

Article

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 sceleritum 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 Okhlopko, 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, gallic acid, 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-secoisolaricresinol; carotenoids: β -apo-12'carotenal, apocarotenal, 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.

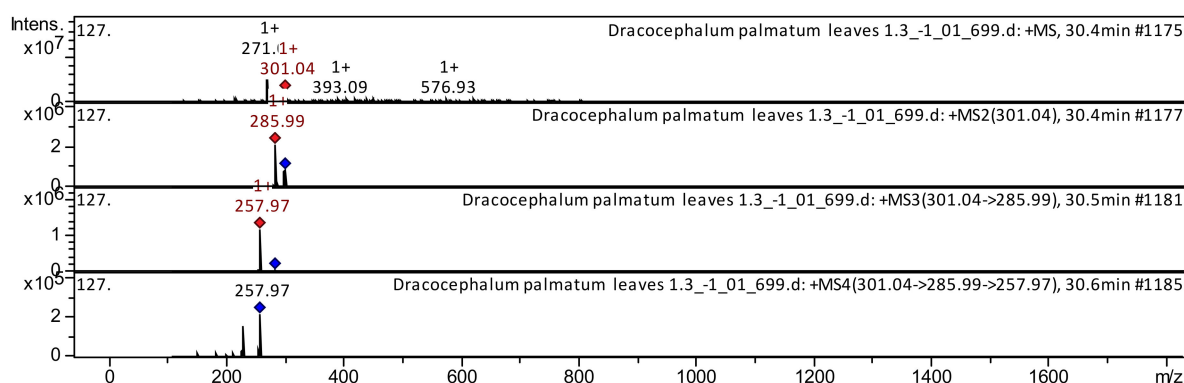


Figure 3. CID spectrum of diosmetin from extracts of *D. palmatum*, m/z 301.

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.

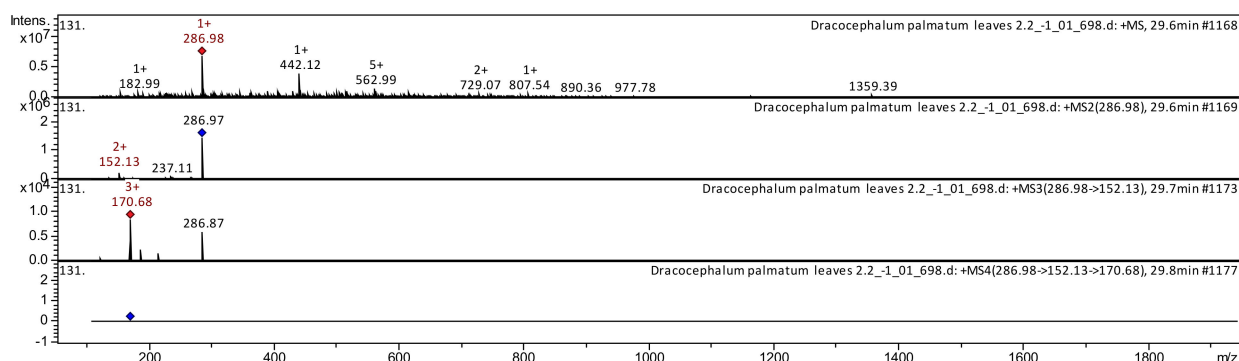


Figure 4. CID spectrum of luteolin from extracts of *D. palmatum*, m/z 286.98.

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.

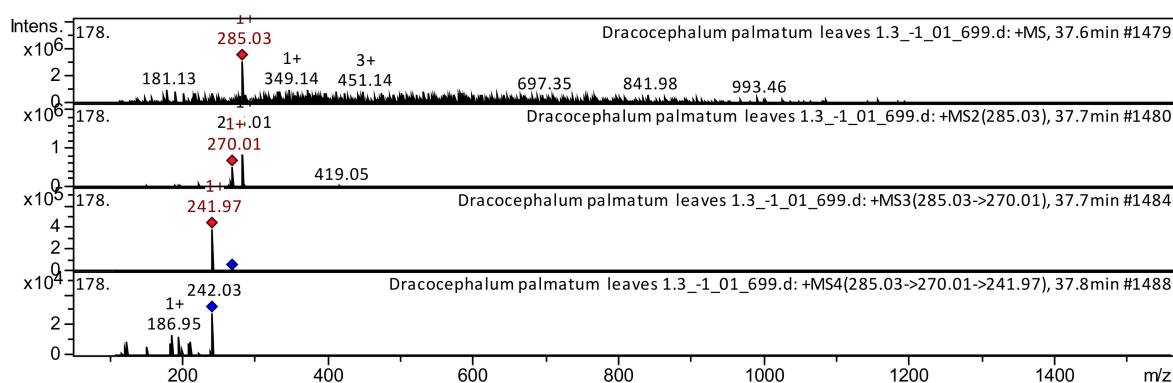


Figure 5. CID spectrum of negletein from extracts of *D. palmatum*, m/z 285.03.

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.

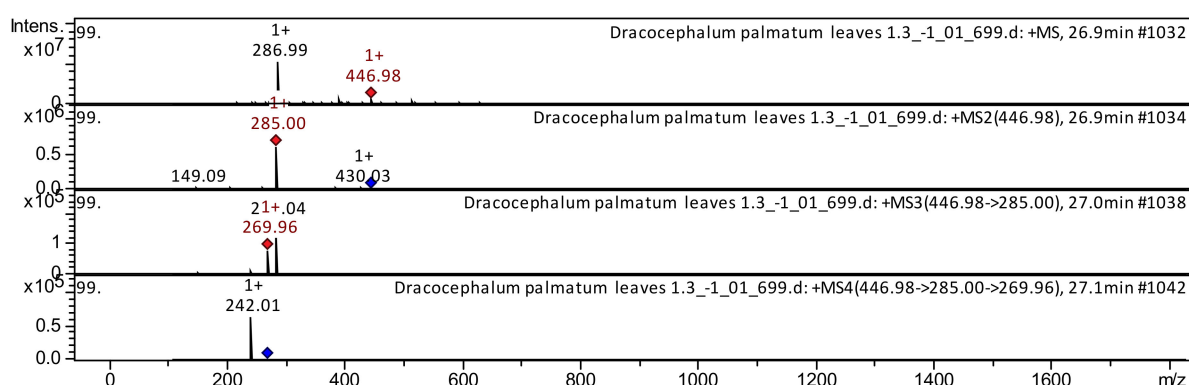


Figure 6. CID spectrum of acacetin 7-*O*-glucoside from *D. palmatum*, *m/z* 446.98.

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.

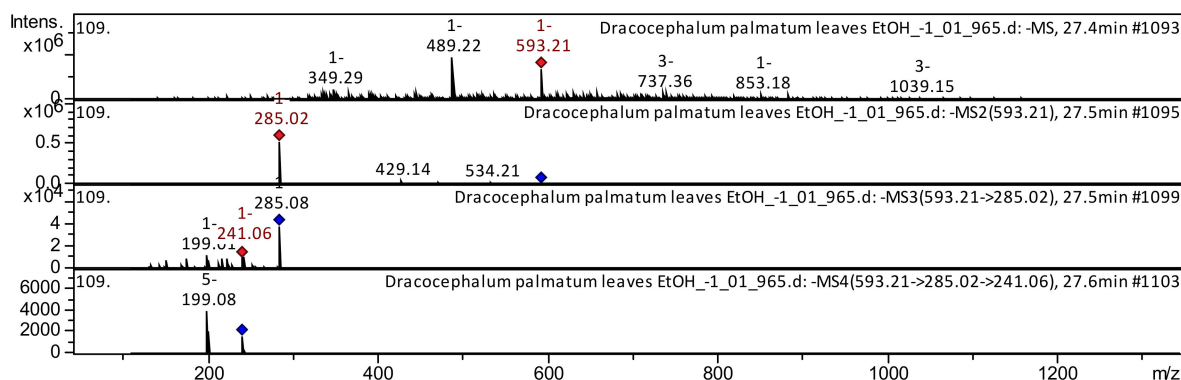


Figure 7. CID spectrum of kaempferol 3-O-rutinoside from extracts of *D. palmatum*, m/z 593.21.

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.

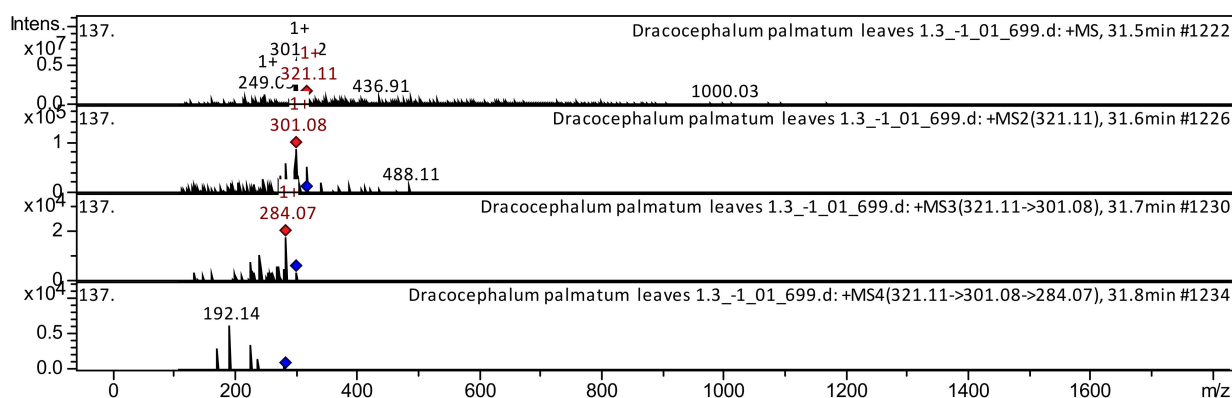


Figure 8. CID spectrum of ampelopsin from extracts of *D. palmatum*, m/z 321.11.

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.

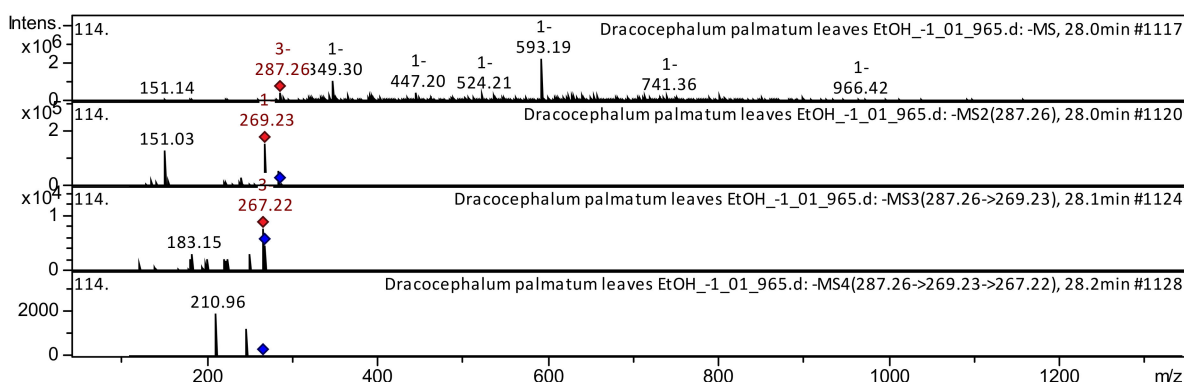


Figure 9. CID spectrum of dihydrokaempferol from extracts of *D. palmatum*, m/z 287.26.

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 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].

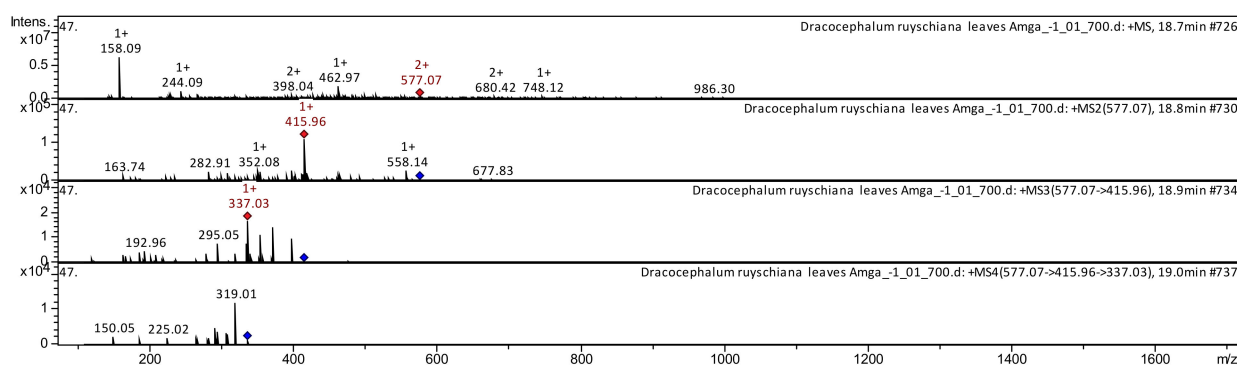


Figure 10. CID spectrum of procyanidin from extracts of *D. ruyschiana*, m/z 577.07.

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-secoisolaricresinol, 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	<i>D. ruyschiana</i>	<i>D. palmatum</i>
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 ₈ S		
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		

Table 1. Cont.

No.	Class of Compounds	Identified Compounds	Formula	<i>D. ruyschiana</i>	<i>D. palmatum</i>
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 ₉ H ₈ O ₄		
47	Phenolic acid	Methylgallic acid (methyl gallate)	C ₈ H ₈ O 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 ₇ H ₆ O ₃		
51	Hydroxybenzoic acid	Ellagic acid	C ₁₄ H ₆ O 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 ₉ Na		
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		

Table 1. Cont.

No.	Class of Compounds	Identified Compounds	Formula	<i>D. ruyschiana</i>	<i>D. palmatum</i>
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 sceleium; 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% CH₃CN; 5–45 min, 100–25% CH₃CN; 45–55 min, 25–0% CH₃CN; 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 <i>Dracocephalum</i>	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	<i>D. ruyschiana</i>	Flavone	Apigeninidin	C ₁₅ H ₁₁ O ₄	255.2454		256	168	122		<i>Triticum</i> [46]
2	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Flavone	Apigenin (5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one)	C ₁₅ H ₁₀ O ₅	270.2369		269	225	181	117	<i>Dracocephalum palmatum</i> [4], Andean blueberry [10], <i>Lonicera japonicum</i> [11], Mexican lupine species [12]
3	<i>D. palmatum</i>	Flavone	Negletein (5,6-dihydroxy-7-methoxy-flavone)	C ₁₆ H ₁₂ O ₅	284.2635		285	271	241	187	<i>Actinocarya tibetica</i> [19]
4	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Flavone	Acacetin (linarigenin, buddleoflavanol)	C ₁₆ H ₁₂ O ₅	284.2635		285	268	211; 143		<i>Dracocephalum palmatum</i> [4], Mexican lupine species [12], <i>Mentha</i> [14], <i>Dracocephalum moldavica</i> [15], <i>Wissadula periplocifolia</i> [18]
5	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Flavone	Luteolin	C ₁₅ H ₁₀ O ₆	286.2363		287	286; 153	171	153	<i>Dracocephalum palmatum</i> [4], <i>Eucalyptus</i> [16], <i>Lonicera japonicum</i> [11]
6	<i>D. palmatum</i>	Flavone	Apigenin-7, 4'-dimethyl ether	C ₁₇ H ₁₄ O ₅	298.2901		299	284	256		<i>Ocimum</i> [20]
7	<i>D. palmatum</i>	Flavone	Diosmetin (luteolin 4'-methyl ether, salinigriflavanol)	C ₁₆ H ₁₂ O ₆	300.2629		301	286	258		Andean blueberry [10], <i>Lonicera japonicum</i> [11], <i>Cirsium japonicum</i> [13], <i>Mentha</i> [14], <i>Dracocephalum moldavica</i> [15]
8	<i>D. palmatum</i>	Flavone	Salvigenin	C ₁₈ H ₁₆ O ₆	328.3160		329	314; 240	154		<i>Dracocephalum palmatum</i> [4], <i>Ocimum</i> [20]
9	<i>D. palmatum</i>	Flavone	Nevadensin	C ₁₈ H ₁₆ O ₇	344.3154		345	311	284	149	<i>Mentha</i> [14], <i>Ocimum</i> [20]
10	<i>D. ruyschiana</i>	Flavone	Apigenin 7-sulfate	C ₁₅ H ₁₀ O ₆ S	350.3001	349		269	223		sulfates [18], <i>G. linguiforme</i> [28],
11	<i>D. ruyschiana</i>	Flavone	Chrysin 6-C-glucoside	C ₂₁ H ₂₀ O ₉	416.3781		417	51; 127	333; 267	165	<i>Passiflora incarnata</i> [26]
12	<i>D. ruyschiana</i>	Flavone	Chrysin glucuronide	C ₂₁ H ₁₈ O ₁₀	430.3616		431	255	255; 153	171	<i>F. pottsii</i> [28]
13	<i>D. palmatum</i>	Flavone	Apigenin-5-O-glucoside	C ₂₁ H ₂₀ O ₁₀	432.3775		433	414; 274; 215; 145	371; 245; 147	327	Rice [22]

Table A1. Cont.

Nº	Variety of <i>Dracocephalum</i>	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
14	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Flavone	Apigenin-7- <i>O</i> -glucoside (apigetrin, cosmosiin)	C ₂₁ H ₂₀ O ₁₀	432.3775		433	271	153		<i>Dracocephalum palmatum</i> [4], <i>Mentha</i> [24], Mexican lupine species [12]
15	<i>D. ruyschiana</i>	Flavone	Apigenin 7- <i>O</i> -glucuronide	C ₂₁ H ₁₈ O ₁₁	446.361		447	271	153	271; 171	Pear [25], <i>Bougainvillea</i> [27]
16	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Flavone	Acacetin 7- <i>O</i> -glucoside (tilianin)	C ₂₂ H ₂₂ O ₁₀	446.4041		447	285; 149	270	242	<i>Dracocephalum palmatum</i> [4], <i>Bougainvillea</i> [27]
17	<i>D. palmatum</i>	Flavone	Acacetin 8- <i>C</i> -glucoside	C ₂₂ H ₂₂ O ₁₀	446.4041		447	428; 344	343; 230; 133	232	Mexican lupine species [12]
18	<i>D. palmatum</i>	Flavone	Luteolin 7- <i>O</i> -glucoside (cynaroside, luteoloside)	C ₂₁ H ₂₀ O ₁₁	448.3769		449	287; 199	153		<i>Lonicera japonicum</i> [11], Pear [25], <i>Passiflora incarnata</i> [26]
19	<i>D. ruyschiana</i>	Flavone	Acacetin 7- <i>O</i> -beta-D-glucuronide	C ₂₂ H ₂₀ O ₁₁	460.3876	459		283; 343; 175	268	267	<i>Dracocephalum moldavica</i> [15]
20	<i>D. ruyschiana</i>	Flavone	Luteolin-7- <i>O</i> -beta-glucuronide	C ₂₁ H ₁₈ O ₁₂	462.3604		463	287	268	245; 119	<i>Mentha</i> [14], rat plasma [32], <i>Newbouldia laevis</i> [30]
21	<i>D. ruyschiana</i>	Flavone	Diosmetin-7- <i>O</i> -beta-glucoside	C ₂₂ H ₂₂ O ₁₁	462.4035		463	287	168	123	<i>Dracocephalum moldavica</i> [15], <i>Oxalis corniculata</i> [23]
22	<i>D. palmatum</i>	Flavone	Luteolin <i>O</i> -acetyl-hexoside	C ₂₃ H ₂₂ O ₁₂	490.4136	489		285; 450	199	155	<i>Dracocephalum palmatum</i> [4]
23	<i>D. palmatum</i>	Isoflavone	Apigenin 7- <i>O</i> -beta-D-(6''- <i>O</i> -malonyl)-glucoside	C ₂₄ H ₂₂ O ₁₃	518.4237		519	502; 184	125		<i>Dracocephalum moldavica</i> [14], <i>Zostera marina</i> [21]
24	<i>D. palmatum</i>	Flavone	Acacetin 8- <i>C</i> -glucoside malonylated	C ₂₅ H ₂₄ O ₁₃	532.4503		533	497; 205	377; 335		Mexican lupine species [12]
25	<i>D. palmatum</i>	Isoflavone	2'-Hydroxygenistein <i>O</i> -glucoside malonylated	C ₂₄ H ₂₂ O ₁₄	534.4231	533		489	285; 326	284	Mexican lupine species [12]
26	<i>D. palmatum</i>	Flavone	Luteolin 7- <i>O</i> -beta-D-(6''- <i>O</i> -malonyl)-glucoside	C ₂₄ H ₂₂ O ₁₄	534.4231		535	436; 354; 287; 214	328; 238		<i>Dracocephalum moldavica</i> [15], <i>Zostera marina</i> [21]
27	<i>D. palmatum</i>	Flavone	Acacetin <i>C</i> -glucoside methylmalonylated	C ₂₆ H ₂₆ O ₁₃	546.4758		547	529; 496; 369	343		Mexican lupine species [12]
28	<i>D. ruyschiana</i>	Flavone	Apigenin 8- <i>C</i> -hexoside-6- <i>C</i> -pentoside	C ₂₆ H ₂₈ O ₁₄	564.4921		565	547; 511; 427	529; 499	511	<i>Triticum aestivum</i> L. [47,48], <i>Bituminaria</i> [49], <i>Licania Rigida</i> [50]

Table A1. Cont.

Nº	Variety of <i>Dracocephalum</i>	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
29	<i>D. ruyschiana</i>	Flavone	Apigenin 8-C-pentoside-6-C-hexoside	C ₂₆ H ₂₈ O ₁₄	564.4921		565	547; 274	529; 474; 247	390	<i>Triticum aestivum</i> L. [47,48], <i>Bituminaria</i> [49], <i>Licania Rigida</i> [50]
30	<i>D. palmatum</i>	Flavone	Apigenin 6-C-[6''-acetyl-2''-O-deoxyhexoside]-glucoside	C ₂₉ H ₃₂ O ₁₅	620.5554		621	561; 218	533	445; 222	<i>Passiflora incarnata</i> [26]
31	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Flavonol	Kaempferol (3,5,7-trihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one)	C ₁₅ H ₁₀ O ₆	286.2363		287	269; 202	233; 205	216	Andean blueberry [10], <i>Lonicera japonicum</i> [11], <i>Rhus coriaria</i> (Sumac) [36], potato leaves [37], rapeseed petals [38]
32	<i>D. palmatum</i>	Flavonol	Dihydrokaempferol (aromadendrin, katuranin)	C ₁₅ H ₁₂ O ₆	288.2522		287	269; 151	267; 183	211	<i>F. glaucescens</i> [28], <i>Camellia kucha</i> [34], <i>Rhodiola rosea</i> [51]
33	<i>D. palmatum</i>	Flavonol	Dihydroquercetin (taxifolin, taxifoliol)	C ₁₅ H ₁₂ O ₇	304.2516		305	287	286; 186	185	Andean blueberry [10], <i>Eucalyptus</i> [16], <i>Camellia kucha</i> [34], strawberry [40]
34	<i>D. palmatum</i>	Flavonol	Ampelopsin (dihydromyricetin, ampeloptin)	C ₁₅ H ₁₂ O ₈	320.251		321	301	284	192	<i>Rhus coriaria</i> [36], <i>Impatiens glandulifera</i> Royle [39]
35	<i>D. palmatum</i>	Flavonol	Astragalin (kaempferol 3-O-glucoside, kaempferol-3-beta-monoglucoside)	C ₂₁ H ₂₀ O ₁₁	448.3769		447	285; 327	241	199	<i>Lonicera japonicum</i> [11], Mexican lupine species [12], pear [25], <i>Camellia kucha</i> [34]
36	<i>D. ruyschiana</i>	Flavonol	Kaempferol-3-O-glucuronide	C ₂₁ H ₁₈ O ₁₂	462.3604		463	287	268; 169	241; 119	<i>A. cordifolia</i> , <i>G. linguiforme</i> [28], Strawberry [35], <i>Rhus coriaria</i> [36]
37	<i>D. palmatum</i>	Flavonol	Kaempferol 3-O-rutinoside	C ₂₇ H ₃₀ O ₁₅	594.5181		593	285	241; 199	199	<i>Lonicera japonicum</i> [11], Pear [25], <i>Camellia kucha</i> [34], strawberry [35], <i>Rhus coriaria</i> [36],
38	<i>D. ruyschiana</i>	Flavan-3-ol	(Epi)catechin	C ₁₅ H ₁₄ O ₆	290.2681		291	273; 117	255; 145		Andean blueberry [10], <i>C. edulis</i> [28], <i>Camellia kucha</i> [34], <i>Radix polygoni multiflori</i> [52], cranberry [53],

Table A1. Cont.

Nº	Variety of <i>Dracocephalum</i>	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
39	<i>D. palmatum</i>	Flavan-3-ol	Gallocatechin (+(-)gallocatechin)	C ₁₅ H ₁₄ O ₇	306.2675		307	289	259		<i>Licania ridigna</i> [50], <i>G. linguiforme</i> [28], <i>Vaccinium myrtillus</i> [43], <i>Rhodiola rosea</i> [51]
40	<i>D. palmatum</i>	Flavanone	Naringenin (naringetol, naringenin)	C ₁₅ H ₁₂ O ₅	272.5228		273	153; 256	125		<i>Dracocephalum palmatum</i> [4], Andean blueberry [10], <i>Eucalyptus</i> [16], Mexican lupine species [12], rapeseed petals [38]
41	<i>D. palmatum</i>	Flavanone	Eriodictyol (3',4',5,7-tetrahydroxy-flavanone)	C ₁₅ H ₁₂ O ₆	288.2522		289	163; 271	145	117	<i>Dracocephalum palmatum</i> [4], Andean blueberry [10], <i>Eucalyptus</i> [16], <i>Mentha</i> [24], peppermint [29]
42	<i>D. ruyschiana</i>	Flavanone	Fustin (2,3-dihydrofistein)	C ₁₅ H ₁₂ O ₆	288.2522	287		269; 141	267; 185	249	<i>F. glaucescens</i> , <i>F. pottsii</i> [28]
43	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Flavanone	Prunin (naringenin-7-O-glucoside)	C ₂₁ H ₂₂ O ₁₀	434.3934	433		271; 151	269; 151		<i>Dracocephalum palmatum</i> [4], rapeseed petals [38], tomato [54]
44	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Flavanone	Eriodictyol-7-O-glucoside (pyracanthoside, miscanthoside)	C ₂₁ H ₂₂ O ₁₁	450.3928	449		285; 151	243; 151		<i>Dracocephalum palmatum</i> [4], <i>Impatiens glandulifera</i> Royle [39], peppermint [29], <i>Mentha</i> [24]
45	<i>D. palmatum</i>	Flavanone	Eriodictyol O-malonyl-hexoside	C ₂₄ H ₂₄ O ₁₄	536.4390	535		491; 287	287; 151	269; 151	<i>Dracocephalum palmatum</i> [4]
46	<i>D. palmatum</i> ; <i>D. ruyschiana</i>	Hydroxycinnamic acid	Caffeic acid	C ₉ H ₈ O ₄	180.1574		181	135	119		<i>Dracocephalum palmatum</i> [4], <i>Eucalyptus</i> [16], <i>Triticum</i> [46], <i>Salvia miltiorrhiza</i> [55]
47	<i>D. palmatum</i>	Phenolic acid	Methylgallic acid (methyl gallate)	C ₈ H ₈ O ₅	184.1461	183		139	137	119	<i>Eucalyptus</i> [16], papaya [35], <i>Rhus coriaria</i> [36]
48	<i>D. ruyschiana</i>	Phenolic acid	Hydroxy methoxy dimethylbenzoic acid	C ₁₀ H ₁₂ O ₄	196.1999		197	179	161	133	<i>F. herrerae</i> , <i>F. glaucescens</i> [28]
49	<i>D. palmatum</i>	Phenolic acid	Ethyl caffeate (ethyl 3,4-dihydroxycinnamate)	C ₁₁ H ₁₂ O ₄	208.2106	207		179	135		<i>Lepechinia</i> [56]

Table A1. Cont.

N ^o	Variety of <i>Dracocephalum</i>	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
50	<i>D. palmatum</i>	Hydroxybenzoic acid	4-Hydroxybenzoic acid (PHBA, benzoic acid, p-hydroxybenzoic acid)	C ₇ H ₆ O ₃	138.1207		139	122			Bougainvillea [27], Triticum [46], Bituminaria [49], Vigna unguiculata [57], Eucalyptus globulus [58],
51	<i>D. ruyschiana</i>	Hydroxybenzoic acid	Ellagic acid (benzoic acid, elagostasine, lagistase, eleagic acid)	C ₁₄ H ₆ O ₈	302.1926	301		284	221	112	Rhus coriaria [36], Eucalyptus [16], Eucalyptus globulus [58], Rubus occidentalis [59]
52	<i>D. palmatum</i>	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	<i>D. ruyschiana</i>	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	<i>D. palmatum</i>	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	<i>D. ruyschiana</i>	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	<i>D. palmatum</i>	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	<i>D. palmatum</i>	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	<i>D. palmatum</i> , <i>D. ruyschiana</i>	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	<i>D. palmatum</i>	Phenolic acid	Prolithospermic acid	C ₁₈ H ₁₄ O ₈	358.2990		359	341; 207	314; 267; 149		Mentha [14], Salvia miltiorrhiza [55]
60	<i>D. palmatum</i>	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]

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Nº	Variety of <i>Dracocephalum</i>	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
61	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Phenolic acid	Caffeic acid derivative	C ₁₆ H ₁₈ O ₉ Na	377.2985	377		341; 215	179		<i>Bougainvillea</i> [27]
62	<i>D. palmatum</i>	Phenolic acid	Salvianic acid C	C ₁₈ H ₁₈ O ₉	378.3301	377		359; 315	289	229	<i>Salviae multiorrhiza</i> [55], <i>Lepechinia</i> [56]
63	<i>D. ruyschiana</i>	Phenolic acid	3,4- <i>O</i> -dicaffeoylquinic acid (isochlorogenic acid B)	C ₂₅ H ₂₄ O ₁₂	516.4509		517	397	337; 135		<i>Lonicera japonicum</i> [11], Pear [25], <i>Stevia rebaudiana</i> [64]
64	<i>D. ruyschiana</i>	Stilbene	Pinosylvin (3,5-stilbenediol, trans-3,5-dihydroxystilbene)	C ₁₄ H ₁₂ O ₂	212.2439		213	168	126		<i>Pinus sylvestris</i> [50], <i>Pinus resinosa</i> [65]
65	<i>D. ruyschiana</i>	Stilbene	Resveratrol (trans-resveratrol, 3,4',5-trihydroxystilbene, stilbentriol)	C ₁₄ H ₁₂ O ₃	228.2433		229	142; 210	114		<i>A. cordifolia</i> , <i>F. glaucescens</i> , <i>F. herrerae</i> [28], <i>Radix polygoni multiflori</i> [52]
66	<i>D. palmatum</i>	Lignan	Hinokinin	C ₂₀ H ₁₈ O ₆	354.3533		355	337; 189	319; 226		<i>Triticum aestivum</i> L. [46], <i>Rhodiola rosea</i> [51], lignans [66]
67	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Lignan	Dimethyl-secoisolariciresinol	C ₂₂ H ₃₀ O ₆	390.4700		391	373; 249; 121	355; 225	313; 226	Lignans [66]
68	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Anthocyanidin	Petunidin	C ₁₆ H ₁₃ O ₇₊	317.2702		318	166; 300	121		<i>A. cordifolia</i> , <i>C. edulis</i> [28]
69	<i>D. palmatum</i>	Anthocyanidin	Cyanidin <i>O</i> -pentoside	C ₂₀ H ₁₉ O ₁₀	419.3589		419	287	219	201	Andean blueberry [10], <i>Gaultheria mucronata</i> , <i>Gaultheria antarctica</i> [60], Myrtle [67]
70	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Anthocyanidin	Pelargonidin-3- <i>O</i> -glucoside (callistephin)	C ₂₁ H ₂₁ O ₁₀	433.3854		433	271	153; 225	171	strawberry [61], <i>Triticum aestivum</i> [68], <i>Rubus ulmifolius</i> [69]
71	<i>D. palmatum</i>	Anthocyanidin	Peonidin <i>O</i> -pentoside	C ₂₁ H ₂₁ O ₁₀	433.3854		433	301; 215; 145	229; 139		Andean blueberry [10], Myrtle [67],
72	<i>D. palmatum</i>	Anthocyanidin	Cyanidin-3- <i>O</i> -glucoside (cyanidin 3- <i>O</i> -beta-D-glucoside, kuromarin)	C ₂₁ H ₂₁ O ₁₁₊	449.3848		449	287	153		rice [22], <i>Triticum</i> [46,68], acerola [70]
73	<i>D. palmatum</i>	Anthocyanidin	Peonidin-3- <i>O</i> -glucoside	C ₂₂ H ₂₃ O ₁₁₊	463.4114		463	301	286	258; 140	<i>Berberis ilicifolia</i> , <i>Berberis empetrifolia</i> [60], Andean blueberry [10], strawberry [61], <i>Triticum aestivum</i> [68]
74	<i>D. palmatum</i>	Anthocyanidin	Cyanidin 3-(acetyl)hexose	C ₂₃ H ₂₃ O ₁₂₊	491.4215		491	287	245; 153	171	<i>Acerola</i> [70]

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75	<i>D. palmatum</i>	Anthocyanidin	Cyanidin 3-(6''-malonylglucoside)	C ₂₄ H ₂₃ O ₁₄	535.4310		535	287	285; 179	242; 153	strawberry [40], strawberry [61], <i>Triticum aestivum</i> [68]
76	<i>D. palmatum</i>	Anthocyanidin	Cyanidin 3-O-coumaroyl hexoside	C ₃₀ H ₂₇ O ₁₃	595.533		595	287	153		Grape vine varieties [71]
77	<i>D. palmatum</i>	Anthocyanidin	7-O-Methyl-delphinidin-3-O-(2''galloyl)-galactoside	C ₂₉ H ₂₆ O ₁₆	630.5071		631	317; 519			<i>Rhus coriaria</i> [36]
78	<i>D. ruyschiana</i>	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], <i>Vaccinium myrtillus</i> [43]
OTHERS											
79	<i>D. palmatum</i>	Amino acid	L-Leucine ((S)-2-amino-methylpentanoic acid)	C ₆ H ₁₃ NO ₂	131.1729		132	130			<i>Lonicera japonica</i> [11], <i>Camellia kucha</i> [34], Potato leaves [37], <i>Vigna unguiculata</i> [57]
80	<i>D. palmatum</i>	Alpha-omega dicarboxylic acid	Hydroxymethylglutaric acid	C ₆ H ₁₀ O ₅	162.1406		163	145	117		Potato leaves [37]
81	<i>D. palmatum</i>	Cyclohexenecarboxylic acid	Perillic acid	C ₁₀ H ₁₄ O ₂	166.217		167	149	121		<i>Mentha</i> [14]
82	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Amino acid	L-tryptophan (tryptophan; (S)-tryptophan)	C ₁₁ H ₁₂ N ₂ O ₂	204.2252		205	188	144	118	<i>Passiflora incarnata</i> [26], <i>Camellia kucha</i> [34], <i>Vigna unguiculata</i> [57]
83	<i>D. palmatum</i>	Aminoalkylindole	5-Methoxydimethyltryptamine	C ₁₃ H ₁₈ N ₂ O	218.2948		219	201	159; 118		<i>Camellia kucha</i> [34]
84	<i>D. palmatum</i>	Sesquiterpenoid	Epiglobulol ((–)-globulol)	C ₁₅ H ₂₆ O	222.3663		223	205; 153	133		Olive leaves [72]
85	<i>D. palmatum</i>	Omega-5 fatty acid	Myristoleic acid (cis-9-tetradecanoic acid)	C ₁₄ H ₂₆ O ₂	226.3550		227	209	139		<i>F. glaucescens</i> [28]
86	<i>D. palmatum</i>	Medium-chain fatty acid	Hydroxydodecanoic acid	C ₁₂ H ₂₂ O ₅	246.3001		247	229	216		<i>F. glaucescens</i> [28]
87	<i>D. palmatum</i>	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		<i>F. glaucescens</i> [28]
88	<i>D. ruyschiana</i>	Propionic acid	Ketoprofen	C ₁₆ H ₁₄ O ₃	254.2806	253		210	180		<i>Ginkgo biloba</i> [73]
89	<i>D. palmatum</i> ; <i>D. ruyschiana</i>	Ribonucleoside composite of adenine (purine)	Adenosine	C ₁₀ H ₁₃ N ₅ O ₄	267.2413		268	136; 258			<i>Lonicera japonica</i> [11]
90	<i>D. palmatum</i>	Sceletium alkaloid	O-Methyl-dehydrojoubertiamine	C ₁₇ H ₂₁ NO ₂	271.3541		272	256	242	226	<i>A. cordifolia</i> [28]
91	<i>D. ruyschiana</i>	Sceletium alkaloid	4'-O-desmethyl mesembranol	C ₁₆ H ₂₃ NO ₃	277.3587		278	258	240	141	<i>A. cordifolia</i> [28]

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92	<i>D. palmatum</i>	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			<i>Sanguisorba officinalis</i> [74], <i>Pinus sylvestris</i> [75]
93	<i>D. palmatum</i>	2-Hydroxy fatty acid	2-Hydroxyheptadecanoic acid	C ₁₇ H ₃₄ O ₃	286.4501	285		265	186		<i>F. pottsii</i> [28]
94	<i>D. palmatum</i>	Alkaloid	Mesembrenol	C ₁₇ H ₂₃ NO ₃	289.3694		290	242; 122	184; 149		<i>Sceletium</i> [76]
95	<i>D. palmatum</i> , <i>D. ruyschiana</i>	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		<i>Salviae miltiorrhiza</i> [77]
96	<i>D. palmatum</i>	Alpha-omega dicarboxylic acid	Octadecanedioic acid (1,16-hexadecanedicarboxylic acid)	C ₁₈ H ₃₄ O ₄	314.4602		315	297; 179	212		<i>F. glaucescens</i> [28]
97	<i>D. palmatum</i>	Unsaturated essential fatty acid	Oxo-eicosatetraenoic acid	C ₂₀ H ₃₀ O ₃	318.4504		319	300	282; 167	240	<i>F. pottsii</i> [28]
98	<i>D. ruyschiana</i>	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	<i>Bituminaria</i> [49], <i>Phyllostachys nigra</i> [63]
99	<i>D. ruyschiana</i>	Oxylipins	Trihydroxyoctadecadienoic acid	C ₁₈ H ₃₂ O ₅	328.4437	327		211; 171	183		Potato leaves [37]
100	<i>D. ruyschiana</i>	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	<i>D. palmatum</i> , <i>D. ruyschiana</i>	Oxylipins	13- Trihydroxy-octadecenoic acid (THODE)	C ₁₈ H ₃₄ O ₅	330.4596	329		229; 311	211	167	<i>Bituminaria</i> [49], <i>Sasa veitchii</i> [63], <i>Brassica oleracea</i> [79]
102	<i>D. ruyschiana</i>	Carotenoid	Beta-apo-12'-carotenal	C ₂₅ H ₃₄ O	350.5369		351	259; 147	231; 145		Carotenoids [80,81]
103	<i>D. palmatum</i>	Sterol	Stigmasterol (stigmasterin, beta-stigmasterol)	C ₂₉ H ₄₈ O	412.6908		413	301	188		<i>A. cordifolia</i> , <i>F. pottsii</i> [28], Olive leaves [72], <i>Hedyotis diffusa</i> [82]
104	<i>D. ruyschiana</i>	Carotenoid	Apocarotenal ((all-E)-beta-apo-caroten-8'-al)	C ₃₀ H ₄₀ O	416.6380		417	399; 200	351	267	<i>Carica papaya</i> [83]
105	<i>D. palmatum</i>	Tetrahydroxyxanthen	Mangiferin	C ₁₉ H ₁₈ O ₁₁	422.3396		423	387; 238	345		[84,85]
106	<i>D. palmatum</i>	Long-chain fatty acid	Nonacosanoic acid	C ₂₉ H ₅₈ O ₂	438.7696		439	395; 353; 245	245		<i>C. edulis</i> [28]
107	<i>D. palmatum</i>	Anabolic steroid, androgen, androgen ester	Vebonol	C ₃₀ H ₄₄ O ₃	452.6686		453	435; 336; 226	336	209	<i>Rhus coriaria</i> [36], <i>Hylocereus polyrhizus</i> [86]

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108	<i>D. ruyschiana</i>	Triterpenic acid	Oleanolic acid (oleanic acid, cariophyllin, astrantiagenin C, virgaureagenin B)	C ₃₀ H ₄₈ O ₃	456.7003		457	410; 325	342; 164		<i>C. edulis</i> [28], <i>Hedyotis diffusa</i> [82], <i>Folium Eriobotryae</i> [87], <i>Eleutherococcus</i> [88]
109	<i>D. palmatum</i>	Indole sesquiterpene alkaloid	Sespendole	C ₃₃ H ₄₅ NO ₄	519.7147		520	184; 359	124		<i>Rhus coriaria</i> [36], <i>Hylocereus polyrhizus</i> [86]
110	<i>D. ruyschiana</i>	Carotenoid	(Z)-lutein	C ₄₀ H ₅₄ O	550.8562		551	533			<i>Physalis peruviana</i> [89], carotenoids [90]
111	<i>D. palmatum</i>	Carotenoid	5,8-epoxy-α-carotene	C ₄₀ H ₅₆ O	552.872		553	536; 412; 207	299; 261		<i>Physalis peruviana</i> [89]
112	<i>D. ruyschiana</i>	Carotenoid	Cryptoxanthin (beta-cryptoxanthin)	C ₄₀ H ₅₆ O	552.872		553	535; 325; 223	517		Carotenoids [81,91], <i>Smilax aspera</i> [92]
113	<i>D. ruyschiana</i>	Carotenoid	Violaxanthin (zeaxanthin dieperoxide, all-trans-violaxanthin)	C ₄₀ H ₅₆ O ₄	600.8702		601	364; 582	346; 202; 142	114	Carotenoids [91]
114	<i>D. palmatum</i>	Macrocyclic glycolipid lactone	Resinoside A	C ₃₁ H ₃₄ O ₁₃	614.5939		615	287; 203	162		<i>Eucalyptus</i> genus [93]

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