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INFLUENCE OF SOME HERBICIDES ON THE CONTENT OF ESTERS, HIGHER ALCOHOLS, ALDEHYDES AND TERPENES IN RED WINES OF THE CABERNET SAUVIGNON

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Abstract
Study on the effect of herbicides flumioxazin (Pledge 50 WP); s-metolachlor + terbuthylazine + mesotrione (Lumax 538 SC) and pyraflufen-ethyl + glyphosate (Guild) on the content of esters, higher alcohols, aldehydes and terpenes in red wines from Cabernet Sauvignon variety was conducted. The gas chromatographic (GC-FID) analysis identified 14 volatile compounds in the variants. The highest total amount of volatile compounds was found in the wine obtained after treatment with Pledge 50 WP (326.62 mg.dm^{-3}). Five higher alcohols, five esters, two terpenes, one aldehyde and methyl alcohol have been identified. Higher levels of higher alcohols in the wines obtained after treatment of the experimental variants with herbicides have been established. The dominant higher alcohol was 3-methyl-1-butanol. There was a trend of higher ethyl alcohol levels in the wines from experimental variants compared to the untreated control variant. The highest ester content in the Pledge 50 WP variant wine (65.61 mg.dm^{-3}) was found. The esters were dominated by ethyl acetate which in the established concentrations (15.28 – 21.01 mg.dm^{-3}) produced the pleasant fruity flavor. Lower levels of acetaldehyde were found in the wines from experimental variants compared to the control. The herbicidal treatments have a positive effect on the synthesis of geraniol terpene in the vine. Treating the areas with the studied herbicides led to an improved overall volatile and aromatic profile of the red wines obtained from Cabernet Sauvignon variety. This study demonstrated the advantages of conventional agriculture by the observed beneficial effects of the treatment with herbicides. They were a guarantee for stable and controlled development of the vine from Cabernet Sauvignon variety, which reflected in the improved volatile and aromatic quality in red wines produced from it.

Keywords: Herbicides, Cabernet Sauvignon, red wines, esters, higher alcohols, aldehydes, terpenes, ethanol, methanol.

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1. INTRODUCTION

The need for an increasingly high production of low-cost foods and raw materials undoubtedly imposes the chemical method for control of the unwanted plants as a major technological element in the field of the conventional agriculture. Today, 80-90% of the world's main crops - wheat, corn, cotton, sugar beet, vine and fruits are being treated with herbicides. There are more than 300 herbicidal active substances which, either alone or in various combinations, form the basis of a large number of commercial products (Kolev, 1963; Fetvadzhieva, 1966; Fetvadzhieva, 1973; Tonev, 2000; Tonev et al., 2007).
By effectively weeds inhibiting, the herbicides block the competition for nutrients (Guerra and Steenworth, 2012). A number of studies have shown that a large number of herbicides (diuron, oxifluorfen, dichlobenil, glyphosate, etc.) have a positive influence on the vines growth (Neury, 1985; Elmore et al., 1997; Paulo et al., 1997; Guéry, 1998). Despite the positive results obtained in many studies, there is always have a risk for toxicity to the vine and the consumer due to the accumulation of higher levels of herbicides residues in the vine product (Tourte et al., 2008).
There is evidence that the herbicide flumioxazine, applied to the soil, leads to a stress reduction of leaf carbohydrates and free amino acids decrease, which can affect the vine vitality for the long term period (Saladin et al., 2003).
Reduced iron levels in the leaves of young vines after flumioxazine treatment with no apparent herbicidal effect were found, which indicate for hidden phytotoxicity (Prodanova-Marinova and Staneva, 2018).

The influence of herbicides on the composition and quality of grapes and wines is of interest. The use of the most common herbicide glyphosate on the Ancellotta variety (*Vitis vinifera* L.) has been found to reduce the pH and the anthocyanins concentration in grapes and increase its titratable acids as compared to the untreated control, but the concentration of anthocyanins, flavonoids and phenolic acids in wine remains unchanged (Donnini et al., 2016). Karl et al. (2016) investigated the impact of certain technological measures (including glyphosate treatment) on vines, grapes and wine of the Cabernet Franc variety. They found that the use of glyphosate resulted in high yields, comparability in the chemical composition of the grape juice, and lack of sensory differences in the wine.

A study on the influence of the density of the weed species *Lolium perenne* L. on the yield of grapes and the quality of wine from the region of Northern Portugal was conducted (Martins et al., 2015). The team found that treatment with herbicides (glyphosate or combinations of other herbicides with glyphosate or glyphosate + ACCAse or ALS - inhibitors) has an inhibitory effect on *L. perenne* and led to an increased grape yield but the wine quality was constant regardless of the weed reduction level.

The aromatic wine profile is a complex combination of different groups of compounds (esters, higher alcohols, aldehydes and terpenes) (Vilanova et al., 2013; Robinson et al., 2014).

They are indicators for wine quality. The esters have the most important aromatic influence because of their significantly lower threshold of aromatic perception. They are the product of yeast metabolism (during alcoholic fermentation) and chemical formation (during wine aging, based on the esterification process) (Chobanova, 2012). Esters are formed in grapes in very small amounts (10.00 - 30.00 $mg.dm^{-3}$) (Abrasheva et al., 2008). They increase in the young wines after alcoholic fermentation (up to 500.00 $mg.dm^{-3}$) (Cobanova, 2012) and reach very high concentrations in old aged wines (792.00 - 800.00 $mg.dm^{-3}$) (Yankov et al., 2000).

The higher alcohols are metabolic products of *Saccharomyces cerevisiae* (Bell and Henschke, 2005). Their amount ranges from 150.00 - 500.00 $mg.dm^{-3}$ (Abrasheva et al., 2008). They are a precursor for the formation of esters in the wine aging process (Meng et al., 2011).

The group of aldehydes is quantitatively dominated by acetaldehyde. Its quantity in dry wines is in the range of 10.00 - 200.00 $mg.dm^{-3}$ (Velkov, 1996; Chobanova, 2012).

The wine terpenes are mainly represented by terpene alcohols – α - terpineol, β-citronellol, linalool, linalool oxide, nerol, geraniol (Luan, 2006; Oliveira, 2008).

The herbicide Guild has a totally leaf-like effect and provides a good microclimate in the perennials. Pledge 50 WP and LUMAX 538 SC have both soil and leaf action. The duration of their effect in soil is over 90 days.

Their leaf application does not exclude accumulation in the soil and long-lasting influence on both some weed species and on the vine and wine.

The aim of this study was to investigate the effects of three herbicides on the content of esters, higher alcohols, aldehydes and terpenes in red wines of the Cabernet Sauvignon variety.

2. MATERIALS AND METHODS

2.1. Plant Material, Setting of the Trial, Herbicides and Application Details

The experiment was done in 2017 on the territory of the Experimental Base of the Institute of Viticulture and Enology (IVE), Pleven, Bulgaria. The Cabernet Sauvignon variety plantation (Berlandieri x Riparia Selection Oppenheim 4) was created in 2003 and located at 43.42 ° N 24.62 ° E and 140 meters altitude.

The soil type of the area, on which the plantation was located, was leached black earth formed on clayey loess. The mechanical composition was a heavy sandy clay, with good hidrophysical properties, fully satisfying the vine biological requirements (Krastanov and Dilkova, 1963).

Table 1. Herbicides, their doses and time of application

	Herbicides applied (formulated product)	Time of application	Active substance (g /l; g/kg)	Doses (l/da)
1	Pledge 50 WP	postem	500 g/kg flumioxazin	0.02
2	Lumax 538 SC	postem	375 g/l s-metolachlor + 125 g/l terbuthylazine + 337.50 g/l mesotrione	0.60
3	Guild	postem	1.71 g/l pyraflufen-éthyl + 261 g/l glyphosate	0.56

This type of soil is considered to be the most suitable for cultivation of varieties intended for the production of red table wines (Kurtev et al., 1979).

The formation was a modified Moser. The distance between the rows was 2.5 m and the inter-row distance was 1.3 m.

The study included 3 herbicides: Pledge 50 WP, Lumax 538 SC and Guild (Table 1). The types, composition of herbicides and their application doses are presented in Table 1.

In order to study the herbicide's foliar action, the treatment was performed once (29^{th} May), when most dicotyledonous weeds were in the butonization phase - the beginning of flowering. The herbicides were applied once in the stripe of the row with a backspray sprayer at 40 l/ha and a nozzle pressure P max of 300 kPa.

2.2. Vinification

The grapes was harvested (30 kg for each variant) and were vinified at the Experimental Wine Cellar of IVE. A classic scheme for the production of dry red wines (Yankov et al., 1992) was applied – crushing and destemming, sulphitation (50 $mg.kg^{-1}$ SO_2), inoculating with pure culture dry yeasts *Saccharomyces cerevisiae* Siha Rubio Cru (EATON Begerow) - 20 $g.100\ dm^{-3}$, temperature of fermentation - 28°C, separation from solids, further sulphitation, storage.

The corresponding variants of the wines obtained were as follows:

CONTROL - red wine of the Cabernet Sauvignon variety, unprocessed with herbicides;

V1 - red wine of the Cabernet Sauvignon variety, treated with herbicide Pledge 50 WP;

V2 - red wine of the Cabernet Sauvignon variety, treated with herbicide LUMAX 538 SC;

V3 - red wine of the Cabernet Sauvignon variety, treated with herbicide Guild.

2.3. Determination of alcohol content of obtained wines

The alcohol content of the obtained wines was defined by specialized equipment with high precision – automatic distillation unit - DEE Destillation Unit with Densimat and Alcomat, Gibertini, Milan, Italy.

2.4. Volatile content determination by Gas Chromatography (Gas Chromatograph with Flame Ionization Detector)

Gas chromatographic determination of the volatile components in wine distillates was done. The content of major volatile compounds was determined on the basis of stock standard solution prepared in accordance with the IS method 3752:2005. The method describes the preparation of standard solution with one congener, but the step of preparation was followed for the preparation of a solution with more compounds. The standard solution in this study include the following compounds (purity > 99.0%): acetaldehyde, ethyl acetate, methanol, isopropyl acetate, 1-propanol, 2-butanol, propyl acetate, 2-methyl-propanol, 1-butanol, isobutyl acetate, ethyl butyrate, butyl acetate, 2-methyl-1-butanol, 3-methyl-1-butanol, ethyl isovalerate, 1-pentanol, pentyl acetate, 1-hexanol, ethyl hexanoate, hexyl acetate, 1-heptanol, linalool oxide, phenyl

acetate, ethyl caprylate, α-terpineol, β-citronellol, nerol, geraniol. As an internal standard 1-octanol was used.
The 2 μl of prepared standard solution was injected in gas chromatograph Varian 3900 (Varian Analytical Instruments, Walnut Creek, California, USA) with a capillary column VF max MS (30 m, 0.25 mm ID, DF = 0.25 μm), equipped with a flame ionization detector (FID). The used carrier gas was Helium. Hydrogen to support combustion was supplied to the chromatograph via a hydrogen bottle. The injection was manually by microsyringe.
The parameters of the gas chromatographic determination were: injector temperature – 220 °C; detector temperature – 250 °C, initial oven temperature – 35 °C for 1 min, up to 55 °C with step of 2 °C/min for 11 min, up to 230 °C with step of 15 °C/min for 3 min. Total time of chromatography analysis – 25.67 min.
After determination of the retention times: acetaldehyde (3.256), ethyl acetate (4.017), methanol (4.186), isopropyl acetate (5.897), 1-propanol (6.763), 2-butanol (7.215), propyl acetate (7.427), 2-methyl-1-propanol (7.665), 1-butanol (8.473), isobutyl acetate (8.675), ethyl butyrate (9.868), butyl acetate (12.277), 2-methyl-1-butanol (13.408), 3-methyl-1-butanol (13.542), ethyl isovalerate (13.589), 1-pentanol (14.192), pentyl acetate (14.273), 1-hexanol (15.621), ethyl hexanoate (16.410), hexyl acetate (16.677), 1-heptanol (16.727), linalool oxide (16.981), phenyl acetate (18.400), ethyl caprylate (18.949), α-terpineol (19.387), β-citronellol (19.691), nerol (20.022), geraniol (20.730) of the volatile compounds in the standard solution, the identification and quantification of the volatile substances in the wines was established. The volatile composition was determined based on injection of wine distillates. Prepared samples were injected in a gas chromatograph and was carried out an identification and quantification of the aromatic substances in each of them.

3. RESULTS AND DISCUSSION

The results obtained for the volatile profile of the studied red wines are presented in Table 2. The chromatographic profiles of the examined red wines of the Cabernet Sauvignon variety are presented in Figures 1 - 4.

Table 2. Identified volatile compounds in red wines of the Cabernet Sauvignon variety after herbicide treatment of the plantation areas.

IDENTIFIED COMPOUNDS, mg.dm^{-3}	WINES (CABERNET SAUVIGNON)			
	CONTROL	V1 PLEDGE 50 WP	V2 LUMAX 538 SC	V3 GUILD
Ethyl alcohol, vol. %	12.43	13.56	13.16	13.51
Acetaldehyde	27.55	13.68	0.05	0.05
Methanol	8.73	12.00	21.20	17.78
2-methyl-1-butanol	36.20	34.66	ND	ND
3-methyl-1-butanol	144.89	166.53	200.15	174.88
1-butanol	0.05	33.40	31.90	22.91
1-hexanol	17.01	0.05	0.05	0.05
1-heptanol	ND	0.05	ND	ND
Total higher alcohols	***198.15***	***234.69***	***232.10***	***197.84***
Ethyl acetate	21.01	15.28	20.12	18.67
Propyl acetate	ND	50.28	0.05	38.69
Isobutyl acetate	35.03	ND	ND	ND
Pentyl acetate	0.05	ND	ND	ND
Ethyl decanoate	ND	0.05	ND	ND
Total esters	***56.09***	***65.61***	***20.17***	***57.36***
Linalool oxide	0.79	ND	ND	ND
Geraniol	0.31	0.64	0.24	0.89
Total terpenes	***1.10***	***0.64***	***0.24***	***0.89***
TOTAL CONTENT	***291.62***	***326.62***	***273.81***	***273.92***

** ND /not detected/*

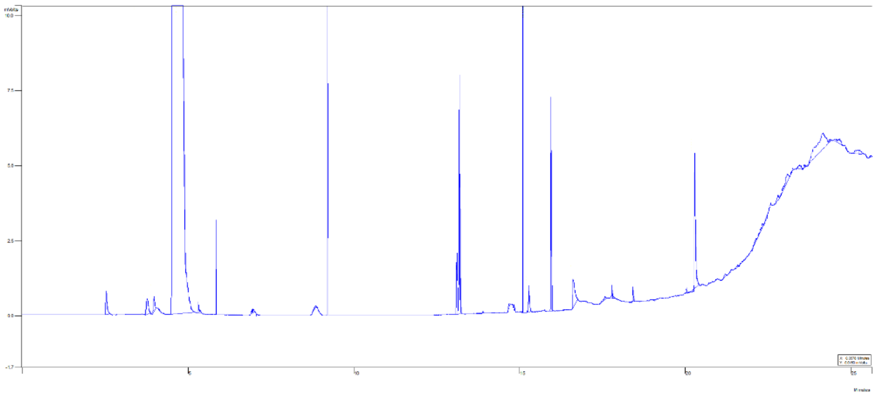

Figure 1. Chromatographic profile of wine from the Cabernet Sauvignon variety, CONTROL variant (without herbicide treatment)

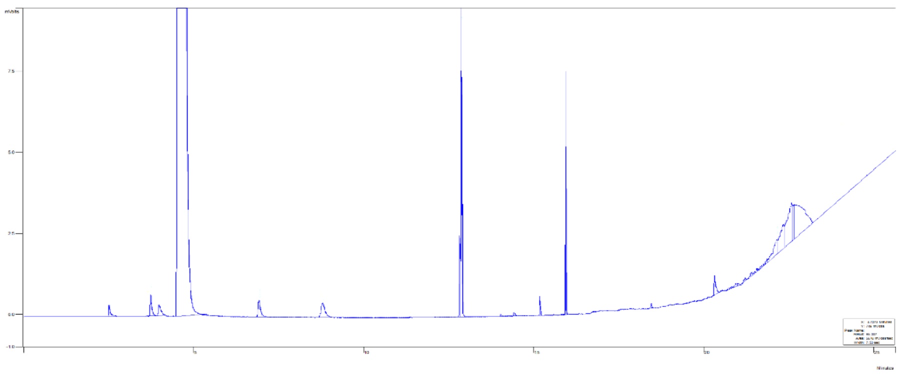

Figure 2. Chromatographic profile of wine from the Cabernet Sauvignon variety V1 variant (treated with herbicide PLEDGE 50 WP)

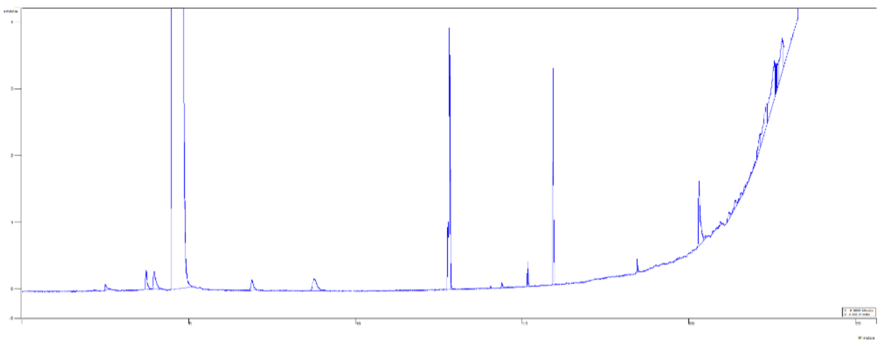

Figure 3. Chromatographic profile of wine from the Cabernet Sauvignon variety V2 variant (treated with herbicide LUMAX 538 SC)

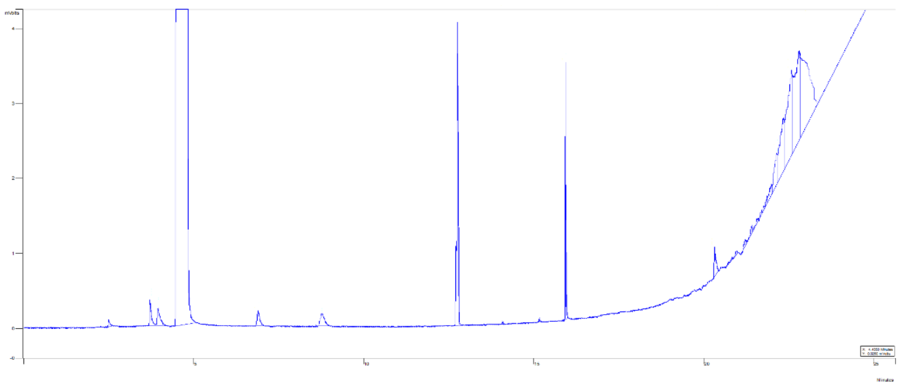

Figure 4. Chromatographic profile of wine from the Cabernet Sauvignon variety V3 variant (treated with herbicide GUILD)

Fourteen volatile compounds from different aromatic groups in the investigated wines were identified. The highest total amount of volatile components was found in the wine obtained from Cabernet Sauvignon variety, variant V1 (PLEDGE 50 WP) - 326.62 $mg.dm^{-3}$. The wines of variants V2 and V3 (LUMAX 538 SC and GUILD) shown an almost comparable content of volatile components (273.81 $mg.dm^{-3}$ and 273.92 $mg.dm^{-3}$, respectively). This volatile content was close to that found in the control sample (291.62 $mg.dm^{-3}$). The variant obtained after treatment with PLEDGE 50 WP shown a distinct difference in the total volatile content both between it and the other two variants, as compared to the untreated control.

Differences in the ethyl alcohol content of the wines were also found. The lowest alcohol content was found in the control sample (12.43% vol. %). In the three experimental samples, the ethyl alcohol was present in noticeably higher amounts. The highest was its content in the V1 wine obtained after treatment of the herbicide PLEDGE 50 WP (13.56% vol. %).

The higher ethyl alcohol content found in the experimental samples was an indirect evidence of better sugar accumulation in the grapes. The reduced density of weeds decreased the competition and created better conditions for metabolic expression of the grapevine. This reflected in higher carbohydrate synthesis, which subsequently generated higher ethyl alcohol levels in wines.

The higher alcohols were represented by 5 identified compounds. There were marked differences in their total content between the variants. The total amount of higher alcohols found in the control sample (198.15 $mg.dm^{-3}$) was very similar to that found in variant V3 (197.84 $mg.dm^{-3}$) treated with the herbicide GUILD. The treatments with PLEDGE 50 WP (V1) and LUMAX 538 SC (V2) also showed close values for total content of higher alcohols (234.69 $mg.dm^{-3}$ and 232.10 $mg.dm^{-3}$ respectively), but they were noticeably higher than those in the control (198.15 $mg.dm^{-3}$).

The results obtained for the total content of higher alcohols were evidence for the effectiveness of herbicidal treatments. Treating with tested herbicides probably helped the amino acid metabolism of the vine and created conditions for generating of more amino acids in the grapes. Since they are a precursor for the synthesis of higher alcohols from yeasts *Saccharomyces cerevisiae*, their increased content probably led to increased synthesis of higher alcohols. It was reported for variants V1 and V2.

The improved and increased total content of higher alcohols in V1 and V2 variants, compared with the control, led to complication of the aromatic profile of the wines produced by the treatment of vines with the respective herbicides. The higher content of higher alcohols was a precondition for complicating of the ester content of wines in the aging process. For V3 variant, the content of higher alcohols were comparable to those found in the control.

The total amount of higher alcohols found was typical for young red wines and correlated with the quantitative variations presented by Abrasheva et al. (2008).

Examining the component composition of the individual identified representatives of higher alcohols, there was a predominant presence of 3-methyl-1-butanol. It was found in all studied variants. A tendency of higher content of this higher alcohol in the experimental variants was reported compared to the control (144.89 $mg.dm^{-3}$). The highest content was secreted in the red wine, variant V2 (200.15 $mg.dm^{-3}$), obtained from grapevines, where the weeds were treated with LUMAX 538 SC. The 3-methyl-1-butanol is one of the main components of the aromatic group of higher alcohols. It gives typical notes of malt and whiskey in the wine aroma (Francis and Newton, 2005). This compound is one of those with an important aromatic effect found in the study of red wines from Merlot and Cabernet Sauvignon varieties produced in California and Australia (Gürbüz et al. 2006).

The higher concentration of 1-hexanol found in the wine of the control sample (17.01 $mg.dm^{-3}$) was noticeable as compared to the experimental variants in which the alcohol was found in traces. Hexanol is an indicator of

herbaceous and bitter taste in wines when it exceeds its normal quantitative presence (4.00 – 10.00 mg.dm^{-3}) (Chobanova, 2012). This disadvantage was observed only in the control sample, because in the experimental variants it was found in very low quantities.
1-butanol has been identified in all wines studied. The lowest was the quantity in the control sample (0.05 mg.dm^{-3}), and the highest in the wine of variant V2 (33.40 mg.dm^{-3}), where the weeds were treated with PLEDGE 50 WP.
The group of esters was represented by 5 identified compounds. Considering the total ester content of the variants, a quantitative predominance in the red wine of variant V1 (65.61 mg.dm^{-3}) obtained after treatment with PLEDGE 50 WP herbicide was observed. In the variant with LUMAX 538 SC treatment the total ester content was lowest (20.17 mg.dm^{-3}). The concentration of esters in red wine of variant V3 (GUILD) (57.36 mg.dm^{-3}) was close to that reported in the control (56.89 mg.dm^{-3}). The data were in correlation with the normal ranges of presence of esters in red wines indicated by Chobanova (2012).
The presence of ethyl acetate was obvious and predominant. It was established in all variants. The lowest was its quantity (15.28 mg.dm^{-3}) in the wine obtained after treatment with herbicide PLEDGE 50 WP (V1). The highest content (21.01 mg.dm^{-3}) was found in the wine of the control variant. Ethyl acetate is an ester which, depending on its concentration, can have both a positive and a negative impact on the sensory characteristics of the wine. The range of its normal presence (30.00 - 200.00 mg.dm^{-3}) determines the appearance of its pleasant fruity character (Chobanova, 2012). Exceeding these values it gives negative acetic-acidic tone. The results obtained in this study testify to the positive effect of the ester, because its concentrations were typical and normal for young red dry wines.
The aldehyde fraction was represented by acetaldehyde. It was found in the highest amount in the control sample (27.55 mg.dm^{-3}). The experimental variants shown significantly lower aldehyde concentrations. The acetaldehyde is a product of the yeast metabolism. The results obtained indicate a possible reduction in the synthesis of acetaldehyde in the application of herbicidal treatments.
In all tested variants, the presence of methyl alcohol was found. Its presence in the wines is normal. Its presence is due to its precursor - pectin, which, due to pectolytic enzyme complex of the fruit, is degraded to methyl alcohol (Marinov, 2005). It was allowed in wines at concentrations of 60.00 – 230.00 mg.dm^{-3} (Abrasheva et al., 2008). Above these values, it is toxic. In this study methanol was found in very low concentrations. The lowest was its content in the control sample (8.73 mg.dm^{-3}), and the highest in the variant V2 of wine treated with the LUMAX 538 SC herbicide (21.20 mg.dm^{-3}). The concentrations of methyl alcohol in wines were low and in correlation with the safety criteria.
The group of terpenes was represented by only two compounds - linalool oxide and geraniol. Linalool oxide was identified only in the control sample (0.79 mg.dm^{-3}). Geraniol was found in all samples studied. It was noticeable its higher concentration in two of the experimental variants compared to the control. In variant V1 (treatment with PLEDGE 50 WP) it was found to be more than twice as high (0.64 mg.dm^{-3}) as compared to the control (0.31 mg.dm^{-3}).
In variant V3 (treatment with GUILD) its content (0.89 mg.dm^{-3}) was nearly three times higher than the control. In variant V2 (LUMAX 538 SC), the established amount of this terpene was lower (0.24 mg.dm^{-3}) than that of the control. The highest total terpenic content was found in the control (1.10 mg.dm^{-3}), and the lowest in the wine of variant V2 (0.24 mg.dm^{-3}).
The results testify to the direct influence of the two herbicide treatments (V1 and V3) on the geraniol synthesis in the vines. Since terpenes are the metabolic products of the vine (Martin et al., 2010), the herbicide treatment applied in this study created favorable conditions for improved metabolism of geraniol in the vine from where it passing into the wine.

4. CONCLUSIONS

From the results obtained from the study, the following conclusions can be made:

• Fourteen volatile aromatic compounds were identified and quantified in red wines of Cabernet Sauvignon after treatment of vine plantation with herbicides;

• The highest content of volatile compounds (326.62 mg.dm^{-3}) was found in the wine of variant V1 treated with herbicide PLEDGE 50 WP;

• Higher levels of ethanol were found in the experimental variants compared to the control. This was an indirect evidence of improved carbohydrate metabolism of the vine after treatment of the test areas with herbicides;

• Five higher alcohols have been identified. The highest content was found in variants V1 (PLEDGE 50 WP) and V2 (LUMAX 538 SC) (234.69 mg.dm^{-3} and 232.10 mg.dm^{-3}, respectively). Treating with the used herbicides probably improved the amino acid metabolism of the vines and created conditions for increasing of their content in the grapes. The predominant higher alcohol in the wines studied was 3-methyl-1-butanol which have a positive impact of the general wine aroma;

• The highest ester content (65.61 mg.dm^{-3}) was found in the wine obtained after treatment of the test area with the herbicide PLEDGE 50 WP. The dominant ester found in all experimental variants was ethyl acetate, which in the established concentrations has a strong positive fruity impact in the wines;

• Acetaldehyde was found at the highest concentration in the control sample (27.55 mg.dm^{-3}). In the experimental variants it was present in low concentrations. This was evidence of a possible reduction in the synthesis of acetaldehyde when applying herbicidal treatments;

• In all wines, methyl alcohol was found. It is a normal component of the wine-based volatile composition. Its concentrations met of the safety criteria;

• The terpene fraction was dominated by geraniol. The results testify to the direct positive effect of foliar treatment with PLEDGE 50 WP and GUILD in the applied doses (V1 and V3) on the geraniol synthesis in the vine from where it passes into the wine.

Treating of the vineyards from the Cabernet Sauvignon variety with the herbicides studied led to an improved total volatile and aromatic profile of the red wines produced.

This study demonstrated the advantages of conventional agriculture by the observed beneficial effects of the treatment with herbicides. They are a guarantee for stable and controlled development of the vine from Cabernet Sauvignon variety, which reflected in the improved volatile and aromatic quality in red wines produced from it.

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