality grapes for high quality wine production. Except the variety, on high quality of wine, a location of vineyard – «terroir» also has a very strong impact.

The objective of this research was to establish how different locations of vineyards influenced on grape and wine quality of Istrian Malvasia. Four specific locations have been chosen for this research. Those are: Pula – southern part of Istrian peninsula, with shallow red soils and low amount of rain in vegetation, Visnjan – western part of peninsula, with characteristics deep red soils and good physical and chemical properties, Motovun – central part of peninsula, with gray («flysch») soils, rich with clay, and bad physical and chemical properties and cold winter period and Buje – northwestern part of peninsula, with brown soils, good physical and chemical properties and good rain distribution through year. On all locations a growing form was Guyot – single or double branched.

Grapes and wine were analyzed from each location for harvest 2002. The content of acetate and ethyl esters, fatty acids and free monoterpenes was analyzed from wine extracts obtained by the solid phase extraction (SPE) method using C18 as a sorbent. SPE has already been applied for the analysis of aroma compounds from wine and grapes (Wada et al., 1997., Carballeira et al., 2001., López et al., 2002.). The content of higher alcohols was analyzed from wine distillates. All aromatic compounds were analyzed by gas chromatography. Wine from Buje location contains higher level of volatile esters, particularly iso-amyl acetate (average 2,04 mg/L), significantly higher then on the other locations. The wine from Buje location also contains significantly higher amount of free monoterpenes, especially linalool (average 27 µg/L) and geraniool (average 49 µg/L). The wine from Motovun location contains higher amount of higher alcohols, especially 2-phenyl ethanol (average 26,42 mg/L), significantly higher then on the other locations.

Summarized, all results show how not only the variety but also location of vineyard – «terroir» has a strong impact on the quality of grape and wine.

La qualité du raisin et du vin de la Malvasie d'Istrie en fonction du terroir

La culture de la vigne et la production du vin sur le territoire d'Istrie est une tradition centenaire. Les premiers écrits qui en témoignent date de l'époque antique. La variété de raisin la plus répandue et la plus connue en Istrie est la «Malvazija Istarska Bijela» aujourd'hui présente sur environ 60% des plantations vinicole. «Malvazija Istarska Bijela» est une variété autochtone en Istrie, et une des meilleures variétés de la grande famille de Malvasie en Méditerrané. «Malvazija Istarska Bijela» donne des raisins de qualité permettant ainsi la production d'un vin fin. La qualité de ce vin est également déterminée par le terroir.

Le but de cette étude était de spécifier la façon dont le terroir influence la qualité de raisin et ainsi le vin de la «Malvazija Istarska Bijela». Pour le besoin de cette étude, quatre localités avaient été choisies. Il s'agit de « Medulin »,- la partie sud de la presqu'île ayant un sol rouge et peu profond et où les précipitations sont moins importantes durant la période de végétation ; « Zenodragi » - la partie ouest de la presqu'île dont le sol rouge et profond a d'excellentes caractéristiques physico-chimiques; « Motovun » – la partie centrale de la presqu'île, ayant un sol riche en argile et d'une moins bonne caractéristique physico-chimiques, et où les périodes hivernales sont assez froides, et « Buje » – la partie nord-ouest de la presqu'île ayant un sol brun, de bonnes caractéristiques physico-chimiques et

où la répartition des précipitations durant toute l'année est avantageuse. Sur toutes ces localités, le cépage cultivé est le Guyot (simple ou double branche).
Les analyses du raisin et de vin des vendanges 2002 ont été effectuées pour chacune des quatre localités. Les paramètres aromatiques de vin (les esters d'acétate et d'éthyle, les acides gras et le monoterpenes libres) sont analysés à partir des extraits de vin (l'extraction de phase solide) et les distillats de vin (les alcools supérieurs) par la méthode de chromatographie gazeuse (ref).
Le vin de « Buje » contient plus d'esters volatiles et tout particulièrement l'acétate iso amyle en comparaison avec les autre régions (la moyenne étant de 2,04 mg/l). Le vin provenant de « Buje » est significativement plus riche en monoterpen libres notamment de linalole (0,027 mg/l) et de geranides (0,049 mg/l). Le vin de la région de « Motovun » contient plus d'éthanol 2 phenyle comparé aux vins des autre régions (la moyenne était de 26, 42 mg/l).
Les résultats de nos investigations démontrent que la qualité du vin est déterminé de manière importante par uniquement par la variété mais aussi par le terroir où la vigne est cultivé.

Introduction

Viticulture and wine production are a part of historical tradition in Istria. First written document of vine cultivation in this area date since antiquity. The most wide spread vine variety in Istria is white Istrian Malvasia. The Istrian Malvasia is a native grape variety in Istria and it is one of the best varieties in a huge family of Malvasian varieties from Mediterranean basin. It gives quality grapes for high quality wine production (Persuric et al., 2003). Except the variety, on wine quality, a location of vineyard - "terroir" also have a very strong impact (Staver et al., 1999.; Persuric et al., 2000).
From climatic influences, soil type appears to be the least significant factor affecting grape and wine quality or to be poorly correlated with wine characteristic. Soil influences tend to be expressed indirectly through features such as heat retention, water-holding capacity, and nutritional status. The geologic origin of the parental material of the soil has little direct influence on grape quality. Fine wines are produced from grapes grown on soils derived from all three basic rock types – igneous, sedimentary and metamorphic. Examples of wine regions where the soils are primarily derived from a single rock type are Champagne (chalk), Jerez (limestone) and Mosel (schist). However, equally famous regions have soils derived from a mixture of rock types, namely, Rheingau (Germany) or Bordeaux (France) (Jackson 2000).
Similar to the data on soil attributes, much of the information on the influences of slope on grape quality is circumstantial. The effects tend to be most marked at high latitudes or altitudes.
Quality wine is produced from quality grapes. These can be estimated through chemical composition and primary and secondary aromatic profile. Istrian Malvasia is placed into variety group with considerable aromatic flower potential. Terpenes are an important group of aromatic compounds characterizing the odor. Unlike many of the aromatic constituents of wine, terpenes are primary derived from grapes. They exist in grapes in three forms. Most are found as free monoterpene alcohols or oxides. In this form they are volatile and may contribute to the fragrance of a wine. Compounds component of fermentation (secondary) aroma (volatile esters, fatty acids, higher alcohols) depend on various factors: vine variety, wine yeasts set, alcohol fermentation temperature, and particularly high influence has a chemical composition of must, especially sugar and aminoacids content, precursors of these aromas.
The objective of this research was to establish how different locations of vineyard influenced on grape and wine quality of Istrian Malvasia, with special regard to aromatic grape and wine profile. These are the first year results of a longer ongoing project.

Materials and Methods

For this research the grape from harvest 2002. from four different locations was considered. The first one was location named Pula, southern part of peninsula, with shallow red soils and low amount of rain in vegetation period. The altitude is 30 m above see level. The vineyard has a south slope. The second one was location named Visnjan; on western part of Istrian peninsula, with characteristic deep red soil and good physical and chemical properties. The altitude is 180 m above see level. The vineyard have south-west slope.
Next one was location named Motovun, in central part of peninsula, with gray ("flysch") soils, rich

with clay, and bad physical and chemical properties and cold winter period. The altitude is 220 m above see level. The vineyard have east slope. The last one was location named Buje, on northwestern part of peninsula, with brown soils, good physical and chemical properties and good rain distribution through year. The altitude is 140 m above see level. The vineyard has southeast slope.

On all locations a training form is Guyot – single or double branched. Each vineyard have as rootstock Kobber 5BB. The grape were harvested as follows; Buje at September 16th, Motovun at September 17th, Pula at September 18th and Visnjan at September 19th. From each location three grape samples were taken for sugars, titrable acidity and pH measuring.

From each location was harvested 500 kg of grape and then was divided on three equal parts, three repetitions. Each repetition was stemmed, crushed and pressed. The fermentation was controlled and guided on 17°C. Elementary grape processing and alcohol fermentation (for each site in three repetitions) have been performed in a wine minivinification of the Institute for Agriculture and Tourism in Porec. In obtained musts was determined a sugar content, total acidity and pH. Since from some sites obtained grape had unusually low sugar concentration (due to climatic circumstances), obtained wine would have very low alcohol concentration. That's why a sugar adding (2 kg/hl) was performed in all samples, resulting with particularly high alcohol content in some wines. Sulphurisation with 20 g of metabisulfit per hectoliter and sediment for 24 hours on 12 C° was performed.

Clear musts were inoculated with selectioned commercial yeasts (Saccharomyces cerevisiae VB1). Controlled alcohol fermentation on temperature 17 C° was performed in inox tanks volume 100 L.

The content of acetate and ethyl esters, fatty acids and free monoterpenes was analyzed from wine extracts obtained by the solid phase extraction method using C18 as a sorbent. SPE has already been applied for the analysis of aroma compounds from wine and grapes (Wada et al., 1997., Carballeira etal., 2001., López et al., 2002.). The content of higher alcohols was analyzed from wine distillates. All aromatic compounds were analyzed by gas chromatography.

Gas chromatographic (GC) analyses of acetaldehyde, ethyl acetate, methanol, 1-propanol, isobutyl alcohol and isoamyl alcohol were performed on Varian 3350 gas chromatograph equipped with a split/splitless injector and a flame ionization detector. 2 μl of the doubly diluted wine distillate were injected and injection mode was split (1:20). Prior to the injection, 1 ml of the internal standard solution (n-amyl alcohol) was added to the diluted distillate. Separations of compounds were performed using a 30m/0.25mmID/0.25μm df capillary column Rtx-WAX (Restek, USA) with the following parameters: initial oven temperature was 40°C for 4 minutes, raised at 5°C/min to 90°C, at 15°C/min to 235°C and then kept at 235°C for 10 minutes. The injector and detector temperatures were 160°C and 240°C, respectively. The carrier gas was helium at velocity of 1.5 ml/min. Quantification was performed by the internal standard method using Varian Star Chromatography Workstation, version 4.51 software.

The other compounds of interest were isolated from wine samples by the solid-phase extraction method using Varian Bond Elut C_{18} sorbent, packed in a 500 mg/6 ml cartridges, in combination with vacuum manifold VacElut 20 (Varian, USA). A 12.5 ml volume of wine was diluted to 25 ml with de-ionized water in a 25 ml volumetric flask and 1 ml of the internal standards solution (ethyl heptanoate and 1-undecanol) was added. C_{18} cartridges were activated by passing 5 ml of methanol and 5 ml of de-ionized water through them. Sample solution was passed through the activated sorbent and the sorbent was washed with 4 ml of de-ionized water and dried under vacuum. Compounds of interest were eluted from the sorbent with 5 ml of dichloromethane. The extract was dried over anhydrous sodium sulfate and then concentrated under the stream of nitrogen until the extract volume was reduced to 1 ml.

GC analyses were performed on a same gas chromatograph as described above. Separations of compounds of interest were done using the same chromatographic column with the following parameters: initial oven temperature was 40°C, then raised at 10°C/min to 60°C and kept for 2 min, then it was programmed at 2°C/min to 176°C followed by the raise at 10°C/min to 240°C and then kept for 20 minutes. The injector and detector temperatures were 235°C and 245°C, respectively. The carrier gas was helium at velocity of 1.5 ml/min. 2 μl of the extract were injected and injection mode was splitless for 0.75 minutes. Quantifications were performed by the internal standard method using Varian Star Chromatography Workstation, version 4.51 software.

All obtained data from analysis was performed by ANOVA, on Student-Newman-Keulse test by significance level p=0,05, p=0,01 and p=0,001 respectively.

Results and Discussion

Climatic conditions
The year 2002 had a usual temperature value, with hot summer period. But value for rainfall was not so usually. The unusual dry months was June, with only 31,2 mm and then follow very humid period, from July to September, any months over 100 mm. In September, the rainfall was 189,8 mm (Figure 1.). Such unusually bad climatic conditions affected a grape quality.

Principal chemical analyses
In such climatic conditions, the value of sugars, titrable acidity and pH in musts was very variable for each location (Table 1.). The highest content of sugars was measured by Buje and Visnjan location. For all location is evident unusually high level of acidity. The worst results were marked on Motovun location, as a consequence of bad soil chemical and physical properties and bad vineyard orientation, on east direction.
Likewise for the original musts, obtained wines were characterized by high total acidity (caused by unfavorable climatic circumstances), which ranged from 6,7 – 9,2 g/L, and it's considerably higher than usual (5 – 6,5 g/L) (Table 2.). Wines from all sites were characterized by high extracts ((20.5 – 27.0 g/L) and fullness with no regard to climatic conditions during vegetation.

Primary (variety) wine aroma

Monoterpenes
The main carriers of primary or variety aromas are monoterpenes, chemical compounds characteristic for aromatic vine varieties, in which a composition of fragrance compounds on grape is so expressed that its easy recognizable (Riberrou-Gayon 2000).
Quantity of singular monoterpenic compounds, as well as a total sum of these compounds in grape depends on variety, sanitary status, grape maturity, land and microclimatic conditions, and concentration of these compounds in wine also depends on technological processing procedure and wine care.
Concentration of free total monoterpenes in analyzed wines range between 112-225 μg/L, which are notable values (Dalla Serra et al., 2000.). According to the same authors, Istrian Malvasia is placed into variety group with considerable aromatic flower potential.
Significantly the highest concentration of total free monoterpenes was measured in wines from Buje site (224,33 mg/L), and especially big difference of 100% was in comparison with wines from site Motovun (Table 3.). Wines from other sites didn't differ significantly regarding a total monoterpenes sum.
The same as for total monoterpenes concentration, wines from Buje site had higher concentrations of singular free monoterpenes: linalool, citronelol, nerol and geraniol, while for free α - terpineol analyzed wines didn't differ significantly.

Secondary (fermentation) wine aroma

Compounds component of fermentation aroma (volatile esters, fatty acids, higher alcohols) depend on various factors: vine variety, wine yeasts set, alcohol fermentation temperature, and particularly high influence has a chemical composition of must, especially sugar and aminoacids content, precursors of these aromas (Versini, Rapp 1991).

Ethyl esters
In wines from sites Buje (3,84 mg/L) was measured a significantly higher quantity of ethyl esters, and in comparison with wine from Motovun site is for 77% higher (Table 4).
Concentrations of ethyl hexanoate, octanoate and decanoate in wines from all sites surmount olfactive threshold, and contribute to fruit wine aroma expressed in wines from all sites. Particularly should be mentioned a concentration of ethyl octanoate (which is characterized by a fragrance on green apple) in wines of Buje site (1,87 mg/L) which is significantly higher in relation to wines on other three sites.

Acetate esters
As well as for ethyl esters, total sum of acetate esters is significantly higher in wines from Buje site in relation to other sites (Table 5.). In all analyzed wines the most represented was ethyl acetate, which according to Riberrau-Gayon et al. (1999) in concentrations up to 80 mg/L contribute to olfactive wine complexness, and has a positive influence on its quality.
Regarding the other acetate esters responsible for forming of fruit-flower wine aroma should be highlighted a significantly higher concentration of isoamyl acetate in wines from Buje site, which average value of 2,04 mg/L surmount olfactive threshold, and gives a fine fragrance on banana.

Higher alcohols
Higher alcohol sum of Malvasia from four different sites range from 202,53 – 235,95 mg/L, and there are no significant differences between singular sites (Table 6.). Considering a relatively low content of higher alcohols can be concluded that these concentrations positively contribute to wanted aromatic wine profile (confirmed also by literature data, Versini, Rapp 1991). Namely, higher alcohols in concentration up to 300 mg/L contribute to a development of wanted wine aroma, while concentrations higher that 400mg/L negatively influence its aromatic characteristics.
Regarding singular higher alcohols should be mentioned a concentration of 2-phenyl ethanol (which unlike the other higher alcohols with smell on dilutant, has a very pleasant smell on roses) in wines from Motovun site (26,42 mg/L), which is significantly higher in relation to wines from other locations for 40-85%.
Regarding singular higher alcohols should be mentioned a concentration of 2-fenil ethanol (very fine rose fragrance) in Malvasia wine from site Motovun (26,42 mg/L), which is significantly higher in relation to wine from other sites for 40-85 %.

Fatty acids
Total sum of middle chain (C_6 – C_{10}) fatty acids is rather uniform and range about 20 mg/L, for exception of wine from Motovun site, with significantly the lowest concentration of 15.5 mg/L (Table 7.).
From singular fatty acids with major share is present a caprylic acid in wines from all sites.
From showed data is visible that concentration of singular fatty acids in analyzed samples doesn’t surmount olfactive thresholds, but in interaction with other volatile wine compounds (Tamborra et al., 1990.) positively influence its aromatic characteristics.

Conclusions

1. All sites gave grape and wine of high quality in a climatically unfavorable year.
2. From presented results of must chemical analysis, it is visible that Buje site gave grape with better quality characteristics in comparison with other sites.
3. Likewise, concentration of primary and secondary aromas was significantly higher in wines from Buje site in comparison with other sites.
4. Since all factors influencing a final substances of primary and secondary aromas were stable, it follows from this one year study that differences in their concentration is due to “terroir” influence.

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Figure 1. Temperature and rainfall in 2002 (data from meteorological station Porec)

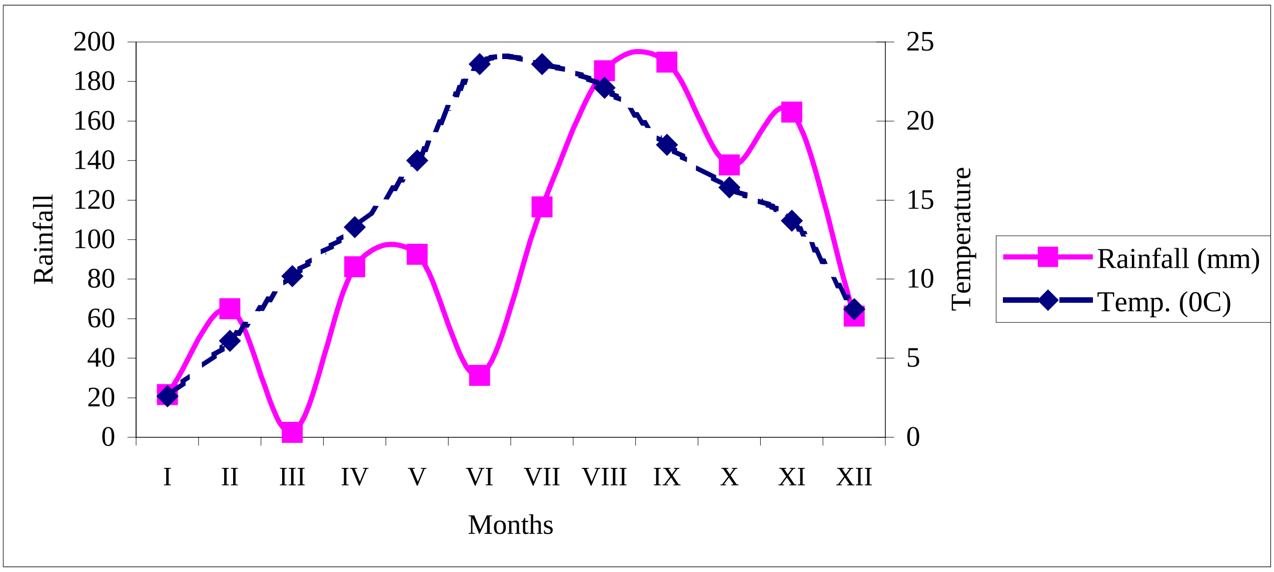

Table 1. Content of sugars, titrable acidity and pH value in must of Istrian Malvasia

Location	Visnjan	Motovun	Pula	Buje
Sugars (°Kl)	17,0	14,8	16,6	19,6
Titrable acidity (g/L tartaric acid)	10,18	9,66	8,51	9,84
pH	3,30	3,16	3,21	3,32

Table 2. Principal chemical wine analyses

SITE	WINE ANALYSES						
	Alcoh. (vol.%)	Total acids (g/L)	Extract without sugar (g/L)	Total extract (g/L)	Sugars (g/L)	Ash (g/L)	pH
Visnjan	12,7	9,2	24,1	26,6	3,5	3,3	3,2
Motovun	10,8	8,2	20,7	22,8	3,1	2,5	3,2
Pula	12,0	6,7	19,0	20,5	2,5	2,4	3,1
Buje	14,3	8,0	24,5	27,0	3,5	2,4	3,2

Table 3. Content of primary aromatic compounds in wine of Istrian Malvasia, harvest 2002(µg/L)

Site	Linalool	Alfa terpineol	Citronelol	Nerol	Geraniol	Total
Visnjan	12,33 b	23,33	12,33 b	67,67 b	35 b	150,66 b
Motovun	5,33 b	30,00	6 b	48,67 c	22,33 b	112,33 b
Pula	17 b	34,67	7,67 b	43,33 c	30,67 b	133,34 b
Buje	27,33 a	30,33	17,67 a	100,33 a	48,67 a	224,33 a
Signif.	***	ns	*	***	**	***

Table 4. Content of ethyl esters in wine of Istrian Malvasia, for harvest 2002 (mg/L)

Site	Etil heksanoat	Etil octanoat	Etil decanoat	Total
Visnjan	1,13 a	1,59 b	0,66 ab	3,38 ab
Motovun	0,68 b	1,05 c	0,45 b	2,18 c
Pula	1,04 a	1,55 b	0,62 ab	3,21 b
Buje	1,12 a	1,87 a	0,85 a	3,84 a
Signif.	***	***	**	***

Table 5. Content of acetate esters in wine of Istrian Malvasia, harvest 2002 (mg/L)

Site	Heksil acetat	2-fenil etil acetat	Etil acetat	Izo amil acetat	Total
Visnjan	0,01 c	0,05 c	26,12 bc	0,77 b	26,95 bc
Motovun	0,02 b	0,08 b	29,54 b	0,52 c	30,16 b
Pula	0,02 b	0,07 bc	21,36 c	0,63 bc	22,08 c
Buje	0,05 a	0,14 a	48,94 a	2,04 a	51,17 a
Signif.	***	***	***	***	***

Table 6. Content of higher alcohols in wine of Istrian Malvasia, harvest 2002 (mg/L)

Site	2-fenil-etanol	1-propanol	Iso-butanol	Iso-amil alcohol	1-heksanol	Total
Visnjan	17,33 b	18,06 b	33,59 a	166,19	0,78 a	235,95 a
Motovun	26,42 a	10,44 c	23,51 b	159,22	0,71 b	220,30 a
Pula	18,61 b	16,7 b	19,15 b	147,46	0,61 b	202,53 a
Buje	14,21 b	29,16 a	23,00 b	161,93	0,67 b	228,97 a
Signif.	**	***	**	ns	***	ns

Table 7. Content of fatty acids in wine of Istrian Malvasia, -harvest 2002 (mg/L)

Site	Caproic acid	Caprylic acid	Capric acid	Total
Visnjan	2,93	7,42 a	0,05 b	10,4 a
Motovun	2,63	5,18 b	0,02 b	7,83 b
Pula	3,06	7,27 a	0,04 b	10,37 a
Buje	3,25	6,9 a	0,18 a	10,33 a
Signif.	ns	*	*	*