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The Global Metabolome Profiles of Four Varieties of *Lonicera caerulea*, Established via Tandem Mass Spectrometry

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Abstract: Blue honeysuckle (*Lonicera caerulea* L.) bears dietary fruits that are rich in bioactive compounds. However, information on the metabolome profiles of honeysuckle varieties grown in Russia is limited. In this study, we employed tandem mass spectrometry to study the metabolome profiles of four *L. caerulea* varieties (Volhova, Tomichka, Goluboe vereteno, and Amfora) grown in two geographical locations in Russia, i.e., the Russian Far East and St. Petersburg. We observed that the metabolome profiles of the four varieties grown in two locations differ significantly, particularly in the polyphenol's other compound classes. We were able to identify 122 bioactive compounds in extracts from honeysuckle berries, 75 compounds from the polyphenol group and 47 compounds from other chemical groups. Thirty chemical constituents from the polyphenol group (flavones jaceosidin, cirsiliol, sophoraisoflavone A, chrysoeriol-*O*-hexoside, flavonols dimethylquercetin-3-*O*-dehexoside, rhamnocitrin, rhamnetin II, stilbenes pinosylvin, resveratrol, dihydroresveratrol, etc.) and twenty-seven from other chemical groups were identified. The largest number of unique polyphenols is characteristic of the variety Tomichka, the selection of the regional state unitary enterprise "Bakcharskoye", from the free pollination of *L. caerulea*, originating in the Primorsky Territory of Russia (*L. caerulea* subspecies Turczaninow). This genotype has the highest number of similar unique polyphenols, regardless of where it was grown. Blue honeysuckle genotypes originating from Primorsky Krai in Russia can be used in various breeding programs in order to improve and enrich the biochemical composition of fruits. It should also be noted that, regardless of the place of cultivation, the total amount of unique polyphenols remains quite large. Attention should be paid to the Volhova honeysuckle variety, obtained through gamma irradiation of the Pavlovskaya variety (Kamchatka ecotype). This sample is characterized by a stable composition of biologically active substances, regardless of the growing area. These data could support future research on the production of a variety of pharmaceutical products containing ultrapure extracts of *L. caerulea*.

Keywords: *Lonicera caerulea*; metabolome profile; tandem mass spectrometry; polyphenols; blue honeysuckle

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1. Introduction

Blue honeysuckle (*Lonicera caerulea* L.) is a young small-fruit crop belonging to the Caprifoliaceae family. The interest in *L. caerulea* has increased due to its early ripening and, especially in the northern regions, due to its high winter hardiness, palatability, and rich biochemical composition of berries. It is grown in China, Canada, Poland, and other European countries. In Russia, it was grown on >700 hectares (https://haskapru.com/, e.g., accessed on 1 August 2022) in 2022. A significant part of the acreage is occupied by varieties that belong to the first generation selected from wild flora, indicating a huge potential in honeysuckle breeding.

Honeysuckle berries contain a wide variety of polyphenolic compounds, including bioflavonoids, hydroxycinnamic acids, flavonols, polyphenols, anthocyanins, and compounds that are rare for berry crops such as iridoids, the high content of which has a positive effect on human health. The content of iridoids is mainly represented by derivatives of loganic acid and loganin and ranges from 78.0 to 406.4 mg/100 g depending on the genotype [1,2]. Scientific studies report the antimicrobial and anti-inflammatory activity of iridoids [3]. Fresh honeysuckle fruits are classified as dietary fruits, due to the high content of biologically active substances [4,5]. *L. caerulea* berries are characterized by a high content of dry matter (up to 19%) and sugars (up to 12.5%, represented by sucrose, glucose, and fructose, the content of the latter being higher than 55%). The combined action of ascorbic acid (up to 150 mg/100 g) and P-active substances (total up to 2500 mg/100 g) have a positive effect on the human body [6]. The beneficial effect of *L. caerulea* berries on reducing the negative effects of ultraviolet radiation and diabetes mellitus, as well as neurodegenerative diseases and atherosclerosis, has been reported [7,8]. The positive effect on human health is associated with a high content of polyphenolic compounds, primarily anthocyanins (anthocyanins, proanthocyanins, and iridoids). The content of these bioactive constituents depends on the variety and genotype [9]. The content of polyphenols is also influenced by the time of harvest, as well as solar radiation and temperature. An earlier study indicated that the geographical location can influence the accumulation of primary and secondary metabolites in the blue honeysuckle *L. caerulea* subsp. edulis (Turcz. ex Herder) Hultén [10]. However, such information is not available for honeysuckle varieties grown in different territories of Russia. Therefore, the determination of the composition and quantity of metabolome profiles of honeysuckle varieties from Russia will reveal a wealth of knowledge for future health-related studies and breeding strategies.

Plant metabolomic strategies are based on two analytical technologies, namely, MS and nuclear magnetic resonance (NMR). However, NMR-based approaches are inferior to MS-based approaches due to it being able to separate fewer compounds, given its relatively lower sensitivity [11]. Despite continuous progress in MS technology, the study of the plant metabolome is a major challenge in plant metabolomics research. Currently, only a few thousand metabolites (>14,000) can be measured, while in the plant kingdom, 200,000 to 1 million metabolites are expected, and its analysis is concentration dependent. However, it is difficult to predict the full extent of the complete plant metabolome, because, unlike the transcriptome and proteome, it is genome-independent [12,13]. Moreover, due to the wide dynamic range of plant metabolite concentrations and high chemical diversity, no single analytical technology can cover the entire plant metabolome, so various extraction methods and a combination of additional analytical technologies are often used for analysis.

We used tandem mass spectrometry to conduct a metabolomic study involving a detailed analysis of *L. caerulea*'s bioactive compounds.

2. Materials and Methods

2.1. Materials

The object of this study was the berries of the four *L. caerulea* varieties (Volhova, Tomichka, Goluboe vereteno, and Amfora), harvested from plantations by N.I. Vavilov All-Russian Institute of Plant Genetic Resources, Primorsky Territory (43°6′34″ N, 131°52′41″ E) and St.-Petersburg (Pushkin, 59°42′51″ N, 30°23′47″ E) (Figure 1).

A. **B.**

Figure 1. (**A**) Berries of *L. caerulea*. A. Variety "Atlant"; (**B**) Variety "Vilyuyka" (Photo by E. Rusakova).

The varieties of *L. caerulea* presented in this article were obtained from the following scientific departments: variety "Goluboe vereteno" from the M.A. Lisavenko Scientific-Research Institute of Horticulture of Siberia; variety "Tomichka" from the Regional State Unitary Enterprise "Bakcharskoye"; variety "Amfora" (also known as variety "Roxana" (Kamchatka)) from free pollination; and variety "Volhova" from the N.I. Vavilov All-Russian Institute of Plant Genetic Resources.

The berries were harvested at the end of July 2022 from two-year-old plants. All samples morphologically corresponded to the pharmacopoeial standards of the State Pharmacopoeia of the Russian Federation [14].

2.2. Chemicals and Reagents

HPLC-grade acetonitrile was purchased from Fisher Scientific (Southborough, UK), MS-grade formic acid was from Sigma-Aldrich (Steinheim, Germany). Ultrapure water was prepared from a SIEMENS ULTRA clear (SIEMENS water technologies, Günzburg, Germany), and all other chemicals were analytical grade.

2.3. Extraction

Fractional maceration technique was applied to obtain highly concentrated extracts [15]. Aqueous ethanol (80%) was selected for the extraction process due to its high efficiency in extracting polyphenol compounds and compounds of other chemical groups from plant samples. From 500 g of the berries, 50 g of berries of each variety were randomly selected for maceration. The total amount of the extractant (aqueous ethanol) was divided into 3 parts, and the plant parts were consistently infused with the first, second, and third parts. The infusion of each part of the extractant lasted seven days at room temperature. Three replicates of the extraction process were carried out on each plant sample. The extract was filtered through Whatman filter paper. The filtrates were diluted with acetonitrile to final working concentration for analysis.

2.4. Liquid Chromatography

The HPLC analyses were performed on a HPLC instrument of Shimadzu LC-20 Prominence HPLC (Shimadzu, Kyoto, Japan), equipped with a UV sensor and C18 silica reverse-phase column (4.6 × 150 mm, particle size: 2.7 μm). The gradient elution program with two mobile phases (A, deionized water; B, acetonitrile with formic acid 0.1% (*v*/*v*)) was as follows: 0–2 min, 0% B; 2–50 min, 0–100% B; control washing 50–60 min 100% B. The entire HPLC analysis was performed with a UV–vis detector SPD- 20A (Shimadzu, Kyoto, Japan) at a wavelength of 230 nm for identification compounds; the temperature was 50 °C, and the total flow rate was 0.25 mL min^{-1}. The injection volume was 10 μL. Additionally, liquid chromatography was combined with a mass spectrometric ion trap to identify compounds.

2.5. Mass Spectrometry

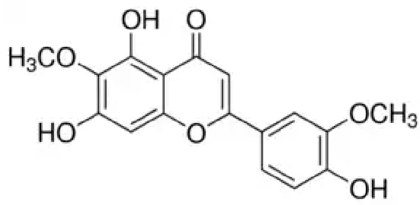
Mass spectrometry analysis was performed on an ion trap amaZon SL (BRUKER DALTONIKS, Bremen, Germany), equipped with an ESI source in positive and negative ion modes. The optimized parameters were obtained as follows: ionization source temperature: 70 °C, gas flow: 4 L/min, nebulizer gas (atomizer): 7.3 psi, capillary voltage: 4500 V, end plate bend voltage: 1500 V, fragmentary: 280 V, and collision energy: 60 eV. An ion trap was used in the scan range of *m*/*z* 100–1.700 for MS and MS/MS. The chemical constituents were characterized by their retention behavior, molecular formula, MS/MS spectral patterns, and the home-library database built by the Group of Biotechnology, Bioengineering and Food Systems at the Far-Eastern Federal University (Russia), based on data from other spectroscopic techniques, such as nuclear magnetic resonance, ultraviolet spectroscopy, and MS, as well as data from the literature that is continually updated and revised. The capture rate was one spectrum/s for MS and two spectrum/s for MS/MS. Data collection was controlled by Windows software for BRUKER DALTONIKS. All experiments were repeated three times. A four-stage ion separation mode (MS/MS mode) was implemented.

3. Results and Discussion

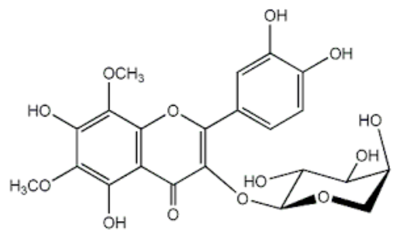
The HPLC conditions were optimized to obtain maximal resolution and signal within a minimal run time. Various chromatographic conditions such as the mobile phase composition, injection volume, flow rate, column temperature, and gradient program were studied and optimized for the separation of polyphenol compounds. Different mobile phase compositions (ethanol–water, ethanol-0.1% (*v*/*v*) formic acid aqueous solution, acetonitrile–water, and acetonitrile –0.1% (*v*/*v*) formic acid aqueous solution) were tested in the gradient program at a 0.25 mL/flow rate. A mobile phase composed of 0.1% (*v*/*v*) formic acid aqueous solution (A) and acetonitrile (B) at a 0.25 mL/min flow rate and 50 °C column temperature was found optimal for resolution of the maximum number of peaks in extracts of *L. caerulea* within 60 min.

The purpose of this study was to establish, as fully as possible, the composition of secondary metabolites in *L. caerulea* extracts from different geographic regions of origin and to further compare these compositions of chemical compounds both across the presented cultivars and across different geographic origins. Chemical compounds were characterized by their retention behavior, molecular formula, MS/MS spectral patterns, and the home-library database built by the Group of Biotechnology, Bioengineering and Food Systems at the Far-Eastern Federal University (Russia), which is based on data from other spectroscopic techniques, such as nuclear magnetic resonance, ultraviolet spectroscopy, and MS, as well as data from the literature and is continually updated and revised.

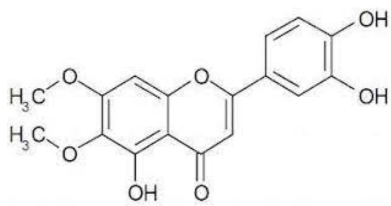
We were able to identify 122 chemical compounds from extracts of *L. caerulea*: 75 chemical compounds from the polyphenol group and 47 chemical compounds from other chemical groups. The chemical structures of some of the identified polyphenols are shown in Figure 2. All the identified polyphenols and other compounds, along with molecular formulas and MS/MS data for *L. caerulea*, are summarized in Table 1. Polyphenols are represented by the following chemical groups: flavones, flavonols, flavan-3-ols, flavanones, phenolic acids, anthocyanidins, lignans, and coumarins. For the first time, thirty-two compounds from the polyphenol group and twenty-seven compounds from other chemical groups were identified in berries of *L. caerulea*. These are flavones, such as formononetin, acacetin, rhamnocitrin, 5,7-dimethoxyluteolin, and eupatolitin-di-*O*-hexoside; flavonols, such as herbacetin, rhamnetin I, isorhamnetin, padmatin, myricetin-3-*O*-glucuronide, rhamnetin-di-*O*-hexoside, myricetin-*O*-galloyl-hexoside; flavan-3-ols (epi)-galoocatechin-3-gallate; (epi)-afzelechin derivative; flavanone hemiphloin; lignans, such as secoisolariciresinol, dimethyl-secoisolariciresinol, coumarin fraxin; etc. The chemical compounds from other chemical groups are benzofuran loliolide; aminoalkylindole 5-methoxydimethyltryptamine; sesquiterpenoid caryophyllene oxide; aporphine alkaloid anonaine; etc.



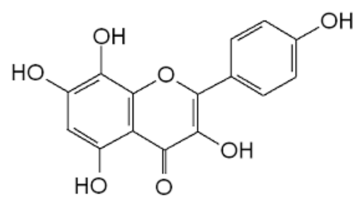
Jaceosidin



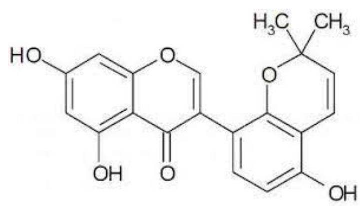
Pentahydroxy dimethoxyflavone



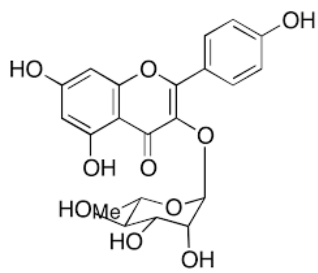
Cirsiliol



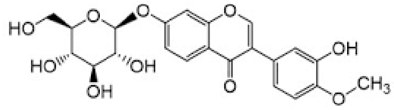
Herbacetin



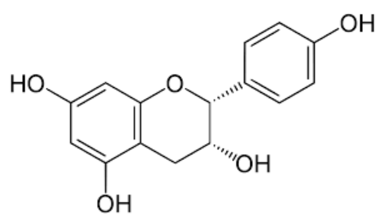
Sophoraisoflavone A



Kaempferol-3-*O*-*α*-*L*-rhamnoside



Calycosin-7-*O*-beta-*D*-glucoside-6″-*O*-malonate



(epi)-Afzelechin

Figure 2. Chemical structure of some identified polyphenols in extracts of *L. caerulea*.

Table 1. Characterization of the constituents of the extracts of *L. caerulea* in positive and negative ionization modes via HPLC-ion trap-MS/MS.

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
1	Flavone	Apigenin	$C_{15}H_{10}O_5$	20.2		271	225	179		*Phlomis* (Lamiaceae) [16]; Olive oil [17]; *Mentha* [18]; *L. henryl* [19]
2	Flavone	Trihydroxy(iso)flavone	$C_{15}H_{10}O_5$	25.6		271	197	129		Propolis [20]
3	Flavone	5,6,4′-Trihydroxy-7,8-dimethoxyflavone	$C_{17}H_{14}O_7$	24.4		331	303; 185	203	157	*Mentha* [21]; *F. glaucescens*; *F. herrerae* [22]
4	Flavone	Jaceosidin [5,7,4′-trihydroxy-6′,5′-dimetoxyflavone] *	$C_{17}H_{14}O_7$	33.2		331	303; 203	203; 157	175	*Mentha* [18,21]
5	Flavone	Cirsiliol *	$C_{17}H_{14}O_7$	34.0	329		229; 311	211	211	Ocimum [23]
6	Flavone	Sophoraisoflavone A *	$C_{20}H_{16}O_6$	33.7		353	335; 294; 235; 195	317; 277; 229		Chinese herbal formula Jian-Pi-Yi-Shen pill [24]
7	Flavone	Pentahydroxy dimethoxyflavone *	$C_{17}H_{14}O_9$	35.6		363	344; 300; 256	238; 146		*G. linguiforme* [22]
8	Flavone	Dihydroxy-tetramethoxy(iso)flavone *	$C_{19}H_{18}O_8$	27.5		375	345	245	175; 227	Propolis [20]
9	Flavone	Luteolin 7-*O*-glucoside [Cynaroside]	$C_{21}H_{20}O_{11}$	27.1		449	297	269	241	*L. henryi* [19]; *V. macrocarpon* [25]; *L. japonica* [26]
10	Flavone	Chrysoeriol *O*-hexoside *	$C_{22}H_{22}O_{11}$	7.3		463	445; 243			*T. aestivum* L. [27]; *Ipomoea batatas* [28]
11	Flavone	Formononetin-7-*O*-glucoside-6″-*O*-malonate *	$C_{25}H_{24}O_{12}$	18.7		517	271	243		*Astragali radix* [29,30]
12	Flavone	Acacetin 8-C-glucoside malonylated *	$C_{25}H_{24}O_{13}$	44.6		533	471; 411; 315	424; 281	305; 263	*Mexican lupine* species [31]
13	Flavone	Calycosin-7-*O*-*β*-*D*-glucoside-6″-*O*-malonate *	$C_{25}H_{24}O_{13}$	7.5		533	287	273; 236		*Radix astragali* [29,30]
14	Flavone	Chrysin derivative	$C_{26}H_{24}O_{14}$	44.8	559		277	233; 177		*Embelia* [32]
15	Flavone	C-hexosyl-apigenin O-rhamnoside *	$C_{27}H_{30}O_{14}$	36.2		579	561; 337; 317	319; 262	161	*T. aestivum* [33]
16	Flavone	Lonicerin [Luteolin-7-*O*-Rhamnoside; Veronicastroside; Scolymoside; Luteolin-7-Rhamnoglucoside]	$C_{27}H_{30}O_{15}$	22.8		595	449; 287	287	287; 153	*L. japonica* [26]; *Exocarpium Citri Grandis* [34]
17	Flavone	Luteolin 7-*O*-(6-*O*-arabinosyl-glucoside)	$C_{26}H_{28}O_{15}$	22.9		581	287	153; 241; 287		*L. henryi* [19]
18	Flavonol	Kaempferol	$C_{15}H_{10}O_6$	23.0		287	269; 149	239; 181		*L. japonica* [26]; *P. sibirica* [35]; *Rhus coriaria* [36]; *R. meyeri* [37]; *Andean blueberry* [38]

Table 1. *Cont.*

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
19	Flavonol	Dihydrokaempferol	$C_{15}H_{12}O_6$	25.4	287		259	215	173	*Andean blueberry* [38]; *Camellia kucha* [39]; *Strawberry* [40]
20	Flavonol	Rhamnocitrin *	$C_{16}H_{12}O_6$	27.5		301	273	245	217; 177; 131	*Astragali radix* [29]; *Mentha* [41]
21	Flavonol	Quercetin	$C_{15}H_{10}O_7$	31.3		303	257; 146	229	201; 145	Propolis [20]; *Ocimum* [23]; *V. macrocarpon* [25,42]; *Rhus coriaria* [36]; *R. meyeri* [37]
22	Flavonol	Herbacetin [3,5,7,8-Tetrahydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one] *	$C_{15}H_{10}O_7$	26.6		303	203	175		*Rhodiola rosea* [43]
23	Flavonol	Rhamnetin II *	$C_{16}H_{12}O_7$	32.9		317	302	274; 153; 121	229; 153; 121	*P. sibirica* [35]; *Rhus coriaria* L. (*Sumac*) [36]; *Spondias purpurea* [44]
24	Flavonol	Isorhamnetin [Isorhamnetol; Quercetin 3′-Methyl ether; 3-Methylquercetin]	$C_{16}H_{12}O_7$	24.4	315		283	255; 211	227	*Andean blueberry* [38]; *V. macrocarpon* [42]; *Spondias purpurea* [44]
25	Flavonol	Kaempferol-3-*O*-α-L-rhamnoside *	$C_{21}H_{20}O_{10}$	22.9		433	287	187		*C.edulis; F. glaucescens* [22]; *Rhus coriaria* [36]; *P. aculeata* [45]; *Cassia abbreviata* [46]
26	Flavonol	Quercetin 3-*O*- glucoside [Isoquercitrin; Hirsutrin; Quercetin-3-*O*-Glucopyranoside; 3-Glucosylquercetin]	$C_{21}H_{20}O_{12}$	23.4		465	303	229; 165	201; 161	*L. henryi* [19]; *L. japonica* [26]; *Ribes meyeri* [37]; *Andean blueberry* [38]; *Spondias purpurea* [44]; *R. occidentalis* [47]; *Cranberry* [48]; *V. myrtillus* [49]
27	Flavonol	Kaempferol 3-*O*-rutinoside	$C_{27}H_{30}O_{15}$	22.6		595	449; 287	287	287	*L. japonica* [26]; *R. meyeri* [37]; *Spondias purpurea* [44]; *Strawberry* [50]
28	Flavonol	Quercetin 3-*O*-pentosyl hexoside	$C_{26}H_{28}O_{16}$	21.9		597	303; 257; 211	257; 195; 165	229	*F. pottsii* [22]; *Spondias purpurea* [44]; *V. myrtillus* [51]
29	Flavonol	Rutin (Quercetin 3-*O*-rutinoside)	$C_{27}H_{30}O_{16}$	22.1		611	303	257; 165	229	*L. henryi* [19]; *L. japonica* [26]; *Ribes meyeri* [37]; *Spondias purpurea* [44]; *R. occidentalis* [47]; *R. magellanicum* [52]

Table 1. *Cont.*

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
30	Flavonol	Isorhamnetin 3-*O*-(6″-*O*-rhamnosyl-hexoside)	$C_{28}H_{32}O_{16}$	24.3		625	317	302		*L. henryi* [19]; *Bee-pollen* [53]
31	Flavonol	Dimethylquercetin-3-*O*-dehexoside *	$C_{29}H_{34}O_{17}$	38.4	653		507; 353; 311	329	287; 190	*Capsicum annuum* [54]
32	Flavonol	Derivative of Quercetin rhamnosyl hexoside	$C_{36}H_{46}O_{22}$	8.5	829		609	301	300	Pubchem
33	Flavan-3-ol	Epiafzelechin [(epi)Afzelechin] *	$C_{15}H_{14}O_5$	19.4		275	245; 219; 175	215; 193; 175; 157; 127	175; 157; 145	*A. cordifolia; F. glaucescens; F. herrerae* [22]; *Cassia abbreviata* [46]
34	Flavan-3-ol	(Epi)-catechin	$C_{15}H_{14}O_6$	22.6		291	273; 137			*V. macrocarpon* [25]; *Andean blueberry* [38]; *Rubus occidentalis* [47]; *Cranberry* [48]; *V. myrtillus* [49,51]
35	Flavan-3-ol	Gallocatechin [+(−)Gallocatechin]	$C_{15}H_{14}O_7$	55.3		307	261; 243; 163; 137	187; 159	131	*G. linguiforme* [22]; *Embelia* [32]; *R. meyeri* [37]; *V. myrtillus* [51]
36	Flavan-3-ol	(Epi)-afzelechin derivative	$C_{18}H_{16}O_{10}$	19.1		393	275; 245; 215	245; 175	175; 127	*Zostera marina* [55]
37	Flavan-3-ol	(Epi)-catechin derivative	$C_{18}H_{16}O_{11}$	19.4		409	291; 275	261; 242; 208; 173	244; 214; 191; 173; 160; 124	Pubchem
38	Flavan-3-ol	(−)-Epicatechin Gallate [(−)-Epicatechin-3-*O*-Gallate; L-Epicatechin Gallate] *	$C_{22}H_{18}O_{10}$	23.3	441		330; 139	150		Chinese herbal formula Jian-Pi-Yi-Shen pill [24]; *R. meyeri* [37]; *Camellia kucha* [39]; *Cassia abbreviates* [46]; *Terminalia arjuna* [56]
39	Flavanone	Naringenin [Naringetol; Naringenine] *	$C_{15}H_{12}O_5$	31.3		273	153; 189	111		*G. linguiforme* [22]; *Mexican lupine* species [31]; *Exocarpium Citri Grandis* [33]; *Andean blueberry* [38]; *Rapeseed petals* [57]
40	Flavanone	Butin [7,3′,4′-Trihydroxyflavanone] *	$C_{15}H_{12}O_5$	31.7		273	153	171	153	*Ribes meyeri* [38]
41	Anthocyanin	Anthocyanidin [cyanidin chloride; Cyanidin]	$C_{15}H_{11}O_{6+}$	7.9		287	286; 270; 247; 205	221		*F. herrerae* [22]; *Andean blueberry* [38]; *Phoenix dactylifera* [58]
42	Anthocyanin	Petunidin	$C_{16}H_{13}O_{7+}$	35.6		318	256	238; 113	238	*A. cordifolia; C. edulis* [22]
43	Anthocyanin	Pelargonidin-3-*O*-glucoside (callistephin)	$C_{21}H_{21}O_{10}$	25.9		431	257; 331	227	215	*R. ulmifolius* [59]; *Black currant, Elderberry* [60]

Table 1. *Cont.*

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
44	Anthocyanin	Delphinidin 3-*O*-glucoside	$C_{21}H_{21}O_{12+}$	23.3		465	303	257; 165	229; 201	*R. magellanicum* [52]; *Black currant* [60]; *B. lycium* [61]; *B. ilicifolia; B.s empetrifolia; R. maellanicum; R. cucullatum; M. nummalaria* [62]; *B. microphylla* [63]
45	Anthocyanin	Pelargonidin 3-*O*-(6-*O*-malonyl-*β*-*D*-glucoside)	$C_{24}H_{23}O_{13}$	11.8		519	271	243	197	*Gentiana lutea* [64]; *T. aestivum* [65]
46	Anthocyanin	Delphinidin 3-*O*-*β*-*D*-sambubioside	$C_{26}H_{29}O_{16}$	21.6		597	303; 465; 229	229; 165	201; 172	*Red currant* [60]; *B. microphylla* [63]; *T. aestivum* [65]
47	Anthocyanin	Delphinidin 3-*O*-rutinoside [Tulipanin; Delphinidin 3-Rhamnosyl-Glucoside]	$C_{27}H_{31}O_{16}$	22.4		611	303	257; 165	229	*Black currant* [60]; *B. ilicifolia; B. empetrifolia; R. maellanicum; R. cucullatum* [62]; *B. microphylla* [63]
48	Anthocyanin	Petunidin-3-rutinoside	$C_{28}H_{33}O_{16}$	24.2		625	317; 479	302; 139	274; 229; 153	*Black currant* [60]; *B. ilicifolia; B. empetrifolia* [62]; *B. microphylla* [63]
49	Hydroxybenzoic acid (Phenolic acid)	Protocatechuic acid	$C_7H_6O_4$	29.8		155	127			*V. macrocarpon* [25]; *L. japonica* [26]; *R. meyeri* [37]
50	Hydroxycinnamic acid	Caffeic acid [(2E)-3-(3,4-Dihydroxyphenyl)acrylic acid]	$C_9H_8O_4$	13.3		181	135	119		*V. macrocarpon* [25]; *L. japonica* [26]; *R. meyeri* [37]; *Strawberry* [40]; *R. occidentalis* [47]; *V. myrtillus* [49]
51	Methylbenzoic acid	Methylgallic acid [Methyl gallate] *	$C_8H_8O_5$	15.3		185	139	111		*Rhus coriaria* [36]; Papaya [50]; *Eucalyptus* [66]
52	Trans-cinnamic acid	Ferulic acid	$C_{10}H_{10}O_4$	7.3	193		176	132		*V. macrocarpon* [25]; *L. japonica* [26]; *Andean blueberry* [38]; *R. nigrum* [67];
53	Phenolic acid	Hydroxy methoxy dimethylbenzoic acid *	$C_{10}H_{12}O_4$	20.4		197	188	179		*F. herrerae; F. glaucescens* [22]
54	Phenolic acid	2,3,4,5,6-pentahydroxybenzoic acid *	$C_7H_6O_7$	8.6		203	156	129		*Jatropha* [68]
55	Hydroxycinnamic acid	Hydroxyferulic acid *	$C_{10}H_{10}O_5$	8.1		211	193	75; 147	157; 129	*Andean blueberry* [38]; *Strawberry* [40]; *Rosa davurica* [69]

Table 1. *Cont.*

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
56	Hydroxycinnamic acid	Sinapic acid [trans-Sinapic acid]	$C_{11}H_{12}O_5$	29.2		225	207; 179	151; 123	123	*V. macrocarpon* [25]; *Cranberry* [48]; *Andean blueberry* [38]
57	Phenolic acid	2,4,6-Trihydroxy-3,5-dimethoxybenzoic acid *	$C_9H_{10}O_7$	35.6		230	212	195		*Actinidia* [70]
58	Hydroxybenzoic acid (Phenolic acid)	Ellagic acid [Benzoaric acid; Elagostasine; Lagistase; Eleagic acid]	$C_{14}H_6O_8$	21.7	301		257	229	201	*Rubus occidentalis* [47]; *Eucalyptus* [66]
59	Phenolic acid	6-Hydroxy-3-methoxy-4-*O*-*β*-*D*-glucopyranoside *	$C_{14}H_{20}O_{10}$	8.4	347		301; 165	165; 137		*Actinidia* [70]
60	Phenylpropanoid (cinnamic acid derivative glycoside); Hydroxycinnamic acid;	Chlorogenic acid [3-*O*-Caffeoylquinic acid]	$C_{16}H_{18}O_9$	18.5	353		191	127		*L. henryi* [19]; *L. japonica* [26]; *V. macrocarpon* [25,42]; *Andean blueberry* [38]; *Strawberry* [40]; *Spondias purpurea* [44]; *Cranberry* [48]; *V. myrtillus* [49]; *R. magellanicum* [52]
61	Hydroxycinnamic acid;	3-*O*-Hydroxydihydrocaffeoylquinic acid	$C_{16}H_{20}O_{10}$	6.7	6.7		191	173; 127		*L. henryi* [19]
62	Phenolic acid	Caffeoylquinic acid derivative		25.5	381		179; 135	135		*V. myrtillus* [51]
63	Flavonoid	*p*-Coumaroylhexose-4-*O*-hexoside *	$C_{25}H_{28}O_{10}$	23.3		489	327	299; 253	253; 225	*Strawberry* [40]; *Gmelina arborea* [71]
64	Phenolic acid	3,4-*O*-dicaffeoylquinic acid [Isochlorogenic acid B]	$C_{25}H_{24}O_{12}$	23.7	515		353	191	173	*L. henryi* [19]; *L. japonica* [26]; *Stevia rebaudiana* [72]
65	Phenolic acid	4,5-*O*-dicaffeoylquinic acid [Isochlorogenic acid C]	$C_{25}H_{24}O_{12}$	24.7	515		353	191	171	*L. henryi* [19]; *L. japonica* [26]; Lemon [50]
66	Phenolic acid	*p*-Coumaroyl malonyldihexose		23.8		575	413; 335; 188	395; 340; 226; 188	346; 290; 211	*V. myrtillus* [51]
67	Phenolic acid	Dicaffeoylferuoylquinic acid *		42.5		693	353; 261	335; 261; 135	243; 149	*Artemisia annua* [73]
68	Stilbene	Pinosylvin [3,5-Stilbenediol; Trans-3,5-Dihydroxystilbene] *	$C_{14}H_{12}O_2$	32.7		213	167; 139	139		*P. resinosa* [74]; *P. sylvestris* [75]
69	Stilbene	Resveratrol [trans-Resveratrol; 3,4′,5-Trihydroxystilbene; Stilbentriol] *	$C_{14}H_{12}O_3$	20.3		229	211	183; 127	138	*A. cordifolia; F. glaucescens; F. herrerae* [22]; *Embelia* [32]; *Radix polygoni multiflori* [76]

Table 1. *Cont.*

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
70	Stilbene	Dihydroresveratrol [Alpha, Beta-Dihydroresveratrol] *	$C_{14}H_{14}O_3$	19.4		231	214; 158	196; 168		*Maackia amurense* [77]
71	Hydroxycoumarin	Umbelliferone [Skimmetin; Hydragin] *	$C_9H_6O_3$	16.5		163	145	117		*F. glaucescens* [22]; *Actinidia* [70]; *Zostera marina* [55]; *S. officinalis* [78]
72	Coumarin	Fraxetin *	$C_{10}H_8O_5$	23.7		209	191	117		*Embelia* [32]; *Actinidia* [70]; *Jatropha* [68]
73	Coumarin	3,4/6,8-Dihydro-5,7-dihydroxy-2-oxo-2H-1-benzopyran-3-acetic acid	$C_{11}H_{10}O_6$	7.3		239	221	203	185	*Actinidia* [70]
74	Coumarin	Umbelliferone hexoside *	$C_{15}H_{16}O_8$	52.8		325	289; 127	271; 127	253; 146	*G. linguiforme* [22]
75	Coumarin	7-(*β-D*-Glucopyranoside/galactopyranoside)-2-oxo-2H-1-benzopyran-4-acetic acid	$C_{17}H_{18}O_{10}$	6.7		383	163; 365	145		*Actinidia* [70]
	OTHERS									
76	Amino acid	L-Proline [(2-Pyrrolidinecarboxylic acid]	$C_5H_9NO_2$	16.3		116	70			*L. japonica* [26]; *V. unguiculata* [79]
77	Non-proteinogenic L-alpha-amino acid	L-Pyroglutamic acid [Pidolic acid; 5-Oxo-L-Proline] *	$C_5H_7NO_3$	7.8		130	111			*Potato leaves* [80]
78	Amino acid	L-Histidine	$C_6H_9N_3O_2$	26.2		156	129	110		*L. japonica* [26]; *Camellia kucha* [39]; *Actinidia deliciosa* [81]
79	Amino acid	L-threanine	$C_7H_{14}N_2O_3$	7.6		175	157; 129	129; 115		*Camellia kucha* [39]
80	Amino acid	L-Arginine	$C_6H_{14}N_4O_2$	9.9		175	130	111		*L. japonica* [26]; *Hylocereus polyrhizus* [82]
81	Cyclohexenecarboxylic acid	Shikimic acid [L-Schikimic acid] *	$C_7H_{10}O_5$	8.1		175	157	129	111	*A. cordifolia* [22]; *R. meyeri* [37]; *Camellia kucha* [39]
82	Tricarboxylic acid	Citric acid [Anhydrous; Citrate]	$C_6H_8O_7$	6.7	191		111; 173			*Mentha* [18]; Strawberry, Lemon, Cherimoya, Papaya, Passion fruit [50]; *V. unguiculata* [79]; *Potato leaves* [80]
83	Polyhydroxycarboxylic acid	Quinic acid	$C_7H_{12}O_6$	7.9	191		111; 173	111		*L. japonica* [26]; *R. meyeri* [37]; *Andean blueberry* [38]; *Potato leaves* [80]

Table 1. *Cont.*

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
84	Pentahydroxy hexanoic acid	Gluconic acid [Dextronic acid; Maltonic acid; Glycogenic acid; Pentahydroxy hexanoic acid] *	$C_6H_{12}O_7$	19.1		197	188; 179; 156; 119	156; 148		*R. meyeri* [37]; *Colchicum micranthum* [83]
85	Benzofuran	Loliolide *	$C_{11}H_{16}O_3$	20.7		197	179; 127	111		*Jatropha* [68]
86	Alpha, omega dicarboxylic acid	Sebacic acid [Decanedioic acid] *	$C_{10}H_{18}O_4$	17.6		203	185	139	111; 157	*Jatropha* [68]
87		4-Dihydroxy-3-methoxy-benzenepropanoic acid *	$C_{10}H_{12}O_5$	25.7		213	193; 167; 139; 119			*Actinidia* [70]
88	Sesquiterpenoid	Caryophyllene oxide [Caryophyllene-alpha-oxide] *	$C_{15}H_{24}O$	16.4	219		173; 111	111		*R. davurica* [69]; Olive leaves [84]
89	Carboxylic acid	Myristoleic acid [Cis-9-Tetradecanoic acid] *	$C_{14}H_{26}O_2$	20.2		227	209; 165	121		*F. glaucescens* [22]; *Maackia amurensis* [85]
90	Pyrimidine nucleoside	Cytidine	$C_9H_{13}N_3O_5$	29.2		244	225; 179	179	151	*L. japonica* [26]
91	Glycosylated pyrimidine analog	Uridine	$C_9H_{12}N_2O_6$	28.3		245	145	117		*L. japonica* [26]; *Potato leaves* [80]
92	Hydroxy tetradecanoic acid	Hydroxy myristic acid [2S-Hydroxytetradecanoic acid; Alpha-Hydroxy Myristic acid] *	$C_{14}H_{28}O_3$	30.8		245	228	183		*F. pottsii* [22]
93	Medium-chain fatty acid	Hydroxy dodecanoic acid *	$C_{12}H_{22}O_5$	27.5		247	229; 201	187	159; 145	*F. glaucescens* [22]
94		Caffeic acid isoprenyl ester	$C_{14}H_{16}O_4$	25.4		249	203	157	129	*Eucalyptus* [66]; Brazilian propolis [86]
95	Sesquiterpene lactone	Artemisinin C *	$C_{15}H_{20}O_3$	25.7		249	202; 157; 125	157; 185	129	*Artemisia annua* [87]
96	Aporphine alkaloid	Anonaine *	$C_{17}H_{15}NO_2$	25.8		266	249	203	157	*R. rugosa* [69]; *Magnolia* [88]
97	Ribonucleoside composite of adenine (purine)	Adenosine	$C_{10}H_{13}N_5O_4$	20.2		268	250	204; 158	157	*L. japonica* [26]; *R. acicularis* [69]; Huolisu Oral Liquid [89]
98		3,4,8,9,10-Penthahydroxydibenzo [b,d]pyran-6-one *	$C_{13}H_8O_7$	33.3		277	203	157	129	*Terminalia arjuna* [56]
99	Omega-3-fatty acid	Stearidonic acid [6,9,12,15-Octadecatetraenoic acid; Moroctic acid] *	$C_{18}H_{28}O_2$	40.0		277	261	215; 115	129	*G. linguiforme* [22]; *Rhus coriaria* [36]; *Jatropha* [68]; *Salviae Miltiorrhizae* [90]
100	Omega-3-fatty acid	Linolenic acid (Alpha-Linolenic acid; Linolenate) *	$C_{18}H_{30}O_2$	42.2		279	261	219	163	*Jatropha* [68]; *P. sylvestris* [75]; *Maackia amurensis* [85]; *Salviae Miltiorrhizae* [90]

Table 1. *Cont.*

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
101	Mixture of diastereomers	Fructose-leucine	$C_{12}H_{23}NO_7$	7.8		294	276	258	210	*Potato leaves* [80]
102	Cyclohexenecarboxylic acid	Coumaroyl shiikimic acid	$C_{16}H_{16}O_7$	19.4		321	219; 173	201; 173	155	*Andean blueberry* [38]
103	Oxylipin	13- Trihydroxy-Octadecenoic acid [THODE] *	$C_{18}H_{34}O_5$	32.6	329		229; 171	210	209; 183	*Phoenix dactylifera* [58]; *Jatropha* [68]; *Broccoli* [91]
104	Alpha, omega-dicarboxylic acid	Eicosatetraenedioic acid *	$C_{20}H_{30}O_4$	32.1	333		287; 197; 151	151		*G. linguiforme* [22]
105	Cyclohexenecarboxylic acid	Caffeoyl shikimic acid	$C_{16}H_{16}O_8$	38.0		337	273; 173	128		*R. meyeri* [37]
106	Alpha, omega-dicarboxylic acid	Trihydroxy eicosatetraenoic acid *	$C_{20}H_{32}O_5$	45.6		353	261	243	159	*F. glaucescens* [22]
107	Dicarboxylic acid sugar	Caffeoyl gluconic acid	$C_{15}H_{18}O_{10}$	21.6		359	340; 312; 284; 228; 196			*R. meyeri* [37]
108	Iridoid glucoside	Sweroside	$C_{16}H_{22}O_9$	21.6		359	197; 127	179	111	*L. japonica* [26]
109	Cyclopentapyran	Loganin acid	$C_{16}H_{24}O_{10}$	18.9		377	158; 359	130		*L. japonica* [26]
110		7-(*β*-*D*-Galactopyranosyloxy)-6,8-dimethoxy-2H-1-benzopyran-2-one	$C_{17}H_{20}O_{10}$	6.7	383		191	172; 127	171	*Actinidia* [70]
111	Iridoid	Monotropein *	$C_{16}H_{22}O_{11}$	31.2		391	373; 329; 251; 187	311; 202	203	*V. myrtillus* [51,92]
112	Sterol	Beta-Sitostenone [Stigmast-4-En-3-One; Sitostenone] *	$C_{29}H_{48}O$	2.1		413	301; 171	189		*F. herrerae* [22]; *Terminalia laxiflora* [93]
113	Anabolic steroid	Vebonol *	$C_{30}H_{44}O_3$	24.9		453	435; 210	226; 336	210	*Rhus coriaria* [36]; *Hylosereus polyrhizus* [82]
114	Phenylpropanoid glucoside	Grayanoside A [Hydroxyphenylethyl feruloyl glucopyranoside] *	$C_{24}H_{28}O_{10}$	23.4	475		375; 275	347; 275; 175	247; 175	*Strawberry* [40]
115	Thromboxane receptor antagonist	Vapiprost *	$C_{30}H_{39}NO_4$	44.7		478	337	263; 121	119	*Rhus coriaria* [36]; *Hylosereus polyrhizus* [82]
116	Indole sesquiterpene alkaloid	Sespendole *	$C_{33}H_{45}NO_4$	45.7		520	184	125		*Rhus coriaria* [36]
117	Iridoid glucoside	*p*-Coumaroyl monotropein *	$C_{25}H_{28}O_{13}$	44.6		537	375; 256; 185			*Cranberry* [52]; *V. myrtillus* [49,51]
118	Iridoid glucoside	*p*-Coumaroyl-6,7-dihydromonotropein *	$C_{25}H_{30}O_{13}$	20.2		540	373; 229; 179	179		*Cranberry* [48]; *V. myrtillus* [51]
119	Carotenoid	Zeaxanthin [All-Trans-Zeaxanthin; Anchovyxanthin]	$C_{40}H_{56}O_2$	28.4		570	552; 412; 184	534; 317; 184	487; 404; 321; 149	Sarsaparilla [94]; Carotenoids [95]

Table 1. *Cont.*

	Class of Compounds	Identification	Formula	Retention Time	Observed Mass [M-H]-	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
120	Carotenoid	(*all-E*)-lutein 3-*O*-C(4:0)		41.8		638	620; 554	536; 335; 220	414; 276; 241	Carotenoids [96]
121	Iridoid	*p*-Coumaroyl monotropein hexoside *		42.5		699	537; 347; 259	375; 259; 185		*V. myrtillus* [51]
122	Product of chlorophyll degradation	Pheophytin A	$C_{55}H_{74}N_4O_5$	0.6		872	593	533	461	*Physalis peruviana* [97]; Capsicum [98]

* Chemical constituents identified for the first time in *L. caerulea*.

The new tentatively identified polyphenols belonged to six classes, including eleven flavones, three flavonols, two flavan-3-ols, two flavanone, seven phenolic acids and their conjugates, four stilbenes, and two coumarins (Table 1). The new tentatively identified compounds from other chemical groups belonged to 12 classes, including 1 L-alpha-amino acid, 1 cyclohexanecarboxylic acid, 3 alpha, omega dicarboxylic acid, 1 pentahydroxy hexanoic acid, 1 benzofuran, 1 sesquiterpenoid and 1 sesquiterpene lactone, 1 hydroxytetradecanoic acid, 2 omega-3 fatty acids, 1 aporphine alkaloid, 1 oxylipin, 3 iridoids, 1 sterol, and others. An approximate comparison of the chemical constituents identified in the *L. caerulea* varieties obtained from two different regions is shown in Appendix A, Table A1.

3.1. Flavones

3.1.1. 7-Hydroxy(iso)flavones

We identified flavone calycosin-7-*O*-*β*-*D*-glucoside-6″-*O*-malonate (compound **13** in Table 1) in extracts from the berries of *L. caerulea*. The CID spectrum (collision-induced spectrum), in positive ion modes, of flavone calycosin-7-*O*-*β*-*D*-glucoside-6″-*O*-malonate from the berries of *L. caerulea* is shown in Figure 3.

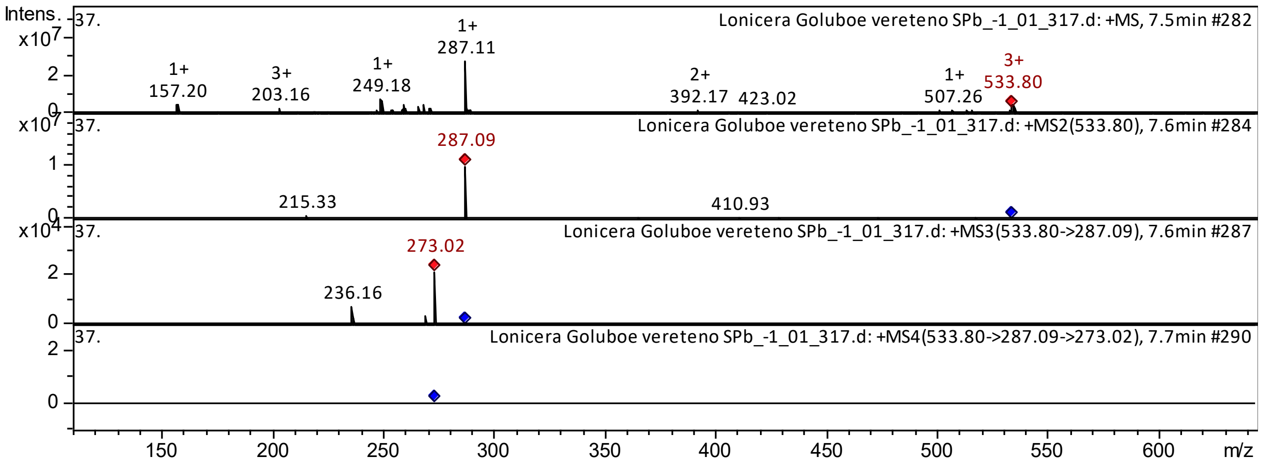


Figure 3. CID spectrum of calycosin-7-*O*-*β*-*D*-glucoside-6″-*O*-malonate from *L. caerulea* (variety Goluboe vereteno from Saint-Petersburg), *m*/*z* 533.80.

The [M+H]+ ion produced two fragment ions with *m*/*z* 287.09 and *m*/*z* 215.33 (Figure 3). The fragment ion with *m*/*z* 287.09 produced two characteristic daughter ions with *m*/*z* 273.02 and *m*/*z* 236.16. However, this flavone has already been reported from *Astragali Radix* [29,30]. Calycosin-7-*O*-*β*-D-glucoside-6″-*O*-malonate (flavonoid glycoside) is biosynthesized by the conversion of flavonoid glycoside malonate, as shown in Figure 4 [99–101].

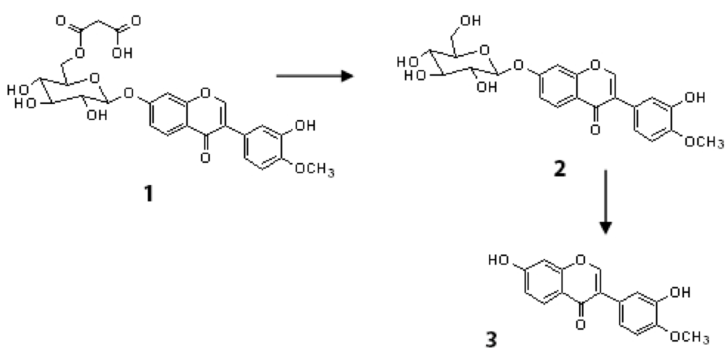


Figure 4. Chemical structure analysis of conversion of flavonoid glycoside malonate to their related flavonoid glycoside (**1**. calycosin-7-*O*-*β*-D-glucoside-6″-*O*-malonate; **2**. calycosin-7-*O*-*β*-D-glucoside; **3**. ononin).

3.1.2. Dihydroxyflavones

The flavones acacetin 8-*C*-glucoside malonylated (compound **12** in Table 1) and chrysin derivative (compound **14** in Table 1) have already been characterized as components of *Mexican lupine* species [31] and *Embelia* [32]. These flavones were tentatively identified in extracts from the berries of *L. caerulea*. The CID spectrum, in positive ion modes, of acacetin 8-C-glucoside malonylated from extracts from the berries of *L. caerulea* is shown in Figure 5.

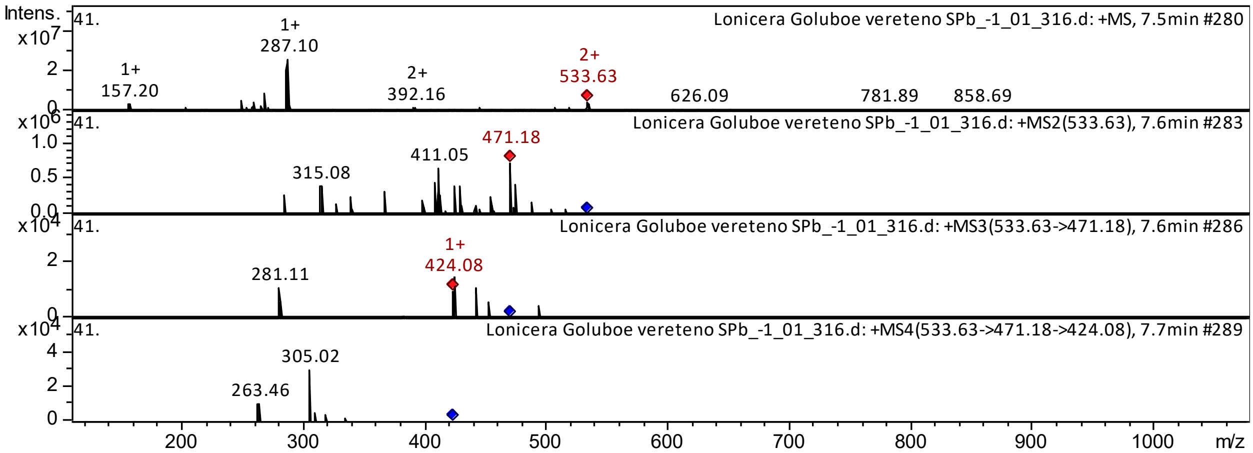


Figure 5. CID spectrum of acacetin 8-C-glucoside from *L. caerulea* (variety Goluboe vereteno from Saint-Petersburg), *m/z* 533.63.

The $[M+H]^+$ ion produced three fragment ions with *m/z* 471.18, *m/z* 411.05, and *m/z* 315.08 (Figure 5). The fragment ion with *m/z* 471.18 produced two characteristic daughter ions with *m/z* 424.08 and *m/z* 281.11. The fragment ion with *m/z* 424.08 produced two characteristic ions with *m/z* 305.02 and *m/z* 263.46. The acacetin 8-*C*-glucoside has been previously reported in the extract from *Mexican lupine* species [31].

3.1.3. Trihydroxyflavones

The flavones apigenin (compound **1** in Table 1), trihydroxy(iso)flavone (compound **2** in Table 1), luteolin 7-*O*-glucoside (compound **9** in Table 1), chrysoeriol *O*-hexoside (compound **10** in Table 1), C-hexosyl-apigenin *O*-rhamnoside (compound **15** in Table 1), lonicerin (compound **16** in Table 1), luteolin 7-*O*-(6-*O*-arabinosyl-glucoside) (compound **17** in Table 1), rhamnocitrin (compound **20** in Table 1), and kaempferol 3-*O*-rutinoside (compound **27** in Table 1) have already been characterized as a components of *Phlomis* (Lamiaceae) [16], Olive oil [17], *Mentha* [18,41], *L. henryi* [19], Propolis [20], *V. macrocarpon* [25], *L. japonica* [26], *T. aestivum* L. [27], *Ipomoea batatas* [28], *Astragali radix* [29], *Exocarpium Citri Grandis* [34], *Strawberry* [50], *R. meyeri* [37], and *Spondias purpurea* [44]. The trihydroxyflavones were tentatively identified in extracts from the berries of *L. caerulea*. The CID spectrum, in positive ion modes, of Lonicerin from extracts from the berries of *L. caerulea* is shown in Figures 6 and 7.

The $[M+H]^+$ ion produced two fragment ions with *m/z* 449.11 and *m/z* 287.11 (Figure 7). The fragment ion with *m/z* 449.11 produced one characteristic daughter ion with *m/z* 287.12. The fragment ion with *m/z* 287.12 produced two characteristic daughter ions with *m/z* 287.08 and *m/z* 153.14. The Lonicerin was identified, using the bibliography, in extracts from *L. japonica* [26] and *Exocarpium Citri Grandis* [34].

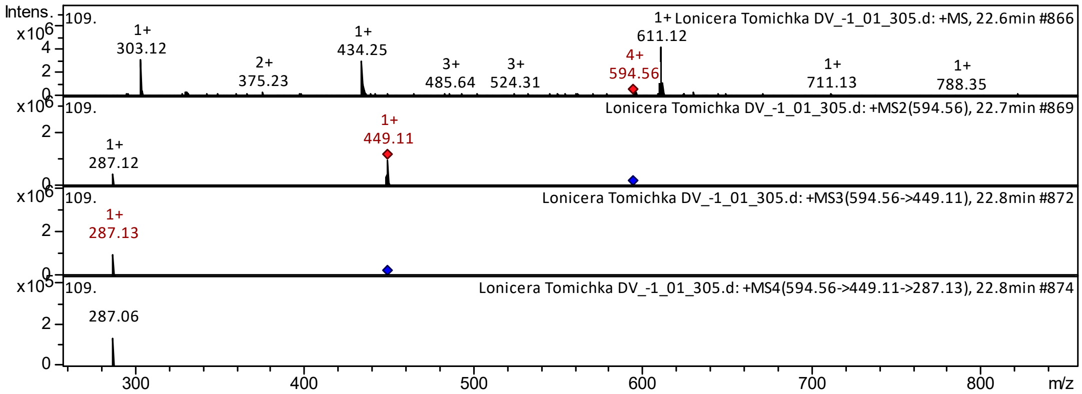


Figure 6. CID spectrum of lonicerin from *L. caerulea* (variety Tomichka from Far East), m/z 594.56.

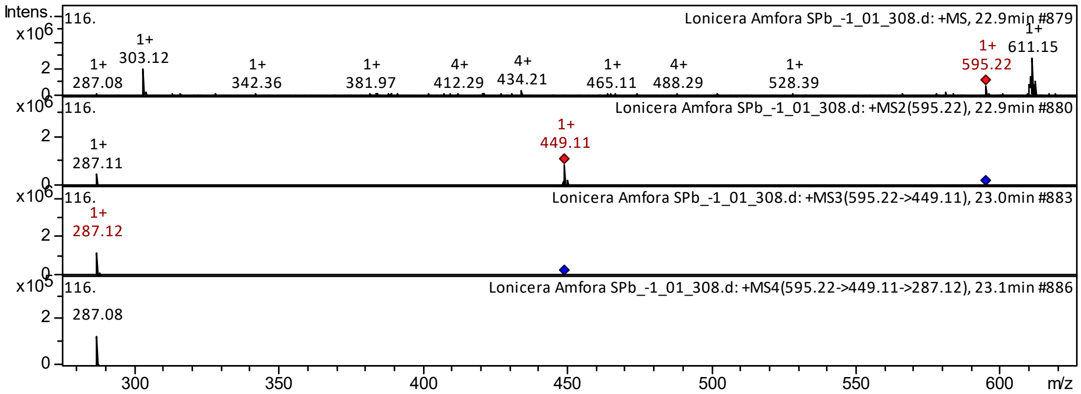


Figure 7. CID spectrum of lonicerin from *L. caerulea* (variety Amfora from Saint-Petersburg), m/z 595.22.

3.1.4. Tetrahydroxyflavones

The flavonols kaempferol (compound **18** in Table 1), dihydrokaempferol (compound **19** in Table 1), rhamnetin II (compound **23** in Table 1), isorhamnetin (compound **24** in Table 1), and rutin (compound **29** in Table 1) have already been characterized as components of *L. henryi* [19], *L. japonica* [26], *P. sibirica* [35], *Rhus coriaria* [36], *R. meyeri* [37], *Andean blueberry* [38], *Camellia kucha* [39], *Strawberry* [40], *Spondias purpurea* [44], *R. occidentalis* [47], and *R. magellanicum* [52]. These tetrahydroxyflavones were tentatively identified in extracts from the berries of *L. caerulea*. The CID spectrum, in positive ion modes, of Rhamnetin II from the berries of *L. caerulea* is shown in Figure 8.

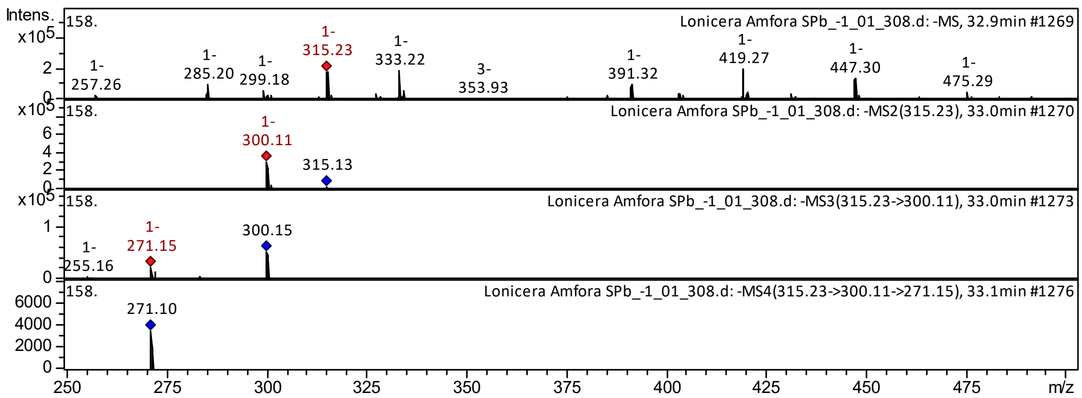


Figure 8. CID spectrum of rhamnetin II from berries of *L. caerulea* (variety Amfora from Saint-Petersburg), m/z 315.23.

The [M–H]$^-$ ion produced one fragment ion with m/z 300.11 (Figure 8). The fragment ion with m/z 300.11 produced three characteristic daughter ions with m/z 271.15, m/z 227.19, and m/z 151.23. The fragment ion with m/z 271.15 produced one characteristic daughter ion with m/z 227.16. The rhamnetin II was identified, using the bibliography, in extracts from *P. sibirica* [35], *Rhus coriaria* L. [36], and *Spondias purpurea* [44].

3.1.5. Pentahydroxyflavones

The flavonols quercetin (compound **21** in Table 1), herbacetin (compound **22** in Table 1), and pentahydroxy dimethoxyflavone (compound **7** in Table 1) have already been characterized as components of Propolis [20], *G. linguiforme* [22], Ocimum [23], *V. macrocarpon* [25,42], *Rhus coriaria* [36], *R. meyeri* [37], and *Rhodiola rosea* [43]. These pentahydroxyflavones were tentatively identified in extracts from the berries of *L. caerulea*. The CID spectrum, in positive ion modes, of the herbacetin from berries of *L. caerulea* is shown in Figure 9.

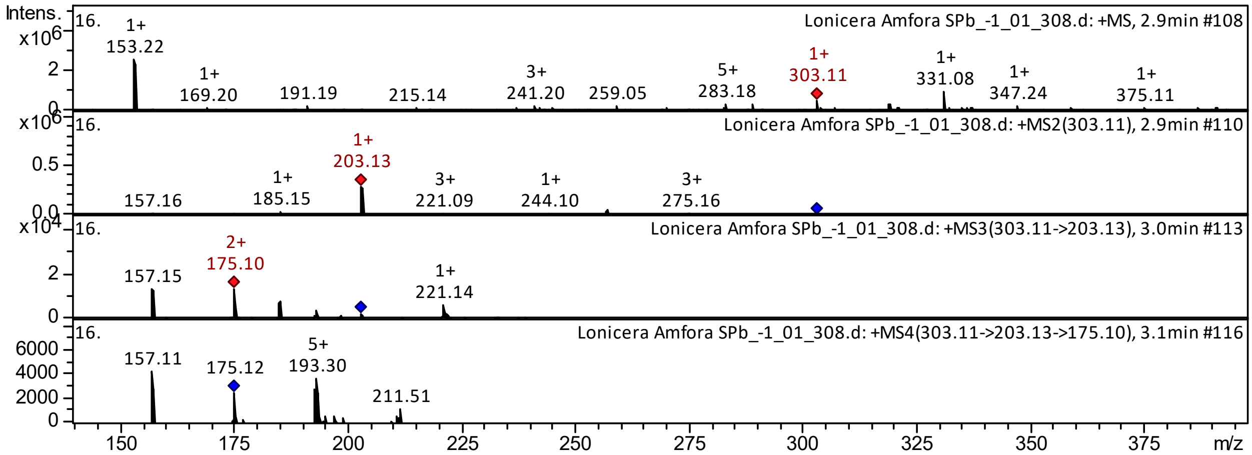


Figure 9. CID spectrum of herbacetin from berries of *L. caerulea* (variety Amfora from Saint-Petersburg), m/z 303.11.

The [M+H]$^+$ ion produced two fragment ions with m/z 203.13 and m/z 257.10 (Figure 9). The fragment ion with m/z 203.13 produced two characteristic daughter ions with m/z 157.15 and m/z 175.10. The fragment ion with m/z 175.10 produced one characteristic daughter ion with m/z 157.11. The herbacetin was identified, using the bibliography, in extracts from Ocimum [23] and *Rhodiola rosea* [43].

3.2. Phenolic Acids

3.2.1. Hydroxycinnamic Acids and Cinnamate Esters

The caffeic acid (compound **50** in Table 1), ferulic acid (compound **52** in Table 1), hydroxyferulic acid (compound **55** in Table 1), sinapic acid (compound **56** in Table 1), chlorogenic acid (compound **60** in Table 1), 3-*O*-hydroxydihydrocaffeoylquinic acid (compound **61** in Table 1), 3,4-*O*-dicaffeoylquinic acid (compound **64** in Table 1), 4,5-*O*-dicaffeoylquinic acid (compound **65** in Table 1), and dicaffeoylferuoylquinic acid (compound **67** in Table 1) have already been characterized as components of *L. henryi* [19], *V. macrocarpon* [25], *L. japonica* [26], *R. meyeri* [37], *Andean blueberry* [38], *Strawberry* [40], *R. occidentalis* [47], *V. myrtillus* [49], *R. nigrum* [67], and *Stevia rebaudiana* [72]. These acids were tentatively identified in the extracts from berries of *L. caerulea*. The chemical structure analysis of chlorogenic acid is shown in Figure 10.

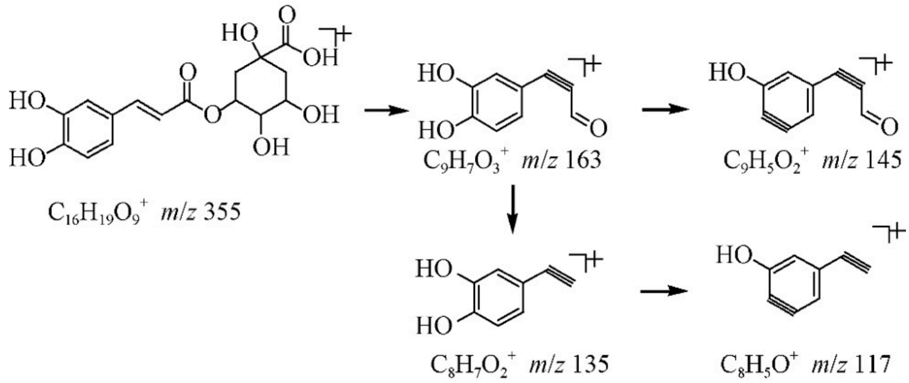


Figure 10. The chemical structure analysis of chlorogenic acid.

The CID spectrum, in positive ion modes, of chlorogenic acid from the berries of *L. caerulea* is shown in Figure 11.

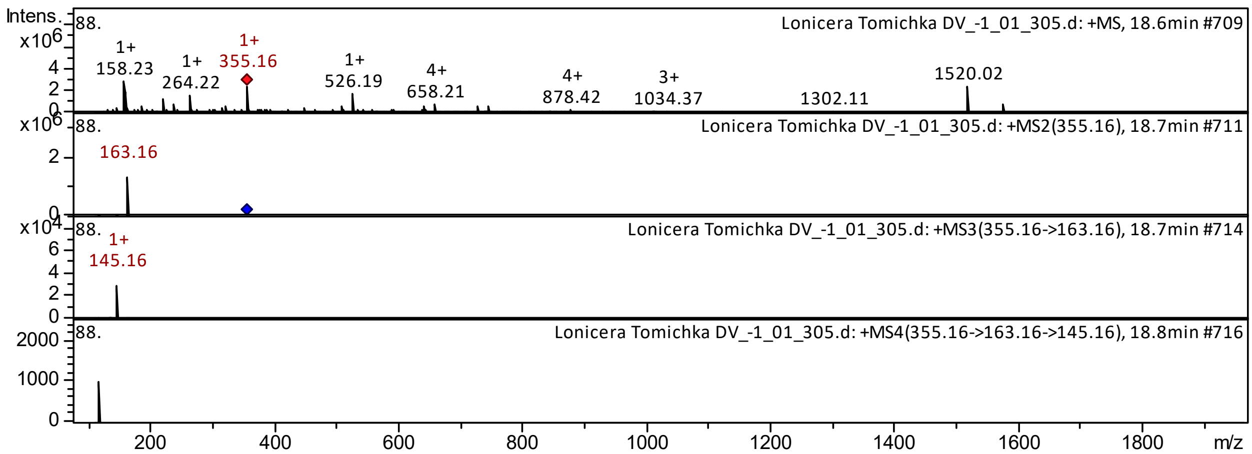


Figure 11. CID spectrum of chlorogenic acid from berries of *L. caerulea* (variety Tomichka from Far East), *m/z* 355.16.

The $[M+H]^+$ ion produced one fragment ion with *m/z* 203.13 (Figure 11). The fragment ion with *m/z* 163.16 produced one characteristic daughter ion with *m/z* 145.16. The chlorogenic acid was tentatively identified, using the bibliography, in extracts from *L. henryi* [19], *L. japonica* [26], *V. macrocarpon* [25,42], *Andean blueberry* [38], *Strawberry* [40], *Spondias purpurea* [44], *cranberry* [48], *V. myrtillus* [49], and *R. magellanicum* [52].

3.2.2. Hydroxybenzoic and Methylbenzoic Acids

The hydroxy methoxy dimethylbenzoic acid (compound **53** in Table 1), 2,3,4,5,6-pentahydroxybenzoic acid (compound **54** in Table 1), methylgallic acid (compound **51** in Table 1), 2,4,6-trihydroxy-3,5-dimethoxybenzoic acid (compound **57** in Table 1), ellagic acid (compound **58** in Table 1), and 6-hydroxy-3-methoxy-4-*O*-*β*-D-glucopyranoside (compound **59** in Table 1) have already been characterized as components of *F. herrerae*, *F. glaucescens* [22], *Rhus coriaria* [36], *R. occidentalis* [47], Papaya [50], *Eucalyptus* [66], *Jatropha* [68], and *Actinidia* [70]. These acids were tentatively identified in the extracts from berries of *L. caerulea*. The CID spectrum, in positive ion modes, of the methylgallic acid from berries of *L. caerulea* is shown in Figure 12.

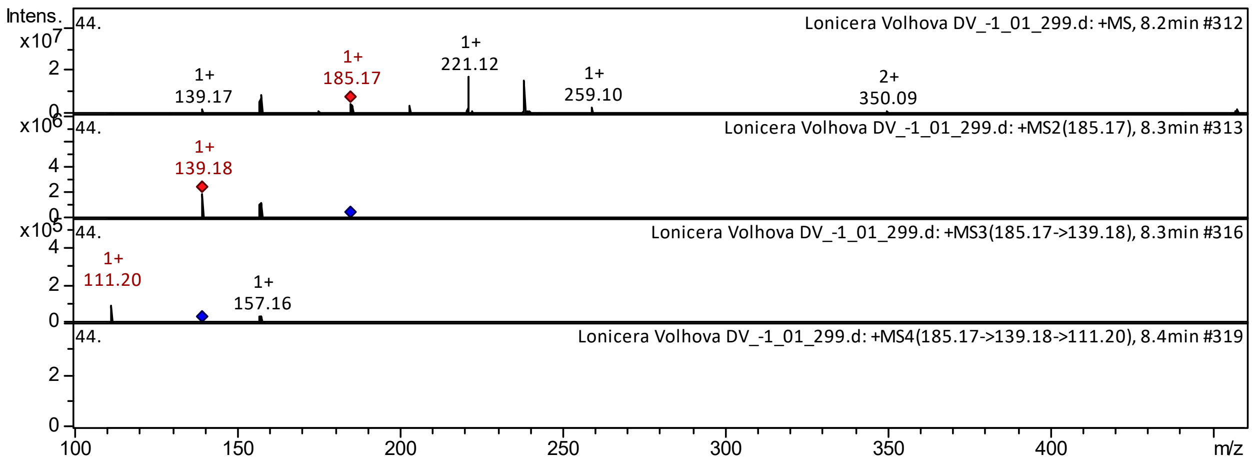


Figure 12. CID spectrum of methylgallic acid from berries of *L. caerulea* (variety Volhova from Far East), m/z 185.17.

The $[M+H]^+$ ion produced one fragment ion with m/z 139.18 (Figure 12). The fragment ion with m/z 139.18 produced one characteristic daughter ion with m/z 111.2. The methylgallic acid was identified, using the bibliography, in extracts from *Rhus coriaria* [36]; Papaya [50]; and *Eucalyptus* [66].

A Vienna diagram showing the similarities and differences in the presence of various chemical groups in the Far Eastern *L. caerulea* varieties (Amfora; Tomichka; Goluboe vereteno; Volhova) is shown in Figure 13.

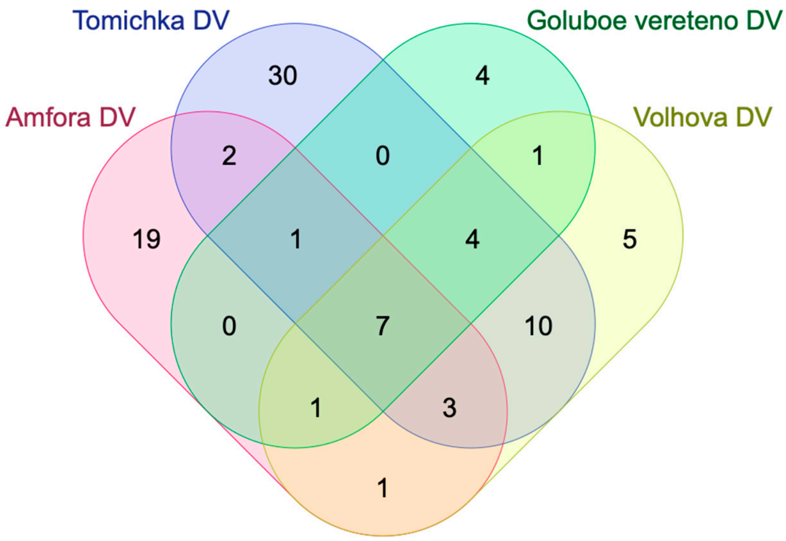


Figure 13. Vienna diagram showing similarities and differences in the presence of various chemical groups in Far Eastern *L. caerulea* varieties.

Table 2 below shows the distribution of the chemical groups in *L. caerulea* samples from the Far East presented in this study.

Table 2. The distribution of the constituents in extracts of *L. caerulea* samples from the Far East.

Names	Total	Elements
Amfora; Goluboe vereteno; Tomichka; Volhova	7	kaempferol; herbacetin; 2,3,4,5,6-pentahydroxybenzoic acid; caffeic acid isoprenyl ester; L-histidine; anonaine; 8,9,10-penthahydroxydibenzo [bd]pyran-6-one
Amfora; Goluboe vereteno; Tomichka	1	hydroxyferulic acid
Amfora; Tomichka; Volhova	3	quercetin; hydroxy dodecanoic acid; rhamnocitrin
Amfora; Goluboe vereteno; Volhova	1	jaceosidin
Goluboe vereteno; Tomichka; Volhova	4	pheophytin A; sebacic acid; fructose-leucine; myristoleic acid
Amfora; Tomichka	2	sespendole; fraxetin
Amfora; Volhova	1	stearidonic acid
Tomichka; Volhova	10	*p*-coumaroyl shiikimic acid; isorhamnetin 3-*O*-(6″-*O*-rhamnosyl-hexoside); *p*-coumaroyl malonyldihexose; isorhamnetin; ellagic acid; resveratrol; methylgallic acid; delphinidin 3-*O*-glucoside; hydroxy methoxy dimethylbenzoic acid; quinic acid
Goluboe vereteno; Volhova	1	(epi)-afzelechin derivative
Amfora	19	4/6,8-dihydro-5,7-dihydroxy-2-oxo-2H-1-benzopyran-3-acetic acid; trihydroxyisoflavone; dimethylquercetin-3-*O*-dehexoside; chrysoeriol *O*-hexoside; 6-hydroxy-3-methoxy-4-*O*-*β*-*D*-glucopyranoside; formononetin-7-*O*-glucoside-6″-*O*-malonate; 13-trihydroxy-Octadecenoic acid; linolenic acid; cirsiliol; adenosine; pelargonidin-3-*O*-glucoside; citric acid; apigenin; gallocatechin; grayanoside A; pelargonidin 3-*O*-(6-*O*-malonyl-*β*-*D*-glucoside); *C*-hexosyl-apigenin *O*-rhamnoside; artemisinin C; vapiprost
Tomichka	30	rutin; 7-(*β*-*D*-glucopyranoside/galactopyranoside)-2-oxo-2H-1-benzopyran-4-acetic acid; umbelliferone; sinapic acid; vebonol; umbelliferone hexoside; lonicerin; (−)-epicatechin gallate; caffeic acid; L-arginine; quercetin 3-*O*-glucoside; ferulic acid; L-threanine; quercetin 3-*O*-pentosyl hexoside; *p*-coumaroyl-6,7-dihydromonotropein; *p*-coumaroylhexose-4-*O*-hexoside; 5-*O*-dicaffeoylquinic acid; eicosatetraenedioic acid; uridine; delphinidin 3-*O*-*β*-*D*-sambubioside; chlorogenic acid; delphinidin 3-*O*-rutinoside; caffeoyl gluconic acid; caffeoylquinic acid derivative; cytidine; naringenin; petunidin-3-rutinoside; dicaffeoylferuoylquinic acid; kaempferol 3-*O*-rutinoside; zeaxanthin; pentahydroxy dimethoxyflavone
Goluboe vereteno	4	caffeoyl shikimic acid; calycosin-7-*O*-*β*-*D*-glucoside-6″-*O*-malonate; pinosylvin; dihydroxy-tetramethoxy(iso)flavone
Volhova	5	trihydroxy eicosatetraenoic acid; 4-*O*-dicaffeoylquinic acid; derivative of quercetin rhamnosyl hexoside; monotropein; butin

From Table 2, it follows that there are several compounds commonly present in the four different samples. Also, the following chemical compounds have a fairly significant repeatability in varieties from the Far East: hydroxyferulic acid; quercetin; hydroxy dodecanoic acid; rhamnocitrin; jaceosidin; pheophytin A; sebacic acid; fructose-leucine; myristoleic acid; sespendole; fraxetin; stearidonic acid; coumaroyl shiikimic acid; isorhamnetin 3-*O*-(6″-*O*-rhamnosyl-hexoside); *p*-coumaroyl malonyldihexose; isorhamnetin; ellagic acid; resveratrol; methylgallic acid; delphinidin 3-*O*-glucoside; hydroxy methoxy dimethylbenzoic acid; quinic acid; and (epi)-afzelechin derivative.

A Vienna diagram showing the similarities and differences in the presence of various chemical groups in the Saint-Petersburg *L. caerulea* varieties (Amfora; Tomichka; Goluboe vereteno; Volhova) is shown in Figure 14.

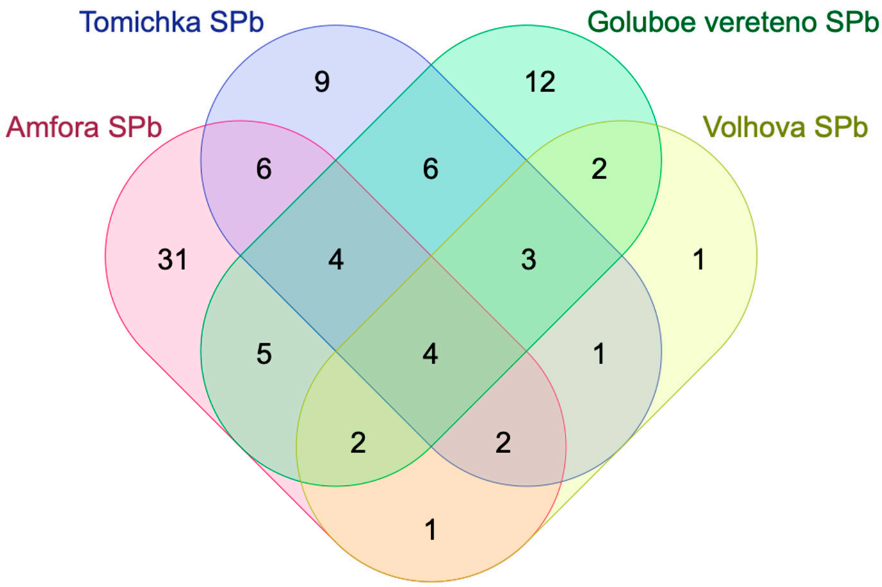


Figure 14. Vienna diagram showing similarities and differences in the presence of various polyphenolic groups in Saint-Petersburg *L. caerulea* varieties.

Table 3 below shows the distribution of the chemical groups in *L. caerulea* samples from the Saint-Petersburg varieties presented in the study.

From Table 3, it follows that in all four different samples, a certain number of chemical compounds is exactly repeated, and these are the following constituents: Petunidin; Sebacic acid; Apigenin; Pentahydroxy dimethoxyflavone; (*Epi*)-afzelechin derivative; L-Histidine; Anonaine; and Myristoleic acid.

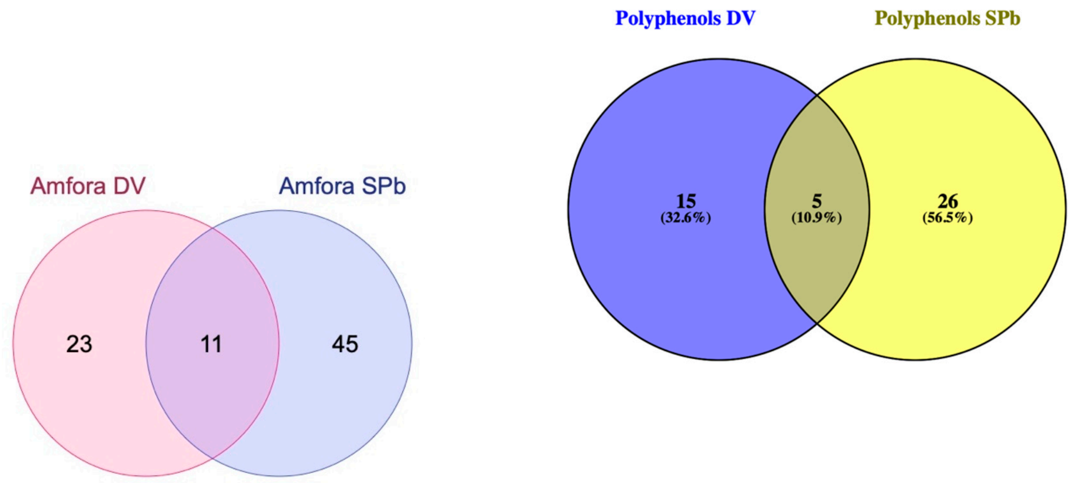
Also, the following chemical compounds have a fairly significant repeatability in varieties from Saint-Petersburg: isorhamnetin; ellagic acid; caffeic acid isoprenyl ester; quercetin; herbacetin; (*epi*)-afzelechin; (*epi*)-catechin; 7-(*β*-*D*-glucopyranoside/galactopyranoside)-2-oxo-2H-1-benzopyran-4-acetic acid; shikimic acid; cirsiliol; methylgallic acid; hydroxy dodecanoic acid; dihydroxy-tetramethoxy(iso)flavone; *p*-coumaroyl monotropein hexoside; resveratrol; fructose-leucine; quinic acid; artemisinin C; 5,6,4′-trihydroxy-7,8-dimethoxyflavone; 2,3,4,5,6-pentahydroxybenzoic acid; sespendole; linolenic acid; gallocatechin; 6-trihydroxy-3,5-dimethoxybenzoic acid; 4-dihydroxy-3-methoxy-benzenepropanoic acid; 8,9,10-penthahydroxydibenzo [b d]pyran-6-one; citric acid; and hydroxy methoxydimethylbenzoic acid.

Below are Venn diagrams (Figures 15A,B, 16A,B, 17A,B, and 18A,B showing the similarities and differences in the general complex of isolated chemical compounds from *L. caerulea* extracts (Amfora, Tomichka, Goluboe vereteno, and Volhova varieties) and specifically in the complex of polyphenolic compounds. Accordingly, the chemical data on secondary metabolites obtained from plantations at widely separated geographic locations are compared.

A general analysis of the degree of similarity and divergence, in particular in terms of the polyphenolic component, with a greater degree of probability, shows approximately the same percentage of occurrence of both polyphenolic compounds and compounds of other chemical classes in the same *L. caerulea* varieties grown at two geographical points far apart from each other. These diagrams allow us to reach a preliminary conclusion about the large geographical variability in terms of secondary metabolites of the same variety of the presented *L. caerulea*.

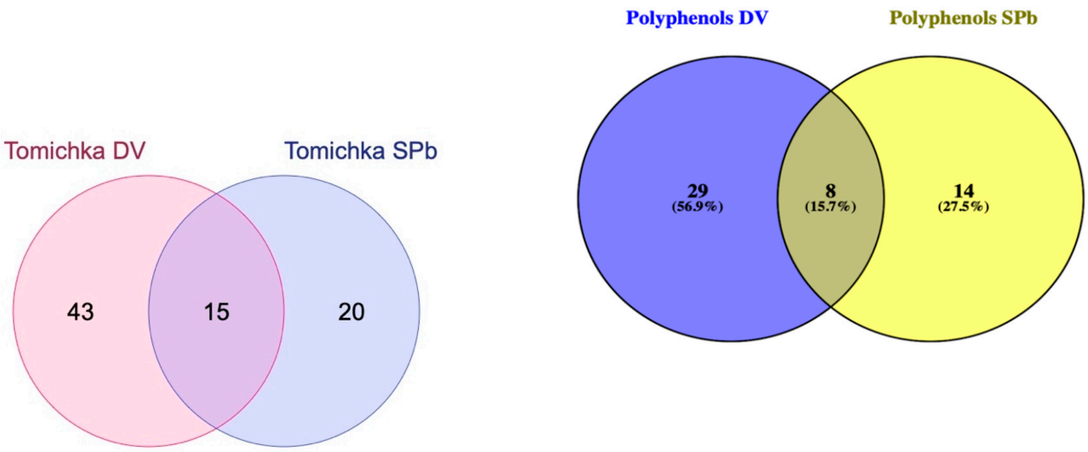
Table 3. Distribution of chemicals in extracts of *L. caerulea* cultivars from Saint-Petersburg, shown in detail by variety of sample.

Names	Total	Elements
Amfora SPb Goluboe vereteno SPb Tomichka SPb Volhova SPb	4	(*epi*)-afzelechin derivative; L-histidine; anonaine; myristoleic acid
Amfora SPb Goluboe vereteno SPb Tomichka SPb	4	petunidin; sebacic acid; apigenin; pentahydroxy dimethoxyflavone
Amfora SPb Tomichka SPb Volhova SPb	2	isorhamnetin; ellagic acid
Amfora SPb Goluboe vereteno SPb Volhova SPb	2	caffeic acid isoprenyl ester; quercetin
Goluboe vereteno SPb Tomichka SPb Volhova SPb	3	herbacetin; (*epi*)-afzelechin; (*epi*)-catechin
Amfora SPb Tomichka SPb	6	7-(*β*-*D*-glucopyranoside/galactopyranoside)-2-oxo-2H-1-benzopyran-4-acetic acid; shikimic acid; cirsiliol; methylgallic acid; hydroxy dodecanoic acid; dihydroxy-tetramethoxy(iso)flavone
Amfora SPb Goluboe vereteno SPb	5	*p*-coumaroyl monotropein hexoside; resveratrol; fructose-leucine; quinic acid; artemisinin C
Amfora SPb Volhova SPb	1	5,6,4′-trihydroxy-7,8-dimethoxyflavone
Goluboe vereteno SPb Tomichka SPb	6	2,3,4,5,6-pentahydroxybenzoic acid; sespendole; linolenic acid; gallocatechin; 6-trihydroxy-3,5-dimethoxybenzoic acid; 4-dihydroxy-3-methoxy-benzenepropanoic acid
Tomichka SPb Volhova SPb	1	8,9,10-penthahydroxydibenzo [b d]pyran-6-one
Goluboe vereteno SPb Volhova SPb	2	citric acid; hydroxy methoxy dimethylbenzoic acid
Amfora SPb	31	coumaroyl shiikimic acid; loganin acid; isorhamnetin 3-*O*-(6″-*O*-rhamnosyl-hexoside); 2,4,6-trihydroxy-3,5-dimethoxybenzoic acid; lonicerin; *p*-coumaroyl malonyldihexose; caryophyllene oxide; L-pyroglutamic acid; 3,8,9,10-penthahydroxydibenzo [bd]pyran-6-one; hydroxyferulic acid; caffeic acid; L-arginine; 3-*O*-hydroxydihydrocaffeoylquinic acid; quercetin 3-*O*-glucoside; pheophytin A; L-proline; eicosatetraenedioic acid; rhamnetin II; rhamnocitrin; loliolide; 7-(*β*-*D*-galactopyranosyloxy)-6,8-dimethoxy-2H-1-benzopyran-2-one; *p*-coumaroyl-6,7-dihydromonotropein; delphinidin 3-*O*-*β*-*D*-sambubioside; chlorogenic acid; delphinidin 3-*O*-rutinoside; kaempferol-3-*O*-*α*-L-rhamnoside; caffeoyl gluconic acid; pinosylvin; caffeoylquinic acid derivative; dihydroresveratrol; sweroside; luteolin 7-*O*-(6-*O*-arabinosyl-glucoside)
Tomichka SPb	9	trihydroxy eicosatetraenoic acid; dimethylquercetin-3-*O*-dehexoside; sophoraisoflavone A; (*all-E*)-lutein 3-*O*-C(4:0); dihydrokaempferol; hydroxy myristic acid; jaceosidin; luteolin 7-*O*-glucoside; naringenin
Goluboe vereteno SPb	12	acacetin 8-*C*-glucoside malonylated; gluconic acid; kaempferol; stearidonic acid; *β*-Sitostenone; *p*-coumaroyl monotropein; anthocyanidin; adenosine; (*epi*)-catechin derivative; protocatechuic acid; calycosin-7-*O*-*β*-*D*-glucoside-6″-*O*-malonate; chrysin derivative
Volhova SPb	1	2,3,4,6-pentahydroxybenzoic acid



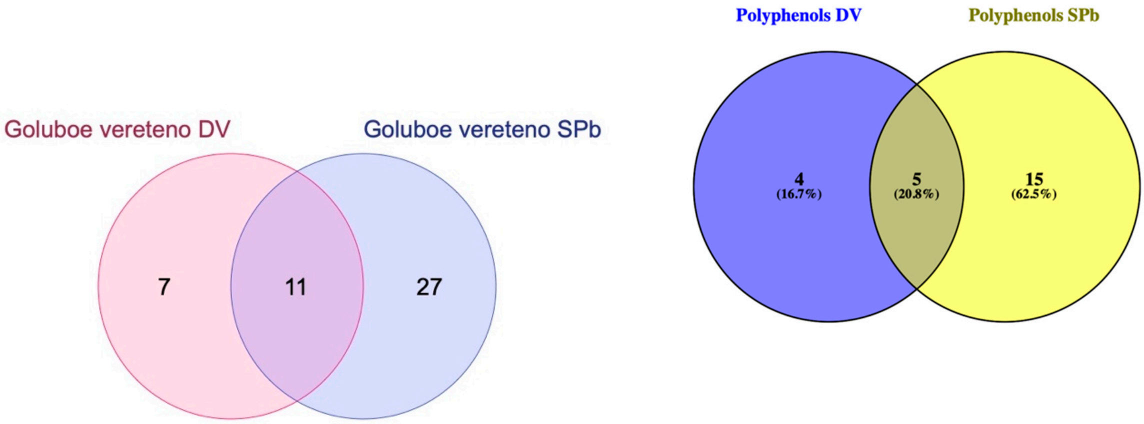
A. **B.**

Figure 15. (**A**) The similarities and differences in the overall complex of isolated chemical constituents from extracts of *L. caerulea* (variety Amfora); (**B**) The similarities in the complex of polyphenolic compounds of *L. caerulea* (variety Amfora).



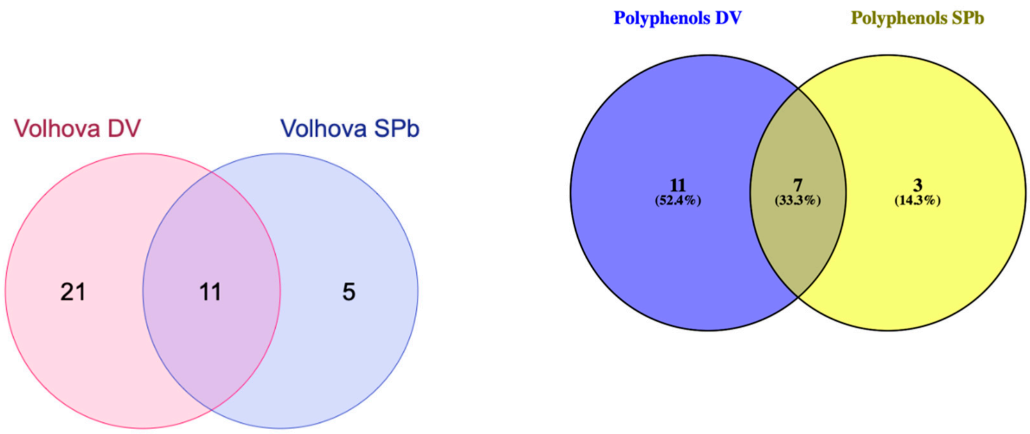
A. **B.**

Figure 16. (**A**) The similarities and differences in the overall complex of isolated chemical constituents from extracts of *L. caerulea* (variety Tomichka); (**B**) The similarities in the complex of polyphenolic compounds of *L. caerulea* (variety Tomichka).



A. **B.**

Figure 17. (**A**) The similarities and differences in the overall complex of isolated chemical constituents from extracts of *L. caerulea* (variety Goluboe vereteno); (**B**) The similarities in the complex of polyphenolic compounds of *L. caerulea* (variety Goluboe vereteno).



A. **B.**

Figure 18. (**A**) The similarities and differences in the overall complex of isolated chemical constituents from extracts of *L. caerulea* (variety Volhova); (**B**) The similarities in the complex of polyphenolic compounds of *L. caerulea* (variety Volhova).

4. Conclusions

In summary, the present study described a systematic comparative screening of phenolics and other chemical groups in *L. caerulea* extracts using a HPLC-ESI—ion trap. A total of 122 compounds, including 75 polyphenols and 47 chemical constituents from other chemical groups were identified from *L. caerulea* extracts of four blue honeysuckle species. They were characterized by their retention behavior, molecular formula, MS/MS spectral patterns, and using the home-library database built by the Group of Biotechnology, Bioengineering and Food Systems at the Far-Eastern Federal University (Russia), which is based on data from other spectroscopic techniques, such as nuclear magnetic resonance, ultraviolet spectroscopy, and MS, as well as data from the literature, and is continually updated and revised. For the first time, thirty chemical constituents from the polyphenol group (flavones Jaceosidin, Cirsiliol, Sophoraisoflavone A, Chrysoeriol-O-hexoside, stilbenes Pinosylvin, Resveratrol, Dihydroresveratrol, etc.) and twenty-seven chemical constituents from other chemical groups were identified in the berries of *L. caerulea*.

The largest number of unique polyphenols is found in the variety Tomichka, the selection of the regional state unitary enterprise "Bakcharskoye", obtained from the free pollination of *L. caerulea* and originating from the Primorsky Territory of Russia (*L. caerulea* subspecies Turczaninow). This genotype has the highest number of similar unique polyphenols, regardless of where it was grown. Blue honeysuckle genotypes originating from Primorsky Krai in Russia can be used in various breeding programs in order to improve and enrich the biochemical composition of fruits. It should also be noted that, regardless of the place of cultivation, the total amount of unique polyphenols remains quite significant. Attention should be paid to the Volhova honeysuckle variety, obtained through gamma irradiation of the Pavlovskaya variety (Kamchatka ecotype). This sample is characterized by a stable composition of biologically active substances, regardless of the growing area. These data could support future research on the production of a variety of pharmaceutical products containing ultrapure extracts of *L. caerulea*. The richness of various biologically active compounds, including compounds of the polyphenol group and compounds of other chemical groups (oxylipins, Omega- fatty acids, sterols, iridoids, etc.), provides great opportunities for the design of new nutritional and dietary supplements based on supercritical extracts from the leaves, stems, and berries of *L. caerulea*.

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Appendix A

Table A1. Approximate comparison of chemical constituents identified in *L. caerulea* varieties obtained from two different regions.

Class of Compounds	Identification	Amfora Far East	Amfora SPb	Tomichka Far East	Tomichka SPb	Goluboe Far East	Goluboe SPb	Volhova Far East	Volnova SPb
Flavone	Apigenin	■	■		■		■		
Flavone	Trihydroxy(iso)flavone	■							
Flavone	5,6,4′-Trihydroxy-7,8-dimethoxyflavone		■						■
Flavone	Jaceosidin	■			■	■		■	
Flavone	Cirsiliol	■	■		■				
Flavone	Sophoraisoflavone A				■				
Flavone	Pentahydroxy dimethoxyflavone		■	■	■		■		
Flavone	Dihydroxy-tetramethoxy(iso)flavone		■		■	■			
Flavone	Luteolin 7-*O*-glucoside				■				
Flavone	Chrysoeriol *O*-hexoside	■							
Flavone	Formononetin-7-*O*-glucoside-6″-*O*-malonate	■							
Flavone	Acacetin 8-C-glucoside malonylated						■		
Flavone	Calycosin-7-*O*-beta-*D*-glucoside-6″-*O*-malonate					■	■		
Flavone	Chrysin derivative						■		
Flavone	C-hexosyl-apigenin *O*-rhamnoside	■							
Flavone	Lonicerin		■	■					
Flavone	Luteolin 7-*O*-(6-*O*-arabinosyl-glucoside)		■						
Flavonol	Kaempferol	■		■		■	■	■	
Flavonol	Dihydrokaempferol				■				
Flavone	Rhamnocitrin	■	■	■				■	
Flavonol	Quercetin	■	■	■			■	■	■
Flavone	Herbacetin	■		■	■	■	■	■	■
Flavonol	Rhamnetin II		■						
Flavonol	Isorhamnetin		■	■	■			■	■
Flavonol	Kaempferol-3-*O*-α-*L*-rhamnoside		■						
Flavonol	Quercetin 3-*O*-glucoside		■	■					
Flavonol	Kaempferol 3-*O*-rutinoside			■					
Flavonol	Quercetin 3-*O*-pentosyl hexoside			■					
Flavonol	Rutin			■					
Flavonol	Isorhamnetin 3-*O*-(6″-*O*-rhamnosyl-hexoside)		■	■				■	
Flavonol	Dimethylquercetin-3-*O*-dehexoside	■			■				
Flavonol	Derivative of Quercetin rhamnosyl hexoside							■	
Flavan-3-ol	Epiafzelechin				■		■		■
Flavan-3-ol	(*Epi*)-catechin				■		■		■
Flavan-3-ol	Gallocatechin	■			■		■		
Flavan-3-ol	(*Epi*)-afzelechin derivative		■		■	■	■	■	■
Flavan-3-ol	(*Epi*)-catechin derivative						■		
Flavan-3-ol	(−)-Epicatechin Gallate			■					
Flavanone	Naringenin			■	■				
Flavanone	Butin							■	
Anthocyanin	Anthocyanidin						■		
Anthocyanin	Petunidin		■		■		■		
Anthocyanin	Pelargonidin-3-*O*-glucoside	■							
Anthocyanin	Delphinidin 3-*O*-glucoside			■				■	
Anthocyanin	Pelargonidin 3-*O*-(6-*O*-malonyl-*β*-*D*-glucoside)	■							
Anthocyanin	Delphinidin 3-*O*-*β*-*D*-sambubioside		■	■					
Anthocyanin	Delphinidin 3-*O*-rutinoside		■	■					
Anthocyanin	Petunidin-3-rutinoside			■					
Hydroxybenzoic acid (Phenolic acid)	Protocatechuic acid						■		
Hydroxycinnamic acid	Caffeic acid		■	■					
Methylbenzoic acid	Methylgallic acid		■	■	■			■	
Trans-cinnamic acid	Ferulic acid			■					
Phenolic acid	Hydroxy methoxy dimethylbenzoic acid			■			■	■	■
Phenolic acid	2,3,4,5,6-pentahydroxybenzoic acid	■		■	■	■	■	■	■
Hydroxycinnamic acid	Hydroxyferulic acid	■	■	■		■			
Hydroxycinnamic acid	Sinapic acid			■					
Phenolic acid	2,4,6-Trihydroxy-3,5-dimethoxybenzoic acid		■		■		■		
Hydroxybenzoic acid (Phenolic acid)	Ellagic acid		■	■	■			■	■
Phenolic acid	6-Hydroxy-3-methoxy-4-*O*-*β*-*D*-glucopyranoside	■							

Table A1. *Cont.*

Class of Compounds	Identification	Amfora Far East	Amfora SPb	Tomichka Far East	Tomichka SPb	Goluboe Far East	Goluboe SPb	Volhova Far East	Volnova SPb
Hydroxycinnamic acid	Chlorogenic acid		■	■					
Hydroxycinnamic acid	3-*O*-Hydroxydihydrocaffeoylquinic acid		■						
Phenolic acid	Caffeoylquinic acid derivative		■	■					
Flavonoid	*p*-Coumaroylhexose-4-*O*-hexoside			■					
Phenolic acid	3,4-*O*-dicaffeoylquinic acid							■	
Phenolic acid	4,5-*O*-dicaffeoylquinic acid			■					
Phenolic acid	*p*-Coumaroyl malonyldihexose		■	■				■	
Phenolic acid	Dicaffeoylferuoylquinic acid			■					
Stilbene	Pinosylvin		■			■			
Stilbene	Resveratrol		■	■			■	■	
Stilbene	Dihydroresveratrol		■						
Hydroxycoumarin	Umbelliferone			■					
Coumarin	Fraxetin	■		■					
Coumarin	3,4/6,8-Dihydro-5,7-dihydroxy-2-oxo-2H-1-benzopyran-3-acetic acid	■							
Coumarin	Umbelliferone hexoside			■					
Coumarin	7-(*β*-*D*-Glucopyranoside/galactopyranoside)-2-oxo-2H-1-benzopyran-4-acetic acid		■	■	■				
OTHERS									
Amino acid	L-Proline		■						
Non-proteinogenic L-alpha-amino acid	L-Pyroglutamic acid		■						
Amino acid	L-Histidine	■	■	■	■	■	■	■	■
Amino acid	L-threanine			■					
Amino acid	L-Arginine		■	■					
Cyclohexenecarboxylic acid	Shikimic acid		■		■				
Tricarboxylic acid	Citric acid	■					■		■
Polyhydroxycarboxylic acid	Quinic acid		■	■			■	■	
Pentahydroxyhexanoic acid	Gluconic acid						■		
Benzofuran	Loliolide		■						
Alpha, omega dicarboxylic acid	Sebacic acid		■	■	■	■	■	■	
	4-Dihydroxy-3-methoxy-benzenepropanoic acid				■		■		
Sesquiterpenoid	Caryophyllene oxide		■						
Carboxylic acid	Myristoleic acid		■	■	■	■	■	■	■
Pyrimidine nucleoside	Cytidine			■					
Glycosylated pyrimidine analog	Uridine			■					
Hydroxytetradecanoic acid	Hydroxy myristic acid				■				
Medium-chain fatty acid	Hydroxy dodecanoic acid	■	■	■	■			■	
	Caffeic acid isoprenyl ester	■	■	■		■	■	■	■
Sesquiterpene lactone	Artemisinin C	■	■				■		
Aporphine alkaloid	Anonaine	■	■	■	■	■	■	■	■
Ribonucleoside composite of adenine (purine)	Adenosine	■					■		
	3,4,8,9,10-Penthahydroxydibenzo [b,d]pyran-6-one	■	■	■	■	■		■	■
Omega-3-fatty acid	Stearidonic acid	■					■	■	
Omega-3-fatty acid	Linolenic acid	■			■		■		
Mixture of diastereomers	Fructose-leucine		■	■		■	■	■	
Cyclohexenecarboxylic acid	Coumaroyl shiikimic acid		■	■				■	
Oxylipin	13-Trihydroxy-Octadecenoic acid	■							
Alpha, omega-dicarboxylic acid	Eicosatetraenedioic acid		■	■					
Cyclohexenecarboxylic acid	Caffeoyl shikimic acid					■			
Alpha, omega-dicarboxylic acid	Trihydroxy eicosatetraenoic acid				■			■	
Dicarboxylic acid sugar	Caffeoyl gluconic acid		■	■					

Table A1. *Cont.*

Class of Compounds	Identification	Amfora Far East	Amfora SPb	Tomichka Far East	Tomichka SPb	Goluboe Far East	Goluboe SPb	Volhova Far East	Volnova SPb
Iridoid glucoside	Sweroside								
Cyclopentapyran	Loganin acid								
	7-(*β*-*D*-Galactopyranosyloxy)-6,8-dimethoxy-2H-1-benzopyran-2-one								
Iridoid	Monotropein								
Sterol	Beta-Sitostenone								
Anabolic steroid	Vebonol								
Phenylpropanoid glucoside	Grayanoside A								
Thromboxane receptor antagonist	Vapiprost								
Indole sesquiterpene alkaloid	Sespendole								
Iridoid glucoside	*p*-Coumaroyl monotropein								
Iridoid glucoside	*p*-coumaroyl-6,7-dihydromonotropein								
Carotenoid	Zeaxanthin								
Carotenoid	(*all*-*E*)-lutein 3-*O*-C(4:0)								
Iridoid	p-Coumaroyl monotropein hexoside								
Product of chlorophyll degradation	Pheophytin A								

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