

SUPPLEMENTARY FILE

Figure S1. Fingerprints of the analyzed extracts in the negative ionization mode.

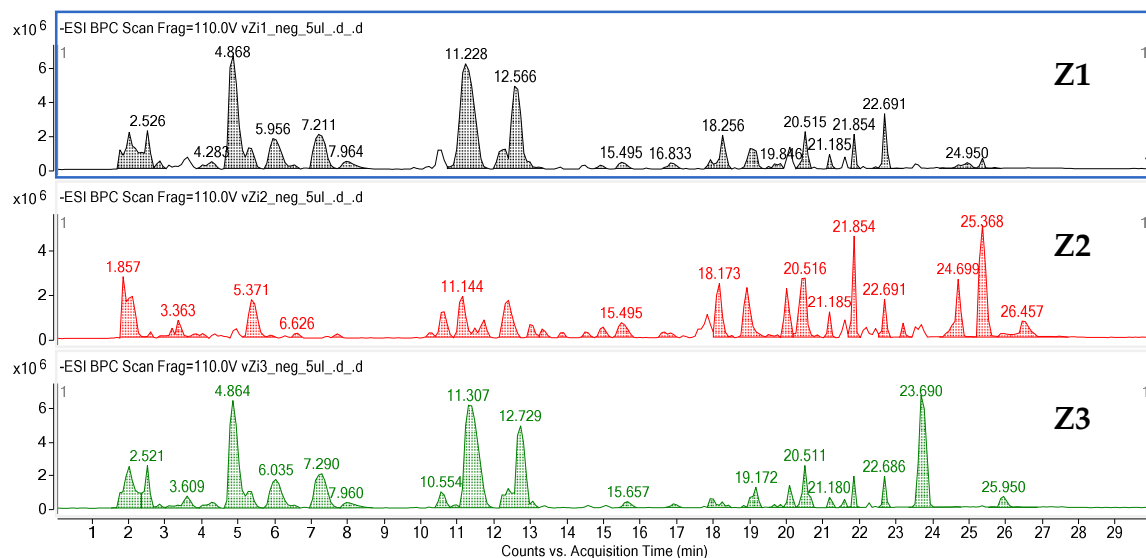


Figure S2. Fingerprints of the analyzed extracts in the positive ionization modes.

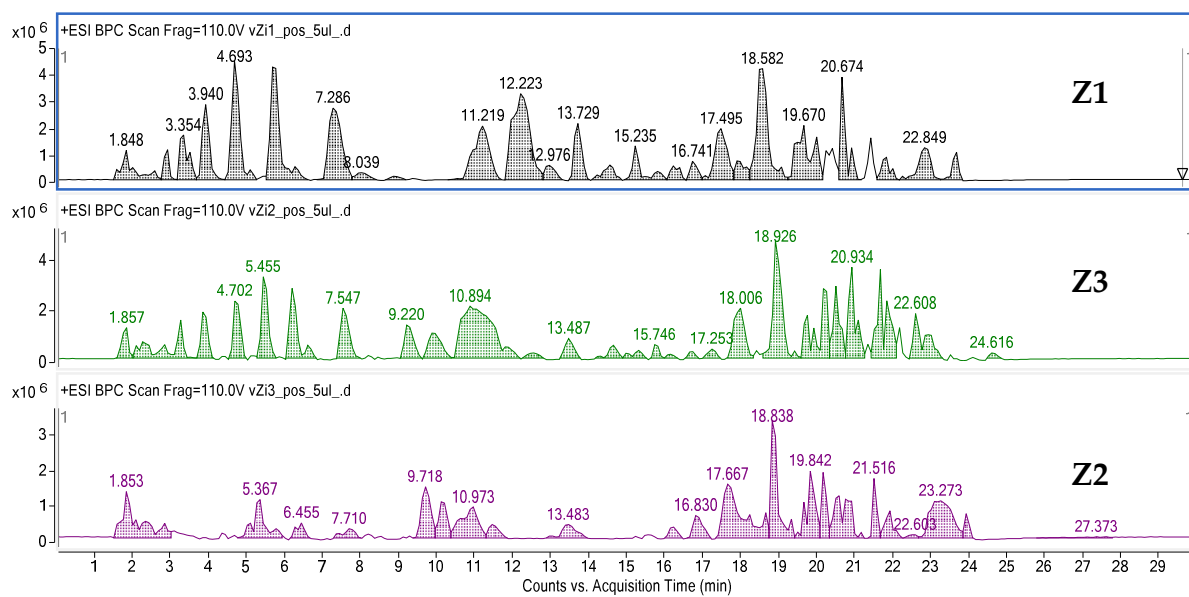


Table S1. MS/MS spectra of the identified compounds.

Compound	Spectrum
Apigenin	<p>ESI Product Ion (rt: 21.832 min) Frag=130.0V CID@20.0 (269.0467[z=1] -> **) vZi3_neg_5ul_d_d</p>
Chlorogenic acid	<p>ESI Product Ion (rt: 3.128 min) Frag=120.0V CID@10.0 (353.0885[z=1] -> **) vZi1_neg_5ul_d_d</p>
Neochlorogenic acid	<p>ESI Product Ion (rt: 3.998 min) Frag=120.0V CID@10.0 (353.0885[z=1] -> **) vZi1_neg_5ul_d_d</p>
(Z)-Chlorogenic acid	<p>ESI Product Ion (rt: 4.333 min) Frag=120.0V CID@10.0 (353.0885[z=1] -> **) vZi1_neg_5ul_d_d</p>
Luteolin	<p>ESI Product Ion (rt: 21.302 min) Frag=130.0V CID@20.0 (285.0396[z=1] -> **) vZi1_neg_5ul_d_d</p>
Thymonin and a dimer	<p>ESI Product Ion (rt: 19.110 min) Frag=120.0V CID@10.0 (359.0772[z=1] -> **) vZi1_neg_5ul_d_d</p>

	<p>Mass spectrum of Thymonin isomer (rt: 19.143 min). The x-axis represents mass-to-charge ratio (m/z) from 120 to 800, and the y-axis represents relative intensity from 0 to 1.2. The base peak is at m/z 359.0775. Other significant peaks are labeled at m/z 161.0246, 197.0455, and 719.1591.</p> <p>ES-Product Ion (rt: 19.143 min) Frag=120.0V CID@10.0 (719.1606[z=1] -> **) vZi1_neg_5ul_d_d</p>
Thymonin isomer	<p>Mass spectrum of Acacetin (rt: 21.820 min). The x-axis represents mass-to-charge ratio (m/z) from 110 to 450, and the y-axis represents relative intensity from 0 to 8. The base peak is at m/z 359.0772. Other significant peaks are labeled at m/z 329.0303, 344.0537, and 359.0772.</p> <p>ES-Product Ion (rt: 21.820 min) Frag=120.0V CID@10.0 (359.0772[z=1] -> **) vZi1_neg_5ul_d_d</p>
Acacetin	<p>Mass spectrum of Diosmetin (rt: 22.719 min). The x-axis represents mass-to-charge ratio (m/z) from 90 to 380, and the y-axis represents relative intensity from 0 to 2.5. The base peak is at m/z 288.0385. Other significant peaks are labeled at m/z 240.0430, 283.0617, and 288.0385.</p> <p>ES-Product Ion (rt: 22.719 min) Frag=130.0V CID@20.0 (283.0615[z=1] -> **) vZi3_neg_5ul_d_d</p>
Diosmetin	<p>Mass spectrum of Diosmetin (rt: 22.334 min). The x-axis represents mass-to-charge ratio (m/z) from 100 to 370, and the y-axis represents relative intensity from 0 to 4. The base peak is at m/z 284.0331. Other significant peaks are labeled at m/z 135.0459, 165.0194, 256.0349, and 299.0563.</p> <p>ES-Product Ion (rt: 22.334 min) Frag=130.0V CID@20.0 (299.0578[z=1] -> **) vZi3_neg_5ul_d_d</p>
Diosmetin	<p>Mass spectrum of 5,7,21-trihydroxyflavone-21-O-glucopyranoside (rt: 20.059 min). The x-axis represents mass-to-charge ratio (m/z) from 100 to 1600, and the y-axis represents relative intensity from 0 to 5. The base peak is at m/z 269.0610. Other significant peaks are labeled at m/z 561.1609, 607.1661, and 269.0610.</p> <p>ES-Product Ion (rt: 20.059 min) Frag=120.0V CID@10.0 (607.1661[z=1] -> **) vZi3_neg_5ul_d_d</p>
5,7,21-trihydroxyflavone-21-O-glucopyranoside	<p>Mass spectrum of Thymonin isomer (rt: 18.469 min). The x-axis represents mass-to-charge ratio (m/z) from 100 to 580, and the y-axis represents relative intensity from 0 to 1.6. The base peak is at m/z 269.0464. Other significant peaks are labeled at m/z 103.0055, 113.0245, 137.0248, 157.0132, 175.0283, 242.9426, 307.0822, 408.0251, 429.1333, and 445.0802.</p> <p>ES-Product Ion (rt: 18.469 min) Frag=120.0V CID@10.0 (445.0786[z=1] -> **) vZi3_neg_5ul_d_d</p>

Caffeic acid	<p>x10⁴ -ESI Product Ion (rt: 6.487 min) Frag=130.0V CID@20.0 (179.0355[z=1] -> **) vZi3_neg_5ul_d_d</p> <p>Counts vs. Mass-to-Charge (m/z)</p>
Ethyl ester of caffeic acid	<p>x10³ -ESI Product Ion (rt: 7.642 min) Frag=120.0V CID@10.0 (207.0669[z=1] -> **) vZi3_neg_5ul_d_d</p> <p>Counts vs. Mass-to-Charge (m/z)</p>
Oleanolic acid	<p>x10⁵ -ESI Product Ion (rt: 22.920 min) Frag=130.0V CID@20.0 (455.3532[z=1] -> **) vZi3_neg_5ul_d_d</p> <p>Counts vs. Mass-to-Charge (m/z)</p>
Ursolic acid	<p>x10³ -ESI Product Ion (rt: 24.309 min) Frag=130.0V CID@20.0 (455.3532[z=1] -> **) vZi3_neg_5ul_d_d</p> <p>Counts vs. Mass-to-Charge (m/z)</p>
Maslinic acid	<p>x10⁴ -ESI Product Ion (rt: 23.338 min) Frag=130.0V CID@20.0 (471.3478[z=1] -> **) vZi3_neg_5ul_d_d</p> <p>Counts vs. Mass-to-Charge (m/z)</p>
Thymol	<p>x10⁴ +ESI Product Ion (rt: 22.674 min) Frag=130.0V CID@20.0 (151.1127[z=1] -> **) vZi2_pos_5ul_d</p> <p>Counts vs. Mass-to-Charge (m/z)</p>

Carvacrol	<p>+ESI Product Ion (rt: 19.859 min) Frag=120.0V CID@10.0 (151.1124[z=1] -> **) vZi3_pos_5ul_d</p> <table border="1"><thead><tr><th>m/z</th><th>Relative Intensity (x10⁻⁴)</th></tr></thead><tbody><tr><td>105.0703</td><td>~0.8</td></tr><tr><td>109.0649</td><td>~1.2</td></tr><tr><td>123.1163</td><td>~1.0</td></tr><tr><td>133.1000</td><td>~0.5</td></tr><tr><td>151.1131</td><td>2.5</td></tr><tr><td>153.1288</td><td>~0.5</td></tr></tbody></table>	m/z	Relative Intensity (x10 ⁻⁴)	105.0703	~0.8	109.0649	~1.2	123.1163	~1.0	133.1000	~0.5	151.1131	2.5	153.1288	~0.5
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105.0703	~0.8														
109.0649	~1.2														
123.1163	~1.0														
133.1000	~0.5														
151.1131	2.5														
153.1288	~0.5														
Ziziphoroside A	<p>+ESI Product Ion (rt: 10.500 min) Frag=130.0V CID@20.0 (353.1603[z=1] -> **) vZi3_pos_5ul_d</p> <table border="1"><thead><tr><th>m/z</th><th>Relative Intensity (x10⁻⁴)</th></tr></thead><tbody><tr><td>201.0403</td><td>~1.5</td></tr><tr><td>353.1593</td><td>5.0</td></tr></tbody></table>	m/z	Relative Intensity (x10 ⁻⁴)	201.0403	~1.5	353.1593	5.0								
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201.0403	~1.5														
353.1593	5.0														
Ziziphoroside B	<p>+ESI Product Ion (rt: 12.876 min) Frag=130.0V CID@20.0 (353.1603[z=1] -> **) vZi1_pos_5ul_d</p> <table border="1"><thead><tr><th>m/z</th><th>Relative Intensity (x10⁻⁵)</th></tr></thead><tbody><tr><td>119.0484</td><td>~0.5</td></tr><tr><td>147.0446</td><td>~0.8</td></tr><tr><td>201.0401</td><td>~0.5</td></tr><tr><td>353.1605</td><td>2.0</td></tr></tbody></table>	m/z	Relative Intensity (x10 ⁻⁵)	119.0484	~0.5	147.0446	~0.8	201.0401	~0.5	353.1605	2.0				
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119.0484	~0.5														
147.0446	~0.8														
201.0401	~0.5														
353.1605	2.0														
Ziziphoroside C	<p>+ESI Product Ion (rt: 13.528 min) Frag=120.0V CID@10.0 (353.1603[z=1] -> **) vZi1_pos_5ul_d</p> <table border="1"><thead><tr><th>m/z</th><th>Relative Intensity (x10⁻⁴)</th></tr></thead><tbody><tr><td>147.0430</td><td>~0.8</td></tr><tr><td>165.0558</td><td>~0.5</td></tr><tr><td>201.0388</td><td>~0.8</td></tr><tr><td>353.1601</td><td>3.5</td></tr></tbody></table>	m/z	Relative Intensity (x10 ⁻⁴)	147.0430	~0.8	165.0558	~0.5	201.0388	~0.8	353.1601	3.5				
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147.0430	~0.8														
165.0558	~0.5														
201.0388	~0.8														
353.1601	3.5														
Schizonepetaside E	<p>+ESI Product Ion (rt: 3.961 min) Frag=120.0V CID@10.0 (349.1844[z=1] -> **) vZi3_pos_5ul_d</p> <table border="1"><thead><tr><th>m/z</th><th>Relative Intensity (x10⁻⁴)</th></tr></thead><tbody><tr><td>163.0416</td><td>~0.8</td></tr><tr><td>281.0342</td><td>~0.5</td></tr><tr><td>349.1849</td><td>3.5</td></tr></tbody></table>	m/z	Relative Intensity (x10 ⁻⁴)	163.0416	~0.8	281.0342	~0.5	349.1849	3.5						
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163.0416	~0.8														
281.0342	~0.5														
349.1849	3.5														

Table S2. The relative compositions of the Z1–Z3 extracts. For the each studied compound (1–26), the HPLC peak areas representing the absolute amounts of a given compound within Z1, Z2 and Z3 extracts were rescaled, in order to sum to 1 in every row of the table below, expressing the relative compositions of the Z1–Z3 extracts.

		Absolute Compositions			Relative Compositions (C _{rel})		
		Z1	Z2	Z3	Z1	Z2	Z3
1	Chlorogenic acid	1540451	616767	1428191	0.4296	0.1720	0.3983
2	Neochlorogenic acid	3809788	1204722	4321964	0.4081	0.1290	0.4629
4	(Z)-Chlorogenic acid	7447554	1204722	4720773	0.5569	0.0901	0.3530
6	Caffeic acid	6243017	5526195	5075319	0.3706	0.3281	0.3013
9	Ziziphoroside isomer 1	559519	362891	241409	0.4808	0.3118	0.2074
10	Ziziphoroside isomer 2	175140	0	24764	0.8761	0.0000	0.1239
11	Ziziphoroside isomer 3	344946	251998	320946	0.3758	0.2745	0.3497
13	Rosmarinic acid	32458496	23080201	13968651	0.4670	0.3321	0.2010
15	Diosmin	12139796	21723047	12863281	0.2598	0.4649	0.2753
23	Acacetin	1838989	1331696	5276971	0.2177	0.1576	0.6247
26	Ursolic acid	11308	1391069	3039741	0.0025	0.3132	0.6843

Table S3. The relative biological activities of the Z1–Z3 extracts. Biological activities represented by ‘survivability’ of cells/enzymes (S) were taken from Figure 6 for the Z1–Z3 extracts of concentrations equal to 200 ug/mL and used to calculate biological activity (A) using formula $A = 100\% - S$. For each biological activity test (I–VIII), the values of A for the Z1, Z2 and Z3 extracts were rescaled in order to sum to 1 in every row of the table below.

		A = 100%-S [%]			Relative Activities (A _{rel})		
		Z1	Z2	Z3	Z1	Z2	Z3
I	Cytotoxicity B16F10-10%	2.02	4.42	15.31	0.0929	0.2032	0.7039

II	Cytotoxicity B16F10-1%	2.22	6.4	16.95	0.0868	0.2503	0.6629
III	Cytotoxicity HaCat-10%	0	26.2	0	0.0000	1.0000	0.0000
IV	A375-10%	19.31	28.07	0	0.4076	0.5924	0.0000
V	SKMEL-3	8.14	23.12	0	0.2604	0.7396	0.0000
VI	MurT	29.93	49.75	17.4	0.3083	0.5125	0.1792
VII	MushT	7.6	9.07	0	0.4559	0.5441	0.0000
VIII	SOD	7.41	36.14	24.88	0.1083	0.5281	0.3636