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Biochemistry

Phytoalexin Stilbenoids of Saperavi and Rkatsiteli (*Vitis vinifera* L.) as Biomarkers of Resistance to Gray Mold (*Botrytis cinerea*)

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(Presented by Academy Member Ramaz Gakhokidze)

Among the diverse biological activities of grape stilbenoids, phytoalexin activity is important. Regarding to this we studied in some Georgian wine grape varieties, the correlation between the phytoalexin stilbenoids synthesis and the level of bacterial and fungal attacks. Presented materials shows the results of the study of the change of phytoalexin stilbenoids under gray mold infection in different microzones of Georgia: for Saperavi - Mukuzani and Napareuli, for Rkatsiteli - Tsarapi and Tibaani. In August 2022, we infected grape varieties with the conidial water suspension of *Botrytis cinerea* under different soil and climatic conditions, and we observed the development of gray mold on the grape barries in the period of August-September. In experimental vineyards trans-resveratrol and its products - glycosides and polymeric stilbenoids in the healthy grape skins of Saperavi and Rkatsiteli were found. In Saperavi berries skin stilbenoids concentration was higher compared to Rkatsiteli berries skin. In both infected varieties the stress-metabolite phytoalexin stilbenoids were identified: trans-resveratrol, trans-ε-viniferin, trans-piceid, trans-astringin and cis-piceid. Stilbenoids concentration changes were observed regarding the vine variety and soil-climatic factors, especially the high daily air temperature. The impact of the above mentioned factors was established with different experiments carried out in the lab and in natural conditions (in the vineyard). The received results are important data for further research to determine the stilbenoid biomarker of Saperavi and Rkatsiteli grapes, resistance against gray mold disease. *© 2023 Bull. Georg. Natl. Acad. Sci.*

Saperavi, Rkatsiteli, stilbenoids, phytoalexins, gray mold, Botrytis cinerea

Stilbenoids belong to a wide class of phenolic compounds. They include resveratrol and its derivatives (glucosides, dimers, trimers, tetramers, etc.) *cis*- and *trans*-isomeric forms [1]. Stilbenoids are characterized by several high biological activities and among them is important the phytoalexin activity for the plant, especially for the grapevine. The most important phytoalexin stilbenoids are:

resveratrol [2], pterostilbene [3], piceid [4], viniferins [5]. Phytoalexins, under plant infection conditions, are actively synthesized and act against disease-causing microorganisms (for example *Botrytis cinerea* and *Plasmopara viticola*). Beside the biotic factors, phytoalexins also respond to abiotic stresses such as UV rays and AlCl3 [6,7]. Studied the variability of stilbenoids in the berry skin of red (Pinot noir, Gamay) and white (Chardonnay)winegrape varieties infected by *Botrytis cinerea* and treated with UV rays. All samples infected with *B. cinerea* showed a decreased amount of resveratrol and an increased concentration after UV irradiation. Pterostilbene was found in low concentrations in infected berries of Chardonnay and Gamay. Pterostilbene was also observed in low concentrations in grape skins by other authors [8]. According to Pezet and Pont [9], pterostilbene plays an important role in the resistance of immature grapes against disease-causing microorganisms. Other authors studies the interaction betweenstilbenoids and *Botrytis cinerea* in gapevine.

According to Bezhuashvili et al [10] stilbenoids have been identified in healthy and naturally diseased Georgian winegrape varieties – Rkatsiteli (white), Tsolikouri (white), Alexandrouli (red), Mujuretuli (red). *Trans*-resveratrol and *trans*-ε-viniferin were dominant for red varieties; moreover, *trans*-resveratrol was lower than *trans*-ε-viniferin in healthy grape skins, and the concentration of *trans*-resveratrol was significantly higher under gray mold infection than *trans*-ε-viniferin; it decreased under disease conditions [10]. In white wine grape varieties (Rkatsiteli and Tsolikouri), the main stress metabolite was *trans*-resveratrol, which increased significantly in gray mold disease conditions [11]. The inhibitory effect of *trans*-resveratrol on *Botrytis cinerea* activity and consequently the spread of gray mold on grapes, has been established under laboratory conditions (in petri dishes) [12]. Stilbenoids had an inhibitory effect of the fungus- *Botrytis cinerea* pure culture in food areas placed in petri dishes and there was a negative correlation between the fungal propagation and the stilbenoids concentration According to Adrian et al. [13] a resveratrol concentration of 100 µg/ml completely inhibited the development of *B. cinerea* mycelium, while concentrations of pterostilbene at 20–40–60 µg/ml caused 50%, 80% and 100% inhibition of*B.cinerea* mycelium development. According to Pezet and Pont [9] a concentration of pterostilbene of 18 µg/ml caused a 50% inhibition of *B. cinerea* mycelium development while a concentration of 52 µg/ml resulted in an inhibition of 52%.

Evidences have been obtained on the capability of some highly pathogenic *B. cinerea* strains to circumvent the defence by detoxifying resveratrol through an oxidative process [14]. Other stilbenoids can be detoxified by enzymatic (laccase) activity of *B. cinerea*, resulting in the release of compounds like pterostilbene-trans-dehydrodimer, pterostilbene-cis-dehydrodimer, resveratrol trans-dehydrodimer [15]. All the physiopathological aspects of stilbenoids are addressed.

Materials and Methods

The objects of the study were healthy and gray mold-infected grape skins from Saperavi (red) and Rkatsiteli (white) vineyards located in viticulture microzones in Eastern Georgia. As concerning to the experiment Saperavi berries were sampled, as follows: a) Mukuzani microzone – from a 17-year-old vineyard located on Eutric Cambisols and calcic Kastanozems type of soil, b) Napareuli microzone cultivated from 40 year old vineyard on Eutric Cambisols and calcic Kastanozems type of soil; Rkatsiteli grape varieties were sampled from a) Tsarapi microzone cultivated from 40 year old vineyard grown on meadow cinnamonic-calcaric cambisols and calcic kastanozems type of soil, b) Tibaani microzone – from 17 year old vineyard grown on cinnamonic calcareous-calcaric cambisols and calcic kastanozemstype of soil.

Stilbenoids containing fractions were isolated from healthy and diseased grape skins. Trans-resveratrol and ε-viniferin were individually isolated from one-year-old vine shoots by ethylacetate extraction and column separation.

Stilbenoids were determined by the method of highperformance liquid chromatography (HPLC) [17]. For this purpose, we used the chromatograph Varian; Column- Supelcosil PM LC18, 250 x 4.6 mm; Eluents: A. 0.025% trifluoroacetic acid,B.Acetonitrile: A80/20. Gradient mode: 0-35 min, 20-50% B, 48-53 min, 200% B. Flow rate of the eluent – 0,8 ml/min; fractions were filtered using a membrane filter (0.45 µ) before the chromatographic procedure.

Lab experiment Healthy berries of red winegrape varieties (*V. vinifera* L.) Saperavi and Rkatsiteli were sampled at technological maturity (September, 2022) in the following environments of Georgia: a) Saperavi berries from vineyard lokaled in Mukuzani and Nafareuli microzone; b) Rcatsiteli berries from vineyard localed in Tsarafi and Tibaani microzone. The experimental design included the following treatments: 1) berry pre-treatment with 5 mg/100 mL of ε-viniferin, and then fungal infection; 2) berry pre-treatment with 5mg/100mL of *trans*-resveratrol, and then fungal infection; 3) control berries with fungal infection but without pretreatments.The pre-treatments were done by soaking 12 berries per variety in the previously described solutions (or just water in the case of the control), while fungal infection was done by spraying *Botrytis cinerea* conidial suspension over the berries placed on damp filter paper inside petri dishes. The fungal inoculum was prepared by recovering conidia from infected berries grown in the field.

Vineyard experiment As concerning the vineyard trial, healthy clusters of Saperavi (red winegrape variety) and Rkatsiteli (white winegrape variety) from the experimental (notsprayed by pesticides) vineyards, located in the above-mentioned microzones were considered. An experiment was conducted between 11 August-28 September 2022. The experimental design was as follows: 1) cluster pre-treatment with 5 mg/100 mL of trans-resveratrol and then fungal infection; 2) cluster pre-treatment with 5 mg/100 mL ε-viniferin and then fungal infection; 3) control vines with fungal infection but without any pre-treatment. while fungal infection was done by spraying Botrytis cinerea conidial suspension.

Three clusters of different sizes were selected per each treatment, according to the following chart.

Results and Discussion

Considering the results of the research it should be noted that the accumulation of phytoalexin stilbenoids in the skin of Saperavi and Rkatsiteli grapes is studied under the influence of abiotic (soil, air temperature) and biotic (gray mold – *Botrytis cinerea*) factors. In August-September of 2022 year, in the experimental microzones, were mostly rainless weather and the daily air temperature varied in the intervals indicated in Table 1.

Table 1. Daily air temperature range in experimental viticulture microzones

Microzones	Temperature ^{0}C	
	August, 2022	September, 2022
Mukuzani	25-35	22-28
Napareuli	27-38	20-30
Tsarapi	25-36	21-38
Tibaani	24-37	23-29

Temperature is one of the important abiotic factors impacting the biosynthesis of stilbenoids in grapevine. The inhibitory effect of high temperature on the biosynthesis of stilbenoids has been established by a number of researchers [18-20]. It is known that the temperature of normal biosynthesis of resveratrol is 15-20^{0}C for prolonged biosynthesis 5^{0}C, and for inhibition -20^{0}C and heat treatment at 65^{0}C for 2 hours [21].

In the experimental vineyards at the indicated temperature in the skin of healthy Saperavi and

Rkatsiteli grapes resveratrol and its derivatives – in the form of glycosides, dimers and trimers were accumulated. The stilbenoid profiles are dominated by glucosidic forms: trans-piceide, trans-astringin and cis-piceide (Table 2). Phytoalexin stilbenoids: trans-resveratrol, trans-ε viniferin, trans-piceide, trans-astringin and cis-piceide were identified from the comparison of stilbenoids of healthy and gray mold-infected grape skins.

The change of stilbenoids under infection with *Botrytis cinerea* is different.

The special attention deserves the significant increase of the concentration of trans-resveratrol in the skin of Rkatsiteli grapes grown in the micro-zones of Tsarapi and Tibaani: 7.2→22.3 mg/kg and 10.8→18.3 mg/kg. The concentration of stilbe-noids accumulated in the skin of healthy Saperavi grapes exceeds the concentration of stilbenoids in the skin of Rkatsiteli grapes. Moreover, the amount of trans-resveratrol exceeds the amount of trans-viniferin. The concentration of trans astringin in the skin of Saperavi and Rkatsiteli grapes increases with infection, except in the Rkatsiteli variant of the Tibaani microzone.

The concentration of cis-piceide increases with the infection of Saperavi by *"Botrytis cinerea"*.

The concentration of trans-piceide increases with the infection of Mucuzani Saperavi, Tsarafi and Tibaani Rkatsiteli.

It was tested inhibitory effect of trans-resvera-trol and trans-ε viniferin on the activity of the fungus *Botrytis cinerea* in laboratory and natural conditions in the vineyard. The results of the experiment are given in Tables 3,4. In lab *Botrytis cinerea* spreaded 100% on untreated Saperavi and Rkatsiteli berries. In pre-treated vines with trans-resveratrol the infection was reduced to 8.3% on Saperavi berries and with trans-ε-viniferin the fun-gus did not develop at all. We obtained a similar re-sult in the lab regarding to the Rkatsiteli grape, but

Table. 2. Change of Stilbenoids of grape skin of Saperavi and Rkatsiteli under Gray mold infection

Stilbenoids, mg/kg	Saperavi Mukuzani		Napareuli		Rkatsiteli Tsarafi		Tibaani	
	healthy	infected	healthy	infected	healthy	infected	healthy	infected
trans-resveratrol	12.0	9.3	11.4	14.9	7.2	22.3	10.8	18.3
trans- ε-viniferin	7.5	6.7	6.8	5.9	4.7	8.1	3.5	8.9
trans-piceid	13.3	19.5	14.2	11.3	10.7	15.0	11.7	16.6
trans- astringin	25.0	15.8	18.7	20.0	15.6	18.4	13.5	10.5
cis-piceid	16.7	17.8	17.1	18.7	16.5	10.2	17.3	14.8

Table 3. Lab.trial. Impact of phytoalexins stilbenoids on the gray mold infection of Saperavi and Rkatsiteli grape berries

Pre-treatments	Number of berries in each petri dish		Number on infected berries in each		Degree of infection (%)		Biological efficiency (%)	
Saperavi	Mukuzani	Napareuli	Mukuzani	Napareuli	Mukuzani	Napareuli	Mukuzani	Napareuli
Control	12	12	12	12	100	100	0	0
R-5mg/100ml	12	12	1	1	8.3	8.3	91.7	91.7
V-5mg/100ml	12	12	0	0	0	0	100	100
Rkatsiteli	Tsarapi	Tibaani	Tsarapi	Tibaani	Tsarapi	Tibaani	Tsarapi	Tibaani
Control	12	12	12	12	100	100	0	0
R-5mg/100ml	12	12	2	1	16.7	8.3	83.3	91.7
V-5mg/100ml	12	12	0	0	0	0	100	100

*R-*trans*-resveratrol, V- *trans*-ε-viniferin

Table 4. Vineyard trial. Impact of trans-resveratrol and trans- ε-viniferin solutions on gray mold infection of Saperavi and Rkatsiteli clusters

Pre-treatments	Number of berries/cluster		Number of infected berries		Degree of infection (%)		Biological efficiency (%)	
Saperavi	Mukuzani	Napareuli	Mukuzani	Napareuli	Mukuzani	Napareuli	Mukuzani	Napareuli
Control	81	87	41	45	50.6	51.7	49.4	48.3
	123	127	63	58	51.2	45.7	48.8	54.3
	265	260	130	135	49.1	51.9	50.9	48.1
R-5mg/100ml	88	84	35	32	39.8	38.1	60.2	61.9
	135	145	50	56	37.0	38.6	63.0	61.4
	194	210	72	80	37.1	38.1	62.9	61.9
V-5mg/100ml	80	89	28	32	35.0	36.0	65.0	64.0
	127	140	45	48	35.4	35.0	64.6	65.0
	180	205	62	70	34.4	34.1	65.6	65.9
Rkatsiteli	Tsarapi	Tibaani	Tsarapi	Tibaani	Tsarapi	Tibaani	Tsarapi	Tibaani
Control	70	75	40	40	57.1	53.3	42.9	46.7
	105	110	55	57	52.4	51.8	47.6	48.2
	155	170	83	90	53.5	52.9	48.4	47.7
R-5mg/100ml	65	68	34	32	52.3	47.1	47.7	52.9
	100	103	52	52	51.0	49.5	49.0	50.5
	130	157	67	80	51.3	50.9	48.7	49.1
V-5mg/100ml	67	75	32	35	47.7	46.6	52.3	53.4
	110	122	52	57	47.2	46.7	52.8	53.3
	140	148	66	69	47.1	48.0	52.9	52.0

unlike viniferin, the grape barries in Tsarapi microzone were infected 2 times more than in Tibaani (Table 3) with *trans*-resveratrol pre-treatment.

We obtained different results from the same experiments (on the same grape variety) under field conditions. In contrast to lab conditions *Botrytis cinerea* partially developed in the control variants. In pre-treatment with trans-resveratrol and trans-ε-viniferin the degree of infection was somewhat reduced on Saperavi and Rkatsiteli grapes but at a lower extent. Similar to the results of the laboratory experiments *trans*-ε-viniferin inhibition degree was higher as compared to *trans*-resveratrol (Table 4).

Table 4. Vineyard trial. Impact of trans-resveratrol and trans- ε-viniferin solutions on gray mold infection of Saperavi and Rkatsiteli clusters

This difference was caused most likely by high daily air temperature, which decreased the intensity of *Botrytis cinere*a reproduction and at the same time inhibited the phytoalexin ability of stilbenoids.

Conclusion

It was established the variation of phytoalexin stilbenoids of wine grape varieties – Saperavi (Mukuzani, Nafareuli) and Rkatsiteli (Tsarapi, Tibaani) grown in different microzones of Georgia under gray mold attack . It was studied the impact of abiotic (soil, air temperature) and biotic (*Botrytis cinerea*) factors. The presented materials are the research results of the first year of the 3-year project and are important for further research.

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ბიოქიმია

საფერავის და რქაწითელის (*Vitis vinifera* L.) ფიტოალექსინი სტილბენოიდები, როგორც რეზისტენტობის ბიომარკერი ნაცრისფერი სიდამპლის მიმართ (*Botrytis cinerea*)

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(წარმოდგენილია აკადემიის წევრის რ. გახოკიძის მიერ)

ვაზის სტილბენოიდების მრავალფეროვანი ბიოლოგიური აქტივობიდან მნიშვნელოვანია ფიტოალექსინური აქტივობა. ამასთან დაკავშირებით ჩვენ მიერ შესწავლილია საქართველოს ზოგიერთი საღვინე ვაზის ჯიშის იმუნიტეტის კორელაცია ფიტოალექსინ სტილბენოიდებთან ბაქტერიული და სოკოვანი დაავადებების პირობებში. წინამდებარე მასალები კი, წარმოადგენს საფერავის და რქაწითელის ფიტოალექსინი სტილბენოიდების ცვალებადობის კვლევის შედეგებს ნაცრისფერი სიდამპლით ინფიცირებისას მევენახეობის სხვადასხვა მიკროზონაში. კონკრეტულად, საფერავისთვის-მუკუზნის და ნაფარეულის, რქაწითელისთვის - წარაფის და ტიბაანის მიკროზონებში. აღნიშნული ვაზის ჯიშების ხელოვნური დაინფიცირება ჩავატარეთ 2022 წლის აგვისტოში *Botrytis cinerea*- ს კონიდიალური წყლიანი სუსპენზიით განსხვავებულ ნიადაგურ-კლიმატურ პირობებში და ყურძნის მტევნებზე ნაცრისფერი სიდამპლის განვითარებას/გამრავლებას დავაკვირდით აგვისტო-სექტემბრის პერიოდში. საექსპერიმენტო მიკროზონების ვენახებში საფერავის და რქაწითელის ჯანსაღი ყურძნის კანში აღმოჩნდა სტილბენოიდები ტრანს-რესვერატროლის და მისი წარმოებულების-გლიკოზიდების და პოლიმერული სტილბენოიდების სახით. საფერავის ყურძნის კანში დაფიქსირდა სტილბენოიდების რაოდენობრივი უპირატესობა რქაწითელის სტილბენოიდებთან შედარებით. ნაცრისფერი სიდამპლით დაავადებულ საფერავის და რქაწითელის ყურძნის კანში სტრეს-მეტაბოლიტ ფიტოალექსინ სტილბენოიდებად გამოვლინდა: ტრანს-რესვერატროლი, ტრანს-ε-ვინიფერინი, ტრანს-პიცეიდი, ტრანს-ასტრინგინი და ცის-პიცეიდი. გამოვლინდა მათი ცვალებადობის დამოკიდებულება ვაზის ჯიშის და ნიადაგურ-კლიმატურ ფაქტორებზე, განსაკუთრებით, აღსანიშნავია ჰაერის დღიური მაღალი ტემპერატურა. აღნიშნული ფაქტორების გავლენა დადასტურდა ლაბორატორიულ და ბუნებრივ პირობებში-ვენახში ჩატარებული ხელოვნური დაინფიცირების განსხვავებული ხარისხით. ექსპერიმენტის შედეგები მნიშვნელოვანი მონაცემებია შემდგომი კვლევების გასაგრძელებლად-საფერავის და რქაწითელის სტილბენოიდური ბიომარკერის, როგორც ნაცრისფერი სიდამპლის მიმართ რეზისტენტობის დასადგენად.

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