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Study of the effect of some herbicides on the volatile composition of red wines from Cabernet sauvignon

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Abstract
Gas chromatographic study (GC-FID) to determine the volatile composition of wines (two harvests - 2018 and 2019) of the Cabernet Sauvignon variety with the treatment of experimental plantations with herbicides Pledge 50 WP (flumioxazin), Lumax 538 SC (s-metolachlor + terbuthylazine + mesotrione) and Guild (pyraflufen-ethyl + glyphosate) was performed. The results were compared with untreated control. The wines of the 2018 harvest showed a higher total content of volatile compounds compared to the 2019 harvest. Herbicide treatment had the effect of increasing the content of higher alcohols in the experimental wines. This was a possible effect of blocking competition for nutrients needful for the vine metabolism by weeds elimination. The wines of the 2018 harvest contain 9 higher alcohols, the main ones were 1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol and 4-methyl-2-pentanol. The wines from the next harvest showed a poorer species composition of higher alcohols - 5 representatives, with the main presence of 2-methyl-1-butanol and 3-methyl-1-butanol. The experimental variants for the wines of the 2018 harvest showed a higher total ester content compared to the control and the main esters were ethyl acetate and ethyl decanoate. In the next harvest this tendency was absent, and the main representative of the esters was propyl acetate. The aldehyde fraction was represented by acetaldehyde. A low total terpene content in the wines was found, which was normal, as Cabernet Sauvignon is a non-muscat variety. Methyl alcohol concentrations were defined. They were many times lower than the maximum allowable, which characterized wines as toxicologically harmless. The study showed that the treatment with the herbicides Guild, Lumax 538 SC and Pledge 50 WP of experimental plantations of Cabernet Sauvignon led to improved synthesis of higher alcohols and esters in wines, which reflected in improving of their volatile and aromatic quality.

Keywords: Red wines, herbicides, volatile composition, higher alcohols, esters, aldehydes, terpenes

Introduction

The application of herbicides today is a widely used practice to control weeds in conventional agriculture, and in particular viticulture. The advantages of applying these control chemicals are efficiency, low cost and easy application, and the disadvantages include the development of herbicide-resistant weeds, risks of toxicity to the vine and the accumulation of herbicide residues in grapes and their corresponding products (Tourte *et al*., 2008; Guerra and Steenworth, 2012) [25, 7].

The treatment of vineyards with herbicides reduces the competition for nutrients and water between the vine and the weeds. (Keller, 2015; Prodanova-Marinova and Staneva, 2018, 2019) [11, 18]. This creates conditions for normal and improved development of the vine plant. Herbicides produced on the basis of the active substances - glyphosate, glufosinate, a combination of glyphosate and flazasulfuron, etc. are the most often applied in the vineyards. (Bauer *et al*., 2017) [1].

There is a little information in the literature regarding the direct complex effect of herbicide treatments on the volatile composition of wines. It is one of the main indicators of their quality. Its origin is associated with grapes (so-called varietal aroma), the metabolism of yeasts, lactic acid bacteria and other microflora during fermentation processes (so-called fermentation aroma), and last but not least - directly influence of the wine aging process (forming the so-called bouquet) (Callejon *et al*., 2010) [2].

The main groups of volatile compounds identified in wines are: esters (products of yeasts metabolism and chemical bonding between acids and alcohols - esterification), higher alcohols (produced on the basis of metabolic breakdown of amino acids by the yeasts), aldehydes (yeasts metabolites) and terpenes (vine plant metabolites) (Kim *et al*. 2018; Nan *et al*., 2021; Meng *et al*., 2011; Tomasino *et al*., 2020) [12, 16, 15, 23]. The methanol should be added to them as a component of the volatile fraction without aromatic influence. This compound is formed on the basis of the degradation of grape pectin (during fermentation) by the pectolytic enzyme complex (Hodson *et al*., 2017) [9]. According to OIV, the methyl alcohol content of red wines is limited to a maximum of 400.00 mg/dm3 (OIV, 2015) [10], which defines wine as toxicologically harmless.

The aim of the present study was to investigate the effect of treatment of Cabernet Sauvignon vine (two harvests) experimental areas with certain herbicides on the volatile composition formed in their wine.

Materials and Methods

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

The experiment was done in 2018 and 2019 on the territory of the Experimental Base of the Institute of Viticulture and Enology (IVE), Pleven, Bulgaria. 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) [13]. 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) [26].

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, when most dicotyledonous weeds were in the butonization phase - the beginning of flowering (51-63 BBCH). 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.

Table 1: Herbicides, 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 + 337.5 g/l mesotrione	0.60
3	Guild	Postem	1,71 g/l pyraflufen-éthyl + 261 g/l glyphosate	0.56

Vinification

The grapes was harvested (30 kg for each variety) 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 SO_2), inoculating with pure culture dry yeasts *Saccharomyces cerevisiae* Siha Rubio Cru (EATON Begerow) - 20 g/100 dm3, 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 Cabernet Sauvignon variety, untreated plantation with herbicides; V1 - red wine of Cabernet Sauvignon variety, treated plantation with herbicide Pledge 50 WP;

V2 - red wine of Cabernet Sauvignon variety, treated plantation with herbicide LUMAX 538 SC; V3 - red wine of Cabernet Sauvignon variety, treated plantation with herbicide Guild.

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 - Gibertiny BEE RV 10326 (Gibertiny Electronics Srl., Milano, Italy) and Gibertiny Densi Mat CE AM 148 (Gibertiny Electronics Srl., Milano, Italy).

Volatile content determination by Gas Chromatography (GC-FID)

Gas chromatographic determination (GC-FID) 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, isobutanol, 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-propanol (7.665), isobutanol (7.921), 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.

Results and Discussion

The data obtained from the gas chromatographic analysis of red wines (harvests 2018 and 2019) are presented in Tables 2 and 3.

Table 2: Identified volatile compounds in red wines of Cabernet Sauvignon variety, after herbicide treatment of the plantation areas, harvest 2018

Identified Compounds, mg/dm3	Wines			
	Cabernet Sauvignon			
	Control	V1 Pledge 50 WP	V2 Lumax 538 SC	V3 Guild
Ethyl alcohol, vol.%	14.28	13.28	13.27	13.82
Acetaldehyde	218.20	0.05	0.05	57.21
Methanol	39.27	118.50	53.65	59.28
1-propanol	0.05	0.05	10.58	13.96
2-propanol	ND	0.05	0.05	125.39
2- butanol	38.44	98.96	47.33	41.14
2-methyl-1-butanol	31.83	60.21	37.82	41.59
3-methyl-1-butanol	149.71	331.69	158.67	177.09
4-methyl-2-pentanol	0.05	0.05	0.05	0.05
1-butanol	ND	ND	0.05	ND
1-pentanol	0.05	ND	13.51	0.05
2-phenylethanol	0.05	ND	ND	ND
Total higher alcohols	220.18	491.01	268.06	399.27
Ethyl acetate	40.28	46.93	23.46	0.05
Phenyl acetate	ND	ND	ND	0.05
Pentyl acetate	ND	ND	0.05	ND
Ethyl decanoate	0.05	0.05	62.36	412.37
Total esters	40.33	46.98	85.87	412.47
α-terpineol	ND	ND	0.05	ND
β-citronellol	0.05	ND	ND	ND
Nerol	0.05	ND	0.05	ND
Geraniol	ND	ND	0.05	0.05
Total terpenes	0.10	-	0.15	0.05
Total Content	518.08	656.54	407.78	928.28

* ND - Not Detected

Analyzing the total amount of volatile compounds in the wines from 2018 harvest, it became clear that they had the lowest content in the wine of variant V2, when the plantations was treated with Lumax 538 CK. However, the other two variants (V1 - Pledge 50 WP and V3 - Guild) showed a higher total content of volatile compounds (656.54 mg/dm3 and 928.28 mg/dm3, respectively) compared to the untreated control (518.08 mg/dm3). The variant V3 (Guild) showed the highest accumulation of volatile compounds.

Table 3: Identified volatile compounds in red wines of Cabernet Sauvignon variety, after herbicide treatment of the plantation areas, harvest 2019

Identified Compounds, mg/dm3	WINES			
	Cabernet Sauvignon			
	Control	V1 Pledge 50 WP	V2 Lumax 538 SC	V3 Guild
Ethyl alcohol, vol. %	14.45	14.07	14.53	14.40
Acetaldehyde	129.45	65.51	35.44	124.29
Methanol	23.51	78.12	28.88	48.54
2-propanol	ND	ND	ND	11.47
2- butanol	ND	0.05	119.36	13.63
2-methyl-1-butanol	21.25	41.97	21.14	43.91
3-methyl-1-butanol	42.60	95.99	38.82	83.13
2-phenylethanol	0.05	0.05	0.05	ND
Total higher alcohols	63.90	138.06	179.37	152.14
Propyl acetate	12.20	54.69	10.86	63.01
Isopentyl acetate	0.05	0.05	ND	6.35
Ethyl decanoate	ND	207.69	ND	ND

Ethyl butyrate	0.05	ND	ND	ND
Total esters	12.25	262.43	10.86	69.36
Linalool oxide	ND	ND	ND	0.05
β-citronellol	0.05	ND	0.05	0.05
Nerol	ND	0.05	0.05	ND
Geraniol	0.05	0.10	0.13	ND
Total terpenes	0.10	0.15	0.23	0.10
Total Content	229.21	544.27	254.78	394.43

* ND - Not Detected

The analysis of the results of 2019 harvest showed a slightly different trend. The lowest detected total amount of volatile compounds was identified in the control (229.21 mg/dm3). All experimental variants showed a higher quantitative presence of volatile compounds compared to the control. They ranged from 254.78 mg/dm3 (V3 - Lumax 538 SC) to 544.27 mg/dm3 (V1 - Pledge 50 WP).

It was noteworthy that the wines from the 2018 harvest had accumulated more volatile compounds than the wines from the next harvest. This was due to the characteristic individual climatic features of each of the two years.

The established total content of higher alcohols in the wines of the 2018 harvest defined the control as a variant with the lowest content of these components (220.18 mg/dm3). Significantly higher amounts of higher alcohols were identified in the experimental variants, ranging from 268.06 mg/dm3 (V2 - Lumax 538 SC) to 491.01 mg/dm3 (V1 - Pledge 50 WP).

An identical trend was observed for wines from the 2019 harvest. The lowest content of higher alcohols was identified in the control (63.90 mg/dm3). The experimental variants showed a higher total amount of higher alcohols, ranging from 138.06 mg/dm3 (V1 - Pledge 50 WP) to 179.37 mg/dm3 (V2 - Lumax 538 SC). The trend of higher amounts of higher alcohols in wines from the 2018 harvest, compared to those of the 2019 was visible again (the same trend like that of the total content of volatile compounds).

As a number of identified representatives of the fraction of higher alcohols in wines from the harvest 2018 were identified 9 compounds, and in those of the harvest 2019 - 5. The main representatives identified in all studied variants of wines from the harvest 2018 were: 1-propanol, 2-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol and 4-methyl-2-pentanol. The wines of the 2019 harvest were dominated by 2-methyl-1-butanol and 3-methyl-1- butanol.

From the fraction of higher alcohols in wines from the 2018 harvest at the highest concentration was identified 3-methyl-1-butanol. Its lowest amount was identified in the control sample (149.71 mg/dm3). In the experimental variants it varied from 158.67 mg/dm3 (V2 – Lumax 538 SC) to 331.69 mg/dm3 (V1 - Pledge 50 WP). In the wines of the 2019 harvest, this higher alcohol was also dominant quantitatively. The lowest detected amount (38.82 mg/dm3) was identified in variant V2 (Lumax 538 SC). The other two experimental variants (V1 - Pledge 50 WP and V3 - Guild) showed higher concentration of 3-methyl-1-butanol (95.99 mg/dm3 and 83.13 mg/dm3, respectively) compared to the untreated control (42.60 mg/dm3). 3-methyl-1-butanol was the main higher alcohol of wine. The data obtained in the present study correlated with other studies that detected this higher alcohol in amounts between 200.00 - 500.00 mg/dm3 (Gil *et al*., 2006; Chobanova, 2012) [3, 6].

2-methyl-1-butanol was also a major higher alcohol in the wine volatile fraction. In wines from the 2018 harvest, it was identified in the lowest concentration in the control sample (31.83 mg/dm3). All experimental variants contained it in a higher amount, which varied from 37.82 mg/dm3 (V2 Lumax 538 SC) to 60.21 mg/dm3 (V1 - Pledge 50 WP). A similar trend was observed in the wines of the 2019 harvest. Very close, almost identical concentrations of 2-methyl-1-butanol were observed in control and experimental variant V2, 21.25 mg/dm3 and 21.14 mg/dm3, respectively. The other variants showed higher concentrations, 43.91 mg/dm3 (V3- Guild) and 41.97 mg/dm3 (V1-Pledge 50 WP), respectively. According to other studies, the content of 2-methyl-1-butanol in wines varied from 19.22 - 231.00 mg/dm3 (Oliva *et al*., 1999; Pozo-Bayon *et al*., 2010; Martinez-Gil *et al*., 2012). Gutierrez-Gamboa *et al*. (2017) [17, 20, 8] investigated the effect of foliar nitrogen fertilization of Cabernet Sauvignon and found the presence of 2-methyl-1-butanol in a control sample of a wine from the variety (without treatment) of 52.84 mg/dm3. The data in our study were fully correlated with the above studies.

2-butanol was the main representative in the wines of the 2018 harvest. The trend of its established concentration was similar to that of the other main higher alcohols, namely - the lowest concentration found in the control variant (38.44 mg/dm3). In the experimental variants, it ranged from 41.14 mg/dm3 (V3 - Guild) to 98.16 mg/dm3 (V1 - Pledge 50 WP). In the wines of the next harvest (2019) 2-butanol was absent in the control. In the experimental variants it was found in a concentration of 0.05 mg/dm3 (V1 - Pledge 50 WP) to 119.36 mg/dm3 (V2 - Lumax 538 SC). 2-butanol was identified as a major representative of higher alcohols in another study (Slaghenaufi *et al*., 2020) [21].

Another major representative of the higher alcohols for the wines of the 2018 harvest, which was absent in those of the next harvest, was 1-propanol. Its concentration in the control sample was identical to that of the wine of variant V1 (0.05 mg/dm3). The other two variants showed higher concentration of this alcohol, as in V3 (Guild) it was 13.96 mg/dm3, and in V2 (Lumax 538 SC) - 10.58 mg/dm3. This component was found in red wines at concentrations averaging 29.50 - 71.50 mg/dm3 (Gil *et al*., 2006) [6]. In another study of the volatile composition of 11 wines, it was found in concentrations from 47.62 mg/dm3 to 507.29 mg/dm3 (Chung *et al*., 2015) [4].

4-methyl-2-pentanol was been identified only in wines from the 2018 harvest. Its amounts were identical in absolutely all variants (0.05 mg/dm3).

2-propanol was not been identified only in the control sample of wines from harvest 2018. In the experimental variants, this compound varied in concentrations from 0.05 mg/dm3 (V1 - Pledge 50 WP and V2 - Lumax 538 SC) to 125.39 mg/dm3 (V3 - Guild). In the wines of the 2019 harvest, 2-propanol was identified only in variant V3 (11.47 mg/dm3).

In the wines of the 2018 harvest, in separate variants, 1-butanol, 1-pentanol and 2-phenylethanol were identified. The first was found only in variant V2 (0.05 mg/dm3), the second was not identified only in variant V1, in the others it ranged from 0.05 - 13.51 mg/dm3, and 2-phenylethanol was identified only in the control sample (0.05 mg/dm3). This higher alcohol was also identified in three of the 2019 harvest variants (control, V1 and V2) in the same concentration.

The results obtained for the quantitative presence of higher alcohols in the studied wines in summary indicated that the treatment of experimental plantations with herbicides led to higher concentrations of individual higher alcohols, as in almost all cases their quantities were higher than that in the untreated control, which as a result increased the chemical complexity of the wines.

Considering the total content of esters in the wines of the 2018 harvest, it could See that it was the lowest in the control variant (40.33 mg/dm3). All experimental variants showed higher esters levels, with a very high final concentration (412.27 mg/dm3) secreted in variant V3 (Guild). For the wines of the next harvest (2019), the content of esters was the lowest in variant V3 (Guild) (10.86 mg/dm3), followed by the control, in which a slightly higher content of esters (12.25 mg/dm3) was identified. The highest was the quantitative presence of esters in the wine of variant V1 (Pledge 50 VP) - 262.43 mg/dm3. In general, this harvest was characterized by a lower quantitative ester accumulation compared to the 2018 harvest. By species representatives in the wines of the 2018 and 2019 harvests, four esters have been identified.

In the wines of the 2018 harvest, the main ester representatives (identified in all studied variants) were ethyl acetate and ethyl decanoate. Ethyl acetate ranged from 0.05 mg/dm3 (V3-Guild) to 46.93 mg/dm3 (V1-Pledge 50 WP). In young wines, the ester rarely exceeds 50.00 - 80.00 mg/dm3 (Chobanova, 2012) [3], and Cortez-Dieguez *et al*. (2015) found this ester in young red wines from northwestern Spain in amounts of 23.48 mg/dm3 - 78.36 mg/dm3. The data in our study were fully correlated with the cited studies.

Ethyl decanoate was the other main ester present in the wines of the 2018 harvest. It varied from 0.05 mg/dm3 (control V1) to 412.37 mg/dm3 (V3 - Guild). In the wines of this harvest, very low amounts of phenyl acetate and pentyl acetate were identified in some of the samples. The main ester for the wines of the next harvest (2019) was propyl acetate. It was identified in the lowest amount (10.86 mg/dm3) in variant V2 (Lumax 538 SC). In the other wines it varied from 12.20 mg/dm3 (control) to 63.01 mg/dm3 (V3 - Guild). Isopentyl acetate was identified in three of the variants (control, V1 and V3), with concentrations ranging from 0.05 mg/dm3 to 6.35 mg/dm3. The other two esters identified were ethyl decanoate (found only in variant V1 - 207.69 mg/dm3) and ethyl butyrate (found in very low amounts - 0.05 mg/dm3), only in the control.

The aldehyde fraction was represented by acetaldehyde. For the wines of the 2018 harvest, it was found in the highest concentration (218.20 mg/dm3) in the control. In the experimental variants, it ranged from 0.05 mg/dm3 (V1 and V2) to 57.21 mg/dm3 (V3). In the wines of the next harvest, acetaldehyde was again found in the highest concentration in the control (129.45 mg/dm3). In the experimental variants, it ranged from 35.44 mg/dm3 (V2 - Lumax 538 SC) to 124.29 mg/dm3 (V3 - Guild). The normal concentration of acetaldehyde is in the range of 10.00 - 200.00 mg/dm3 (Chobanova, 2012) [3]. Almost all results in the current study correlated with this range, with the exception of the control in the 2018 harvest, where the amount of this aldehyde was found to be slightly above 200.00 mg/dm3. Cabernet Sauvignon is a non-muscat variety in which the amount of terpenes is normally lower. The wines of the 2018 harvest had the highest total terpene content in variant V2 (0.15 mg/dm3). Terpenes was not found in variant V1, and variant V3 showed a lower terpene content (0.05 mg/dm3) than the control (0.10 mg/dm3).

The wines of the 2019 harvest showed a slightly higher total terpene content compared to those of the previous harvest. It was highest again in variant V2 (0.23 mg/dm3). In the other variants it varied from 0.10 mg/dm3 (control and V3) to 0.15 mg/dm3 (V1).

Four terpenes were identified as species representatives in the wines of the 2018 and 2019 harvests. Their quantities in the 2018 harvest were low and individual terpenes were identified in separate variants. In the wines of the 2019 harvest, only geraniol was identified in slightly higher concentrations. It was not established only in variant V3. In the control sample, this terpene was identified in the lowest amount (0.05 mg/dm3) and the highest geraniol content was established in variant V2 (Lumax 538 SC) (0.13 mg/dm3).

Methanol was also a constant and normal component of the volatile composition. Its content in the control sample of wines from the 2018 harvest was the lowest (39.27 mg/dm3). In the experimental variants it varied from 53.65 mg/dm3 (V2 - Lumax 538 SC) to 118.50 mg/dm3 (V1 - Pledge 50 WP). In the wines of the next harvest (2019) again its content was the lowest in the control (23.51 mg/dm3). In the experimental variants of this harvest, it varied in lower concentrations compared to the previous harvest, namely from 28.88 mg/dm3 (V2 - Lumax 538 SC) to 78.12 mg/dm3 (V1 - Pledge 50 WP). According to the OIV, the normal presence of methanol in red wines is allowed up to 400.00 mg/dm3 (OIV, 2015). All wines analyzed in the present study contained it in concentrations several times lower than the maximum allowable, which made wines absolutely toxicologically harmless.

Conclusions

The following conclusions can be made from the study Wines from the 2018 harvest were characterized by a higher total content of volatile compounds compared to those of the 2019 harvest. This was due to the individual climatic conditions of the year.

- All experimental variants, in both harvests, were characterized by higher levels of higher alcohols compared to controls. This confirmed the effectiveness of herbicide treatment of experimental plantations on improving of the synthesis of higher alcohols in the fermentation process.
- Nine higher alcohols were identified in the wines of the 2018 harvest, the main representatives of which are: 1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol and 4-methyl-2-pentanol. Their species composition in the wines of the next harvest (2019) was poorer, with 5 representatives identified, of which 2-methyl-1- butanol and 3-methyl-1-butanol quantitatively dominate.
- For the wines of the 2018 harvest, the lowest total ester content was found in the control. All experimental wines from this harvest contained higher amount of esters. At the

next harvest (2019) the lowest ester concentration was found in variant V3, followed by the control. The other two variants had higher amounts of esters.

- The main esters in the wines of the 2018 harvest were ethyl acetate and ethyl decanoate, and in the 2019 harvest - propyl acetate.
- The one aldehyde - acetaldehyde was identified in wines.
- The wines of both harvests were characterized by low total terpene content. This is a normal trend, because Cabernet Sauvignon is a non-muscat variety.
- The established concentrations of methyl alcohol in wines were normal, many times lower than the maximum permissible, which made wines toxicologically harmless.
- The study showed that the treatment with the herbicides Guild, Lumax 538 SC and Pledge 50 WP of experimental plantations of Cabernet Sauvignon led to improved synthesis of higher alcohols and esters in wines, which reflected in improving of their volatile and aromatic quality.

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