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Phenolic Compounds of Six Unexplored Asteraceae Species from Asia: Comparison of Wild and Cultivated Plants

Daniil N. Olennikov [1,*] and Nadezhda K. Chirikova [2]

[1] Laboratory of Biomedical Research, Institute of General and Experimental Biology, Siberian Division, Russian Academy of Science, 6 Sakhyanovoy Street, 670047 Ulan-Ude, Russia
[2] Department of Biochemistry and Biotechnology, North-Eastern Federal University, 58 Belinsky Street, 677027 Yakutsk, Russia; hofnung@mail.ru
* Correspondence: olennikovdn@mail.ru; Tel.: +7-902-160-0627

Abstract: The Asteraceae family in Siberian Asia exhibits remarkable biodiversity and has long served as a valuable resource for domesticating various beneficial plants with medicinal, therapeutic, and industrial significance to humanity. In this work, we studied for the first time the chemical composition of six understudied or previously unexplored plant species, *Artemisia jacutica* (AJ), *Carduus nutans* subsp. *leiophyllus* (CL), *Cirsium heterophyllum* (CH), *Echinops davuricus* (ED), *Ixeris chinensis* subsp. *versicolor* (IV), and *Lactuca sibirica* (LS), which were successfully cultivated under open-field conditions as biennial or perennial crops. We profiled these species, employing a liquid chromatography–mass spectrometry approach, identifying over 100 phenolic compounds. Among these compounds were hydroxybenzoic acid glucosides, hydroxybenzoyl/*p*-coumaroyl/feruloyl quinic acids, hydroxycoumarin *O*-glucosides, caffeoyl/*p*-coumaroyl/feruloyl glucaric/tartaric acids, *O*- and *C*-glucosides of apigenin, acacetin, luteolin, chrysoeriol, 6-hydroxyluteolin, pectolinarigenin, kaempferol, quercetin, isorhamnetin, and tri-/tetra-*O*-*p*-coumaroyl spermines and spermidines. All examined species exhibited a significant accumulation of phenolic compounds throughout the experimental period, reaching levels comparable to or exceeding those found in wild samples (WSs), with the best total phenolic content for AJ at 26.68 mg/g (vs. 26.68 mg/g in WS; second year), CL at 50.23 mg/g (vs. 38.32 mg/g in WS; second year), CH at 51.14 mg/g (vs. 40.86 mg/g in WS; sixth year), ED at 86.12 mg/g (vs. 78.08 mg/g in WS; seventh year), IV at 102.49 mg/g (vs. 88.58 mg/g in WS; fourth year), and LS at 127.34 mg/g (vs. 110.64 mg/g in WS; fifth year). Notably, in the first year of cultivation, approximately 40–60% of the wild-level target compounds accumulated in the plants, with even higher levels detected in subsequent years, particularly in the second and third years. This study highlights the potential of cultivation to produce new Asteraceae plants rich in bioactive phenolics.

Keywords: *Artemisia jacutica*; *Carduus nutans*; *Cirsium heterophyllum*; *Echinops davuricus*; *Ixeris chinensis*; *Lactuca sibirica*; liquid chromatography–mass spectrometry

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1. Introduction

For over 11 thousand years, humanity has relied on a primary agrotechnical technique—the deliberate domestication of wild plants possessing beneficial properties aimed at their utilization as food, medicinal, and industrial crops. Despite the long history of this breeding practice, there is a pressing need to broaden the range of cultivated plants, driven by the increasing demands of society and the pursuit of new practical insights into utilizing plant resources. Plant populations exhibiting unique chemical compositions, inherent biological activities, or potential economic uses have historically faced indiscriminate exploitation during the initial stages of human interaction [1]. Such activities can result in the decline in plant communities within their native habitats and, in severe cases, lead to the extinction of entire biological species [2]. Existing measures, such as restrictions on

the collection of natural species [3], the establishment of reserves and protected areas [4], and the creation of seed banks for endangered species [5], though implemented with the intention of conservation, may not always be successful.

An effective strategy for protecting natural plant populations is the introduction studies of wild species [6], facilitating the cultivation of desired biological material under controlled conditions in the field [7] or greenhouse environments [8]. Most plants integral to human daily life as sources of food (such as wheat, oats, and rye), medicines (including calendula, chamomile, and ginseng), or industrial resources (such as flax, hemp, and pine) were once wild species whose potential for cultivation under controlled conditions was subsequently demonstrated [9]. These studies allow the conservation of plant species and offer opportunities to improve their inherent qualities through selective breeding practices, thereby increasing their productivity and enhancing their valuable properties [10].

With the growing interest in new herbal medicines and the treatment of socially significant diseases, extensive research over the past century has focused on integrating local flora into practical crop rotations. This approach allows us to satisfy the increasing demands of the pharmaceutical industry [11]. Currently, it is commonplace for people to forego foraging natural thickets for plants like plantain, rhodiola, and valerian, among thousands of other species, opting instead to cultivate them for medicinal raw materials. These studies are particularly relevant for regions where traditional medical systems based on local ecosystems have long been practiced, utilizing plants from nearby fields, forests, and steppes. The Baikal natural territory is intertwined with the heritage of traditional Buryat medicine, which continues to play a pivotal role in the Republic of Buryatia and beyond [12]. Decades of successful research into the introduction of wild species have yielded cultivated varieties of well-known medicinal plants such as *Ferulopsis hystrix* [13], *Phlojodicarpus sibiricus* [14], and *Geum aleppicum* [15], among many others, with cultivation histories spanning over half a century.

Plants belonging to the Asteraceae (Compositae) family have long been used for their medicinal properties owing to their widespread distribution [16] and diverse range of biological activities, encompassing cardiovascular benefits [17], antidiabetic effects [18], antimicrobial properties [19], antioxidant activity [20], cytotoxic potential [21], and more. The Asteraceae family exhibits a rich biological diversity in the Baikal region, comprising 61 genera and over 250 species [22]. Certain genera within the Asteraceae family, such as *Arnica*, *Bidens*, *Centaurea*, *Gnaphalium*, *Solidago*, *Tanacetum*, and *Tussilago*, are well known for their medicinal properties but remain as poorly studied and unstudied genera of scientific interest. Employing a similar globally used approach, scientists have successfully cultivated select Asteraceae species like *Acmella oleracea* [23], *Ageratum conyzoides* [24], *Calendula officinalis* [25], *Tagetes minuta*, *T. patula*, and *T. erecta* [26] for personal use. Furthermore, significant achievements in the cultivation of Siberian species include *Artemisia frigida* [27], *Klasea centauroides* [28], *Parasenecio hastatus* [29], and *Rhaponticum uniflorum* [30], all of which have found application in medicinal production.

The vast diversity of Asteraceae, the largest plant family, makes it a reservoir for nearly all categories of natural metabolites. Among these, phenolic compounds are particularly important, encompassing flavonoids [31], coumarins [32], and hydroxycinnamates [33], each exhibiting diverse bioactivities [34,35] and practical applications [36]. Building upon previous studies that have introduced over 100 wild plant species [37] and identified species of paramount cultivation importance [38], this study presents findings on the phenolic composition of six underexplored or previously unstudied Asian species within the Asteraceae family, both before and after introduction into cultivation.

2. Materials and Methods

2.1. Plant Material

Plant samples (consisting of flowering herbs and seeds from 41 species) were collected at the Altacheisky Nature Reserve, Republic of Buryatia, Russia (https://baikalzapovednik.ru/altacheisky#rec54745054; accessed on 10 April 2024), from 2010 to 2020 (Table S1).

Professor N.I. Kashchenko, Doctor of Pharmacy (IGEB SB RAS, Ulan-Ude, Russia) authenticated the species (without age determination because in most cases, this is not possible). Subsequently, the plant material was dried in a ventilated heat oven at 40 °C for 5 days and stored at 3–4 °C until the analysis. Seeds were air-dried (1 month, 20 °C) and stored at 0 °C before planting. All species were germinated under grow box conditions (Secret Jardin Hydro Shoot HS480W System, Secret Jardin Agomoon SRL, Manage, Belgium), utilizing Plagron Soil Promix (Plagron, Weert, Netherlands) as an artificial ground. Next, the plants were grown under open-field conditions at Experimental Plantation Site No. 24-1b (Mukhorshibir, Republic of Buryatia, Russia; 51°02′46.4″ N, 107°46′52.7″ E, 830 m a.s.l.), without fertilizer application, with water supplied by an automatic drip irrigation system, GWB3240 (ELGO, Caesarea, Israel) [39]. The territory of the plantation site is located in similar pedo-climatic conditions to Altacheisky Nature Reserve, which minimizes all potential negative influence on the chemical composition of cultivated plants. Samples exhibiting successful cultivation after the first year were cultivated further. From the initial species list, only six species (*Artemisia jacutica*, *Carduus nutans* subsp. *leiophyllus*, *Cirsium heterophyllum*, *Echinops davuricus*, *Ixeris chinensis* subsp. *versicolor*, *Lactuca sibirica*) demonstrated clear potential for biennial or perennial cultivation under selected cultivation conditions (Table S2). Herbal parts of six plants were collected in a flowering phase of vegetation once per season, followed by the drying in an IPLS-131 convection drying oven (Besteq Engineering, Inc., Rostov-On-Don, Russia) at 35 °C to a moisture < 10%, and stored in a D-450A Edry auto-dry cabinet (Edry Co., Ltd., Taichung, Taiwan; humidity 2%) before an HPLC analysis. One HPLC sample was collected from 3–5 experimental fields with 4–6 repetitions; five HPLC samples were applied to obtain the mean value (Table S3).

2.2. Chemicals

The reference compounds utilized in this study were purchased from Cayman Chemicals (Ann Arbor, MI, USA), ChemFaces (Wuhan, Hubei, China), Extrasynthese (Lyon, France), MCE Med Chem Express (Monmouth, NJ, USA), and Sigma-Aldrich (St. Louis, MO, USA), or were isolated and characterized in our laboratory [40–55] (Table S4).

2.3. Liquid Chromatography–Mass Spectrometry (LS–MS) Profiling and Quantification

The LS–MS profiling of phenolic compounds in *A. jacutica*, *C. nutans* subsp. *leiophyllus*, *C. heterophyllum*, *E. davuricus*, *I. chinensis* subsp. *versicolor*, and *L. sibirica* plants was conducted using a high-performance liquid chromatography with photodiode array detection and electrospray ionization triple quadrupole mass-spectrometric detection (HPLC–PDA–ESI–tQ–MS) system. This comprehensive analysis employed an LC-20 Prominence liquid chromatograph coupled with the photodiode array detector SPD-M30A (with a wavelength range of 200–600 nm) and a triple-quadrupole mass spectrometer, LCMS 8050 (all from Shimadzu, Columbia, MD, USA). Chromatographic separation was achieved using a C18 column, ReproSil-Pur 120 C18-AQ (250 mm × 4.6 mm × 5 µm; Dr. Maisch, Ammerbuch, Germany), with successful compound separation facilitated by a two-eluent gradient elution system employing two chromatographic modes (HPLC conditions), as detailed in Table S5. Metabolite identification was accomplished by correlating retention times, ultraviolet spectra (Figure S1), and mass spectra with reference standards and the existing literature. This process was managed using LabSolutions^{TM} LCGC software ver. 5.80 (Shimadzu), which contains an internal LC–MS library.

To prepare the extract samples for HPLC profiling and quantification, 100 mg of milled plant material was weighed and combined with 5 mL of methanol. The mixture was then sonicated for 30 min at 40 °C twice. Subsequently, the extracts were filtered through a 0.21 µm cellulose acetate syringe filter and combined. The volume was adjusted to 10 mL in a conical flask using methanol. The prepared samples were stored at 10 °C for less than an hour before the analysis.

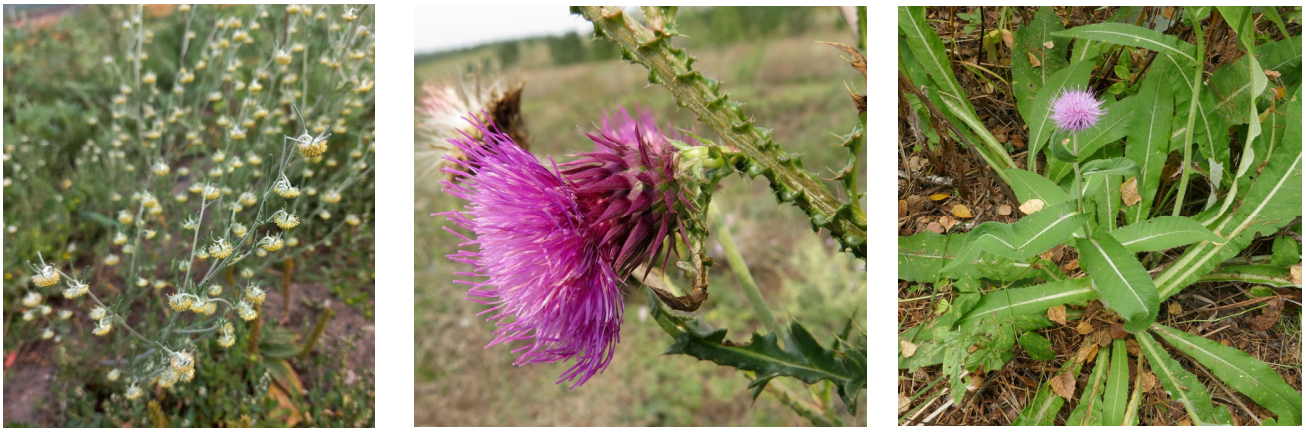
Quantification was performed using the abovementioned LC–MS conditions, with full-scan MS peak area used for calculations. A quantitative analysis of all described compounds was conducted using 55 reference standards (Table S4). Each compound was carefully weighed (10 mg) and dissolved in a methanol–DMSO mixture (1:1) in volumetric flasks (10 mL). Calibration curves for the reference standards were established using stock solutions in methanol (1–100 μg/mL). Mass-spectrometric peak area data were utilized to plot 'concentration–peak area' graphs, and validation criteria (correlation coefficients, r^2; standard deviation, S_{YX}; limits of detection, LODs; limits of quantification, LOQs; and linear ranges) were calculated as described previously [51] (Table S6). All quantitative analyses were performed five times, and the data are presented as the mean value ± standard deviation (S.D.).

2.4. Statistical Analysis

Statistical analyses were performed using a one-way analysis of variance, with the significance of means distinguished using Fisher's least significant difference (LSD) test ($\alpha = 0.05$). Statistical significance was determined at $p < 0.05$. The results are presented as means ± S.D. A linear regression analysis and calibration graph generation were performed using Advanced Grapher 2.2 (Alentum Software, Inc., Ramat-Gan, Israel).

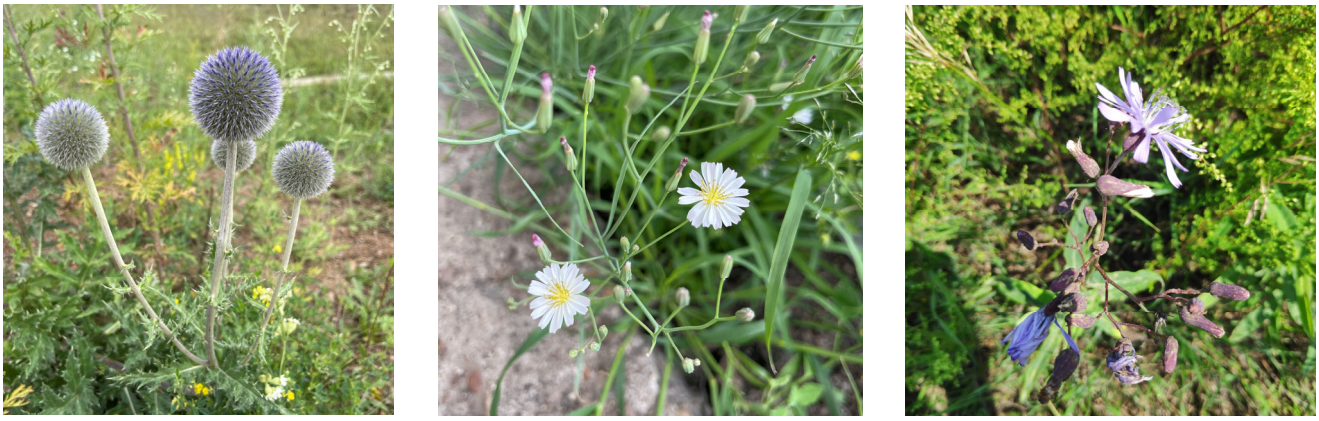
3. Results and Discussion

The selection of research objects was guided by the wealth of knowledge derived from traditional Buryat medicine regarding the use of Asteraceae family plants in treating various socially significant diseases (cancer, diabetes, and atherosclerosis, among others) [56]. Consequently, 41 plant species were collected and subjected to cultivation trials under open-field conditions (Figure S2). Despite the ecological adaptability of wild plants and the expected ease of cultivation under more favorable conditions, only 6 out of the 41 species exhibited consistent and successful reproduction in open-field culture during our experiment. The plants selected for further long-term cultivation include *Artemisia jacutica*, *Carduus nutans* subsp. *leiophyllus*, *Cirsium heterophyllum*, *Echinops davuricus*, *Ixeris chinensis* subsp. *versicolor*, and *Lactuca sibirica*, all of which were either poorly studied or entirely unexplored (Figure 1).



(**a**) (**b**) (**c**)

Figure 1. *Cont.*



(**d**) (**e**) (**f**)

Figure 1. Six Asteraceae species from Asia: (**a**) *Artemisia jacutica*; (**b**) *Carduus nutans* subsp. *leiophyllus*; (**c**) *Cirsium heterophyllum*; (**d**) *Echinops davuricus*; (**e**) *Ixeris chinensis* subsp. *versicolor*; (**f**) *Lactuca sibirica*.

3.1. Artemisia jacutica (Yakut wormwood)

Artemisia jacutica Drobow is an annual or biennial species commonly found in peat bogs, lake shores, and old arable lands. The entire plant is grayish; is adorned with dense, white, and adjacent hairs; and reaches 25–40 cm in height. Its flower baskets are steep, hemispherical, 6–8 mm wide, pedunculated, and often deflected or drooping, forming a wide, loose, and paniculate inflorescence [22]. In traditional Buryat medicine, lamas use decoctions made from the flowering tops of *A. jacutica* to treat various ailments, including cancers, throat disorders such as tonsillitis, and lung ailments, and use it as an antipyretic for diphtheria [56]. The plant contains essential oil with a high chamazulene content [57]. However, the presence of non-terpene metabolites remains largely unexplored.

A total of 32 compounds were identified in the wild sample of *A. jacutica,* including 27 definitively identified compounds and 5 tentatively annotated phenolics (Figure S3 and Table S7). Among these, caffeic acid derivatives included four mono-caffeoyl glucaric acids acylated at 2-*O*-, 3-*O*-, 4-*O*-, and 5-*O*-positions [58] and eight well-known mono- and di-caffeoyl quinic acids [59]. Additionally, a distinct UV pattern featuring maxima at 298 and 308 nm was observed for four N-containing metabolites, which are characteristic of phenolamides such as coumaroyl spermines [55]. The presence of *p*-coumaroyl fragments, inferred from the loss of fragments weighing 146 a.m.u., elucidated the structures of tri- *p* -coumaroyl spermines (compounds Aj-16, -18, and -19) and tetra-*p*-coumaroyl spermines (compound Aj-28) [60].

In *A. jacutica*, flavonoid components encompassed two flavone glycosides (schaftoside and an unknown 6-hydroxyluteolin di-*O*-hexoside), ten flavonol glycosides related to quercetin (quercetin 3-*O*-gentiobioside, calendoflavobioside, rutin, calendosides I/II, quercetin 3-*O*-(2″/4″/6″-*O*-acetyl)-glucosides) and isorhamnetin (isorhamnetin 3-*O*-(2″/6″-*O*-acetyl)-glucosides), and four flavonoid aglycones (cirsiliol, axyllarin, cirsilineol, and chrysosplenetin).

Most compounds identified in *A. jacutica* are commonly encountered in the genus, including caffeoyl quinic acids (prevalent in various wormwoods [51]), quercetin and isorhamnetin glycosides [61], and flavonoid aglycones [62]. However, some metabolites are rare in the *Artemisia* genus, such as caffeoyl glucaric acids (previously reported only in *A. annua* [63] and *A. absinthium* [64]) and *p*-coumaroyl spermines (detected in *A. caruifolia* [65]).

A comparative analysis of the HPLC profiles of wild and cultivated samples of *A. jacutica* revealed promising acclimatization progress in the second year following introduction. While first-year plants exhibited an incomplete phenolic profile, with losses observed in flavone glycosides, certain phenolamides, and flavonol glycosides, the second-year plants successfully accumulated all phenolics characteristic of their wild counterparts (Table 1).

Table 1. Content of phenolic compounds found in wild and cultivated samples of *Artemisia jacutica* herb, mg/g of dry plant weight (±S.D.).

Comp. No.	Compound	Wild Sample	Cultivated Samples	
			1st Year	2nd Year
	Caffeoyl glucaric acids			
Aj-1	3-*O*-Caffeoyl glucaric acid	0.39 ± 0.00 ^{c}	0.14 ± 0.00 ^{a}	0.25 ± 0.00 ^{b}
Aj-2	4-*O*-Caffeoyl glucaric acid	0.80 ± 0.02 ^{b}	0.34 ± 0.01 ^{a}	0.97 ± 0.02 ^{c}
Aj-4	2-*O*-Caffeoyl glucaric acid	1.10 ± 0.02 ^{b}	0.52 ± 0.01 ^{a}	2.35 ± 0.05 ^{c}
Aj-6	5-*O*-Caffeoyl glucaric acid	0.76 ± 0.02 ^{b}	0.32 ± 0.00 ^{a}	0.93 ± 0.02 ^{c}
	Caffeoyl quinic acids			
Aj-3	4-*O*-Caffeoyl quinic acid (*trans*-)	0.22 ± 0.00 ^{a}	<0.01	0.20 ± 0.00 ^{a}
Aj-5	4-*O*-Caffeoyl quinic acid (*cis*-)	0.20 ± 0.00 ^{b}	<0.01	0.14 ± 0.00 ^{a}
Aj-7	5-*O*-Caffeoyl quinic acid (*trans*-)	6.64 ± 0.14 ^{a}	2.18 ± 0.05 ^{a}	7.35 ± 0.15 ^{c}
Aj-8	3-*O*-Caffeoyl quinic acid (*trans*-)	0.11 ± 0.00 ^{a}	<0.01	0.22 ± 0.00 ^{b}
Aj-9	5-*O*-Caffeoyl quinic acid (*cis*-)	0.19 ± 0.00 ^{b}	<0.01	0.15 ± 0.00 ^{a}
Aj-22	3,4-Di-*O*-caffeoyl quinic acid	0.25 ± 0.00 ^{a}	<0.01	0.52 ± 0.01 ^{b}
Aj-23	3,5-Di-*O*-caffeoyl quinic acid	7.10 ± 0.16 ^{b}	3.29 ± 0.07 ^{a}	8.27 ± 0.17 ^{c}
Aj-25	4,5-Di-*O*-caffeoyl quinic acid	0.34 ± 0.00 ^{b}	0.25 ± 0.00 ^{a}	0.69 ± 0.02 ^{c}
	Phenolamides			
Aj-16	Tri-*O*-*p*-coumaroyl spermine	0.08 ± 0.00 ^{a}	–	0.09 ± 0.00 ^{a}
Aj-18	Tri-*O*-*p*-coumaroyl spermine	0.11 ± 0.00 ^{b}	<0.01	0.05 ± 0.00 ^{a}
Aj-19	Tri-*O*-*p*-coumaroyl spermine	2.15 ± 0.05 ^{b}	1.53 ± 0.04 ^{a}	3.69 ± 0.07 ^{c}
Aj-28	Tetra-*O*-*p*-coumaroyl spermine	0.74 ± 0.02 ^{b}	0.39 ± 0.00 ^{a}	0.79 ± 0.02 ^{b}
	Flavone glucosides			
Aj-10	6-Hydroxyluteolin di-*O*-hexoside	0.05 ± 0.00 ^{a}	–	<0.01
Aj-11	Schaftoside	0.11 ± 0.00 ^{a}	–	<0.01
	Flavonol glucosides			
Aj-12	Quercetin 3-*O*-gentiobioside	0.10 ± 0.00 ^{a}	–	<0.01
Aj-13	Calendoflavobioside	0.08 ± 0.00 ^{a}	–	0.12 ± 0.00 ^{a}
Aj-14	Rutin	0.25 ± 0.00 ^{b}	0.05 ± 0.00 ^{a}	0.39 ± 0.01 ^{c}
Aj-15	Calendoside II	0.57 ± 0.01 ^{b}	0.29 ± 0.00 ^{a}	0.93 ± 0.02 ^{c}
Aj-17	Calendoside I	0.02 ± 0.00 ^{a}	–	0.03 ± 0.00 ^{a}
Aj-20	Quercetin 3-*O*-(2″-*O*-acetyl)-glucoside	0.02 ± 0.00 ^{a}	–	<0.01
Aj-21	Quercetin 3-*O*-(6″-*O*-acetyl)-glucoside	0.18 ± 0.00 ^{a}	<0.01	<0.01
Aj-24	Quercetin 3-*O*-(4″-*O*-acetyl)-glucoside	0.08 ± 0.00 ^{a}	n.d.	<0.01
Aj-26	Isorhamnetin 3-*O*-(2″-*O*-acetyl)-glucoside	0.10 ± 0.00 ^{a}	<0.01	<0.01
Aj-27	Isorhamnetin 3-*O*-(6″-*O*-acetyl)-glucoside	0.12 ± 0.00 ^{a}	<0.01	<0.01
	Flavonoid aglycones			
Aj-29	Cirsiliol	0.27 ± 0.00 ^{a}	<0.01	<0.01
Aj-30	Axyllarin	0.56 ± 0.01 ^{b}	0.34 ± 0.01 ^{a}	0.39 ± 0.00 ^{a}
Aj-31	Cirsilineol	1.81 ± 0.04 ^{b}	0.51 ± 0.01 ^{a}	0.59 ± 0.01 ^{a}
Aj-32	Chrysosplenetin	1.18 ± 0.03 ^{b}	0.29 ± 0.00 ^{a}	0.32 ± 0.00 ^{a}
	Subtotal caffeoyl glucaric acids	3.05	1.32	4.50
	Subtotal caffeoyl quinic acids	15.05	5.72	17.54
	Total caffeic acid derivatives	18.10	7.04	22.04
	Total phenolamides	3.08	1.92	4.62
	Subtotal flavone glucosides	0.16	–	<0.01
	Subtotal flavonol glucosides	1.52	0.34	1.47
	Subtotal flavonoid aglycones	3.82	1.14	1.30
	Total flavonoids	5.50	1.48	2.77
	Total phenolic compounds	26.68	10.44	29.43

For compound numeration, see Figure S1. Means with the same letters for each parameter in a row are not significantly different at $p < 0.05$ by Fisher's protected least significant test.

Quantitative assessment underscored cultivated plants' enhanced synthetic capacity in producing caffeic acid derivatives and phenolamides. Notably, the levels of major compounds, including 2-*O*-caffeoyl glucaric acid, 5-*O*-*trans*-caffeoyl quinic acid, 3,5-di-*O*-

caffeoyl quinic acid, and tri-*O*-*p*-coumaroyl spermine, significantly increased ($p < 0.05$) from 1.10, 6.64, 7.10, and 2.15 mg/g in wild samples to 2.35 (+114%), 7.35 (+11%), 8.27 (+16%), and 3.69 mg/g (+72%) in two-year cultivated plants, respectively. Furthermore, calendoside II and rutin concentrations demonstrated consistent growth, increasing from 0.57 and 0.25 mg/g to 0.93 and 0.39 mg/g, respectively. However, the total content of flavonoid groups in cultivated plants did not reach wild plant levels owing to low concentrations of acylated derivatives and aglycones. Nevertheless, the total phenolic content in two-year cultivated plants surpassed that of wild plants by 10%.

3.2. Carduus nutans subsp. leiophyllus (Thoermer's Thistle, Abducted Thistle)

Carduus nutans subsp. *leiophyllus* (Petrovič) Arènes (syn. *C. thoermeri* Weinm.) is a biennial species commonly found in fields and pastures, characterized by its branched, cobwebby–pubescent appearance, reaching heights of up to 1 m [22]. It is considered a valuable honey plant because it produces large quantities of nectar, and its seeds contain up to 30% fatty oil. The leaves of Siberian thistles have long been utilized in local traditional medicines to treat various ailments, including indigestion, stomach disorders, vomiting, and pulmonary diseases [56]. Early studies on European samples of *C. nutans* subsp. *leiophyllus* have revealed the presence of lipids [66], polysaccharides [67], and some phenolic acids and flavonoids [68]. However, the chemical composition of Asian samples remains largely unexplored.

The analysis of wild samples of *C. nutans* subsp. *leiophyllus* via HPLC profiling revealed the presence of 20 compounds, among which 11 were identified using external standards. These identified components include protocatechuic acid 4-*O*-glucoside, monocaffeoyl quinic acid (3-*O*-, 4-*O*-, 5-*O*-), mono-*p*-coumaroyl quinic acid (3-*O*-, 4-*O*-, 5-*O*-), mono-feruloyl quinic acid (3-*O*-, 4-*O*-, 5-*O*-), and luteolin 7-*O*-sophoroside (Figure S4 and Table S8). Additionally, two flavonoids (Cn-16 and Cn-20) were successfully isolated from the methanolic extract of *C. nutans* subsp. *leiophyllus* leaves, purified through column chromatography, and identified using UV, NMR, and mass-spectrometric analyses as luteolin 7-*O*-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucoside (linariifolioside) and chrysoeriol 7-*O*-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucoside, respectively (Table S9) [69,70]. Furthermore, seven compounds were tentatively characterized as protocatechuic acid *O*-hexosides (Cn-1/2), caffeoyl quinic acid (Cn-4), luteolin *O*-hexoside-*O*-pentoside (Cn-15), luteolin di-*O*-hexoside-*O*-acetate (Cn-17), and apigenin di-*O*-hexoside-*O*-acetate (Cn-18/19).

Bulgarian samples of *C. nutans* subsp. *leiophyllus* exhibited the presence of various benzoic acids (such as salicylic, protocatechuic, vanillic, and syringic) and cinnamic acids (including cinnamic, *p*-coumaric, caffeic, ferulic, sinapic, and chlorogenic), alongside several flavonoids including luteolin, kaempferol, myricetin, hyperoside, and rutin [68]. Chlorogenic acid was the only compound similar in both European and Asian samples. Thus, 19 components unique to this species were identified for the first time. Linariifolioside and chrysoeriol 7-*O*-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucoside were isolated from *C. crispus* [70], and luteolin 7-*O*-sophoroside was detected in *C. nutans* [71]. The presence of hydroxycinnamoyl quinic acids and luteolin derivatives is typical for the *Carduus* genus [72], which makes *C. nutans* subsp. *leiophyllus* similar to other representatives of the genus. However, its more diverse composition sets it apart from its counterparts.

The cultivation of *C. nutans* subsp. *leiophyllus* as a biennial crop has yielded plant material that exhibits a phenolic profile similar to that of natural samples (Table 2).

Notably, the total content of caffeoyl quinic acids and flavone glucosides was slightly higher in two-year cultivated plants, measuring at 13.96 and 36.02 mg/g, respectively, compared to 10.28 and 26.51 mg/g in wild samples. Of particular interest is the observation that the levels of acetylated flavones, specifically luteolin 7-*O*-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucoside and chrysoeriol 7-*O*-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucoside, were significantly higher in two-year samples compared to wild plants, exhibiting increments of 33% ($p < 0.05$) and 43% ($p < 0.05$), respectively. This suggests a greater stability of flavonoid esters under cultivation conditions, which may undergo hydrolysis under natural conditions.

Table 2. Content of phenolic compounds found in wild and cultivated samples of *Carduus nutans* subsp. *leiophyllus* herb, mg/g of dry plant weight (±S.D.).

Comp. No.	Compound	Wild Sample	Cultivated Samples	
			1st Year	2nd Year
	Benzoic acids			
Cn-1	Protocatechuic acid *O*-hexoside	0.37 ± 0.01	–	<0.01
Cn-2	Protocatechuic acid *O*-hexoside	0.44 ± 0.01	–	<0.01
Cn-3	Protocatechuic acid 4-*O*-glucoside	0.72 ± 0.02 [b]	0.22 ± 0.00 [a]	0.25 ± 0.00 [a]
	Hydroxycinnamoyl quinic acids			
Cn-4	4-*O*-Caffeoyl quinic acid (*cis*-)	1.75 ± 0.03 [b]	0.92 ± 0.02 [a]	2.14 ± 0.04 [c]
Cn-5	Caffeoyl quinic acid (Cn-4/7/8 isomer)	0.45 ± 0.01 [a]	–	0.69 ± 0.01 [b]
Cn-6	4-*O*-*p*-Coumaroyl quinic acid	0.04 ± 0.00 [a]	–	0.05 ± 0.00 [a]
Cn-7	5-*O*-Caffeoyl quinic acid (*trans*-)	0.27 ± 0.00 [a]	–	0.25 ± 0.00 [a]
Cn-8	3-*O*-Caffeoyl quinic acid (*trans*-)	6.82 ± 0.14 [b]	3.84 ± 0.09 [a]	9.97 ± 0.12 [c]
Cn-9	4-*O*-Feruloyl quinic acid	0.02 ± 0.00 [a]	–	0.05 ± 0.00 [b]
Cn-10	5-*O*-*p*-Coumaroyl quinic acid	0.25 ± 0.00 [b]	–	0.14 ± 0.00 [a]
Cn-11	3-*O*-*p*-Coumaroyl quinic acid	0.36 ± 0.01 [b]	0.25 ± 0.00 [a]	0.35 ± 0.00 [b]
Cn-12	5-*O*-Feruloyl quinic acid	0.11 ± 0.00 [a]	–	0.07 ± 0.00 [a]
Cn-13	3-*O*-Feruloyl quinic acid	0.21 ± 0.00 [b]	0.03 ± 0.00 [a]	0.25 ± 0.00 [b]
	Flavone glucosides			
Cn-14	Luteolin 7-*O*-(2″-*O*-glucosyl)-glucoside	0.46 ± 0.01 [b]	0.27 ± 0.00 [a]	0.33 ± 0.00 [a]
Cn-15	Luteolin *O*-hexoside-*O*-pentoside	0.54 ± 0.01 [c]	0.04 ± 0.00 [a]	0.39 ± 0.01 [b]
Cn-16	Luteolin 7-*O*-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucoside	14.10 ± 0.31 [b]	5.74 ± 0.14 [a]	18.79 ± 0.43 [c]
Cn-17	Luteolin di-*O*-hexoside-*O*-acetate	0.14 ± 0.00 [a]	–	0.33 ± 0.00 [b]
Cn-18	Apigenin di-*O*-hexoside-*O*-acetate	0.29 ± 0.00 [a]	–	0.35 ± 0.01 [b]
Cn-19	Apigenin di-*O*-hexoside-*O*-acetate	0.11 ± 0.00 [a]	–	0.30 ± 0.00 [b]
Cn-20	Chrysoeriol 7-O-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucoside	10.87 ± 0.22 [b]	5.09 ± 0.12 [a]	15.53 ± 0.31 [c]
	Subtotal benzoic acids	1.53	0.22	0.25
	Subtotal caffeoyl quinic acids	10.28	5.04	13.96
	Subtotal flavone glucosides	26.51	11.14	36.02
	Total phenolic compounds	38.32	16.40	50.23

For compound numeration, see Figure S2. Means with the same letters for each parameter in a row are not significantly different at $p < 0.05$ by Fisher's protected least significant test.

3.3. *Cirsium heterophyllum* (Diversifolious Thistle)

Cirsium heterophyllum (L.) Hill is a perennial herbaceous plant that can reach heights of up to 1.5 m, commonly found in sparse mixed forests, larch forests, forest meadows, and forest–steppe zones. Its large basal leaves gradually transition into small bracts as the plant grows taller [22]. The plant bears medium-sized purple flowers with a pleasant scent, making it a valuable honey plant. In Eastern medicine, the leaves of *C. heterophyllum* have been used to treat bone diseases and fractures [67]. Existing knowledge regarding the chemical composition of *C. heterophyllum* includes the presence of luteolin 7-*O*- and 4′-*O*-glucosides in the herb [73].

Twenty-six compounds were identified in *C. heterophyllum* leaves, comprising benzoic acids (protocatechuic acid glucosides Ch-1 and -2), hydroxycinnamoyl quinic acids (mono-(3-*O*-, 4-*O*-, 5-*O*-) and di-caffeoyl quinic acids (3,4-*O*-, 3,5-*O*-, 4,5-*O*), and *p*-coumaroyl quinic acids (3-*O*-, 4-*O*-, 5-*O*-)), and flavonoids (Figure S5 and Table S10). All flavonoids identified were flavones, featuring luteolin, chrysoeriol, apigenin, acacetin, and pectolinarigenin as aglycones. Luteolins comprised known 7-*O*-rutinoside (scolymoside), and 7-*O*-, 3′-*O*-, and 4′-*O*-glucosides, while chrysoeriols were present as 7-*O*- and 4′-*O*-glucosides and two acetyl-glucosides of chrysoeriol 7-*O*-glucoside (denoted as Ch-16 and -19). Apigenin derivatives included di-*C*-glucoside schaftoside and apigenin 7-*O*-glucoside, with two 7-*O*-glucosides identified for acacetin and pectolinarigenin.

Flavones represent the predominant phenolic compounds in *Cirsium* plants, commonly detected in over 30 species as 7-*O*-glycosides [74]. Less common are the classes of 3′/4′-*O*-glucosides and *C*-glucosides. In an earlier study on Asian thistles, pectolinarigenin

7-*O*-rutinoside (pectolinarin) was isolated from 25 samples [75], indicating its frequent occurrence in the genus. Only pectolinarigenin 7-*O*-glucoside was identified in our investigation, possibly suggesting a distinct chemical profile of *C. heterophyllum* specific to the Heterophylla tribe of *Cirsium*. This assertion is further supported by the presence of scolymoside, isorhoifolin, schaftoside, dracocephaloside, chrysoeriol 4′-*O*-glucoside, and *p*-coumaroyl quinic acids, which were identified in the genus for the first time [72].

For this research, cultivated *C. heterophyllum* plants were observed over six years, allowing us to conclude that the plant's chemical composition was completely reproducible in culture (Table 3).

Table 3. Content of phenolic compounds found in wild and cultivated samples of *Cirsium heterophyllum* herb, mg/g of dry plant weight (±S.D.).

Comp. No.	Compound	Wild Sample	Cultivated Samples			
			1st Year	2nd Year	4th Year	6th Year
	Benzoic acids					
Ch-1	Protocatechuic acid *O*-hexoside (Ch-2 isomer)	0.18 ± 0.00 ^{b}	–	–	0.10 ± 0.00 ^{a}	0.24 ± 0.00 ^{c}
Ch-2	Protocatechuic acid 4-*O*-glucoside	0.08 ± 0.00 ^{b}	–	<0.01	0.01 ± 0.00 ^{a}	0.11 ± 0.00 ^{b}
	Hydroxycinnamoyl quinic acids					
Ch-3	4-*O*-Caffeoyl quinic acid (*trans*-)	0.40 ± 0.01 ^{b}	0.22 ± 0.00 ^{a}	0.25 ± 0.00 ^{a}	0.48 ± 0.01 ^{bc}	0.47 ± 0.01 ^{c}
Ch-4	4-*O*-Caffeoyl quinic acid (*cis*-)	0.04 ± 0.00	<0.01	<0.01	0.01 ± 0.00	0.01 ± 0.00
Ch-5	4-*O*-*p*-Coumaroyl quinic acid	0.01 ± 0.00	<0.01	<0.01	<0.01	<0.01
Ch-6	5-*O*-Caffeoyl quinic acid (*trans*-)	5.21 ± 0.12 ^{c}	2.69 ± 0.05 ^{a}	3.17 ± 0.06 ^{b}	7.83 ± 0.16 ^{d}	7.54 ± 0.15 ^{d}
Ch-7	3-*O*-Caffeoyl quinic acid (*trans*-)	1.24 ± 0.03 ^{b}	0.54 ± 0.01 ^{a}	1.62 ± 0.03 ^{c}	1.97 ± 0.04 ^{d}	2.02 ± 0.04 ^{e}
Ch-8	5-*O*-Caffeoyl quinic acid (*cis*-)	0.32 ± 0.00 ^{a}	<0.01	<0.01	0.25 ± 0.00 ^{a}	0.29 ± 0.00 ^{a}
Ch-9	5-*O*-*p*-Coumaroyl quinic acid	0.49 ± 0.01 ^{d}	<0.01	0.06 ± 0.00 ^{a}	0.14 ± 0.00 ^{b}	0.32 ± 0.01 ^{c}
Ch-11	3-*O*-*p*-Coumaroyl quinic acid	0.30 ± 0.00 ^{b}	<0.01	<0.01	0.04 ± 0.00 ^{a}	0.29 ± 0.00 ^{b}
Ch-17	3,4-Di-*O*-caffeoyl quinic acid	0.85 ± 0.02 ^{c}	0.20 ± 0.00 ^{a}	0.57 ± 0.01 ^{b}	1.14 ± 0.02 ^{d}	1.15 ± 0.02 ^{d}
Ch-20	3,5-Di-*O*-caffeoyl quinic acid	1.94 ± 0.04 ^{d}	0.69 ± 0.02 ^{a}	0.93 ± 0.02 ^{b}	1.76 ± 0.03 ^{c}	1.84 ± 0.04 ^{d}
Ch-23	4,5-Di-*O*-caffeoyl quinic acid	1.22 ± 0.02 ^{c}	0.52 ± 0.01 ^{a}	0.79 ± 0.02 ^{b}	1.41 ± 0.03 ^{d}	1.52 ± 0.03 ^{d}
	Flavone glucosides					
Ch-10	Schaftoside (apigenin 6-*C*-glucoside-8-*C*-arabinoside)	1.00 ± 0.02 ^{cd}	0.25 ± 0.00 ^{a}	0.79 ± 0.02 ^{b}	0.93 ± 0.02 ^{c}	1.11 ± 0.02 ^{d}
Ch-12	Scolymoside (veronicastroside, luteolin 7-*O*-rutinoside)	1.85 ± 0.03 ^{b}	0.79 ± 0.02 ^{a}	1.93 ± 0.04 ^{b}	2.85 ± 0.05 ^{c}	3.15 ± 0.06 ^{d}
Ch-13	Cynaroside (luteolin 7-*O*-glucoside)	3.16 ± 0.06 ^{c}	1.14 ± 0.02 ^{a}	2.73 ± 0.06 ^{b}	3.51 ± 0.07 ^{d}	3.44 ± 0.07 ^{d}
Ch-14	Chrysoeriol 7-*O*-glucoside	10.69 ± 0.22 ^{b}	5.67 ± 0.11 ^{a}	10.39 ± 0.11 ^{b}	15.86 ± 0.32 ^{c}	17.21 ± 0.36 ^{d}
Ch-15	Isorhoifolin (apigenin 7-*O*-rutinoside)	1.04 ± 0.02	0.63 ± 0.02	1.27 ± 0.02	2.93 ± 0.06	3.84 ± 0.08
Ch-16	Chrysoeriol 7-*O*-(2″-*O*-acetyl)-glucoside	0.94 ± 0.02 ^{c}	<0.01	<0.01	0.09 ± 0.00 ^{a}	0.14 ± 0.00 ^{b}
Ch-18	Dracocephaloside (luteolin 3′-*O*-glucoside)	0.05 ± 0.00 ^{b}	<0.01	<0.01	0.01 ± 0.00 ^{a}	0.02 ± 0.00 ^{a}
Ch-19	Chrysoeriol 7-*O*-(6″-*O*-acetyl)-glucoside	0.06 ± 0.00 ^{b}	<0.01	<0.01	0.02 ± 0.00 ^{a}	0.03 ± 0.00 ^{a}
Ch-21	Cosmosiin (apigenin 7-*O*-glucoside)	0.54 ± 0.01 ^{b}	0.63 ± 0.02 ^{a}	0.94 ± 0.02 ^{c}	1.64 ± 0.03 ^{e}	1.24 ± 0.02 ^{d}
Ch-22	Chrysoeriol 4′-*O*-glucoside	0.07 ± 0.00 ^{b}	<0.01	<0.01	0.02 ± 0.00 ^{a}	0.01 ± 0.00 ^{a}
Ch-24	Acacetin 7-*O*-glucoside	7.71 ± 0.15 ^{e}	2.69 ± 0.05 ^{a}	3.14 ± 0.12 ^{b}	3.52 ± 0.03 ^{c}	3.93 ± 0.04 ^{d}
Ch-25	Luteolin 4′-*O*-glucoside	0.01 ± 0.00	<0.01	<0.01	<0.01	<0.01
Ch-26	Pectolinarigenin 7-*O*-glucoside	1.46 ± 0.03 ^{d}	0.93 ± 0.02 ^{a}	1.57 ± 0.03 ^{d}	1.50 ± 0.03 ^{cd}	1.22 ± 0.02 ^{b}
	Subtotal benzoic acids	0.26	–	<0.01	0.11	0.35
	Subtotal hydroxycinnamoyl quinic acids	12.02	4.86	7.39	15.03	15.45
	Subtotal flavone glucosides	28.58	12.73	22.76	32.88	35.34
	Total phenolic compounds	40.86	17.59	30.15	48.01	51.14

For compound numeration, see Figure S3. Means with the same letters for each parameter in a row are not significantly different at $p < 0.05$ by Fisher's protected least significant test.

From the first to the sixth year, a gradual increase in benzoic acids (from 0 to 0.35 mg/g), hydroxycinnamoyl quinic acids (from 4.86 to 15.45 mg/g), and flavonoid content (from 12.73 to 35.34 mg/g) was noted. The final concentration levels in cultivated samples were significantly higher ($p < 0.05$) compared to wild samples, showing an increase of 35% for benzoic acids, 29% for hydroxycinnamoyl quinic acids, and 24% for flavonoids. Significantly elevated values ($p < 0.05$) were observed for predominant compounds such as 5-*O*-caffeoyl quinic acid (7.83 mg/g; +50% vs. wild sample, WS), 3-*O*-caffeoyl quinic acid (2.02 mg/g; +63% vs. WS), scolymoside (3.15 mg/g; +70% vs. WS), chrysoeriol 7-*O*-glucoside (17.21 mg/g; +61% vs. WS), isorhoifolin (3.84 mg/g; +269% vs. WS), and cosmosiin (1.24 mg/g; +129% vs. WS). However, it is worth noting that some flavonoids did not reach the wild level, such as chrysoeriol 7-*O*-glucoside acetates, acacetin 7-*O*-glucoside, and pectolinarigenin 7-*O*-glucoside, suggesting that the cultivation of wild plants may not always result in a complete replication of the quantitative characteristics of the parent metabolome.

3.4. Echinops davuricus (Dahurian Globe Thistle)

Echinops davuricus Fisch. ex Hornem. (syn. *E. latifolius* Tausch) is a perennial low to medium (reaching a height of up to 60 cm) tomentose, weakly branched plant covered with spines with flowers in the form of large bright blue spherical heads [22]. It thrives in diverse habitats, including the steppe and rocky slopes of the Angara–Sayan and Daurian territories. The roots of this plant, locally known as *ru rta*, are used in Buryat traditional medicine for treating throat and lung ailments, wound cleansing, stomach tumors, and diphtheria [67]. Despite its wide distribution, the intensive excavation of its roots has led to a rapid decline in population numbers. Cultivation techniques have been developed to address this issue and cater to consumer demands sustainably, alleviating pressure on natural populations. The roots of *E. davuricus* are a source of bioactive thiophenes, exhibiting efficacy against human malignant melanoma and human cervical carcinoma [76]. However, the aerial parts of the plant remain unexplored chemically.

The phenolic compounds identified in the herb of *E. davuricus* have previously been reported in other species of the *Echinops* genus, such as monocaffeoyl quinic acids and luteolin 7-*O*-glucoside in *E. grijsii* Hance [77], and dicaffeoyl quinic acids in *E. galalensis* Schweinf. [78] (Figure S6 and Table S11). Additionally, two known *Echinops* apigenin 7-*O*-glucoside *p*-coumarates (echitin and echinacin), originally isolated from *E. echinatus* Roxb. [79], were found in the low-polarity fraction of the chromatogram, alongside N^1,N^5,N^{10}-tri-*O*-(*EEE*)-*p*-coumaroyl-spermidine, identified in the *Echinops* genus for the first time through comparison with a reference standard. Furthermore, several other compounds were identified as new metabolites of *Echinops*, including protocatechuic acid 4-*O*-glucoside, *p*-coumaroyl quinic acids, isoquercitrin, hyperoside, chrysoeriol 7-*O*-glucoside, and 5-*O*- and 3′-*O*-glucosides of luteolin.

E. davuricus is a slow-growing plant. Therefore, the duration of the experiment was nine years (Table 4).

Over this period, cultivated plants gradually accumulated compounds, slowly reaching the levels found in wild samples. The total phenolic compound content in the *E. davuricus* herb was 38.10 mg/g after the first year (49% of the wild level, WL), 65.74 mg/g after the third year (84% of WL), 82.59 mg/g after the fifth year (106% of WL), 86.12 mg/g after the seventh year (110% of WL), and 85.15 mg/g after the ninth year (109% of WL). The maximum concentration of hydroxycinnamoyl quinic acids was observed after the fifth year (50.48 mg/g; 115% of WL), reflecting the accumulation dynamics of individual compounds. For flavonoids, the highest accumulation levels were recorded only at the end of the experiment (ninth year; 38.34 mg/g; 121% of WL), corresponding to the revealed dynamics for non-acylated flavonol and flavone glycosides. Luteolin 7-*O*-glucoside *p*-coumarates surpassed the levels detected in wild plants, possibly owing to more favorable agricultural conditions.

Table 4. Content of phenolic compounds found in wild and cultivated samples of *Echinops davuricus* herb, mg/g of dry plant weight (±S.D.).

Comp. No.	Compound	Wild Sample	Cultivated Samples				
			1st Year	3rd Year	5th Year	7th Year	9th Year
	Benzoic acids						
El-1	Protocatechuic acid 4-*O*-glucoside	0.39 ± 0.01 ^{c}	–	<0.01	0.14 ± 0.00 ^{a}	0.22 ± 0.00 ^{b}	0.25 ± 0.00 ^{b}
	Hydroxycinnamoyl quinic acids						
El-2	4-*O*-Caffeoyl quinic acid (*trans*-)	2.14 ± 0.04 ^{d}	0.52 ± 0.01 ^{a}	1.18 ± 0.02 ^{b}	2.02 ± 0.04 ^{cd}	2.15 ± 0.04 ^{d}	1.87 ± 0.04 ^{c}
El-3	5-*O*-Caffeoyl quinic acid (*trans*-)	28.47 ± 0.64 ^{d}	15.93 ± 0.32 ^{a}	25.69 ± 0.52 ^{b}	30.89 ± 0.62 ^{e}	29.14 ± 0.60 ^{de}	27.63 ± 0.58 ^{c}
El-4	3-*O*-Caffeoyl quinic acid (*trans*-)	0.18 ± 0.00 ^{d}	<0.01	0.05 ± 0.00 ^{a}	0.10 ± 0.00 ^{b}	0.12 ± 0.00 ^{bc}	0.14 ± 0.00 ^{c}
El-5	5-*O*-Caffeoyl quinic acid (*cis*-)	0.27 ± 0.00 ^{b}	<0.01	<0.01	0.18 ± 0.00 ^{a}	0.22 ± 0.00 ^{ab}	0.25 ± 0.00 ^{b}
El-6	5-*O*-*p*-Coumaroyl quinic acid	0.33 ± 0.00 ^{b}	<0.01	0.35 ± 0.00 ^{b}	0.41 ± 0.01 ^{c}	0.32 ± 0.00 ^{ab}	0.29 ± 0.00 ^{a}
El-7	3-*O*-*p*-Coumaroyl quinic acid	0.25 ± 0.00 ^{a}	<0.01	<0.01	0.27 ± 0.00 ^{ab}	0.25 ± 0.00 ^{a}	0.29 ± 0.00 ^{b}
El-12	3,4-Di-*O*-caffeoyl quinic acid	0.45 ± 0.01 ^{c}	0.08 ± 0.00 ^{a}	0.12 ± 0.00 ^{b}	0.63 ± 0.02 ^{d}	0.69 ± 0.01 ^{d}	0.83 ± 0.02 ^{e}
El-15	3,5-Di-*O*-caffeoyl quinic acid	10.11 ± 0.22 ^{b}	6.38 ± 0.12 ^{a}	12.69 ± 0.28 ^{d}	14.22 ± 0.29 ^{e}	10.82 ± 0.21 ^{bc}	11.63 ± 0.23 ^{c}
El-16	4,5-Di-*O*-caffeoyl quinic acid	1.69 ± 0.03 ^{c}	0.96 ± 0.02 ^{a}	1.59 ± 0.03 ^{bc}	1.76 ± 0.03 ^{c}	1.52 ± 0.03 ^{b}	0.90 ± 0.02 ^{a}
	Flavonol glycosides						
El-8	Isoquercitrin (quercetin 3-*O*-glucoside)	5.02 ± 0.11 ^{d}	1.14 ± 0.02 ^{a}	2.96 ± 0.04 ^{b}	4.62 ± 0.10 ^{c}	5.39 ± 0.11 ^{de}	5.42 ± 0.11 ^{e}
El-9	Hyperoside (quercetin 3-*O*-galactoside)	4.73 ± 0.09 ^{c}	<0.01	<0.01	0.96 ± 0.02 ^{a}	3.74 ± 0.08 ^{b}	4.69 ± 0.07 ^{c}
	Flavone glycosides						
El-10	Cynaroside (luteolin 7-*O*-glucoside)	3.54 ± 0.07 ^{ab}	3.29 ± 0.06 ^{a}	3.94 ± 0.08 ^{b}	4.73 ± 0.10 ^{c}	5.82 ± 0.11 ^{d}	5.12 ± 0.10 ^{d}
El-11	Chrysoeriol 7-*O*-glucoside	0.75 ± 0.02 ^{c}	<0.01	0.22 ± 0.00 ^{a}	0.31 ± 0.00 ^{b}	0.25 ± 0.00 ^{a}	0.39 ± 0.01 ^{b}
El-13	Luteolin 5-*O*-glucoside	5.57 ± 0.11 ^{c}	2.69 ± 0.05 ^{a}	4.22 ± 0.09 ^{b}	4.63 ± 0.09 ^{b}	5.58 ± 0.11 ^{c}	5.63 ± 0.11 ^{c}
El-14	Dracocephaloside (luteolin 3′-*O*-glucoside)	3.08 ± 0.06 ^{b}	2.52 ± 0.06 ^{a}	3.89 ± 0.07 ^{c}	3.96 ± 0.08 ^{c}	4.63 ± 0.09 ^{e}	4.22 ± 0.08 ^{d}
El-17	Echitin (apigenin 7-*O*-(2″-*O*-*p*-coumaroyl)-glucoside)	1.58 ± 0.03 ^{b}	1.12 ± 0.02 ^{a}	2.57 ± 0.06 ^{c}	3.38 ± 0.06 ^{d}	3.57 ± 0.07 ^{de}	3.62 ± 0.07 ^{e}
El-19	Echinacin (apigenin 7-*O*-(6″-*O*-*p*-coumaroyl)-glucoside)	7.37 ± 0.14 ^{c}	2.84 ± 0.04 ^{a}	5.33 ± 0.10 ^{b}	7.93 ± 0.16 ^{d}	9.11 ± 0.18 ^{e}	9.25 ± 0.21 ^{f}
	Phenolamides						
El-18	N^1,N^5,N^{10}-Tri-*O*-(*EEE*)-*p*-coumaroyl-spermidine	2.16 ± 0.04 ^{d}	0.63 ± 0.02 ^{a}	0.94 ± 0.02 ^{b}	1.45 ± 0.03 ^{c}	2.58 ± 0.05 ^{e}	2.73 ± 0.06 ^{e}
	Subtotal benzoic acids	0.39	–	<0.01	0.14	0.22	0.25
	Subtotal hydroxycinnamoyl quinic acids	43.89	23.87	41.67	50.48	45.23	43.83
	Subtotal flavonol glycosides	9.75	1.14	2.96	5.58	9.13	10.11
	Subtotal flavone glycosides	21.89	12.46	20.17	24.94	28.96	28.23
	Total flavonoids	31.64	13.60	23.13	30.52	38.09	38.34
	Subtotal phenolamides	2.16	0.63	0.94	1.45	2.58	2.73
	Total phenolic compounds	78.08	38.10	65.74	82.59	86.12	85.15

For compound numeration, see Figure S4. Means with the same letters for each parameter in a row are not significantly different at $p < 0.05$ by Fisher's protected least significant test.

3.5. *Ixeris chinensis subsp. versicolor (Variegated Ixeris)*

Ixeris chinensis subsp. *versicolor* (Fisch. ex Link) Kitam. (syn. *Ixeridium gramineum* (Fisch.) Tzvelev) is a perennial deciduous plant commonly found in meadows, rocky slopes, and bushy areas. It features greenish-blue leaves and a multiheaded stem, the ends of which are covered with versicolor flowers [22]. The entire plant contains a bitter, milky juice (latex), historically utilized in local medicine in the Baikal region as a vasoconstrictor [67]. There is no scientific information about the chemical composition of *I. chinensis* subsp. *versicolor*, although the plant is characterized by a high adaptability and ease of cultivation, giving a significant increase in green biomass already in the first year.

Mass-spectrometric profiling revealed the presence of 25 compounds in the herb of *I. chinensis* subsp. *versicolor*, including hydroxycinnamoyl quinic/tartaric acids, coumarins, flavonoids, and sesquiterpenes (Figure S7 and Table S12). Among these, the known *Ixeris* hydroxycinnamates, including four mono-caffeoyl quinic acids (4-*O*-*trans*; 3-*O*-*trans*; 5-*O*-*trans*/*cis*), caftaric acid, and cichoric acid, previously detected in *I. sonchifolia* (Maxim.) Hance [80], were identified in *I. chinensis* subsp. *versicolor*. Notably, cichoric acid exhibited

two peaks typical for di-*trans* and *cis*-*trans* isomers [81], a phenomenon not uncommon in plants but observed for the first time in the genus. Additionally, some non-flavonoid phenolics were identified as potential new components of *Ixeris*, including cichoriin (esculetin 7-*O*-glucoside), coutaric acid (*p*-coumaroyl tartaric acid), *p*-coumaroyl-caffeoyl-tartaric acid, and feruloyl-caffeoyl-tartaric acid. Among the ten flavonoids detected, several known flavonols were found, such as baimaside, quercetin 3-*O*-gentiobioside, quercetin 3-*O*-(2″-*O*-arabinosyl)-glucoside, peltatoside, sophoraflavonoloside, kaempferol 3-*O*-gentiobioside, calendoflavobioside, rutin, and populnin, along with one flavone chrysoeriol 7-*O*-glucoside. None of these compounds have been previously found in *Ixeris* plants. Compound Ic-10 was tentatively identified as kaempferol di-*O*-hexoside, an isomer of kaempferol 3-*O*-gentiobioside. The flavonoids found in *Ixeris* primarily consist of flavones derived from apigenin and luteolin [82], a composition atypical for *I. chinensis* subsp. *versicolor*. Some flavonols have also been identified in the parent species *I. chinensis* (Thunb.) Nakai [83], indicating that this composition is acceptable for selected species inside the genus.

The quantitative analysis of wild samples revealed a high concentration of cichoric acid (68.07 mg/g) and caftaric acid (5.31 mg/g), comprising over 94% of the total hydroxycinnamate content and more than 82% of the total phenolic content in the plant (Table 5).

Table 5. Content of phenolic compounds found in wild and cultivated samples of *Ixeris chinensis* subsp. *versicolor* herb, mg/g of dry plant weight (±S.D.).

Comp. No.	Compound	Wild Sample	Cultivated Samples			
			1st Year	2nd Year	3rd Year	4th Year
	Hydroxycinnamoyl quinic/tartaric acids					
Ic-1	4-*O*-Caffeoyl quinic acid (*trans*-)	0.02 ± 0.00 ^{a}	–	<0.01	0.01 ± 0.00 ^{a}	0.01 ± 0.00 ^{a}
Ic-3	Caftaric acid isomer	0.09 ± 0.00 ^{c}	–	<0.01	0.02 ± 0.00 ^{a}	0.05 ± 0.00 ^{b}
Ic-4	Caftaric acid	5.22 ± 0.11 ^{b}	3.86 ± 0.07 ^{a}	5.29 ± 0.11 ^{b}	5.93 ± 0.12 ^{bc}	6.07 ± 0.12 ^{c}
Ic-6	5-*O*-Caffeoyl quinic acid (*trans*-)	1.95 ± 0.04 ^{c}	0.98 ± 0.02 ^{a}	1.78 ± 0.04 ^{b}	2.14 ± 0.04 ^{d}	2.23 ± 0.05 ^{d}
Ic-7	3-*O*-Caffeoyl quinic acid (*trans*-)	0.52 ± 0.01 ^{b}	<0.01	0.29 ± 0.00 ^{a}	0.57 ± 0.02 ^{bc}	0.61 ± 0.02 ^{c}
Ic-12	5-*O*-Caffeoyl quinic acid (*cis*-)	0.05 ± 0.00 ^{b}	–	<0.01	0.01 ± 0.00 ^{a}	0.01 ± 0.00 ^{a}
Ic-15	Coutaric acid	0.07 ± 0.00 ^{b}	–	<0.01	0.05 ± 0.00 ^{a}	0.06 ± 0.00 ^{ab}
Ic-20	Cichoric acid (di-*trans* isomer)	64.84 ± 1.29 ^{b}	35.16 ± 0.70 ^{a}	62.82 ± 1.55 ^{b}	78.11 ± 1.59 ^{c}	78.03 ± 1.61 ^{b}
Ic-21	Cichoric acid (*cis*-*trans* isomer)	3.23 ± 0.06 ^{b}	0.96 ± 0.02 ^{a}	3.52 ± 0.07 ^{bc}	3.86 ± 0.08 ^{c}	3.94 ± 0.08 ^{c}
Ic-22	*p*-Coumaroyl-caffeoyl-tartaric acid	0.66 ± 0.02 ^{ab}	<0.01	0.56 ± 0.02 ^{a}	0.72 ± 0.02 ^{b}	0.94 ± 0.02 ^{c}
Ic-23	Feruloyl-caffeoyl-tartaric acid	0.67 ± 0.02 ^{b}	0.02 ± 0.00 ^{a}	0.63 ± 0.02 ^{b}	0.84 ± 0.02 ^{c}	0.97 ± 0.02 ^{d}
	Coumarins					
Ic-2	Cichoriin	1.52 ± 0.03 ^{b}	1.12 ± 0.02 ^{a}	1.69 ± 0.03 ^{b}	2.14 ± 0.05 ^{c}	2.54 ± 0.05 ^{d}
	Flavonol glycosides					
Ic-5	Baimaside	0.11 ± 0.00 ^{b}	–	<0.01	<0.01	0.04 ± 0.00 ^{a}
Ic-8	Quercetin 3-*O*-gentiobioside	1.69 ± 0.03 ^{d}	0.72 ± 0.02 ^{a}	0.96 ± 0.02 ^{b}	1.37 ± 0.03 ^{c}	1.74 ± 0.04 ^{d}
Ic-9	Quercetin 3-*O*-(2″-*O*-arabinosyl)-glucoside	0.63 ± 0.02 ^{c}	<0.01	0.23 ± 0.00 ^{a}	0.34 ± 0.01 ^{a}	0.52 ± 0.02 ^{b}
Ic-10	Kaempferol di-*O*-hexoside	0.03 ± 0.00	–	<0.01	<0.01	<0.01
Ic-11	Peltatoside	0.85 ± 0.02 ^{d}	0.21 ± 0.00 ^{a}	0.58 ± 0.02 ^{b}	0.73 ± 0.02 ^{c}	0.79 ± 0.02 ^{cd}
Ic-13	Sophoraflavonoloside	0.27 ± 0.00 ^{b}	<0.01	0.14 ± 0.00 ^{a}	0.25 ± 0.00 ^{b}	0.39 ± 0.01 ^{c}
Ic-14	Kaempferol 3-*O*-gentiobioside	0.20 ± 0.00 ^{c}	<0.01	<0.01	0.05 ± 0.00 ^{a}	0.09 ± 0.00 ^{b}
Ic-16	Calendoflavobioside	0.12 ± 0.00 ^{c}	–	<0.01	0.02 ± 0.00 ^{a}	0.07 ± 0.00 ^{b}
Ic-17	Rutin	0.02 ± 0.00	–	<0.01	<0.01	<0.01
Ic-18	Populnin	0.95 ± 0.02 ^{c}	0.53 ± 0.02 ^{a}	0.79 ± 0.02 ^{b}	0.93 ± 0.02 ^{c}	1.14 ± 0.02 ^{d}
	Flavone glycosides					
Ic-19	Chrysoeriol 7-*O*-glucoside	2.27 ± 0.04 ^{d}	1.04 ± 0.02 ^{a}	1.41 ± 0.03 ^{b}	1.94 ± 0.04 ^{c}	2.25 ± 0.04 ^{d}
Subtotal hydroxycinnamoyl quinic/tartaric acids		77.32	40.98	74.89	92.26	92.92
	Subtotal coumarins	1.52	1.12	1.69	2.14	2.54
	Subtotal flavonol glycosides	4.87	1.46	2.70	3.69	4.78

Table 5. *Cont.*

Comp. No.	Compound	Wild Sample	Cultivated Samples			
			1st Year	2nd Year	3rd Year	4th Year
	Subtotal flavone glycosides	2.27	1.04	1.41	1.94	2.25
	Total flavonoids	9.74	2.16	4.11	5.63	7.03
	Total phenolic compounds	88.58	44.26	80.69	100.03	102.49

For compound numeration, see Figure S5. Means with the same letters for each parameter in a row are not significantly different at $p < 0.05$ by Fisher's protected least significant test.

These compounds are unique bioactive metabolites with antiviral, antidiabetic, and immunostimulant properties [84,85]. Previous research on cichoric acid levels in plants has indicated 0.15–2.30% concentrations in chicory and echinacea products [86], underscoring the significance of the *I. chinensis* subsp. *versicolor* herb as a novel source of this compound. The remaining phenolic compounds collectively accounted for approximately 12% of the plant's phenolic content. Among the basic flavonoids present in the herb, chrysoeriol 7-*O*-glucoside (2.27 mg/g), quercetin 3-*O*-gentiobioside (1.69 mg/g), and populnin (0.95 mg/g) were predominant, contributing to a total value of 9.74 mg/g in dry plant material. In comparison, coumarins accounted for 1.52 mg/g.

A four-year cultivation experiment showed that *I. chinensis* subsp. *versicolor* could accumulate cichoric acid (66.34 mg/g) and caftaric acid (5.29 mg/g) by the second year, reaching levels comparable to those found in wild-growing samples. In subsequent years (third and fourth), there was a gradual increase in the concentration of these target compounds, with cichoric acid reaching 81.97 mg/g and caftaric acid reaching 8.30 mg/g. A similar accumulation pattern was observed for cichoriin, with its content reaching 2.54 mg/g by the fourth year, representing a 67% increase compared to wild samples ($p < 0.05$). The level of flavonoid deposition at the end of the experiment was measured at 72% of the wild level ($p < 0.05$), suggesting that an extended cultivation period is necessary to achieve the desired concentration of flavonoids in cultivated plants.

3.6. Lactuca sibirica (Siberian Lettuce)

Lactuca sibirica (L.) Benth. ex Maxim., alongside wormwoods and dandelions, is one of the most prevalent perennial plant species in Siberia's field and steppe communities [87]. This weedy species is more than one meter high and has a highly developed root system. The species has an erect, densely leafed plant with bluish-green leaves and numerous purple-to-lilac flowers. Despite the bitter latex present throughout the plant, it is considered a valuable forage species owing to its ability to regenerate green foliage rapidly after grazing by cattle [88]. In traditional Transbaikalian medicine, the *L. sibirica* herb (known locally as *srol-gon sngon-bo*) is used to treat injured head bones and heat caused by intoxication [67]. This species is a close relative of common lettuce, which has been domesticated since approximately 4000 BC [89], as evidenced by the use of young, non-bitter greens of *L. sibirica* in salads. Chemical analyses of *L. sibirica* have revealed the presence of lactucin-like guaianolides (8-deoxylactucin, jacquinelin, 11β,13-dihydrolactucin, and crepidiaside B) and furofuran lignans (lactucaside) in its herb [90]. At the same time, its roots contain guaianolides (8-deoxylactucin, jacquinelin, 13-dihydrolactucin, crepidiaside B, vernoflexuoside, 11β,13-dihydroglucozaluzanin C, macrocliniside A, ixerin F) and 3β,14-dihydroxy-11β,13-dihydrocostunolide-3-*O*-glucoside [91]. Despite these findings, the phenolic compounds of *L. sibirica* remain largely unexplored.

HPLC–MS profiling of the *L. sibirica* herb revealed the presence of 43 compounds encompassing hydroxybenzoates, hydroxycinnamates, flavonoids, and phenolamides (Figure S8 and Table S13). In the hydrophilic compound zone, seven components exhibiting specific UV-absorbance characteristics relative to vanilloyl derivatives (λ_{max}: 289 and 316 nm; Figure S1) [40] were identified and tentatively classified as mono-vanilloyl quinic acids (Ls-1, -5, -7, -9) and di-vanilloyl quinic acids (Ls-15, -16, -19). These rare plant pheno-

lics were previously found only in Apocynaceae (*Carissa spinarum* L.) [40], Convolvulaceae (*Erycibe obtusifolia* Benth.) [42], and Rutaceae (*Zanthoxylum zanthoxyloides* (Lam.) Zepern. & Timler) [41], and for the first time in the Asteraceae family. Three hydrophilic phenolics eluting from 5.32 to 7.41 min were identified as protocatechuic glucosides, also present in *Carduus nutans* subsp. *leiophyllus*, *Cirsium heterophyllum*, and *Echinops davuricus*. Mono- and dicaffeoylquinic acids (3/4/5-*O*-, 3,4/3,5/4,5-di-*O*-) similar to typical *Lactuca* caffeates [92] were detected in *L. sibirica*, alongside hydroxycinnamoyl-tartaric acids such as caftaric acid and di-*trans*-cichoric acid, previously found in *L. sativa*, *L. virosa* [93], and *L. orientalis* [94], as well as cichoric acid *cis-trans*-/di-*cis*-isomers and *p*-coumaroyl/feruloyl-caffeoyl-tartaric acids detected in the genus for the first time.

The flavonoids identified in *L. sibirica* encompassed luteolin and its derivatives (7/3′/4′-*O*-glucosides, along with two tri-*O*-hexosides with unknown structures), apigenin and its 7-*O*-glucuronide, chrysoeriol 7-*O*-glucoside, two kaempferols (3-*O*-neohesperidoside, 3-*O*-rutinoside), and four quercetins (3-*O*-rutinoside, 3-*O*-(3″/4″/6″-*O*-acetyl)-glucosides). Apigenin, luteolin, kaempferol, and quercetin in the form of aglycones and various *O*-glucosides have been isolated from eight *Lactuca* species [92]. However, flavone 3′/4′-*O*-glucosides, chrysoeriols, and acetylated flavonol *O*-glucosides are newly discovered in the genus.

A compact chromatographic zone, characterized by closely spaced retention times, contained at least four compounds eluted in a low-polarity compound region. Their distinctive UV-absorption profile (λ_{max}: 297 and 309 nm; Figure S1), molecular formulas ($C_{46}H_{50}N_4O_8$), and mass-spectral patterns led to the identification of Ls-39–Ls-42 as isomeric phenolamines with a *tetra-O-p*-coumaroyl spermine basic structure [95] previously undescribed in *Lactuca*. The differences between these compounds are likely attributed to the number and location of *cis* and *trans* bonds in the structure of the *p*-coumaroyl fragments.

The quantitative analysis of wild *L. sibirica* samples revealed a high phenolic content (110.64 mg/g), with the predomination of hydroxycinnamoyl quinic/tartaric acids (66.79 mg/g) and a medium level of flavonoids (26.94 mg/g) and hydroxybenzoyl quinic acids (13.58 mg/g) (Table 6).

Table 6. Content of phenolic compounds found in wild and cultivated samples of *Lactuca sibirica* herb, mg/g of dry plant weight (±S.D.).

Comp. No.	Compound	Wild Sample	Cultivated Samples			
			1st Year	2nd Year	3rd Year	5th Year
	Hydroxybenzoyl quinic acids					
Ls-1	Vanilloyl quinic acid (1-*O*-isomer *)	11.63 ± 0.22 ^{b}	8.63 ± 0.17 ^{a}	12.58 ± 0.26 ^{c}	15.39 ± 0.30 ^{d}	15.28 ± 0.31 ^{d}
Ls-5	Vanilloyl quinic acid (4-*O*-isomer *)	1.53 ± 0.03 ^{a}	<0.01	1.65 ± 0.03 ^{a}	2.12 ± 0.04 ^{b}	2.14 ± 0.04 ^{b}
Ls-7	Vanilloyl quinic acid (5-*O*-isomer *)	<0.01	–	<0.01	<0.01	0.08 ± 0.00
Ls-9	Vanilloyl quinic acid (5-*O*-isomer *)	<0.01	–	<0.01	<0.01	0.02 ± 0.00
Ls-15	Divanilloyl quinic acid (3,4-isomer *)	0.42 ± 0.01 ^{b}	<0.01	<0.01	0.14 ± 0.00 ^{a}	0.16 ± 0.00 ^{a}
Ls-16	Divanilloyl quinic acid (3,5-isomer *)	<0.01	–	<0.01	<0.01	<0.01
Ls-19	Divanilloyl quinic acid (4,5-isomer *)	<0.01	–	<0.01	<0.01	<0.01
	Benzoic acids					
Ls-2	Protocatechuic acid *O*-hexoside	0.27 ± 0.00 ^{c}	<0.01	0.10 ± 0.00 ^{a}	0.15 ± 0.00 ^{ab}	0.19 ± 0.00 ^{b}
Ls-3	Protocatechuic acid *O*-hexoside	0.31 ± 0.00 ^{b}	<0.01	0.22 ± 0.00 ^{a}	0.31 ± 0.00 ^{b}	0.35 ± 0.01 ^{b}
Ls-4	Protocatechuic acid 4-*O*-glucoside	<0.01	<0.01	<0.01	0.08 ± 0.00 ^{a}	0.12 ± 0.00 ^{a}
	Hydroxycinnamoyl quinic/tartaric acids					
Ls-6	4-*O*-Caffeoyl quinic acid (*trans*-)	0.08 ± 0.00	<0.01	<0.01	<0.01	<0.01
Ls-8	Caftaric acid	6.73 ± 0.014 ^{b}	4.63 ± 0.09 ^{a}	7.69 ± 0.15 ^{c}	8.55 ± 0.16 ^{d}	9.27 ± 0.18 ^{e}
Ls-10	5-*O*-Caffeoyl quinic acid (*trans*-)	3.93 ± 0.07 ^{c}	1.95 ± 0.04 ^{a}	2.77 ± 0.05 ^{b}	3.97 ± 0.07 ^{c}	4.12 ± 0.08 ^{cd}
Ls-11	3-*O*-Caffeoyl quinic acid (*trans*-)	<0.01	<0.01	<0.01	<0.01	<0.01
Ls-13	5-*O*-Caffeoyl quinic acid (*cis*-)	0.35 ± 0.00 ^{b}	<0.01	0.26 ± 0.00 ^{a}	0.35 ± 0.00 ^{b}	0.37 ± 0.00 ^{b}
Ls-23	3,4-Di-*O*-caffeoyl quinic acid	0.22 ± 0.00	<0.01	<0.01	<0.01	<0.01
Ls-26	3,5-Di-*O*-caffeoyl quinic acid	12.06 ± 0.24 ^{c}	5.21 ± 0.10 ^{a}	10.59 ± 0.21 ^{b}	14.27 ± 0.29 ^{d}	14.06 ± 0.28 ^{d}
Ls-27	Cichoric acid (di-*trans* isomer)	39.71 ± 0.78 ^{b}	22.17 ± 0.45 ^{a}	40.25 ± 0.82 ^{b}	45.63 ± 0.91 ^{c}	46.02 ± 0.92 ^{c}
Ls-29	4,5-Di-*O*-caffeoyl quinic acid	<0.01	<0.01	<0.01	<0.01	<0.01
Ls-33	Cichoric acid (*cis-trans* isomer)	1.12 ± 0.02 ^{bc}	0.63 ± 0.02 ^{a}	0.96 ± 0.02 ^{b}	1.14 ± 0.02 ^{bc}	1.25 ± 0.02 ^{c}
Ls-34	Cichoric acid (*cis-cis* isomer)	0.31 ± 0.01 ^{b}	<0.01	<0.01	0.23 ± 0.00 ^{a}	0.25 ± 0.00 ^{ab}
Ls-35	*p*-Coumaroyl-caffeoyl-tartaric acids	1.44 ± 0.03 ^{b}	0.50 ± 0.01 ^{a}	1.27 ± 0.03 ^{a}	1.42 ± 0.03 ^{b}	1.45 ± 0.03 ^{b}

Table 6. *Cont.*

Comp. No.	Compound	Wild Sample	Cultivated Samples			
			1st Year	2nd Year	3rd Year	5th Year
Ls-36	Feruloyl-caffeoyl-tartaric acid	0.62 ± 0.02 ^{c}	0.02 ± 0.00 ^{a}	0.52 ± 0.02 ^{b}	0.63 ± 0.02 ^{c}	0.54 ± 0.02 ^{b}
Ls-37	*p*-Coumaroyl-caffeoyl-tartaric acid	0.22 ± 0.00 ^{c}	<0.01	<0.01	0.04 ± 0.00 ^{a}	0.11 ± 0.00 ^{b}
	Flavones					
Ls-12	Luteolin tri-*O*-hexoside	<0.01	–	<0.01	<0.01	<0.01
Ls-14	Luteolin tri-*O*-hexoside	<0.01	–	<0.01	<0.01	<0.01
Ls-20	Cynaroside (luteolin 7-*O*-glucoside)	6.20 ± 0.12 ^{d}	2.18 ± 0.04 ^{a}	4.53 ± 0.09 ^{b}	5.94 ± 0.06 ^{c}	6.34 ± 0.12 ^{d}
Ls-22	Chrysoeriol 7-*O*-glucoside	7.00 ± 0.14 ^{d}	2.86 ± 0.05 ^{a}	3.89 ± 0.07 ^{b}	6.29 ± 0.14 ^{c}	7.55 ± 0.14 ^{e}
Ls-25	Dracocephaloside (luteolin 3′-*O*-glucoside)	0.05 ± 0.00	–	<0.01	<0.01	<0.01
Ls-30	Apigenin 7-*O*-glucuronide	5.37 ± 0.011 ^{d}	1.17 ± 0.02 ^{a}	1.29 ± 0.02 ^{a}	3.86 ± 0.07 ^{b}	4.29 ± 0.08 ^{c}
Ls-31	Luteolin 4′-*O*-glucoside	<0.01	–	<0.01	<0.01	<0.01
Ls-38	Luteolin	1.18 ± 0.02 ^{c}	0.24 ± 0.00 ^{a}	0.96 ± 0.02 ^{b}	1.14 ± 0.02 ^{bc}	1.96 ± 0.03 ^{d}
Ls-43	Apigenin	1.93 ± 0.03 ^{e}	0.20 ± 0.00 ^{a}	1.27 ± 0.02 ^{b}	1.52 ± 0.03 ^{c}	1.70 ± 0.03 ^{d}
	Flavonol glycosides					
Ls-17	Kaempferol 3-*O*-neohesperidoside	0.06 ± 0.00	–	<0.01	<0.01	<0.01
Ls-18	Rutin (quercetin 3-*O*-rutinoside)	3.14 ± 0.06 ^{c}	0.53 ± 0.02 ^{a}	2.14 ± 0.04 ^{b}	4.26 ± 0.08 ^{d}	4.57 ± 0.09 ^{d}
Ls-21	Nicotiflorin (kaempferol 3-*O*-rutinoside)	0.05 ± 0.00	–	<0.01	<0.01	<0.01
Ls-24	Quercetin 3-*O*-(6″-*O*-acetyl)-glucoside	1.88 ± 0.04 ^{d}	0.52 ± 0.02 ^{a}	1.14 ± 0.02 ^{b}	1.56 ± 0.03 ^{c}	1.60 ± 0.03 ^{c}
Ls-28	Quercetin 3-*O*-(3″-*O*-acetyl)-glucoside	0.08 ± 0.00	–	–	<0.01	<0.01
Ls-32	Quercetin 3-*O*-(4″-*O*-acetyl)-glucoside	<0.01	–	<0.01	<0.01	<0.01
	Phenolamides					
Ls-39-42	Tetra-*O*-*p*-coumaroyl spermines	2.75 ± 0.05 ^{b}	1.95 ± 0.04 ^{a}	2.89 ± 0.05 ^{b}	3.14 ± 0.06 ^{c}	3.55 ± 0.07 ^{d}
	Subtotal hydroxybenzoyl quinic acids	13.58	8.63	14.23	17.51	17.68
	Subtotal benzoic acids	0.58	<0.01	0.32	0.54	0.66
	Subtotal hydroxycinnamoyl quinic/tartaric acids	66.79	35.11	64.31	76.23	77.44
	Subtotal flavones	21.73	6.65	11.94	18.75	21.84
	Subtotal flavonol glycosides	5.21	1.05	3.28	5.82	6.17
	Total flavonoids	26.94	7.70	15.22	24.57	28.01
	Total phenolamides	2.75	1.95	2.89	3.14	3.55
	Total phenolic compounds	110.64	53.39	96.97	121.99	127.34

For compound numeration, see Figure S6. * Tentative identification. Means with the same letters for each parameter in a row are not significantly different at $p < 0.05$ by Fisher's protected least significant test.

The contents of the total benzoic acids and phenolamides were measured at 0.58 and 2.75 mg/g, respectively. The bioactive hydroxycinnamates, cichoric and caftaric acids, exhibited levels of 41.14 and 6.73 mg/g, respectively, surpassing known data for the highest content of these compounds in edible lettuces such as *L. sativa* (15 and 1.5 mg/g), *L. virosa* (15 and 2.0 mg/g), *L. serriola* (25 and 2.2 mg/g) [93], and *L. orientalis* (6.6 and 0.6 mg/g) [94]. Values for basic hydroxycinnamoyl quinic acids were determined as 12.06 and 3.93 mg/g for 3,5-di-*O*- and 5-*O*-caffeoyl quinic acids, respectively, exceeding the corresponding parameters in *L. sativa* (1.2 and 3.3 mg/g), *L. virosa* (2.8 and 3.9 mg/g), *L. serriola* (1.1 and 3.1 mg/g) [93], and *L. orientalis* (0.4 and 0.0 mg/g) [94]. The primary vanilloyl quinic acid, Ls-1, exhibited a content of approximately 11.63 mg/g, indicating a potentially high level. However, quantitative data on the content of hydroxybenzoyl quinic acids in plants are currently unavailable.

Considering the data on flavonoid content, it is evident that flavones greatly outnumbered flavonols (21.73 vs. 5.21 mg/g in total). Chrysoeriol 7-*O*-glucoside (7.00 mg/g), luteolin 7-*O*-glucoside (6.20 mg/g), and apigenin 7-*O*-glucuronide (5.37 mg/g) collectively contributed to over 86% of the total flavone content or 69% of the total flavonoid content. Rutin, as a basic flavonol with a value of 3.14 mg/g, accounted for no more than 12% of the total flavonoids. Flavonoids have not been previously described as the primary phytocomponents of lettuces. In *L. sativa*, the total flavonoid variations are 0.03–22.9 mg/100 g [96], 0.1–1.35 mg/100 g [97], and 0.14–2.81 mg/100 g [98], which is significantly lower than that in *L. sibirica*.

The cumulative content of four tetra-*O*-*p*-coumaroyl spermines amounted to 2.75 mg/g. Although there is a lack of known content data for other *Lactuca* species, it is noteworthy that phenolamides can be present at levels reaching 70 μg/g in peanut flowers [99],

120 μg/g in apple flowers [55], and 200 μg/g in tea flower buds [100]. This underscores the potential of the *L. sibirica* herb as a source of this group of metabolites.

A five-year study on the potential introduction of *L. sibirica* revealed its potential as a perennial crop, with phenolic compound levels reaching those found in the wild by the third year of cultivation. The total phenolic content in the first, second, third, and fifth years of cultivation measured at 53.39, 96.97, 121.99, and 127.34 mg/g, respectively, reaching 48%, 88%, 110%, and 115% ($p < 0.05$) of the wild level (WL), respectively. The main components, such as hydroxycinnamoyl quinic/tartaric acids, approached wild levels by the second year (64.31 mg/g; 96% of WL), along with hydroxybenzoyl quinic acids (14.23 mg/g; 105% of WL) and phenolamides (2.89 mg/g; 105% of WL). The accumulation of flavonoids and individual groups occurred more gradually, achieving 101% of the WL for flavones in the fifth year and 112% of the WL for flavonols in the third year ($p < 0.05$). Large increases in the concentration of individual compounds after the first year of cultivation were observed for vanilloyl quinic acid Ls-1 (74% of WL), tetra-*O*-*p*-coumaroyl spermines (71% of WL), caftaric acid (68% of WL), and cichoric acid (56% of WL), which are basic components of *L. sibirica*, accounting for over 70% of the total phenolic content. Furthermore, the absolute contents of chicoric and caftaric acids in one-year samples were measured at 22.17 and 4.63 mg/g, respectively, exceeding the values found in *L. sativa* cv. British Hilde leaves (15 and 1.5 mg/g, respectively) [93]. These findings suggest the potential of *L. sibirica* as a promising annual crop that, with further breeding research, could be more widely integrated into the human diet.

3.7. New Asian Asteraceae Species for Cultivation: What's Next?

The investigation of six Asteraceae species revealed the presence of over one hundred phenolic compounds (Table S14) belonging to various chemical groups, including benzoates, coumarins, hydroxycinnamates, flavonoids, and phenylamines (Table 7).

Table 7. Synopsis of compound groups found in six Asteraceae species.

Compound Groups	Species *					
	Aj	**Cn**	**Ch**	**Ed**	**Ic**	**Ls**
		Benzoates				
Hydroxybenzoic acid glucosides		√	√	√		√
Hydroxybenzoyl quinic acids						√
		Coumarins				
Hydroxycoumarin *O*-glucosides					√	
		Hydroxycinnamates				
Caffeoyl glucaric acids	√					
Caffeoyl tartaric acids					√	√
p-Coumaroyl tartaric acids					√	
Mixed tartaric acids					√	√
p-Coumaroyl quinic acids		√	√	√		
Caffeoyl quinic acids	√	√	√	√	√	√
Feruloyl quinic acids		√				
		Flavonoids				
Apigenin *O*-glucosides		√	√	√		√
Apigenin *C*-glucosides	√		√			
Acacetin *O*-glucosides			√			
Luteolin *O*-glucosides		√	√	√		√
Chrysoeriol *O*-glucosides		√	√	√	√	
6-Hydroxyluteolin *O*-glucosides	√					
Pectolinarigenin *O*-glucosides			√			
Kaempferol *O*-glucosides					√	√
Quercetin *O*-glucosides	√			√	√	√
Isorhamnetin *O*-glucosides	√					
Flavone aglycones	√					√
Flavonol aglycones	√					
		Phenylamines				
Tri-*O*-*p*-coumaroyl spermines	√					
Tetra-*O*-*p*-coumaroyl spermines	√					√
Tri-*O*-*p*-coumaroyl-spermidine				√		

* Aj—*Artemisia jacutica*, Cn—*Carduus nutans* subsp. *leiophyllus*, Ch—*Cirsium heterophyllum*, Ed—*Echinops davuricus*, Ic—*Ixeris chinensis* subsp. *versicolor*, Ls—*Lactuca sibirica*.

Unique compounds identified only in one species included caffeoyl glucaric acids, 6-hydroxyluteolin *O*-glucosides, tri-*O*-*p*-coumaroyl spermines, and flavonol aglycones from *A. jacutica*, feruloyl quinic acids from *C. nutans* subsp. *leiophyllus*, acacetin *O*-glucosides and pectolinarigenin *O*-glucosides from *C. heterophyllum*, tri-*O*-*p*-coumaroyl-spermidine from *E. davuricus*, hydroxycoumarin *O*-glucosides and *p*-coumaroyl tartaric acids from *I. chinensis* subsp. *versicolor*, and hydroxybenzoyl quinic acids from *L. sibirica*. Despite the similarities in plant composition, these species exhibited differences in phenolic profiles. These differences were particularly pronounced in terms of the quantitative levels of individual compounds, underscoring the cultivated species as sources of specific phenolic compounds: 3,5-di-*O*-caffeoyl- and 5-O-caffeoyl quinic acids in *A. jacutica*, luteolin and chrysoeriol 7-*O*-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucosides in *C. nutans* subsp. *leiophyllus*, chrysoeriol 7-*O*-glucoside in *C. heterophyllum*, 3,5-di-*O*-caffeoyl- and 5-*O*-caffeoyl quinic acids, and echinacin in *E. davuricus*, cichoric acid in *I. chinensis* subsp. *versicolor* and *L. sibirica*, and vanilloyl quinic acid, tetra-*O*-*p*-coumaroyl spermines, and caftaric acid in *L. sibirica*.

Based on the chemical composition data of the studied species and existing literature on the biological activity of specific metabolite groups, we can outline potential avenues for a further medical exploration of extracts from cultivated samples. Protocatechuic acid glucosides are identified as potential sources of free protocatechuic acid, known for their antibacterial, antiviral, antifibrotic [101], antioxidant [102], anti-inflammatory, and antihyperglycemic properties [103]. *Lactuca sibirica*'s vanilloyl quinic acids, exhibiting unique antisickling activity similar to the isomeric burkinabins A–C from *Zanthoxylum zanthoxyloides* [41], also demonstrate antioxidant protection and tyrosinase inhibition capabilities [42]. Cichoriin from *I. chinensis* subsp. *versicolor* is recognized for its antiobesity and antioxidant properties [104], alongside antidiabetic [105], antiproliferative, and photoprotective effects [106]. Caffeoyl glucaric acids from *A. jacutica* demonstrate moderate hepatoprotection [107] and ROS production inhibition [108]. The immune-active and anti-inflammatory action of caffeoyl tartaric acids [84,85] from *I. chinensis* subsp. *versicolor* and *L. sibirica* may influence the activity of their respective extracts. Derivatives of apigenin, acacetin, luteolin, chrysoeriol, pectolinarigenin, kaempferol, quercetin, and isorhamnetin, differing in proportions across species, exhibit anticancer, anti-inflammatory, enzyme inhibitory [109], cardioprotective, antidiabetic, anti-aging [110], coronary heart disease prevention, and hepatoprotective activities [111]. Open-chain coumaroylated spermidine and spermine alkaloids (or phenylamines) from various sources demonstrate analgesic effects and μ-opioid receptor agonist activity [112], inhibit NO production in RAW 264.7 cells [113], and scavenge free radicals [114].

The diverse biological activities exhibited by the identified secondary metabolites suggest a polyvalent effect inherent in the total extracts. The next phase of exploring the potential practical applications of these plants requires conducting biological experiments to evaluate their medicinal utility. Based solely on preliminary data, we expect antioxidant activity across all studied species, given their rich antioxidant content. The presence of individual compounds with confirmed immunostimulatory, anti-inflammatory, and hepatoprotective properties suggests the potential for these plants in these therapeutic applications. This study shows that the domestication of six wild plant species allows the cultivation of plant material with a high phenolic compound content, thereby paving the way for exploiting its beneficial properties to improve human life.

4. Conclusions

This is the first report describing phenolic profiles of *Artemisia jacutica*, *Echinops davuricus*, *Ixeris chinensis* subsp. *versicolor*, and *Lactuca sibirica* herbs, significantly enriching the chemical dataset for *Carduus nutans* subsp. *leiophyllus* and *Cirsium heterophyllum*. Wild plants can be successfully cultivated under open-field conditions, with the qualitative composition and quantitative content of target compounds aligning entirely with those of their parent organisms. These findings are significant because the studied plants thrive not only

in Siberia but also in Europe and the Baltic States (e.g., *Carduus nutans* subsp. *leiophyllus*, *Cirsium heterophyllum*, and *Lactuca sibirica*), as well as in China, Mongolia, Korea (*Echinops davuricus*), and Qinghai, Tibet, Vietnam, and Xinjiang (*Ixeris chinensis* subsp. *versicolor*), rendering them potentially valuable plants across diverse geographic areas. The results underscore the feasibility of transferring ethnochemical and ethnopharmacological research into the controlled conditions of modern science to obtain reliable data, which could serve as a foundation for developing novel pharmaceuticals in the future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/horticulturae10050486/s1, Figure S1: Typical UV spectra of the basic phenolic compounds found in six Asteraceae species; Figure S2: Flow chart for the experimental design; Figure S3: HPLC-MS chromatograms of *Artemisia jacutica* herb in SIM mode; Figure S4: HPLC-MS chromatograms of *Carduus nutans* subsp. *leiophyllus* herb in SIM mode; Figure S5: HPLC-MS chromatograms of *Cirsium heterophyllum* herb in SIM mode; Figure S6: HPLC-MS chromatograms of *Echinops davuricus* herb in SIM mode; Figure S7: HPLC-MS chromatograms of *Ixeris chinensis* subsp. *versicolor* herb in SIM mode; Figure S8: HPLC-MS chromatograms of *Lactuca sibirica* herb in SIM mode; Table S1: Description of wild samples of Asteraceae species collected in Altacheiskii reserve for the period 2010–2020 and information on cultivation success; Table S2: Plant cultivation conditions of six Asteraceae species; Table S3: Plant sample description for HPLC assay; Table S4: Reference standards used for HPLC profiling and quantification; Table S5: HPLC and mass-spectral conditions used for metabolite separation; Table S6: Regression equations, correlation coefficients, standard deviation, limits of detection, limits of quantification, and linear ranges for 55 reference standards; Table S7: Retention times, molecular formulas, mass-spectral data for negative ionization, and identification level of compounds Aj-1–Aj-32 found in *Artemisia jacutica* herb; Table S8: Retention times, molecular formulas, mass-spectral data for negative ionization, and identification level of compounds Cn-1–Cn-20 found in *Carduus nutans* subsp. *leiophyllus* herb; Table S9: Extraction/chromatography conditions and spectral data of luteolin 7-*O*-(2″-*O*-(6‴-*O*-acetyl)-glucosyl)-glucoside and chrysoeriol 7-*O*-(2″-*O*(6‴-*O*-acetyl)-glucosyl)-glucoside isolated from *Carduus nutans* subsp. *leiophyllus* leaves; Table S10: Retention times, molecular formulas, mass-spectral data for negative ionization, and identification level of compounds Ch-1–Ch-24 found in *Cirsium heterophyllum* herb; Table S11: Retention times, molecular formulas, mass-spectral data for negative ionization, and identification level of compounds El-1–El-19 found in *Echinops davuricus* herb; Table S12: Retention times, molecular formulas, mass-spectral data for negative ionization, and identification level of compounds Ic-1–Ic-25 found in *Ixeris chinensis* subsp. *versicolor* herb; Table S13: Retention times, molecular formulas, mass-spectral data for negative ionization, and identification level of compounds Ls-1–Ls-41 found in *Lactuca sibirica* herb; Table S14: Synopsis of compounds found in six Asteraceae species.

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