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The colours, pigment and phenol contents of young port wines: Effects of cultivar, season and site

by

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Färbung, Pigment- und Phenolgehalt junger Portweine: Der Einfluß von Sorte, Jahrgang und Standort

Zusammenfassung: Im Kleinausbau wurden unter standardisierten Bedingungen 95 sortenreine Portweine hergestellt. Die Trauben der Jahrgänge 1977—83 stammten von 16 Rebsorten auf 5 Standorten im Douro-Tal (nördliches Portugal). Das spezifische Gewicht und der pH - Wert des Traubensaftes wurden bestimmt. Die Portweine wurden unmittelbar nach dem Aufspriten auf Färbung, Pigment- und Phenolgehalt sowie pH analysiert. Die sortenbedingte Variabilität konnte beträchtlich sein — bis zu 12fach bei den Gesamtpigmenten, 14fach bei der Farbintensität, aber nur 3,6fach bei den Gesamtphenolen. Die jahrgangsbedingten Schwankungen waren nur bis zu 2fach bei den Gesamtpigmenten und der Farbintensität und 1,6fach bei den Gesamtphenolen.

Die Portweine aus den Sorten Souzão, Tinta da Barca und Touriga Nacional (alle aus Tua) waren am kräftigsten gefärbt und enthielten die meisten Pigmente; Mourisco (Tua) und Tinto Cão (Baixo Corgo) lieferten die am schwächsten gefärbten Weine mit den wenigsten Pigmenten. Die Portweinfärbung war in erster Linie vom Pigmentgehalt und pH abhängig, konnte aber in geringerem Maße auch durch Selbst-Assoziation der Anthocyane und Co-Pigmentierung von Anthozyanen mit anderen Komponenten erhöht werden. Die Unterschiede zwischen den Standorten waren im allgemeinen nicht signifikant.

Key words: port wine, variety of vine, pigment, phenol.

Introduction

Portuguese ports are traditionally blends made from a large number of grape cultivars which are often planted randomly in the vineyard. There are little data on the characteristics of individual cultivars other than a rough classification of their quality as very good, good, normal, poor and bad (GOSWELL 1966). Hence, small quantities (10—20 kg) of grapes of 16 selected cultivars were air-freighted from Portugal to Long Ashton and processed into single cultivar ports under controlled pilot scale conditions. The main objective was to study the colour of port wine since this is considered the most important component of quality. Only young, freshly-made ports are described here. Immediately after processing, the ports were analysed for colour, pigment and phenol contents and pH. Seasonal variation was investigated for up to 7 harvests and the effects of 5 different sites were examined.

Materials and methods

Port wines

The grapes were picked at commercial maturity, flown to Bristol from the Douro valley in Portugal, and processed in Long Ashton as soon as possible after arrival,

using special Portuguese fortifying spirit. The ports were made under standard conditions in order to allow comparisons between ports made from different grape cultivars or between ports made in different years. The grapes were weighed, crushed with an addition of SO_2 and specific gravity (SG), and pH values of the crushed grapes were measured. In 1977—79, amounts between 75 and 150 mg l^{-1} SO_2 were added according to wine pH; thereafter, 150 mg l^{-1} SO_2 was added consistently. The crushed grapes were transferred into 20 l stainless steel vessels, kept at a temperature of 28 °C and after approximately 6 h inoculated with Montrachet yeast (10^7 cells ml^{-1}; inoculum 1 ml kg^{-1}). At SG 1.045 the fermenting mash was pressed, and the wine was fortified with fortifying spirit (77 % alcohol by volume) to give a calculated alcoholic strength of 19.5 % (v/v). All particulate matter was removed by centrifuging and the ports were stored in tightly corked glass jars of suitable size (5—20 l) in a dark, temperature-controlled room at 15 °C.

The numbers of single cultivar ports made between 1977 and 1983 were specified for each site:

Year	Tua	Baixo Corgo	Santa Barbara	Pinhão	Vilariça
1977	5	1	—	—	—
1978	8	3	—	—	—
1979	9	3	2	—	—
1980	9	2	3	—	—
1981	10	3	3	2	1
1982	12	3	3	2	2
1983	6	1	1	—	1

Ports were analysed as soon as possible after processing.

Analyses

Measurements of wine colour (at its own pH) and total pigments (in 1 M HCl) were made as described previously (TIMBERLAKE and BRIDLE 1976; JACKSON *et al.* 1978), except that wine colour was measured at its λ_{max} rather than at exactly 520 nm. Since λ_{max} was always very near (± 5 nm) to 520 nm, the measurements at λ_{max} were in very close agreement with the traditional ones at 520 nm. During 1981—83, colour was also measured after adjustment of the ports to pH 3.50. Polymeric pigments were determined by the spectral method (SOMERS and EVANS 1977) and also by high performance liquid chromatography (HPLC) (BAKKER *et al.* 1985).

Total phenols were measured spectrally as $A_{280nm} - 4$ (SOMERS and EVANS 1977). While these arbitrary units of absorbance are adequate for relative measurements on a range of wines, some indication of the actual phenol content in terms of gallic acid (the usually employed standard) is desirable. Hence, total phenols in 33 of the young ports were determined both by the above UV absorption method and the method of SINGLETON and ROSSI (1965) using the Folin-Ciocalteu reagent. To the plotted results a linear regression line could be fitted as follows:

$y = 29.5x + 210$, where

y = Total phenols as gallic acid (mg l^{-1})

x = Total phenols as $A_{280nm} - 4$.

The correlation coefficient was 0.956. The line did not go through the origin but indicated a Folin Ciocalteu reading of 210 mg l^{-1} gallic acid for zero A_{280nm} − 4. This may be due to approximations inherent in both methods, i.e. interference by SO_2 giving false positive readings in the Folin-Ciocalteu method (SOMERS and ZIEMELIS 1980) and the use of 4 as an approximate measure of non-phenolic interference in the absorbance method (SOMERS and EVANS 1977). The slope of the line indicated that 1 absorbance unit is equivalent to 29.5 mg l^{-1} of gallic acid.

The percentage ratio of pigments/phenols

From the spectral curve of malvidin 3-glucoside in 1 M HCl the ratio of its absorbance at 280 nm to that at 520 nm is 0.6. The contribution of the pigments to the total phenol (both pigmented and colourless) absorption at 280 nm is then approximately 0.6 A_{520nm}, so that the ratio of pigments to phenols is given by 0.6 total pigments/total phenols.

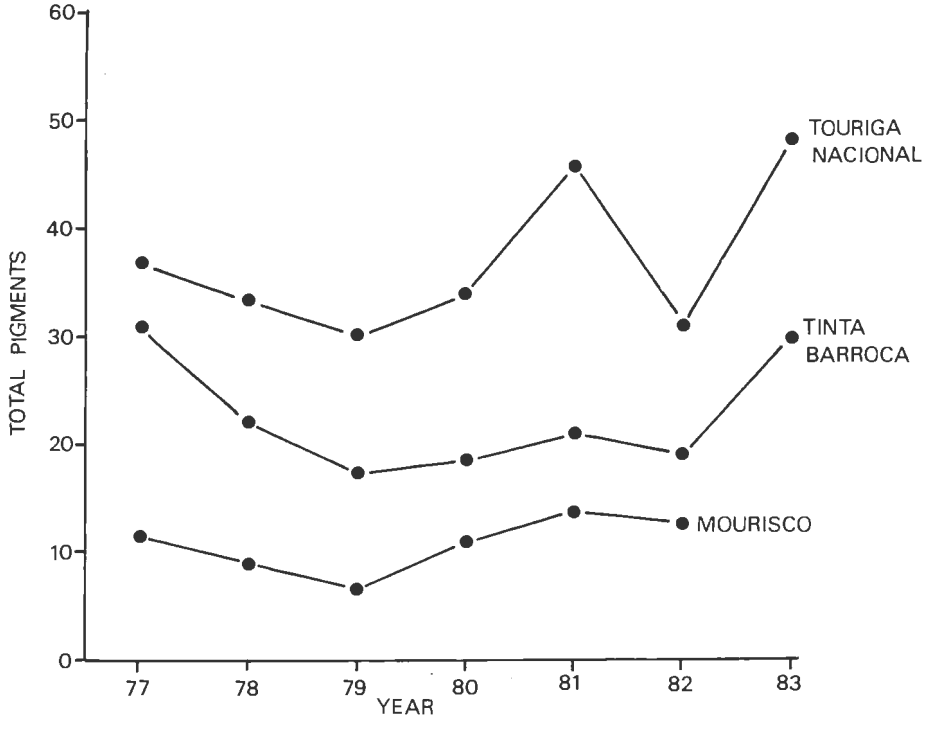

Fig. 1: Variation in total pigment contents of young single cultivar ports of Touriga Nacional, Tinta Barroca and Mourisco in 1977—83. Total pigments are expressed as A_{520nm} in 1 M HCl measured at 10 mm path-length.

Die Schwankungen des Gesamtpigmentgehaltes junger sortenreiner Portweine: Touriga Nacional, Tinta Barroca und Mourisco, Jahrgänge 1977—83. Die Gesamtpigmente sind als A_{520nm} für 10 mm Schichtdicke bei Messung in 1 M HCl angegeben.

Results and discussion

Seasonal variations in total pigments and in colour density of 3 cultivars, representative of the range of these attributes found in young ports, are illustrated in Figs. 1 and 2. Differences were not always consistent and a more definite indication of the effect of season is given by the variation in the means of several cultivars during the period 1977—82 (Figs. 3 and 4). Total pigments and colour were greatest in 1977 and 1981 and least in 1979.

Because of seasonal effects and also variation in the number of years (1—7) that any cultivar was examined, comparisons of individual cultivars could not be made on

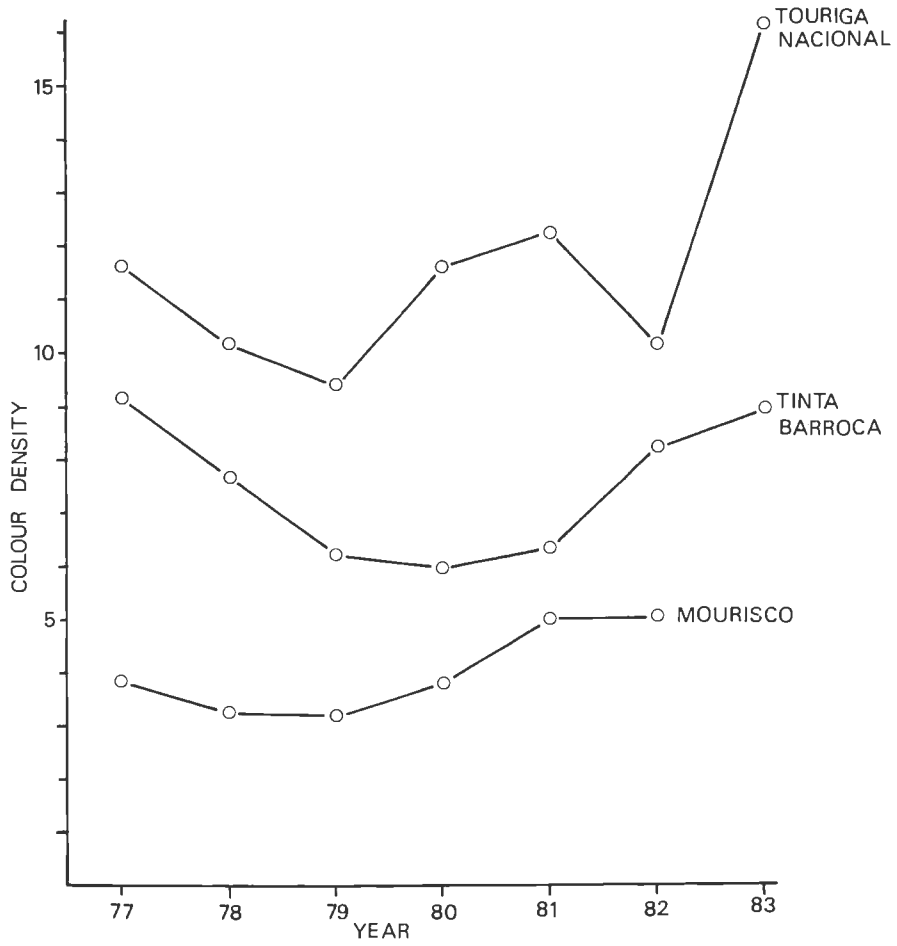

Fig. 2: Variation in colour densities of young Touriga Nacional, Tinta Barroca and Mourisco ports in 1977—83. Values are expressed as absorbance units for 10 mm path-length, derived from measurements at 1 mm path-length.

Die Schwankungen der Farbintensität junger Portweine der Sorten Touriga Nacional, Tinta Barroca und Mourisco, Jahrgänge 1977—83. Die Werte sind in Absorptionseinheiten bei 10 mm Schichtdicke angegeben; gemessen wurde bei 1 mm Schichtdicke.

the basis of their mean values. Rather, one cultivar (Touriga Nacional, Tua) was chosen as a standard, and parameters for the other cultivars were expressed as ratios of the values for this standard cultivar in each year. Means of the ratios were then calculated for all the years investigated. Selected results according to this procedure are given in Table 1. Actual overall mean values together with standard errors of the means for 1977—83 for grape specific gravity, and port total pigments, $A_{\lambda max}$, colour density, tint, total phenols, the ratio of total pigments/total phenols, and pH are given only for the cultivar Touriga Nacional (Tua). For all other cultivars the values quoted are the relative mean values compared with Touriga Nacional (Tua) which is given the arbitrary score of 1.00. The variability of each of these means can be calculated from the overall standard deviation at the foot of each column; the standard error of a mean is given by: standard deviation/$n^{1/2}$, where n is the number of years.

In this way the cultivars can be listed according to the parameter of interest. Thus, in Table 1 the cultivars are listed in order of decreasing contents of total pigments, regarded as the most important parameter for port wines. Whether any two means (μ_1

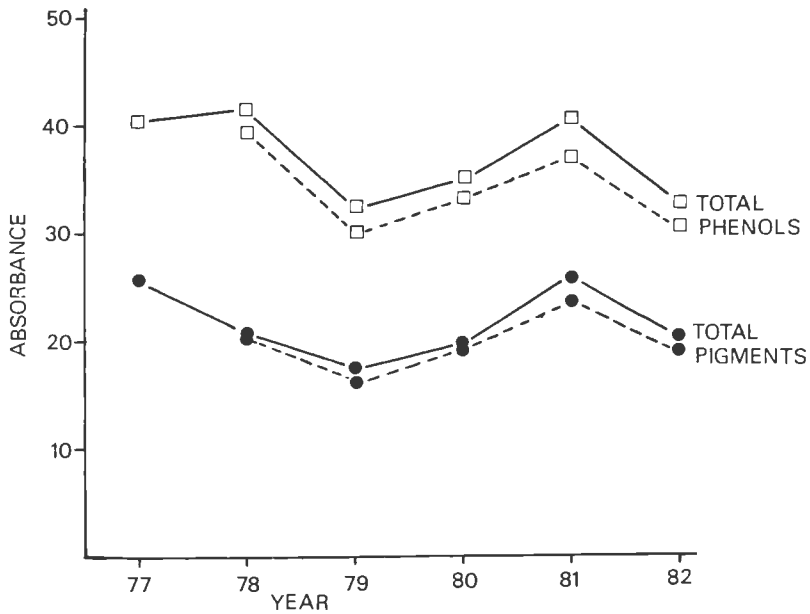

Fig. 3: Mean values of total pigments and total phenols of (i) 5 single cultivar ports (Touriga Nacional, Tinta Santarem, Tinta Barroca, Rufete and Mourisco, all from Tua) during 6 years (1977—82) and (ii) 9 single cultivar ports (those above plus Tinta Roriz, Tinta Cão, Tinta Francisca, all from Tua, and Tinta Barroca from Baixo Corgo) during 5 years (1978—82). Total pigments are expressed as A_{520nm} and total phenols as $A_{280nm} - 4$ measured in 1 M HCl at 10 mm path-length. —— = (i), – – – – = (ii).

Mittelwerte der Gesamtpigmente und Gesamtphenole (1) von 5 sortenreinen Portweinen (Touriga Nacional, Tinta Santarem, Tinta Barroca, Rufete und Mourisco, alle aus Tua) über 6 Jahre (1977—82); (2) von 9 sortenreinen Portweinen (obige Sorten sowie Tinta Roriz, Tinta Cão, Tinta Francisca, alle aus Tua, ferner Tinta Barroca aus Baixo Corgo) über 5 Jahre (1978—82). Die Gesamtpigmente sind als A_{520nm}, die Gesamtphenole als $A_{280nm} - 4$ für 10 mm Schichtdicke bei Messung in 1 M HCl angegeben. —— = (1), – – – – = (2).

Table 1

Summary of analyses of single cultivar grapes and young port wines during 1977—83 · Total pigments, $A_{\lambda max}$, colour density and total phenols are expressed in absorbance units for 10 mm pathlength

Zusammengefaßte Analysen von Beeren und sortenreinen jungen Portweinen der Jahrgänge 1977—83 · Gesamtpigmente, $A_{\lambda max}$, Farbintensität und Gesamtphenole sind in Absorptionseinheiten bei 10 mm Schichtdicke angegeben

Cultivar	Site[1])	No. of years	Grape SG	Ports						
				Total pigments	$A_{\lambda max}$	Colour density	Tint	Total phenols	Ratio pigments/ phenols	pH
				Absolute means						
Touriga Nacional	Tua	7	93.8±3.1[2])	37.0±2.1	7.64±0.69	11.59±0.94	0.530±0.035	52.4±2.4	0.425±0.021	3.81±0.051
				Relative means						
Souzão	Tua	2	0.94	1.65	2.91	2.68	0.77	1.40	1.20	2.17 (3.47)
Tinta da Barca	Tua	2	0.90	1.07	1.05	1.10	1.34	1.28	0.86	0.68 (3.97)
Touriga Nacional	Tua	7	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00 (3.81)
Touriga Francesa	SB	5	0.99	0.86	0.89	0.88	1.10	0.94	0.94	0.90 (3.86)
Touriga Nacional	V	3	1.04	0.88	0.85	0.90	1.20	0.99	0.88	0.69 (3.97)
Viera da Natividade	V	1	0.88	0.83	1.11	1.07	0.91	1.05	0.79	1.82 (3.55)
Malvesia Preta	SB	4	1.07	0.83	1.07	1.04	0.97	0.85	0.96	1.88 (3.54)
Tinta Santarem	Tua	6	0.87	0.75	0.90	0.88	0.94	0.76	1.00	1.94 (3.53)
Touriga Francesa	BC	4	0.93	0.74	0.80	0.79	0.95	0.75	0.99	1.50 (3.63)
Tinta Amarela	Tua	4	0.98	0.70	0.67	0.67	1.02	0.63	1.14	1.21 (3.73)
Tinta Roriz	Tua	6	0.94	0.62	0.53	0.57	1.21	0.76	0.81	0.66 (3.99)
Tinta Barroca	Tua	7	1.05	0.62	0.63	0.66	1.11	0.80	0.78	1.11 (3.76)
Tinta Amarela	BC	4	0.95	0.61	0.67	0.66	0.94	0.55	1.13	1.75 (3.57)
Cornifesto	P	2	0.94	0.59	0.57	0.60	1.14	0.79	0.77	1.22 (3.72)
Touriga Nacional	P	2	0.83	0.58	0.57	0.60	1.21	0.79	0.75	0.89 (3.86)
Tinta Francisca	SB	3	0.95	0.55	0.48	0.55	1.39	0.71	0.80	0.49 (4.12)
Tinta Francisca	BC	1	0.80	0.53	0.50	0.47	0.86	0.49	1.08	1.91 (3.53)
Tinta Francisca	Tua	5	0.96	0.52	0.49	0.52	1.11	0.61	0.88	0.99 (3.81)
Tinto Cão	Tua	6	0.93	0.50	0.42	0.44	0.91	0.48	1.06	1.37 (3.67)
Donzelinho	Tua	2	1.02	0.49	0.51	0.48	1.12	0.60	0.81	1.52 (3.63)
Tinta Barroca	BC	6	0.88	0.49	0.42	0.42	1.01	0.56	0.89	1.27 (3.71)
Rufete	Tua	6	0.98	0.43	0.46	0.49	1.19	0.59	0.73	1.21 (3.73)
Tinto Cão	BC	1	0.85	0.35	0.22	0.23	1.14	0.37	0.96	0.96 (3.83)
Mourisco	Tua	6	1.06	0.30	0.36	0.37	1.24	0.43	0.69	1.31 (3.69)
Standard deviation for relative means			0.09	0.13	0.18	0.17	0.14	0.15	0.10	0.42

[1]) Abbreviations: SB = Santa Barbara, V = Vilariça, BC = Baixo Corgo, P = Pinhão.

[2]) To calculate the mean and standard deviation of the SG's, 1.000 was substracted and the remainder multiplied by 1000, e.g. mean SG of Touriga Nacional was 1.0938.

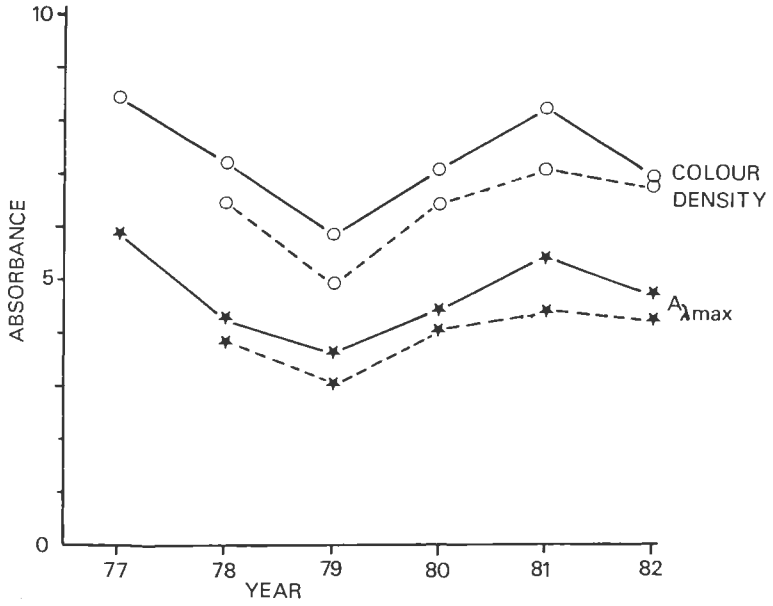

Fig. 4: Mean values of colour densities and $A_{\lambda max}$ of (i) 5 single cultivar ports during 6 years (1977—82) and (ii) 9 single cultivar ports during 5 years (1978—82). Cultivars as in Fig. 3. Values are expressed for 10 mm path-length, derived from measurements at 1 mm path-length. —— = (i), – – – – = (ii).

Mittelwerte von Farbintensität und $A_{\lambda max}$ (1) von 5 sortenreinen Portweinen über 6 Jahre (1977—82) und (2) 9 sortenreinen Portweinen über 5 Jahre (1978—82). Sorten wie in Fig. 3. Die Werte sind für 10 mm Schichtdicke angegeben; gemessen wurde bei 1 mm Schichtdicke. —— = (1), – – – – = (2).

and μ_2) in a given column are significantly different can be tested by calculating their standard error of difference (SED) from the following equation: $SED = s\,(1/n_1 + 1/n_2)^{1/2}$, where s is the standard deviation and n_1 and n_2 are the number of years that the cultivars were examined. Using this SED, a t-test can then be used to test for a significant difference between these means (65 df).

Also given in Table 1 is the mean port pH value of Touriga Nacional together with the relative means for port hydrogen ion concentrations compared with Touriga Nacional (1.00). Since pH is a logarithmic function, it was necessary to convert pH to H^+ concentration to calculate mean values. The logarithm of a relative value gives the equivalent difference in pH for that cultivar compared with Touriga Nacional (Tua), since $\log_{10}(H_1^+/H_2^+) = -pH_1 + pH_2$. A ratio greater than 1 implies a pH less than Touriga Nacional (Tua) and vice-versa. For clarity, mean pH values calculated in this way are given in brackets following each ratio, but the ratios should be used to test for significance.

Variation of analytical parameters

Grape specific gravity and grape and port pH

The specific gravity of the grape must varied from year to year and from cultivar to cultivar. The sweetest grapes were Malvesia Preta, Mourisco and Tinta Barroca (Tua)

and the least sweet were Tinto Cão and Tinta Barroca (Baixo Corgo) and Tinta Santarem (Tua). Malvesia Preta (SG 1.075—1.119) and Tinta Roriz (SG 1.071—1.101) showed wide ranges while other cultivars varied over a much narrower range e.g. Mourisco (SG 1.093—1.100), Tinto Cão (Tua; SG 1.085—1.094) and Tinta Barroca (Baixo Corgo; SG 1.076—1.085). Likewise cultivars varied in grape pH values, those of lowest pH being Tinta Francisca (Baixo Corgo; 3.27), Tinta Amarela (Baixo Corgo; 3.31) and Tinto Cão (Tua; 3.33) and those of highest pH being Tinta Francisca (Santa Barbara; 3.80), Touriga Nacional (Vilariça; 3.65) and Tinta Roriz (Tua; 3.61). The largest pH variations occurred in Mourisco (3.30—3.92) and Tinta Barroca (Tua, 3.30—3.90) and the least variation in Tinta Amarela (Tua; 3.59—3.68). Port pH correlated significantly with grape pH ($P < 0.01$) and was always higher, the mean difference being 0.29 ± 0.10. Ports of lowest pH were Tinta Francisca (Baixo Corgo; 3.53), Tinta Santarem (3.53), Malvesia Preta (3.54) and Viera da Natividade (3.55) and of highest pH Tinta Francisca (Santa Barbara; 4.12), Tinta Roriz (3.99) and Tinta da Barca (3.97).

Although the correlation between grape SG and pH was significant (0.634, $P < 0.05$), this was due to the large number of degrees of freedom (93) and no obvious relationship was evident when values were plotted graphically. Cultivars examined for at least 5 years showed significant correlations ($P < 0.05$) between SG and grape or port pH in only two cultivars (Tinto Cão and Mourisco). Of the Tua cultivars only Tinta Santarem was significantly different from Touriga Nacional; its grapes were less sweet ($P < 0.01$) and its port was of lower pH ($P < 0.001$). Malvesia Preta, Tinta Amarela (Baixo Corgo) and Souzão all had lower pH values ($P < 0.01$) than Touriga Nacional (Tua), but no significant differences in grape pH or SG values. Comparing sites, Tinta Barroca (Baixo Corgo) must was significantly less sweet ($P < 0.01$) than Tinta Barroca (Tua) but showed no significant pH differences. Touriga Nacional (Pinhão) must was less sweet ($P < 0.05$) than Touriga Nacional (Tua and Vilariça). The grapes of Tinta Amarela (Baixo Corgo) had lower pH values ($P < 0.05$) than this cultivar grown at Tua. The port of Touriga Francesa (Baixo Corgo) was of lower pH ($P < 0.05$) than Touriga Francesa (Santa Barbara) and the pH of Tinta Francisca port was lower in Baixo Corgo than in Santa Barbara ($P < 0.01$).

Total pigments

Port pigment contents varied nearly 12-fold from 6.5 (Mourisco, Tua, 1979) to 77.1 (Souzão, Tua, 1983). Souzão was exceptional in containing 1 ½ times the total pigments of Tinta da Barca (Tua), the next highest in pigment content. Souzão apart, the other ports ranged 8-fold from 6.5 to 50.7. Of these Tinta da Barca and Touriga Nacional (Tua) contained consistently large amounts, while Mourisco and Rufete contained consistently small amounts of pigments.

Tinta da Barca, Touriga Francesa (Santa Barbara), Touriga Nacional (Vilariça) and Viera da Natividade were not significantly different from Touriga Nacional (Tua) but all other cultivars were significantly different from the latter, most of them at $P < 0.001$. With only one exception (1980) ports made from Tinta Barroca grown at Tua contained more pigments than ports made from Tinta Barroca from Baixo Corgo, but overall the difference was not quite significant. The only significant difference between sites concerned Touriga Nacional (Pinhão) which contained less pigments ($P < 0.05$) than this cultivar grown at Tua or Vilariça.

It was of interest to ascertain the importance of cultivar compared with year on total pigments. Data were analysed (i) for 5 cultivars over 6 years and (ii), for 9 cultivars over 5 years. The percentages of the total variance which could be accounted for by cul-

tivar and year, respectively, were 81 % and 9 % for (i) and 66 % and 18 % for (ii), the remainder in each case being unaccounted for. Thus, variation due to cultivar was much greater (3.7—9 times) than that due to year.

Port pigment contents can be expressed as malvidin 3-glucoside chloride equivalents using the absorptivity value (a) of 28,000 (NIKETIC-ALEKSIC and HRAZDINA 1972); the range is then 123—1,457 mg l^{-1}. However, the ports contained not only anthocyanins but pigments resistant to the bleaching action of SO_2 and indicative of condensed or polymerised anthocyanins, despite being analysed as young as possible. The content of polymeric pigments was 2—24 %, mean 7 %, of the total pigments as estimated by the spectral method of SOMERS and EVANS (1977) and was even greater when measured by HPLC (BAKKER *et al.* 1985). Hence, it is preferable to express total pigments as absorbance values rather than in equivalents of malvidin 3-glucoside.

Total phenols

Total phenols in the ports varied from 18.0 (Mourisco, Tua, 1979) to 65.4 (Souzão, Tua, 1983). Using the conversion factor already discussed (Materials and methods), this corresponds to 741—2,139 mg l^{-1} of gallic acid, a range typical of red wines (SINGLETON and ESAU 1969). Although Souzão, Tinta da Barca and Touriga Nacional contained most total phenols (as for total pigments), the relative order of cultivars was not the same for total phenols as for total pigments. The ratio of total pigments to total phenols varied from 0.51 (Souzão) to 0.24 (Tinta Barroca, Tua); a decreasing ratio signifies an increasing proportion of colourless to coloured phenols.

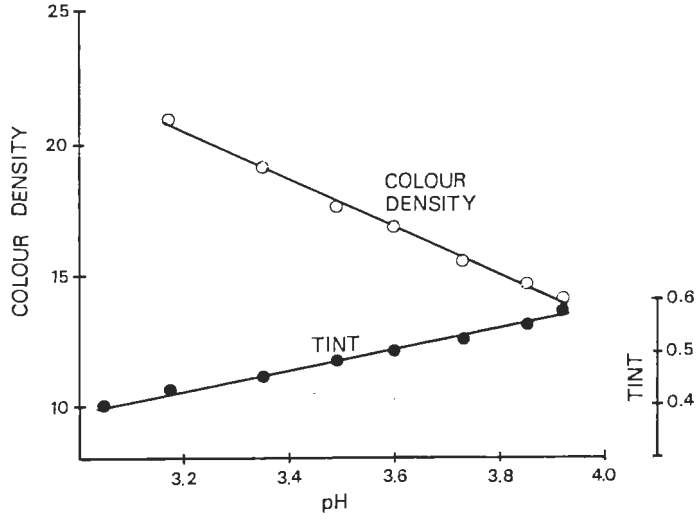

Fig. 5: The influence of pH on colour density (absorbance units) and tint in a young port (Touriga Nacional, 1981).

Der Einfluß des pH auf die Farbintensität (Absorptionseinheiten) und -tönung eines jungen Portweins (Touriga Nacional, 1981).

Colour

Souzão (1983) was the most highly coloured port examined; $A_{\lambda max}$ was 34.0 and colour density was 45.5 Mourisco and Tinto Cão (Baixo Corgo) were the least coloured. Although the order of $A_{\lambda max}$ and colour density generally followed that of total pigments, it was not identical. Differences in order appear largely due to pH differences. Notably Touriga Francesa (Santa Barbara), Touriga Nacional (Vilariça), Tinta Roriz and Tinto Cão (Baixo Corgo) had less colour than anticipated from their total pigment contents because of their high pH values. The colour density of Tinta Barroca (Tua) port although greater than Tinta Barroca (Baixo Corgo) port (except in 1980) was not quite significantly so. As with the total pigments, the only significant difference between sites concerned Touriga Nacional; the colour density of the port made from Pinhão fruit was significantly lower ($P < 0.05$) than from Tua fruit. Since Pinhão is considered a high quality port area, these differences are attributed to the particular strain (Canario) of Touriga Nacional grown at Pinhão.

Tint varied from 0.34 (Souzão, 1983) to 1.00 (Mourisco, 1979). The brownest ports were Tinta Francisca (Santa Barbara), Tinta da Barca and Mourisco, while the reddest ports were Souzão, Tinta Francisca (Baixo Corgo) and Viera da Natividade.

Influence of pH on colour density and tint

The influence of pH on colour characteristics was determined by adjusting the pH values of young ports within the range 3.0—4.0. Typically, colour density decreased linearly and tint values increased linearly with increasing pH (Fig. 5).

Interpretation of colour differences

The major factors affecting port colour are pigment content and pH; the greater the pigment content and the lower the pH, the greater the colour and vice-versa. However, previous work has shown that colour can be affected by additional subtle phenomena involving anthocyanins (TIMBERLAKE and BRIDLE 1983). These are a) self-association of anthocyanins, in which colour increases more than linearly with increasing anthocyanin concentration and b) co-pigmentation of anthocyanins with other components, notably colourless phenols, resulting also in colour augmentation. Mechanisms a) and b) occur simultaneously to extents depending upon actual and relative contents

Table 2

The effect of co-pigmentation on port colour (α values) · Total pigments is expressed in absorbance units for 10 mm path-length

Der Einfluß der Co-Pigmentierung auf die Portweinfärbung (α-Werte) · Die Gesamtpigmente sind in Absorptionseinheiten bei 10 mm Schichtdicke angegeben

Year	Cultivar	Total pigments	Ratio pigments/ phenols	$\alpha_{3.5}$ (%)
1981	Tinto Cão (Tua)	20.7	0.44	18.8
	Touriga Nacional (Pinhão)	21.0	0.36	23.8
1982	Tinto Cão (Tua)	14.4	0.41	27.1
	Rufete (Tua)	14.1	0.32	34.4

Table 3

The influence of site on port colour (α values)

Der Einfluß des Standortes auf die Portweinfärbung (α- Werte)

Year	Cultivar	Site	$\alpha_{3.5}$ (%)
1981	Tinta Barroca	Tua	27.1
	Tinta Barroca	Baixo Corgo	20.7
1982	Tinta Barroca	Tua	35.1
	Tinta Barroca	Baixo Corgo	28.1
1983	Tinto Cão	Tua	26.1
	Tinto Cão	Baixo Corgo	20.1

of anthocyanins and co-pigments. Self-association predominates at high anthocyanin concentrations and co-pigmentation at high ratios of co-pigment to anthocyanin. Since the variable effect of pH must be eliminated in order to reveal the extent of operation of these mechanisms in ports, colours were measured at pH adjusted to a suitable constant value of 3.50. The percentage ratio of port pigments colour (at λ_{max}) at pH 3.50 to the total pigments colour in 1 M HCl was then designated $\alpha_{3.5}$, by analogy with similar ratios for monomeric anthocyanins (SOMERS and EVANS 1977; JACKSON *et al.* 1978). For many ports differences in colour (at constant pH 3.50) could then be interpreted from values of $\alpha_{3.5}$, total pigments content and the ratio of total pigments to total phenols.

The influence of self-association was shown by comparing ports with similar pigments/phenols ratios i.e. similarly co-pigmented. Thus, in 1982 Souzão (Tua) and Malvesia Preta (Santa Barbara) had similar pigments/phenols ratios (0.51 and 0.49, respectively), but Souzão (52.5) had a greater pigments content than Malvesia Preta (29.5). The greater $\alpha_{3.5}$ value of Souzão (34.5 %) compared with Malvesia Preta (31 %) reflects an increased colour over and above that expected in proportion to its increased pigments content and indicates increased self-association. Likewise in 1983 Tinto Cão (Baixo Corgo) and Touriga Nacional (Tua) had similar pigments/phenols ratios (0.51 and 0.54, respectively), but contained widely different pigment contents viz. 17.1 (Tinto Cão) and 48.3 (Touriga Nacional). The much higher $\alpha_{3.5}$ value of Touriga Nacional (33.8 %) compared with Tinto Cão (20.1 %) reflects increased anthocyanin self-association in the Touriga Nacional port. Colour augmentation is evident also in these ports at their natural pH values, since they were very similar (3.73 and 3.75, respectively); thus, Touriga Nacional had 2.8 times the pigments content of Tinto Cão, but exhibited 4.5 times its colour ($A_{\lambda max}$) (Table 1).

In contrast, when port pigment contents are similar, those ports more coloured at pH 3.5 (higher $\alpha_{3.5}$ values) usually contained the larger excess of phenols over pigments (lower ratio pigments/phenols). Two pairs which illustrate this effect, attributable to co-pigmentation, are shown in Table 2.

Differences between pairs of ports were not always explicable in this way, probably because the ports contained not only monomeric anthocyanins but also some oligomeric or polymeric pigments of uncertain behaviour.

Considerations of $\alpha_{3.5}$ are also useful in amplifying differences between sites (Table 3). These observations provide a possible explanation of the inferior status of Baixo Corgo fruit; excepting Tinta Francisca, their pigments are not only lower in amount (Table 1) but are also less coloured.

Summary

95 port wines were made under standard small scale conditions from grapes of 16 individual cultivars grown at 5 different sites in the Douro valley in northern Portugal during 1977—1983. Grape specific gravity and pH values were measured. The ports were analysed immediately after fortification for colour, pigment and phenol contents and pH. Cultivar variations were up to 12-fold in total pigments, 14-fold in colour density, but only 3.6-fold in total phenols. Seasonal variations were up to 2-fold in total pigments and colour density and 1.6-fold in total phenols. Because of seasonal effects and variation in the numbers of each cultivar examined, cultivar characteristics were compared by their mean values with reference to an arbitrarily chosen standard cultivar (Touriga Nacional). Statistical analysis confirmed that the variation in total pigments was affected much more by cultivar than by season.

Souzão, Tinta da Barca and Touriga Nacional ports (all from Tua) were the most coloured and contained most pigments. Mourisco (Tua) and Tinta Cão (Baixo Corgo) were the least coloured and contained least pigments. Port colour was dependent principally on pigments content and pH, but small effects attributed to anthocyanin self-association and co-pigmentation were also discerned. Differences between sites were generally not significant, apart from some characteristics of Touriga Nacional from Pinhão compared with Tua and Vilariça, which were attributed to the particular strain of fruit at Pinhão. Nevertheless, there was some indication that the inferior status of Baixo Corgo compared with Cima Corgo fruit may be attributed not only to its generally lower pigments content, but also to smaller percentages of the pigments being expressed in coloured forms.

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