

# Preliminary Characterisation of Sardinian Red Grape Cultivars (*Vitis vinifera* L.) According to Their Phenolic Potential

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Submitted for publication: Feb 2009 Accepted for publication: May 2009

Key words: Cultivar, red grapes, polyphenolic composition, skins, seeds

Fourteen cultivars and clones, mainly selected from the island of Sardinia (Italy) and grown in a collection field, showed significant quantitative differences in phenolic potential. An extraction method designed to reproduce the winemaking process was used to determine the amounts of extractable polyphenols, anthocyanins, catechins and proanthocyanidins reactive to vanillin, and the proanthocyanidins in grape skins and seeds. The Sardinian cultivar Nieddera and the Spanish cultivar Graciano had the highest concentrations of extractable polyphenols, anthocyanins, catechins and proanthocyanidins reactive to vanillin. Four clones of the Cannonau cultivar (synonym Grenache) exhibited fairly high variability, with significant differences in berry and seed phenolic contents.

Historically, grape-growing has been one of the most important agricultural activities in Europe and has a great impact on the European economy. Innovations in agronomic, technological and marketing strategies have been adapted to optimise the quality of wines.

In the last ten years, there has been great interest in red grape cultivars throughout the world, especially in view of the scientific evidence for the so-called "French Paradox", which is associated with the antioxidant properties of the phenolic compounds in red grapes. In fact, the health benefits of red wines have been well documented in numerous scientific papers (Renaud & De Logeril, 1992; Kanner *et al.*, 1994; Burns *et al.*, 2000; Lòpez-Vèlez *et al.*, 2003; Corder *et al.*, 2006). The importance of phenolic compounds for wine quality is also very well known, as they are responsible for important properties such as colour, bitterness and astringency (Gawel, 1998; Boulton, 2001; Brossaud *et al.*, 2001).

In the last 40 years, the incidence of red cultivars has increased in Sardinia, a large island located in the Mediterranean Sea off southern Italy. Today, the most important red grape cultivar is Cannonau (synonym Grenache, cultivated in 31% of the 27 000-hectare regional vine-growing area), followed by the white grape cultivar Nuragus (15% of the Sardinian vine-growing area), which for many decades was the main Sardinian cultivar. Other red grape cultivars grown in Sardinia are Monica and Carignano (12% and 7% of the regional vine-growing area respectively) and Bovale and Pascale di Cagliari (6% of the vine-growing area respectively) (Nieddu et al., 2006b). Other traditional Sardinian red grape cultivars like Girò and Cagnulari are currently showing a strong decline, with growing areas of less than 250 hectares. The reduction in grape genetic variability is due to the sharp decrease of the vine-growing area (in comparison to 74 000 hectares in the 1980s) and the increasing spread of "international" cultivars like Sangiovese, Cabernet Sauvignon, Merlot and Syrah, which are characterised by very good adaptation to the environment and good technological and agronomical characteristics.

The traditional Sardinian range of varieties is not well characterised and there is information about the ampelographic patrimony of Sardinia, particularly the polyphenolic composition of red grape cultivars, regarding only a few cultivars (Castia *et al.*, 1992a,b; Deidda *et al.*, 1994; Del Caro *et al.*, 1994). Moreover, it is very difficult to compare the data because they were obtained in different geographical areas and in vineyards subjected to different cultivation techniques, which could have influenced the productivity, berry size and area/volume ratio (Matthews *et al.*, 1987; Matthews & Matthews, 1988; Fernandez de Simon *et al.*, 1992; Bergqvist *et al.*, 2001).

Phenolic composition is used by scientists to differentiate wine cultivars (Mattivi *et al.*, 1991; Castia *et al.*, 1992b; De La Presa-Owens *et al.*, 1995; Gonzalez-Neves *et al.*, 2001; Rossouw & Marais, 2003). It is very important to know the concentration of phenolic compounds in grapes, both for cultivar characterisation and because of their role in the winemaking process. In fact, the total amount and the different concentrations of the various fractions give important information to oenologists with regard to the winemaking techniques that should be adopted for these grapes (Mattivi *et al.*, 2002a).

The polyphenolic content is related to the grape composition and the oenological practices, and wine ageing can modify the phenolic composition (Fulcrand *et al.*, 2006). Indeed, these compounds are involved in many chemical reactions during wine maturation and ageing that modify characteristics such as colour, flavour, taste (bitterness and astringency) and antioxidant activity (Pérez-Magariño & Gonzales-SanJosè, 2004).

Wines with more stable and intense colour come from grapes with good phenolic maturity (Mattivi *et al.*, 2002b; Jensen *et al.*, 2008). Hence, grapes that produce wines suitable for ageing

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contain more phenolic compounds, especially anthocyanins and tannins with a low degree of polymerisation that are able to be transformed into proanthocyanidins or condensed tannins during storage. For this reason, grapes for wines to be aged for a long time should have a very high ratio between tannins with a low degree of polymerisation and those with a high degree of polymerisation.

There is very little information in the literature about the contribution of the polyphenolic compounds in the different parts of the grape to wine quality (Jensen *et al.*, 2008). Therefore, the aim of this study was to characterise the most important Sardinian red grape cultivars according to the polyphenolic contents of the grape skins and seeds in order to evaluate their most appropriate oenological uses.

#### MATERIALS AND METHODS

#### Sampling

Research was carried out in 2007 on 14 grape cultivars collected during their technological maturity (soluble solids %/titratable acidity ratio stable) and belonging to a varietal collection field planted at Sassari University's experimental agricultural station at Fenosu-Oristano (N 39°53'42", E 8°37'01") in 2006. These cultivars were cultivated in three randomised plots (VSP trellised with gujot pruning, rootstock 1103 P, spacing 2.5 m x 1 m). The following red grape varieties and clones were studied: four Cannonau clones (CAPVS 1, CAPVS 2, CAPVS 5 selected in Sardinia and VCR1 selected in northern Italy) and the traditional Sardinian varieties Monica, Bovale grande, Pascale di Cagliari, Nieddera, Gregu nieddu, Caricagiola, Nieddu mannu and Girò. Two Spanish varieties, Mazuela and Graciano, which are genetically identical in 12 SSR markers to Carignano and Bovale sardo respectively but with a different adaptation to the environment, were included in the comparison (Nieddu et al., 2006a). Carignano and Bovale sardo could not be included in the study because they did not produce a sufficient number of homogeneous clusters during the study year, as required by the sampling protocol.

In September, 12 representative clusters per variety were sampled, one for each vine in the three plots. Clusters between 1 m and 20 cm above the soil were chosen. Titrable acidity, pH and total soluble solids were measured in musts of the different grape varieties. Two replicates of 500 g of berries for each variety were frozen at -18°C until polyphenol extraction. The following were determined in the extracts of the grape skins and seeds: extractable polyphenols, extractable anthocyanins (only on skin extracts), catechins and proanthocyanidins reactive to vanillin, and extractable proanthocyanidins.

### Polyphenol extraction

Various methods have been reported in the literature for the extraction of grape polyphenols (Di Stefano & Cravero, 1991; Amrani & Glories, 1994; Mattivi *et al.*, 2002a). We adopted the Mattivi method, as it is able to extract polyphenols from grape skins and seeds, simulating the maceration process of red winemaking.

A 12% hydroalcoholic solution of ethyl alcohol with 5 g/L of tartaric acid neutralised to pH 3 with NaOH, and supplemented with 200 mg/L of potassium metabisulphite, was prepared for the polyphenol extraction. Skins and seeds from 200 g of berries were

manually separated and poured into two flasks, each containing 200 mL of hydroalcoholic solution. The flasks were put in a stove at 30°C for 5 days; each flask was stirred once a day. At the end of the extraction, the seed extract was directly poured into a 260 mL bottle, while the skin extract, obtained by gravity and manual pressing of the skins, was centrifuged for 8 min at 8000 rpm to remove the lees and then poured into a 260 mL bottle. The bottles were filled with the hydroalcoholic solution, closed with a screw cap and stored at 4°C until the analysis.

#### **Spectrophotometric determinations**

Spectrophotometric determinations were carried out on the extracts according to the methods of Di Stefano *et al.* (1989), which allow isolation of the phenolic compounds on a Sep-Pak C18 cartridge to eliminate interference due to salts, sugars and proteins (HP 8453 UV-VIS spectrophotometer, Palo Alto, CA).

Extractable polyphenols: Extracts diluted with 1 N sulphuric acid were passed through a previously activated Sep-Pak cartridge and the phenolic compounds were eluted with 2 mL of methanol and 5 mL of water in 25 mL flasks. A volume of 1 mL of Folin-Ciocalteu reagent was added to the diluted samples, followed after 3 min by 4 mL of 10% sodium carbonate plus water up to volume. After 90 min, the absorbance value was taken at 700 nm on a 1 cm cell against a blank obtained in the same way but with water instead of extract. The results (mg/kg of grape) were expressed as (+) catechin = 186.5\* E700 \* d; d = dilutions.

Extractable anthocyanins: Extracts diluted with 1 N sulphuric acid were passed through a previously activated Sep-Pak cartridge. After washing of the cartridge with 0.01 N sulphuric acid, anthocyanins were eluted with 3 mL of methanol in 25 mL flasks; then 3 mL of HCl were added and made up to volume with a solution of ethanol:water:hydrochloric acid (70:30:1). The extractable anthocyanins were quantified on the basis of maximum absorbance in the visible light interval of 536 to 540 nm and calculated as malvidin (mg/kg of grape) = E (1 cm, 1 max vis) \*26.6 \*d; d = dilutions.

Extractable catechins and proanthocyanidins reactive to vanillin (Vanillin Index): After dilution with 1 N sulphuric acid, the samples were passed through a previously activated Sep-Pak cartridge and eluted with 5 mL of methanol; then 1 mL of this solution was poured into a dark glass flask, to which were added 6 mL of a 4% vanillin solution in methanol and the flask was placed in a cold water bath. After 3 min, 3 mL of HCl were added. A blank was prepared in the same way but with 6 mL of methanol instead of vanillin. Absorbance values at 500 nm were taken after 15 min and the results were expressed as (+) catechin (mg/kg of grape) =  $290.8*\Delta E*$  d.  $\Delta E=$  difference in absorbance between sample and blank, d = dilutions.

Extractable proanthocyanidins: after dilution with 0.1 N sulphuric acid, 2 mL of diluted extracts were passed through a previously activated Sep-Pak cartridge, and proanthocyanidins were eluted with 3 mL of methanol and collected in 100 mL distillation flasks. 9.5 mL of absolute ethanol and 12.5 mL of hydrochloric acid containing 300 mg/L of FeSO<sub>4</sub>:7H<sub>2</sub>O were added to the flasks and they were heated in a bath of boiling water for 50 min. The flasks were then put in a cold water bath in the dark for 10 min. A blank was prepared in the same way but the flasks were not subjected to heating and the acid solution

was added after chilling. The absorbance spectrum at 380 to 700 nm was recorded for both sample and blank. A tangent to the absorbance curve was plotted starting at the minimum point and ending at the maximum point. The height of the line drawn between the maximum and the tangent was read and expressed in absorbance units. The same procedure was followed for the blank. The difference between the two values (sample and blank) is the  $\Delta E$ '. For the final calculation, the content was expressed in cyanidin chloride (mg/kg of grape) =  $\Delta E$ '1cm \*1162.5 \*d. d = dilutions.

The values of the different parameters derive from calculations that consider the quantity of berries used, the millilitres of extract used, the molar extinction coefficients (obtained with calibration curves) and the molecular weights of the different compounds.

#### Statistical analysis

One-way analysis of variance (ANOVA) and HSD Tukey's test (significance level p < 0.05) were applied to the data (Statistica 6.0 for Windows).

#### RESULTS AND DISCUSSION

#### Chemical parameters of musts

The results reported in Table 1 indicate significant differences between the compared varieties. Most of them showed very low acidity and high pH, typical of musts from grapes harvested in a warm climate and with a high sugar level. Mazuela had significantly higher acidity than all the other cultivars (5.40 g/L of tartaric acid); Bovale grande had the next highest value (4.61 g/L), while Gregu nieddu had the lowest value (2.06 g/L).

The highest pH values were found in Graciano and Gregu nieddu (4.31 and 4.25 respectively), while the highest value among the

Cannonau clones was found in CAPVS1. Pascale di Cagliari had the lowest value for total soluble solids content (19.45%), while Graciano and Monica showed significantly higher values (25.95 and 25.90% respectively). Among the four clones of Cannonau, CAPVS1 had the highest value (24.95%) and VCR1 the lowest (20.90%).

#### Phenolic profiles of grape skin extracts

The one-way ANOVA of grape skin phenolic profiles is reported in Table 2. The highest extractable phenolic contents were found in Nieddera, Graciano, Caricagiola, Cannonau CAPVS 1 and Bovale grande, while all the other cultivars had significantly lower values. The highest extractable anthocyanin content was found in Graciano, while the Cannonau clones VCR1 and CAPVS 2, and the Girò, Gregu nieddu and Pascale di Cagliari cultivars had lower values. The different cultivars showed fairly high variability in low molecular weight polyphenols (Vanillin Index). Extractable proanthocyanidins were significantly higher in Nieddera, Caricagiola and Cannonau CAPVS 5 than in all the other varieties.

#### Phenolic profiles of seed extracts

The contents of different phenolic classes in the seeds are reported in Table 3. Nieddera had a significantly higher value of extractable polyphenols than the other cultivars, while Mazuela had the lowest value. Graciano showed a significantly higher content of catechins reactive to vanillin than the other cultivars, confirming what has been reported in the literature (Monagas *et al.*, 2003); Bovale grande and Mazuela had the lowest values. In contrast, the content of extractable proanthocyanidins was significantly higher in Monica than in the other cultivars, while Bovale grande and Mazuela had the lowest values.

TABLE 1
Titratable acidity, pH and total soluble solids of the different cultivars (means ± standard deviations).

Cultivar	Titratable acidity (g/L tartaric acid)	рН	Total soluble solids (°Brix %)
Cannonau CAPVS 1	$3.19 \pm 0.05$ fg*	$3.90 \pm 0.00$ cd	$24.95 \pm 0.07c$
Cannonau CAPVS 2	$3.71 \pm 0.06c$	$3.81 \pm 0.00e$	$24.10 \pm 0.00$ d
Cannonau CAPVS 5	$3.22 \pm 0.00 f$	$3.82 \pm 0.01$ de	$24.10 \pm 0.00$ d
VCR1 biotype Tocai rosso	$3.30 \pm 0.00$ ef	$3.77 \pm 0.01$ efg	$20.90 \pm 0.00 h$
Bovale grande	$4.61 \pm 0.06b$	$3.69 \pm 0.01$ g	$20.00\pm0.00i$
Caricagiola	$3.04 \pm 0.05$ g	$4.18 \pm 0.04$ b	$23.50 \pm 0.00e$
Girò	$3.34 \pm 0.05 def$	$4.19 \pm 0.01b$	$25.50 \pm 0.07$ b
Gregu Nieddu	$2.06 \pm 0.06 h$	$4.25 \pm 0.01$ ab	$23.55 \pm 0.07e$
Monica	$3.34 \pm 0.05 def$	$3.98 \pm 0.04c$	$25.90 \pm 0.00$ a
Nieddera	$3.82 \pm 0.00c$	$3.96 \pm 0.01c$	$22.70\pm0.00\mathrm{f}$
Nieddu Mannu	$3.67 \pm 0.00c$	$3.79 \pm 0.02$ ef	$21.55 \pm 0.07$ g
Pascale di Cagliari	$3.49 \pm 0.05$ d	$3.94 \pm 0.01c$	$19.45 \pm 0.071$
Graciano	$3.41 \pm 0.06$ de	$4.31 \pm 0.02a$	$25.95 \pm 0.07a$
Mazuela	$5.40 \pm 0.00$ a	$3.71 \pm 0.04 \mathrm{fg}$	$17.95 \pm 0.07$ m

<sup>\*</sup> Values are the mean of two replicates for each extraction.

Data followed by different letters within each column differ significantly according to HSD Tukey's Test at p < 0.05.

TABLE 2 Phenolic profile in the skins of different cultivars of red grapes (mg/kg of grape).

Cultivar	Extractable polyphenols (mg/kg of catechin)	Extractable anthocyanins (mg/kg malvidin)	Vanillin Index (mg/kg of catechin)	Extractable proanthocyanidins (mg/kg of cyanidin chloride)
Cannonau CAPVS 1	1074ab*	431e	966abc	915cd
Cannonau CAPVS 2	812def	304gh	919abcd	907cd
Cannonau CAPVS 5	791def	404efg	881abcd	1611ab
Cannonau VCR1 biotipo Tocai rosso	632ef	257h	564cde	911cd
Bovale grande	1034abc	888b	682bcde	1236bc
Caricagiola	1156a	417ef	1025ab	1715a
Girò	889bcd	270h	713bcde	1075c
Gregu Nieddu	599f	321fgh	717bcde	641de
Monica	721def	576d	660bcde	448ef
Nieddera	1224a	735c	1231a	1717a
Nieddu Mannu	702def	634cd	375e	1093c
Pascale di Cagliari	754def	347efgh	686bcde	1249bc
Graciano	1212a	2468a	1010ab	547f
Mazuela	819cde	701c	545de	1092c

<sup>\*</sup> Values are the mean of two replicates for each extraction.

Data followed by different letters within each column differ significantly according to HSD Tukey's Test at p < 0.05.

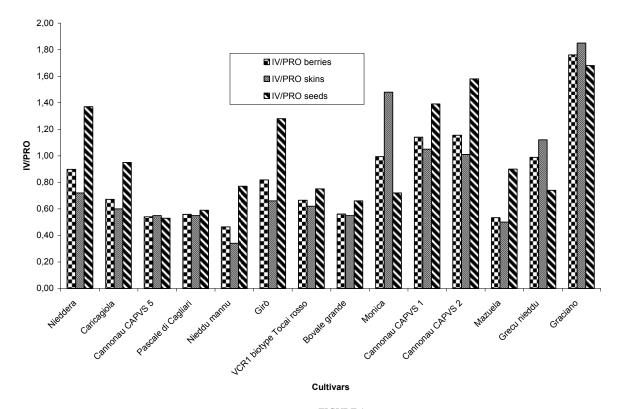


FIGURE 1 IV/PRO ratio of berries, skins and seeds in different red grape cultivars.

TABLE 3 Phenolic profile in the seeds of different cultivars of red grapes (mg/kg of grape)

Cultivar	Extractable polyphenols (mg/kg of catechin)	Vanillin index (mg/kg of catechin)	Extractable proanthocyanidins (mg/kg of cyanidin chloride)
Cannonau CAPVS 1	409*c	440cde	317gh
Cannonau CAPVS 2	440c	476cd	301h
Cannonau CAPVS 5	368cd	212fg	398ef
Cannonau VCR1 biotipo Tocai rosso	415c	364def	484c
Bovale grande	131ef	77h	117i
Caricagiola	415c	440cde	464cd
Girò	454c	460cde	358fg
Gregu Nieddu	259de	243f	328gh
Monica	619b	578c	799a
Nieddera	852a	909b	664b
Nieddu Mannu	366cd	338ef	432de
Pascale di Cagliari	250def	226fg	383ef
Graciano	635b	1093a	651b
Mazuela	93f	94gh	105i

<sup>\*</sup>Values are the mean of two replicates for each extraction.

Data followed by different letters within each column differ significantly according to HSD Tukey's Test at p < 0.05.

TABLE 4 Range of extractable polyphenols contents in different red grape cultivars.

Range	Cultivar
800 – 1100*	Gregu nieddu, Mazuela, Pascale di Cagliari, VCR1 biotype Tocai rosso, Nieddu mannu
1100 - 1400	Cannonau CAPVS 5, Bovale grande, Cannonau CAPVS 2, Monica, Girò
1400 - 1700	Cannonau CAPVS 1, Caricagiola
1700 - 2000	Graciano
> 2000	Nieddera

<sup>\*</sup>Data are expressed as catechin, mg/kg of grape.

#### Extractable polyphenols in the berries

Extractable polyphenols varied from 859 mg/kg in Gregu nieddu grapes to 2 076 mg/kg in Nieddera grapes (Table 4). The different cultivars were distributed in five groups of increasing value. Ten of the 14 cultivars were in the low-value groups (five from 800 to 1100 mg/kg, five from 1100 to 1400 mg/kg), while the other four varieties showed higher concentrations (Nieddera, Graciano, Caricagiola and Cannonau CAPVS 1). In a comparison with a large number of Italian red grape varieties, with values ranging from 1500 to 4200 mg/kg (Mattivi et al., 2002b), the Sardinian

TABLE 5 Range of extractable anthocyanin content in different red grape cultivars.

Range	Cultivar
200 – 400*	Girò, Cannonau VCR1 biotype Tocai rosso, Cannonau CAPVS 2, Gregu nieddu, Pascale di Cagliari
400 - 600	Cannonau CAPVS 5, Caricagiola, Cannonau CAPVS 1, Monica
600 - 800	Nieddu mannu, Mazuela, Nieddera
800 - 1000	Bovale grande
1000 - 2500	Graciano

<sup>\*</sup>Data are expressed as malvidin 3-monoglucoside chloride, mg/kg of grape.

red grapes exhibit a medium or low-medium level of polyphenols. This comparison is particularly significant, as our results were obtained with the same methods of extraction and analysis of the different phenolic classes, although we used frozen grapes instead of fresh grapes.

Therefore, we can conclude that only Nieddera, Graciano, Caricagiola and Cannonau CAPVS 1 can yield wines suitable for long ageing, as confirmed by the excellent ageing possibilities reported for Graciano (Nunez et al., 2004). The other varieties are indicated more for young, fruity wines.

TABLE 6
Range of extractable catechins and proanthocyanidins reactive to vanillin content in different red grape cultivars.

Range	Cultivar
600 – 1000*	Mazuela, Nieddu mannu, Bovale grande, Pascale of Cagliari, Cannonau VCR1 biotype Tocai rosso, Gregu nieddu
1000 - 1400	Cannonau CAPVS 5, Girò, Monica, Cannonau CAPVS 2
1400 - 1800	Cannonau CAPVS 1, Caricagiola
1800 - 2200	Nieddera, Graciano

<sup>\*</sup>Data are expressed as catechin, mg/kg of grape.

TABLE 7
Range of extractable proanthocyanidin content in different red grape cultivars.

Range	Cultivar
700 – 1000*	Gregu nieddu
1000 - 1300	Graciano, Mazuela, Cannonau CAPVS 2, Cannonau CAPVS 1, Monica
1300 - 1600	Bovale grande, Cannonau VCR1 biotype Tocai rosso, Girò, Nieddu mannu
1600 - 1900	Pascale di Cagliari
1900 - 2200	Cannonau CAPVS 5, Caricagiola
2200 - 2500	Nieddera

<sup>\*</sup>Data are expressed as cyanidin chloride, mg/kg of grape.

#### Extractable anthocyanins in the berries

Table 5 shows a similar situation to the above-mentioned phenolic class, with nine of 14 varieties having a very low anthocyanin content (200 to 600 mg/kg), and four varieties with mean concentrations of between 600 and 1 000 mg/kg. Only Graciano had a very high anthocyanin content (2464 mg/kg). The nine cultivars with low contents could be indicated for monovarietal wines with low or medium colour intensity. In fact, even if the maceration time is extended, the extraction from the skins is very quick (Mattivi *et al.*, 2003). However, these cultivars could also be used to produce rosé and red wines, the latter from the more coloured varieties. Nieddu mannu, Mazuela, Nieddera, Bovale grande and obviously Graciano, which contain medium and high concentrations of anthocyanins, are the varieties most indicated to produce strongly coloured wines (Nunez *et al.*, 2004).

## Extractable catechins and proanthocyanidins reactive to vanillin (Vanillin Index) in the berries

In Table 6, the cultivars are separated into four groups at intervals of 400 mg/kg, ranging from a minimum of 639 mg/kg for Mazuela to a maximum of 2 163 mg/kg for Graciano. Again, most varieties were in the low-value groups (Mazuela, Nieddu mannu, Bovale

TABLE 8

Percentage of extractable catechins and proanthocyanidins reactive to vanillin and extractable proanthocyanidins in the seeds of the different red grape cultivars. The remaining percentage is localised in the skins.

Cultivar	% Extractable catechins and proanthocyanidins reactive to vanillin	% Extractable proanthocyanidins
Cannonau CAPVS 1	31.3	25.7
Cannonau CAPVS 2	34.1	24.9
Cannonau CAPVS 5	19.4	19.8
Cannonau VCR1 biotype Tocai rosso	39.2	34.7
Bovale grande	10.1	8.6
Caricagiola	30.0	21.3
Girò	39.2	25.0
Gregu Nieddu	25.3	33.9
Monica	46.7	64.1
Nieddera	42.5	27.9
Nieddu Mannu	47.1	28.3
Pascale di Cagliari	24.8	23.5
Graciano	52.0	54.3
Mazuela	14.7	8.8

grande, Pascale, Cannonau VCR1 biotype Tocai rosso, Gregu nieddu), while the other cultivars showed higher values.

#### Extractable proanthocyanidins in the berries

In Table 7, the cultivars are separated into six groups at intervals of 300 mg/kg, from a minimum of 969 mg/kg for Gregu nieddu to a maximum of 2 381 mg/kg for Nieddera. Nine of the varieties (> 50%) are in the intermediate concentration (1000 to 1600 mg/kg).

We also calculated the Vanillin Index/proanthocyanidin ratio (VI/PRO), as it is correlated with the degree of polymerisation of flavanols and thus effectively describes the condensation reaction course. In fact, this ratio is defined as the "tannin condensation index": the lower the ratio, the higher the tannin molecular weight and hence the degree of polymerisation of these compounds. Contrarily, if the ratio is high, the degree of polymerisation of flavanols is lower and these molecules are more reactive and astringent (Cagnasso *et al.*, 2005, 2006). For this reason, only varieties with a high value of this ratio (from 0.8 upwards) are considered suitable for wines that can withstand a decrease in the tannic character and thus a softening of the taste during storage (Mattivi *et al.*, 1991). In our cultivars (Fig. 1), the mean value of the ratio was 0.84 (0.77 without Graciano), with extreme values

of 0.46 for Nieddu mannu and 1.76 for Graciano. As reported in the literature, the flavanols in the seeds are less polymerised than those in the skins (Prieur *et al.*, 1994; Souquet *et al.*, 1996). This is confirmed by our results for 10 of the 14 varieties analysed, although Cannonau CAPVS 5, Gregu nieddu, Monica and Graciano presented higher values in the skins. In particular, Graciano had a very high VI/PRO ratio for the skins (1.85), indicating a higher content of monomeric and/or low molecular weight flavonols (Monagas *et al.*, 2003).

#### Distribution of catechins and proanthocyanidins in the berries

Table 8 shows that 10 of the 14 varieties had less than 40% of the catechins and proanthocyanidins reactive to vanillin located in the seeds; among them, Mazuela, Bovale and especially Cannonau CAPVS 5 had a very low percentage in the seeds. Of the other four varieties, only Graciano exceeded 50% located in the seeds. The content of extractable proanthocyanidins in the seeds did not exceed 35% in 12 of the 14 varieties; only Monica and Graciano exhibited a high percentage in the seeds.

#### CONCLUSIONS

The analysis of the phenolic potential of the main Sardinian red grape cultivars resulted in a better technological characterisation, which could be useful to improve wine production. Nieddera is distinguished by the high concentration of extractable polyphenols, extractable anthocyanins (together with Bovale grande and Nieddu Mannu), catechins and proanthocyanidins reactive to vanillin, and extractable proanthocyanidins (together with Caricagiola and the Cannonau CAPVS 5 clone). This cultivar can be considered very good for wines suitable for long ageing. Its aptitude is confirmed by the VI/PRO ratio, which shows a high value (0.90) due to cultivar's richness in monomeric and/or low molecular weight phenols. Regarding the Spanish Graciano and Mazuela varieties, cultivated in Sardinia, only the former deserves attention on account of its high anthocyanin content and its VI/PRO ratio, the highest among all the cultivars, confirming its suitability for wines that are suitable for long ageing. The best use for the other cultivars would be the production of young wines or those to be aged for a medium term, although in the latter case great attention would have to be given to the use of suitable winemaking procedures or blending with grapes with a high phenolic content.

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