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QUANTIFICATION OF CATECHINS AND PROANTHOCYANIDINS IN SEVERAL PORTUGUESE GRAPEVINE VARIETIES AND RED WINES

QUANTIFICAÇÃO DAS CATEQUINAS E PROANTOCIANIDINAS EM ALGUMAS VARIEDADES DE VIDEIRA E VINHOS TINTOS PORTUGUESES

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SUMMARY

Catechins, oligomeric proanthocyanidins (degree of polymerization ranging from 2 to 12-15) and polymeric proanthocyanidins (degree of polymerization > 12-15) in several Portuguese grapevine varieties (Fernão Pires, Castelão, Vital, Vinhão, Espadeiro, Azal Tinto) harvested from the west and the north of Portugal in 1993 and 1994, and in some red wines from several Portuguese regions (Estremadura, Dão and Vinhos Verdes), were quantified using modified vanillin assay.

In most grapevine varieties studied, the levels of catechins and proanthocyanidins in seeds in 1993 were roughly equal to those in 1994, although the climatological conditions were different between the two years. However, these values in skins of all tested varieties except *Fernão Pires*, obtained in 1994, were much smaller than those in 1993. Catechins and proanthocyanidins were located essentially in seeds, being 77,2% of total catechins of grape berry, 80,8% of total oligomeric proanthocyanidins of grape berry and 60,3% of total polymeric proanthocyanidins of grape berry, then in skins, being 19,7% of total catechins of grape berry, 19,0% of total oligomeric proanthocyanidins of grape berry and 38,9% of total polymeric proanthocyanidins of grape berry, and very little in pulp, being 3,1% of total catechins of grape berry, 0,2% of total oligomeric proanthocyanidins of grape berry and 0,8% of total polymeric proanthocyanidins of grape berry (mean values of two years). In seeds, the percentages of catechins, oligomeric and polymeric proanthocyanidins were respectively 4,2%, 29,4% and 66,4%; in skins, on the other hand, these values were respectively 1,8%, 13,0% and 85,2% (mean values of two years). The results also show the differences between the grapevine varieties from the west of Portugal and those from the north of Portugal.

For all red wines analyzed, polymeric proanthocyanidins were predominant (averaging 65.5%), followed by oligomeric proanthocyanidins (averaging 27.9%), and catechins were presented in the lowest concentration (averaging 6.6%). Furthermore, the distribution of catechins, oligomeric and polymeric proanthocyanidins in red wines was similar to that in grapes.

Key Words: grapevine varieties, wines, catechins, proanthocyanidins.
Palavras chave: Variedades de videira, vinhos, catequinas, proantocianidinas

INTRODUCTION

Proanthocyanidins (PA) are at least partially responsible for some major organoleptic properties of wines, in particular astringency and bitterness (Haslam, 1974; Arnold *et al*., 1980; Singleton, 1992; Spranger *et al*., 2000). They play an important role in red wine aging due to their high reactivity (polymerisation, condensation with anthocyanins and oxidation reactions) (Timberlake and Bridle, 1976; Ricardo da Silva *et al.*, 1991b; Cheynier *et al*., 1997). Some low molecular weight PA (dimers and trimers) have been identified as potent oxygen free radical scavengers (Ricardo da Silva *et al.*, 1991c) and effective antioxidants *in vivo* (Teissedre *et al*., 1996). The presence of high quantities of these compounds in grapes and red wines, as compared with other fruits and beverages, has brought considerable interest to enologists.

A large number of measurements have been made of catechin and PA contents in grapes and wines. The majority of these measurements have involved analysis of some individual dimeric and trimeric PA by HPLC (Lea *et al*., 1979; Bourzeix *et al*., 1986; Oszmianski and Lee, 1990; Ricardo da Silva *et al*., 1992) and very few works have concerned with quantification of total PA contents (Revilla *et al*., 1991; Vivas *et al*., 1994; Sun *et al*., 1998b). The reason for this is due essentially to lack of standard global estimation method. Evaluation of total phenolic compounds or "*tannins*" in grape or wine, for which the most common method was the Folin-Ciocalteu (Singleton and Rossi, 1965), quantified not only PA but also other phenolics. Otherwise, recent investigation revealed that both in grape and in wine, PA existed essentially in highly polymerized forms (Sun *et al*., 1996, 1998a, 1999; Cheynier, 1997). Furthermore, the chemical properties of PA depend largely their structures and their degree of polymerization (Cheynier, 1997; Spranger *et al*., 2000). As a consequence, quantitative analysis of PA content and distribution according to their degree of polymerization is undoubtedly important.

In our previous work (Sun *et al*., 1998a), one method for separation of PA according to their polymerization degree was described. This method was used to quantitatively separate grape and wine PA into three fractions containing respectively catechins, oligomeric PA and polymeric PA. Each fraction can be further studied or analyzed. The modified vanillin assay as recently described (Sun *et al*., 1998b) permits quantitative analysis of total PA in each fraction.

The purpose of present work is to evaluate catechins, oligomeric and polymeric PA contents in various Portuguese grapevine varieties and red wines.

MATERIALS AND METHODS

Fernão Pires, Castelão and Vital grapes (*Vitis vinifera* L.) from vineyards of the INIA-Estação Vitivinícola Nacional (Dois Portos, Portugal), Vinhão, Espadeiro, and Azal Tinto grapes (*Vitis vinifera* L.) from vineyards of Comissão de Viticultura da Região dos Vinhos Verdes (Portugal), were harvested both in September 1993 and in September 1994. The mode of sampling and the extraction of total phenolic compounds from each part of grapes were performed as described by Bourzeix *et al*. (1986).

Five one-year-old wines were used in this study, in which one was from the Quinta das Maias (Portugal) and made with several typical cultivars (*Vitis vinifera* L.) of Dão region (referred as **D**). The other four wines were made at the INIA-Estação Vitivinícola Nacional (Dois Portos, Portugal), one of which was from the Quinta d'Almoinha and made with several cultivars (*Vitis vinifera* L.) of Estremadura region (referred as **E**), and three of which were elemental wines made respectively with the following grapevine varieties (*Vitis vinifera* L.): Tinta Miúda of Estremadura region (referred as **TM**), Espadeiro and Vinhão of Vinhos Verdes region (referred respectively as **Es** and **V**). For each of elemental wines, 50-kg lots of corresponding grape cluster was crushed, treated with 80 mg/L SO_2 and then transferred into 60-L stainless steel tanks, and maintained at 25ºC. The cap was punched down three times daily until it remained submerged. After alcoholic fermentation was finished (about seven days), the mash was pressed. Free-run and press wines were combined and stored in 20-L vessels at room temperature. After one month when the malo-lactic fermentation was finished, the wines were racked, treated with 30 mg/L SO_2 and stored at room temperature for another three months. The wines were then racked, treated with 30 mg/L SO_2, bottled and stored at room temperature for eight months prior to analysis.

The fractionation of proanthocyanidins of grapes and wines into catechins, oligomers and polymers was realized by percolation on C_{18} Sep-Pak cartridges, according to method described earlier (Sun *et al*., 1998a). Quantification of total flavan-3-ols in each fraction was carried out by the modified vanillin assay (Sun *et al*., 1998b).

General composition of juices from each grapevine variety studied, *i.e.* density, total acidity, pH, total sugar and potential alcohol, were analyzed using the standard methods as recommended by OIV (OIV, 1990).

Significant differences at 95% level among varieties and between the two years for catechin, oligomeric and polymeric proanthocyanidin contents in

each part of grapes were separately assessed with multifactor analysis of variance using Statgraphic 5 v. (STSC Inc., Rockville, USA).

RESULTS AND DISCUSSION

Catechin and proanthocyanidin contents in different parts of grapes

Catechin and proanthocyanidin contents in the pulp, skins and seeds of grape are presented in table I, II and III, respectively.

According to the data from table I, II and III, the relative percentage of different types of flavan-3-ols in each part of grape cluster can be calculated. These results are presented in table IV.

Considering that in the literature the phenolic contents in grapes were generally expressed either in w/w of fresh cluster or by w/w of fresh solid, the data given in these tables include both the two types of expression. In fact, the first expression reflects the variation of cluster weight, whereas the second indicates the concentration in the solid part.

TABLE I

Catechin and proanthocyanidin contents in the pulp from grapevine varieties studied
Teores em catequinas e proantocianidinas na polpa da uva de diversas cultivares estudadas

variety	year	catechins		oligomers		polymers	
		mg/g fresh seed	mg/kg fresh cluster	mg/g fresh seed	mg/kg fresh cluster	mg/g fresh seed	mg/kg fresh cluster
Fernão Pires	1993	**4.0**b ± 0.3	**141.7**abc ± 11.3	**26.0**a ± 2.2	**915.5**a ± 78.7	**78.3**a ± 6.1	**2751.8**c ± 214.6
	1994	**4.2**b ± 0.3	**129.2**abc ± 9.7	**22.5**a ± 1.5	**684.4**a ± 45.9	**67.4**a ± 4.1	**2050.4**c ± 125.1
Castelão	1993	**3.5**ab ± 0.3	**86.1**ab ± 8.3	**27.6**a ± 2.5	**689.7**a ± 62.8	**64.0**a ± 5.4	**1597.2**ab ± 135.8
	1994	**3.3**ab ± 0.2	**57.1**ab ± 4.0	**23.7**a ± 2.5	**416.5**a ± 43.7	**73.5**a ± 6.7	**1290.7**ab ± 117.5
Vital	1993	**1.0**a ± 0.1	**20.4**a ± 2.6	**19.0**a ± 2.3	**377.7**a ± 45.7	**56.0**a ± 5.9	**1113.7**a ± 116.9
	1994	**1.1**a ± 0.1	**20.9**a ± 1.9	**21.3**a ± 1.8	**408.9**a ± 35.2	**54.7**a ± 4.0	**1049.8**a ± 76.6
Vinhão	1993	**3.1**ab ± 0.2	**195.3**bc ± 11.9	**27.4**a ± 1.5	**1724.5**b ± 94.8	**58.0**a ± 3.7	**3648.4**d ± 229.8
	1994	**2.1**ab ± 0.1	**101.7**bc ± 6.9	**24.1**a ± 1.5	**1199.8**b ± 73.2	**60.5**a ± 4.6	**3007.0**d ±228.5
Espadeiro	1993	**12.1**c ± 0.5	**465.5**d ± 17.7	**39.0**b ± 2.3	**1500.2**b ± 87.0	**45.2**a ± 3.3	**1742.6**bc ± 127.2
	1994	**9.0**c ± 0.8	**298.8**d ± 26.6	**37.7**b ± 3.5	**1245.9**b ± 115.9	**73.0**a ± 6.8	**2413.4**bc ± 224.4
Azal Tinto	1993	**4.5**b ± 0.2	**312.7**c ± 14.4	**37.7**b ± 2.0	**2641.2**c ± 140.0	**72.0**a ± 4.2	**5040.8**e ± 297.4
	1994	**2.6**b ± 0.2	**176.6**c ± 16.4	**42.7**b ± 3.0	**2897.3**c ± 205.7	**75.2**a ± 6.0	**5106.3**e ± 408.5

Mean values ± SD (n = 2); means followed by the same letter in a column are not significantly different (LSD, 5%); symbol * indicates that for the same variety there was significant difference (LSD, 5%) between the two years.

TABLE II

Catechin and proanthocyanidin contents in the seeds from grapevine varieties studied
Teores em catequinas e proantocianidinas na polpa da uva de diversas cultivares estudadas

variety	year	catechins		oligomers		polymers	
		mg/kg fresh pulp	mg/kg fresh cluster	mg/kg fresh pulp	mg/kg fresh cluster	mg/kg fresh pulp	mg/kg fresh cluster
Fernão Pires	1993	**0.0**a ± 0.0	**0.0**a ± 0.0	**0.3**a * ± 0.1	**0.2**a * ± 0.1	**0.9**a ± 0.2	**0.7**a ± 0.2
	1994	**1.2**a ± 0.3	**1.0**a ± 0.3	**1.0**a * ± 0.2	**0.8**a * ± 0.2	**26.5**a ± 3.0	**21.8**a ± 2.5
Castelão	1993	**2.7**a ± 0.9	**2.2**a ± 0.7	**1.6**a * ± 0.6	**1.3**a * ± 0.5	**13.1**a ± 3.0	**10.9**a ± 2.5
	1994	**5.2**a ± 1.2	**4.4**a ± 1.0	**0.0**a * ± 0.0	**0.0**a * ± 0.0	**50.3**a ± 5.0	**42.4**a ± 4.2
Vital	1993	**3.6**a ± 1.1	**2.9**a ± 0.9	**4.5**a * ± 1.6	**3.5**a * ± 1.2	**47.6**a ± 7.6	**37.7**a ± 6.0
	1994	**3.2**a ± 1.4	**2.6**a ± 1.1	**1.4**a * ± 0.5	**1.1**a * ± 0.4	**13.4**a ± 3.3	**11.0**a ± 2.7
Vinhão	1993	**2.6**a ± 1.2	**1.9**a ± 0.9	**7.3**a * ± 2.4	**5.4**a * ± 1.8	**81.9**a ± 10.7	**60.2**a ± 7.8
	1994	**7.2**a ± 2.2	**5.8**a ± 1.8	**0.0**a * ± 0.0	**0.0**a * ± 0.0	**88.0**a ± 10.6	**70.7**a ± 8.5
Espadeiro	1993	**7.4**a ± 2.4	**5.5**a ± 1.8	**7.1**a * ± 2.1	**5.3**a * ± 1.6	**78.0**a ± 10.1	**58.0**a ± 7.5
	1994	**4.5**a ± 1.6	**3.5**a ± 1.2	**0.8**a * ± 0.3	**0.6**a * ± 0.2	**12.8**a ± 2.4	**10.1**a ± 1.9
Azal Tinto	1993	**11.6**a ± 3.8	**9.0**a ± 3.0	**9.6**a * ± 2.7	**7.5**a * ± 2.1	**25.7**a ± 7.2	**20.0**a ± 5.6
	1994	**8.3**a ± 1.9	**6.5**a ± 1.5	**1.0**a * ± 0.3	**0.8**a * ± 0.3	**90.8**a ± 10.9	**71.3**a ± 8.6

Mean value ± SD (n = 2); means followed by the same letter in a column are not significantly different (LSD, 5%); for all grapevine varieties, there was no significant difference (LSD, 5%) between the two years both on the basis of mg/g fresh seed and on the basis of mg/kg fresh cluster.

Although both catechins and proanthocyanidins in the pulp were detected for all varieties studied except for Fernão Pires (table I), the values obtained were relatively small or negligible, as compared with those obtained in the skins and the seeds. This is agreement with other authors (Bourzeix *et al*., 1986; Ricardo-da-Silva *et al*., 1992). Furthermore, catechins and proanthocyanidins detected in the pulp might be due to the contamination of skins during its separation from the pulp.

In the seeds, as presented in table II, proanthocyanidins were essentially present in polymeric forms (averaging 66,4%), to less extent in oligomeric forms (averaging 29,4%), and small amount in monomeric forms (catechins) (averaging 4,2%). For a given variety, the concentrations of each type of flavanols between the two years were roughly equal. This may indicate that the concentration of such compounds in the seeds was generally not dependent on the vintage.

In the skins, as can be seen in table III, the great majority of proanthocyanidins

TABLE III

Catechin and proanthocyanidin contents in the skins from grapevine varieties studied
Teores em catequinas e proantocianidinas na polpa da uva de diversas cultivares estudadas

variety	year	catechins		oligomers		polymers	
		mg/kg fresh skins	mg/kg fresh cluster	mg/kg fresh skins	mg/kg fresh cluster	mg/kg fresh skins	mg/kg fresh cluster
Fernão Pires	1993	**141.1**a * ± 8.6	**22.6**a * ± 1.4	**1827.0**a ± 127.9	**292.9**a ± 20.5	**7680.1**a ± 559.0	**1231.1**a * ± 96.0
	1994	**150.7**a * ± 13.9	**15.9**a * ± 1.5	**2606.8**a ± 198.1	**275.0**a ± 20.9	**9064.5**a ± 625.5	**956.4**a * ± 66.0
Castelão	1993	**221.3**a * ± 19.5	**27.1**a * ± 2.4	**2692.9**a ± 218.1	**329.2**a ± 26.7	**19733.4**a ± 1401.1	**2412.0**a * ± 171.3
	1994	**155.6**a * ± 11.4	**18.2**a * ± 1.3	**1997.7**a ± 141.8	**233.7**a ± 16.6	**15926.9**a ± 1210.4	**1863.5**a * ± 141.6
Vital	1993	**140.8**a * ± 14.2	**22.2**a * ± 2.2	**1250.1**a ± 118.8	**197.1**a ± 18.7	**8786.2**a ± 597.5	**1385.5**a * ± 94.2
	1994	**20.4**a * ± 2.3	**2.8**a * ± 0.3	**283.5**a ± 34.9	**38.7**a ± 4.8	**1932.1**a ± 202.9	**263.6**a * ± 27.7
Vinhão	1993	**681.5**b * ± 46.3	**120.5**a * ± 8.2	**3534.8**a ± 229.8	**624.9**a ± 40.6	**10480.4**a ± 597.4	**1852.9**a * ± 105.6
	1994	**237.6**b * ± 22.8	**30.5**a * ± 2.9	**821.6**a ± 80.5	**105.5**a ± 10.3	**10320.9**a ± 650.2	**1325.7**a * ± 83.5
Espadeiro	1993	**362.3**ab * ± 33.7	**62.9**a * ± 5.8	**1624.8**a ± 121.9	**282.0**a ± 21.2	**16734.2**a ± 987.3	**2904.0**a * ± 171.3
	1994	**133.3**ab * ± 16.8	**20.5**a * ± 2.6	**1414.3**a ± 145.7	**217.4**a ± 22.4	**10784.4**a ± 884.3	**1657.5**a * ± 135.9
Azal Tinto	1993	**646.3**b * ± 37.5	**73.8**a * ± 4.3	**2182.0**a ± 137.5	**249.2**a ± 15.7	**19232.3**a ± 980.8	**2196.5**a * ± 112.0
	1994	**358.8**b * ± 40.2	**41.8**a * ± 4.7	**1209.0**a ± 104.0	**140.7**a ± 12.1	**20974.0**a ± 1384.3	**2441.4**a * ± 161.1

Mean value ± SD (n = 2); means followed by the same letter in a column are not significantly different (LSD, 5%); symbol * indicates that for the same variety there was significant difference (LSD, 5%) between the two years.

were presented in polymeric forms (averaging 85,3%). The percentages of oligomeric proanthocyanidins and catechins are relatively small, averaging 13,0% and 1,8%, respectively. On the other hand, both catechin and proanthocyanidin concentrations varied markedly between the two years for all varieties studied. In other words, catechin and proanthocyanidin concentrations in the skins may depend on the physiological states of grapes.

Although catechin and proanthocyanidin concentrations in skins were much lower than those in seeds, the skins may have greater practical importance because catechin and proanthocyanidins in such soft tissues should be most easily released during maceration stage of winemaking. In addition, since the skins have a higher percentage of the total grape weight than the seeds, they account for an important proportion of phenolic compounds in the whole grape berry. In fact, the relative percentage ratios of catechins, oligomeric and polymeric proanthocyanidins in different parts of grape berry based on fresh cluster weight can be calculated from the data given in table I, table II and table III. The mean values obtained were as follows: for catechins, 3,1% in pulp, 19,7% in skins, 77,2% in seeds; for oligomeric proanthocyanidins, 0,2%

TABLE IV

Relative percentage (%) of different types of flavan-3-ols in each part of grape berry
Percentagem relativa (%) de diferentes tipos de 3-flavanois em cada parte do bago de uva

variety	year	pulp			seeds			skins		
		catechins	oligomers	polymers	catechins	oligomers	polymers	catechins	oligomer	polymers
Fernão Pires	1993	**0.0**a ± 0.0	**27.0**a * ± 8.9	**73.0**a ± 24.0	**3.7**a ± 0.4	**24.0**a ± 2.5	**72.3**b ± 7.1	**1.5**a ± 0.1	**18.9**a ± 1.8	**79.6**a ± 8.0
	1994	**4.3**a ± 1.2	**3.4**a * ± 0.8	**92.3**a ± 14.5	**4.5**a ± 0.4	**23.9**a ± 2.0	**71.6**b ± 5.5	**1.3**a ± 0.1	**22.1**a ± 2.1	**76.7**a ± 6.8
Castelão	1993	**15.5**a ± 5.7	**9.1**a * ± 3.6	**75.5**a ± 22.2	**3.7**a ± 0.4	**29.0**a ± 3.2	**67.3**b ± 7.1	**1.0**a ± 0.1	**11.9**a ± 1.2	**87.1**a ± 8.2
	1994	**9.4**a ± 2.3	**0.0**a * ± 0.0	**90.6**a ± 12.4	**3.3**a ± 0.3	**23.6**a ± 3.0	**73.1**b ± 8.4	**0.9**a ± 0.1	**11.0**a ± 1.1	**88.1**a ± 8.9
Vital	1993	**6.5**a ± 2.2	**8.0**a * ± 3.0	**85.5**a ± 18.2	**1.3**a ± 0.2	**25.0**a ± 3.7	**73.7**b ± 9.9	**1.4**a ± 0.2	**12.3**a ± 1.4	**86.3**a ± 7.8
	1994	**17.8**a ± 8.5	**7.6**a * ± 3.4	**74.6**a ± 24.1	**1.4**a ± 0.2	**27.6**a ± 2.9	**70.9**b ± 6.6	**0.9**a ± 0.1	**12.7**a ± 1.9	**86.4**a ± 12.1
Vinhão	1993	**2.9** a ± 1.3	**7.9**a * ± 2.8	**89.2**a ± 15.8	**3.5**a ± 0.3	**31.0**a ± 2.2	**65.5**b ± 5.1	**4.6**a ± 0.4	**24.1**a ± 1.9	**71.3**a ± 5.1
	1994	**7.6**a ± 2.5	**0.0**a * ± 0.0	**92.4**a ± 15.3	**2.4**a ± 0.2	**27.8**a ± 2.3	**69.8**b ± 6.6	**2.1**a ± 0.2	**7.2**a ± 0.8	**90.7**a ± 7.7
Espadeiro	1993	**8.0**a ± 2.7	**7.6**a * ± 2.5	**84.3**a ± 14.6	**12.6**b ± 0.7	**40.5**a ± 2.9	**46.9**a ± 3.9	**1.9**a ± 0.2	**8.7**a ± 0.8	**89.4**a ± 7.1
	1994	**24.8**a ± 9.6	**4.3**a * ± 1.8	**70.9**a ± 17.7	**7.5**b ± 0.8	**31.5**a ± 3.6	**61.0**a ± 6.9	**1.1**a ± 0.2	**11.5**a ± 1.4	**87.5**a ± 9.6
Azal Tinto	1993	**24.8**a ± 9.4	**20.4**a * ± 6.8	**54.8**a ± 18.3	**3.9**a ± 0.2	**33.0**a ± 2.2	**63.0**ab ± 4.5	**2.9**a ± 0.2	**9.9**a ± 0.8	**87.2**a ± 5.9
	1994	**8.3**a ± 2.1	**1.0**a * ± 0.3	**90.7**a ± 14.8	**2.2**a ± 0.2	**35.4**a ± 3.2	**62.4**ab ± 6.1	**1.6**a ± 0.2	**5.4**a ± 0.6	**93.0**a ± 8.4

Mean value ± SD (n = 2); means followed by the same letter in a column are not significantly different (LSD, 5%); symbol * indicates that for the same variety there was significant difference (LSD, 5%) between the two years.

in pulp, 19,0% in skins, 80,8% in seeds; for polymeric proanthocyanidins, 0,8% in pulp, 38,9% in skins, 60,3% in seeds. From these values, it should be especially noted that, nearly 40% of total polymeric proanthocyanidins in the grape berry were located in grape skins. Moreover, Souquet *et al.* (1996) reported that the highest DP of proanthocyanidins in grape skins might reach 83. It is a reasonable suggestion that the skins should be an important source of polymeric proanthocyanidins in red wine.

It is generally accepted that chemical composition of grapes varies according to the variety, the climatological conditions, the grapevine age, etc. For this reason, the general composition (*i.e.* density, total acidity, pH, total sugar and potential alcohol) of juices from the grapevine varieties studied was analyzed. These results are given in table V.

As already mentioned above, catechin and proanthocyanidin concentrations in skins were generally much higher in 1993 than in 1994. From table V, it can be seen that the ripening index for each of the varieties from the West (*i.e.* Fernão Pires, Castelão and Vital) was much higher in 1993 than in 1994. So

we may suggest that, for the varieties from the West catechin and proanthocyanidin concentrations in skins were positively related to the grape ripeness. However, this correlation is not observed for the varieties from the North for which the ripening indexes were similar between the two years (table V).

From table I, II and III, it can also be noted that catechin and proanthocyanidin levels in the varieties from the North were generally higher than those from the West. The reason for this could be due to the different varieties, the different physiological state of grape and the different cultivated and climatic conditions between the two regions.

Catechin and proanthocyanidin contents in wines

Catechin and proanthocyanidin contents in several one-year-old red wines were presented in table VI.

For all wines analyzed, polymeric proanthocyanidins were predominant (averaging 65.5%), followed by oligomeric proanthocyanidins (averaging 27.9%), and monomeric flavan-3-ols (catechins) were presented in the lowest concentration (averaging 6.6%). Furthermore, the distribution of each type of flavan-3-ols (monomers, oligomers and polymers) in red wines is similar to that in grapes.

TABLE V

General composition of juices from various grapevine varieties
Composição geral dos mostos de diversas cultivares de videiras

variety	Year	Density (d_{20}^{20})	Total acidity (g/L tart. ac.)	pH	Total sugar (g/L)	potential alcohol (º)	Ripening index (Total sugar/total acidity)
Fernão Pires	1993	1,085	5,6	3,3	195,1	10,5	34,8
	1994	1,081	10,5	3,2	184,0	10,8	17,5
Castelão	1993	1,091	5,3	3,2	208,6	12,3	39,4
	1994	1,103	9,3	3,2	238,2	14,0	25,6
Vital	1993	1,073	6,7	3,2	164,1	9,6	24,5
	1994	1,067	11,2	3,3	151,0	8,9	13,5
Vinhão	1993	1,060	15,5	2,7	133,8	7,9	8,6
	1994	1,077	15,4	2,8	175,1	10,3	11,4
Espadeiro	1993	1,063	14,1	2,6	140,2	8,2	9,9
	1994	1,067	16,9	2,7	151,0	8,9	8,9
Azal Tinto	1993	1,063	16,4	2,8	140,2	8,2	8,5
	1994	1,080	19,6	2,8	181,8	10,7	9,3

Table VI

Catechin and proanthocyanidin contents in several one-year-old red wines*
Teores em catequinas e proantocianidinas em alguns vinhos com um ano de envelhecimento

wine	concentration (mg/L)			relative percentage (%)		
	catechins	oligomers	polymers	catechins	oligomers	polymers
TM	76.2 ± 6.2	205.6 ± 13.5	479.5 ± 31.3	10.0 ± 0.9	27.0 ± 2.2	63.0 ± 5.0
D	50.4 ± 5.1	279.6 ± 12.7	412.4 ± 32.6	6.8 ± 0.8	37.7 ± 2.5	55.5 ± 5.1
E	34.7 ± 2.6	175.2 ± 10.9	334.8 ± 21.2	6.4 ± 0.6	32.2 ± 2.5	61.5 ± 4.7
Es	55.2 ± 5.3	262.4 ± 15.3	466.8 ± 28.7	7.0 ± 0.7	33.5 ± 2.4	59.5 ± 4.4
V	18.6 ± 2.8	65.2 ± 6.1	611.2 ± 37.9	2.7 ± 0.4	9.4 ± 1.0	87.9 ± 7.3

* mean value ± SD (n = 3). **TM** = Tinta Miúda elemental wine of Estremadura region; **D** = wine made with several typical cultivars of Dão region; **E** = wine made with several typical cultivars of Estremadura region; **Es** = Espadeiro elemental wine of Vinhos Verdes region; **V** = Vinhão elemental wine of Vinhos Verdes region.

CONCLUSION

Although only several grapevine varieties from Portugal and some one-year-old red wines were selected as tested samples in the present work, the results obtained could be generalized to other grapevine varieties and red wines. It gives us some important information as follows: (1) catechins, oligomeric proanthocyanidins and polymeric proanthocyanidins were located essentially in the seeds, then in the skins and very little in the pulp; (2) in wines and in each solid part of grape berry, proanthocyanidins were mainly present in polymeric forms, to a much less extent in oligomeric forms and very little in monomeric flavan-3-ols (catechins); (3) the percentages of polymeric proanthocyanidins in the skins were generally higher than those in the grape seeds.

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RÉSUMÉ

Quantification des catéchines et des proanthocyanidines dans certains cépages et vins rouges portugais.

Catéchines, proanthocyanidines oligomères (degré de polymérisation comprenant entre 2 et 12-15) et proanthocyanidines polymères (degré de polymérisation > 12-15) de certains cépages portugais (Fernão Pires, Castelão, Vital, Vinhão, Espadeiro, Azal Tinto) récoltés de l'Ouest et du Nord du Portugal en 1993 et 1994 et de quelques vins rouges de différentes régions portugaises

(Dão, Estremadura et Vinhos Verdes) ont été quantifiées en utilisant la méthode à la vanilline.

Dans la plupart des cépages étudiés, le contenu de catéchines et de proanthocyanidines des pépins était très similaire dans les deux années, malgré les différentes conditions climatiques entre eux. Par contre, les teneurs de ces composés dans les pellicules de toutes les cépages étudiés excepté *Fernão Pires*, étaient beaucoup plus basses en 1994. En outre, catéchines et proanthocyanidines sont présentes essentiellement dans les pépins, ce qui représente 77,2% de catéchines, 80,8% de proanthocyanidines oligomères et 60,3% de proanthocyanidines polymères du total de la baie. Les valeurs correspondantes dans les pellicules représentent seulement 19,7%, 19,0% et 38,9% du total de la baie et la pulpe est presque dépourvue de ces composés, soit 3,1% de catéchines totales de la baie, 0,2% de proanthocyanidines oligomères totales de la baie et 0,8% de proanthocyanidines polymères totales de la baie. Dans les pépins, la répartition de catéchines, proanthocyanidines oligomères et proanthocyanidines polymères était respectivement 4,2%, 29,4% et 66,4% et dans les pellicules 1,8%, 13,0% et 85,2% (valeur moyenne). Les résultats ont montré aussi la différence entre les cépages de l'Ouest et du Nord du Portugal.

Pour tous les vins analysés, proanthocyanidines polymères étaient prédominantes, soit 65,5%, ensuite proanthocyanidines oligomères, soit 27,9%, et les catechines, seulement 6,6% (valeur moyenne). Donc, la distribution de catéchines, proanthocyanidines oligomères et proanthocyanidines polymères dans les vins était semblable à celle dans les raisins.

RESUMO

Quantificação das catequinas e proantocianidinas em algumas variedades de videira e vinhos tintos portugueses

Neste trabalho, o teor total de catequinas, proantocianidinas oligoméricas (grau de polimerização compreendido entre 2 e 12-15) e proantocianidinas poliméricas (grau de polimerização > 12-15) de uvas de algumas variedades de videira portuguesas (Fernão Pires, Castelão, Vital, Vinhão, Espadeiro, Azal Tinto) colhidas no Oeste e Norte de Portugal em 1993 e 1994, e vinhos de diferentes regiões portuguesas (Dão, Estremadura e Vinhos Verdes), foi determinado utilizando o método de reacção com vanilina.

Para a maioria das variedades de videira estudadas, o teor de catequinas, proantocianidinas oligoméricas e proantocianidinas poliméricas nas graínhas das uvas, foi aproximadamente igual nos dois anos de estudo, apesar das diferentes condições climatéricas entre os dois anos. No entanto, na película das uvas de todas as variedades ensaiadas, com excepção de Fernão Pires, os teores determinados foram muito mais baixos na colheita de 1994 do que na de 1993. As catequinas e proantocianidinas localizam-se essencialmente nas graínhas, atingindo em média 77,2% do total de catequinas do bago, 80,8% do total de oligómeros do bago e 60,3% do total de polímeros do bago, enquanto que nas películas as catequinas representam, em média, apenas 19,7%, os oligómeros 19,0% e os polímeros 38,9% do teor total respectivo no bago. A contribuição da polpa para o teor total de catequinas e procianidinas do bago é diminuta (3,1% de catequinas, 0,2% de oligómeros e 0,8% de polímeros). Por outro lado, a distribuição percentual de catequinas, proantocianidinas oligoméricas e proantocianidinas poliméricas nas graínhas, foi respectivamente de 4,2%, 29,4% e 66,4% (valores médios), sendo nas películas de 1,8%, 13,0% e 85,2%. Os resultados mostraram também diferenças entre as variedades das regiões do Oeste e do Norte de Portugal.

Em todos os vinhos analisados, as proantocianidinas poliméricas foram predominantes (valor médio 65,5%), seguidas pelas proantocianidinas oligoméricas (valor médio 27,9%) e pelas catequinas, cujo valor médio foi apenas de 6,6%. Além disso, a distribuição de catequinas, proantocianidinas oligoméricas e proantocianidinas poliméricas nos vinhos tintos era semelhante à da uva.

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