PROFILO AROMATICO DI MALVASIA ODOROSISSIMA

AROMATIC PROFILE OF MALVASIA ODOROSISSIMA

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6° simposio internazionale delle Malvasie nel bacino del Mediterraneo
ITALIAN VITIS DATABASE (IVD)

Approximately 600 accessions which presumably belong to 300 varieties of *Vitis vinifera subsp. sativa*

A multidisciplinary approach for a better knowledge, safeguard, and valorization of Italian grapevine biodiversity. [http://www.vitisdb.it/](http://www.vitisdb.it/)

The local varieties have a multiple importance within the Italian grapevine germplasm. This is due to their ability to determine several *typical sensory* and *hedonistic characteristics of the wine* as well as to evocate historical and cultural values related to the viticulture.

IVD is an *online informative system* that allows a straightforward consultation and application addressed to researchers, technicians, and operators of the viticulture and the oenological sectors.
ITALIAN VITIS DATABASE (IVD)

Activities:

• **Ampelographic and phenological studies**, according to the minimal list of the European project GrapeGen06 based on the second edition of the OIV descriptor list for grape varieties and *Vitis spp.*
• Ampelometric measurements by using the SUPERAMPELO software
• **Analysis of the polymorphism**
  9 loci microsatellites
  some tri-, tetra- and penta-nucleotides microsatellite loci
  analysis of polymorphism of some SNPs
• **Histo-anatomical observations of berry and leaf** by optical and electronic microscopy
• Analysis of berry juice composition
• Analysis of the grape **phenolic and aroma profiles**
• Investigation on the viticultural performance
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MALVASIA

**Malvasia odorosissima** (MO; also known as Malvasia aromatica di Parma)

White aromatic varieties belonging to the Malvasia family

**Malvasia di Candia aromatica** (MC)

**Malvasia grape family**

A large group of cultivars commonly considered to be born in Greece (Monemvasía) and widely cultivated in the Mediterranean area, as well as North America, South America, and Australia.
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MC vs. MO

**MC** is a well-known **aromatic** cultivar in the worldwide vine and wine scenario.

**MO** is another **aromatic** cultivar Known at least since the XIX century in Emilia, MO is **currently on the brink of extinction** because of its low productivity and it has often been replaced in the vineyards by the higher yielding MC.

Almost unknown internationally, but historical records and local tradition attest its oenological potential, which require analytical confirmations for a targeted exploitation.
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Grape aroma compounds

**Quality indexes** that influence the wine sensory expression:

- Terpenoids
- C₁₃-Norisoprenoids
- Benzenoids
- Aliphatic alcohols
- Esters
- Methoxypyrazines
- Sulfur-containing compounds
MALVASIA

Grape aroma compounds

Many of these compounds are present in grapes in 2 forms:
• Free
• Glycosylated

Their relative proportion varies according to the cultivar.

Glycosides are considered an aromatic potential, since they are susceptible of releasing volatile aglycones through enzymatic or acid hydrolysis.
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Grape aroma compounds

Many of these compounds in 2 forms:
- Free
- Glycosylated
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Grape aroma compounds

A different classification of the aromatic varieties can be carried out according to the prevalence of either linalool and its derivatives or geraniol and its derivatives.

![Linalool](image1.png) ![Geraniol](image2.png)
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Grape aroma compounds

AIMS

Provide the aromatic characterization of MO and MC to highlight each distinctive aromatic profile and support the use for winemaking and product differentiation

Safeguard the local biodiversity

The effects of climatic conditions in two consecutive vintages were also considered
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MALVASIA SAMPLING

The plants of MO and MC were cultivated in contiguous and homogeneous plots of the same germplasm collection located in the Reggio Emilia area (I.T.A. A. Zanelli, latitude 44.675420° N, longitude 10.584984° E)

METEOROLOGICAL TRENDS

- I year - low rainfall (700 mm) and a quite warm summer season (24.8 °C seasonal average temperature; 38.9 °C maximum seasonal temperature)

- II year - the summer was cooler, with a mean and maximum seasonal temperature of 23.4 °C and 37.2 °C, and the annual rainfall was higher than in the previous year (989 mm)

ORCHARDS

- Silty clay soil: sand 10.9%, clay 41.3%, and silt 47.8%
- pH = 7.5
- Organic matter = 17.5 g/kg
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MALVASIA

SAMPLING

The plants of MO and MC were cultivated in contiguous and homogeneous plots of the same germplasm collection located in the Reggio Emilia area (I.T.A. A. Zanelli, latitude 44.675420° N, longitude 10.584984° E)

SAMPLING DESIGN

- 10 bunches in good sanitary conditions were collected from 3 plants of each variety
- When sugar accumulation (soluble solids) almost became constant around 21 °Brix
- Harvest dates were 10 September in the I year and 17 September in the II year

GENETIC RECOGNITION

- The accessions were previously screened using a standard set of 9 microsatellite (SSR) markers.
MALVASIA SAMPLE PREPARATION

- 100 berries
- peeled and the skins were placed in 20 mL of methanol for 1 h in order to deactivate the enzymes and to promote the extraction of the aromatic compounds

- Deseeded pulps in a beaker with 100 mg of Na$_2$S$_2$O$_5$ to prevent oxidation, and temporarily kept at -20°C during the time of skins extraction

- Then the pulps were added to the methanolic suspension of skins and they were ground and homogenized after the addition of 20 mL of "must-like" tartaric solution at pH 3.2.

- Suspension centrifuged at rpm 15 min (4°C)
- Supernatant recovered and the pellet washed with 20 mL of buffer solution at pH 3.2
- Final extract volume: 250 mL
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MALVASIA SAMPLE PREPARATION

SOLID PHASE EXTRACTION (SPE)
- Free and glycosylated volatile fractions were isolated by solid phase extraction (SPE).
- Each extract was spiked with 50 μL of internal standard (2-heptanol, 1000 mg/L in ethanol).

- **Free volatiles** were loaded onto a 5-g C\textsubscript{18}-endcapped cartridge and recovered with 15 mL of CH\textsubscript{2}Cl\textsubscript{2}.
- **Glycosylated compounds** were subsequently eluted with 30 mL of MeOH, then eliminated under vacuum.
- The residue was re-dissolved in 5 mL of a phosphate–citrate buffer at pH 5 and spiked with the IS.
- A commercial glycosidase enzyme with β-glycosidase activity was added at 40°C for 24 h in order to release the aglycons.

- This hydrolyzed sample was eluted through a 1-g C\textsubscript{18}-endcapped cartridge.
- Free aglycons were recovered with 6 mL of CH\textsubscript{2}Cl\textsubscript{2}.
- Concentration up to about 50 μL.
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MALVASIA
FREE AND GLYCOSYLATED VOLATILE DETERMINATION

• GC/MS
  • Stabilwax-DA capillary column 0.25 mm i.d. × 30 m length × 0.25 µm df
  • Helium as carrier gas at a flow rate of 0.9 mL/min
  • Injector port (splitless mode) and transfer line were set at 240°C
  • Initial temperature 30°C. Rate 4.25°C/min up to 230°C and finally held for 20 min (66 min in total)
  • Ionization energy set at 70 eV
  • Mass range at 33-350 m/z, in full scan acquisition mode

Laboratory of Mass Spectrometry, at CIGS of University of Modena and Reggio Emilia. Thanks the Bank Foundation “Cassa di Risparmio di Modena”
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MALVASIA
FREE VOLATILE DETERMINATION

- 11 Aliphatics (herbaceous scent)
- 14 Benzenoids
- 3 C13-Norisoprenoids (fruity floral scent)
- 24 Terpenoids (floral scent)
- 52 Total

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Aliphatics sum

Benzenoids sum

C_{13}-Norisoprenoids sum

MALVASIA
FREE VOLATILES
MALVASIA ODOROSISSIMA

Terpenoids sum

MALVASIA FREE VOLATILES
ROSE OXIDE ISOMERS
Pleasant volatiles associated with a very low threshold of perception

Detected only in MO, thus supporting a sensory and a genetic similarity between MO and White Muscat.
Unlike aromatic Malvasia grapes, White Muscat is a variety characterized by both a prevalence of linalool and its derivatives and the presence of rose oxide isomers.
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MALVASIA GLYCOSYLATED VOLATILE DETERMINATION

- 11 Aliphatics (herbaceous scent)
- 15 Benzenoids
- 5 C_{13}-Norisoprenoids (fruity floral scent)
- 25 Terpenoids (floral scent)
- 56 Total

Laboratory of Mass Spectrometry, at CIGS of University of Modena and Reggio Emilia. Thanks the Bank Foundation “Cassa di Risparmio di Modena”
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**Aliphatics sum**

- **MO I year**: 20 µg/kg
- **MO II year**: 30 µg/kg
- **MC I year**: 60 µg/kg
- **MC II year**: 40 µg/kg

**Benzenoids sum**

- **MO I year**: 100 µg/kg
- **MO II year**: 200 µg/kg
- **MC I year**: 400 µg/kg
- **MC II year**: 300 µg/kg

**C$_{13}$-Norisoprenoids sum**

- **MO I year**: 10 µg/kg
- **MO II year**: 5 µg/kg
- **MC I year**: 15 µg/kg
- **MC II year**: 10 µg/kg

MALVASIA GLYCOSYLATED VOLATILES
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**Linalool-like sum**

- MO I year: [Graph 1]
- MO II year: [Graph 1]

**Geraniol-like sum**

- MO I year: [Graph 1]
- MO II year: [Graph 1]

**MC I year**
- Linalool-like sum: [Graph 2]
- Geraniol-like sum: [Graph 2]

**MC II year**
- Linalool-like sum: [Graph 2]
- Geraniol-like sum: [Graph 2]

**Terpenoids sum**

- MO I year: [Graph 3]
- MO II year: [Graph 3]
- MC I year: [Graph 3]
- MC II year: [Graph 3]

MALVASIA GLYCOSYLATED VOLATILES
ROSE OXIDE ISOMERS

Pleasant volatiles associated with a very low threshold of perception

(Z)-Rose oxide was solely present in MO, albeit in lower concentrations in comparison with the free forms of the same variety.
CONCLUSIONS

The richness of the aromatic profile of MO is an important feature for the oenological exploitation of this variety, which is currently on the brink of extinction and erroneously confused with MC, even by winemakers.

In addition, MO seemed to be less susceptible to seasonal variations in terms of quantitative expression of volatiles, as otherwise showed by MC. This supposed stability is of considerable interest and deserves further insights in the current climate change situation affecting grape and wine quality.

Some evidence renders the MO aromatic profile similar to White Muscat one, thus giving value to the proximity already demonstrated by the genetic analysis between the two aromatic varieties.

The increasing interest in Malvasia wines on the international market opens good perspective for the re-proposal of underexploited Malvasia cultivars for the oenological products diversification.
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Grazie per l’attenzione