



Élelmiszertudományi Kar

**A REVIEW OF THE EFFECT OF WINE
TECHNOLOGY PROCEDURES ON THE
POLYPHENOLIC COMPOUNDS AND SENSORY
ANALYSIS IN RED WINES**

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PhD Dissertation Theses

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1. INTRODUCTION

The Bull's Blood is one of the most famous red wine in Hungary. More than twenty years of history can be traced back to the definition of the modern concept of Bull's Blood. These issues are analyzed: what else can the Bull's Blood is different for the other blending red wine rest of the world, what kind of grape variety we use to the blending, and what technologies use for the wine process. The Bull's Blood was awarded in origin protection in vintage of 1997.

As a result of the efforts and regulations in the domestic and foreign market the Bull's Blood perception is improving. However the consumers cannot determine the concept of Bull's Blood, because both in price and quality there are a wide range unfolds before them.

During these transformations the quality winegrowing and winemaking has come into the foreground opposite to quantity centred yield. The quality yield is influenced by many factors: the vine itself, the habitat, the microclimate and the technology. The economical and market needs require the high-quality yield, but besides this the production of unique products is emphasized. For the sake of constant and balanced yield safety and for quality the world vines have come into foreground.

The researchers studied several aspects of red wines, as well as Bull's Blood opportunities for quality improvement, but there is a need for

focused research and for the safety of production and to develop a detailed understanding and improvement of the Bull's Blood.

During my research the grape varieties of Bull's Blood were investigated in terms of phenolic compounds. In this search of us the chemical and organoleptic characteristic of the ten grapes, wines and Bull's Blood has been mapped, and the connection between the two parameters has been examined in the vintage of 2007, 2008 and 2009.

2. AIMS

1. During my research I was studied ten grape varieties in terms of physiologically active compound. Investigated these contents where accumulation in a part of bunches. These results allow a limited yield method for the future.

2. In my research I studied ten wines and blending wine: the Bull's Blood, in terms of deeper level of analysis and sensory analysis.

3. In my search of us the chemical and organoleptic characteristic of the ten grapes, wines and Bull's Blood has been mapped, and the connection between the two parameters.

4. In my search I investigated the blending and ageing effect, which influence the chemical and organoleptic parameters.

3. MATERIALS AND METHODS

The quality of viticulture and wine making is influenced by several factors. The geographical origin, the wine district, plays a prominent role. The thirteen studied grape and wine samples and the Bull's Blood of Eger comes from three vineyards: Kőlyuktető, Szarkás-wine district, Kolompos-wine district. The processing, the treatment of wines, the blending and aging were happened in Research Institute of Viticulture and Enology of KRF.

The experiments were carried out on three consecutive vintages between 2007 and 2009. The samples were harvested in stage of full ripeness. The wine processing was happened in microvinification conditions. The new blending wine was investigated. After ageing we measured the blending and basic wines once more in order to reveal how the phenolic compounds developed in the ageing wine, because these parameters influence the wine quality.

The protected origin classic Bull's Blood can be made at least three varieties of wine by blending. The useable grape varieties are: Kékfrankos, Kékoportó, Kadarka, Blauburger, Zweigelt, Cabernet franc, Cabernet Sauvignon, Merlot, Pinot noir, Kékmedoc. The 102/2009 V.11. regulation was modification. The useable grape varieties were flared with Turán, Bíbor kadarka and Syrah. With regard to the regulation of Bull's Blood during my research were

investigated ten grapes and wine samples until 2009, than were analyzed thirteen grapes and wine samples.

All kinds of grapes were harvested in full ripeness. I was investigated the berry skin, the berry pulp, and the wine (new and ageing), which were processed in a microvinification conditions. Frozen bunches were weighed and along the longitudinal axis divided into three equal parts. Ten berry skin samples were extracted with a 6:4 ratio of methanol: water solvent containing 1 V/V% cc. hydrochloric acid. The tests were carried out in the berry skin extracts and musts.

All vintages (2007; 2008; 2009) the harvest was happened in a stage of full ripeness. Grapes were harvested by hand, cases in bold. The processing was happened in a condition of microvinification. After the destemming the yeast, fertilizer and sulphurous acid solution were added into the mash. All of wines the skin maceration times were 20 days. After the pressing part of the new wines (NW) were bottled for analysis. The other part of wines (AW) were aged one year in glass ballons of 25 L in volume, than we were analysed again. The blending ratios were the same every year. The rates are as follows: Kékfrankos: 35%, Cabernet Sauvignon: 10%, Cabernet franc: 10%, Merlot: 10%, Blauburger: 10%, Zweigelt: 10%, Menoire: 5%, Pinot noir: 5%, Kadarka: 5%, Kékoportó/Portugieser: 5%.

The routine chemical analysis were carried out in Research Institute of Viticulture and Enology of KRF in accordance with national standards and the Hungarian wine-making practices.

The sugar content were analysed with Rebelein-method by the Hungarian standard MSZ 9479-1980, the titratable acid content by the Hungarian standard MSZ 9472-1986, the sugar free extract by Hungarian standard MSZ 9463-1985 with picnometer, the pH-value by the Hungarian standard MSZ 14849-1979 by potentiometric method and the alcohol content by the Hungarian standard MSZ 9458-1972.

The spectrophotometric analysis were carried out in the Budafok Laboratory of the Department of Oenology of Corvinus University of Budapest.

Absorbance measurements were recorded on MOM Spektromom 195 spectrophotometer. The amount of total polyphenolic content (TP) in wine samples was determined by the Folin-Ciocalteu's reagent (Slinkard & Singleton, 1977) and was expressed in mg/L of gallic acid. Anthocyanins (A) were estimated according to Ribereau-Gayon and Stonestreet (Ribereau-Gayon & Stonestreet, 1966), and was expressed in mg/L. The content of leucoanthocyanins (LA) were measured after heating with 40:60 hydrochloric acid and buthanol, containing 300 mg/L ferro-sulphate (Flanzy, Aubert, Marinos, 1969). Catechin (C) was determined using the Rebelein method (Rebelein, 1965), after diluting the wine with alcohol and reacting with

sulphuric acid vanillin. The colour parameters, absorbances at 420 and 520 nm were measured. The colour intensity (CI) ($A_{420+520}$), the hue (CH) ($A_{420/520}$) were estimated (Sudraud, 1958).

Concentrations of stilbenes were determined using HPLC method with isocratic elution. This method was elaborated at the Department of Oenology of Corvinus University of Budapest (Kállay, Török, 1997). The samples of wine were filtered using Sartorius μm filter. The type of this instrument: HP Series 1050. This instrument has got a variable wavelength detectors, the system is connected to a Data Station (HP 3396A) for collection and data analysis. All samples were analysed four stilbenes compounds: trans-piceid; trans-resveratrol; cis-piceid; cis-resveratrol.

Determination of stilbenes compounds (circumstances and settings):

Column: LiChrospher[®] 100 CN (125 × 4 mm; 5 μm); (Merck, Germany).

Detector: HP Series 1050.

Flow: 2 mL/min.

Wavelength: 306 nm.

Temperature: 30 °C.

Eluent: 5:5:90 = acetonitril:metil-alcohol:distilled water.

LQD: 0,1 mg/L.

LOQ: 0,05 mg/L.

Wine is a hedonistic creation, so in addition to the analytical tests should cast the wine organoleptic under criticism. The wine samples were analysed in new and ageing status. The organoleptic analysis of the wines has been carried out by a five-man expert jury, using a hundred-point evaluation system. The basic wines and the blending wines (Bull's Blood) were criticized by the judges.

Statistical analyses were performed using the analysis of variance (ANOVA). Tukey's test was used as comparison test when samples were significantly different after ANOVA ($p < 0,005$). Results were evaluated by a two-factor analysis of variance (MANOVA). The statistical evaluation were done with a software package of IBM SPSS 20. The statistical analyses were done in a Department of Biometrics and Agricultural Informatics in Corvinus University of Budapest.

4. RESULTS

Results of berry skin extract

During my research I investigated the physiologically active compounds within the cluster. I tried to find the answer, where the phenolic compounds localized within the bunch.

In the vintage of 2007 three grape varieties were studied: Blauburger, Kékfrankos and Zweigelt. In the grape variety of Blauburger the maximum amount of the phenolic compounds (total polyphenolic content, anthocyanins, content of leucoanthocyanins, catechins) were accumulated in the end part of the cluster. The minimum quantity of phenolic contents were found in the shoulder of cluster. Trans-piceid was detected in the berry skin extracts of Blauburger grape variety with chromatography method. This fact corresponds to the literature statements, since the skin is mostly present in the form of piceid. Among the part of bunches the statistics were not showed significant difference due to the high standard deviations. In the grape variety of Kékfrankos the maximum quantity of the physiologically active contents were localized in the shoulder of the cluster. Trans-piceid was detected in the tip of cluster. In the grape variety of Zweigelt the maximum amount of phenolic contents were found in the shoulder of bunch. The maximum quantity of physiologically active compounds in Kékfrankos and Zweigelt grapes were localized in the shoulder of cluster in the vintage of 2007. The MANOVA test is based on a

significant difference between the varieties (Wilks $\lambda=0,004$, $p<0,001$). Despite these differences, there is no significant difference between distributions within the cluster (Wilks $\lambda=0,411$, $p=0,168$), (BLAU, KF, ZW). The normality damaged due to outliers, and the standard deviations were high. According to the Tukey test the anthocyanin component failure, however, resulted in a significant difference.

In the vintage of 2008 three grape varieties were studied: Pinot noir, Merlot and Cabernet franc. The Pinot noir grape varieties in the terms of the maximum amount of total-polyphenol and anthocyanin compounds were accumulation in the middle part of bunches. The maximum quantity of catechins and leucoanthocyanins were found in the tip of cluster. The maximum amount of cis-piceid was detected in the middle part of cluster. At the Merlot grape variety all quality parameters (total polyphenol, anthocyanins, leucoanthocyanins, catechins, stilbenes) were localized in the shoulder of cluster. For Cabernet franc grapes the phenolic compounds were found in the tip of bunch, except the catechin content. In the vintage of 2008 both in terms of quantity of phenolic compounds in three different varieties were accumulated in different part of bunches. The statistic method was showed a difference on a total polyphenol and leucoanthocyanin contents. Among the classes of phenolic compounds is also a significant difference emerged.

In the vintage of 2009 three grape varieties were studied: Turán, Bíbor kadarka and Syrah. These three grape varieties can be

blending for the Bull's Blood from this year. The maximum amount of total polyphenols, anthocyanins, leucoanthocyanins and catechins were measured in the shoulder of cluster, going down the cluster, and then a downward trend can be observed. Trans-piceid, trans-resveratrol and cis-resveratrol were detected in berry skin extract of Turán grape. The part of bunches was a significant differences with regard to the trans-resveratrol concentrations. In the berry skin extract of Bíbor kadarka grape were measured the phenolic contents in the shoulder of cluster. In the berry skin extract the maximum amount of trans-resveratrol was localized in the tip of cluster. The maximum quantity of phenolic compounds was detected in the shoulder of Syrah grape variety. The 2009 vintage can be outstanding. In this vintage in all three grape varieties were localized the phenolic compounds in the upper part of the cluster. MANOVA test is showed significant differences between the varieties (Wilks $\lambda=0,06$, $p<0,001$). The 2009 vintage in spite of the differences were not a significant difference between the distributions of species within the part of bunches (Wilks $\lambda=0,88$, $p=0,9$) (TU, BK, SY). Normality damaged due to outliers, and the standard deviations were high.

Results of must

Reducing sugar content of musts from the vintage of 2007 were provided to be the average, which due to the climatic situation of the year. The titrable acidity of must were changed between 4,8 and 8,2 g/L in ten grape variety. For determination the optimal harvest date

the addition of sugar and titrable acidity content must take notice of the pH value. In the vintage of 2007 the pH values were ranged between 2,84 and 3,45.

In the vintage of 2008 the highest reducing sugar content was measured in Kékfrankos grape variety, the lowest reducing content was measured in Kékoportó grape variety. In the vintage of 2008 the titrable acidity of musts was lower than the previous vintage. In the vintage of 2008, the pH values were directly proportional to the titrable acidity values.

In the vintage of 2009 the reducing sugar content of musts had very high values which due to the climatic situation of the year. The titratable acidity and pH are closely related. In the vintage of 2009 the titrable acidity of musts were changed between 4,9 and 8,6 g/L. In the vintage of 2009 the pH values were ranged between 3,14 and 3,55.

Results of Wines

Routine analytical studies of the wines were made in all three vintages new and old wine state. The results were mainly due to the significant additional for wine treatments.

Wine analysis in all three vintages (2007, 2008, 2009) were evaluated by ANOVA and MANOVA statistically method. During my research examined the effects of aging and blending for the phenolic composition of wines. The results of the multivariate

ANOVA significant for the year [Wilk λ = 0,17, $p < 0,001$], for the grape variety [Wilk λ = 0,19, $p < 0,001$], and for the ageing [Wilk λ = 0,585, $p < 0,001$].

The colour of the grapes and red wines determine the compounds of anthocyanins. During the development the anthocyanin monomers of wine undergo different physical, chemical and biochemical processes. During the ageing each basic and, as well as the blending wines also decreased this number, which probably due to the processes of polycondensation. The average values of anthocyanin in new wines were ranged between 159 and 563 mg /L, in aged wines were ranged between 142 and 428 mg/L. The effect of ageing were reduced the concentration of anthocyanins in the basic and blending wine too.

The total polyphenol content in new wines were ranged between 1076 mg/L (Merlot) and 2126 mg/L (Cabernet Sauvignon) based on the average of three years. The value of total polyphenol in Bull's Blood was 1633 mg/L. In the aged wines the values of total polyphenol contents were ranged between 1033 mg/L (Kadarka) and 2072 mg/L (Cabernet Sauvignon). In aged Bull's Blood was detected 1284 mg/L value. The effect of ageing the catechin content variously formed, which sometimes falling, sometimes growing. Due to the aging the catechin content decreased in the Bull's Blood, which owing for the polycondensation. Catechin monomers in condensation reactions form of different degrees of polymerization and molecular weight of tannins. The catechin reduction of the wine sensory

perspective may be advantageous, as in this case also the Bull's Blood.

Leucoanthocyanin content of wines like the catechins followed decreasing and increasing trend due to the aging which in most cases correlates with the sensory results. Effect of the ageing the leucoanthocyanin content was decreased in Bull's Blood, which owing the polymerization, or causes the oxidative reaction of Fe (II).

The elegant red colour is the basic consumer expectations. The colour intensity and colour hue is the determining traction of the colour of wine. The colour intensity of wine were ranged between 2,2 and 9,8. The effect of ageing all of wines was happened the colour deposit. According to the literature of the new wine is of greater value relative color strength of the aged wines. The colour hue were changed between 0,57 and 1,11. The effect of ageing the values of colour hue was increased in all wines.

I was detected stilben compounds: trans-piceid, cis-piceid, trans-resveratrol and cis-resveratrol. In the three vintages was not detected in all species of each form, and due to the aging the values have changed. Differences have been observed between the vintages in terms of resveratrol content. In aged wine the trans- piceid content was increased. The cis form is labile. Variable relative to the trans form of increasing and decreasing trends between new and old wine. Established of three years, that not all new wines have in been detected the trans-resveratrol content. Due to the ageing in the aged

wine piceides evolved form of trans-resveratrol. Cis-resveratrol content of wine was much lower than that of trans-resveratrol content. In some new wine samples could not detected this form.

We measured the wine with sensory analysis method too. In new and aged wine stage several parameters were analyzed according to the judges. There were great differences between the wines both between species as well as between the ageing states. In the vintage of 2007 the aged wines get higher values, than new wines. In the vintage of 2008 in each aged wine the colour deepened, slightly browned which affected the ageing. The judges noticed that. Effect the ageing the wines become more harmony. The vintage of 2009 can be more impressive than the previous years. The judges were given higher points for new wines.

5. NEW SCIENTIFIC RESULTS

1. During my research was measured berry skin extract in three vintages.

The quantity and quality of physiologically active compounds were showed differences between the varieties. The phenolic compounds were localized a different part of bunches.

2. All wines were measured with a routine, spectrophotometer and high-performance method.

The ten grape varieties were showed a differences both the routine and instrumental analysis. The amount of the physiologically active compounds were changed all vintages.

3. During my research I examined the effect of ageing for the basic and blending wines.

It can be concluded that in all three vintages the phenolic component were showed a differences. The role of the aging has a great importance for the quality wine making.

4. All wines were measured with a sensory analysis method.

Between the grape varieties were showed differences. The ageing has a positive influence on the sensory properties of wine. The analysis was observed correlation between the analytical parameters and sensory attributes.

5. During my research examined the effects of aging and blending process for the phenolic composition of wines.

Necessary for a deeper chemical understanding of basic wines, that we can do a quality blending wine.

The ageing was influenced the chemical and sensory parameters in a basic and blending wine too.

6. The sensory results were in close contact with the analytical parameters.

The analysis was showed significant differences between the vintages and ageing states.

6. SCIENTIFIC PUBLICATIONS

Journals with IF:

Leskó, A; Nyitrai-Sárdy, D; Kállay, M; *Balga, I.* (2012) : Changes of the anthocyanin characteristic in model solution due to the used yeast. Acta Alimentaria; Impact Factor (2011): 0,444.

Balga, I; Leskó, A; Kállay, M; Ladányi, M. (2014): Ageing influence on the changes of polyphenolic compounds in red wines. Czech Journal of Food Science, Prague, ISSN 1805-9317; Impact Facort (2013): 0,741.

Hungarian Journals without IF:

Balga, I; Kállay, M; Leskó, A. (2012): Egy „hungarica” szőlőfajta, a Turán borának fenolos összetételének és organoleptikus tulajdonságainak tanulmányozása az érlelés függvényében. Borászati Füzetek, 23. évfolyam, 5. szám, 12-17.

Hungarian Conferences, full paper:

Balga, I; Kállay; M. (2011): Vörösborok fenolos összetételének változása. XVII. Ifjúsági Tudományos Fórum, Keszthely.

Balga, I; Kállay, M; Nagy, B; Nyitrainé Sárdy, D; Leskó, A. (2013): A Kékfrankos szőlőfajta finomösszetételének vizsgálata az Egri borvidéken. XIX. Tudományos Ifjúsági Fórum, Keszthely. CD kiadvány, ISBN 978-963-9639-51-5.

International Conferences, full paper:

Balga, I; Kiss, A; Gál, L; Leskó, A; Kállay, M. (2014): Evaluation of the correlation between the chemical and sensory compounds in red wine. Proceedings of the Third Edition of the International Conference Series on Wine Active Compounds, Bourgogne. Edited by Pr. Régis Gougeon, Université de Bourgogne.

Balga, I; Leskó, A; Nyitrai Sárdy, D; Nagy, B; Kállay, M. (2014): Chemical and sensory evaluation of the Hungarian wines in vinedistrict of Eger. 20th Youth Scientific Forum, Keszthely. ISBN: 978-963-9639-57-7.