Study of the phenolic composition of Vernaccia di San Gimignano vine

Franco Giannetti*, Anna Maria Epifani, Marco Leprini and Giordano Martini
CREA, Research Centre for Viticulture and Enology, 52100 Arezzo, Italy

Abstract. Vernaccia di San Gimignano is a Tuscan white wine, with a great historical tradition, produced mostly from the homonymous grapevine. One of the peculiarities of the vine, apart from producing fruity and sapid young wines, is the ability to generate structured wines, suitable for the aging process of “riserva” type. For a better understanding of the Vernaccia di San Gimignano characteristics, a research protocol has been set up. It specifically concerns the phenolic composition of the grapes observed by HPLC analysis. The hydroxycinnamic acids, the flavanols and the flavonols of the skins, the flavanols of the seeds and the hydroxycinnamic acids of the juice have been determined. The trans-caftaric acid is the predominant form in the juice (70-120 mg/L) and in the skins (5-12 mg/Kg) where there are higher values of quercetin (4-20 mg/Kg) and procyanidins (18-35 mg/Kg). Catechins (30-80 mg/Kg) prevail in the seeds.

1 Introduction
In a region where excellent red wines are produced, a remarkable white wine named Vernaccia di San Gimignano, derived mostly from the homonymous grapevine, stands out [1]. The first traces of this wine date back to the Middle Ages. It was the first wine in Italy to receive the “D.O.C” quality assurance label in 1966 and the “D.O.C.G” origin assurance label in 1993. Furthermore, the territory of San Gimignano (Tuscany, Italy) was one of the first in Italy to be analyzed through viticulture zoning studies and where researches on clonal selections were promoted [2].

One of the peculiarities of the grapevine, apart from producing fruity and sapid young wines, is the ability to generate structured wines, suitable for aging process of “riserva” typology.

2 Materials and methods
Vernaccia di San Gimignano (clone VP 6) is one of the cultivars grown in the experimental field of the CREA-VE labs of Arezzo. The oenological characteristic parameters were evaluated for three consecutive years. The harvest date was decided on the basis of sugar accumulation, about 21 ° Brix and titratable acidity not less than 6 g/L; the fresh grape extracts were analysed by High-Performance-Liquid-Chromatography (HPLC-DAD) for the determination of phenolic compounds [3, 4].

An Agilent 1100 chromatograph with auto sampler set at 10 µl and a Phenomenex Luna C18 5 µm 250x3 mm column with a flow rate of 0.7 mL/min were used. The spectra were recorded at the optimal wavelengths for the various compounds (280, 320 and 360 nm), eluted in gradient of solution A (Acetonitrile 50% + solution B 50%) which from initial value of 5% passes to 10% in 10 min, to 30% in 20 min, to 60% in 30 min and to 100% in 40 min. The analysis ended at 50 minutes. Solution B is H3PO4 0,07%. The compounds were quantified comparing the peak areas with external standard values [5, 6].

3 Results

![Average grape composition by weight (%).](image)

The average grape composition was the following: the juice represented 80,45%, the skins 16,79% and the seeds 2,76% (Fig. 1). There were 171 seeds per 100 berries. The must had an average sugar content of 21...
°Brix, a titratable acidity of 6.25 g/L and a pH of 3.15. The average weight of the berries was 2.32 g (Fig. 2).

![Fig. 2. Average analytical values of the grapes at harvest.](image)

Must chromatographic analysis recorded the presence of about 90 mg/L of hydroxycinnamic acid represented by more than 90% by trans-caftaric acid (Tab. 1).

| Hydroxycinnamic acids of the must. Average values for the three years ±SD. |
|------------------|------------------|------------------|------------------|------------------|
| cis CAFTARIC     | trans CAFTARIC   | cis COUTARIC     | trans COUTARIC   | trans FERTARIC   |
| 0.33 ± 0.03      | 80.89 ± 7.06     | 0.47 ± 0.04      | 3.34 ± 0.31      | 2.02 ± 0.17      |
| 0.38%            | 92.92%           | 0.54%            | 3.84%            | 2.32%            |

These compounds have also been detected in the skins, mostly in the trans form, with a prevalence of trans-caftaric acid (12 mg/Kg in the global extracts and 5.5 mg/Kg in the extractable part).

Other compounds present in significant quantities are the flavanol monomers, mainly catechin (13.4 mg/Kg in the global extracts and 7 mg/Kg in the extractable part) and epicatechin at a lower rate (9.6 mg/Kg and 4.2 mg/Kg respectively). Among the procyanidins, the B1 dimeric compounds show the highest values.

In the flavonols group, there are three forms of quercetin and two of kaempferol. The main compound is quercetin-3-O-glucoside (17.8 mg/Kg in the global extracts and 12.4 mg/Kg in the extractable part) (Fig. 3). Relative to the phenolic grape seed composition, a considerable amount of flavonols monomers, mainly catechin, were detected (Fig. 4).

![Fig. 3. Phenolic compounds of skin extracts (mg/kg grapes). Bars represent standard deviation between vintages.](image)

**Conclusions**

A global control of the grapes at harvest, beyond essential information about sugar content, pH, total acidity and relative acid composition, implies further parameters that can indicate the best potential technological processes.

Also in white grapes, the polyphenol indexes measured on the berries portions can be useful to establish the phenolic composition of the must and to determinate the eventual skin contact times and temperatures during the vinification process.

Seeds polyphenols are not easily extractable in vinification, but they have a varietal value and they can be useful for various health purposes [7].

For a better understanding of the Vernaccia di San Gimignano characteristics, a research protocol has been established that involves the use of HPLC analysis to observe, in depth, the phenolic composition of the grapes. The must and the skin extractable fraction of
Vernaccia di San Gimignano present a moderate and balanced content of phenolic compounds that allow some alternative vinification choices, such as the use of barrrique or amphorae, which entail a better micro-oxygenation and a consequent sensorial enrichment. The results obtained showed that the extractable phenolic compounds from skins amounts to 60% of the total grape phenolic substances contained, while for the seeds the extraction rate stands around 40%.

References

2. R. Bandinelli, P. Storchi, L’Enologo 5, 30-34 (2016)