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Bentonite and Gelatine Impact on the Young Red Wine Coloured Matter

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Summary

This paper deals with the impact of two fining agents (bentonite and gelatine) on the coloured matters of young red wines Vranac, Pinot Noir and Gamay Noir. Both agents caused decrease in these substances. The effect is more intensive with the dose of bentonite of 1 g/L, but the variability depends on variety. Higher decrease was found in the colour intensity, coloured anthocyanins and polymers (up to 44 %), but lower in the colourless anthocyanins (up to 20 %). The intensity of red and blue colours decreases, while that of yellow colour increases. The use of bentonite in dosages higher than those recommended may cause the wine to obtain more pronounced »brick red« colour (the colour tint increases while the value of the spectrum form decreases). Fewer changes occurred in the coloured matters after treating the wine with gelatine. The colour intensity, colourless and coloured anthocyanins showed a decrease of up to 10 % and polymers of up to 16 %. The intensity of yellow colour decreases, while that of red increases as well as the $\Delta A/\%$ value.

Key words: red wine, wine colour, anthocyanins, fining, bentonite, gelatine

Introduction

In the practice of producing red wines it is of great importance to obtain good colour and clearness of wines and to possibly keep them for a prolonged period of time. Stabilisation of red wines provides, first of all, stability of colour and clearness. Preparation of wines for the market should be relatively quick, *i.e.* quicker than achieving approximately the same effect by spontaneous fining. Not only turbid wines are fined, but also those inclined to turbidity and precipitation. Agents of different origin are used for fining, but they must not affect or cause such changes of the chemical composition that would negatively affect the wine quality. They should only remove the components that make wine unstable (*1*).

For fining of red wines (*2*) the following agents are recommended: bentonite, gelatine, albumin and casein, as well as dosages to be applied. The most frequent use is that of gelatine and bentonite. Some enochemical characteristics of these agents are well known, but we are not fully familiarised with their effects on the phenolic matters in wines except on some conventional parameters such as colour intensity and tint, quantity of free anthocyanins and tanning substances (*3*).

For the purpose of better explanation of the effects of bentonite and gelatine usage on red wine coloured matters, we have studied fining of wines made from the cultivars Vranac, Pinot Noir and Gamay Noir.

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Materials and Methods

Grapes

The experiments were carried on the young wines made from the cultivars Vranac (native cultivar originated from Montenegro), Pinot Noir and Gamay Noir, produced in 2001 at the Centre for Viticulture and Winemaking in Niš. Fining of these wines was carried out during April 2002, using bentonite-sodium montmorillonite clay called »Clarol«, manufactured by the Agricultural and Industrial Combine »Aleksinac« based in Aleksinac and Gelatine Animale 80 B1 manufactured by »Italo-gelatine s.p.a.« based in Italy, according to Food Chemicals Codex.

Use of bentonite and gelatine

The following experiment was set up: T_0 – control, T_1 – bentonite (0.3 g/L), T_2 – bentonite (0.6 g/L), T_3 – bentonite (1.0 g/L), T_4 – gelatine (0.05 g/L), and T_5 – gelatine (0.1 g/L). For each variant, 200 mL of wine were used. Variants T_1, T_2 and T_3 were treated with 2 mL of the bentonite suspension and variants T_4 and T_5 were treated with the gelatine solution. After 8 days the wines were separated from the precipitation and analysed.

Analyses

The pH was measured with a pH-meter (Hanna Instruments), standardised to pH=4.0 and 7.0 with standard buffer solutions. The iodometric determination of free sulphur dioxide was done by titration in acid solution according to Ripper, as cited in Daničić (*4*).

Anthocyanins, colour intensity, tint and spectrum form

Content of free, coloured (flavilium cation and quinodal base) and colourless anthocyanins (carbinol pseudo-base and bisulphite compound) and polymers was determined after the addition of excess of SO_2 and at pH=1 by measuring absorbance of the wine at 520 nm, according to Sommers and Evans method (*5*).

Colour intensity (I) and tint (T) according to the official method OIV (*6*) are:

$$I = A_{420} + A_{520} + A_{620}$$

$$T = A_{420} / A_{520}$$

Intensity of yellow (A_{420}/%), red (A_{520}/%) and blue (A_{620}/%) colours as well as the spectrum form (ΔA/%) according to Glories (*7*) are:

$$A_{420}/\% = (A_{420}/I)\cdot 100 \quad A_{520}/\% = (A_{520}/I)\cdot 100$$

$$A_{620}/\% = (A_{620}/I)\cdot 100$$

$$\Delta A = (1-(A_{420} + A_{620})/2\cdot A_{520})\cdot 100$$

Total phenols

Total phenols were determined by a spectroscopic method using Folin-Ciocalteu reagent and sodium carbonate, method OIV (*6*) and the measurement of absorbance at 280 nm (A_{280}) of the wine samples diluted at the ratio of 1:50, according to Ribereau-Gayon method (*8*).

HPLC analysis

For the purpose of high quality determination of certain anthocyanins, chromatographic separation was done on the Hewlett-Packard High Pressure Liquid Chromatography (HPLC) equipment, type HP 1100, according to the method of Eder *et al.* (*9*). The detection of separated anthocyanins was carried out by means of the Pye Unicam UV-VIS detector. The separation of anthocyanins was done on chromatographic column by reverse phase using Licrospher type 100 RP 18 with 5-μm particles. Solvents used for separation were as follows: A – 5 mM phosphate buffer, pH=1.8 and B – methanol with the addition of HCl.

Standard substances used were: cyanidine-3-glucoside (Cn 3-G), delphinidine-3-glucoside (Dp 3-G), peonidine-3-glucoside (Pn 3-G), petunidine-3-glucoside (Pt 3-G) and malvidine-3-glucoside (Mv 3-G). Based on the retention times anthocyanins were determined individually.

Results and Discussion

Some relevant analytical parameters of the control wines are given in Table 1, where it can be seen that wines differ in many analytical parameters such as: colour intensity and tint, total phenolic matters, content of free, coloured and colourless forms of anthocyanins.

From Table 2 it can be seen that the treatments with bentonite resulted in a considerable decrease in colour intensity, which is particularly distinct with a dosage of 1 g/L of bentonite. The highest decrease in colour intensity was that of the wine made from Vranac (from 18 to 36 %), and the lowest was that in the wine made from Pinot Noir (from 11.2 to 27.4 %). The intensity of yellow colour increases and that of red and blue colours decreases. The colour tint increases, while the values for determining the spectrum form decrease, which points to a mild »brick red« colour of the wine that is more distinctly expressed by a higher dosage of bentonite. Treatments with gelatine had lower impact on the colour intensity, which decreased for about 10 % in all the wines studied, except in the wine made from Vranac, where the impact of gelatine was the lowest (decrease to

Table 1. Some relevant analytical parameters in the control wines

Parameter	Cultivar		
	Vranac	Pinot Noir	Gamay Noir
Colour intensity	0.717	0.465	0.507
Tint	0.469	0.628	0.499
γ(free anthocyanins)/(mg/L)	276.5	166.2	218.6
γ(coloured anthocyanins)/(mg/L)	49.7	27.8	39.0
γ(colourless anthocyanins)/(mg/L)	226.8	138.4	178.7
Total phenols (IFC)	34.5	25.5	27.9
Total phenols (A_{280})	29.7	24.2	26.3
pH	3.05	3.22	3.18
γ(free SO_2)/(mg/L)	15.4	14.3	14.8

Table 2. Impact of agents used for fining red wines on the changes of some parameters of colour

Colour parameters	Treatments					
	T_0	T_1	T_2	T_3	T_4	T_5
			Vranac			
Colour intensity	0.717	0.588	0.521	0.459	0.695	0.662
Tint	0.469	0.506	0.516	0.526	0.476	0.461
A_{420}/%	30.0	31.6	32.1	32.5	30.0	29.7
A_{520}/%	63.9	62.4	62.2	61.8	63.7	64.4
A_{620}/%	6.1	6.0	5.7	5.7	6.0	5.9
ΔA/%	71.80	69.87	69.62	69.13	71.67	72.36
			Pinot Noir			
Colour intensity	0.465	0.413	0.378	0.338	0.431	0.415
Tint	0.628	0.666	0.684	0.698	0.618	0.606
A_{420}/%	35.5	36.8	37.5	38.0	35.2	34.9
A_{520}/%	56.5	55.2	54.7	54.4	57.0	57.5
A_{620}/%	8.0	8.0	7.8	7.6	7.8	7.6
ΔA/%	61.51	59.45	58.61	58.04	62.22	63.10
			Gamay Noir			
Colour intensity	0.507	0.432	0.389	0.355	0.475	0.453
Tint	0.499	0.509	0.521	0.533	0.490	0.484
A_{420}/%	31.0	31.5	32.0	32.5	30.7	30.5
A_{520}/%	62.1	61.8	61.4	60.9	62.6	62.9
A_{620}/%	6.9	6.7	6.6	6.6	6.7	6.6
ΔA/%	69.41	69.09	68.58	67.97	70.18	70.54

7.7 %). Fining the wines by means of this agent resulted in the removal of yellow colour, increasing at the same time the intensity of red colour, which caused the colour tint to decrease for about 3 % in the variant with the higher dosage of gelatine, while the values for the spectrum form increased.

The impact of agents and dosages applied for fining on the changes in phenolic composition in the wines made from Vranac, Pinot Noir and Gamay Noir are given in Figs. 1–3. From these graphs it can be seen that the bentonite treatments resulted in considerable decrease in polymers (from 14.7 to 37.8 %) and coloured anthocyanins (from about 20 to 44.4 %), while the decrease in colourless anthocyanins was from 10 to 21 %. Higher decrease in these components was in the wine made from Vranac, which is correlated with higher decrease in colour intensity. Considerable losses in these components were found after treating the wines with gelatine. Decrease in free, colourless and coloured forms of anthocyanins ranged from 2 to 10 %, while that of polymers ranged from 6 to 16 %.

Based on these studies it can be observed that the treatments of fining red wines resulted in the variation of colour parameters. The highest decrease was obtained in colour intensity, polymers and coloured forms of free anthocyanins, while lower decrease was that of the colourless anthocyanins. Higher decrease occurred with bentonite, where the colour tint increased after the treatment and so did the intensity of yellow colour. Treatment of wines with gelatine resulted in lower decrease of phenolic substances (IFC), except in the case of index A_{280}.

Gelatine, compared to other fining agents, both removes anthocyanins and provides their stability to a lesser degree during further storage of the wines (*10*).

Revilla *et al.* (*3*) studied the effect of sodium bentonite, sodium montmorillonite and hectorite in dosages of 0.5 and 1 g/L on the phenolic composition of eight young wines. The greatest changes were caused by sodium bentonite and sodium montmorillonite in dosages of 1 g/L. The decrease in catechin, proanthocyanidols and free anthocyanins was high (in certain wines even over 60 %).

Bentonite proved to be an important agent intended to remove colloidal coloured matters constituted of flavilium cations (ionised anthocyanins), tanning agents, polysaccharides and proteins. Therefore, the loss in colour is not irrelevant. Bentonite is added to eliminate unstable complexes and to stabilise wines, which remain stable at low temperatures and do not change over a period of several months (*8*).

Our results for the wine made from Pinot Noir are not in agreement with the results reported by Radić and Puškaš (*11*), which showed high decrease in colour intensity and free anthocyanins when gelatine was used in a dosage of 4 g/hL (even to 74.1 %), while these parameters were less affected by bentonite.

A proportional presence of some anthocyanins in wines is given in Table 3. Thus, the amount of Dp 3-G, Cn 3-G and acylated anthocyanins decreased in the Vranac accompanied by the increase in the amount of Pt 3-G, Pn 3-G and Mv 3-G. Dp 3-G and Pt 3-G decreased in the wine made from Pinot Noir and the amount of Pn 3-G and Mv 3-G increased, while the share of Dp 3-G, Pt

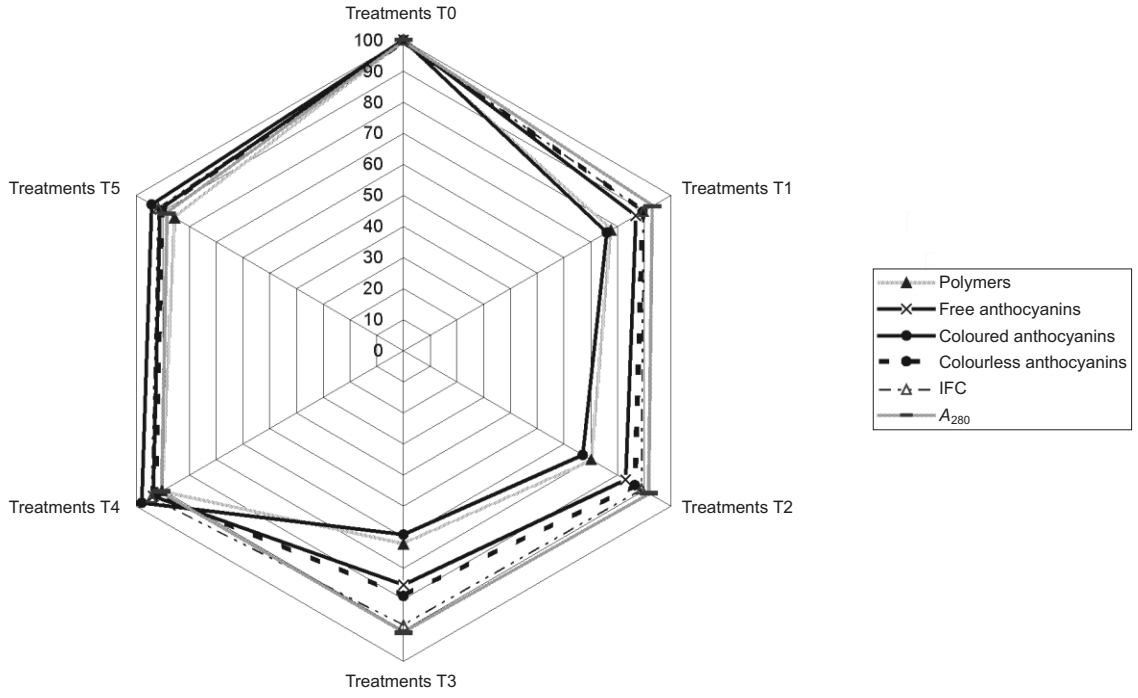

Fig. 1. Impact of fining agents on the changes of phenolic composition in Vranac

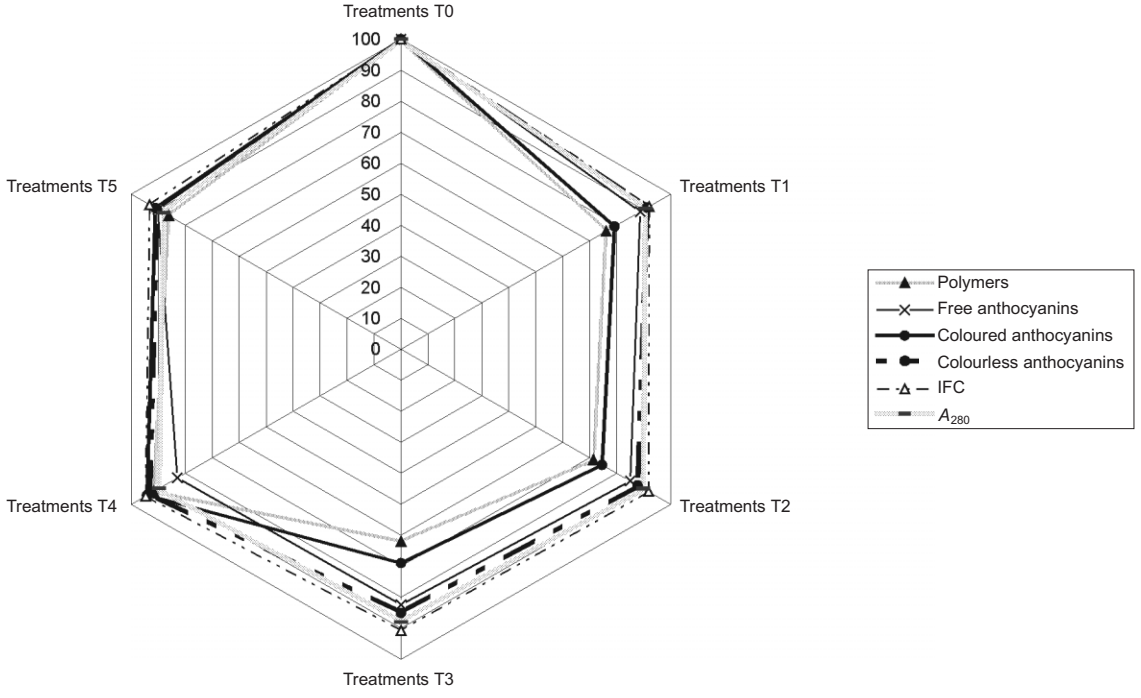

Fig. 2. Impact of fining agents on the changes of phenolic composition in Pinot Noir

3-G and acylated anthocyanins decreased in Gamay Noir and that of Pn 3-G and Mv 3-G increased.

The most stable anthocyanins are those containing methoxy groups (Mv 3-G, Pn 3-G and Pt 3-G), while acylated anthocyanins are unstable. According to McCloskey and Yengoyan (*12*) acylated monoglucoside pigments degrade faster than the other monoglucosides in wine.

Conclusions

Based on the obtained results it can be concluded that the use of agents intended for fining young red wines caused the decrease in the content of phenolic compounds, but the quantitative effect varied depending on the type of agents, dosage applied, nature of different groups of phenolic substances and characteristics of each wine.

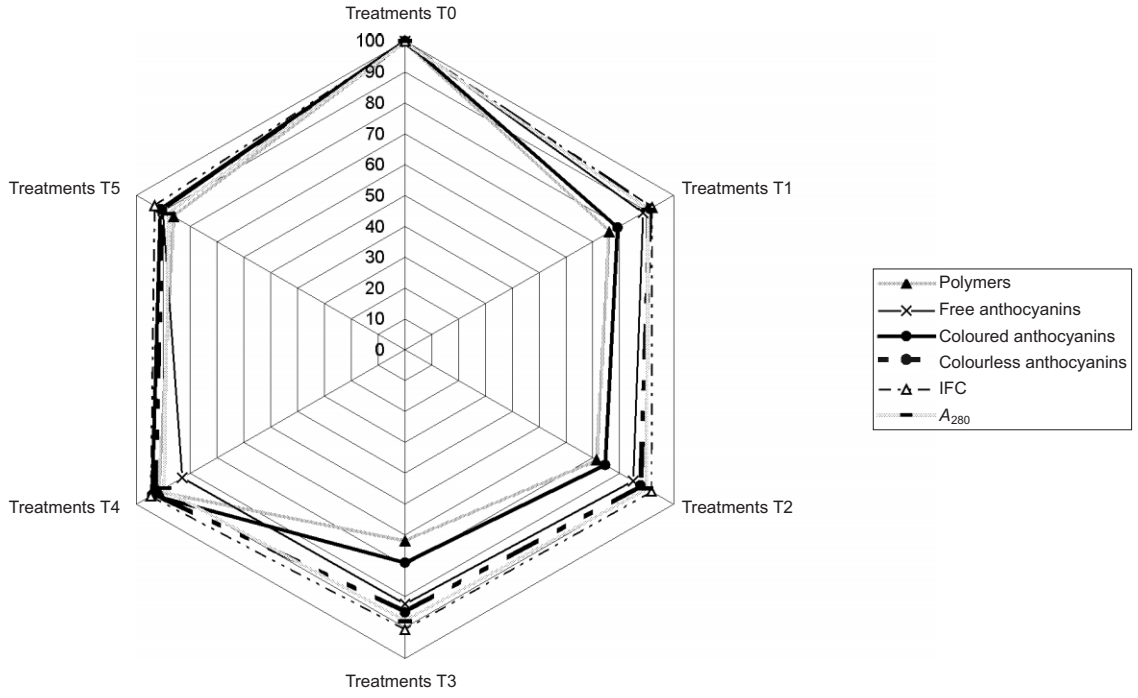

Fig. 3. Impact of fining agents on the changes of phenolic composition in Gamay Noir

Table 3. Impact of fining of red wines on the proportional presence of certain anthocyanins

Wine	Variant	*w*(anthocyanins)/%					
		Dp 3-G	Cn 3-G	Pt 3-G	Pn 3-G	Mv 3-G	Total acylated anthocyanins
Vranac	T_0	6.8	2.5	11.6	18.2	46.1	14.8
	T_1	6.1	2.4	11.6	18.2	47.5	14.0
	T_2	5.8	2.2	11.8	18.6	47.9	13.7
	T_3	5.3	2.2	11.8	18.6	48.5	13.6
	T_4	6.5	2.6	11.6	18.1	46.8	14.4
	T_5	6.2	2.4	11.5	18.3	47.4	14.2
Pinot Noir	T_0	5.5	0	8.6	21.0	64.9	0
	T_1	4.8	0	8.0	21.2	66.0	0
	T_2	4.1	0	7.6	21.6	66.7	0
	T_3	3.6	0	7.0	21.7	67.7	0
	T_4	5.4	0	8.5	21.0	65.1	0
	T_5	5.0	0	8.3	21.2	65.5	0
Gamay Noir	T_0	4.2	0	7.6	15.8	60.9	11.5
	T_1	4.1	0	7.7	16.0	62.1	10.1
	T_2	3.6	0	7.3	16.4	63.4	9.3
	T_3	3.2	0	7.0	16.6	64.4	8.8
	T_4	4.2	0	7.4	15.9	61.5	11.0
	T_5	3.9	0	7.3	16.1	62.0	10.7

Greater changes in the colours of wines were caused by bentonite, which is particularly evident in the treatment with 1 g/L. Higher decrease was that in the wine colour, polymers and ionised anthocyanins (up to 45 %) and lower in the colourless anthocyanins (up to 20 %). Higher decrease in anthocyanins as well as that in the colour intensity was seen in the wine made from Vranac. The intensity of red and blue colours decreases and that of yellow colour increases, which affects the increase in colour tint. Bentonite, used in dosages higher than those recommended may cause the wine to obtain more pronounced »brick red« colour (ΔA/% decrease). The wine fined by means of bentonite showed a decrease of Cn 3-G and Dp 3-G, as well as of acylated anthocyanins (less stable antocyanins), while the amount of Mv 3-G partly increased.

Fewer changes occurred in the phenolic composition after treating red wines with gelatine. The colour intensity, free, colourless and coloured anthocyanins decrease for about 10 % and polymers for 16 %. In contrast, gelatine decreases the intensity of yellow colour and increases the intensity of red colour, which affects the decrease in the tint and increase in the spectrum form value.

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Utjecaj bentonita i želatine na bojene sastojke mladoga crvenog vina

Sažetak

U ovom je radu ispitivan utjecaj dvaju sredstava za bistrenje (bentonita i želatine) na bojene sastojke mladih crvenih vina Vranac, Burgundac crni i Game crni. Oba su sredstva utjecala na smanjenje tih tvari. Učinak je intenzivniji s primjenom bentonita u količini od 1 g/L, ali je različit od vina do vina. Najviše je smanjen intenzitet boje u obojenim spojevima antocijanina i polimerima (do 44 %), a manje u bezbojnim antocijaninima (do 20 %). Smanjuje se intenzitet crvene i plave, a povećava udjel žute boje. Uporaba bentonita više od preporučene doze može uzrokovati ciglasto-crvenu boju vina (povećava se nijansa boje, a smanjuje vrijednost veličine spektra). Manje promjene uočene su u bojenim sastojcima nakon obrade vina želatinom. Intenzitet boje, bezbojni i obojeni antocijani smanjili su se do 10 %, a polimeri do 16 %. Smanjuje se intenzitet žute boje, a povećava udjel crvene, kao i vrijednosti razlika u postotku apsorbancije.