



Supplementary Material

Sagan Dalya Tea, a New “Old” Probable Adaptogenic Drug: Metabolic Characterization and Bioactivity Potentials of *Rhododendron adamsii* Leaves

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Table S1. Reference standards used for the qualitative and quantitative analysis by HPLC-DAD-ESI-tQ-MS and HPLC-UV assays.

No	Compound	Purity (≥), %	Manufacturer (cat. No)*	Used for analysis (compound No in Table 2)
3	Malic acid	99	Sigma (W265501)	3
4	Citric acid	99	Sigma (251275)	4
5	Tartaric acid	99	Sigma (W304401)	5
6	Succinic acid	99	Sigma (W471920)	6
7	Fumaric acid	99	Sigma (47910)	7
10	Phlorin (phloroglucinol <i>O</i> -glucoside)	90	Sigma (PHL85690)	8, 9, 10, 11, 12, 13, 14
17	Arbutin (hydroquinone <i>O</i> -glucoside)	98	Sigma (A4256)	15, 16, 17, 19, 20
21	Sakakin (orcinol <i>O</i> -glucoside)	90	Sigma (PHL83267)	18, 21, 24
45	Dihydroquercetin 3- <i>O</i> -rhamnoside	95	Sigma (PHL80356)	42, 43, 44, 45, 102, 109, 112, 113
50	Myricetin 3- <i>O</i> -rutinoside	98	Wuhan (TBW01950)	50
51	Myricetin 3- <i>O</i> -galactoside	85	Sigma (SML00249)	51
52	Isomyricitrin (myricetin 3- <i>O</i> -glucoside)	99	Extrasynthese (1357S)	36, 37, 46, 47, 49, 56, 91, 92, 93, 94, 97, 99, 106, 107, 108, 111, 118, 119, 165, 166, 167, 168, 169
53	Rutin (quercetin 3- <i>O</i> -rutinoside)	95	Sigma (R2303)	53
54	Hyperoside (quercetin 3- <i>O</i> -galactoside)	98	Extrasynthese (1027S)	54
55	Isoquercitrin (quercetin 3- <i>O</i> -glucoside)	98	Sigma (16654)	38, 48, 100, 101, 103, 104, 110, 114, 115, 121, 122
57	Avicularin (quercetin 3- <i>O</i> -arabinoside)	95	Sigma (75759)	57
58	Myricitrin (myricetin 3- <i>O</i> -rhamnoside)	99	Sigma (91255)	58
59	Quercitrin (quercetin 3- <i>O</i> -rhamnoside)	98	Sigma (740580)	59
60	Juglanin (kaempferol 3- <i>O</i> -arabinoside)	95	MCE (HYN3433)	60
61	Afzelin (kaempferol 3- <i>O</i> -rhamnoside)	98	Sigma (PHL83864)	61
62	Dihydroquercetin (taxifolin)	95	Sigma (PHL89284)	62
63	Phloretin	99	Sigma (P7912)	63
64	Dihydrokaempferol (aromadendrin)	95	Sigma (SMB00175)	64
65	Myricetin	96	Sigma (70050)	65
66	Quercetin	95	Sigma (Q4951)	66
67	Luteolin	98	Sigma (L9283)	67
68	Apigenin	95	Sigma (10798)	68
69	Isorhamnetin	95	Sigma (17794)	69
73	Kaempferol	99	Extrasynthese (1124S)	73
74	Farrerol	99	MCE (HYN0344)	74
86	1- <i>O</i> -Caffeoylquinic acid	98	ChemFaces (CFN99121)	86
89	Vanillic acid 4- <i>O</i> -glucoside	98	ChemFaces (CFN95257)	89
95	5- <i>O</i> -Caffeoylquinic acid	95	Sigma (C3878)	95
96	3- <i>O</i> -Caffeoylquinic acid	98	Sigma (94419)	96
98	4- <i>O</i> -Caffeoylquinic acid	98	Sigma (65969)	98
105	Miquelianin (quercetin 3- <i>O</i> -glucuronide)	90	Sigma (90733)	105
120	Cannabigerorcinic acid	98	Cayman (23258)	70, 71, 72, 75, 76, 77, 78, 79, 80, 81, 82, 83, 120, 116, 117, 123, 124, 129
137	Grifolic acid	98	ChemFaces (CFN97284)	125, 126, 127, 128, 130, 131, 132, 137, 138, 139, 140
141	Daurichromenic acid	98	ChemFaces (CFN97302)	133, 134, 135, 136, 141, 141, 142, 143, 144, 145
148	Gallic acid	97	Sigma (G7384)	146, 147, 148, 149, 150, 151
151	Gallic acid <i>O</i> -methyl ester	98	Sigma (274194)	151
154	Procyanidin B ₁	90	Extrasynthese (0983)	154
155	Catechin	99	Extrasynthese (0976S)	152, 153, 155, 157

Table S1. Cont.

No	Compound	Purity (≥), %	Manufacturer (cat. No)*	Used for analysis (compound No in Table 2)
158	Procyanidin B ₂	90	Sigma (PHL89552)	158
159	Epicatechin	99	Extrasynthese (0977S)	159
160	Procyanidin C ₁	90	Extrasynthese (0988)	160
161	Catechin 3-O-gallate	98	Extrasynthese (0972S)	156, 161, 162
164	Epicatechin 3-O-gallate	97.5	Extrasynthese (0978S)	164
170	Quercetin 3-O-(6''-O-galloyl)-glucoside	98	ChemFaces (CFN91064)	170, 171
	Saccharose	99	Sigma (S7903)	1
	Glucose	99	Sigma (49161)	2
	Ursolic acid	90	Sigma (216753)	22, 23, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35
	Dihydromyricetin	98	Sigma (SML0295)	39, 40, 41
	Protocatechuic acid	97	Sigma (37580)	84, 85
	Vanillic acid	97	Sigma (H36001)	88, 89, 90

* Manufacturers list: Cayman—Cayman Chemicals (Ann Arbor, MI, USA); ChemFaces—ChemFaces (Wuhan, Hubei, PRC); Extrasynthese—Extrasynthese (Lyon, France); MCE—MCE Med Chem Express (Monmouth, NJ, USA); Sigma—Sigma-Aldrich (St. Louis, MO, USA); Wuhan—Wuhan Chem Norm Biotech Co., Ltd. (Wuhan, PRC).

Table S2. Regression equations, correlation coefficients (r^2), standard deviation (S_{yx}), limits of detection (LOD), limits of quantification (LOQ) and linear ranges for 55 reference standards.

Compound	Ionization ^a	CE ^b (eV)	Regression equation ^c		r^2	S_{yx}	LOD/ LOQ ($\mu\text{g/mL}$)	Linear range ($\mu\text{g/mL}$)
			a	$b \cdot 10^6$				
1- <i>O</i> -Caffeoylquinic acid	N	-15	2.5394	-1.2360	0.9994	$0.45 \cdot 10^{-2}$	0.006/0.02	0.02–300.0
3- <i>O</i> -Caffeoylquinic acid	N	-15	2.4176	-1.5647	0.9994	$0.40 \cdot 10^{-2}$	0.005/0.02	0.02–300.0
4- <i>O</i> -Caffeoylquinic acid	N	-15	2.7365	-1.0690	0.9996	$0.51 \cdot 10^{-2}$	0.006/0.02	0.02–300.0
5- <i>O</i> -Caffeoylquinic acid	N	-15	2.9021	-1.4184	0.9998	$0.39 \cdot 10^{-2}$	0.004/0.01	0.02–300.0
Afzelin (kaempferol 3- <i>O</i> -rhamnoside)	N	-20	2.0859	-0.9171	0.9980	$6.18 \cdot 10^{-2}$	0.03/0.09	0.10–100.0
Apigenin	N	-15	5.8022	-0.8040	0.9990	$1.14 \cdot 10^{-2}$	0.007/0.02	0.02–500.0
Arbutin (hydroquinone <i>O</i> -glucoside)	N	-10	0.1756	-0.0144	0.9967	$3.01 \cdot 10^{-2}$	0.56/1.71	2.00–850.0
Avicularin (quercetin 3- <i>O</i> -arabinoside)	N	-20	1.4412	-0.6211	0.9930	$11.25 \cdot 10^{-2}$	0.26/0.78	0.80–100.0
Cannabigerorcinic acid	N	-15	1.1123	-1.0289	0.9862	$0.41 \cdot 10^{-2}$	0.01/0.04	0.05–400.0
Catechin	N	-20	0.9562	-0.0521	0.9971	$7.79 \cdot 10^{-2}$	0.27/0.82	0.90–100.0
Catechin 3- <i>O</i> -gallate	N	-20	1.3387	-0.0284	0.9981	$9.50 \cdot 10^{-2}$	0.23/0.71	0.80–100.0
Citric acid	N	-10	0.9518	-0.0267	0.9990	$1.03 \cdot 10^{-2}$	0.03/0.10	0.10–100.0
Daurichromenic acid	N	-30	1.1269	-0.9560	0.9864	$0.93 \cdot 10^{-2}$	0.02/0.08	0.10–400.0
Dihydrokaempferol (aromadendrin)	N	-15	3.6748	-0.7069	0.9987	$0.90 \cdot 10^{-2}$	0.008/0.02	0.02–400.0
Dihydromyricetin	N	-15	4.9634	-0.5047	0.9972	$0.63 \cdot 10^{-2}$	0.004/0.01	0.01–400.0
Dihydroquercetin (taxifolin)	N	-15	4.1069	-0.5637	0.9989	$0.77 \cdot 10^{-2}$	0.006/0.02	0.02–400.0
Dihydroquercetin 3- <i>O</i> -rhamnoside	N	-20	2.5078	-0.6342	0.9991	$0.96 \cdot 10^{-2}$	0.01/0.03	0.04–400.0
Epicatechin	N	-20	1.0828	-0.0456	0.9973	$6.85 \cdot 10^{-2}$	0.21/0.63	0.70–100.0
Epicatechin 3- <i>O</i> -gallate	N	-20	1.5152	-0.0523	0.9979	$12.67 \cdot 10^{-2}$	0.28/0.84	0.90–100.0
Farrerol	N	-10	6.3710	-0.9634	0.9985	$0.92 \cdot 10^{-2}$	0.004/0.01	0.02–400.0
Fumaric acid	N	-10	0.8615	-0.0364	0.9982	$2.03 \cdot 10^{-2}$	0.03/0.07	0.10–100.0
Gallic acid	N	-10	2.6538	-0.1376	0.9990	$1.17 \cdot 10^{-2}$	0.01/0.04	0.10–100.0
Gallic acid <i>O</i> -methyl ester	N	-15	1.9478	-0.2369	0.9984	$1.03 \cdot 10^{-2}$	0.02/0.05	0.05–250.0
Glucose	N	-10	1.5632	-0.0376	0.9983	$5.14 \cdot 10^{-2}$	0.11/0.33	0.40–100.0
Grifolic acid	N	-25	1.0627	-1.2531	0.9893	$0.62 \cdot 10^{-2}$	0.02/0.06	0.10–400.0
Hyperoside (quercetin 3- <i>O</i> -galactoside)	N	-20	1.4689	-0.3641	0.9990	$5.69 \cdot 10^{-2}$	0.12/0.38	0.40–400.0
Isomyricitrin (myricetin 3- <i>O</i> -glucoside)	N	-20	2.6340	-0.2411	0.9973	$2.74 \cdot 10^{-2}$	0.03/0.10	0.10–350.0
Isoquercitrin (quercetin 3- <i>O</i> -glucoside)	N	-20	1.8267	-0.4160	0.9990	$11.73 \cdot 10^{-2}$	0.21/0.67	0.70–400.0
Isorhamnetin	N	-15	1.1541	-0.4691	0.9987	$1.06 \cdot 10^{-2}$	0.03/0.10	0.10–350.0
Juglanin (kaempferol 3- <i>O</i> -arabinoside)	N	-20	2.0384	-0.3640	0.9975	$2.02 \cdot 10^{-2}$	0.03/0.10	0.10–350.0
Kaempferol	N	-10	1.2416	-0.3615	0.9901	$3.02 \cdot 10^{-2}$	0.08/0.24	0.3–100.0
Luteolin	N	-15	7.064	-1.533	0.9992	$1.92 \cdot 10^{-2}$	0.009/0.03	0.03–500.0
Malic acid	N	-10	0.9911	-0.0379	0.9988	$2.05 \cdot 10^{-2}$	0.07/0.21	0.3–100.0
Miquelianin (quercetin 3- <i>O</i> -glucuronide)	N	-20	1.6705	-0.4374	0.9988	$12.79 \cdot 10^{-2}$	0.25/0.77	0.8–100.0
Myricetin	N	-15	0.9375	-0.7631	0.9982	$1.42 \cdot 10^{-2}$	0.05/0.15	0.20–350.0
Myricetin 3- <i>O</i> -galactoside	N	-20	2.4751	-0.2081	0.9976	$2.04 \cdot 10^{-2}$	0.03/0.10	0.10–350.0

Table S2. Cont.

Compound	Ionization ^a	CE ^b (eV)	Regression equation ^c		r^2	S_{YX}	LOD/ LOQ ($\mu\text{g/mL}$)	Linear range ($\mu\text{g/mL}$)
			a	$b \cdot 10^6$				
Myricetin 3- <i>O</i> -rutinoside	N	-25	1.9634	-0.7458	0.9963	$2.59 \cdot 10^{-2}$	0.04/0.14	0.20–350.0
Myricitrin (myricetin 3- <i>O</i> -rhamnoside)	N	-20	1.8233	-0.7962	0.9975	$2.02 \cdot 10^{-2}$	0.04/0.11	0.20–350.0
Phloretin	N	-15	2.0330	-0.2516	0.9992	$1.09 \cdot 10^{-2}$	0.02/0.05	0.05–300.0
Phlorin (phloroglucinol <i>O</i> -glucoside)	N	-10	0.1537	-0.0189	0.9960	$3.83 \cdot 10^{-2}$	0.82/2.49	2.50–850.0
Procyanidin B ₁	N	-30	1.3722	-0.0829	0.9973	$9.93 \cdot 10^{-2}$	0.24/0.72	0.80–100.0
Procyanidin B ₂	N	-30	1.3620	-0.0820	0.9961	$9.91 \cdot 10^{-2}$	0.21/0.72	0.80–100.0
Procyanidin C ₁	N	-20	1.0634	-0.0933	0.9902	$10.01 \cdot 10^{-2}$	0.31/0.94	1.00–100.0
Protocatechuic acid	N	-10	1.9610	-0.5271	0.9993	$0.94 \cdot 10^{-2}$	0.02/0.05	0.05–250.0
Quercetin	N	-15	1.1105	-0.3211	0.9937	$4.18 \cdot 10^{-2}$	0.12/0.38	0.40–400.0
Quercetin 3- <i>O</i> -(6''- <i>O</i> -galloyl)-glucoside	N	-25	1.1492	-0.6010	0.9980	$4.68 \cdot 10^{-2}$	0.14/0.41	0.50–400.0
Quercitrin (quercetin 3- <i>O</i> -rhamnoside)	N	-20	1.9871	-0.6871	0.9984	$5.63 \cdot 10^{-2}$	0.09/0.28	0.40–400.0
Rutin (quercetin 3- <i>O</i> -rutinoside)	N	-20	1.2716	-0.7389	0.9897	$9.14 \cdot 10^{-2}$	0.23/0.72	0.80–400.0
Sucrose	N	-10	1.6278	-0.0428	0.9990	$7.11 \cdot 10^{-2}$	0.14/0.44	0.50–100.0
Sakakin (orcinol <i>O</i> -glucoside)	N	-10	0.2569	-0.0316	0.9973	$2.52 \cdot 10^{-2}$	0.33/1.00	1.00–750.0
Succinic acid	N	-10	1.4611	-0.0731	0.9982	$4.08 \cdot 10^{-2}$	0.09/0.27	0.30–100.0
Tartaric acid	N	-10	1.5330	-0.0863	0.9985	$4.15 \cdot 10^{-2}$	0.09/0.27	0.30–100.0
Ursolic acid	N	-20	2.6370	-0.5733	0.9952	$2.85 \cdot 10^{-2}$	0.03/0.11	0.20–250.0
Vanillic acid	N	-10	1.5379	-0.6220	0.9990	$0.99 \cdot 10^{-2}$	0.02/0.06	0.10–250.0
Vanillic acid 4- <i>O</i> -glucoside	N	-15	1.0864	-0.5271	0.9983	$1.04 \cdot 10^{-2}$	0.03/0.10	0.10–500.0

^a Ionization mode : N—negative. ^b CE—collision energy. ^c Regression equation: $y = a \cdot x + b$.

Table S3. Retention times (t_R), UV- and ESI-MS spectral data of compounds **1–171** found in *Rhododendron adamsii*.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ⁻ ^e	MS/MS (I , %) ^f	
1	0.62 ¹	O-Hexosyl-hexose ^L [26]	Nil	-10	341		
2	0.76 ¹	Hexose ^L [26]	Nil	-10	179		
3	0.92 ¹	Malic acid ^R [26,29]	Nil	-10	133		
4	1.05 ¹	Citric acid ^R [26,29]	Nil	-10	191		
5	1.26 ¹	Tartaric acid ^R [26,29]	Nil	-10	149		
6	1.42 ¹	Succinic acid ^R [26,29]	Nil	-10	117		
7	1.51 ¹	Fumaric acid ^R [26,29]	Nil	-10	115		
8	2.48 ¹	Phloroglucinol di-O-hexoside ^L [44]	PGL	-10	449	[449]: 287 (12), 125 (100)	
9	2.67 ¹	Phloroglucinol di-O-hexoside ^L [44]	PGL	-10	449	[449]: 287 (12), 125 (100)	
10	2.75 ¹	Phlorin (phloroglucinol O-glucoside) ^R [44]	PGL	-10	287	[287]: 125	
11	2.93 ¹	Phloroglucinol di-O-hexoside-O-acetate ^L [44]	PGL	-15	491	[491]: 449 (22), 287 (10), 125 (100)	
12	3.09 ¹	Phloroglucinol di-O-hexoside-O-acetate ^L [44]	PGL	-15	491	[491]: 449 (18), 287 (9), 125 (100)	
13	3.18 ¹	Phloroglucinol di-O-hexoside-di-O-acetate ^L [44]	PGL	-15	533	[533]: 491 (5), 449 (26), 287 (12), 125 (100)	
14	3.24 ¹	Phloroglucinol di-O-hexoside-di-O-acetate ^L [44]	PGL	-15	533	[533]: 491 (3), 449 (20), 287 (10), 125 (100)	
15	3.31 ¹	Hydroquinone di-O-hexoside ^L [45,46]	HQU	-10	433	[433]: 271 (100), 109 (12)	
16	3.43 ¹	Hydroquinone di-O-hexoside ^L [45,46]	HQU	-10	433	[433]: 271 (100), 109 (9)	
17	3.64 ¹	Arbutin (hydroquinone O-glucoside) ^R [45,46]	HQU	-10	271	[271]: 109	
18	3.69 ¹	Orcinol di-O-hexoside ^L [47]	ORC	-10	447	[447]: 285 (36), 123 (100)	
19	3.81 ¹	Hydroquinone di-O-hexoside-O-methyl ester ^L [45,46]	HQU	-10	447	[447]: 285 (23), 123 (100), 109 (12)	
20	3.92 ¹	Hydroquinone O-hexoside-O-methyl ester ^L [45,46]	HQU	-10	285	[285]: 123 (100), 109 (22)	
21	4.09 ¹	Sakakin (orcinol O-glucoside) ^R [47]	ORC	-10	285	[285]: 123	
22	4.26 ¹	Ursolic acid tri-O-hexoside ^L [33,48]	Nil	-20	941	[941]: 779 (10), 617 (100), 455 (54)	
23	4.31 ¹	Ursolic acid tri-O-hexoside ^L [33,48]	Nil	-20	941	[941]: 779 (14), 617 (100), 455 (43)	
24	4.47 ¹	Orcinol O-hexoside-O-acetate ^L [47]	ORC	-15	327	[327]: 285 (16), 123 (100)	

Table S3. Cont.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ^{-e}	MS/MS (I , %) ^f	
25	4.58 ^I	Ursolic acid di- <i>O</i> -hexoside ^L [33,48]	Nil	-20	779	[779]: 617 (100), 455 (37)	
26	4.74 ^I	Ursolic acid di- <i>O</i> -hexoside ^L [33,48]	Nil	-20	779	[779]: 617 (100), 455 (34)	
27	4.79 ^I	Ursolic acid tri- <i>O</i> -hexoside- <i>O</i> -acetate ^L [33,48]	Nil	-20	983	[983]: 941 (26), 779 (8), 617 (100), 455 (43)	
28	4.97 ^I	Ursolic acid tri- <i>O</i> -hexoside- <i>O</i> -acetate ^L [33,48]	Nil	-20	983	[983]: 941 (20), 779 (4), 617 (100), 455 (35)	
29	5.18 ^I	Ursolic acid di- <i>O</i> -hexoside- <i>O</i> -acetate ^L [33,48]	Nil	-20	821	[821]: 779 (18), 617 (100), 455 (29)	
30	5.46 ^I	Ursolic acid <i>O</i> -hexoside ^L [33,48]	Nil	-20	617	[617]: 455	
31	5.53 ^I	Ursolic acid di- <i>O</i> -hexoside-di- <i>O</i> -acetate ^L [33,48]	Nil	-20	863	[863]: 821 (9), 779 (22), 659 (8), 617 (100), 455 (31)	
32	5.74 ^I	Ursolic acid di- <i>O</i> -hexoside-di- <i>O</i> -acetate ^L [33,48]	Nil	-20	863	[863]: 821 (11), 779 (25), 659 (4), 617 (100), 455 (25)	
33	7.87 ^I	Ursolic acid <i>O</i> -hexoside- <i>O</i> -acetate ^L [33,48]	Nil	-20	659	[659]: 617 (100), 455 (30)	
34	8.28 ^I	Ursolic acid <i>O</i> -hexoside- <i>O</i> -acetate ^L [33,48]	Nil	-20	659	[659]: 617 (100), 455 (35)	
35	10.26 ^I	Ursolic acid <i>O</i> -hexoside-di- <i>O</i> -acetate ^L [33,48]	Nil	-20	701	[701]: 659 (3), 617 (100), 455 (29)	
36	2.72 ^{II}	Myricetin tri- <i>O</i> -hexoside-tri- <i>O</i> -desoxyhexoside ^L [49–51]	MYR	-30	1241	[1241]: 1095 (100), 949 (22), 933 (2) [949]: 803 (100), 641 (36), 479 (7) [479]: 317	
37	2.79 ^{II}	Myricetin tri- <i>O</i> -hexoside-di- <i>O</i> -desoxyhexoside ^L [49–51]	MYR	-30	1095	[1095]: 949 (100), 803 (27), 641 (9) [803]: 641 (100), 479 (31) [479]: 317	
38	2.97 ^{II}	Quercetin tri- <i>O</i> -hexoside-di- <i>O</i> -desoxyhexoside ^L [12,13]	QUE	-25	1079	[1079]: 933 (100), 787 (21), 625 (3) [787]: 625 (100), 463 (23) [463]: 301	
39	3.22 ^{II}	Dihydromyricetin di- <i>O</i> -hexoside ^L [12,52]	DHM	-20	643	[643]: 481 (100), 319 (27)	
40	3.45 ^{II}	Dihydromyricetin <i>O</i> -hexoside ^L [12,52]	DHM	-20	481	[481]: 319	
41	3.52 ^{II}	Dihydroquercetin di- <i>O</i> -hexoside-di- <i>O</i> -desoxyhexoside ^L [12,52]	DHQ	-25	919	[919]: 773 (12), 627 (100), 611 (35) [627]: 465 (100), 303 (5)	

Table S3. Cont.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ^{-e}	MS/MS (I , %) ^f	
42	3.64 ^{II}	Dihydroquercetin di- <i>O</i> -hexoside- <i>O</i> -desoxyhexoside ^L [12,52]	DHQ	-25	773	[773]: 627 (100), 465 (32) [465]: 303	
43	3.72 ^{II}	Dihydroquercetin <i>O</i> -hexoside- <i>O</i> -desoxyhexoside ^L [12,52]	DHQ	-25	611	[611]: 465 (100), 303 (28)	
44	3.78 ^{II}	Dihydroquercetin <i>O</i> -hexoside ^L [12,52]	DHQ	-20	465	[465]: 303	
45	3.83 ^{II}	Dihydroquercetin 3- <i>O</i> -rhamnoside ^R [12,52]	DHQ	-20	449	[449]: 303	
46	4.09 ^{II}	Myricetin di- <i>O</i> -hexoside-di- <i>O</i> -desoxyhexoside ^L [49–51]	MYR	-25	933	[933]: 787 (25), 641 (100) [641]: 479 (100), 317 (27)	
47	4.18 ^{II}	Myricetin di- <i>O</i> -hexoside- <i>O</i> -desoxyhexoside ^L [49–51]	MYR	-25	787	[787]: 641 (100), 479 (35) [479]: 317	
48	4.26 ^{II}	Quercetin di- <i>O</i> -hexoside- <i>O</i> -desoxyhexoside ^L [12,13]	QUE	-25	771	[771]: 625 (21), 463 (100), 301 (12)	
49	4.31 ^{II}	Myricetin <i>O</i> -hexoside- <i>O</i> -desoxyhexoside ^L [49–51]	MYR	-25	625	[625]: 479 (100), 317 (25)	
50	4.43 ^{II}	Myricetin 3- <i>O</i> -rutinoside ^R [49–51]	MYR	-25	625	[625]: 479 (100), 317 (3)	
51	4.51 ^{II}	Myricetin 3- <i>O</i> -galactoside ^R [49–51]	MYR	-20	479	[479]: 317	
52	4.58 ^{II}	Isomyricitrin (myricetin 3- <i>O</i> -glucoside) ^R [49–51]	MYR	-20	479	[479]: 317	
53	4.74 ^{II}	Rutin (quercetin 3- <i>O</i> -rutinoside) ^R [12,13]	QUE	-20	609	[609]: 463 (100), 301 (15)	
54	4.78 ^{II}	Hyperoside (quercetin 3- <i>O</i> -galactoside) ^R [12,13]	QUE	-20	463	[463]: 301	
55	4.83 ^{II}	Isoquercitrin (quercetin 3- <i>O</i> -glucoside) ^R [12,13]	QUE	-20	463	[463]: 301	
56	4.97 ^{II}	Myricetin <i>O</i> -pentoside ^L [49–51]	MYR	-20	449	[449]: 317	
57	5.11 ^{II}	Avicularin (quercetin 3- <i>O</i> -arabinoside) ^R [12,13]	QUE	-20	433	[433]: 301	
58	5.26 ^{II}	Myricitrin (myricetin 3- <i>O</i> -rhamnoside) ^R [49–51]	MYR	-20	463	[463]: 317	
59	5.63 ^{II}	Quercitrin (quercetin 3- <i>O</i> -rhamnoside) ^R [12,13]	QUE	-20	433	[433]: 301	
60	5.77 ^{II}	Juglanin (kaempferol 3- <i>O</i> -arabinoside) ^R [35]	KAE	-20	417	[417]: 285	
61	6.29 ^{II}	Afzelin (kaempferol 3- <i>O</i> -rhamnoside) ^R [35]	KAE	-20	431	[431]: 285	
62	8.25 ^{II}	Dihydroquercetin (taxifloin) ^R [12,52]	DHQ	-15	303		
63	8.68 ^{II}	Phloretin ^R [35]	PHL	-15	273		

Table S3. Cont.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ^{-e}	MS/MS (I , %) ^f	
64	8.83 ^{II}	Dihydrokaempferol (aromadendrin) ^R [12,52]	DHK	-15	287		
65	9.01 ^{II}	Myricetin ^R [49–51]	MYR	-15	317		
66	9.23 ^{II}	Quercetin ^R [12,13]	QUE	-15	301		
67	9.27 ^{II}	Luteolin ^R [35]	LUT	-15	285		
68	9.37 ^{II}	Apigenin ^R [35]	API	-15	269		
69	9.51 ^{II}	Isorhamnetin ^R [35]	QUE	-15	315		
70	9.76 ^{II}	Cannabigerorcinic acid O-methyl ester di-O-hexoside ^L [53,54]	CGA	-15	641	[641]: 479 (26), 317 (100), 303 (5) [317]: 303 (28), 285 (100) [303]: 285 (18), 275 (43), 234 (100), 166 (18)	
71	9.93 ^{II}	Cannabigerorcinic acid O-methyl ester di-O-hexoside ^L [53,54]	CGA	-15	641	[641]: 479 (23), 317 (100), 303 (7) [317]: 303 (24), 285 (100) [303]: 285 (16), 275 (51), 234 (100), 166 (22)	
72	10.04 ^{II}	Cannabigerorcinic acid O-methyl ester O-hexoside-O-desoxyhexoside ^L [53,54]	CGA	-15	625	[625]: 479 (31), 317 (100) [317]: 303 (25), 285 (100) [303]: 285 (18), 275 (45), 234 (100), 166 (26)	
73	10.24 ^{II}	Kaempferol ^R [35]	KAE	-10	285		
74	10.48 ^{II}	Farrerol ^R [35]	FAR	-10	299		
75	10.63 ^{II}	Cannabigerorcinic acid methyl ester O-hexoside ^L [53,54]	CGA	-20	479	[479]: 317 (42), 303 (100), 285 (93) [303]: 285 (15), 275 (38), 234 (100), 166 (16)	
76	10.97 ^{II}	Cannabigerorcinic acid di-O-methyl ester O-hexoside ^L [53,54]	CGA	-22	493	[493]: 331 (19), 317 (5), 303 (100), 285 (14) [303]: 285 (22), 275 (40), 234 (100), 166 (19)	
77	11.05 ^{II}	Cannabigerorcinic acid di-O-methyl ester O-hexoside ^L [53,54]	CGA	-22	493	[493]: 331 (22), 317 (7), 303 (100), 285 (11) [303]: 285 (26), 275 (42), 234 (100), 166 (20)	
78	11.22 ^{II}	Cannabigerorcinic acid di-O-methyl ester O-hexoside ^L [53,54]	CGA	-22	493	[493]: 331 (21), 317 (5), 303 (100), 285 (14) [303]: 285 (31), 275 (49), 234 (100), 166 (25)	
79	11.47 ^{II}	Cannabigerorcinic acid O-methyl ester ^L [53,54]	CGA	-30	317	[317]: 303 (27), 285 (100) [303]: 285 (21), 275 (43), 234 (100), 166 (22)	635 ^{2M-H}
80	11.52 ^{II}	Cannabigerorcinic acid O-methyl ester ^L [53,54]	CGA	-30	317	[317]: 303 (26), 285 (100) [303]: 285 (22), 275 (46), 234 (100), 166 (27)	
81	11.74 ^{II}	Cannabigerorcinic acid di-O-methyl ester ^L [53,54]	CGA	-30	331	[331]: 317 (10), 303 (100), 285 (73) [303]: 285 (24), 275 (47), 234 (100), 166 (23)	
82	12.04 ^{II}	Cannabigerorcinic acid di-O-methyl ester ^L [53,54]	CGA	-30	331	[331]: 317 (9), 303 (100), 285 (75) [303]: 285 (27), 275 (40), 234 (100), 166 (18)	

Table S3. Cont.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ^{-e}	MS/MS (I , %) ^f	
83	13.15 ^{III}	Cannabigerorcinic acid tri- <i>O</i> -methyl ester ^L [53,54]	CGA	-30	345	[345]: 331 (5), 317 (63), 303 (100), 285 (52) [303]: 285 (24), 275 (49), 234 (100), 166 (16)	
84	0.68 ^{III}	Protocatechuic acid di- <i>O</i> -hexoside ^L [35]	PCA	-15	477	[477]: 315 (22), 153 (100)	
85	0.89 ^{III}	Protocatechuic acid <i>O</i> -hexoside ^L [35]	PCA	-15	315	[315]: 153	
86	2.42 ^{III}	1- <i>O</i> -Caffeoylquinic acid ^R [55]	CQA	-15	353	[353]: 191 (100), 179 (15), 173 (3), 135 (5)	
87	2.71 ^{III}	Vanillic/isovanillic acid <i>O</i> -hexoside ^L [35]	VA	-15	329	[329]: 167	
88	2.76 ^{III}	Vanillic/isovanillic acid <i>O</i> -hexoside ^L [35]	VA	-15	329	[329]: 167	
89	2.81 ^{III}	Vanillic acid 4- <i>O</i> -glucoside ^R [35]	VA	-15	329	[329]: 167	
90	2.95 ^{III}	Vanillic/isovanillic acid <i>O</i> -hexoside ^L [35]	VA	-15	329	[329]: 167	
91	3.42 ^{III}	Myricetin di- <i>O</i> -hexoside-di- <i>O</i> -hexuronide ^L [49–51]	MYR	-30	993	[993]: 817 (82), 655 (100) [655]: 479 (100), 317 (23)	
92	3.54 ^{III}	Myricetin di- <i>O</i> -hexoside-di- <i>O</i> -hexuronide ^L [49–51]	MYR	-30	993	[993]: 817 (89), 655 (100) [655]: 479 (100), 317 (21)	
93	3.74 ^{III}	Myricetin di- <i>O</i> -hexoside- <i>O</i> -hexuronide ^L [49–51]	MYR	-25	817	[817]: 641 (100), 479 (35) [479]: 317	
94	4.11 ^{III}	Myricetin <i>O</i> -hexoside-di- <i>O</i> -hexuronide ^L [49–51]	MYR	-25	831	[831]: 655 (12), 479 (100), 317 (20)	
95	4.26 ^{III}	5- <i>O</i> -Caffeoylquinic acid ^R [55]	CQA	-15	353	[353]: 191 (100), 179 (4), 165 (15)	
96	4.51 ^{III}	3- <i>O</i> -Caffeoylquinic acid ^R [55]	CQA	-15	353	[353]: 191 (100), 179 (81), 135 (22)	
97	4.67 ^{III}	Myricetin <i>O</i> -hexoside- <i>O</i> -hexuronide ^L [49–51]	MYR	-25	655	[655]: 479 (100), 317 (25)	
98	4.72 ^{III}	4- <i>O</i> -Caffeoylquinic acid ^R [55]	CQA	-15	353	[353]: 191 (19), 179 (100), 173 (91), 135 (12)	
99	4.89 ^{III}	Myricetin <i>O</i> -hexuronide ^L [49–51]	MYR		493	[493]: 317	
100	5.03 ^{III}	Quercetin di- <i>O</i> -hexoside- <i>O</i> -hexuronide ^L [12,13]	QUE	-25	801	[801]: 625 (11), 463 (100), 301 (14)	
101	5.14 ^{III}	Quercetin <i>O</i> -hexoside-di- <i>O</i> -hexuronide ^L [12,13]	QUE	-25	815	[801]: 639 (5), 463 (100), 301 (12)	
102	5.26 ^{III}	Dihydroquercetin <i>O</i> -hexuronide ^L [12,51]	DHQ	-25	479	[479]: 303	

Table S3. Cont.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ^{-e}	MS/MS (I , %) ^f	
103	5.38 ^{III}	Quercetin <i>O</i> -hexoside- <i>O</i> -hexuronide ^L [12,13]	QUE	-25	639	[639]: 463 (100), 301 (10)	
104	5.63 ^{III}	Quercetin <i>O</i> -hexoside- <i>O</i> -hexuronide ^L [12,13]	QUE	-25	639	[639]: 463 (100), 301 (15)	
105	5.69 ^{III}	Miquelianin (quercetin 3- <i>O</i> -glucuronide) ^R [12,13]	QUE	-20	477	[477]: 301	
106	6.01 ^{III}	Myricetin <i>O</i> -hexuronide- <i>O</i> -acetate ^L [48–50]	MYR	-30	535	[535]: 493 (100), 317 (28)	
107	6.78 ^{III}	Myricetin <i>O</i> -hexoside-di- <i>O</i> -acetate ^L [49–51]	MYR	-30	563	[563]: 521 (25), 479 (100), 317 (33)	
108	6.92 ^{III}	Myricetin <i>O</i> -hexouronide-di- <i>O</i> - acetate ^L [49–51]	MYR	-30	577	[577]: 535 (3), 493 (100), 317 (18)	
109	7.22 ^{III}	Dihydroquercetin <i>O</i> -hexuronide- <i>O</i> -acetate ^L	DGQ	-25	521	[521]: 479 (100), 303 (9)	
110	7.36 ^{III}	Quercetin <i>O</i> -hexuronide- <i>O</i> -acetate ^L	QUE	-25	519	[519]: 477 (100), 301 (12)	
111	7.92 ^{III}	Myricetin <i>O</i> -hexoside-di- <i>O</i> -acetate ^L [49–51]	MYR	-30	563	[563]: 521 (21), 479 (100), 317 (41)	
112	8.14 ^{III}	Dihydroquercetin <i>O</i> -hexuronide-di- <i>O</i> -acetate ^L [12,52]	DHQ	-25	563	[563]: 521 (7), 479 (100), 303 (9)	
113	8.26 ^{III}	Dihydroquercetin <i>O</i> -hexuronide-di- <i>O</i> -acetate ^L [12,52]	DHQ	-25	563	[563]: 521 (5), 479 (100), 303 (5)	
114	8.47 ^{III}	Quercetin <i>O</i> -hexuronide-di- <i>O</i> -acetate ^L [12,13]	QUE	-25	561	[561]: 519 (12), 477 (100), 301 (14)	
115	8.69 ^{III}	Quercetin <i>O</i> -hexuronide-di- <i>O</i> -acetate ^L [12,13]	QUE	-25	561	[561]: 519 (10), 477 (100), 301 (18)	
116	8.92 ^{III}	Cannabigerorcinic acid di- <i>O</i> -hexoside ^L [53,54]	CGA	-25	627	[627]: 465 (14), 303 (100), 285 (57) [303]: 285 (25), 275 (42), 234 (100), 166 (20)	
117	9.01 ^{III}	Cannabigerorcinic acid <i>O</i> -hexoside ^L [53,54]	CGA	-25	465	[465]: 303 (73), 285 (100) [303]: 285 (22), 275 (43), 234 (100), 166 (25)	
118	9.18 ^{III}	Myricetin <i>O</i> -hexoside-tri- <i>O</i> -acetate ^L [49–51]	MYR	-25	605	[605]: 563 (5), 479 (100), 317 (25)	
119	9.24 ^{III}	Myricetin <i>O</i> -hexoside-tri- <i>O</i> -acetate ^L [49–51]	MYR	-25	605	[605]: 563 (2), 479 (100), 317 (31)	

Table S3. Cont.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ^{-e}	MS/MS (I , %) ^f	
120	9.33 ^{III}	Cannabigerorcinic acid ^R	CGA	-20	303	[303]: 285 (37), 275 (50), 234 (100), 166 (25)	607 ^{2M-H}
121	9.46 ^{III}	Quercetin <i>O</i> -hexoside-tri- <i>O</i> -acetate ^L [12,13]	QUE	-25	589	[589]: 547 (2), 505 (14), 463 (100), 301 (11)	
122	9.53 ^{III}	Quercetin <i>O</i> -hexoside-tri- <i>O</i> -acetate ^L [12,13]	QUE	-25	589	[589]: 547 (1), 505 (10), 463 (100), 301 (18)	
123	9.72 ^{III}	Cannabigerorcinic acid <i>O</i> -acetate ^L	CGA	-20	345	[345]: 303 (82), 285 (100) [303]: 285 (31), 275 (43), 234 (100), 166 (22)	
124	9.81 ^{III}	Cannabigerorcinic acid di- <i>O</i> -acetate ^L	CGA	-20	387	[387]: 345 (18), 303 (100), 285 (53) [303]: 285 (29), 275 (42), 234 (100), 166 (18)	
125	9.93 ^{III}	Hydroxy-grifolic acid di- <i>O</i> -hexoside ^L [53]	GRA	-20	711	[711]: 549 (18), 387 (100), 369 (73) [387]: 369 (27), 318 (53), 250 (100), 196 (18)	
126	9.98 ^{III}	Hydroxy-grifolic acid <i>O</i> -hexoside ^L [53]	GRA	-20	549	[549]: 387 (28), 369 (100) [387]: 369 (25), 318 (50), 250 (100), 196 (14)	
127	10.09 ^{III}	Hydroxy-grifolic acid <i>O</i> -hexoside ^L [53]	GRA	-20	549	[549]: 387 (31), 369 (100) [387]: 369 (29), 318 (48), 250 (100), 196 (16)	
128	10.27 ^{III}	Hydroxy-grifolic acid <i>O</i> -pentoside ^L [53]	GRA	-20	519	[519]: 387 (25), 369 (100) [387]: 369 (25), 318 (50), 250 (100), 196 (18)	
129	10.40 ^{III}	Cannabigerorcinic acid tri- <i>O</i> -acetate ^L [53,54]	CGA	-20	429	[429]: 387 (3), 345 (12), 303 (100) [303]: 285 (35), 275 (52), 234 (100), 166 (21)	
130	10.67 ^{III}	Hydroxy-grifolic acid ^L [53]	GRA	-20	387	[387]: 369 (27), 318 (53), 250 (100), 196 (22)	
131	10.75 ^{III}	Grifolic acid di- <i>O</i> -hexoside ^L [53]	GRA	-20	695	[695]: 533 (23), 371 (100), 353 (83) [371]: 353 (10), 302 (63), 234 (100), 180 (5)	
132	10.86 ^{III}	Grifolic acid <i>O</i> -hexoside ^L [53]	GRA	-20	533	[533]: 371 (51), 353 (100) [371]: 353 (14), 302 (61), 234 (100), 180 (9)	
133	10.86 ^{III}	Daurichromenic acid di- <i>O</i> -hexoside ^L [53,54]	DCA	-25	693	[693]: 531 (52), 369 (100) [369]: 351 (12), 300 (100), 232 (31)	
134	11.06 ^{III}	Daurichromenic acid <i>O</i> -hexoside ^L [53,54]	DCA	-25	531	[531]: 369 [369]: 351 (10), 300 (100), 232 (29)	
135	11.26 ^{III}	Hydroxy-daurichromenic acid ^L [53,54]	HDCA	-30	385	[385]: 367 (22), 316 (100), 248 (39)	769 ^{2M-H}
136	11.43 ^{III}	Hydroxy-daurichromenic acid <i>O</i> -methyl ester ^L [53,54]	HDCA	-30	399	[399]: 385 (15), 367 (100) [385]: 367 (25), 316 (100), 248 (42)	
137	11.64 ^{III}	Grifolic acid ^R [53]	GRA	-25	371	[371]: 353 (15), 327 (33), 302 (62), 234 (100), 180 (12)	741 ^{2M-H}

Table S3. Cont.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ^{-e}	MS/MS (I , %) ^f	
138	12.72 ^{III}	Grifolic acid <i>O</i> -methyl ester ^L [53]	GRA	-25	385	[385]: 371 (23), 353 (100) [371]: 353 (14), 302 (59), 234 (100), 180 (10)	
139	12.81 ^{III}	Grifolic acid di- <i>O</i> -methyl ester ^L [53]	GRA	-25	399	[399]: 385 (26), 367 (100) [385]: 371 (20), 353 (100) [371]: 353 (16), 302 (58), 234 (100), 180 (12)	
140	12.92 ^{III}	Grifolic acid <i>O</i> -methyl ester- <i>O</i> -acetate ^L [53]	GRA	-25	427	[427]: 385 (62), 371 (21), 353 (100) [371]: 353 (18), 302 (60), 234 (100), 180 (14)	
141	13.14 ^{III}	Daurichromenic acid ^R [53,54]	DCA	-30	369	[369]: 351 (12), 300 (100), 232 (35)	737 ^{2M-H}
142	13.42 ^{III}	Daurichromenic acid <i>O</i> -acetate ^L [53,54]	DCA	-32	411	[411]: 369 (100), 351 (18) [369]: 351 (14), 300 (100), 232 (32)	
143	13.58 ^{III}	Daurichromenic acid <i>O</i> -methyl ester ^L [53,54]	DCA	-35	383	[383]: 369 (25), 351 (100) [369]: 351 (12), 300 (100), 232 (30)	
144	13.74 ^{III}	Daurichromenic acid <i>O</i> -methyl ester- <i>O</i> -acetate ^L [53,54]	DCA	-35	425	[425]: 383 (35), 369 (53), 351 (100) [369]: 351 (14), 300 (100), 232 (31)	
145	14.23 ^{III}	Daurichromenic acid di- <i>O</i> -methyl ester ^L [53,54]	DCA	-35	397	[397]: 383 (5), 369 (63), 351 (100) [369]: 351 (9), 300 (100), 232 (28)	
146	2.70 ^{IV}	Gallic acid di- <i>O</i> -hexoside ^L [28]	GA	-10	493	[493]: 331 (52), 169 (100) [169]: 151 (100), 141 (10)	
147	3.27 ^{IV}	Gallic acid <i>O</i> -hexoside ^L [28]	GA	-10	331	[331]: 169 [169]: 151 (100), 141 (14)	
148	3.94 ^{IV}	Gallic acid ^R [28]	GA	-10	169	[169]: 151 (100), 141 (12)	
149	4.32 ^{IV}	Gallic acid <i>O</i> -methyl ester <i>O</i> -hexoside ^L [28]	GA	-15	345	[345]: 183 (100), 169 (24) [169]: 151 (100), 141 (9)	
150	4.91 ^{IV}	Gallic acid <i>O</i> -methyl ester <i>O</i> -hexoside ^L [28]	GA	-15	345	[345]: 183 (100), 169 (22) [169]: 151 (100), 141 (7)	
151	5.60 ^{IV}	Gallic acid <i>O</i> -methyl ester ^R [28]	GA	-15	183	[183]: 169 [169]: 151 (100), 141 (11)	
152	7.82 ^{IV}	Catechin/epicatechin di- <i>O</i> -hexoside ^L [28]	CAT	-20	613	[613]: 451 (53), 289 (100)	
153	8.51 ^{IV}	Catechin/epicatechin <i>O</i> -hexoside ^L [28]	CAT	-20	451	[451]: 289	
154	9.03 ^{IV}	Procyanidin B ₁ ^R [28]	CAT	-30	577	[577]: 289	
155	9.82 ^{IV}	Catechin ^R [28]	CAT	-20	289	[289]: 247 (100), 191 (28), 123 (9)	
156	10.76 ^{IV}	Catechin/epicatechin <i>O</i> -hexoside- <i>O</i> -gallate ^L [28]	CAT	-20	603	[603]: 451 (33), 289 (100)	
157	12.15 ^{IV}	Catechin/epicatechin <i>O</i> -hexoside ^L [28]	CAT	-20	451	[451]: 289	
158	13.02 ^{IV}	Procyanidin B ₂ ^R [28]	CAT	-30	577	[577]: 289	
159	13.54 ^{IV}	Epicatechin ^R [28]	CAT	-20	289	[289]: 247 (14), 191 (58), 123 (100)	
160	15.51 ^{IV}	Procyanidin C ₁ ^R [28]	CAT	-20	865	[865]: 577 (82), 289 (100)	
161	19.67 ^{IV}	Catechin 3- <i>O</i> -gallate ^R [28]	CAT	-20	441	[441]: 289 (9), 125 (15), 109 (100)	
162	20.52 ^{IV}	Catechin/epicatechin dimer <i>O</i> -gallate ^L [28]	CAT	-30	729	[729]: 577 (100), 289 (53)	

Table S3. Cont.

No	t_R (min) ^a	Compound ^b	UV pattern ^c	CE (eV) ^d	ESI-MS (m/z)		Adduct ions
					[M-H] ⁻ ^e	MS/MS (I , %) ^f	
163	21.48 ^{IV}	Catechin/epicatechin dimer di- <i>O</i> -gallate ^L [28]	CAT	-30	881	[729]: 577 (100), 289 (44)	
164	22.26 ^{IV}	Epicatechin 3- <i>O</i> -gallate ^R [28]	CAT	-20	441	[441]: 289 (15), 125 (42), 109 (100)	
165	22.97 ^{IV}	Myricetin tri- <i>O</i> -hexoside-di- <i>O</i> -gallate ^L [49–51]	MYR	-30	1107	[1107]: 955 (14), 803 (83), 641 (100) [641]: 479 (100), 317 (27)	
166	23.67 ^{IV}	Myricetin di- <i>O</i> -hexoside-di- <i>O</i> -gallate ^L [49–51]	MYR	-30	945	[945]: 793 (41), 641 (100) [641]: 479 (100), 317 (25)	
167	24.43 ^{IV}	Myricetin di- <i>O</i> -hexoside- <i>O</i> -gallate ^L [49–51]	MYR	-30	793	[793]: 641 (14), 479 (100), 317 (21)	
168	25.63 ^{IV}	Myricetin <i>O</i> -hexoside- <i>O</i> -gallate ^L [49–51]	MYR	-25	631	[631]: 479 (100), 317 (25)	
169	25.83 ^{IV}	Myricetin <i>O</i> -hexoside- <i>O</i> -gallate ^L [49–51]	MYR	-25	631	[631]: 479 (100), 317 (30)	
170	26.74 ^{IV}	Quercetin 3- <i>O</i> -(6''- <i>O</i> -galloyl)-glucoside ^R [12,13]	QUE	-25	615	[615]: 463 (100), 301 (12)	
171	28.02 ^{IV}	Quercetin <i>O</i> -hexoside-di- <i>O</i> -gallate ^L [12,13]	QUE	-25	767	[767]: 615 (8), 463 (100), 301 (15)	

^a Chromatographic conditions: I—mode 1; II—mode 2; III—mode 3; IV—mode 4. ^b Compound identification was based on comparison of retention time, UV and MS spectral data with reference standard (^R) or interpretation of UV and MS spectral data and comparison with literature data (^L). ^c UV-patterns as listed in Table S4. ^d CE—collision energy. ^e Mass spectrometric data: deprotonated ion [M-H]⁻. ^f Signal intensity (percentage).

Table S4. UV-spectral patterns of compounds found in *R. adamsii*.

Name of UV-pattern	Group of compound	λ_{\max} , nm
API	Apigenin	270, 335
CAT	Catechins	275 (± 1)
CGA	Cannabigerorcinic acid (CGA) / CGA derivatives	220 (± 2), 270 (± 2), 305 (± 3)
CQA	Caffeoylquinic acids	290 (± 2) sh, 324 (± 2)
DCA	Daurichromenic acid (DCA) / DCA derivatives	260 (± 2)
DHQ	Dihydroquercetin (DHQ) / DHQ glycosides	290 (± 2), 325 (± 2) sh
DHK	Dihydrokaempferol (DHK) / DHK glycosides	291 (± 2) sh, 330 (± 2)
DHM	Dihydromyricetin (DHM) / DHM glycosides	295 (± 2) sh, 320 (± 4)
FAR	Farrerol	260, 330
GA	Gallic acid (GA) / GA derivatives	271 (± 2)
GRA	Grifolic acid (GRA) / GRA derivatives	220 (± 2), 270 (± 2), 310 (± 3)
HDCA	Hydroxy-daurichromenic acid (HDCA) / HDCA derivatives	230 (± 3), 260 (± 2)
HQU	Hydroquinone (HQU) / HQU derivatives	282 (± 1)
KAE	Kaempferol (Ka) / Ka glycosides	265 (± 3), 360 (± 5)
LUT	Luteolin	255 sh, 265, 355
MYR	Myricetin (My) / My glycosides	255 (± 3), 370 (± 5)
Nil	No absorption > 200 nm	-
ORC	Orcinol (ORC) / ORC derivatives	230 (± 2), 275 (± 2), 280 (± 3)
QUE	Quercetin (Qu) / Qu glycosides	256 (± 3), 267 (± 2), 362 (± 4)
PCA	Protocatechuic acid glycosides	260 (± 1), 291 (± 2)
PGL	Phloroglucinol (PGL) / PGL derivatives	266 (± 2)
PHL	Phloretin	220, 260
VA	Vanillic/isovanillic acid (VA) / VA derivatives	260 (± 1), 292 (± 2)

sh—shoulder.

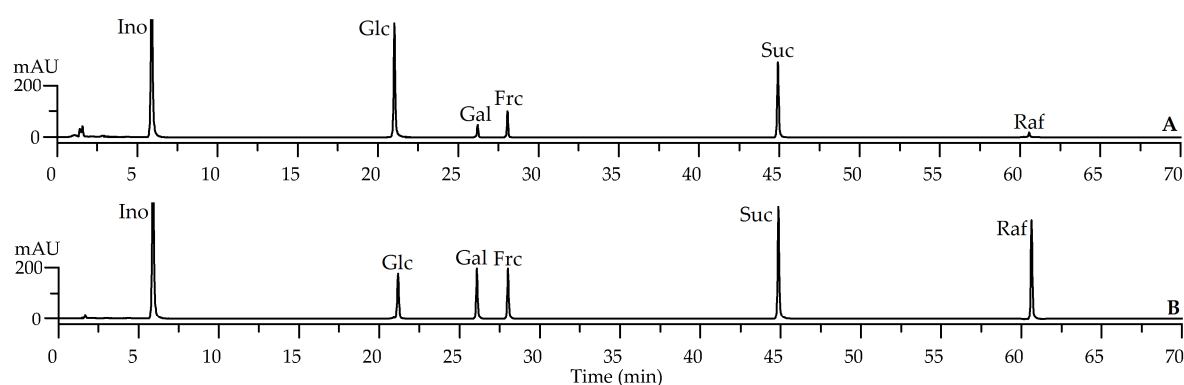


Figure S1. High-performance anion-exchange chromatography with photodiode detection (HPAEC-PDA) chromatograms of free carbohydrates of *Rhododendron adamsii* leaves (July sample, **A**) and reference standards (**B**). Chromatographic conditions: liquid chromatograph LC-20 Prominence coupled with photodiode array detector SPD-M30A (all Shimadzu, Columbia, MD, USA) and column Dionex CarboPac MA1 (4 × 250 mm, 8.5 µm; Thermo Fisher Scientific, Sunnyvale, CA, USA); isocratic elution; eluent 0.6 M NaOH; flow rate: 400 µL/min; column temperature 25 °C; sample volume 5 µL; detection wavelength 190 nm. Inositol (Ino) was used as an internal standard. Carbohydrates were signed as Frc—fructose, Gal—galactose, Glc—glucose, Raf—raffinose, and Suc—sucrose.

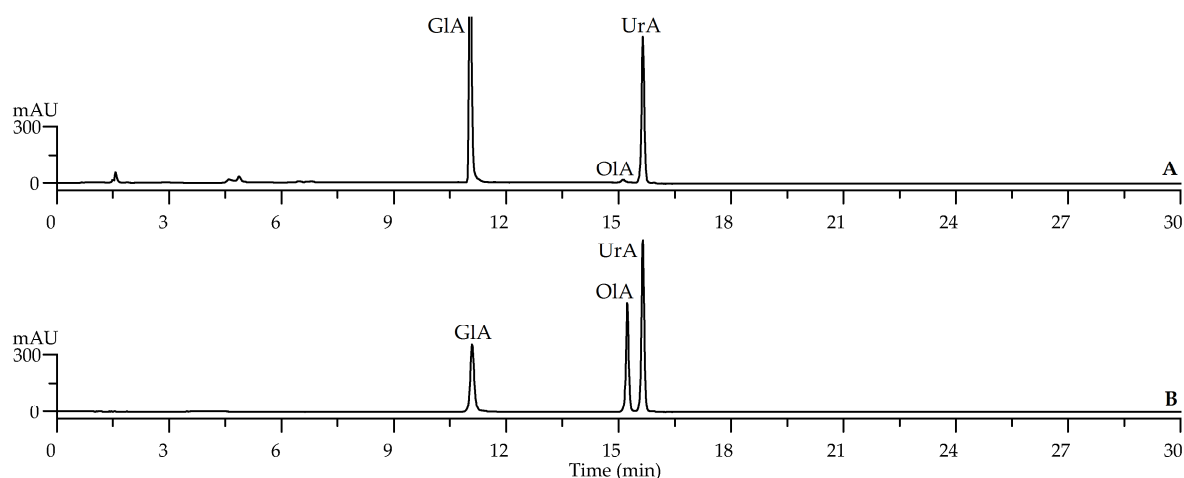


Figure S2. High-performance liquid chromatography with photodiode detection (HPLC-PDA) chromatograms of triterpenic acids of *R. adamsii* leaves (July sample, **A**) and reference standards (**B**). Sample preparation: The extract of *R. adamsii* (100 mg) was dissolved in 90% methanol (1 mL) followed by dilution of 20% methanol (8 mL), then centrifuged (6000 g, 15 min), and the supernatant was transferred in the volumetric flask (10 mL). Aliquot of internal standard (glycyrrhetic acid, 200 μ L; 1000 μ g/mL in methanol) was added to a volumetric flask and the final volume reached 10 mL with 25% methanol in the volumetric flask (solution A). Solution A (2 mL) was passed through polyamide SPE-cartridge and eluted with water (40 mL; solution B). Solution B was concentrate in a vacuum to dryness and 5 mL of 20% HCl in acetone was added. The mixture was boiled under a reflux 60 min and after cooling it was diluted to 20 mL and transferred into a separating funnel. Liquid-liquid extraction with ethyl acetate (3×20 mL) was used to separate triterpenic acid aglycones. The combined organic phase was concentrated in a vacuum and the dry residue was dissolved in 5 mL of methanol. The methanolic solution was passed through Al_2O_3 SPE-cartridge, eluted with methanol (50 mL) followed with solvent removal in a vacuum, dissolving in 5 mL of methanol and HPLC-PAD analysis. Chromatographic conditions: liquid chromatograph LC-20 Prominence coupled with photodiode array detector SPD-M30A (all Shimadzu, Columbia, MD, USA) and column AcclaimTM C30 (4.6×250 mm, 5 μ m; Thermo Fisher Scientific, Sunnyvale, CA, USA); gradient elution; eluent A 1% $\text{CH}_3\text{COONH}_3$ in water, eluent B MeCN-MeOH 3:1; flow rate: 1000 μ L/min; column temperature 30 $^\circ\text{C}$; sample volume 4 μ L; detection wavelength 190 nm. Glycyrrhetic acid (GLA) was used as an internal standard. Triterpenic acids were signed as OIA—oleanolic acid and UrA—ursolic acid.

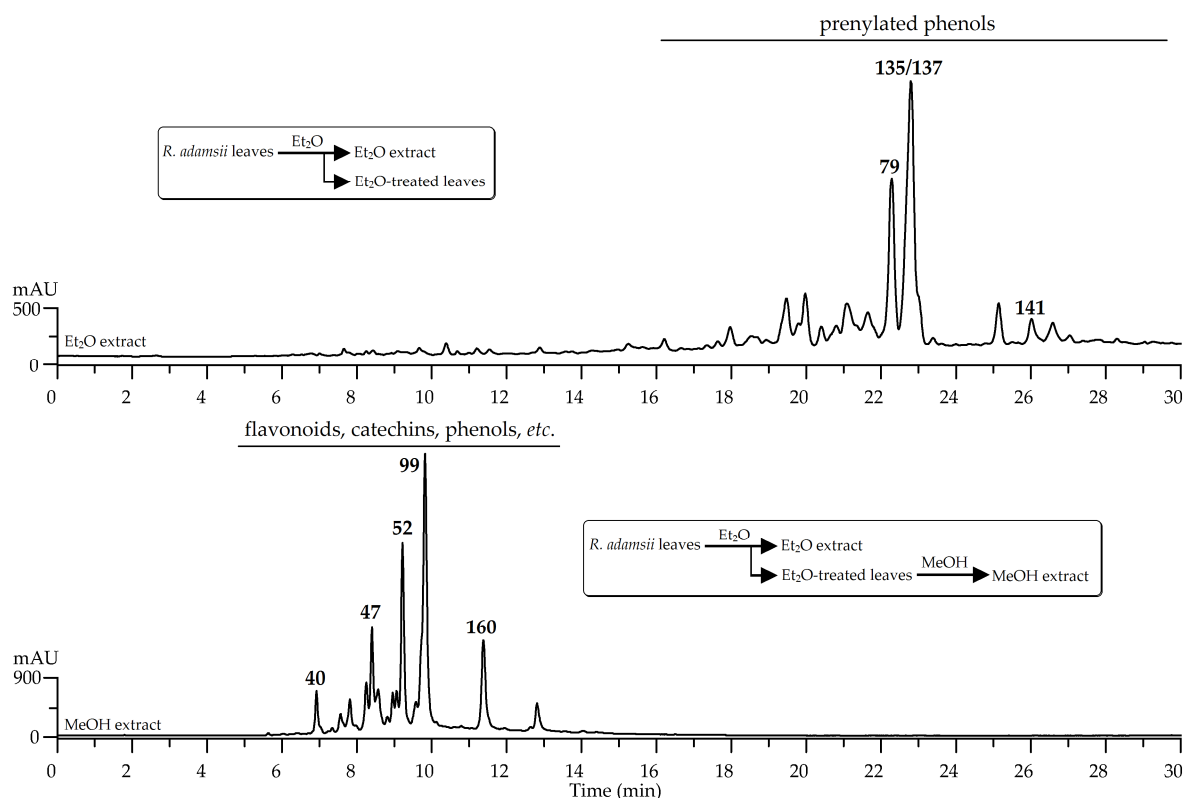


Figure S3. HPLC-PDA chromatograms of ether (Et₂O) and methanolic (MeOH) extracts of fresh *R. adamsii* leaves (January sample). The basic peaks numbered as described in Table 2. Sample preparation: Intact fresh *R. adamsii* leaves (5 g) were rinsed (10 min) three times in Et₂O (100 mL, each time; 20°C) and combined Et₂O-extract was concentrated in vacuum to dryness. The leaves of *R. adamsii* after Et₂O treatment were powdered and extracted with boiled MeOH twice (50 mL, each extraction) followed by concentration in vacuum to dryness to prepare MeOH-extract. Both extracts were dissolved in MeOH (ca. 5 mg in 1 mL), filtered through a 0.22-μm PTFE syringe filter before injection into the HPLC system. Chromatographic conditions used to separation of ethereal and methanolic extracts described in section 2.9 of Material and Methods.

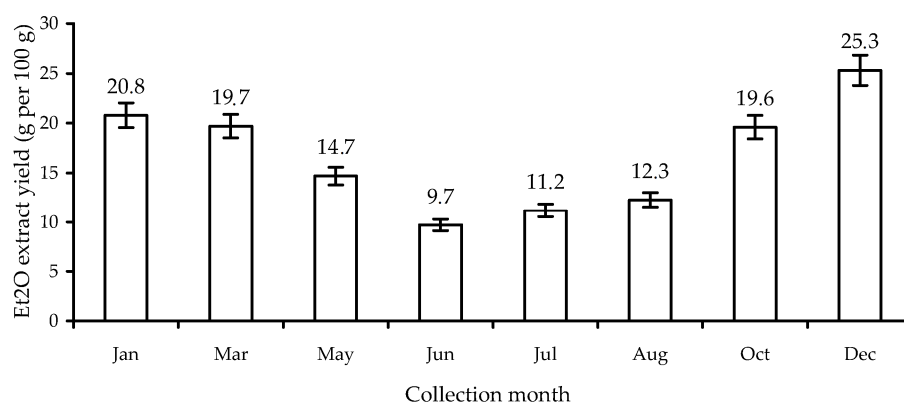


Figure S4. Yield of ether extract from *R. adamsii* leaves collected in various months. Sample preparation: Powdered *R. adamsii* leaves (1 g) were extracted three times with Et₂O (30 mL, each time; 20°C) and combined Et₂O-extract was concentrated in vacuum to dryness. The dry residue was weighted and the yield of ether extract was expressed as g per 100 g of dry leaves. All the analyses were carried out three times.