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Dracocephalum palmatum S. and *Dracocephalum ruyschiana* L. Originating from Yakutia: A High-Resolution Mass Spectrometric Approach for the Comprehensive Characterization of Phenolic Compounds

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Abstract: *Dracocephalum palmatum* S. and *Dracocephalum ruyschiana* L. contain a large number of target analytes, which are biologically active compounds. High performance liquid chromatography (HPLC) in combination with an ion trap (tandem mass spectrometry) was used to identify target analytes in extracts of *D. palmatum* S. and *D. ruyschiana* L. originating from Yakutia. The results of initial studies revealed the presence of 114 compounds, of which 92 were identified for the first time in the genus *Dracocephalum*. New identified metabolites belonged to 17 classes, including 16 phenolic acids and their conjugates, 18 flavones, 5 flavonols, 2 flavan-3-ols, 1 flavanone, 2 stilbenes, 10 anthocyanins, 1 condensed tannin, 2 lignans, 6 carotenoids, 3 oxylipins, 2 amino acids, 3 sceletium alkaloids, 3 carboxylic acids, 8 fatty acids, 1 sterol, and 3 terpenes, along with 6 miscellaneous compounds. It was shown that extracts of *D. palmatum* are richer in the spectrum of polyphenolic compounds compared with extracts of *D. ruyschiana*, according to a study of the presence of these compounds in extracts, based on the results of mass spectrometric studies.

Keywords: *Dracocephalum palmatum; Dracocephalum ruyschiana*; ion trap; tandem mass spectrometry; polyphenolic compounds

1. Introduction

The genus *Dracocephalum* L. (family *Lamiaceae*) is represented on the territory of the Republic of Sakha (Yakutia) by five species—*Dracocephalum jacutense* Peschkova, *D. nutans* L., *D. palmatum* Stephan, *D. ruyschiana* L., and *D. stellerianum* Hiltebr [1]. These are perennial herbaceous plants, differing in both origin and habitat and belonging to the divisions of vegetation cover. The ranges of *Dracocephalum* are unequal, from extremely small (endemic *D. jacutense* Peschkova) to extensive Eurasian (*D. nutans* L., *D. ruyschiana* L.). The two species of *D. palmatum* Stephan and *D. stellerianum* Hiltebr are widespread in the Asian territory [2]. *Dracocephalum palmatum* Steph. ex Willd. is found in the northeastern regions of Yakutia. It grows on dry stony, gravelly slopes, rocks, stony tundra, and mountain steppes. It is a perennial evergreen plant with creeping shoots and a very dense turf, which forms beneath [3]. *Dracocephalum palmatum* forms continuous "carpet" populations on dry stony mountain slopes under the conditions of the Pole of Cold Oymyakon (N 63°13′32.0″ E 142°53′56.2″) (Figure 1).

Figure 1. *Dracocephalum palmatum* S. in the Oymyakon area of Yakutia (photo taken by Okhlopkova, July 2019).

A total of 23 compounds (phenylpropanoids, coumarins, flavonoids, and triterpenes) were isolated from a crude alcoholic extract of the aerial parts of *Dracocephalum palmatum* in studies by Olennikov et al. (2013) [4]. A research by Kim et al. (2020) aimed to evaluate the tumor suppressive effect of *D. palmatum* extract in diffuse large B cell lymphoma (DLBCL) and its underlying mechanism. The effect of *D. palmatum* extracts on several DLBCL cell lines significantly reduced cell viability and increased apoptosis and, at the same time, did not affect the survival of normal cells in vitro and in vivo. These studies indicate that the cytotoxic effect may be specific to cancer cells [5]. Lee et al. (2020) studied the anticancer potential of dried leaves of *D. palmatum* Stephan using human prostate cancer PC-3 cells. The results showed that the use of *D. palmatum* extract induces apoptosis and has intracellular ROS (reactive oxygen species)—independent antitumor effects on prostate cancer cells associated with increased expression of superoxide dismutase (SOD2) [6].

The habitat of *Dracocephalum ruyschiana* L. extends far to the north; its growth was noted in the Lena and Vilyui river basins, in grass, larch, birch, and mixed forests and meadow steppes. This species has erect stems 20–55 cm high, sparsely shortly pubescent at the nodes and in the upper part, with shortened vegetative shoots in the leaf axils. *Dracocephalum ruyschiana* forms continuous "carpet" populations in the Amga River valley in the conditions of Central Yakutia (N 60°31′09.0″ E 131°26′26.7″) (Figure 2). Kakasy et al. (2006) identified the composition of *D. ruyschiana* L. extracts using HPLC and GC–MS with particular emphasis on their flavonoids, aliphatic, aromatic carboxylic acids, and sugars. GC–MS analysis identified and quantified as the main components monosaccharides, sugar alcohols, disaccharides, and trisaccharides, 33 components in total [7].

A review by Zeng et al. (2010) is devoted to the study of the chemical compositions of plants of the genus *Dracocephalum* L. Since the 1970s, 246 compounds, including terpenoids, steroids, flavonoids, alkaloids, lignans, phenols, and coumarins, have been identified from the genus *Dracocephalum*. As can be seen, terpenoids are the dominant constituents within the genus *Dracocephalum* [8].

Figure 2. *Dracocephalum ruyschiana* L. in the Amga area of Yakutia (photo taken by Okhlopkova, July 2019).

Five new flavone tetraglycosides, 5 new benzyl alcohol glycosides, and 19 known compounds were isolated from the extract of the aerial parts of *D. ruyschiana*. *D. ruyschiana* L. (*Lamiaceae*) is a traditional medicinal plant in Mongolia [9].

In this work, we used an HPLC–MS/MS–ion trap to carry out a phytochemical study involving a detailed metabolomic and comparative analysis of *D. palmatum* and *D. ruyschiana* extracts. Aboveground, phytomass of *D. palmatum* was collected during expedition work on the territory of the Pole of Cold Oymyakon during the period of seed ripening (from 15 to 25 July 2019). Phytomass of *D. ruyschiana* was collected on the territory of the river Amga, Yakutia, in June 2019.

2. Results

Extracts of *D. palmatum* S. and *D. ruyschiana* L. were analyzed by an HPLC–MS/MS ion trap to better interpret the diversity of available phytochemicals. All of them have a rich bioactive composition. The structural identification of each compound was carried out on the basis of their accurate mass and MS/MS fragmentation by HPLC–ESI–ion trap–MS/MS. A total of 114 compounds were successfully characterized in extracts of *D. palmatum* and *D. ruyschiana* based on their accurate MS and fragment ions by searching online databases and the reported literature.

All the identified compounds along with molecular formulas, MS/MS data, and their comparative profile for two varieties of *Dracocephalum* are summarized in Table A1 (Appendix A). These are flavones: apigenin 8-*C*-pentoside-6-*C*-hexoside, nevadensin, apigenin 7-*O*-glucuronide, chrysin 6-*C*-glucoside chrysin glucuronide, and acacetin 7-*O*-glucoside; flavanols: dihydrokaempferol, dihydroquercetin, astragalin, kaempferol 3-*O*-rutinoside, and ampelopsin; flavan-3-ols: catechin, gallocatechin, and flavanone fustin; phenolic acids: methylgallic acid, hydroxy methoxy dimethylbenzoic acid, ellagic acid, caffeoylshikimic acid, prolithospermic acid, salvianolic acid G, and 3,4-*O*-dicaffeoylquinic acid; stilbenes: pinosylvin and resveratrol; anthocyanins: pelargonidin-3-*O*-glucoside, peonidin *O*-pentoside, cyanidin 3-(6″-malonylglucoside), and cyanidin 3-(acetyl)hexose; lignans: hinokinin and dimethyl-secoisolariciresinol; carotenoids: *β-apo*-12′carotenal, apo-carotenal, 5,8-*epoxy*-*α*-carotene, cryptoxanthin, and violaxanthin; and so forth.

3. Discussion

A total of 114 compounds were identified in extracts of *D. palmatum* and *D. ruyschiana*, and 92 compounds were identified for the first time in the genus *Dracocephalum*. New identified metabolites belonged to 17 classes, including 16 phenolic acids and their conjugates, 18 flavones, 5 flavonols, 2 flavan-3-ols, 1 flavanone, 2 stilbenes, 10 anthocyanins, 1 condensed tannin, 2 lignans, 6 carotenoids, 3 oxylipins, 2 amino acids, 3 sceletium alkaloids, 3 carboxylic acids, 8 fatty acids, 1 sterol, and 3 terpenes, along with 6 miscellaneous compounds. Metabolomic screening of polyphenols by *D. palmatum* and *D. ruyschiana* included flavones, flavonols, flavan-3-ols, flavanones, anthocyanins, condensed tannins, lignans, stilbenes, and phenolic acids.

3.1. Flavones

3.1.1. Trihydroxyflavones

The flavones apigenin (compound **2**) and diosmetin (compound **7**) have already been characterized as a component of Andean blueberry [10], *Lonicera japonicum* [11], Mexican lupine species [12], *Cirsium japonicum* [13], *Mentha* [14], *and Dracocephalum moldavica* [15]. The flavone apigenin was found in extracts of *D. palmatum* and *D. ruyschiana.* The flavone diosmetin was found in extracts of *D. palmatum.* The CID spectrum in positive ion modes of diosmetin from extracts of *D. palmatum* is shown in Figure 3.

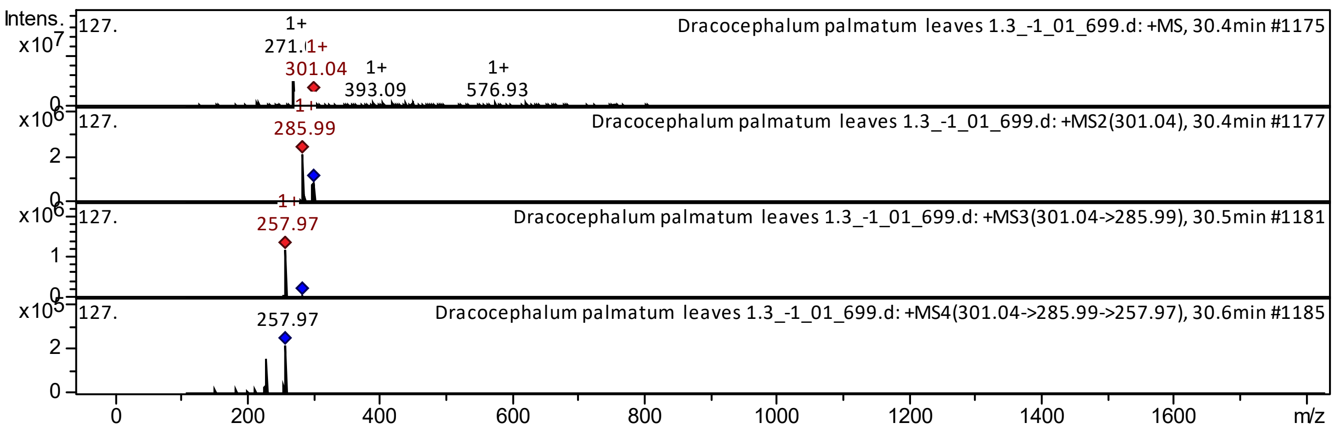

Figure 3. CID spectrum of diosmetin from extracts of *D. palmatum*, *m/z* 301.

The $[M + H]^+$ ion produced one fragment ion at *m/z* 286 (Figure 3). The fragment ion with *m/z* 286 yields a daughter ion at *m/z* 258. It was identified in the bibliography in extracts of Andean blueberry [10], *Lonicera japonicum* [11], Mexican lupine species [12], *Cirsium japonicum* [13], *Mentha* [14], and *Dracocephalum moldavica* [15].

3.1.2. Tetrahydroxyflavones

The flavone luteolin (compound **5**) has already been characterized as a component of *Eucalyptus* [16], and *Triticum aestivum* [17]. The flavone luteolin was found in extracts of *D. palmatum* and *D. ruyschiana.* The CID spectrum in positive ion modes of luteolin from extracts of *D. palmatum* is shown in Figure 4.

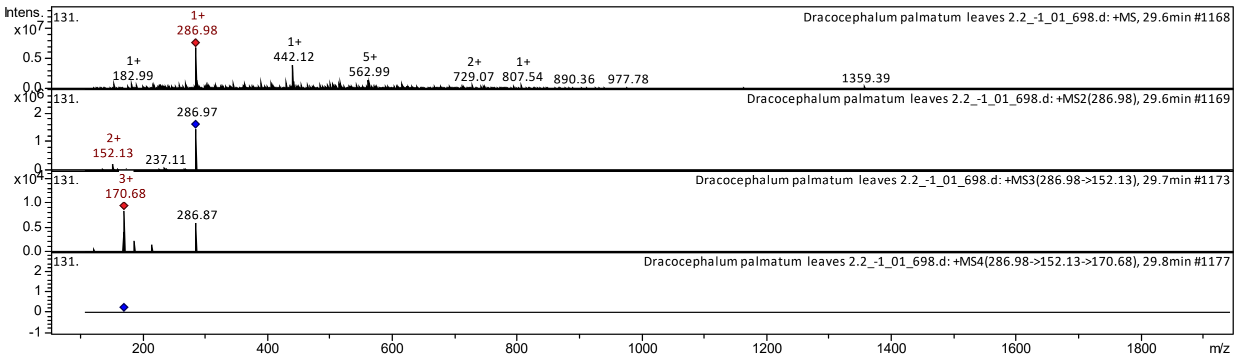

Figure 4. CID spectrum of luteolin from extracts of *D. palmatum*, *m/z* 286.98

The $[M + H]^+$ ion produced two fragment ions at *m/z* 152 and *m/z* 237 (Figure 4). It was identified in the bibliography in extracts of *Eucalyptus* [16], and *Triticum aestivum* [17].

3.1.3. Dimethoxyflavones

The flavones negletein (compound **3**) and acacetin (compound **4**) have already been characterized as a component of *Wissadula periplocifolia* [18], and *Actinocarya tibetica* [19]. Flavone acacetin was found in extracts of *D. palmatum* and *D. ruyschiana.* The CID spectrum in positive ion modes of negletein from extracts of *D. palmatum* is shown in Figure 5.

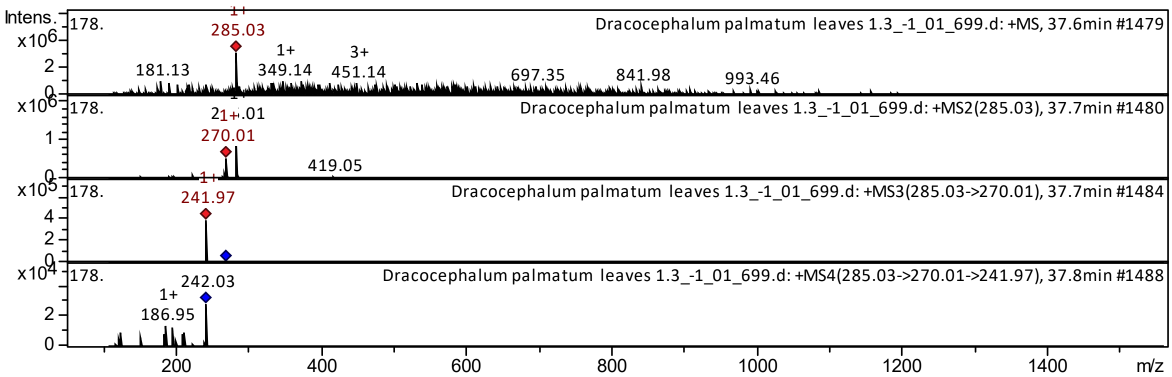

Figure 5. CID spectrum of negletein from extracts of *D. palmatum*, *m/z* 285.03.

The $[M + H]^+$ ion produced one fragment ion at *m/z* 270 (Figure 5). The fragment ion with *m/z* 270 yields a daughter ion at *m/z* 241. The fragment ion with *m/z* 241 yields daughter ions at *m/z* 187. It was identified in the bibliography in extracts of *Wissadula periplocifolia* [18], and *Actinocarya tibetica* [19].

3.1.4. Trimethoxyflavone

The flavones salvigenin (compound **8**) and nevadensin (compound **9**) have already been characterized as components of *Ocimum* [20]. The trimethoxyflavones salvigenin and nevadensin were found in an extract of *D. palmatum.*

3.1.5. Isoflavones

The isoflavones apigenin 7-*O*-*β*-D-(6″-O-malonyl)-glucoside (compound **23**) and 2′-hydroxygenistein *O*-glucoside malonylated (compound **25**) have already been characterized as a component of, Mexican lupine species [12], and *Zostera marina* [21]. Both isoflavones were found in extracts of *D. palmatum.*

3.1.6. Flavone Glucoside

The flavones apigenin 5-*O*-glucoside (compound **13**), apigenin 7-*O*-glucoside (compound **14**), acacetin 7-*O*-glucoside (compound **16**), acacetin 8-*O*-glucoside (compound **17**), luteolin 7-*O*-glucoside (compound **18**), and diosmetin 7-*O*-*β*-glucoside (compound **21**) have already been characterized as a component of rice [22], *Oxalis corniculata* [23], *Mentha* [24], pear [25], and *Passiflora incarnata* [26]. The flavones apigenin 7-*O*-glucoside (compound **14**) and acacetin 7-*O*-glucoside (compound **16**) were found in an extract of *D. palmatum* and *D. ruyschiana.*

The flavones apigenin 5-*O*-glucoside (compound **13**), acacetin 8-*C*-glucoside (compound **17**), and luteolin 7-*O*-glucoside (compound **18**) were found in an extract of *D. palmatum.* The CID spectrum in positive ion modes of acacetin 7-*O*-glucoside from *D. palmatum* is shown in Figure 6.

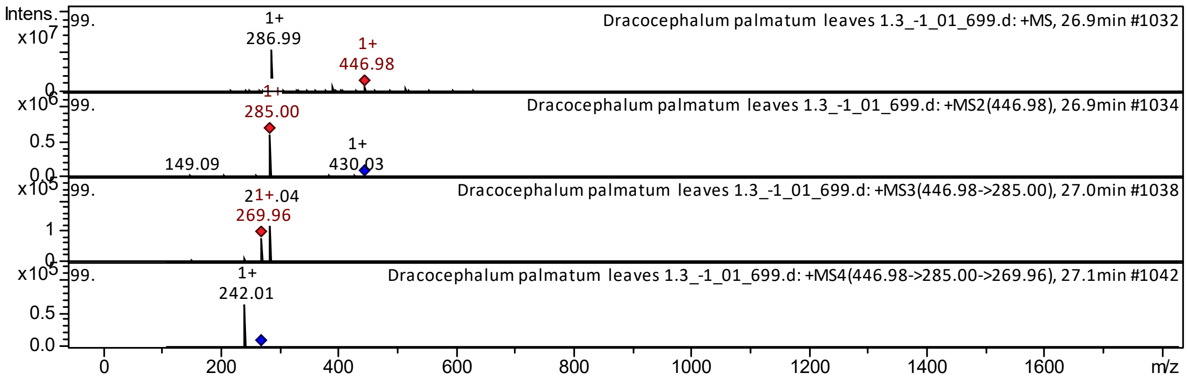

Figure 6. CID spectrum of acacetin 7-*O*-glucoside from *D. palmatum*, *m*/*z* 446.98.

The $[M + H]^+$ ion produced three fragment ions at *m*/*z* 285, *m*/*z* 430, and *m*/*z* 149 (Figure 6). The fragment ion with *m*/*z* 285 yields a daughter ion at *m*/*z* 269. The fragment ion with *m*/*z* 269 yields daughter ions at *m*/*z* 242. It was identified in the bibliography in extracts from *Bougainvillea* [27].

3.1.7. Flavone Glucuronide

The flavone chrysin glucuronide (compound **12**) has already been characterized as a component of *F. pottsii* [28]. The flavone apigenin 7-*O*-glucuronide (compound **15**) has already been characterized as a component of peppermint [29] and *Newbouldia laevis* [30]. The flavone luteolin 7-*O*-*β*-D-glucuronide (compound **20**) has already been characterized as a component of *Mentha* [31], rat plasma [32], and *Thymus vulgaris* [33]. All flavone glucuronides were found in an extract of *D. ruyschiana.*

3.2. Flavonols

3.2.1. Trihydroxyflavones

The flavonols astragalin (compound **35**) and kaempferol 3-*O*-rutinoside (compound **37**) have already been characterized as a component of *Camellia kucha* [34], strawberry [35], and *Rhus coriaria* [36]. Both flavonols were found in extracts of *D. palmatum.* The CID spectrum in negative ion modes of kaempferol 3-*O*-rutinoside from extracts of *D. palmatum* is shown in Figure 7.

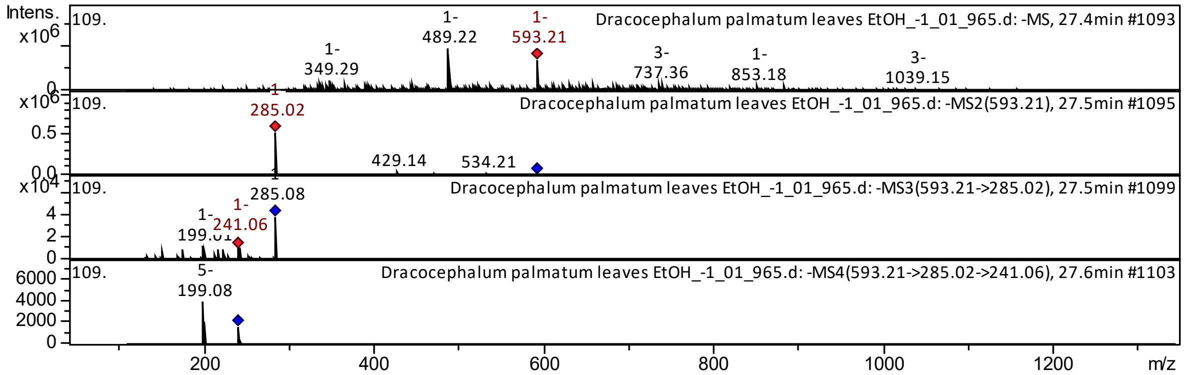

Figure 7. CID spectrum of kaempferol 3-*O*-rutinoside from extracts of *D. palmatum*, *m/z* 593.21.

The [M − H]⁻ ion produced three fragment ions at *m/z* 285, *m/z* 534, and *m/z* 429 (Figure 7). The fragment ion with *m/z* 285 yields two daughter ions at *m/z* 241 and *m/z* 199. It was identified in the bibliography in extracts from *Camellia kucha* [34], strawberry [35], and *Rhus coriaria* [36].

3.2.2. Tetrahydroxyflavone

The flavonol kaempferol (compound **31**) has already been characterized as a component of potato leaves [37], and rapeseed petals [38]. Flavonol kaempferol was found in extracts of *D. palmatum* and *D. ruyschiana.*

3.2.3. Hexahydroxyflavone

The hexahydroxyflavone ampelopsin (compound **34**) has already been characterized as a component of *Impatiens glandulifera* Royle [39]. It was identified in extracts of *D. palmatum*. The CID spectrum in positive ion modes of ampelopsin from extracts of *D. palmatum* is shown in Figure 8.

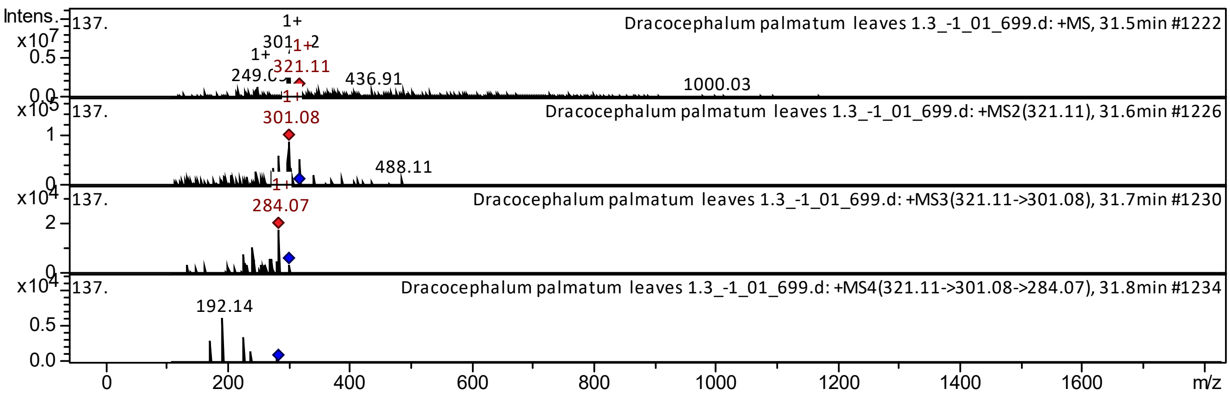

Figure 8. CID spectrum of ampelopsin from extracts of *D. palmatum*, *m/z* 321.11.

The [M + H]⁺ ion produced one fragment ion at *m/z* 301 (Figure 8). The fragment ion with *m/z* 301 yields a daughter ion at *m/z* 284. The fragment ion with *m/z* 284 yields daughter ions at *m/z* 192. It was identified in the bibliography in extracts from *Impatiens glandulifera* Royle [39].

3.2.4. Dihydroflavonols

The dihydroflavonols dihydrokaempferol (compound **32**) and dihydroquercetin (compound **33**) have already been characterized as a component of strawberry [40] and *Solanum tuberosum* [41]. The flavonols dihydrokaempferol and dihydroquercetin were found in extracts of *D. palmatum*. The CID spectrum in negative ion modes of kaempferol 3-*O*-rutinoside from extracts of *D. palmatum* is shown in Figure 9.

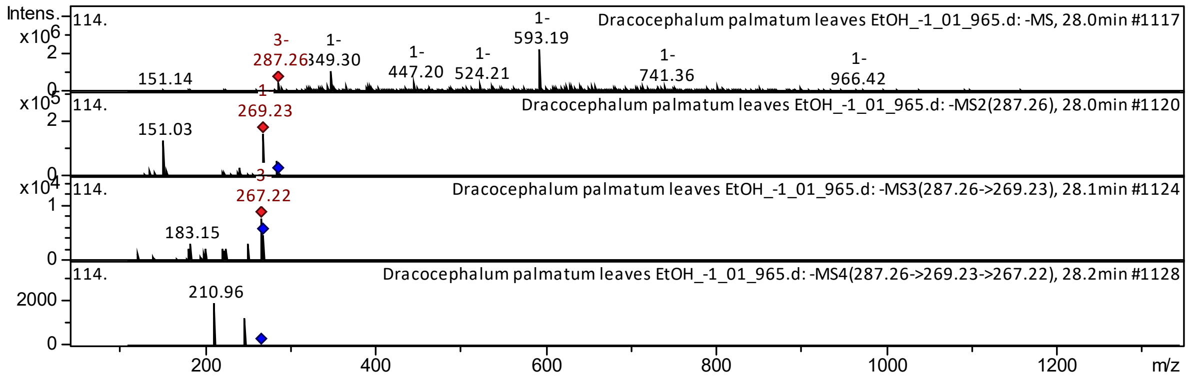

Figure 9. CID spectrum of dihydrokaempferol from extracts of *D. palmatum*, *m/z* 287.26.

The $[M - H]^-$ ion produced two fragment ions at *m/z* 269 and *m/z* 151 (Figure 9). The fragment ion with *m/z* 269 yields two daughter ions at *m/z* 267 and *m/z* 183. This compound was identified in the bibliography in extracts from of strawberry [40] and *Solanum tuberosum* [41].

3.3. Condensed Tannin

The procyanidin A-type dimer (compound **78**) has already been characterized as a component of *Vaccinium macrocarpon* [42] and *Vaccinium myrtillus* [43]. The CID spectrum in positive ion modes of procyanidin A-type dimer from *D. ruyschiana* is shown in Figure 10. The $[M + H]^+$ ion produced four fragment ions at *m/z* 415, *m/z* 352, *m/z* 283, and *m/z* 164 (Figure 10). The fragment ion with *m/z* 415 yields three daughter ions at *m/z* 337, *m/z* 295, and *m/z* 193. This compound was identified in the bibliography in extracts from *Vaccinium macrocarpon* [42] and *Vaccinium myrtillus* [43].

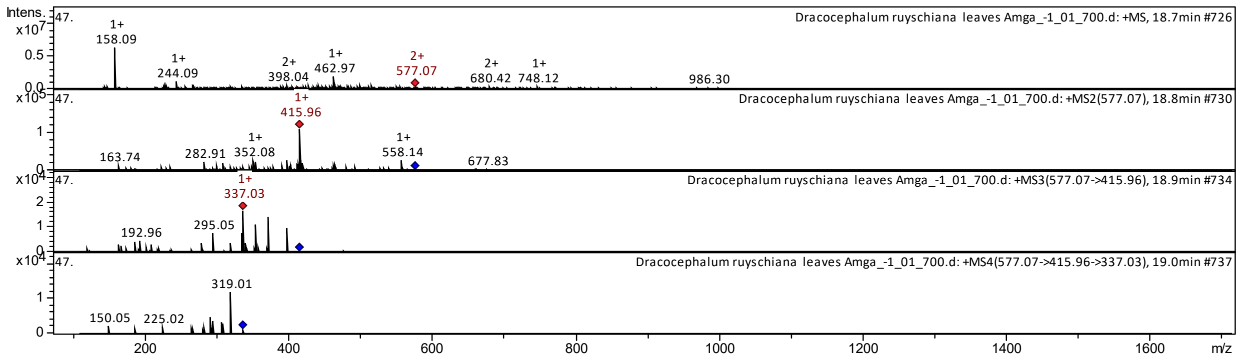

Figure 10. CID spectrum of procyanidin from extracts of *D. ruyschiana*, *m/z* 577.07.

The polyphenol composition distribution table is shown below (Table 1). The comparison table shows the presence of some flavonoids in both types of the genus *Dracocephalum* (apigenin, acacetin, luteolin, apigenin 7-*O*-glucoside, acacetin 7-*O*-glucoside, kaempferol, prunin, eriodictyol 7-*O*-glucoside, caffeic acid, caffeic acid-*O*-hexoside, dimethyl-secoisolariciresinol, petunidin, and pelargonidin 3-*O*-glucoside). Mass spectrometric studies have convincingly shown that the amount of polyphenolic compounds in the extracts of *D. palmatum* is greater than in the extracts of *D. ruyschiana*. The number of polyphenolic compounds identified as a result of the study in the extracts of *D. palmatum* is 57 compounds. In extracts of *D. ruyschiana*, 35 compounds.

Table 1. The flavonoid composition distribution of the genus *Dracocephalum* L. Blue square—presence in extracts of *D. ruyschiana*; magenta square—in extracts of *D. palmatum.*

No.	Class of Compounds	Identified Compounds	Formula	*D. ruyschiana*	*D. palmatum*
1	Flavone	**Apigeninidin**	$C_{15}H_{11}O_4$	■	
2	Flavone	**Apigenin**	$C_{15}H_{10}O_5$	■	■
3	Flavone	**Negletein** (5,6-dihydroxy-7-methoxyflavone)	$C_{16}H_{12}O_5$		■
4	Flavone	**Acacetin** (linarigenin, buddleoflavonol)	$C_{16}H_{12}O_5$	■	■
5	Flavone	**Luteolin**	$C_{15}H_{10}O_6$	■	■
6	Flavone	**Apigenin-7, 4′-dimethyl ether**	$C_{17}H_{14}O_5$		■
7	Flavone	**Diosmetin**	$C_{16}H_{12}O_6$		■
8	Flavone	**Salvigenin**	$C_{18}H_{16}O_6$		■
9	Flavone	**Nevadensin**	$C_{18}H_{16}O_7$		■
10	Flavone	**Apigenin 7-sulfate**	$C_{15}H_{10}O_8S$	■	
11	Flavone	**Chrysin 6-*C*-glucoside**	$C_{21}H_{20}O_9$	■	
12	Flavone	**Chrysin glucuronide**	$C_{21}H_{18}O_{10}$	■	
13	Flavone	**Apigenin-5-*O*-glucoside**	$C_{21}H_{20}O_{10}$		■
14	Flavone	**Apigenin-7-*O*-glucoside**	$C_{21}H_{20}O_{10}$	■	■
15	Flavone	**Apigenin 7-*O*-glucuronide**	$C_{21}H_{18}O_{11}$	■	
16	Flavone	**Acacetin 7-*O*-glucoside**	$C_{22}H_{22}O_{10}$	■	■
17	Flavone	**Acacetin 8-*C*-glucoside**	$C_{22}H_{22}O_{10}$		■
18	Flavone	**Luteolin 7-*O*-glucoside** (cynaroside, luteoloside)	$C_{21}H_{20}O_{11}$		■
19	Flavone	**Acacetin 7-*O*-*beta*-D-glucuronide**	$C_{22}H_{20}O_{11}$	■	
20	Flavone	**Luteolin-7-*O*-beta-glucuronide**	$C_{21}H_{18}O_{12}$	■	
21	Flavone	**Diosmetin-7-*O*-beta-glucoside**	$C_{22}H_{22}O_{11}$	■	
22	Flavone	**Luteolin *O*-acetyl-hexoside**	$C_{23}H_{22}O_{12}$		■
23	Isoflavone	**Apigenin 7-*O-beta-D-(6″ -O*-malonyl)-glucoside**	$C_{24}H_{22}O_{13}$		■
24	Flavone	**Acacetin 8-*C*-glucoside malonylated**	$C_{25}H_{24}O_{13}$		■
25	Isoflavone	**2′-Hydroxygenistein *O*-glucoside malonylated**	$C_{24}H_{22}O_{14}$		■
26	Flavone	**Luteolin 7-*O-beta-D-(6″ -O*-malonyl)-glucoside**	$C_{24}H_{22}O_{14}$		■
27	Flavone	**Acacetin *C*-glucoside methylmalonylated**	$C_{26}H_{26}O_{13}$		■
28	Flavone	**Apigenin 8-*C*-hexoside-6-*C*-pentoside**	$C_{26}H_{28}O_{14}$	■	
29	Flavone	**Apigenin 8-*C*-pentoside-6-*C*-hexoside**	$C_{26}H_{28}O_{14}$	■	
30	Flavone	**Apigenin 6-*C*-[6″ -acetyl-2″ -*O*-deoxyhexoside]-glucoside**	$C_{29}H_{32}O_{15}$		■
31	Flavonol	**Kaempferol**	$C_{15}H_{10}O_6$	■	■
32	Flavonol	**Dihydrokaempferol** (aromadendrin; katuranin)	$C_{15}H_{12}O_6$		■
33	Flavonol	**Dihydroquercetin** (taxifolin, taxifoliol)	$C_{15}H_{12}O_7$		■
34	Flavonol	**Ampelopsin** (dihydromyricetin, ampeloptin)	$C_{15}H_{12}O_8$		■
35	Flavonol	**Astragalin** (kaempferol 3-*O*-glucoside; kaempferol-3-beta-monoglucoside, astragaline)	$C_{21}H_{20}O_{11}$		■
36	Flavonol	**Kaempferol-3-*O*-glucuronide**	$C_{21}H_{18}O_{12}$	■	
37	Flavonol	**Kaempferol 3-*O*-rutinoside**	$C_{27}H_{30}O_{15}$		■
38	Flavan-3-ol	**(epi)catechin**	$C_{15}H_{14}O_6$	■	
39	Flavan-3-ol	**Gallocatechin** [+(−)gallocatechin]	$C_{15}H_{14}O_7$		■
40	Flavanone	**Naringenin** (naringetol, naringenin)	$C_{15}H_{12}O_5$		■
41	Flavanone	**Eriodictyol** (3′,4′,5,7-tetrahydroxy-flavanone)	$C_{15}H_{12}O_6$		■

42	Flavanone	**Fustin** (2,3-dihydrofistein)	$C_{15}H_{12}O_6$		
43	Flavanone	**Prunin** (naringenin-7-*O*-glucoside)	$C_{21}H_{22}O_{10}$		
44	Flavanone	**Eriodictyol-7-O-glucoside**	$C_{21}H_{22}O_{11}$		
45	Flavanone	**Eriodictyol *O*-malonyl-hexoside**	$C_{24}H_{24}O_{14}$		
46	Hydroxycinnamic acid	**Caffeic acid**	$C_9H_8O_4$		
47	Phenolic acid	**Methylgallic acid** (methyl gallate)	$C_8H_8O_5$		
48	Phenolic acid	**Hydroxy methoxy dimethylbenzoic acid**	$C_{10}H_{12}O_4$		
49	Phenolic acid	**Ethyl caffeate** (ethyl 3,4-dihydroxycinnamate)	$C_{11}H_{12}O_4$		
50	Hydroxybenzoic acid	**4-Hydroxybenzoic acid**	$C_7H_6O_3$		
51	Hydroxybenzoic acid	**Ellagic acid**	$C_{14}H_6O_8$		
52	Hydroxycinnamic acid	**Sinapic acid** (trans-sinapic acid)	$C_{11}H_{12}O_5$		
53	Hydroxycinnamic acid	**1-O-(4-Coumaroyl)-glucose**	$C_{15}H_{18}O_8$		
54	Gallate ester	**Beta-glucogallin**	$C_{13}H_{16}O_{10}$		
55	Phenolic acid	**Caffeoylshikimic acid** (5-O-caffeoylshikimate)	$C_{16}H_{15}O_8$		
56	Phenolic acid	**Salvianolic acid G**	$C_{18}H_{12}O_7$		
57	Phenolic acid	**1-caffeoyl-beta-D-glucose**	$C_{15}H_{18}O_9$		
58	Phenolic acid	**Caffeic acid-*O*-hexoside** (caffeoyl-*O*-hexoside)	$C_{15}H_{18}O_9$		
59	Phenolic acid	**Prolithospermic acid**	$C_{18}H_{14}O_8$		
60	Phenolic acid	**Rosmarinic acid**	$C_{18}H_{16}O_8$		
61	Phenolic acid	**Caffeic acid derivative**	$C_{16}H_{18}O_9Na$		
62	Phenolic acid	**Salvianic acid C**	$C_{18}H_{18}O_9$		
63	Phenolic acid	**3,4-*O*-dicaffeoylquinic acid** (Isochlorogenic acid B)	$C_{25}H_{24}O_{12}$		
64	Stilbene	**Pinosylvin**	$C_{14}H_{12}O_2$		
65	Stilbene	**Resveratrol**	$C_{14}H_{12}O_3$		
66	Lignan	**Hinokinin**	$C_{20}H_{18}O_6$		
67	Lignan	**Dimethyl-secoisolariciresinol**	$C_{22}H_{30}O_6$		
68	Anthocyanidin	**Petunidin**	$C_{16}H_{13}O_{7+}$		
69	Anthocyanidin	**Cyanidin *O*-pentoside**	$C_{20}H_{19}O_{10}$		
70	Anthocyanidin	**Pelargonidin-3-*O*-glucoside** (callistephin)	$C_{21}H_{21}O_{10}$		
71	Anthocyanidin	**Peonidin *O*-pentoside**	$C_{21}H_{21}O_{10}$		
72	Anthocyanidin	**Cyanidin-3-*O*-glucoside** (cyanidin 3-*O*-beta-D-glucoside, kuromarin)	$C_{21}H_{21}O_{11}$+		
73	Anthocyanidin	**Peonidin-3-O-glucoside**	$C_{22}H_{23}O_{11}$ +		
74	Anthocyanidin	**Cyanidin 3-(acetyl)hexose**	$C_{23}H_{23}O_{12+}$		
75	Anthocyanidin	**Cyanidin 3-(6″ -malonylglucoside)**	$C_{24}H_{23}O_{14}$		
76	Anthocyanidin	**Cyanidin 3-*O*-coumaroyl hexoside**	$C_{30}H_{27}O_{13}$		
77	Anthocyanidin	**7-O-Methyl-delphinidin-3-O-(2″ galloyl)-galactoside**	$C_{29}H_{26}O_{16}$		
78	Condensed tannin	**Procyanidin A-type dimer**	$C_{30}H_{24}O_{12}$		

A total of 114 metabolome compounds were identified in the extracts of *D. palmatum* and *D. ruyschiana*, many of which are characteristic of the genus *Dracocephalum*. Of these, 92 components were identified for the first time in this plant species. These are flavones: apigenin 8-*C*-pentoside-6-*C*-hexoside, nevadensin, apigenin 7-*O*-glucuronide, negletein, chrysin 6-*C*-glucoside, luteolin 7-*O*-*β*-glucuronide, chrysin glucuronide, and acacetin 7-*O*-glucoside; flavanols: dihydrokaempferol, dihydroquercetin, astragalin, kaempferol 3-*O*-rutinoside, and ampelopsin; flavan-3-ols: catechin, gallocatechin, and flavanone fustin; phenolic acids: 4-hydroxybenzoic acid, methylgallic acid, hydroxy methoxy dimethylbenzoic acid, ellagic acid, caffeoylshikimic acid, prolithospermic acid, salvianolic acid G, and 3,4-*O*-dicaffeoylquinic acid; stilbenes: pinosylvin and resveratrol; anthocyanins: pelargonidin-3-*O*-glucoside, peonidin *O*-pentoside, cyanidin 3-(6″-malonylglucoside), cyanidin 3-(acetyl)hexose, and condensed tannin procyanidin A-type dimer; lignans: hinokinin and dimethyl-secoisolariciresinol; stilbenes: resveratrol and pinosylvin; carotenoids: *β-apo*-12′carotenal, apocarotenal, 5,8-*epoxy*-*α*-carotene, cryptoxanthin, violaxanthin, and sceletium; alkaloids: mesembrenol and 4′-O-desmethyl mesembranol; oxylipins: oxo-DHOD, THODE, and tetrahydroxyxanthen mangiferin; and so forth.

4. Materials and Methods

4.1. Materials

Aboveground, phytomass of *D. palmatum* S. was collected during expedition work on the territory of the Pole of Cold Oymyakon during the period of seed ripening (from 15 to 25 July 2019). Phytomass of *D. ruyschiana* L. was collected on the territory of the river Amga, Yakutia, in June 2019. The identification of the species was carried out by E. G. Nikolin, PhD (IBPK SB RAS). All samples were morphologically authenticated according to the current standard of Pharmacopoeia of the Eurasian Economic Union [44]. Herbariums of plants are kept in the collection of the educational and scientific laboratory “Molecular Genetic and Cellular Technologies” of the Institute of Natural Sciences of North-Eastern Federal University (Yakutsk, Republic of Sakha (Yakutia), Russian Federation).

4.2. Chemicals and Reagents

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

4.3. Fractional Maceration

Fractional maceration technique was applied to obtain highly concentrated extracts [45]. From 500 g of the sample, 10 g of leaves was randomly selected for maceration. The total amount of the extractant (ethyl alcohol of reagent grade) was divided into three parts and consistently infused to the grains with the first, second, and third parts. A solid–solvent ratio was 1:20. The infusion of each part of the extractant lasted 7 days at room temperature.

4.4. Liquid Chromatography

HPLC was performed using Shimadzu LC-20 Prominence HPLC (Shimadzu, Kyoto, Japan), equipped with a UV sensor and C18 silica reverse phase column (4.6 × 150 mm, particle size: 2.7 μm) to perform the separation of multicomponent mixtures. The gradient elution with two mobile phases’ program (A, deionized water; B, acetonitrile with formic acid 0.1% *v*/*v*) was as follows: 0.01–5 min, 100% CH_3CN; 5–45 min, 100–25% CH_3CN; 45–55 min, 25–0% CH_3CN; control washing, 55–60 min, 0% CH3CN. The entire HPLC analysis was performed with a UV–VIS detector, SPD-20A (Shimadzu, Kyoto, Japan), at a wavelength of 230 nm; the temperature was 50 °C, and the total flow rate was 0.25 mL/min. The injection volume was 10 μL. Additionally, liquid chromatography was combined with a mass spectrometric ion trap to identify compounds.

4.5. Mass Spectrometry

MS analysis was performed on an ion trap, amaZon SL (Bruker Daltonics, Bremen, Germany), equipped with an ESI source in negative and positive ion modes. The optimized parameters were obtained as follows: ionization source temperature: 70 °C, gas flow: 4 L/min, nebulizer gas (atomizer): 7.3 psi, capillary voltage: 4500 V, end plate bend voltage: 1500 V, fragmentary: 280 V, collision energy: 60 eV. A four-stage ion separation mode (MS/MS mode) was implemented. An ion trap was used in the scan range *m/z* 100–1.700 for MS and MS/MS. All experiments were repeated three times. A four-stage ion separation mode (MS/MS mode) was implemented.

5. Conclusions

The extracts of *D. palmatum* S. and *D. ruyschiana* L. contain a large number of polyphenolic complexes, which are biologically active compounds. For the most complete and safe extraction, the method of maceration with MeOH was used. To identify target analytes in extracts, HPLC was used in combination with an ion trap. The results of the preliminary study showed the presence of 114 compounds corresponding to the genus *Dracocephalum*, of which 92 were identified for the first time in the genus *Dracocephalum* L.

The data obtained will help to intensify future research on the development and production of various medical products containing targeted extracts of *D. palmatum* S. and *D. ruyschiana* L. A wide variety of biologically active polyphenolic compounds open up rich opportunities for the creation of new drugs, as well as biologically active additives based on extracts from the genus *Dracocephalum*.#

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Appendix A

Table A1. Compounds identified from the extracts of *D. palmatum* S. and *D. ruyschiana* L. in positive and negative ionization modes by HPLC–ion trap–MS/MS.

№	Variety of *Dracocephalum*	Class of Compounds	Identified Compounds	Formula	Mass	Molecular Ion $[M-H]^-$	Molecular Ion [M + H]+	2 Fragmentation MS/MS	3 Fragmentation MS/MS	4 Fragmentation MS/MS	References
			POLYPHENOLS								
1	*D. ruyschiana*	Flavone	**Apigeninidin**	$C_{15}H_{11}O_4$	**255.2454**		**256**	**168**	**122**		*Triticum* [46]
2	*D. palmatum*, *D. ruyschiana*	Flavone	**Apigenin** (5,7-dixydroxy-2-(40hydroxyphenyl)-4H-chromen-4-one)	$C_{15}H_{10}O_5$	**270.2369**		**269**	**225**	**181**	**117**	*Dracocephalum palmatum* [4], Andean blueberry [10], *Lonicera japonicum* [11], Mexican lupine species [12]
3	*D. palmatum*	Flavone	**Negletein** (5,6-dihydroxy-7-methoxyflavone)	$C_{16}H_{12}O_5$	**284.2635**		**285**	**271**	**241**	**187**	*Actinocarya tibetica* [19]
4	*D. palmatum*, *D. ruyschiana*	Flavone	**Acacetin** (linarigenin, buddleoflavonol)	$C_{16}H_{12}O_5$	**284.2635**		**285**	**268**	**211; 143**		*Dracocephalum palmatum* [4], Mexican lupine species [12], *Mentha* [14], *Dracocephalum moldavica* [15], *Wissadula periplocifolia* [18]
5	*D. palmatum*, *D. ruyschiana*	Flavone	**Luteolin**	$C_{15}H_{10}O_6$	**286.2363**		**287**	**286; 153**	**171**	**153**	*Dracocephalum palmatum* [4], *Eucalyptus* [16], *Lonicera japonicum* [11]
6	*D. palmatum*	Flavone	**Apigenin-7, 4′-dimethyl ether**	$C_{17}H_{14}O_5$	**298.2901**		**299**	**284**	**256**		*Ocimum* [20]
7	*D. palmatum*	Flavone	**Diosmetin** (luteolin 4′-methyl ether, salinigricoflavonol)	$C_{16}H_{12}O_6$	**300.2629**		**301**	**286**	**258**		Andean blueberry [10], *Lonicera japonicum* [11], *Cirsium japonicum* [13], *Mentha* [14], *Dracocephalum moldavica* [15]
8	*D. palmatum*	Flavone	**Salvigenin**	$C_{18}H_{16}O_6$	**328.3160**		**329**	**314; 240**	**154**		*Dracocephalum palmatum* [4], *Ocimum* [20]

9	*D. palmatum*	Flavone	**Nevadensin**	$C_{18}H_{16}O_7$	344.3154		345	311	284	149	*Mentha* [14], *Ocimum* [20]
10	*D. ruyschiana*	Flavone	**Apigenin 7-sulfate**	$C_{15}H_{10}O_8S$	350.3001	349		269	223		sulfates [18], *G. linguiforme* [28],
11	*D. ruyschiana*	Flavone	**Chrysin 6-*C*-glucoside**	$C_{21}H_{20}O_9$	416.3781		417	51; 127	333; 267	165	*Passiflora incarnata* [26]
12	*D. ruyschiana*	Flavone	**Chrysin glucuronide**	$C_{21}H_{18}O_{10}$	430.3616		431	255	255; 153	171	*F. pottsii* [28]
13	*D. palmatum*	Flavone	**Apigenin-5-*O*-glucoside**	$C_{21}H_{20}O_{10}$	432.3775		433	414; 274; 215; 145	371; 245; 147	327	Rice [22]
14	*D. palmatum*, *D. ruyschiana*	Flavone	**Apigenin-7-*O*-glucoside** (apigetrin, cosmosiin)	$C_{21}H_{20}O_{10}$	432.3775		433	271	153		*Dracocephalum palmatum* [4], *Mentha* [24], Mexican lupine species [12]
15	*D. ruyschiana*	Flavone	**Apigenin 7-*O*-glucuronide**	$C_{21}H_{18}O_{11}$	446.361		447	271	153	271; 171	Pear [25], *Bougainvillea* [27]
16	*D. palmatum*, *D. ruyschiana*	Flavone	**Acacetin 7-*O*-glucoside** (tilianin)	$C_{22}H_{22}O_{10}$	446.4041		447	285; 149	270	242	*Dracocephalum palmatum* [4], *Bougainvillea* [27]
17	*D. palmatum*	Flavone	**Acacetin 8-*C*-glucoside**	$C_{22}H_{22}O_{10}$	446.4041		447	428; 344	343; 230; 133	232	Mexican lupine species [12]
18	*D. palmatum*	Flavone	**Luteolin 7-*O*-glucoside** (cynaroside, luteoloside)	$C_{21}H_{20}O_{11}$	448.3769		449	287; 199	153		*Lonicera japonicum* [11], Pear [25], *Passiflora incarnata* [26]
19	*D. ruyschiana*	Flavone	**Acacetin 7-*O*-*beta*-D-glucuronide**	$C_{22}H_{20}O_{11}$	460.3876	459		283; 343; 175	268	267	*Dracocephalum moldavica* [15]
20	*D. ruyschiana*	Flavone	**Luteolin-7-*O*-beta-glucuronide**	$C_{21}H_{18}O_{12}$	462.3604		463	287	268	245; 119	*Mentha* [14], rat plasma [32], *Newbouldia laevis* [30]
21	*D. ruyschiana*	Flavone	**Diosmetin-7-*O*-beta-glucoside**	$C_{22}H_{22}O_{11}$	462.4035		463	287	168	123	*Dracocephalum moldavica* [15], *Oxalis corniculata* [23]
22	*D. palmatum*	Flavone	**Luteolin *O*-acetyl-hexoside**	$C_{23}H_{22}O_{12}$	490.4136	489		285; 450	199	155	*Dracocephalum palmatum* [4]
23	*D. palmatum*	Isoflavone	**Apigenin 7-*O*-*beta-D*-(6″-*O*-malonyl)-glucoside**	$C_{24}H_{22}O_{13}$	518.4237		519	502; 184	125		*Dracocephalum moldavica* [14], *Zostera marina* [21]

24	*D. palmatum*	Flavone	**Acacetin 8-*C*-glucoside malonylated**	$C_{25}H_{24}O_{13}$	**532.4503**		**533**	**497; 205**	**377; 335**		Mexican lupine species [12]
25	*D. palmatum*	Isoflavone	**2′-Hydroxygenistein *O*-glucoside malonylated**	$C_{24}H_{22}O_{14}$	**534.4231**	**533**		**489**	**285; 326**	**284**	Mexican lupine species [12]
26	*D. palmatum*	Flavone	**Luteolin 7-*O*-*beta*-*D*-(6″ -*O*-malonyl)-glucoside**	$C_{24}H_{22}O_{14}$	**534.4231**		**535**	**436; 354; 287; 214**	**328; 238**		*Dracocephalum moldavica* [15], *Zostera marina* [21]
27	*D. palmatum*	Flavone	**Acacetin *C*-glucoside methylmalonylated**	$C_{26}H_{26}O_{13}$	**546.4758**		**547**	**529; 496; 369**	**343**		Mexican lupine species [12]
28	*D. ruyschiana*	Flavone	**Apigenin 8-*C*-hexoside-6-*C*-pentoside**	$C_{26}H_{28}O_{14}$	**564.4921**		**565**	**547; 511; 427**	**529; 499**	**511**	*Triticum aestivum* L. [47,48], *Bituminaria* [49], *Licania Rigida* [50]
29	*D. ruyschiana*	Flavone	**Apigenin 8-*C*-pentoside-6-*C*-hexoside**	$C_{26}H_{28}O_{14}$	**564.4921**		**565**	**547; 274**	**529; 474; 247**	**390**	*Triticum aestivum* L. [47,48], *Bituminaria* [49], *Licania Rigida* [50]
30	*D. palmatum*	Flavone	**Apigenin 6-*C*-[6″ -acetyl-2″ -*O*-deoxyhexoside]-glucoside**	$C_{29}H_{32}O_{15}$	**620.5554**		**621**	**561; 218**	**533**	**445; 222**	*Passiflora incarnata* [26]
31	*D. palmatum*, *D. ruyschiana*	Flavonol	**Kaempferol** (3,5,7-trihydroxy-2-(4-hydro-xyphenyl)-4H-chromen-4-one)	$C_{15}H_{10}O_{6}$	**286.2363**		**287**	**269; 202**	**233; 205**	**216**	Andean blueberry [10], *Lonicera japonicum* [11], *Rhus coriaria* (Sumac) [36], potato leaves [37], rapeseed petals [38]
32	*D. palmatum*	Flavonol	**Dihydrokaempferol** (aromadendrin, katuranin)	$C_{15}H_{12}O_{6}$	**288.2522**	**287**		**269; 151**	**267; 183**	**211**	*F. glaucescens* [28], *Camellia kucha* [34], *Rhodiola rosea* [51]
33	*D. palmatum*	Flavonol	**Dihydroquercetin** (taxifolin, taxifoliol)	$C_{15}H_{12}O_{7}$	**304.2516**		**305**	**287**	**286; 186**	**185**	Andean blueberry [10], *Eucalyptus* [16], *Camellia kucha* [34], strawberry [40]
34	*D. palmatum*	Flavonol	**Ampelopsin** (dihydromyricetin, ampeloptin]	$C_{15}H_{12}O_{8}$	**320.251**		**321**	**301**	**284**	**192**	*Rhus coriaria* [36], *Impatiens glandulifera* Royle [39]
35	*D. palmatum*	Flavonol	**Astragalin** (kaempferol 3-*O*-glucoside, kaempferol-3-beta-monoglucoside)	$C_{21}H_{20}O_{11}$	**448.3769**	**447**		**285; 327**	**241**	**199**	*Lonicera japonicum* [11], Mexican lupine species

											[12], pear [25], *Camellia kucha* [34]
36	*D. ruyschiana*	Flavonol	**Kaempferol-3-*O*-glucuronide**	$C_{21}H_{18}O_{12}$	**462.3604**		**463**	**287**	**268; 169**	**241; 119**	*A. cordifolia*, *G. linguiforme* [28], Strawberry [35], *Rhus coriaria* [36]
37	*D. palmatum*	Flavonol	**Kaempferol 3-*O*-rutinoside**	$C_{27}H_{30}O_{15}$	**594.5181**	**593**		**285**	**241; 199**	**199**	*Lonicera japonicum* [11], Pear [25], *Camellia kucha* [34], strawberry [35], *Rhus coriaria* [36],
38	*D. ruyschiana*	Flavan-3-ol	**(Epi)catechin**	$C_{15}H_{14}O_6$	**290.2681**		**291**	**273; 117**	**255; 145**		Andean blueberry [10], *C. edulis* [28], *Camellia kucha* [34], *Radix polygoni multiflori* [52], cranberry [53],
39	*D. palmatum*	Flavan-3-ol	**Gallocatechin** (+(−)gallocatechin)	$C_{15}H_{14}O_7$	**306.2675**		**307**	**289**	**259**		*Licania ridigna* [50], *G. linguiforme* [28], *Vaccinium myrtillus* [43], *Rhodiola rosea* [51]
40	*D. palmatum*	Flavanone	**Naringenin** (naringetol, naringenin)	$C_{15}H_{12}O_5$	**272.5228**		**273**	**153; 256**	**125**		*Dracocephalum palmatum* [4], Andean blueberry [10], *Eucalyptus* [16], Mexican lupine species [12], rapeseed petals [38]
41	*D. palmatum*	Flavanone	**Eriodictyol** (3′,4′,5,7-tetrahydroxy-flavanone)	$C_{15}H_{12}O_6$	**288.2522**		**289**	**163; 271**	**145**	**117**	*Dracocephalum palmatum* [4], Andean blueberry [10], *Eucalyptus* [16], *Mentha* [24], peppermint [29]
42	*D. ruyschiana*	Flavanone	**Fustin** (2,3-dihydrofistein)	$C_{15}H_{12}O_6$	**288.2522**	**287**		**269; 141**	**267; 185**	**249**	*F. glaucescens*, *F. pottsii* [28]

43	*D. palmatum*, *D. ruyschiana*	Flavanone	**Prunin** (naringenin-7-*O*-glucoside)	**$C_{21}H_{22}O_{10}$**	**434.3934**	**433**		**271; 151**	**269; 151**		*Dracocephalum palmatum* [4], rapeseed petals [38], tomato [54]
44	*D. palmatum*, *D. ruyschiana*	Flavanone	**Eriodictyol-7-O-glucoside** (pyracanthoside, miscanthoside)	**$C_{21}H_{22}O_{11}$**	**450.3928**	**449**		**285; 151**	**243; 151**		*Dracocephalum palmatum* [4], *Impatiens glandulifera* Royle [39], peppermint [29], M*entha* [24]
45	*D. palmatum*	Flavanone	**Eriodictyol *O*-malonyl-hexoside**	**$C_{24}H_{24}O_{14}$**	**536.4390**	**535**		**491; 287**	**287; 151**	**269; 151**	*Dracocephalum palmatum* [4]
46	*D. palmatum*; *D. ruyschiana*	Hydroxycinnamic acid	**Caffeic acid**	**$C_9H_8O_4$**	**180.1574**		**181**	**135**	**119**		*Dracocephalum palmatum* [4], *Eucalyptus* [16], *Triticum* [46], *Salvia miltiorrhiza* [55]
47	*D. palmatum*	Phenolic acid	**Methylgallic acid** (methyl gallate)	**$C_8H_8O_5$**	**184.1461**	**183**		**139**	**137**	**119**	*Eucalyptus* [16], papaya [35], *Rhus coriaria* [36]
48	*D. ruyschiana*	Phenolic acid	**Hydroxy methoxy dimethylbenzoic acid**	**$C_{10}H_{12}O_4$**	**196.1999**		**197**	**179**	**161**	**133**	*F. herrerae*, *F. glaucescens* [28]
49	*D. palmatum*	Phenolic acid	**Ethyl caffeate** (ethyl 3,4-dihydroxycinnamate)	**$C_{11}H_{12}O_4$**	**208.2106**	**207**		**179**	**135**		*Lepechinia* [56]
50	*D. palmatum*	Hydroxybenzoic acid	**4-Hydroxybenzoic acid** (PHBA, benzoic acid, p-hydroxybenzoic acid)	**$C_7H_6O_3$**	**138.1207**		**139**	**122**			*Bougainvillea* [27], *Triticum* [46], *Bituminaria* [49], *Vigna unguiculata* [57], *Eucalyptus globulus* [58],
51	*D. ruyschiana*	Hydroxybenzoic acid	**Ellagic acid** (benzoic acid, elagostasine, lagistase, eleagic acid)	**$C_{14}H_6O_8$**	**302.1926**	**301**		**284**	**221**	**112**	*Rhus coriaria* [36], *Eucalyptus* [16], *Eucalyptus globulus* [58], *Rubus occidentalis* [59]
52	*D. palmatum*	Hydroxycinnamic acid	**Sinapic acid** (trans-sinapic acid)	**$C_{11}H_{12}O_5$**	**224.21**		**225**	**206**	**138**		Andean blueberry [10], rapeseed petals [38], *Triticum* [46], Cranberry [53], *Cherimoya* [60]

53	*D. ruyschiana*	Hydroxycinnamic acid	**1-O-(4-coumaroyl)-glucose**	**$C_{15}H_{18}O_8$**	**326.2986**	**325**		**145**	**117**		Cranberry [53], strawberry [40], *Rubus occidentalis* [59]
54	*D. palmatum*	Gallate ester	**Beta-glucogallin** (1-O-galloyl-beta-d-glucose, galloyl glucose]	**$C_{13}H_{16}O_{10}$**	**332.2601**		**333**	**314**	**271; 151**	**244; 159**	Strawberry [40,61], carao tree seeds [62]
55	*D. ruyschiana*	Phenolic acid	**Caffeoylshikimic acid** (5-O-caffeoylshikimate)	**$C_{16}H_{15}O_8$**	**335.2855**	**335**		**179**	**135**	**133**	Andean blueberry [10], pear [25], passion fruits [35], *Vaccinium myrtillus* [43]
56	*D. palmatum*	Phenolic acid	**Salvianolic acid G**	**$C_{18}H_{12}O_7$**	**340.2837**		**341**	**296; 208**	**278; 208**	**235; 164**	*Mentha* [14], *Salvia miltiorrhiza* [55]
57	*D. palmatum*	Phenolic acid	**1-caffeoyl-beta-D-glucose** (caffeic acid-3-*O*-beta-D-glucoside)	**$C_{15}H_{18}O_9$**	**342.298**	**341**		**178; 119**	**135**		*Passiflora incarnata* [26], strawberry [40], Cranberry [53]
58	*D. palmatum*, *D. ruyschiana*	Phenolic acid	**Caffeic acid-*O*-hexoside** (caffeoyl-*O*-hexoside)	**$C_{15}H_{18}O_9$**	**342.298**	**341**		**178; 113**			pear [25], *Cherimoya*, papaya [35], *Sasa veitchii* [63]
59	*D. palmatum*	Phenolic acid	**Prolithospermic acid**	**$C_{18}H_{14}O_8$**	**358.2990**		**359**	**341; 207**	**314; 267; 149**		*Mentha* [14], *Salvia miltiorrhiza* [55]
60	*D. palmatum*	Phenolic acid	**Rosmarinic acid**	**$C_{18}H_{16}O_8$**	**360.3148**	**359**		**161**	**133**		*Dracocephalum palmatum* [4], *Mentha* [14], *Zostera marina* [21], peppermint [29], *Salvia miltiorrhiza* [55], *Lepechinia* [56]
61	*D. palmatum*, *D. ruyschiana*	Phenolic acid	**Caffeic acid derivative**	**$C_{16}H_{18}O_9Na$**	**377.2985**	**377**		**341; 215**	**179**		*Bougainvillea* [27]
62	*D. palmatum*	Phenolic acid	**Salvianic acid C**	**$C_{18}H_{18}O_9$**	**378.3301**	**377**		**359; 315**	**289**	**229**	*Salviae miltiorrhiza* [55], *Lepechinia* [56]
63	*D. ruyschiana*	Phenolic acid	**3,4-*O*-dicaffeoylquinic acid** (isochlorogenic acid B)	**$C_{25}H_{24}O_{12}$**	**516.4509**		**517**	**397**	**337; 135**		*Lonicera japonicum* [11], Pear [25], *Stevia rebaudiana* [64]

64	*D. ruyschiana*	Stilbene	**Pinosylvin** (3,5-stilbenediol, trans-3,5-dihydroxystilbene)	$C_{14}H_{12}O_2$	**212.2439**	**213**	**168**	**126**		*Pinus sylvestris* [50], *Pinus resinosa* [65]
65	*D. ruyschiana*	Stilbene	**Resveratrol** (trans-resveratrol, 3,4′,5-trihydroxystilbene, stilbentriol)	$C_{14}H_{12}O_3$	**228.2433**	**229**	**142; 210**	**114**		*A. cordifolia*, *F. glaucescens*, *F. herrerae* [28], *Radix polygoni multiflori* [52]
66	*D. palmatum*	Lignan	**Hinokinin**	$C_{20}H_{18}O_6$	**354.3533**	**355**	**337; 189**	**319; 226**		*Triticum aestivum* L. [46], *Rhodiola rosea* [51], lignans [66]
67	*D. palmatum*, *D. ruyschiana*	Lignan	**Dimethyl-secoisolariciresinol**	$C_{22}H_{30}O_6$	**390.4700**	**391**	**373; 249; 121**	**355; 225**	**313; 226**	Lignans [66]
68	*D. palmatum*, *D. ruyschiana*	Anthocyanidin	**Petunidin**	$C_{16}H_{13}O_7{}^+$	**317.2702**	**318**	**166; 300**	**121**		*A. cordifolia*, *C. edulis* [28]
69	*D. palmatum*	Anthocyanidin	**Cyanidin *O*-pentoside**	$C_{20}H_{19}O_{10}$	**419.3589**	**419**	**287**	**219**	**201**	Andean blueberry [10], *Gaultheria mucronata*, *Gaultheria antarctica* [60], Myrtle [67]
70	*D. palmatum*, *D. ruyschiana*	Anthocyanidin	**Pelargonidin-3-*O*-glucoside (callistephin)**	$C_{21}H_{21}O_{10}$	**433.3854**	**433**	**271**	**153; 225**	**171**	strawberry [61], *Triticum aestivum* [68], *Rubus ulmifolius* [69]
71	*D. palmatum*	Anthocyanidin	**Peonidin *O*-pentoside**	$C_{21}H_{21}O_{10}$	**433.3854**	**433**	**301; 215; 145**	**229; 139**		Andean blueberry [10], Myrtle [67],
72	*D. palmatum*	Anthocyanidin	**Cyanidin-3-*O*-glucoside** (cyanidin 3-*O*-beta-D-glucoside, kuromarin)	$C_{21}H_{21}O_{11}{}^+$	**449.3848**	**449**	**287**	**153**		rice [22], *Triticum* [46,68], acerola [70]
73	*D. palmatum*	Anthocyanidin	**Peonidin-3-O-glucoside**	$C_{22}H_{23}O_{11}{}^+$	**463.4114**	**463**	**301**	**286**	**258; 140**	*Berberis ilicifolia*, *Berberis empetrifolia* [60], Andean blueberry [10], strawberry [61], *Triticum aestivum* [68]
74	*D. palmatum*	Anthocyanidin	**Cyanidin 3-(acetyl)hexose**	$C_{23}H_{23}O_{12}{}^+$	**491.4215**	**491**	**287**	**245; 153**	**171**	*Acerola* [70]

75	*D. palmatum*	Anthocyanidin	**Cyanidin 3-(6″-malonylglucoside)**	$C_{24}H_{23}O_{14}$	**535.4310**	**535**	**287**	**285; 179**	**242; 153**	strawberry [40], strawberry [61], *Triticum aestivum* [68]
76	*D. palmatum*	Anthocyanidin	**Cyanidin 3-*O*-coumaroyl hexoside**	$C_{30}H_{27}O_{13}$	**595.533**	**595**	**287**	**153**		Grape vine varieties [71]
77	*D. palmatum*	Anthocyanidin	**7-O-Methyl-delphinidin-3-O-(2″galloyl)-galactoside**	$C_{29}H_{26}O_{16}$	**630.5071**	**631**	**317; 519**			*Rhus coriaria* [36]
78	*D. ruyschiana*	Condensed tannin	**Procyanidin A-type dimer**	$C_{30}H_{24}O_{12}$	**576.501**	**577**	**416; 352; 283; 164**	**337; 295; 193**	**319; 225; 150**	pear [25], *Vaccinium myrtillus* [43]
			OTHERS							
79	*D. palmatum*	Amino acid	**L-Leucine** ((S)-2-amino-methylpentanoic acid)	$C_6H_{13}NO_2$	**131.1729**	**132**	**130**			*Lonicera japonica* [11], *Camellia kucha* [34], Potato leaves [37], *Vigna unguiculata* [57]
80	*D. palmatum*	Alpha-omega dicarboxylic acid	**Hydroxymethylglutaric acid**	$C_6H_{10}O_5$	**162.1406**	**163**	**145**	**117**		Potato leaves [37]
81	*D. palmatum*	Cyclohexenecarboxylic acid	**Perillic acid**	$C_{10}H_{14}O_2$	**166.217**	**167**	**149**	**121**		*Mentha* [14]
82	*D. palmatum*, *D. ruyschiana*	Amino acid	**L-tryptophan** (tryptophan; (S)-tryptophan)	$C_{11}H_{12}N_2O_2$	**204.2252**	**205**	**188**	**144**	**118**	*Passiflora incarnata* [26], *Camellia kucha* [34], *Vigna unguiculata* [57]
83	*D. palmatum*	Aminoalkylindole	**5-Methoxydimethyltryptamine**	$C_{13}H_{18}N_2O$	**218.2948**	**219**	**201**	**159; 118**		*Camellia kucha* [34]
84	*D. palmatum*	Sesquiterpenoid	**Epiglobulol** ((−)-globulol)	$C_{15}H_{26}O$	**222.3663**	**223**	**205; 153**	**133**		Olive leaves [72]
85	*D. palmatum*	Omega-5 fatty acid	**Myristoleic acid** (cis-9-tetradecanoic acid)	$C_{14}H_{26}O_2$	**226.3550**	**227**	**209**	**139**		*F. glaucescens* [28]
86	*D. palmatum*	Medium-chain fatty acid	**Hydroxydodecanoic acid**	$C_{12}H_{22}O_5$	**246.3001**	**247**	**229**	**216**		*F. glaucescens* [28]

87	*D. palmatum*	Omega-3 unsaturated fatty acid	**Hexadecatrienoic acid** (hexadeca-2,4,6-trienoic acid)	**$C_{16}H_{26}O_2$**	**250.3764**		**251**	**233; 191**	**187**		*F. glaucescens* [28]
88	*D. ruyschiana*	Propionic acid	**Ketoprofen**	**$C_{16}H_{14}O_3$**	**254.2806**	**253**		**210**	**180**		*Ginkgo biloba* [73]
89	*D. palmatum; D. ruyschiana*	Ribonucleoside composite of adenine (purine)	**Adenosine**	**$C_{10}H_{13}N_5O_4$**	**267.2413**		**268**	**136; 258**			*Lonicera japonica* [11]
90	*D. palmatum*	Sceletium alkaloid	***O*-Methyl-dehydrojoubertiamine**	**$C_{17}H_{21}NO_2$**	**271.3541**		**272**	**256**	**242**	**226**	*A. cordifolia* [28]
91	*D. ruyschiana*	Sceletium alkaloid	**4′-*O*-desmethyl mesembranol**	**$C_{16}H_{23}NO_3$**	**277.3587**		**278**	**258**	**240**	**141**	*A. cordifolia* [28]
92	*D. palmatum*	Omega-9 unsaturated fatty acid	**Oleic acid** (cis-9-octadecenoic acid, cis-oleic acid)	**$C_{18}H_{34}O_2$**	**282.4614**		**283**	**209; 114**			*Sanguisorba officinalis* [74], *Pinus sylvestris* [75]
93	*D. palmatum*	2-Hydroxy fatty acid	**2-Hydroxyheptadecanoic acid**	**$C_{17}H_{34}O_3$**	**286.4501**	**285**		**265**	**186**		*F. pottsii* [28]
94	*D. palmatum*	Alkaloid	**Mesembrenol**	**$C_{17}H_{23}NO_3$**	**289.3694**		**290**	**242; 122**	**184; 149**		*Sceletium* [76]
95	*D. palmatum, D. ruyschiana*	Diterpenoid	**Tanshinone IIB** ((S)-6-(hydroxymethyl)-1,6-dimethyl-6,7,8,9-tetrahydrophenanthro[1,2-B]furan-10,11-dione)	**$C_{19}H_{18}O_4$**	**310.3438**		**311**	**283; 137**	**119**		*Salviae miltiorrhiza* [77]
96	*D. palmatum*	Alpha-omega dicarboxylic acid	**Octadecanedioic acid** (1,16-hexadecanedicarboxylic acid)	**$C_{18}H_{34}O_4$**	**314.4602**		**315**	**297; 179**	**212**		*F. glaucescens* [28]
97	*D. palmatum*	Unsaturated essential fatty acid	**Oxo-eicosatetraenoic acid**	**$C_{20}H_{30}O_3$**	**318.4504**		**319**	**300**	**282; 167**	**240**	*F. pottsii* [28]
98	*D. ruyschiana*	Oxylipins	**9,10-Dihydroxy-8-oxooctadec-12-enoic acid** (oxo-DHODE; oxo-dihydroxy-octadecenoic acid)	**$C_{18}H_{32}O_5$**	**328.4437**	**327**		**229**	**209**	**183**	*Bituminaria* [49], *Phyllostachys nigra* [63]
99	*D. ruyschiana*	Oxylipins	**Trihydroxyoctadecadienoic acid**	**$C_{18}H_{32}O_5$**	**328.4437**	**327**		**211; 171**	**183**		Potato leaves [37]

100	*D. ruyschiana*	Long-chain polyunsaturated fatty acid	**Docosahexaenoic acid**	$C_{22}H_{32}O_2$	**328.4883**	**327**		**309; 201**	**291; 171**	**273**	Marine extracts [78]
101	*D. palmatum*, *D. ruyschiana*	Oxylipins	**13- Trihydroxy-octadecenoic acid** (THODE)	$C_{18}H_{34}O_5$	**330.4596**	**329**		**229; 311**	**211**	**167**	*Bituminaria* [49], *Sasa veitchii* [63], *Brassica oleracea* [79]
102	*D. ruyschiana*	Carotenoid	**Beta-apo-12′-carotenal**	$C_{25}H_{34}O$	**350.5369**		**351**	**259; 147**	**231; 145**		Carotenoids [80,81]
103	*D. palmatum*	Sterol	**Stigmasterol** (stigmasterin, beta-stigmasterol)	$C_{29}H_{48}O$	**412.6908**		**413**	**301**	**188**		*A. cordifolia*, *F. pottsii* [28], Olive leaves [72], *Hedyotis diffusa* [82]
104	*D. ruyschiana*	Carotenoid	**Apocarotenal** ((all-E)-beta-apo-caroten-8′-al)	$C_{30}H_{40}O$	**416.6380**		**417**	**399; 200**	**351**	**267**	*Carica papaya* [83]
105	*D. palmatum*	Tetrahydroxyxanthen	**Mangiferin**	$C_{19}H_{18}O_{11}$	**422.3396**		**423**	**387; 238**	**345**		[84,85]
106	*D. palmatum*	Long-chain fatty acid	**Nonacosanoic acid**	$C_{29}H_{58}O_2$	**438.7696**		**439**	**395; 353; 245**	**245**		*C. edulis* [28]
107	*D. palmatum*	Anabolic steroid, androgen, androgen ester	**Vebonol**	$C_{30}H_{44}O_3$	**452.6686**		**453**	**435; 336; 226**	**336**	**209**	*Rhus coriaria* [36], *Hylocereus polyrhizus* [86]
108	*D. ruyschiana*	Triterpenic acid	**Oleanolic acid** (oleanic acid, cariophyllin, astrantiagenin C, virgaureagenin B)	$C_{30}H_{48}O_3$	**456.7003**		**457**	**410; 325**	**342; 164**		*C. edulis* [28], *Hedyotis diffusa* [82], *Folium Eriobotryae* [87], *Eleutherococcus* [88]
109	*D. palmatum*	Indole sesquiterpene alkaloid	**Sespendole**	$C_{33}H_{45}NO_4$	**519.7147**		**520**	**184; 359**	**124**		*Rhus coriaria* [36], *Hylocereus polyrhizus* [86]
110	*D. ruyschiana*	Carotenoid	**(Z)-lutein**	$C_{40}H_{54}O$	**550.8562**		**551**	**533**			*Physalis peruviana* [89], carotenoids [90]
111	*D. palmatum*	Carotenoid	***5,8-epoxy-alpha*-carotene**	$C_{40}H_{56}O$	**552.872**		**553**	**536; 412; 207**	**299; 261**		*Physalis peruviana* [89]
112	*D. ruyschiana*	Carotenoid	**Cryptoxanthin** (beta-cryptoxanthin)	$C_{40}H_{56}O$	**552.872**		**553**	**535; 325; 223**	**517**		Carotenoids [81,91], *Smilax aspera* [92]

113	*D. ruyschiana*	Carotenoid	**Violaxanthin** (zeaxanthin dieperoxide, all-trans-violaxanthin)	$\mathbf{C_{40}H_{56}O_4}$	**600.8702**	**601**	**364; 582**	**346; 202; 142**	**114**	Carotenoids [91]
114	*D. palmatum*	Macrocyclic glycolipid lactone	**Resinoside A**	$\mathbf{C_{31}H_{34}O_{13}}$	**614.5939**	**615**	**287; 203**	**162**		*Eucalyptus genus* [93]

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