Research of 5 extracts of wild Amur grape *Vitis amurensis* Rupechr. and identification of its polyphenolic composition by tandem mass spectrometry (HPLC-MS / MS)

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Abstract. *Vitis amurensis* Rupechr contains a large number of polyphenolic compounds which are biologically active components. For the most efficient and safe extraction supercritical carbon dioxide was used. In this work, for the first time, a comparative metabolomic study of biologically active substances of wild grapes collected from five different places of the Primorsky and Khabarovsk territories is carried out. To identify target analytes in ethanol extracts of grape berries, high performance liquid chromatography (HPLC) was used in combination with an amaZon SL ion trap (manufactured by BRUKER DALTONIKS, Germany) equipped with an ESI electrospray ionization source in negative and positive ion modes. The mass spectrometer was used in the scan range m/z 100 - 1.700 for MS and MS / MS. Used fragmentation of the 4th order. Primary mass spectrometric results showed the presence of 89 biologically active compounds corresponding to the species *V. amurensis*, moreover, salvianolic acids F, D and G, oleanolic, ursolic, myristoleic acids, berberinicin, mearisetin, esculin, nevadensin, stigmasterol, fucosterol, phlorizin, L-tryptophan identified for the first time in *V. amurensis*.

1 Introduction

Researchers attribute the appearance of the first representatives of the *Vitaceae* family, belonging to the genus *Vitis*, to the Upper Cretaceous period, when there were already types of plants that were very similar in leaves to vines. The absence of seeds does not allow, however, to have complete confidence in their belonging to the genus *Vitis* [1, 2]. To these types, researchers include the *Vitis dakotana* Berry vine found in the Upper Cretaceous
sediments in Harding County in South Dakota, which is very similar in appearance to modern vines [3, 4].

The evolution of grape plants approaching the cultivated vine, judging by the fossil finds, took place especially intensively in Central and Southern Europe during the second half of the Tertiary period and then especially in the Quaternary period. On the territory of Russia, quite a lot of finds of fossils are also known belonging to the genera *Cissites, Ampelopsis, Parthenocissus* and especially to the genus *Vitis*: *V. sachalinensis* Krysht. and *V. crenata* Heer on Sakhalin, *V. teutonica* A. Br. – near Taganrog and on the Irtysh River, as well as *V. praevinifera* Sap. - on the Krynka river. All these data show that the evolution of the vine on the territory of Russia proceeded from ancient times. And now in Russia in many areas wild grapes *V. sylvestris* Gmel grow [5, 6, 7].

Very little information is available about the culture of East Asian grape varieties. *V. lanata* Roxb is cultivated in eastern India. and *V. tomentosa* Heyne, in Japan and in Korea – *V. Thunbergii* Sieb. et Zucc. called *V. Seiboldii* hort [8]. More complete information is available regarding *V. amurensis* Rupr., which was first introduced into the culture by I.V. Michurin. In his work "Results of half a century of work" I.V. Michurin describes four forms of *V. amurensis* Rupr., which were isolated in the Far East [9, 10].

For the isolation of biologically active substances, ripe fruits, fruit skins, combs, leaves, seeds, vine bark, red grape wine are used. Fruits contain 65-85% water, 10-33% sugar (glucose and fructose), phlobaphene, gallic acid, quercetin, enin, glycosides - monodelphinidin and didelphinidin, acids (malic, silicic, salicylic, phosphoric, tartaric, citric, etc.) pectin and tannins, potassium, magnesium, calcium, manganese, cobalt, iron and vitamins: B1, B2, Ba, B12, A, C, P, PP, folic acid, and enzymes.

The dominant class of biologically active compounds of fruits, and especially grape ridges, are bioflavonoids and, in particular, the so-called complexes of oligomeric proanthocyanidins or condensed tannins, which are polymeric forms of flavonoids from the group of catechins [11].

In European medicine, until recently, grapes were widely used as a means of therapy and rehabilitation for a wide range of diseases: chronic recurrent inflammatory processes, tuberculosis, kidney disease, arterial hypertension, etc.

The aim of this work was a comparative metabolomic study of biologically active substances of wild grapes harvested in five different places in the Russian Far Eastern taiga in the Primorsky and Khabarovsk territories. High performance liquid chromatography (HPLC) in combination with a BRUKER DALTONIKS ion trap (tandem mass spectrometry) was used to identify target analytes in extracts. This paper presents a detailed study of the metabolomic composition of grape juice from fruits taken from five habitats of *V. amurensis* in the Far East: Pakhtusov Islands and Rikord Island (Peter the Great Bay, Sea of Japan), the vicinity of Artem (Primorsky Territory), the vicinity of the river Arsenyevka (Primorsky Territory), environs of Vyazemsky (Khabarovsk Territory).

### 2 Materials and methods

#### 2.1 Materials

The object of the study was the berries of the wild grape *V. amurensis*, collected in the floodplain of the Arsenyevka River, Primorsky Territory (N. 44 ° 52'18 ”, E 133 ° 35'12”; brown-gley bleached soils) in the vicinity of Vyazemsky, Khabarovsk Territory (N47 ° 32'15 ”, E 134 ° 45'20”; podzolic-brown forest heavy loamy soils), in the vicinity of Artem, Primorsky Territory (St. lat. 43 ° 21'34 ”, E 132 ° 11'19”; yellow-brown earth soils), on Rikord Island, Peter the Great Bay (N 42 ° 52'54 ”, E 131 ° 40'06 ”; yellow-brown earth
soils), on Pakhtusov Islands, Peter the Great Bay (N 42 ° 53’57”, E 131 ° 38’45”; yellow-
brown soil). The grapes were harvested at the end of August and September 2020. All
samples morphologically corresponded to the pharmacopoeial standards of the State
Pharmacopoeia of the Russian Federation [12].

2.2 Methods

2.2.1 Fractional maceration
To obtain highly concentrated extracts, fractional maceration was applied. In this case, the
total amount of the extractant (ethyl alcohol of reagent grade) is divided into 3 parts and is
consistently infused with grapes with the first part, then with the second and third. The
infusion time of each part of the extractant was 7 days.

2.2.2 High performance liquid chromatography
To perform the separation of multicomponent mixtures, a Shimadzu LC-20 Prominence
HPLC high pressure liquid chromatograph (Shimadzu, Japan) was used, equipped with a UV
detector and a Shodex ODP-40 4E reverse phase column. The gradient elution program is as
follows: 0.0 – 4 min, 100% CH₃CN; 4 - 60 min, 100% – 25% CH₃CN; 60 - 75 min, 25% –
0% CH₃CN; control wash 75 - 120 min 0% CH₃CN. All HPLC analysis was done with an
SPD-20A UV-VIS detector (Kanda-Nishikicho 1-chrome, Shimadzu, Chiyoda-ku, Tokyo,
Japan) at 230 ηm and 330 ηm; temperature 17 °C. The injection volume was 1 ml.

2.2.3 Tandem mass spectrometry
Mass spectrometric data were obtained using an amaZon SL ion trap (manufactured by
BRUKER DALTONIKS, Germany) equipped with an ESI electrospray ionization source in
negative and positive ion modes. The optimized parameters are obtained as follows:
ionization source temperature: 70 °C, gas flow: 4 L / min, nebulizer gas (nebulizer): 7.3 psi,
capillary voltage: 4500 V, end plate bend voltage: 1500V, fragmentary: 280V, collision
energy: 60 eV. The mass spectrometer was used in the scan range m / z 100 – 1.700 for MS
and MS / MS. Used fragmentation of the 4th order.

3 Research results
Clarification of the metabolomic composition is an extremely important result in the system
of biochemical analysis. In this work, the HPLC-MS / MS method was used with additional
ionization and analysis of fragmented ions. High-precision mass spectrometric data were
recorded on an AMAZON SL BRUKER DALTONIKS ion trap equipped with an ESI source
in the negative / positive ion mode. A total of 300 peaks of the isolated target analytes were
found on the ion chromatogram (Fig. 1).
Fig. 1. Distributed graph of tandem mass spectrometry of the analyzed target analytes of the EtOH extract of *V. amurensis* (Vyazemsky, Khabarovsk Territory), represented by an ion chromatogram (Brown line – graph of the intensity of the signal of positive ions; blue line – graph of the intensity of the signal of negative ions; black line – total intensity of positive ions; blue line – total intensity of negative ions).

Based on the measurement results, a unified system table of molecular masses and fragmented ions of target analytes isolated in extracts of *V. amurensis* was compiled. (Table 1).

**Table 1.** Metabolome analysis of biologically active substances isolated from extracts of *V. amurensis*

| №  | Identification          | Formula    | Observed mass [M-H]- | Observed mass [M+H]+ | MS/MS Stage 1 fragmentation | MS/MS Stage 2 fragmentation | MS/MS Stage 2 fragmentation | References  |
|----|-------------------------|------------|-----------------------|-----------------------|----------------------------|----------------------------|----------------------------|-------------|
| 1  | Malic acid              | C₄H₆O₅    | 133                   | 115                   |                            |                            |                            | [22, 32, 57, 66] |
| 2  | Tartaric acid           | C₄H₆O₆    | 149                   | 131                   |                            |                            |                            | [32, 66]    |
| 3  | Umbelliferone           | C₁₉H₉O₅   | 161                   | 115                   |                            |                            |                            | [29, 36]    |
| 4  | *p*-Coumaric acid       | C₉H₇O₃    | 165                   | 146                   | 119                        |                            |                            | [13, 21, 22, 26, 29, 46] |
| 5  | Gallic acid             | C₁₇H₁₀O₇  | 171                   | 126                   |                            |                            |                            | [13, 20, 29, 36, 53] |
| 6  | Indole-3-carboxylic acid| C₁₀H₉NO₂  | 176                   | 130                   |                            |                            |                            | [50]        |
| 7  | Esculetin               | C₁₆H₁₂O₅  | 179                   | 133                   | 115                        |                            |                            | [29, 71]    |
| 8  | Caffeic acid            | C₁₅H₁₀O₄  | 179                   | 133                   |                            |                            |                            | [13, 15, 29, 46, 55] |
| 9  | Citric acid             | C₇H₆O₇    | 191                   | 111; 173; 143; 127    |                            |                            |                            | [42, 57, 59, 66] |
| 10 | Quinic acid             | C₉H₁₂O₅   | 191                   | 111; 173; 111         |                            |                            |                            | [22, 29, 30, 42, 53, 57, 61] |
| No. | Compound                       | Molecular Formula | MW  | Molar Mass   | Data References |
|-----|--------------------------------|-------------------|-----|-------------|----------------|
| 11  | Dihydroferulic acid            | C_{10}H_{12}O_{4} | 195 | 159; 129; 113; 122 | [27, 30, 38]    |
| 12  | Ethyl gallate                  | C_{9}H_{10}O_{5}  | 197 | 169; 125     | [31]           |
| 13  | L-Tryptophan                   | C_{11}H_{12}N_{2}O_{2} | 205 | 188; 146; 170; 118; 144; 118 | [43, 59] |
| 14  | Sinapic acid                   | C_{11}H_{10}O_{5} | 225 | 179; 153; 115; 133; 115; 115 | [13, 19, 29, 56, 57] |
| 15  | Myristoleic acid               | C_{14}H_{26}O_{2} | 227 | 209; 181; 155; 199; 181; 127 | [30] |
| 16  | Resveratrol                    | C_{14}H_{12}O_{3} | 229 | 142; 184; 114 | [30, 60] |
| 17  | Apigenin                       | C_{15}H_{10}O_{5} | 271 | 253; 181; 137 | [13, 34, 43, 58, 67] |
| 18  | Naringenin                     | C_{15}H_{12}O_{5} | 273 | 227; 155; 209; 139 | [29, 53, 60, 62] |
| 19  | Linolenic acid                 | C_{18}H_{36}O_{2} | 279 | 260; 176; 120 | [19, 71] |
| 20  | Kaempferol                     | C_{15}H_{10}O_{4} | 287 | 269; 227; 153 | [29, 42, 45, 68] |
| 21  | Luteolin                       | C_{15}H_{10}O_{4} | 287 | 271; 225; 175; 158 | [34, 43, 60, 67] |
| 22  | Dihydrokaempferol              | C_{15}H_{12}O_{6} | 289 | 271; 199; 127; 243; 189; 118 | [24, 41, 54] |
| 23  | Catechin                       | C_{15}H_{14}O_{6} | 289 | 245; 205; 203; 188 | [13, 25, 29, 53, 57, 60] |
| 24  | Epicatechin                    | C_{15}H_{16}O_{6} | 291 | 272; 175; 130; 157; 140 | [13, 29, 46, 53] |
| 25  | 9-Oxo-10E,12Z-octadecanoic acid| C_{18}H_{30}O_{3} | 295 | 249; 165; 220; 125 | [30, 71] |
| 26  | Caffeoylmalic acid             | C_{12}H_{12}O_{8} | 295 | 133; 179; 148; 119; 115 | [57] |
| 27  | Coutaric acid                  | C_{13}H_{12}O_{8} | 295 | 163; 119; 119 | [29] |
| 28  | Kaempferide                    | C_{16}H_{12}O_{6} | 301 | 283; 265; 239; 211; 185; 133; 211; 151 | [45, 70, 74] |
| 29  | Ellagic acid                   | C_{14}H_{6}O_{8}  | 303 | 172; 158; 144; 127; 116 | [29, 46, 52, 59] |
| 30  | Quercetin                      | C_{15}H_{10}O_{7} | 303 | 285; 163; 267; 159; 239 | [13, 25, 29, 51, 56, 60, 62, 68] |
| 31  | Hesperitin                     | C_{15}H_{14}O_{6} | 301 | 257; 151; 228; 189 | [16, 29, 60] |
| No. | Compound                                      | Formula      | MW | M/z  | Literature |
|-----|-----------------------------------------------|--------------|-----|------|------------|
| 32  | Dihydroquercetin                              | C_{15}H_{12}O_{7} | 305 | 259; 149 | [29, 60, 64] |
| 33  | Caftaric acid                                 | C_{13}H_{12}O_{6} | 311 | 149; 221 | [17, 22, 29, 55] |
| 34  | Salvianolic acid F                            | C_{17}H_{14}O_{6} | 315 | 269; 243; 213; 185; 144 | [22] |
| 35  | Protocatechuic acid-O-hexoside                | C_{13}H_{10}O_{6} | 315 | 153; 298 | [22, 57, 62] |
| 36  | Dihydroxybenzoylhexoside                      | C_{13}H_{16}O_{6} | 315 | 153; 253 | [44] |
| 37  | Myricetin                                     | C_{15}H_{16}O_{8} | 317 | 273; 191 | [29, 30, 36, 51, 60] |
| 38  | Fertaric acid [Fertarate]                     | C_{14}H_{14}O_{5} | 325 | 193; 149 | [29] |
| 39  | p-Coumaric acid-O-hexoside                    | C_{15}H_{15}O_{8} | 325 | 193; 163 | [30, 50, 51, 57, 62] |
| 40  | Galloyl glucose                               | C_{13}H_{16}O_{10} | 331 | 313; 195 | [59] |
| 41  | Gallic acid hexoside                          | C_{13}H_{16}O_{10} | 331 | 271; 169; 125 | 125 | [48] |
| 42  | Mearnsetin                                    | C_{15}H_{12}O_{8} | 333 | 318; 301; 273; 245; 193; 165; 139 | 301; 289; 271; 219; 192; 153; 136 | [52] |
| 43  | Esculin                                       | C_{15}H_{10}O_{9} | 339 | 177; 293 | [29, 30, 34, 71] |
| 44  | Salvianolic acid G                            | C_{16}H_{12}O_{7} | 341 | 323; 295; 255; 195; 159 | 305 | [35, 69] |
| 45  | Nevadensin                                    | C_{16}H_{16}O_{7} | 343 | 328; 259 | 313 | 269 | [45, 69] |
| 46  | Palmatine                                     | C_{21}H_{22}NO_{4} | 353 | 335; 235 | 317; 235; 137 | [18, 71] |
| 47  | Hexose-hexose-N-acetyl                       | C_{14}H_{26}NO_{10} | 366 | 186; 142 | 142 | [40] |
| 48  | Fraxin                                       | C_{14}H_{18}O_{10} | 371 | 208; 352 | 135 | [29] |
| 49  | Fraxetin-7-O-beta-glucuronide                 | C_{16}H_{16}O_{11} | 385 | 367; 272; 209; 175; 143 | 158 | [73] |
| 50  | Polydatin                                     | C_{26}H_{12}O_{6} | 389 | 227; 343 | 184 | 143 | [46, 60] |
|   | Compound                     | Formula      | Molecular Weight | Mass (Da)          |     |     |     |     |     |
|---|------------------------------|--------------|------------------|-------------------|-----|-----|-----|-----|-----|
|51 | Fucosterol                   | C_{29}H_{48}O| 413              | 395; 355; 271; 194; 119 | 297; 199 | 268; 187 |     | [30] |
|52 | Stigmasterol                 | C_{29}H_{48}O| 413              | 301; 259; 189      | 171 | 287; 209 |     | [14, 20, 30] |
|53 | Salvianolic acid D           | C_{20}H_{18}O_{10} | 417             | 373; 329          | 287; 209 |     |     | [21, 22] |
|54 | Apigenin-7-O-glucoside       | C_{21}H_{20}O_{10} | 433              | 414; 287; 186      | 241; 158 |     |     | [15, 17, 29, 34, 42, 43, 58] |
|55 | Pelargonidin-3-O-glucoside (callistephin) | C_{21}H_{21}O_{10} | 433              | 414; 271; 172      | 172; 226 | 116 |     | [23, 59, 65] |
|56 | Phlorizin                    | C_{22}H_{12}O_{10} | 437              | 397; 217          | 377 |     |     | [26, 29, 30, 46, 53, 57] |
|57 | Catechin gallate             | C_{22}H_{18}O_{10} | 441              | 289; 169          | 245; 205 | 203 |     | [29, 33] |
|58 | Kaempferol-3-O-galactoside   | C_{21}H_{20}O_{11} | 449              | 287               | 269; 217 |     |     | [25, 29] |
|59 | Eriodictyol-7-O-glucoside    | C_{21}H_{21}O_{11} | 449              | 269               | 207; 251 | 165 |     | [16, 29, 42, 63] |
|60 | Dihydrokaempferol glucoside  | C_{21}H_{22}O_{11} | 449              | 287               | 227; 269 | 225; 149 |     | [46] |
|61 | Oleanoic acid                | C_{10}H_{48}O_{3} | 457              | 439; 411; 365; 337; 293; 248; 205 | 364; 337; 309; 219 | 337; 319; 301; 279; 247; 232; 219 |     | [45, 61] |
|62 | Ursolic acid                 | C_{10}H_{45}O_{3} | 457              | 411; 393; 365; 337; 279; 247 | 365; 337; 292; 279; 247; 219; 205 |     |     | [20, 44, 61, 69] |
|63 | Isorhamnetin 3-O-rhamonoside | C_{22}H_{22}O_{11} | 461              | 315; 152; 219     |     |     |     | [52, 53] |
|64 | Peonidin-3-O-glucoside       | C_{21}H_{23}O_{11} | 463              | 301               | 286; 258 | 268; 258; 230; 202; 174; 121 |     | [28, 29, 37, 59, 65] |
|65 | Hyperoside                   | C_{21}H_{20}O_{12} | 463              | 301; 179          | 257; 179 | 255; 147 |     | [13, 25, 26, 29, 51, 60, 63] |
|66 | Quercetin 3-O-glucoside      | C_{21}H_{20}O_{12} | 465              | 303               | 285; 257; 229; 201; 150 | 229; 201; 155 |     | [15, 25, 29, 34, 43, 46] |
| No. | Compound                             | Molecular Formula | M (Da) | m/z (relative intensity) | Retention Time (s) | Refs. |
|-----|--------------------------------------|-------------------|--------|-------------------------|-------------------|-------|
| 67  | Taxifolin-3-O-glucoside              | C_{12}H_{22}O_{12} | 467    | 449; 303; 188; 287; 132; 260 | 29              | [29]  |
| 68  | Quercetin-3-O-glucuronide            | C_{21}H_{19}O_{13} | 477    | 301; 179; 273; 179; 151  | 25, 29, 57, 65   |       |
| 69  | Isorhamnetin 3-O-glucoside           | C_{22}H_{22}O_{12} | 479    | 317; 287; 301; 257; 274; 228; 149 | 15, 29, 52     |       |
| 70  | Myricetin-3-O-galactoside            | C_{21}H_{20}O_{13} | 479    | 299; 153; 271; 243; 171 | 13, 25, 29, 51, 63 |       |
| 71  | Dimethyllellagic acid hexose         | C_{22}H_{20}O_{12} | 493    | 331; 299; 270; 242; 179; 150; 270; 225 | 59              |       |
| 72  | Malvidin 3-O-glucoside               | C_{23}H_{25}O_{12} | 493    | 331; 315; 179; 315; 179 | 29, 37, 65      |       |
| 73  | 5-O-(4'-O-p-coumaroyl glucosyl)quinic acid | C_{22}H_{26}O_{13} | 501    | 339; 277; 323; 257; 277 | 34              |       |
| 74  | P-Coumaroylcaffaoylquinic acid       | C_{22}H_{26}O_{11} | 501    | 355; 483; 181; 409; 391; 367; 339; 293; 323; 293; 233; 205 | 61              |       |
| 75  | Coumaric acid derivative             | C_{20}H_{18}O_{7}  | 503    | 457; 411; 382; 339; 293; 409; 391; 367; 339; 293; 323; 293; 233; 205 | 57              |       |
| 76  | Malvidin acetyl hexoside             | C_{24}H_{27}O_{13} | 537    | 331; 299; 261; 243; 211; 154; 111 | 30              |       |
| 77  | Procyanidin A-type dimer              | C_{30}H_{24}O_{12} | 577    | 425; 397; 373; 287; 245; 181; 245; 218; 189; 123 | 13, 25, 51, 61  |       |
| 78  | Isovitexin 6"-O-deoxyhexoside         | C_{27}H_{30}O_{14} | 579    | 415; 297; 177; 397; 344; 362 | 44              |       |
| 79  | Vitexin 2"-O-glucoside                | C_{27}H_{28}O_{15} | 595    | 415; 353; 283; 265; 176 | 44              |       |
| 80  | Kaempferol-3,7-Di-O-glucoside        | C_{27}H_{26}O_{16} | 611    | 449; 287; 229; 165; 213; 111 | 39, 47          |       |
| 81  | Cyanidin 3,5-O-dihexoside             | C_{27}H_{31}O_{16} | 611    | 287; 449; 287; 287 | 23, 49          |       |
| 82  | Cyanidin 3,5-O-diglucoside            | C_{27}H_{31}O_{16} | 611    | 287; 449; 287; 269; 231; 199; 161; 231; 213; 189; 175; 147 | 37, 65         |       |
| 83  | Apigenin 6-C-[6"-acetyl-2"-O-deoxyhexoside]-glucoside | C_{29}H_{32}O_{15} | 621    | 561; 547; 461; 533; 461; 433; 433 | 44              |       |
Research carried out using tandem mass spectrometry showed the presence of 89 biologically active compounds corresponding to the *V. amurensis* species. Salvianolic acids F, D and G, oleanolic, ursolic, myristoleic acids, berbercinin, mearnsetin, esculin, nevadensin, stigmasterol, fucosterol, Phlorizin, L-Tryptophan are identified for the first time in *V. amurensis*.

The identification of compounds (m/z values and fragmented ions) was carried out by comparing the obtained experimental data with known scientific results or mass spectrometric libraries. Anthocyanins have been identified in the extracts: Malvidin-3-O-glucoside, Pelargonidin-3-O-glucoside (callistephin), Peonidin-3-O-glucoside, Cyanidin-3,5-dihexoside, Cyanidin-3,5-diglucoside, Peonidin-3,5-diglucoside, Malvidin 3-(6-O-coumaroyl) glucoside, Petunidin-3-O-glucoside-5-O-glucoside, Malvidin 3-(6'-p-caffeoyl glucoside), Malvidin 3,5-diglucoside. Obtained mass spectrometry data correlate with scientific sources [13, 23, 28, 29, 37, 49, 51, 59, 61, 65]. A large group of flavonoids identified; flavonols Kaempferol, Aromadendrin, Kaempferide, Quercetin, Dihydroquercetin, Kaempferol-3-O-galactoside, Quercetin 3-O-galactoside, Taxifolin-3-O-glucoside, Quercetin-3-O-glucuronic acid, Isorhamnetin-3-O-rhamonoside, Isorhamnetin-3-O-glucoside, Myricetin-3-O-galactoside, Kaempferol-3,7-Di-O-glucoside [13, 24, 25, 29, 41, 42, 45, 51, 54, 56, 57, 60, 62, 64, 65, 68, 70, 74]; flavones: Apigenin, Luteolin, Nevadensin, Apigenin-7-O-glucoside, Isovitexin 6"-O-deoxyhexoside, Vitexin 2"-O-glucoside, Apigenin 6-C-[6"-acetyl-2"-O-deoxyhexoside]-glucoside [13, 15, 17, 34, 43, 44, 45, 48, 58, 60, 67, 69]; flavanones: Naringenin, Hesperitin, Eriodictyol-7-O-glucoside [16, 29, 42, 53, 60, 62, 63]; Flavan-3-ols: Catechin, Epicatechin [13, 25, 29, 46, 53, 57, 60].

Glycosylated coumarins have also been identified: Umbelliferone, Esculin, Fraxin, Fraxetin-7-O-beta-glucuronide [29, 30, 34, 36, 71, 73], berberine Palmatine [18, 71], stilbenes Polydatin and trans-Resveratrol, [30, 46, 60], sterols: Fucosterol, Stigmasterol [14, 20, 30], dihydrochalcone Phlorizin [26, 29, 30, 46, 53, 57].

It should be noted that compounds such as coumarins Umbelliferone, Fraxin and Esculin, flavone Nevadensin, flavan-3-ol Epicatechin, sterol Fucosterol, flavanol Taxifolin-3-O-glucoside were identified by mass spectrometry only in island samples of wild grapes. *V. amurensis* (Pakhtusov Islands and Rikord Island, Peter the Great Bay, Sea of Japan).
4 Conclusions

Amur grape *V. amurensis* Ruprecht contains a large number of polyphenolic complexes, which are biologically active compounds. In this work, we have tried for the first time to conduct a comparative metabolic study of biologically active substances of wild grapes obtained from five different places in the Primorsky and Khabarovsk territories. HPLC in combination with a BRUKER DALTONIKS ion trap (tandem mass spectrometry) was used to identify target analytes in extracts. The results showed the presence of 89 biologically active compounds corresponding to the species *V. amurensis*, and Salvianolic acids F, D and G, Oleanolic, Ursolic, Myristoleic acids, Berbericinin, Mearsetin, Esculin, Nevadensin, Stigmasteryl, Fucosterol, Phlorizin, L-Tryptophan were identified for the first time in *V. amurensis*.

The findings may support future research into the production of various pharmaceutical and dietary supplements containing *V. amurensis* extracts. A wide variety of biologically active polyphenolic compounds opens up rich opportunities for the creation of new drugs and biologically active additives based on extracts from this family of grapes (*Vitaceae*).

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