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Dracocephalum jacutense Peschkova from Yakutia: Extraction and Mass Spectrometric Characterization of 128 Chemical Compounds

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Abstract: *Dracocephalum jacutense* Peschkova is a rare and endangered species of the genus *Dracocephalum* of the Lamiaceae family. The species was first described in 1997 and listed in the Red Data Book of Yakutia. Significant differences in the multicomponent composition of extracts from *D. jacutense* collected in the natural environment and successfully introduced in the Botanical Garden of Yakutsk were identified by a team of authors earlier in a large study. In this work, we studied the chemical composition of the leaves, stem, and inflorescences of *D. jacutense* using the tandem mass spectrometry method. Only three cenopopulations of *D. jacutense* were found by us in the territory of the early habitat—in the vicinity of the village of Sangar, Kobyaysky district of Yakutia. The aboveground phytomass of the plant was collected, processed and dried as separate parts of the plant: inflorescences, stem and leaves. Firstly, a total of 128 compounds, 70% of which are polyphenols, were tentatively identified in extracts of *D. jacutense*. These polyphenol compounds were classified as 32 flavones, 12 flavonols, 6 flavan-3-ols, 7 flavanones, 17 phenolic acids, 2 lignans, 1 dihydrochalcone, 4 coumarins, and 8 anthocyanidins. Other chemical groups were presented as carotenoids, omega-3-fatty acids, omega-5-fatty acids, amino acids, purines, alkaloids, and sterols. The inflorescences are the richest in polyphenols (73 polyphenolic compounds were identified), while 33 and 22 polyphenols were found in the leaves and stems, respectively. A high level of identity for polyphenolic compounds in different parts of the plant is noted for flavanones (80%), followed by flavonols (25%), phenolic acids (15%), and flavones (13%). Furthermore, 78 compounds were identified for the first time in representatives of the genus *Dracocephalum*, including 50 polyphenolic compounds and 28 compounds of other chemical groups. The obtained results testify to the unique composition of polyphenolic compounds in different parts of *D. jacutense*.

Keywords: *Dracocephalum*; polyphenols; tandem mass spectrometry; ion trap

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1. Introduction

The genus *Dracocephalum* (family Lamiaceae) includes a total of 77 species. They are annual and perennial herbaceous plants, and occasionally dwarf shrubs. The species are native to Europe, Eurasia, North Asia and North America. The genus *Dracocephalum* is of high practical interest due to the accumulation of secondary metabolites, especially polyphenolic compounds, in its vegetative and generative organs. Terpenoids, steroids,

flavonoids, alkaloids, lignans, phenols, coumarins, cyanogenic compounds, and glucosides have been identified in the chemical composition of representatives of the genus *Dracocephalum* [1–5]. Some components have antioxidant, antihypoxic, immunomodulatory, and anticancer effects [6–9].

Many scientific studies have been carried out on the phytochemical composition of representatives of the genus *Dracocephalum* in recent years. Four new (undescribed) terpenoids have been isolated from dried aerial parts of *D. moldavica*, including a monoterpenoid glycoside, an iridoid glycoside, a sesquiterpene and a triterpenoid, as well as nine known terpenoids. The chemical structure of the compounds was established using spectroscopy, HRESIMS data analysis and acid hydrolysis. Of these, five compounds were found in the genus *Dracocephalum* for the first time [10]. The UPLC-Q-TOF-MS method was used to study the qualitative and quantitative composition of secondary metabolites (flavonoids, phenolic acids, and coumarins) in the aerial part of *D. moldavica*, depending on the growth period and geographical location [11]. The study of polyphenolic compounds in *D. moldavica* using LC-MS revealed the content of rosmarinic acid as the main component, in the range of 5.337 ± 0.0411 and 6.320 ± 0.0535 mg/mL [12].

Five species of *Dracocephalum* grow in the territory of Yakutia, which is characterized by a sharply continental climate, close continuous occurrence of permafrost, and snow cover that is preserved for almost seven months a year. Among these species, *D. jacutense* is the only one listed in the Red Data Book of Yakutia [13]. *D. jacutense* grows in stony sparse steppe phytocenoses (Figure 1). To date, only a few cenopopulations of the plant have survived. The comparative analysis of the chemical composition of aerial parts of *D. jacutense* Peschkova collected both in controlled conditions (the Botanical Garden of Yakutia) and in a natural-growth area (the vicinity of the village of Sangar, Kobyaysky district of Yakutia) was performed by a team of authors in a previous large study [14]. A total of 156 bioactive compounds were successfully characterized in extracts of *D. jacutense* based on their accurate MS (Mass Spectrometry) fragment ions by searching online databases and the reported literature. A detailed study of the composition by tandem mass spectrometry revealed a significant difference in the polyphenol composition of the samples.

Figure 1. *D. jacutense* Peschkova (Kobyaysky district of Yakutia, photo taken by Rhozina, July 2022).

Wild-grown plant samples had a higher number of polyphenolic compounds (92 compounds) than plant samples grown in the Botanical Garden (56 compounds), which was not previously described in the genus *Dracocephalum*. In addition, a total of 37 compounds of other chemical groups were identified that were not previously identified in the genus *Dracocephalum*. In general, the extract of *D. jacutense* grown in wild conditions was found to be a richer source of flavones, flavanols, flavan-3-ols, phenolic acids, and anthocyanidins than plants grown in controlled conditions in the Botanical Garden.

In general, studies of the phytochemical composition of representatives of the genus *Dracocephalum* are of great importance for determining their potential use in medicine, the development of new drugs and other pharmaceutical industries. The aim of this work is

a comparative analysis of the phytochemical profile of various parts of *D. jacutense*, i.e., leaves, inflorescences, and stems, collected in the vicinity of the village of Sangar in the Kobyaysky district of Yakutia during an expedition in July 2022. Maceration extracts of *D. jacutense* were analyzed by ion trap HPLC-MS/MS and showed a greater diversity of chemical compounds present in different parts of the plant. The ion trap was used in the scan range m/z 100–1700 for MS. A four-stage ion separation mode (MS/MS mode) was implemented. Extracts of plant inflorescences, leaves and stems were analyzed separately. The extracts from *D. jacutense* were analyzed by high-performance liquid chromatography (HPLC) coupled with the ion trap in order to characterize chemical compounds from different parts of *D. jacutense*. The compounds were characterized by interpreting the mass spectrum provided by the ion trap-MS/MS, as well as comparing with information from the literature.

2. Results

A total of 128 compounds were tentatively identified in the plant extracts, of which 70% were polyphenols. These polyphenol compounds were classified as 32 flavones, 12 flavonols, 6 flavan-3-ols, 7 flavanones, 17 phenolic acids, 2 lignans, 1 dihydrochalcone, 4 coumarins, and 8 anthocyanidins. Other chemical groups were presented as carotenoids, omega-3-fatty acids, omega-5-fatty acids, amino acids, purines, alkaloids, and sterols.

All the identified compounds, along with MS/MS data, molecular formulas, and their comparative profile for *D. jacutense*, are summarized in Table A1 (Appendix A). Of the identified compounds, 70% are polyphenols, and 30% are amino acids, fatty acids, purine, alkaloid, sterol, carotenoids, etc. Compounds of the polyphenol group were represented in inflorescences by 73 variations, in leaf extracts by 33 compounds, and in stem extracts by 22 polyphenols.

Of these compounds, 78 were identified for the first time in the genus *Dracocephalum;* 50 were polyphenolic compounds and 28 were from other chemical groups (amino acids, fatty acids, triterpenic acids, etc.). Furthermore, 36 polyphenolic compounds and compounds of other chemical groups (fatty acids, naphthoquinone, pterocarpan, amino acids, triterpenic acids, zeaxanthin, etc.) were found for the first time in extracts from the inflorescences, while 6 polyphenolic compounds were found for the first time in leaf extracts, and 2 polyphenolic compounds were found in stem extracts. Figures A1–A3 (from Appendix A) below show ion chromatograms separately for extracts from inflorescences, stems, and leaves of *D. jacutense*.

The greatest similarity in the identified chemical compounds is found in representatives of the genera *Mentha*, *Vaccinium*, *Rosmarinus*, *Astragali*, and *Eucalyptus*. In addition, Rhodioloside C (monoterpene glycoside), previously described in *Rhodiola rosea*, was found in leaf extracts [15–17] and *Rhodiola crenulata* [18].

The newly identified polyphenols belonged to nine classes, including 11 phenolic acids and their conjugates, 14 flavones, 6 flavonols, 4 flavan-3-ols, 3 flavanone, 5 anthocyanins, 2 lignans, 4 coumarins, and 1 dihydrochalcone (Table 1). Newly identified compounds from other chemical groups belonged to 11 classes, including 1 benzenediol, 3 amino acid and their conjugates, 2 fatty amides, 3 omega-3 fatty acids, 1 omega-5 fatty acid, 4 carotenoids, 1 monoterpene glycoside, 1 diterpenoid naphthoquinone, 4 triterpenic acids, 1 pterocarpan, 1 dihydrochalcone, and others.

2.1. Flavones

2.1.1. 7-Hydroxy(iso)flavones

The flavones formononetin (compound **1**), and calycosin [3′-Hydroxyformononetin] (compound **4**) have already been characterized as a component of *Astragali Radix* [19–21], Huolisu Oral Liquid [22], and the Chinese herbal formula Jian-Pi-Yi-Shen pill [23]. The flavone formononetin and calycosin were found in extracts from leaves of *D. jacutense.* The CID-spectrum in positive ion mode of flavone calycosin from extracts of leaves of *D. jacutense* is shown in Figure 2.

Table 1. Polyphenols identified in the extracts of *D. jacutense* in positive and negative ionization modes using HPLC-ion trap-MS/MS.

No	Class of Compound	Identified Polyphenol	Formula
1	Flavone	**Formononetin** [Biochanin B; Formononetol] *	$C_{16}H_{12}O_4$
2	Flavone	**Apigenin** [5,7-Dixydroxy-2-(40Hydroxyphenyl)-4H-Chromen-4-One]	$C_{15}H_{10}O_5$
3	Flavone	**Acacetin** [Linarigenin; Buddleoflavonol]	$C_{16}H_{12}O_5$
4	Flavone	**Calycosin** [3′-Hydroxyformononetin] *	$C_{16}H_{12}O_5$
5	Flavone	**Genkwanin** [Gengkwanin; Puddumetin; Apigenin 7-Methyl Ether]	$C_{16}H_{12}O_5$
6	Flavone	**Luteolin**	$C_{15}H_{10}O_6$
7	Flavone	**Diosmetin** [Luteolin 4′-Methyl Ether; Salinigricoflavonol]	$C_{16}H_{12}O_6$
8	Flavone	**Chrysoeriol** [Chryseriol]	$C_{16}H_{12}O_6$
9	Flavone	**Cirsimaritin** *	$C_{17}H_{14}O_6$
10	Flavone	**Dihydroxy-dimethoxy(iso)flavone** *	$C_{17}H_{14}O_6$
11	Flavone	**5,7-Dimethoxyluteolin** *	$C_{17}H_{14}O_6$
12	Flavone	**Myricetin** *	$C_{15}H_{10}O_8$
13	Flavone	**Isothymusin**	$C_{17}H_{14}O_7$
14	Flavone	**Cirsiliol** *	$C_{17}H_{14}O_7$
15	Flavone	**Dimethoxy-trihydroxy(iso)flavone** *	$C_{17}H_{14}O_7$
16	Flavone	**Nevadensin**	$C_{18}H_{16}O_7$
17	Flavone	**Gardenin B** [Demethyltangeretin] *	$C_{19}H_{18}O_7$
18	Flavone	**5-Hydroxy-6,7,8,3′,4′-pentamethoxyflavone** *	$C_{20}H_{20}O_8$
19	Flavone	**Apigenin *O*-hexoside**	$C_{21}H_{20}O_{10}$
20	Flavone	**Apigenin-7-*O*-glucoside** [Apigetrin; Cosmosiin]	$C_{21}H_{20}O_{10}$
21	Flavone	**Apigenin 7-*O*-glucuronide**	$C_{21}H_{18}O_{11}$
22	Flavone	**Acacetin 7-*O*-glucoside** [Tilianin]	$C_{22}H_{22}O_{10}$
23	Flavone	**Luteolin 7-*O*-glucoside** [Cynaroside; Luteoloside]	$C_{21}H_{20}O_{11}$
24	Flavone	**Acacetin 7-*O*-*β*-D-glucuronide**	$C_{22}H_{20}O_{11}$
25	Flavone	**6,4′-Dimethoxyisoflavone-7-*O*-glucoside** *	$C_{23}H_{24}O_{10}$
26	Flavone	**Diosmetin-7-*O*-*β*-glucoside**	$C_{22}H_{22}O_{11}$
27	Flavone	**Apigenin-*O*-rhamnoside** *	$C_{22}H_{22}O_{11}$
28	Flavone	**Chrysoeriol-7-*O*-glucuronide** *	$C_{22}H_{20}O_{12}$
29	Flavone	**Acacetin 7-*β*-*O*-(6″-acetyl)-glucoside**	$C_{24}H_{24}O_{11}$
30	Isoflavone	**Apigenin 7-*O*-*β* - D-(6″-*O*-malonyl)-glucoside**	$C_{24}H_{22}O_{13}$
31	Flavone	**Acacetin 7-*O*-*β*-D-(6″-*O*-malonylated)-glucoside**	$C_{25}H_{24}O_{13}$
32	Flavone	**Chrysoeriol *O*-hexoside *C*-hexoside** *	$C_{28}H_{32}O_{16}$
33	Flavonol	**Kaempferol**	$C_{15}H_{10}O_6$
34	Flavonol	**Quercetin**	$C_{15}H_{10}O_7$
35	Flavonol	**Dihydroquercetin** (Taxifolin; Taxifoliol)	$C_{15}H_{12}O_7$
36	Flavonol	**Isorhamnetin** *	$C_{16}H_{12}O_7$
37	Flavonoid	**3,5-Diacetyltambulin** *	$C_{22}H_{20}O_9$
38	Flavonol	**Astragalin** [Kaempferol 3-*O*-glucoside; Astragaline]	$C_{21}H_{20}O_{11}$
39	Flavonol	**Quercitrin** [Quercetin 3-*O*-rhamnoside; Quercetrin] *	$C_{21}H_{20}O_{11}$
40	Flavonol	**Kaempferol-3-*O*-glucuronide**	$C_{21}H_{18}O_{12}$

Table 1. *Cont.*

No	Class of Compound	Identified Polyphenol	Formula
41	Flavonol	**Taxifolin-3-*O*-hexoside** [Dihydroquercetin-3-*O*-hexoside] *	$C_{21}H_{22}O_{12}$
42	Flavonol	**Kaempferol 3-*O*-rutinoside**	$C_{27}H_{30}O_{15}$
43	Flavonol	**Kaempferol-3,7-Di-*O*-glucoside** *	$C_{27}H_{30}O_{16}$
44	Flavonol	**Kaempferol dihexoside rhamnoside** *	$C_{33}H_{40}O_{20}$
45	Flavan-3-ol	**(epi)Afzelechin** *	$C_{15}H_{14}O_5$
46	Flavan-3-ol	**Catechin** [D-Catechol] *	$C_{15}H_{14}O_6$
47	Flavan-3-ol	**(epi)catechin**	$C_{15}H_{14}O_6$
48	Flavan-3-ol	**Gallocatechin** [+(−)Gallocatechin]	$C_{15}H_{14}O_7$
49	Flavan-3-ol	**Catechin 3-*O*-gallate** *	$C_{22}H_{18}O_{10}$
50	Flavan-3-ol	**Epigallocatechin-3-gallate** *	$C_{22}H_{18}O_{11}$
51	Flavanone	**Naringenin** [Naringetol; Naringenine]	$C_{15}H_{12}O_5$
52	Flavanone	**Eriodictyol** [3′,4′,5,7-tetrahydroxy-flavanone]	$C_{15}H_{12}O_6$
53	Isoflavanone	**Ferreirin** *	$C_{16}H_{14}O_6$
54	Trihydroxyflavanone	**Homoeriodictyol** *	$C_{16}H_{14}O_6$
55	Flavanone	**Prunin** [Naringenin-7-*O*-glucoside]	$C_{21}H_{22}O_{10}$
56	Flavanone	**Eriodictyol-7-*O*-glucoside** [Pyracanthoside; Miscanthoside]	$C_{21}H_{22}O_{11}$
57	Flavanone	**Eriodictyol-7-*O*-glucuronide** *	$C_{21}H_{20}O_{12}$
58	Hydroxycinnamic acid	***p*-Coumaric acid** *	$C_9H_8O_3$
59	Hydroxycinnamic acid	**3,4-Dihydroxyhydrocinnamic acid** *	$C_9H_{10}O_4$
60	Phenolic acid	**2,3,4,5-Tetrahydroxybenzoic acid** *	$C_7H_6O_6$
61	Phenolic acid	**Salvianic acid A** [Danshensu] *	$C_9H_{10}O_5$
62	Hydroxybenzoic acid	**Ellagic acid** [Benzoaric acid; Elagostasine; Lagistase; Eleagic acid]	$C_{14}H_6O_8$
63	Phenolic acid	**Protocatechuic acid-*O*-hexoside** *	$C_{13}H_{16}O_9$
64	Phenolic acid	**Caffeic acid-4-*O*-*β*-D-hexoside** [Caffeoyl-*O*-hexoside]	$C_{15}H_{18}O_9$
65	Phenolic acid	**Chlorogenic acid** [3-*O*-Caffeoylquinic acid]	$C_{16}H_{18}O_9$
66	Phenolic acid	**Isochlorogenic acid** *	$C_{16}H_{18}O_9$
67	Phenolic acid	**Rosmarinic acid**	$C_{18}H_{16}O_8$
68	Phenolic acid	**Caffeic acid derivative**	$C_{16}H_{18}O_9Na$
69	Phenolic acid	**1/3/4/5-*p*-Coumaroylquinic acid * + C_2H_2O**	$C_{18}H_{20}O_9$
70	Phenolic acid	**8,8′-Aryl-Diferulic acid** *	$C_{20}H_{18}O_8$
71	Phenolic acid	**Caffeic acid hexoside dimer** *	$C_{31}H_{40}O_{17}$
72	Phenolic acid	**Salvianolic acid B** [Danfensuan B] *	$C_{36}H_{30}O_{16}$
73	Phenylpropanoic acid	**Sagerinic acid**	$C_{36}H_{32}O_{16}$
74	Phenolic acid	**Clerodendranoic acid H** *	$C_{36}H_{32}O_{16}$
75	Lignan	**Phillygenin** [Sylvatesmin; Phyllygenol; Forsythigenol] *	$C_{21}H_{24}O_6$
76	Lignan	**Medioresinol** *	$C_{21}H_{24}O_7$
77	Dihydrochalcone	**Phloretin** [Dihydronaringenin; Phloretol] *	$C_{15}H_{14}O_5$
78	Hydroxycoumarin	**Umbelliferone** [Skimmetin; Hydragin] *	$C_9H_6O_3$
79	Coumarin	**Fraxetin** [7,8-Dihydroxy-6-methoxycoumarin] *	$C_{10}H_8O_5$
80	Hydroxycoumarin	**Umbelliferone hexoside** *	$C_{15}H_{16}O_8$
81	Coumarin glycoside	**Fraxin** [Fraxetin-8-*O*-glucoside] *	$C_{16}H_{18}O_{10}$

Table 1. *Cont.*

No	Class of Compound	Identified Polyphenol	Formula
82	Anthocyanidin	**Petunidin**	$C_{16}H_{13}O_{7+}$
83	Anthocyanidin	**Pelargonidin-3-*O*-glucoside (callistephin)**	$C_{21}H_{21}O_{10}$
84	Anthocyanidin	**Cyanidin-3-*O*-glucoside** [Cyanidin 3-*O*-beta-D-Glucoside; Kuromarin]	$C_{21}H_{21}O_{11+}$
85	Anthocyanidin	**Cyanidin 3,5-*O*-diglucoside** *	$C_{27}H_{31}O_{16}$
86	Anthocyanidin	**Peonidin-3,5-diglucoside** [Peonin; Peonidin 3-Glucoside-5-Glucoside] *	$C_{28}H_{33}O_{16}$
87	Anthocyanidin	**Cyanidin-3-*O*-rutinoside-5-*O*-glucoside** *	$C_{33}H_{41}O_{20}$
88	Anthocyanidin	**Delphinidin 3-*O*-rutinoside-5-*O*-glucoside** *	$C_{33}H_{41}O_{21}$
89	Anthocyanidin	**Malonyl-shisonin** *	$C_{39}H_{39}O_{21+}$

* Polyphenols identified for the first time in genus *Dracocephalum*.

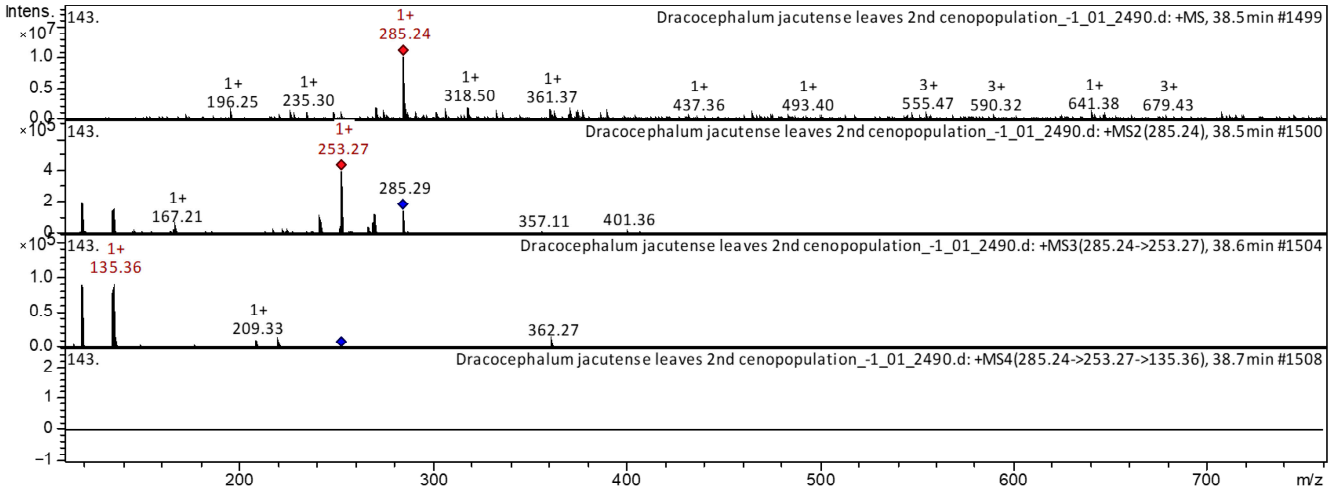

Figure 2. CID-spectrum of calycosin [3′-Hydroxyformononetin] from extracts of leaves of *D. jacutense*, at *m*/*z* 285.24.

The $[M + H]^+$ ion produced two fragment ions at *m*/*z* 253.27 [aglycone-CH_3OH] and *m*/*z* 167.21 (Figure 2). The fragment ion with *m*/*z* 253.3 yielded two daughter ions at *m*/*z* 209.33 and *m*/*z* 135.36. It was identified in the bibliography in extracts of *Astragali radix* [19–21] and Huolisu Oral Liquid [22]. The CID-spectrum in positive ion mode of formononetin from extracts of leaves of *D. jacutense* is shown in Figure 3.

The $[M + H]^+$ ion produced six fragment ions at *m*/*z* 213.3, *m*/*z* 199.35, *m*/*z* 185.29, *m*/*z* 161.24, *m*/*z* 133.33, and *m*/*z* 117.3 (Figure 3). The fragment ion for *m*/*z* 213.3 yielded four daughter ions at *m*/*z* 169.21, *m*/*z* 157.26, *m*/*z* 143.24, and *m*/*z* 129.29. The fragment ion for *m*/*z* 169.21 yielded two daughter ions at *m*/*z* 143.27 and *m*/*z* 129.33. It was identified in the bibliography in extracts of *Astragali radix* [19–21], Huolisu Oral Liquid [22] and the Chinese herbal formula Jian-Pi-Yi-Shen pill [23]. The base peak ion chromatogram in positive ion mode and base peak ion chromatogram in negative ion mode of *D. jacutense* (experiment 2484) are shown in Figure 4.

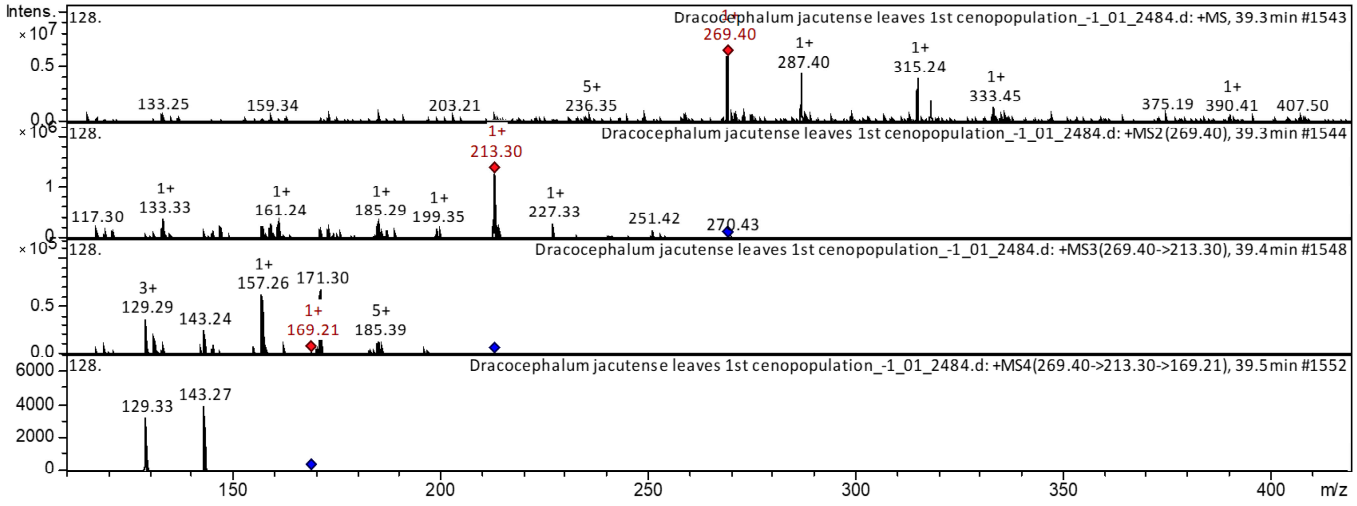

Figure 3. CID-spectrum of formononetin from extracts of leaves of *D. jacutense*, at *m*/*z* 269.4.

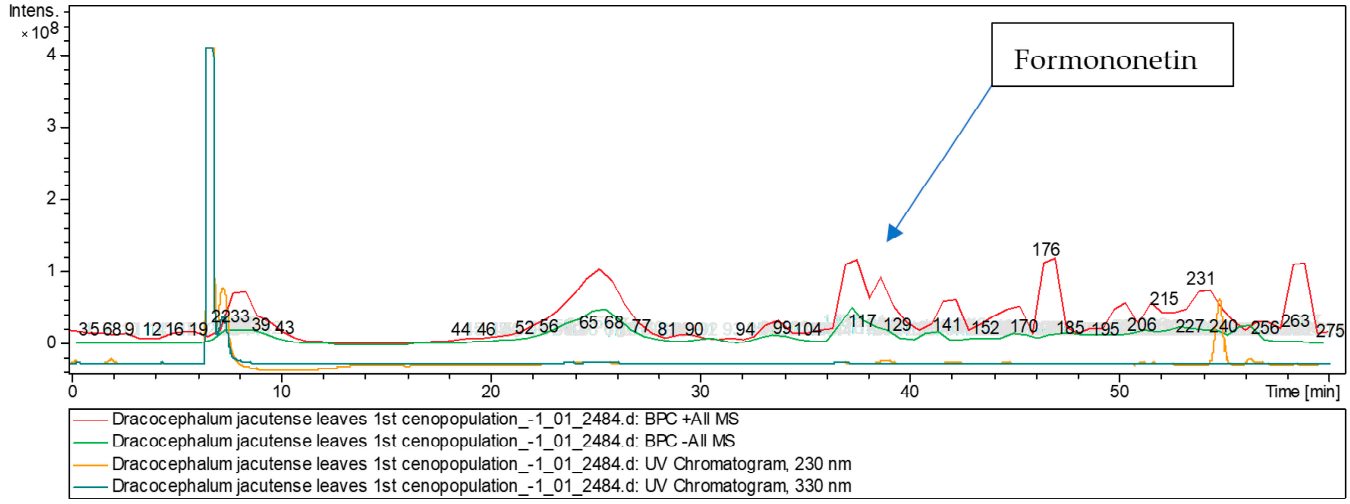

Figure 4. Base peak ion chromatogram in positive ion mode and base peak ion chromatogram in negative ion mode of *D. jacutense* (experiment 2484).

2.1.2. Dihydroxyflavones

The flavones genkwanin (compound **5**) and Dihydroxy-dimethoxy(iso)flavone (compound **10**) have already been characterized as a component of *D. palmatum* [1], *Astragali radix* [20], *Rosmarinus officinalis* [24], propolis [25], etc. These flavones were found in extracts from leaves and flowers of *D. jacutense*. The CID-spectrum in positive ion mode of genkwanin from extracts of leaves of *D. jacutense* is shown in Figure 5.

The $[M + H]^+$ ion produced three fragment ions at *m*/*z* 270, *m*/*z* 242, and *m*/*z* 167 (Figure 5). The fragment ion for *m*/*z* 270 yielded daughter ions at *m*/*z* 242. The fragment ion for *m*/*z* 242 yielded daughter ions at *m*/*z* 213, *m*/*z* 197, and *m*/*z* 124. It was identified in the bibliography in extracts of *D. palmatum* [1,5], *Rosmarinus officinalis* [24], and *Menthae Haplocalycis* [26]. The base peak ion chromatogram in positive ion mode and base peak ion chromatogram in negative ion mode of *D. jacutense* (experiment 2490) are shown in Figure 6.

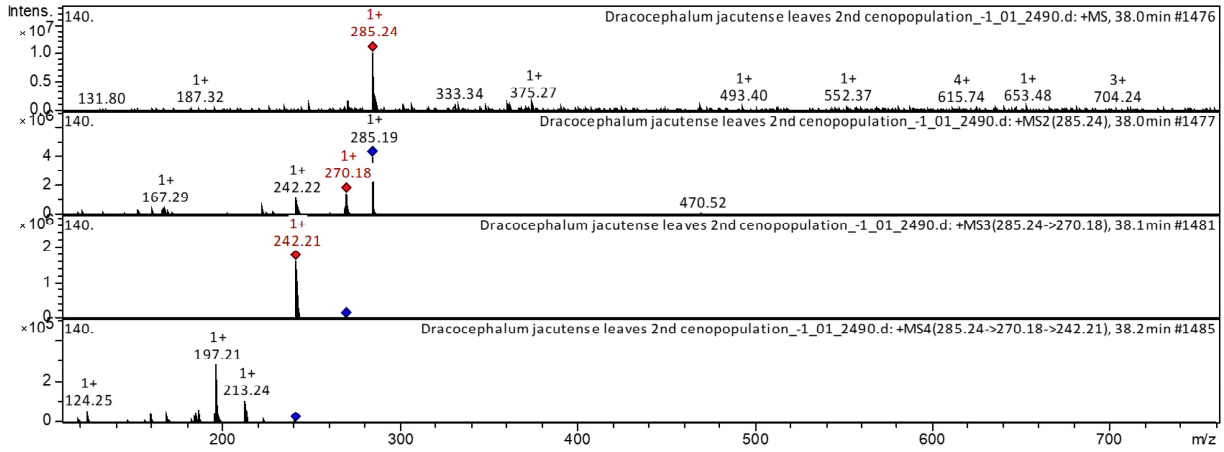

Figure 5. CID-spectrum (experiment 2490) of genkwanin from extracts of leaves of *D. jacutense*, at *m*/*z* 285.

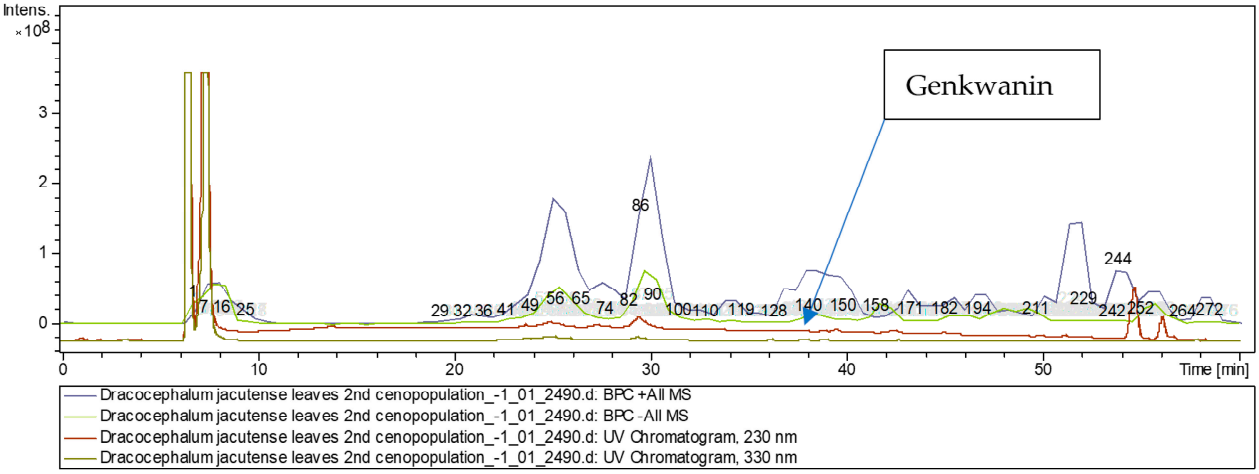

Figure 6. Base peak ion chromatogram in positive ion mode and base peak ion chromatogram in negative ion mode of *D. jacutense* (experiment 2490).

2.1.3. Trihydroxyflavones

The flavones apigenin (compound **2**), diosmetin (compound **7**), and chrysoeriol (compound **8**) have already been characterized as a component of *D. palmatum* [1], *Dracocephalum* [5,14], propolis [25], *D. moldavica* [27], *Rhus coriaria* [28], etc. The flavones diosmetin, and chrysoeriol were found in extracts from the leaves of *D. jacutense,* and the flavone apigenin was found in extracts of the flowers of *D. jacutense.*

2.1.4. Hexahydroxyflavone

The flavone myricetin (compound **12**) has already been characterized as a component of *Vaccinium macrocarpon* [29] and Andean blueberry [30]. This flavone was found in extracts from inflorescences of *D. jacutense.*

2.2. Flavan-3-ols

The flavan-3-ols catechin (compound **46**), (epi)catechin (compound **47**), gallocatechin (compound **48**), catechin-3-*O*-gallate (compound **49**), and epigallocatechin-3-gallate (compound **50**) have already been characterized as a component of *Dracocephalum* [1,5,14], *Sanguisorba officinalis* [31], *C. edulis* [32], *and Camellia kucha* [33]. The flavan-3-ol catechin-3-*O*-gallate was found in extracts from leaves of *D. jacutense.*

3. Discussion

The polyphenol composition distribution table is shown in Table A2 (Appendix B). The comparison table shows the presence of some flavonoids in all three types of extracts, including the polyphenols acacetin, luteolin, cirsimaritin, luteolin 7-*O*-glucoside, kaempferol, astragalin, kaempferol-3-*O*-glucuronide, naringenin, eriodictyol, prunin, eriodictyol 7-*O*-glucoside, rosmarinic acid, and caffeic acid derivative. The results of the research turned out to be more representative, finding 73 polyphenols in extracts from inflorescences, 33 polyphenols in extracts from leaves and 22 polyphenols in extracts from stems of *D. jacutense.*

The analysis shows that the overwhelming presence of the polyphenolic group was found in the inflorescence of *D. jacutense*. Moreover, the majority of this group of flavonoids are flavones, amounting to 21 chemical compounds, 29% of the total compounds of the polyphenol group. In second place in terms of the number of identified polyphenol groups are hydroxybenzoic and hydroxycinnamic acids, amounting to 15 chemical compounds, 21% of the total compounds. In third place in terms of the number of detected compounds are flavonols, amounting to 12 chemical compounds, 16% of the total amount of polyphenols.

It should be noted that some of the chemical compounds found in *D. jacutense* were first tentatively identified in the genus *Dracocephalum*. These include the polyphenol compounds formononetin, calycosin, cirsimaritin, 5,7-dimethoxyluteolin, myricetin, cirsiliol, taxifolin-3-*O*-hexoside, catechin 3-*O*-gallate, epigallocatechin-3-gallate, ferreirin, homoeriodictyol, salvianic acid, protocatechuic acid-*O*-hexoside, etc.

Figure 7 shows a Venn diagram built on the data obtained during the mass spectrometric study of the presence of polyphenols in different parts of the plant. The Venn diagram data shows that 13 compounds (14.6%) are present in all three parts of the plant, 8 polyphenolic compounds (9%) are present in both the inflorescences and in the leaves, and 4 polyphenolic compounds (4.5%) are present in both the inflorescences and in the stems of the plant.

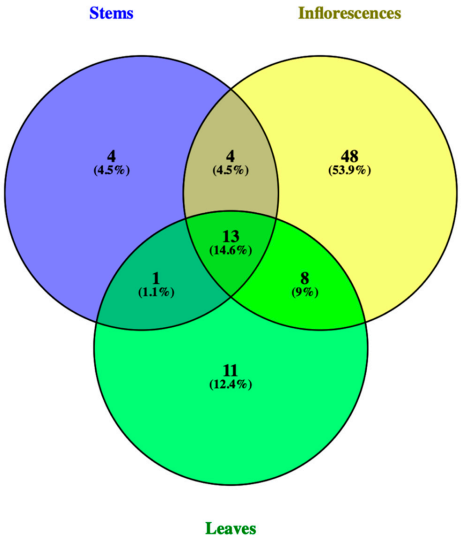

Figure 7. Venn diagram representing a study of the polyphenolic composition of compounds in the inflorescences, leaves, and stems of *D. jacutense*.

A detailed interpretation of the identified compounds in inflorescences, leaves, and stems of *D. jacutense* is presented in Table 2.

Table 2. Detailed interpretation of the identified compounds in inflorescences, leaves, and stems of *D. jacutense*.

Names	Total	Elements
Inflorescences Leaves Stems	13	Prunin; Kaempferol-3-*O*-glucuronide; Naringenin; Eriodictyol; Rosmarinic acid; Caffeic acid derivative; Luteolin 7-*O*-glucoside; Luteolin; Acacetin; Eriodictyol-7-*O*-glucoside; Cirsimaritin; Kaempferol; Astragalin;
Inflorescences Stems	4	Apigenin-7-*O*-glucoside; Apigenin; Acacetin 7-*O*-glucoside; Homoeriodictyol;
Leaves Stems	1	Diosmetin;
Inflorescences Leaves	8	Petunidin; Fraxetin; Isorhamnetin; Genkwanin; Gallocatechin; Apigenin 7-*O*-beta-D-(6″-*O*-malonyl)-glucoside; Catechin; Cyanidin-3-*O*-glucoside;
Stems	4	Phloretin; Acacetin 7-beta-*O*-(6″-acetyl)-glucoside; 1/3/4/5-p-Coumaroylquinic acid; Ellagic acid;
Inflorescences	48	3,4-Dihydroxyhydrocinnamic acid; Epigallocatechin-3-gallate; Chrysoeriol-7-*O*-glucuronide; Delphinidin 3-*O*-rutinoside-5-*O*-glucoside; Protocatechuic acid-*O*-hexoside; Pelargonidin-3-O-glucoside; Eriodictyol-7-*O*-glucuronide; Cyanidin-3-*O*-rutinoside-5-*O*-glucoside; Quercetin; Diosmetin-7-*O*-beta-glucoside; Ferreirin; Quercetrin; (epi)Afzelechin; Kaempferol-3,7-Di-*O*-glucoside; Fraxin; Apigenin 7-*O*-glucuronide; 3,5-Diacetyltambulin; 2,3,4,5-Tetrahydroxybenzoic acid; Salvianic acid A; Apigenin *O*-hexoside; Caffeic acid hexoside dimer; Cirsiliol; Salvianolic acid B; Chlorogenic acid; (epi)catechin; Apigenin-*O*-rhamnoside; Acacetin 7-*O*-beta-D-glucuronide; Cyanidin 3,5-*O*-diglucoside; Umbelliferone; Medioresinol; Malonyl-shisonin; 8,8′-Aryl-Diferulic acid; Phillygenin; p-Coumaric acid; Kaempferol dihexoside rhamnoside; 6,4′-Dimethoxyisoflavone-7-*O*-glucoside; Sagerinic acid; Taxifolin-3-*O*-hexoside; Caffeic acid-4-*O*-beta-D-hexoside; Umbelliferone hexoside; Clerodendranoic acid H; Myricetin; Chrysoeriol *O*-hexoside C-hexoside; 5,7-Dimethoxyluteolin; Isochlorogenic acid; 5-Hydroxy-6,7,8,3′,4′-pentamethoxyflavone; Dihydroquercetin; Kaempferol 3-*O*-rutinoside;
Leaves	11	Gardenin B; Nevadensin; Peonidin-3,5-diglucoside; Isothymusin; Chrysoeriol; Formononetin; Calycosin; Dihydroxy-dimethoxy(iso)flavone; Acacetin 7-*O*-beta-D-(6″-*O*-malonylated)-glucoside; Catechin 3-*O*-gallate; Dimethoxy-trihydroxy(iso)flavone;

The polyphenol composition distribution of *D. jacutense* is summarized in Table A2 (Appendix B). It should be noted that some of the chemical compounds found in *D. jacutense* were first tentatively identified in the genus *Dracocephalum*. These include the polyphenol compounds formononetin, calycosin, cirsimaritin, 5,7-dimethoxyluteolin, myricetin, cirsiliol, taxifolin-3-*O*-hexoside, catechin 3-*O*-gallate, epigallocatechin-3-gallate, ferreirin, homoeriodictyol, salvianic acid, protocatechuic acid-*O*-hexoside, etc.

4. Materials and Methods

4.1. Plant Material

Separate parts (leaves, stems, inflorescences) of *D. jacutense* Peschkova were collected during expedition work in the territory of the Kobyaysky district of Yakutia from July 14 to 19 July 2022 (Figure 8). The aboveground phytomass was collected at the stage of full flowering of the plant. A few seeds were at the stage of milky ripeness and were husked (extracted) from inflorescences during office processing before drying the phytomass. All samples were morphologically authenticated according to the current standard of the State Pharmacopoeia of the Russian Federation [34].

Figure 8. Collection areas of *D. jacutense* Peschkova in the territory of the Kobyaysky district of Yakutia (Russian Federation).

4.2. Chemicals and Reagents

HPLC-grade acetonitrile was purchased from Fisher Scientific (Southborough, UK), and MS-grade formic acid was obtained from Sigma-Aldrich (Steinheim, Germany). Ultrapure water was prepared using a Siemens Ultra Clear system (Siemens Water Technologies, Gunzburg, Germany), and all other chemicals were analytical grade.

4.3. Fractional Maceration

Fractional maceration (repeated infusion) provides for a change in the concentration difference at the phase boundary due to the renewal of the extractant. In this case, the amount of the extractant is divided into portions, and the infusion time is divided into periods. [35]. From 300 g of the sample, 10 g of inflorescences, leaves, and stems were randomly selected for maceration. The total amount of the extractant (ethyl alcohol of reagent grade) was divided into three parts, and the parts of plant were consistently infused in the first, second, and third parts. The solid–solvent ratio was 1:20. The infusion of each part of the *D. jacutense* samples continued for 7 days at room temperature.

4.4. Liquid Chromatography

A Shimadzu LC-20 Prominence HPLC Pump (Shimadzu, Kyoto, Japan) equipped with a UV sensor and C18 silica reverse phase column (4.6 × 150 mm, particle size: 2.7 µm) was used to perform the separation of multicomponent mixtures. The gradient elution program with two mobile phases (A, deionized water; B, CH_3CN with formic acid 0.1% v/v) was as follows: 0, 0–4 min, 100% CH_3CN; 4–60 min, 100–25% CH_3CN; 60–75 min, 25–0% CH_3CN; control washing 50–60 min, 100% A. 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, a temperature of 50 °C, and a total flow rate of 0.25 mL min^{-1}. The liquid chromatography equipment was combined into one line with an ion trap amaZon SL (Bruker Daltoniks, Bremen, Germany) for the identification of biologically active compounds.

4.5. Mass Spectrometry

The chemical compounds were identified by comparing their mass spectra, mass spectrometry fragmentation, and retention time with a home-library database built by the Food Products Group at the Far East Federal University (Russian Federation), based on data from other spectroscopic equipment and data from scientific literature. MS analysis was performed on an ion trap amaZon SL (Bruker Daltonics, Germany) equipped with an ESI source in negative and positive ion modes. The optimized parameters were 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.

5. Conclusions

In total, 128 chemical compounds were identified in the extracts of the rare species *D. jacutense*, which grows only in the environs of the village of Sangar, the Kobyaysky district of Yakutia, using HPLC-MS/MS with an ion trap and database comparison. Of these, 73 polyphenolic compounds were found in extracts from inflorescences, 33 in extracts from leaves, and 22 in extracts from stems. Of the total number of polyphenols found, 14% of the compounds are found in all types of extracts. These include four flavones, three flavanols, four flavanones and two phenolic acids. A large share of the identity for polyphenolic compounds in different parts of *D. jacutense* is noted for flavanones, for which the identity is 80%, then for flavonols (25%), phenolic acids (15%), and flavones (13%).

Thus, in terms of the individuality of the classes of polyphenolic compounds in *D. jacutense*, it can be noted that flavonoids, isoflavanone, phenylpropanoic acid, hydroxycinnamic acids, lignans, hydroxycoumarins, coumarins, and coumarin glucoside are found only in inflorescences, while hydroxybenzoic acid and dihydrochalcone are found only in stems.

All obtained data testify to the unique phytochemical composition of extracts from different parts of *D. jacutense*. This plant species is characterized by a narrow local distribution; at present, only three cenopopulations have been preserved in the sparse steppe phytocenoses of the Kobyaysky district of Yakutia.

Author Contributions: Conceptualization, M.P.R. and Z.M.O.; methodology, Z.G.R., P.S.E. and K.S.G.; software, M.P.R. and K.S.G.; validation, Z.M.O., M.P.R. and K.S.G.; formal analysis, M.P.R. and Z.M.O.; investigation, Z.M.O. and K.S.G.; resources, K.S.G.; data curation, Z.G.R. and P.S.E.; writing—original draft preparation, M.P.R. and Z.M.O.; writing—review and editing, M.P.R. and K.S.G.; visualization, M.P.R. and Z.M.O.; supervision, K.S.G.; project administration, Z.M.O. and K.S.G. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement: Not applicable.

Informed consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

Sample Availability: Not applicable.

Appendix A

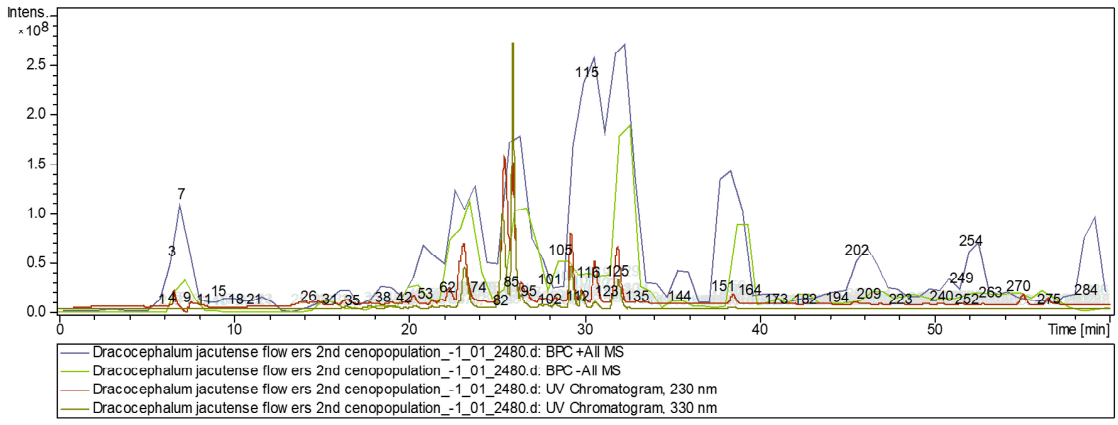

Figure A1. Base peak ion chromatogram in positive ion mode (violet line), base peak ion chromatogram in negative ion mode (green line), UV Chromatogram, 230 nm (brown line), UV Chromatogram, 330 nm (gray line) of extracts from inflorescences of *D. jacutense*.

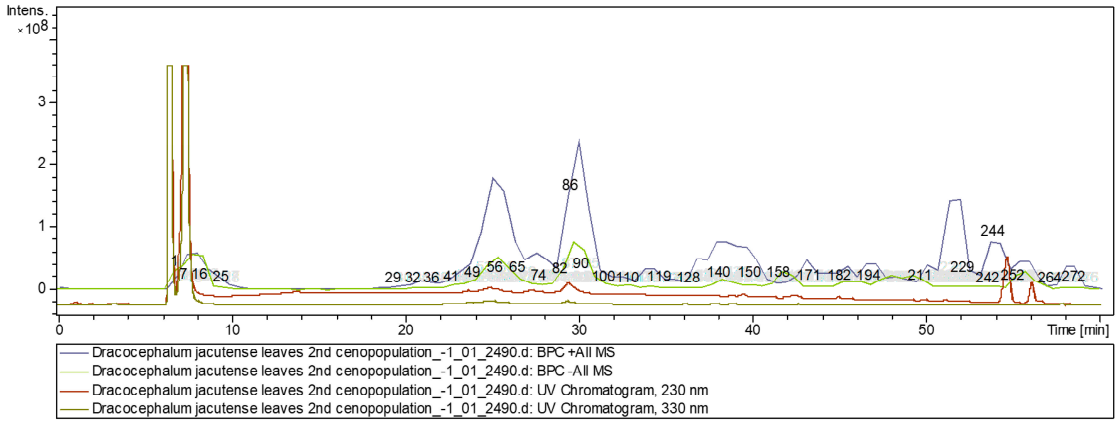

Figure A2. Base peak ion chromatogram in positive ion mode (violet line), base peak ion chromatogram in negative ion mode (green line), UV Chromatogram, 230 nm (brown line), UV Chromatogram, 330 nm (gray line) of extracts from leaves of *D. jacutense*.

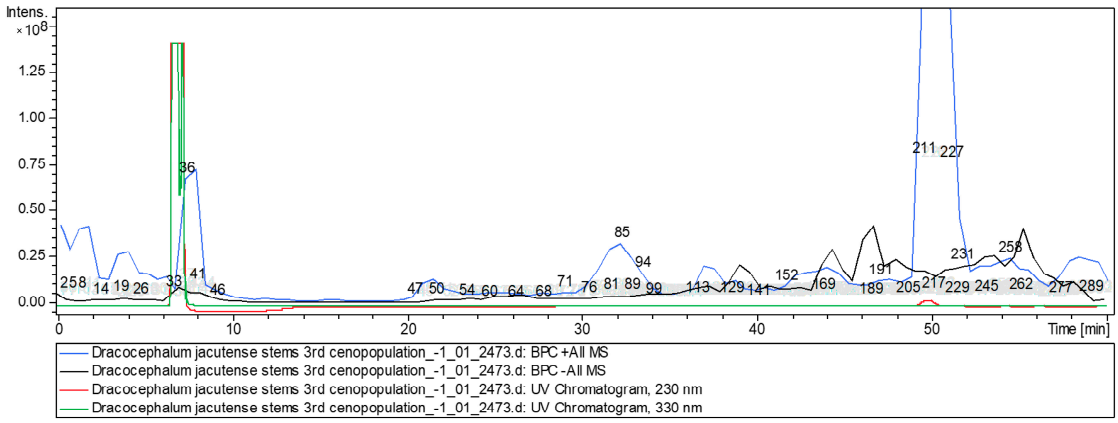

Figure A3. Base peak ion chromatogram in positive ion mode (violet line), base peak ion chromatogram in negative ion mode (gray line), UV Chromatogram, 230 nm (red line), UV Chromatogram, 330 nm (green line) of extracts from stems of *D. jacutense*.

Table A1. Compounds identified from the extracts of *D. jacutense* in positive and negative ionization modes by HPLC-ion trap-MS/MS.

No	Class of Compounds	Identified Compounds	Formula	Retention Time, min	Molecular Ion $[M-H]^-$	Molecular Ion $[M+H]^+$	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
		POLYPHENOLS								
1	Flavone	**Formononetin** [Biochanin B; Formononetol] *	$C_{16}H_{12}O_4$	**31.9**		**269**	**213**	**170; 156; 129**	**141**	*Astragali Radix* [19–21]; Huolisu Oral Liquid [22]
2	Flavone	**Apigenin** [5,7-Dixydroxy-2-(40Hydroxyphenyl)-4H-Chromen-4-One]	$C_{15}H_{10}O_5$	**8.0**		**269**	**225**	**181**	**117**	*D. palmatum* [1]; *Dracocephalum* [5]; Andean blueberry [30]; *Lonicera japonicum* [36]; Mexican lupine species [37]
3	Flavone	**Acacetin** [Linarigenin; Buddleoflavonol]	$C_{16}H_{12}O_5$	**35.7**		**285**	**268**	**211; 143**		*D. palmatum* [1]; *Dracocephalum* [5]; *Mentha* [26]; *D. moldavica* [27]; Mexican lupine species [37]
4	Flavone	**Calycosin** [3′-Hydroxyformononetin] *	$C_{16}H_{12}O_5$	**38.5**		**285**	**253; 242; 225; 200**	**235; 221; 209; 203**		*Astragali Radix* [19–21]; Huolisu Oral Liquid [22]
5	Flavone	**Genkwanin** [Gengkwanin; Puddumetin; Apigenin 7-Methyl Ether]	$C_{16}H_{12}O_5$	**38.0**		**285**	**165**			*D. palmatum* [1]; *Rosmarinus officinalis* [24]; *Mentha* [27]
6	Flavone	**Luteolin**	$C_{15}H_{10}O_6$	**7.9**		**287**	**286; 153**	**171**	**153**	*D. palmatum* [1]; *Dracocephalum* [5]; *Lonicera japonicum* [36]
7	Flavone	**Diosmetin** [Luteolin 4′-Methyl Ether; Salinigricoflavonol]	$C_{16}H_{12}O_6$	**8.8**		**301**	**286**	**258**		*Dracocephalum* [1]; Mentha [26]; *D. moldavica* [27]; Andean blueberry [30]; *Lonicera japonicum* [36]
8	Flavone	**Chrysoeriol** [Chryseriol]	$C_{16}H_{12}O_6$	**9.0**		**301**	**286; 167**	**258**	**203**	*D. jacutense* [14]; Propolis [25]; *Rhus coriaria* [28]
9	Flavone	**Cirsimaritin** [Scrophulein; 4′,5-Dihydroxy-6,7-Dimethoxyflavone; 7-Methylcapillarisin] *	$C_{17}H_{14}O_6$	**30.9**		**315**	**282**	**254**	**226; 119**	*Rosmarinus officinalis* [24]; *Ocimum* [38]
10	Flavone	**Dihydroxy-dimethoxy(iso)flavone** *	$C_{17}H_{14}O_6$	**38.1**		**315**	**300; 272**	**272**	**257; 243; 217; 201; 185; 167**	*Astragali radix* [21]; *Rosmarinus officinalis* [24]; Propolis [25]
11	Flavone	**5,7-Dimethoxyluteolin** *	$C_{17}H_{14}O_6$	**38.2**	**313**		**285; 213; 185**	**185; 145**		*Syzygium aromaticum* [39]; *Rosa rugosa* [40]
12	Flavone	**Myricetin** *	$C_{15}H_{10}O_8$	**2.9**		**319**	**291; 219; 143**	**191; 143**	**173**	Propolis [25]; *Vaccinium macrocarpon* [29]; Andean blueberry [30]; *Sanguisorba officinalis* [31]; *F. glaucescens* [32]
13	Flavone	**Isothymusin**	$C_{17}H_{14}O_7$	**24.2**		**331**	**303; 203**	**203; 275**	**203**	*D. palmatum* [1]
14	Flavone	**Cirsiliol** *	$C_{17}H_{14}O_7$	**34.2**		**331**	**316; 298; 233; 157**	**297; 187; 134**		*Ocimum* [38]
15	Flavone	**Dimethoxy-trihydroxy(iso)flavone** *	$C_{17}H_{14}O_7$	**28.4**		**331**	**316; 226**	**298; 226**	**270; 226**	Propolis [25]; Jatropha [41]
16	Flavone	**Nevadensin**	$C_{18}H_{16}O_7$	**34.1**		**345**	**312; 241; 147**	**284; 269**	**269; 213; 135**	*Dracocephalum* [1]; *Mentha* [26]; *Ocimum* [40]

Table A1. *Cont.*

No	Class of Compounds	Identified Compounds	Formula	Retention Time, min	Molecular Ion $[M-H]^-$	Molecular Ion $[M+H]^+$	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
		POLYPHENOLS								
17	Flavone	**Gardenin B** [Demethyltangeretin] *	$C_{19}H_{18}O_7$	**40.3**		**359**	**326; 298**	**298**	**270; 239; 162**	*Mentha* [26]; *Ocimum* [38]; *Actinocarya tibetica* [42]
18	Flavone	**5-Hydroxy-6,7,8,3′,4′-pentamethoxyflavone** *	$C_{20}H_{20}O_8$	**40.2**		**389**	**356**	**313**	**295; 221; 149**	*Mentha* [26]
19	Flavone	**Apigenin *O*-hexoside**	$C_{21}H_{20}O_{10}$	**25.5**	**431**		**269**	**269; 225; 149**	**224; 157**	*D. palmatum* [1]; *F. glaucescens*; *F. pottsii* [32]; *Chamaecrista nictitans* [43]
20	Flavone	**Apigenin-7-*O*-glucoside** [Apigetrin; Cosmosiin]	$C_{21}H_{20}O_{10}$	**25.8**		**433**	**271**	**153**		*D. palmatum* [1]; *Dracocephalum* [5]; *Mexican lupine species* [37]; *Mentha spicata* [44]
21	Flavone	**Apigenin 7-*O*-glucuronide**	$C_{21}H_{18}O_{11}$	**25.5**		**447**	**271**	**153**	**271; 171**	*Dracocephalum* [5]; *Pear* [45]; Bougainvillea [46]
22	Flavone	**Acacetin 7-*O*-glucoside** [Tilianin]	$C_{22}H_{22}O_{10}$	**30.1**		**447**	**285; 149**	**270**	**242**	*D. palmatum* [1]; *Dracocephalum* [5]; Bougainvillea [46]
23	Flavone	**Luteolin 7-*O*-glucoside** [Cynaroside; Luteoloside]	$C_{21}H_{20}O_{11}$	**23.6**		**449**	**287; 199**	**153**		*Dracocephalum* [5]; *Lonicera japonicum* [36]; Pear [45]; *Passiflora incarnata* [47]
24	Flavone	**Acacetin 7-*O*-beta-D-glucuronide**	$C_{22}H_{20}O_{11}$	**24.5**		**461**	**270; 242; 153**	**242**		*Dracocephalum* [5]; *D. moldavica* [27]
25	Flavone	**6,4′-Dimethoxyisoflavone-7-*O*-glucoside** *	$C_{23}H_{24}O_{10}$	**30.1**		**461**	**285**	**270; 242; 153**	**242**	*Astragali radix* [19–21]
26	Flavone	**Diosmetin-7-*O*-beta-glucoside**	$C_{22}H_{22}O_{11}$	**9.3**		**463**	**287**	**168**	**123**	*Dracocephalum* [5]; *D. moldavica* [27]; *Oxalis corniculata* [48]
27	Flavone	**Apigenin-*O*-rhamnoside** *	$C_{22}H_{22}O_{11}$	**27.1**		**463**	**273; 153**	**153; 171**	**171**	*Passion fruit* [49]
28	Flavone	**Chrysoeriol-7-*O*-glucuronide** *	$C_{22}H_{20}O_{12}$	**26.5**		**477**	**301**	**286**	**258**	Propolis [25]
29	Flavone	**Acacetin 7-beta-*O*-(6″-acetyl)-glucoside**	$C_{24}H_{24}O_{11}$	**6.6**		**489**	**472; 354; 296; 223**			*D. moldavica* [27]
30	Isoflavone	**Apigenin 7-*O*-beta-D-(6″-*O*-malonyl)-glucoside**	$C_{24}H_{22}O_{13}$	**43.1**		**519**	**184; 500; 466; 371; 258**	**125**		*Dracocephalum* [5]; *D. moldavica* [27]; *Zostera marina* [50]
31	Flavone	**Acacetin 7-*O*-beta-D-(6″-*O*-malonylated)-glucoside**	$C_{25}H_{24}O_{13}$	**29.4**		**533**	**371; 285; 191; 165**	**353; 285; 191; 165**	**147**	*D. moldavica* [27]
32	Flavone	**Chrysoeriol *O*-hexoside *C*-hexoside** *	$C_{28}H_{32}O_{16}$	**42.8**		**625**	**445; 463; 377; 347**	**357; 217**		*Triticum aestivum L.* [51,52]
33	Flavonol	**Kaempferol** [3,5,7-Trihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one]	$C_{15}H_{10}O_6$	**5.5**		**287**	**269; 202**	**233; 205**	**216**	*Dracocephalum* [5]; *Rhus coriaria* [28]; Andean blueberry [30]; *Lonicera japonica* [36]; Rapeseed petals [53]
34	Flavonol	**Quercetin**	$C_{15}H_{10}O_7$	**9.0**		**303**	**285; 228; 165**	**229; 165**	**141**	Propolis [25]; *Rhus coriaria* [28]; *Vaccinium macrocarpon* [29,54]

Table A1. *Cont.*

No	Class of Compounds	Identified Compounds	Formula	Retention Time, min	Molecular Ion $[M - H]^-$	Molecular Ion $[M + H]^+$	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
		POLYPHENOLS								
35	Flavonol	**Dihydroquercetin** (Taxifolin; Taxifoliol)	$C_{15}H_{12}O_7$	**28.0**		**305**	**287**	**286; 186**	**185**	*Dracocephalum* [5]; Andean blueberry [30]; *Camellia kucha* [33]
36	Flavonol	**Isorhamnetin** [Isorhamnetol; Quercetin 3′-Methyl ether; 3-Methylquercetin] *	$C_{16}H_{12}O_7$	**45.4**		**317**	**299; 257; 214; 173**	**281; 188**		*Rosmarinus officinalis* [24]; Propolis [25]; *Vaccinium macrocarpon* [29]; Andean blueberry [30]; *Embelia* [55]
37	Flavonoid	**3,5-Diacetyltambulin** *	$C_{22}H_{20}O_9$	**22.3**	**427**		**381; 249**	**249; 161**	**161; 124**	*A. cordifolia* [32]
38	Flavonol	**Astragalin** [Kaempferol 3-*O*-glucoside; Astragaline]	$C_{21}H_{20}O_{11}$	**31.0**	**447**		**285; 327**	**241**	**199**	*Dracocephalum* [5]; *Camellia kucha* [33]; *Lonicera japonicum* [36]; Mexican lupine species [37]; *pear* [45]
39	Flavonol	**Quercitrin** [Quercetin 3-*O*-rhamnoside; Quercetrin] *	$C_{21}H_{20}O_{11}$	**24.2**		**449**	**302**	**202; 174; 127**	**175**	Propolis [25]; *Rhus coriaria* [28]; *Vaccinium macrocarpon* [29,54]; *Camellia kucha* [33]; *Bryophyllum pinnatum* [48]; *Embelia* [55]; *Euphorbia hirta* [56]
40	Flavonol	**Kaempferol-3-*O*-glucuronide**	$C_{21}H_{18}O_{12}$	**23.9**		**463**	**287**	**268; 169**	**241; 119**	*Dracocephalum* [5]; *Rhus coriaria* [28]; *A. cordifolia*; *G. linguiforme* [32]
41	Flavonol	**Taxifolin-3-*O*-hexoside** [Dihydroquercetin-3-*O*-hexoside] *	$C_{21}H_{22}O_{12}$	**18.5**		**467**	**305; 259; 195; 153**	**259; 195; 153**	**231; 149**	Andean blueberry [30]; *Euphorbia hirta* [56]; millet grains [57]
42	Flavonol	**Kaempferol 3-*O*-rutinoside**	$C_{27}H_{30}O_{15}$	**28.3**		**595**	**287; 345; 389; 449**	**287; 245; 153**	**171**	*Dracocephalum* [5]; *Rhus coriaria* [28]; *Camellia kucha* [33]; *Lonicera japonica* [36]; Pear [45]
43	Flavonol	**Kaempferol-3,7-Di-*O*-glucoside** *	$C_{27}H_{30}O_{16}$	**15.8**		**611**	**287; 449**	**287; 213; 185; 137**	**185; 157**	Rapeseed petals [53]; Tomato [58]; *Taraxacum officinale* [59]
44	Flavonol	**Kaempferol dihexoside rhamnoside** *	$C_{33}H_{40}O_{20}$	**21.5**		**757**	**595; 287**	**287; 213; 137**	**185; 168**	*C. edulis* [32]
45	Flavan-3-ol	**(epi)Afzelechin** *	$C_{15}H_{14}O_5$	**8.7**		**275**	**228; 210; 175; 157; 132**	**212; 203; 183; 170**	**194**	*A. cordifolia*; *F. glaucescens*; *F. herrerae* [32]; *Cassia granidis* [60]; *Cassia abbreviata* [61]
46	Flavan-3-ol	**Catechin** [D-Catechol] *	$C_{15}H_{14}O_6$	**34.4**		**291**	**207; 123**	**123**		*C. edulis* [32]; *Camellia kucha* [33]; *Vaccinium macrocarpon* [54]; Actinidia [62]
47	Flavan-3-ol	**(epi)catechin**	$C_{15}H_{14}O_6$	**18.6**		**291**	**273; 117**	**255; 145**		*Dracocephalum* [5]; Andean blueberry [30]; *C. edulis* [32]; *Camellia kucha* [33]
48	Flavan-3-ol	**Gallocatechin** [+(−)Gallocatechin]	$C_{15}H_{14}O_7$	**8.3**		**307**	**289**	**259**		*Dracocephalum* [5]; *G. linguiforme* [32]; *Rhodiola rosea* [63]

Table A1. *Cont.*

No	Class of Compounds	Identified Compounds	Formula	Retention Time, min	Molecular Ion $[M - H]^-$	Molecular Ion $[M + H]^+$	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
		POLYPHENOLS								
49	Flavan-3-ol	**Catechin 3-*O*-gallate** *	$C_{22}H_{18}O_{10}$	**7.2**		**443**	**273; 205**	**263; 211; 171; 143**		*Camellia kucha* [33]; Rhododendron [64]; *Terminalia arjuna* [65]
50	Flavan-3-ol	**Epigallocatechin-3-gallate** *	$C_{22}H_{18}O_{11}$	**6.3**		**459**	**290; 207**	**207; 123**		*F. glaucescens* [32]; *Camellia kucha* [33]; *Clidemia rubra* [66]
51	Flavanone	**Naringenin** [Naringetol; Naringenine]	$C_{15}H_{12}O_5$	**8.4**		**273**	**153; 256**	**125**		*D. palmatum* [1]; *Dracocephalum* [5]; Andean blueberry [30]; Mexican lupine species [37]; Rapeseed petals [53]
52	Flavanone	**Eriodictyol** [3′,4′,5,7-tetrahydroxy-flavanone]	$C_{15}H_{12}O_6$	**20.5**		**289**	**163; 271**	**145**	**117**	*D. palmatum* [1]; *Dracocephalum* [5]; Andean blueberry [30]; *Mentha* [44]
53	Isoflavanone	**Ferreirin** *	$C_{16}H_{14}O_6$	**27.0**		**303**	**177; 285**	**163**	**135**	*Mentha* [44]
54	Trihydroxyflavanone	**Homoeriodictyol** *	$C_{16}H_{14}O_6$	**27.1**		**303**	**285; 177**	**163**	**145**	*Mentha* [26]
55	Flavanone	**Prunin** [Naringenin-7-*O*-glucoside]	$C_{21}H_{22}O_{10}$	**22.7**	**433**		**271; 151**	**269; 151**		*D. palmatum* [1]; *Dracocephalum* [5]; Rapeseed petals [53]
56	Flavanone	**Eriodictyol-7-O-glucoside** [Pyracanthoside; Miscanthoside]	$C_{21}H_{22}O_{11}$	**6.3**	**449**		**285; 151**	**243; 151**		*D. palmatum* [1]; *Dracocephalum* [5]; *Mentha* [44]
57	Flavanone	**Eriodictyol-7-O-glucuronide** *	$C_{21}H_{20}O_{12}$	**23.3**	**463**		**285; 151**	**285; 243; 151**		*Thymus vulgaris* [67]
58	Hydroxycinnamic acid	***p*-Coumaric acid** [4-Hydroxycinnamic acid; P-Hydroxycinnamic acid; 4-Coumarate] *	$C_9H_8O_3$	**16.7**		**165**	**147**	**119**		*F. pottsii* [32]; *Rhus coriaria* [28]; Andean blueberry [30]; Rapeseed petals [53]; *Vaccinium macrocarpon* [54]
59	Hydroxycinnamic acid	**3,4-Dihydroxyhydrocinnamic acid***	$C_9H_{10}O_4$	**33.6**		**183**	**137**			*Eucalyptus Globulus* [68]
60	Phenolic acid	**2,3,4,5-Tetrahydroxybenzoic acid** [2-Hydroxygallussaure; 3,4,5-Trihydroxysalicylic acid] *	$C_7H_6O_6$	**5.9**		**187**	**144**			PubChem
61	Phenolic acid	**Salvianic acid A** [Danshensu] *	$C_9H_{10}O_5$	**15.3**	**197**		**179; 135**	**135**		Huolisu Oral Liquid [22]; *Hedyotis diffusa* [69]
62	Hydroxybenzoic acid	**Ellagic acid** [Benzoaric acid; Elagostasine; Lagistase; Eleagic acid]	$C_{14}H_6O_8$	**5.5**	**301**		**284**	**221**	**112**	*Dracocephalum* [5]; *Rhus coriaria* [28]; *Eucalyptus Globulus* [68]
63	Phenolic acid	**Protocatechuic acid-*O*-hexoside** *	$C_{13}H_{16}O_9$	**16.1**	**315**		**153; 123**	**123**		*Rhus coriaria* [28]; *Euphorbia hirta* [56]; *Eucalyptus Globulus* [68]
64	Phenolic acid	**Caffeic acid-4-*O*-beta-D-hexoside** [Caffeoyl-*O*-hexoside]	$C_{15}H_{18}O_9$	**6.7**	**341**		**179; 119**	**143; 131**		*Dracocephalum* [5]; pear [45]; *Cherimoya, papaya* [49]; *Sasa veitchii* [70]

Table A1. *Cont.*

No	Class of Compounds	Identified Compounds	Formula	Retention Time, min	Molecular Ion $[M - H]^-$	Molecular Ion $[M + H]^+$	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
		POLYPHENOLS								
65	Phenolic acid	**Chlorogenic acid** [3-*O*-Caffeoylquinic acid]	$C_{16}H_{18}O_9$	**17.9**		**355**	**179; 338; 227**	**127**		*D. palmatum* [1]; *Vaccinium macrocarpon* [29,54]; Andean blueberry [30]; *Rhus coriaria* [28]; *Camellia kucha* [33]; *Lonicera japonica* [36]; Bougainvillea [46]; Rapeseed petals [53]
66	Phenolic acid	**Isochlorogenic acid** *	$C_{16}H_{18}O_9$	**29.5**		**355**	**323; 269; 165**	**295; 208; 133**	**295; 249; 221**	*Actinidia* [62]
67	Phenolic acid	**Rosmarinic acid**	$C_{18}H_{16}O_8$	**24.5**	**359**		**161**	**133**		*D. palmatum* [1]; *Mentha* [26]; *Dracocephalum* [5]; *Salvia miltiorrhiza* [71]
68	Phenolic acid	**Caffeic acid derivative**	$C_{16}H_{18}O_9Na$	**6.8**	**377**		**341; 215**	**179**		*Dracocephalum* [5]; Bougainvillea [46]
69	Phenolic acid	**1/3/4/5-*p*-Coumaroylquinic acid** * + C_2H_2O	$C_{18}H_{20}O_9$	**7.3**		**381**	**321; 275; 233**	**260; 218; 143**		*Actinidia* [62]
70	Phenolic acid	**8,8′-Aryl-Diferulic acid** *	$C_{20}H_{18}O_8$	**36.9**	**385**		**193; 285**	**193; 161**		millet grains [57]
71	Phenolic acid	**Caffeic acid hexoside dimer** *	$C_{31}H_{40}O_{17}$	**6.9**	**683**		**341**	**179; 161**	**143**	*Strawberry, Lemon, Cherimoya, Passion fruit* [49]
72	Phenolic acid	**Salvianolic acid B** [Danfensuan B] *	$C_{36}H_{30}O_{16}$	**26.3**	**717**		**519; 321**	**321; 279**	**279; 185**	Huolisu Oral Liquid [22]; *Mentha* [26]; Bougainvillea [46]; *Salvia miltiorrhiza* [71]
73	Phenylpropanoic acid	**Sagerinic acid**	$C_{36}H_{32}O_{16}$	**25.7**	**719**		**359**	**161; 197**	**133**	*D. palmatum* [1]; Huolisu Oral Liquid [22]; *Rosmarinus officinalis* [24]; *Mentha* [26]; *Salvia miltiorrhiza* [71]
74	Phenolic acid	**Clerodendranoic acid H** *	$C_{36}H_{32}O_{16}$	**26.1**	**719**		**359**	**161**		*Lepechinia* [72]
75	Lignan	**Phillygenin** [Sylvatesmin; Phyllygenol; Forsythigenol] *	$C_{21}H_{24}O_6$	**16.7**	**371**		**163; 325**	**119**		Lignans [73]
76	Lignan	**Medioresinol** *	$C_{21}H_{24}O_7$	**20.8**	**387**		**207; 163; 119**	**163**		*Rosmarinus officinalis* [24]; Lignans [73]; *Bituminaria* [74]
77	Dihydrochalcone	**Phloretin** [Dihydronaringenin; Phloretol] *	$C_{15}H_{14}O_5$	**7.6**		**275**	**255; 229; 131**	**237; 209; 164**		*G. linguiforme* [32]; *Rosa rugosa* [40]; *Punica granatum* [75]
78	Hydroxycoumarin	**Umbelliferone** [Skimmetin; Hydragin] *	$C_9H_6O_3$	**26.2**		**163**	**145; 135; 117**	**117**		*Sanguisorba officinalis* [31]; *F. glaucescens* [32]; *Zostera marina* [50]; *Actinidia* [62]
79	Coumarin	**Fraxetin** [7,8-Dihydroxy-6-methoxycoumarin] *	$C_{10}H_8O_5$	**20.5**		**209**	**191; 149**	**149**	**147**	*Jatropha* [41]; *Embelia* [56]; *Actinidia* [62]
80	Hydroxycoumarin	**Umbelliferone hexoside** *	$C_{15}H_{16}O_8$	**7.1**		**325**	**307; 288; 271; 253; 241**	**127; 118**		*G. linguiforme* [32]
81	Coumarin glycoside	**Fraxin** [Fraxetin-8-O-glucoside] *	$C_{16}H_{18}O_{10}$	**7.3**		**371**	**209**			*Rosa davurica* [40]; *Actinidia* [62]
82	Anthocyanidin	**Petunidin**	$C_{16}H_{13}O_{7+}$	**35.6**		**318**	**166; 300**	**121**		*Dracocephalum* [1]; *A. cordifolia*; *C. edulis* [32]

Table A1. *Cont.*

No	Class of Compounds	Identified Compounds	Formula	Retention Time, min	Molecular Ion $[M-H]^-$	Molecular Ion $[M+H]^+$	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
		POLYPHENOLS								
83	Anthocyanidin	**Pelargonidin-3-*O*-glucoside (callistephin)**	$C_{21}H_{21}O_{10}$	**25.8**		**433**	**271**	**153; 225**	**171**	*Dracocephalum* [1]; *Triticum aestivum* [76]; *Rubus ulmifolius* [77]
84	Anthocyanidin	**Cyanidin-3-*O*-glucoside** [Cyanidin 3-*O*-beta-D-Glucoside; Kuromarin]	$C_{21}H_{21}O_{11}+$	**7.5**		**449**	**287**	**153**		*Dracocephalum* [1]; *Triticum aestivum* [76]; *Malpighia emargınata* [78]
85	Anthocyanidin	**Cyanidin 3,5-*O*-diglucoside** *	$C_{27}H_{31}O_{16}$	**16.1**		**611**	**287; 449**	**287; 241; 213; 175; 149**	**213; 185; 172; 157; 145**	Rapeseed petals [53]; Muscadine pomace [79]; *Berberis microphylla* [80]
86	Anthocyanidin	**Peonidin-3,5-diglucoside** [Peonin; Peonidin 3-Glucoside-5-Glucoside] *	$C_{28}H_{33}O_{16}$	**44.1**		**625**	**463; 374; 301**	**445; 373**		*Triticum aestivum* [76]; Muscadine pomace [79]
87	Anthocyanidin	**Cyanidin-3-*O*-rutinoside-5-*O*-glucoside** *	$C_{33}H_{41}O_{20}$	**21.1**		**757**	**287; 449; 595**	**287; 213; 137**	**185**	*Camellia kucha* [33]
88	Anthocyanidin	**Delphinidin 3-*O*-rutinoside-5-*O*-glucoside** *	$C_{33}H_{41}O_{21}$	**20.5**		**773**	**303; 465; 611**	**257; 303; 229; 165**	**257; 229; 201; 116**	*Berberis microphylla* [80]; *Iris dichotoma* [81]; *Solanium nigrum* [82]
89	Anthocyanidin	**Malonyl-shisonin** *	$C_{39}H_{39}O_{21}+$	**23.0**		**843**	**595; 535; 491; 287**	**287; 259; 213; 147**	**213; 185**	*Perilla frutescens* [83,84]
		OTHERS								
90	Benzenediol	**Catechol derivative** *	$C_6H_6O_3$	**5.9**		**127**	**124; 118**			*Embelia* [55]
91	Amino acid	**Phenylalanine** [L-Phenylalanine] *	$C_9H_{11}NO_2$	**8.7**		**166**	**120**			*G. linguiforme* [32]; *Camellia kucha* [33]; *Lonicera japonica* [36]; Rapeseed petals [53]; *Potato leaves* [85]
92	Amino acid	**Tyrosine** [(2S)-2-Amino-3-(4-Hydroxyphnyl)Propanoic acid] *	$C_9H_{11}NO_3$	**8.1**		**182**	**165; 150**	**113**		*Euphorbia hirta* [56]; *Hylocereus polyrhizus* [86]
93	Monobasic carboxylic acid	**Hydroxyphenyllactic acid** *	$C_9H_{10}O_4$	**17.6**	**181**		**163; 135**	**119**		*Mentha* [87]
94	Amino acid	**L-Tryptophan** [Tryptophan; (S)-Tryptophan]	$C_{11}H_{12}N_2O_2$	**9.2**		**205**	**188**	**144**	**118**	*Dracocephalum* [1]; *Camellia kucha* [33]; *Rosa acicularis* [40]; Rapeseed petals [53]
95	Omega-5 fatty acid	**Myristoleic acid** [Cis-9-Tetradecanoic acid]	$C_{14}H_{26}O_2$	**20.5**		**227**	**209**	**139**		*Dracocephalum* [1]; *F. glaucescens* [32]
96	Xanthone	**Mangiferitin** [Norathyriol; 1,3,6,7-Tetrahydroxyxanthone] *	$C_{13}H_8O_6$	**9.7**		**261**	**193; 135**	**179; 124**	**111**	*Rhus coriaria* [28]
97	Ribonucleoside composite of adenine (purine)	**Adenosine**	$C_{10}H_{13}N_5O_4$	**9.2**		**268**	**136; 258**			*Dracocephalum* [1]; *Lonicera japonica* [36]

Table A1. *Cont.*

No	Class of Compounds	Identified Compounds	Formula	Retention Time, min	Molecular Ion $[M - H]^-$	Molecular Ion $[M + H]^+$	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
		POLYPHENOLS								
98	Omega 3-fatty acid	**Stearidonic acid** [6,9,12,15-Octadecatetraenoic acid; Moroctic acid] *	$C_{18}H_{28}O_2$	**17.9**		**277**	**177; 247**	**175**		*Rhus coriaria* [28]; *G. linguiforme* [32]; Jatropha [41]; *Salviae miltiorrhiza* [88]
99	Omega 3-fatty acid	**Linolenic acid** [Alpha-Linolenic acid; Linolenate] *	$C_{18}H_{30}O_2$	**10.9**		**279**	**219; 259**	**159**		Jatropha [41]; *Salviae miltiorrhiza* [88]
100	Fatty amide	**Linoleic acid amide** *	$C_{18}H_{33}NO$	**8.2**		**280**	**262; 244**	**244; 234; 216; 196; 172**	**196; 168; 151**	Propolis [25]; *Rhus coriaria* [28]
101	Fatty amide	**Oleamide** *	$C_{18}H_{35}NO$	**7.1**		**282**	**263; 246; 192**	**245; 228; 217; 197; 170**		Propolis [25]
102	Alkaloid	**Mesembrenol**	$C_{17}H_{23}NO_3$	**35.6**		**290**	**242; 122**	**184; 149**		*Dracocephalum* [1]; *Sceletium* [89]
103	Diterpenoid naphthoquinone	**Tanshinone IIA** [Tanshinone B] *	$C_{19}H_{18}O_3$	**8.1**		**295**	**277; 259; 193; 149**	**259; 241; 199; 149**	**241; 147**	Huolisu Oral Liquid [22]
104	Unsaturated hydroxy fatty acid	**Hydroxyoctadecatrienoic acid***	$C_{18}H_{30}O_3$	**44.9**	**293**		**275; 235; 185; 172**	**231; 205; 177**	**231; 163**	Jatropha [41]
105	Polyunsaturated fatty acid	**Alpha-Kamlolenic Acid** [18-Hydroxy-9Z,11E,13E-Octadecatrienoic Acid] *	$C_{18}H_{30}O_3$	**43.9**	**293**		**275; 231; 171**	**231; 177**	**231**	*G. linguiforme*; *F. glaucescens*; *F. pottsii* [32]
106	Essential fatty acid	**Hydroxyoctadecadienoic acid** *	$C_{18}H_{32}O_3$	**46.5**	**295**		**277; 251; 195; 171; 152**	**233; 179; 155**		*A. cordifolia*; *F. glaucescens*; *F. herrerae* [32]; *Jatropha* [41]
107	Pterocarpans	**3-Hydroxy-9,10-dimethoxypterocarpan**	$C_{17}H_{16}O_5$	**28.9**		**301**	**286; 257; 229; 177; 153**	**163; 149**	**145**	*Astragali radix* [19–21]; Huolisu Oral Liquid [22]
108		**p-hydroxyphenacyl-β-D-glucopyranoside** *	$C_{14}H_{18}O_8$	**31.1**	**313**		**161; 213**	**133; 161**	**133**	*Rhodiola crenulata* [18,90]
109	Long-chain fatty acid	**Hydroxy eicosenoic acid** *	$C_{20}H_{38}O_3$	**42.8**		**327**	**295; 268; 181; 125**	**268**	**237; 135**	*A. cordifolia*; *F. pottsii* [32]
110	Amino acid	**Fructose-phenylalanine** *	$C_{15}H_{21}NO_7$	**8.1**		**328**	**310; 292**	**292; 264; 244; 216; 198; 178**	**244; 216; 198; 171; 156**	Potato leaves [85]
111	Oxylipins	**9,10-Dihydroxy-8-oxooctadec-12-enoic acid** [oxo-DHODE; oxo-Dihydroxy-octadecenoic acid]	$C_{18}H_{32}O_5$	**8.1**	**327**		**229**	**209**	**183**	*Dracocephalum* [1]; *Phyllostachys nigra* [70]; *Bituminaria* [74]
112	Oxylipins	**13- Trihydroxy-Octadecenoic acid** [THODE]	$C_{18}H_{34}O_5$	**34.1**	**329**		**229; 293; 211; 171**	**211; 229; 155**	**183; 211**	*Dracocephalum* [1]; *Sasa veitchii* [70]; *Bituminaria* [74]
113	Unsaturated omega-3 fatty acid	**Trihydroxy eicosatetraenoic acid** *	$C_{20}H_{32}O_5$	**40.5**		**353**	**261; 293; 243; 207**	**243; 201; 159; 132**	**162**	*F. glaucescens* [32]
114	Tetrasyclic diterpenoid	**Komaroviquinone**	$C_{21}H_{28}O_5$	**1.9**		**361**	**343; 302**	**310; 269; 218; 161**	**282**	*D. komarovii* [91]
115	Sterol	**Stigmasterol** [Stigmasterin; Beta-Stigmasterol]	$C_{29}H_{48}O$	**3.5**		**413**	**395; 301; 237; 189**	**189**		*Dracocephalum* [1]; *A. cordifolia*; *F. pottsii* [32]; *Hedyotis diffusa* [69]

Table A1. *Cont.*

No	Class of Compounds	Identified Compounds	Formula	Retention Time, min	Molecular Ion $[M - H]^-$	Molecular Ion $[M + H]^+$	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
		POLYPHENOLS								
116	Anabolic steroid; Androgen; Androgen ester	**Vebonol**	$C_{30}H_{44}O_3$	**25.2**		**453**	**435; 336; 226**	**336**	**209**	*Dracocephalum* [1]; *Rhus coriaria* [28]; *Hylocereus polyrhizus* [86]
117	Triterpenic acid	**Betulonic acid** [Betunolic acid; Liquidambaric acid] *	$C_{30}H_{46}O_3$	**47.8**		**455**	**436; 353; 313; 249**	**393; 336; 319; 282**	**154**	*Rhus coriaria* [28]; *Rosa rugosa* [40]
118	Triterpenic acid	**1-Hydroxy-3-oxours-12-en-28-oic acid** *	$C_{30}H_{46}O_4$	**41.0**		**471**	**453; 425; 407; 389**	**365; 335; 283; 205**	**177; 121**	*Pear* [45]
119	Triterpenic acid	**Pomolic acid** *	$C_{30}H_{48}O_4$	**45.8**		**473**	**454; 371; 302; 144**			*Sanguisorba officinalis* [31]; *Pear* [45]; *Malus domestica* [92]
120	Triterpenic acid	**Tormentic acid** [Jacarandic acid; Tomentic acid] *	$C_{30}H_{48}O_5$	**42.2**	**487**		**470; 423; 372**	**403; 377**		*Sanguisorba officinalis* [31]; *Pear* [45]; *Actinidia* [62]
121	Monoterpene glycoside	**Rhodioloside C** [(2E,4R)-4-hydroxy-3,7-dimethyl-2,6-octadienyl β-D-glucopyranosyl(1-3)-β-D-glucopyranoside] *	$C_{22}H_{38}O_{12}$	**30.7**	**493**		**447; 329; 285**	**309; 285**	**294; 187**	*Rhodiola rosea* [15–17]; *Rhodiola crenulata* [18]
122	Carotenoid	**(all-E)-lutein 3′-*O*-myristate** *	$C_{40}H_{54}O$	**0.6**		**551**	**533; 509; 429; 385; 355**	**133**		Carotenoids [93]; *Rosa rugosa* [94]
123	Carotenoid	**Cryptoxanthin** [Beta-cryptoxanthin]	$C_{40}H_{56}O$	**5.3**		**553**	**535; 325; 223**	**517**		*Dracocephalum* [1]; Carotenoids [93]; *Sarsaparilla* [95]
124	Carotenoid	**Zeaxanthin** [All-Trans-Zeaxanthin; Anchovyxanthin] *	$C_{40}H_{56}O_2$	**3.6**		**569**	**553; 534; 471; 359**	**534; 486; 326; 262**	**516; 473; 308; 262**	*Sarsaparilla* [95]; Carotenoids [96]
125	Product of Chlorophylle breakdown	**Pheophorbide a** *	$C_{35}H_{34}N_4O_6$	**0.3**		**607**	**547; 503; 461**	**461; 433**	**433**	Chlorophyll derivatives [97]
126	Cycloartanol	**Cyclopassifloic acid glucoside** *	$C_{37}H_{62}O_{12}$	**40.4**		**699**	**537**	**375; 331; 259; 185**		*Passiflora incarnata* [47]
127	Carotenoid	**Carotenoid** *	$C_{41}H_{59}O_{10}$	**2.8**		**712**	**695; 605; 543; 474; 456**	**412; 369; 200; 143**		Carotenoids [98]
128	Carotenoid	***(all-E)-beta*-cryptoxanthin laurate** [Beta-Cryptoxanthin-Laurate] *	$C_{52}H_{78}O_2$	**29.5**		**735**	**323; 521; 277**	**295; 163**	**249; 173; 134**	Carotenoids [93]; Sarsaparilla [95]; *Carica papaya* [99]

* Compounds identified for the first time in genus *Dracocephalum*.

Appendix B

Table A2. The polyphenol composition distribution of *D. jacutense*. Green squares—presence in extracts from stems; violet squares—in extracts from inflorescences; emerald squares—in extracts from leaves.

No	Class of Compounds	Identified Compounds	Stems	Inflorescences	Leaves
1	Flavone	**Formononetin** [Biochanin B; Formononetol] *			
2	Flavone	**Apigenin** [5,7-Dixydroxy-2-(40Hydroxyphenyl)-4H-Chromen-4-One]			
3	Flavone	**Acacetin** [Linarigenin; Buddleoflavonol]			
4	Flavone	**Calycosin** [3′-Hydroxyformononetin] *			
5	Flavone	**Genkwanin** [Gengkwanin; Puddumetin; Apigenin 7-Methyl Ether]			
6	Flavone	**Luteolin**			
7	Flavone	**Diosmetin** [Luteolin 4′-Methyl Ether; Salinigricoflavonol]			
8	Flavone	**Chrysoeriol** [Chryseriol]			
9	Flavone	**Cirsimaritin** [Scrophulein] *			
10	Flavone	**Dihydroxy-dimethoxy(iso)flavone** *			
11	Flavone	**5,7-Dimethoxyluteolin** *			
12	Flavone	**Myricetin** *			
13	Flavone	**Isothymusin**			
14	Flavone	**Cirsiliol** *			
15	Flavone	**Dimethoxy-trihydroxy(iso)flavone** *			
16	Flavone	**Nevadensin**			
17	Flavone	**Gardenin B** [Demethyltangeretin] *			
18	Flavone	**5-Hydroxy-6,7,8,3′,4′-pentamethoxyflavone** *			
19	Flavone	**Apigenin *O*-hexoside**			
20	Flavone	**Apigenin-7-*O*-glucoside** [Apigetrin; Cosmosiin]			
21	Flavone	**Apigenin 7-*O*-glucuronide**			
22	Flavone	**Acacetin 7-*O*-glucoside** [Tilianin]			
23	Flavone	**Luteolin 7-*O*-glucoside** [Cynaroside; Luteoloside]			
24	Flavone	**Acacetin 7-*O*-beta-D-glucuronide**			
25	Flavone	**6,4′-Dimethoxyisoflavone-7-*O*-glucoside** *			
26	Flavone	**Diosmetin-7-*O*-beta-glucoside**			
27	Flavone	**Apigenin-*O*-rhamnoside** *			
28	Flavone	**Chrysoeriol-7-*O*-glucuronide** *			
29	Flavone	**Acacetin 7-beta-*O*-(6″-acetyl)-glucoside**			
30	Isoflavone	**Apigenin 7-*O*-beta-D-(6″-*O*-malonyl)-glucoside**			
31	Flavone	**Acacetin 7-*O*-beta-D-(6″-*O*-malonylated)-glucoside**			
32	Flavone	**Chrysoeriol *O*-hexoside *C*-hexoside** *			
33	Flavonol	**Kaempferol**			
34	Flavonol	**Quercetin**			
35	Flavonol	**Dihydroquercetin (Taxifolin; Taxifoliol)**			
36	Flavonol	**Isorhamnetin** [Isorhamnetol; Quercetin 3′-Methyl ether; 3-Methylquercetin] *			
37	Flavonoid	**3,5-Diacetyltambulin** *			
38	Flavonol	**Astragalin** [Kaempferol 3-*O*-glucoside; Kaempferol-3-Beta-Monoglucoside; Astragaline]			
39	Flavonol	**Quercitrin** [Quercetin 3-*O*-rhamnoside; Quercetrin] *			
40	Flavonol	**Kaempferol-3-*O*-glucuronide**			
41	Flavonol	**Taxifolin-3-*O*-hexoside** [Dihydroquercetin-3-*O*-hexoside] *			
42	Flavonol	**Kaempferol 3-*O*-rutinoside**			
43	Flavonol	**Kaempferol-3,7-Di-*O*-glucoside** *			
44	Flavonol	**Kaempferol dihexoside rhamnoside** *			
45	Flavan-3-ol	**(epi)Afzelechin** *			
46	Flavan-3-ol	**Catechin** [D-Catechol] *			
47	Flavan-3-ol	**(epi)catechin**			
48	Flavan-3-ol	**Gallocatechin** [+(−)Gallocatechin]			
49	Flavan-3-ol	**Catechin 3-*O*-gallate** *			
50	Flavan-3-ol	**Epigallocatechin-3-gallate** *			
51	Flavanone	**Naringenin** [Naringetol; Naringenine]			
52	Flavanone	**Eriodictyol** [3′,4′,5,7-tetrahydroxy-flavanone]			
53	Isoflavanone	**Ferreirin** *			
54	Trihydroxyflavanone	**Homoeriodictyol** *			

Table A2. *Cont.*

No	Class of Compounds	Identified Compounds	Stems	Inflorescences	Leaves
55	Flavanone	**Prunin** [Naringenin-7-*O*-glucoside]			
56	Flavanone	**Eriodictyol-7-O-glucoside** [Pyracanthoside; Miscanthoside]			
57	Flavanone	**Eriodictyol-7-O-glucuronide** *			
58	Hydroxycinnamic acid	***p*-Coumaric acid** [4-Hydroxycinnamic acid; P-Hydroxycinnamic acid; 4-Coumarate] *			
59	Hydroxycinnamic acid	**3,4-Dihydroxyhydrocinnamic acid** *			
60	Phenolic acid	**2,3,4,5-Tetrahydroxybenzoic acid** [2-Hydroxygallussaure; 3,4,5-Trihydroxysalicylic acid] *			
61	Phenolic acid	**Salvianic acid A** [Danshensu] *			
62	Hydroxybenzoic acid	**Ellagic acid** [Benzoaric acid; Elagostasine; Lagistase; Eleagic acid]			
63	Phenolic acid	**Protocatechuic acid-O-hexoside** *			
64	Phenolic acid	**Caffeic acid-4-*O*-beta-D-hexoside** [Caffeoyl-*O*-hexoside]			
65	Phenolic acid	**Chlorogenic acid** [3-*O*-Caffeoylquinic acid]			
66	Phenolic acid	**Isochlorogenic acid** *			
67	Phenolic acid	**Rosmarinic acid**			
68	Phenolic acid	**Caffeic acid derivative**			
69	Phenolic acid	**1/3/4/5-*p*-Coumaroylquinic acid** * **+ C_2H_2O**			
70	Phenolic acid	**8,8′-Aryl-Diferulic acid** *			
71	Phenolic acid	**Caffeic acid hexoside dimer** *			
72	Phenolic acid	**Salvianolic acid B** [Danfensuan B] *			
73	Phenylpropanoic acid	**Sagerinic acid**			
74	Phenolic acid	**Clerodendranoic acid H** *			
75	Lignan	**Phillygenin** [Sylvatesmin; Phyllygenol; Forsythigenol] *			
76	Lignan	**Medioresinol** *			
77	Dihydrochalcone	**Phloretin** [Dihydronaringenin; Phloretol] *			
78	Hydroxycoumarin	**Umbelliferone** [Skimmetin; Hydragin] *			
79	Coumarin	**Fraxetin** [7,8-Dihydroxy-6-methoxycoumarin] *			
80	Hydroxycoumarin	**Umbelliferone hexoside** *			
81	Coumarin glycoside	**Fraxin** [Fraxetin-8-O-glucoside] *			
82	Anthocyanidin	**Petunidin**			
83	Anthocyanidin	**Pelargonidin-3-*O*-glucoside (callistephin)**			
84	Anthocyanidin	**Cyanidin-3-*O*-glucoside** [Cyanidin 3-*O*-beta-D-Glucoside; Kuromarin]			
85	Anthocyanidin	**Cyanidin 3,5-*O*-diglucoside** *			
86	Anthocyanidin	**Peonidin-3,5-diglucoside** [Peonin; Peonidin 3-Glucoside-5-Glucoside] *			
87	Anthocyanidin	**Cyanidin-3-O-rutinoside-5-O-glucoside** *			
88	Anthocyanidin	**Delphinidin 3-O-rutinoside-5-O-glucoside** *			
89	Anthocyanidin	**Malonyl-shisonin** *			
		TOTAL	22	73	33

* Compounds identified for the first time in genus *Dracocephalum*.

References

1. Olennikov, D.N.; Chirikova, N.K.; Kim, E.; Kim, S.W.; Zulfugarov, I.S. New glycosides of eriodictyol from *Dracocephalum palmatum*. *Chem. Nat. Compd.* **2018**, *54*, 860–863. [CrossRef]
2. Toshmatov, Z.O.; Li, J.; Eshbakova, K.A.; Tang, D.; Xin, X.L.; Aisa, H.A. New monoterpene glucosides from *Dracocephalum komarovi* and their anti-inflammatory activity. *Phytochem. Lett.* **2019**, *33*, 102–105. [CrossRef]
3. Zhang, H.R.; Xu, L.T.; Liu, X.Q.; Fan, J.J.; Wang, X.N.; Shen, T.; Wang, S.Q.; Ren, D.M. Dracomolphesin A–E, five 3,4-seco-phenylpropanoids with Nrf2 inducing activity from *Dracocephalum moldavica*. *Chin. Chem. Lett.* **2020**, *31*, 1259–1262. [CrossRef]
4. Zhang, H.R.; Wang, S.Q.; Liu, Q.Y.; Zheng, H.; Liu, X.Q.; Wang, X.N.; Shen, T.; Ren, D.M. Dracomolphin A–E, new lignans from *Dracocephalum moldavica*. *Fitoterapia* **2021**, *150*, 104841. [CrossRef] [PubMed]
5. Okhlopkova, Z.M.; Razgonova, M.P.; Pikula, K.S.; Zakharenko, A.M.; Piekoszewski, W.; Manakov, Y.A.; Ercisli, S.; Golokhvast, K.S. *Dracocephalum palmatum* S. and *Dracocephalum ruyschiana* L. originating from Yakutia: A high-resolution mass spectrometric approach for the comprehensive characterization of phenolic compounds. *Appl. Sci.* **2022**, *12*, 1766. [CrossRef]
6. Khodaei, M.; Amanzadeh, Y.; Faramarzi, M.A.; Pirali-Hamedani, M.; Adhami, H.R. Cholinesterase Inhibitory, Anti-oxidant and Anti-tyrosinase Activities of Three Iranian Species of Dracocephalum. *Res. J. Pharmacogn.* **2019**, *6*, 25–31.
7. Kim, J.; Kim, J.N.; Park, I.; Sivtseva, S.; Okhlopkova, Z.; Zulfugarov, I.S.; Kim, S.-W. *Dracocephalum palmatum* Stephan extract induces caspase- and mitochondria-dependent apoptosis via Myc inhibition in diffuse large B cell lymphoma. *Oncol. Rep.* **2020**, *44*, 2746–2756. [CrossRef]
8. Lee, S.-E.; Okhlopkova, Z.; Lim, C.; Cho, S. *Dracocephalum palmatum* Stephan extract induces apoptosis in human prostate cancer cells via the caspase-8-mediated extrinsic pathway. *Chin. J. Nat. Med.* **2020**, *18*, 793–800. [CrossRef]

9. Song, E.S.; Choi, J.Y.; Gwon, H.E.; Lee, K.Y.; Choi, S.G.; Islam, M.A.; Chun, J.Y.; Hwang, J.N. Phytochemical profile and antioxidant activity of *Dracocephalum moldavica* L. seed extracts using different extraction methods. *Food Chem.* **2021**, *350*, 128531. [CrossRef] [PubMed]
10. Wang, J.; Sun, J.; Jin, L.; Huang, Y.; Wang, M.; Jin, M.; Diao, S.; Zhou, W.; Li, G. Four new terpenoids and other metabolites with potential anti-complementary activities from the aerial parts of *Dracocephalum moldavica* (Lamiaceae). *Nat. Prod. Res.* **2022**, *22*, 1–9. [CrossRef]
11. Wu, C.; Liu, H.; Rong, X.; Liu, J.; Ding, W.; Cheng, X.; Xing, J.; Wang, C. Phytochemical Composition Profile and Space–Time Accumulation of Secondary Metabolites for Dracocephalum Moldavica Linn. via UPLC–Q/TOF–MS and HPLC–DAD Method. *Biomed. Chromatogr.* **2020**, *34*, e4865. [CrossRef] [PubMed]
12. Simea, Ș.; Ielciu, I.; Hanganu, D.; Niculae, M.; Pall, E.; Burtescu, R.F.; Olah, N.-K.; Cenariu, M.; Oniga, I.; Benedec, D.; et al. Evaluation of the Cytotoxic, Antioxidative, and Antimicrobial Effects of *Dracocephalum moldavica* L. Cultivars. *Molecules* **2023**, *28*, 1604. [CrossRef] [PubMed]
13. Red Book of the Republic of Sakha (Yakutia). *V. 1: Rare and Endangered Species of Plants and Fungi*; Danilova, N.S., Ed.; Publishing House "Reart": Moscow, Russia, 2017; 412p. (In Russian)
14. Razgonova, M.P.; Okhlopkova, Z.M.; Rozhina, Z.G.; Egorova, P.S.; Ercisli, S.; Golokhvast, K.S. Comparison of Wild and Introduced *Dracocephalum jacutense* P.: Significant Differences of Multicomponent Composition. *Horticulturae* **2022**, *8*, 1211. [CrossRef]
15. Troshchenko, A.T.; Kutikova, G.A. Rhodioloside from *Rhodiola rosea* and *R. quadrifida* I. *Chem. Nat. Compd.* **1967**, *3*, 244–249. [CrossRef]
16. Saratikov, A.S.; Krasnov, E.A.; Chnikina, L.A.; Duvidson, L.M.; Sotova, M.I.; Marina, T.F.; Nechoda, M.F.; Axenova, R.A.; Tscherdinzeff, S.G. Rhodiolosid, a new glycoside from *Rhodiola rosea* and its pharmacological properties. *Pharmazie* **1968**, *23*, 392–395.
17. van Diermen, D.; Marston, A.; Bravo, J.; Reist, M.; Carrupt, P.A.; Hostettmann, K. Monoamine oxidase inhibition by *Rhodiola rosea* L. roots. *J. Ethnopharmacol.* **2009**, *122*, 397–401. [CrossRef]
18. Han, F.; Li, Y.; Ma, L.; Liu, T.; Wu, Y.; Xu, R.; Song, A.; Yin, R. A rapid and sensitive UHPLC-FT-ICR MS/MS method for identification of chemical constituents in *Rhodiola crenulata* extract, rat plasma and rat brain after oral administration. *Talanta* **2016**, *160*, 183–193. [CrossRef]
19. Huang, X.; Liu, Y.; Song, F.; Liu, Z.; Liu, S. Studies on principal components and antioxidant activity of different *Radix astragali* samples using high-performance liquid chromatography/electrospray ionization multiple-stage tandem mass spectrometry. *Talanta* **2009**, *78*, 1090–1101. [CrossRef]
20. Zhang, J.; Xu, X.-J.; Xu, W.; Huang, J.; Zhu, D.; Qui, X.-H. Rapid Characterization and Identification of Flavonoids in *Radix astragali* by Ultra-High-Pressure Liquid Chromatography Coupled with Linear Ion Trap-Orbitrap Mass Spectrometry. *J. Chromatogr. Sci.* **2015**, *53*, 945–952. [CrossRef] [PubMed]
21. Wang, F.; Zhao, S.; Li, F.; Zhang, B.; Qu, Y.; Sun, T.; Luo, T.; Li, D. Investigation of Antioxidant interactions between *Radix Astragali* and Cimicifuga foetida and Identification of Synergistic Antioxidant Compounds. *PLoS ONE* **2014**, *9*, e87221. [CrossRef]
22. Yin, Y.; Zhang, K.; Wei, L.; Chen, D.; Chen, Q.; Jiao, M.; Li, X.; Huang, J.; Gong, Z.; Kang, N.; et al. The Molecular Mechanism of Antioxidation of Huolisu Oral Liquid Based on Serum Analysis and Network Analysis. *Front. Pharma.* **2021**, *12*, 710976. [CrossRef] [PubMed]
23. Wang, F.; Huang, S.; Chen, Q.; Hu, Z.; Li, Z.; Zheng, P.; Liu, X.; Li, S.; Zhang, S.; Chen, J. Chemical characterisation and quantification of the major constituents in the Chinese herbal formula Jian-Pi-Yi-Shen pill by UPLC-Q-TOF-MS/MS and HPLC-QQQ-MS/MS. *Phytochem. Anal.* **2020**, *31*, 915–929. [CrossRef]
24. Mena, P.; Cirlini, M.; Tassotti, M.; Herrlinger, K.A.; Dall'Asta, C.; Del Rio, D. Phytochemical Profiling of Flavonoids, Phenolic Acids, Terpenoids, and Volatile Fraction of a Rosemary (*Rosmarinus officinalis* L.) Extract. *Molecules* **2016**, *21*, 1576. [CrossRef]
25. Belmehdi, O.; Bouyahya, A.; Jeko, J.; Cziaky, Z.; Zengin, G.; Sotkó, G.; El Baaboua, A.; Senhaji, N.S.; Abrini, J. Synergistic interaction between propolis extract, essential oils, and antibiotics against *Staphylococcus epidermidis* and methicillin resistant *Staphylococcus aureus*. *Int. J. Second Metab.* **2021**, *8*, 195–213. [CrossRef]
26. Xu, L.L.; Xu, J.J.; Zhong, K.R.; Shang, Z.P.; Wang, F.; Wang, R.F.; Liu, B. Analysis of non-volatile chemical constituents of *Menthae Haplocalycis* herba by ultra-high performance liquid chromatography—High resolution mass spectrometry. *Molecules* **2017**, *22*, 1756. [CrossRef]
27. Martinez-Vazquez, M.; Estrada-Reyes, R.; Martinez-Laurrabaquio, A.; Lopez-Rubalcava, C.; Heinze, G. Neuropharmacological study of *Dracocephalum moldavica* L. (Lamiaceae) in mice: Sedative effect and chemical analysis of an aqueous extract. *J. Ethnopharmacol.* **2012**, *141*, 908–917. [CrossRef] [PubMed]
28. Abu-Reidah, I.M.; Ali-Shtayeh, M.S.; Jamous, R.M.; Arraes-Roman, D.; Segura-Carretero, A. HPLC–DAD–ESI-MS/MS screening of bioactive components from *Rhus coriaria* L. (Sumac) fruits. *Food Chem.* **2015**, *166*, 179–191. [CrossRef]
29. Rafsanjany, N.; Senker, J.; Brandt, S.; Dobrindt, U.; Hensel, A. In Vivo Consumption of Cranberry Exerts ex Vivo Antiadhesive Activity against FimH-Dominated Uropathogenic *Escherichia coli*: A Combined in Vivo, ex Vivo, and in Vitro Study of an Extract from *Vaccinium macrocarpon*. *J. Agric. Food Chem.* **2015**, *63*, 8804–8818. [CrossRef]
30. Aita, S.E.; Capriotti, A.L.; Cavaliere, C.; Cerrato, A.; Giannelli Moneta, B.; Montone, C.M.; Piovesana, S.; Lagana, A. Andean Blueberry of the Genus Disterigma: A High-Resolution Mass Spectrometric Approach for the Comprehensive Characterization of Phenolic Compounds. *Separations* **2021**, *8*, 58. [CrossRef]

31. Kim, S.; Oh, S.; Noh, H.B.; Ji, S.; Lee, S.H.; Koo, J.M.; Choi, C.W.; Jhun, H.P. In Vitro Antioxidant and Anti-Propionibacterium acnes Activities of Cold Water, Hot Water, and Methanol Extracts, and Their Respective Ethyl Acetate Fractions, from *Sanguisorba officinalis* L. Roots. *Molecules* **2018**, *23*, 3001. [CrossRef]
32. Hamed, A.R.; El-Hawary, S.S.; Ibrahim, R.M.; Abdelmohsen, U.R.; El-Halawany, A.M. Identification of Chemopreventive Components from Halophytes Belonging to Aizoaceae and Cactaceae Through LC/MS—Bioassay Guided Approach. *J. Chrom. Sci.* **2021**, *59*, 618–626. [CrossRef]
33. Qin, D.; Wang, Q.; Li, H.; Jiang, X.; Fang, K.; Wang, Q.; Li, B.; Pan, C.; Wu, H. Identification of key metabolites based on non-targeted metabolomics and chemometrics analyses provides insights into bitterness in Kucha [*Camellia kucha* (Chang et Wang) Chang]. *Food Res. Int.* **2020**, *138 Pt B*, 109789. [CrossRef]
34. Pharmacopoeia of the Eurasian Economic Union, Approved by Decision of the Board of Eurasian Economic Commission No. 100 dated 11 August 2020. Available online: http://www.eurasiancommission.org/ru/act/texnreg/deptexreg/LSMI/Documents/%D0%A4%D0%B0%D1%80%D0%BC%D0%B0%D0%BA%D0%BE%D0%BF%D0%B5%D1%8F%20%D0%A1%D0%BE%D1%8E%D0%B7%D0%B0%2011%2008.pdf (accessed on 15 July 2021).
35. Azmir, J.; Zaidul, I.S.M.; Rahman, M.M.; Sharif, K.; Mohamed, A.; Sahena, F.; Jahurul, M.; Ghafoor, K.; Norulaini, N.; Omar, A. Techniques for extraction of bioactive compounds from plant materials: A review. *J. Food Eng.* **2013**, *117*, 426–436. [CrossRef]
36. Cai, Z.; Wang, C.; Zou, L.; Liu, X.; Chen, J.; Tan, M.; Mei, Y.; Wei, L. Comparison of Multiple Bioactive Constituents in the Flower and the Caulis of *Lonicera japonica* Based on UFLC-QTRAP-MS/MS Combined with Multivariate Statistical Analysis. *Molecules* **2019**, *24*, 1936. [CrossRef]
37. Wojakowska, A.; Piasecka, A.; Garcia-Lopez, P.M.; Zamora-Natera, F.; Krajewski, P.; Marczak, L.; Kachlicki, P.; Stobiecki, M. Structural analysis and profiling of phenolic secondary metabolites of Mexican lupine species using LC–MS techniques. *Phytochem* **2013**, *92*, 71–86. [CrossRef]
38. Pandey, R.; Kumar, B. HPLC–QTOF–MS/MS-based rapid screening of phenolics and triterpenic acids in leaf extracts of *Ocimum* species and their interspecies variation. *J. Liq. Chromatogr. Relat. Tech.* **2016**, *39*, 225–238. [CrossRef]
39. Fanthoni, A.; Saepudin, E.; Cahyana, A.H.; Rahayu, D.U.C.; Haib, J. Identification of Nonvolatile Compounds in Clove (*Syzygium aromaticum*) from Manado. In Proceedings of the International Symposium on Current Progress in Mathematics and Sciences 2016 (ISCPMS 2016), Depok City, Indonesia, 1–2 November 2016; Volume 1862, pp. 030079-1–030079-10.
40. Razgonova, M.P.; Bazhenova, B.B.; Zabalueva, Y.Y.; Burkhanova, A.G.; Zakharenko, A.M.; Kupriyanov, A.N.; Sabitov, A.S.; Ercisli, S.; Golokhvast, K.S. *Rosa davurica* Pall., *Rosa rugosa* Thumb., and *Rosa acicularis* Lindl. originating from Far Eastern Russia: Screening of 146 Chemical Constituents in Tree Species of the Genus Rosa. *Appl. Sci.* **2022**, *12*, 9401. [CrossRef]
41. Zengin, G.; Mahomoodally, M.F.; Sinan, K.I.; Ak, G.; Etienne, O.K.; Sharmeen, J.B.; Brunetti, L.; Leone, S.; Di Simone, S.C.; Recinella, L.; et al. Chemical composition and biological properties of two *Jatropha* species: Different parts and different extraction methods. *Antioxidants* **2021**, *10*, 792. [CrossRef] [PubMed]
42. Singh, B.; Jain, S.K. Simultaneous Quantification of Five Bioactive Flavonoids in High Altitude Plant *Actinocarya tibetica* by LC-ESI-MS/MS. *J. AOAC Int.* **2015**, *98*, 907–912. [CrossRef]
43. Mateos-Martin, M.L.; Fuguet, E.; Jimenez-Ardon, A.; Herrero-Uribe, L.; Tamayo-Castillo, G.; Torres, J.L. Identification of polyphenols from antiviral *Chamaecrista nictitans* extract using high-resolution LC–ESI–MS/MS. *Anal. Bioanal. Chem.* **2014**, *406*, 5501–5506. [CrossRef]
44. Li, X.; Tian, T. Phytochemical Characterization of *Mentha spicata* L. Under Differential Dried-Conditions and Associated Nephrotoxicity Screening of Main Compound with Organ-on-a-Chip. *Front. Pharmacol.* **2018**, *9*, 1067. [CrossRef]
45. Sun, L.; Tao, S.; Zhang, S. Characterization and Quantification of Polyphenols and Triterpenoids in Thinned Young Fruits of Ten Pear Varieties by UPLC-Q TRAP-MS/MS. *Molecules* **2019**, *24*, 159. [CrossRef] [PubMed]
46. El-Sayed, M.A.; Abbas, F.A.; Refaat, S.; El-Shafae, A.M.; Fikry, E. UPLC-ESI-MS/MS Profile of The Ethyl Acetate Fraction of Aerial Parts of Bougainvillea 'Scarlett O'Hara' Cultivated in Egypt. *Egypt. J. Chem.* **2021**, *64*, 22. [CrossRef]
47. Ozarowski, M.; Piasecka, A.; Paszel-Jaworska, A.; de Siqueira, A.; Chaves, D.; Romaniuk, A.; Rybczynska, M.; Gryszczynska, A.; Sawikowska, A.; Kachlicki, P.; et al. Comparison of bioactive compounds content in leaf extracts of *Passiflora incarnata*, *P. caerulea* and P. alata and in vitro cytotoxic potential on leukemia cell lines. *Braz. J. Pharmacol.* **2018**, *28*, 179–191. [CrossRef]
48. Pandey, B.P.; Pradhan, S.P.; Adhikari, K. LC-ESI-QTOF-MS for the Profiling of the Metabolites and in Vitro Enzymes Inhibition Activity of *Bryophyllum pinnatum* and *Oxalis corniculata* Collected from Ramechhap District of Nepal. *Chem. Biodivers.* **2020**, *17*, e2000155.
49. Spinola, V.; Pinto, J.; Castilho, P.C. Identification and quantification of phenolic compounds of selected fruits from Madeira Island by HPLC-DAD-ESI-MSn and screening for their antioxidant activity. *Food Chem.* **2015**, *173*, 14–30. [CrossRef]
50. Razgonova, M.P.; Tekutyeva, L.A.; Podvolotskaya, A.B.; Stepochkina, V.D.; Zakharenko, A.M.; Golokhvast, K.S. *Zostera marina* L. Supercritical CO_2-Extraction and Mass Spectrometric Characterization of Chemical Constituents Recovered from Seagrass. *Separations* **2022**, *9*, 182. [CrossRef]
51. Cavaliere, C.; Foglia, P.; Pastorini, E.; Samperi, R.; Laganà, A. Identification and mass spectrometric characterization of glycosylated flavonoids in *Triticum durum* plants by high-performance liquid chromatography with tandem mass spectrometry. *Rapid Commun. Mass Spectrom. Int. J. Devoted Rapid Dissem. Up—Minute Res. Mass Spectrom.* **2005**, *19*, 3143–3158. [CrossRef] [PubMed]
52. Wojakowska, A.; Perkowski, J.; Góral, T.; Stobiecki, M. Structural characterization of flavonoid glycosides from leaves of wheat (*Triticum aestivum* L.) using LC/MS/MS profiling of the target compounds. *J. Mass Spectrom.* **2013**, *48*, 329–339. [CrossRef]

53. Yin, N.-W.; Wang, S.-X.; Jia, L.-D.; Zhu, M.-C.; Yang, J.; Zhou, B.-J.; Yin, J.-M.; Lu, K.; Wang, R.; Li, J.-N.; et al. Identification and Characterization of Major Constituents in Different-Colored Rapeseed Petals by UPLC−HESI-MS/MS. *J. Agric. Food Chem.* **2019**, *67*, 11053–11065. [CrossRef]
54. Abeywickrama, G.; Debnath, S.C.; Ambigaipalan, P.; Shahidi, F. Phenolics of selected cranberry genotypes (*Vaccinium macrocarpon* Ait.) and their antioxidant efficacy. *J. Agr. Food Chem.* **2016**, *64*, 9342–9351. [CrossRef]
55. Vijayan, K.P.R.; Raghu, A.V. Tentative characterization of phenolic compounds in three species of the genus *Embelia* by liquid chromatography coupled with mass spectrometry analysis. *Spectrosc. Lett.* **2019**, *52*, 653–670. [CrossRef]
56. Mekam, P.N.; Martini, S.; Nguefack, J.; Tagliazucchi, D.; Stefani, E. Phenolic compounds profile of water and ethanol extracts of *Euphorbia hirta* L. leaves showing antioxidant and antifungal properties. *South Afr. J. Bot.* **2019**, *127*, 319–332. [CrossRef]
57. Chandrasekara, A.; Shahidi, F. Determination of antioxidant activity in free and hydrolyzed fractions of millet grains and characterization of their phenolic profiles by HPLC-DAD-ESI-MSn. *J. Funct. Foods* **2011**, *3*, 144–158. [CrossRef]
58. Le Gall, G.; DuPont, M.S.; Davis, A.L.; Collins, G.J.; Verhoeyen, M.E.; Colquhoun, I.J. Characterization and Content of Flavonoid Glycosides in Genetically Modified Tomato (*Lycopersicum esculentum*) Fruits. *Roots. Agric. Food Chem.* **2003**, *51*, 2438–2446. [CrossRef]
59. Aabideen, Z.U.; Mumtaz, M.W.; Akhtar, M.T.; Mukhtar, H.; Raza, S.A.; Touqeer, T.; Saari, N. Anti-Obesity Attributes; UHPLC-QTOF-MS/MS-Based Metabolite Profiling and Molecular Docking Insights of *Taraxacum officinale*. *Molecules* **2020**, *25*, 4935. [CrossRef]
60. Marcia Fuentes, J.A.; Lopez-Salas, L.; Borras-Linares, I.; Navarro-Alarcon, M.; Segura-Carretero, A.; Lozano-Sanchez, J. Development of an Innovative Pressurized Liquid Extraction Procedure by Response Surface Methodology to Recover Bioactive Compounds from Carao Tree Seeds. *Foods* **2021**, *10*, 398. [CrossRef]
61. Sobeh, M.; Mahmoud, M.F.; Abdelfattah, M.A.O.; Cheng, H.; El-Shazly, A.M.; Wink, M. A proanthocyanidin-rich extract from *Cassia abbreviata* exhibits antioxidant and hepatoprotective activities in vivo. *J. Ethnopharmacol.* **2018**, *213*, 38–47. [CrossRef] [PubMed]
62. Chen, Y.; Cai, X.; Li, G.; He, X.; Yu, X.; Wang, C.; Xiao, Q.; Xiang, Z. Chemical constituents of radix *Actinidia chinensis* planch by UPLC–QTOF–MS. Biomedical Chromatography. *Biomed. Chromatogr.* **2021**, *35*, e5103. [CrossRef]
63. Zakharenko, A.M.; Razgonova, M.P.; Pikula, K.S.; Golokhvast, K.S. Simultaneous determination of 78 compounds of *Rhodiola rosea* extract using supercritical CO_2-extraction and HPLC-ESI-MS/MS spectrometry. HINDAWY. *Biochem. Res. Int.* **2021**, *2021*, 9957490. [CrossRef]
64. Jaiswal, R.; Jayasinghe, L.; Kuhnert, N. Identification and characterization of proanthocyanidins of 16 members of the *Rhododendron* genus (Ericaceae) by tandem LC–MS. *J. Mass Spectrom.* **2012**, *47*, 502–515. [CrossRef]
65. Singh, A.; Bajpai, V.; Kumar, S.; Sharma, K.R.; Kumar, B. Profiling of Gallic and Ellagic Acid Derivatives in Different Plant Parts of *Terminalia arjuna* by HPLC-ESI-QTOF-MS/MS. *Nat. Prod. Com.* **2016**, *11*, 239–244. [CrossRef]
66. Gordon, A.; Schadow, B.; Quijano, K.E.; Marx, F. Chemical characterization and antioxidant capacity of berries from *Clidemia rubra* (Aubl.) Mart. (Melastomataceae). *Food Res. Int.* **2011**, *44*, 2120–2127. [CrossRef]
67. Justesen, U. Negative atmospheric pressure chemical ionisation low-energy collision activation mass spectrometry for the characterisation of flavonoids in extracts of fresh herbs. *J. Chromatogr. A* **2000**, *902*, 369–379. [CrossRef] [PubMed]
68. Pan, M.; Lei, Q.; Zang, N.; Zhang, H. A Strategy Based on GC-MS/MS, UPLC-MS/MS and Virtual Molecular Docking for Analysis and Prediction of Bioactive Compounds in *Eucalyptus Globulus* Leaves. *Int. J. Mol. Sci.* **2019**, *20*, 3875. [CrossRef] [PubMed]
69. Chen, X.; Zhu, P.; Liu, B.; Wei, L.; Xu, Y. Simultaneous determination of fourteen compounds of *Hedyotis diffusa* Willd extract in rats by UHPLC-MS/MS method: Application to pharmacokinetics and tissue distribution study. *J. Pharmaceut. Biomed. Analys.* **2018**, *159*, 490–512. [CrossRef]
70. Van Hoyweghen, L.; De Bosscher, K.; Haegeman, G.; Deforce, D.; Heyerick, A. In Vitro Inhibition of the Transcription Factor NF-kB and Cyclooxygenase by Bamboo Extracts. *Phytother. Res.* **2014**, *28*, 224–230. [CrossRef]
71. Jiang, R.-W.; Lau, K.-M.; Hon, P.-M.; Mak, T.C.W.; Woo, K.-S.; Fung, K.-P. Chemistry and Biological Activities of Caffeic Acid Derivatives from *Salvia miltiorrhiza*. *Curr. Med. Chem.* **2005**, *12*, 237–246.
72. Serrano, C.A.; Villena, G.K.; Rodriguez, E.F. Phytochemical profile and rosmarinic acid purification from two Peruvian *Lepechinia* Willd. species (Salviinae, Mentheae, Lamiaceae). *Sci. Rep.* **2021**, *11*, 7260. [CrossRef]
73. Eklund, P.C.; Backman, M.J.; Kronberg, L.A.; Smeds, A.I.; Sjoholm, R.E. Identification of lignans by liquid chromatography-electrospray ionization ion-trap mass spectrometry. *J. Mass Spectr.* **2008**, *43*, 97–107. [CrossRef]
74. Llorent-Martinez, E.J.; Spinola, V.; Gouveia, S.; Castilho, P.C. HPLC-ESI-MSn characterization of phenolic compounds, terpenoid saponins, and other minor compounds in *Bituminaria bituminosa*. *Industr. Crops Prod.* **2015**, *69*, 80–90. [CrossRef]
75. Mena, P.; Calani, L.; Dall'Asta, C.; Galaverna, G.; Garcia-Viguera, C.; Bruni, R.; Crozier, A.; Del Rio, D. Rapid and Comprehensive Evaluation of (Poly)phenolic Compounds in Pomegranate (*Punica granatum* L.) Juice by UHPLC-MSn. *Molecules* **2012**, *17*, 14821–14840. [CrossRef]
76. Garg, M.; Chawla, M.; Chunduri, V.; Kumar, R.; Sharma, S.; Sharma, N.K.; Kaur, N.; Kumar, A.; Mundey, J.K.; Saini, M.K.; et al. Transfer of grain colors to elite wheat cultivars and their characterization. *J. Cereal Sci.* **2016**, *71*, 138–144. [CrossRef]
77. Da Silva, L.P.; Pereira, E.; Pires, T.C.S.P.; Alves, M.J.; Pereira, O.R.; Barros, L.; Ferreira, I.C.F.R. *Rubus ulmifolius* Schott fruits: A detailed study of its nutritional, chemical and bioactive properties. *Food Res. Int.* **2019**, *119*, 34–43. [CrossRef] [PubMed]

78. Vera de Rosso, V.; Hillebrand, S.; Cuevas Montilla, E.; Bobbio, F.O.; Winterhalter, P.; Mercadante, A.Z. Determination of anthocyanins from acerola (*Malpighia emarginata* DC.) and ac-ai (Euterpe oleracea Mart.) by HPLC–PDA–MS/MS. *J. Food Composit. Analys.* **2008**, *21*, 291–299. [CrossRef]
79. Anari, Z.; Mai, C.; Sengupta, A.; Howard, L.; Brownmiller, C.; Wickramasinghe, R. Combined Osmotic and Membrane Distillation for Concentration of Anthocyanin from Muscadine Pomace. *J. Food Sci.* **2019**, *84*, 2199–2208. [CrossRef] [PubMed]
80. Ruiz, A.; Hermosín-Gutiérrez, I.; Vergara, C.; von Baer, D.; Zapata, M.; Hitschfeld, A.; Obando, L.; Mardones, C. Anthocyanin profiles in south Patagonian wild berries by HPLC-DAD-ESI-MS/MS. *Food Res. Int.* **2013**, *51*, 706–713. [CrossRef]
81. Xu, W.; Luo, I.; Vergara, G.; Yu, F.; Jia, Q.; Zeng, Y.; Bi, X.; Lei, J. Characterization of anthocyanins in the hybrid progenies derived from *Iris dichotoma* and *I. domestica* by HPLC-DAD-ESI/MS analysis. *Phytochem* **2018**, *150*, 60–74. [CrossRef]
82. Chhon, S.; Jeon, J.; Kim, J.; Park, S.Y. Accumulation of Anthocyanins through Overexpression of AtPAP1 in *Solanum nigrum* Lin. (Black Nightshade). *Biomolecules* **2020**, *10*, 277. [CrossRef] [PubMed]
83. Yamazaki, M.; Nakajima, J.; Yamanashi, M.; Sugiyama, M.; Makita, Y.; Springob, K.; Awazuhara, M.; Saito, K. Metabolomics and differential gene expression in anthocyanin chemo-varietal forms of *Perilla frutescens*. *Phytochem* **2003**, *62*, 987–995. [CrossRef]
84. He, Y.-K.; Yao, Y.-Y.; Chang, Y.-N. Characterization of Anthocyanins in *Perilla frutescens* var. acuta Extract by Advanced UPLC-ESI-IT-TOF-MSn Method and Their Anticancer Bioactivity. *Molecules* **2015**, *20*, 9155–9169. [CrossRef]
85. Rodriguez-Perez, C.; Gomez-Caravaca, A.M.; Guerra-Hernandez, E.; Cerretani, L.; Garcia-Villanova, B.; Verardo, V. Comprehensive metabolite profiling of *Solanum tuberosum* L. (potato) leaves T by HPLC-ESI-QTOF-MS. *Food Res. Int.* **2018**, *112*, 390–399. [CrossRef]
86. Wu, Y.; Xu, J.; He, Y.; Shi, M.; Han, X.; Li, W.; Zhang, X.; Wen, X. Metabolic Profiling of Pitaya (*Hylocereus polyrhizus*) during Fruit Development and Maturation. *Molecules* **2019**, *24*, 1114. [CrossRef]
87. Cirlini, M.; Mena, P.; Tassotti, M.; Herrlinger, K.A.; Nieman, K.M.; Dall'Asta, C.; Del Rio, D. Phenolic and volatile composition of a dry spearmint (*Mentha spicata* L.) extract. *Molecules* **2016**, *21*, 1007. [CrossRef]
88. Yang, S.T.; Wu, X.; Rui, W.; Guo, J.; Feng, Y.F. UPLC/Q-TOF-MS analysis for identification of hydrophilic phenolics and lipophilic diterpenoids from Radix *Salviae Miltiorrhizae*. *Acta Chromatogr.* **2015**, *27*, 711–728. [CrossRef]
89. Patnala, S.; Kanfer, I. Medicinal use of Sceletium: Characterization of Phytochemical Components of Sceletium Plant Species using HPLC with UV and Electrospray Ionization—Tandem Mass Spectroscopy. *J. Pharm. Pharm. Sci.* **2015**, *18*, 414–423. [CrossRef]
90. Chen, D.; Fan, J.; Wang, P.; Zhu, L.; Jin, Y.; Peng, Y.; Du, S. Isolation, identification and antioxidative capacity of water-soluble phenylpropanoid compounds from *Rhodiola crenulata*. *Food Chem.* **2012**, *134*, 2126–2133. [CrossRef] [PubMed]
91. Uchiyama, N.; Kiuchi, F.; Ito, M.; Honda, G.; Takeda, Y.; Khodzhimatov, O.K.; Ashurmetov, O.A. New Icetexane and 20-Norabietane Diterpenes with Trypanocidal Activity from *Dracocephalum komarovi*. *J. Nat. Prod.* **2003**, *66*, 128–131. [CrossRef]
92. Sut, S.; Zengin, G.; Maggi, F.; Malagoli, M.; Dall'Acqua, S. Triterpene Acid and Phenolics from Ancient Apples of Friuli Venezia Giulia as Nutraceutical Ingredients: LC-MS Study and In Vitro Activities. *Molecules* **2019**, *24*, 1109. [CrossRef]
93. Mercadante, A.Z.; Rodrigues, D.B.; Petry, F.C.; Barros Mariutti, L.R. Carotenoid esters in foods—A review and practical directions on analysis and occurrence. *Food Res. Int.* **2017**, *99*, 830–850. [CrossRef] [PubMed]
94. Al-Yafeai, A.; Malarski, A.; Bohm, V. Characterization of carotenoids and vitamin E in *R. rugosa* and *R. canina*: Comparative analysis. *Food Chem.* **2018**, *242*, 435–442. [CrossRef] [PubMed]
95. Delgado-Pelayo, R.; Homero-Mendez, D. Identification and Quantitative Analysis of Carotenoids and Their Esters from Sarsaparilla (*Smilax aspera* L.) Berries. *J. Chromatogr. A* **2012**, *60*, 8225–8232. [CrossRef] [PubMed]
96. Zoccali, M.; Giuffrida, D.; Salafia, F.; Giofre, S.V.; Mondello, L. Carotenoids and apocarotenoids determination in intact human blood samples by online supercritical fluid extraction-supercritical fluid chromatography-tandem mass spectrometry. *J. Pharmaceut. Biomed. Analys.* **2018**, *1032*, 40–47. [CrossRef]
97. van Breemen, R.B.; Canjura, F.L.; Schwartz, S.J. Identification of Chlorophyll Derivatives by Mass Spectrometry. *J. Agric. Food Chem.* **1991**, *39*, 1452–1456. [CrossRef]
98. Murador, D.C.; Salafia, F.; Zoccali, M.; Martins, P.L.G.; Ferreira, A.; Dugo, P.; Mondello, L.; de Rosso, V.V.; Giuffrida, D. Green Extraction Approaches for Carotenoids and Esters: Characterization of Native Composition from Orange Peel. *Antioxidants* **2019**, *8*, 613. [CrossRef]
99. Lara-Abia, S.; Lobo-Rodrigo, G.; Welti-Chanes, J.; Pilar Cano, M. Carotenoid and Carotenoid Ester Profile and Their Deposition in Plastids in Fruits of New Papaya (*Carica papaya* L.) Varieties from the Canary Islands. *Foods* **2021**, *10*, 434. [CrossRef] [PubMed]