Influence of foliar fertilizers application on the volatile composition of red wines

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Abstract

Introduction.The aim of the present study was to determine the influence of different foliar fertilizers (in four harvests – 2019, 2020, 2021, and 2022) on the composition of volatile and aromatic compounds of red wines from the Bulgarian hybrid variety Storgozia.

Materials and methods. Gas chromatography-flame ionization detection was used to determine the volatile compounds in red wines.

Results and discussion. The results obtained regarding the total content of volatile compounds in the analyzed wines showed that the variant of vine treatment with fertiliser MaxGrow NS, consist of N, 20%, S, 7%, Mg, 14%, P, 5%, Mn, 1%, Zn, 0.01%, Cu, 0,05%, Fe, 0.05), Cu, 0.01%, Zn, 0.01%, B, 0.025%, Mo, 0.002%, demonstrated final high levels of volatile and aroma compounds in wines of three from the four investigated harvests (2019, 2020 and 2021). As individual representatives from the group of higher alcohols, 2-methyl-1-butanol and 3-methyl-1-butanol dominated in all four harvests. The two alcohols are the main metabolites of the yeast microflora. The application of different foliar fertilizers did not negatively affect the acetaldehyde content in the resulting wines. Its presence corresponded to the appearance of its positive influence. From the obtained results, it could be concluded that in the 2020 and 2022 harvests, the foliar application of nitrogen and mineral sources affected the content of esters. In the other two harvests, individual variants showed higher ester accumulation than the untreated control, but others demonstrated lower levels. As a result, no specific conclusion could be made about the influence of foliar fertilizers on the final wines ester concentrations. A major ester from this fraction was ethyl acetate. Foliar fertilization affects the synthesis of ß-citronellol, leading to increased levels of this terpene. Conversely, for geraniol, a decrease in its concentrations was observed in the wines obtained after the application of foliar fertilization.

Conclusions. The application of foliar fertilizers led to changes in composition of volatile compounds of the researched red wines and influenced both on the different groups of volatiles and individual compounds.

Introduction

The need for organic and ecological agriculture at the current stage is fundamental due to the significant climate changes. They are a stress factor not only for vine plants but also for different crops. This stress is formed because of extreme, unpredictable and unexpected changes in weather, which can lead to a significant reduction in the yield of the vine and the composition of the grapes (Azabard, 2022; van Leeuwen and Dariet, 2016). The vine is a plant with high sensitivity to extreme high temperatures, and the heat stress caused by them significantly affects the content of organic acids, the titratable acidity and pH of the grapes (Hewitt et al., 2023; Venios et al., 2020). Increasing temperatures and decreasing rainfalls, intensifying grape ripening, lead to a deterioration of the aromatic wine profile (Gutiérrez-Gamboa, 2018). This necessitates the application of various viticultural practices to ensure controlled metabolic development of the vine, improving the yield and quality of its grapes. One of the essential treatments in this aspect is mineral fertilization. Nitrogen has a significant impact on the metabolomics and life cycle of the grapevine, and directly affects the yield, composition and quality of its fruit (Delas et al., 1991; Soubeyrand et al., 2014). Foliar fertilization is an effective strategy for improving crop nutrition when the soil is poor in nutrients and under dry climatic conditions (Lv et al., 2017). It essentially represents spraying of nutrients on the canopy of the crops, which leads to the direct absorption of these substances by the crop leaves and stems (Cooper, 2003). It is actively entering in viticulture, due to the improved and efficient assimilation of nitrogen and mineral components, improving the vitality of the vine and the qualitative composition of grapes and wine (Rubio-Bretón et al., 2018).

Wine, being a product of grape juice fermentation by the yeast belonging to the genus *Saccharomyces*, contains many volatile compounds produced mostly due to the yeast metabolic activity. These compounds includes higher alcohols, aldehydes and ketones, esters, terpenes, lactones, phenols, the amounts of which varied from a few ng/l to hundreds of mg/l (Delgado et al., 2020; Manolache et al., 2018; Tang et al., 2019). However, it was reported that some of volatile compounds present in wine come into wine directly from the grapes (Cordente et al., 2012; González-Barreiro et al., 2015).

Higher alcohols are synthesized by yeasts that metabolize sugars and amino acids (direct precursors for higher alcohols formation) (Bell and Henschke, 2005).The biological synthesis of esters is also associated with yeasts metabolism during alcoholic fermentation. This is a clear indicator that the presence of nitrogen in the must (vitally necessary for the yeasts) is extremely important for the proper course of fermentation and generating aromatic compounds that determine the wine quality (Lacroux et al., 2008; Miller et al., 2007).

In the scientific literature, there are not many studies determining the influence of foliar fertilization directly on the wine's aromatic profile. Trdenić et al. (2020) determined the effect of foliar application of K, B and other microelements on the content of aromatic compounds in grapes of the white variety Škrlet bijeli from Croatia. The team identified the presence of 24 volatile compounds in the three years study. In two of the harvests (2013 and 2014) Trdenić et al. (2020) found high contents of 1-hexanol, linalool, ß-damascenone, trans-2-hexenal and geranyl-acetone. Lacroux et al. (2008) found that N and S foliar fertilization of Sauvignon Blanc vines improved the aromatic profile of wines by increasing the volatile thiols and glutathione. On the other hand, Rubio-Bretón et al. (2012) when studying the foliar application of two nitrogen sources – phenylalanine and urea, applied as fertilizers to vines of the red Tempranillo variety, concluded that the studied nitrogen sources did not change the wine aromatic profile. Gutiérrez-Gamboa et al. (2018) investigated the effect of applying different foliar nitrogen fertilizers on Cabernet Sauvignon wines. The team found that the urea + sulfur treatments and the application of a commercial BA preparation had a positive effect by increasing the amounts of three very important wine esters – ethyl hexanoate, ethyl octanoate and ethyl decanoate. When treated with urea and arginine, the team found an accumulation of high total levels of terpenes, which are a product of the vine.

The aim of the present study was to determine the influence of different foliar fertilizers on the production of volatile and aromatic compounds in red wines from the Bulgarian hybrid variety Storgozia.

Materials and methods

Variety and plantation

The red hybrid grapevine variety Storgozia grafted on the rootstock Berlandieri x Riparia selection Oppenheim 4 was used in the study. The plantation was located on the territory of the Experimental Base of Institute of Viticulture and Enology (IVE)-Pleven in the area "Tomovskoto". The variety was planted according to a scheme of 1 m intra-row and 2.5 m inter-row distance, in which there were 4000 vines per hectare. They were trained monostemmed and with a single cordon at a height of 1 m. The rows were oriented in the southeast-northwest direction. The exposure had a slight slope to the north. The support structure consisted of one supporting wire 100 cm from the ground, and two pairs for shoots tucking in, respectively 30 and 60 cm above it. The load on the vines was leveled at 20 buds provided through spurs and fruit canes.

Experimental variants of foliar fertilization

The Ka-Bor liquid fertilizers (Agro-Bio Trading Ltd., Bulgaria) and the Max Grow series (Maxgrow Chemical Ltd. Bulgaria), recommended for vineyards, were tested. Applied fertilizers differed by their elemental composition. Content of macronutrients – nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), magnesium (Mg) and micronutrients – iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), chlorine (Cl), molybdenum (Mo). The influence of every single nutrient on vine is related with: nitrogen stimulates growth, grape berries size, bunch weight, it is component of enzymes, vitamins and chlorophyll; phosphorus participates in nucleic acids, phosphoric esters, lipids and nucleotides, participates in energy transfer and has a direct effect on the grapes quality and yield; potassium increases the growth of the vine root system, increases the disease resistance and the content of sugars in grapes; sulfur is a component of enzymes and proteins, participates in photosynthesis, increases resistance to diseases; calcium is extremely important for grape berries strength, leaf growth and disease resistance; magnesium participates in photosynthesis, protein synthesis, grapes quality and yield; boron improves the growth of the root system and aerial parts, increases the content of sugars and increases the yield; zinc stimulates general root growth, increases sugar content, berries strength and yield; Mn, Cu, and Fe increase photosynthetic activity and the development of leaf mass.

The scheme of the experiment contained six variants; each with four repetitions of five vines is shown (Table 1).

The soil type was chernozem. The vineries were grown without irrigation. For the purpose of the research, soil fertilization was excluded from the plantation agrotechnics. Foliar feeding was carried out four times and with doses recommended by the manufacturer.

Table 1

Experimental vines variants and doses of fertilizers application

Vines	Fertilizer	Content of elements, %	Amount of fertilizer, ml/ha
V1	Control – untreated	-	-
V2	Ka-Bor	K, 12; Ca, 6; B, 1.5	600
V3	Max Grow 999	N, 9; P, 9; K, 9; Fe, 0.05; Mn, 0.025; Cu, 0.01; Zn, 0.01; B, 0.025; Mo, 0.02	5000
V4	Max Grow PK	N, 3; P, 20; K, 22; Fe, 0.05; Mn, 0.025; Cu,0.01; Zn, 0.01; B, 0.025; Mo, 0.002	4000
V5	Max Grow NS	N, 20; S, 7; Mg, 14; P, 5; Mn, 1; Zn, 0.01; Cu, 0.5	5000
V6	Max Grow Co.	Max Grow 999*, Max Grow PK, Max Grow NS as 2V3 + V4 + V5	Dose for fertilizer was indicated above

* Max Grow 999 was taken in double dose

Vinification. The study was conducted at the IVE – Pleven. The object of the present study were red wines obtained from four harvests (2019, 2020, 2021 and 2022) of the Storgozia variety. The grapes for each studied variant (30 kg each) were picked and vinified in the IVE Experimental Wine Cellar in the conditions of microvinification, according to the classic scheme for the production of red wines (González-Neves et al., 2013): crushing – destemming – sulphitation (50 mg/kg SO_2) – alcoholic fermentation with SIHA Rubio Cru yeast *Saccharomyces cerevisiae* from Eaton's Begerow: 20 g of dry yeast per 100 l at temperature 28°C – separation from solids – additional sulphitation – storage.

Gas chromatography-flame ionization detection (GC-FID) of the wine's volatile composition. The content of the main volatile and aromatic compounds was determined based on a stock standard solution prepared in accordance with IS 3752:2005 method. The method describes the preparation of a standard solution of one congener, but the preparation step was followed to prepare a solution of more compounds. The standard solution in the present study included the following compounds (purity > 99.0%): acetaldehyde, ethyl acetate, methanol, 2-propanol, isopropyl acetate, 1-propanol, 2-butanol, propyl acetate, 1-butanol, isobutyl acetate, ethyl butyrate, 2-butyl acetate, 2-methyl-1-butanol, 3-methyl-1-butanol, 4-methyl-2-pentanol, 1-pentanol, pentyl acetate, 1-hexanol, ethyl hexanoate, hexyl acetate, 1-heptanol, linalool oxide, dimethyl succinate, phenyl acetate, linalool , ethyl caprylate, 2-phenylethanol, α-terpineol, nerol, ß-citronellol, geraniol, ethyl decanoate.

The prepared standard solution containing all compounds was injected in an amount of 2 µl into a 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 flame ionization detector (FID). The carrier gas was helium. Hydrogen to support combustion was supplied to the chromatograph via a hydrogen bottle. The injection was manual, using a microsyringe.

The gas chromatographic determination parameters were: injector temperature – 220 °C, detector temperature – 250 °C, initial oven temperature – 35 °C/1 min retention, rise to 55 °C with a step of 2 °C/min for 11 min, rise to 230 °C with a step of 15 °C/min for 3 min. Total chromatography time – 25.67 min. After the retention times of the compounds in the standard solution were determined, the identification and quantification of the volatile compounds in the wines were conducted. The volatile composition was determined based on the injection of wine distillates. Samples were injected in an amount of 2 µl into a gas chromatograph and identification and quantification of volatile compounds was performed.

Statistical data processing. Statistical processing of the data was performed, including determination of average content and standard deviation (±SD), with four replications (four harvests) for the main compounds identified in all of the four analized harvests. The statistical data processing was carried out using the Excel 2007 program (Microsoft Corporation, USA).

Results and discussion

The obtained results of the performed gas-chromatographic analysis of the wines from the respective four harvests (2019, 2020, 2021 and 2022) are presented in Tables 2 – 5.

Changes of the wines total volatile content by harvests

The highest total content of volatile compounds in the wines of the 2019 harvest was found in the variant V6. The determined concentration of volatile compounds in this combined variant of foliar fertilization was more than 4 times higher, compared to the untreated control. High levels of total volatile compounds were also reported in variants V5 and V3. Variant V2 showed a lower content of volatile components than the control, and variant V4 demonstrated a slightly lower level than the control. For the total amount of volatile compounds in the wines from the next harvest (2020) a different trend was observed. In this harvest, all experimental wines accumulated a significantly higher amount of volatile compounds, compared to the control. Very high concentration of total volatile compounds was found here in variants V2 and V5. They were respectively more than 24 times and more than 14 times higher compared to the untreated control. In the third harvest (2021), the wine of variant V5 dominated in terms of total volatile compounds concentration. In this harvest, it was noticeable that the levels of volatile compounds in the experimental variants were not significantly higher than those of the control variant. A correlation could be drawn here with the first harvest (2019), where variants V2 and V4 also showed lower total volatile content than the control variant. In contrast, for all three harvests (2019, 2020 and 2021) a high final amount of volatile compounds was observed for variant V5. In the last harvest (2022), only variant V2 showed levels of volatile compounds lower than the control. The highest total content of volatile compounds in this harvest was found in variant V3. The V4 variant also showed high levels.

The results obtained regarding the total content of volatile compounds in the analyzed wines indicated that in three of the harvests – 2019, 2021 and 2022, the V2 variant showed levels of total volatile compounds lower than the control. The most constant in terms of high final content of volatile compounds turned out to be variant V5, which demonstrated final high levels in wines of three from the four investigated harvests (2019, 2020 and 2021). In this variant of used foliar fertilizer, the amounts of nitrogen are the highest. This led to more nitrogen in the grapes and during fermentation has led to the stimulation of the yeasts metabolic action and the secretion of higher amounts of volatiles.

Table 2

Gas-chromatographic analysis, harvest 2019

Identified compounds	Content in wines, mg/l, from vines					
	V1	V2	V3	V4	V5	V6
Ethyl alcohol, vol.%	13.63	14.25	13.02	13.06	12.56	12.66
Acetaldehyde	45.81	22.85	52.08	10.39	308.85	511.77
Methanol	7.33	7.01	35.27	65.74	198.72	115.14
2-methyl-1-butanol	45.69	3.85	28.16	46.28	110.94	302.46
3-methyl-1-butanol	102.25	8.39	17.07	96.20	230.08	71.57
2-phenyl ethanol	nd	24.75	320.65	nd	nd	nd
1-propanol	nd	nd	22.59	9.00	ND	153.48
2-propanol	nd	nd	19.92	7.23	304.51	nd
Total higher alcohols	147.94	36.99	408.39	158.71	645.53	527.51
Ethyl acetate	22.17	38.55	247.35	6.31	155.36	286.95
Pentyl acetate	nd	nd	54.13	nd	nd	nd
Isopentyl acetate	23.48	ND	66.74	31.54	nd	116.86
Propyl acetate	27.69	12.46	119.69	77.03	nd	nd
Isopropyl acetate	nd	nd	5.63	1.51	nd	nd
Ethyl hexanoate	50.58	nd	nd	nd	nd	nd
Phenyl acetate	nd	nd	85.20	nd	nd	168.59
Ethyl caprylate	16.62	nd	nd	nd	nd	nd
Hexyl acetate	28.13	nd	nd	2.67	nd	nd
Total esters	168.67	51.01	578.74	119.06	155.36	572.40
Nerol	nd	nd	0.10	0.20	nd	nd
β – citronellol	nd	0.56	nd	0.63	nd	nd
Geraniol	0.75	nd	0.14	0.12	nd	nd
Total terpenes	0.75	0.56	0.24	0.95	nd	nd
Total content	370.50	118.42	1074.72	354.85	1308.46	1726.82

*nd – not detected
**Statistical data (Average ± SD) for four main compounds (acetaldehyde, methanol, 3-methyl-1-butanol and ethyl actate) identified in all harvests analysed is shown in Table 6.

Table 3

Gas-chromatographic analysis of wines, harvest 2020

Identified compounds	Content in wines, mg/l, from vines					
	V1	V2	V3	V4	V5	V6
Ethyl alcohol, vol.%	12.64	12.18	12.30	12.02	12.35	13.01
Acetaldehyde	8.58	102.44	200.88	119.41	162.63	81.25
Methanol	9.47	193.44	86.03	166.11	270.62	199.69
2-methyl-1-butanol	8.69	586.46	134.12	nd	169.13	nd
3-methyl-1-butanol	18.89	1500.35	137.58	126.60	439.75	66.36
1-propanol	0.05	0.05	nd	0.05	68.36	nd
2-propanol	nd	nd	nd	nd	nd	56.26
1-pentanol	nd	0.05	0.05	nd	nd	nd
1-heptanol	0.05	nd	nd	nd	nd	nd
2-phenylethanol	0.05	nd	nd	305.88	nd	0.05

Table 3 ***(Continue)***

Identified compounds	Content in wines, mg/l, from vines					
	V1	V2	V3	V4	V5	V6
Total higher and aromatic alcohols	27.73	2086.91	271.75	432.53	677.24	122.67
Ethyl acetate	47.78	72.30	174.94	263.15	212.37	205.71
Pentyl acetate	nd	nd	0.05	0.05	nd	nd
Isopentyl acetate	6.03	86.35	119.10	109.13	167.90	72.68
Propyl acetate	9.37	199.35	nd	nd	138.97	nd
Isopropyl acetate	nd	0.05	0.05	0.05	0.05	0.05
Phenyl acetate	nd	nd	nd	nd	0.05	nd
Ethyl caprylate	nd	nd	nd	nd	0.05	0.05
Total esters	63.18	358.05	294.14	372.38	519.39	278.49
Linalool oxide	0.32	nd	nd	0.05	nd	nd
α – terpineol	0.05	nd	nd	nd	nd	0.05
Nerol	0.05	nd	nd	0.65	nd	0.74
β – citronellol	0.05	0.05	0.14	nd	0.05	0.05
Geraniol	0.53	0.69	nd	0.41	0.10	0.23
Total terpenes	1.00	0.74	0.14	1.11	0.15	1.07
Total content	109.96	2741.58	852.94	1091.54	1630.03	683.17

*nd – not detected
**Statistical data (Average ± SD) for four main compounds (acetaldehyde, methanol, 3-methyl-1-butanol and ethyl actate) identified in all harvests analysed is shown in Table 6.

Table 4

Gas-chromatographic analysis of wines, harvest 2021

Identified compounds	Content in wines, mg/l, from vines					
	V1	V2	V3	V4	V5	V6
Ethyl alcohol, vol.%	11.69	12.11	12.36	12.10	10.83	15.44
Acetaldehyde	13.92	13.45	8.77	67.26	27.56	19.33
Methanol	64.95	79.20	50.08	33.00	173.43	173.35
2-methyl-1-butanol	36.45	19.66	19.28	13.63	30.45	21.35
3-methyl-1-butanol	62.91	35.31	33.88	38.85	41.83	36.54
2-propanol	nd	nd	13.35	9.74	nd	nd
1-pentanol	nd	nd	18.79	nd	21.43	nd
2-butanol	ND	24.32	nd	nd	18.12	31.77
1-heptanol	43.20	nd	76.02	nd	nd	nd
2-phenylethanol	193.93	70.17	257.14	nd	nd	nd
Total higher and aromatic alcohols	336.49	149.46	418.46	62.22	111.83	89.66
Ethyl acetate	58.82	27.27	20.04	18.18	71.06	58.71
Pentyl acetate	nd	nd	nd	nd	39.78	nd
Isopentyl acetate	5.22	nd	nd	6.30	30.98	6.91
Propyl acetate	nd	nd	nd	14.68	nd	nd
Isopropyl acetate	nd	6.52	7.98	11.41	20.03	7.67
Phenyl acetate	nd	29.41	nd	nd	38.68	9.48

Table 4 *(Continue)*

Identified compounds	Content in wines, mg/l, from vines					
	V1	V2	V3	V4	V5	V6
Ethyl hexanoate	nd	nd	nd	nd	112.74	nd
Total esters	64.04	63.20	28.02	50.57	313.27	82.77
Linalool oxide	0.42	nd	0.43	0.96	nd	nd
α – terpineol	nd	0.15	0.20	0.55	nd	nd
Nerol	nd	0.10	nd	nd	nd	nd
β – citronellol	0.12	0.24	0.33	0.15	nd	0.12
Geraniol	0.29	nd	0.15	nd	0.94	0.17
Total terpenes	0.83	0.49	1.11	1.66	0.94	0.29
Total content	480.23	305.80	506.44	214.71	627.03	365.40

*nd – not detected
**Statistical data (Average ± SD) for four main compounds (acetaldehyde, methanol, 3-methyl-1-butanol and ethyl actate) identified in all harvests analysed is presented in Table 6.

Table 5

Gas-chromatographic analysis of wines, harvest 2022

Identified compounds	Content in wines, mg/l, from vines					
	V1	V2	V3	V4	V5	V6
Ethyl alcohol, vol.%	13.15	12.77	11.59	11.90	12.53	12.76
Acetaldehyde	68.44	46.98	69.02	67.22	103.75	7.83
Methanol	7.64	2.07	18.26	8.00	8.02	4.14
2-methyl-1-butanol	22.26	13.41	16.21	12.07	6.61	12.99
3-methyl-1-butanol	26.09	45.53	90.81	52.78	43.61	94.34
4-methyl-2-pentanol	nd	nd	nd	nd	2.57	nd
1-propanol	4.84	2.49	nd	12.31	3.05	3.49
2-propanol	nd	nd	2.18	nd	nd	nd
1-pentanol	nd	nd	nd	nd	4.36	nd
1-butanol	21.44	nd	nd	112.75	nd	44.19
2-butanol	nd	nd	139.39	5.89	nd	nd
Isobutanol	nd	nd	nd	1.55	nd	nd
1-heptanol	15.81	8.13	nd	nd	nd	nd
1-hexanol	nd	12.97	nd	nd	nd	nd
2-phenylethanol	55.11	nd	nd	60.86	165.28	40.65
Total higher and aromatic alcohols	145.55	82.53	248.59	258.21	225.48	195.66
Ethyl acetate	21.68	4.96	106.55	31.91	15.18	29.77
Pentyl acetate	13.79	14.18	7.81	nd	nd	nd
Diethyl succinate	nd	nd	49.85	ND	18.97	nd
Propyl acetate	nd	nd	1.69	nd	nd	nd
Isopropyl acetate	nd	nd	nd	10.44	nd	nd
Butyl acetate	nd	nd	12.60	nd	1.79	nd
Isobutyl acetate	36.73	nd	nd	nd	102.56	nd

Table 5 ***(Continue)***

Identified compounds	Content in wines, mg/l, from vines					
	V1	**V2**	**V3**	**V4**	**V5**	**V6**
Phenyl acetate	nd	nd	72.39	220.26	nd	nd
Ethyl hexanoate	nd	nd	182.85	78.21	nd	46.87
Ethyl butyrate	nd	nd	70.76	nd	nd	nd
Ethyl caprylate	23.59	173.25	nd	nd	nd	nd
Hexyl acetate	nd	nd	153.84	nd	nd	90.27
Ethyl decanoate	23.43	nd	nd	nd	nd	nd
Total esters	119.22	192.39	656.65	340.82	138.50	166.91
Linalool oxide	nd	nd	nd	nd	nd	0.36
Linalool	0.11	0.64	nd	nd	0.16	0.86
β – citronellol	0.19	nd	nd	nd	nd	nd
Geraniol	nd	0.16	0.82	0.14	nd	nd
Total terpenes	0.30	0.80	0.82	0.14	0.16	1.22
Total content	341.15	324.77	993.34	674.39	475.91	375.76

*nd – not detected
**Statistical data (Average ± SD) for four main compounds (acetaldehyde, methanol, 3-methyl-1-butanol and ethyl actate) identified in all harvests analysed is shown in Table 6.

Changes of total and individual content of higher and aromatic alcohols in the analyzed wines by harvests.

Higher alcohols are a product of yeast amino acid metabolism. In the present study, the analysis of their total and individual concentrations was directly related to the presence of free nitrogen and amino acids in the grapes of the vine, which were directly affected by the applied foliar fertilizers. The concentration of higher alcohols in red wines can reach 600.00 mg/l (Chobanova, 2012).

In Storgozia wines from the 2019 harvest, only variant V2 showed total levels of higher alcohols significantly lower than the control. The highest content of higher alcohols was found in variants V5 and V6, which was respectively 4.36 and 3.56 times higher than that generated in the control wine.V3 variant also showed high final levels of higher alcohols. In the next harvest (2020), in all experimental wine variants, significantly higher quantitative levels of higher alcohols were obtained, comparing them with the control variant. Very high final level in variant V2 was obtained – 75 times higher than that found in the control variant. High final levels of higher alcohols in this harvest were also found in the variants V5 and V4. They were respectively 24 and 15 times higher than the control. In the wines of the 2021 harvest, however, the trends were significantly different. Almost all experimental variants in this harvest showed total higher alcohol levels lower than the control. Only variant V3 accumulated more in comparison with the control. In the last harvest (2022), the trend of higher alcohols accumulation was similar to the first two. In this harvest, only variant V2 accumulated a lower amount of total higher alcohols than the control. The highest levels of higher alcohols in this year had the wines of variants V4, V3 and V5.

The different foliar fertilizers had a positive effect on the accumulation of higher alcohols in three of the four investigated harvests. Significant amounts of these wine aroma components were established. Variant V5 showed consistent accumulation of high amounts higher alcohols in three of the four harvests examined – 2019, 2020 and 2022, and variant V4 showed high levels in two of the harvests examined – 2020 and 2021. Moreover, since the formation of higher alcohols by yeasts during alcoholic fermentation is directly influenced by the accumulation of assimilable nitrogen in the must, the positive influence on the higher alcohols yeasts production based on the application of foliar fertilization of vines from the hybrid variety Storgozia could be outlined.

As individual representatives from the group of higher alcohols, 2-methyl-1-butanol and 3-methyl-1-butanol dominated in all four harvests. The two alcohols are the main metabolites of the yeast microflora. Only two of the experimental variants of the investigated wines from the 2019 harvest showed a significantly higher amount of 2-methyl-1-butanol – V5 and V6, compared to the control variant. Variant V4 showed a very close (almost comparable) concentration of this compound to the control, while the other two variants – V2 and V3 showed lower levels of this higher alcohol and in the V2 variant they were very low. The trend of the presence of 2-methyl-1-butanol in the next harvest (2020) was not identical. In this particular harvest, high levels of this higher alcohol were found in variant V2, exceeding those found in the control. In the wines of the 2021 harvest, a trend towards lower levels of 2-methyl-1-butanol was found in the experimental variants, compared to the control. Thus, in the experimental wines of this harvest, the content of 2-methyl-1-butanol was lower than the control V1. In the last harvest (2022), the trend in the content of 2-methyl-1-butanol was analogous to the previous one. The level found in the control sample V1 dominated those of the experimental wine variants. The influence of this higher alcohol on the wine aroma has been associated with fruity nuances (Carpena et al., 2021). Analyzing the results for this individual component (given the results obtained in the more significant part of the experimental variants from the four harvests) of the higher alcohols fraction, it could be concluded that the application of the different foliar fertilizers did not affect the content of 2-methyl-1-butanol, because the results indicated that in the most cases the untreated control showed higher levels of this component.The obtained results correlated with the data of Rubio-Bretón et al. (2018), who applied foliar different nitrogen fertilizers to vines of the red Tempranillo variety and found that wines obtained from grapes of untreated vines showed a higher content of 2-methyl-1-butanol, compared to treated ones. Gutiérrez-Gamboa et al. (2018) in a study of foliar fertilization of Cabernet Sauvignon found that wines from vines treated with Arg, Ur and commercial preparations – NT and BA accumulated a smaller amount of 2-methyl-1-butanol than the untreated control variant. These data are also consistent with what was found in our study.

Regarding the content of 3-methyl-1-butanol in the wines of the 2019 harvest, a higher content than the control was found only in the variant V5. All other experimental variants showed levels of this alcohol lower than the control, and in variant V2 and V3 they were very low. In the next harvest (2020), however, the trend was reversed. The lowest levels of this higher alcohol were found in control V1. All experimental variants showed higher level of 3-methyl-1-butanol, and in variant V2 it was very high. Experimental variant V5 also showed a much higher concentration than the control. The trend in the 2021 harvest was the same as in 2020. The detected amounts of 3-methyl-1-butanol in the experimental wines were lower than that found in the control. The last harvest (2022) had a similar trend to 2020: 3-methyl-1-butanol was found in the lowest concentration in wine of the control variant V1. In the experimental wines, its concentration was higher. The data in two of the studied harvests (2019 and 2021) correlated with the results of Rubio- Bretón et al. (2018), who found that the concentration of 3-methyl-1-butanol in Tempranillo red wines, under foliar treatment with nitrogen fertilizers, was lower in the experimental variants than in the control. 3-methyl-

1-butanol is a higher alcohol that has a strong aromatic fruity influence on wine (Cameleyre et al., 2015; Cometto-Muñiz and Abraham, 2008).

This reduction in the two major higher alcohols (2-methyl-1-butanol and 3-methyl-1-butanol) was also been demonstrated with soil nitrogen fertilization (Webster et al., 1993). The data on the content of 3-methyl-1-butanol in the 2020 and 2022 harvests were correlated with data obtained by Gutiérez-Gamboa et al. (2018) who applied foliar fertilization with different nitrogen sources to Cabernet Sauvignon vines. In the wines of the Urea + Sulfur treatment variants, they proved a higher concentration of 3-methyl-1-butanol and 2-methyl-1-butanol.

2-phenylethanol was the only aromatic alcohol that was identified in the studied wines. In the wine of the 2019 harvest, it was found only in two of the experimental variants – V2 and V3. In the wines from the next harvest (2020), it was identified in traces in the control variant V1 and variant V6. A high amount of 2-phenyl ethanol was found in the wine of variant V4 from this harvest. In the wines of the 2021 harvest, 2-phenylethanol was identified in three of the variants – V1, V2 and V3. In the last harvest (2022), this aromatic alcohol was found in four of the variants – V1, V4, V5 and V6. This aromatic alcohol has a strong influence on the wines aroma, giving a rose aroma, and its concentrations vary widely – on average 10.00 – 150.00 mg/l (Chobanova, 2012).

1-propanol was identified in three experimental wine variants from the 2019 harvest – V3, V4 and V6. Its concentrations between these variants varied from 9.00 mg/l to 153.48 mg/l. In the wines of the next harvest (2020), it was identified in four variants – V1, V2, V4 and V5, and in the first three, it was in very low amounts (traces). In the wines of the 2021 harvest, 1-propanol was not identified. In the last harvest (2022), this compound was identified in almost all variants examined, except for V3. In the wines of this harvest, its concentrations ranged from 2.49 mg/l to 12.31 mg/l. 1-propanol is a compound that imparts alcoholic-bitter notes in wine aroma (Zhang et al., 2015).

Other higher alcohols identified in individual samples between harvests were 2-propanol, 1-pentanol, 2-butanol, 1-heptanol, 1-hexanol, isobutanol.

The changes of the aldehyde content in the analyzed wines by harvests. Acetaldehyde was identified in all analyzed wines by variants and harvests. This compound is the main dominant representative of the wine aldehyde fraction.

In the wines of the 2019 harvest, only the variants V2 and V4 showed levels of this aldehyde lower than that found in the control variant V1. The rest of the experimental wines demonstrated higher aldehyde concentrations, and in the variants V5 and V6 they are very high, 308.85 mg/l and 511.77 mg/l, respectively. Analyzing the results of the next harvest (2020), it was found that all experimental wines accumulated acetaldehyde levels higher than that found in the control. The variation in the presence of aldehyde between the experimental wines ranged from 81.25 mg/l (V6) to 200.88 mg/l (V3), compared to 8.58 mg/l in the control V1. The trend in the next harvest (2021) was almost similar. Of all the analyzed experimental wines, only variants V2 and V3 showed aldehyde levels lower than the control V1, and even the concentration in variant V2 was marginally lower than the control. In the remaining variants of this harvest, the aldehyde was present in higher concentrations than the control, varying between samples from 19.33 mg/l to 67.26 mg/l. In the last harvest (2022), a lower concentration of acetaldehyde than the control was found in variants V2, V6 and V4. Variant V3 showed a concentration slightly higher, but almost comparable to the control. Of all the examined wines of this harvest, only variant V5 showed a distinctly higher aldehyde content than the control.

Acetaldehyde is a compound with dual nature with respect to the dry wines aroma. At concentrations up to 130.00 mg/l it gives a fruity character to the wine, while at higher concentrations it causes an oxidized tone in the aroma (Ribéreau-Gayon et al., 2000; Noble et al., 1987). In almost all the dry red wines examined in the present study, the aldehyde was identified in concentrations positively influencing the aromatic quality. The only exceptions were variants V5 and V6 from the 2019 harvest (where high aldehyde levels were found) and variants V3 and V5 from the 2020 harvest.

The conducted research indicated that the application of different foliar fertilizers did not negatively affect the acetaldehyde content in the resulting wines. Its presence corresponded to the appearance of its positive influence on the wine's aromatic profile.

The changes of total and individual content of esters in the analyzed wines by harvests. The ester fraction has an important and strong impact on the wine aromatic profile. The total amount of esters in young wines varies from 200.00 to 400.00 mg/l (Chobanova, 2012).

In the wines of the 2019 harvest, only two variants showed significantly higher than the control level of total esters – variant V3 and V6. All other variants accumulated less esters than the control wine. In the next harvest (2020), the trend was different. In it, all experimental variants showed levels of total esters significantly exceeding that found in the control. In the 2021 harvest, three of the variants (V2, V5 and V6) accumulated higher amounts of esters than the control, with the highest concentration of esters found in variant V5. The last researched harvest (2022) showed a similar trend to that found in the 2020 harvest. The amount of esters accumulated in the control was the lowest, compared to the experimental variants, where it varied from 138.50 to 656.65 mg/l.

From the obtained results, it could be concluded that in the 2020 and 2022 harvests, the foliar application of nitrogen and mineral sources affected the content of esters. In the other two harvests, individual variants showed higher ester accumulation than the untreated control, but others demonstrated lower levels. As a result, no specific conclusion could be made about the influence of foliar fertilizers on the final wines ester concentrations. Further studies are needed to determine how fertilization affects the metabolic accumulation of esters in grapes and their biosynthesis by yeasts during fermentation.

A major ester from this fraction was ethyl acetate. In the 2019 harvest, it was found in a lower concentration than the control only in the wine of variant V4. All other variants showed higher levels, ranged from 38.55 to 286.95 mg/l. In the next harvest (2020), higher content of this ester was noticed in the experimental wines, compared to the control. In the 2021 harvest, only variant V5 showed ethyl acetate levels higher than the control. In the other experimental variants, the ester varied from 18.18 to 58.71 mg/l. In the last harvest (2022), two of the variants – V2 and V5 accumulated less ethyl acetate, compared to the control. In the other variants, its quantities were higher.

Ethyl acetate has a dual effect on the wine's aromatic quality and it is synthesized normally in young wines biologically by the yeast microflora. In concentrations up to 80.00 – 100.00 mg/l, it positively affects the wine aroma; above them, the wine acquires a characteristic unpleasant acetic-acidic and chemical nuance in the aroma (Plata et al., 2003). Based on this, it was clear from the obtained results that in the 2019 harvest, variants V3, V5 and V6 accumulated ester in high levels (155.36 mg/l – 286.95 mg/l), over the upper limit of its positive influence. In the 2020 harvest, variants V3, V4, V5 and V6 also demonstrated high ester levels ranging from 174.94 mg/l to 263.15 mg/l. It was noteworthy that in both harvests the wines obtained from variants with applied foliar fertilization with the presence of Mg in the fertilizer accumulated high levels of ethyl acetate. The last two harvests (2021 and 2022) showed normal ester levels, which in the first harvest ranged from 18.18 mg/l to 71.06 mg/l, and in the second from 4.96 mg/l to 106.55 mg/l. Within these concentrations, it had a positive effect on the wine's aromatic quality.

Two other esters with a more substantial presence in the analyzed wines were propyl acetate and isopentyl acetate. In the wines of the 2019 harvest, propyl acetate was identified in four of the studied variants (V1 – V4). Its levels varied from 12.46 mg/l to 119.69 mg/l. In the next harvest (2020), the ester was found in three variants – V1, V2 and V5, with variations from 9.37 mg/l to 199.35 mg/l. In the wines of the 2021 harvest, propyl acetate was identified only in the V4 variant. In the last harvest (2022), this ester was identified again in only one variant – V3.

Isopentyl acetate in the 2019 harvest was identified in three of the experimental variants – V1, V3 and V4. Its amounts ranged from 23.48 mg/l to 66.74 mg/l. The lowest concentration was found in the control. In the next harvest (2020) it was identified in all studied variants, making the impression that in the control V1 it was present in a lower concentration (6.03 mg/l) compared to the experimental wines, where it varied from 72.68 mg/l to 167.90 mg/l. In the wines of the 2021 harvest, isopentyl acetate was found in four experimental variants – V1, V4, V5 and V6, and again, as in the other two harvests, its concentration in the control sample V1 was lower compared to the experimental variants.In the last harvest (2022), isopentyl acetate was not identified. Isopentyl acetate, like ethyl acetate, is a key compound for the wine aroma profile (Plata et al., 2003). From the results in the present study, it was evident that the application of foliar fertilizers affects the synthesis of this ester, leading to an increase in its concentrations in the experimental wines. Such a tendency was also observed for other ethyl esters. The data correlated with studies of Martinez-Gil et al. (2012), who reported a relationship between the ethyl esters formed in wines and the must nitrogen content.

Pentyl acetate, ethyl hexanoate, phenyl acetate, ethyl caprylate, hexyl acetate, ethyl butyrate, butyl acetate, diethyl succinate, isobutyl acetate and ethyl decanoate were also identified in the wines by harvests in separate variants.

Changes of total and individual terpene content in the analyzed wines by harvests

The terpene fraction has an important, fundamental relation to the aroma of wines from muscat varieties and formes so-called muscat aroma. Storgozia variety investigated in the present study is non-muscat. However, terpenes, as a product of the vine, exert an aromatic influence on the wines and the study of their presence is an important indicator of the complex wine aroma.

Regarding the total amount of terpenes identified in the wines of the 2019 harvest, only variant V4 accumulated an amount higher than the control. Terpenes were not identified in variants V5 and V6, and the other two variants showed a total terpene concentration lower than control. In the next harvest (2020), variant V4 showed again total terpene levels higher than control (1.00 mg/l). Variant V6 also accumulated more terpenes. All other experimental variants were characterized by terpene levels lower than control. In the wines of the 2021 harvest, variants V3, V4 and V5 accumulated amounts of total terpenes ranging from 0.94 mg/l to 1.66 mg/l, higher than control. In this harvest as well, it was noticeable that variant V4 accumulated a high amount of terpenes, as in previous two harvests. In the last studied harvest (2022), higher total terpenes were found in variants V2, V3 and V6, ranging from 0.80 mg/l to 1.22 mg/l, comparing them with the control level for this harvest (0.30 mg/l). According to Chobanova (2012), the average content of total terpenes in wine is about 2.00 mg/l. The data in the present study were in absolute correlation with this concentration range.

The data also correlated with the results of Vilanova et al. (2007) who investigated Albariño wines from northern and southern Spain. They found a concentration of total free terpenes in northern wines of 1757.15 $\mu g/L^{-1}$ (1.75 mg/l) and in the south – lower, respectively 458.99 $\mu g/L^{-1}$ (0.45 mg/l).

From the obtained results, it could not be concluded that the foliar fertilizers applied to the vines have a constant effect on increasing the concentration of total terpenes in the wines obtained from them.

Geraniol was found as the representative species of terpenes in the 2019 harvest in most of the tested variants (three of them). It was noteworthy that in the control its concentrations were higher compared to the other two experimental variants – V3 and V4. In the next harvest (2020) a dominant presence was reported, in addition to geraniol, and also ß-citronellol. The latter was found in almost all samples (except variant V4), but only in the wine of variant V3 it was in a higher amount. In the remaining variants (including control) it was present in low concentrations. Geraniol, on the other hand, in this harvest was also identified in almost all the wines examined (with the exception of variant V3). It was noteworthy that of all the experimental variants, only variant V2 showed levels of this terpene higher than the control. All other variants contained it in lower amounts. For the 2021 harvest, the situation was identical. Again, the dominant terpenes were ß-citronellol and geraniol. ß-citronellol was identified in almost all the wines analyzed (except variant V5). Its concentration in the experimental wines was comparable in one variant (V6) and higher (0.12 mg/l – 0.33 mg/l) than the control V1 (0.12 mg/l). Geraniol in this harvest was identified in variants V1, V3, V5 and V6 and only variant V5 showed levels higher than the control.The last harvest (2022) was distinguished by a dominant presence of linalool and geraniol. Linalool was identified in four of the investigated wines – V1, V2, V5 and V6. Its concentration in the control wine was lower than that found in the experimental variants. Geraniol was identified in three of the investigated variants – V2, V3 and V4, where it varied from 0.14 mg/l to 0.82 mg/l.

It looks that foliar fertilization affects the synthesis of ß-citronellol, leading to increase levels of this terpene in the experimental wines. Conversely, for geraniol, a decrease in its concentrations was observed in the wines obtained after the application of foliar fertilization, compared to the untreated ones.

Changes in the amounts of methanol in the analyzed wines

Methyl alcohol is a normally present component of wines that is produced from fruit pectin by pectinesterase enzymatic degradation, and in red wines, it is accumulated to a maximum of 350.00 mg/l (Chobanova, 2012). It was identified in all examined wines from the four harvests. In the wines of the 2019 harvest, only variant V2 showed methanol levels slightly lower than the control. All other variants showed higher levels of this component, ranging from 35.27 mg/l to 198.72 mg/l. In the next harvest (2020), the trend was maintained. Control V1 accumulated an amount of methyl alcohol, which was lower than that found in all experimental variants. In the wines of the 2021 harvest, lower methanol levels than the control were found in two of the experimental variants – V3 and V4. The rest showed a methanol content higher than the control. In the last harvest (2022), only variants V2 and V6 contained this component in amounts lower than the control. The tendency for the remaining variants was towards a higher accumulation, which varied from 8.00 mg/l to 18.26 mg/l.

In all wines, in all four harvests, normal levels of methanol, inherent in red wines, were found. It was noteworthy, however, that most experimental variants accumulated higher levels of this component compared to the untreated controls. It is likely that foliar fertilization accelerates the metabolism of the vine and has the effect of increasing the pectin content of the fruit, which is a factor for the final wines methanol levels.

Statistical data analysis of the main compounds identified in all four harvests

The statistical data is presened on table 6. Statistical processing of the data was performed, including the determination of the average values and standard deviation of four compounds (acetaldehyde, methanol, 3-methyl-1-butanol and ethyl acetate) that were identified practically in all studied variants and in the four harvests. The four replicates were taken from each single concentration of the compound found in a particular harvest. The results processed in this way can give an idea of whether these compounds show high variability considering the many factors that influence their presence in the wine – climatic conditions of the year, soils, agrotechnical measures and others. Acetaldehyde showed a very high standard deviation for variants V3, V5 and V6. In the V6 variant, it even surpassed the average value. This is an indicator that led to the conclusion that the content of this aldehyde in these variants was influenced by various factors and can vary significantly between different harvests. For methanol, a distinctly high standard deviation was observed for variants V2 and V4. And here it could be concluded that these variants showed a high variability in the concentration of methanol, which could vary significantly between harvests. The trend was similar for variants V2 and V5 for 3-methyl-1-butanol and V4 for ethyl acetate (basic wine ester).

Table 6

Statistical data (average ± SD) of main compounds for four harvests analyzed

Compounds, mg/l	Content in wines, mg/l, from vines					
	V1	**V2**	**V3**	**V4**	**V5**	**V6**
Acetaldehyde	34.18 ±28.13	46.43 ±39.92	82.68 ±82.77	66.07 ±44.52	150.69 ±119.05	155.04 ±239.99
Methanol	22.25 ±28.23	70.43 ±89.26	47.41 ±28.84	68.21 ±69.41	162.69 111.03±	123.08 ±86.80
3-methyl-1-butanol	52.53 ±38.34	397.35 ±735.47	69.83 ±55.09	78.60 ±40.25	188.81 ±189.17	67.20 ±23.77
Ethyl acetate	37.36 ±18.94	35.77 ±28.06	137.22 ±96.99	79.88 ±122.62	113.49 ±87.55	145.28 ±121.87

Conclusions

- It was proved that the variant of vine treatment with fertilizer MaxGrow NS, demonstrated final high levels of volatile and aroma compounds in wines of three from the four investigated harvests (2019, 2020 and 2021).
- A positive influence of foliar fertilization on the content of higher alcohols was outlined. This was due to the likely higher amounts of assimilable nitrogen in the must, which directly increased the final higher alcohol content of the analyzed wines.
- Dominant representatives of the higher alcohols fraction were 2-methyl-1-butanol and 3-methyl-1-butanol. The application of foliar fertilizers did not affect an increase in the content of 2-methyl-1-butanol in wines. In most cases, the untreated control showed

higher levels of this higher alcohol than the experimental variants. No increasing trend could be outlined in the content of 3-methyl-1-butanol either. In two of the harvests (2019 and 2022) this higher alcohol was present in lower amounts than the control. In the other two harvests (2020 and 2021) the trend was reversed and it dominated quantitatively in the experimental wines compared to their controls.

– A single aromatic alcohol was identified – 2-phenyl ethanol. 1-propanol was also found to be a major component of the higher alcohols fraction.
– From the group of aldehydes, its main representative – acetaldehyde – was present in the volatile fraction. The different foliar fertilizers did not have negative effect on the acetaldehyde secretion.
– No specific conclusion can be drawn about the influence of foliar fertilizers on the final total ester concentrations of the wines. Further studies related to the influence of fertilization on the metabolic accumulation of esters in grapes and their biosynthesis by the yeasts during fermentation are needed.
– Ethyl acetate was the main one, followed with propyl acetate and isopentyl acetate. The application of foliar fertilizers affected the accumulation of isopentyl acetate, leading to an increase in its concentrations in the experimental wines.
– The obtained results indicated that foliar fertilizers did not consistently affect increased total terpene content in the wines, but foliar fertilization affected the concentrations of ß-citronellol, leading to an increase in the levels of this terpene in the experimental wines. A decrease of concentration of another terpene – geraniol in the experimental wines (treated with foliar fertilizers) compared to the untreated control was observed.
– Normal levels of methanol inherent in red wines were found. Most experimental variants accumulated higher levels of this component compared to the untreated controls. It is likely that foliar fertilization accelerates the metabolism of the vine and had the effect of increasing the pectin content of the fruit, which is a main factor for the final wines methanol levels.

The application of foliar fertilizers led to changes in contents of volatile compounds in the researched wines.

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