

MECHANICAL HARVESTING OPTIMIZATION AND POSTHARVEST TREATMENTS TO IMPROVE WINE QUALITY

G. ARFELLI^{1*}, E. SARTINI², F. BORDINI³, C. CAPRARA³ and F. PEZZI³

1: Università degli Studi di Teramo, Facoltà di Agraria
Dipartimento di Scienze degli Alimenti, via C. Lerici 1, 64023 Mosciano S. Angelo, TE, Italy
2: Alma Mater Studiorum, Università di Bologna, Facoltà di Agraria
Dipartimento di Scienze degli Alimenti, p.zza G. Goidanich, 60, 47023 Cesena, FC, Italy
3: Alma Mater Studiorum, Università di Bologna, Facoltà di Agraria
Dipartimento di Economia e Ingegneria Agrarie, via G. Fanin 50, 40127 Bologna, Italy

Abstract

Aims: The aim of this work was to verify the influence of mechanical harvesting and postharvest treatments on wine composition.

Methods and results: Trials were carried out in triplicate on cv. Montuni grapes. The estimated best setting frequency for the mechanical harvester was 410 shakes/min. Comparing hand-picked and mechanically harvested grapes, the reduced extract and pH results were lower for the hand-picked grapes, showing a more evident berry breakage caused by the mechanical harvester. The wines obtained from mechanically harvested grapes had a lower phenolic compound content than wines produced with hand-picked grapes, indicating that oxidation phenomena occurred; the trend for postharvest treated grapes was different. The significantly lower amount of higher alcohols in the hand-picked grapes trial than in the mechanically harvested ones could be explained by a lower amount of their precursors and oxygen in musts. The sensory differences among the trials were significant for some parameters, but an overall view of the data suggested that the differences were not remarkable and all the wines were good.

Conclusion: Postharvest treatments reduce the loss of natural antioxidant compounds found in wines produced from mechanically harvested grapes. Mechanical harvesting does not have a negative influence on wine composition if matched with the proper vineyard characteristics, machine settings and postharvest treatments. The typicality of Montuni wine is maintained in the cases of grapes harvested mechanically with, but also without, any postharvest treatment. The use of these treatments is otherwise useful to obtain wines with a better stability.

Significance and impact of the study: With respect to mechanical harvesting, this study highlights the importance of maintaining and/or improving the quality of mechanically harvested grapes containing the harvesting costs.

Keywords: antioxidant adjuvants, mechanical harvesting, postharvest treatments, solid carbon dioxide

Résumé

Buts : Le but de ce travail de recherche était de vérifier l'influence de différents traitements mécaniques pendant et après la vendange sur la composition du vin.

Méthode et résultats : Les essais ont été menés en triple sur les raisins du cépage Montuni. La meilleure fréquence estimée pour la machine à vendanger était de 410 impulsions par minute. L'extrait réduit et le pH étaient plus bas pour la vendange manuelle, ce qui met en évidence l'écrasement de la baie du raisin en raison de la vendange mécanique. Les vins issus de raisins récoltés mécaniquement avaient une teneur en composés phénoliques plus basse que ceux obtenus avec des raisins récoltés mécaniquement, à cause du phénomène d'oxydation. La tendance pour les raisins traités après récolte était différente. La quantité significativement plus basse des alcools supérieurs dans l'essai des raisins vendangés manuellement peut être expliquée par une quantité moindre des précurseurs et de l'oxygène dans les moûts. Les différences sensorielles entre les essais étaient significatives pour quelques paramètres, mais la plupart des résultats indiquaient que les différences n'étaient pas importantes et que tous les vins étaient bons.

Conclusion : Les traitements après vendange réduisent la perte des composés antioxydants naturels dans les vins issus de raisins récoltés mécaniquement. La vendange mécanique n'a pas une influence négative sur la composition des vins, si on prend en compte les caractéristiques du vignoble, les réglages de la machine à vendanger ainsi que les traitements après la vendange. La typicité du vin issu du cépage Montuni est conservée dans le cas de vendanges mécaniques, avec, mais aussi sans, traitements après vendange. L'usage de ces traitements est utile pour obtenir des vins ayant une meilleure stabilité.

Signification : Cette étude a souligné l'importance de maintenir et/ou d'améliorer la qualité des raisins récoltés à la machine, en limitant les dépenses liées à la vendange.

Keywords : produits antioxydants, vendange mécanique, traitements après vendange, glace carbonique

manuscript received the 6th July 2009 - revised manuscript received the 13th May 2010

INTRODUCTION

The first studies about mechanical harvesters started in the United States and the first experimental mechanical harvesting of grapes began in California in 1952 (MORRIS, 1994). Major developments in juice and wine grape harvest mechanization occurred in the early and mid-1960's (SHAULIS *et al.*, 1966, SHEPARDSON *et al.*, 1969, STUDER and OLMO, 1969) and mechanization was commercially practiced by the late 1960's (BENEDICT *et al.*, 1971). Later, the technique was also developed in Europe.

Improvements in harvesting equipment over the years have made possible extensive operations. Collecting and transporting a high percentage of the production yield to the processors is economically important, but it is also essential to maintain the quality of the harvested grapes (MORRIS, 1994).

The most important parameters to be monitored during mechanical harvest are:

a. Characteristics of harvested grapes : This aspect may be specified in terms of damaged bunch, amount of the dispersed must (from damaged grapes) and presence of impurities (leaves and debris) (INTRIERI and PONI, 1990).

b. Damage to plants and to the support system for production : This is a direct cause of impurities in the harvested grapes.

c. Losses during harvesting : Losses may consist of the amount of unpicked grapes, the ones fallen to the ground, or the must dispersed on leaves during harvesting or just after, during the machine cleaning operations. These last two losses are generally grouped in the so-called hidden losses, because they are less visible (INTRIERI and PONI, 1990). Hidden losses are difficult to detect during harvesting but they are important to improve the machine settings.

The main characteristic of mechanically harvested grapes is the berry damage that induces the release of free run must (INTRIERI and PONI, 1990). Free run must is exposed to some biochemical reactions such as enzymatic phenolic oxidation and uncontrolled microbial growth that penalizes the mechanical harvesting over the manual picking.

The oxidation of phenolic compounds leads to very important modifications in grape composition, inducing the formation of polymers with a different condensation grade, evidenced by a brown colour that negatively affects both the colour and the sensorial characteristic of wine (MACHEIX *et al.*, 1991).

The postharvest handling system (MORRIS, 1983) and the use of some technological adjuvants to reduce must oxidation can improve wine quality (MORRIS *et al.*, 1972; NELSON and AHMEDULLAH, 1972; O'BRIEN and STUDER, 1977; MORRIS *et al.*, 1979; ARFELLI *et al.*, 2005). Furthermore, temperature from the time of harvest to the time of processing probably influences the quality of machine-harvested grapes more than any other factor (JONES *et al.*, 1969; MARSHALL *et al.*, 1971; O'BRIEN and STUDER, 1977; MORRIS *et al.*, 1979; PETERSON, 1979). High temperatures (above 25 °C) at the time of harvest are usually not a problem in cool areas (MOYER *et al.*, 1961; JONES *et al.*, 1969; MARSHALL *et al.* 1971), but in hot areas (such as the San Joaquin Valley in California and the Southern United States), grapes should be harvested during cool periods of the day or at night to avoid quality loss (JONES *et al.*, 1969; MORRIS *et al.*, 1979).

The cultivation of the Montuni variety is widespread in Pianura Padana, but it is very difficult to find scientific references to this grape and its characteristics. The little information about Montuni wines is provided below. Montuni grapes produce a pale yellow wine, with a delicate, pleasant and persistent aroma. The flavour is fresh and pleasantly bitter. The wine's aromatic profile is characterized by floral and herbaceous flavours. On the palate, the most important note is the sapidity with a low acidity and a medium body. This wine is delicate and harmonious.

The aim of this work was to verify the influence of mechanical harvesting and postharvest treatments on wine composition and to compare the wines produced from mechanical harvesting to those produced from hand-picked grapes. For this purpose, the optimization of mechanical harvesting regarding fruit yield, quality of the harvested product and precautions to avoid grape deterioration was initially done. Finally, the effects of mechanical harvester and some postharvest technology applications (SO₂, tannins and CO₂ addition) were studied.

MATERIALS AND METHODS

1. Grape variety and vineyard characteristics

The experiment was carried out in the Padana Valley examining the cultural conditions of this area; in particular, the Montuni white vine variety (an autochthonous vine variety, widespread in the area) which was used to carry out the trials.

The choice to carry out trials on Montuni grapes is due to the presence of this variety in a particular area of Italy where the mechanization of the vineyard is growing and the majority of this variety is already harvested by machine.

Harvest was performed on September 19, 2005. About 200 kg of sound grapes were harvested for each trial. The main characteristics of the vineyard were the following: the training system was a free cordon planted in 1995, the plantation distance was 2.5 x 1.5 m and the vertical height of the cordon was 1.75 m. The vineyard productivity was 20.4 tons/ha.

Grape characteristics were the following: sugar level 21.54 °Brix, pH 3.32, titratable acidity 9.17 g/L (expressed as tartaric acid), average weight of 100 berries 186 g, average weight of bunch 75.09 g, and detached force 2.1 N. The detached force value was a medium/low value, considered as normal for Montuni grapes. The raining period before harvest did not seem to influence this parameter.

The average bunch weight was calculated by picking all the production from three vines, weighting and counting the number of bunches. Then, the weight was divided by the number of bunches.

The average berry weight was determined by picking and weighting 1000 berries from ten different vines (100 berries per vine). The total weight was divided by 1000.

Detachment force was determined by a Texture Analyzer TA-HDi (Stable Micro System UK) equipped with a load cell of 2,5 kN and 1N of sensitivity. The data were acquired by the software integrated with the instrumentation at 200 pps of resolution.

2. Mechanical harvester settings

Manual picking and mechanical harvesting carried out using different machine settings were compared.

A VL 660 Braud (CNH group) grape harvester was used. This machine harvester is characterized by horizontal bow beaters with collecting buckets as transport system. It has a cleaning system characterized by 4 pneumatic aspirators and a mechanic ginner-separator.

Mechanical harvester speed was set at 2.8 km/h and kept constant with varying shaker frequency (360, 410, 460 shakes/min).

The vibration transmitted to the plants by the grape harvester was measured with 3 piezoelectric accelerometers (Brüel & Kjaer) connected to a load amplifier (Brüel & Kjaer, Nexus 2692) and a digital recorder (Teak, 135 t). The first accelerometer was installed on the permanent cordon of the row, whereas the other two were positioned upon the shoots at a distance of 10 and 20 cm from the first one (PEZZI and CAPRARA 2009).

The three harvesting treatments were conducted in triplicate on nine 30 m long plots prepared in the vineyard, formed by homogeneous rows without failed vines. Each plot was isolated by eliminating clusters and leaves at the ends.

The total amount of picked grapes, the visible and hidden losses, and the level of resulted mashing and plant defoliation were measured in each trial.

Product losses were expressed as a percentage of the overall production (harvested fruit + visible losses + hidden losses).

Visible losses are represented by the fruit left on the vines and ground losses. Ground losses were collected in plastic sheets while the unpicked bunches were hand-picked after the machine had passed.

Hidden losses are represented by the must adhering to the leaves left on the plants and the must dispersed by the machine's cleaning apparatus. The must on the leaves was quantified by determining the leaf moisture content, before and after harvest, corrected with the Brix degrees value, using the following:

$$M = L - \frac{D - L(1 - W_m)}{(W_m - W_l)}$$

where M, is the juice losses (g); L, is the mass of leaves with juice, after the harvester has passed (g); D, is the dry matter of the L mass (g); W_m, is the water fraction of the juice; W_l, is the water fraction of the leaves before the harvester has passed (PEZZI and CAPRARA, 2009).

The must dispersed by the fans was recovered through a hygroscopic system made of a close-mesh net (3 mm) in a jute bag and placed at the exit of the cleaning system. The juice absorbed by the bag was quantified as increased weight.

In the harvested product, the amount of released must was determined by allowing the mass to drain for 30 minutes [Must released (%) = (Must drained weight/Total mass weight) x 100].

The level of defoliation was calculated as the ratio between the average weight of the leaves lost during the passage of the grape harvester (calculated by collecting the remaining leaves) and the corresponding initial average weight measured prior to the start of the trial [Level of defoliation (%) = [(Total leaves weight - Remaining leaves weight)/ Total leaves weight] x 100].

3. Postharvest treatments

All machine settings were similar in results, therefore 410 shakes/min were chosen as the intermediate regulation. Grapes were transported to the cellar within

two hours and kept at 23 °C (MAPG, MEHGC and MEHGSO₂T) and 15 °C (MEHGCO₂). The following trials were carried out:

MAPG: hand-picked grapes.

Regarding the mechanically harvested grapes, the trials were set as follows:

- MEHGC: mechanically harvested grapes without any field treatments (control).

- MEHGCO₂: mechanically harvested grapes were added with solid CO₂ until the temperature reached 15 °C.

- MEHGSO₂T: mechanically harvested grapes were added with SO₂ (60 mg/kg by adding 120 mg/kg of potassium metabisulfite) and oenological tannins (100 mg/kg).

All grape field treatments were carried out in triplicate.

4. Winemaking operations

A traditional winemaking process was used to produce the wine from all the grapes described above. All trials were carried out in triplicate (120 L of must for each different replicate). All grapes were destemmed, crushed and pressed using a pneumatic press. Pressing was carried out using two pressing cycles of 30 and 10 minutes at 0.8 and 1.2 bars, respectively. The pressing yield was about 60 %.

Musts were added with sulphur dioxide (up to 50 mg/L), gelatine (5 mg/L), pectolitic enzymes (3 mg/L) and bentonite (200 mg/L).

Must clarification was carried out in refrigerated tanks at 4 °C for about 48 hours, in order to have the same turbidity in all trials. At the end of this process, must was devatted and temperature was increased to 18 °C to improve yeast growth. Alcoholic fermentation was induced with a starter prepared with 250 mg/L (2.5 x 10⁶ cells/mL) of dry yeasts (*Saccharomyces cerevisiae* 404 IMIA strain) and was carried out at controlled temperature (18 °C) in jacketed stainless steel tanks (160 L). All trials were added with nitrogen adjuvant up to a FAN value of 200 mg/L. The addition was carried out at the beginning and halfway through fermentation. Alcoholic fermentation showed a regular trend and finished within 8 days for all trials. Seven days after the end of alcoholic fermentation, wines were devatted and put into a refrigerated cell (-4 °C) for 4 weeks to improve tartaric stabilization. At the end of tartaric stabilization, wines were added with sulphur dioxide to 80 mg/L, and filtered through a cartridge line with a decreasing porosity (10, 8, 5, 1.2, 0.8, 0.65 µm). After filtration, samples were bottled, stored at 4 °C for 8 weeks and then analysed.

5. Chemical analysis

pH, titratable acidity, ethanol, volatile acidity, reduced extract, refractometric determination of sugar content (Brix degree), free and total sulphur dioxide and potassium were determined as stated by the Commission Regulation (OFFICIAL JOURNAL ECC 1990). Reducing sugars were determined as described by LANE and EYNON (1923). Malic and lactic acids were determined as described by CASTELLARI *et al.* (2000). Total phenolic index was evaluated as gallic acid using the optical density (OD) at 280 nm (RIBÉREAU-GAYON, 1970). Optical density at 420 nm (OD) (SUDRAUD, 1958), catechins (ZIRONI *et al.*, 1992), and phenolic fractions by HPLC (CASTELLARI *et al.*, 2002) were also determined. The Browning test (Δ OD 420 nm) was carried out by putting 20 mL of wine into a 70 mL test-tube closed with a teflon (polytetrafluoroethylene) screw top. These tubes were put into a stove at 50 °C for 48 hours and then the OD at 420 nm was determined. Δ OD = OD 420 nm (after the browning test) - OD 420 nm (before the browning test). Turbidity was measured using a nephelometer (NTU, Nephelometric Turbidity Units). Chemical analyses were carried out 13 weeks after the end of alcoholic fermentation.

6. Microbiological analysis

Microbiological analyses were carried out immediately after pressing. Total yeasts were grown on Sabouraud 4 % Glucose Agar at 28 °C for 3 days. Apiculate yeasts were grown on WL Agar supplemented with Cycloheximide (10 mg/L) at 28 °C for 4 days. Green colonies were analysed using a microscope to confirm the microorganism nature. Acetic bacteria were grown on GYC Agar supplemented with Cycloheximide (10 mg/L) at 28 °C for 4 days. Lactic bacteria were grown on MRS Agar enriched with tomato juice broth and supplemented with Cycloheximide (10 mg/L) under anaerobic conditions at 30 °C for 6 days. Cell counts in musts (CFU/mL) were determined by plating 1 mL of the appropriate dilution, in duplicate, on the respective growth substrates.

7. GC-MS analysis

GC-MS analysis was carried out using a GC-mass spectrometer Finnigan Trace DSQ Quadrupole (Thermo Finnigan, San Jose, CA) equipped with a Stabilwax (30 m, 0.25 mm ID, 0.25 µm) (Restek, Bellefonte, PA). GC settings were as described by GERBI *et al.* (1992). Mass spectrometer settings were: Ion Source: electron Ionization (EI), Ion Polarity: POS, Ion Source Temperature: 250 °C, MS transfer line: 220 °C, Turbomolecular Pump: 70 L/sec, Acquisition: full Scan, Mass range: 30-400 m/z, Carrier gas: He, Gas flow: 1.0 mL/min, and SSL: 250 °C. The data were processed using Xcalibur Data System Software 1.4.1 SP3 (Thermo

Finnigan, San Jose, CA). Compounds identification was carried out based on the comparison of the spectra of the unknown compounds with the spectra of the standard compounds. GC-MS analyses of wine were carried out in triplicate 60 days after bottling.

8. Sensory analysis

Sensory analyses were carried out in a sensory room designed according to ISO 8589:2007 rules. Descriptive analysis was carried out in only one session. Sensory profile was determined using 10 descriptors chosen by the panel in a preliminary session as stated by the ISO 11035: 1994 rules and according to their importance in Montuni wines. Skilled judges (n=12) were trained as required by the ISO 8586-1: 1993 rules. Regarding each descriptor, judges were asked to evaluate the samples on a 7-point scale of intensity. Zero (0) corresponded to the absence of perception while seven (7) corresponded to the highest perception level.

9. Statistical treatments

Statistical treatment of data was performed using Statistica 5.0 for Windows (StatSoft, Inc., Tulsa, OK). An ANOVA and a Tukey test were used to highlight the effects and interactions of the independent variables on chemical data. The data reported in tables correspond to the mean of three replicates for fixed compounds and nine replicates (three replicates of trials and three replicates of analysis) for volatile compounds.

RESULTS

1. Mechanical harvester settings

Table 1 shows the maximum acceleration and the number of more relevant accelerations (> 300 m/s²). Different settings induced different mechanical effects on the vines. Accordingly, the shaker frequency

improvement was found significantly related to the number and intensity of accelerations.

The above cited differences were not so significant when considering the parameters presented in table 2. This could be due to the condition of grapes at harvest because of the rainfall during the final ripening phase. This climatic trend could have affected the skin toughness of berries.

The acceleration increase was different according to the different positions: higher values were detected at the maximum distance from the permanent cordon (20 cm). Increasing the beater frequency induced an evident increase of the defoliation index, while it didn't modify the percentage of released must which was quite high in all trials.

The total product losses were limited and characterized by small differences between the different trials (from 7.2 to 7.7 %). The most important losses were ground losses favoured by an easy fall-off of berries to the ground in front of the grape harvester. The beater setting affected the different types of losses: increasing the shaking frequency didn't modified substantially the amount of ground losses but decreased the unharvested fruit fraction and increased the hidden losses caused by the must dispersed on leaves and by the harvester cleaning system. For this reason, as reported in materials and methods, the shaking frequency was set to 410 shakes/min for the subsequent trials.

2. Oenological results

Table 3 shows the must data.

Reducing sugars and total titratable acidity didn't show any statistical differences, thus confirming a sufficient homogeneity of the grapes used for the trials. pH and potassium data were higher in all the mechanically harvested grape trials than in the MAPG trial.

Table 1. Influence of shaking frequencies on transmitted acceleration.

| Shaking Frequency (shakes/min) | Maximum acceleration (m/s ²) | | | | | | Number of accelerations > 300 m/s ² | | | | | |
|---|--|---|------|---|------|---|--|---|-----|---|-----|---|
| | 360 | | 410 | | 460 | | 360 | | 410 | | 460 | |
| On cordon | 545 | A | 577 | A | 1222 | B | 4 | A | 20 | A | 108 | B |
| On shoot (10 cm far from the cordon) | 727 | A | 1035 | B | 1393 | C | 11 | A | 50 | B | 131 | C |
| On shoot (20 cm far from the cordon) | 986 | A | 1520 | B | 1763 | C | 47 | A | 184 | B | 273 | C |

Values are the mean of ten replicates. Values not identified by the same letters are different for p ≤ 0.01

Table 2. Influence of shaking frequencies on defoliation and losses.

| Shaking Frequency (shakes/min) | | 360 | | 410 | | 460 | |
|-------------------------------------|---|-------|-----|-------|-----|-------|-----|
| Defoliation index | % | 10,07 | A | 21,94 | B | 24,51 | B |
| Must released | % | 16,05 | n.s | 16,20 | n.s | 16,39 | n.s |
| <i>Visible losses</i> | | | | | | | |
| On ground losses | % | 4,009 | n.s | 4,470 | n.s | 4,290 | n.s |
| Unpicked bunch | % | 1,750 | b | 0,480 | ab | 0,050 | a |
| <i>Hidden losses</i> | | | | | | | |
| Must dispersed on the leaves | % | 0,780 | n.s | 1,040 | n.s | 1,640 | n.s |
| On harvester cleaning system | % | 0,640 | n.s | 1,530 | n.s | 1,690 | n.s |
| Total losses | % | 7,18 | n.s | 7,52 | n.s | 7,67 | n.s |

Values are the mean of three replicates. Values not identified by the same letters are different for $p \leq 0.01$ (capital letters) and $p \leq 0.05$ (small letters)

Table 3. Musts composition

| Trials | | MAPG | | MEHGC | | MEHGCO ₂ | | MEHGSO ₂ T | |
|----------------------------|------|----------|------|----------|------|---------------------|------|-----------------------|------|
| Reducing sugars | g/L | 212 | n.s. | 214 | n.s. | 203 | n.s. | 207 | n.s. |
| pH | | 3,11 | A | 3,36 | B | 3,32 | B | 3,35 | B |
| Titrateable acidity | g/L | 9,2 | n.s. | 9,2 | n.s. | 9,3 | n.s. | 9,0 | n.s. |
| Total phenols | mg/L | 398 | a | 435 | b | 443 | b | 511 | c |
| Potassium | mg/L | 1276 | A | 1471 | C | 1374 | B | 1569 | D |
| Turbidity | ntu | 13 | A | 106 | C | 70 | B | 80 | B |
| Total yeasts | cfu | 1,50E+05 | A | 2,70E+06 | B | 2,30E+06 | B | 3,60E+05 | A |
| Apiculate yeasts | cfu | 4,50E+04 | A | 1,80E+06 | C | 1,60E+06 | C | 2,20E+05 | B |
| Acetic bacteria | cfu | 6,20E+04 | B | 1,50E+05 | C | 1,50E+05 | C | 2,00E+02 | A |
| Lactic bacteria | cfu | 2,60E+04 | B | 1,20E+05 | C | 1,10E+05 | C | <100 | A |

Values are the mean of three replicates (*). Values not identified by the same letters are different for $p = 0.01$ (capital letters) and $p \leq 0.05$ (small letters).

Turbidity was higher in the mechanically harvested grape must trials than in the hand-picked grape musts trial. The highest turbidity value was related to the mechanically harvested grapes without any post-treatments.

Phenolic compound content was higher in mechanically harvested grape musts than in MAPG musts. The trend of phenolic compounds was not the same for mechanically harvested grapes. The phenolic content in MEHGSO₂T was higher than in the musts obtained from the other mechanically harvested grapes. Yeast and bacterial counts were lower in MAPG musts than in mechanically harvested grape musts with or without carbon dioxide addition. The use of sulphur dioxide and tannins led to the lowest yeast and bacterial count.

The wine data (Table 4) confirmed the good randomization of the grapes used for the trials, as reported above. A difference of 0.8 % (v/v), even if not statistically significant, was detected in ethanol content. Reducing sugars and volatile acidity didn't show any statistical differences confirming that there wasn't a significant development of microorganisms before alcoholic fermentation (see Table 3) and that the fermentation process was normally carried out in all trials.

The MAPG trial showed the lowest pH value, while the mechanical harvest trials were not significantly different.

The total phenols data (Table 4) indicated that the amount of these compounds in wines obtained using mechanically harvested grapes without any field treatment (MEHGC) was lower than in MAPG. The wine colour

Table 4. Wine composition: fixed compounds.

| Trials | | MAPG | | MEHGC | | MEHGCO₂ | | MEHGSO₂T | |
|------------------------------|-------------|-------------|------|--------------|------|---------------------------|------|----------------------------|------|
| Ethanol | g/L | 13,28 | n.s. | 13,53 | n.s. | 12,79 | n.s. | 13,04 | n.s. |
| Reducing sugars | g/L | 3,7 | n.s. | 4,7 | n.s. | 4,1 | n.s. | 4,3 | n.s. |
| Reduced extract | g/L | 19,1 | A | 20,7 | B | 20,7 | B | 21,1 | B |
| pH | | 3,08 | a | 3,24 | b | 3,23 | b | 3,28 | b |
| Titrateable acidity | g/L | 7,75 | n.s. | 7,76 | n.s. | 7,63 | n.s. | 7,48 | n.s. |
| Volatile acidity | g/L | 0,31 | n.s. | 0,29 | n.s. | 0,35 | n.s. | 0,35 | n.s. |
| Total sulphur dioxide | mg/L | 79 | n.s. | 83 | n.s. | 85 | n.s. | 86 | n.s. |
| Total phenols | mg/L | 338 | B | 294 | A | 323 | B | 398 | C |
| Δ OD | | 0,012 | A | 0,015 | BC | 0,014 | AB | 0,018 | C |
| OD 420 nm | | 0,103 | A | 0,130 | C | 0,114 | B | 0,133 | C |
| Catechins | mg/L | 16,6 | n.s. | 12,4 | n.s. | 12,8 | n.s. | 17,0 | n.s. |
| Gallic acid | mg/L | 1,876 | B | 1,017 | A | 1,829 | B | 3,070 | C |
| (+) Catechin | mg/L | 4,373 | C | 2,313 | A | 3,308 | B | 4,593 | C |
| (-) epicatechin | mg/L | 5,933 | C | 4,246 | A | 4,944 | B | 5,539 | C |
| Caftaric acid | mg/L | 26,6 | C | 16,7 | A | 21,1 | B | 26,9 | C |
| Coutaric acid | mg/L | 2,128 | A | 2,057 | A | 2,954 | B | 3,457 | C |
| Rutin | mg/L | nd | A | 0,489 | C | 0,373 | B | 0,747 | D |

Values are the mean of three replicates (*). Values not identified by the same letters are different for $p \leq 0.01$ (capital letters) and $p \leq 0.05$ (small letters).

was statistically lighter in the MAPG trial than in all the others.

The highest oxidative stability was found in the MAPG trial.

Gallic acid and flavans concentrations were statistically lower using mechanically harvested grapes without any treatments (MEHGC) than in the MAPG trial.

Caftaric acid content was lower in the mechanically harvested grape trials without sulphur dioxide protection than in the MAPG trial.

Rutin was not detected in MAPG, trial confirming that a skin damage occurred in the other trials.

Higher alcohols (Table 5) were quantitatively the largest group of flavour compounds in our wines, as normally in alcoholic beverages (NYKÄNEN 1986). The sum of alcohols in no case exceeded the concentration of 400 mg/L, described by RAPP and MANDERY (1986) as the threshold where they would contribute in a negative way to the wine's aroma.

Half of the higher alcohols detected (Table 5) were not statistically different, some were even detected in high concentration. Eight compounds were statistically different

but only four of them showed concentrations higher than their olfactory threshold: isoamyl alcohol (sweet flavour) (LI *et al.*, 2008), 3-ethoxy 1-propanol (fruit flavour) (MOYANO *et al.*, 2002), 3-methylthio 1-propanol (cooked vegetables flavour) (CULLERÉ *et al.*, 2004) and phenyl-ethyl alcohol (flower and rose flavour) (LI *et al.* 2008). No threshold is known for tyrosol in wine (GARDE-CERDÁN *et al.* 2008), while in beer it is an important component of bitter flavour with a threshold of 200 mg/L (HARWICK, 1994). Phenyl-ethyl alcohol content was within the range (10-75 mg/L) described by RIBÉREAU-GAYON and SAPIS (1965).

Propanoic and butyric acid (Table 6) didn't show any statistical differences among all trials. Hexanoic, octanoic and decanoic acids were lower in the MAPG trial than in the mechanically harvested ones; this is probably due to the substrate availability.

Also phenyl-acetic acid was lower in MAPG trials than in MEHGC, but its amount was not statistically different when compared with MEHGSO₂T and MEHGCO₂ and it was below the olfactory threshold (GOMEZ-MIGUEZ *et al.*, 2007). Isobutyric and isovaleric acid content was higher with hand-picked grapes than with the mechanically harvested ones.

As for esters (Table 7), only four compounds showed statistically significant differences. Generally, their levels were lower in MAPG trial wines. Among the statistically different compound concentrations, only hexyl acetate was below the olfactory threshold (LI *et al.*, 2008), hence the other compounds affected the aroma profile of the wines. Ethyl esters of fatty acids were more abundant than higher alcohol acetates; therefore according to FERREIRA *et al.* (1995), the fruity character attributed to the aroma of Montuni wines is mainly related to fruity notes (apple, pear, cherry, etc.).

The amount of other compounds (Table 8) affecting the wine's aromatic profile was lower than their olfactory threshold (when reported in literature). The majority of these substances were lower in wines obtained from hand-

picked grapes probably for the reasons reported above. A different trend was observed for dihydro-2-methyl-3(2H)-thiophenone, 4-O-methyl mannose and 2,3-dihydro-thiophen, even if they were not always statistically higher than in the other trials.

Figure 1 shows the differences among the different trials from a sensorial point of view. Descriptive analysis put in evidence that some sensorial parameters (yellow hue, floral and banana aromas, acidity, body and intensity) were influenced by the different picking methods and postharvest treatments.

3. Discussion

The pH data (see table 3) confirm what POCOCK and WATERS (1998) have found. The highest level of

Table 5. Wine composition: higher alcohols.

| Trials | | MAPG | | MEHGC | | MEHGCO ₂ | | MEHGSO ₂ T | | Odour threshold |
|-------------------------|------|--------|-----|--------|------|---------------------|------|-----------------------|------|---------------------|
| 1-Propanol | µg/L | 49571 | n.s | 55644 | n.s. | 56312 | n.s. | 60120 | n.s. | 314000 ^a |
| 2 Methyl-1-Propanol | µg/L | 13152 | n.s | 13450 | n.s. | 11890 | n.s. | 10525 | n.s. | 40000 ^b |
| 1-Butanol | µg/L | 503 | n.s | 556 | n.s. | 504 | n.s. | 576 | n.s. | 150000 ^d |
| 3-Penten-2ol | µg/L | 75 | n.s | 60 | n.s. | 68 | n.s. | 77 | n.s. | unknown |
| Isoamyl alcohol | µg/L | 214251 | C | 180715 | B | 180369 | B | 163512 | A | 30000 ^c |
| 2-methyl-5-hexen-3-ol | µg/L | 157 | n.s | 161 | n.s. | 197 | n.s. | 174 | n.s. | unknown |
| 1- Hexanol | µg/L | 454 | A | 539 | C | 484 | B | 487 | B | 8000 ^b |
| 3 Ethoxy-1-Propanol | µg/L | 485 | A | 684 | B | 824 | C | 795 | BC | 100 ^a |
| (2R,3R)-2,3-Butanediol | µg/L | 10728 | n.s | 10617 | n.s. | 10129 | n.s. | 10461 | n.s. | 120000 ^c |
| (Z)-3-Hexen-1-ol | µg/L | 45 | A | 92 | B | 88 | B | 100 | B | 400 ^b |
| (2S,3S)-2,3-Butanediol | µg/L | 1489 | A | 2226 | B | 2091 | B | 2306 | B | 120000 ^c |
| 3-Methylthio-1-Propanol | µg/L | 1254 | n.s | 1187 | n.s. | 1196 | n.s. | 1104 | n.s. | 1000 ^b |
| Benzyl alcohol | µg/L | 9 | a | 18 | b | 11 | ab | 18 | b | 200000 ^c |
| Phenethyl alcohol | µg/L | 47995 | B | 38645 | A | 45734 | B | 37861 | A | 14000 ^b |
| Tyrosol | µg/L | 22952 | A | 33280 | C | 34673 | C | 28933 | B | unknown |

Values are the mean of nine replicates (*). Values not identified by the same letters are different for $p \leq 0.01$ (capital letters) and $p \leq 0.05$ (small letters).
^a - Moyano *et al.*, 2002; ^b - Culleré L. *et al.*, 2004; ^c - Gómez-Míguez M.J. *et al.*, 2007; ^d - Li H. *et al.*, 2008.

Table 6. Wine composition: volatile acids.

| Trials | | MAPG | | MEHGC | | MEHGCO ₂ | | MEHGSO ₂ T | | Odour threshold |
|-------------------|------|------|-----|-------|------|---------------------|------|-----------------------|------|-------------------|
| Propanoic acid | µg/L | 1231 | n.s | 1033 | n.s. | 1037 | n.s. | 1280 | n.s. | 8100 ^c |
| Isobutyric acid | µg/L | 3070 | C | 2603 | B | 2433 | B | 2208 | A | 230 ^c |
| Butyric acid | µg/L | 3620 | n.s | 4069 | n.s. | 4029 | n.s. | 3723 | n.s. | 173 ^b |
| Isovaleric acid | µg/L | 2015 | B | 1380 | A | 1343 | A | 1199 | A | 33.4 ^c |
| Hexanoic acid | µg/L | 4133 | A | 4881 | B | 4923 | B | 5032 | B | 420 ^b |
| Octanoic acid | µg/L | 7430 | A | 7713 | A | 8720 | B | 8420 | B | 500 ^b |
| n-decanoic acid | µg/L | 2383 | A | 2885 | B | 3148 | B | 3185 | B | 1000 ^b |
| Phenylacetic acid | µg/L | 94 | AB | 264 | C | 132 | B | 40 | A | 1000 ^b |

Values are the mean of nine replicates (*). Values not identified by the same letters are different for $p \leq 0.01$

^b - Culleré L. *et al.*, 2004; ^c - Gómez-Míguez M.J. *et al.*, 2007

Table 7. Wine composition: esters

| Trials | | MAPG | | MEHGC | | MEHGCO ₂ | | MEHGSO ₂ T | | Odour threshold |
|-----------------------------|------|------|------|-------|------|---------------------|------|-----------------------|------|---------------------|
| Isoamyl acetate | µg/L | 2728 | A | 3318 | B | 3858 | C | 4206 | D | 30 ^c |
| Ethyl hexanoate | µg/L | 793 | n.s. | 864 | n.s. | 902 | n.s. | 920 | n.s. | 14 ^b |
| Hexyl acetate | µg/L | 71 | A | 90 | AB | 118 | C | 113 | BC | 1500 ^b |
| Ethyl lactate | µg/L | 4742 | n.s. | 4595 | n.s. | 4256 | n.s. | 4621 | n.s. | 14000 ^d |
| Ethyl octanoate | µg/L | 1443 | n.s. | 1505 | n.s. | 1620 | n.s. | 1671 | n.s. | 5 ^d |
| Ethyl 3-hydroxybutyrate | µg/L | 173 | n.s. | 238 | n.s. | 204 | n.s. | 196 | n.s. | 20000 ^c |
| Ethyl decanoate | µg/L | 780 | n.s. | 661 | n.s. | 699 | n.s. | 723 | n.s. | 200 ^d |
| Diethyl succinate | µg/L | 115 | n.s. | 148 | n.s. | 128 | n.s. | 175 | n.s. | 200000 ^b |
| Phenylethyl acetate | µg/L | 1370 | n.s. | 1187 | n.s. | 1449 | n.s. | 1368 | n.s. | 250 ^d |
| Diethyl malate | µg/L | 343 | n.s. | 329 | n.s. | 287 | n.s. | 302 | n.s. | 10000 ^a |
| N-Acetylglycine ethyl ester | µg/L | 83 | n.s. | 93 | n.s. | 75 | n.s. | 69 | n.s. | unknown |
| Ethyl hydrogen succinate | µg/L | 6588 | C | 3327 | A | 2612 | A | 5602 | B | unknown |
| Ethyl p-hydroxycinnamate | µg/L | 177 | A | 205 | A | 207 | A | 608 | B | 1.6 ^c |

Values are the mean of nine replicates (*). Values not identified by the same letters are different for $p \leq 0.01$

^a - Moyano *et al.*, 2002; ^b - Culleré L. *et al.*, 2004; ^c - Gómez-Míguez M.J. *et al.*, 2007; ^d - Li H. *et al.*, 2008.

potassium in musts obtained using mechanically harvested grapes confirms their hypothesis regarding the increase of inorganic cations caused by skin maceration occurring during transport (OUGH 1969; OUGH and BERG 1971; GUERZONI *et al.* 1981). Moreover, a lower potassium amount in MEHGCO₂ than in the MEHGC and MEHGSO₂T trials could be related to a co-precipitation of this metal with tartaric acid due to the low temperature.

After pressing, the higher turbidity value in all the mechanically harvested grape musts than in the MAPG trial musts is due to cell wall damage during harvesting and to the subsequent high diffusion of colloidal substances such as protein, pectin, etc., from skin into the juice.

The higher level of total phenols in mechanically harvested grape musts confirms the above reported data and previous reports from OUGH (1969), OUGH and BERG (1971), and GUERZONI *et al.* (1981). This result was expected considering the enhanced extraction phenomena in mechanically harvested grapes. The highest level of phenolics in MEHGSO₂T was logically related to: 1) oxidation prevention due to antioxidant activity of tannins (HAGERMAN *et al.* 1998) and sulphur dioxide (USSEGLIO-TOMASSET 1992), 2) extraction phenomena related to maceration with sulphur dioxide (BAKKER *et al.* 1998), and 3) addition of commercial tannins (100 mg/kg). Considering what we reported above, the amount of total phenols detected in MEHGSO₂T was lower than expected (100-130 mg/L over the other mechanically harvested trials). This could be due to the interaction between the tannins and proteins released from the mechanically harvested grape pomace (MAC MANUS *et al.*, 1985; FELDMAN *et al.*, 1999).

The lower yeasts and bacterial counts in musts obtained from hand-picked grapes than from MEHGC and MEHGCO₂ is due to a limited break of the berries. This type of berry damage could lead to the formation of a juice and to microbial dispersion and growth which doesn't happen with hand picked grapes. In these trials, the influence of temperature (lower in MEHGCO₂) on microbial growth was not as important as found by other authors (MORRIS *et al.*, 1979). The addition of sulphur dioxide and tannins during harvest minimizes the microbial growth, therefore resulting in the lowest bacterial population.

Reduced extract and pH data, lower in hand-picked than in mechanically harvested grape wines (see table 4), point out the higher berry damage caused by the harvester

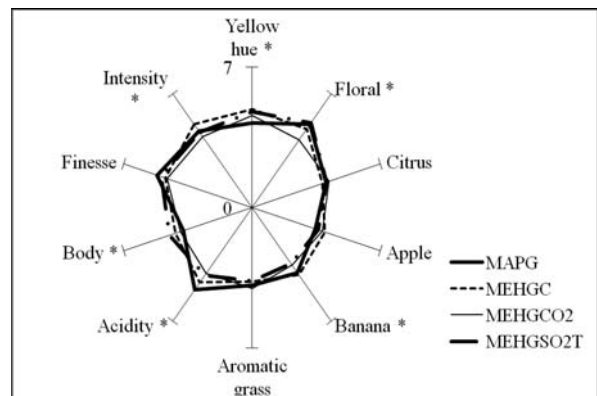


Figure 1 - Wines descriptive analysis

In sensorial parameters indicate with an asterisk (*) a difference among some trials is verified for $p = 0.01$.

Table 8. Wine composition: other volatile compounds

| Trials | | MAPG | | MEHGC | | MEHGCO ₂ | | MEHGSO ₂ T | | Odour threshold |
|---|------|------|------|-------|------|---------------------|------|-----------------------|------|--------------------|
| 3 hydroxy-2-Butanone | µg/L | 1912 | A | 2320 | BC | 2235 | AB | 2610 | C | unknown |
| Dihydro-2-methyl-3(2H)-thiophenone | µg/L | 41 | C | 15 | A | 19 | AB | 32 | BC | unknown |
| Butyrolactone | µg/L | 3557 | A | 6852 | D | 4015 | B | 5372 | C | 20000 ^a |
| N-Ethyl-Acetamide | µg/L | 106 | A | 205 | C | 174 | BC | 168 | B | unknown |
| 4-O-Methyl mannose | µg/L | 1217 | B | 1622 | C | 995 | A | 1022 | A | unknown |
| N-(3-Methylbutyl)acetamide | µg/L | 1072 | A | 1578 | B | 1870 | BC | 2031 | C | unknown |
| 1,4-Diacetoxybutane | µg/L | 148 | n.s. | 165 | n.s. | 127 | n.s. | 193 | n.s. | unknown |
| Pantolactone | µg/L | 279 | n.s. | 347 | n.s. | 325 | n.s. | 353 | n.s. | 2200 ^a |
| 2,3-dihydro-thiophen | µg/L | 101 | B | 28 | A | 25 | A | 90 | B | unknown |
| 5-hydroxymethylfurfural | µg/L | 33 | A | 65 | B | 24 | A | 84 | B | unknown |
| n-acetyltyramine | µg/L | 66 | A | 233 | B | 88 | A | 170 | B | unknown |
| 1H-indole-3-ethanol | µg/L | 5041 | A | 5035 | A | 3880 | A | 11925 | B | unknown |

Values are the mean of nine replicates (*). Values not identified by the same letters are different for $p \leq 0.01$
a - Moyano *et al.*, 2002.

machine (POCOCK and WATERS, 1998). These data confirm the must data reported in table 3.

The lowest total phenol content of MEHGC indicates that oxidation of phenolic compounds occurred, and started during harvesting. In the trials with postharvest treatments (MEHGCO₂ and MEHGSO₂T), the content of phenolic compounds was similar (MEHGCO₂) or higher (MEHGSO₂T) than in MAPG trial wines. The total phenol content of MEHGCO₂ was similar to MAPG. This can be explained by the low temperature of grapes, caused by CO₂ addition, which decreases the extraction of phenols during transport. Solid CO₂ has two effects: 1) drop in temperature which results in a lower oxidase activity and a lower extraction from skins, and 2) sublimation that leads to a CO₂ gas release with partial removal of oxygen from the environment. The first effect can also be obtained by picking the grapes when the temperature is lower (at night), while the second is typical of inert gases. The phenolic content of MEHGSO₂T was higher for the same reason reported above for musts.

The wine colour results confirm that « white wine made from machine-harvested grapes was significantly darker by visual assessment » (NOBLE *et al.*, 1975). This could confirm the oxidation of grape phenols (POULARD *et al.*, 1980) in MEHGC and the extractive effect due to sulphur dioxide on phenolic compounds in MEHGSO₂T. The highest amount of phenolic compounds detected in MEHGSO₂T could explain the higher optical density result.

The higher stability towards oxidation in MAPG is probably due to its lower content of oxidizable compounds, while the high value detected in MEHGSO₂T could be related to its high amount of antioxidant compounds exposed to oxidation.

The lower amount of gallic acid and flavans in MEHGC than in MEHGCO₂ could be due to more important oxidation phenomena in trials carried out without any protection. Instead, the same trend for gallic acid and flavans found in MEHGCO₂ compared to MEHGSO₂T could be due to the lower diffusion of these compounds from the skins into the juice at low temperatures. The concentration of flavans in MAPG and MEHGSO₂T didn't show any statistical differences. This may result from a good equilibrium between oxidation, oxidation prevention and extraction phenomena in MEHGSO₂T that led to a similar amount of flavans compared to MAPG, in which these phenomena did not occur.

The lowest concentration of caftaric acid in MEHGC confirms the importance of oxidative phenomena. As a matter of fact, this compound is an excellent substrate for grape polyphenol-oxidase (GUNATA *et al.* 1987; CHEYNIER *et al.* 1986) and its loss was expected in samples without any protection against oxidation phenomena. The above considerations related to flavans content were confirmed also to explain the different amounts of caftaric acid. Coumaric acid showed a different trend and its behaviour is difficult to explain. The significantly different amounts of rutin were mainly due to extraction phenomena, as reflected by the lack of this

compound in the MAPG trial. Furthermore, the highest concentration of rutin in the MEHGSO₂T trial could be related to extraction phenomena (due to mechanical harvest and sulphur dioxide addition) but also to protection against oxidation phenomena (linked to sulphur dioxide addition).

The significantly lower amount of 1-hexanol, 3-ethoxy 1-propanol, (Z)-3-hexen 1-ol, (2S,3S) 2,3-butanediol, benzyl alcohol and tyrosol in the MAPG trial than in the mechanically harvested ones can be explained by the lowest amount of amino acids and oxygen in the musts (see Table 5). ÄYRÄPÄÄ (1971) has demonstrated that both the catabolic process from amino acids and the anabolic process from sugars are involved in the formation of fusel alcohols via 2-keto acids. The different amount of these compounds could be related to the precursor availability, fermentation conditions (yeast strain, oxygen (VALERO *et al.* 2002), temperature, pH (MARAIS 1978)), and insoluble material in grape must (EDWARDS *et al.* 1990). In our conditions, some variables reported above were the same in all trials (yeast strain, fermentation temperature, and insoluble materials) because all the wines were fermented after clarification at controlled temperature and inoculated with the same yeast strain to obtain similar values of insoluble materials in all trials. Some other parameters, particularly the precursor availability (PAETZOLD *et al.* 1990; POCOCK and WATERS 1998), dissolved oxygen and pH (POCOCK and WATERS 1998), were affected by harvest conditions. The concentration of amino acids in musts influences the production of higher alcohols; the total concentration of higher alcohols increases as the concentration of the corresponding amino acids increases (SCHULTHESS and ETTLINGER 1978). In our trials, mechanical harvesting induced the breaking of grape skin, causing a higher extraction of amino acids than in manual harvesting (data not reported). Moreover, hand-picked grapes produced musts with the lowest amount of oxygen. LAMBRECHTS and PRETORIUS (2000), ZOECKLEIN *et al.* (1995) and VALERO *et al.* (2002) put in evidence that yeasts produce low quantity of higher alcohols without must oxygenation. Moreover, grape juice obtained from hand picked grapes has a lower pH value than the one obtained from mechanically harvested grapes, and this low pH value can reduce the level of proteins in juice (MORETTI and BERG 1965 and MURPHEY *et al.* 1989). The higher amount of 1-hexanol in MEHGC than in the other mechanically harvested grape trials is related to a higher enzymatic activity that could promote the 1-hexanol formation from C18 compounds. The reduced enzymatic activity in trials with postharvest treatments is related to the lower temperature (MEHGCO₂) and to antiseptic addition (MEHGSO₂T). The lower amount of 3 ethoxy-1-propanol in MEHGC trial than in

MEHGCO₂ trial could be justified by the higher presence of 3 ethoxy-1-propanol precursor in MEHGCO₂.

Isoamyl alcohol was higher in the MAPG trial wines and this could be difficult to explain considering that the amount of precursor amino acids should be higher in mechanically harvested grapes than in hand-picked grapes because of the higher grape skin damage and the lower amount of oxygen than in mechanically harvested musts. Moreover, the higher concentration of phenyl-ethyl alcohol in the MAPG trial than in MEHGC and MEHGSO₂T ones is not easy to explain. Different pH could influence the enzymatic pathway in yeast leading to the synthesis of isoamyl and phenyl-ethyl alcohols.

Considering oxygen availability, a higher amount of fatty acids in the mechanically harvested grape trials (see Table 6) could be expected, as reported by HOUTMAN *et al.* (1980). Moreover, the lower amount of isobutyric and phenylacetic acids in MEHGSO₂T trial (double addition of antioxidant compounds) than in the other mechanically harvested grape trials confirms this hypothesis. However, RADLER (1978) found that synthesis of saturated fatty acids is generally carried out at the beginning of fermentation, although it can continue throughout the fermentation process in anaerobic conditions. Therefore, the iso-butyric and iso-valeric acid trends could be due to different oxygen availability and pH value, but no report in literature could give us any confirmation.

The lowest level of esters in wines obtained from hand-picked grapes (see Table 7) could be explained by the lower amount of acid and alcohol precursors in this type of grapes. In fact, KEYZERS R. A. and BOSS P.K. (2010) have observed that the production of many fermentation esters was enhanced when grape juice concentration was increased. Moreover, VALERO *et al.* (2002) have proven that the concentration of esters was lower without oxygenation, which can be linked to a decreased cellular growth under these conditions. In particular, a lower amount of isoamyl acetate, hexyl acetate and ethyl p-hydroxycinnamate was observed using hand picked grapes. However, this last hypothesis cannot be confirmed by the general trend of these compounds in the mechanically harvested grape trials. As a matter of fact, the amount of these esters significantly increases (particularly for some compounds) starting from the highest oxygenated trial (MEHGC) to the lowest (double addition of antioxidant compounds) oxygenated one (MEHGSO₂T).

The low amount of isoamyl acetate in the MAPG trial doesn't agree with previous work (NYKÄNEN, 1986), which has reported a higher content of isoamyl acetate in anaerobic conditions than in semi-aerobic conditions. In accordance with NYKÄNEN (1986), a high correlation

coefficient ($r^2 = 0.8617$, data not reported) is found between ethyl octanoate and ethyl hexanoate content. The highest amount of ethyl hydrogen succinate in the MAPG trial could be due to a different metabolism in yeasts at lower pH.

Some sensorial parameters are significantly influenced by the picking method and postharvest techniques as shown in Figure 1. The lowest yellow hue, the highest acidity and the lowest body in the MAPG trial wines reflect the chemical findings. In fact, MAPG showed the lowest values of optical density at 420 nm, pH and reduced extract. In particular, the yellow hue was significantly lower in MAPG than MEHGC and MEHGSO₂T. This could be due to the absence of oxidative protection in the MEHGC trial and to the extractive action of sulphur dioxide in MEHGSO₂T. In the latter trial the influence of tannin addition on colour hue could also be considered. The acidity was significantly higher in the MAPG trial than in the MEHGC and MEHGSO₂T ones. This evidence could be due to the more considerable extraction of cations that react with tartaric acid and significantly increase the pH values. The extraction phenomena are related to cell walls breaking due to the action of dried ice (solid carbon dioxide) or antiseptic compound (sulphur dioxide). The body was significantly lower in the MAPG trial than in the MEHGSO₂T trial. This could be partially related to significant differences in reduced extract (see table 4). This parameter was also significantly higher in MEHGC and MEHGC₂, but this evidence couldn't be confirmed by the sensory profiles. This is difficult to explain and could be related to a different yeast metabolism, due to the addition of sulphur dioxide in postharvest treatment that can produce a higher amount of glycerol.

The MEHGC₂ wine is characterized by a significantly lower floral sensation than the other trials. This could be due to a lower dissolution of aromatic compounds or their precursors related to the lower temperature during transport. This evidence is, however, difficult to explain since a significantly higher amount of phenethyl alcohol, related to a flowery character, was monitored in MEHGC₂ than in MEHGC and MEHGSO₂T (see table 5). On the contrary, other compounds related to flowery sensation such as ethyl octanoate and phenyl ethyl acetate did not show significant differences (see table 7). Still, the aromatic expression of an odour descriptor is not only linked to the content of the compounds generating this sensation. Synergic and antithetic interactions between aromatic compounds must be considered in order to have a complete evaluation of a wine's aroma.

The significantly higher level of banana aroma in MAPG and MEHGC than in the other two trials is very

difficult to explain. In fact, the characteristic « banana » aroma is related to the isoamyl acetate content (GÓMEZ-MÍGUEZ *et al.*, 2007) and this compound is present in a significantly higher amount in MEHGC₂ and MEHGSO₂T (see table 7). Furthermore, other compounds related to banana aroma, such as ethyl hexanoate and ethyl octanoate, didn't show any significant differences.

The significantly higher intensity (taste-olfactory) in the MEHGC than MEHGC₂ trial can be linked to a higher dissolution of fixed and aromatic compounds.

CONCLUSION

This study shows that to obtain good results from mechanical harvesting, the harvester settings and the appropriate planned oenological control of the harvested products should be carefully considered.

As far as our concern, these choices can not be standardized and depend on the vine characteristics and its conditions at harvest time. The results obtained in this study could indicate some practical conditions but they can't be generalized. Concerning the harvester settings, using berries characterized by a low detachment force and a low must yield, as Montuni, the choice of settings affects the losses less sensitively and a higher beater frequency could be used to obtain an almost complete detachment of the product.

The quality of the musts obtained from mechanically harvested grapes resulted generally good. pH level was lower in the MAPG trial owing to a lower breaking of skins. The quantity of phenolics was higher in the mechanically harvested trials, but the level was not so high as to induce oxidation for the following winemaking procedures.

Postharvest treatments reduce the losses of natural antioxidant compounds in wines obtained from mechanically harvested grapes. Solid CO₂ addition is useful to decrease temperature of berries. While similar results could be obtained by picking the grapes at night, CO₂ addition could also be used to create an inert environment around the grapes. Volatile compounds characterized by a pleasant and favourable aroma are positively affected by postharvest treatments. Mechanical harvesting does not have a negative influence on wine composition if proper vineyard characteristics, machine settings and postharvest treatments are followed.

The sensorial differences among the trials are significant for some parameters, but an overall view of the data suggests that the differences are not remarkable and all the wines are good. The characteristics of Montuni wine are maintained with mechanically harvested grapes

also without any postharvest treatments. The use of these treatments is otherwise useful to obtain wines with a better stability, as observed by the chemical data.

BIBLIOGRAPHIC REFERENCES

- ARFELLI G., BORDINI F. and PEZZI F., 2005. Vendemmia meccanica e tecnologie post raccolta. *VQ in vite qualitas, in vino excellentia*, **1**, 80-82.
- ÄYRÄPÄÄ T., 1971. Formation of higher alcohols by yeasts and its dependence on nitrogenous nutrients. *Kem. Tidskr.*, **83**, 79-90.
- BAKKER J., BRIDLE P., BELLWORTHY S.J., GARCIA-VIGUERA C., READER H.P. and WATKINS S.J., 1998. Effect of sulphur dioxide and must extraction on colour, phenolic composition and sensory quality of red table wine. *J. Sci. Food Agr.*, **78**, 297-307.
- BENEDICT R.H., FLEMING J.W. and MORRIS J.R., 1971. Post-harvest changes in quality of mechanically harvested 'Concord' grapes. *Ark. Farm Res.*, **20**, 1, 10.
- CASTELLARI M., VERSARI A., SPINABELLI U., GALASSI S. and AMATI A., 2000. An improved HPLC method for the analysis of organic acids, carbohydrates, and alcohols in grape musts and wines. *J. Liq. Chrom. & Rel. Technol.*, **23**, 2047-2056.
- CASTELLARI M., SARTINIE, FABIANI A., ARFELLI G. and AMATI A., 2002. Analysis of wine phenolics by high performance liquid chromatography using a monolithic column. *J. Chrom. A*, **973**, 221-227.
- CHEYNIER V.E., TROUSDALE E., SINGLETON V.L., SALGUES M. and WYLDE R., 1986. Characterization of 2-S-glutathionyl tartaric acid and its hydrolysis in relation to grape wines. *J. Agr. Food Chem.*, **34**, 217-221.
- CULLERÉ L., ESCUDERO A., CACHO J. and FERREIRA V., 2004. Gas chromatography-olfactometry and chemical quantitative study of the aroma of six premium quality Spanish aged red wines. *J. Agr. Food Chem.*, **52**, 1653-1660.
- EDWARDS C.G., BEELMAN R.B., BARTLEY C.E. and MCCONNELL A.L., 1990. Production of decanoic acid and other volatile compounds and the growth of yeast and malolactic bacteria during vinification. *Am. J. Enol. Vitic.*, **41**, 48-56.
- FELDMAN K.S., SAMBANDAM A., LEMIN S.T., NICEWONGER R.B., LONG G.S., BATTAGLIA D.F., ENSEL S.M. and LACI M.A., 1999. Binding affinities of gallotannin analogs with bovine serum albumin: ramification for polyphenol-protein molecular recognition. *Phytochemistry*, **51**, 867-872.
- FERREIRA B., HARY C., BARD M.H., TAISANT C., OLSSON A. and LEFUR Y., 1995. Effect of skin-contact and setting on the level of the C18:2, C18:3 fatty acids and C6 compounds in Burgundy Chardonnay musts and wines. *Food Quality Preference*, **6**, 35-41.
- GARDE-CERDAN T., JARAUTA I., ROSARIO SALINAS M. and ANCIN-AZPILICUETA C., 2008. Comparative study of the volatile composition in wines obtained from traditional vinification and from Ganimede method. *J. Sci. Food Agr.*, **88**, 1777-1785.
- GERBI V., ZEPPA G. and CARNICINI A., 1992. Rapid extraction of volatile compounds in wine and vinegar using extrelut resin. *Italian J. Food Sci.*, **4**, 259-267.
- GOMEZ-MIGUEZ M.J., CACHO J.F., FERREIRA V., VICARIO I.M. and HEREDIA F.J., 2007. Volatile components of Zalema white wines. *Food Chem.*, **100**, 1464-1473.
- GUERZONI M.E., ZIRONI R., INTRIERI C. and MAGNANINI E., 1981. Stabilization of white wine by early hyperoxidation of must. *Food Technology Australia*, **33**, 444-446.
- GUNATA Z.Y., SAPIS J.P. and MOUTOUNET M., 1987. Substrate and carboxylic acid inhibitors of grape polyphenoloxidases. *Phytochemistry*, **26**, 1573-1575.
- HAGERMAN A.E., RIEDL K.M., JONES A., SOVIK K.N., RITCHARD N.T., HARTZFELD P.W. and RIECHEL T.L., 1998. High molecular weight plant polyphenolics (tannins) as biological antioxidants. *J. Agr. Food Chem.*, **46**, 1887-1892.
- HARWICK W.A., 1994. The properties of beer, 551-586. In: *Handbook of brewing*, ed. W.A. Harwick, Marcel Dekker Publisher, New York, 741 p.
- HOUTMAN A.C., MARAIS J. and DU PLESSIS S., 1980. The possibilities of applying present day knowledge of wine aroma components influence of several juice factors on fermentation rate and esters production during fermentation. *S. Afr. J. Enol. Vitic.*, **1**, 27-33.
- INTRIERI C. and PONI S., 1990. A new integrated approach between training system and mechanical equipment for full mechanization of quality vineyards. In: *Proc. 7th Aust. Wine Ind. Techn. Conf., Adelaide*, Australia, Eds Williams P.J., Davidson D.M. and Lee T.H. p. 35-50.
- ISO, 2007. Sensory analysis - General guidance for the design of test room. International Organization for Standardization, ISO 8589:2007.
- ISO, 1994. Sensory Analysis - Identification and selection of descriptors for establishing a sensory profile by multidimensional approach. International Organization for Standardization, ISO 11035:1994.
- ISO, 1993. Sensory Analysis -General guidance for the selection, training, and monitoring of assessors.- Part 1: Selected assessors. International Organization for Standardization, ISO 8586-1:1993.
- JONES M.D., BENEDICT R.H. AND FLEMING J.W., 1969. Effects of southern temperatures on quality of mechanically harvested grapes. *Trans. Amer. Soc. Agr. Eng.*, **12**, 739-740.
- KEYZERS R. A. AND BOSS P.K., 2010. Changes in the volatile compound production of fermentations made from musts with increasing grape content. *J. Agric. Food Chem.*, **58**, 1153-1164.
- LAMBRECHTS M.G. and PRETORIUS I.S., 2000. Yeast and its importance to wine aroma - a review. *S. Afr. J. Enol. Vitic.*, **21**, 97-125.
- LANE J.H. and EYNON L., 1923. Determination of reducing sugars by Fehling solution with methylene blue indicator. *J. Soc. Chem. Ind.*, **42**, 32-37T.

- LI H., TAO Y.S., WANG H. and ZHANG L., 2008. Impact odorants of Chardonnay dry white wine from Ch'angli County (China). *Eur. Food Res. Technol.*, **227**, 287-292.
- MACHEIX J.J., SAPIS J.C. and FLEURIET A., 1991. Phenolic compounds and polyphenol oxidase in relation to browning in grapes and wines. *Crit. Rev. Food Sci. Nutr.*, **30**, 441-486.
- MARAIS J., 1978. The effect of pH on esters and quality of Colombar wine during maturation. *Vitis*, **17**, 396-403.
- MARSHALL D.E., LEVIN J.H. and CARGILL B.F., 1971. Properties of 'Concord' grapes related to mechanical harvesting and handling. *Trans. Amer. Soc. Agr. Eng.*, **14**, 373-376.
- MC MANUS J.P., DAVIS K.G., BEART J.E., GAFFNEY S.H., LILLEY T.H. and HASLAM E., 1985. Polyphenol interactions. Part I. Introduction; some observations on the reversible complexation of polyphenols with proteins and polysaccharides. *J. Chem. Soc. Perkin Trans.*, **2**, 1429-1438.
- MORETTI R.H. and BERG H.W., 1965. Variability among wines to protein clouding. *Am. J. Enol. Vitic.*, **16**, 69-78.
- MORRIS J.R., 1983. Effects of mechanical harvesting on the quality of small fruits and grapes. *Amer. Soc. Agric. Engin.*, **5**, 84, 332-348
- MORRIS J.R., 1994. Mechanical harvesting and vineyard mechanization. <http://www.uark.edu/depts/ifse/grapeprog/articles/webg94-4vm.pdf>
- MORRIS J.R., FLEMING J.W., BENEDICT R.H. and MCCASKILL D.R., 1972. Effects of sulfur dioxide on postharvest quality of mechanically harvested grapes. *Ark. Farm Res.*, **21**, 2, 5.
- MORRIS J.R., CAWTHON D.L. and FLEMING J. W., 1979. Effects of temperature and SO₂ addition on quality and postharvest behavior of mechanically-harvested juice grapes in Arkansas. *J. Amer. Soc. Hort. Sci.*, **104**, 166-169.
- MOYANO L., ZEA L., MORENO J. and MEDINA M., 2002. Analytical study of aromatic series in Sherry wines subjected to biological aging. *J. Agric. Food Chem.*, **50**, 7356-7361.
- MOYER J.C., SHAULIS N.J. and SHEPARDSON E.S., 1961. Grape harvesting research at Cornell. In: *Proc. 1961 N.Y. State Hort. Soc.*, p. 250-255.
- MURPHEY J.M., SPAYD S.E. and POWERS J.R., 1989. Effect of grape maturation on soluble protein characteristics of Gewürztraminer and white Riesling juice and wine. *Am. J. Enol. Vitic.*, **40**, 199-207.
- NELSON K.E. and AHMEDULLAH M., 1972. Influence of depth of pack on quality of grapes stored in unvented containers. *Am. J. Enol. Vitic.*, **23**, 39-42.
- NOBLE A.C., OUGH C.S. and KASIMATIS A.N., 1975. Effects of leaf content and mechanical harvest on wine « quality ». *Am. J. Enol. Vitic.*, **26**, 158-163.
- NYKÄNEN L., 1986. Formation and occurrence of flavour compounds in wine and distilled alcoholic beverages. *Am. J. Enol. Vitic.*, **37**, 84-96.
- O'BRIEN M. and STUDER H.E., 1977. Closed and open transport and sampling of wine grapes. *Trans. Amer. Soc. Agr. Eng.*, **20**, 631-634.
- OFFICIAL JOURNAL L 272, 3.10.1990, Commission Regulation (EEC) No 2676/90 of 17 September 1990 determining Community methods for the analysis of wines, 1-192.
- OUGH C.S., 1969 Substances extracted during skin contact with white musts. I. General wine composition and quality changes with contact time. *Am. J. Enol. Vitic.*, **20**, 93-100.
- OUGH C.S. and BERG H.W., 1971. Simulated mechanical harvest and gondola-transport. Effect of temperature, atmosphere, and skin-contact on chemical and sensory qualities of white wines. *Am. J. Enol. Vitic.*, **22**, 194-198.
- PAETZOLD M., DULAU I. and DUBOURDIEU D., 1990. Fractionnement et caractérisation des glycoprotéines dans les moûts de raisins blancs. *J. Int. Sci. Vigne Vin.*, **24**, 13-28.
- PETERSON R., 1979. Most important machine picker feature may be night-time use. Calif. Western States Grape Grower, Dec., p. 14.
- PEZZI F. and CAPRARA C., 2009. Mechanical grape harvesting: investigation of the transmission of vibrations. *Biosystems Engineering*, **103**, 281-286.
- POCOCK K.F. and WATERS E.J., 1998. The effect of mechanical harvesting and transport of grapes, and juice oxidation, on the protein stability of wines. *Austr. J. Grape Wine Res.*, **4**, 136-139.
- POULARD A.M., BRELET M. and ROUSSET Y., 1980. Incidences de la récolte mécanique sur la qualité des moûts et la composition des vins. *Vignes et Vins*, **293**, 54-59.
- RADLER F., 1978. Les activateurs du développement anaérobie de la levure. *Ann. Technol. Agric.*, **27**, 203-213.
- RAPP A. and MANDERY H., 1986. Wine aroma. *Experientia*, **42**, 873-884.
- RIBÉREAU-GAYON P. and SAPIS J.C., 1965. Sur la présence dans les vin de tyrosol, de tryptophol, d'alcool phényléthylique et de γ -obutirolactone, produits secondaires de la fermentation alcoolique. *C.R. Hebdomadaires des Séances de l'Academie des Sciences, Serie D Science Naturelles*, **261**, 1915-1916.
- RIBÉREAU-GAYON P., 1970. Les dosages des composés phénoliques totaux dans le vin rouge. *Chim. Anal.*, **52**, 627-631.
- SCHULTHESS D. and ETTLINGER L., 1978. Influence of the concentration of branched chain amino acids on the formation of fusel alcohols. *J. Institute Brewing*, **84**, 240-243.
- SHAULIS N.J., SHEPARDSON E.S. and JORDAN T.D., 1966. The Geneva Double Curtain for Concord Grapes. *New York State Agricultural Experiment Station Bulletin*, Agricultural Experiment Station, Cornell Univ., Geneva, **811**, 1-16.
- SHEPARDSON E.S. SHAULIS N. and MOYER J.C., 1969. Mechanical harvesting of grape varieties grown in New York State. In: *Fruit and vegetable harvest mechanization: technological implications*. RMC Rep. No. 16, Rural Manpower Center, Michigan State Univ., East Lansing. Eds Cargill B.F. and Rossmiller G.E., p. 571-579
- STUDER H.E. and OLMO H.P., 1969. Mechanical harvesting of grapes in California: cultural practices and machines. In: *Fruit and vegetable harvest mechanization: technological*

- implications*. RMC Rep. No. 16, Rural Manpower Center, Michigan State Univ., East Lansing. Eds Cargill B.F. and Rossmiller G.E., p. 611-621.
- SUDRAUD P., 1958. Interprétation des courbes d'absorption des vins rouges. *Ann. Technol. Agr.*, **7**, 203-208.
- USSEGLIO-TOMASSET L., 1992. Properties and use of sulphur dioxide. *Food Addit. Contam.*, **9**, 399-404.
- VALERO E., MOYANO L., MILLAN M.C., MEDINA M. and ORTEGA J.M., 2002. Higher alcohols and ester production by *Saccharomyces cerevisiae*. Influence of initial oxygenation of grape must. *Food Chem.*, **78**, 57-61.
- ZIRONI R., BUIATTI S. and CELOTTI E., 1992., Evaluation of a new colorimetric method for the determination of catechins in musts and wines. *Wein Wissenschaft*, **47**, 1-7.
- ZOECKLEIN B.W., FUGELSANG K.C., GUMP B.H. and NURY E.S., 1995. Alcohols and extract, 97-114. In: *Wine analysis and production*, Aspen Publishers New York, 607 p.