LC-MS/MS Screening of Phenolic Compounds in Wild and Cultivated Grapes *Vitis amurensis* Rupr

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**Abstract:** This work represents a comparative metabolomic study of extracts of wild grapes obtained from six different places in the Primorsky and Khabarovsk territories (Far East Russia) and extracts of grapes obtained from the collection of N.I. Vavilov All-Russian Institute of Plant Genetic Resources (St. Petersburg). The metabolome analysis was performed by liquid chromatography in combination with ion trap mass spectrometry. The results showed the presence of 118 compounds in ethanolic extracts of *V. amurensis* grapes. In addition, several metabolites were newly annotated in *V. amurensis*. The highest diversity of phenolic compounds was identified in the samples of the *V. amurensis* grape collected in the vicinity of Vyazemsky (Khabarovsk Territory) and the floodplain of the Arsenyevka River (Primorsky Territory), compared to the other wild samples and cultivated grapes obtained in the collection of N.I. Vavilov All-Russian Institute of Plant Genetic Resources.

**Keywords:** Amur grape; identification; mass spectrometry; metabolites; metabolomics

1. **Introduction**

The appearance of the first representatives of the *Vitaceae* family (genus *Vitis*) dates from the Upper Cretaceous period [1]. Several types of fossil grapes of genus *Vitis* have been found in different parts of North America [2]. In the Eocene, representatives of the genus *Vitis* were widespread in Eurasia and the Far North [2]. In the Paleogene, one of the best-preserved species of fossil grapes *Vitis sachelinensis* Krysh. was found and described in the sediments of the Sakhalin Island, the Russian Far East. These data show that the evolution of the vine in the territory of Russia proceeded from ancient times. Moreover, now wild grapes of the genus *Vitis* grow in many Russian regions [3,4]. At the same time, there is very little information about the culture of East Asian grapes.

Grape berries contain 65–85% water; 10–33% sugar (glucose and fructose); flofaben; gallic acid; quercetin; oenin; the glycosides monodelphinidin and delphinidin; the acids malic, hydrosilic, *ortho*-hydroxybenzoic, phosphoric, tartaric, citric, succinic, formic, pectin, and tannins; salts of potassium; magnesium; calcium; manganese; cobalt; iron vitamins B1, B2, B6, B12, A, C, P, and PP; folic acid; and enzymes. The dominant class of biologically active compounds of fruits and especially grape ridges are flavonoids, in par-
ticular complexes of oligomeric proanthocyanidins (condensed tannins), which are polymeric forms of flavonoids from the group of catechins, and their monomeric units, namely catechins and leucoanthocyanidins [5].

Many studies have been devoted to the biological activity of flavonoids and complexes of oligomeric proanthocyanidins [6,7]. Complexes of oligomeric proanthocyanidins act as traps of free radicals and block the process of lipid peroxidation of biological membranes [8,9]. Their antioxidant activity is many times higher than that of vitamins E and C. They can inhibit the activity of many enzymes (hydrolase, oxidoreductase, kinase, transferase, among others) [10]. Due to the wide spectrum of action, the active compounds of the grapes V. amurensis have a pronounced positive effect on various organs and systems of the body, such as antihypertensive and vasostrengthening effects, as well as antidiabetic, anti-inflammatory, antiallergy, anticarcinogenic, antistress, radioprotective, and antirheumatic effects. Moreover, flavonoids have an anti-Alzheimer’s activity [11–13].

This work presents a detailed comparative study of the metabolomic composition of wild V. amurensis grape berry extracts taken from six different locations of the Russian Far East and four cultural specimens of V. amurensis obtained from the collection of N.I. Vavilov All-Russian Institute of Plant Genetic Resources (St. Petersburg). High-performance liquid chromatography (HPLC) in combination with tandem mass spectrometry was used to identify target analytes in the extracts. Previously, the authors carried out metabolomic studies of Far Eastern plant species, such as Schizandra chinensis, Rhodiola rosea, Rhododendron adamsii, and Panax ginseng [14,15].

2. Results

The metabolome of ten samples of wild and cultural V. amurensis was analyzed and compared. A combination of both ionization modes (positive and negative) in MS full scan mode was applied for the molecular mass determination of the compounds in ethanolic extracts of V. amurensis. Compound identification was performed by comparing the observed m/z values and the fragmentation patterns with the literature. The list of compounds identified in the ethanolic extract of V. amurensis are represented in Table A1. The 118 compounds shown in Table A1 belong to different phenolic families, namely anthocyanins, flavones, flavonols, flavan-3-ols, flavanones, hydroxycinnamic acids, hydroxybenzoic acids, stilbenes, and tannins.

2.1. Anthocyanidins and Anthocyanins

A total of 18 anthocyanin compounds have been identified in the analyzed samples of V. amurensis (Table 1). The anthocyanins pelargonidin-3-O-glucoside, cyanidin-3-O-glucoside, and petunidin-3-(6-O-coumaroyl) glucoside have already been characterized as a component of Far East V. amurensis [16]. The anthocyanins malvidin-3-O-acetylhexo-side, delphinid-3,5-O-diglucoside, malvidin-3-O-rutinoside, malvidin 3-acetyl-5-glucoside, petunidin 3-coumaroylglucoside-5-O-glucoside, and malvidin 3-coumaroylglucoside-5-O-glucoside were only found in the extracts of cultivated V. amurensis (St. Petersburg).

| No. | Identified Compound                          | ARS  | ART  | KAL  | PAK  | RIK  | VZK  | SPB-1 | SPB-2 | SPB-3 | SPB-4 |
|-----|---------------------------------------------|------|------|------|------|------|------|-------|-------|-------|-------|
| 1.  | Cyanidin 3,5-O-diglucoside                  |      |      |      |      |      |      |       |       |       |       |
| 2.  | Cyanidin-3-O-glucoside                      |      |      |      |      |      |      |       |       |       |       |
|     | [Cyanidin 3-O-beta-D-glucoside]             |      |      |      |      |      |      |       |       |       |       |
| 3.  | Delphinidin 3-O-glucoside                   |      |      |      |      |      |      |       |       |       |       |
| 4.  | Delphinidin-3,5-O-diglucoside               |      |      |      |      |      |      |       |       |       |       |
| 5.  | Malvidin 3-(6-O-acetyl) glucoside           |      |      |      |      |      |      |       |       |       |       |
| 6.  | Malvidin 3-(6-O-coumaroyl) glucoside        |      |      |      |      |      |      |       |       |       |       |
7. Malvidin 3-(6′-p-cafeoylglucoside)  +  +  +  +  +  +  +  +  +
8. Malvidin 3,5-diglucoside  +  +  +  +  +  +  +  +  +
9. Malvidin 3-coumaroylglucoside-5-O-glucoside  +
10. Malvidin 3-O-acetyl hexoside  +
11. Malvidin 3-O-glucoside  +  +  +  +  +  +  +
12. Pelargonidin-3-O-glucoside (callistephin)  +
13. Peonidin-3,5-O-diglucoside [peonin; peonidin 3-glucoside-5-glucoside]  +  +  +  +  +  +
14. Peonidin-3-O-glucoside  +  +  +
15. Petunidin 3-(6-O-coumaroyl) glucoside  +
16. Petunidin 3-coumaroylglucoside-5-O-glucoside  +
   Petunidin 3-O-glucoside-5-O-glucoside [Petunidin 3,5-di-O-beta-D-glucoside]  +  +  +  +  +
18. Petunidin-3-O-glucoside  +

| Total number | 2 | 10 | 5 | 1 | 3 | 8 | 7 | 8 | 6 | 6 |
|--------------|---|----|---|---|---|---|---|---|---|---|

ARS, wild V. amurensis sample obtained from floodplain of the Arsenyevka River (Primorsky Territory); ART, wild V. amurensis sample obtained from the vicinity of Artem (Primorsky Territory); KAL, wild V. amurensis sample obtained from the vicinity of Kalinovka (Primorsky Territory); PAK, wild V. amurensis sample obtained from the Pakhtusov Islands (Sea of Japan); RIK, wild V. amurensis sample obtained from Rikord Island (Sea of Japan); VZK, wild V. amurensis sample obtained from the vicinity of Vyazemsky (Khabarovsky Territory); SPB-1, SPB-2, SPB-3, and SPB-4, samples of cultivated V. amurensis provided by N.I. Vavilov All-Russian Institute of Plant Genetic Resources (St. Petersburg).

2.2. Other Flavonoid Compounds

A total of 42 flavonoid compounds were identified in analyzed V. amurensis samples (Table 2). The flavonols dihydrokaempferol, kaempferide, mearnsit, kaempferol-3-O-glucoside, dihydrokaempferol glucoside,isorhamnetin 3-O-rhamnside, hyperoside, taxifolin-3-O-glucoside, kaempferol 3,7-di-O-glucoside, and quercetin-O-dihexoside have been already characterized as components of Far East V. amurensis.

Table 2. Other flavonoid compounds identified in the ethanolic extracts of V. amurensis.

| No. | Identified Compound                     | ARS | ART | KAL | PAK | RIK | VZK | SPB-1 | SPB-2 | SPB-3 | SPB-4 |
|-----|----------------------------------------|-----|-----|-----|-----|-----|-----|-------|-------|-------|-------|
| 1.  | Quercetin-3-O-glucuronide               | +   | +   | +   | +   | +   | +   | +     | +     | +     | +     |
| 2.  | Kaempferol                              | +   | +   | +   | +   | +   |     |       |       |       |       |
| 3.  | Quercetin                               | +   | +   | +   | +   | +   | +   |       |       |       |       |
| 4.  | Isorhamnetin [isorhamnetol; Quercetin 3′-Methyl ether] | +   |     | +   |     | +   |     |       |       |       |       |
| 5.  | Isorhamnetin 3-O-glucoside             | +   | +   | +   | +   |     |     |       |       |       |       |
| 6.  | Myricetin-3-O-galactoside              | +   |     | +   | +   |     |     |       |       |       |       |
| 7.  | Quercetin 3-O-glucoside [isouercitin; Hirsutrin] | +   |     | +   | +   |     |     |       |       |       |       |
| 8.  | Myricetin                               | +   | +   |     |     |     |     |       |       |       |       |
| 9.  | Dihydrokaempferol                      |     |     |     |     |     | +   |       |       |       |       |
| 10. | Dihydroquercetin (Taxifolin; Taxifoliol) |     |     |     |     |     | +   |       |       |       |       |
| Molecules 2021, 26, 3650 | 4 of 17 |
|------------------------|--------|
| 11. Hyperoside (Quercetin 3-O-galactoside; Hyperin) | + |
| 12. Kaempferol diglycoside | + |
| 13. Kaempferol glycoside | + |
| 14. Dihydrokaempferol glucoside | + |
| 15. Herbacetin | + |
| 16. Isohamnetin 3-O-rhamnoside | + |
| 17. Kaempferide | + |
| 18. Mearnssetin | + |
| 19. Quercetin-3-O-dihexoside | + |
| 20. Rutin (Quercetin 3-O-rutinoside) | + |
| 21. Taxifolin-3-O-glucoside | + |
| **Total number:** | 3 9 2 1 4 8 3 6 2 4 |
| 22. Apigenin | + |
| 23. Syringetin | + |
| 24. Luteolin diglycoside | + |
| 25. Nevadensin | + |
| 26. Vitexin 2"-O-glucoside [Apigenin 8-C-glucoside 2"-O-glucoside] | + |
| 27. Luteolin | + |
| 28. Diosmetin [Luteolin 4'-Methyl Ether; Salinigrifloravonol] | + |
| 29. Pentahydroxy trimethoxy flavone | + |
| 30. Apigenin diglycoside | + |
| 31. Vitexin [Apigenin 8-C-Glucoside] | + |
| 32. Vitexin glucoside | + |
| 33. Apigenin glucoside | + |
| **Total number:** | 2 3 2 2 1 3 2 4 2 3 |
| 34. Cirsimaretin [Scrophulein; 4',5-dihydroxy-6,7-dimethoxyflavone; 7'-methylcapillarisin] | + |
| 35. Catechin [D-Catechol] | + |
| 36. Epicatechin | + |
| 37. Galloカテchin [+(-)Gallocatechin] | + |
| 38. Catechin gallate | + |
| **Total number:** | 0 2 0 1 2 1 2 1 1 |
| 39. Naringenin [Naringetol; Naringenine] | + |
| 40. Eriodictyol-7-O-glucoside [Pyracanthoside; Miscanthoside] | + |
| 41. Hesperitin [Hesperetin] | + |
| 42. Hexahydroxyflavanone hexoside | + |
| **Total number:** | 0 1 0 2 1 2 0 0 0 1 |

ARS, wild *V. amurensis* sample obtained from floodplain of the Arsenyevka River (Primorsky Territory); ART, wild *V. amurensis* sample obtained from the vicinity of Artem (Primorsky Territory); KAL, wild *V. amurensis* sample obtained from the vicinity of Kalinovka (Primorsky Territory); PAK, wild *V. amurensis* sample obtained from the Pakhtusov Islands (Sea of Japan); RIK, wild *V. amurensis* sample obtained from Rikord Island (Sea of Japan); VZK, wild *V. amurensis* sample obtained from the vicinity of Vyazemsky (Khabarovsk Territory); SPB-1, SPB-2, SPB-3, and SPB-4, samples of cultivated *V. amurensis* provided by N.I. Vavilov All-Russian Institute of Plant Genetic Resources (St. Petersburg).
2.3. Phenolic Acids and Other Compounds

In addition, 22 phenolic acids and 37 other compounds were identified in analyzed *V. amurensis* samples (Table 3). It should be noted that the coumarins umbelliferone and fraxin; the sterol fucosterol; and the flavanols taxifolin-3-O-glucoside, kaempferol-3,7-di-O-glucoside; hydroxycinnamic acids 3-p-coumaroyl-4-cafeoylquinic acid, and 5-O-(4'-O- p-coumaroyl glucosyl) quinic acid were identified by mass spectrometry only in samples of wild *V. amurensis* grapes collected from the Pakhtusov Islands and Rikord Island, Peter the Great Bay, Sea of Japan.

Table 3. Phenolic acids and other compounds identified in the ethanolic extracts of *V. amurensis*.

| No. | Identified Compound                                      | ARS | ART | KAL | PAK | RIK | VZK | SPB-1 | SPB-2 | SPB-3 | SPB-4 |
|-----|--------------------------------------------------------|-----|-----|-----|-----|-----|-----|-------|-------|-------|-------|
|     | Hydroxybenzoic acids                                   |     |     |     |     |     |     |       |       |       |       |
| 1.  | Salvianolic acid D                                     | +   | +   | +   | +   | +   | +   | +     | +     | +     | +     |
| 2.  | Salvianolic acid G                                     | +   |     |     | +   | +   |     |       |       |       |       |
| 3.  | Ellagic acid [Benzoic acid; Elagostasine]              | +   |     |     |     |     |     | +     | +     |       |       |
| 4.  | 4-Hydroxybenzoic acid                                  |     |     |     |     |     |     |       |       |       |       |
| 5.  | Protocatechuic acid                                    |     |     |     |     |     |     |       |       |       |       |
| 6.  | Gallic acid                                            |     |     |     |     |     |     |       |       |       |       |
| 7.  | Syringic acid [Benzoic acid; Cedar acid]              |     |     |     |     |     |     |       |       |       |       |
| 8.  | Salvianolic acid F                                     |     |     |     |     |     |     | +     |       |       |       |
| 9.  | Dihydroxybenzoyl-hexoside                              |     |     |     |     |     |     |       |       |       |       |
|     | Total number:                                          | 1   | 1   | 0   | 1   | 0   | 6   | 2     | 3     | 1     | 1     |
|     | Hydroxycinnamic acids                                  |     |     |     |     |     |     |       |       |       |       |
| 10. | Caftaric acid [cis-caftaric acid; 2-cafeoyl-L-tartaric acid] | +   |     |     | +   | +   | +   | +     | +     | +     | +     |
| 11. | Di-O-cafeoylquinic acid                               | +   |     |     |     |     |     | +     | +     |       |       |
| 12. | Sinapic acid [trans-Sinapic acid]                     |     |     |     |     |     |     | +     | +     |       |       |
| 13. | Coutaric acid [Trans-p-Coumaroyltartaric acid]        |     |     |     |     |     |     |       |       |       |       |
| 14. | Fertaric acid [Fertarate]                             |     |     |     |     |     |     |       |       |       |       |
| 15. | p-Coumaric acid-O-hexoside [Trans-p-Coumaric acid 4-glucoside] | +   |     |     |     |     |     |       |       |       |       |
| 16. | Caffeic acid-O-(sinapoyl-O-hexoside)                  |     |     |     |     |     |     | +     | +     |       |       |
| 17. | p-Coumaric acid                                       |     |     |     |     |     |     | +     |       |       |       |
| 18. | Caffeoylmalic acid                                    |     |     |     |     |     |     |       |       |       |       |
| 19. | 1-Caffeoyl-beta-D-glucose [Caffeic acid-glucoside]    |     |     |     |     |     |     |       |       |       | +     |
| 20. | 5-O-(4'-O-p-coumaroyl glucosyl) quinic acid            |     |     |     |     |     |     |       |       |       |       |
| 21. | 3-p-coumaroyl-4-cafeoylquinic acid                    |     |     |     |     |     |     |       |       |       |       |
| 22. | Coumaric acid derivative                              |     |     |     |     |     |     |       |       |       |       |
|     | Total number:                                          | 0   | 1   | 0   | 3   | 2   | 2   | 1     | 1     | 0     | 4     |
|     | Other compounds                                        |     |     |     |     |     |     |       |       |       |       |
| 23. | Ethyl gallate                                         | +   | +   | +   | +   | +   | +   | +     | +     | +     | +     |
| 24. | Malic acid                                            | +   | +   | +   | +   | +   | +   | +     | +     | +     | +     |
| 25. | Hexose-hexose-N-acetyl                                | +   | +   |     | +   | +   | +   | +     | +     | +     | +     |
| 26. | Citric acid                                           | +   | +   |     | +   | +   | +   | +     | +     | +     | +     |
| 27. | Quinic acid                                           | +   | +   | +   | +   | +   | +   | +     | +     | +     | +     |
28. Galloyl glucose [Beta-Glucogallin; 1-O-Galloyl-Beta-D-Glucose]  
29. L-Tryptophan [Tryptophan; (S)-Tryptophan]  
30. Cyclopasifloric acid glucoside  
31. Indole-3-carboxylic acid  
32. Myristoleic acid [Cis-9-Tetradecanoic acid]  
33. Resveratrol [trans-Resveratrol; Stilbentriol]  
34. Protocatechuic acid-O-hexoside  
35. Palmitic acid [Berbericinine; Burasaine]  
36. Polydatin [Piceid; trans-Piceid]  
37. Procyandin A-type dimer  
38. Shikimic acid  
39. Esculetin [Cichorigenin; Aesculetin]  
40. 9-oxo-10E,12Z-octadecanoic acid [9-Oxo-ODE]  
41. Gallic acid hexoside  
42. Esculetin [Aesculin; Esculoside; Polychrome]  
43. 1-O-Sinapoyl-beta-D-glucose  
44. Stigmasterol [Stigmasterin; Beta-Stigmasterol]  
45. Oleanoic acid  
46. Tartaric acid  
47. Umbelliferone  
48. Dihydroferulic acid  
49. Linolenic acid (Alpha-Linolenic acid; Linolenate)  
50. Nonadecadienoic acid  
51. Bilobalide [(-)-Bilobalide]  
52. 3,7-Dimethylevercetin  
53. Erucic acid (Cis-13-Docosenoic acid)  
54. Fraxin (Fraxetin-8-O-glucoside)  
55. Fucosterol [Fucostein; Trans-24-Ethylidenecholesterol]  
56. Floridzin: phlorhizin: Phloretin 2'-Glucoside; Phloretin-O-hexoside  
57. Ursolic acid  
58. Anmunricoic acid  
59. Dimethylellagic acid hexose

| Molecules 2021, 26, 3650 | 6 of 17 |

| Total number | 7 | 15 | 7 | 17 | 11 | 11 | 5 | 5 |

ARS, wild *V. amurensis* sample obtained from floodplain of the Arsenyevka River (Primorsky Territory); ART, wild *V. amurensis* sample obtained from the vicinity of Artem (Primorsky Territory); KAL, wild *V. amurensis* sample obtained from the vicinity of Kalinovka (Primorsky Territory); PAK, wild *V. amurensis* sample obtained from the Pakhtusov Islands (Sea of Japan); RIK, wild *V. amurensis* sample obtained from Rikord Island (Sea of Japan); VZK, wild *V. amurensis* sample obtained from the vicinity of Vyazemsky (Khabarovsk Territory); SPB-1, SPB-2, SPB-3, and SPB-4, samples of cultivated *V. amurensis* provided by N.I. Vavilov All-Russian Institute of Plant Genetic Resources (St. Petersburg).
3. Discussion

In general, the diversity of phytochemicals identified in wild and cultural grape V. amurensis resulted in the following descending order (number of metabolites in parenthesis): VZK (52) > ART (46) > SPB-2 (39) > SPB-1 (28) > SPB-4 (27) > PAK (25) > RIK (22) > KAL (20) > SPB-3 (19) > ARS (18). The most diverse metabolome was identified in the grapes collected in the vicinity of Vyazemsky, Khabarovsk Territory, which was rich in flavanols and phenolic acids.

The anthocyanins identified in V. amurensis in this study were previously identified and annotated in the vines [17] Solanum nigrum [18], Gaultheria Antarctica [19], and Vitis vinifera [20] and wheat [21]. Our identification of flavonoid compounds agrees with bibliographic data for Echinops [22], Rhodiola rosea [23], Ocimum [24], Alpinia officinarum [25], Brazilian propolis [26], Vitis vinifera [20], Rubus occidentalis [27], C. edulis [28], and Vaccinium macrocarpon [29].

Although wild grapes tend to be more diverse than cultivated varieties [30], this number of anthocyanins in one form is quite rare and more likely to occur in other berries, such as blueberries [31]. We hypothesize that many different anthocyanins are associated with rather low temperatures in summer and monsoon climates. To respond to adverse conditions, various anthocyanins are produced [32]. In addition, V. amurensis have an increased acidity of the fruit, which is also associated with unfavorable growing conditions [33]. As it is known, anthocyanins and many other phenolic compounds participating in the protective processes of plants are more stable in an acidic environment [34].

4. Materials and Methods

4.1. V. amurensis Samples

Ten samples of wild and cultivated grape V. amurensis were selected for the performance of metabolomics study. Six samples of wild V. amurensis were collected from different places in the Primorsky and Khabarovsk territories, Far Eastern Russia (Table 4, Figure 1). Four samples of cultivated V. amurensis, namely SPB-1, SPB-2, SPB-3, and SPB-4, were obtained from the collection of N.I. Vavilov All-Russian Institute of Plant Genetic Resources, St. Petersburg. The grapes were harvested at the end of August and September 2020. Each sample included 100 g of grape berries.

| Code Name of the Sample | Location | Geographical Values | Soil Type |
|-------------------------|----------|---------------------|-----------|
| ARS                     | Floodplain of the Arsenyevka River, Primorsky Territory | N. 44°52'18", E 133°35'12" | brown grey bleached soils |
| ART                     | The vicinity of Artem, Primorsky Territory | N 43°21'34", E 132°11'19" | yellow-brown soil |
| KAL                     | The vicinity of Kalinovka, Primorsky Territory | N 43°07'27", E 133°12'30" | layered floodplains |
| PAK                     | The Pakhtusov Islands, Peter the Great Bay, Sea of Japan | N 42°53'57", E 131°38'45" | yellow-brown soil |
| RIK                     | Rikord Island, Peter the Great Bay, Sea of Japan | N 42°52'54", E 131°40'06" | yellow-brown earth soils |
| VZK                     | The vicinity of Vyazemsky, Khabarovsk Territory | N 47°32'15", E 134°45'20" | podzolic brown forest heavy loamy soils |
Figure 1. Region of wild V. amurensis grape collection.

4.2. Chemicals and Reagents

HPLC-grade acetonitrile was purchased from Fisher Scientific (Southborough, UK), and MS-grade formic acid was purchased from Sigma-Aldrich (Steinheim, Germany). Ultra-pure water was obtained with Siemens Ultra-Clear TWF EDI UV UF TM Water Purification System (Siemens, Munich, Germany). All the other chemicals were of analytical grade.

4.3. Fractional Maceration

Fractional maceration with ethyl alcohol was applied to obtain highly concentrated extracts of V. amurensis. Each sample of V. amurensis was divided into three parts and consistently infused. The infusion time of each part of the extractant was seven days.

4.4. Liquid Chromatography

The separation of multicomponent mixtures was performed by a Shimadzu LC-20 Prominence HPLC (Shimadzu, Kyoto, Japan) equipped with a UV detector and a Shodex ODP-40 4E reverse-phase column (4.6 × 250 mm, particle size 4 μm). The gradient elution program with two mobile phases (A, deionized water; B, acetonitrile with formic acid 0.1% v/v) was as follows: 0.01–2 min, 100% B; 2–50 min, 100–0% B; control washing 50–60 min, 0% B. The entire HPLC analysis was done with an SPD-20A detector at wavelengths of 230 and 330 nm; the temperature corresponded to 40 °C. The injection volume was 10 μL.
4.5. Mass Spectrometry

MS analysis was performed on an ion trap amaZon SL (Bruker Daltonics, Bremen, Germany). Four-stage ion separation (MS/MS mode) was implemented. All the chemical profiles of the samples were obtained by the HPLC–ESI–MS/MS method. The working parameters were as follows: ionization source temperature 50 °C, gas flow 4 L/min, nebulizer gas (atomizer) 7.3 psi, capillary voltage 4500 V, endplate bend voltage 1500 V, fragmentation voltage 280 V, and collision energy 60 eV. The ion trap was used in the scan range of 100–1700 m/z for MS and MS/MS. The capture rate was one spectrum/s for MS and two spectrum/s for MS/MS. The mass spectra were recorded in negative and positive ion mode. Data collection was controlled by Hystar DataAnalysys 4.1 software (Bruker Daltonics, Bremen, Germany). All the measurements were performed in triplicate.

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Appendix A

Table A1. The list of compounds identified in ethanolic extracts of V. amurensis.

| No. | Identified Compound                  | Molecular Formula | Calculated Mass | Precursor Ion, m/z [M-H] | Fragment Ions, m/z | References |
|-----|-------------------------------------|-------------------|-----------------|--------------------------|-------------------|------------|
| 1.  | Cyanidin 3,5-O-diglucoside          | C27H21O16         | 611.5335        | 611                      | 287; 449; 269; 231; 199; 161; 231; 213; | [35,36] |
| 2.  | Cyanidin-3-O-glucoside             | C27H21O11         | 449.3848        | 449                      | 287; 206; 143     | [19,20,35,37,38] |
| 3.  | Delphinidin 3-O-glucoside          | C21H21O12+        | 465.3905        | 465                      | 165; 239; 213; 173; | [19–21,39] |
| 4.  | Delphinidin-3,5-O-diglucoside      | C27H21O17         | 626.5169        | 627                      | 465; 303; 257; 153; | [18,40] |
| 5.  | Malvidin 3,5-O-diglucoside         | C28H23O13         | 655.5795        | 655                      | 493; 331; 315; 179; 313 | [17,20,21] |
| 6.  | Malvidin 3-(6-O-acetyl) glucoside  | C28H23O13         | 535.478         | 537                      | 331; 299; 261; 243; 211; 154; 111 | [20,39] |
| 7.  | Malvidin 3-(6-O-coumaroyl) glucosi | C28H23O14         | 639.5801        | 639                      | 242; 179; 150; 287; 213 | [20,39,40] |
| 8.  | Malvidin 3-coumaroylglucoside-5-O- | C28H23O11         | 801.7192        | 801                      | 639; 493; 331; 315; 287; 270; 242; 300 | [39] |
| 9.  | Malvidin 3-O-acetyl hexoside       | C27H23O14         | 535.479         | 537                      | 331; 305; 261; 207; 185; 255; 229; 211 | [17] |
| 10. | Malvidin 3-O-glucoside             | C28H21O12         | 493.4374        | 493                      | 331; 315; 179     | [20,39,40] |
|   | Name                                                                 | Molecular Formula | Molar Mass | Molar Masses | References       |
|---|----------------------------------------------------------------------|-------------------|------------|-------------|-----------------|
|11. | Pelargonidin-3-O-glucoside (callistephen)                           | C_{21}H_{21}O_{10} | 433.3854   | 414; 271; 172; 226; 116 | [35,39,41]       |
|12. | Peonidin-3,5-O-diglucoside [Peonin; Peonidin 3-glucoside-5-glucoside] | C_{28}H_{33}O_{16} | 625.5520   | 301; 463; 286; 258; 214; 121 | [21,39,40]       |
|13. | Peonidin-3-O-glucoside                                              | C_{27}H_{32}O_{11} | 463.4114   | 301; 286; 268; 258; 230; 202; 174; 121 | [20,39,41]       |
|14. | Petunidin 3-(6-O-coumaronyl) glucoside                              | C_{30}H_{38}O_{14} | 625.553    | 317; 302; 274; 218 | [20,39,40]       |
|15. | Petunidin 3-coumaroylglucoside-5-O-glucoside                        | C_{32}H_{41}O_{21} | 787.6926   | 625; 479; 317; 301; 246; 302; 274; 228 | [39,40]          |
|16. | Petunidin 3-galactoside                                             | C_{27}H_{32}O_{12} | 479.4108   | 317; 302; 273 | [19–21,39]       |
|17. | Petunidin 3,5-diglucoside                                          | C_{29}H_{34}O_{17} | 641.5514   | 317; 479; 420; 257; 302; 274; 228 | [39,40]          |

**Flavonols**

|   | Name                                                                 | Molecular Formula | Molar Mass | Molar Masses | References       |
|---|----------------------------------------------------------------------|-------------------|------------|-------------|-----------------|
|18. | Dihydrokaempferol                                                    | C_{13}H_{16}O_{5} | 288.2522   | 271; 199; 127; 243; 189; 118 | [22,42]       |
|19. | Dihydrokaempferol glucoside                                         | C_{13}H_{20}O_{6} | 450.3928   | 287; 227; 269; 225; 149 | [27]          |
|20. | Dihydroquercetin (taxifolin; taxifoliol)                             | C_{13}H_{18}O_{5} | 304.2516   | 259; 149; 199; 214; 19; 171 | [20,43,44]   |
|21. | Herbacetin [3,5,7,8-tetrahydroxy-2-(4-hydroxy-xyphenyl)-4H-chromen-4-one] | C_{13}H_{18}O_{7} | 302.2357   | 179; 273; 121; 151 | [24,45]       |
|22. | Hyperoside (quercetin 3-O-galactoside; hyperin)                      | C_{13}H_{18}O_{2} | 464.3763   | 301; 179; 257; 255; 147 | [43,46–48]      |
|     | Isorhamnetin [isorhamnetol; quercetin 3'-methyl ether; 3-methylquercetin] | C_{13}H_{20}O_{7} | 316.2623   | 299; 270; 230; 207; 177; 165; 147; 123; 147; 123; 119 | [49,50]       |
|23. | Isorhamnetin 3-O-galactoside                                         | C_{13}H_{20}O_{7} | 478.4029   | 317; 301; 257; 274; 228; 150 | [20,47,51]   |
|24. | Isorhamnetin 3-O-rhamonoside                                         | C_{13}H_{20}O_{7} | 462.4035   | 315; 152; 219 | [28,49]         |
|25. | Kaempferide                                                          | C_{13}H_{20}O_{7} | 300.2629   | 283; 265; 239; 211; 185; 133; 151 | [20,24,26] |
|26. | Kaempferol                                                           | C_{13}H_{18}O_{6} | 286.2363   | 269; 227; 153 | [20,24,50] |
|27. | Kaempferol diglycoside                                              | C_{27}H_{30}O_{6} | 610.5175   | 449; 287; 229; 165; 213; 111 | [52,53]       |
|28. | Kaempferol glycoside                                                | C_{27}H_{30}O_{6} | 448.3769   | 287; 269; 217; 318; 301; 273; 245; 193; 165; 139; 289; 271; 219; 153; 136; 273; 191; 255; 229; 205; 187; 163; 125; 227 | [20,47] |
|29. | Mearmetin                                                           | C_{13}H_{20}O_{8} | 332.2617   | 333 | [49]          |
|30. | Myricetin                                                           | C_{13}H_{18}O_{8} | 318.2351   | 317 | [20,28,54] |
|31. | Myricetin-3-O-galactoside                                           | C_{13}H_{20}O_{7} | 480.3757   | 299; 153; 271; 243; 171 | [47,48,55] |
|32. | Quercetin                                                           | C_{13}H_{18}O_{7} | 302.2357   | 285; 163; 267; 159; 239 | [20,24,37,43] |
|33. | Quercetin 3-O-glucoside [Isoqueretin; Hirsutrin]                    | C_{13}H_{20}O_{7} | 464.3763   | 303; 285; 257; 229; 201; 150; 155 | [20,27,47,56] |
|34. | Quercetin 3-O-glucuronide                                           | C_{13}H_{18}O_{7} | 478.3598   | 301; 179; 273; 151 | [39,47,57] |
|35. | Quercetin-O-dihexoside                                              | C_{13}H_{18}O_{7} | 626.5179   | 303; 257; 150; 229 | [51,58] |
|36. | Rutin (quercetin 3-O-rutinoside)                                     | C_{27}H_{30}O_{8} | 610.5175   | 303; 229; 257 | [27,35,37,56] |
| No. | Molecule                                      | Formula     | MW       | M/z       | References                  |
|-----|-----------------------------------------------|-------------|----------|-----------|----------------------------|
| 38  | Taxifolin-3-O-glucoside                       | C_{21}H_{22}O_{12} | 466.3922 | 467       | 449; 303; 188; 287; 132; 260 | [20] |
|     | **Flavones**                                  |             |          |           |                            |
| 39  | Apigenin [5,7-dixydoxy-2-(40hydroxyphenyl)-4H-chromen-4-one] | C_{15}H_{10}O_{5} | 270.2369 | 271       | 253; 181; 137              | [56,59,60] |
| 40  | Luteolin                                      | C_{15}H_{10}O_{5} | 286.2633 | 287       | 271; 225; 175; 158         | [43,56,59,60] |
| 41  | Diosmetin [luteolin 4'-methyl ether; salinigricoflavonol] | C_{15}H_{10}O_{5} | 300.2629 | 301       | 286; 258; 229; 184; 153; 124 | [61–63] |
|     | Cirsimaritin [scrohulein; 4',5-dihydroxy-6,7-dimethoxyflavone; 7-methylcapillarin] | C_{15}H_{10}O_{5} | 314.2895 | 313       | 298; 247; 151; 270         | [24] |
| 42  | Nevadensin                                    | C_{15}H_{10}O_{5} | 344.3154 | 343       | 328; 259; 313; 269         | [24,63] |
|     |                                              |             |          |           | 330; 315; 246; 151; 163    | [24,63] |
| 43  | Syringetin                                    | C_{15}H_{10}O_{5} | 346.2883 | 345       | 287; 271; 203; 183; 163    | [28] |
|     |                                              |             |          |           | 378; 347; 317; 284; 246; 206; 349; 321; 284; 193; 322; 304; 282; 196; 154 | [28] |
| 44  | Pentahydroxy trimethoxy flavone               | C_{15}H_{10}O_{10} | 392.3136 | 393       | 414; 287; 186; 241; 158    | [20,56,64,65] |
| 45  | Apigenin diglycoside                          | C_{15}H_{10}O_{10} | 432.3775 | 433       | 249; 221; 192              | [57,66,67] |
| 46  | Vitexin [apigenin 8-C-glucoside]               | C_{15}H_{10}O_{10} | 432.3775 | 431       | 287; 213; 137; 185         | [20,55,56,66,68] |
|     | Luteolin diglycoside                          | C_{15}H_{10}O_{11} | 448.3769 | 449       | 249; 221; 192              | [57,66,67] |
| 47  | Isovitexin 6''-O-deoxyhexoside [apigenin 6-C-glucoside 6''-O-deoxyhexoside] | C_{15}H_{10}O_{14} | 578.5187 | 579       | 415; 297; 177; 397; 344; 362 | [66] |
| 48  | Apigenin glucoside                            | C_{15}H_{10}O_{15} | 594.5181 | 595       | 415; 353; 283; 265; 176    | [66] |
| 49  | Apigenin glucoside                            | C_{15}H_{10}O_{15} | 620.5554 | 621       | 561; 547; 461; 533; 461; 433 | [66] |
|     | **Flavan-3-ols**                              |             |          |           |                            |
| 50  | Catechin [D-catechol]                         | C_{15}H_{10}O_{6} | 290.2681 | 289       | 245; 205; 203; 188         | [43,49,55,57] |
|     |                                              |             |          |           | 272; 175; 130; 157; 140    | [20,49,55] |
| 51  | Epicatechin                                   | C_{15}H_{10}O_{6} | 290.2681 | 291       | 245; 205; 203; 188         | [43,49,55,57] |
|     |                                              |             |          |           | 272; 175; 130; 157; 140    | [20,49,55] |
| 52  | Gallatechin [(+)-gallocatechin]                | C_{15}H_{10}O_{7} | 306.2675 | 305       | 179; 125                   | [20,28,43,44] |
| 53  | Catechin gallate                             | C_{15}H_{10}O_{10} | 442.3723 | 441       | 289; 169; 245; 205; 203    | [20,56] |
|     |                                              |             |          |           |                            | [20,56] |
| 54  | Naringenin [Naringetol; Naringenine]          | C_{15}H_{10}O_{5} | 272.5228 | 273       | 227; 155; 209; 139         | [20,43,49] |
| 55  | Hesperitin [Hesperetin]                       | C_{15}H_{10}O_{5} | 302.2788 | 301       | 257; 151; 228; 189         | [20,43,49] |
| 56  | Eriodictyol-7-O-glucoside [Pyrancthioside; miscanthoside] | C_{15}H_{20}O_{11} | 450.3928 | 449       | 269; 207; 251; 165         | [48,65,68] |
| 57  | Hexahydroxyflavanone hexoside                 | C_{15}H_{20}O_{13} | 482.3916 | 483       | 437; 359; 263; 231; 298; 255; 225; 155 | [28] |
|     | **Hydroxybenzoic acids**                      |             |          |           |                            |
| 58  | 4-hydroxybenzoic acid                        | C_{6}H_{4}O_{3} | 138.1207 | 139       | 121                        | [20,69,70] |
| 59  | Protocatechuic acid                          | C_{6}H_{4}O_{4} | 154.1201 | 155       | 127                        | [20,28,55] |
| 60  | Gallic acid                                  | C_{6}H_{4}O_{5} | 170.1195 | 171       | 126                        | [20,54,55] |
| 61  | Syringic acid [benzoic acid; cedar acid]      | C_{6}H_{4}O_{5} | 198.1727 | 199       | 154; 140; 111; 140; 123; 125 | [20,55,71] |
| No. | Name                                                                 | Molecular Formula | Molar Mass | Molar Mass | Molar Mass | Ref. |
|-----|----------------------------------------------------------------------|------------------|------------|------------|------------|------|
| 64  | Ellagic acid [benzoic acid; elagostasine]                             | C₁₄H₁₀O₈         | 302.1926   | 303        | 172; 158; 144; 127; 116 | [27,41,44] |
| 65  | Salvianolic acid F                                                   | C₁₇H₁₄O₆         | 314.2895   | 315        | 144; 207; 181; 153; 179; 161; 133 | [69] |
| 66  | Dihydroxybenzoyl-hexoside                                           | C₁₇H₁₂O₄         | 316.2607   | 315        | 153; 253; 151; 184 | [66] |
| 67  | Salvianolic acid G                                                   | C₁₈H₁₂O₇         | 340.2837   | 341        | 323; 295; 255; 195; 159; 305 | [63,72] |
| 68  | Salvianolic acid D                                                   | C₂₈H₃₈O₁₈        | 418.3509   | 417        | 373; 329; 287; 209 | [69,73] |
|     | **Hydroxycinnamic acids**                                            |                  |            |            |            |      |
| 69  | *p*-Coumaric acid                                                   | C₇H₆O₅           | 164.16     | 165        | 146; 119 | [20,46,55,73] |
| 70  | Sinapic acid [trans-sinapic acid]                                    | C₁₇H₁₄O₆         | 224.2100   | 225        | 179; 153; 115; 133; 115 | [20,37,55,74] |
| 71  | Caffeoylmalic acid                                                  | C₁₇H₁₂O₆         | 296.2296   | 295        | 133; 179; 148; 119; | [28] |
| 72  | Coutaric acid [trans-p-Coumaroyltartaric acid]                       | C₁₇H₁₄O₆         | 296.2296   | 295        | 163; 119 | [20] |
| 73  | Caftaric acid [cis-coumaric acid; 2-coumene-1-ol; 2-coumaroyl-L-tartaric acid; caffeoyl tartaric acid] | C₁₇H₁₄O₆         | 312.23     | 311        | 149; 221; 131 | [20,38,64,69] |
| 74  | Ferutaric acid [fertaric acid]                                       | C₁₇H₁₄O₆         | 326.2556   | 325        | 193; 149; 134 | [20] |
| 75  | p-Coumaric acid-O-hexoside [trans-p-Coumaroyl-4-glucoside]           | C₁₇H₁₄O₆         | 326.2986   | 325        | 193; 163; 119 | [28,57,75] |
| 76  | 1-Caffeoyl-beta-D-glucose [caffeic acid-glucoside]                   | C₁₇H₁₂O₆         | 342.2987   | 341        | 179; 161; 135 | [20,66] |
| 77  | 5-O-(4'-O-p-coumaroyl glucosyl) quinic acid                          | C₂₈H₃₈O₁₄        | 500.4499   | 501        | 339; 277; 203 | [56] |
| 78  | 3-p-coumaroyl-4-caffeylquinic acid                                  | C₂₈H₃₈O₁₄        | 500.4515   | 501        | 355; 483; 181; 225; 281; 193; 120; 133 | [76] |
| 79  | Coumaric acid derivative                                             | C₁₇H₁₄O₆         | 502.5550   | 503        | 293; 409; 391; 367; 323; 293; 233; 205 | [57] |
| 80  | Di-O-cafeoylquinic acid                                             | C₂₈H₃₈O₁₄        | 516.4509   | 517        | 355; 339; 202 | [58,66,76] |
| 81  | Caffeic acid-O-(sinapoyl-O-hexoside)                                 | C₂₈H₃₈O₁₄        | 566.5080   | 567        | 405; 520; 249; 234 | [57,77] |
|     | **Other compounds**                                                 |                  |            |            |            |      |
| 82  | Malic acid                                                          | C₄H₆O₅           | 134.0874   | 133        | 115 | [57,69,78] |
| 83  | Tartaric acid                                                       | C₄H₆O₅           | 150.0900   | 149        | 131 | [78,79] |
| 84  | Umbelliferone                                                       | C₅H₈O₅           | 162.1421   | 161        | 115 | [20,28,54] |
| 85  | Shikimic acid                                                       | C₇H₆O₅           | 174.1513   | 175        | 112 | [28,78] |
| 86  | Indole-3-carboxylic acid                                            | C₁₄H₁₀O₄         | 175.1840   | 176        | 130 | [75] |
| 87  | Esculetin [Cichorigenin; Aesculetin]                                 | C₁₇H₁₄O₈         | 178.1415   | 179        | 133; 115 | [20] |
| 88  | Citric acid                                                         | C₇H₆O₇           | 192.1235   | 191        | 111; 173; 143; 127 | [57,59,79] |
| 89  | Quinic acid                                                         | C₇H₆O₇           | 192.1666   | 191        | 111; 173 | [20,28,57,59] |
| 90  | Dihydroferulic acid                                                | C₁₇H₁₂O₆         | 196.1999   | 195        | 159; 129; 113; 122 | [28,80,81] |
| 91  | Ethyl gallate                                                       | C₁₇H₂₁O₅         | 198.1727   | 197        | 169; 125 | [45] |
| 92  | L-Tryptophan [tryptophan; (S)-tryptophan]                           | C₁₇H₁₄N₂O₂        | 204.2252   | 205        | 188; 146; 170; 118 | [41,66] |
| 93  | Myristoleic acid [cis-9-tetradecanoic acid]                         | C₁₈H₃₈O₂          | 226.3550   | 227        | 209; 181; 155; 199; 181; 127 | [28] |
| 94  | Resveratrol [trans-resveratrol; stilbenetriol]                      | C₁₄H₁₂O₃         | 228.2433   | 229        | 142; 184; 114 | [28,43] |
| No. | Name of Compound                                                                 | Molecular Formula | Mass 1 | Mass 2 | Mass 3 | Mass 4 | Mass 5 | Mass 6 | Mass 7 | References |
|-----|----------------------------------------------------------------------------------|-------------------|--------|--------|--------|--------|--------|--------|--------|------------|
| 95  | Linolenic acid (alpha-linolenic acid; linolenate)                                | C18H30O2          | 278.4296 | 279  | 260; 176; 120 | [62,74] |
| 96  | 9-oxo-10E,12Z-octadecanoic acid [9-oxo-ODE]                                     | C18H30O3          | 294.4290 | 295  | 249; 165; 220; 125 | [62,82] |
| 97  | Nonadecadienoic acid                                                             | C19H32O2          | 294.4721 | 295  | 278; 250; 211; 172; 204; 181; 176 | [28] |
| 98  | Protocatechuic acid-O-hexoside                                                   | C18H26O7          | 316.2607 | 315  | 153; 298; 151 | 57,69,75 |
| 99  | Bilobalide [(-)-Bilobalide]                                                       | C18H26O8          | 326.2986 | 325  | 183; 261; 119; 183; 314; 297; 255; 228; | 46,50,75 |
| 100 | 3,7-dimethylquercetin                                                             | C13H16O7          | 330.2889 | 331  | 203; 146; 267; 227; 203; 186; 164; 134 | [75] |
| 101 | Galloyl glucose [beta-glucogallin; 1-O-galloyl-beta-D-glucose]                   | C17H20O10         | 332.2601 | 333  | 313; 195; 166 | [41] |
| 102 | Gallic acid hexoside                                                             | C17H18O10         | 332.2601 | 331  | 271; 169; 125 | [83] |
| 103 | Erucic acid (cis-13-docosenoic acid)                                             | C22H36O7          | 338.5677 | 339  | 132; 293 | [65] |
| 104 | Esculin [aesculin; esculoside; polychrome]                                        | C17H16O7          | 340.2821 | 339  | 177; 293; 131 | 20,28,56 |
| 105 | Palmatine [berbericine; Burasaine]                                               | C20H28O11         | 352.4037 | 353  | 335; 235; 317; 235; 137 | [84] |
| 106 | Hexose-hexose-N-acetyl                                                           | C15H20O10         | 367.3490 | 366  | 186; 142 | [85] |
| 107 | Fraxin (fraxetin-8-O-glucoside)                                                  | C17H20O10         | 370.3081 | 371  | 208; 352; 135 | [20] |
| 108 | 1-O-sinapoyl-beta-D-glucose                                                      | C22H36O7          | 386.5356 | 387  | 205; 130 | [20] |
| 109 | Polydatin [piceid; trans-piceid]                                                 | C17H20O10         | 390.3839 | 389  | 227; 343; 184; 143; 395; 355; 271; 194; | 27,43 |
| 110 | Fucosterol [fucosteine; trans-24-ethylidenecolesterol]                           | C25H41O10         | 412.6908 | 413  | 119; 297; 199; 268; 187 | [28] |
| 111 | Stigmasterol [stigmasterin; beta-stigmasterol]                                  | C25H38O10         | 412.6908 | 413  | 301; 259; 189; 171 | 28,86,87 |
| 112 | Phlorizin [phloridzin; phlorizoside; floridzin; phloretin 2'-glucoside; phloretin-O-hexoside] | C21H16O10       | 436.4093 | 437  | 397; 217; 377 | [20,27,46,49,57] |
| 113 | Oleanoic acid                                                                   | C23H36O3          | 456.7003 | 457  | 439; 411; 365; 337; 293; 248; 205; 364; 309; 219; 319; 301; 279; 247; 232 | 24,76 |
| 114 | Ursolic acid                                                                    | C23H36O3          | 456.7003 | 457  | 411; 393; 365; 337; 279; 247; 292; 247; 219; 205 | 63,76,86 |
| 115 | Anmurcoic acid                                                                   | C25H40O3          | 486.6922 | 487  | 325; 307; 304; 261; 279 | [76] |
| 116 | Dimethylellagic acid hexose                                                      | C23H36O3          | 492.3864 | 493  | 331; 299; 270; 242; 179; 150; 225 | 41 |
| 117 | Procyanidin A-type dimer                                                          | C20H26O7          | 576.501  | 577  | 245; 181; 245; 218; 189; 123 | 20,55,57 |
| 118 | Cyclopassifloic acid glucoside                                                   | C20H26O7          | 698.8810 | 699  | 537; 347; 271; 259; 185 | [66] |
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