Article

Zostera marina L.: Supercritical CO₂-Extraction and Mass Spectrometric Characterization of Chemical Constituents Recovered from Seagrass

Mayya P. Razgonova 1,2,*; Lyudmila A. Tekutyeva 2,*; Anna B. Podvolotskaya 2; Varvara D. Stepochkina 2; Alexander M. Zakharenko 3,4 and Kirill Golokhvast 2,3

1. N.I. Vavilov All-Russian Institute of Plant Genetic Resources, B. Morskaya 42-4, 190000 Saint-Petersburg, Russia
2. Department of Bioeconomy and Food Security, Far Eastern Federal University, Sukhanova 8, 690950 Vladivostok, Russia; apodvolot7777@mail.ru (A.B.P.); vdksi6stsyna@gmail.com (V.D.S.); golokhvast@sfica.ru (K.G.)
3. Laboratory of Supercritical Fluid Research and Application in Agrobiotechnology, Tomsk State University, Lenin Str. 36, 634050 Tomsk, Russia; rarfeyandex.ru
4. Siberian Federal Scientific Centre of Agrobiotechnology, Centralnaya, Presidium, 633501 Krasnoyarsk, Russia
*
Correspondence: m.razgonova@vir.ru (M.P.R.); lat7777@mail.ru (L.A.T.)

Abstract: Three types of Zostera marina L. collection were extracted using the supercritical CO₂-extraction method. For the purposes of supercritical CO₂-extraction, old seagrass ejection on the surf edge, fresh seagrass ejection on the surf edge and seagrass collected in water were used. Several experimental conditions were investigated in the pressure range 50–350 bar, with the used volume of co-solvent ethanol in the amount of 1 % in the liquid phase at a temperature in the range of 31–70 °C. The most effective extraction conditions are: pressure 250 Bar and temperature 60 °C for Z. marina collected in shallow water. Z. marina contain various phenolic compounds and sulfated polyphenols with valuable biological activity. Tandem mass-spectrometry (HPLC-ESI-ion trap) was applied to detect target analytes. 77 different biologically active components have been identified in Z. marina supercritical CO₂-extracts. 38 polyphenols were identified for the first time in Z. marina.

Keywords: Zostera marina; CO₂-extraction; tandem mass spectrometry; polyphenols; sulfated polyphenols

1. Introduction

Zostera marina L. is a perennial marine herbaceous plant, genus Zostera, family Zosteraceae. Zostera lives mainly in the coastal waters of the northern hemisphere, it grows in the Azov, Black, Caspian, White and Far Eastern seas (Figure 1). For the most part, the plant lives in shallow water or at a depth of 1–4 m (sometimes 10 m), mainly on soft sandy or muddy bottoms in the calm waters of bays and bays. In the 30s of the last century, Zostera began to die, the reason for this was a special type of animal—the labyrinutha [1]. During the epidemic, Zostera disappeared from the coasts of North America, the Atlantic and Southern Europe and still does not grow in these places.

Zostera has a branched root system, forms underwater meadows, sometimes with a very high herbage up to 100 cm high. Plants bloom and pollinate under water, pollen is carried by streams of water. In order to survive in harsh conditions that are not intended for the life of higher plants, that is, in salty sea water, the plant has acquired a number of biochemical features that determines its adaptation to a specific habitat. The plant produces a special pectin, which has no analogues in other plants. Firstly, it was isolated in 1940 by the Russian scientist V.I. Miroshnikov, who named it zosterin. Zosterin from a
chemical point of view is a polysaccharide of pectin nature. It is a highly active polyanionic adsorbent, which, passing through the gastrointestinal tract, binds and removes heavy metal ions, bile acids, pathogenic microorganisms, etc. from the body [2].

Interested in the unique nature of zosterin, Yu. S. Ovodov engaged in serious research, the result of which showed that these pectins are among the most complex in structure of objects of natural origin, and this unique feature gives them a high adsorption capacity. Because of this, a pectin called zosterin has found extensive use in medicine [3].

The pectin from **Zostera marina** has unique features that distinguish it from the glycans of other land plants. Numerous studies have shown that zosterin has a more complex structure than land plant pectins. Although it, like other pectins, has a linear backbone of rhamnogalacturonan and a branched region, however, the latter is a much more complex configuration. Another “block” is attached to it—xylogalacturonan (chains consisting of rings of galacturonic acid and xylose). Xylogalacturonans were found earlier in pectins of some terrestrial plants (for example, in mountain pine pollen). However, in zosterin, this fragment has additional branches that increase the volume of macromolecules.

The use of zosterin as a dietary supplement has an antiulcer effect, normalizes the function of the gastrointestinal tract, enhances the feeling of satiety, thereby facilitating the tolerance of low-calorie diets. An important property of pectin is its ability to reduce blood cholesterol, which provides an anti-sclerotic effect. Features of the metabolism of pectins allow the use of zosterin in diabetes mellitus as an auxiliary antidiabetic agent. Of exceptional interest are experimental data on the antitumor properties of zosterin and its ability to prolong life, i.e., act as a potential geroprotector. The observed effects indicate the multifunctional nature of the impact of this pectin on the body [4,5]. The therapeutic effect of rosmarinic acid, luteolin and its sulfated derivatives—these are one of the most active components of **Z. marina**—are considered in detail in experimental studies in diseases associated with impaired carbohydrate and lipid metabolism [6].

In this research, supercritical CO₂-extraction of three samples of **Z. marina** was used to obtain an effective amount of polyphenolic substances: old storm seagrass waste, fresh storm seagrass waste, and seagrass collected in water. We used a tandem mass spectrometry to carry out a phytochemical study involving a detailed metabolomic analysis of **Z. marina**. Eelgrass was collected during expedition work near Vityaz Bay, Primorsky Krai, Russia (N 42°36′10″ E 131°10′55″), during the period from 10 to 20 August 2021.
2. Results and Discussion

Three samples of *Z. marina* were subjected to a detailed research: 1. old *Z. marina* ejection on the surf edge, 2. fresh *Z. marina* ejection on the surf edge, 3. *Z. marina* collected in the water. All three *Z. marina* samples were subjected to supercritical CO2-extraction under different extraction conditions. The applied supercritical pressures ranged from 50 to 350 bar, and the extraction temperature ranged from 31 to 70 °C. The co-solvent EtOH was used in an amount of 1% of the total amount of solvent. Used different extraction conditions for different seagrass samples showed the best result for bagging in water (Extraction conditions: pressure 250 bar and temperature 60 °C). The total yield of biologically active substances under these extraction conditions was 4.2 mg per 100 mg of supercritical CO2-extract. The quantitative ratio of the extract of biologically active substances obtained by the method of supercritical extraction was achieved by evaporating the CO2-extract and calculating the ratio of the mass of the extracted plant matrix to the dry mass of the obtained extract. Below are 3D graphs of supercritical extraction of an old *Z. marina* release (Figure 2); fresh release of *Z. marina* (Figure 3); *Z. marina* bagging in water (Figure 4). The structural identification of each compound was carried out on the basis of their accurate mass and MS/MS fragmentation by HPLC–ESI–ion trap–MS/MS. A total of 77 compounds were characterized in three extracts of *Z. marina* based on their accurate MS and fragment ions by searching online databases and the references.

![Graph](image-url)
Figure 3. 3D-graph data of supercritical CO₂-extraction. Total yield of biologically active substances from extracts of Z. marina (fresh seagrass ejection on the surf edge).

Figure 4. 3D-graph data of supercritical CO₂-extraction. Total yield of biologically active substances from extracts of Z. marina (Seagrass collected in water).
There were identified 77 compounds (53 compounds from polyphenol group and 24 compounds from other chemical groups). All the identified polyphenols and other compounds along with molecular formulas, and MS/MS data for Z. marina are summarized in Table A1 (Appendix A). For the first time, 38 polyphenols were identified in this plant. There are polyphenols: flavonoids Kaempferol, Kaempferide, Herbacetic, Dihydroquercetin, Myricetin, Kaempferol 7-sulfate, Isorhamnetin 3-sulfate, Kaempferol-7-O-α-L-rhamnoside, Aromadendrin 7-O-rhamnoside, Quercitrin, Astragalin, Kaempferol 3-(6′-malonylglucoside), Herbacetic-3-O-glucoside-7-O-xilo/ara; flavones Dihydroxy-dimethoxy(iso)flavone, Circumaritin, Cirsimilin, Jaceosidin, 5,6′,4′-Trihydroxy-7,8-dimetoxyflavone, Syringetin, etc.

Figures 5–12 shows examples of the decoding spectra (collision-induced dissociation (CID) spectrum) of the ion chromatogram obtained using tandem mass spectrometry. The CID spectrum in positive ion modes of flavan-3-ol (epi)Afzelechin from Z. marina is shown in Figure 5.

![Figure 5. CID spectrum of (epi)Afzelechin from Z. marina, m/z 275.01.](image)

[M+H]$^+$ ion produced two fragment ions with m/z 245.02 and m/z 175.03 (Figure 5). The fragment ion with m/z 245.02 produced one characteristic daughter ion with m/z 175.01. It was identified in the references in extract from Cassia granatitis [7]; Cassia abbreviata [8]; A. cordifolia; F. glaucescens; F. herrerae [9]. It should be noted separately that the presence of many sulfated polyphenols was found in the supercritical extracts of Z. marina. For example, these are the following chemical compounds: Luteolin 7-sulfate; Diosmetin 7-sulfate, Kaempferol 7-sulfate, Isorhamnetin 3-sulfate, Apigenin7-sulfate, Chrysoeriol 7-sulfate, Luteolin 7,3′-disulfate, (2S)-Naringenin 4′-O-sulfate. The CID spectrum in positive ion modes of flavone Luteolin 7-sulfate from Z. marina is shown in Figure 6.

![Figure 6. CID spectrum of Luteolin 7-sulfate from Z. marina, m/z 366.82.](image)
[M+H]^+ ion produced one fragment ion with m/z 286.89 (Figure 6). The fragment ion with m/z 286.89 produced two characteristic daughter ions with m/z 152.96, and m/z 268.95. It was identified in the bibliography in extracts from Z. marina [10,11]. The CID spectrum in negative ion modes of flavone Apigenin 7-sulfate from Z. marina is shown in Figure 7.

![Figure 7](image7.png)

**Figure 7.** CID spectrum of Apigenin 7-sulfate from Z. marina, m/z 348.95.

[M-H]^− ion produced one fragment ion with m/z 268.96 (Figure 7). The fragment ion with m/z 268.96 produced two characteristic daughter ions with m/z 225.01 and m/z 268.93. The fragment ion with m/z 225.01 formed one daughter ion with m/z 197.01. It was identified in the bibliography in extracts from G. linguiforme [9]; Z. marina [11]; sulphates [12]. We also want to separately note the first identification of the presence of a large class of anthocyanins in Z. marina. Pelargonidin 3-O-glucoside; Cyanidin 3-O-glucoside; Pelargonidin 3-O-(6-O-malonyl-beta-D-glucoside); Cyanidin 3-(6'-malonylglucoside). All these anthocyanins were identified firstly in Z. marina. The CID spectrum in positive ion modes of anthocyanin Pelargonidin 3-O-glucoside from Z. marina is shown in Figure 8.

![Figure 8](image8.png)

**Figure 8.** CID spectrum of Pelargonidin 3-O-glucoside acid from Z. marina, m/z 432.55.

[M+H]^+ ion produced one fragment ion with m/z 270.90. (Figure 8). The fragment ion with m/z 270.90 formed five daughter ions with m/z 152.88, m/z 224.93, m/z 202.95, m/z 162.85, and m/z 118.96. It was identified in the bibliography in extract from Rubus ulmifolius [13]; Strawberry [14]; Vigna unguiculata [15].

The CID spectrum in positive ion modes of anthocyanin Pelargonidin 3-O-(6-O-malonyl-beta-D-glucoside) from Z. marina is shown in Figure 9. [M+H]^+ ion produced two fragment ions with m/z 270.91, and m/z 432.81 (Figure 9). The fragment ion with m/z 270.91 formed two daughter ions with m/z 153.00, m/z 224.93. It was identified in the bibliography in extract from Strawberry [14], Wheat [16].
Figure 9. CID spectrum of Pelargonidin-3-O-(6-O-malonyl-beta-D-glucoside) acid from *Z. marina*, m/z 518.85.

The CID spectrum in negative ion modes of flavonol Kaempferol 7-sulfate from *Z. marina* is shown in Figure 10. [M–H]– ion produced one fragment ion with m/z 284.92 (Figure 10). The fragment ion with m/z 284.92 formed four daughter ions with m/z 266.90, m/z 256.96, m/z 238.98, and m/z 213.03. It was identified in the bibliography in extract from *F. pulverulenta* Frankeniaceae [12].

Figure 10. CID spectrum of Kaempferol 7-sulfate from *Z. marina*, m/z 364.87.

The CID spectrum in negative ion modes of phenolic acid Sagerinic acid from *Z. marina* is shown in Figure 11. [M–H]– ion produced two fragment ions with m/z 358.92 and m/z 197.02 (Figure 11). The fragment ion with m/z 358.92 formed two daughter ions with m/z 179.08, m/z 161.03. It was identified in the bibliography in extract from *Mentha* [17]; *Lamiaceae* spp. [18]; *Lepechinia* [19].
The CID spectrum in positive ion mode of hydroxycoumarin Umbelliferone from Z. marina is shown in Figure 12. [M+H]+ ion produced one fragment ion with m/z 144.99 (Figure 12). The fragment ion with m/z 144.99 produced one characteristic daughter ion with m/z 117.08. It was identified in the bibliography in extracts from F. glaucescens [9]; Sanguisorba officinalis [20]; Actinidia chinensis [21].

Separately, it should be noted that a detailed analysis of the presence of polyphenols and biologically active substances from other chemical groups showed the highest number of compounds in the seagrass collected in water and fresh release on the shore than in the old release on the shore. The ratio was 31 and 30 versus 26 for polyphenols, respectively (Table 1).

**Table 1.** Identified polyphenols by tandem mass-spectrometry in three samples: eelgrass collected in water; fresh eelgrass ejection on the surf edge; old eelgrass ejection on the surf edge.

| №  | Class of Compounds | Identified Polyphenols                          | Seagrass Collected in Water | Fresh Seagrass Ejection on the Surf Edge | Old Seagrass Ejection on the Surf Edge |
|----|-------------------|-----------------------------------------------|-----------------------------|----------------------------------------|---------------------------------------|
| 1  | Flavonol          | Kaempferol [3,5,7-Trihydroxy-2-(4-hydroxyxyphenyl)-4H-chromen-4-one] * | Green                       | Blue                                   | Red                                   |
| 2  | Flavonol          | Kaempferide [4'-O-Methylkaempferol] *          |                             |                                       |                                       |
| 3  | Flavonol          | Herbacetin [3,5,7,8-Tetrahydroxy-2-(4-hydroxyxyphenyl)-4H-chromen-4-one] * | Green                       | Blue                                   | Red                                   |
| 4  | Flavonol          | Dihydroquercetin [Taxifolin; Taxifolin] *     |                             |                                       |                                       |
| No. | Flavonoid | Structure |
|-----|-----------|-----------|
| 5   | Flavonol  | Myricetin [3,5,7-Trihydroxy-2-(3,4,5-Trihydroxyphenyl)-4H-Chromen-4-One] * |
| 6   | Flavonol  | Kaempferol 7-sulphate * |
| 7   | Flavonol  | Isoharnetin 3-sulphate * |
| 8   | Flavonol  | Kaempferol-7-O-α-L-rhamnopyranoside * |
| 9   | Flavonol  | Aromadendrin 7-O-rhamnoside * |
| 10  | Flavonol  | Quercitrin [Quercetin 3-L-rhamnopyranoside; Quercetin] * |
| 11  | Flavonol  | Astragalin * |
| 12  | Flavonol  | Kaempferol 3-(6''-malonylglucoside) * |
| 13  | Flavonol  | Herbacetin-3-O-glucoside-7-O-xyl/ara * |
| 14  | Flavone   | Luteolin |
| 15  | Flavone   | Diosmetin |
| 16  | Flavone   | Chrysoeriol [Chryseriol] |
| 17  | Flavone   | Dihydroxy-dimethoxy(iso)flavone * |
| 18  | Flavone   | Cirsimaritin * |
| 19  | Flavone   | Cirsiliol * |
| 20  | Flavone   | Jaceosidin [5,7,4'-trihydroxy-6',5'-dimethoxyflavone] * |
| 21  | Flavone   | 5,6,4'-Trihydroxy-7,8-dimethoxyflavone * |
| 22  | Flavone   | Syringetin * |
| 23  | Flavone   | Apigenin 7-sulfate |
| 24  | Flavone   | Hydroxy-tetramethoxy(iso) flavone * |
| 25  | Flavone   | Luteolin 7-sulphate |
| 26  | Flavone   | Chrysoeriol-7-sulphate |
| 27  | Flavone   | Diosmetin-7-sulphate |
| 28  | Flavone   | Luteolin 7-O-glucoside [Cynaroside; Luteoloside] |
| 29  | Flavone   | Linarin [Acaciin; Buddleoside; Acacetin-7-O-Rutinoside; Linarigenin Glycoside] * |
| 30  | Flavone   | Apigenin 6-C[6''-acetyl-2''-O-deoxyhexosid]glucoside * |
| 31  | Flavone   | Acacetin-acetyl-glucoside-rhamnoglucoside |
| 32  | Flavone   | Luteolin 7,3'-disulphate |
| 33  | Flavan-3-ol| Epiafzelechin [epiafzelechin] * |
| 34  | Flavan-3-ol| Derivative of (epiafzelechin) * |
| 35  | Flavan-3-ol| Catechin [D-Catechin] * |
| 36  | Flavan-3-ol| (epi)Catechin * |
| 37  | Flavan-3-ol| (epi)Afzelechin derivative * |
| 38  | Flavan-3-ol| Catechin derivative * |
| 39  | Flavanone  | (2S)-Naringenin 4'-O-sulfate * |
| 40  | Anthocyanin| Pelargonidin-3-O-glucoside (callistephin) * |
| 41  | Anthocyanin| Cyanidin-3-O-glucoside [Cyanidin 3-O-beta-D-Glucoside; Kuromanin] * |
| 42  | Anthocyanin| Pelargonidin 3-O-(6' O-malonyl-beta-D-glucoside) * |
| 43  | Anthocyanin| Cyanidin 3-6''-malonylglucoside) * |
| 44  | Phenolic acids and derivatives | Zosteric acid [P-Sulfoxyccinnamic acid; 4-Hydroxycinnamate Sulfate] |
| 45  | Phenolic acids and derivatives | Caffeic acid [(2E)-3-(3,4-Dihydroxyphenyl)acrylic acid] |
| 46  | Phenolic acids and derivatives | Caffeic acid derivative |
| 47  | Phenolic acids and derivatives | 3-O-cafeoylshikimic acid [3-Csa] * |
| 48  | Phenolic acids and derivatives | Rosmarinic acid |
| 49  | Phenolic acids and derivatives | Caffeic acid derivative |
Thus, it can be stated that as a result of the most detailed study by tandem mass spectrometry, new data on the content of biologically active substances in Z. marina have been obtained.

3. Materials and Methods

3.1. Materials

Phytomass of Z. marina was collected during expedition work near Vityaz Bay, Primorsky Krai, Russia (N 42°36′10″ E 131°10′55″), during the period from 10 to 20 August 2021. All samples were morphologically authenticated according to the current standard of Pharmacopeia of the Eurasian Economic Union [22].

3.2. Chemicals and Reagents

HPLC-grade acetonitrile was purchased from Fisher Scientific (Southborough, UK), MS-grade formic acid was from Sigma-Aldrich (Steinheim, Germany). Ultra-pure water was prepared from a SIEMENS ULTRA clear (SIEMENS water technologies, Munich, Germany), and all other chemicals were analytical grade.

3.3. SC-CO₂: Extraction

SC-CO₂ extraction was performed using the SFE-500 system (Thar SCF Waters, Milford, CT, USA) supercritical pressure extraction apparatus. System options include: Co-solvent pump (Thar Waters P-50 High Pressure Pump), for extracting polar samples. CO₂ flow meter (Siemens, Germany), to measure the amount of CO₂ being supplied to the system, multiple extraction vessels, to extract different sample sizes or to increase the throughput of the system. Flow rate was 10–25 mL/min for liquid CO₂ and 1.00 mL/min for EtOH. Extraction samples of 20 g Z. marina were used. The extraction time was counted after reaching the working pressure and equilibrium flow, and it was 60–90 min for each sample.

3.4. Liquid Chromatography

HPLC was performed using Shimadzu LC-20 Prominence HPLC (Shimadzu, Japan) was used, equipped with an UV-sensor and a Shodex ODP-40 4E reverse phase column to perform the separation of multicomponent mixtures. The gradient elution program was as follows: 0.01–4 min, 100% C₅H₇N; 4–60 min, 100–25% C₅H₇N; 60–75 min, 25–0% C₅H₇N; control washing 75–120 min 0% C₅H₇N. The entire HPLC analysis was performed using a UV-VIS detector SPD-20A (Shimadzu, Japan) at wavelengths of 230 and 330 nm, at 17 °C provided with column oven CTO-20A (Shimadzu, Japan) with an injection volume of 20 μL.

3.5. Mass Spectrometry

MS analysis was performed on an ion trap amaZon SL (BRUKER DALTONIKS, Germany) equipped with an ESI source in negative ion mode. The optimized parameters were obtained as follows: ionization source temperature: 70°C; gas flow: 4 L/min, nebulizer gas (atomizer): 7.3 psi, capillary voltage: 4500 V, end plate bend voltage: 1500V, fragmentary: 280 V, collision energy: 60 eV. An ion trap was used in the scan range m/z 100 -1.700 for MS and MS/MS. The mass spectra were recorded in negative and positive ion mode. The capture rate was one spectrum/s for MS and two spectrum/s for MS/MS. Data collection was controlled by Hystar Data Analysis 4.1 software (BRUKER DALTONIKS, Bremen, Germany). All experiments were repeated three times. A four-stage ion separation mode
(MS/MS mode) was implemented. After a comparison of the m/z values, retention times, and the fragmentation patterns with the MS/MS spectral data retrieved from the cited articles and after a database search (MS2T, MassBank, HMDB), a comprehensive table was compiled of the molecular masses of the analytes isolated from CO2 extracts of Z. marina for ease of annotation (Appendix A (Table A1)).

4. Conclusions

Three types of Zostera marina L. collection were extracted using the supercritical CO2-extraction method. For the purposes of supercritical CO2-extraction, old seagrass ejection on the surf edge, fresh seagrass ejection on the surf edge and seagrass collected in water were used. Several experimental conditions were investigated in the pressure range 50–350 bar, with the used volume of co-solvent ethanol in the amount of 1% in the liquid phase at a temperature in the range of 31–70 °C. The most effective extraction conditions are: pressure 250 Bar and temperature 60 °C for Z. marina collected in sea water. Z. marina contain various phenolic compounds and sulfated polyphenols with valuable biological activity. Tandem mass-spectrometry (HPLC-ESI-ion trap) was applied to detect target analytes. High-accuracy mass spectrometric data were recorded on an ion trap amaZon SL BRUKER DALTONIKS equipped with an ESI source in the mode of negative and positive ions. The four-stage ion separation mode was implemented. 77 different biologically active components have been identified in Z. marina supercritical CO2-extracts. 38 polyphenols were identified for the first time in Z. marina.

These data could support future research for the production of a variety of pharmaceutical products containing extracts of Z. marina. The richness of various biologically active compounds, including compounds of polyphenol group, amino acids, carotenoids, Omega-fatty acids, sterols, triterpenoids, iridoids, etc., provides great opportunities for the design of new nutritional and dietary supplements based on extracts from this genus Zostera.

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

Funding: This research was carried out with financial support of the Ministry of Education and Science of the Russian Federation within the framework of the implementation of a complex project for the creation of high-tech production provided by the Decree of the Russian Federation Government dated 9 April 2010 № 218. The project is entitled “Development of industrial technology and organization in the Far Eastern Federal District of the high-tech production of feed Vitamin A of increased stability and bioavailability”, agreement No. 075-11-2021-065, 25 June 2021.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are available from the corresponding author upon request.

Acknowledgments: Research work according to “Development of industrial technology and organization in the Far Eastern Federal District of the high-tech production of feed Vitamin A of increased stability and bioavailability”, agreement No. 075-11-2021-065, 25 June 2021.

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

Table A1. Compounds identified from the CO₂-extracts of Zostera marina in positive and negative ionization modes by HPLC-ion trap-MS/MS.

| №  | Class of Compounds | Identified Compounds                                                                 | Formula   | Mass | Molecule ion [M-H]- | Molecule ion [M+H]+ | 2 fragmentations MS/MS | 3 fragmentations MS/MS | 4 fragmentations MS/MS | References |
|----|--------------------|--------------------------------------------------------------------------------------|-----------|------|----------------------|----------------------|------------------------|------------------------|------------------------|------------|
| 1  | Flavonol           | Kaempferol [3,5,7-Trihydroxy-2-((4-hydroxy-xyphenyl)-4H-chromen-4-one) *]            | C_{15}H_{10}O_{6} | 286.24 | 287                  | 258; 241; 187; 137   | 229; 213; 153          | 203; 132               | Rhus coriaria [23]; Andean blueberry [24]; Potato leaves [25]; Impatiens glandulifera Royle [26]; Rapeseed petals [27]; Rh. sichotense [28] |
| 2  | Flavonol           | Kaempferide [4’-O-Methylkaempferol] *                                                 | C_{16}H_{12}O_{6} | 300.262 | 9                    | 301                  | 286                    | 258                    | 229; 201; 153          | Ocmium [30]; Alpinia officinarum [31]; Brazilian propolis [32] |
| 3  | Flavonol           | Herbacetin [3,5,7,8-Tetrahydroxy-2-(4-hydroxy-xyphenyl)-4H-chromen-4-one] *          | C_{15}H_{10}O_{7} | 302.235 | 7                    | 303                  | 275; 202; 185; 157    | 175; 157               | Ocmium [30]; Rhodiola rosea [33] |
| 4  | Flavonol           | Dihydroquercetin [Taxifolin; Taxifoliol] *                                           | C_{15}H_{10}O_{7} | 304.25  | 303                  | 285                  | 267; 241; 215; 135    | 171                    | Andean blueberry [24]; millet grains [34]; Camellia kucha [35]; Rosa rugosa [36] |
| 5  | Flavonol           | Myricetin [3,5,7-Trihydroxy-2-(3,4,5-Trihydroxyphenyl)-4H-Chromen-4-One] *           | C_{15}H_{10}O_{8} | 318.235 | 1                    | 319                  | 289; 261; 239; 219; 191; 173 | 261; 243; 214; 191; 173 | 159; 233; 215; 191; 161; 143 | Sanguisorba officinalis [20]; Andean blueberry [24]; millet grains [34]; Rosa rugosa [36]; Vaccinium macrocarpon [37] |
| 6  | Flavonol           | Kaempferol 7-sulphate *                                                              | C_{18}H_{10}O_{9} | 366.299 | 5                    | 365                  | 285                    | 241; 199; 151; 197; 171; 143 | F. pulverulenta Frankeniaceae [12] |
| 7  | Flavonol           | Isorhamnetin 3-sulphate *                                                            | C_{15}H_{10}O_{7} | 394.309 | 6                    | 393                  | 313                    | 298                    | 269                    | Senecio galicus Asteraceae; Polygonum hydropiper Polygoniaceae [12] |
| 8  | Flavonol           | Kaempferol-7-O-α-L-rhamnositne *                                                    | C_{15}H_{10}O_{8} | 432.377 | 5                    | 431                  | 257                    | 227; 157               | 215; 145               | Rhodiola crenulata [38]; Rhodiola sachalinensis [39] |
| 9  | Flavonol           | Aromadendrin 7-O-rhamnoside *                                                       | C_{15}H_{10}O_{8} | 434.393 | 4                    | 433                  | 259; 229               | 227; 199; 157          | 215; 199               | Eucalyptus [40] |
| 10 | Flavonol           | Quercitin [Quercetin 3-L-rhamnoside; Quercetrin] *                                  | C_{19}H_{10}O_{11} | 448.376 | 9                    | 449                  | 303; 203               | 203                    | 185                    | Rhus coriaria [23]; Camellia kucha [35]; Vaccinium macrocarpon [37,41]; Propolis [42] |
| 11 | Flavonol | Astragalin [Kaempferol 3-O-glucoside; Kaempferol-3-Beta-Monoglucoside; Astragaline] * | C_{21}H_{20}O_{11} | 448.376 | 9 | 449 | 287; 367 | 153; 240 |
| 12 | Flavonol | Kaempferol 3-(6''-malonylglucoside) * | C_{21}H_{20}O_{11} | 534.423 | 1 | 535 | 449; 287 | 263; 219; 153 |
| 13 | Flavonol | Herbacetin-3-O-glucoside-7-O-xylo/ara * | C_{21}H_{20}O_{11} | 596.490 | 9 | 597 | 436 | 389; 327; 240; 221; 194 | 194; 150 |
| 14 | Flavone | Luteolin | C_{15}H_{10}O_{6} | 286.236 | 3 | 287 | 152; 241; 187 |
| 15 | Flavone | Diosmetin | C_{15}H_{10}O_{6} | 300.262 | 9 | 299 | 283; 256 |
| 16 | Flavone | Chrysoeriol [Chrysoeriol] | C_{15}H_{10}O_{6} | 300.262 | 9 | 301 | 286; 244; 203 | 258 | 229 |
| 17 | Flavone | Dihydroxydimethoxy(iso)flavone * | C_{17}H_{14}O_{6} | 314.289 | 5 | 315 | 299; 271; 215; 169 | 297; 271; 253; 229; 186 | 269; 253; 145 |
| 18 | Flavone | Cirsimaritin * | C_{17}H_{14}O_{6} | 314.289 | 5 | 315 | 299; 282; 254 | 254 | 226; 197; 181; 169; 153 |
| 19 | Flavone | Cirsiliol * | C_{17}H_{14}O_{6} | 330.288 | 9 | 331 | 298; 203 | 270 | 241 |
| 20 | Flavone | Jacosidin [5,7,4''-trihydroxy-6',5'-dimetoxyflavone] * | C_{17}H_{14}O_{6} | 330.288 | 9 | 331 | 303; 285; 257; 231 | 203; 184; 157 | 185; 157; 127 |
| 21 | Flavone | 5,6,4''-Trihydroxy-7,8-dimetoxyflavone * | C_{17}H_{14}O_{6} | 330.288 | 9 | 331 | 303; 257; 223; 203 | 275; 221; 203 | 245; 175; 143 |
| 22 | Flavone | Syringetin * | C_{17}H_{14}O_{6} | 346.288 | 3 | 347 | 318; 291; 247; 219 | 291; 261; 219 | 273; 261; 243; 191 |
| 23 | Flavone | Apigenin 7-sulfate | C_{17}H_{14}O_{6} | 350.300 | 1 | 349 | 269 | 225; 197; 159 | 197 |
| 24 | Flavone | Hydroxy-tetramethoxy(iso)flavone * | C_{17}H_{14}O_{6} | 358.342 | 359 | 315 | 256; 190 |
| 25 | Flavone | Luteolin 7-sulphate | C_{17}H_{14}O_{6} | 366.299 | 5 | 367 | 287 | 153; 259; 241; 219; 199; 179 | 123 |
| 26 | Flavone | Chrysoeriol-7-sulphate | C_{17}H_{14}O_{6} | 380.326 | 1 | 381 | 301; 286 | 258 | Zostera marina [10] |

* Actinidia chinensis [21]; Rapeseed petals [27]; Spondias purpurea [29]; Camellia kucha [35]; Lonicera japonicum [43]; A. cordifolia [9]; Impatiens glandulifera Royle [26]; Mexican lupine species [44].

Zostera marina [11]; Propolis [42]; Lonicera japonicum [43]; Dracocephalum palatum [46]; Andean blueberry [24]; Lonicera japonicum [43]; Cirsium japonicum [47]; Mentha [48]; Rhus coriaria [23]; Mexican lupine species [44]; Dracocephalum palatum [46]; Mentha [48]; Ocimum [30]; Rosmarinus officinalis [49]; Astragalus radix [50]; F. glaucescens; F. herrerae [9]; Mentha [48]; C. edulis [9]; Zostera marina [11]; G. linguiforme [9]; sulphates [12].
| 27 | Flavone | Diosmetin-7-sulphate | C_{16}H_{12}O_{9}S | 380.326 | 1 | 379 | 299 | 284 | Zostera marina [10; 11] |
| 28 | Flavone | Luteolin 7-O-glucoside (Cynaroside; Luteoloside) | C_{21}H_{20}O_{11} | 448.376 | 9 | 449 | 287 | 213; 137 | 185 |
| 29 | Flavone | Linarin [Acaciin; Buddleioside; Acacetin-7-O-Rutinoside; Linarigenin Glycoside] * | C_{16}H_{12}O_{6} | 592.545 | 3 | 593 | 575; 377; 197 | 377 | 197 | Dracecephalum palmatum [46]; Mentha [48,51,53] |
| 30 | Flavone | Apigenin 6-C-[6'-acetyl-2'-O-deoxyhexoside]-glucoside * | C_{21}H_{20}O_{10} | 620.555 | 4 | 621 | 561 | 461 | 433 | Passiflora incarnata [54] |
| 31 | Flavone | Acacetin-acetyl-glucoside-rhamnoglucoside | C_{16}H_{12}O_{11} | 796.636 | 4 | 797 | 519 | 240; 185 | Zostera marina [10] |
| 32 | Flavone | Luteolin 7,3'-disulphate | C_{15}H_{10}O_{12}S_{2} | 446.362 | 7 | 447 | 287; 366 | 241 | Zostera marina [10] |
| 33 | Flavan-3-ol | Epiafzelechin [(epi)Afzelechin] * | C_{18}H_{12}O_{6} | 274.268 | 7 | 275 | 244; 233; 216; 193 | 237; 213; 192; 175; 15; 145 | Cassia grandis [7]; Cassia abbreviata [8]; A. cordifolia; F. glaucescens; F. herrerae [9] |
| 34 | Flavan-3-ol | Derivative of (epi)Afzelechin * | C_{18}H_{12}O_{6} | 276.284 | 5 | 277 | 245; 229; 216; 207 | 233; 215 | 211 | millet grains [34]; Camellia kucha [35]; Vaccinium macrocarpon [41]; Eucalyptus [55]; Radix polygoni multiflori [56]; Rh. rosea [57] |
| 35 | Flavan-3-ol | Catechin [D-Catechol] * | C_{21}H_{20}O_{11} | 290.268 | 1 | 291 | 261; 173 | 243; 191; 173; 143 | 143; 125 | Andean blueberry [24]; millet grains [34]; Vaccinium macrocarpon [41]; Eucalyptus [55]; Rubus occidentalis [58] |
| 36 | Flavan-3-ol | (epi)Catechin * | C_{21}H_{20}O_{11} | 290.268 | 1 | 291 | 261; 231; 209; 191; 173 | 243; 215; 199; 179; 161 | 233; 206; 180; 161; 138 | Tamarix africana [59] |
| 37 | Flavan-3-ol | (epi)Afzelechin derivative * | C_{21}H_{20}O_{10} | 392.313 | 6 | 393 | 274 | 245; 221; 205; 191; 175; 157 | 237; 192; 176; 157 | Rubus ulmifolius [13]; Strawberry [14]; Vigna unguiculata [15] |
| 38 | Flavan-3-ol | Catechin derivative * | C_{21}H_{20}O_{11} | 424.355 | 4 | 425 | 291 | 261; 173 | 173 | Rubus ulmifolius [13]; Rapeseed petals [27]; Berberis ilicifolia; Berberis empetrifolia; Ribes maellanicum; |
| 39 | Flavanone | (2S)-Naringenin 4'-O-sulfate * | C_{15}H_{12}O_{4}S | 352.316 | 0 | 351 | 271 | 269 | 225 | Rubus ulmifolius [13]; Strawberry [14]; Vigna unguiculata [15] |
| 40 | Anthocyanin | Pelargonidin-3-O-glucoside (callistephin) * | C_{21}H_{20}O_{6} | 433.385 | 4 | 433 | 271 | 153; 247; 225; 187; 163 | 127 | Rubus ulmifolius [13]; Rapeseed petals [27]; Berberis ilicifolia; Berberis empetrifolia; Ribes maellanicum; |
| 41 | Anthocyanin | Cyanidin-3-O-glucoside (Cyaniun 3-O-beta-D-Glucoside; Kuromarin) * | C_{21}H_{20}O_{6} | 449.384 | 8 | 449 | 287 | 241; 153 | Rubus ulmifolius [13]; Rapeseed petals [27]; Berberis ilicifolia; Berberis empetrifolia; Ribes maellanicum; |
| 42 | Anthocyanin | Pelargonidin-3-O-(6-O-malonyl-beta-D-glucoside) * | C_{26}H_{32}O_{17} | 519.438 | 8 | 519 | 271; 433 | 153; 224 | Strawberry [14]; Wheat [16] |
| 43 | Anthocyanin | Cyanidin 3-(6”-malonylglucoside) * | C_{28}H_{34}O_{18} | 535.431 | 0 | 535 | 287; 449 | 241; 153 | Wheat [16]; Strawberry [14,62] |
| 44 | Phenolic acids and derivatives | Zosteric acid [P-Sulfoxyccinnamic acid; 4-Hydroxycinnamate Sulfate] | C_{16}H_{16}O_{5}S | 244.221 | 2 | 245 | 145; 202 | 141 | Zostera marina [11] |
| 45 | Phenolic acids and derivatives | Caffeic acid [(2E)-3-(3,4-Dihydroxyphenyl)acrylic acid] | C_{16}H_{18}O_{4} | 180.157 | 4 | 181 | 135; 163; 145; 121 | 119 | |
| 46 | Phenolic acids and derivatives | Caffeic acid derivative | C_{16}H_{16}O_{5} | 222.235 | 6 | 221 | 181 | 142 | Embelia [63] |
| 47 | Phenolic acids and derivatives | 3-O-caffeoylshikimic acid [3-Csa] * | C_{26}H_{32}O_{15} | 336.293 | 4 | 337 | 191; 173; 153 | 123 | Gratagi Fructus [64] |
| 48 | Phenolic acids and derivatives | Rosmarinic acid | C_{16}H_{18}O_{8} | 360.314 | 8 | 359 | 161; 135 | 133 | |
| 49 | Phenolic acids and derivatives | Caffeic acid derivative | C_{23}H_{24}O_{7} | 377.298 | 5 | 376 | 341; 215 | 179 | 119 | Embelia [63]; Bougainvillea [66] |
| 50 | Phenolic acids and derivatives | Ellagic acid pentoside [Ellagic acid 4-O-xylpyranoside] * | C_{28}H_{32}O_{15} | 434.307 | 3 | 433 | 257 | 227; 157 | 215 | Escalliptus [40]; Strawberry [62]; Punica granatum [67] |
| 51 | Phenolic acids and derivatives | Sagerinic acid * | C_{26}H_{32}O_{16} | 720.629 | 7 | 719 | 359 | 161 | Mentha [17]; Lamiaceae spp. [18]; Lepechinia [19] |
| 52 | Hydroxycoumarin | Umbelliferone [Skimmetin; Hydragin] * | C_{16}H_{14}O_{4} | 162.142 | 1 | 163 | 145 | 117 | F. glaucescens [9]; Sanguisorba officinalis [20]; Actinidia chinensis [21] |
| 53 | Dihydrochalcone | Phloretin [Dihydronaringenin; Phloretol] * | C_{26}H_{32}O_{12} | 274.268 | 7 | 275 | 245; 175; 214; 175 | | G. linguiiforme [9]; Escalliptus [55]; Punica granatum [67] |

**OTHERS**
| 54 | Cyclohexane carbonyl oxalic acid | Perilllic | C₂₁H₂₆N₃O₈ | 219 | 166.217 | 167 | 149 | 147 | 137 | Mentha [48] |
| 55 | Amino acid | L-threonine | C₉H₁₈N₂O₃ | 174.197 | 7 | 271 | 175 | 157; 147; 125 | 147; 129 | Camelia kucha [35] |
| 56 | Omega-5 fatty acid | Myristoleic acid [Cis-9-Tetradecanoic acid] * | C₁₄H₂₉O₂ | 226.355 | 0 | 227 | 175 | 192; 139 | 122 | F. glaucescens [9] |
| 57 | Carotenoid | 3-OH-beta-apo-11-carotenal | C₂₉H₄₈O₂ | 234.334 | 0 | 235 | 175 | 157 | 140 | Carotenoids [68] |
| 58 | Peptide | 5-Oxo-L-propyl-L-isoleucine | C₁₆H₂₈N₄O₇ | 242.271 | 6 | 243 | 175 | 141 | 131 | Potato leaves [25] |
| 59 | Carotenoid | beta-apo-13-carotenal | C₂₉H₄₈O₂ | 258.498 | 4 | 260 | 175 | | | Carotenoids [68] |
| 60 | Aporphine alkaloid | Anonaine | C₂₃H₃₂N₂O₄ | 265.306 | 5 | 266 | 175 | 202 | | Magnolia [69] |
| 61 | Anthraquinone | Emolin [6-Methyl-1,3,8-trihydroxyanthraquinone] | C₂₃H₂₆O₉ | 270.236 | 9 | 271 | 175 | 162 | | |
| 62 | Omega-3 fatty acid | Linolenic acid (Alpha-Linolenic acid; Linolenate) | C₁₈H₃₀O₃ | 278.429 | 6 | 277 | 175 | 205 | 273 | Salviae [71]; rice [72]; Pinus sylvestris [73] |
| 63 | Omega-9 unsaturated fatty acid | Oleic acid (Cis-9-Octadecenoic acid; Cis-Oleic acid) | C₁₈H₃₂O₂ | 282.461 | 4 | 283 | 175 | 197 | | Zosperma marina [11]; Sanguisorba officinalis [20]; Huolisu Oral Liquid [65] |
| 64 | Carotenoid | Apo-14'-Zeaxanthinal | C₂₉H₄₈O₂ | 326.473 | 5 | 327 | 175 | 222 | | Carotenoids [74] |
| 65 | Amino disaccharide | Trehalosyl 2,4,6'-triamine | C₂₉H₄₈O₄ | 340.350 | 1 | 341 | 175 | 331 | | [75] |
| 66 | Omega-hydroxy-long-chain-fatty acid | Hydroxy docosanoic acid | C₂₉H₄₈O₂ | 356.583 | 355 | 309 | 175 | 287 | A. cordifolia [9] |
| 67 | Sterol | Stigmasterol [Stigmasterin; Beta-Stigmasterol] | C₂₃H₃₆O₃ | 412.690 | 8 | 413 | 175 | 189 | 171 | A. cordifolia; F. pottsii [9]; Oryza sativa [61]; Olive leaves [76]; Hedoptis diffusa [77] |
| 68 | Sterol | Fucosterol [Fucosten; Trans-24-Ethylidenecholesterol] * | C₂₃H₃₆O₃ | 412.690 | 8 | 413 | 175 | 189 | 189 | F. pottsii [9]; Oryza sativa [61] |
| 69 | Sterol | Beta-Sitostenone [Stigmaster-4-En-3-One; Sitostenone] | C₂₃H₃₆O₃ | 412.690 | 8 | 413 | 175 | 189 | 171 | F. herrerana [9]; Cryptomeria japonica bark [78]; Xanthium sibiricum [79]; Terminalia laxiflora [80] |
| 70 | Iridoid monoterpenoid | Dihydroxysovaltrate | C₂₀H₂₆O₈ | 424.484 | 7 | 425 | 175 | 235 | 253 | Rhus coriaria [23] |
| 71 | Sterol | Sigmast-4-en-6-beta-ol-3-one | C₂₀H₂₆O₈ | 428.690 | 2 | 429 | 175 | 261 | | Xanthium sibiricum [79] |
| 72 | Anabolic steroid; Androgen; Androgen ester | Vebonol | C₁₈H₂₆O₂ | 452.668 | 6 | 453 | 175 | 226 | 139 | Rhus coriaria [23]; Hylocereus polyrhizus [81] |
| 73 | Triterpenic acid | 1-Hydroxy-3-oxo-12-en-28-oic acid | C₂₀H₃₄O₈ | 470.683 | 8 | 471 | 175 | 182 | | Pear [82] |
| 74 | Carotenoid | (all-E)-lutein 3'-O-myristate | C₂₀H₂₆O₈ | 550.856 | 2 | 551 | 175 | 303 | | Carotenoids [83]; Rosa rugosa [84] |
| 75 | Carotenoid | Antheraxanthin [All-Trans-Antheraxanthin] | C₂₀H₂₆O₈ | 584.870 | 8 | 585 | 175 | 377 | | Carotenoids [83]; Sarsaparilla [85]; Arbutus unedo [86] |
| 76  | Carotenoid (all-E)-Violaxanthin | C₂₅H₃₄MgN₂O₆ | 600.870 | 2 | 601 | 581; 540; 501; 415; 301 | 523; 442; 290 | Rosa rugosa [84]; Arbutus unedo [86]; Carica papaya [87]; Physalis peruviana [88] |
| 77  | Chlorophyll derivative | Chlorophyllide a | C₄₀H₅₆O₄ | 614.973 | 3 | 615 | 579; 545; 528; 478 | 508 | [89,90] |

* Compounds identified for the first time in *Z. marina*.

References

1. Seshagiri, R. Ecology of the marine protists, the Labyrinthulomycetes (Thraustochytrids and Labyrinthulids). *Eur. J. Protistol.* 2002, 38, 127–145.
2. Loenko, U.N.; Artyukov, A.A.; Kozlovskaya, E.P. *Zosterin*; Dal’nauka: Vladivostok, Russia, 1997; 212p.
3. Ovodova, Y.; Ovodova, R.; Bondarenko, O.; Krasikova, I. The pectic substances of zosteraceae: Part IV. Pectinase digestion of zostericine. *Carbohydr. Res.* 1971, 18, 311–318.
4. Wang, H.; Tang, X.; Chen, J.; Shang, S.; Zhu, M.; Liang, S.; Zang, Y. Comparative studies on the response of Zostera marina leaves and roots to ammonium stress and effects on nitrogen metabolism. *Aquat. Toxicol.* 2021, 240, 105965.
5. Zhao, W.; Yang, X.-Q.; Zhang, Q.-S.; Tan, Y.; Liu, Z.; Ma, M.-Y.; Wang, M.-X.; Xu, B. Photoinactivation of the oxygen-evolving complex regulates the photosynthetic strategy of the seagrass Zostera marina. *J. Photochem. Photobiol. B Biol.* 2021, 222, 112529.
6. Popov, A.M.; Krivoshapko, O.N.; Klimovich, A.A.; Artyukov, A.A. Biological activity and mechanisms of therapeutic action of rosmarynic acid, luteolin and its sulphated derivatives. *Biomeditsinskaya Khimiya* 2016, 62, 22–30.
7. Fuentes, J.A.M.; López-Salas, L.; Borras-Linares, I.; Navarro-Alarcón, M.; Segura-Carretero, A.; Lozano-Sánchez, J. Development of an Innovative Pressurized Liquid Extraction Procedure by Response Surface Methodology to Recover Bioactive Compounds from Carao Tree Seeds. *Foods* 2021, 10, 398.
8. Sobeh, M.; Mahmoud, M.; Abdelfattah, M.A.; Cheng, H.; El-Shazly, A.M.; Wink, M. A proanthocyanidin-rich extract from Cassia abbreviata exhibits antioxidant and hepatoprotective activities in vivo. *J. Ethnopharmacol.* 2018, 213, 38–47.
9. Hamed, A.R.; El-Hawy, S.S.; Ibrahim, R.M.; Abdelmolsen, U.R.; El-Halawany, A.M. Identification of Chemopreventive Components from Halophytes Belonging to Aizoaceae and Cactaceae Through LC/MS—Bioassay Guided Approach. *J. Chromatogr. Sci.* 2020, 59, 618–626.
10. Enerstvedt, K.H.; Jordheim, M.; Andersen, M. Isolation and Identification of Flavonoids Found in Zostera marina Collected in Norwegian Coastal Waters. *Am. J. Plant Sci.* 2016, 7, 1163–1172.
11. Papazian, S.; Parrot, D.; Buryyskova, B.; Weinberger, F.; Tasdemir, D. Surface chemical defence of the eelgrass *Zostera marina* against microbial foulers. *Sci. Rep.* 2019, 9, 3323.
12. Teles, Y.C.F.; Souza, M.S.R.; de Fatima Vanderlei de Souza, M. New Sulphated Flavonoids: Biosynthesis, Structures, and Biological Activities. *Molecules* 2018, 23, 480.
13. Da Silva, L.P.; Pereira, E.; Pires, T.C.S.P.; Alves, M.J.; Pereira, O.R.; Barros, L.; Ferreira, I.C.F.R. Rubus ulmifolius Schott fruits: A detailed study of its nutritional, chemical and bioactive properties. *Food Res. Int.* 2019, 119, 34–43.
14. Kajdzanovska, M.; Gjamovski, V.; Stefova, M. HPLC-DADA-ESI-MSn identification of phenolic compounds in cultivated strawberries from Macedonia. *Maced. J. Chem. Chem. Eng.* 2010, 29, 181–194.
15. Ha, T.J.; Lee, M.H.; Park, C.H.; Pae, S.B.; Shim, K.B.; Ko, J.M.; Park, K.Y. Identification and Characterization of Anthocyanins in Yard-Long Beans (Vigna unguiculata ssp. sesquipedalis L.) by High-Performance Liquid Chromatography with Diode Array Detection and Electrospray Ionization/Mass Spectrometry (HPLC-DAD-ESI/MS) Analysis. *J. Agric. Food Chem.* 2010, 58, 2571–2576.
16. Garg, M.; Chawla, M.; Chunduri, V.; Kumar, R.; Sharma, S.; Sharma, N.K.; Kaur, N.; Kumar, A.; Mundey, J.K.; Saini, M.K.; et al. Transfer of grain colors to elite wheat cultivars and their characterization. *J. Cereal Sci.* 2016, 71, 138–144.
17. Cirilini, M.; Mena, P.; Tassotti, M.; Herrlinger, K.A.; Nieman, K.; Dall’Astá, C.; Del Rio, D. Phenolic and Volatile Composition of a Dry Spearmint (*Mentha spicata* L.) Extract. *Molecules* 2016, 21, 1007.
18. Del Mar Contreras, M.; Algieri, F.; Rodriguez-Nogales, A.; Galvez, J.; Segura-Carretero, A. Evaluation of the Antifungal Activity of the Licania Rigida Leaf Ethanolic Extract against Biofilms Formed by *Candida* Sp. Isolates in Acrylic Resin Discs. *Antibiotics* 2019, 8, 250.
19. Serrano, C.A.; Villena, G.K.; Rodriguez, E.F. Phytochemical profile and rosmarinic acid purification from two Peruvian Lepechinia Willd. species (Salviiniaceae, Mentheae, Lamiaceae). *Sci. Rep.* 2021, 11, 7260.
20. Kim, S.; Oh, S.; Noh, H.B.; Ji, S.; Lee, S.H.; Koo, J.M.; Choi, C.W.; Jhuu, H.P. In Vitro Antioxidant and Anti-Propionibacterium acnes Activities of Cold Water, Hot Water, and Methanol Extracts, and Their Respective Ethyl Acetate Fractions, from *Sanguisorba officinalis* L. *Roots. Molecules* 2018, 23, 3001.
21. Chen, Y.; Cai, X.; Li, G.; He, X.; Yu, X.; Yu, X.; Wang, C. Chemical constituents of radix Actinidia chinensis planch by UPLC–QTOF–MS. *Biomed. Chromatogr.* 2021, 35, e5103.
22. Pharmacopoeia of the Eurasian Economic Union, Approved by Decision of the Board of Eurasian Economic Commission No. 100 dated August 11, 2020. Available online:
Separations 2022, 9, 182

http://www.eurasiancommission.org/ru/act/textreg/deptexreg/LSM/Documents/%D0%9F%D0%BE%D0%B4%D0%BE%D0%B1%D0%B0%D1%80%D1%82%D0%BE%202011%2008.pdf
(accessed on 15 July 2022).

23. Abu-Reidah, I.M.; Ali-Shtayeh, M.S.; Jamous, R.M.; Arraes-Roman, D.; Segura-Carretero, A. HPLC–DAD–ESI–MS/MS screening of bioactive components from Rhizoria L. (Sumac) fruits. Food Chem. 2015, 166, 179–191.

24. Aita, S.E.; Capriotti, A.L.; Cavaliere, C.; Cerrato, A.; Moneta, B.G.; Montone, C.M.; Piovesana, S.; Laganà, A. Andean Blueberry of the Genus Disterigma: A High-Resolution Mass Spectrometric Approach for the Comprehensive Characterization of Phenolic Compounds. *Separations* 2021, 8, 58.

25. Rodriguez-Pérez, C.; Gómez-Caravaca, A.M.; Guerra-Hernández, E.; Cerretani, L.; García-Villanova, B.; Verardo, V. Comprehensive metabolite profiling of Solanum tuberosum L. (potato) leaves by HPLC–ESI–QTOF–MS. *Food Res. Int.* 2018, 112, 390–399.

26. Viera, M.N.; Winterhalter, P.; Jerz, G. Flavonoids from the flowers of Impatiens glandulifera Royle isolated by high performance countercurrent chromatography. *Phytochem. Anal.* 2016, 27, 116–125.

27. Yin, N.-W.; Wang, S.-X.; Jia, L.-D.; Zhu, M.-C.; Yang, J.; Zhou, B.-J.; Yin, J.-M.; Lu, K.; Wang, R.; Li, J.-N.; et al. Identification and Characterization of Major Constituents in Different-Colored Raspased Petals by UPLC–HESI–MS/MS. *Agric. Food Chem.* 2019, 67, 11053–11065.

28. Razgonova, M.P.; Zakharenko, A.M.; Grudev, V.; Ercisi, S.; Golokhvat, K.S. Comparative analysis of the multicomponent composition of Far East Sibkhotinsky Rhododendron (Rh. sikkotense) and East Siberian Rhododendron (Rh. adamsii) using supercritical CO2-extraction and HPLC–MS/MS spectroscopy. *Molecules* 2020, 25, 3774.

29. Engels, C.; Gräter, D.; Esquivel, P.; Jiménez, V.M.; Gänzle, M.G.; Schieber, A. Characterization of phenolic compounds in jocote (Spondias purpurea) L. peels by ultra-high-performance liquid chromatography/electrospray ionization mass spectrometry. *Food Res. Int.* 2012, 46, 557–562.

30. Pandey, R.; Kumar, B. HPLC–QTOF–MS/MS-based rapid screening of phenolics and triterpenic acids in leaf extracts of *Ocimum* species and their interspecies variation. *J. Liq. Chromatogr. Relat. Technol.* 2016, 39, 225–238.

31. Zhang, W.-X.; Chao, J.-C.; Hu, D.-J.; Shakerian, F.; Ge, L.; Liang, X.; Wang, Y.; Zhao, J.; Li, S.-P. Comparison of Antioxidant Activity and Main Active Compounds Among Different Parts of Alpinia officinarum Hance Using High-Performance Thin Layer Chromatography-Bioautography. *J. AOAC Int.* 2019, 102, 726–733.

32. Xu, X.; Yang, B.; Wang, D.; Zhu, Y.; Miao, X.; Yang, W. The Chemical Composition of Brazilian Green Propolis and Its Protective Effects on Mouse Aortic Endothelial Cells against Inflammatory Injury. *Molecules* 2020, 25, 4612.

33. Zapesochnaya, G.G.; Kurkin, V.A.; Shchavlinlski, A.N. Flavonoids of the above-ground part of Rhodiola rosea. II. Structure of novel glycosides of herbacetin and gossypetin. *Chem. Nat. Connect.* 1985, 4, 496–507.

34. Chandrasekara, A.; Shahidi, F. Determination of antioxidant activity in free and hydrolyzed fractions of millet grains and characterization of their phenolic profiles by HPLC–DAD–ESI–MSn. *J. Funct. Foods* 2011, 3, 144–158.

35. Qin, D.; Wang, Q.; Li, H.; Jiang, X.; Fang, K.; Wang, Q.; Li, B.; Pan, C.; Wu, H. Identification of key metabolites based on non-targeted metabolomics and chemometrics analyses provides insights into bitterness in Kucha [Camellia kucha (Chang et Wang) Chang]. *Food Res. Int.* 2020, 138, 109789.

36. Olech, M.; Pietrzak, W.; Nowak, R. Characterization of Free and Bound Phenolic Acids and Flavonoid Aglycones in Rosa rugosa Thunb. Leaves and Achenes Using LC–ESI–MS/MS–MRM Methods. *Molecules* 2020, 25, 1804.

37. Rafsanjany, N.; Senker, J.; Brandt, S.; Dobrindt, U.; Hensel, A. In Vivo Consumption of Cranberry Exerts ex Vivo Antiadhesive Activity against FimH-Dominated Uropathogenic Escherichia coli: A Combined in Vivo, ex Vivo, and in Vitro Study of an Extract from Vaccinium macrocarpon. *J. Agric. Food Chem.* 2015, 63, 8804–8818.

38. Yang, Y.; Feng, Z.; Jiang, J.; Zhang, P. Chemical constituents of roots of *Rhodiola crenulata*. *Chin. Pharm. J.* 2013, 48, 410–413.

39. Zhang, S.; Liu, C.; Bi, H.; Wang, C. Extraction of flavonoids from *Rhodiola sachalinensis* A. Bor by UPE and the antioxidant activity of its extract. *Nat. Prod. Res.* 2008, 22, 178–187.

40. Santos, S.A.O.; Freire, C.S.R.; Domingues, M.R.M.; Silvestre, A.J.D.; Neto, C.P. Characterization of Phenolic Components in Polar Extracts of Eucalyptus globulus Labill. Bark by High-Performance Liquid Chromatography–Mass Spectrometry. *Agric. Food Chem.* 2011, 59, 9386–9393.

41. Abeywickrama, G.; Debnath, S.C.; Ambigaipalan, P.; Shahidi, F. Phenolics of Selected Cranberry Genotypes (*Vaccinium macrocarpon* Att.) and Their Antioxidant Efficacy. *J. Agric. Food Chem.* 2016, 64, 9324–9331.

42. Belmehdi, O.; Bouyahya, A.; Jeko, J.; Czakiy, Z.; Zengin, G.; Sotkó, G.; Abrini, J. Synergistic interaction between propolis extract, essential oils, and antibiotics against Staphylococcus epidermidis and meticillin resistant Staphylococcus aureus. *Int. J. Second. Metab.* 2021, 8, 195–213.

43. Cai, Z.; Wang, C.; Zou, L.; Liu, X.; Chen, J.; Tan, M.; Mei, Y.; Wei, L. Comparison of Multiple Bioactive Constituents in the Flower and the Caulis of *Lonicera japonica* Based on UFLC–QTRAP–MS/MS Combined with Multivariate Statistical Analysis. *Molecules* 2019, 24, 1936.

44. Wojakowska, A.; Piasiecka, A.; Garcia-Lopez, P.M.; Zamora-Natera, F.; Krajewski, P.; Marczak, L.; Kachlicki, P.; Stobiecki, M. Structural analysis and profiling of phenolic secondary metabolites of Mexican lupine species using LC–MS techniques. *Phytochemistry* 2013, 92, 71–86.

45. Petsalo, A.; Jalonen, J.; Tolonen, A. Identification of flavonoids of *Rhodiola rosea* by liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A* 2006, 1112, 224–231.
46. Olennikov, D.N.; Chirikova, N.K.; Okhlopkova, Z.M.; Zulfugarov, I.S. Chemical Composition and Antioxidant Activity of Tānara Ōto (Draecocephalum palmatum Stephan), a Medicinal Plant Used by the North-Yakutian Nomads. Molecules 2013, 18, 14105.

47. Zhang, Z.; Jia, P.; Zhang, X.; Zhang, Q.; Yang, H.; Shi, H.; Zhang, L. LC-MS/MS determination and pharmacokinetic study of seven flavonoids in rat plasma after oral administration of Cirsium japonicum DC. extract. J. Ethnopharmacol. 2014, 158, 66–75.

48. Xu, L.L.; Xu, J.J.; Zhong, K.R.; Shang, Z.P.; Wang, F.; Wang, R.F.; Liu, B. Analysis of non-volatile chemical constituents of Menthae Haplocalycis herba by ultra-high performance liquid chromatography-high resolution mass spectrometry. Molecules 2017, 22, 1756.

49. Mena, P.; Cirilini, M.; Tassotti, M.; Herrlinger, K.A.; Dall’Ast, C.; Del Rio, D. Phytochemical Profiling of Flavonoids, Phenolic Acids, Terpenoids, and Volatile Fraction of a Rosemary (Rosmarinus officinalis L.) Extract. Molecules 2016, 21, 1576.

50. Zhang, J.; Xu, X.-J.; Xu, W.; Huang, J.; Zhu, D.; Qiu, X.-H. Rapid Characterization and Identification of Flavonoids in Radix Astragali by Ultra-High-Pressure Liquid Chromatography Coupled with Linear Ion Trap-Orbitrap Mass Spectrometry. J. Chromatogr. Sci. 2014, 53, 945–952.

51. Marzouk, M.M.; Hussein, S.R.; Elkhateeb, A.; El-shabrawy, M.; Abdel-Hameed, E.-S. S.; Kawashy, S.A. Comparative study of Mentha species growing wild in Egypt: LC-ESI-MS analysis and chemosystematic significance. J. Appl. Pharm. Sci. 2018, 8, 116–122.

52. Justesen, U. Negative atmospheric pressure chemical ionisation low-energy collision activation mass spectrometry for the characterisation of flavonoids in extracts of fresh herbs. J. Chromatogr. A 2000, 902, 369–379.

53. Chen, X.; Zhang, S.; Xuan, Z.; Ge, D.; Chen, X.; Zhang, J.; Wang, Q.; Wu, Y.; Liu, B. The Phenolic Fraction of Mentha haplocalyx and Its Constituent Linarin Ameliorate Inflammatory Response through Inactivation of NF-kB and MAPKs in Lipopolysaccharide-Induced RAW264.7 Cells. Molecules 2017, 22, 811.

54. Ozarowski, M.; Piasecka, A.; Paszel-Jaworska, A.; de Chaves DS, A.; Romaniuk, A.; Rybczynska, M.; Thiem, B. Comparison of bioactive compounds content in leaf extracts of Passiflora incarnata, P. caerulea and P. alata and in vitro cytotoxic potential on leukemia cell lines. Braz. J. Pharm. Sci. 2018, 27, 199–121.

55. Santos, S.A.; Vilela, C.; Freire, C.; Neto, C.; Silvestre, A. Ultra-high performance liquid chromatography coupled to mass spectrometry applied to the identification of valuable phenolic compounds from Eucalyptus wood. J. Chromatogr. B 2013, 938, 65–74.

56. Zhu, Z.-W.; Li, J.; Gao, X.-M.; Amponsem, E.; Kang, L.-Y.; Hu, L.-M.; Zhang, B.-L.; Chang, Y.-X. Simultaneous determination of stilbenes, phenolic acids, flavonoids and anthraquinones in Radix polygoni multiflori by LC-MS/MS. J. Pharm. Biomed. Anal. 2012, 62, 162–166.

57. Zakharenko, A.M.; Razgonova, M.P.; Pikula, K.S.; Golokhvast, K.S. Simultaneous determination of 78 compounds of Rhodiola rosea extract using supercritical CO2-extraction and HPLC-ESI-MS/MS spectrometry. Biochem. Res. Commun. 2021, 2021, 9957490.

58. Paudel, L.; Wyzgoski, F.J.; Scheeren, J.C.; Chanon, A.M.; Reese, R.N.; Smiljanić, D.; Wessdemioti, C.; Blakeslee, J.J.; Riedl, K.M.; Rinaldi, P.L. Nonanthocyanin Secondary Metabolites of Black Raspberry (Rubus occidentalis L.) Fruits: Identification by HPLC-DAD, NMR, HPLC-ESI-MS, and ESI-MS/MS Analyses. J. Agric. Food Chem. 2013, 61, 12032–12043.

59. Karker, M.; De Tommasi, N.; Smoou, A.; Abdelly, C.; Ksouri, R.; Braca, A. New Sulphated Flavonoids from Tamarix africana and Biological Activities of Its Polar Extract. Planta Med. 2016, 82, 1374–1380.

60. Ruiz, A.; Hermosín-Gutiérrez, I.; Vergara, C.; von Baer, D.; Zapata, M.; Hitschfeld, A.; Abando, L.; Mandores, C. Anthocyanin profiles in south Patagonian wild berries by HPLC-DAD-ESI-MS/MS. Food Res. Int. 2013, 51, 706–713.

61. Seekhaw, P.; Mahatheeranont, S.; Sookwong, P.; Luangkamin, S.; Na Lampang Neonlab, A.; Puangsombat, P. Phytochemical Constituents of Thai Dark Purple Glutinous Rice Bran Extract Cultivar Luem Pua (Oryza sativa L.). Chiang Mai J. Sci. 2018, 45, 1383–1395.

62. Sun, J.; Liu, X.; Yang, T.; Slovin, J.; Chen, P. Profiling polyphenols of two diploid strawberry (Fragaria vesca) inbred lines using UHPLC-HRMSn. Food Chem. 2013, 146, 289–298.

63. Vijayan, K.P.R.; Raghu, A.V. Tentative characterization of phenolic compounds in three species of the genus Embelia by liquid chromatography with mass spectrometry analysis. Spectrosc. Lett. 2019, 52, 653–670.

64. Huang, Y.; Yao, P.; Leung, K.W.; Wang, H.-Y.; Kong, X.P.; Wang, L.; Dong, T.T.X.; Chen, Y.; Tsim, K.W.K. The Yin-Yang Property of Chinese Medicinal Herbs Relates to Chemical Composition but Not Anti-Oxidative Activity: An Illustration Using Spleen-Meridian Herbs. Front. Pharmacol. 2018, 9, 1304.

65. Yin, Y.; Zhang, K.; Wei, L.; Chen, D.; Chen, Q.; Jiao, M.; Li, X.; Huang, J.; Gong, Z.; Kang, N.; et al. The Molecular Mechanism of Antioxidation of Huolisu Oral Liquid Based on Serum Analysis and Network Analysis. Front. Pharmacol. 2021, 12, 710976.

66. El-Sayed, M.A.; Abbas, F.A.; Refaat, S.; El-Shafae, A.M.; Fikry, E. UPLC-ESI-MS/MS Profile of The Ethyl Acetate Fraction of Aerial Parts of Bougainvillea ‘Scarlett O’Hara’ Cultivated in Egypt. Egypt. J. Chem. 2021, 64, 22.

67. Mena, P.; Calani, L.; Dall’asta, C.; Galaverna, G.; García-Viguera, C.; Bruni, R.; Crozier, A.; Del Rio, D. Rapid and Comprehensive Evaluation of (Poly)phenolic Compounds in Pomegranate (Punica granatum L.) Juice by UHPLC-MSn. Molecules 2012, 17, 14821–14840.

68. Mi, J.; Jia, K.-P.; Wang, J.Y.; Al-Babili, S. A rapid LC-MS method for qualitative and quantitative profiling of plant apocarotenoids. Anal. Chim. Acta 2018, 1035, 87–95.

69. Guo, K.; Tong, C.; Fu, Q.; Xu, J.; Shi, S.; Xiao, Y. Identification of minor lignans, alkaloids, and phenylpropanoid glycosides in Magnolia officinalis by HPLC-DAD-QTOF-MS/MS. J. Pharm. Biomed. Anal. 2019, 170, 153–160.
70. Luo, D.-Q.; Jia, P.; Zhao, S.-S.; Zhao, Y.; Liu, H.-J.; Wei, F.; Ma, S.-C. Identification and Differentiation of Polygonum multiflorum Radix and Polygoni multiﬁlori Radix Preparata through the Quantitative Analysis of Multicomponents by the Single-Marker Method. J. Anal. Methods Chem. 2019, 7430717.

71. Yang, S.; Wu, X.; Rui, W.; Guo, J.; Feng, Y.F. UPLC/Q-TOF-MS Analysis for Identification of Hydrophilic Phenolics and Lipophilic Diterpenoids from Radix Salviae Miltiorrhizae. Acta Chromatogr. 2015, 27, 711–728.

72. Chen, W.; Gong, L.; Guo, Z.; Wang, W.; Zhang, H.; Liu, X.; Yu, S.; Xiong, L.; Luo, J. A Novel Integrated Method for Large-Scale Detection, Identification, and Quantification of Widely Targeted Metabolites: Application in the Study of Rice Metabolomics. Mol. Plant 2013, 6, 1769–1780.

73. Ekeberg, D.; Flate, P.-O.; Eikenes, M.; Fongen, M.; Naess-Andresen, C.F. Qualitative and quantitative determination of extracts in heartwood of Scots pine (Pinus sylvestris L.) by gas chromatography. J. Chromatogr. A 2006, 1109, 267–272.

74. Zoccali, M.; Giuffrida, D.; Salafia, F.; Giofrè, S.V.; Mondello, L. Carotenoids and apocarotenoids determination in intact human blood samples by online supercritical fluid extraction-supercritical fluid chromatography-tandem mass spectrometry. Anal. Chim. Acta 2018, 1032, 40–47.

75. Lu, Y.C.; Mondal, S.; Wang, C.-C.; Lin, C.-H.; Mong, K.-K.T. Diverse Synthesis of Natural Trehalosamines and Synthetic 1,1′-Disaccharide Aminoglycosides. ChemBioChem 2018, 20, 287–294.

76. Montenegro, Z.S.; Álvarez-Rivera, G.; Mendiola, J.; Ibáñez, E.; Cifuentes, A. Extraction and Mass Spectrometric Characterization of Terpenes Recovered from Olive Leaves Using a New Adsorbent-Assisted Supercritical CO2 Process. Foods 2021, 10, 1301.

77. Chen, X.; Zhu, P.; Liu, B.; Wei, L.; Xu, Y. Simultaneous determination of fourteen compounds of Hedysotis diffusa Willd extract in rats by UHPLC-MS/MS method: Application to pharmacokinetics and tissue distribution study. J. Pharm. Biomed. Anal. 2018, 159, 490–512.

78. Li, W.-H.; Chang, S.-T.; Chang, S.-C.; Chang, H.-T. Isolation of antibacterial diterpenoids from Cryptomeria japonica bark. Nat. Prod. Res. 2008, 22, 1085–1093.

79. Kan, S.; Chen, G.; Han, C.; Chen, Z.; Song, X.; Ren, M.; Jiang, H. Chemical constituents from the roots of Xanthium sibiricum L. Nat. Prod. Res. 2011, 25, 1243–1249.

80. Salih, E.Y.; Julkunen-Titto, R.; Lampi, A.-M.; Kanninen, M.; Luukkanen, O.; Sipi, M.; Lehtonen, M.; Vuorela, H.; Fyrquisp, T. Terminalia laxiflora and Terminalia brownii contain a broad spectrum of antimycobacterial compounds including ellagitannins, ellagic acid derivatives, triterpenes, fatty acids and fatty alcohols. J. Ethnopharmacol. 2018, 227, 82–96.

81. Wu, Y.; Xu, J.; He, Y.; Shi, M.; Han, X.; Li, W.; Zhang, X.; Wen, X. Metabolic Profiling of Pitaya (Hylocereus polyrhizus) during Fruit Development and Maturation. Molecules 2019, 24, 1114.

82. Sun, L.; Tao, S.; Zhang, S. Characterization and Quantitation of Polyphenols and Triterpenoids in Thinned Young Fruits of Ten Pear Varieties by UPLC-Q TRAP-MS/MS. Molecules 2019, 24, 159.

83. Mercadante, A.Z.; Rodrigues, D.B.; Petry, F.C.; Mariutti, L. Carotenoid esters in foods—A review and practical directions on analysis and occurrence. Food Res. Int. 2017, 99, 830–850.

84. Al-Yafeai, A.; Malarski, A.; Böhm, V. Characterization of carotenoids and vitamin E in R. rugosa and R. canina: Comparative analysis. Food Chem. 2018, 242, 435–442.

85. Delgado-Pelayo, R.; Hornero-Méndez, D. Identification and Quantitative Analysis of Carotenoids and Their Esters from Sarsaparilla (Smilax aspera L.) Berries. J. Agric. Food Chem. 2012, 60, 8225–8232.

86. Delgado-Pelayo, R.; Gallardo-Guerrero, L.; Hornero-Méndez, D. Carotenoid composition of strawberry tree (Arbutus unedo L.) fruits. Food Chem. 2016, 199, 165–175.

87. Lara-Abia, S.; Lobo-Rodrigo, G.; Welti-Chanes, J.; Pilar Cano, M. Carotenoid and Carotenoid Ester Profile and Their Deposition in Plastids in Fruits of New Papaya (Carica papaya L.) Varieties from the Canary Islands. Foods 2021, 10, 434.

88. Eitzbach, L.; Pfeiffer, A.; Weber, F.; Schieber, A. Characterization of carotenoid profiles in goldenberry (Physalis peruviana L.) fruits at various ripening stages and in different plant tissues by HPLC-DADAPCI-MSn. Food Chem. 2018, 245, 508–517.

89. Van Breemen, R.B.; Canjura, F.L.; Schwartz, S.J. Identification of Chlorophyll Derivatives by Mass Spectrometry. J. Agric. Food Chem. 1991, 39, 1452–1456.

90. Milenkovic, S.M.; Zvezdanovic, J.B.; Andelkovic, T.D.; Markovic, D.Z. The identification of chlorophyll and its derivatives in the pigment mixtures: HPLC-chromatography, Visible and spectroscopy studies. Adv. Technol. 2012, 1, 16–24.