

## Article

# Chemodiversity of Arctic Plant *Dryas oxyodonta*: LC-MS Profile and Antioxidant Activity

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**Abstract:** *Dryas oxyodonta* Yuz. is a perennial evergreen shrub from the Rosaceae family. *D. oxyodonta* thrives in subalpine and subarctic regions, as well as in highlands spanning from Central Asia to Siberia and Mongolia. Owing to a lack of information on its chemical composition, we conducted qualitative and quantitative chromatographic analyses on extracts from the leaves and flowers of *D. oxyodonta* sourced from various Siberian habitats. Employing high-performance liquid chromatography with photodiode-array detection and electrospray ionization triple-quadrupole mass spectrometric detection, we identified 40 compounds, encompassing gallotannins, hydroxycinnamates, procyanidins, catechins, flavonoids, and triterpenes. All Siberian populations of *D. oxyodonta* exhibited a notable abundance of phenolic compounds. Furthermore, we identified rare glycosides, such as sexangularetin and corniculatusin, as potential markers of the chemodiversity within the *Dryas* genus. Extracts from the flowers and leaves were effective scavengers of free radicals, including DPPH•, ABTS•<sup>+</sup>, O<sub>2</sub>•<sup>-</sup>, and •OH radicals. Our findings unequivocally establish *D. oxyodonta* as a rich source of phenolic compounds with potent antioxidant activity, suggesting its potential utility in developing novel functional products.

**Keywords:** Dryadoideae; Rosaceae; flavonols; sexangularetin; corniculatusin; quercetin; kaempferol; DPPH; ABTS



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## 1. Introduction

The Rosaceae family is horticulturally important, containing various economically significant fruiting and ornamental species [1]. Chemotaxonomic investigations into Rosaceae have been conducted worldwide, examining botanical [2], genomic [3], and chemical perspectives [4]. Despite extensive research, debates persist regarding the classification of certain genera within the Rosaceae family. One such controversial genus is *Dryas*, which belongs to the subfamily Dryadoideae [5], although it has historically been classified as a separate family (Dryadaceae), tribe (Dryadeae), or subtribe (Dryadinae) [6]. Thriving predominantly in the cold regions of the Northern Hemisphere, particularly in subalpine and subarctic zones, the *Dryas* genus plays a significant role in the vegetation of high-mountain arctic and alpine tundras, often symbolizing these environments [7]. The ability of *Dryas* to form dense alpine thickets is likely attributable to the structure of its fruit—an achene characterized by a long, persistent, and feathery shaft. *Dryas* has limited distribution in snowy conditions because achenes fall very close to the parent plant [8].

*Dryas oxyodonta* Juz. is a perennial evergreen shrub, forming cushion-shaped growths with creeping, branched stems reaching heights of up to 8 cm (Figure 1). Its leaves, simple and petiolate, have oblong blades measuring 1–3 cm in length. These leaves exhibit a two-toned appearance, with dark green tops and whitish, tomentose undersides adorned with blunt serrations along the edges. The solitary white flowers bloom on 3–6-centimeter-long peduncles [9]. *D. oxyodonta* is distributed in subalpine and subarctic regions and in

highlands stretching from Central Asia to Siberia and Mongolia [10]. Among Siberian ethnic groups, particularly the Yakuts and Buryats, *D. oxyodonta* is used in traditional folk medicine for treating diarrhea and aiding digestion [11,12].



**Figure 1.** *Dryas oxyodonta* Juz. (Okinsky District, Buryatia Republic, Russia; CC BY-NC).

Despite its medicinal significance, the chemical composition of *D. oxyodonta* remains largely unexplored. Currently, there are no data regarding its chemical makeup. Among the *Dryas* genus, *D. octopetala* is the most studied species. It is known that the leaves of *D. octopetala*, collected in the mountains of France and Norway, contain procyanidin, propylarganidin, quercetin, kaempferol, isorhamnetin, corniculatusin, sexangularetin, limocitrin, and gossypetin [13]. Leaves of *D. octopetala*, collected in the mountain valleys of the Dolomites, yielded (+)-epicatechin and six flavonol glycosides: corniculatusin 3-*O*-arabinofuranoside, corniculatusin 3-*O*-galactopyranoside, sexangularetin 3-*O*-galactoside, hyperoside, avicularin, and guaijaverin [14]. In traditional medicine, the flowers and leaves of *D. octopetala* are used as digestive, antidiarrheal [14], cardiovascular, and neurological remedies [15].

The similarity in chemical composition and the identification of patterns in the metabolomes of plant species from the same family offer insights into their chemodiversity. Chemical compounds aid in species identification and quality control of herbal medicinal products that are increasing in popularity [16]. To perform chemodiversity studies, advanced analytical tools like high-performance liquid chromatography with photodiode-array detection and electrospray ionization triple-quadrupole mass spectrometric detection (HPLC–PDA–ESI–tQ–MS) are indispensable, serving as instrumental tools for fingerprinting plant extracts.

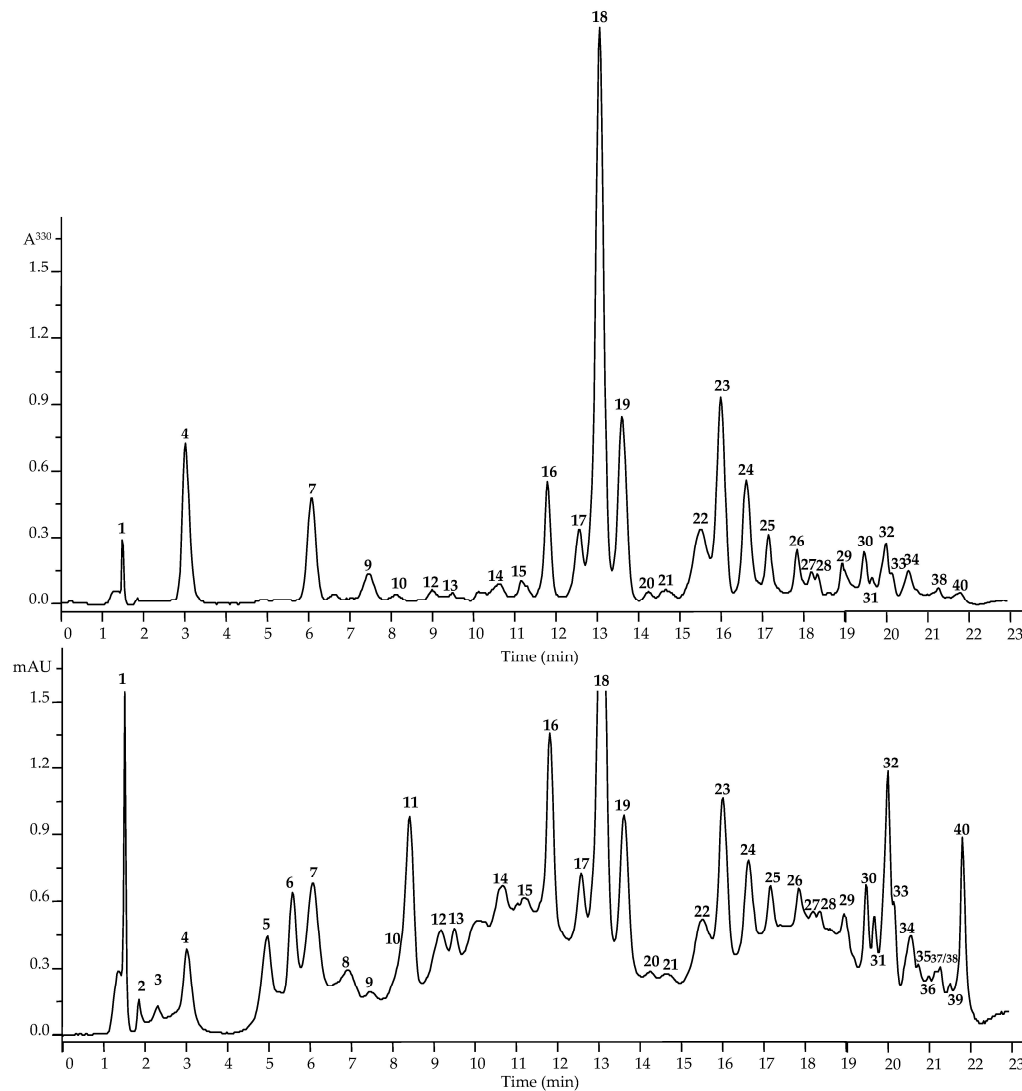
As part of our ongoing investigation into the metabolomes of Rosaceae family members [17–19], we conducted, for the first time, a comprehensive qualitative and quantitative chromatographic analysis of extracts from *D. oxyodonta*'s leaves and flowers, collected from diverse Siberian habitats. Employing HPLC–PDA–ESI–tQ–MS, we evaluated these extracts for their chemical constituents and antioxidant potential. Additionally, we identified specific chemotaxonomic markers characteristic of the *Dryas* genus.

## 2. Results and Discussion

### 2.1. Metabolome of *Dryas oxyodonta*

The analysis of metabolites in *D. oxyodonta* extracts was conducted using the HPLC–PDA–ESI–tQ–MS methodology. This comprehensive analysis allowed us to identify 40 distinct compounds (Figures 2 and S1; Table 1). The identification process adhered to the recommended minimum reporting standards for chemical analysis, as outlined by the Chemical Analysis Working Group. Specifically, compounds were identified using reten-

tion times, UV and MS spectra, and by comparison with standard compounds and the existing literature [20]. Metabolite identification was performed at two levels, with nineteen compounds fully characterized at the first level and twenty-one provisionally annotated at the second level.



**Figure 2.** High-performance liquid chromatography data of *Dryas oxyodonta* extracts (top figure—HPLC-PDA chromatogram,  $\lambda$  330 nm; bottom figure—HPLC-MS chromatogram, TIC, negative ionization). The numbering of the compounds is indicated as in Table 1.

**Table 1.** Retention times ( $t_R$ ), ultraviolet (UV), and mass spectrometric (ESI-MS) information of 1–40 detected in *Dryas oxyodonta*.

| No. | $t_R$ , min | UV Pattern <sup>a</sup> | Molecular Formula                               | ESI-MS, $m/z$<br>(Deprotonated ion<br>[M – H] <sup>–</sup> :<br>Daughter Ions) | Compound [Ref.]           | IL <sup>b</sup> |
|-----|-------------|-------------------------|---|--|---------------------------|-----------------|
| 1   | 1.48        | A                       | C <sub>15</sub> H <sub>18</sub> O <sub>9</sub>  | 341: 179   | 6-O-Caffeoyl glucose [21] | 1               |
| 2   | 1.92        | B                       | C <sub>13</sub> H <sub>16</sub> O <sub>10</sub> | 331: 169   | Galloyl glucose [22]      | 2               |
| 3   | 2.29        | B                       | C <sub>13</sub> H <sub>16</sub> O <sub>10</sub> | 331: 169   | 1-O-Galloyl glucose [22]  | 1               |
| 4   | 3.02        | A                       | C <sub>15</sub> H <sub>18</sub> O <sub>9</sub>  | 341: 179   | 1-O-Caffeoyl glucose [21] | 1               |
| 5   | 4.96        | C                       | C <sub>30</sub> H <sub>26</sub> O <sub>12</sub> | 577  | Procyanidin B1 [23]       | 1               |
| 6   | 5.63        | C                       | C <sub>15</sub> H <sub>14</sub> O <sub>6</sub>  | 289  | (+)-Catechin [22]         | 1               |

Table 1. Cont.

| No. | $t_R$ , min | UV Pattern <sup>a</sup> | Molecular Formula                               | ESI-MS, $m/z$<br>(Deprotonated ion<br>[M – H] <sup>–</sup> ;<br>Daughter Ions) | Compound [Ref.]   | IL <sup>b</sup> |
|-----|-------------|-------------------------|---|--|---|-----------------|
| 7   | 6.08        | D                       | C <sub>15</sub> H <sub>18</sub> O <sub>8</sub>  | 325: 163   | 1- <i>O-p</i> -Coumaroyl glucose [21]   | 1               |
| 8   | 6.97        | C                       | C <sub>30</sub> H <sub>26</sub> O <sub>12</sub> | 577  | Procyanidin B2 [23]   | 1               |
| 9   | 7.38        | A                       | C <sub>16</sub> H <sub>20</sub> O <sub>9</sub>  | 355: 193   | 1- <i>O</i> -Feruloyl glucose [21]  | 1               |
| 10  | 8.08        | A                       | C <sub>24</sub> H <sub>24</sub> O <sub>14</sub> | 503: 341, 179  | 1,6-Di- <i>O</i> -caffeoyl glucose [21]   | 1               |
| 11  | 8.31        | C                       | C <sub>15</sub> H <sub>14</sub> O <sub>6</sub>  | 289  | (–)-Epicatechin [22]  | 1               |
| 12  | 9.00        | E                       | C <sub>33</sub> H <sub>40</sub> O <sub>22</sub> | 787: 625, 463, 301   | Quercetin 3- <i>O</i> -trihexoside [24]   | 2               |
| 13  | 9.42        | E                       | C <sub>32</sub> H <sub>38</sub> O <sub>21</sub> | 757: 625, 595, 463, 301  | Quercetin<br>3- <i>O</i> -pentoside- <i>O</i> -dihexoside<br>[25]                 | 2               |
| 14  | 10.67       | E                       | C <sub>27</sub> H <sub>30</sub> O <sub>17</sub> | 625: 463, 301  | Quercetin 3- <i>O</i> -dihexoside [24]  | 2               |
| 15  | 11.12       | E                       | C <sub>26</sub> H <sub>28</sub> O <sub>16</sub> | 595: 463, 301  | Quercetin<br>3- <i>O</i> -pentoside- <i>O</i> -hexoside [25]                      | 2               |
| 16  | 11.87       | F                       | C <sub>22</sub> H <sub>22</sub> O <sub>13</sub> | 493: 331   | Corniculatusin <i>O</i> -hexoside<br>[26]   | 2               |
| 17  | 12.76       | F                       | C <sub>21</sub> H <sub>20</sub> O <sub>12</sub> | 463: 331   | Corniculatusin <i>O</i> -pentoside<br>[26]  | 2               |
| 18  | 13.0.8      | E                       | C <sub>21</sub> H <sub>20</sub> O <sub>12</sub> | 463: 301   | Quercetin 3- <i>O</i> -galactoside<br>(hyperoside) [27]                           | 1               |
| 19  | 13.67       | E                       | C <sub>20</sub> H <sub>18</sub> O <sub>11</sub> | 433: 301   | Quercetin<br>3- <i>O</i> -arabinopyranoside<br>(guajaverin) [28]                  | 1               |
| 20  | 14.22       | G                       | C <sub>22</sub> H <sub>22</sub> O <sub>12</sub> | 477: 315   | Sexangularetin <i>O</i> -hexoside<br>[29]   | 2               |
| 21  | 14.79       | G                       | C <sub>21</sub> H <sub>20</sub> O <sub>11</sub> | 447: 315   | Sexangularetin <i>O</i> -pentoside<br>[29]  | 2               |
| 22  | 15.55       | E                       | C <sub>20</sub> H <sub>18</sub> O <sub>11</sub> | 433: 301   | Quercetin 3- <i>O</i> -xyloside<br>(reynoutrin) [28]                              | 1               |
| 23  | 16.01       | E                       | C <sub>20</sub> H <sub>18</sub> O <sub>11</sub> | 433: 301   | Quercetin<br>3- <i>O</i> -arabinofuranoside<br>(avicularin) [28]                  | 1               |
| 24  | 16.71       | H                       | C <sub>21</sub> H <sub>20</sub> O <sub>11</sub> | 447: 285   | Kaempferol 3- <i>O</i> -galactoside<br>(trifolin) [30]                            | 1               |
| 25  | 17.11       | H                       | C <sub>20</sub> H <sub>18</sub> O <sub>10</sub> | 417: 285   | Kaempferol<br>3- <i>O</i> -arabinofuranoside<br>(juglanin) [30]                   | 1               |
| 26  | 17.89       | I                       | C <sub>35</sub> H <sub>34</sub> O <sub>19</sub> | 757: 625, 595, 463, 301  | Quercetin <i>O</i> -caffeoyl- <i>O</i> -<br>pentoside- <i>O</i> -hexoside<br>[31] | 2               |
| 27  | 18.09       | J                       | C <sub>31</sub> H <sub>28</sub> O <sub>16</sub> | 655: 493, 331  | Corniculatusin<br><i>O</i> -caffeoyl- <i>O</i> -hexoside [26]                     | 2               |
| 28  | 18.19       | J                       | C <sub>30</sub> H <sub>26</sub> O <sub>15</sub> | 625: 463, 331  | Corniculatusin<br><i>O</i> -caffeoyl- <i>O</i> -pentoside [26]                    | 2               |
| 29  | 18.97       | I                       | C <sub>30</sub> H <sub>26</sub> O <sub>15</sub> | 625: 463, 301  | Quercetin<br><i>O</i> -caffeoyl- <i>O</i> -hexoside [31]                          | 2               |
| 30  | 19.42       | I                       | C <sub>29</sub> H <sub>24</sub> O <sub>14</sub> | 595: 433, 301  | Quercetin<br><i>O</i> -caffeoyl- <i>O</i> -pentoside [31]                         | 2               |
| 31  | 19.63       | K                       | C <sub>31</sub> H <sub>28</sub> O <sub>15</sub> | 639: 477, 315  | Sexangularetin<br><i>O</i> -caffeoyl- <i>O</i> -hexoside [29]                     | 2               |
| 32  | 19.94       | K                       | C <sub>30</sub> H <sub>26</sub> O <sub>14</sub> | 609: 447, 315  | Sexangularetin<br><i>O</i> -caffeoyl- <i>O</i> -pentoside [29]                    | 2               |
| 33  | 20.02       | I                       | C <sub>29</sub> H <sub>24</sub> O <sub>14</sub> | 595: 433, 301  | Quercetin<br><i>O</i> -caffeoyl- <i>O</i> -pentoside [31]                         | 2               |
| 34  | 20.53       | I                       | C <sub>29</sub> H <sub>24</sub> O <sub>14</sub> | 595: 433, 301  | Quercetin<br><i>O</i> -caffeoyl- <i>O</i> -pentoside [31]                         | 2               |
| 35  | 20.82       | L                       | C <sub>30</sub> H <sub>48</sub> O <sub>5</sub>  | 487  | Tormentic acid [19]   | 1               |

Table 1. Cont.

| No. | $t_R$ , min | UV Pattern <sup>a</sup> | Molecular Formula                               | ESI-MS, $m/z$<br>(Deprotonated ion<br>[M – H] <sup>–</sup> ;<br>Daughter Ions) | Compound [Ref.]                           | IL <sup>b</sup> |
|-----|-------------|-------------------------|---|--|---|-----------------|
| 36  | 21.02       | L                       | C <sub>30</sub> H <sub>48</sub> O <sub>4</sub>  | 471  | Corosolic acid [19]                       | 1               |
| 37  | 21.12       | L                       | C <sub>30</sub> H <sub>48</sub> O <sub>3</sub>  | 455  | Ursolic acid [19]                         | 1               |
| 38  | 21.20       | M                       | C <sub>30</sub> H <sub>26</sub> O <sub>14</sub> | 609: 447, 285  | Kaempferol<br>O-caffeoyl-O-hexoside [30]  | 2               |
| 39  | 21.53       | L                       | C <sub>30</sub> H <sub>48</sub> O <sub>3</sub>  | 455  | Ursolic acid isomer [19]                  | 2               |
| 40  | 21.89       | M                       | C <sub>29</sub> H <sub>24</sub> O <sub>13</sub> | 579: 417, 285  | Kaempferol<br>O-caffeoyl-O-pentoside [30] | 2               |

<sup>a</sup> UV patterns: A—328 ± 2 nm; B—217 ± 2, 277 ± 2 nm; C—278 ± 1 nm; D—314 ± 1 nm; E—254 ± 1, 265 ± 1, 352 ± 2 nm; F—273 ± 2, 360 ± 2 nm; G—270 ± 2, 356 ± 2 nm; H—250 ± 3, 350 ± 2 nm; I—253 ± 1, 265 ± 1, 333 ± 3 nm; J—273 ± 2, 343 ± 3 nm; K—271 ± 2, 335 ± 2 nm; L—205 ± 4 nm; M—252 ± 3, 332 ± 2 nm.

<sup>b</sup> Identification levels: 1 identified compounds after comparison of UV and MS data and retention times with reference standards; 2 putatively annotated compounds after comparison of UV and MS data with data from the literature.

### 2.1.1. Gallotannins, Hydroxycinnamates, Procyanidins, and Catechins

The analysis of *D. oxyodonta* revealed representatives from six compound groups, encompassing gallotannins, hydroxycinnamates, procyanidins, catechins, flavonoids, and triterpenes. Notably, two gallotannins were discerned, each at varying levels of identification. The presence of 1-*O*-galloyl glucose (3), also known as glucogallin, was confirmed by comparing retention times and spectral characteristics with a reference standard. Additionally, the nature of galloyl glucose (2) was elucidated by comparing UV and MS data with the existing literature, particularly focusing on the deprotonated ion and the loss of particles with  $m/z$  152 (a gallic acid fragment) [22].

Five hydroxycinnamates were identified in the *D. oxyodonta* extract through comparison with reference standards [21]. Among these, three derivatives of caffeic acid—6-*O*-caffeoyl glucose (1), 1-*O*-caffeoyl glucose (4), and 1,6-di-*O*-caffeoyl glucose (10)—were confirmed, along with derivatives of *p*-coumaric and ferulic acids, identified as 1-*O*-*p*-coumaroyl glucose (7) and 1-*O*-feruloyl glucose (9), respectively. Furthermore, two procyanidins, B1 (5) and B2 (8), along with two catechins, (+)-catechin (6) and (–)-epicatechin (11), were characterized at the first level of metabolite identification through comparison of retention times, UV spectra, and MS data with reference compounds [22,23]. Notably, procyanidin and (+)-epicatechin were previously detected in *D. octopetala* leaves [13,14].

### 2.1.2. Flavonoids

Flavonoids were the predominant group of compounds in the *D. oxyodonta* extracts. The detected flavonol-*O*-glycosides, identified based on absorption spectra and deglycosylated fragment sizes, primarily belonged to derivatives of quercetin (12–15, 18, 19, 22, 23, 26, 29, 30, 33, and 34; 254 ± 1, 265 ± 1, 352 ± 2 nm; 253 ± 1, 265 ± 1, and 333 ± 3 nm; aglycone with  $m/z$  301), kaempferol (24, 25, 38, and 40; 250 ± 3 nm, 350 ± 2 nm; 252 ± 3, and 332 ± 2 nm; aglycone with  $m/z$  285), sexangularetin (20, 21, 31, and 32; 270 ± 2, 356 ± 2 nm; 271 ± 2, and 335 ± 2 nm; aglycone with  $m/z$  315), and corniculatusin (16, 17, 27, and 28; 273 ± 2, 360 ± 2 nm; 273 ± 2, and 343 ± 3 nm; aglycone with  $m/z$  331).

Four quercetin derivatives—hyperoside (18; 463 → 301), guaijaverin (19; 433 → 301), reynoutrin (22; 433 → 301), and avicularin (23; 433 → 301)—were identified through comparison of retention times, UV spectra, and MS data with reference compounds. Additionally, compounds 12 and 14, displaying similar UV and MS characteristics to quercetin derivatives, yielded deprotonated ions [M – H]<sup>–</sup> with  $m/z$  787 and 625, respectively, along with specific daughter ions following the elimination of three and two *O*-bonded hexose moieties ( $m/z$  787 → 625 → 463 → 301 and  $m/z$  625 → 463 → 301, respectively) [24]. The tentative structures of compounds 12 and 14 were identified as quercetin 3-*O*-trihexoside and quercetin 3-*O*-dihexoside, respectively. Compounds 13 and 15 were also determined to

be quercetin glycosides, containing pentose and hexose fragments within their structures. The presence of these fragments was further validated by a mass loss of 162 and 132 a.m.u., corresponding to hexose and pentose, respectively [25]. The proposed formulae of **13** and **15** were detected to be quercetin 3-*O*-pentoside-*O*-dihexoside and quercetin 3-*O*-pentoside-*O*-hexoside, respectively. Compounds **12–15** exhibited UV patterns that were consistent with flavonol glycosides ( $254 \pm 1$ ,  $265 \pm 1$ , and  $352 \pm 2$  nm), while compounds **26**, **29**, **30**, **33**, and **34** displayed UV data characteristic of flavonol caffeoylglycosides ( $253 \pm 1$ ,  $265 \pm 1$ , and  $333 \pm 3$  nm). The provisional structures of compounds **26**, **29**, **30**, **33**, and **34** were determined based on a specific hypsochromic shift of band I in the UV spectrum, along with the loss of the caffeoyl moiety (162 a.m.u.) in the mass spectrum. The assumed structures for compounds **26** and **30** were identified as quercetin *O*-caffeoyl-*O*-pentoside-*O*-hexoside and quercetin *O*-caffeoyl-*O*-pentoside, respectively. Compounds **30**, **33**, and **34** were characterized as quercetin *O*-caffeoyl-*O*-pentoside [31].

Two kaempferol derivatives—trifolin (kaempferol 3-*O*-galactoside, **24**;  $447 \rightarrow 285$ ) and juglanin (kaempferol 3-*O*-arabinofuranoside, **25**;  $417 \rightarrow 285$ )—were characterized at the first level of identification through comparison of retention times, UV spectra, and MS data with reference compounds. The proposed structures of the acylated kaempferol derivatives were inferred from characteristic UV spectra ( $252 \pm 3$  and  $332 \pm 2$  nm), deglycosylated fragments, and daughter ions formed upon the loss of caffeoyl moieties in the mass spectra, indicating kaempferol *O*-caffeoyl-*O*-hexoside and kaempferol *O*-caffeoyl-*O*-pentoside as tentative formulae for compounds **38** and **40**, respectively [30].

Derivatives **20**, **21**, **31**, and **32** were identified as containing either sexangularetin or 8-methoxykaempferol as an aglycone moiety, making them rare compounds. Tentatively identified non-acylated sexangularetins were observed to be glycosides with an aglycone daughter ion at  $m/z$  315 and carbohydrate moieties as either hexose (sexangularetin *O*-hexoside, **20**;  $477 \rightarrow 315$ ) or pentose (sexangularetin *O*-pentoside, **21**;  $447 \rightarrow 315$ ) [29]. Compounds **20** and **21** are likely sexangularetin 3-*O*-galactoside and sexangularetin 3-*O*-arabinoside, respectively, because these compounds have been previously detected in the leaves of *D. octopetala* [14]. Acylated sexangularetin glycosides include proposed structures such as sexangularetin *O*-caffeoyl-*O*-hexoside (**31**) and sexangularetin *O*-caffeoyl-*O*-pentoside (**32**). These compounds showed specific bands in the UV spectrum ( $271 \pm 2$  and  $335 \pm 2$  nm) and the loss of the caffeoyl moiety in the mass spectrum ( $m/z$   $639 \rightarrow 477$  and  $609 \rightarrow 447$ , respectively) [29].

Another group of rare flavonols in the *D. oxydonta* extract includes corniculatusin or 8-methoxyquercetin derivatives. Non-acylated corniculatusin *O*-hexoside (**16**) and corniculatusin *O*-pentoside (**17**) were presumably identified after a comparison of UV and MS data with information from the literature [14]. Possible structures of **16** and **17** are corniculatusin 3-*O*-galactoside and corniculatusin 3-*O*-arabinoside, respectively, which were previously isolated from the leaves of *D. octopetala* [14]. Acylated corniculatusin glycosides demonstrated typical bands in the UV spectra ( $273 \pm 2$  and  $343 \pm 3$  nm). Compound **27** (deprotonated ion at  $m/z$  655) demonstrated a loss of caffeoyl and hexose ( $m/z$   $655 \rightarrow 493$ , 331), which is characteristic of corniculatusin *O*-caffeoyl-*O*-hexoside. Compound **28** yielded an  $[M - H]^-$  ion with  $m/z$  625 and two fragment ions, resulting from the loss of caffeoyl and pentose. The structure of **28** was determined to be corniculatusin *O*-caffeoyl-*O*-pentoside [14].

Previously, the flavonoids hyperoside, avicularin, and guaijaverin were identified in *D. octopetala* leaves [14]. It is also worth noting that the aglycones quercetin, kaempferol, corniculatusin, and sexangularetin were previously discovered in the same plant [13]. However, in the *D. oxydonta* extract, we only identified flavonoid glycosides. Therefore, the compounds reynoutrin, trifolin, and juglanin were identified for the first time in the *Dryas* genus.

### 2.1.3. Triterpenes

Four triterpenes were discerned in the *D. oxyodonta* extract, including tormentic (35), corosolic (36), and ursolic (37) acids. Their identification was achieved by comparing their UV spectra, MS data, and  $t_R$  with those of reference compounds. The ursolic acid isomer (39) was provisionally annotated by comparing its UV and MS spectra with data from the literature. Notably, triterpenoids have not been previously reported in species of the *Dryas* genus.

Thus, this study's metabolomic profile of the *D. oxyodonta* extract provides comprehensive insights into its chemical composition and unveils novel compounds within the *Dryas* genus.

### 2.2. Chemodiversity Significance of *D. oxyodonta* Metabolites for the *Dryas* Genus

We attempted to identify specific markers of chemodiversity for the *Dryas* genus to clarify its potential taxonomic position from a chemical perspective. Our investigation focused on several compound groups (gallotannins, hydroxycinnamates, procyanidins, catechins, triterpenes, and flavonoids), comparing them with existing data on *D. octopetala* and representatives from other subfamilies.

Gallotannins are widely distributed in representatives of the Rosaceae family [32]. Gallotannins, in particular glucogallin, are known to participate in the biosynthesis of 1,2,3,4,6-pentagalloylglucose, a precursor to ellagitannins [33] frequently found in the Rosoideae subfamily [19,34,35]. Notably, ellagitannins were not detected in *D. oxyodonta* despite the fact that the genus *Dryas* was previously included in the Rosoideae subfamily [36]. Given the widespread distribution of gallotannins in the Rosaceae family, their presence in the *Dryas* genus does not serve as a unique chemodiversity marker. Moreover, the absence of 2-pyrone-4,6-dicarboxylic acid in *D. oxyodonta* extracts is noteworthy, because this compound is a chemotaxonomic marker of the Rosoideae subfamily and has been identified in numerous genera, such as *Agrimonia*, *Filipendula*, *Fragaria*, *Geum*, *Potentilla*, *Rosa*, *Rubus*, and *Sanguisorba* [37,38].

Hydroxycinnamates are common metabolites in the Rosaceae family [39–41]. Specifically, caffeic, coumaric, and ferulic acid derivatives are prevalent within the Rosoideae subfamily [42–45]. Although derivatives of hydroxycinnamic acids were identified in the *D. oxyodonta* extract, there are no records of their discovery in *D. octopetala*, likely owing to the lack of comprehensive knowledge about this species. Procyanidins and catechins, characteristic of the Dryadoideae subfamily, have also been found in other subfamilies, such as Rosoideae and Amygdaloideae, across genera like *Agrimonia* [46], *Prunus* [47], *Malus* [48], and *Pyrus* [49]. Therefore, establishing a distinct chemodiversity pattern for procyanidins and catechins is challenging due to their ubiquitous presence in the plant metabolome. This situation mirrors the one observed with triterpenes. In *D. oxyodonta*, all detected triterpenes belonged to the ursane type, a common triterpenoid found in various members of the Rosaceae family [19,50,51]. Consequently, this triterpenoid type cannot serve as a distinguishing criterion for chemodiversity within the *Dryas* genus.

The presence of derivatives of the flavonols quercetin and kaempferol is a common characteristic of the Rosaceae family, as validated by this study [52]. Additionally, derivatives of the flavonols sexangularetin and corniculatusin are more specific to the *Dryas* genus, identified in *D. oxyodonta* in this study and previously in *D. octopetala* [14]. Previously, the presence of sexangularetin derivatives has been observed in certain representatives of the Amygdaloideae (genera *Crataegus*, *Sorbus*, and *Prunus*) [1,53] and Rosoideae (*Fragaria*) subfamilies [54]. Conversely, corniculatusin derivatives have only been documented within the Rosaceae family in the Dryadoideae subfamily, specifically in the *Cowania*, *Purshia*, and *Dryas* genera [14,55]. Consequently, sexangularetin and corniculatusin glycosides are a phytochemical fingerprint for the *Dryas* genus, because these 8-methoxyflavonol derivatives have not been observed together in other species of the Rosaceae family. A similar occurrence of sexangularetin and corniculatusin in one botanical specimen has previously been reported for *Lotus corniculatus* (Fabaceae) [56,57]. Thus, the phenolic fingerprint pro-

files, specifically the flavonol glycosides of sexangularetin and corniculatusin, along with the presence of gallotannins and the absence of ellagitannins and 2-pyrone-4,6-dicarboxylic acid, could serve as markers in chemodiversity and potentially chemotaxonomy investigations within the *Dryas* genus. Regarding the question of whether the *Dryas* genus should be included in a separate subfamily, it is important to note that the metabolome of the studied representatives of this genus differs from existing data on the chemical composition patterns of members of other subfamilies within the Rosaceae family. This difference justifies the presence of a separate subfamily for *Dryas*.

### 2.3. Quantitative Analysis of Metabolites in *Dryas oxyodonta* Extracts

For the quantitative analysis of compounds using HPLC–PDA–ESI–tQ–MS, as well as for a comparative qualitative analysis of the components, samples of *D. oxyodonta* (flowers and leaves) were collected from three different regions of the high-mountain alpine tundra belt in Siberia: Sakha (1000 m), Buryatia (1900 m), and Altai (2300 m) (Table 2). These regions have a sharply continental climate, wide daily and annual temperature fluctuations, and moderate precipitation [58,59].

**Table 2.** Contents of compounds 1–40 in leaves and flowers of *Dryas oxyodonta* collected from three locations in Siberia, mg/100 g FW ( $\pm$ S.D.).

| No. | Compound   | Sakha 1000 m<br>(n = 14) |                  | Buryatia 1900 m (n = 14) |                  | Altai 2300 m<br>(n = 12) |                  |
|-----|--|--------------------------|------------------|--------------------------|------------------|--------------------------|------------------|
|     |  | Flowers                  | Leaves           | Flowers                  | Leaves           | Flowers                  | Leaves           |
| 1   | 6-O-Caffeoyl glucose                             | 0.93 $\pm$ 0.02          | 0.90 $\pm$ 0.02  | 1.03 $\pm$ 0.02          | tr.              | tr.                      | tr.              |
| 2   | Galloyl glucose                                  | 1.87 $\pm$ 0.03          | 5.11 $\pm$ 0.11  | 1.69 $\pm$ 0.04          | 2.83 $\pm$ 0.05  | tr.                      | tr.              |
| 3   | 1-O-Galloyl glucose                              | 2.14 $\pm$ 0.04          | 3.73 $\pm$ 0.07  | 1.53 $\pm$ 0.03          | 1.65 $\pm$ 0.03  | 0.93 $\pm$ 0.02          | tr.              |
| 4   | 1-O-Caffeoyl glucose                             | 3.75 $\pm$ 0.06          | 0.93 $\pm$ 0.02  | 4.83 $\pm$ 0.10          | 1.27 $\pm$ 0.02  | 1.11 $\pm$ 0.02          | 1.24 $\pm$ 0.02  |
| 5   | Procyanidin B1                                   | 55.11 $\pm$ 0.99         | 73.84 $\pm$ 1.40 | 42.14 $\pm$ 0.88         | 40.83 $\pm$ 0.86 | 21.15 $\pm$ 0.38         | 20.53 $\pm$ 0.41 |
| 6   | (+)-Catechin                                     | 14.82 $\pm$ 0.27         | 45.77 $\pm$ 0.96 | 26.84 $\pm$ 0.51         | 39.14 $\pm$ 0.82 | 14.22 $\pm$ 0.27         | 22.83 $\pm$ 0.43 |
| 7   | 1-O- <i>p</i> -Coumaroyl glucose                 | 2.63 $\pm$ 0.04          | 1.73 $\pm$ 0.04  | 3.79 $\pm$ 0.08          | 0.61 $\pm$ 0.01  | 0.27 $\pm$ 0.01          | tr.              |
| 8   | Procyanidin B2                                   | 19.25 $\pm$ 0.35         | 29.16 $\pm$ 0.61 | 10.06 $\pm$ 0.19         | 11.29 $\pm$ 0.24 | 9.57 $\pm$ 0.19          | 8.27 $\pm$ 0.17  |
| 9   | 1-O-Feruloyl glucose                             | 0.83 $\pm$ 0.02          | tr.              | 0.93 $\pm$ 0.02          | tr.              | 0.52 $\pm$ 0.01          | tr.              |
| 10  | 1,6-Di-O-caffeoyl glucose                        | 0.24 $\pm$ 0.00          | tr.              | 0.12 $\pm$ 0.00          | tr.              | 0.14 $\pm$ 0.00          | tr.              |
| 11  | (–)-Epicatechin                                  | 26.84 $\pm$ 0.51         | 52.17 $\pm$ 1.04 | 42.03 $\pm$ 0.84         | 73.15 $\pm$ 1.61 | 22.82 $\pm$ 0.46         | 35.11 $\pm$ 0.70 |
| 12  | Quercetin 3-O-trihexoside                        | 1.01 $\pm$ 0.02          | tr.              | 0.12 $\pm$ 0.00          | tr.              | 1.09 $\pm$ 0.02          | 0.14 $\pm$ 0.00  |
| 13  | Quercetin<br>3-O-pentoside-O-dihexoside          | 0.67 $\pm$ 0.01          | tr.              | 0.09 $\pm$ 0.00          | tr.              | 1.72 $\pm$ 0.04          | 0.21 $\pm$ 0.00  |
| 14  | Quercetin 3-O-dihexoside                         | 1.43 $\pm$ 0.03          | tr.              | 0.53 $\pm$ 0.01          | tr.              | 4.35 $\pm$ 0.09          | 0.41 $\pm$ 0.01  |
| 15  | Quercetin<br>3-O-pentoside-O-hexoside            | 1.24 $\pm$ 0.02          | tr.              | 0.72 $\pm$ 0.02          | tr.              | 2.09 $\pm$ 0.04          | 0.52 $\pm$ 0.01  |
| 16  | Corniculatusin 3-O-galactoside                   | 7.83 $\pm$ 0.15          | 2.73 $\pm$ 0.05  | 5.79 $\pm$ 0.12          | 0.50 $\pm$ 0.01  | 0.11 $\pm$ 0.00          | 0.08 $\pm$ 0.00  |
| 17  | Corniculatusin 3-O-arabinoside                   | 6.33 $\pm$ 0.11          | 1.29 $\pm$ 0.03  | 4.25 $\pm$ 0.09          | 0.41 $\pm$ 0.01  | 0.23 $\pm$ 0.00          | 0.09 $\pm$ 0.00  |
| 18  | Quercetin 3-O-galactoside<br>(hyperoside)        | 43.27 $\pm$ 0.69         | 8.21 $\pm$ 0.16  | 58.33 $\pm$ 1.22         | 12.63 $\pm$ 0.21 | 27.63 $\pm$ 0.58         | 2.63 $\pm$ 0.06  |
| 19  | Quercetin 3-O-arabinopyranoside<br>(guaijaverin) | 10.52 $\pm$ 0.19         | 5.27 $\pm$ 0.10  | 14.63 $\pm$ 0.28         | 6.24 $\pm$ 0.12  | 22.85 $\pm$ 0.48         | 11.81 $\pm$ 0.26 |
| 20  | Sexangularetin 3-O-galactoside                   | 1.52 $\pm$ 0.03          | 0.40 $\pm$ 0.01  | 0.84 $\pm$ 0.01          | tr.              | 0.28 $\pm$ 0.01          | 0.15 $\pm$ 0.00  |
| 21  | Sexangularetin 3-O-arabinoside                   | 2.16 $\pm$ 0.04          | 0.52 $\pm$ 0.01  | 0.92 $\pm$ 0.02          | tr.              | 0.37 $\pm$ 0.01          | 0.06 $\pm$ 0.00  |
| 22  | Quercetin 3-O-xyloside<br>(reynoutrin)           | 5.27 $\pm$ 0.10          | tr.              | 6.83 $\pm$ 0.14          | 0.83 $\pm$ 0.01  | 11.64 $\pm$ 0.23         | 9.83 $\pm$ 0.17  |
| 23  | Quercetin 3-O-arabinofuranoside<br>(avicularin)  | 9.83 $\pm$ 0.17          | 1.53 $\pm$ 0.03  | 14.95 $\pm$ 0.31         | 3.86 $\pm$ 0.08  | 27.82 $\pm$ 0.53         | 5.22 $\pm$ 0.09  |
| 24  | Kaempferol 3-O-galactoside<br>(trifolin)         | 4.03 $\pm$ 0.08          | 0.93 $\pm$ 0.02  | 5.29 $\pm$ 0.09          | 1.95 $\pm$ 0.04  | 9.65 $\pm$ 0.18          | 2.10 $\pm$ 0.04  |
| 25  | Kaempferol<br>3-O-arabinofuranoside (juglanin)   | 0.52 $\pm$ 0.01          | tr.              | 1.89 $\pm$ 0.04          | 0.52 $\pm$ 0.01  | 3.76 $\pm$ 0.07          | 1.52 $\pm$ 0.03  |
| 26  | Quercetin O-caffeoyl-O-pentoside-<br>O-hexoside  | 0.41 $\pm$ 0.01          | tr.              | 1.22 $\pm$ 0.02          | 0.21 $\pm$ 0.00  | 1.73 $\pm$ 0.03          | tr.              |
| 27  | Corniculatusin<br>O-caffeoyl-O-hexoside          | 2.67 $\pm$ 0.05          | 0.63 $\pm$ 0.01  | 0.72 $\pm$ 0.02          | tr.              | tr.                      | 0.27 $\pm$ 0.00  |
| 28  | Corniculatusin<br>O-caffeoyl-O-pentoside         | 1.54 $\pm$ 0.03          | 1.14 $\pm$ 0.03  | 0.70 $\pm$ 0.01          | tr.              | 0.44 $\pm$ 0.01          | 0.19 $\pm$ 0.00  |
| 29  | Quercetin O-caffeoyl-O-hexoside                  | 0.24 $\pm$ 0.00          | tr.              | 0.63 $\pm$ 0.01          | 0.08 $\pm$ 0.00  | 1.14 $\pm$ 0.02          | tr.              |



Table 2. Cont.

| No. | Compound  | Sakha 1000 m<br>(n = 14) |             | Buryatia 1900 m (n = 14) |             | Altai 2300 m<br>(n = 12) |             |
|-----|---|--------------------------|-------------|--------------------------|-------------|--------------------------|-------------|
|     |   | Flowers                  | Leaves      | Flowers                  | Leaves      | Flowers                  | Leaves      |
| 30  | Quercetin <i>O</i> -caffeoyl- <i>O</i> -pentoside         | 0.12 ± 0.00              | tr.         | 0.69 ± 0.01              | 0.05 ± 0.00 | 1.52 ± 0.03              | tr.         |
| 31  | Sexangularetin<br><i>O</i> -caffeoyl- <i>O</i> -hexoside  | 0.53 ± 0.01              | 0.04 ± 0.00 | 0.08 ± 0.00              | tr.         | 0.02 ± 0.00              | tr.         |
| 32  | Sexangularetin<br><i>O</i> -caffeoyl- <i>O</i> -pentoside | 2.67 ± 0.06              | 0.22 ± 0.00 | 1.10 ± 0.02              | 0.09 ± 0.00 | tr.                      | tr.         |
| 33  | Quercetin <i>O</i> -caffeoyl- <i>O</i> -pentoside         | tr.                      | tr.         | 0.54 ± 0.01              | tr.         | 0.97 ± 0.02              | tr.         |
| 34  | Quercetin <i>O</i> -caffeoyl- <i>O</i> -pentoside         | tr.                      | tr.         | 0.63 ± 0.01              | tr.         | 1.49 ± 0.03              | tr.         |
| 35  | Tormentolic acid  | 6.85 ± 0.14              | 7.39 ± 0.14 | 2.94 ± 0.06              | 3.85 ± 0.08 | 1.41 ± 0.03              | 2.53 ± 0.05 |
| 36  | Corosolic acid  | 2.74 ± 0.06              | 3.67 ± 0.07 | 0.53 ± 0.01              | 1.02 ± 0.02 | 0.92 ± 0.02              | 1.14 ± 0.02 |
| 37  | Ursolic acid  | 2.22 ± 0.04              | 1.29 ± 0.03 | 0.60 ± 0.01              | 0.42 ± 0.01 | 0.57 ± 0.01              | 1.69 ± 0.03 |
| 38  | Kaempferol<br><i>O</i> -caffeoyl- <i>O</i> -hexoside      | tr.                      | tr.         | 0.63 ± 0.01              | tr.         | 0.90 ± 0.02              | 0.52 ± 0.01 |
| 39  | Ursolic acid isomer<br>Kaempferol                         | 1.14 ± 0.02              | 0.93 ± 0.02 | 0.83 ± 0.02              | 0.92 ± 0.02 | 1.14 ± 0.02              | 0.95 ± 0.02 |
| 40  | Kaempferol<br><i>O</i> -caffeoyl- <i>O</i> -pentoside     | tr.                      | tr.         | 0.69 ± 0.01              | tr.         | 2.11 ± 0.04              | 0.92 ± 0.02 |
|     | Total cinnamoyl glucoses                                  | 8.38                     | 3.56        | 10.70                    | 1.88        | 2.04                     | 1.24        |
|     | Total galloyl glucoses                                    | 4.01                     | 8.84        | 3.22                     | 4.48        | 0.93                     | tr.         |
|     | Total procyanidins  | 74.36                    | 103.00      | 52.20                    | 52.12       | 30.72                    | 28.80       |
|     | Total catechins   | 41.66                    | 97.94       | 68.87                    | 112.29      | 37.04                    | 57.94       |
|     | Total flavonoids, including:                              | 103.81                   | 22.91       | 122.81                   | 27.37       | 123.91                   | 36.67       |
|     | Kaempferol glucosides                                     | 4.55                     | 0.93        | 8.50                     | 2.47        | 16.42                    | 5.06        |
|     | Quercetin glucosides                                      | 74.01                    | 15.01       | 99.91                    | 23.90       | 106.04                   | 30.77       |
|     | Sexangularetin glucosides                                 | 6.88                     | 1.18        | 2.94                     | 0.09        | 0.67                     | 0.21        |
|     | Corniculatusin glucosides                                 | 18.37                    | 5.79        | 11.46                    | 0.91        | 0.78                     | 0.63        |
|     | Total phenolics   | 232.22                   | 236.25      | 257.80                   | 198.14      | 194.64                   | 124.65      |
|     | Total triterpenes   | 12.95                    | 13.28       | 4.90                     | 6.21        | 4.04                     | 6.31        |

tr.—traces (&lt;limit of quantification).

Procyanidin B1 was identified as the primary compound in both flowers and leaves of *D. oxyodonta* collected from the Sakha region (55.11 and 73.84 mg/g, respectively). Additionally, both flowers and leaves of the same samples exhibited notably high levels of (–)-epicatechin (26.84 and 52.17 mg/g, respectively) and (+)-catechin (14.82 and 45.77 mg/g, respectively). Furthermore, the analysis revealed that the hyperoside content in *D. oxyodonta* flowers exceeded that in leaves by more than fivefold (43.27 vs. 8.21 mg/g, respectively). The primary compound in *D. oxyodonta* flowers from Buryatia was identified as hyperoside (58.33 mg/g), while (–)-epicatechin accumulated in the leaves (73.15 mg/g). High levels of procyanidin B1 and (+)-catechin were also observed in both flowers and leaves, similar to the samples from Sakha. However, the flowers from Altai had a different composition, with the flavonols avicularin (27.82 mg/g) and hyperoside (27.63 mg/g) being the predominant compounds. In the leaves from Altai and those from Buryatia, epicatechin was the dominant compound, with a concentration of 35.11 mg/g. However, similar to the samples from other regions, the flowers and leaves of specimens from Altai also exhibited high levels of procyanidin B1 and (+)-catechin. The overall flavonoid content was highest in the *D. oxyodonta* flowers from Altai samples (123.91 mg/g), and the maximum concentration of phenolic compounds was observed in the flowers from Buryatia (257.80 mg/g).

Notably, all of the studied samples contained potential marker compounds, namely, glycosides of sexangularetin and corniculatusin. Higher concentrations of glycosides were observed in the flowers, while the leaves contained lesser amounts or even trace quantities. This pattern of sexangularetin and corniculatusin derivatives' accumulation in flowers was previously described for *L. corniculatus*, where the authors proposed it as a taxonomic and ecological characteristic [56]. However, quercetin and kaempferol unsubstituted at the 8 position accumulated maximally in *L. corniculatus* leaves, a trend that was not observed in the leaves of *D. oxyodonta*. Therefore, all populations of *D. oxyodonta* collected in Siberia exhibited a high concentration of phenolic compounds, indicating the presence of antioxidant activity.

#### 2.4. Antioxidant Activity of *D. oxyodonta* Extracts

We conducted a comparative analysis of the antioxidant potential of *D. oxyodonta* extracts derived from flowers and leaves collected from various locations in Siberia (Table 3). The scavenging capacities of the analyzed extracts were assessed using four radical assays: DPPH<sup>•</sup>, ABTS<sup>•+</sup>, O<sub>2</sub><sup>•-</sup>, and <sup>•</sup>OH.

**Table 3.** Radical scavenging activity of *D. oxyodonta* extracts.

| Extracts            | DPPH <sup>•</sup> <sup>a</sup> | ABTS <sup>•+</sup> <sup>a</sup> | O <sub>2</sub> <sup>•-</sup> <sup>a</sup> | <sup>•</sup> OH <sup>a</sup> |
|---------------------|--------------------------------|---------------------------------|---|------------------------------|
| SFE                 | 9.23 ± 0.18                    | 5.04 ± 0.10                     | 26.13 ± 0.52                              | 14.92 ± 0.29                 |
| SLE                 | 11.08 ± 0.22                   | 7.12 ± 0.14                     | 37.16 ± 0.74                              | 8.08 ± 0.16                  |
| BFE                 | 8.67 ± 0.17                    | 3.99 ± 0.08                     | 21.59 ± 0.43                              | 12.78 ± 0.25                 |
| BLE                 | 11.90 ± 0.23                   | 4.36 ± 0.09                     | 41.14 ± 0.82                              | 19.36 ± 0.39                 |
| AFE                 | 15.01 ± 0.30                   | 8.07 ± 0.16                     | 58.22 ± 1.16                              | 36.05 ± 0.72                 |
| ALE                 | 18.33 ± 0.36                   | 10.85 ± 0.21                    | 73.01 ± 1.46                              | 49.32 ± 0.99                 |
| Trolox <sup>b</sup> | 10.17 ± 0.20                   | 4.67 ± 0.09                     | 109.28 ± 2.18                             | 16.37 ± 0.33                 |

SFE—Sakha flower extract. SLE—Sakha leaf extract. BFE—Buryatia flower extract. BLE—Buryatia leaf extract. AFE—Altai flower extract. ALE—Altai leaf extract. <sup>a</sup> IC<sub>50</sub>, µg/mL ± SD. <sup>b</sup> Reference compound.

*D. oxyodonta* extracts from flowers collected in Buryatia and Sakha exhibited the most pronounced antioxidant activity, while leaf extracts from the same locations showed less pronounced activity. These results align with expectations because the active extracts are characterized by high levels of potent antioxidants such as catechins, flavonoids, and procyanidins [60,61]. In a previous study, the highest antioxidant activity among the examined species of Arctic plants was found in the *D. octopetala* extract [62]. Consequently, herbal tea made from the vegetative parts of *D. oxyodonta* can be considered to be a valuable source of antioxidants, owing to its high phenolic compound contents.

### 3. Materials and Methods

#### 3.1. Plant Material

Plant samples of *Dryas oxyodonta* (flowers and leaves) were collected from three different regions of Siberia: the Republic of Buryatia, Tunkinsky District (21 July 2022; 51°51′47.2″ N 101°43′34.6″ E, 1900 m a.s.l.); the Republic of Sakha (Yakutia), Oymyakonskii District, Tas-Kystabyt Mountains (26 July 2022; 62°59′33.1″ N 145°01′47.8″ E, 1000 m a.s.l.); and the Altai Republic, Ust Koksinkii District (16 July 2022; 49°56′26.7″ N 85°59′11.3″ E, 2300 m a.s.l.). Samples were collected at eight points in the alpine tundra (12–14 samples each). Fresh materials were dried in an IPLS-131 drying oven (Bestek Engineering LLC, Rostov-on-Don, Russia) under the following conditions: convection mode, 40 °C. After the samples reached a humidity of 9–12%, they were stored in an Edry D-450A auto-drying cabinet (Edry Co., Ltd., Taichung, Taiwan) before HPLC separation.

#### 3.2. Reagents

The reference standards were purchased from BenchChem (Pasadena, CA, USA): 1-*O*-feruloyl-glucose (Cat. No. B135945); ChemFaces (Wuhan, China): juglanin (Cat. No. CFN96238, ≥98%), trifolin (Cat. No. CFN92079, ≥98%); Scientific Laboratory Supplies (Nottingham, UK): 1-*O*-galloyl glucose (Cat. No. 69288, ≥90%); Selleck Chemicals LLC (Houston, TX, USA): procyanidin B1 (Cat. No. E0240, ≥97%); Sigma-Aldrich (St. Louis, MO, USA): (+)-catechin (Cat. No. 43412, ≥99%), corosolic acid (Cat. No. PHL80065, ≥90%), 2,2-diphenyl-1-picrylhydrazyl (Cat. No. D9132), (–)-epicatechin (Cat. No. E4018, ≥98%), lithium perchlorate (Cat. No. 205281, ≥95%), perchloric acid (Cat. No. 244252, ≥70%), procyanidin B2 (Cat. No. 42157, ≥90%), avicularin (Cat. No. 44006, ≥90%), guaijaverin (Cat. No. PHL80986, ≥95%), hyperoside (Cat. No. 83388, ≥97%), reynoutrin (Cat. No. 83390, ≥97%), tormentic acid (Cat. No. PHL85836, ≥95%), Trolox (Cat. No. 648471), ursolic acid (Cat. No. U6753, ≥90%); 1-*O*-caffeoyl-glucose and 1-*O*-*p*-coumaroyl

glucose were previously isolated from *Spiraea salicifolia* [63], while 6-*O*-caffeoyl-glucose and 1,6-di-*O*-caffeoyl-glucose were isolated from *Filipendula ulmaria* [64].

### 3.3. Extract Preparation

To prepare the *D. oxyodonta* extracts, 10 g of the ground plant materials (leaves and flowers) was treated twice with 100 mL of 70% methanol using an ultrasonic bath (Sapphire Ltd., Moscow, Russia) with the following sonication parameters: 30 min, 40 °C, frequency 35 kHz, and ultrasound power 100 W. The obtained liquid extracts were combined and centrifuged. The supernatants were filtered through cellulose filters and concentrated until dryness. The yields of the *D. oxyodonta* extracts were 4.3 g (Altai flower extract), 4.6 g (Altai leaf extract), 3.8 (Buryatia flower extract), 4.1 (Buryatia leaf extract), 4.4 g (Sakha flower extract), and 4.2 (Sakha leaf extract). The final dry extracts were conserved at 4 °C for subsequent usage in chromatographic experiments and antioxidant activity studies.

### 3.4. Liquid Chromatography–Mass Spectrometry Detection of Metabolites in *D. oxyodonta* Extracts

Fingerprinting of *D. oxyodonta* metabolites was carried out using liquid chromatography–mass spectrometry (Table S1). LabSolutions LCMS software (ver. 5.6) was applied to operate the LC-MS system [65]. To identify metabolites, a set of chromatographic and spectral parameters (retention time and UV/MS spectra, respectively) were analyzed in comparison with data from reference compounds, data from the literature, and our own mass spectrometry library. For the preparation of the analyzed solution, *D. oxyodonta* extract (5 mg) was dissolved in methanol in a volumetric flask (5 mL) by shaking, followed by filtration through syringe filters with a pore size of 0.22 µm.

### 3.5. HPLC-PDA-ESI-tQ-MS Quantification of Metabolites in *D. oxyodonta* Extracts

The quantification of *D. oxyodonta* compounds was performed using liquid chromatography–mass spectrometry conditions (Section 3.4). The full-scan MS peak areas were applied for calculation. Nineteen reference standards were utilized to build calibration curves: 6-*O*-caffeoyl glucose, 1-*O*-galloyl glucose, 1-*O*-caffeoyl glucose, procyanidin B1, (+)-catechin, 1-*O*-*p*-coumaroyl glucose, procyanidin B2, 1-*O*-feruloyl glucose, 1,6-di-*O*-caffeoyl glucose, (–)-epicatechin, hyperoside, guaijaverin, reynoutrin, avicularin, trifolin, juglanin, tormentic acid, corosolic acid, and ursolic acid. The reference compounds were carefully weighed (10 mg), dissolved in 10 mL volumetric flasks with the usage of a methanol–DMSO (1:1) solvent, and then “concentration–mass spectral peak area” graphs were plotted (1–100 µg/mL). The values of the correlation coefficient ( $r^2$ ), standard deviation ( $S_{YX}$ ), limit of detection (LOD), limit of quantification (LOQ), and linear range were calculated in Advanced Grapher 2.2 (Alentum Software Inc., Ramat-Gan, Israel), using calibration curve data [66] and the results of three sufficient HPLC runs (Table 4). Intra-day precision, inter-day precision, and the recovery of spiked samples were studied using the known assay [67]. The results were expressed as mean values  $\pm$  standard deviation (S.D.).

### 3.6. Antioxidant Activity of *D. oxyodonta* Extracts

Spectrophotometric assays in microplates were used to evaluate the antioxidant potential of *D. oxyodonta* extracts via four radical tests: DPPH• (2,2-diphenyl-1-picrylhydrazyl radical) [68], ABTS•<sup>+</sup> (2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) cation radical) [69], O<sub>2</sub>•<sup>-</sup> (superoxide radical) [70], and •OH (hydroxyl radical) [71]. The results of the DPPH•, ABTS•<sup>+</sup>, O<sub>2</sub>•<sup>-</sup>, and •OH assays were measured as IC<sub>50</sub> values (the half-maximal inhibitory concentration). To calculate the IC<sub>50</sub> correlations, “concentration (µg/mL or mg/mL)—antioxidant activity (%)” graphs were used. All tests were carried out five times, and the data obtained were presented as the mean value  $\pm$  standard deviation (SD).

### 3.7. Statistical Analysis

Statistical analyses were carried out with the usage of one-way analysis of variance. Duncan's multiple range test was applied to find the significance of the mean differences. Differences were presumed to be statistically significant at  $p < 0.05$ . The results were provided as the mean  $\pm$  S.D. Advanced Grapher 2.2 (Alentum Software, Inc., Ramat Gan, Israel) was applied for linear regression analysis, as well as for generating the calibration graphs.

**Table 4.** Regression equations, correlation coefficients ( $r^2$ ), standard deviation ( $S_{yx}$ ), limits of detection (LOD), limits of quantification (LOQ), and linear ranges for 19 reference standards used for HPLC-MS quantification.

| Compound                         | Regression Equation <sup>a</sup> |                 | $r^2$  | $S_{yx}$               | LOD/LOQ ( $\mu\text{g/mL}$ ) | Linear Range ( $\mu\text{g/mL}$ ) | RSD% (Intra-Day) | RSD% (Inter-Day) | Recovery of Spiked Sample REC% |
|----------------------------------|----------------------------------|-----------------|--------|------------------------|------------------------------|-----------------------------------|------------------|------------------|--------------------------------|
|                                  | $a$                              | $b \times 10^6$ |        |                        |                              |                                   |                  |                  |                                |
| 6-O-Caffeoyl glucose             | 1.3387                           | −0.0284         | 0.9981 | $9.50 \times 10^{-2}$  | 0.23/0.71                    | 1.0–100.0                         | 1.45             | 1.92             | 101.27                         |
| 1-O-Galloyl glucose              | 1.3586                           | −0.0663         | 0.9987 | $9.69 \times 10^{-2}$  | 0.24/0.71                    | 1.0–100.0                         | 0.97             | 1.16             | 98.34                          |
| 1-O-Caffeoyl glucose             | 1.5824                           | −0.1078         | 0.9965 | $16.25 \times 10^{-2}$ | 0.34/1.03                    | 1.0–100.0                         | 0.89             | 1.29             | 100.64                         |
| Procyanidin B1                   | 1.3722                           | −0.0829         | 0.9973 | $9.93 \times 10^{-2}$  | 0.24/0.72                    | 1.0–100.0                         | 1.09             | 1.36             | 99.12                          |
| (+)-Catechin                     | 0.9562                           | −0.0521         | 0.9971 | $7.79 \times 10^{-2}$  | 0.27/0.82                    | 1.0–100.0                         | 1.23             | 1.54             | 100.07                         |
| 1-O- <i>p</i> -Coumaroyl glucose | 1.4238                           | −0.0891         | 0.9901 | $7.33 \times 10^{-2}$  | 0.17/0.52                    | 1.0–100.0                         | 1.38             | 1.88             | 101.14                         |
| Procyanidin B2                   | 1.3620                           | −0.0820         | 0.9961 | $9.91 \times 10^{-2}$  | 0.21/0.72                    | 1.0–100.0                         | 1.47             | 1.64             | 100.78                         |
| 1-O-Feruloyl glucose             | 1.5152                           | −0.0523         | 0.9979 | $12.67 \times 10^{-2}$ | 0.28/0.84                    | 1.0–100.0                         | 1.33             | 1.61             | 100.11                         |
| 1,6-Di-O-caffeoyl glucose        | 1.7552                           | −0.0569         | 0.9982 | $8.89 \times 10^{-2}$  | 0.18/0.51                    | 1.0–100.0                         | 1.40             | 1.98             | 100.39                         |
| (−)-Epicatechin                  | 1.0828                           | −0.0456         | 0.9973 | $6.85 \times 10^{-2}$  | 0.21/0.63                    | 1.0–100.0                         | 1.12             | 1.42             | 99.23                          |
| Hyperoside                       | 1.4689                           | −0.3641         | 0.9990 | $5.69 \times 10^{-2}$  | 0.12/0.38                    | 1.0–100.0                         | 1.22             | 1.43             | 101.22                         |
| Guaijaverin                      | 1.3436                           | −0.4406         | 0.9981 | $17.58 \times 10^{-2}$ | 0.43/1.31                    | 1.0–100.0                         | 0.99             | 1.60             | 102.55                         |
| Reynoutrin                       | 1.5364                           | −0.3614         | 0.9927 | $10.07 \times 10^{-2}$ | 0.22/0.66                    | 1.0–100.0                         | 1.34             | 1.78             | 102.03                         |
| Avicularin                       | 1.4041                           | −0.3270         | 0.9992 | $14.02 \times 10^{-2}$ | 0.33/1.00                    | 1.0–100.0                         | 1.31             | 1.57             | 99.83                          |
| Trifolin                         | 2.0859                           | −0.9171         | 0.9980 | $6.18 \times 10^{-2}$  | 0.03/0.09                    | 1.0–100.0                         | 1.23             | 1.83             | 101.23                         |
| Juglanin                         | 2.2126                           | −0.5160         | 0.9987 | $8.11 \times 10^{-2}$  | 0.12/0.37                    | 1.0–100.0                         | 1.08             | 1.60             | 98.33                          |
| Tormentic acid                   | 1.5330                           | −0.0863         | 0.9985 | $4.15 \times 10^{-2}$  | 0.09/0.27                    | 1.0–100.0                         | 1.39             | 1.78             | 100.09                         |
| Corosolic acid                   | 2.3312                           | −0.4563         | 0.9803 | $14.92 \times 10^{-2}$ | 0.21/0.64                    | 1.0–100.0                         | 1.24             | 1.85             | 101.40                         |
| Ursolic acid                     | 1.2820                           | −0.9634         | 0.9697 | $11.64 \times 10^{-2}$ | 0.30/0.91                    | 1.0–100.0                         | 1.41             | 1.91             | 99.54                          |

<sup>a</sup> Regression equation:  $y = a \times x + b$ .

## 4. Conclusions

The *Dryas oxyodonta* species thrives across extensive territories in the subalpine and subarctic zones of the Northern Hemisphere, creating valuable reserves. This study elucidates the chemical composition of this species, which has not been previously examined. In exploring the chemodiversity of *D. oxyodonta*, we established the marker role of certain rare flavonoids. The propensity of *Dryas* to accumulate phenolic compounds, alongside its associated high antioxidant activity, positions the studied species as a promising source of raw medicinal plant materials.

**Supplementary Materials:** The following supporting information are available at: <https://www.mdpi.com/article/10.3390/plants13060868/s1>. Figure S1: Structures of compounds identified in *Dryas oxyodonta*. Table S1: Conditions for liquid chromatography–mass spectrometry detection of metabolites in *Dryas oxyodonta* extracts.

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