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# Study on Tămâioasă Românească Wine Composition Obtained Throught Different Prefermentative Treatments

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**Abstract.** In this study a number of seven prefermentative treatments were conducted in order to improve the compositional characteristics of certain wines obtained from Tămâioasă românească grape varieties. The samples were treated with: oxalic acid, lactic acid, succinic acid, ellagic tannins, bentonite, chitosan and oenological carbon. Folin-Ciocâlteu index showed that the use of pre-fermentative treatments decreased the amount of phenolic compounds from 410.38 mg/L to 202.17 mg/L.Major color and hue differences for Tămâioasă românească wines are found in the samples treated with oxalic acid and activated carbon. Metal content revealed that bentonite treatment contributed at increasing the amount of sodium in wines. Calcium content increased due prefermentative treatments application from 10.67 mg/L to 41.29 mg/L. Coper conent was under detection limit of 0.01 mg/L (SLD <0.01 mg/L).

**Keywords:** prefermentative treatments, Tămâioasă românească, wine, chitosan, oenological carbon

## INTRODUCTION

In order to obtain high quality wines, besides the grape processing technology, the treatments applied to the must before fermentation also have an important role in deciding the wine's quality (Cotea and Zănoagă, 2009). For this purpose many studies have been performed on the effect of the used enological practices and their influence on the wine's composition (Losada *et al.*, 2010; Puig-Deu *et al.*, 1996; Villanõ *et al.*, 2006). The increasing of acidity can be achieved by lactic acid, oxalic acid and succinic acid (***OIV, 2013, Ribéreau-Gayon and Glories, 2006; Jackson, 2008). Tannins are added to wines during the winemaking process for a number of reasons: to stabilize colour, to modify mouth-feel, to mask green characters, to increase polyphenolics and aromatic stability (Harbertson *et al.*, 2011; Parker *et al.*, 2007). Treating must with bentonite is recommended for wines which are to be clarified shortly after the completion of alcoholic fermentation (Ribéreau-Gayon and Dubourdieu, 2006). Chitosan treatment can be an effective method to clarify the must and to prevent protein haze (Rao *et al.*, 2010; Domingues *et al.*, 2011). Activated charcoal is use to to eliminate, possible contaminants, to correct the colour from white musts derived from the white juice of red grapes, from very yellow musts derived from white grape varieties and from oxidized musts (Ribéreau-Gayon and Glories, 2006).

## MATERIALS AND METHODS

Regents for pre-fermentative treatments: tannin (Taniblanc® - from AEB Spa, Italy), bentonite (Bentonita Clarit PLV 45 – Sodinal, România). Oxalic acid, lactic acid, succinic acid, chitosan and activated charcoal were purchased from Sigma-Aldrich, Germany.

Reagents for metal content. Stock solutions of each metal (sodium, potassium, calcium, iron, copper, zinc) were used, from Merck (Germany). Working standard solutions were obtained by suitable dilution from stock solution; for reagents preparation and for dilution bidistilled water was used. Cesium chloride and lanthanum chloride were purchased from Sigma-Aldrich, Germany.

Reagents for polyphenolic compounds determination. Folin-Ciocâlteu reagent, sodium carbonate and gallic acid were purchased from Sigma-Aldrich, Germany.

Grape samples and winemaking. Tămâioasă românească grapes were harvested from Cotnari vineyard (Romania) in 2012 at technical maturity and processed following the classical wine-making technique. The substances used were: oxalic acid - 0,6g/L (V1), lactic acid - 3g/L (V2), succinic acid - 2g/L (V3), tannin - 5g/L (V4), bentonite -100g/L (V5), chitosan - 100g/L (V6), activated carbon -100g/L (V7). After alcoholic fermentation, wines from Tămâioasă românească were filtered using a filtration-filling device-Tenco Enomatic® followed by sulphur dioxide addition (40 mg/L) to preserve wine from microbiological damage. Bottling was done with a semi-automatic device. After six months of storage the wines were analysed. Also, for each grape variety, a control sample (V) was obtained without prefermentative treatment.

After decarbonisation, the next parameters were analysed: sulfur dioxide (Iodometry) OIV-MA-AS323-04B,volatile acidity OIV-MA-AS313-02, total acidity OIV-MA-AS313-01, alcoholic strength by frequency oscillator OIV-MA-AS312-01A, reducing substances OIV-MA-AS311-01A, pH OIV-MA-AS313-15, total dry matter, and non-reducing substances OIV-MA-AS2-03B were done according to present standards (***OIV, 2013) and specific literature (Ribereau-Gayon *et al.*, 2006). The used analysis methods for compositional characteristics were: Folin-Ciocâlteu Index, CIE Lab 76. Metal content was determined by Shimadzu AA – 6300 Spectrophotometer.

Total content of phenolic compounds was determined by spectroscopic method Folin-Ciocâlteu by using a Spectrophotometer Analytik Jena S 200 at 765 nm. The results were expressed in mg gallic acid/L (Singleton&Rossi, 1965 modified by Waterhouse, 2001). Calibration curve equation was: $y=78.693 \cdot x-179.09$. Correlation coefficient (R) for calibration curve was 0.9761.

Evaluation of chromatic characteristics of wine. Analytik Jena S 200 spectrophotometer was used to determine the chromatic characteristics according to CIE Lab 76 (OIV, 2013). The CIELab76 colour or space system is based on a sequential or continuous Cartesian representation of 3 orthogonal axes: *L*, *a* and *b*. L is clarity, *a* is component of green/red colour and *b* is component of blue/yellow colour. The chromatic characteristics were calculated by equations:

$$L = 116(Y/Yn)^{1/3}-16$$
$$b = 200-[(Y/Yn)^{1/3}-(Z/Zn)^{1/3}$$
$$a = 500[(X/Xn)-(Y/Yn)]$$
$$C = (a^2+b^2)^{1/2}$$
$$H = tg^{-1}(b/a)$$
$$\Delta H = [(\Delta E)^2-(\Delta L)^2-(\Delta C)^2]^{1/2}$$
$$\Delta E = [(\Delta L)^2+(\Delta C)^2+(\Delta H)^2]^{1/2}$$

Metal content was determined by Shimadzu AA-6300 Spectrophotometer. Potassium and sodium were determined directly in diluted wine by atomic absorption spectrophotometry after the addition of cesium chloride to suppress ionization of potassium and sodium. For sample preparation, 2.5 mL of wine were pipetted (previously diluted 1/10) into a 50 mL volumetric flask, and then 1 mL cesium chloride solution was added. The volumetric flask was filled up to the mark with distilled water. The used atomic absorption spectrophotometer

was equipped with an air-acetylene burner and potassium and sodium hollow cathode lamps. The absorbance wavelength was set to 769.9 nm for potassium determination and 589 nm for sodium determination (Method OIV-MA-AS322-02A-Potassium, Method OIV-MA-AS322-03A-Sodium). Calibration curve equation for sodium was Abs = 0.242772 × Conc. + 0.0044680 with r = 0.9986, and for potassium Abs. = 0.080540 × Conc. + 0.041700, r = 0.9902.

Calcium was determined directly on diluted wine by atomic absorption spectrophotometry after the addition of an ionization suppression agent. For this determination atomic absorption spectrophotometer was fitted with an air-acetylene burner and calcium hollow cathode lamp. For sample preparation 1 mL of wine and 2 mL lanthanum chloride solution were placed in a 20 mL volumetric flask and filled up to the mark with distilled water. The absorbance wavelength was set to 422.7 nm. Calibration curve equation was Abs. = 0.024900 × Conc. + 0.0093200, r = 0.9997 (Method OIV-MA-AS322-04-Calcium).

Iron was determined after suitable dilution of the wine and removal of alcohol directly by atomic absorption spectrophotometry. For this, atomic absorption spectrophotometer was equipped with an air-acetylene burner and iron hollow cathode lamp. The absorption wavelength was set to 248.3 nm. Calibration curve equation was Abs. = 0.0022540 × Conc. – 0.0026000, r = 0.9884 (Method OIV-MA-AS322-05A-Iron). For copper determination, the atomic absorption spectrophotometer was equipped with an air-acetylene burner and copper hollow cathode lamp. In a 100 mL volumetric flask were placed 20 mL of wine and then filled up to the mark with distilled water. Absorbance was measured at 324.8 nm (Method OIV-MA-AS322-06-Copper). Zinc was determined directly in the wine by atomic absorption spectrophotometry at 213.9 nm after removal of alcohol. The atomic absorption spectrophotometer was equipped with an air-acetylene burner and zinc hollow cathode lamp. Calibration curve equation was Abs. = 0.23122 × Conc. + 0.011520, r = 0.9984 (Method OIV-MA-AS322-08-Zinc). In all cases, analyses were performed in triplicate, and a mean value was calculated.

## RESULTS AND DISCUSSIONS

The volatile acidity of Tămâioasă românească wines ranged between 0.19 g/L in the control sample, lactic acid and bentonite treatments and 0.27 g/L in chitosan sample, the treatments with lactic and succinic acid having a positive influence on the total acidity.

Tab 1.

Quality parameters of wines obtained through different prefermentative treatments

| No. | pH | Free $SO_2$ (mg/L) | Total $SO_2$ (mg/L) | Volatile acidity (g acetic acid/L) | Total acidity (g tartaric acid/L) | Alcohol (% vol.) | Reductive substances (g/L) | Total dry extract (g/L) | Non reductive extract (g/L |
|---|---|---|---|---|---|---|---|---|---|
| V | 3.3 | 12.39 | 49.55 | 0.19 | 6.22 | 13.91 | 1.66 | 18.3 | 16.64 |
| V1 | 3.22 | 18.27 | 52.34 | 0.21 | 6.42 | 13.94 | 1.77 | 17.7 | 15.9 |
| V2 | 3.18 | 15.17 | 46.76 | 0.19 | 8.63 | 13.6 | 1.81 | 21.1 | 19.2 |
| V3 | 3.29 | 11.77 | 38.4 | 0.22 | 8.83 | 13.73 | 1.8 | 19.6 | 17.8 |
| V4 | 3.32 | 15.17 | 46.76 | 0.21 | 6.02 | 13.97 | 1.71 | 18.5 | 16.79 |
| V5 | 3.29 | 15.48 | 46.45 | 0.19 | 6.42 | 13.71 | 1.45 | 17.7 | 16.25 |
| V6 | 3.43 | 15.17 | 52.03 | 0.27 | 5.92 | 13.75 | 1.82 | 20.9 | 19.08 |
| V7 | 3.25 | 11.46 | 39.02 | 0.2 | 6.42 | 13.81 | 1.26 | 18.8 | 17.54 |

The values of the alcoholic concentration were higher in the Tămâioasă românească samples that were treated with oxalic acid and tannin (V1 and V4). For evaluating the total dry extract and the non-reductive extract, the lower values were found in the samples treated with oxalic acid and bentonite. It was observed that the wines were dry, the reductive substances having small quantities (Tab. 1). If the quantity of phenolic compounds grew after addition of tannins ($V_4$), in general the use of other treatments decreased the amount of these compounds (fig. 1).

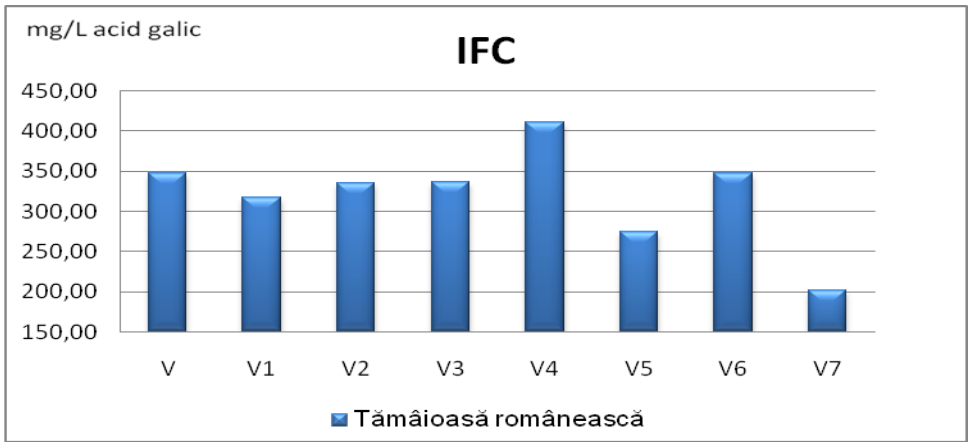


Fig. 1. Content of phenolic compounds in wines by Folin-Ciocâlteu method

The chromatic parameters of the Tămâioasă românească wines were calculated according to the CIE Lab 76 methods and to the registered absorption spectrum of each wine sample. The values of L parameter showed that the wines obtained by applying charcoal were the most clear. Generally the colour of the wines is yellow greenish (Tab. 2). Major colour and hue differences were found in the samples treated with oxalic acid (V1), and activated carbon (V7).

Tab 2.

Chromatic characteristics of wines obtained from Tămâioasă românească variety

| Sample | Clarity L | Cromaticity | | Chrome C | Tonality H | Luminosity | Tenta | ΔE | ΔH |
|---|---|---|---|---|---|---|---|---|---|
| | | a | b | | | | | | |
| V | 97.75 | 0.40 | 4.58 | 4.60 | 84.98 | 0.12 | 2.54 | | |
| V1 | 97.82 | 5.13 | 4.53 | 4.53 | 89.32 | 0.12 | 2.65 | 4.72 | 4.72 |
| V2 | 97.86 | 0.17 | 5.05 | 5.05 | 88.10 | 0.12 | 2.79 | 0.53 | 0.26 |
| V3 | 97.67 | 0.37 | 4.98 | 5.00 | 85.75 | 0.13 | 2.60 | 0.41 | 0.07 |
| V4 | 97.81 | 0.36 | 5.54 | 5.55 | 86.27 | 0.13 | 2.80 | 0.95 | 0.10 |
| V5 | 97.71 | 0.20 | 4.88 | 4.88 | 87.61 | 0.13 | 2.65 | 0.36 | 0.22 |
| V6 | 98.01 | -0.24 | 4.88 | 4.88 | -87.21 | 0.12 | 3.05 | 0.75 | 0.64 |
| V7 | 99.72 | -0.18 | 1.43 | 0.84 | -78.69 | 0.00 | -4.62 | 3.76 | 3.67 |

Sodium content increased after bentonite addition (V5) while, by succinic acid treatment (V3), the level of sodium reached the lowest values. Regarding the potassium content, its level decreased after bentonite treatment (V5). Due to calcium oxalate precipitation, the level of calcium significantly decreased in wines at sample treated with oxalic acid (V1), the rest of prefermentative treatments contributed at increasing the level of

calcium in wine. High level of iron were found in wine treated with succinic acid (V3) and chitosan (V6). Small values of zinc concentration were registered in Tămâioasă românească wines at bentonite (V5), succinic acid (V3) and chitosan (V6) treatments. Copper content was below the limit of detection (SLD<0.01 mg/L) in wine treated with tannin (V4).

Tab 3.

Mean values and standard deviation of different metals (mg/L) in Tămâioasă românească wines

| Sample | Na | K | Ca | Fe | Cu | Zn |
|---|---|---|---|---|---|---|
| V | 11.95 ±0.0004 | 467.87±0.0056 | 14.51±0.0001 | 5.11±0.0009 | 0.52±0.0005 | 9.35±0.0027 |
| V1 | 11.69 ±0.0003 | 477.68±0.0037 | 10.67±0.0007 | 10.04±0.0097 | 0.33±0.0003 | 1.61±0.0006 |
| V2 | 12.59±0.0001 | 434.48±0.0316 | 41.29±0.0004 | 4.95±0.0023 | 0.44±0.0004 | 4.21±0.0019 |
| V3 | 9.96±0.0004 | 467.05±0.0479 | 31.25±0.0011 | 9.58±0.0046 | 0.54±0.0002 | 0.13±0.0003 |
| V4 | 20.63±0.0005 | 447.54±0.0118 | 34.15±0.0022 | 2.36±0.0008 | - | 7.57±0.0037 |
| V5 | 23.39±0.0003 | 353±0.0763 | 20.54±0.0005 | 7.19±0.0009 | 0.23±0.0007 | 0.006±0.0002 |
| V6 | 20.89±0.0004 | 472.69±0.0095 | 32.59±0.0068 | 11.86±0.0022 | 0.66±0.0008 | 0.27±0.0004 |
| V7 | 11.92±0.0006 | 470.18±0.0072 | 20.76±0.0006 | 3.22±0.0003 | 0.291±0.0003 | 6.11±0.0021 |

## CONCLUSION

The quantity of phenolic compounds grew after addition of tannins. Visible colorimetric and tone difference compared to the control sample were observed in case of oxalic acid and activated carbon addition. The most clear wines were obtained through activated carbon treatment. Prefermentative treatments contributed at increasing the level of calcium in wine, except oxalic acid addition. Succinic acid (V3) and chitosan (V6) contributed at increasing the iron content in wine. Copper content was below the limit of detection (SLD<0.01 mg/L) in wine treated with tannin (V4).

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