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PAPER

RELATIONSHIP BETWEEN GRAPE PHENOLIC MATURITY AND RED WINE PHENOLIC COMPOSITION

RELAZIONE TRA LA MATURITÀ FENOLICA DELLE UVE E LA COMPOSIZIONE FENOLICA DEI VINI ROSSI

E. CAGNASSO, L. ROLLE, A. CAUDANA and V. GERBI*
Dipartimento Valorizzazione e Protezione delle Risorse Agroforestali, Di.Va.P.R.A., Microbiologia agraria e Tecnologie Alimentari, Università di Torino, Via L. da Vinci 44, 10095 Grugliasco (TO) Italy
*Corresponding author: Tel. +39 0116708552, Fax +39 0116708549, e-mail: vincenzo.gerbi@unito.it

ABSTRACT

Phenolic maturity of red Piedmont grape varieties Nebbiolo and Barbera was monitored during the grape harvest in 16 vineyards in 2000 and 2001. The study used the Glories' method which was modified to avoid some critical parts of the original protocol, mainly regarding the extraction solution used at pH 1. Experimental winemaking processes were performed on a part of the grapes from the vineyards being monitored. The analytical data revealed a correlation between the an-

RIASSUNTO

Nelle annate 2000 e 2001 è stato condotto un monitoraggio della maturità fenolica di uve rosse piemontesi Nebbiolo e Barbera, che ha riguardato 16 vigneti. Il lavoro ha permesso di mettere a punto modifiche al metodo per la valutazione della maturità fenolica proposto da Glories per ovviare ad alcune criticità dello stesso, segnatamente per quanto riguarda l'estrazione a pH 1. Parte delle uve dei vigneti sottoposti a monitoraggio sono state vinificate sperimentalmente. Lo studio dei dati analitici dei vini otte-

- Key words: Barbera, Nebbiolo, phenolic maturity, polyphenols, previsional indexes, wine -

thocyanins and flavonoid indexes of grapes and color indexes of wines. The cell maturity index (EA%) is representative of how quickly anthocyanins can be extracted. Moreover, a correlation was found between the seed maturity index (Mp%) and the content of low molecular weight flavanols in the wine. In 2002-2004 this correlation was studied on Nebbiolo, Barbera and Dolcetto grape varieties on an industrial scale. Winemaking carried out using different systems of maceration confirmed the experimental results.

nuti ha evidenziato correlazioni positive tra gli indici degli antociani e dei flavonoidi delle uve e quelli del colore del vino. L'indice EA% si è dimostrato rappresentativo della velocità di cessione della materia colorante. Inoltre è stato evidenziato un collegamento tra l'indice di maturità dei vinaccioli (Mp%) e il contenuto di flavanoli a bassa massa molecolare del vino. Negli anni 2002-2004 le correlazioni rilevate sono state nuovamente valutate su Nebbiolo, Barbera e Dolcetto in vinificazioni condotte su scala industriale con sistemi diversi di macerazione confermando i risultati già ottenuti su scala ridotta.

INTRODUCTION

Phenolic compounds, extractable from grape skins and seeds, have a notable influence on the sensorial properties of red wines, especially their chromatic characteristics, astringency and bitterness (ARNOLD *et al.*, 1980; ROBICHAUD and NOBLE, 1990). The phenolic compounds, together with the aroma precursors are the main factors that affect wine quality. Consequently they have been studied extensively in grapes and wine (AMRANI-JOUTEI *et al.*, 1994; MOUTOUNET *et al.*, 1996; CHEYNIER, 2000; ATASANOVA *et al.*, 2002).

The evaluation of the sugar content and acid profile alone do not fully express the real oenological potential of grapes. Knowing the polyphenolic characteristics of the grapes allows the maceration and winemaking process to be planned so as to allow winemakers to fully exploit the potentiality that the grape reaches in the vineyard (SAINT-CRIQ *et al.*, 1998ab; GONZALEZ-NEVES *et al.*, 2004).

Many studies have been conducted to define the best method to evaluate polyphenolic compounds in grapes (AUBERT and POUX, 1968; RIBEREAU-GAYON, 1971; MARGHERI *et al.*, 1985; BOURZEIX *et al.*, 1986; GUNATA *et al.*, 1987). GLORIES and AUGUSTINE (1993) used the term "grape phenolic maturity" to indicate the concentration of phenolic compounds in grapes, and the ease with which they are released. This definition encompasses the anthocyanin concentration in the skin, their degree of extractability, the flavanol concentration in the seeds and skin and their degree of polymerization. The method proposed by GLORIES consists of extracting the phenolic compounds from the whole berries liquidized under two different conditions, determining the concentration and subsequently comparing the data. Moreover, the authors indicate that the partial break-up of the seeds allows tannins to be partially extracted, and that skin tannins are extracted in proportion to the anthocyanins.

The first stage of the procedure attempts to extract nearly all of the phenolic content using a very low pH (~1) which favours the complete degradation of the

cell membrane (GLORIES and SAUCIER, 2000). The second stage repeats the extraction under normal maceration conditions using a buffer (pH 3.2) which does not cause any further degradation of the cell membrane other than that normally reached during ripening. The smaller the difference in the parameters between pH 1 and pH 3.2, the greater the level of phenolic maturation.

Many compounds are involved in the evolution of the maturation of the grape, so the definition of phenolic maturity cannot be represented by a few parameters and some confusion can arise when the data are interpreted (VENENCIE *et al.*, 1998).

Numerous studies were carried out in the 1990s to evaluate the phenolic potential of grapes using the method proposed by Glories working with whole berries (BARCELO, 1997; SAINT-CRIQ *et al.*, 1998bc; CELOTTI *et al.*, 2000a; GONZÁLES-NEVES *et al.*, 2004; 2007). Other studies were aimed at modifying the nature of the solvent and the working model of extraction while trying to be faithful to the original Glories method, working with skins and seeds separately (RIOU and ASSELIN, 1996; VENENCIE *et al.*, 1997; VENENCIE *et al.*, 1998; PEYRON, 1998; DI STEFANO *et al.*, 2000; MATTIVI *et al.*, 2002a) or with whole berries (LAMADON, 1995; CAYALA *et al.*, 2002; CRESPY, 2002; ROMERO-CASCALES *et al.*, 2005; MATTIVI, 2006).

Other methods for assessing the phenolic quality of grapes which differ drastically from the Glories method, such as the use of chromatic parameters (CELOTTI *et al.*, 2000b; 2007) or grape sensorial analysis, have also been developed (ROUSSEAU and DELTEIL, 2000; MARTINEZ, 2002).

The use of whole berries to evaluate phenolic maturity has been criticized (DI STEFANO *et al.*, 2000), but there have also been studies that have supported the technological validity of the Glories method (ROMERO-CASCALES *et al.*, 2005; GONZÁLES-NEVES *et al.*, 2004, GONZÁLES-NEVES *et al.*, 2007).

In this study, autochthonous grapes from the Piedmont region were used to study the relationship between the level of grape phenolic maturity and the characteristics of the various wines obtained at the experimental and industrial levels.

MATERIALS AND METHODS

Grape maturity

During the 2000-2001 vintage, the technological and phenolic maturity of the grapes were monitored, in eight vineyards of Barbera grapes and eight of Nebbiolo. The vineyards are located in the Langhe area (Cuneo province, Piedmont, northwestern Italy, where Barbera d'Alba DOC and Barbaresco DOCG wines are produced) and in the Alto Monferrato area (Asti province, Piedmont, where Barbera d'Asti DOC is produced).

A representative sampling of the grapes was made during harvesting. Three samples (ca. 500 berries) from all parts of the vine as well as from throughout the vineyard were gathered. Technological parameters and the anthocyanin profile of the grapes were determined on half of the berries from each sample. The remaining berries were used to determine the phenolic maturity parameters.

The technological maturity index: density (soluble solids), total acidity and pH according to official methods (EEC, 1990), was determined. Moreover the varietal anthocyanin profile was analysed by HPLC. Sample preparation was carried out as described by DI STEFANO and CRAVERO (1991): the berry skin extract was applied to a 300 mg SEP-PAK C18 cartridge (Waters Corporation, Milford, MA, USA) and eluted with methanol. The cartridge was preconditioned with methanol (2 mL) and H_2SO_4 (0.005 M; 2 mL)

before use. The chromatograph was a P100 equipped with a AS3000 auto-sampler (Spectra Physics Analytical, Inc, San Jose, CA, USA) and a 20 mL Rheodyne sample loop. A LiChroCART analytical column (25 cm x 0.4 cm i.d.) from Merck (Darmstadt, Germany) packed with LiChrosphere 100 RP-18 5-μm particles by Alltech (Deerfield, IL, USA) and a Spectra Focus Diode Array Detector (Spectra Physics Analytical, Inc, San Jose, CA, USA) operating at 520 nm was used.

The following conditions were used: solvent A=10% formic acid in water. Solvent B=10% formic acid with 50% methyl alcohol in water. These solvents were filtered through a 0.20 μm filter. The solvent flow rate was 1mL/min. The solvent program used was 72% A to 55% A over 15 min; to 30% A over 20 min; to 10% A over 10 min; to 1% A over 5 min; to 72% A over 3 min; an equilibrium time of 10 min was used (ROLLE and GUIDONI, 2007; ZEPPA *et al.*, 2001). Data treatment was carried out using the ChromQuest™ chromatography data system (ThermoQuest, Inc, San Jose, CA, USA).

The identification of the free form anthocyanins, in the berry skin extract was performed by comparison with external standards (delphinidin-3-O-glucoside chloride, malvidin-3-O-glucoside chloride, peonidin-3-O-glucoside chloride, petunidin chloride, cyanidin chloride; Extrasynthèse, Genay, France); the acylated forms of anthocyanins were identified by comparing the retention time of each chromatographic peak with available data in the literature (DI STEFANO *et al.* 1995). The percentages of individual anthocyanins were determined by comparing the area of the individual peak with the total peak area (HEBRERO *et al.*, 1988; LETAIEF *et al.*, 2007).

The Glories' protocol used to determine phenolic maturity is described by SAINT-CRIQ *et al.* (1998c). This protocol was modified to simplify the handling process and minimise the effect of the buffering capacity of the juice to improve the extraction yield:

- the pH 1 extractant solution was prepared immediately before use by mixing equal volumes of the following solutions: 1) HCl 1.0 M (to stabilise the pH value in extraction solution near 1 unit); 2) $K_2S_2O_5$ 2.0 g/L (to improve the cell membrane permeability according to AMRANI-JOUTEI and GLORIES, 1994, AMRANI-JOUTEI and GLORIES 1995a);

- the extracts after the maceration period were separated from the solid parts using a centrifuge at 3,500 rpm for 5 min.

The following parameters were determined in pH 1 and 3.2 solutions: phenolic richness (expressed as Absorbance at 280 nm, A280) according to RIBEREAU-GAYON (1970) and total anthocyanins (A1 and A3.2), total flavonoids (TF1 and TF3.2) and non-anthocyanin flavonoids (NAF1 and NAF3.2) as reported in the wine analysis. The analytical data were in reference to berry mass.

The indexes of phenolic maturity calculated are those defined by GLORIES and AUGUSTINE (1993): potential anthocyanins (A1), extractible anthocyanins (A3.2), cell maturity index (EA%) and seed maturity index (Mp%). The latter index was determined, according to the indications of the authors, by taking into consideration the medium ratio (TAR) between the total polyphenols (expressed as the absorbance at 280 nm) and the total anthocyanins of the skin (expressed as g/L), equal to the value 40.

The EA% and Mp% indexes were calculated as follows:

$$EA\% = \frac{A1 - A3.2}{A1} \times 100 \qquad Mp\% = \frac{A280 - ((A1/1000) \times TAR)}{A280} \times 100$$

Preliminary assays showed that the TAR value of 40 was too low for the Nebbiolo grapes and that the value of 70 was more correct. To evaluate the mean of Nebbiolo TAR, the skins of 50 grams of berries were liquidized with 2V mL of pH 3.2 extractant solution (where V is the volume corresponding to the must from 50 grams of berries as described to SAINT-CRIQ *et al.*, 1998) and the protocol of grape phenolic maturity was applied. For twenty Nebbiolo grape samples a mean TAR of 70±5.1 was obtained. The variability was in agreement with Glories' data (GLORIES, 2001). Therefore this value was used in the calculations for the Nebbiolo grapes.

Experimental winemaking

The grapes that were used to monitor the maturity came from six vineyards and three for each cultivar, were fermented. Winemaking was carried out using an experimental protocol. It was repeated three times per vineyard.

The winemaking was done in stainless steel tanks using about 500 kg of grapes for each trial. Fifty mg/L of SO_2 (as potassium metabisulfite) and 150 mg/L of ammonium sulphate were added to the must obtained from crushing and destemming. The must was inoculated with 200 mg/L of dry yeasts BRL97 Lalvin (Lallemand, Grenaa, Denmark). The pomace floating cap was punched down twice a day during maceration. Skin contact was continued for 120 h, after which draining off was carried out.

Industrial winemaking

Industrial scale (ca. 10,000 kg grapes) winemaking was carried out in 2002, 2003 and 2004 to evaluate the provisional index efficacy of phenolic maturity assessed on a reduced scale in the previous harvests (2000, and 2001). Nebbiolo, Barbera and Dolcetto grapes were harvested from vineyards in the provinces of Cuneo and Asti.

Various fermenters with different functions were used: horizontal rotating types with vanes, model VMO 100 (Velo spa, Altivole, TV, Italy) and a punching-down device (Tosto spa, Chieti Scalo, CH, Italy) during the first two years. In 2004 a rotating tank was used exclusively. Winemaking was carried out using the following vinification protocol. During skin contact rotating fermentors and punching-down devices were put into action three times a day for five min each time. For all the vinifications, the temperature of the must in fermentation was controlled so that it did not exceed 30°C (Nebbiolo), 29°C (Barbera) and 28°C (Dolcetto).

Wine analysis

The first racking off (15 days after the draining off) wines were analysed using the following parameters: alcoholic strength, total acidity, pH and total dry matter (EEC, 1990). Wine acids were determined by HPLC (SCHNEIDER *et al.*, 1987). Phenolic compound indexes were determined as described by DI STEFANO *et al.* (1989): total phenols (TP), total flavonoids (TF), non-anthocyanin flavonoids (NAF) and flavanols reactive to vanillin (flavanols vanillin assay, FVA) all expressed as (+)-catechin (mg/L), proanthocyanidins (PR) expressed as cyanidin chloride (mg/L). Total anthocyanins (AT) and monomeric anthocyanins (AM) were expressed as malvidin-3-glucoside chloride (mg/L) (DI STEFANO *et al.*, 1991). The relative standard deviation of phenolic indexes based on repeated analyses (n=10) of seven red wines were: 1.39% (TP), 0.93% (TF), 2.80% (FVA), 1.14% (AT), 3.90% (AM). Anthocyanins was determined by HPLC as described above in grape maturity.

Chromatic properties were determined: colour intensity (CI), tone (CT) and yellow (A420), red (A520) and blue (A620) components according to GLORIES (1984). The CIELAB index values

were determined with reference to illuminant C (PIRACCI, 1994): clarity (L*), red-green component (a*), yellow-blue component (b*), chroma (C*) and hue (H*). All absorbance measurements were made using a UV-1601PC spectrophotometer (Shimazdu Scientific Instruments Inc., Columbia, MD, USA) and chromatic properties were carried out using a glass cuvette (2 mm optical path).

The kinetics of extraction of the anthocyanin (AT) and flavonoid compounds (TF) was also monitored during the 2001 winemaking.

Statistical analysis

The data were analysed using STATISTICA for Windows Release 6.0 (StatSoft Inc., Tulsa, OK, USA).

RESULTS AND DISCUSSION

Table 1 shows the combined descriptive experimental parameters of the technological and phenolic maturity determined at harvest time. Analogous parameters are shown in Table 2 for the industrial trial grapes (2002-2004).

The grapes reached a good level of technological maturation as shown by the sugar content (Brix) data. The total acidity was lower in the 2000 vintage due to intense respiration favoured by the higher average summer temperatures. The pH values are in accordance with those described previously; the 2001 values are lower due to notable rains. The absolute values of the total anthocyanin and flavonoid indexes at harvest obtained under various extraction conditions (pH 1: A1, TF1; pH 3.2: A3.2, TF3.2), show a notable disparity in the anthocyanin potential (A1) between Nebbiolo and Barbera confirming data of other authors (CRAVERO and DI STEFANO, 1992; MATTIVI *et al.*, 2002b). In particular, the A1 values for the Nebbiolo cultivar varied between the minimum value of 332 (in 2001) and 574 mg/kg (in 2000). The variability between the minimum and maximum for different vineyards in the same year were ca. 180 mg/

Table 1 - Grape maturity indexes of Barbera and Nebbiolo at harvest in 2000 and 2001 (mean±standard deviation). Data from eight vineyards.

		Barbera		Nebbiolo	
Harvest-period	beginning end	2000 21 Sept. 2 Oct.	2001 24 Sept. 28 Sept.	2000 25 Sept. 9 Oct.	2001 2 Oct. 3 Oct.
Berry weight[a] (g)		262.5±23.5	268.0±29.5	188.6±15.4	178.2±19.4
Soluble solids (Brix)		24.1±1.5	23.7±1.5	25.2±0.9	23.6±1.0
Total acidity (g/kg)		8.5±1.2	9.6±2.0	7.1±0.4	7.0±0.6
pH		3.17±0.07	2.99±0.05	3.26±0.08	3.04±0.08
Anthocyanins pH 1 - A1 (mg/kg)		983±175	1131±197	494±51	428±60
Anthocyanins pH 3.2 - A3.2 (mg/kg)		538±104	658±76	318±23	366±53
Flavonoids pH 1 - FT1(mg/kg)		2768±348	2588±369	2582±146	2406±339
Flavonoids pH 3.2 - FT3.2 (mg/kg)		1304±224	1777±200	2130±150	2287±324
Absorbance at 280 nm - A280		44.8±4.9	72.3±4.6	62.0±11.7	64.9±6.2
EA%		50.3±3.9	41.2±4.3	35.3±3.4	14.3±5.6
Mp%[b]		52.0±7.5	60.5±3.0	58.9±8.9	56.8±4.6

[a]Expressed as weight of 100 berries; [b]Mp% data were calculated using a tannins/anthocyanins ratio (TAR) equal to 40 for Barbera grapes and 70 for Nebbiolo grapes.

Table 2 - Grape maturity indexes at harvest in 2002, 2003 and 2004 (mean±standard deviation).

	Year	2002	2003	2004
Number of	Barbera	2	4	7
Vineyards	Dolcetto	2	2	2
	Nebbiolo	1	3	1
Berry weight[a] (g)	Barbera	250.1±14.1	198.0±14.4	218.4±16.1
	Dolcetto	192.8±4.2	169.5±21.9	155.0±24.0
	Nebbiolo	110.3	188.3±3.2	156-1
Soluble solids (Brix)	Barbera	20.2±0.3	25.3±0.4	24.7±0.8
	Dolcetto	19.3±0.4	23.9±0.6	22.2±3.0
	Nebbiolo	23.0	24.6±0.4	24.3
Total acidity (g/kg)	Barbera	13.0±0.1	6.8±0.6	10.4±1.3
	Dolcetto	8.2±0.1	4.3±0.7	6.5±0.4
	Nebbiolo	10.3	5.0±0.2	5.6
pH	Barbera	2.92±0.05	3.16±0.07	3.01±0.05
	Dolcetto	3.19±0.02	3.52±0.25	3.08±0.04
	Nebbiolo	3.04	3.32±0.02	3.10
Anthocyanins pH 1 - A1 (mg/kg)	Barbera	1027±148	1062±100	1171±119
	Dolcetto	958±62	801±39	1107±32
	Nebbiolo	757	500±27	696
Anthocyanins pH 3.2 - A3.2 (mg/kg)	Barbera	572±71	523±64	607±38
	Dolcetto	576±16	487±25	667±33
	Nebbiolo	466	314±1	470
Flavonoids pH 1 - FT1 (mg/kg)	Barbera	2828±416	3151±290	3052±136
	Dolcetto	3723±301	3814±307	3500±419
	Nebbiolo	4284	3511±272	3526
Flavonoids pH 3.2 - FT3.2 (mg/kg)	Barbera	1621±235	1934±123	1651±57
	Dolcetto	2565±309	2789±344	2226±385
	Nebbiolo	3345	2745±229	2922
Absorbance at 280 nm - A280	Barbera	64.3±1.6	69.6±8.2	61.2±4.4
	Dolcetto	68.0±3.4	76.9±4.3	59.5±9.2
	Nebbiolo	71-1	67.9±5.0	70.8
EA%	Barbera	44.0±1.4	50.4±4.9	47.9±4.2
	Dolcetto	39.5±2.1	39.0±0.1	39.7±0.9
	Nebbiolo	38.1	36.1±2.6	32.4
Mp%	Barbera	61.5±3.5	70.4±2.8	55.9±3.1
	Dolcetto	62.5±0.7	71.8±0.3	51-7±4.4
	Nebbiolo	49.0	64.7±2.5	48.7

kg. In 2001, the values were lower with a minimum value of 332 mg/kg.

The FT1 values in both cultivars were high. The ratio between TF3.2 and TF1, which represents an assessment of the extractability fraction of the flavonoids, is characteristic of the cultivar. This ratio is on average >80% for Nebbiolo and <60% for Barbera.

The EA% values for cultivar Barbera were higher than Nebbiolo in both vintages (Δ=15-16). The Barbera grape values are due to a more rigid cell wall structure according to ROMERO-CASCALES *et al.* (2005).

The EA% values from the 2001 vintage were lower than those of 2000 because of a greater cell wall fragility that facilitated anthocyanin extraction (AMRANI-JOUTEI and GLORIES, 1994; 1995a).

The contribution wine tannins (Mp%) from the seeds in Barbera grapes was

Table 3A - Anthocyanin pattern of grapes produced in 2001 vintages (±standard deviation); n=3.

	N1	N2	N3	B1	B2	B3
Delphynidin-3-glucoside (%)	6.2±0.3	6.8±0.2	6.4±0.3	11.8±1.1	12.0±1.4	14.3±1.3
Cyanidin-3-glucoside (%)	16.0±1.3	18.9±1.9	16.4±1.4	10.3±1.0	11.4±1.2	9.4±1.0
Petunidin-3-glucoisde (%)	5.4±0.5	6.2±0.5	5.1±0.6	11.2±1.1	11.1±1.0	13.0±1.3
Peonidin-3-glucoside (%)	42.6±0.9	43.6±0.7	44.0±0.7	24.9±2.0	27.5±2.2	21.7±2.4
Malvidin-3-glucoside (%)	20.1±1.9	16.4±1.7	18.9±2.0	36.4±2.1	33.0±1-9	36.9±2.2
Σ acetylglucoside anthocyanins (%)	3.6±0.4	3.1±0.4	3.8±0.3	1.3±0.1	1.4±0.1	1.1±0.2
Σ cinnamoylglucoside anthocyanins (%)	6.2±0.5	5.1±0.6	5.4±0.6	4.1±0.1	3.6±0.2	3.6±0.2

[a]Abbreviation: B (Barbera), N (Nebbiolo).

higher in 2001 – a clear sign of incomplete maturation. In fact, according to AMRANI-JOUTEI and GLORIES (1994), DE FREITAS *et al.* (2000) and GLORIES (2001), the proanthocyanidin extraction decreases to the seed maturation level. The Mp% values in Nebbiolo show a limited variability between the vintages.

The anthocyanin profile was determined on the six grape stocks used in winemaking (Table 3A). The percentages of anthocyanidins examined were similar to those reported in the literature (CRAVERO and DI STEFANO, 1992; GUIDONI *et al.*, 1997).

Fig. 1 shows that anthocyanin extraction during maceration reached its highest value after three days for trial B2 (Barbera grapes); the EA% value was lower (41.0). Trial B1 yielded the anthocyanins more slowly, the EA% value was 45.6. The differences were less in the Nebbiolo grapes because of the low anthocyanin content values as well as the cell maturity index EA (9-20%).

The situation described above is also valid for the total flavonoid extraction (Fig. 2), where the slope of the extraction curve for Barbera was higher, with a decreasing EA% value. After the third day of maceration, the formation of ethanol tended to influence the extraction kinetics, making the trends more uniform. The cell maturity index (EA%) values are therefore a measure of the facili-

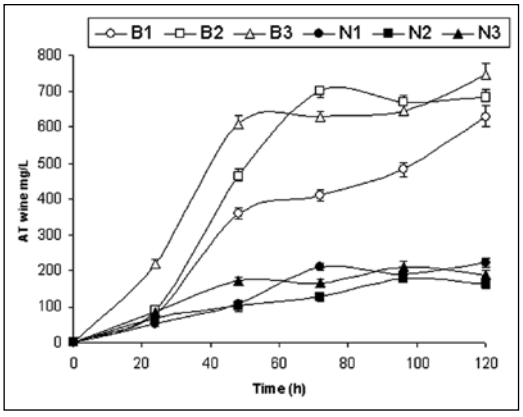

Fig. 1 - Evolution of the mean total anthocyanin (AT) contents during skin contact (2001); data as malvidin-3-glucoside chloride equivalent, mg/L. Grape: Barbera (B) and Nebbiolo (N).

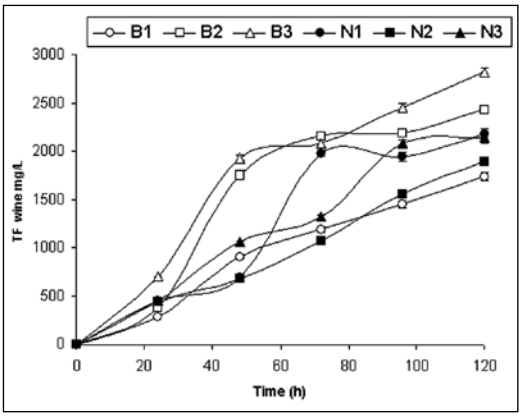

Fig. 2 - Evolution of the mean total flavonoid (TF) contents during skin contact (2001); data as (+)-catechin equivalent, mg/L. Grape: Barbera (B) and Nebbiolo (N).

Table 3B - Anthocyanin pattern of wines produced in 2000 and 2001 vintages (±standard deviation); n=3.

Sample[a]	N1		N2		N3		B1		B2		B3
year	2000	2001	2000	2001	2000	2001	2000	2001	2000	2001	2001
Delphynidin-3-glucoside (%)	0.2±0.1	0.2±0.1	0.2±0.1	0.6±0.2	4.5±0.7	2.0±0.5	0.3±0.2	9.3±0.6	0.3±0.1	1.0±0.6	4.0±0.6
Cyanidin-3-glucoside (%)	0.1±0.1	0.9±0.4	0.2±0.1	1.3±0.2	4.5±0.6	1.8±0.3	0.3±0.1	2.8±0.2	0.3±0.1	1.1±0.6	2.4±0.4
Petunidin-3-glucoisde (%)	1.9±0.4	3.7±0.4	1.0±0.2	3.2±0.3	10.8±0.7	3.6±0.4	4.2±0.5	13.3±0.6	2.4±0.4	9.0±0.5	11.2±0.7
Peonidin-3-glucoside (%)	25.2±2.5	30.3±1.2	22.2±0.9	27.4±0.9	10.6±1.3	7.4±0.9	4.9±0.9	6.1±0.9	4.4±0.7	4.0±0.7	4.9±0.7
Malvidin-3-glucoside (%)	63.5±2.3	58.4±1.8	69.8±2.0	59.4±1.1	53.5±1.3	57.8±1.8	68.8±2.5	50.4±1.2	67.8±1.7	61.4±1.2	55.2±1.5
Σ acetylglucoside anthocyanins (%)	8.7±1.1	5.8±0.6	6.7±1.0	6.9±0.5	5.7±0.6	24.9±0.9	21.0±1.0	12.6±0.4	24.7±1.2	19.0±0.7	16.8±1.3
Σ cinnamoylglucoside anthocyanins (%)	0.6±0.2	0.6±0.2	0.1±0.1	1.1±0.4	1.3±0.3	2.2±0.6	0.2±0.1	5.5±0.6	0.3±0.1	4.3±0.6	5.4±0.6

[a]Abbreviation: B (Barbera), N (Nebbiolo).

ty with which the polyphenols, especially of the anthocyanins, were extracted during the first phases of maceration. Decreasing values correspond to increased ease of extraction.

The wines obtained in the 2000 and 2001 vintages from grapes taken from vineyards in which the phenolic maturity was monitored are described by general analytical parameters (Table 4A) and chromatic parameters (Table 4B).

The percentage recovery of anthocyanin pigments, expressed as the ratio between the average index of total anthocyanins in the wine (AT) and the corresponding index evaluated in grapes (A1 and A3.2) in the 2000 vintage, shows that there was 50% recovery in Nebbiolo wines compared to A3.2, and only 35% of the potential value at pH 1. Barbera wines presented better results especially with regard to the A3.2 values (on average 80%). These results were repeated in the 2001 vintage.

The amount of anthocyanins in the wines is dependent on the grape variety. In fact, in Barbera, the grapevine has an anthocyanin profile made up mainly of molecules tri-substituted in the B-ring (CRAVERO and DI STEFANO, 1992, DI STEFANO *et al.*, 2002; GERBI *et al.*, 2004) and therefore more protected against oxidation. The decrease in concentration of these pigments appears remarkably inferior to that of the Nebbiolo variety.

The wine anthocyanin profile (Table 3B) shows a considerable drop in di-substituted anthocyanins compared to the grape, particularly those with a catechol type structure on the B-ring. Moreover, a prevalence of the malvidin-3-glucoside (Mv3G) emerges as well in the case of Nebbiolo, instead of peonidin-3-glucoside (Pe3G), as in the grapes. Generally, a ratio Pe3G/Mv3G >1 is found in Nebbiolo wines (CAGNASSO *et al.*, 2001), but the opposite has also been found (GERBI *et al.*, 2002). The remarkable loss of di-substituted anthocyanins, easily extractable since the first phases of maceration,

Table 4A - Physicochemical characteristics of wines in 2000 and 2001 vintages (± standard deviation); n=3.

Sample[a]:	N1		N2		N3		B1		B2		B3
Vintage:	2000	2001	2000	2001	2000	2001	2000	2001	2000	2001	2001
Alcohol (% vol.)	14.39±0.25	13.83±0.10	13.16±0.19	12.47±0.32	13.18±0.08	13.02±0.19	11.85±0.11	13.66±0.22	13.99±0.10	14.06±0.08	15.53±0.24
Reducing Sugars (g/L)	3.1±1.0	1.5±0.8	1.7±0.4	1.4±0.2	1.4±0.4	1.4±0.4	1.8±0.5	2.9±0.5	2.9±0.6	2.2±0.2	4.5±0.7
Total Dry Matter (g/L)	32.6±1.5	nd[b]	31.0±1.4	nd	29.2±0.8	nd	28.9±0.7	nd	35.4±0.7	nd	nd
pH	3.39±0.02	3.57±0.02	3.34±0.04	3.37±0.02	3.25±0.02	3.38±0.03	3.20±0.07	3.23±0.003	3.30±0.07	3.19±0.02	3.28±0.03
Total Acidity (g/L as tartaric acid)	6.7±0.1	6.2±0.2	7.2±0.5	8.8±0.4	7.8±0.4	7.2±0.2	10.8±0.6	10.2±0.3	8.5±0.4	8.0±0.1	8.2±0.4
Volatile Acidity (g/L as acetic acid)	0.28±0.04	0.26±0.06	0.21±0.04	0.23±0.02	0.27±0.05	0.23±0.05	0.35±0.06	0.44±0.04	0.40±0.02	0.40±0.02	0.45±0.02
Tartaric Acid (g/L)	2.2±0.1	2.2±0.2	2.5±0.4	2.4±0.1	2.5±0.2	2.3±0.2	3.7±0.2	3.7±0.2	3.2±0.2	4.2±0.2	3.2±0.1
Malic Acid (g/L)	1.7±0.5	1.8±0.25	2.3±0.2	1.7±0.3	2.3±0.2	2.3±0.2	5.4±0.4	3.7±0.2	2.2±0.3	1.4±0.1	1.8±0.1
Citric Acid (g/L)	0.38±0.07	0.26±0.04	0.4±0.1	0.18±0.05	0.30±0.15	0.23±0.04	0.3±0.0	0.40±0.06	0.72±0.07	0.48±0.03	0.35±0.04
Lactic Acid (g/L)	0.62±0.13	1.3±0.2	0.89±0.09	1.8±0.2	1.0±0.1	1.9±0.1	1.0±0.3	1.2±0.2	1.0±0.1	0.90±0.04	1.1±0.2
Succinic Acid (g/L)	0.7±0.1	nd	0.9±0.2	nd	0.8±0.1	nd	0.6±0.3	nd	0.5±0.1	nd	nd
Total Anthocyanins (mg/L as malvidin-3-glucoside chloride)	184±13	195±14	200±18	231±12	149±13	168±14	454±23	707±30	519±22	547±25	663±32
Combined Anthocyanins (%)	36.4±2.9	43.5±0.9	43.0±1.2	35.0±1.0	31.5±0.9	43.5±0.4	19.2±0.5	31.1±0.4	22.7±0.6	25.8±0.4	36.6±0.8
Total polyphenols (mg/L as (+)-catechin)	1863±43	2750±84	2351±58	2838±53	1883±78	2750±62	1453±54	2329±50	1854±38	2217±40	2880±63
Total Flavonoids (mg/L as (+)-catechin)	1458±53	2245±78	1846±63	2484±47	1372±79	1994±75	1337±53	2192±51	1504±47	2126±35	2657±56
Flavanols Vanillin Assay- FVA (mg/L as (+)-catechin)	1067±68	1348±91	1360±51	1539±49	1080±50	1517±68	360±21	721±30	340±21	741±33	917±42
Proanthocyanidins - PR (mg/L as cyanidin chloride)	2791±155	4370±149	3349±102	4801±110	2697±106	3976±110	1110±84	2244±107	1360±86	2139±109	2953±112
FVA / PR	0.38±0.01	0.31±0.01	0.41±0.00	0.32±0.00	0.42±0.01	0.38±0.01	0.32±0.01	0.32±0.00	0.25±0.00	0.35±0.02	0.35±002

[a]Abbreviation: B (Barbera), N (Nebbiolo);

[b]nd: not detected.

Table 4B - Chromatic characteristics of wines in 2000 and 2001 vintages (± standard deviation); n=3.

Sample[a]:	N1		N2		N3		B1		B2		B3
Vintage:	2000	2001	2000	2001	2000	2001	2000	2001	2000	2001	2001
Clarity – L*	24.7±0.8	27.3±1.0	25.3±0.7	22.0±0.7	33.0±0.9	27.1±0.8	14.2±0.7	5.3±0.6	10.8±0.6	7.6±0.5	2.8±0.3
Hue – H* (rad)	0.599±0.003	0.610±0.002	0.606±0.002	0.581±0.003	0.618±0.002	0.613±0.002	0.471±0.002	0.259±0.004	0.399±0.002	0.322±0.002	0.234±0.003
Chroma – C*	71.2±0.06	72.7±0.4	72.9±0.5	66.1±0.4	79.2±0.5	69.8±0.4	53.8±0.5	34.8±0.4	47.7±0.5	41.3±0.4	21.1±0.3
Colour Intensity – CI (1 mm)	0.731±0.011	0.6658±0.009	0.773±0.007	0.878±0.012	0.572±0.010	0.840±0.010	1.421±0.009	2.693±0.012	1.778±0.011	2.114±0.008	2.697±0.013
Colour Tone – CT	0.651±0.004	0.693±0.003	0.602±0.004	0.570±0.005	0.588±0.004	0.648±0.004	0.451±0.002	0.399±0.004	0.437±0.003	0.411±0-003	0.439±0.004
% Yellow (A420/CI)	35.5±0.4	37.1±0.3	34.3±0.2	32.9±0.5	34.2±0.3	36.1±0.5	28.2±0.2	26.1±0.4	28.0±0.2	26.7±0.2	27.6±0.3
% Red (A520/CI)	54.9±0.7	54.0±0.4	57.1±0.3	58.1±0.7	58.4±0.3	55.7±0.2	63.2±0.4	65.5±0.6	63.1±0.4	64.7±0.3	62.2±0.4
% Blue (A620/CI)	9.5±0.2	8.9±0.1	8.1±0.2	8.9±0.3	7.4±0.1	8.2±0.2	8.5±0.1	8.4±0.2	8.8±0.1	8.7±0.1	10.1±0.2

[a]Abbreviation: B (Barbera), N (Nebbiolo).

is probably due to the complex processes of combination, oxidation and insolubilization that characterise anthocyanin-like substances during the course of winemaking (CHEYNIER *et al.*, 1994; 1997; CHEYNIER, 2000).

The situation regarding flavonoids in wine (TF) differs between the two cultivars studied. For Nebbiolo, the percentage found in wine with respect to grape is relatively low (≈ 60-70%) for TF3.2 and only 50-60% for TF1 in the 2000 vintage. Instead, higher values were found in 2001 with an increase in both percentages recovered.

Wines from Barbera show a TF content in wine greater than the potential shown in grapes at pH 3.2 (TF3.2) in both vintages. When TF wine was compared to the TF1 of grapes, the recovery factor varied, on average, from 50% in 2000 to 70% in 2001. Barbera grapes have few skin extractable proanthocyanidins (CRAVERO and DI STEFANO, 1992). The apparent anomaly of recovery percentage of TF3.2 can be explained on the basis of the high extractability of the seed proanthocyanidins during winemaking that depends, above all, on the ethanol concentration of the product. The aqueous solution (especially the pH 3.2 extraction) allows tannins with a low molecular mass only to be easily extracted.

A good correlation between wine and grape composition was recorded (Table 5). Total anthocyanins (AT) and chromatic parameters of the wine were highly correlated with the grape indexes (A1 and A3.2). The correlation associated with anthocyanin pigments highlights a secondary role of the cell maturity index (EA%) in determining the overall anthocyanin extraction. In fact, it seems that technology and the time of maceration produce a levelling action. Nevertheless, EA% does not appear superfluous because it provides information about how quickly anthocyanins can be extracted during the skin contact phase (Fig. 2).

The EA% parameter is useful for pro-

gramming the winemaking process in particular for grape varieties rich in easily degradable anthocyanins (Nebbiolo, Sangiovese, Pinot noir, Freisa).

The correlations found between the colour indexes of wine (Glories' and CIELAB parameters) with the same A1 and A3.2 indexes is significant for the colour of the future wine. They are characterised by correlation coefficients >0.93 and, in both cases, they are better than those carried out with the A3.2 index (Table 5).

The proanthocyanidin concentrations in red wines are represented by the PR and FVA indexes. These parameters were well correlated with the non-anthocyanin flavonoids (NAF1 and NAF3.2) and total flavonoids (TF1) in grapes. In particular, NAF3.2 seems better for assessing the flavanols that are reactive to vanillin (low-molecular proanthocyanidins). Considering that the seeds usually contain principally low-molecular weight flavanols (PRIEUR *et al.*, 1994; SOUQUET *et al.*, 1996) compared to the skin, the NAF3.2 value will tend to increase when the seed is less mature.

The linear regression equations of the best correlation, found when all data were considered, are shown (Table 6). The high R^2 value confirms that the grape indexes are useful for predicting the composition of the future wine by expressing the quantitative potential of the grape.

Industrial scale winemaking was carried out during the 2002, 2003 and 2004 vintages. Climatic conditions were very different during the three years; 2002 had a rainy pre-harvest period, 2003 had high temperatures for the entire ripening period along with widespread drought. 2004 was generally favourable with intermediate conditions between vintages. The correlation coefficients recorded in the industrial winemaking are shown in Table 7. The data refer to the single years; substantial improvements in the correlation coefficients in all three years were only noted in a few cases.

There was a good correlation between the total anthocyanins (AT) and colour parameters of the industrial wines with the A1 and A3.2 indexes of the grapes. These data seem to be in agreement with the ex-

Table 5 - Correlation coefficient between grape indexes and wine colour components in experimental winemaking (2000 and 2001).

Grape wine	A1	A3.2	A280	FT1	FNA1	FT3.2	FNA3.2
TP	-0.191	-0.040	0.650*	-0.125	0.202	0.703*	0.543
FT	0.129	0.263	0.645*	0.136	-0.059	0.560	0.301
FVA	-0.735**	-0.663*	0.549	-0.407	0.767**	0.798**	0.906***
PR	-0.643*	-0.533	0.574	-0.438	0.613*	0.762**	0.818**
AT	0.973***	0.978***	-0.074	0.695*	-0.874***	-0.380	-0.742**
L*	-0.946***	-0.964***	0.115	-0.668*	0.854***	0.347	0.711*
a*	-0.934***	-0.960***	-0.020	-0.735**	0.782**	0.207	0.605*
b*	-0.959***	-0.973***	0.078	-0.698*	0.849***	0.341	0.711*
H*	-0.949***	-0.969***	0.032	-0.716*	0.819**	0.268	0.654*
C*	-0.939***	-0.970***	0.045	-0.685*	0.829**	0.250	0.642*
TC	-0.909***	-0.877***	0.105	-0.666*	0.808**	0.470	0.762**
IC	0.946***	0.968***	-0.011	0.717**	-0.814**	-0.239	-0.633*
A420 (yellow)	0.935***	0.964***	0.001	0.710*	-0.804**	-0.212	-0.610*
A520 (red)	0.947***	0.966***	-0.018	0.715*	-0.818**	-0.254	-0.643*
A620 (blue)	0.934***	0.962***	0.007	0.729*	-0.788**	-0.199	-0.600

* p>0.95; ** p>0.99; *** p>0.999.

Table 6 - Regression coefficient (y=a+bx) between grape indexes and wine phenols and colour components in experimental winemaking (confidence interval for p=0.95).

Y wine	X grape	a	b	R^2	F
AT	**A1**	-28.94±79.12	0.5049±0.090	0.946	159.5***
AT	**A3.2**	-199.8±97.5	1.193±0.194	0.956	193.3***
IC	**A1**	-0.1045±0.4097	0.001887±0.000468	0.902	83.1***
IC	**A3.2**	-0.7553±0.4432	0.004495±0.000882	0.936	132.9***
TC	**A1**	0.7209±0-0719	-0.000241±0.000082	0.826	42.8***
TC	**A3.2**	0.7907±0.1120	-0.000540±0.000223	0.769	30.0***
C*	**A1**	91.14±10.11	-0.04316±0.01156	0.888	71.3***
C*	**A3.2**	106.54±9.80	-0.1039±0.0195	0.942	145.1***
H*	**A1**	0.7571±0.0778	-0.000350±0.000089	0.899	80.1***
H*	**A3.2**	0.8830±0.0816	-0.000850±0.000162	0.939	139.0***
L*	**A1**	36-66±5.33	-0.02367±0.00610	0.895	77.0***
L*	**A3.2**	45.04±5.91	-0.05670±0.0118	0.929	118.7***
A420	**A1**	0.0631±0.1092	0.000437±0.000125	0.875	62.8***
A420	**A3.2**	-0.0976±0.1108	0.00106±0.00022	0.929	118-3***
A520	**A1**	-01242±0.2782	0.001249±0.000318	0.898	78-9***
A520	**A3.2**	-0.5682±0.3019	0.002996±0.000601	0.934	127.2***
A620	**A1**	-0.01523±0.0440	0.000175±0.000050	0.873	61.9***
A620	**A3.2**	-0.07931±0.04564	0.000424±0.000091	0.925	111.5***
FVA	**FNA3.2**	29.3±358.1	0.7724±0.2722	0.821	41.2***

* p>0.95; ** p>0.99; *** p>0.999.

perimental wines described. The correlation coefficients are lower but still significant and are better if compared with A1. The regression equations (Table 8) have different values for the *a* and *b* coefficients for all three years; the values are less than those obtained in the experimental trials (Table 6). In 2003, a year with high temperatures during the ripening period, the AT values in wine were higher than those (AT3.2) in the grapes. The variability is mostly due to the different states of cell wall fragility which favoured easier extractions in 2002 and 2004 (AMRANI-JOUTEI and GLORIES, 1994; AMRANI-JOUTEI and GLORIES 1995ab). The lower A3.2 values in the 2003 harvest seems to have been due to lower efficiency of aque-

Table 7 - Correlation coefficient between grape indexes and wine phenols and colour composition in industrial winemaking (2002-2004).

Grape wine	A1	A3.2	A280	FT1	FT3.2
FT	-0.557**	-0.516**	0.626**	0.645***	0.708***
AT	0.930***	0.850***	-0.271	-0.338	-0.673***
TC	-0.705***	-0.750***	0.155	0.249	0.434*
IC	0.904***	0.786***	-0.310	-0.420*	-0.727***
A420 (yellow)	0.853***	0.723***	-0.300	-0.380	-0.685***
A520 (red)	0.934***	0.821***	-0.322	-0.449*	-0.756***
A620 (blue)	0.716***	0.624**	-0.226	-0.300	-0.556**

* p>0.95; ** p>0.99; *** p>0.999.

ous pH 3.2 extracting solution with low cell wall fragility.

The comparison of the TF indexes (Table 8) is good when the three years are grouped together, while the data for 2003 alone are not significant. This appears to have been due to cell walls that were less brittle which prevented the release of tannic flavonoids enclosed in the more complex cellular structures of anthocyanins (AMRANI-JOUTEI *et al.*, 1994; AMRANI-JOUTEI and GLORIES, 1994;1995a,b). In fact, the very high temperatures in July and August were excessively stressful to the vines in 2003, slowing down the enzymatic degradation of the polysaccharide structures.

In 2004 a non-linear relationship between TF wine and TF3.2 grape indexes was recorded (Fig. 3); this seems to indicate a lower estimate of the potential flavonoids in grapes (to medium-low concentrations). In fact, this is actually due to the low extraction efficiency of the aqueous buffer (pH 3.2) for the Barbera grape samples and to the more rigid cell wall structure.

In a less favourable vintage, the extraction of tannic substances is more standardized in industrial winemaking. This effect, caused by maceration conditions, tends to annul the grape variety differences.

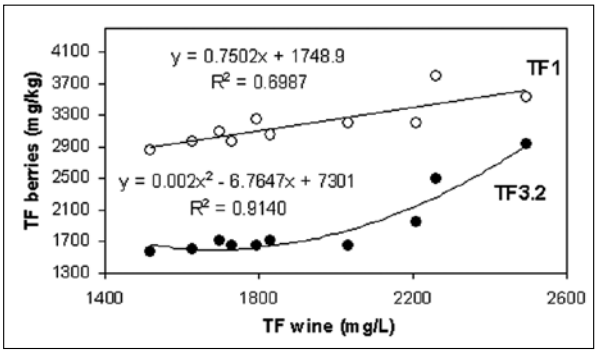

Fig. 3 - Regression between total flavonoids (TF) of the wine (industrial scale) and corresponding grape indexes to pH1 (TF1) and pH 3.2 (TF3.2) in 2004 (n=10).

CONCLUSIONS

The various parameters evaluated, including flavonoid indexes, have shown a clear connection with the phenolic composition indexes of wines. The phenolic parameters of the grapes considered can function as good prediction indexes of the future wine and are therefore of special technological interest. The EA% index measures the ease with which anthocyanins can be extracted in the first phase of skin contact.

It has been shown at the experimental level, and later verified in industrial winemaking, that the modality and time

Table 8 - Regression coefficient (y=a+bx) between grape indexes and wine phenols and colour components in industrial winemaking (confidence interval for p=0.95).

Y wine	X grape	a	b	R^2	F
AT	**A1**	-160.5±157.1	0.8163±0.1571	0.853	116.1***
AT	**A3.2**	-280.3±253.4	1.699±0.465	0.723	57.3***
IC	**A1**	-0.7101±0.6974	0.003104±0.000697	0.810	85.2***
IC	**A3.2**	-1.022±1.205	0.006274±0.002231	0.630	34.0***
TC	**A1**	0.8944±0.1480	-0.000385±0.000148	0.593	29.1***
TC	**A3.2**	1.0220±0.1622	-0.000947±0.00300	0.681	42.7***
A420	**A1**	-0.0872±0.2279	0.000777±0.000228	0.714	50.0***
A420	**A3.2**	-0.1343±0.3677	0.001513±0.000681	0.515	21.2***
A520	**A1**	-0.5769±0.3629	0.002001±0-000363	0.867	130.8***
A520	**A3.2**	-0.8224±0.6724	0.004129±0.001245	0.703	47.3***

* p>0.95; ** p>0.99; *** p>0.999.

of maceration can make the yield of the extraction process more uniform even for each variety studied. It is also true that different, carefully selected extraction modalities can highlight the differences between different grapes thus affecting the final characteristics of the wine. When designing a wine it is indispensable to choose the best-suited extraction conditions for the desired results.

The phenolic maturity indexes described here play an important role in the timing and modality during the maceration process so as to highlight the inherent potential of the grape.

The simplicity of the model showed that the correlation was strongly influenced by vintage. To interpret the data, a specific vintage reference must be defined. Therefore, new studies are indispensable if this limitation is to be overcome.

REFERENCES

Amrani-Joutei K., Glories Y. and Mercier M. 1994. Localisation des tanins dans la pellicule de baies de raisin. Vitis. 33: 133.

Amrani-Joutei K. and Glories Y. 1994. Etudes en conditions modèles de l'extractibilité des composes phénoliquesndes pellicules et des pépins de raisin rouge. J. Int. Sci. Vigne Vin, 28: 303.

Amrani-Joutei K. and Glories Y. 1995a. Tanins et anthocyanes: localisation dans la baie de raisin et mode d'extraction. Rev. Fra. Oenol., 153: 28.

Amrani-Joutei K. and Glories Y. 1995b. Etude de la localisation et de l'extrabilité des tannins et des anthocyanes de la pellicule de raisin. In Œnologie 95, 5e Symposium Internationald'Oenologie (Proceedings), p. 119. Bordeaux-Lac, 15 to 17 June 1995, Coordonnateur Lonvaud-Funel, Technique & Documentation, Paris.

Arnold R.A., Noble A.C. and Singleton V.L. 1980. Bitterness and astringency of phenolics fraction in wine. J. Agric. Food Chem. 28: 675.

Atasavova V., Fulcrand H., Cheynier V. and Moutounet M. 2002. Effect of oxygenation on polyphenol changes occurring in the course of wine-making. Anal. Chim. Acta. 458: 15.

Auberts S. and Poux C. 1968. Extractions des composés phénoliques du raisin. Ann. Technol. Agric. 18: 93.

Barcelo J.M. 1997. La gestion de la maturation: le premier acte oenologique. Incidence sur les profils de vins de Syrah dans les Côtes du Rhône. Prog. Agric. Vitic. 114: 281.

Bourzeix M., Weyland D. and Heredia N. 1986. A study of catechins and procyanidins of grape clusters, the wine and other by-products of the vine. Bull. OIV. 59: 1171.

Cagnasso E., Ummarino I. and Di Stefano R. 2001. Estrazione dei polifenoli di uve Nebbiolo da Barolo con sistemi diversi di vinificazione. L'Enologo 37: 87.

Cayala L., Cottereau Ph. and Renard R. 2002. Estimation de la maturité phénolique des raisin rouges par la méthode I.T.V. standard. Rev. Fr. Oenol., 193: 10.

Celotti E. and Carcereri De Prati G. 2000a. Studio della maturità fenolica delle uve rosse per valorizzare l'area viticola dei Colli Berici. L'Enologo. 36: 79.

Celotti E. and Carcereri De Prati G. 2000b. La qualità fenolica delle uve rosse. Valutazione oggettiva mediante misura del colore. Ind. Bevande. 29: 378.

Celotti E., Della Vedova T., Ferrarini R. and Martinand S. 2007. The use of reflectance for monitoring phenolic maturity curves in red grapes. Ital. J. Food Sci. 19:91.

Cheynier V., Souquet J.M., Kontek A. and Moutounet M. 1994. Anthocyanin degradation in oxidising grape musts. J. Sci. Food Agric. 66: 283.

Cheynier V., Hidalgo-Arellano I., Souquet J.M. and Moutounet M. 1997. Estimation of the oxidative changes in phenolic compounds of Carignane during winemaking. Am. J. Enol.Vitic. 48: 225.

Cheynier V. 2000. Grape polyphenols and their reactions in wine. In Polyphenols 2000. Freising-Weihenstephan Germany, September 10-15, S. Martens, D. Treutter, and G. Forkmann (Eds.), p. 1. Freising, Germany.

Cravero M.C. and Di Stefano R. 1992. Composizione fenolica di alcune varietà di vite cultivate in Piemonte. Vignevini. 19: 47.

Crespy A. 2002. La maturité polyphénolique. Rev. Oenol. 105: 40.

De Freitas V.A.P., Glories Y. and Monique A. 2000. Developmental changes of procyanidins in grapes of red *Vitis vinifera* varieties and their composition in respective wines. Am. J. Enol. Vitic. 51: 397.

Di Stefano R., Cravero M.C. and Gentilini N. 1989. Metodi per lo studio dei polifenoli dei vini. L'Enotecnico. 25: 83.

Di Stefano R. and Cravero M.C. 1991. Metodi per lo studio dei polifenoli dell'uva. Riv. Vitic. Enol. 44: 37.

Di Stefano R., Borsa D., Maggiorotto G. and Corino L. 1995. Terpeni e polifenoli di uve aromatiche a frutto colorato prodotte in Piemonte. L'Enotecnico. 29: 75.

Di Stefano R., Borsa D., Bosso A. and Garcia-Moruno E. 2000. Sul significato e sui metodi di determinazione dello stato di maturità dei polifenoli. L'Enologo. 36: 73.

Di Stefano R, Borsa D., Ummarino I., Gentilizi N. and Follis R. 2002. Evoluzione della composizione polifenolica di uve da cultivars diverse durante la maturazione. L'Enologo. 38: 81.

EEC. 1990. Commission Regulation N. 2676 of 17 September 1990 Determining Community methods for analysis of wines. OJ L272, 3.10.1990.

Gerbi V., Zeppa G. and Rolle L. 2002. Evoluzione delle antocianine nel corso della vinificazione delle uve nebbiolo. In "Ricerche e Innovazioni nell'Industria Alimentare", a cura di S. Porretta, Vol. V, p. 420. Chiriotti Editori, Pinerolo, TO, Italy.

Gerbi V., Rolle L., Guidoni S., Zeppa G. and Schneider A. 2004 Indagine sul profilo antocianico di vitigni autoctoni piemontesi. In "Ricerche e Innovazioni nell'Industria Alimentare", a cura di S.

Porretta, vol. VI, p. 377. Chiriotti Editori, Pinerolo, TO, Italy.
Glories Y. 1984. La couleur des vins rouges. 2me partie. Mesure, origine et interprétation. Conn. Vigne Vin. 18: 253.
Glories Y. 2001. Caractérisation du potentel phénolique: adaptation de la vinification- Prog. Agric. Vitic.118: 347.
Glories Y. and Augustin M. 1993. Maturité phénolique du raisin, consèquences technologiques: applications aux millésimes 1991 et 1992. In Actes du Colloque "Journée Technique du CIVB" 21 Janvier, p. 56. CIVB, Bordeaux, France.
Glories Y. and Saucier C. 2000. Tannin evolution from grape to wine. Effects on wine taste. In Proceedings of the ASEV 50th Anniversary Annual Meeting, Seattle, WA. J.M. Rantz (Ed.), p. 353. ASEV, Davis, CA.
González-Neves G., Charamelo D., Balado J., Barreiro L., Bochicchio R., Gato G., Gil G., Tessore A., Carboneau A. and Moutounet M. 2004. Phenolic potential of Tannat, Cabernet Sauvignon and Merlot grapes and their correspondence with wine composition. Anal. Chim. Acta 513: 191.
González-Neves G., Franco J., Ferrer M., Moutounet M. and. Carboneau A. 2007. Predicción de la composición fenólica y el color de los vinos tintos de acuerdo con el potencial polifenólico de la uva. XXXth OIV World Congress, Budapest 10-16 June.
Guidoni S., Mannini F., Ferrandino A., Argamante N. and Di Stefano R. 1997. The effect of Grapevine Leafroll and Rugose Wood sanitation on agronomic performance and berry and leaf phenolic content of a Nebbiolo clone (*Vitis vinifera* L.). Am. J. Enol. Vitic. 48: 438.
Gunata Z., Pineau J. and Cordonnier R. 1987. Determination de la qualitè de la vendange par sa richesse en composés phenoliques. Applications a la vinification. Rev. Fr. Oenol. 107: 7.
Hebrero E., Santos-Buelga C. and Rivas Ponzalo J.C. 1988. High performance liquid chromatography-diode array spectroscopy identification of anthocyanins of *Vitis vinifera* variety Tempranillo. Am. J. Enol. Vitic. 39: 227.
Lamadon F. 1995. Protocole pour l'évalutation de la richesse polyphénolique des raisins. Rev. Oenol., 76: 37.
Letaief H., Rolle L., Zeppa G., Orriols I. and Gerbi V. 2007. Phenolic characterization of grapevine cultivars from Galicia (Spain) Brancellao, Merenzao and Mencia (*Vitis vinifera* L.). Ital. J. Food Sci. 19: 101.
Margheri G., Tonon T., Pellegrini R. and Sartori G. 1985. Correlazione tra la composizione biochimica dell'uva, le tecniche di vinificazione e la qualità dei vini. L'Enotecnico. 21: 1129.
Martinez L. 2002. La dégustation des baies de raisin. Rev. Oenol. 105: 19.
Mattivi F., Prast A., Nicolini G. and Valenti L. 2002a. Validazione di un nuovo metodo per la misura del potenziale polifenolico delle uve rosse e discussione del suo campo di applicazione in enologia. Riv. Vitic. Enol. 56: 55.
Mattivi F., Zulian C., Nicolini G. and Valenti L. 2002b. Wine, biodiversity, technology, and antioxidants. Ann. N.Y. Acad. Sci. 957: 37.
Mattivi F. 2006. Gli indici di maturazione delle uve e la loro importanza. Quad. Vitic. Enol Univ. Torino, 28: 27.
Moutounet M., Rigaud J., Souquet J.M. and Cheynier V. 1996. Caractérisation structurale des tanins de la baie du raisin. Bull. OIV. 69: 433.
Peyron D. 1998. Le potentiel polyphénolique du Pinot Noir. Rev. Fr. Oenol. 170: 42.
Piracci A. 1994. Evaluation instrumentale de la couleur. J. Int. Sci. Vigne Vin. 28: 247.
Prieur C., Rigaud J., Cheynier V. and Moutounet M. 1994. Oligomeric and polymeric procyanidins from grape seeds. Phytochem. 36: 781.
Ribereau-Gayon P. 1970. Le dosage des composés phénoliques totaux dans le vins rouges. Chimie Anal. 52: 627.
Ribereau-Gayon P. 1971. Evolution des composés phénoliques au cours de la maturation du raisin. I. Expérimentation 1969. Connaiss. Vigne Vin. 5: 247.
Riou V. and Asselin C. 1996. Potentiel polyphénolique disponible du raisin. Estimation rapide par extraction partielle à chaud. Prog. Agric. Vitic., 113: 382.
Robichaud J.L. and Noble A.C. 1990. Astringency and bitterness of selected phenolics in wine. J. Sci. Food Agric. 53: 343.
Rolle L. and Guidoni S. 2007. Color and anthocyanin evaluation of red winegrapes by CIE L*, a*,b* parameters. J. Int. Sci. Vigne Vin. 41: 193.
Romero-Cascales I., Ortega-Regules A., López-Roca J.M., Fernández-Fernández J.I. and Gómez-Plaza E. 2005. Differences in anthocyanin extractability from grapes to wines according to variety. Am. J. Vitic. Enol. 56: 212.
Rousseau J. and Delteil D. 2000. Présentation d'une méthode d'analyse sensorielle des raisins. Principe, méthode et grille d'interprétation. Rev. Fr. Oenol. 173: 10.
Saint-Criq N., Vivas N. and Glories Y. 1998a. Apports récents à l'interprétation des critéres de la qualité des vin rouges. Rev. Fr. Oenol. 169: 19.
Saint-Criq N., Vivas N. and Glories Y. 1998b. Maturation phénolique des raisins rouges relation avec la qualité des vins. Comparaison des cépges Merlot et Tempranillo. Prog. Agric. Vitic. 115: 306.
Saint-Criq N., Vivas N. and Glories Y. 1998c. Maturité phénolique: définition et contrôle. Rev. Fr. Oenol. 173: 22.
Schneider A., Gerbi V. and Redoglia M. 1987. A rapid HPLC method for separation and determination of major organic acids in grape musts and wines. Am. J. Enol. Vitic. 38: 151.
Souquet J-M., Cheynier V., Brossaud F. and Moutounet M. 1996. Polymeric proanthocyanidins from grape skins. Phytochem. 43: 509.
Venencie C., Uveira M.N. and Guiet S. 1997. Maturité polyphénolique du raisin mise en place d'une méthode d'analyse de routine. Rev. Fr. Oenol. 167: 36.
Venencie C., Videau B. and Michel D. 1998. Contrôle maturité: analyse des pellicules ou des baies entiéres? Rev. Fr. Oenol. 169: 13.
Zeppa G., Rolle L., Gerbi V. and Guidoni S. 2001. Anthocyanin composition of four autochthonous *Vitis vinifera* grapevine varieties from the Piedmont. Ital. J. Food Sci. 13: 405.

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