Vitis **47** (4), 241–243 (2008)

# Free and glycoconjugated volatiles of *V. vinifera* grape 'Falanghina'

S. A. Lamorte[1)], A. Gambuti [2)], A. Genovese [1)], S. Selicato [1)], L. Moio [2)]

[1)] Dipartimento di Scienze degli Alimenti, Facoltà di Agraria, Università degli Studi di Foggia, Foggia, Italy
[2)] Dipartimento di Scienza degli Alimenti, Università degli Studi di Napoli Federico II, Portici, Italy

## Summary

**The potential aroma of *Vitis vinifera* Falanghina was investigated by means of qualitative and semi-quantitative determinations of volatile free and glycosidically bound secondary metabolites. Glycosilated geranic acid, α-terpineol, eugenol and 2-exo-hydroxy-1,8-cineole play a central role in characterizing the potential aromatic expression of this cultivar. In particular glycosilated 2-exo-hydroxy-1,8-cineole found in Falanghina must may be discriminant and hypothetically contributes to identify Falanghina wine origin and affiliation because of its high chemical and biological stability.**

K e y w o r d s : must, *Vitis vinifera* 'Falanghina', grape aroma, free and potential volatiles, GC-MS.

## Introduction

Some wines possess a characteristic and distinctive aroma even if they are obtained from neutral grape varieties. The perceived aroma derives from specific compounds often presented as glycosilated precursors. The knowledge of the specific pattern of free and glycosidically bound odorous volatiles of grapes could be successfully used to defend high value monovarietal wines against fraudulent misdescription.

'Falanghina' grape is used to obtain typical Italian wines and in particular numerous DOC (Designation of Controlled Origin) and IGT (Typical Geographical Indication) wines. The aroma of 'Falanghina' wine is mainly characterized by floral and fruity notes (Moio 2005). However there is lack of knowledge on the aromatic composition of this grape variety.

The purpose of this study was to define free and bound secondary metabolites of 'Falanghina' grape with the aim to understand expressed and potential aromas, and to evaluate the possibility of employing some of these compounds as characterising markers.

## Material and Methods

M u s t s a m p l e s : More than 2 kg of 'Falanghina' grapes were randomly hand-picked at technological maturity during the 2004 vintage from 10 different vineyards of the Benevento area (Campania, Italy) and divided into aliquots of 400 g each. For each sample an aliquot was used to determine the total acidity, pH and sugar content according to the Official European Methods of Commission Regulation EEC N° 2676/90. Remaining berries were selected and rapidly frozen and stored at -20 °C until must preparation.

E x t r a c t i o n o f f r e e a n d b o u n d s e c o n d a r y m e t a b o l i t e s : Each centrifuged must (from 400 g of berries) was divided into three samples (3 x 40 ml), then spiked with 200 µl of 2-octanol (Sigma-Aldrich, 200 mg·l$^{-1}$ in methanol) and extracted as reported by Di Stefano (1991).

C h r o m a t o g r a p h i c a n a l y s i s : A 1.4 µl aliquot of each concentrated juice extract was injected in splitless mode into a Hewlett-Packard 5890 series II gas chromatograph equipped with split/splitless injector (Hewlett-Packard, Avondale, PA) and with flame ionization detector. The column used was a DBWax from J&W Scientific (Folsom, CA), 60 m length x 0.32 mm with 0.5 µm film thickness. The temperature program was the following: 40 °C for 5 min, 3 °C·min$^{-1}$ rate to 220 °C maintained for 25 min. The carrier gas was He flowing at 37 cm·s$^{-1}$. Detector and injector were maintained at 250 °C.

A n a l y s i s o f f r e e a n d b o u n d v o l a t i l e c o m p o u n d s : Identification was performed by GC/MS consisting of a 6890 series Agilent Technologies gas chromatograph and 5973 Network series mass selective detector (Agilent Technologies) fitted with a quadrupole electronic impact source. Electron impact mass spectra were recorded with ion-source energy of 70 eV. Peaks were identified by comparing their mass fragmentation pattern with that of standard compounds as well as from the data available in the spectral libraries (Wiley 275, NIST) of the instruments. Compounds were quantified comparing their chromatographic peak area with that of the internal standard.

## Results and Discussion

G e n e r a l a n a l y s i s : Soluble solids for the grapes harvested at technological maturity from 10 vineyards changed from 19.0 °Brix to 23.6 °Brix. Total acidity values, as tartaric acid, from 7.05 g·l$^{-1}$ to 11.10 g·l$^{-1}$ and pH values from 2.83 to 3.45 were observed. A general tendency to low pH and high total acidity is observed for this grape variety confirming data previously reported for 'Falanghina' wines (Moio 2005).

F r e e v o l a t i l e c o m p o u n d s : Eleven alcohols, 5 terpenoids, 4 aldehydes and eugenol were identified and quantified in the free fraction (Table).

Corrrespondence to. Dr. S. A. Lamorte, Dipartimento di Scienze degli Alimenti, Facoltà di Agraria, Università degli Studi di Foggia, Via Napoli 25, 71100 Foggia, Italy. Fax: +39-0825-78468. E-mail: simonalamorte@gmail.com

Table

Mean, minimum, median and maximum values of concentration (micrograms per liter equivalents of 2-octanol) of free and glycoconjugated volatile secondary metabolites from Falanghina grapes from the 2004 vintage. [Each value was calculated from three repetitions for ten samples coming from different vineyards]

| compounds | | free volatiles | | | | glycosidically bound volatiles | | | |
|---|---|---|---|---|---|---|---|---|---|
| alcohols | a | mean | min | median | max | mean | min | median | max |
| 3-methyl-1-butanol | *A, B* | 31.7 | 18.4 | 32.6 | 47.8 | 41.5 | 13.5 | 43.9 | 73.1 |
| 1-pentanol | *A, B* | 16.6 | 12.8 | 17.1 | 21.4 | 33.5 | 13.3 | 33.6 | 58.8 |
| 1-hexanol | *A, B* | 128.9 | 86.5 | 110.6 | 275.0 | 60.0 | 32.6 | 62.5 | 82.3 |
| (E)-3-hexen-1-ol | *A* | 1.9 | 0.0 | 1.6 | 4.3 | 3.2 | 0.9 | 3.0 | 5.5 |
| (Z)-3-hexen-1-ol | *A* | 14.1 | 7.4 | 13.6 | 21.5 | 10.6 | 5.0 | 11.8 | 17.1 |
| 4-methyl-3-penten-1-ol | *A* | 3.3 | 2.0 | 2.9 | 6.4 | 0.6 | 3.6 | 6.4 | 8.4 |
| (E)-2-hexen-1-ol | *A, B* | np [b] | | | | 6.6 | 2.9 | 6.2 | 11.8 |
| 1-octen-3-ol | *A, B* | 1.2 | 0.9 | 1.8 | 3.5 | 0.7 | 1.6 | 4.3 | 6.4 |
| 1-heptanol | *A, B* | np | | | | 7.1 | 2.9 | 6.6 | 12.0 |
| 2-ethyl-1-hexanol | *A* | 17.5 | 5.9 | 16.5 | 30.4 | 1.0 | 3.5 | 4.7 | 6.9 |
| 1-phenylethanol | *A, B* | 0.3 | 0.6 | 0.7 | 1.3 | 6.0 | 1.8 | 5.4 | 13.7 |
| benzyl alcohol | *A, B* | 114.1 | 50.3 | 126.7 | 153.8 | 464.0 | 149.9 | 420.2 | 1032.4 |
| 2-phenylethanol | *A, B* | 204.4 | 107.2 | 226.8 | 314.0 | 324.6 | 102.3 | 348.9 | 574.1 |
| total | | 534.1 | | | | 959.3 | | | |
| terpenoids | | | | | | | | | |
| (Z)-linalool oxide | *A* | 0.9 | 2.0 | 2.1 | 4.8 | 1.9 | 1.2 | 1.7 | 3.0 |
| linalool | *A, B* | np | | | | 7.5 | 1.6 | 5.7 | 19.6 |
| α-terpineol | *A, B* | 2.5 | 0.8 | 1.1 | 23.1 | 156.4 | 116.5 | 152.1 | 202.7 |
| pyranic linalool oxide | *A* | np | | | | 14.5 | 7.5 | 13.8 | 21.8 |
| citronellol | *A, B* | np | | | | 6.3 | 2.2 | 6.1 | 10.2 |
| nerol | *A, B* | nd [c] | | | | nd | | | |
| geraniol | *A, B* | 0.2 | 2.0 | 2.0 | 2.0 | 96.9 | 69.5 | 99.3 | 120.4 |
| exo-2-hydroxy-1,8-cineole | *A* | | | | | 27.6 | 10.8 | 26.7 | 56.3 |
| geranic acid | *A* | 19.7 | 7.5 | 21.5 | 31.0 | 53.2 | 36.2 | 50.9 | 76.3 |
| total | | 23.3 | | 21.6 | | 364.4 | | | |
| aldehydes | | | | | | | | | |
| hexanal | *A, B* | 53.9 | 33.6 | 48.2 | 97.9 | 5.6 | 4.0 | 5.6 | 7.2 |
| (E)-2-hexenal | *A, B* | 74.9 | 36.2 | 64.7 | 195.9 | 5.7 | 1.8 | 4.6 | 11.0 |
| furfural | *A, B* | 1.5 | 1.3 | 2.1 | 5.0 | 2.6 | 2.3 | 2.6 | 3.3 |
| benzaldehyde | *A, B* | 19.7 | 9.2 | 21.6 | 30.8 | 51.1 | 25.3 | 37.6 | 94.7 |
| 1H-pirrole-2-carboxaldehyde | *A* | | | | | 18.4 | 14.7 | 16.7 | 26.1 |
| total | | 150.0 | | | | 83.4 | 53.7 | | |
| 3-oxo-α-ionol | *A* | nd | | | | nd | | | |
| eugenol | *A, B* | 28.2 | 1.9 | 11.4 | 183.3 | 29.9 | 15.9 | 27.6 | 54.4 |

([a]) Identity assignment: A, electron impact mass spectrometry, identity tentatively assigned by comparing mass spectra with those obtained from the literature [The Wiley 275 Registry of Mass Spectral Data; Wiley: New York]; B, reference substances, identities confirmed by comparing mass spectra and retention time with those of authentic standards; ([b]) np, not present; ([c]) nd, not determinated since the relative peak contained more than one component as proved by mass-spectrometry.

As expected for non-floral grape varieties (Schreier 1979), non terpenic alcohols were the most abundant class and accounted for 72.6 % of the total for the free fraction, being 1-hexanol and (Z)-3-hexen-1-ol the dominant alcohols. Aldehydes accounted for 20.4 % of the total in the free fraction (150 µg·l$^{-1}$). (E)-2-hexenal and hexanal are the most abundant aldehydes. $C_6$ alcohols and aldehydes arise from the enzymatic oxidation of linoleic and linolenic acids during grape crushing and pressing (Drawert *et al.* 1973).

The free fraction contained an average of 23 µg·l$^{-1}$ of terpenoids accounting for 3.2 % of the total evaluated content. The level of free α-terpineol was similar to that reported for grapes such as 'Muscat à pétit grains' (Sanchez Palomo *et al.* 2006) and 'Chardonnay' (Sefton *et al.* 1993). Geranic acid was detected at a free level higher than for 'Chardonnay' variety (Sefton *et al.* 1993).

'Falanghina' grapes exhibit levels around 30 µg·l$^{-1}$ of free eugenol (2-methoxy-4-(2-propenyl)phenol). Volatile phenols are important secondary metabolites in grape berries and are strongly influenced by *Vitis vinifera* variety (Brander *et al.* 1980).

Bound volatile compounds: A total of 29 bound secondary metabolites 13 alcohols, 9 terpenoids, 5 aldehydes, 3-oxo-α-ionol and eugenol were identified in the 'Falanghina' extracts (Table).

Aldehydes can be included in this group even with the quoted attention about their possible origin. Aldehydes can be generated from oxidation during extraction of corresponding alcohols released as aglycones.

Non-terpenic alcohols were the most abundant class accounting for 68.8 % of the total compounds, benzyl alcohol (464 $\mu g \cdot l^{-1}$) and 2-phenylethanol (325 $\mu g \cdot l^{-1}$) are the main components.

Glycosidically bound volatiles exhibited a level of 364 $\mu g \cdot l^{-1}$ of terpenoids accounting for 25.4 % of the total in 'Falanghina' grapes. This percentage is higher than that reported for 'Chardonnay' (Sefton *et al.* 199, Castro-Vásquez *et al*. 2002) and 'Sauvignon', 'Tocai friulano', 'Pinot gris', 'Pinot blanc' (Di Stefano *et al.* 2000).

Several terpenols such as linalool, pyranic linalool oxide, citronellol, exo-2-hydroxy-1,8-cineol were observed only in the bound volatile fractions. The most abundant terpenoids were α-terpineol (156.4 $\mu g \cdot l^{-1}$), geraniol (96.9 $\mu g \cdot l^{-1}$) and geranic acid (53.2 $\mu g \cdot l^{-1}$).

The level of α-terpineol was greater than that found in 'Chardonnay' (Sefton *et al.* 1993; Castro-Vásquez *et al.* 2002), 'Malvasia istriana', aromatic 'Traminer', 'Sauvignon', 'Ribolla gialla', 'Tocai friulano', 'Pinot gris' and 'Pinot blanc' (Di Stefano *et al.* 2000), 'Airen', 'Macabeo' (Castro-Vásquez *et al.* 2002), 'Gewürztraminer' (Girard *et al*. 2002), 'Muscat of Bornova', 'Narince' (Selli *et al.* 2003) and 'Muscat à pétit grains' (Sanchez Palomo *et al.* 2006).

The concentration of glycosilated geraniol is similar to that of 'Muscat of Bornova' (Selli *et al*. 2003), 'Tocai friulano' and 'Rhine Riesling' (Di Stefano *et al.* 2000). Glycosilated citronellol level is similar to typical floral varieties such as 'Muscat à pétit grains' (Sanchez Palomo *et al.* 2006), 'Muscat of Bornova' (Selli *et al.* 2003) and 'Malvasia istriana' (Di Stefano *et al*. 2000).

The level of linalool found in 'Falanghina' grapes is similar to that of 'Pinot gris' and it is very low if compared with those detected in floral white varieties as expected (Di Stefano *et al.* 2000).

Geranic acid was detected at bound levels higher than those found in varieties such as 'Chardonnay' (Sefton *et al.* 1993), 'Rhine Riesling', 'Malvasia istriana', 'Ribolla gialla', 'Tocai friulano', 'Pinot gris' and 'Pinot blanc' (Di Stefano *et a*l. 2000).

'Falanghina' grape exhibits high levels of bound 2-exo-hydroxy-1,8-cineole (27.6 $\mu g \cdot l^{-1}$). 2-exo-Hydroxy-1,8- cineole was reported at low bound level in 'Sauvignon' juice (Bitteur *et al.* 1990) and it is now being reported for the first time in the 'Falanghina' variety. 2-exo-Hydroxy-1,8-cineole can originate either from α-terpineol or from 1,8-cineole. Since only α-terpineol was found in 'Falanghina' grape extract the hypothesis proposed by Bitteur and co-workers (1990) for production of 2-exo-hydroxy-1,8-cineole involving epoxidation of the C1 = C2 double bound of α-terpineol is to be put forward.

On the base of data obtained in this study bound geraniol, geranic acid, α-terpineol, eugenol and 2-exo-hydroxy-1,8-cineole play a central role in characterizing the pattern of varietal aromas of *V. vinifera* 'Falanghina'. In particular glycosilated 2-exo-hydroxy-1,8-cineole found in the must of 'Falanghina' grape may be discriminant and could hypothetically contribute to identification of 'Falanghina' wine origin and affiliation because of its known high chemical and biological stability (Bitteur *et al.* 1990).

## Acknowledgement

The authors thank Ms. C. Turner for her helpful assistance in preparing the manuscript. The financial support of Campania region is gratefully acknowledged.

## References

Bitteur, S. M.; Baumes, R. L.; Bayonove, C. L.; Versini, G.; Martin, C. A.; Dalla Serra, A.; 1990: 2-exo-Hydroxy-1,8-cineole: A new component from grape var. Sauvignon. J. Agric. Food Chem. **38**, 1210-1213.

Brander, C. F.; Kepner, R. E.; Webb, A. D.; 1980: Identification of some volatile compounds of wine of *Vitis vinifera* cultivar Pinot Noir. Am. J. Enol. Vitic. **31**, 69-75.

Castro-Vásquez, L.; Pérez-Coello, M. S.; Cabezudo, M. D.; 2002: Effect of enzyme treatment and skin extraction on varietal volatiles in Spanish wines made from Chardonnay, Muscat, Airen and Macabeo grapes. Anal. Chim. Acta **458**, 39-44.

Di Stefano, R.; 1991: Proposal for a method of sample preparation for the determination of free and glycoside terpenes of grapes and wines. Bull. O I V (Off. Int. Vigne Vin) **64**, 219-223.

Di Stefano, R.; Gentilini, N.; Ummarino, I.; 2000: Studio dei profili aromatici di varietà a frutto bianco coltivate nella zona del Collio. L'Enologo dicembre, 95-102.

Drawert, F.; Tressel, R.; Heimann, W.; Emberger, R.; Speck, M.; 1973: Biogenesis of aroma components in plants and fruits. XV. Enzymic-oxidative formation of C6-aldehydes and alcohols and their precursors in apples and grapes. Chem. Mikrob., Technol. Lebensm. **2**, 10-22.

Girard, B.; Fukumoto, L.; Mazza, G.; Delaquis, P.; Ewert, B.; 2002: Volatile terpene constituents in maturing Gewürztraminer grapes from British Columbia. Am. J. Enol. Vitic. **53**, 99-109.

Moio, L.; 2005: Colori, Odori ed Enologia della Falanghina. Prima edizione, Napoli. Poligrafica F.lli Ariello Editori.

Sanchez Palomo, E.; Perez-Coello, M. S.; Diaz-Maroto, M. C.; Gonzales Vinas, M. A.; Cabezudo, M. D.; 2006: Contribution of free and glycosidically-bound volatile compounds to the aroma of muscat "a petit grains" wines and effect of skin contact. Food Chem. **95**, 279-289.

Schreier, P.; 1979: Flavor composition of wines: A review, CRC. Crit. Rev. Food Sci. Nutrit. **11**, 59-111.

Sefton, M. A.; Francis, I. L.; Williams, P. J.; 1993: The volatile composition of Chardonnay juices. A study by flavor precursors analysis. Am. J. Enol. Vitic. **44**, 359-370.

Selli, S.; Cabaroglu, T.; Canbas, A.; Erten, H.; Nurgel, C.; 2003: Effect of skin contact on the aroma composition of the musts of *Vitis vinifera* L. cv. Muscat of Bornova and Narince grown in Turkey. Food Chem. **81**, 341-347.

*Received October 10, 2007*