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Primary Determination of the Composition of Secondary Metabolites in the Wild and Introduced *Artemisia martjanovii* Krasch: Samples from Yakutia

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Abstract: *Artemisia martjanovii* Krasch is a rare representative of the genus Artemisia in Siberia and the Far East. The phytochemical composition of this endangered species is essential for its potential use in medicine. We used tandem mass spectrometry and HPLC-MS/MS methods to describe the metabolome from the stem and leaf extracts of *A. martjanovii* from Yakutia. The metabolome profile analysis of *A. martjanovii* grown in the Botanical Garden of the North-Eastern Federal University, Yakutsk, Russia, and the wild *A. martjanovii* from Khangalassky district, Republic of Sakha (Yakutia) differed significantly both in the polyphenol composition and other compound classes. In total, we identified 104 bioactive constituents from stem and leaf extracts, 56 compounds from the polyphenol group, and 48 from other compound classes. Twenty-seven compounds classified as polyphenol groups, i.e., flavones apigenin, trihydroxy(iso)flavone, salvigenin, cirsiliol, cirsilineol, nevadensin, syringetin, gardenin B, thymonin, and chrysoeriol *C*-hexoside; flavonols: taxifolin, tetrahydroxy-dimethoxyflavone-hexoside, etc.; and 26 compounds from other classes are being reported for the first time in the genus *Artemisia* L.

Keywords: *Artemisia martjanovii*; tandem mass spectrometry; polyphenols; bioactive substances

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1. Introduction

The genus *Artemisia* L., or wormwood, is one of the largest genera of the family *Asteraceae* Dumort (*Compositae* Giseke). It is distributed throughout the northern hemisphere, in the temperate zone of Eurasia, in North and South Africa, and in North America.

Approximately 180 species of the genus *Artemisia* have been recorded on the territory of Russia [1]. In the flora of Yakutia, there are thirty-six species of the genus *Artemisia*, five of which are listed in the "Red Data Book of Yakutia [2]. In the flora of Central Yakutia, there are 22 representatives of the genus *Artemisia*, of which four species are protected. Seventeen species have passed the introduction test in the conditions of Central Yakutia [3].

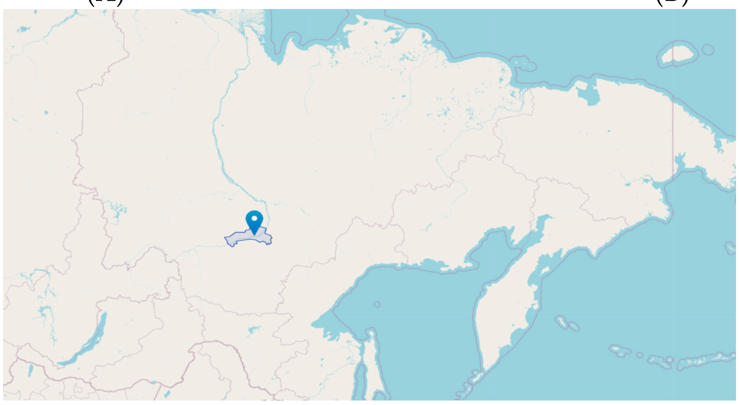
One of the rare representatives of the genus *Artemisia* in Siberia and the Far East is *Artemisia martjanovii* Krasch, ex Poljakov. It is naturally distributed in the south of the

Krasnoyarsk Territory, the north-eastern part of Khakassia, and Central Yakutia. It is listed in the Red Books of the Krasnoyarsk Territory with the status "2" as a vulnerable species, mainly because of its declining and fragmented populations. In Khakassia, however, it is listed with the status "3" as a rare species, and in Yakutia with the status "3d" as an extremely rare subspecies, a relic with a limited geographical area [4].

T. E. Leonova first discovered *A. martjanovii* on the territory of Yakutia in 1967 on the slopes of the banks of the Lena River near the village of Bulgunnyakhtakh. At present, scattered, limited populations of the species can be found along the left bank of the Lena River near the villages of Bulgunnyakhtakh, Elanka, and Tit-Ary on sandy and rocky slopes. Studies of the ontogenesis and the age spectrum of the coenopopulation of the species show that all age stages are represented near the village of Elanka. It is a perennial shrub with lignified branched stems and annual vegetative and flowering shoots up to 20–50 cm in total height (Figure 1). The plant is covered with thick glandular hairs, the leaves are bipinnately divided, and it has a paniculate inflorescence of spherical baskets with a diameter of 4–5 mm.

(**A**)

(**B**)



(**C**)

Figure 1. Habitat (**A**) and plant appearance (**B**): *Artemisia martjanovii* Krasch. ex Poljak (photos by Egorov, June 2022); (**C**): sample collection site of *A. martjanovii*. The blue location icon shows the vicinity of the settlement in the Elanka Khangalassky district of Yakutia (N 61°26′75″; E 128°11′11″), Russia.

Members of the genus *Artemisia* L. are popularly used for their medicinal properties. Within the wormwood group, almost the entire range of terpene compounds is found in the *Asteraceae* family. The essential oils of the studied species of wormwood accumulate valuable constituents. Studies have shown the presence of coumarins in the aerial part of *A. martjanovii*. Additionally, the essential oil of the aerial part of the plant contains monoterpenoids and sesquiterpenoids (pinene, δ-karene, η–cymol, linalool, borneol, and borneol acetate). These essential oil constituents have been shown to have antibacterial and antifungal properties.

In general, studies of the phytochemical composition of representatives of the genus *Artemisia* are of great importance for determining their potential use in medicine, in the development of new drugs, and in other pharmaceutical industries. Thus, the aim of this work is to conduct a comparative analysis of the chemical composition of the above-ground phytomass (leaves, stems) of *A. martjanovii* collected both in controlled grown conditions in the Botanical Garden of the North-Eastern Federal University (NEFU) and in the wild growing conditions in the vicinity of the settlement Elanka, Khangalassky district of Yakutia (N 61°26′75″; E 128°11′11″) during an expedition in June 2022 (Figure 1C).

2. Materials and Methods

2.1. Materials

The object of this study was the aerial parts (leaves, stems) of *A. martjanovii* collected both under controlled conditions in the Botanical Garden of NEFU and under wild growing conditions near the settlement Elanka, Khangalassky district, Yakutia (N 61°26′75″; E 128°11′11″), Russia. Leaves and stems were collected during the growing season of plants in June 2022. *A. martjanovii* has been cultivated in the Botanical Garden of NEFU for 19 years. The plant was introduced into cultivation based on a sample collected in 2004 from a rocky slope on the bank of the Lena River near the village of Elanka.

2.2. Chemicals and Reagents

All chemicals used in this study were of analytical grade. High-performance liquid chromatography (HPLC)-grade acetonitrile was purchased from Fisher Scientific (Southborough, UK). Mass-spectrometry (MS)-grade formic acid was purchased from Sigma-Aldrich (Steinheim, Germany). Ultra-pure water was prepared by using a SIEMENS ULTRA clear (SIEMENS Water Technologies, Günzburg, Germany).

2.3. Extraction

The fractional maceration technique was applied to obtain highly concentrated extracts [5]. Approximately 500 g of the aerial parts of *A. martjanovii* (wild and collected in the Botanical Garden) were randomly selected for maceration. The total amount of the extractant (ethyl alcohol) was divided into three parts, and the parts of the plant were consistently infused with the first, second, and third parts. The solid-to-solvent ratio was 1:15. The infusion of each part of the extractant was completed for 10 days at room temperature.

2.4. Liquid Chromatography

HPLC was performed using a Shimadzu LC-20 Prominence HPLC (Shimadzu, Kyoto, Japan) equipped with a UV sensor and a C18 silica reverse phase column (4.6 × 150 mm, particle size: 2.7 μm) to perform the separation of multicomponent mixtures. 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 40 °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 negative ion mode. 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, collision energy: 60 eV. An ion trap was used in the scan range m/z 100-1.700 for MS and MS/MS. The chemical constituents were identified by comparing their retention index, mass spectra, and MS fragmentation with an in-house, self-built database (Biotechnology, Bioengineering, and Food Systems Laboratory, Far Eastern Federal University, Russia). The in-house, self-built database are based on data from other spectroscopic techniques, such as nuclear magnetic resonance, ultraviolet spectroscopy, and MS, as well as data from the literature that are continuously updated and revised. The capture rate was one spectrum/s for MS and two spectrum/s for MS/MS. Data acquisition were controlled by Windows software for BRUKER DALTONIKS. All experiments were repeated three times. A four-stage ion separation mode (MS/MS mode) was implemented. The structural identification of each compound was carried out on the basis of their accurate mass and MS/MS fragmentation by HPLC–ESI–ion trap–MS/MS.

3. Results and Discussion

We compared the global metabolome profiles of stem and leaf extracts of *A. martjanovii* growing under controlled conditions in the Botanical Garden of NEFU and under wild growing conditions near the settlement of Elanka, Khangalassky district, Yakutia, Russia.

We identified 104 bioactive compounds from extracts of *A. martjanovii* (fifty-six chemical constituents from the polyphenol group and forty-eight chemical constituents from other compound classes). The chemical structures of some tentatively identified polyphenols are shown in Figures 2–4. All the identified polyphenols and compounds from other compound classes, along with molecular formulas and MS/MS data for *A. martjanovii*, are summarized in Appendix A (Table A1). Polyphenols are represented by the following compound classes: flavones, flavonols, flavan-3-ols, flavanones, phenolic acids, anthocyanins, lignans, coumarins, stilbenes, and chalcones (Table 1). For the first time in the genus *Artemisia* L., twenty-seven compounds from the polyphenol group and twenty-six compounds from other compound classes have been tentatively identified. Notably, we found flavones: apigenin, trihydroxy(iso)flavone, salvigenin, cirsiliol, cirsilineol, nevadensin, syringetin, gardenin B, thymonin, chrysoeriol *C*-hexoside; flavonols: taxifolin, tetrahydroxy-dimethoxyflavone-hexoside, isorhamnetin 3-*O*-(6″-*O*-rhamnosyl-hexoside); flavan-3-ol (epi)-catechin; flavanones eriodictyol, (S)-eriodictyol-6-*C*-*β*-*D*-glucopyranoside; stilbene resveratrol; coumarins umbelliferone, fraxetin, tomentin; lignan podophyllotoxin, etc. Constituents of other compound classes include amino acids, carboxylic acids, saturated fatty acids, naphthoquinones, sesquiterpenoids, omega-3 fatty acids, oxylipins, etc.

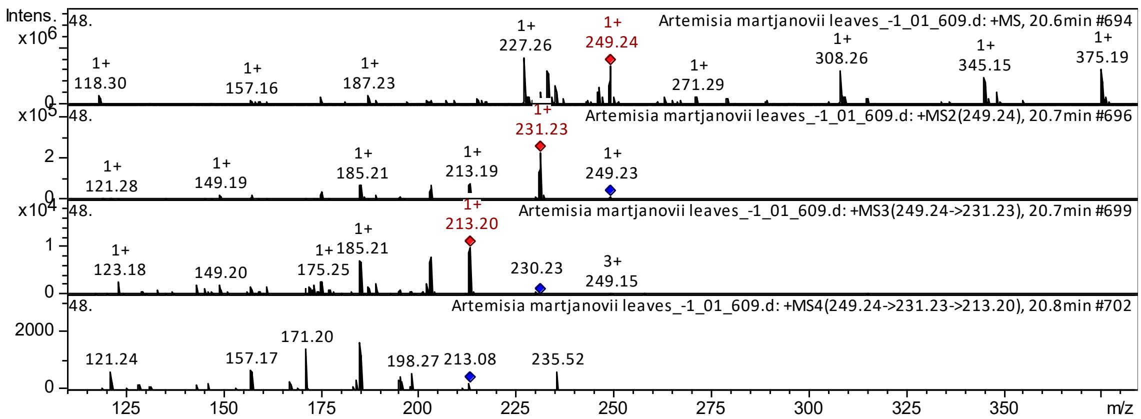


Figure 2. CID-spectrum of artemisinin C from leaf extracts of wild *A. martjanovii*, at *m/z* 249.24.

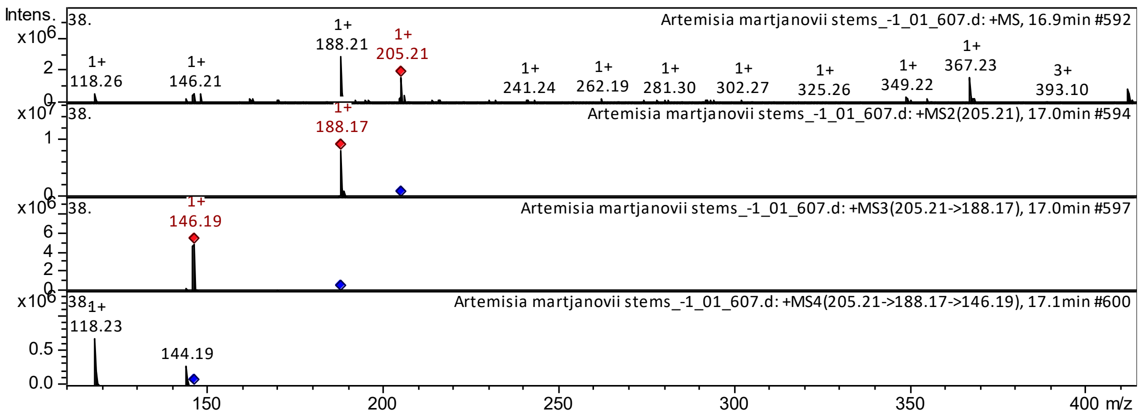


Figure 3. CID-spectrum of L-tryptophan from stems extracts of wild *A. martjanovii*, at *m/z* 205.21.

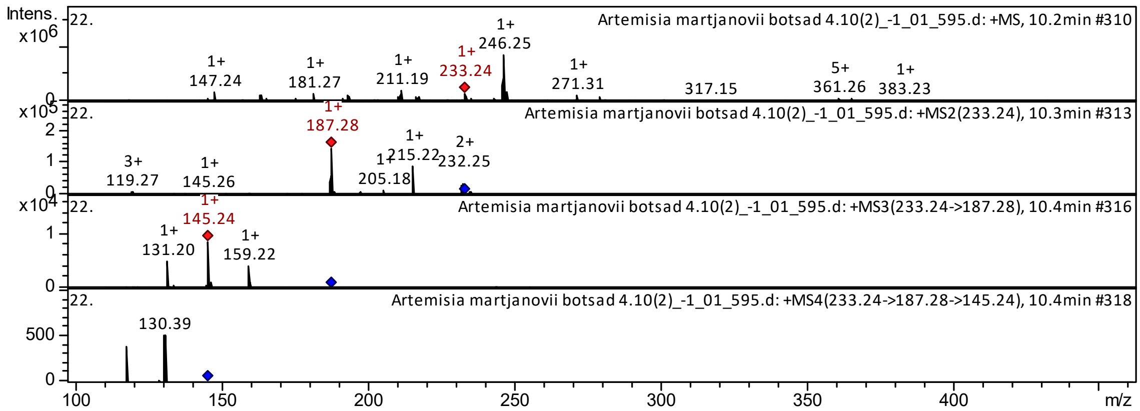


Figure 4. CID-spectrum of atractylenolide II from extracts of introduced *A. martjanovii* growing in the Botanical Garden of NEFU, at *m/z* 233.24.

Below is the distribution of the bioactive compounds recorded in our study in *A. martjanovii* samples from the wild and the Botanical Garden of NEFU.

Figures 2–4 show examples of the decoding spectra (Collision-Induced Dissociation (CID) spectrum) of the ion chromatogram obtained using tandem mass spectrometry. The CID-spectrum in positive ion modes of artemisinin C from extracts of leaves of wild *A. martjanovii* is shown in Figure 2.

The $[M + H]^+$ ion produced five fragment ions at *m/z* 231.23, at *m/z* 213.19, at *m/z* 185.21, at *m/z* 149.19, and at *m/z* 121.28 (Figure 2). The fragment ion with *m/z* 231.23 yields five daughter ions at *m/z* 213.20, *m/z* 185.21, *m/z* 175.25, *m/z* 149.20, and *m/z* 123.18. The fragment ion with *m/z* 213.20 yields four daughter ions at *m/z* 198.27, *m/z* 171.20, *m/z* 157.17, and *m/z* 121.24. It was identified in the bibliography in extracts of *Artemisia annua* [6]. The CID-spectrum in positive ion modes of L-tryptophan from extracts of stems of wild *A. martjanovii* is shown in Figure 3.

The $[M + H]^+$ ion produced one fragment ion at *m/z* 188.17 (Figure 3). The fragment ion with *m/z* 188.17 yields one daughter ion at *m/z* 146.19. The fragment ion with *m/z* 146.19 yields two daughter ions at *m/z* 144.19 and *m/z* 118.23. It has been identified in the bibliography in extracts from Huolisu Oral Liquid [7], *Rosa acicularis* [8], *Camellia kucha* [9], *Euphorbia hirta* [10], *Hylocereus polyrhizus* [11], and rapeseed flower petals [12]. The CID-spectrum in positive ion modes of atractylenolide II from extracts of *A. martjanovii* from the Botanical Garden of NEFU are shown in Figure 4. The $[M + H]^+$ ion produced three fragment ions at *m/z* 187.28, *m/z* 145.26, and *m/z* 119.27 (Figure 4). The fragment ion with *m/z* 187.28 yields three daughter ions at *m/z* 145.24 and *m/z* 131.20. The fragment ion with *m/z* 145.24 yields one daughter ion at *m/z* 130.39. It has been identified in the bibliography in extracts of *Codonopsis Radix*, *Atractylodes macrocephalae rhizoma* [13], and the Chinese herbal formula Jian-Pi-Yi-Shen pill [14].

Table 1. The distribution of the bioactive compounds in wild and introduced *A. martjanovii* from the Botanical Garden of NEFU.

Sample	Number of Compounds	Compound Names
A. martjanovii (wild); *A. martjanovii* (BG)	50	Chrysoeriol C-hexoside; Stearidonic acid methyl ester; Dihydrosantamarin; Undecanedioic acid; Umbelliferone; Trihydroxy(iso)flavone; Deoxyartemisinin I; Petunidin; Syringetin; Vebonol; 3,4-O-dicaffeoylquinic acid; L-Valine; 3-Hydroxy-6,7,4′-trimethoxyflavone; Gardenin B; Dihydroxy tetramethoxyflavone hexoside; Salvigenin; Chrysoeriol 6-*O*-hexoside; Caffeic acid; Dihydroxy-trimethoxyflavone-*O*-hexoside; 3,3′-di-*O*-methyl ellagic acid; Artemisin; Resveratrol; Artemannuin B; Syringic acid; Sespendole; Linolenic acid; Costunolide; Dihydroxy-trimethoxyflavone; Casticin; (Epi)-catechin; Hydroxy myristic acid; Caffeic acid derivative; Hydroxy dodecanoic acid; Pseudosantonin; Dihydroxy-dimethoxyflavone; Centaureidin; Eupatilin; Jaceosidin; Artemetin; Penduletin; Trihydroxymethoxyflavone; Hydroxydodecenoic acid; Myristoleic acid; Atractylenolide I; Artemisinic acid; Atractylenolide II; Artemisinin C; Cirsimaritin; Chrysartemin A; Trihydroxyoctadecadienoic acid
A. martjanovii (wild)	27	Phloretin; Tyrosine; Tri-*O*-methylellagic acid; Isorhamnetin 3-*O*-(6″-*O*-rhamnosyl-hexoside); Santonin; L-Ascorbic acid; Tetrahydroxy-dimethoxyflavone; Dihydroartemisinin; Pheophytin A; 13-Trihydroxy-Octadecenoic acid; Podophyllotoxin; Cirsiliol; Nevadensin; Tomentin; Alpha-Kamlolenic Acid; Dihydroquercetin; Gallic acid; Plumbagin; Methoxyeugenol; Chlorogenic acid; Isololiolide; 1,4,8-Trihydroxy-3-tetralone-methyl formate-4-*O*-*β*-*D*-glucopyranoside; 3,5-Dihydroxy-6,7,3′,4′-tetramethoxyflavone; Cirsilineol; L-Tryptophan; Tanshinone IIA; (S)-eriodictyol-6-C-*β*-*D*-glucopyranoside
A. martjanovii (BG)	27	Artabsinolide A; Stearidonic acid; Eriodictyol; Isorhamnetin 3-*O*-glucoside; Absinthin derivative; Dihydroarteannuin B; Mearnsetin-glucoside; 7-Methoxybenzo[d][1,3] dioxole-5-carboxylic acid; Glucaric acid; Neochlorogenic acid; 3,5-Dihydroxy-6,7,4′-trimethoxyflavone; Ferulic acid; Hispidulin; *cis*-3-Caffeoylquinic acid; Methylgallic acid; Linoleic acid; Apigenin; Absinthin; Hydroxy octadecadienoic acid; Thymonin; 3,4,5-Tri-*O*-caffeoylquinic acid; Quercetin 3-*O*-glucoside; Acacetin C-glucoside methylmalonylated; 3-*O*-acetyl-betulinic acid; Fraxetin; Tetrahydroxy-dimethoxyflavone-hexoside; Tetramethylellagic acid hexose

A Venn diagram showing the similarities and differences in the presence of chemical constituents in wild *A. martjanovii* and introduced *A. martjanovii* from the Botanical Garden of NEFU is shown in Figure 5.

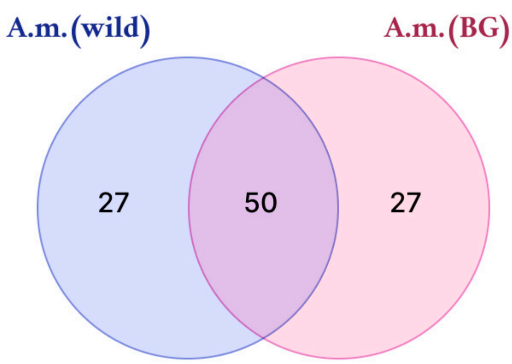


Figure 5. A Venn diagram showing the similarities and differences in the presence of chemical constituents in wild *A. martjanovii* and introduced *A. martjanovii* from the Botanical Garden of NEFU.

A Venn diagram showing the similarities and differences in the presence of chemical constituents in wild and introduced *A. martjanovii* (stems and leaf extracts) from the Botanical Garden of NEFU is shown in Figure 6.

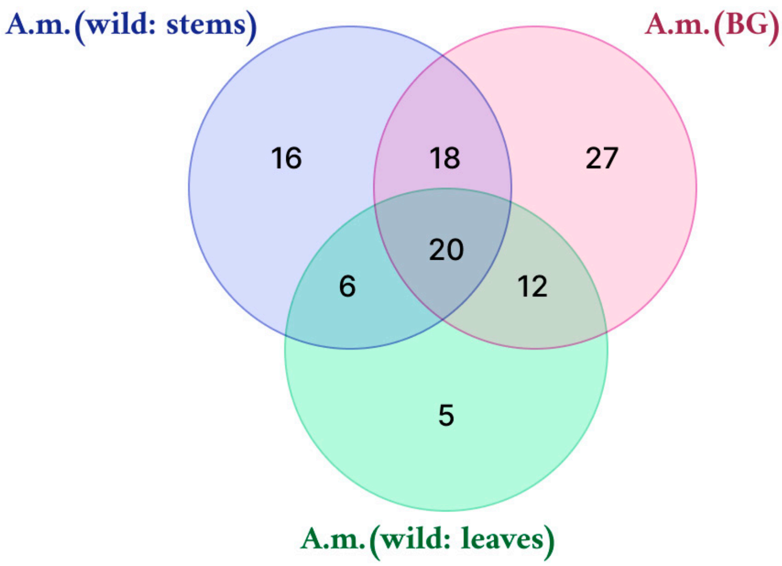


Figure 6. A Venn diagram showing the similarities and differences in the presence of chemical constituents in stem and leaf extracts of wild and introduced *A. martjanovii* from the Botanical Garden of NEFU.

Tables 2 and 3 below show the distribution of the bioactive compounds in the stem and leaf extracts of wild *A. martjanovii* plant samples collected from near the settlement Elanka, Khangalassky district of Yakutia (N 61°26′75″; E 128°11′11″) and from the Botanical Garden of NEFU.

Table 2. The distribution of the constituents in the stem and leaf extracts of wild and introduced *A. martjanovii* from the Botanical Garden of NEFU.

Sample	Number of Compounds	Number of Compounds Identified for the First Time in Genus *Artemisia* L.
A. martjanovii (BG)	77	34
A. martjanovii (wild: leaves)	43	19
A. martjanovii (wild: stems)	61	34

Table 3. The distribution of the constituents in stem and leaf extracts of wild and introduced *A. martjanovii* from the Botanical Garden of NEFU.

Sample	Total Number of Compounds	Compound Names
A. martjanovii (wild: stems)	16	Phloretin; Tyrosine; 3,4-*O*-dicaffeoylquinic acid; Isorhamnetin 3-*O*-(6″-*O*-rhamnosyl-hexoside); L-Ascorbic acid; Tetrahydroxy-dimethoxyflavone; Dihydroartemisinin; 13-Trihydroxy-Octadecenoic acid; Cirsiliol; Nevadensin; Tomentin; Alpha-Kamlolenic Acid; Gallic acid; Methoxyeugenol; 1,4,8-Trihydroxy-3-tetralone-methyl formate-4-*O*-*β*-D-glucopyranoside; L-Tryptophan; (S)-eriodictyol-6-*C*-*β*-*D*-glucopyranoside
A. martjanovii (wild: leaves)	5	Tri-*O*-methylellagic acid; Dihydroquercetin; 3,5-Dihydroxy-6,3′,4′-tetramethoxyflavone; Cirsilineol; Tanshinone IIA

Table 3. *Cont.*

Sample	Total Number of Compounds	Compound Names
A. martjanovii (wild: stems+leaves)	6	Santonin, Pheophytin A; Podophyllotoxin; Plumbagin; Chlorogenic acid; Isololiolide
A. martjanovii (wild: stems + leaves); *A. martjanovii* (BG)	20	Undecanedioic acid; Deoxyartemisinin I; Gardenin B; Salvigenin; Caffeic acid; Artemisin; Dihydroxy-trimethoxyflavone; Casticin; Hydroxy myristic acid; Pseudosantonin; Dihydroxy-dimethoxyflavone; Centaureidin; Eupatilin; Artemetin; Myristoleic acid; Atractylenolide I; Artemisinic acid; Atractylenolide II; Artemisinin C; Cirsimaritin
A. martjanovii (wild: stems); *A. martjanovii* (BG)	18	Dihydrosantamarin; Umbelliferone; Trihydroxy(iso)flavone; Petunidin; Syringetin; Vebonol; L-Valine; Dihydroxy tetramethoxyflavone hexoside; Dihydroxy-trimethoxyflavone-O-hexoside; Resveratrol; Sespendole; Linolenic acid; (Epi)-catechin; Caffeic acid derivative; Hydroxy dodecanoic acid; Hydroxydodecenoic acid; Chrysartemin A; Trihydroxyoctadecadienoic acid
A. martjanovii (wild: leaves); *A. martjanovii* (BG)	12	Chrysoeriol C-hexoside; Stearidonic acid methyl ester; 4-*O*-dicaffeoylquinic acid; 3-Hydroxy-6,7,4′-trimethoxyflavone; Chrysoeriol 6-*O*-hexoside; 3′-di-*O*-methyl ellagic acid; Artemannuin B; Syringic acid; Costunolide; Jaceosidin; Penduletin; Trihydroxymethoxyflavone
A. martjanovii (BG)	27	Artabsinolide A; Stearidonic acid; Eriodictyol; Isorhamnetin 3-*O*-glucoside; Absinthin derivative; Dihydroarteannuin B; Mearnsetin-glucoside; 7-Methoxybenzo[d][13] dioxole-5-carboxylic acid; Glucaric acid; Neochlorogenic acid; 3,5-Dihydroxy-6,7,4′-trimethoxyflavone; Ferulic acid; Hispidulin; *cis*-3-Caffeoylquinic acid; Methylgallic acid; Linoleic acid; Apigenin; Absinthin; Hydroxy octadecadienoic acid; Thymonin; 4,5-Tri-*O*-caffeoylquinic acid; Quercetin 3-*O*-glucoside; Acacetin *C*-glucoside methylmalonylated; 3-*O*-acetyl-betulinic acid; Fraxetin; Tetrahydroxy-dimethoxyflavone-hexoside; Tetramethylellagic acid hexose

From Table 3, it can be seen that a certain number of chemical compounds were commonly detected in the stem and leaf extracts of both wild and Botanical Garden-grown *A. martjanovii*. These are the following constituents: undecanedioic acid; deoxyartemisinin I; gardenin B; salvigenin; caffeic acid; artemisin; dihydroxy-trimethoxyflavone; casticin; hydroxy myristic acid; pseudosantonin; dihydroxy-dimethoxyflavone; centaureidin; eupatilin; artemetin; myristoleic acid; atractylenolide I; artemisinic acid; atractylenolide II; artemisinin C; cirsimaritin.

In addition, the following chemical compounds have a fairly significant repeatability in the extracts from *A. martjanovii* (Botanical Garden) and *A. martjanovii* (wild) stems: dihydrosantamarin; umbelliferone; trihydroxy(iso)flavone; petunidin; syringetin; vebonol; L-valine; dihydroxy tetramethoxyflavone hexoside; dihydroxy-trimethoxyflavone-*O*-hexoside; resveratrol; sespendole; linolenic acid; (Epi)-catechin; caffeic acid derivative; hydroxy dodecanoic acid; hydroxydodecenoic acid; chrysartemin A; trihydroxyoctadecadienoic acid; in varieties from *A. martjanovii* (Botanical Garden) and *A. martjanovii* (wild), leaves: chrysoeriol *C*-hexoside; stearidonic acid methyl ester; 4-*O*-dicaffeoylquinic acid; 3-hydroxy-6,7,4′-trimethoxyflavone; chrysoeriol 6-*O*-hexoside; 3′-di-*O*-methyl ellagic acid; artemannuin B; syringic acid; costunolide; jaceosidin; penduletin; trihydroxymethoxyflavone.

Thus, the analyzed samples of ethanol extracts of the above-ground phytomass of A. *martjanovii*, growing wild and cultivated in the Botanical Garden for 19 years, showed the presence of 50 common compounds of polyphenolic nature and other groups and also contained 27 different compounds. In extracts of plants growing in the wild, a larger number of compounds from other groups were identified (38) compared to plants cultivated under artificial conditions (34). However, a larger number of polyphenolic compounds (43) were identified in cultivated plants than in wild plants (39).

In this study, the qualitative variability of compounds in the phytochemical profile of extracts from above-ground phytomass of wild and cultivated *A. martjanovii* may be associated with differences in geographical location (rocky slope of the riverbank and flat steppe, respectively), soil type, agronomic practices (in the case of the plants grown in the Botanical Garden of NEFU), as well as natural and anthropogenic disturbances in wild nature and artificial cultivation.

Plant secondary metabolites are formed under the influence of many environmental factors and plant growth conditions. The diversity of chemicals in plants indicates their adaptation strategy to changing conditions, and it is specific to each individual species and may vary depending on intraspecific differentiation (population differences). In this regard, *A. martjanovii* samples collected from two different habitats showed intraspecific variability in the qualitative composition of polyphenolic compounds and other groups of compounds identified using tandem mass spectrometry and HPLC-MS/MS methods.

The presence of flavonoids (flavones, flavonols, and flavanones), caffeic acid, chlorogenic acid, and dicaffeoylquinic acid in wild and cultivated *A. martjanovii* shows that this rare plant can be a potential source of antioxidant substances. This can be achieved through introductory cultivation combined with qualitative and quantitative profiling (control) of the constancy of the phytochemical composition. This will reduce the burden on the dwindling wild populations of this rare plant species. The results that we detected stilbene (resveratrol), coumarin, dihydrochalcone, lignan, amino acids, polysaccharides, an abundance of sesquiterpenoids (including santonin, artemisin, etc.), sesquiterpenoid lactones (including artemisinin C and artemannuin B), omega-3 fatty acids, oxylipins, naphthoquinones, and alkaloids (sespendol)—make *A. martjanovii* a potential source of these biologically active substances. In the future, however, it will be worthwhile to investigate the quantitative composition of the identified secondary metabolites.

4. Conclusions

In this study, the phytochemical profile of a rare plant species, *A. martjanovii* Krasch ex Poljakov, growing in Central Yakutia, was investigated for the first time. For this, we used HPLC and tandem mass spectrometry methods.

In total, 104 different individual compounds were identified in extracts of the above-ground phytomass of *A. martjanovii*: various groups of polyphenols, including a whole complex of flavonoids, as well as compounds from other compound classes such as amino acids, polysaccharides, sesquiterpenoids, sesquiterpenoid lactones, fatty acids, naphthoquinones, oxylipins, etc.

We conclude that under conditions of natural growth and introduction, *A. martjanovii* accumulates artemisinin C both in leaves and stems. However, chlorogenic acid was only found in the leaf and stem extracts of wild plants. Twenty-seven chemical constituents from the polyphenol group (flavones apigenin, trihydroxy(iso)flavone, salvigenin, cirsiliol, cirsilineol, nevadensin, syringetin, gardenin B, thymonin, chrysoeriol *C*-hexoside; flavonols: taxifolin, tetrahydroxy-dimethoxyflavone-hexoside, etc.) and 26 chemical constituents from other compound classes were identified in genus *Artemisia* L. for the first time.

In general, *A. martjanovii* from the Central Yakut population is of interest as a potential source of antioxidants and other profiles of pharmacological activity of substances. The declining natural populations of this rare plant species make it urgent to develop in vitro micropropagation technology based on samples of wild plants with subsequent reintroduction in plantation conditions.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Compounds were identified from the ethanol extracts of *A. martjanovii* in positive and negative ionization modes by HPLC-ion trap-MS/MS.

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	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** [5,7-Dixydroxy-2-(40Hydroxyphenyl)-4H-Chromen-4-One] *	$C_{15}H_{10}O_5$	**270.2369**	**49.0**		**271**	225	179		*Lonicera henryi* [15]; Ribes meyeri [16]; *Lonicera japonica* [17]; Mexican lupine species [18]; Exocarpium Citri Grandis [19]; *Stevia rebaudiana* [20]; Propolis [21]; Jatropha [22]
2	**Flavone**	**Trihydroxy(iso) flavone** *	$C_{15}H_{10}O_5$	**270.2369**	**13.0**		**271**	215	173		Propolis [21]
3	**Flavone**	**Hispidulin**	$C_{16}H_{12}O_6$	**300.2629**	**45.8**		**301**	282	254		*Artemisia argyi* [23]; *Cirsium japonicum* [24]; Mentha [25]
4	**Flavone**	**Trihydroxymethoxy flavone**	$C_{16}H_{12}O_6$	**300.2629**	**30.0**		**301**	286; 226; 136	258; 132	189; 162; 135	*Artemisia absinthium* [6]
5	**Flavone**	**Cirsimaritin [Scrophulein; 4′,5-Dihydroxy-6,7-Dimethoxyflavone]**	$C_{17}H_{14}O_6$	**314.2895**	**36.0**		**315**	300	285; 229	257; 229	*Artemisia annua* [6]; Ocimum [26]; *Rosmarinus officinalis* [27]
6	**Flavone**	**Salvigenin** *	$C_{18}H_{16}O_6$	**328.3160**	**52.5**		**329**	296	268	240; 133	*Dracocephalum palmatum* [28]; Ocimum [26]
7	**Flavone**	**Jaceosidin** [5,7,4′-trihydroxy-6′,5′-dimethoxyflavone]	$C_{17}H_{14}O_7$	**330.2889**	**42.3**	**329**		314; 229	299	271	*Artemisia argyi* [23]; *Mentha* [25]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
8	**Flavone**	**Dihydroxy-dimethoxyflavone**	$C_{17}H_{14}O_7$	**330.2889**	**26.5**	**329**		313	299	270	*Artemisia absinthium* [6]
9	**Flavone**	**Cirsiliol ***	$C_{17}H_{14}O_7$	**330.2889**	**35.7**		**331**	316	298	270	Ocimum [26]; *Juglans mandshurica* [29]
10	**Flavone**	**3-Hydroxy-6,7,4′-trimethoxyflavone**	$C_{18}H_{16}O_7$	**344.3154**	**7.8**	**343**		328	313	298; 270	*Artemisia annua* [30]
11	**Flavone**	**Cirsilineol** [Eupatrin; Fastigenin; Cirsileneol] *	$C_{18}H_{16}O_7$	**344.3154**	**9.1**		**345**	312	284; 269	269	Ocimum [26]
12	**Flavone**	**Nevadensin ***	$C_{18}H_{16}O_7$	**344.3154**	**41.0**		**345**	330	312	284; 135	*Mentha* [25]; Ocimum [26]
13	**Flavone**	**Penduletin**	$C_{18}H_{16}O_7$	**344.3154**	**40.4**	**343**		328	313	298	*Artemisia annua* [6]
14	**Flavone**	**Eupatilin**	$C_{18}H_{16}O_7$	**344.3154**	**35.8**		**345**	312	284	269	*Artemisia argyi* [23]
15	**Flavone**	**Syringetin ***	$C_{17}H_{14}O_8$	**346.2883**	**24.3**		**347**	332	317	289	*C. edulis* [31]; Grape [32]
16	**Flavone**	**Tetrahydroxy-dimethoxyflavone**	$C_{17}H_{14}O_8$	**346.2883**	**29.0**	**345**		330	315	287	*Artemisia absinthium* [6]
17	**Flavone**	**Gardenin B** [Demethy ltangeretin] *	$C_{19}H_{18}O_7$	**358.342**	**44.4**		**359**	326; 344; 295	298; 269	283; 269; 227	*Mentha* [25]; Ocimum [26]; *Actinocarya tibetica* [33];
18	**Flavone**	**3,5 -Dihydroxy -6,7,4′-trimethoxyflavone**	$C_{18}H_{16}O_8$	**360.3148**	**35.8**	**358**		343	328	300	*Artemisia annua* [30]
19	**Flavone**	**Centaureidin [5,7,3′-Trihydroxy-3,6,4′-trimethoxyflavone]**	$C_{18}H_{16}O_8$	**360.3148**	**27.5**		**361**	328	300	285	*Artemisia argyi* [23]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
20	**Flavone**	**Dihydroxy-trimethoxyflavone**	$C_{18}H_{16}O_8$	**360.3148**	**30.9**		**361**	346; 142	328; 217	300	*Artemisia absinthium* [6]
21	**Flavone**	**Thymonin** [5,6,4′-trihydroxy-7,8,3′-tri-methoxy flavone] *	$C_{18}H_{16}O_8$	**360.3148**	**32.8**		**361**	345; 187	328; 217	300; 164	Mentha [25,34]
22	**Flavone**	**3,5-Dihydroxy-6,7,3′,4′-tetramethoxyflavone**	$C_{19}H_{18}O_8$	**374.3414**	**37.5**	**373**		358	343	328; 300	*Artemisia annua* [30]
23	**Flavone**	**Casticin [Vitexicarpin; Dihydroxy-tetramethoxyflavone]**	$C_{19}H_{18}O_8$	**374.3414**	**36.5**		**375**	342	313; 151	299; 151	*Artemisia annua* [6,35]; *Artemisia argyi* [23]
24	**Flavone**	**Chrysoeriol *C*-hexoside** *	$C_{22}H_{22}O_{11}$	**462.4036**	**42.2**		**463**	445; 233	427; 229	399; 197	*Triticum aestivum* L. [36,37]
25	**Flavone**	**Chrysoeriol 6-*O*-hexoside** *	$C_{22}H_{22}O_{11}$	**462.4036**	**49.0**		**463**	445; 231	427; 287; 229	409; 229	*Triticum aestivum* L. [38]
26	**Flavone**	**Dihydroxy-trimethoxyflavone-*O*-hexoside**	$C_{23}H_{22}O_{13}$	**506.413**	**29.4**		**507**	345	312	284	Citrus species [39]
27	**Flavone**	**Dihydroxy tetramethoxyflavone hexoside** *	$C_{25}H_{28}O_{13}$	**536.4820**	**27.3**		**537**	375	342	314; 151	*F. pottsii* [31]
28	**Flavone**	**Acacetin C-glucoside methylma lonylated** *	$C_{26}H_{26}O_{13}$	**546.4758**	**48.1**		**547**	529; 327; 231	312; 160	284	Mexican lupine species [18]
29	**Flavonol**	**Dihydroquercetin** (Taxifolin; Taxifoliol) *	$C_{15}H_{12}O_7$	**304.2516**	**8.5**		**305**	286; 234; 175; 147	240; 199; 148	157	*Juglans mandshurica* [29]; *Glycine soja* [40]; millet grains [41]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	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**	**Quercetin 3-O-glucoside** [Isoquercetin; Isoquercitrin; Hirsutrin]	$C_{21}H_{20}O_{12}$	**464.3763**	**50.3**		**465**	447; 231	187	145	*Lonicera henryi* [15]; *Ribes meyeri* [16]; *Lonicera japonica* [17]; Mexican lupine species [18]; *Juglans mandshurica* [29]; *Artemisia annua* [30]; *Vaccinium myrtillus* [42]; *Embelia* [43]
31	**Flavonol**	**Isorhamnetin 3-*O*-glucoside**	$C_{22}H_{22}O_{12}$	**478.4029**	**23.4**		**479**	317	302; 165	274; 153	*Artemisia annua* [30]; *Actinidia valvata* [44]; *Actinidia polygama* [45]
32	**Flavonol**	**Mearnsetin-glucoside**	$C_{22}H_{22}O_{13}$	**494.4023**	**31.3**		**495**	477; 233	459; 244	431; 186	*Artemisia annua* [30]
33	**Dihydroxy-flavonol**	**Tetrahydroxy-dimethoxyflavone-hexoside** [Syringetin-hexoside; dimethyl-myricetin-hexoside] *	$C_{23}H_{24}O_{13}$	**508.4289**	**24.3**		**509**	347	332	317	*Mentha* [46]; Pomegranate [47]; *Vaccinium macrocarpon* [48]
34	**Flavonol**	**Isorhamnetin 3-O-(6″-*O*-rhamnosyl-hexoside) ***	$C_{28}H_{32}O_{16}$	**624.5441**	**24.2**	**623**		315; 300	300; 255	271; 255	*Lonicera henryi* [15]; *Bee-pollen* [49]
35	**Flavan-3-ol**	**(Epi)-catechin ***	$C_{15}H_{14}O_6$	**290.2681**	**7.4**		**291**	272; 216	240; 216; 184	211; 184; 158	*Glycine soja* [40]; *millet grains* [41]; *Vaccinium myrtillus* [42]; *Vaccinium macrocarpon* [50]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
36	**Flavanone**	**Eriodictyol** [3′,4′,5,7-tetrahydroxy-flavanone]	$C_{15}H_{12}O_6$	**288.2522**	**48.5**		**289**	271; 191	201	160	*Artemisia absinthium* [6]; Propolis [21]; *Jatropha* [22]; *Rosmarinus officinalis* [27]; *Juglans mandshurica* [29]; *Embelia* [43]
37	**Flavanone**	**(S)-eriodictyol-6-*C*-*beta*-D-glucopyranoside** *	$C_{21}H_{22}O_{11}$	**450.3928**	**26.3**		**451**	433; 321	247; 167	231	*Aspalathus linearis* [51]
38	**Anthocyanin**	**Petunidin** *	$C_{16}H_{13}O_{7+}$	**317.2702**	**23.4**		**317**	302	274; 153	246; 153	*A. cordifolia; C. edulis* [31]; *Vines* [52]
39	**Hydroxy benzoic acid**	**Gallic acid**	$C_7H_6O_5$	**170.1195**	**15.7**		**171**	152; 138	135		Huolisu Oral Liquid [7]; *Ribes meyeri* [16]; *Juglans mandshurica* [29]; *Vaccinium macrocarpon* [50]; *Punica granatum* [53]; Actinidia [54]
40	**Hydroxy cinnamic acid**	**Caffeic acid** [(2E)-3-(3,4-Dihydroxy phenyl)acrylic acid]	$C_9H_8O_4$	**180.1574**	**8.7**		**181**	163; 135	145; 121	117	*Artemisia argyi* [23]; *Juglans mandshurica* [29]; *Soybean leaves* [55]
41	**Methyl benzoic acid**	**Methylgallic acid** [Methyl gallate] *	$C_8H_8O_5$	**184.1461**	**39.5**		**185**	143	116		Grape [32]; *Rhus coriaria* [56]; *Terminalia arjuna* [57]; Phyllanthus [58]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
42	**Trans-cinnamic acid**	**Ferulic acid**	$C_{10}H_{10}O_4$	**194.184**	**26.2**	**193**		176	132		*Lonicera japonica* [17]; *Juglans mandshurica* [29]; *Soybean leaves* [55]; *Soybean* [59]; *Ribes nigrum* [60];
43	**Hydroxy benzoic acid**	**Syringic acid** [Benzoic acid; Cedar acid] *	$C_9H_{10}O_5$	**198.1727**	**49.8**		**199**	197; 171; 157; 143	142; 129		*Rosa acicularis* [8]; *Juglans mandshurica* [29]; *A. cordifolia*; *G. linguiforme*; *F. glaucescens* [31]; millet grains [41]; *Vaccinium macrocarpon* [50]; *Actinidia* [54]
44	**Cinnamic acid derivative**	**cis-3-Caffeoylquinic acid**	$C_{16}H_{18}O_9$	**354.3087**	**6.4**	**353**		191			*Camellia kucha* [9]; *Lonicera henryi* [15]; *Crataegus monogyna* [61]
45	**Cinnamic acid derivative**	**Chlorogenic acid** [3-O-Caffeoylq Chlorogenic acid [3-O-Caffeoylquinic acid]uinic acid]	$C_{16}H_{18}O_9$	**354.3087**	**16.5**	**353**		191; 321			*Artemisia annua* [6]; *Lonicera henryi* [15]; *Lonicera japonica* [17]; *Artemisia argyi* [23]; *Juglans mandshurica* [29]; *Vaccinium myrtillus* [42]; *Vaccinium macrocarpon* [48,50]; *Rhus coriaria* [56]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
46	**Cinnamic acid derivative**	**Neochlorogenic acid** [5-O-Caffeoylquinic acid]	$C_{16}H_{18}O_9$	**354.3087**	**7.3**	**353**		191; 321	127		*Artemisia annua* [6]; *Lonicera henryi* [15]; *Lonicera japonica* [17]; *Artemisia argyi* [23]; *Dracocephalum palmatum* [28]; *Vaccinium myrtillus* [42]
47		**Caffeic acid derivative**	$C_{16}H_{18}O_9Na$	**377.2985**	**6.4**	**377**		341	179		*Embelia* [43]; Bougainvillea [62]
48	**Phenolic acid**	**3,4-O-dicaffeoylquinic acid [Isochlorogenic acid B]**	$C_{25}H_{24}O_{12}$	**516.4509**	**7.2**	**515**		353	173		*Lonicera henryi* [15]; *Lonicera japonica* [17]; *Stevia rebaudiana* [20]; *Artemisia argyi* [23]; *Artemisia annua* [30]
49	**Phenolic acid**	**Tetramethylellagic acid hexose**	$C_{26}H_{34}O_{11}$	**522.5416**	**27.1**		**523**	361	346	328; 217	*Strawberry* [63]
50	**Phenolic acid**	**3,4,5-Tri-O-caffeoylquinic acid**	$C_{34}H_{30}O_{15}$	**678.5930**	**27.8**	**677**		515; 353	353; 173	173	*Lonicera henryi* [15]; *Artemisia annua* [30]
51	**Stilbene**	**Resveratrol** [trans-Resveratrol; 3,4′,5-Trihydroxystilbene; Stilbentriol] *	$C_{14}H_{12}O_3$	**228.2433**	**7.5**		**229**	172	158; 144		*Embelia* [43]; Grape [32]; *A. cordifolia*; *F. glaucescens*; *F. herrerae* [31]; *Radix polygoni multiflori* [64]
52	**Hydroxycoumarin**	**Umbelliferone** [Skimmetin; Hydragin] *	$C_9H_6O_3$	**162.1421**	**9.2**		**163**	145; 121	117		*F. glaucescens* [31]; Actinidia [54]; *Sanguisorba officinalis* [65]; *Zostera marina* [66]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
53	**Coumarin**	**Fraxetin** *	$C_{10}H_8O_5$	**208.1675**	**36.0**		**209**	191	117		Jatropha [22]; Embelia [43]; Actinidia [54]
54	**Natural plant coumarin**	**Tomentin** *	$C_{11}H_{10}O_5$	**222.1941**	**51.1**		**223**	208	178	165	Jatropha [22]
55	**Dihydro chalcone**	**Phloretin** [Dihydronaringenin; Phloretol] *	$C_{15}H_{14}O_5$	**274.2687**	**31.3**		**275**	257; 147	239; 187	197; 117	*Rosa rugosa* [8]; *G. linguiforme* [31]; *Punica granatum* [53]; *Malus toringoides* [67]
56	**Lignan**	**Podophyllotoxin** [Podofilox; Condylox; Condyline; Podophyllinic acid lactone] *	$C_{22}H_{22}O_8$	**414.4053**	**49.0**		**415**	397; 195	369; 167	351; 179	Lignans [68]
	OTHERS										
57	**Amino acid**	**L-Valine** [(S)-2-Amino-Methylbutanoic acid]	$C_5H_{11}NO_2$	**117.1463**	**7.0**		**118**	116			*Lonicera japonica* [17]; Soybean leaves [55]; *Vigna unguiculata* [69]
58		**L-Ascorbic acid** [Vitamin C]	$C_6H_8O_6$	**176.1241**	**7.1**		**177**	160; 126	158; 141; 132		*Potato leaves* [70]; *Strawberry*, *Lemon*, *Papaya* [71]; *Phoenix dactylifera* [72]
59	**Aromatic amino acid**	**Tyrosine** [(2S)-2-Amino-3-(4-Hydroxyphnyl) Propanoic acid] *	$C_9H_{11}NO_3$	**181.1885**	**8.1**		**182**	165; 136	147; 123	119	*Euphorbia hirta* [10]; *Hylocereus polyrhizus* [11]; Soybean leaves [55]; *Vigna unguiculata* [69]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
60	**Naphtho quinone**	**Plumbagin ***	$C_{11}H_8O_3$	**188.1794**	**16.8**		**189**	187; 133			*Juglans mandshurica* [29]
61	**Propenyl phenol derivative**	**Methoxyeugenol ***	$C_{11}H_{14}O_3$	**194.2271**	**21.0**		**195**	177	133	131	Ocimum [26]
62	**Carboxylic acid**	**7-Methoxybenzo[d][1,3] dioxole-5-carboxylic acid**	$C_9H_8O_5$	**196.1568**	**39.5**		**197**	179	151	123	Actinidia [54]
63	**Benzofuran**	**Isololiolide ***	$C_{11}H_{16}O_3$	**196.2429**	**39.6**		**197**	179	151; 149	123	*Jatropha gossypifolia* [22]; Olive leaves [73]
64	**Essential amino acid**	**L-Tryptophan** [Tryptophan; (S)-Tryptophan] *	$C_{11}H_{12}N_2O_2$	**204.2252**	**16.9**		**205**	188	146	144; 118	Huolisu Oral Liquid [7]; *Rosa acicularis* [8]; *Camellia kucha* [9]; *Euphorbia hirta* [10]; *Hylocereus polyrhizus* [11]; Rapeseed petals [12]
65	**Polysac charides**	**Glucaric acid** [D-Glucaric acid; Saccharic acid; D-Glutarate] *	$C_6H_{10}O_8$	**210.1388**	**8.7**		**211**	193; 147	147	118	Soybean [59]; *Cherimoya*, *Papaya* [71]
66	**Saturated fatty acid**	**Hydroxydodecenoic acid ***	$C_{12}H_{22}O_3$	**214.3013**	**39.0**		**215**	197	195		*Jatropha gossypifolia* [22]
67	**Alpha, omega dicarboxylic acid**	**Undecanedioic acid ***	$C_{11}H_{20}O_4$	**216.2741**	**50.3**		**217**	199; 189; 159	157; 143	143	*Jatropha* [22]; *G. linguiforme* [31]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
68	**Carboxylic acid**	**Myristoleic acid** [Cis-9-Tetradecanoic acid] *	**$C_{14}H_{26}O_2$**	**226.3550**	**20.1**		**227**	209; 165	121		*F. glaucescens* [31]; *Maackia amurensis* [74]
69	**Sesquiter penoid**	**Atractylenolide I ***	**$C_{15}H_{18}O_2$**	**230.3022**	**27.7**		**231**	185	157	142	*Atractylodes macrocephalae rhizoma* [13]; Chinese herbal formula Jian-Pi-Yi-Shen pill [14]
70	**Sesquiter penoid**	**Atractylenolide II** [Asterolide; 2-Atractylenolide] *	**$C_{15}H_{20}O_2$**	**232.3181**	**10.2**		**233**	215; 205; 187; 145	145; 131		*Codonopsis Radix; Atractylodes macrocephalae rhizoma* [13]; Chinese herbal formula Jian-Pi-Yi-Shen pill [14]
71	**Germacranolide**	**Costunolide ***	**$C_{15}H_{20}O_2$**	**232.3181**	**41.4**		**233**	185	143	128	[75]
72	**Monocar boxylic acid**	**Artemisinic acid** [Artemisic acid; arteannuic acid]	**$C_{15}H_{22}O_2$**	**234.3340**	**28.7**		**235**	216	187	145	*Artemisia annua* [30]
73	**Hydroxy tetradecanoic acid**	**Hydroxy myristic acid** [2S-Hydroxytetradecanoic acid; Alpha-Hydroxy Myristic acid] *	**$C_{14}H_{28}O_3$**	**244.3703**	**38.6**		**245**	228	172		*F. pottsii* [31]
74	**Medium-chain fatty acid**	**Hydroxy dodecanoic acid ***	**$C_{12}H_{22}O_5$**	**246.3001**	**26.0**		**247**	229; 201	187	159; 145	*F. glaucescens* [31]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
75	**Sesquiterpenoid**	**Santonin [Alpha-Santonin; Semenen;** Santoninic anhydride]	$C_{15}H_{18}O_3$	**246.3016**	**44.1**		**247**	228	200		*Artemisia absinthium* [6]
76	**Sesquiterpene lactone**	**Artemisinin C**	$C_{15}H_{20}O_3$	**248.3175**	**20.6**		**249**	231	213	171	*Artemisia annua* [6]
77	**Sesquiterpene lactone**	**Artemannuin B**	$C_{15}H_{20}O_3$	**248.3175**	**25.3**	**247**		203	201		*Artemisia annua* [6,30]
78	**Sesquiterpenoid**	**Dihydroarteannuin B**	$C_{15}H_{22}O_3$	**250.3334**	**27.5**		**251**	232	215	187	*Artemisia absinthium* [6]
79	**Sesquiterpenoid**	**Dihydrosantamarin**	$C_{15}H_{22}O_3$	**250.3334**	**39.3**	**249**		205	203; 121	121	*Artemisia absinthium* [6]
80	**Sesquiterpenoid**	**Artemisin**	$C_{15}H_{18}O_4$	**262.3010**	**34.3**		**263**	245	227		Pubchem
81	**Sesquiterpenoid**	**Pseudosantonin**	$C_{15}H_{20}O_4$	**264.3169**	**26.3**		**265**	247	229	201	*Artemisia absinthium* [6]
82	**Sesquiterpenoid**	**Deoxyartemisinin I**	$C_{15}H_{22}O_4$	**266.3328**	**32.1**		**267**	249	229	213	*Artemisia absinthium* [6]
83	**Omega-3-fatty acid**	**Stearidonic acid** [6,9,12,15-Octadecatetraenoic acid; Moroctic acid] *	$C_{18}H_{28}O_2$	**276.4137**	**18.5**		**277**	217	189; 171	161; 134	*Jatropha* [22]; *G. linguiforme* [31]; *Rhus coriaria* [56]; *Salviae Miltiorrhizae* [76]
84	**Sesquiterpenoid**	**Chrysartemin A**	$C_{15}H_{18}O_5$	**278.3004**	**42.7**		**279**	163	145	143	*Artemisia absinthium* [6]
85	**Omega-3-fatty acid**	**Linolenic acid** (Alpha-Linolenic acid; Linolenate) *	$C_{18}H_{30}O_2$	**278.4296**	**17.1**		**279**	261	234; 111	123	Jatropha [22]; *Maackia amurensis* [74]; *Salviae Miltiorrhizae* [76]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
86	**Gamma-lactone**	**Artabsinolide A**	$C_{15}H_{20}O_5$	**280.3163**	**9.1**	**279**		247; 235	203		*Artemisia absinthium* [6]
87	**Sesquiter penoid**	**Dihydroartemisinin**	$C_{15}H_{24}O_5$	**284.3481**	**7.9**		**285**	227	199	130	*Artemisia annua* [30]
88	**Octadeca dienoic acid**	**Linoleic acid** (Linolic acid; Telfairic acid) *	$C_{18}H_{32}O_2$	**280.4455**	**26.5**		**281**	245	228	183	Soybean [59]; Soybean leaves [55]; Jatropha [22];
89	**Omega-3-fatty acid**	**Stearidonic acid methyl ester**	$C_{19}H_{30}O_2$	**290.4403**	**51.6**		**291**	259; 149	241; 161	173	Jatropha [22]
90	**Diterpenoid naphtho-quinone**	**Tanshinone IIA** [Tanshinone II; Tanshinone B] *	$C_{19}H_{18}O_3$	**294.3444**	**49.5**		**295**	277; 241	161	161; 133	Huolisu Oral Liquid [7]; Chinese herbal formula Jian-Pi-Yi-Shen pill [13];
91	**Polyun saturated fatty acid**	**Alpha-Kamlolenic Acid** [18-Hydroxy-9Z,11E,13E-Octadecatrienoic Acid] *	$C_{18}H_{30}O_3$	**294.4290**	**45.3**	**293**		275; 171	231		*G. linguiforme*; *F. glaucescens*; *F. pottsii* [31]
92	**Essential faty acid**	**Hydroxy octadecadienoic acid**	$C_{18}H_{32}O_3$	**296.4449**	**47.5**	**295**		277; 171	275		*Artemisia absinthium* [6]; *Jatropha* [22]; *A. cordifolia*; *F. glaucescens*; *F. herrerae* [31]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
93	Oxylipin	Trihydroxyocta decadienoic acid	$C_{18}H_{32}O_5$	328.4437	32.4	327		229	210	209	*Artemisia absinthium* [6]; Potato leaves [70]
94	Naphtho quinone	3,3′-di-O-methyl ellagic acid *	$C_{16}H_{10}O_8$	330.2458	30.9		331	316	298	270	*Juglans mandshurica* [29]; *Terminalia arjuna* [57]
95	Oxylipin	13- Trihydroxy-Octadecenoic acid [THODE] *	$C_{18}H_{34}O_5$	330.4596	33.0	329		229	209		Jatropha [22]; *Phoenix dactylifera* [72]; *Bituminaria* [77]; *Broccoli* [78]
96	Naphtho quinone	Tri-*O*-methylellagic acid *	$C_{17}H_{12}O_8$	344.2724	29.6	343		328; 300; 247	313; 285	298; 270	*Terminalia arjuna* [57]
97	Sesquiterpene lactone	Artemetin [Artemisetin; Erianthin]	$C_{20}H_{20}O_8$	388.3680	41.4		389	356; 325	313	285; 267	Pubchem
98	Naphtho quinone	1,4,8-Trihydroxy-3-tetralone-methyl formate-4-O-beta-D-glucopyranoside	$C_{18}H_{20}O_{10}$	396.3454	8.7		397	379; 233	217	159	*Juglans mandshurica* [29]
99	Anabolic steroid	Vebonol *	$C_{30}H_{44}O_3$	452.6686	25.6		453	435; 210	226; 336	210	*Hylosereus polyrhizus* [11]; *Rhus coriaria* [56]
100	Sesquiterpene lactone	Absinthin	$C_{30}H_{40}O_6$	496.6350	30.8		497	476; 246	228; 172	172	*Artemisia absinthium* [6]
101	Triterpe	3-O-acetyl-betulinic acid *	$C_{32}H_{50}O_4$	498.7370	41.4		499	480; 233	462; 231	417; 198	*Juglans mandshurica* [29]
102	Sesquiterpene lactone	Absinthin derivative	$C_{30}H_{38}O_7$	510.6185	30.3		511	492; 246	474; 246	228; 172	*Artemisia absinthium* [6]

Table A1. *Cont.*

	Class of Compounds	Identification	Formula	Calculated Mass	Retention Time (min.)	Observed Mass [M-H]−	Observed Mass [M+H]+	MS/MS Stage 1 Fragmentation	MS/MS Stage 2 Fragmentation	MS/MS Stage 3 Fragmentation	References
103	**Indole sesquiterpene alkaloid**	**Sespendole ***	$C_{33}H_{45}NO_4$	**519.7147**	**47.3**		**520**	184	125		*Hylosereus polyrhizus* [11]; *Rhus coriaria* [56]
104	**Product of chlorophyll degradation**	**Pheophytin A**	$C_{55}H_{74}N_4O_5$	**871.1999**	**52.4**		**872**	593	533	461	*Physalis peruviana* [79]; *Capsicum* [80]

* Chemical constituents identified for the first time in genus *Artemisia* L.

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