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Survey of Grapevine *Vitis vinifera* Stem Polyphenols by Liquid Chromatography−Diode Array Detection−Tandem Mass Spectrometry

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Grapes and red wine prepared from *Vitis vinifera* L. contain a variety of polyphenols. Some information is available about the polyphenols of the seeds and leaves of grapevine, but considerably less is known about the polyphenols of woody stems. In this paper, we describe the results of a study of polyphenolic compounds in grapevine stems. We demonstrate how a combination of reversed phase high-performance liquid chromatography with ultraviolet−diode array detection and electrospray ionization−tandem mass spectrometry ion-trap detection enables characterization of a phytochemical mixture of considerable complexity. As the polyphenol source, the stems of three frost-hardy grapevine varieties [Hasaine (Hasansky) sladki, Zilga, and Yubilei Novgoroda] were used. The main group of methanol-extractable polyphenols of stems consists of *trans*-resveratrol and its derivatives including oligomers and glucosides. As minor components of the extract, stilbenoid piceatannol as well as a number of nonstilbenoid polyphenols, mostly flavan-3-ols and phenolic acids glucosides, were determined. The total polyphenol content of the grapevine stems depends on the variety, whereby the stems of cultivar Yubilei Novgoroda with white grapes contain significantly less of both groups of polyphenols.

KEYWORDS: Polyphenols; resveratrols; flavan-3-ols; LC-MS/MS; DAD; grapevine stems

INTRODUCTION

Phytoalexin *trans*-resveratrol, 3,5,4′-trihydroxystilbene (**Figure 1a**), was first isolated in 1940 from the roots of white hellebore (*Veratrum grandiflorum* O. Loes). Since then, *trans*-resveratrol and its derivatives (glycosides and oligomers) as well as analogues (piceatannol, pterostilbene, pinosylvin, rhapontigenin, deoxyrhapontigenin, etc. and their glycosides) have been either isolated or identified in a number of different plants (over 70 species) (*1*).

The most important sources of *trans*-resveratrol are berries of grapevine (*Vitis vinifera* and *Vitis labrusca* L.) and red grape wine, roots of japanese knotweed (*Polygonum cuspidatum* Ziebold et Zucc.), berries of mulberry (*Morus rubra* L.), roots of garden rhubarb (*Rheum rhaponticum* L.), and peanuts (*Arachis hypogaea* L.) (*1*).

trans-Resveratrol is the first stilbene to be synthesized in the plant via the action of the enzyme stilbene synthase in response to fungal infection (*Botrytis cinerea*, *Plasmopara viticola*, etc.) and other stress factors like UV irradiation, ozone, heavy metal ions, injury, or frost (*1*). *trans*-Resveratrol is stable in purified form for a long period if protected from light but is converted to the cis isomer on exposure to UV irradiation (*1*). Other modifications to this base molecule result in the production of piceid and resveratroloside (via glucosylation), pterostilbene (via methylation), and oligomers (via oxidative polymerization) (*2*). There is a hypothesis that namely the resveratrol oligomers and particularly δ-viniferin as well as pterostilbene are highly toxic to downy mildew (*2*).

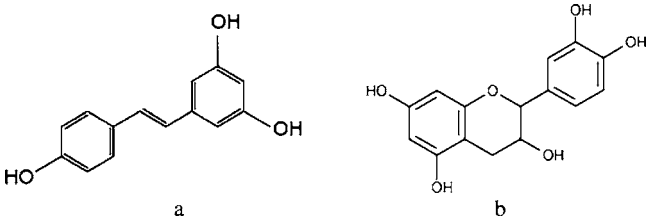

Figure 1. (**a**) *trans*-Resveratrol and (**b**) general formula of catechin and epicatechin.

trans-Resveratrol has been shown to have versatile beneficial physiological effects on mammals. The most important of them are cardioprotective effects (French paradox) (*3*), anticancer

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activities at all three main steps of the carcinogenesis process (*4*), and antioxidant, antibacterial, antiestrogenic, and anti-inflammatory properties (*5*). *trans*-Resveratrol has been shown to be a preventive agent of neurodegenerative processes like Alzheimer's and Parkinson's diseases (*5*, *6*). In addition, it is remarkable that for *trans*-resveratrol, no toxic effects have been established in animal experiments with rats even at very high doses (*7*).

The biological activity of the resveratrol cis isomer as well as resveratrol oligomers has not been studied equally well, but it seems to be true that the biological activity of *cis*-resveratrol is much lower than that of its trans isomer. Resveratrol oligomers usually support the action of *trans*-resveratrol, but they may have different properties (*7*). For example, it has been demonstrated that resveratrol oligomers also strongly suppress HL-60 cell proliferation and induce DNA damage (*8*).

Different parts of grapes contain polyphenols like stilbenes, flavonols quercetin and kaempferol, flavan-3-ols, phenolic acids, leukoanthocyanidins, and anthocyanidins (*9*−*15*). Lately, the seeds of grapes have become a subject of extensive polyphenol studies (*12*, *16*−*20*). Some knowledge has been gained about the polyphenolic composition of grapevine leaves (*21*, *22*). The main analysis method has been high-performance liquid chromatography (HPLC) with ultraviolet (UV), fluorescence, or mass selective (MS) detection. As a rule, only a small number of phenolic compounds are involved in every study. In the stems of *V. vinifera* plants, the presence and structure of several oligostilbenes, mainly resveratrol dimers and tetramers, have been reported (*23*−*25*). Resveratrol dimer ϵ-viniferin is considered to be a biogenetically important precursor of the other dimers like ampelopsins B, D, and F and also tetramers like hopeaphenol and isohopeaphenol, vitisins A, B, and C, and viniferol A (*26*). Despite this, the overall polyphenolic composition of grapevine lignified stems remains largely unknown.

Earlier, we published the results of our study concerning the occurrence and separation of the main polyphenols of the resveratrol group from stems of five grapevine (*V. vinifera*) northern cultivars grown in Estonia (*27*). Since then, we have estimated that these stilbenoids are the major group of polyphenols in grapevines and the ethanol extract of these stems could be used as the basis of health-promoting mixtures possessing a complex of stilbene-originating properties. A very important further step is to identify as much as possible the minor components of this mixture. Here, we report the results of our further study of three vine cultivars by the hyphenated liquid chromatography−diode array detection−tandem mass spectrometry (LC-DAD-MS/MS) method. MS/MS with a mild electrospray ionization and ion-trap detection in combination with UV-DAD in many cases enables simultaneous detection and identification of a number of compounds from a single chromatogram.

MATERIALS AND METHODS

According to the results of our preliminary studies of different *V. vinifera* cultivars growing in the garden of Räpina Gardening College (southeastern of Estonia), relatively resveratrol-rich grapevine cultivars Hasaine (Hasansky) sladki, Zilga (both with blue berries), and Yubilei Novgoroda with white berries were chosen for stem-orientated cultivation.

The meristemic young plants were planted in August, 2003, near Rakvere (Northern Estonia). The terminal parts of the lignified stems were cut off on October 30, 2004, air-dried in the absence of light in a well-ventilated room until December 16, ground with a 1095 Sample Knifetec Mill (Foss Tecator), sieved through a 1 mm sieve, and extracted with methanol (1:10 w/v) for 72 h with eventual shaking. After the extracts were centrifuged with an Eppendorf 5810R cooling centrifuge equipped with a swinging bucket rotor for 15 min at 978 *g*, the supernatants were kept at −20 °C. For the chromatographic analysis, the supernatants were diluted five times with methanol−water (1:1 v/v). The solutions obtained were injected into the chromatographic system without further purification. Main resveratrols and catechins were quantitated by absorbance at $\lambda = 306$ and 280 nm, respectively, using external calibration by *trans*-resveratrol and catechin standards from Sigma. From Sigma also were standard compounds of epigallocatechin, gallocatechin, epicatechin gallate, catechin gallate, and gallocatechin gallate. All solvents (water, acetonitrile, and methanol) were of HPLC grade, and formic acid of MS grade was from Fluka.

Apparatus. For the identification of polyphenols, the LC-MS/MS analyses were performed in both negative and positive ionization modes on an Agilent 1100 Series LC/MSD Trap-XCT equipped with an electrospray interface (ESI). The ion trap was connected to an Agilent 1100 Series HPLC instrument consisting of an autosampler, solvent membrane degasser, binary pump, column thermostat, and UV−vis diode array detector. HPLC 2D ChemStation Software with a ChemStation Spectral SW module was used for the process guidance.

Chromatographic Conditions. The reversed phase HPLC analytical separation was performed on a Zorbax 300SB-C18 column (2.1 mm × 150 mm; 5 μm particle size) with a guard column filled with the same type of sorbent in a stepwise gradient mode of 0.1% formic acid (solvent A) and acetonitrile (solvent B) at a flow rate of 0.3 mL/min at 35 °C. Elution was started with a linear gradient of B from 10 to 30% by 30 min, then to 90% by 40 min, and finished isocratically with 90% of B for 10 min.

The sample injection volume was 10 μL. The DAD was working at an interval of 200−600 nm, and the eluate optical density was continuously monitored at wavelengths 250 (phenolic acids), 280 (flavanols), 306 (*trans*-stilbenes), and 370 (flavonols) nm. Conditions of MS/MS detection were as follows: *m*/*z* interval, 50−1000; target mass, 400; number of fragmented ions, 2; maximal accumulation time, 100 ms; compound stability, 100%; drying gas (N_2 from generator) flow rate, 10 L/min; gas temperature, 350 °C; nebulizer pressure, 30 psi; and collision gas He pressure, 6×10^{-6} mbar.

RESULTS AND DISCUSSION

Figure 2 illustrates UV and MS chromatograms of the methanolic extract of grapevine cultivar Hasaine sladki stems with relatively few major peaks. The chromatograms of the stem extracts of two other cultivars (not shown) are very similar. Some of the peaks are chemically homogeneous; part of them still represents mixtures of several compounds. We have made efforts to determine in these chromatograms as many, both major and minor, compounds as possible. All of the determined compounds are listed in **Tables 1** and **2**.

Identification of Stilbenoids. The major group of phenolics (peaks 3−11 and several minor peaks on **Figure 2**) in vine stems consists of stilbenoid *trans*-resveratrol and closely related compounds. The stilbenic compounds determined in the stem extracts by LC-MS/MS and partly with DAD are presented in **Table 1**. According to their absorbance maxima (λ_{max}) in the near UV region near 320 nm caused by polarized aromatic $\pi-\pi$ electron interaction, most of the hydroxystilbenes including resveratrol itself must have at least one resveratrol monomer moiety in trans configuration (*28*, *34*). In parentheses are respective retention times and wavelengths of maximal absorbance. The only obvious exception is a poorly ionizable resveratrol tetramer eluting at 18.1 min (peak 6), which has the UV spectrum typical of a *cis*-stilbenoid.

MS/MS analysis of the chromatograms gave the following results. Peak 3 in **Figure 2** represents a mixture of resveratrol and piceatannol *O*-glucosides, eluting very close to each other (see **Table 1**). MS^2 spectra of compounds **4** and **5** on **Figure 2** are very similar to the spectra of commercial standards of,

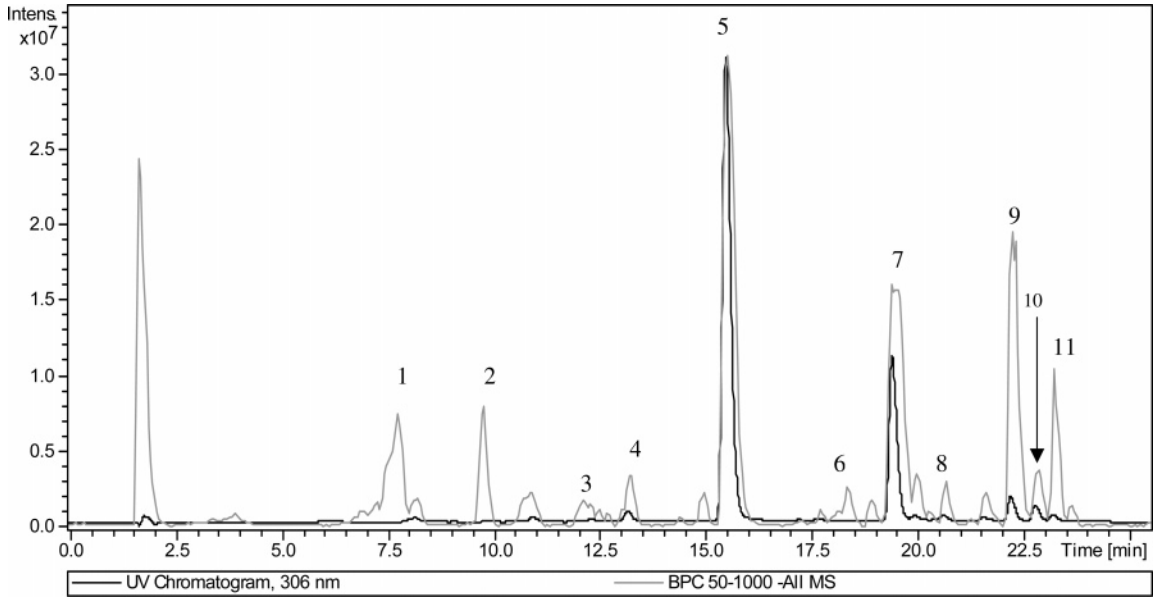

Figure 2. Base peak chromatogram (BPC, all –MS) and UV chromatogram at 306 nm of diluted methanolic extract of *Hasaine sladki* stems. Main identified peaks (compounds): 1, catechin (7.8 min; 278 nm); 2, epicatechin (9.8 min; 278 nm); 3, mixture of resveratrol and piceatannol glucosides (12.4 min); 4, piceatannol (13.2 min; 302 and 321 nm); 5, *t*-resveratrol (15.6 min; 305 nm); 6, *t*-resveratrol tetramer (18.4 min; 282 nm); 7, *t*-resveratrol main dimer ϵ-viniferin (19.7 min; 323 nm); 8, *t*-resveratrol tetramer (20.5 min; 322 nm); 9, *t*-resveratrol trimer (22.2 min; 324 nm); 10, *t*-resveratrol tetramer (22.8 min; 324 nm); and 11, *t*-resveratrol trimer (23.2 min; 322 nm). The peak at 1.8 min represents a mixture of hydrophilic compounds. In parentheses are respective retention times (t_R) and wavelengths of maximal absorbance (λ_{max}).

respectively, piceatannol and *trans*-resveratrol listed also in **Table 1**. The highest peak on EIC (**Figure 3**) with $m/z = 453$, negative mode, eluting at 19.4 min represents a compound characterized by daughter ions 359, 347, 435, 369, 411, 253, etc. with a good match with literature data, and obviously belongs to resveratrol dehydrodimer *trans*-ϵ-viniferin (*15*, *21*, *34*, *35*). We agree with Pezet et al. (*21*) who found that vine stems do not contain any detectable amount of resveratrol dehydrodimer δ-viniferin with the most abundant negative daughter ion 369.1. The stems do not also contain resveratrol trimer α-viniferin with $(M - H)^- = 677$ but contain at least three resveratrol trimers with parent ions $m/z = 679$ (negative mode). Two of them, eluting, respectively, at 22.2 and 23.2 min, are very similar to each other. Their MS^2 spectra contain two intensive fragments with m/z 585 $(M - H - 94)^-$ and 491 $(M - H - 2 \cdot 94)^-$ corresponding, respectively, to the trimer ion without one or two phenolic groups. We have determined three tetramers of resveratrol, also giving a constant neutral loss of 94. In general, the stems contain a real bouquet of resveratrol oligomers. Altogether, there are at least three dimers with $[M - H]^- = 453$ (viniferin type anhydrodimer) (*21*), three dimers with $[M - H]^- = 469$ (caraphenol type dimer) (*29*), and one glucoside of a resveratrol anhydrodimer; two similar trimers with $[M - H]^- = 679$; and three similar tetramers with $[M - H]^- = 905$. The three-dimensional structure of these oligomers is waiting for elucidation.

Actually, the number of resveratrol oligomers can be even higher since in the negative mode extracted ion chromatogram (EIC), there are altogether eight peaks with $m/z = 453$ and three peaks with $m/z = 469$ (both dimers), up to five peaks with $m/z = 679$ (trimers) and nine peaks with $m/z = 905$ (tetramers) (**Figure 3**). Because the concentration of several named ions was too low for fragmentation of the parent ion in MS/MS, these ions could not be identified.

We were able to also determine two *O*-hexosides of *trans*-resveratrol and one *O*-hexoside of the resveratrol dimer, which most likely are glucosides. The difference in their fragmentation patterns can be caused by different positions of the glycosidic group in the resveratrol molecule. The highest peak characterized with $[M - H]^- = 389$ at 10.1 min has neutral loss 120 Da, characteristic of *C*-hexoside (*30*). The presence of resveratrol *C*-glucoside in wine was established earlier (*31*). We also discovered stilbenoid piceatannol and its glucoside in the extract (**Table 1**).

Under our chromatographic conditions, a number of negative ions, mainly of resveratrol derivatives, reached the ion trap in the form of both the $[M - H]^-$ ion and the formic acid adduct of it $[M - H + 46]^-$. These complex ions appeared in the case of piceid $[389 + 46]^-$, resveratrol dimer $[453 + 46]^-$ at $t_R = 14.9$, viniferin $[453 + 46]^-$ at $t_R = 19.4$ min, resveratrol dimer $[453 + 46]^-$ at $t_R = 20.9$ min, and resveratrol trimer $[679 + 46]^-$ at $t_R = 17.7$ min. Positive ions formed no adducts. In spite of this confusing phenomenon and higher sensitivity of the positive mode of ionization, in the case of most ions, the negative ionization was preferred. The main reason is that more polyphenols are negatively ionizable and the sensitivities are more equal to each other than in the case of positive ions.

Determination of Nonstilbenoid Polyphenols. The nonstilbenoid polyphenolic compounds identified in Hasaine sladki stems by either standard compound (catechin, **Figure 1b**; catechin gallate) or literature data by MS/MS (*32*) are listed in **Table 2**.

As can be seen in **Table 2**, most of the identified nonstilbenoid compounds belong to the group of flavan-3-ols (catechin, epicatechin, and their B type dimers), the content of which is significant, and phenolic acid glucosides. Trace amounts of other polyphenolic compounds in the stems remain yet unidentified.

Quantitation of Polyphenols. UV detection at 306 nm, which is the wavelength of the maximum absorbance of *trans*-stilbene type compounds where the absorption of most other polyphenols is low, was used to quantify the content of three main resveratrol variants (*trans*-resveratrol, ϵ-viniferin, and main trimer) in the stem extracts. Analogically, the peaks at 7.8 and 9.8 min at the UV chromatogram at 280 nm were used for quantitation of

Table 1. Stilbenoids in Stems of Vine Cultivar Hasaine sladki Determined by Tandem MS/MS

compound	t_R (min)	$[M-H]^-$ or $[M+H]^+$	main daughter ions (in parentheses the relative intensities – intensity of the first, most abundant ion is taken as 100)
trans-resveratrol *C*-glucoside	10.1	389	269; 241 (11); 299 (2);175 (1); 163 (1)
trans-resveratrol *O*-glucoside	10.9	389	227; 305 (14); 185 (1); 175 (2)
trans-resveratrol *O*-glucoside (piceid)	12.4	389	227; 305 (12); 175 (2); 289 (1)
piceatannol *O*-glucoside	12.7	405	243; 375 (2); 225 (1); 345 (1); 215 (1); 199 (1); 149 (0.5); 173 (0.5)
resveratrol dimer (caraphenol)	13.0	469	451; 363 (23); 375 (19); 281 (1); 423 (0.5)
piceatannol	13.2	243	225; 175 (62); 201 (43); 199 (31); 200 (24)
		+245	135; 236 (44); 227 (25); 199 (24); 219 (21); 214 (18); 124 (15); 209 (12); 203 (9); 185 (8)
piceatannol (standard)	13.2	243	225; 201 (59); 199 (36); 175 (30); 215 (16); 159 (18)
resveratrol dimer	14.9	453	359; 265 (19); 435 (3); 393 (0.6); 297 (0.6)
		+455	361; 349 (17); 267 (3); 293 (2); 251 (2); 255 (2); 215 (1)
trans-resveratrol	15.6	227	185; 183 (48); 159 (33); 157 (33); 143 (20)
		+229	135; 211 (20); 183 (10); 165 (3); 145 (2); 193 (2); 187 (2); 141 (1)
trans-resveratrol (standard)	15.6	227	185; 183 (66); 159 (57); 157 (35); 143 (20)
		+229	135; 211 (17); 183 (8); 165 (3); 145 (2); 193 (3); 187 (2)
resveratrol dimer	15.8	469	345; 375 (46); 251 (9); 241 (5); 423 (3); 357 (3)
resveratrol dimer *O*-glucoside	17.1	615	453; 359 (3), 585 (2); 347 (1); 389 (1), 567 (0.5)
resveratrol trimer	17.7	679	585; 447 (28)491 (11); 385 (2); 479 (1); 465 (1); 567 (1)
		+681	575; 587 (53); 481 (34); 345 (21); 441 (14); 557 (19); 451 (14); 493 (10); 239 (5)
resveratrol dimer	18.0	469	375; 385 (55); 359 (44); 345 (24); 241; 451; 411;
		+471	377; 365 (82); 255 (82); 361 (57); 215 (40); 231 (33); 453 (22); 359 (22); 343 (21); 185 (7)
resveratrol tetramer (*cis*)	18.1	905	811; 717 (78); 357 (14); 451 (7); 611 (7); 887;675 (5)
resveratrol main dimer (ϵ-viniferin)	19.4	453	359; 347 (56); 435 (21); 369 (14); 411 (11); 253 (9)
		+455	349; 361 (86); 215 (70); 343 (57); 437 (51); 199 (39); 255 (32); 251 (18)
ϵ-viniferin (from refs *15* and *21*)	-	453	359; 347; 333; 435; 411; 369
resveratrol tetramer	20.5	905	811; 359 (33); 799 (25); 451 (11); 545 (5); 887 (4); 717 (2)
		+907	559; 361 (45); 453 (12); 651 (8); 813 (8); 541 (4); 783 (2); 801 (1)
resveratrol dimer	20.9	453 + 455	359; 347 (48); 435 (27); 369 (22); 333 (15); 253 (14) 361; 437 (88); 349 (22); 343 (18); 331 (17); 237 (16); 313 (14); 215 (13); 251 (11)
resveratrol main trimer	22.2	679 + 681	585, 447 (18); 491 (9); 661 (6); 479 (6); 567 (4); 423 (4) 587; 575 (81); 481 (43); 463 (36); 557 (42); 569 (40); 215 (34); 493 (34); 347 (19)
resveratrol tetramer	22.8	905	799; 811 (35); 359 (35); 887 (18); 781 (15); 545 (13)
resveratrol trimer	23.2	679	585; 447 (22); 491 (9); 661 (6); 479 (6); 567 (4); 637 (3)
		+681	587; 575 (64); 481 (40); 557 (35); 569 (33); 463 (32); 493 (30); 215 (25); 475 (20)

Table 2. Nonstilbenoid Polyphenolic Compounds Determined in Hasaine sladki Stems

compound	t_R (min)	$[M-H]^-$ or $[M+H]^+$	main daughter ions (in parentheses the relative intensities – intensity of the first, most abundant ion is taken as 100)
caffeic acid *O*-glucoside	1.8	341	179; 161 (18); 143 (13); 149 (3); 131 (3); 125 (2)
procyanidin B1	6.7	577	425; 407 (61); 289 (24); 451 (16); 245 (16);287 (16)
		+579	427; 409 (29); 291 (21); 301 (14); 247 (10); 289 (8); 287 (8)
catechin	7.8	289	245; 205 (27); 179 (13); 203 (11); 227 (3); 165 (3); 161 (3)
		+291	123; 139 (74); 165 (32); 273 (21); 151 (20); 147 (10); 249 (1)
catechin (standard)	7.8	289	245; 205 (28); 179 (13); 203 (11); 175 (6); 227 (4);165 (4)
		+291	123; 139 (76); 165 (33); 273 (22); 151 (21);147 (11)
coumaric acid *O*-glucoside	8.2	325	163; 145 (92); 187 (48); 265 (18); 205 (10); 235 (9); 289 (7)
epicatechin	9.8	289	245; 205 (25); 179 (12); 203 (13); 231 (5); 271 (3): 161 (3)
		+291	123; 139 (78); 165 (32); 151 (25); 273 (19); 147 (10); 231 (2)
taxifolin *O*-glucoside	10.4	465	285; 151 (33); 339 (22); 303 (11); 177 (5); 257 (1)
procyanidin B2	11.1	577	425; 407 (39); 287 (25); 289 (20); 451 (13); 559 (5); 299 (5)
quercetin *O*-glucoside	13.0	463	301; 161 (4); 179 (3); 271 (2); 263 (1); 323 (1)
catechin gallate	13.0	441	289; 395 (22); 169 (17); 331 (8); 245 (5); 193 (6); 405 (6)

flavan-3-ols catechin and epicatechin in stems. Results are presented in **Table 3**.

The cultivar Hasaine sladki has the highest content of resveratrol mono- and oligomers; regarding to catechins, the best was Zilga. The poorest in the polyphenol content was Yubilei Novgoroda, which was the only cultivar studied growing white berries.

For the comparison of *trans*-stilbenoid and flavanol total contents in grapevine stems, the mean areas under UV chromatograms (AUC) at 306 and 280 nm were used (**Table 4**). The numbers listed in **Table 4** for 280 nm do not contain the respective areas of *trans*-resveratrol and ϵ-viniferin peaks. The two cultivars with red berries contained practically equal amounts of nonstilbenoid polyphenols, and the stems of cultivar

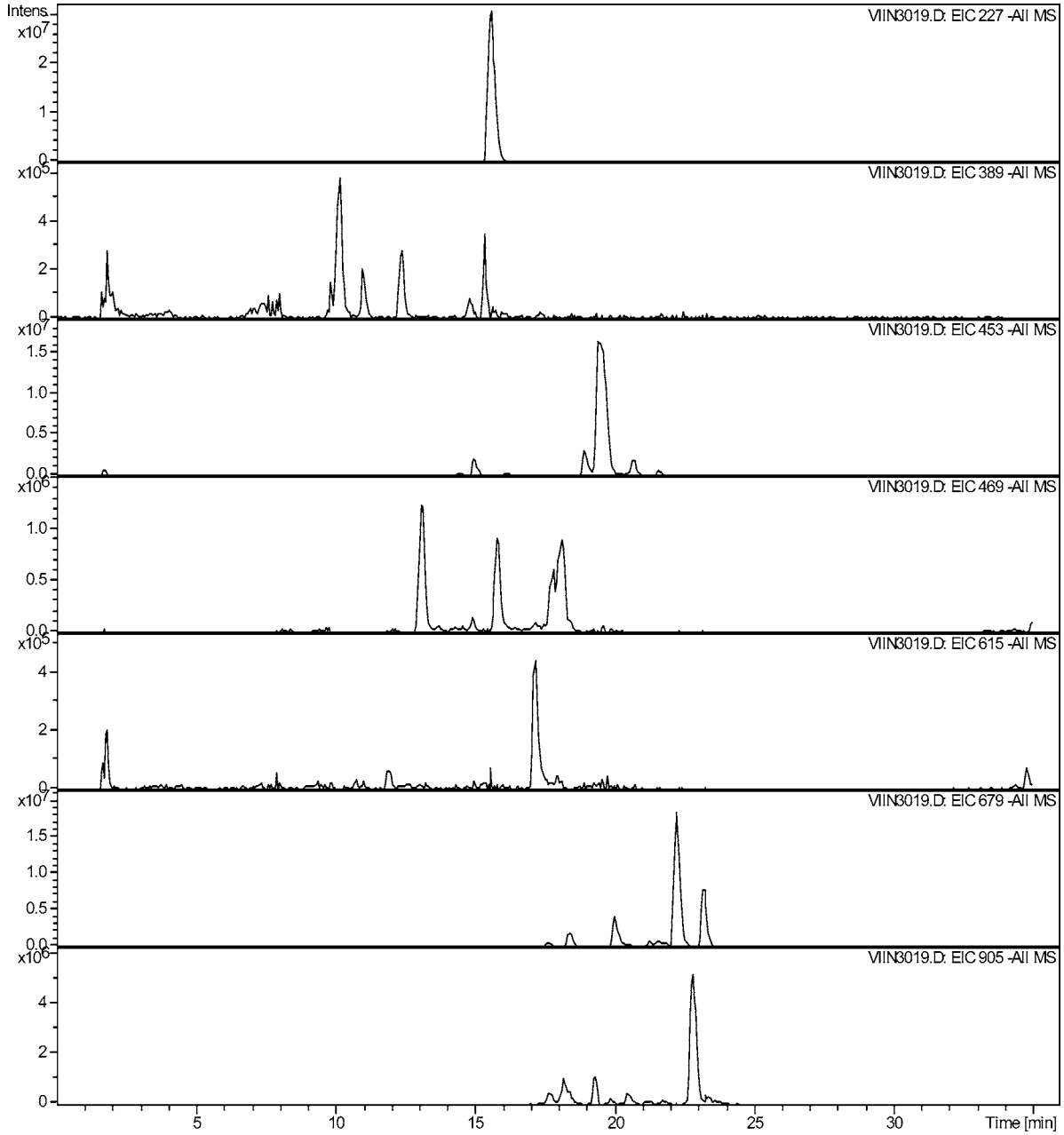

Figure 3. Negative extracted ion chromatograms (EIC) of resveratrol and its main derivatives. From top: resveratrol, $[M - H]^- = 227$; resveratrol glucosides, 389; resveratrol dimers, 453 and 469; resveratrol dimer glucoside, 615; resveratrol trimer, 679; and resveratrol tetramer, 905.

Table 3. Content (mg/g dw) of Three Major Stilbenoids and Two Flavan-3-ols in Grapevine Stems of Different *V. vinifera* Cultivars (Eight Samples from 16 Plants of Each Cultivar)

	mean stilbenoid content				mean catechin content	
cultivar	resveratrol (1)	ϵ-viniferin (2)	main trimer (3)	1 + 2 + 3	catechin	epicatechin
Hasaine sladki	3.2 ± 0.5	1.7 ± 0.3	0.24 ± 0.07	5.1±	1.0 ± 0.02	1.0 ± 0.03
Zilga	2.1 ± 0.3	1.2 ± 0.3	0.11 ± 0.03	3.4±	1.4 ± 0.03	1.3 ± 0.02
Yubilei Novgoroda	1.1 ± 0.3	0.7 ± 0.2	0.04 ± 0.01	1.8±	0.6 ± 0.02	0.6 ± 0.02

Yubilei Novgoroda with white grapes contained significantly less of both groups of polyphenols. Fresh grape skin contains 0.05−0.1 mg/g resveratrol (*33*), and in red wines, the concentration of *trans*-resveratrol has been found to be in the interval of 0.2−7.7 mg/L (*2*).

Conclusion. A hyphenated chromatographic method with DAD and MS/MS detection determined a number of major as well as minor polyphenolic components of the methanol extract of grapevine stems. UV-DAD at different wavelengths (280 and

Table 4. Areas Under Curves of UV Chromatograms (AU × min) at 306 and 280 nm

	mean area (AU × min)	
cultivar	306 nm	280 nm
Hasaine sladki	10780	2700
Zilga	8030	2430
Yubilei Novgoroda	4590	1310

306 nm) was used (i) for estimation of the concentrations of several major individual compounds (*trans*-resveratrol, its main oligomers, and catechins) by the external standard method, (ii) for comparison of total contents of different groups of the polyphenols (stilbenoids and flavonols) in different cultivars of vine, and (iii) as a supporting method of the MS/MS for identification of polyphenols. The lignified stems of northern cultivars of *V. vinifera* grown in Estonia in climatic conditions extreme for this plant are a perfect source of medically and dietarily important hydroxystilbene *trans*-resveratrol and its derivatives. The other larger group of compounds is catechin and its derivatives that in many cases complement and amplify the physiological effect of resveratrol and derivatives. The stilbenoid content is cultivar-dependent.

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