

## Differentiation of Tannat, Cabernet Sauvignon and Merlot grapes from Uruguay according to their general composition and polyphenolic potential

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### Abstract

This paper shows the results of a study carried out during four years (2001-2004). Its aim was the characterization of Tannat, Cabernet Sauvignon and Merlot grapes cultivated in the south of Uruguay. The results were evaluated to qualify the enological potential of these varieties of *Vitis vinifera* L. Typical cultivation situations in the region were included of each variety. The grapes were analysed at harvest for determination of global composition and polyphenolic potential. Tannat grapes presented very different characteristics in relation to other varieties. Tannat had the highest percentage of seeds, berry weight, sugar contents, total acidity, total polyphenols, total anthocyanins, extractable anthocyanins, skin tannins and seed tannins levels. Also, they had the lowest pH values and the highest EA%, corresponding to the lowest extractability of anthocyanins. The effect of vintage on the grape composition was very important, according to the impact of the climatic conditions in the synthesis of quality components of berries. However, the joint consideration of analytical indexes of base composition, polyphenolic potential and structure of the berry allowed a perfect discrimination of samples of each variety.

**Keywords:** Tannat, anthocyanins, polyphenols, Cabernet Sauvignon, Merlot, grape

### Diferenciação de uvas Tannat, Cabernet Sauvignon e Merlot provenientes do Uruguai de acordo com sua composição geral e potencial polifenólico

### Resumo

Este trabalho apresenta os resultados de um estudo realizado durante quatro anos (2001-2004). O objetivo foi a diferenciação e caracterização de uvas de Tannat, Cabernet Sauvignon e Merlot cultivadas no sul do Uruguai. Os resultados foram avaliados para qualificar o potencial enológico das variedades de *Vitis vinifera* L. em situações típicas de cultura na região. As uvas foram analisadas no momento da colheita para determinar a composição geral e o potencial polifenólico. Tannat apresenta características muito diferentes em relação às demais variedades. Tannat apresentou o maior percentual do peso da semente, peso das bagas, teor de açúcar, acidez total, polifenóis totais, antocianinas totais, antocianinas extraíveis, taninos da pele e taninos de sementes. Além disso, ela teve os menores valores de pH e maior EA%, correspondente a uma menor extractabilidade de antocianinas. O efeito da safra sobre a composição foi muito importante, de acordo com o impacto das condições climáticas na síntese de componentes da qualidade dos frutos. No entanto, a análise conjunta da composição global, o potencial de polifenóis e a estrutura da baga permitiu uma perfeita discriminação das amostras de cada variedade.

**Palavras-chave:** Tannat, antocianinas, polifenóis, Cabernet Sauvignon, Merlot, uva

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## Introduction

Tannat is a grape cultivar traditionally cultivated in Uruguay since the end of the 19th century. Nowadays, it is considered the emblematic variety of this country and their red wines are the most recognised and original between the Uruguayan wines. Few studies on these grapes cultivar have been realised in Uruguay (González-Neves et al., 2002, 2004 and 2010) and in other regions around the world, such as Rizzon & Miele (2004). These studies were very important because the enological characterization of grapes is essential for the definition of winemaking conditions (Glories, 2001; González-Neves et al., 2010).

Grapes composition has a primordial incidence on the composition and sensorial properties of wines. The composition of grapes depends on cultivar, soil properties, climatic conditions, crop load and management practices of vineyard (Jackson & Lombard, 1993; Downey et al., 2006). The cultivar is an important factor because the genome regulates the expression of enzymes involved in the synthesis of the grape components, mainly those related to secondary metabolism in grapevines (Downey et al., 2006; Tian et al., 2008). Polyphenols are the most important secondary metabolites and the major bioactive compounds synthesized in the berries. The most important of them are the anthocyanins, pigments responsible for the color of red grapes and young red wines, and the tannins, compounds responsible for astringency and bitterness of grape and wine (Cheynier et al., 2006; Gil-Muñoz et al., 2009).

The structure of the grapes (berry size, ratio skin/flesh) has an enological impact. Different polyphenols have different location within the berry, what modifies its extraction during winemaking. Anthocyanins are found inside the vacuoles of the skin cells and tannins are located in the skin cellules and mainly in seeds. The composition of the cellular walls of skins modifies the anthocyanin diffusion (Ortega-Regules et al., 2008b), whereas the skin tannins extraction is more dependent on the tannin-binding capacity of cell walls (Hanlin et al., 2010). The berry size determines the relationship between skin and juice, and modifies the extraction of the compounds during the skin contact process (Gil-Muñoz et al., 2009; Ortega-Regules et al., 2008a).

The knowledge of polyphenol potential of grapes and their extractability allows a better control of winemaking, using different technologies and defining the conditions of maceration (Di Stefano et al., 2000; Glories, 2001; Cagnasso et al., 2008; González-Neves et al., 2010). Simple spectrophotometric methods permit us to know the polyphenolic potential of grapes and the evaluation of their extractability. The results have technological utility (Glories, 2001; Cagnasso et al., 2008; González-Neves et al., 2010; Torchio et al., 2010), although numerous

criticisms discussing its validity like as indicators of maturity (Di Stefano et al., 2000; González-Neves et al., 2004).

The aim of this work was the differentiation and the enological characterization of Tannat, Cabernet Sauvignon and Merlot grapes cultivated in the south of Uruguay.

## Materials and Methods

### Field trials

The study have been realised for four years (2001 - 2004), considering commercial vineyards of Tannat, Cabernet Sauvignon and Merlot located in the south of Uruguay. In order to obtain a representative variability of the viticultural practices applied in this region for each variety, diverse productive situations were considered. Training systems of lyre and trellis, plants pruned in cordon Royat or Guyot and cluster thinning were included. Three or four vineyards of each variety were considered each year. In all cases, the field trial included 30 plants per vineyard, randomly selected.

### Grape samples

Samples of 250 berries were taken at harvest, with two repetitions for vineyard, employing the method proposed by Carbonneau et al. (1991). Fractions of bunches from 3 to 5 berries were extracted in the middle zone of the spurs. Each fraction was randomly selected, alternatively from the upper and lower parts of the clusters.

The harvest took place in the "technological maturity" in all cases. For that purpose, the relationship between the sugar contents, titratable acidity and pH of grapes were determined once a week.

### Basic analysis of grapes and berry structure

Half of the berries of each sample were used to determinate basic analysis, berry weight, density of musts and the relative proportions of skins, seeds and flesh. The weight of the berry was determined with an Ohaus Scout scale (Ohaus Corp., USA). Then, the berries were manually crushed in a mortar in order to remove the skins, seeds and flesh. The skins and seeds were rinsed under water to completely separate the pulp and dissolve the residual sugars, and, then, they were dried with filter paper and weighed. The weight of the flesh of each sample was calculated by using the difference between the berry weight and the skins and seeds weights. The relative proportion of each part of the grape (flesh, skins and seeds) was calculated.

Basic composition was determined by employing classical analyses (sugar content, total acidity and pH), realized in the juice obtained from the berries manually crushed and the crushing of the pulp with a juice extractor Phillips HR2290 (Phillips, Netherlands). Analyses were carried out according to O.I.V. (2007), using a refractometer

Atago N1 (Atago, Japan) and a pH meter Hanna HI8521 (Hanna instruments, Italie). The must density was estimated from sugar concentrations determined by refractometry.

#### Phenolic potential of the grapes

Half of the berries of each sample were analysed according to Glories & Augustin (1993), in order to determine the total potential in anthocyanins (ApH1), the potential in extractable anthocyanins (ApH3.2) and the phenolic richness of grapes (A280). After grinding the grapes with a blender, model solutions at two different pH values (3.2 and 1.0) were added, homogenised and macerated four hours. The extracts were filtered and centrifuged for 3 min at 3500 rpm before analysis, using a MSE Mistral 2000 centrifuge (Sanyo-Gallenkamp, Great Britain). Anthocyanin contents at pH 3.2 and pH 1.0 were measured according to Ribéreau-Gayon & Stonestreet (1965). The phenolic richness was estimated by measuring the absorbance at 280 nm of the pH 3.2 extract. All the measurements were carried out by duplication with a Shimadzu UV-1240 Mini (Shimadzu, Japan) spectrophotometer, using glass (for the anthocyanin analyses) and quartz (for the absorbance at 280 nm analyses) cells with 1 cm path length.

The indexes were calculated considering the respective dilution of the grape extracts, according to González-Neves et al. (2004). For this purpose, the mean values of the must density and the relative proportion of flesh of each sample were considered.

$$F = (50 + MV) / MV$$

F = Factor of dilution; 50 = volume of pH 3.2 or pH 1.0 solutions in mL; MV = must volume.

$$MV = (50 + P\%) / MD$$

MV = must volume in mL; P% = relative proportion of flesh; MD = must density.

The complementary indexes were calculated as follows:

$$EA\% = [(ApH1 - ApH3.2) / ApH1] \times 100 = \text{anthocyanin extractability index.}$$

$$dpell = (ApH3.2 \times 40) / 1000 = \text{skin tannins levels.}$$

$$dpell\% = (dpell / A280) \times 100 = \text{relative proportion of skin tannins.}$$

$dTpep = A280 - dpell = \text{seed tannins levels.}$

$$Mp\% = [(A280 - dpell) / A280] \cdot 100 = \text{relative proportion of seed tannins.}$$

#### Statistical Analysis

Calculations were performed using the Statgraphics Plus package, 4.1 version (Statgraphics Corp., USA). Analyses of variance and media separation by Tukey at 5% were performed considering the results corresponding to each variety and year.

The incidence of the variety and the vintage on the composition of grapes were evaluated by means of multivariate analysis, employing Principal Component Analyses (PCA) and Discriminant Canonical Analyses (DCA).

## Results and Discussion

### Incidence of the climate

The characteristics of the grapes (composition and berry structure) were strongly modified by the climate conditions of each year. The climatic data as for the four seasons showed very important differences along the maturation period (Figure 1). The year 2001 was the most unfavorable for the ripening of grapes, because it was the warmest (especially in February and March) and rainiest (in January and February) one. Consequently, the lowest levels of sugars, total polyphenols and anthocyanins were obtained in grapes produced in 2001 (Table 1, Figures 2 and 3).

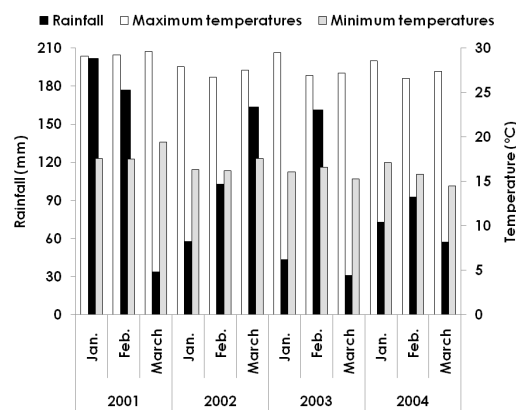
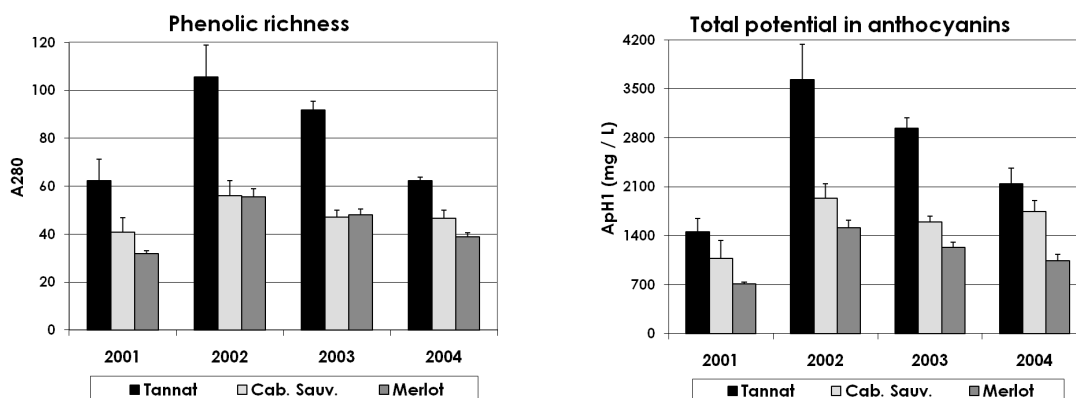


Figure 1. Climate conditions during the maturation of the grapes in each year.

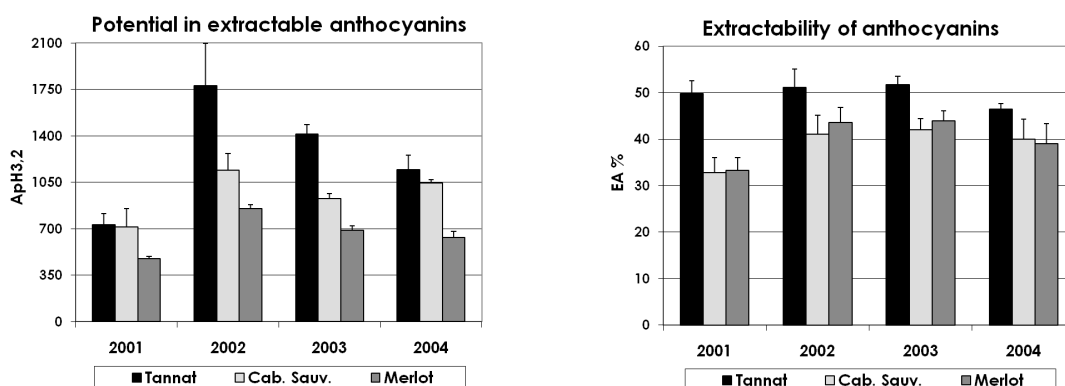
Table 1. Base composition of the grapes of each variety in each year.

		Sugars	Titrateable acidity	pH
Tannat	2001	204.7 ± 11.9	5.6 ± 0.1	3.36 ± 0.08
	2002	243.3 ± 6.5	5.2 ± 0.9	3.33 ± 0.04
	2003	242.0 ± 9.6	5.1 ± 0.8	3.39 ± 0.06
	2004	245.7 ± 9.6	5.7 ± 0.5	3.38 ± 0.04
Cabernet Sauvignon	2001	197.7 ± 5.6	4.4 ± 0.2	3.44 ± 0.03
	2002	219.7 ± 13.8	4.1 ± 0.3	3.52 ± 0.07
	2003	201.3 ± 4.6	4.3 ± 0.2	3.56 ± 0.05
	2004	213.3 ± 4.2	4.1 ± 0.1	3.66 ± 0.06
Merlot	2001	194.3 ± 8.8	4.2 ± 0.3	3.43 ± 0.05
	2002	214.7 ± 3.0	4.3 ± 0.4	3.45 ± 0.03
	2003	192.8 ± 9.0	3.6 ± 0.2	3.58 ± 0.05
	2004	207.8 ± 7.7	3.6 ± 0.2	3.67 ± 0.06

Sugars content expressed in g . L<sup>-1</sup>; titrateable acidity in sulfuric acid g . L<sup>-1</sup>.



**Figure 2.** Phenolic richness (A280) and total potential in anthocyanins (ApH3.2) of the grapes. Mean values and standard deviations, expressed in units of absorbance (A280) and malvidin-3-glucoside  $\text{mg} \cdot \text{L}^{-1}$  (ApH1).



**Figure 3.** Potential in extractable anthocyanins (ApH3.2) and extractability of anthocyanins (EA%) of the grapes. Mean values and standard deviations, expressed in malvidin-3-glucoside  $\text{mg} \cdot \text{L}^{-1}$  (ApH3.2) and percentage (EA%).

The year 2002 was tempered, with moderate drought, except in March. The conditions of this vintage were the most favorable for the synthesis of quality components of grapes. Therefore, the grapes produced in this year had the highest sugar contents, polyphenol richness and anthocyanin potential, especially concerning Tannat variety (Table 1, Figures 2 and 3). The rains of March did not affect the quality of the grapes, as they were produced in a few days, close to harvest.

The year 2003 was sub-humid, warm and with mild nights and the year 2004 was tempered warm, with cool nights and moderate drought. In a previous paper it was signaled that in 2001 and 2003 no water stress was registered in the plants between veraison and harvest. In 2002, water stress was weak, while plant water stress was from moderate to strong in 2004 (Ferrer et al., 2008).

In conclusion, excessive rainfall and higher temperatures had a negative effect on plant metabolism in 2001. In contrast, there were very good conditions for the photosynthesis and anthocyanin synthesis in 2002. There were good conditions for the synthesis of grape quality components in 2003, but high water availability determined an increase of berry size (Table 3), which could determine some dilution effect. In 2004, it was observed a lower synthesis of quality compounds (Table 1, Figures 2 and 3), probably due to the combined effect of high temperatures and strong water stress.

The differences in polyphenolic composition of the grapes produced during different years were more important than the differences in sugars, acidity or pH values (Table 1, Figures 2 and 3). Therefore, in this case, the climatic conditions seem to have a bigger impact on the secondary metabolism than on the primary metabolism of grapevines.

It is known that excessive rainfall and high temperatures may cause inhibition of the biosynthesis of anthocyanins and a general decrease in quality as for grape components (Jackson & Lombard, 1993; Bergqvist et al., 2001; Harbertson et al., 2002; Downey et al., 2006; Mori et al., 2007; Tian et al., 2008). The climatic factors (light, temperature, water availability) have a complex effect on the anthocyanin synthesis, but high temperatures seem to be the most limiting factor for this process (Mori et al., 2007; Cohen et al., 2008).

Climate conditions seem to have impacted more significantly on anthocyanin and skin tannin levels than seed tannin levels, although there were significant differences among years and especially in the grapes of 2004 over the others (Table 2, Figures 2 and 3). There were also differences in the extractability of anthocyanins, which generally was worse in years with higher anthocyanin levels, although the responses of each variety were different in each year (Figures 2 and 3).

**Table 2.** Tannin indexes of the grapes of each variety in each year.

		dpell	dTpep	dpell%	Mp%
Tannat	2001	29.2 ± 3.4	33.2 ± 7.5	47.4 ± 6.7	52.6 ± 6.7
	2002	71.1 ± 12.8	34.5 ± 2.4	66.9 ± 4.4	33.1 ± 4.4
	2003	56.5 ± 2.8	35.2 ± 3.5	61.6 ± 2.9	38.3 ± 2.9
	2004	45.8 ± 4.3	16.4 ± 3.5	73.6 ± 6	26.4 ± 6.0
Cabernet	2001	28.5 ± 5.6	12.2 ± 0.1	69.7 ± 3.7	30.3 ± 3.7
	2002	45.6 ± 5.1	10.5 ± 2.5	81.3 ± 3.4	18.6 ± 3.4
Sauvignon	2003	37.0 ± 1.6	10.0 ± 2.6	78.9 ± 4.8	21.1 ± 4.8
	2004	41.7 ± 1.1	4.8 ± 3.2	90.0 ± 6.1	10.0 ± 6.1
Merlot	2001	19.0 ± 0.6	12.9 ± 0.7	59.5 ± 1.1	40.5 ± 1.1
	2002	34.1 ± 1.1	21.4 ± 2.4	61.5 ± 2	38.5 ± 2.0
	2003	27.5 ± 1.4	20.5 ± 1.9	57.3 ± 2.4	42.6 ± 2.4
	2004	25.3 ± 1.9	13.6 ± 1.8	65.0 ± 4.1	35.0 ± 4.1

dpell and dTpep expressed in absorbance units; dpell% and Mp% in percentage.

#### Basic composition of grapes and berry structure

Tannat grapes had the highest sugar contents and titratable acidity, and the lowest pH values during all years. Merlot and Cabernet Sauvignon grapes have not showed differences between them in the majority of the years (Table 1).

Berry weight of Tannat grapes was significantly higher whereas Cabernet Sauvignon grapes had the lowest berry weight during all years. The highest proportions of skins corresponded to Cabernet Sauvignon grapes, while the highest proportions of seeds were from Tannat (Table 3).

The proportions of skins, seeds and

**Table 3.** Berry structure of the grapes of each variety in each year.

		Berry weight	Skin %	Seed %	Flesh %
Tannat	2001	1.77 ± 0.08	11.9 ± 1.7	5.3 ± 0.6	82.7 ± 2.2
	2002	1.80 ± 0.13	8.5 ± 1.2	4.8 ± 0.4	86.7 ± 1.0
	2003	1.93 ± 0.11	9.0 ± 1.4	4.7 ± 0.5	86.3 ± 1.4
	2004	1.83 ± 0.16	8.1 ± 0.7	4.8 ± 0.3	87.1 ± 0.9
Cabernet	2001	1.51 ± 0.11	12.3 ± 0.8	3.4 ± 0.2	84.3 ± 0.8
	2002	1.35 ± 0.10	9.8 ± 0.8	3.2 ± 0.2	87.0 ± 0.5
Sauvignon	2003	1.54 ± 0.11	11.2 ± 0.9	3.3 ± 0.2	85.5 ± 1.1
	2004	1.28 ± 0.03	13.3 ± 1.0	3.3 ± 0.1	83.3 ± 0.9
Merlot	2001	1.68 ± 0.09	9.8 ± 1.3	3.4 ± 0.1	86.7 ± 1.3
	2002	1.59 ± 0.07	6.6 ± 0.7	3.3 ± 0.2	90.1 ± 0.3
	2003	1.79 ± 0.22	9.0 ± 0.9	3.2 ± 0.3	87.8 ± 1.1
	2004	1.55 ± 0.09	6.5 ± 1.4	3.7 ± 0.2	89.8 ± 1.4

Berry weight expressed in g.

flesh modify the relationship between juice and pomace, modifying the extraction of anthocyanins and tannins during winemaking. Many authors suggest that small berries determine a higher ratio between flesh and skin, what increases the diffusion and solubility into the must of polyphenolic compounds during the skin contact process (Ortega-Regules et al., 2008a; Gil-Muñoz et al., 2009). However, the size of the berries is not strictly correlated to the relationship between skin and flesh (Table 3), what agrees with the results shown by Matthews & Nuzzo (2007). These authors also indicate that the composition of mature berries of each variety is not dependent on a simple way on the size attained by the berry.

#### Phenolic potential of the grapes

Tannat grapes are characterised for the highest values of phenolic richness and total anthocyanin potential in all the years, although there were important differences between the years considered. Moreover, anthocyanin potentials (ApH1 and ApH3.2) were significantly higher in Cabernet Sauvignon than Merlot grapes

in all years studied (Figures 2 and 3).

The extractability of the anthocyanins presented important differences between varieties. Tannat grapes had values of EA% significantly higher than the others, showing that the extraction of the anthocyanins is more difficult as for this variety (Figure 3). Thus, Cabernet Sauvignon and Merlot grapes had anthocyanins easily extracted, without differences in EA% values between them. The differences between the values of EA% verified during all years varies less than the other indexes, particularly for the Tannat grapes. Several authors indicate that the extractability of anthocyanins would be fundamentally a characteristic of the variety (Mori et al., 2007; Ortega-Regules et al., 2008a; Gil-Muñoz et al., 2009).

The highest values in skin and seed tannins were verified in Tannat grapes, with important variations among years (Table 2). Differences found in the tannin proportions of the seeds and skins in each variety were very significant. Tannat grapes presented in both years high proportions of seed tannins and the lowest proportions of

skin tannins. Saint-Cricq de Gaulejac et al. (1998) and Glories (2001) indicate that grape with these characteristics can produce aggressive wines with unstable color, because the tannins of the seeds tend to combine with proteins and polysaccharides instead of stabilizing the anthocyanins.

Cabernet Sauvignon grapes were characterized by the lowest seed tannins levels, the highest proportion of skin tannins and the lowest proportion of seed tannins (Table 2). On the opposite, Merlot grapes had the highest proportion of seeds tannins in three of four years studied.

The results obtained indicate that the winemaking of each variety should be adjusted to obtain wines with good stability of color and proper mouthfeel.

The knowledge of phenolic index values improves the winemaking management (Saint-Cricq et al., 1998; Glories, 2001; González-Neves et al., 2004 and 2010). These indexes, particularly, anthocyanin potential and Mp% values, suggest moderate macerations for Tannat grapes. However, EA% values indicate that during the procession of these grapes, methods to promote the extraction of anthocyanins should be used. The process of skin contact would be conducted with energetic pumping-over at the beginning, to promote the extraction of water-soluble compounds such as anthocyanins, and with little pumping over at the final, due to the high tannins contents of seeds (Saint-Cricq et al., 1998; Glories, 2001). The values of these indexes determined in Merlot suggest short maceration, soft extraction, with moderate pumping over and moderate temperature during the maceration of these grapes. Anthocyanins in Cabernet Sauvignon and Merlot grapes would be equally extracted, though Cabernet Sauvignon grapes presented tannin levels significantly lower in seeds. Consequently, more extended maceration for Cabernet Sauvignon is justified to provide an adequate tannin structure to the wine.

The use of these principles in the winemaking allows improving a good prediction of color and polyphenolic composition of young red wines (González-Neves et al., 2004 and 2010; Cagnasso et al., 2008).

*Multivariate analyses*

Principal Component Analysis (PCA) of data from the basic composition and the phenolic potential of the grapes was performed. The first two components accounted 69.8 % of the total variance. The scores showed a good differentiation of the three varieties in the biplot. The first eigenvector (PC1) essentially differentiates Tannat samples from others (Figure 4). This principal component was positively related principally to the total phenolic richness, anthocyanins potential, extractability of anthocyanins, tannins levels, sugar contents and percentage of seeds. This component was negatively related principally to the pH values (Figure 5). The second

eigenvector (PC2) essentially differentiates Cabernet Sauvignon samples than the others, related to the proportions of tannins in skins and seeds (Figures 4 and 5).

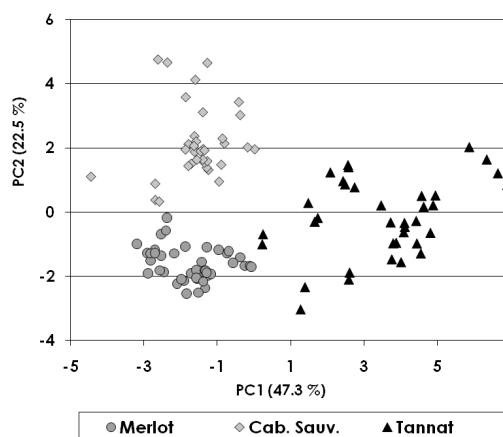


Figure 4. Distribution of the scores of the samples of each variety in the biplot generated for the two first Principal Components.

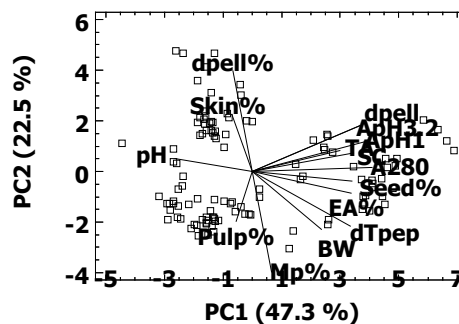


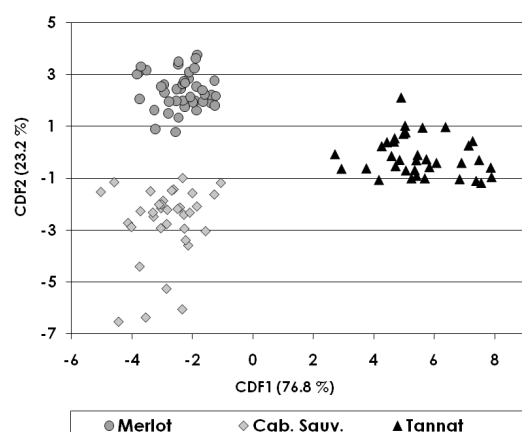
Figure 5. Distribution of the scores of the samples and vectors of variables in the biplot generated for the two first Principal Components. BW = berry weight; Skin% = percentage of skins; Seed% = percentage of seeds; Pulp% = percentage of flesh; SC = sugars contents; TA = titratable acidity; A280 = phenolic richness; ApH1 = total potential in anthocyanins; ApH3.2 = potential in extractable anthocyanins; EA% = extractability of Anthocyanins; dpell = skin tannins; dpell% = percentage of skin tannins; dTpep = seed tannins.

In order to enhance the information obtained from the PCA, the discrimination of the samples based on the variety was verified by a Canonical Discriminant Analysis (CDA). In this analysis, it was not included the proportion of skin tannin (dpell%) because these values and the values of the proportion of seed tannins (Mp%) are interdependent, their correlation is perfect (Figure 6) and both provide the information to be considered redundant. In the same way, the potential in extractable anthocyanins (ApH3.2) is not included because their correlation with the skin tannins (dpell) is perfect, due to the formula used to calculate these values. The two first canonical functions accounted 100 % of the total variance (function 1 explained 76.2 %). Despite the large differences among years, a clear separation among the scores of grapes by variety is observed, what involves a perfect differentiation among them (Figure 6). The first canonical function is principally related to the skin

and seed tannins values, in a positive way, and to the phenolic richness in a negative way. In the second canonical function the same variables are the most important for the varietal differentiation (Table 4). Tannat samples were discriminated by the first function, while Merlot and Cabernet Sauvignon samples were differentiated between them by the second function (Figure 6).

**Table 4.** Standardized coefficients for the two canonical functions based on the varietal differentiation.

	Function 1	Function 2
Berry weight	0.3208	-0.1529
Skin %	-0.4152	0.1105
Seed %	0.7078	-0.21932
Flesh %	-0.5104	-0.6725
Sugars	0.7444	0.0442
Titrateable acidity	0.1766	0.3593
pH	-0.2348	-0.0046
A280	-263.8440	-448.1460
ApH1	1.2239	-0.1773
EA%	0.1204	-0.0274
dpell	196.4320	334.6880
dTpep	127.2860	217.9260
Mp%	0.2010	-2.3181



**Figure 6.** Distribution of the scores of the samples of each variety in the plane generated for the two Canonical Functions.

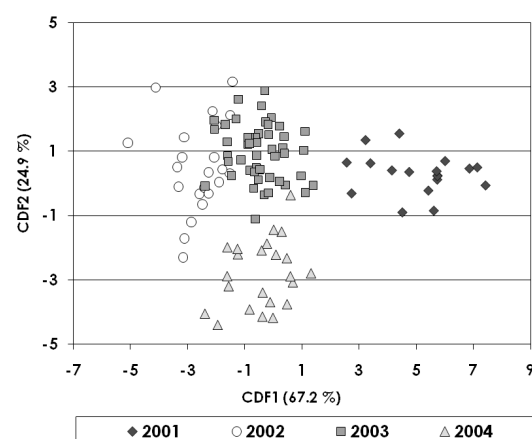
In another hand, the differentiation of the samples based on the vintage was verified by CDA. The two first canonical functions accounted 91.9 % of the total variance. The discrimination of the samples was not perfect, possibly due to the large differences verified between the grapes of the three varieties. However, the two first functions generated classified 95.6 % of the samples correctly, according to their vintage. The scores of the grapes produced in 2001 were clearly separated of the others by the first function. The scores of 2002 and 2003 samples are not clearly separated (Figure 7). The first and the second functions are related principally to the phenolic richness and tannins levels (Table 5).

These results indicate the importance of skin tannin and seed tannin levels for the differentiation and characterization of the varieties included in this analysis. The estimation of skin tannin levels (dpell) is based on a theoretical

relationship with the extractable anthocyanin (ApH3.2), assuming that there is a constant ratio between the extraction of both compounds during winemaking (Saint-Cricq et al., 1998). This principle is not valid in all cases, since it depends on winemaking conditions, and it should be evaluated for each variety of grape (González-Neves et al., 2004; Letaief et al., 2007; Ortega-Regules et al., 2008a). In the same way, the equation for calculating seed tannins (dTpep) is based on the consideration that the phenolic richness of grape depends only on the levels of tannins, underestimating the importance of anthocyanins and other polyphenols (Di Stefano et al., 2000). Despite these criticisms, in a previous paper, it is shown a good correlation between these indexes and the levels of tannins in the wine (González-Neves et al., 2010), what means they are useful for estimating the extractability of tannins, confirming the technological utility of these indexes.

**Table 5.** Standardized coefficients for the two first canonical functions based on the year differentiation.

	Function 1	Function 2
Berry weight	0.3906	-0.3834
Skin %	-0.0276	-0.6719
Seed %	0.1202	1.9457
Flesh %	-1.3204	-0.3628
Sugars	0.4965	1.1439
Titrateable acidity	0.6959	-0.7949
pH	0.0022	0.1387
A280	4325.4800	-3741.8700
ApH1	4.3919	2.2430
EA%	-1.7976	-0.1074
dpell	-2798.3300	2414.0300
dTpep	-2145.7000	1853.4600
Mp%	0.0552	0.7482



**Figure 7.** Distribution of the scores of the samples of each year in the plane generated for the two first Canonical Functions.

## Conclusions

Tannat grapes had very different characteristics from Cabernet Sauvignon and Merlot. Tannat had the highest sugar contents, titrateable acidity, polyphenolic richness, potential in anthocyanins, skin tannins, seed tannins, berry

weight and proportion of seeds, and the lowest pH values and extractability of anthocyanins.

The indexes of general composition, polyphenolic potential and structure of the berry provide valuable information for enological characterization and differentiation of grapes. These data are very important to the control of the winemaking of each variety. The knowledge of the polyphenolic potential and anthocyanin extractability of grapes allows modifying the maceration process in order to seize better the aptitude of the grape to elaborate the best wine.

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