antioxidants

MDPI

Supplementary materials

LC-MS Profile, Gastrointestinal and Gut Microbiota Stability and Antioxidant Activity of *Rhodiola rosea* Herb Metabolites: A Comparative Study with Subterranean Organs

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Content

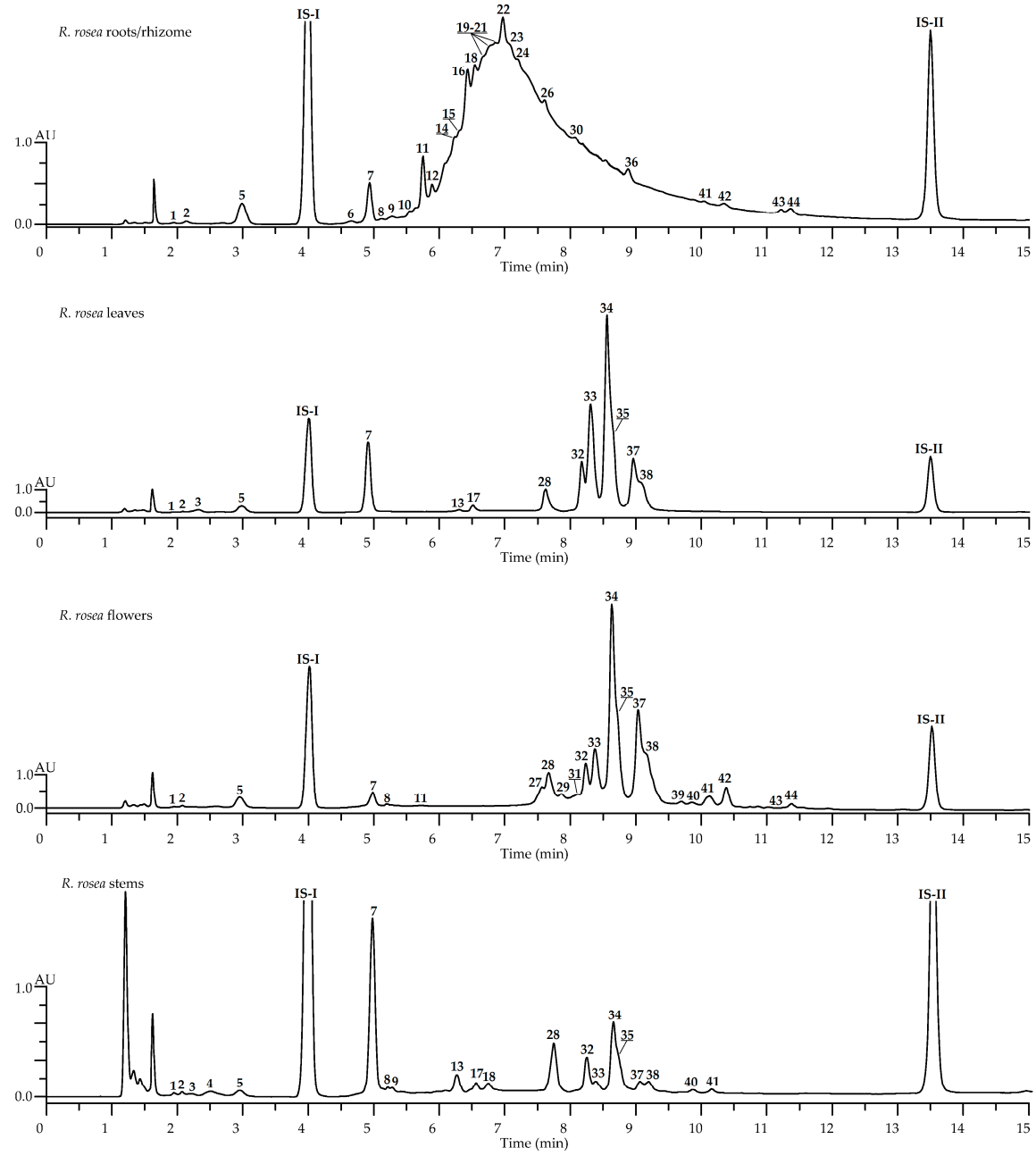


Figure S1. High-Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD) chromatograms (UV detector λ 210 nm) of C_{18} Sep-Pak ethyl acetate-methanol eluates of *Rhodiola rosea* organ extracts. Compounds are numbered as listed in Table 4. IS-I—internal standard I (caffeine, 500 μg/mL); IS-II—internal standard II (benzoic acid, 250 μg/mL).

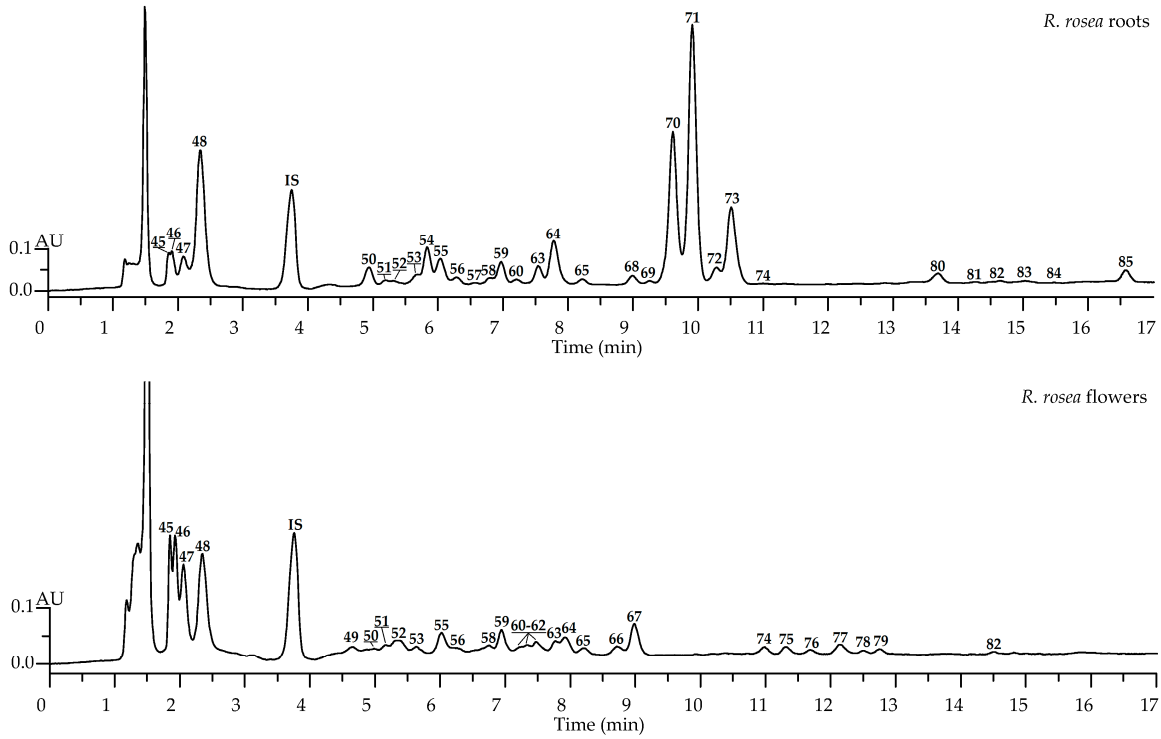


Figure S2. HPLC-DAD chromatograms (UV detector λ 210 nm) of polyamide eluates I of *R. rosea* organ extracts. Compounds are numbered as listed in Table 4. IS—internal standard (picein, 250 μg/mL).

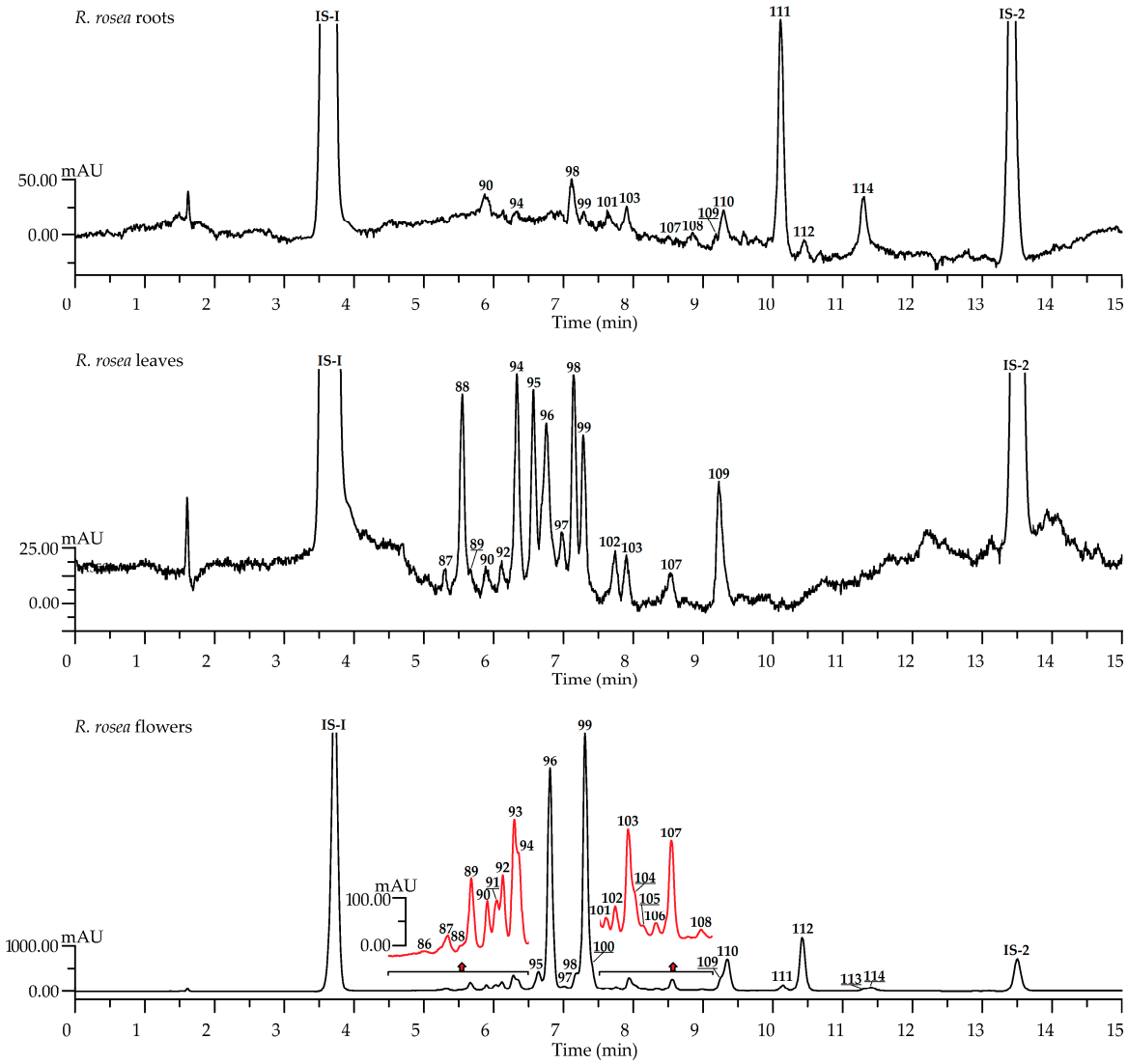


Figure S3. High-Performance Liquid Chromatography with Electrospray Ionization Triple Quadrupole Mass Spectrometric Detection (HPLC-ESI-QQQ-MS) chromatograms (base peak chromatogram or BPC mode, negative ionization) of polyamide eluates II of *R. rosea* organ extracts. Compounds are numbered as listed in Table 4. IS-I—internal standard I (scopoletin-7-*O*-neohesperidoside, 250 μg/mL); IS-II—internal standard II (isorhamnetin, 125 μg/mL). Red inserts—enlarged fragments of chromatogram.

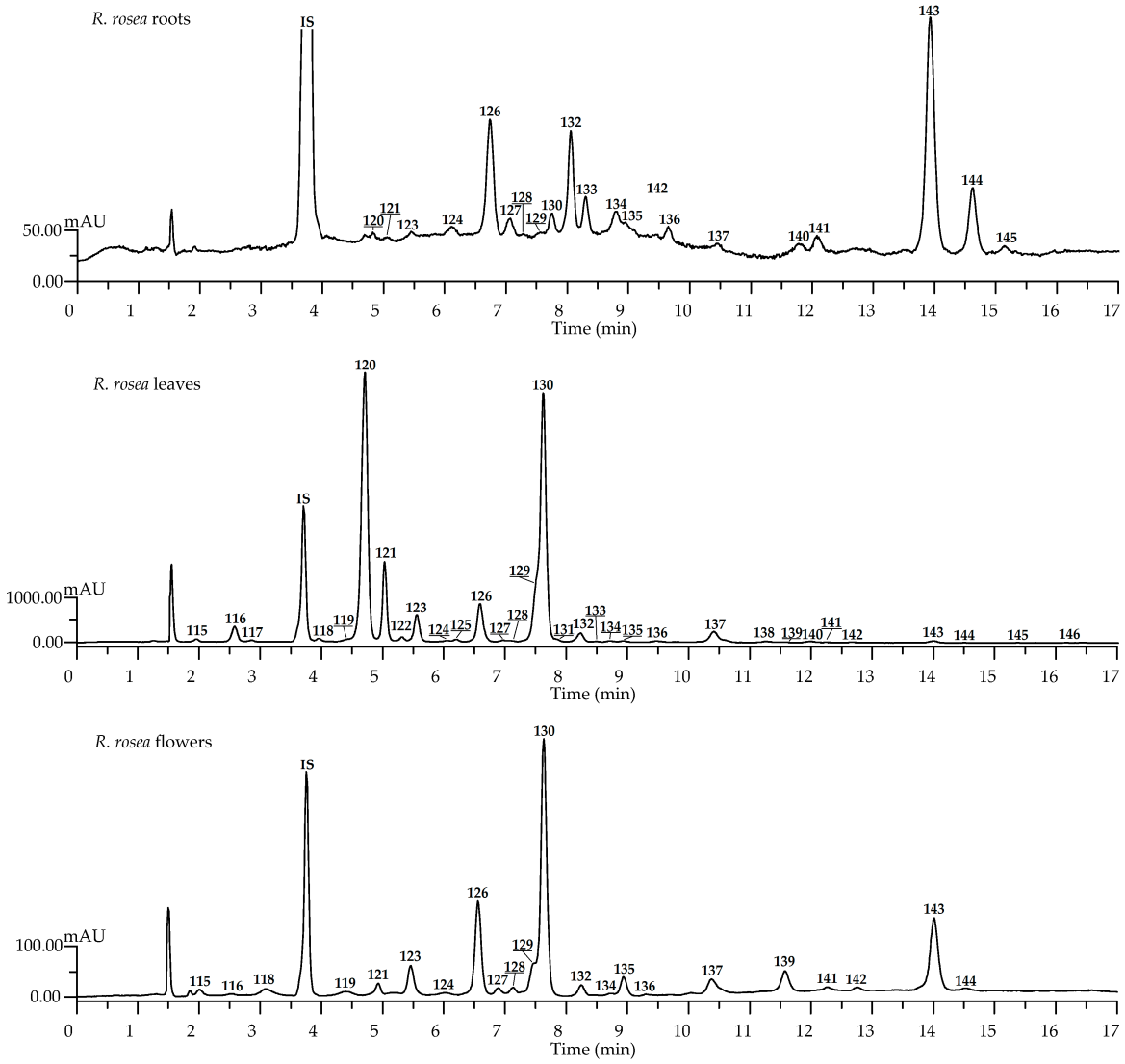


Figure S4. HPLC-ESI-QQQ-MS chromatograms (base peak chromatogram or BPC mode, negative ionization) of polyamide eluates III of *R. rosea* organ extracts. Compounds are numbered as listed in Table 4. IS-I—internal standard (4-*O*-caffeoylquinic acid, 200 μg/mL).

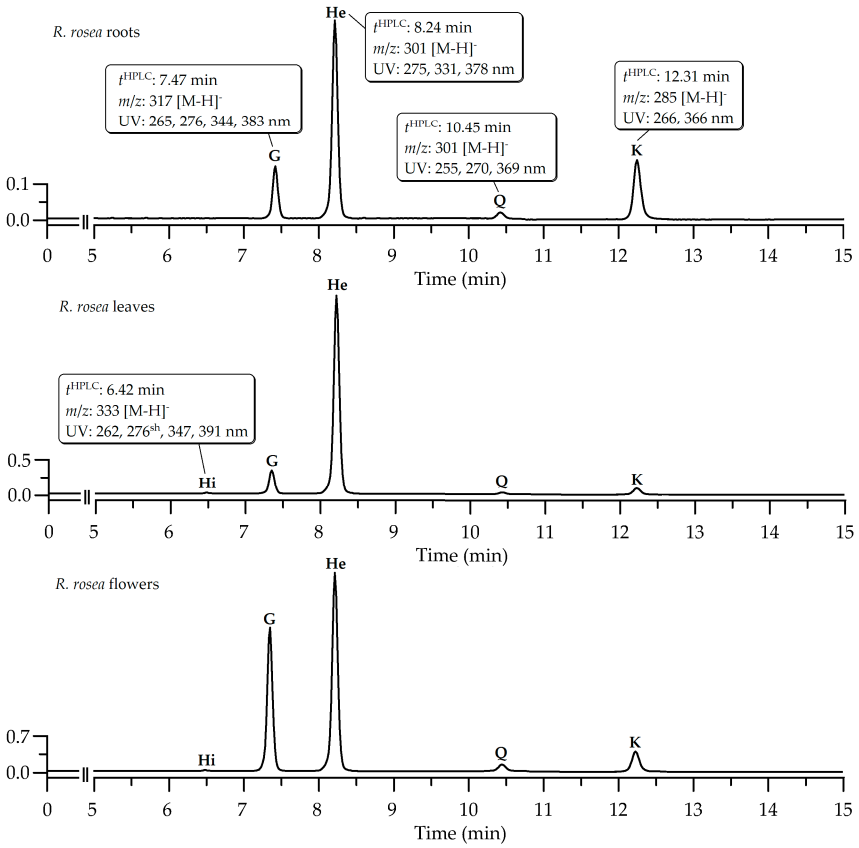


Figure S5. HPLC-DAD chromatograms (detector λ 350 nm) of hydrolysates of total extracts of *R. rosea* organ extracts. G—gossypetin; He—herbacetin; Hi—hibiscetin; K—kaempferol; Q—quercetin. In windows: HPLC retention times (t^{HPLC}), ESI-MS data (*m*/*z*) and UV spectral maxima (UV).

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

No [a]	Compound [b]	Standard	Purity, %	Manufacturer (No) [c]
1 [MS]	1-*O*-Galloyl glucose	1-*O*-Galloyl glucose	≥ 90	Sigma (69288)
2 [MS]	*O*-Galloyl glucose	1-*O*-Galloyl glucose	≥ 90	Sigma (69288)
3 [MS]	*O*-Galloyl glucose	1-*O*-Galloyl glucose	≥ 90	Sigma (69288)
4 [MS]	*O*-Galloyl glucose	1-*O*-Galloyl glucose	≥ 90	Sigma (69288)
5 [MS]	Gallic acid	Gallic acid	≥ 97	Sigma (G7384)
6 [MS]	Di-*O*-galloyl glucose	1,6-Di-*O*-galloyl glucose	≥ 92	Toronto (D293195)
7 [MS,DAD]	1,6-Di-*O*-galloyl glucose	1,6-Di-*O*-galloyl glucose	≥ 92	Toronto (D293195)
8 [MS]	Procyanidin dimer (EGC-EGC)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
9 [MS]	Gallocatechin	(+)Gallocatechin	≥ 98	Extrasynthese (0973S)
10 [MS]	Epigallocatechin	(-)Epigallocatechin	≥ 98	Extrasynthese (0979S)
11 [MS,DAD]	Procyanidin dimer (EGC-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
12 [MS]	Catechin	(+)Catechin	≥ 99	Extrasynthese (0976S)
13 [MS]	Tri-*O*-galloyl glucose	1,3,6-Tri-*O*-galloyl glucose	≥ 90	Sigma (78864)
14 [MS]	Procyanidin dimer (EGCG-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
15 [MS]	Procyanidin trimer (EGC-EGC-EGC)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
16 [MS,DAD]	Procyanidin trimer (EGC-EGC-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
17 [MS]	1,3,6-Tri-*O*-galloyl glucose	1,3,6-Tri-*O*-galloyl glucose	≥ 90	Sigma (78864)
18 [MS]	Tri-*O*-galloyl glucose	1,3,6-Tri-*O*-galloyl glucose	≥ 90	Sigma (78864)
19 [MS]	Procyanidin trimer (EGC-EGCG-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
20 [MS]	Procyanidin trimer (EGCG-EGCG-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
21 [MS]	Procyanidin tetramer (EGC-EGC-EGC-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
22 [MS,DAD]	Epicatechin	(-)Epicatechin	≥ 99	Extrasynthese (0977S)
23 [MS,DAD]	Epigallocatechin gallate	(-)Epigallocatechin gallate	≥ 98	Extrasynthese (0981S)
24 [MS,DAD]	Gallocatechin gallate	(+)Gallocatechin gallate	≥ 98	Extrasynthese (0974S)
25 [MS]	Procyanidin tetramer (EGC-EGC-EGCG-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
26 [MS]	Procyanidin tetramer (EGC-EGCG-EGCG-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
27 [MS]	Tetra-*O*-galloyl glucose	1,2,3,6-Tetra-*O*-galloyl glucose	≥ 98	BioBioPha (BBPP05354)
28 [MS]	1,2,3,6-Tetra-*O*-galloyl glucose	1,2,3,6-Tetra-*O*-galloyl glucose	≥ 98	BioBioPha (BBPP05354)
29 [MS]	Tetra-*O*-galloyl glucose	1,2,3,6-Tetra-*O*-galloyl glucose	≥ 98	BioBioPha (BBPP05354)
30 [MS,DAD]	Epicatechin gallate	(-)Epicatechin gallate	≥ 97.5	Extrasynthese (0978S)
31 [MS]	Tetra-*O*-galloyl glucose	1,2,3,6-Tetra-*O*-galloyl glucose	≥ 98	BioBioPha (BBPP05354)
32 [MS,DAD]	Penta-*O*-galloyl glucose	1,2,3,4,6-Penta-*O*-galloyl glucose	≥ 96	Sigma (67548)
33 [MS,DAD]	1,2,3,4,6-Penta-*O*-galloyl glucose	1,2,3,4,6-Penta-*O*-galloyl glucose	≥ 96	Sigma (67548)
34 [MS,DAD]	Hexa-*O*-galloyl glucose	1,2,3,4,6-Penta-*O*-galloyl glucose	≥ 96	Sigma (67548)
35 [MS,DAD]	Hexa-*O*-galloyl glucose	1,2,3,4,6-Penta-*O*-galloyl glucose	≥ 96	Sigma (67548)
36 [MS]	Catechin gallate	(+)Catechin gallate	≥ 98	Extrasynthese (0972S)
37 [MS,DAD]	Hepta-*O*-galloyl glucose	1,2,3,4,6-Penta-*O*-galloyl glucose	≥ 96	Sigma (67548)
38 [MS,DAD]	Hepta-*O*-galloyl glucose	1,2,3,4,6-Penta-*O*-galloyl glucose	≥ 96	Sigma (67548)
39 [MS]	Octa-*O*-galloyl glucose	1,2,3,4,6-Penta-*O*-galloyl glucose	≥ 96	Sigma (67548)
40 [MS]	Octa-*O*-galloyl glucose	1,2,3,4,6-Penta-*O*-galloyl glucose	≥ 96	Sigma (67548)
41 [MS]	Procyanidin tetramer (EGCG-EGCG-EGCG-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
42 [MS]	Procyanidin pentamer (EGC-EGC-EGC-EGC-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
43 [MS]	Procyanidin pentamer (EGC-EGC-EGC-EGCG-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
44 [MS]	Procyanidin pentamer (EGC-EGC-EGCG-EGCG-EGCG)	Procyanidin B_1	≥ 90	Extrasynthese (0983)
45 [MS]	Hydroquinone *O*-Hex-*O*-Pent	Arbutin	≥ 98	Sigma (A4256)
46 [MS,DAD]	Hydroquinone *O*-Glc (=arbutin)	Arbutin	≥ 98	Sigma (A4256)
47 [MS]	Tyrosol *O*-Hex-*O*-Pent	Salidroside	≥ 98	Sigma (43866)
48 [MS,DAD]	Tyrosol *O*-Glc (=salidroside)	Salidroside	≥ 98	Sigma (43866)
49 [MS]	Tyrosol *O*-dHex	Salidroside	≥ 98	Sigma (43866)
50 [MS]	Tyrosol (=*p*-hydroxyphenethyl alcohol)	Tyrosol	≥ 98	Sigma (188255)
51 [MS]	Benzyl alcohol *O*-Hex-*O*-Pent	Benzyl alcohol	≥ 99.8	Sigma (305197)
52 [MS]	Benzyl alcohol *O*-Hex-*O*-Pent	Benzyl alcohol	≥ 99.8	Sigma (305197)
53 [MS]	Benzyl alcohol *O*-Hex	Benzyl alcohol	≥ 99.8	Sigma (305197)
54 [MS]	*p*-Hydroxycinnamyl alcohol *O*-Hex-*O*-Pent	Triandrin	≥ 98.5	BioBioPha (BBP05330)
55 [MS]	*p*-Hydroxycinnamyl alcohol *O*-Glc (=triandrin)	Triandrin	≥ 98.5	BioBioPha (BBP05330)
56 [MS]	Benzyl alcohol	Benzyl alcohol	≥ 99.8	Sigma (305197)
57 [MS]	Rhodiocyanoside A/D *O*-Pent	Rhodiocyanoside A	≥ 98	ChemFaces (CFN90973)
58 [MS]	Rhodiocyanoside D	Rhodiocyanoside A	≥ 98	ChemFaces (CFN90973)
59 [MS]	Rhodiocyanoside A	Rhodiocyanoside A	≥ 98	ChemFaces (CFN90973)
60 [MS]	Rosiridol di-*O*-Hex-*O*-Pent	Rosiridin	≥ 98	ChemFaces (CFN99181)
61 [MS]	Rosiridol *O*-Hex-di-*O*-Pent	Rosiridin	≥ 98	ChemFaces (CFN99181)
62 [MS]	Rosiridol *O*-Hex-di-*O*-Pent	Rosiridin	≥ 98	ChemFaces (CFN99181)
63 [MS]	Rosiridol *O*-Hex-*O*-Pent	Rosiridin	≥ 98	ChemFaces (CFN99181)
64 [MS]	Rosiridol *O*-Hex-*O*-Pent	Rosiridin	≥ 98	ChemFaces (CFN99181)
65 [MS]	Tyrosol *O*-Hex-*O*-Ac	Salidroside	≥ 98	Sigma (43866)
66 [MS]	Tyrosol *O*-Hex-*O*-Ac	Salidroside	≥ 98	Sigma (43866)
67 [MS]	Tyrosol *O*-Hex-di-*O*-Ac	Salidroside	≥ 98	Sigma (43866)
68 [MS]	Cinnamyl alcohol *O*-Hex-di-*O*-Pent	Rosavin	≥ 98	Sigma (SML0336)
69 [MS]	Cinnamyl alcohol *O*-Hex-di-*O*-Pent	Rosavin	≥ 98	Sigma (SML0336)
70 [MS,DAD]	Cinnamyl alcohol *O*-(6′-*O*-Ara*f*)-Glc (=rosarin)	Rosarin	≥ 98	Sigma (SMB00315)

Table S1. *Cont*.

No	Compound [a]	Standard	Purity, %	Manufacturer (No) [b]
71 MS,DAD	Cinnamyl alcohol *O*-(6′-*O*-Ara*p*)-Glc (=rosavin)	Rosavin	≥ 98	Sigma (SML0336)
72 MS	Cinnamyl alcohol *O*-Hex-*O*-Pent	Rosavin	≥ 98	Sigma (SML0336)
73 MS,DAD	Cinnamyl alcohol *O*-Glc (=rosin)	Rosin	≥ 98	Sigma (PHL89902)
74 MS	Rosiridol 1-*O*-Glc (=rosiridin)	Rosiridin	≥ 98	ChemFaces (CFN99181)
75 MS	*p*-Hydroxycinnamyl alcohol *O*-Hex-*O*-Ac	Rosin	≥ 98	Sigma (PHL89902)
76 MS	*p*-Hydroxycinnamyl alcohol *O*-Hex *O*-Ac	Rosin	≥ 98	Sigma (PHL89902)
77 MS	Rosiridol *O*-Hex-*O*-Ac	Rosiridin	≥ 98	ChemFaces (CFN99181)
78 MS	Rosiridol *O*-Hex-di-*O*-Ac	Rosiridin	≥ 98	ChemFaces (CFN99181)
79 MS	Rosiridol *O*-Hex-di-*O*-Ac	Rosiridin	≥ 98	ChemFaces (CFN99181)
80 MS	*p*-Methoxycinnamyl alcohol *O*-Hex-*O*-Pent	Vimalin	≥ 92	VILAR (0316)
81 MS	*p*-Methoxycinnamyl alcohol *O*-Hex-*O*-Pent	Vimalin	≥ 92	VILAR (0316)
82 MS	*p*-Methoxycinnamyl alcohol *O*-Glc (=vimalin)	Vimalin	≥ 92	VILAR (0316)
83 MS	Cinnamyl alcohol	Cinnamyl alcohol	≥ 98	Sigma (108197)
84 MS	Cinnamic acid	Cinnamic acid	≥ 99	Sigma (C80857)
85 MS	*p*-Methoxycinnamyl alcohol	*p*-Methoxycinnamyl alcohol	≥ 98	ChemFaces (CFN89230)
86 MS	Kaempferol tri-*O*-Hex-*O*-dHex (S37)	Astragalin	≥ 97	Sigma (79851)
87 MS	Herbacetin tri-*O*-Hex-*O*-dHex (S78)	Herbacin	≥ 90	VulcanChem (VC382803)
88 MS	Gossypetin di-*O*-Hex-*O*-dHex (S78)	Hibifolin	≥ 90	Sigma (PHL83580)
89 MS	Quercetin di-*O*-Hex-*O*-dHex (S37)	Isoquercitrin	≥ 98	Sigma (16654)
90 MS	Kaempferol di-*O*-Hex-*O*-dHex (S37)	Kaempferol 7-*O*-Rha	≥ 98	ChemFaces (CFN016224)
91 MS	Gossypetin di-*O*-Hex (S8)	Hibifolin	≥ 90	Sigma (PHL83580)
92 MS	Herbacetin di-*O*-Hex-*O*-dHex (S78)	Herbacin	≥ 90	VulcanChem (VC382803)
93 MS	Gossypetin di-*O*-Hex (S38)	Hibifolin	≥ 90	Sigma (PHL83580)
94 MS	Gossypetin 7-*O*-(3′′-*O*-Glc)-Rha (=rhodioflavonoside)	Herbacin	≥ 90	VulcanChem (VC382803)
95 MS	Herbacetin 7-*O*-(3′′-*O*-Glc)-Rha (=rhodiosin)	Rhodionin	≥ 98	ChemFaces (CFN99758)
96 MS,DAD	Gossypetin 7-*O*-Rha-8-*O*-Glc (=rhodiolgidin)	Herbacin	≥ 90	VulcanChem (VC382803)
97 MS	Kaempferol *O*-Hex-*O*-dHex (S7)	Kaempferol 7-*O*-Rha	≥ 98	ChemFaces (CFN016224)
98 MS	Herbacetin-8-*O*-Xyl (=rhodalin)	Herbacin	≥ 90	VulcanChem (VC382803)
99 MS,DAD	Herbacetin 7-*O*-Rha-8-*O*-Glc (=rhodionidin)	Herbacin	≥ 90	VulcanChem (VC382803)
100 MS	Quercetin 3,7-di-*O*-Glc	Quercetin 3,7-di-*O*-Glc	≥ 92	VILAR (5284-97)
101 MS	Kaempferol 3,7-di-*O*-Glc	Kaempferol 3,7-di-*O*-Glc	≥ 98	ChemFaces (CFN91159)
102 MS	Quercetin 3-*O*-Glc-7-*O*-Rha	Quercetin 3-*O*-Glc-7-*O*-Rha	≥ 98	ChemFaces (CFN90738)
103 MS	Kaempferol 3-*O*-Glc-7-*O*-Rha	Kaempferol 3-*O*-Glc-7-*O*-Rha	≥ 90	VulcanChem (VC383277)
104 MS	Gossypetin 8-*O*-Glc (=gossypin)	Gossypin	≥ 90	Sigma (SML0761)
105 MS	Kaempferol 3,7-di-*O*-Rha (=kaempferitrin)	Kaempferitrin	≥ 98	ChemFaces (CFN98756)
106 MS	Gossypetin 7-*O*-Rha (=rhodiolgin)	Rhodiolgin	≥ 92	VILAR (3710-87)
107 MS	Quercetin 3-*O*-Glc (=isoquercitrin)	Isoquercitrin	≥ 98	Sigma (16654)
108 MS	Quercetin 3-*O*-Rha (=quercitrin)	Quercitrin	≥ 98	Sigma (740580)
109 MS	Herbacetin 8-*O*-Glc (=herbacin)	Herbacin	≥ 90	VulcanChem (VC382803)
110 MS	Herbacetin *O*-dHex (S8)	Herbacin	≥ 90	VulcanChem (VC382803)
111 MS	Kaempferol 3-*O*-Rha (=afzelin)	Afzelin	≥ 98	Sigma (PHL83864)
112 MS	Herbacetin 7-*O*-Rha (=rhodionin)	Rhodionin	≥ 98	ChemFaces (CFN99758)
113 MS	Herbacetin *O*-dHex (S3)	Herbacin	≥ 90	VulcanChem (VC382803)
114 MS	Kaempferol 7-*O*-Rha	Kaempferol 7-*O*-Rha	≥ 98	ChemFaces (CFN016224)
115 MS	Hibiscetin di-*O*-Hex-*O*-HexA (S38)	Hibifolin	≥ 90	Sigma (PHL83580)
116 MS	Gossypetin di-*O*-Hex-*O*-HexA (S378)	Hibifolin	≥ 90	Sigma (PHL83580)
117 MS	Gossypetin *O*-Ac-di-*O*-Hex-*O*-HexA (S378)	Hibifolin	≥ 90	Sigma (PHL83580)
118 MS	Gossypetin *O*-Ac-di-*O*-Hex-*O*-HexA (S378)	Hibifolin	≥ 90	Sigma (PHL83580)
119 MS	Herbacetin di-*O*-Hex-*O*-HexA (S38)	Herbacin	≥ 90	VulcanChem (VC382803)
120 MS,DAD	Herbacetin di-*O*-Hex-*O*-HexA (S378)	Herbacin	≥ 90	VulcanChem (VC382803)
121 MS	Herbacetin *O*-Mal-di-*O*-Hex-*O*-HexA (S378)	Herbacin	≥ 90	VulcanChem (VC382803)
122 MS	Herbacetin *O*-Ac-di-*O*-Hex-*O*-HexA (S378)	Herbacin	≥ 90	VulcanChem (VC382803)
123 MS	Hibiscetin *O*-Hex-*O*-HexA (S38)	Hibifolin	≥ 90	Sigma (PHL83580)
124 MS	Hibiscetin *O*-Mal-*O*-Hex-*O*-HexA (S38)	Hibifolin	≥ 90	Sigma (PHL83580)
125 MS	Hibiscetin *O*-Ac-*O*-Hex-*O*-HexA (S38)	Hibifolin	≥ 90	Sigma (PHL83580)
126 MS	Gossypetin 3-*O*-Glc-8-*O*-GlcA	Hibifolin	≥ 90	Sigma (PHL83580)
127 MS	Gossypetin 3-*O*-(3′′-*O*-Ac)-Glc-8-*O*-GlcA (=rhodiquadrin B)	Hibifolin	≥ 90	Sigma (PHL83580)
128 MS	5-*O*-Feruloylquinic acid	5-*O*-Feruloylquinic acid	≥ 98	ChemFaces (CFN92889)
129 MS	Herbacetin 8-*O*-(2′′-*O*-Glc)-GlcA (=rhodiquadrin C)	Herbacin	≥ 90	VulcanChem (VC382803)
130 MS,DAD	Herbacetin 3-*O*-Glc-8-*O*-GlcA	Herbacin	≥ 90	VulcanChem (VC382803)
131 MS	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA (S3,8)	Herbacin	≥ 90	VulcanChem (VC382803)
132 MS	Herbacetin 3-*O*-(3′′-*O*-Ac)-Glc-8-*O*-GlcA	Herbacin	≥ 90	VulcanChem (VC382803)
133 MS	Gossypetin di-*O*-Ac-*O*-Hex-*O*-HexA (S3,8)	Hibifolin	≥ 90	Sigma (PHL83580)
134 MS	Gossypetin di-*O*-Ac-*O*-Hex-*O*-HexA (S3,8)	Hibifolin	≥ 90	Sigma (PHL83580)
135 MS	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA (S3,8)	Herbacin	≥ 90	VulcanChem (VC382803)
136 MS	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA (S3,8)	Herbacin	≥ 90	VulcanChem (VC382803)
137 MS	Herbacetin di-*O*-Ac-*O*-Hex-*O*-HexA (S3,8)	Herbacin	≥ 90	VulcanChem (VC382803)
138 MS	Gossypetin 8-*O*-GlcA (=hibifolin)	Hibifolin	≥ 90	Sigma (PHL83580)
139 MS	Gossypetin *O*-Mal-*O*-HexA (S8)	Hibifolin	≥ 90	Sigma (PHL83580)
140 MS	Gossypetin *O*-Mal-*O*-HexA (S8)	Hibifolin	≥ 90	Sigma (PHL83580)
141 MS	Gossypetin *O*-Ac-*O*-HexA (S8)	Hibifolin	≥ 90	Sigma (PHL83580)

Table S1. *Cont*.

No	Compound [a]	Standard	Purity, %	Manufacturer (No) [b]
142 [MS]	Gossypetin *O*-Ac-*O*-HexA (S8)	Hibifolin	≥ 90	Sigma (PHL83580)
143 [MS]	Herbacetin 8-*O*-GlcA (=melocorin)	Herbacin	≥ 90	VulcanChem (VC382803)
144 [MS]	Herbacetin *O*-Mal-*O*-HexA (S8)	Herbacin	≥ 90	VulcanChem (VC382803)
145 [MS]	Herbacetin *O*-Ac-*O*-HexA (S8)	Herbacin	≥ 90	VulcanChem (VC382803)
146 [MS]	Herbacetin *O*-Ac-*O*-HexA (S8)	Herbacin	≥ 90	VulcanChem (VC382803)

[a] Standards used in chromatographic assays: [MS]—HPLC-DAD-ESI-QQQ-MS (Sections 2.5–2.7); [DAD]—HPLC-DAD (Section 2.9). [b] Abbreviation used: Ac—acetyl; Ara*f*—arabinofuranose; Ara*p*—arabinopyranose; Glc—glucose; GlcA—glucuronic acid; EGC—epigallocatechin unit; EGCG—epigallocatechin gallate unit; Hex—hexose; HexA—hexuronic acid; Mal—malonyl; Pent—pentose; Rha—rhamnose; Xyl—xylose. Substitution type of flavonol glycoside: S3—3-*O*-substituted; S8—8-*O*-substituted; S37—3,7-di-*O*-substituted; S78—7,8-di-*O*-substituted; S38—3,8-di-*O*-substituted; S378—3,7,8-tri-*O*-substituted; S?—unknown type of *O*-substitution. [c] Manufacturers list: BioBioPha—BioBioPha (Kunming, Yunnan, PRC); ChemFaces—ChemFaces (Wuhan, Hubei, PRC); Extrasynthese—Extrasynthese (Lyon, France); Sigma—Sigma-Aldrich (St. Louis, MO, USA); Toronto—Toronto Research Chemicals (North York, ON, Canada); VILAR—Research Institute of Medical and Aromatic Plants (Moscow, Russia); VulcanChem—VulcanChem (Pasadena, CA, USA).

Table S2. Regression equations, correlation coefficients (r^2), standard deviation (S_{YX}), limits of detection (LOD), limits of quantification (LOQ) and linear ranges for 44 reference standards used in HPLC-MS quantification.

Compound	Ionization [a]	CE [b] (eV)	Regression equation [c]		r^2	S_{YX}	LOD/LOQ (μg/mL)	Linear range (μg/mL)
			a	*b*·10⁶				
Gallic acid	N	-20	2.6538	-0.1376	0.9990	1.17·10⁻²	0.01/0.04	0.1–100.0
1-*O*-Galloyl glucose	N	-20	1.3586	-0.0663	0.9987	9.69·10⁻²	0.24/0.71	0.8–100.0
1,6-Di-*O*-galloyl glucose	N	-20	1.7552	-0.0569	0.9982	8.89·10⁻²	0.18/0.51	0.6–100.0
1,3,6-Tri-*O*-galloyl glucose	N	-25	2.1064	-0.0499	0.9985	8.74·10⁻²	0.14/0.42	0.5–100.0
1,2,3,6-Tetra-*O*-galloyl glucose	N	-25	2.0168	-0.0629	0.9973	9.00·10⁻²	0.15/0.45	0.5–100.0
1,2,3,4,6-Penta-*O*-galloyl glucose	N	-25	2.4561	-0.0171	0.9979	12.33·10⁻²	0.17/0.50	0.6–100.0
(+)Catechin	N	-35	0.9562	-0.0521	0.9971	7.79·10⁻²	0.27/0.82	0.9–100.0
(-)Epicatechin	N	-35	1.0828	-0.0456	0.9973	6.85·10⁻²	0.21/0.63	0.7–100.0
(+)Gallocatechin	N	-35	1.1495	-0.2110	0.9982	17.02·10⁻²	0.48/1.48	1.5–100.0
(-)Epigallocatechin	N	-35	1.2824	-0.1440	0.9987	14.44·10⁻²	0.37/1.12	1.2–100.0
(+)Catechin gallate	N	-35	1.3387	-0.0284	0.9981	9.50·10⁻²	0.23/0.71	0.8–100.0
(-)Epicatechin gallate	N	-35	1.5152	-0.0523	0.9979	12.67·10⁻²	0.28/0.84	0.9–100.0
(+)Gallocatechin gallate	N	-35	1.5279	-0.1846	0.9972	14.95·10⁻²	0.32/1.98	1.0–100.0
(-)Epigallocatechin gallate	N	-35	1.5824	-0.1078	0.9965	16.25·10⁻²	0.34/1.03	1.1–100.0
Procyanidin B_1	N	-25	1.3722	-0.0829	0.9973	9.93·10⁻²	0.24/0.72	0.8–100.0
Arbutin	N	-35	0.1756	-0.0144	0.9967	3.01·10⁻²	0.56/1.71	2.0–100.0
Salidroside	N	-15	2.0674	-0.1255	0.9972	9.34·10⁻²	0.14/0.45	0.5–100.0
Tyrosol	N	-15	2.3277	-0.0933	0.9985	7.59·10⁻²	0.11/0.33	0.4–100.0
Benzyl alcohol	N	-18	0.1408	-0.0193	0.9972	3.91·10⁻²	0.91/2.78	3.0–100.0
Triandrin	N	-28	0.1916	-0.0217	0.9973	3.99·10⁻²	0.68/2.08	2.1–100.0
Rhodiocyanoside A	N	-25	0.6284	-0.0517	0.9975	5.45·10⁻²	0.29/0.87	0.9–100.0
Rosiridin	N	-22	0.8036	-0.0062	0.9979	7.49·10⁻²	0.31/0.93	1.0–100.0
Rosavin	N	-20	0.8115	-0.1006	0.9980	2.25·10⁻²	0.10/0.28	0.3–100.0
Rosarin	N	-20	0.8523	-0.1004	0.9982	2.08·10⁻²	0.08/0.24	0.3–100.0
Rosin	N	-20	1.2374	-0.0924	0.9977	1.88·10⁻²	0.05/0.15	0.2–100.0
Vimalin	N	-35	1.1242	-0.0315	0.9962	9.45·10⁻²	0.28/0.84	0.9–100.0
Cinnamyl alcohol	N	-20	2.7287	-0.0752	0.9994	7.52·10⁻²	0.09/0.28	0.3–100.0
Cinnamic acid	N	-20	2.4493	-0.0938	0.9989	1.85·10⁻²	0.03/0.08	0.1–100.0
p-Methoxycinnamyl alcohol	N	-35	2.2145	-0.1038	0.9985	1.48·10⁻²	0.02/0.07	0.1–100.0
Astragalin	P	+20	2.0859	-0.9171	0.9980	6.18·10⁻²	0.03/0.09	0.1–100.0
Afzelin	P	+30	2.2126	-0.5160	0.9987	8.11·10⁻²	0.12/0.37	0.4–100.0
Kaempferol 7-*O*-Rha	P	+35	2.1821	-0.5407	0.9982	4.21·10⁻²	0.06/0.20	0.2–100.0
Kaempferitrin	P	+35	1.6726	-0.6389	0.9975	8.29·10⁻²	0.16/0.50	0.5–100.0
Kaempferol 3-*O*-Glc-7-*O*-Rha	P	+20	1.5787	-0.3641	0.9981	6.48·10⁻²	0.14/0.41	0.5–100.0
Kaempferol 3,7-di-*O*-Glc	P	+20	1.4196	-0.4514	0.9989	5.76·10⁻²	0.14/0.41	0.5–100.0
Quercitrin	P	+20	1.8267	-0.4160	0.9990	11.73·10⁻²	0.21/0.64	0.7–100.0
Isoquercitrin	P	+20	1.6705	-0.4374	0.9988	12.79·10⁻²	0.25/0.77	0.8–100.0
Quercetin 3-*O*-Glc-7-*O*-Rha	P	+20	1.4041	-0.3270	0.9992	14.02·10⁻²	0.33/1.00	1.0–100.0
Quercetin 3,7-di-*O*-Glc	P	+20	1.3436	-0.4406	0.9981	17.58·10⁻²	0.43/1.31	1.4–100.0
Rhodionin	P	+35	1.5742	-0.7787	0.9972	14.95·10⁻²	0.31/0.95	1.0–100.0
Herbacin	P	+20	1.4663	-0.6790	0.9975	15.01·10⁻²	0.34/1.02	1.1–100.0
Rhodiolgin	P	+30	1.2750	-0.7542	0.9978	15.82·10⁻²	0.41/1.24	1.3–100.0
Gossypin	P	+20	1.1880	-0.8182	0.9967	15.23·10⁻²	0.43/1.29	1.3–100.0
Hibifolin	P	+40	1.1037	-0.4687	0.9962	15.78·10⁻²	0.47/1.43	1.5–100.0
5-*O*-Feruloylquinic acid	N	-20	1.8535	0.0761	0.9989	4.55·10⁻²	0.08/0.25	0.3–100.0

[a] Ionization mode : [N]—negative; [P]—positive. [b] CE—collision energy. [c] Regression equation: $y = a \cdot x + b$.

Table S3. Regression equations, correlation coefficients (r^2), standard deviation (S_{YX}), limits of detection (LOD), limits of quantification (LOQ) and linear ranges for 13 reference standards used in HPLC-DAD quantification.

Compound	Regression equation [a]		r^2	S_{YX}	LOD/ LOQ (μg/mL)	Linear range (μg/mL)
	a	*b*				
1,6-Di-*O*-galloyl glucose	0.0783	-0.0217	0.9991	$2.40 \cdot 10^{-2}$	1.01/3.06	3.5–100.0
1,2,3,4,6-Penta-*O*-galloyl glucose	0.1064	-0.0121	0.9993	$1.88 \cdot 10^{-2}$	0.58/1.77	2.0–100.0
(-)Epicatechin	0.1138	-0.0255	0.9981	$2.96 \cdot 10^{-2}$	0.86/2.60	3.0–100.0
(-)Epicatechin gallate	0.1465	-0.0336	0.9985	$2.67 \cdot 10^{-2}$	0.60/1.82	2.0–100.0
(+)Gallocatechin gallate	0.1217	-0.0155	0.9987	$3.48 \cdot 10^{-2}$	0.94/2.86	3.0–100.0
(-)Epigallocatechin gallate	0.1740	-0.0177	0.9982	$3.28 \cdot 10^{-2}$	0.62/1.89	2.0–100.0
Procyanidin B_1	0.1716	-0.0109	0.9990	$2.50 \cdot 10^{-2}$	0.48/1.46	1.5–100.0
Arbutin	0.0040	-0.0017	0.9972	$0.41 \cdot 10^{-2}$	2.31/7.00	7.0–100.0
Salidroside	0.0148	-0.0146	0.9974	$0.62 \cdot 10^{-2}$	1.38/4.19	4.5–100.0
Rosavin	0.0483	-0.0105	0.9978	$0.82 \cdot 10^{-2}$	0.56/1.70	2.0–100.0
Rosarin	0.0493	-0.0090	0.9974	$0.75 \cdot 10^{-2}$	0.50/1.52	2.0–100.0
Rosin	0.0642	-0.0080	0.9976	$0.91 \cdot 10^{-2}$	0.47/1.42	2.0–100.0
Herbacin	0.0636	-0.0114	0.9985	$1.21 \cdot 10^{-2}$	0.63/1.90	2.0–100.0

[b] Regression equation: $y = a \cdot x + b$.

Table S4. Retention times (t_R), UV- and ESI-MS spectral data of compounds **1–146** found in *R. rosea*.

No	t_R, min [a]	Compound [b]	UV pattern [c]	CE (eV) [d]	ESI-MS, *m/z*	
					MS [e]	MS/MS (*I*, %) [f]
		Negative ionization				
1	1.91 [i]	1-*O*-Galloyl glucose [S]	GA	-20	331	[331]: 169 (100), 125 (19)
2	2.18 [i]	*O*-Galloyl glucose [L]	GA	-20	331	[331]: 169 (100), 125 (26)
3	2.33 [i]	*O*-Galloyl glucose [L]	GA	-20	331	[331]: 169 (100), 125 (9)
4	2.57 [i]	*O*-Galloyl glucose [L]	GA	-20	331	[331]: 169 (100), 125 (24)
5	2.94 [i]	Gallic acid [S]	GA	-20	169	[169]: 125 (100)
6	4.61 [i]	Di-*O*-galloyl glucose [L]	GA	-20	483	[483]: 331 (42), 169 (100), 125 (6)
7	4.78 [i]	1,6-Di-*O*-galloyl glucose [S]	GA	-20	483	[483]: 331 (53), 169 (100), 125 (10)
8	5.11 [i]	Procyanidin dimer (EGC-EGC) [L]	PC	-20	609	[609]: 305 (100)
9	5.27 [i]	Gallocatechin [S]	CT	-35	305	[305]: 168 (37), 125 (100)
10	5.52 [i]	Epigallocatechin [S]	CT	-35	305	[305]: 168 (62), 125 (100)
11	5.76 [i]	Procyanidin dimer (EGC-EGCG) [L]	PC	-20	761	[761]: 457 (82), 305 (100)
12	5.85 [i]	Catechin [S]	CT	-35	289	[289]: 247 (100), 191 (32), 123 (11)
13	6.27 [i]	Tri-*O*-galloyl glucose [L]	GA	-25	635	[635]: 483 (63), 331 (100) [483]: 331 (37), 169 (100), 125 (29)
14	6.31 [i]	Procyanidin dimer (EGCG-EGCG) [L]	PC	-20	913	[913]: 457 (100)
15	6.35 [i]	Procyanidin trimer (EGC-EGC-EGC) [L]	PC	-22	913	[913]: 609 (45), 305 (100)
16	6.48 [i]	Procyanidin trimer (EGC-EGC-EGCG) [L]	PC	-22	1065	[1065]: 761 (31), 609 (100), 457 (18) [609]: 457 (32), 305 (100)
17	6.54 [i]	1,3,6-Tri-*O*-galloyl glucose [S]	GA	-25	635	[635]: 483 (54), 331 (100) [483]: 331 (42), 169 (100), 125 (11)
18	6.78 [i]	Tri-*O*-galloyl glucose [L]	GA	-25	635	[635]: 483 (45), 331 (100) [483]: 331 (31), 169 (100), 125 (16)
19	6.82 [i]	Procyanidin trimer (EGC-EGCG-EGCG) [L]	PC	-22	1217	[1217]: 913 (27), 761 (100), 457 (9) [761]: 457 (100), 305 (63)
20	6.89 [i]	Procyanidin trimer (EGCG-EGCG-EGCG) [L]	PC	-22	1369	[1369]: 913 (23), 457 (100)
21	6.92 [i]	Procyanidin tetramer (EGC-EGC-EGC-EGCG) [L]	PC	-22	1369	[1369]: 1065 (14), 913 (22), 761 (100), 609 (5) [761]: 609 (38), 457 (22), 305 (100)
22	7.02 [i]	Epicatechin [S]	CT	-35	289	[289]: 247 (25), 191 (64), 123 (100)
23	7.12 [i]	Epigallocatechin gallate [S]	CT	-35	457	[457]: 305 (32), 168 (67), 125 (100)
24	7.22 [i]	Gallocatechin gallate [S]	CT	-35	457	[457]: 305 (11), 168 (51), 125 (100)
25	7.41 [i]	Procyanidin tetramer (EGC-EGC-EGCG-EGCG) [L]	PC	-22	1521	[1521]: 1217 (2), 913 (11), 761 (100) [761]: 457 (42), 305 (100)
26	7.53 [i]	Procyanidin tetramer (EGC-EGCG-EGCG-EGCG) [L]	PC	-22	1673	[1673]: 1369 (4), 1217 (2), 913 (100), 761 (5) [913]: 761 (25), 457 (100), 305 (28)
27	7.55 [i]	Tetra-*O*-galloyl glucose [L]	GA	-25	787	[787]: 635 (82), 483 (100), 331 (41) [635]: 483 (67), 331 (100), 169 (59)
28	7.63 [i]	1,2,3,6-Tetra-*O*-galloyl glucose [S]	GA	-25	787	[787]: 635 (53), 483 (100), 331 (45) [635]: 483 (54), 331 (100), 169 (39), 125 (8)
29	7.83 [i]	Tetra-*O*-galloyl glucose [L]	GA	-25	787	[787]: 635 (71), 483 (100), 331 (36) [635]: 483 (52), 331 (100), 169 (27)
30	8.07 [i]	Epicatechin gallate [S]	CT	-35	441	[441]: 289 (12), 125 (43), 109 (100)
31	8.14 [i]	Tetra-*O*-galloyl glucose [L]	GA	-25	787	[787]: 635 (62), 483 (100), 331 (42) [635]: 483 (42), 331 (100), 169 (49)
32	8.26 [i]	Penta-*O*-galloyl glucose [L]	GA	-25	939	[939]: 787 (52), 635 (100), 483 (19) [635]: 483 (12), 331 (56), 169 (100)
33	8.42 [i]	1,2,3,4,6-Penta-*O*-galloyl glucose [S]	GA	-25	939	[939]: 787 (46), 635 (100), 483 (28) [635]: 483 (10), 331 (43), 169 (100)
34	8.63 [i]	Hexa-*O*-galloyl glucose [L]	GA	-30	1091	[1091]: 939 (78), 787 (66), 635 (54), 483 (100) [483]: 331 (57), 169 (100)
35	8.72 [i]	Hexa-*O*-galloyl glucose [L]	GA	-30	1091	[1091]: 939 (72), 787 (59), 635 (48), 483 (100) [483]: 331 (41), 169 (100)
36	8.92 [i]	Catechin gallate [S]	CT	-35	441	[441]: 289 (32), 125 (53), 109 (100)
37	8.98 [i]	Hepta-*O*-galloyl glucose [L]	GA	-30	1243	[1243]: 1091 (6), 939 (38), 787 (100), 635 (11) [787]: 635 (10), 483 (41), 331 (100), 169 (25)
38	9.14 [i]	Hepta-*O*-galloyl glucose [L]	GA	-30	1243	[1243]: 1091 (9), 939 (45), 787 (100), 635 (18) [787]: 635 (12), 483 (46), 331 (100), 169 (31)
39	9.63 [i]	Octa-*O*-galloyl glucose [L]	GA	-30	1395	[1395]: 1243 (4), 1091 (9), 939 (100), 787 (34) [939]: 787 (4), 635 (25), 483 (100), 331 (4) [483]: 331 (25), 169 (100), 125 (11)
40	9.87 [i]	Octa-*O*-galloyl glucose [L]	GA	-30	1395	[1395]: 1243 (8), 1091 (9), 939 (100), 787 (21) [939]: 787 (3), 635 (18), 483 (100), 331 (6) [483]: 331 (11), 169 (100), 125 (15)
41	10.04 [i]	Procyanidin tetramer (EGCG-EGCG-EGCG-EGCG) [L]	PC	-25	1825	[1825]: 1369 (7), 913 (22), 457 (100)
42	10.41 [i]	Procyanidin pentamer (EGC-EGC-EGC-EGC-EGCG) [L]	PC	-25	1673	[1673]: 1369 (2), 1217 (2), 1065 (27), 913 (100), 761 (5); [913]: 761 (18), 609 (100) [609]: 457 (26), 305 (100)

Table S4. *Cont*.

No	t_R, min [a]	Compound [b]	UV pattern [c]	CE (eV) [d]	ESI-MS, *m/z*	
					MS [e]	MS$^{(n)}$ (*I*, %) [f]
43	11.18 [i]	Procyanidin pentamer (EGC-EGC-EGC-EGCG-EGCG) [L]	PC	-25	1825	[1825]: 1521 (1), 1369 (3), 1217 (26), 1065 (100), 913 (11) [1065]: 913 (36), 761 (100), 457 (30), 305 (14)
44	11.43 [i]	Procyanidin pentamer (EGC-EGC-EGCG-EGCG-EGCG) [L]	PC	-25	1977	[1977]: 1673 (1), 1521 (1), 1369 (10), 1065 (15), 913 (100) [913]: 609 (37), 457 (100), 305 (26)
45	1.90 [ii]	Hydroquinone *O*-Hex-*O*-Pent [L]	HQ	-35	403	[403]: 271 (33), 109 (100)
46	1.98 [ii]	Hydroquinone *O*-Glc (=arbutin) [S]	HQ	-35	271	[271]: 109 (100)
47	2.09 [ii]	Tyrosol *O*-Hex-*O*-Pent [L]	TY	-17	431	[431]: 299 (27), 137 (100), 119 (9)
48	2.37 [ii]	Tyrosol *O*-Glc (=salidroside) [S]	TY	-15	299	[299]: 137 (100), 119 (31), 89 (34)
49	4.59 [ii]	Tyrosol *O*-dHex [L]	TY	-15	283	[283]: 137 (100), 119 (27), 89 (21)
50	4.95 [ii]	Tyrosol (=*p*-hydroxyphenethyl alcohol) [S]	TY	-15	137	[137]: 119 (82), 89 (100)
51	5.11 [ii]	Benzyl alcohol *O*-Hex-*O*-Pent [L]	BZ	-18	401	[401]: 269 (25), 107 (100), 77 (38)
52	5.23 [ii]	Benzyl alcohol *O*-Hex-*O*-Pent [L]	BZ	-18	401	[401]: 269 (34), 107 (100), 77 (21)
53	5.56 [ii]	Benzyl alcohol *O*-Hex [L]	BZ	-18	269	[269]: 107 (100), 77 (52)
54	5.82 [ii]	*p*-Hydroxycinnamyl alcohol *O*-Hex-*O*-Pent [L]	pHCA	-28	443	[443]: 311 (14), 149 (100), 131 (9)
55	6.02 [ii]	*p*-Hydroxycinnamyl alcohol *O*-Glc (=triandrin) [S]	pHCA	-28	311	[311]: 149 (100), 131 (54)
56	6.27 [ii]	Benzyl alcohol [S]	BZ	-18	107	[107]: 77 (100)
57	6.55 [ii]	Rhodiocyanoside A/D *O*-Pent [L]	HNG	-25	390	[390]: 258 (41), 96 (100)
58	6.76 [ii]	Rhodiocyanoside D [L]	HNG	-25	258	[258]: 96 (100)
59	6.97 [ii]	Rhodiocyanoside A [S]	HNG	-25	258	[258]: 96 (100)
60	7.18 [ii]	Rosiridol di-*O*-Hex-*O*-Pent [L]	NA	-22	625	[625]: 493 (11), 331 (22), 169 (100)
61	7.27 [ii]	Rosiridol *O*-Hex-di-*O*-Pent [L]	NA	-22	595	[595]: 463 (9), 331 (15), 169 (100)
62	7.47 [ii]	Rosiridol *O*-Hex-di-*O*-Pent [L]	NA	-22	595	[595]: 463 (11), 331 (18), 169 (100)
63	7.52 [ii]	Rosiridol *O*-Hex-*O*-Pent [L]	NA	-22	463	[463]: 331 (21), 169 (100)
64	7.81 [ii]	Rosiridol *O*-Hex-*O*-Pent [L]	NA	-22	463	[463]: 331 (24), 169 (100)
65	8.18 [ii]	Tyrosol *O*-Hex-*O*-Ac [L]	TY	-20	341	[341]: 299 (8), 137 (100), 119 (24)
66	8.72 [ii]	Tyrosol *O*-Hex-*O*-Ac [L]	TY	-20	341	[341]: 299 (5), 137 (100), 119 (11)
67	8.98 [ii]	Tyrosol *O*-Hex-di-*O*-Ac [L]	TY	-20	383	[383]: 299 (34), 137 (100), 119 (5)
68	9.02 [ii]	Cinnamyl alcohol *O*-Hex-di-*O*-Pent [L]	CIN	-20	559	[559]: 427 (8), 295 (14), 133 (100)
69	9.26 [ii]	Cinnamyl alcohol *O*-Hex-di-*O*-Pent [L]	CIN	-20	559	[559]: 427 (11), 295 (27), 133 (100)
70	9.57 [ii]	Cinnamyl alcohol *O*-(6′-*O*-Ara*f*)-Glc (=rosarin) [S]	CIN	-20	427	[427]: 295 (18), 133 (100)
71	9.95 [ii]	Cinnamyl alcohol *O*-(6′-*O*-Ara*p*)-Glc (=rosavin) [S]	CIN	-20	427	[427]: 295 (37), 133 (100)
72	10.26 [ii]	Cinnamyl alcohol *O*-Hex-*O*-Pent [L]	CIN	-20	427	[427]: 295 (22), 133 (100)
73	10.51 [ii]	Cinnamyl alcohol *O*-Glc (=rosin) [S]	CIN	-20	295	[295]: 133 (100)
74	10.98 [ii]	Rosiridol 1-*O*-Glc (=rosiridin) [S]	NA	-22	331	[331]: 169 (100)
75	11.27 [ii]	*p*-Hydroxycinnamyl alcohol *O*-Hex-*O*-Ac [L]	pHCA	-30	353	[353]: 311 (32), 149 (100), 131 (5)
76	11.67 [ii]	*p*-Hydroxycinnamyl alcohol *O*-Hex *O*-Ac [L]	pHCA	-30	353	[353]: 311 (28), 149 (100), 131 (7)
77	12.14 [ii]	Rosiridol *O*-Hex-*O*-Ac [L]	NA	-25	373	[373]: 331 (7), 169 (100)
78	12.48 [ii]	Rosiridol *O*-Hex-di-*O*-Ac [L]	NA	-25	415	[415]: 331 (26), 169 (100)
79	12.81 [ii]	Rosiridol *O*-Hex-di-*O*-Ac [L]	NA	-25	415	[415]: 331 (34), 169 (100)
80	13.65 [ii]	*p*-Methoxycinnamyl alcohol *O*-Hex-*O*-Pent [L]	pMCA	-35	457	[457]: 325 (21), 163 (100), 149 (9)
81	13.94 [ii]	*p*-Methoxycinnamyl alcohol *O*-Hex-*O*-Pent [L]	pMCA	-35	457	[457]: 325 (27), 163 (100), 149 (6)
82	14.57 [ii]	*p*-Methoxycinnamyl alcohol *O*-Glc (=vimalin) [S]	pMCA	-35	325	[325]: 163 (100), 149 (10)
83	15.06 [ii]	Cinnamyl alcohol [S]	CIN	-20	133	
84	15.47 [ii]	Cinnamic acid [S]	CAc	-20	147	
85	16.58 [ii]	*p*-Methoxycinnamyl alcohol [S]	pMCA	-35	163	[163]: 149 (100)
128	7.27 [iv]	3-*O*-Feruloylquinic acid	FQA	-20	367	[367]: 193 (100), 173 (5), 149 (2)
		Positive ionization				
86	5.02 [iii]	Kaempferol tri-*O*-Hex-*O*-dHex [L]	K37	+20	919	[919]: 757 (23), 595 (100), 433 (31) [595]: 433 (100), 287 (21)
87	5.41 [iii]	Herbacetin tri-*O*-Hex-*O*-dHex [L]	H78	+20	935	[935]: 773 (11), 611 (100), 449 (27) [611]: 449 (100), 303 (27)
88	5.56 [iii]	Gossypetin di-*O*-Hex-*O*-dHex [L]	G78	+20	789	[789]: 627 (32), 465 (100), 319 (17)
89	5.63 [iii]	Quercetin di-*O*-Hex-*O*-dHex [L]	Q37	+20	773	[773]: 611 (15), 449 (100), 303 (12)
90	5.97 [iii]	Kaempferol di-*O*-Hex-*O*-dHex [L]	K37	+20	757	[757]: 595 (18), 433 (100), 287 (28)
91	6.18 [iii]	Gossypetin di-*O*-Hex [L]	G8	+20	643	[643]: 481 (15), 319 (100)
92	6.21 [iii]	Herbacetin di-*O*-Hex-*O*-dHex [L]	H78	+20	773	[773]: 611 (38), 449 (100), 303 (8)
93	6.32 [iii]	Gossypetin di-*O*-Hex [L]	G38	+20	643	[643]: 481 (18), 319 (100)
94	6.43 [iii]	Gossypetin 7-*O*-(3′′-*O*-Glc)-Rha (=rhodioflavonoside) [S]	G7	+20	627	[627]: 465 (100), 319 (15)
95	6.63 [iii]	Herbacetin 7-*O*-(3′′-*O*-Glc)-Rha (=rhodiosin) [S]	H7	+20	611	[611]: 449 (100), 303 (21)
96	6.82 [iii]	Gossypetin 7-*O*-Rha-8-*O*-Glc (=rhodiolgidin) [S]	G78	+20	627	[627]: 465 (100), 319 (52)
97	7.02 [iii]	Kaempferol *O*-Hex-*O*-dHex [L]	K7	+20	595	[595]: 433 (100), 287 (31)
98	7.21 [iii]	Herbacetin-8-*O*-Xyl (=rhodalin) [S]	H8	+20	435	[435]: 303 (100)
99	7.35 [iii]	Herbacetin 7-*O*-Rha-8-*O*-Glc (=rhodionidin) [S]	H78	+20	611	[611]: 449 (100), 303 (41)
100	7.43 [iii]	Quercetin 3,7-di-*O*-Glc [S]	Q37	+20	627	[627]: 465 (57), 303 (100)
101	7.54 [iii]	Kaempferol 3,7-di-*O*-Glc [S]	K37	+20	611	[611]: 449 (38), 287 (100)

Table S4. *Cont*.

No	t_R, min [a]	Compound [b]	UV pattern [c]	CE (eV) [d]	ESI-MS, *m/z*	
					MS [e]	$MS^{(n)}$ (*I*, %) [f]
102	7.75 [iii]	Quercetin 3-*O*-Glc-7-*O*-Rha [S]	Q37	+20	611	[611]: 449 (100), 303 (31)
103	7.97 [iii]	Kaempferol 3-*O*-Glc-7-*O*-Rha [S]	K37	+20	595	[595]: 433 (100), 287 (22)
104	8.01 [iii]	Gossypetin 8-*O*-Glc (=gossypin) [S]	G8	+20	481	[481]: 319 (100)
105	8.11 [iii]	Kaempferol 3,7-di-*O*-Rha (=kaempferitrin) [S]	K37	+35	579	[579]: 433 (100), 287 (15)
106	8.41 [iii]	Gossypetin 7-*O*-Rha (=rhodiolgin) [S]	G7	+30	465	[465]: 319 (100)
107	8.57 [iii]	Quercetin 3-*O*-Glc (=isoquercitrin) [S]	Q3	+20	465	[465]: 303 (100)
108	8.98 [iii]	Quercetin 3-*O*-Rha (=quercitrin) [S]	Q3	+20	449	[449]: 303 (100)
109	9.22 [iii]	Herbacetin 8-*O*-Glc (=alginin) [S]	H8	+20	465	[465]: 303 (100)
110	9.43 [iii]	Herbacetin *O*-dHex [L]	H8	+20	449	[449]: 303 (100)
111	10.12 [iii]	Kaempferol 3-*O*-Rha (=afzelin) [S]	K3	+30	433	[433]: 287 (100)
112	10.46 [iii]	Herbacetin 7-*O*-Rha (=rhodionin) [S]	H7	+35	449	[449]: 303 (100)
113	11.27 [iii]	Herbacetin *O*-dHex [L]	H3	+20	449	[449]: 303 (100)
114	11.45 [iii]	Kaempferol 7-*O*-Rha	K7	+35	433	[433]: 287 (100)
115	1.97 [iv]	Hibiscetin di-*O*-Hex-*O*-HexA [L]	Hi38	+35	835	[835]: 673 (18), 511 (100), 335 (22)
116	2.58 [iv]	Gossypetin di-*O*-Hex-*O*-HexA [L]	G378	+35	819	[819]: 657 (90), 495 (100), 319 (29)
117	2.82 [iv]	Gossypetin *O*-Ac-di-*O*-Hex-*O*-HexA [L]	G378	+35	861	[861]: 819 (5), 657 (29), 495 (100), 319 (16)
118	3.15 [iv]	Gossypetin *O*-Ac-di-*O*-Hex-*O*-HexA [L]	G378	+35	861	[861]: 819 (3), 657 (22), 495 (100), 319 (27)
119	4.42 [iv]	Herbacetin di-*O*-Hex-*O*-HexA [L]	H38	+35	803	[803]: 641 (74), 479 (100), 303 (14)
120	4.63 [iv]	Herbacetin di-*O*-Hex-*O*-HexA [L]	H378	+35	803	[803]: 641 (84), 479 (100), 303 (10)
121	5.02 [iv]	Herbacetin *O*-Mal-di-*O*-Hex-*O*-HexA [L]	H378	+35	889	[889]: 803 (25), 641 (37), 479 (100), 303 (29)
122	5.27 [iv]	Herbacetin *O*-Ac-di-*O*-Hex-*O*-HexA [L]	H378	+35	845	[845]: 803 (27), 641 (31), 479 (100), 303 (21)
123	5.52 [iv]	Hibiscetin *O*-Hex-*O*-HexA [L]	Hi38	+35	673	[673]: 511 (100), 335 (18)
124	6.03 [iv]	Hibiscetin *O*-Mal-*O*-Hex-*O*-HexA [L]	Hi38	+35	759	[759]: 673 (21), 511 (100), 335 (18)
125	6.18 [iv]	Hibiscetin *O*-Ac-*O*-Hex-*O*-HexA [L]	Hi38	+35	715	[715]: 673 (25), 511 (100), 335 (15)
126	6.53 [iv]	Gossypetin 3-*O*-Glc-8-*O*-GlcA [S]	G38	+35	657	[657]: 495 (100), 319 (22)
127	6.97 [iv]	Gossypetin 3-*O*-(3''-*O*-Ac)-Glc-8-*O*-GlcA (=rhodiquadrin B) [S]	G38	+35	699	[699]: 523 (100), 319 (46)
129	7.51 [iv]	Herbacetin 8-*O*-(2''-*O*-Glc)-GlcA (=rhodiquadrin C) [S]	H8	+35	641	[641]: 479 (100), 303 (43)
130	7.62 [iv]	Herbacetin 3-*O*-Glc-8-*O*-GlcA [S]	H38	+35	641	[641]: 479 (100), 303 (8)
131	7.90 [iv]	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA [L]	H38	+35	683	[683]: 507 (100), 303 (35)
132	8.23 [iv]	Herbacetin 3-*O*-(3''-*O*-Ac)-Glc-8-*O*-GlcA [S]	H38	+35	683	[683]: 507 (100), 303 (32)
133	8.48 [iv]	Gossypetin di-*O*-Ac-*O*-Hex-*O*-HexA [L]	G38	+35	741	[741]: 565 (100), 319 (31)
134	8.73 [iv]	Gossypetin di-*O*-Ac-*O*-Hex-*O*-HexA [L]	G38	+35	741	[741]: 565 (100), 319 (28)
135	8.98 [iv]	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA [L]	H38	+35	683	[683]: 507 (100), 303 (25)
136	9.49 [iv]	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA [L]	H38	+35	683	[683]: 507 (100), 303 (29)
137	10.47 [iv]	Herbacetin di-*O*-Ac-*O*-Hex-*O*-HexA [L]	H38	+35	725	[725]: 549 (100), 303 (22)
138	11.25 [iv]	Gossypetin 8-*O*-GlcA(=hibifolin) [S]	G8	+40	495	[495]: 319 (100)
139	11.59 [iv]	Gossypetin *O*-Mal-*O*-HexA [L]	G8	+35	581	[581]: 495 (100), 319 (72)
140	11.98 [iv]	Gossypetin *O*-Mal-*O*-HexA [L]	G8	+35	581	[581]: 495 (100), 319 (65)
141	12.26 [iv]	Gossypetin *O*-Ac-*O*-HexA [L]	G8	+35	537	[537]: 495 (100), 319 (62)
142	12.61 [iv]	Gossypetin *O*-Ac-*O*-HexA [L]	G8	+35	537	[537]: 495 (100), 319 (67)
143	14.01 [iv]	Herbacetin 8-*O*-GlcA (=melocorin) [S]	H8	+40	479	[479]: 303 (100)
144	14.50 [iv]	Herbacetin *O*-Mal-*O*-HexA [L]	H8	+35	565	[565]: 479 (100), 303 (82)
145	15.37 [iv]	Herbacetin *O*-Ac-*O*-HexA [L]	H8	+35	521	[521]: 479 (100), 303 (73)
146	16.11 [iv]	Herbacetin *O*-Ac-*O*-HexA [L]	H8	+35	521	[521]: 479 (100), 303 (70)

[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 ([S]) or interpretation of UV and MS spectral data and comparison with literature data ([L]). [c] UV-patterns as listed in Table S5. [d] CE—collision energy. [e] Mass spectrometric data: deprotonated ion $[M–H]^-$, negative ionization / protonated ion $[M+H]^+$, positive ionization. [f] Signal intensity (percentage). Abbreviation used: Ac—acetyl; Ara*f*—arabinofuranose; Ara*p*—arabinopyranose; Glc—glucose; GlcA—glucuronic acid; Hex—hexose; HexA—hexuronic acid; Mal—malonyl; Pent—pentose; Rha—rhamnose; Xyl—xylose.

Table S5. UV-spectral patterns of compounds found in *R. rosea*.

Name of UV-pattern	Group of compound	λ_{max}, nm
BZ	Benzyl alcohol derivatives	205 (±2)
CAc	Cinnamic acid	272
CIN	Cinnamyl alcohol derivatives	250 (±2)
CT	Catechins	275 (±1)
FQA	Feruloylquinic acid	324
G7	Gossypetin 7-*O*-glucosides	260 (±3), 276 sh (±3), 345 (±4), 385 (±5)
G8	Gossypetin 8-*O*-glucosides	256 (±3), 270 sh (±3), 305 (±3), 377 (±5)
G38	Gossypetin 3,8-di-*O*-glucosides	258 (±3), 270 (±2), 355 (±5)
G78	Gossypetin 7,8-di-*O*-glucosides	260 sh (±3), 276 (±3), 304 sh (±4), 340 (±5), 375 sh (±5)
G378	Gossypetin 3,7,8-tri-*O*-glucosides	260 (±3), 270 sh (±3), 365 (±6)
GA	Galloyl glucoses	277 (±2), 300 sh (±4)
H3	Herbacetin 3-*O*-glucosides	282 (±3), 302 (±5), 330 (±5), 375 (±7)
H7	Herbacetin 7-*O*-glucosides	276 (±3), 330 (±5), 385 (±5)
H8	Herbacetin 8-*O*-glucosides	255 sh (±3), 272 (±3), 326 (±4), 374 (±5)
H37	Herbacetin 3,7-di-*O*-glucosides	275 (±3), 306 (±3), 330 (±3), 370 sh (±4)
H38	Herbacetin 3,8-di-*O*-glucosides	272 (±3), 330 sh (±2), 360 (±5)
H78	Herbacetin 7,8-di-*O*-glucosides	276 (±2), 306 (±3), 332 (±3), 370 sh (±6)
H378	Herbacetin 3,7,8-tri-*O*-glucosides	270 (±3), 326 sh (±3), 356 (±4)
Hi38	Hibiscetin 3,8-di-*O*-glucosides	255 sh (±4), 270 (±4), 300 (±2), 365 (±5)
HNG	Hydroxynitrile glucosides	207 (±1)
HQ	Hydroquinone derivatives	282 (±1)
K3	Kaempferol 3-*O*-glucosides	265 (±3), 290 (±2), 320 (±3), 345 (±6)
K7	Kaempferol 7-*O*-glucosides	252 (±3), 265 (±3), 322 (±3), 360 (±5)
K37	Kaempferol 3,7-di-*O*-glucosides	245 sh (±3), 265 (±2), 315 sh (±3), 350 (±6)
NA	No absorption > 200 nm	195–200
PC	Procyanidins	270 (±2)
pHCA	*p*-Hydroxycinnamyl alcohol derivatives	280 (±2)
pMCA	p-Methoxycinnamyl alcohol derivatives	306 (±2)
Q3	Quercetin 3-*O*-glucosides	256 (±3), 267 (±2), 292 (±3), 362 (±4)
Q37	Quercetin 3,7-di-*O*-glucosides	255 (±3), 267 (±3), 355 (±5)
TY	Tyrosol derivatives	225 (±2), 275 (±2)

sh—shoulder.

Table S6. Selected spectra of compounds found in *R. rosea*.

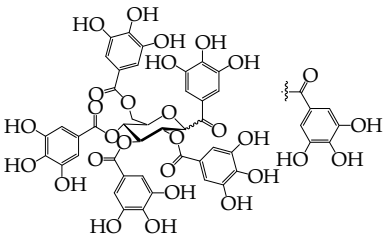
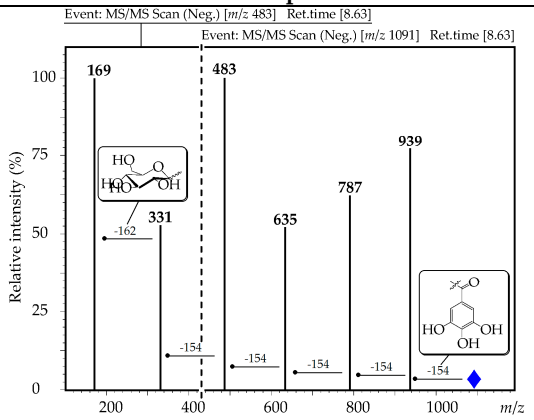
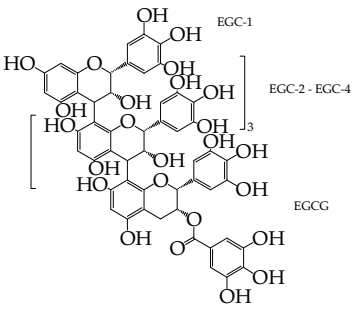
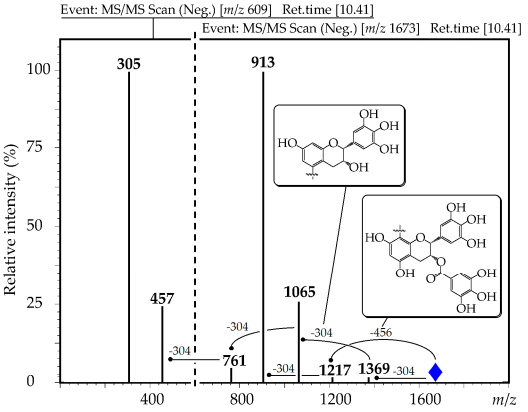
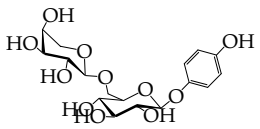
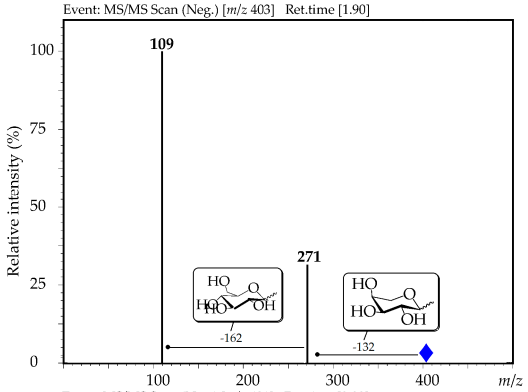
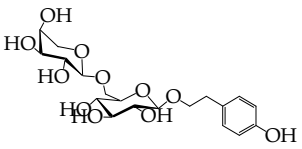
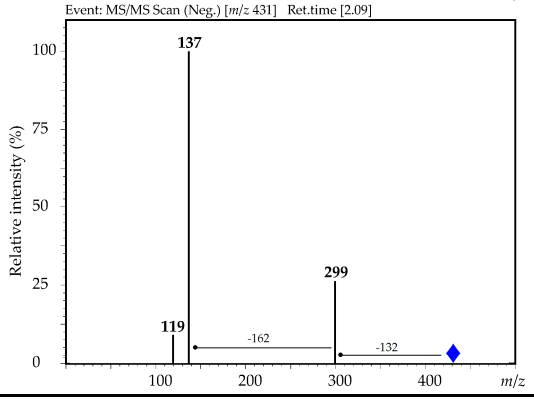
No	Compound	MS/MS spectra
34	Hexa-*O*-galloyl glucose (galloyl *O*-glycoside)  (tentative)	
42	Procyanidin pentamer (EGC-EGC-EGC-EGC-EGCG) (procyanidin)  (tentative)	
45	Hydroquinone *O*-hexoside-*O*-pentoside (hydroquinone derivative)  (tentative)	
47	Tyrosol *O*-hexoside-*O*-pentoside (tyrosol derivative)  (tentative)	

Table S6. *Cont*.

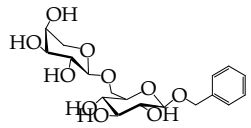
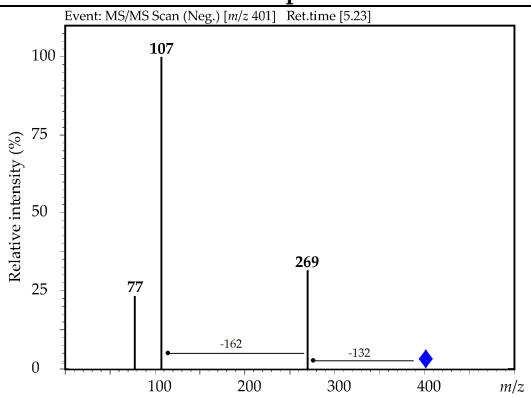
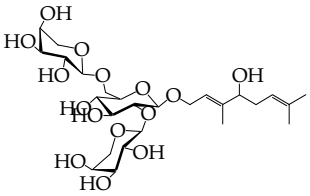
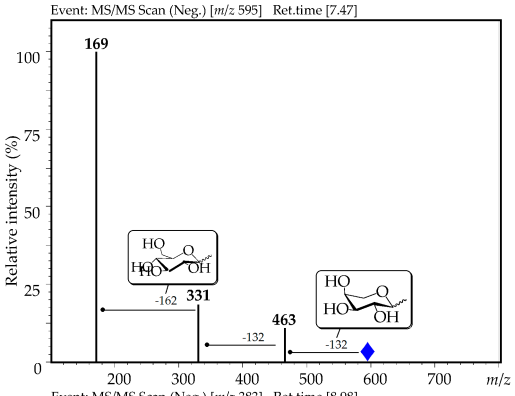
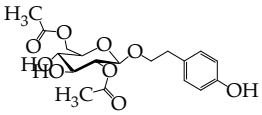
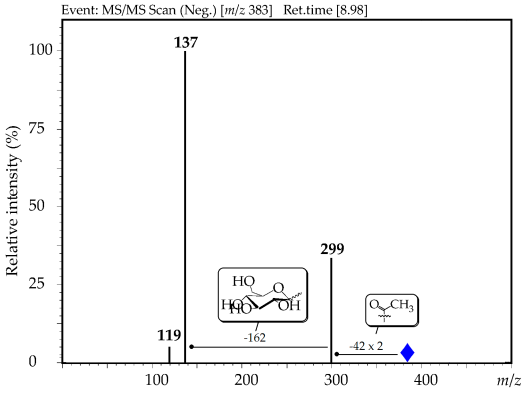
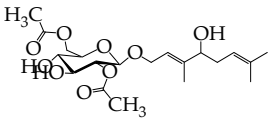
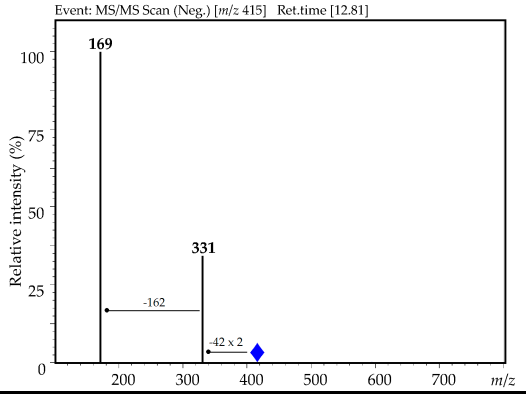
No	Compound	MS/MS spectra
52	Benzyl alcohol *O*-hexoside-*O*-pentoside (benzyl alcohol derivative)  (tentative)	
62	Rosiridol *O*-hexoside-di-*O*-pentoside (rosiridol derivative)  (tentative)	
67	Tyrosol *O*-hexoside-di-*O*-acetate (tyrosol derivative)  (tentative)	
79	Rosiridol *O*-hexoside-di-*O*-acetate (rosiridol derivative)  (tentative)	

Table S6. *Cont*.

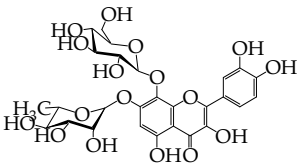
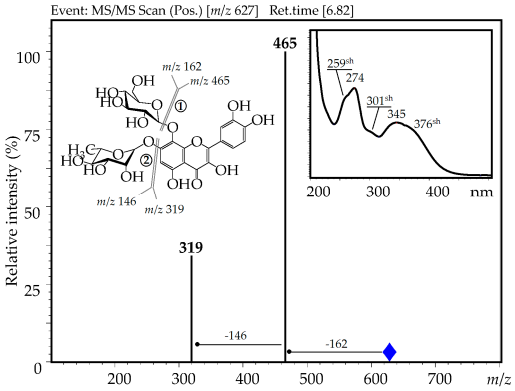
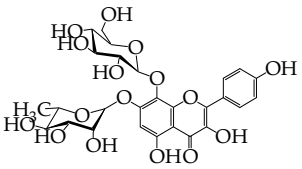
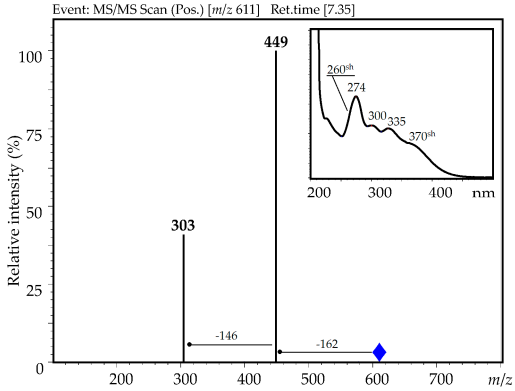
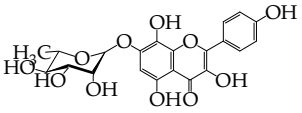
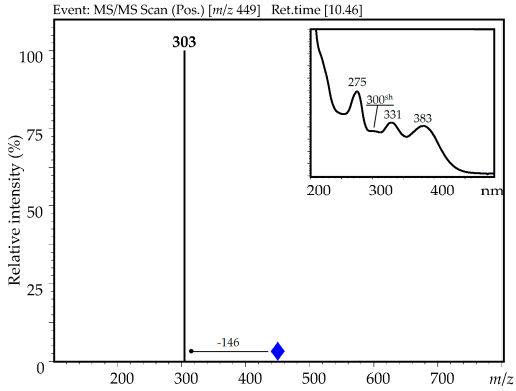
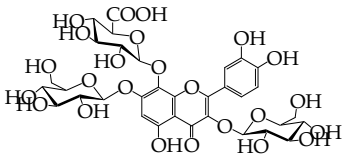
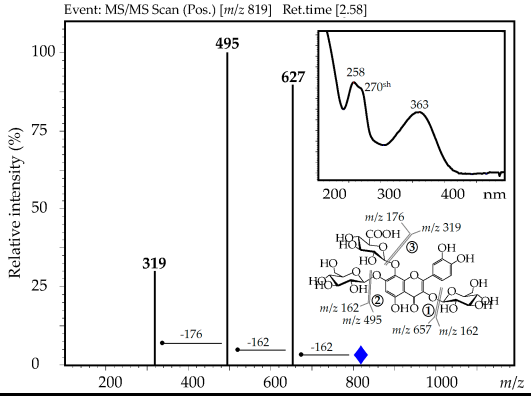
No	Compound	MS/MS, UV spectra (in windows)
96	Gossypetin 7-*O*-Rha-8-*O*-Glc = rhodiolgidin (neutral gossypetin 7,8-di-*O*-glycoside) 	
99	Herbacetin 7-*O*-Rha-8-*O*-Glc = rhodionidin (neutral herbacetin 7,8-di-*O*-glycoside) 	
112	Herbacetin 7-*O*-Rha = rhodionin (neutral herbacetin 7-*O*-glycoside) 	
116	Gossypetin di-*O*-hexoside-*O*-hexuronide (acidic gossypetin 3,7,8-tri-*O*-glycoside)  (tentative)	

Table S6. *Cont*.

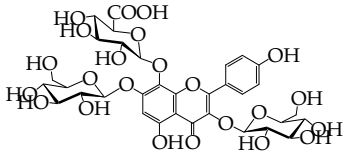
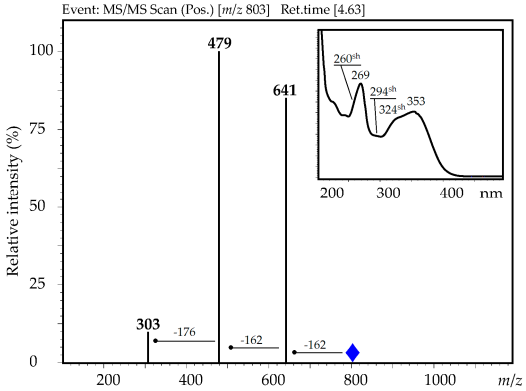
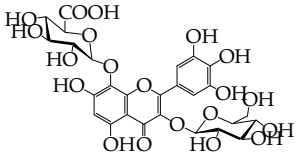
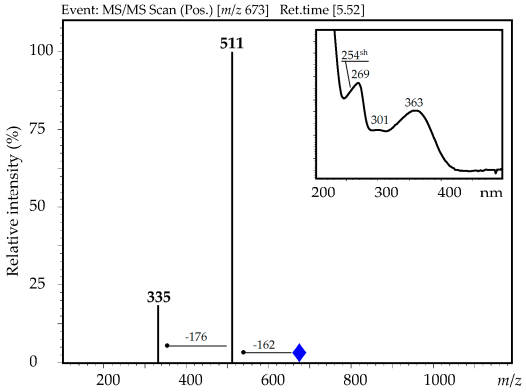
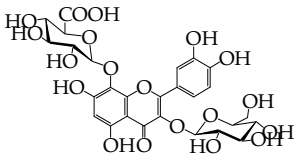
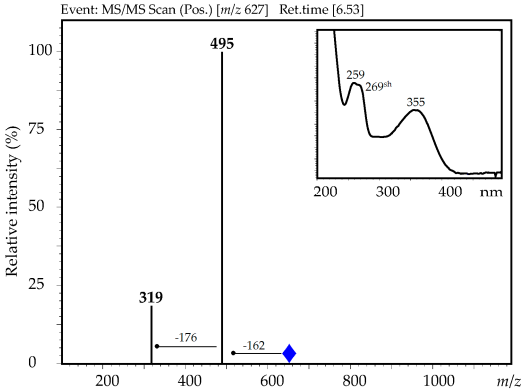
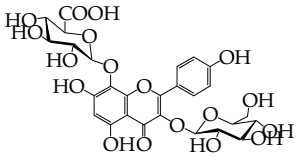
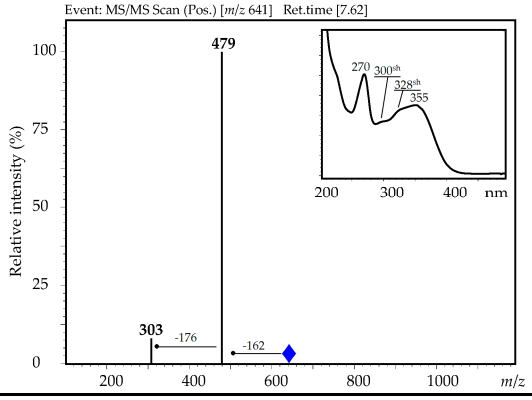
No	Compound	MS/MS, UV spectra (in windows)
120	Herbacetin di-*O*-hexoside-*O*-hexuronide (acidic herbacetin 3,7,8-tri-*O*-glycoside)  (tentative)	
123	Hibiscetin *O*-hexoside-*O*-hexuronide (acidic hibiscetin 3,8-di-*O*-glycoside)  (tentative)	
126	Gossypetin 3-*O*-glucoside-8-*O*-glucuronide (acidic gossypetin 3,8-di-*O*-glycoside) 	
130	Herbacetin 3-*O*-glucoside-8-*O*-glucuronide (acidic herbacetin 3,8-di-*O*-glycoside) 	

Table S6. *Cont*.

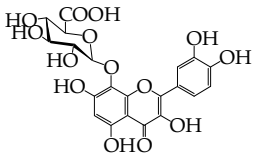
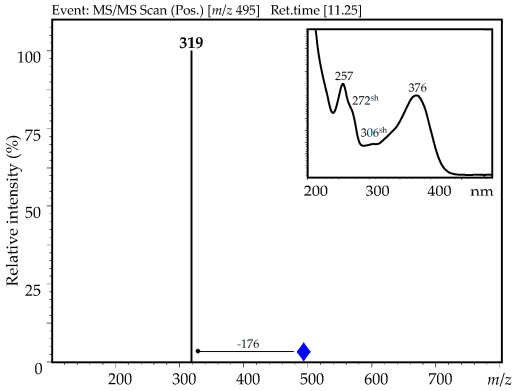
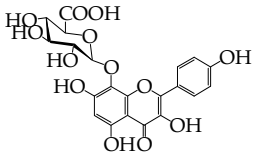
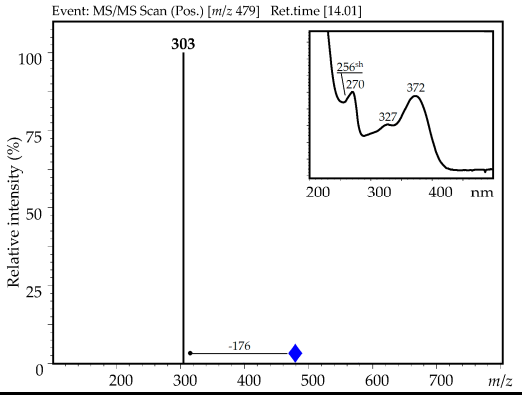
No	Compound	MS/MS, UV spectra (in windows)
138	Gossypetin 8-*O*-glucuronide = hibifolin (acidic gossypetin 8-*O*-glycoside) 	
143	Herbacetin 8-*O*-GlcA = melocorin (acidic herbacetin 8-*O*-glycoside) 	

Table S7. Known flavonol glycosides of *R. rosea*.

Compound	Presence in *R. rosea* organ [ref.]		
	Roots/Rhizomes	Leaves	Flowers
Kaempferol group (9)			
Kaempferol-3-*O*-$^{\alpha L}$Rha*p* (=afzelin)	[2]		
Kaempferol-3-*O*-$^{\beta D}$Glc*p* (=astragalin)	[2]		
Kaempferol-3-*O*-(2''-*O*-$^{\beta D}$Xyl*p*)-$^{\beta D}$Glc*p* (=leucoside)	[54]		
Kaempferol-7-*O*-$^{\alpha L}$Rha*p*	[56]		
Kaempferol-7-*O*-(2''-*O*-$^{\alpha L}$Rha*p*)-$^{\beta D}$Glc*p*	[2]		
Kaempferol-3-*O*-$^{\alpha L}$Rha*p*-7-*O*-$^{\beta D}$Glc*p*		[15]	[15]
Kaempferol-3-*O*-$^{\beta D}$Glc*p*-7-*O*-$^{\alpha L}$Rha*p*	[54]		
Kaempferol-3-*O*-(6''-O-$^{\alpha L}$Rha*p*)-$^{\beta D}$Gal*p*-7-*O*-$^{\alpha L}$Rha*p* (=robinin)	[2]		
Kaempferol-3,7-di-*O*-$^{\beta D}$Glc*p*		[15]	[15]
Quercetin group (2)			
Quercetin-3-*O*-$^{\alpha L}$Rha*p* (=quercitrin)	[2]		
Quercetin-3-*O*-$^{\alpha L}$Rha*p*-7-*O*-$^{\beta D}$Glc*p*		[15]	[15]
Herbacetin group (11)			
Herbacetin 8-*O*-methyl ester	[56]		
Herbacetin-7-*O*-$^{\alpha L}$Rha*p* (=rhodionin)	[55]		[13,14]
Herbacetin-7-*O*-(3''-*O*-$^{\beta D}$Glc*p*)-$^{\alpha L}$Rha*p* (=rhodiosin)	[55]		
Herbacetin-8-*O*-$^{\beta D}$Xyl*p* (=rhodalin)		[14]	[14]
Herbacetin-8-*O*-(3''-*O*-Ac)-$^{\beta D}$Xyl*p* (=acetylrhodalin)	[56]		
Herbacetin-8-*O*-$^{\beta D}$Glc*p* (=alginin, herbacin)	[54]		
Herbacetin-3-*O*-$^{\beta D}$Glc*p*-7-*O*-$^{\alpha L}$Ara*p*		[15]	[15]
Herbacetin-3-*O*-$^{\beta D}$Glc*p*-7-*O*-$^{\beta D}$Xyl*p*		[15]	[15]
Herbacetin-3-*O*-$^{\beta D}$Glc*p*-7-*O*-$^{\alpha L}$Rha*p* (=sinocrassoside C1)	[54]		
Herbacetin-3-*O*-$^{\beta D}$Glc*p*-8-*O*-$^{\beta D}$Xyl*p* (=rhodalidin)		[13,14]	
Herbacetin-7-*O*-$^{\alpha L}$Rha*p*-8-*O*-$^{\beta D}$Glc*p* (=rhodionidin)		[13,14]	[13,14]
Gossypetin group (5)			
Gossypetin-7-*O*-$^{\alpha L}$Rha*p* (=rhodiolgin)			[13,14]
Gossypetin-7-*O*-(3''-*O*-$^{\beta D}$Glc*p*)-$^{\alpha L}$Rha*p* (=rhodioflavonoside)	[53]		
Gossypetin-3-*O*-$^{\beta D}$Glc*p*-7-*O*-$^{\alpha L}$Ara*p*		[15]	[15]
Gossypetin-3-*O*-$^{\beta D}$Glc*p*-7-*O*-$^{\beta D}$Xyl*p*		[15]	[15]
Gossypetin-7-*O*-$^{\alpha L}$Rha*p*-8-*O*-$^{\beta D}$Glc*p* (=rhodiolgidin)		[13,14]	[13,14]
Tricin group (2)			
Tricin-5-*O*-$^{\beta D}$Glc*p*	[70]		
Tricin-7-*O*-$^{\beta D}$Glc*p*	[70]		

Ac—acetyl; $^{\alpha L}$Ara*p*—α-L-arabinopyranose; $^{\beta D}$Gal*p*—β-D-galactopyranose; $^{\beta D}$Glc*p*—β-D-glucopyranose; $^{\alpha L}$Rha*p*—α-L-rhamnopyranose; $^{\beta D}$Xyl*p*—β-D-xylopyranose.

Table S8. Quantitative content of compounds **1–146** in *R. rosea* organs, mg/g dry plant weight ± S.D. [a]

No	Compound [b]	Roots	Rhizome	Leaves	Flowers	Stems
1	1-*O*-Galloyl glucose	0.32 ± 0.01	0.09 ± 0.00	0.12 ± 0.00	0.12 ± 0.00	0.10 ± 0.00
2	*O*-Galloyl glucose	0.29 ± 0.00	0.21 ± 0.00	0.14 ± 0.00	0.36 ± 0.01	0.09 ± 0.00
3	*O*-Galloyl glucose	n.d.	n.d.	0.79 ± 0.02	n.d.	0.10 ± 0.00
4	*O*-Galloyl glucose	n.d.	n.d.	n.d.	n.d.	0.31 ± 0.00
5	Gallic acid	1.72 ± 0.03	1.19 ± 0.02	1.67 ± 0.03	1.52 ± 0.03	0.27 ± 0.00
6	Di-*O*-galloyl glucose	traces	traces	n.d.	n.d.	n.d.
7	1,6-Di-*O*-galloyl glucose	2.29 ± 0.04	1.17 ± 0.02	10.35 ± 0.21	1.56 ± 0.03	3.89 ± 0.06
8	Procyanidin dimer (EGC-EGC)	0.02 ± 0.00	0.34 ± 0.00	n.d.	0.19 ± 0.00	0.15 ± 0.00
9	Gallocatechin	0.29 ± 0.00	2.08 ± 0.04	n.d.	n.d.	0.12 ± 0.00
10	Epigallocatechin	0.12 ± 0.00	1.36 ± 0.02	n.d.	n.d.	n.d.
11	Procyanidin dimer (EGC-EGCG)	3.48 ± 0.07	14.55 ± 0.27	n.d.	traces	n.d.
12	Catechin	1.52 ± 0.03	4.11 ± 0.07	n.d.	n.d.	n.d.
13	Tri-*O*-galloyl glucose	n.d.	n.d.	0.64 ± 0.01	n.d.	0.45 ± 0.01
14	Procyanidin dimer (EGCG-EGCG)	traces	0.59 ± 0.01	n.d.	n.d.	n.d.
15	Procyanidin trimer (EGC-EGC-EGC)	0.11 ± 0.00	0.67 ± 0.01	n.d.	n.d.	n.d.
16	Procyanidin trimer (EGC-EGC-EGCG)	3.36 ± 0.06	10.68 ± 0.22	n.d.	n.d.	n.d.
17	1,3,6-Tri-*O*-galloyl glucose	n.d.	n.d.	1.31 ± 0.02	n.d.	0.27 ± 0.00
18	Tri-*O*-galloyl glucose	0.83 ± 0.02	0.42 ± 0.01	n.d.	n.d.	0.32 ± 0.00
19	Procyanidin trimer (EGC-EGCG-EGCG)	traces	0.49 ± 0.01	n.d.	n.d.	n.d.
20	Procyanidin trimer (EGCG-EGCG-EGCG)	traces	0.45 ± 0.01	n.d.	n.d.	n.d.
21	Procyanidin tetramer (EGC-EGC-EGC-EGCG)	traces	0.22 ± 0.00	n.d.	n.d.	n.d.
22	Epicatechin	4.47 ± 0.09	19.08 ± 0.38	n.d.	n.d.	n.d.
23	Epigallocatechin gallate	1.48 ± 0.03	9.48 ± 0.19	n.d.	n.d.	n.d.
24	Gallocatechin gallate	1.89 ± 0.04	12.44 ± 0.25	n.d.	n.d.	n.d.
25	Procyanidin tetramer (EGC-EGC-EGCG-EGCG)	traces	traces	n.d.	n.d.	n.d.
26	Procyanidin tetramer (EGC-EGCG-EGCG-EGCG)	0.10 ± 0.00	0.68 ± 0.01	n.d.	n.d.	n.d.
27	Tetra-*O*-galloyl glucose	n.d.	n.d.	n.d.	1.94 ± 0.04	n.d.
28	1,2,3,6-Tetra-*O*-galloyl glucose	n.d.	n.d.	4.77 ± 0.09	4.38 ± 0.08	1.42 ± 0.03
29	Tetra-*O*-galloyl glucose	n.d.	n.d.	n.d.	1.67 ± 0.04	n.d.
30	Epicatechin gallate	0.50 ± 0.01	5.12 ± 0.10	n.d.	n.d.	n.d.
31	Tetra-*O*-galloyl glucose	n.d.	n.d.	n.d.	traces	n.d.
32	Penta-*O*-galloyl glucose	n.d.	n.d.	7.15 ± 0.14	5.97 ± 0.11	0.72 ± 0.02
33	1,2,3,4,6-Penta-*O*-galloyl glucose	n.d.	n.d.	18.45 ± 0.37	6.24 ± 0.12	0.22 ± 0.00
34	Hexa-*O*-galloyl glucose	n.d.	n.d.	37.79 ± 0.74[c]	24.02 ± 0.49[c]	2.22 ± 0.04[c]
35	Hexa-*O*-galloyl glucose	n.d.	n.d.			
36	Catechin gallate	0.31 ± 0.00	3.73 ± 0.07	n.d.	n.d.	n.d.
37	Hepta-*O*-galloyl glucose	n.d.	n.d.	17.45 ± 0.34[d]	19.10 ± 0.37[d]	0.51 ± 0.01[d]
38	Hepta-*O*-galloyl glucose	n.d.	n.d.			
39	Octa-*O*-galloyl glucose	n.d.	n.d.	n.d.	0.70 ± 0.02	n.d.
40	Octa-*O*-galloyl glucose	n.d.	n.d.	n.d.	0.61 ± 0.01	0.09 ± 0.00
41	Procyanidin tetramer (EGCG-EGCG-EGCG-EGCG)	0.14 ± 0.00	0.24 ± 0.00	n.d.	1.10 ± 0.02	0.08 ± 0.00
42	Procyanidin pentamer (EGC-EGC-EGC-EGC-EGCG)	traces	1.39 ± 0.02	n.d.	1.34 ± 0.02	n.d.
43	Procyanidin pentamer (EGC-EGC-EGC-EGCG-EGCG)	0.52 ± 0.01	1.79 ± 0.03	n.d.	traces	n.d.
44	Procyanidin pentamer (EGC-EGC-EGCG-EGCG-EGCG)	1.04 ± 0.02	2.72 ± 0.05	n.d.	0.39 ± 0.00	n.d.
45	Hydroquinone *O*-Hex-*O*-Pent	0.52 ± 0.01	2.92 ± 0.06	6.27 ± 0.14	11.39 ± 0.22	traces
46	Hydroquinone *O*-Glc (=arbutin)	4.12 ± 0.08	5.95 ± 0.11	10.35 ± 0.21	12.65 ± 0.25	2.67 ± 0.05
47	Tyrosol *O*-Hex-*O*-Pent	0.93 ± 0.02	2.95 ± 0.05	0.09 ± 0.00	0.59 ± 0.01	traces
48	Tyrosol *O*-Glc (=salidroside)	1.04 ± 0.02	15.06 ± 0.29	0.53 ± 0.01	0.94 ± 0.02	traces
49	Tyrosol *O*-dHex	n.d.	n.d.	traces	traces	traces
50	Tyrosol (=*p*-hydroxyphenethyl alcohol)	traces	1.54 ± 0.03	traces	traces	traces
51	Benzyl alcohol *O*-Hex-*O*-Pent	traces	traces	traces	traces	traces
52	Benzyl alcohol *O*-Hex-*O*-Pent	traces	traces	traces	traces	traces
53	Benzyl alcohol *O*-Hex	traces	traces	traces	traces	traces
54	*p*-Hydroxycinnamyl alcohol *O*-Hex-*O*-Pent	traces	3.44 ± 0.07	n.d.	n.d.	n.d.
55	*p*-Hydroxycinnamyl alcohol *O*-Glc (=triandrin)	traces	2.86 ± 0.05	0.58 ± 0.01	1.10 ± 0.02	0.39 ± 0.00
56	Benzyl alcohol	traces	traces	traces	traces	traces
57	Rhodiocyanoside A/D *O*-Pent	traces	traces	n.d.	n.d.	n.d.
58	Rhodiocyanoside D	traces	traces	traces	traces	traces
59	Rhodiocyanoside A	0.97 ± 0.02	2.64 ± 0.05	1.42 ± 0.03	2.66 ± 0.05	0.58 ± 0.01
60	Rosiridol di-*O*-Hex-*O*-Pent	n.d.	n.d.	traces	traces	traces
61	Rosiridol *O*-Hex-di-*O*-Pent	n.d.	n.d.	traces	traces	traces
62	Rosiridol *O*-Hex-di-*O*-Pent	n.d.	n.d.	n.d.	n.d.	n.d.
63	Rosiridol *O*-Hex-*O*-Pent	traces	2.07 ± 0.04	traces	1.20 ± 0.02	traces
64	Rosiridol *O*-Hex-*O*-Pent	traces	3.11 ± 0.06	0.53 ± 0.01	1.83 ± 0.03	traces
65	Tyrosol *O*-Hex-*O*-Ac	traces	0.57 ± 0.01	traces	traces	traces
66	Tyrosol *O*-Hex-*O*-Ac	n.d.	n.d.	traces	0.09 ± 0.00	traces
67	Tyrosol *O*-Hex-di-*O*-Ac	n.d.	n.d.	traces	0.25 ± 0.00	traces
68	Cinnamyl alcohol *O*-Hex-di-*O*-Pent	traces	0.85 ± 0.01	n.d.	n.d.	n.d.
69	Cinnamyl alcohol *O*-Hex-di-*O*-Pent	traces	traces	n.d.	n.d.	n.d.
70	Cinnamyl alcohol *O*-(6′-*O*-Ara*f*)-Glc (=rosarin)	6.03 ± 0.12	14.20 ± 0.27	n.d.	n.d.	n.d.
71	Cinnamyl alcohol *O*-(6′-*O*-Ara*p*)-Glc (=rosavin)	10.46 ± 0.21	22.95 ± 0.45	n.d.	n.d.	n.d.

Table S8. *Cont.*

No	Compound	Roots	Rhizome	Leaves	Flowers	Stems
72	Cinnamyl alcohol *O*-Hex-*O*-Pent	0.29 ± 0.00	1.54 ± 0.03	n.d.	n.d.	n.d.
73	Cinnamyl alcohol *O*-Glc (=rosin)	3.11 ± 0.06	7.88 ± 0.15	n.d.	n.d.	n.d.
74	Rosiridol 1-*O*-Glc (=rosiridin)	traces	traces	traces	0.86 ± 0.02	traces
75	*p*-Hydroxycinnamyl alcohol *O*-Hex-*O*-Ac	n.d.	n.d.	traces	0.11 ± 0.00	traces
76	*p*-Hydroxycinnamyl alcohol *O*-Hex *O*-Ac	n.d.	n.d.	traces	0.06 ± 0.00	traces
77	Rosiridol *O*-Hex-*O*-Ac	n.d.	n.d.	traces	1.42 ± 0.03	traces
78	Rosiridol *O*-Hex-di-*O*-Ac	n.d.	n.d.	traces	0.46 ± 0.01	traces
79	Rosiridol *O*-Hex-di-*O*-Ac	n.d.	n.d.	traces	0.68 ± 0.01	traces
80	*p*-Methoxycinnamyl alcohol *O*-Hex-*O*-Pent	traces	0.89 ± 0.02	n.d.	n.d.	n.d.
81	*p*-Methoxycinnamyl alcohol *O*-Hex-*O*-Pent	traces	traces	n.d.	n.d.	n.d.
82	*p*-Methoxycinnamyl alcohol *O*-Glc (=vimalin)	traces	traces	n.d.	n.d.	n.d.
83	Cinnamyl alcohol	traces	traces	n.d.	n.d.	n.d.
84	Cinnamic acid	traces	traces	n.d.	n.d.	n.d.
85	*p*-Methoxycinnamyl alcohol	traces	1.15 ± 0.02	n.d.	n.d.	n.d.
86	Kaempferol tri-*O*-Hex-*O*-dHex (S37)	n.d.	n.d.	n.d.	traces	n.d.
87	Herbacetin tri-*O*-Hex-*O*-dHex (S78)	n.d.	n.d.	traces	traces	n.d.
88	Gossypetin di-*O*-Hex-*O*-dHex (S78)	n.d.	n.d.	traces	traces	n.d.
89	Quercetin di-*O*-Hex-*O*-dHex (S37)	n.d.	n.d.	traces	traces	n.d.
90	Kaempferol di-*O*-Hex-*O*-dHex (S37)	traces	traces	traces	traces	n.d.
91	Gossypetin di-*O*-Hex (S8)	n.d.	n.d.	n.d.	traces	n.d.
92	Herbacetin di-*O*-Hex-*O*-dHex (S78)	n.d.	n.d.	traces	traces	n.d.
93	Gossypetin di-*O*-Hex (S38)	n.d.	n.d.	n.d.	traces	n.d.
94	Gossypetin 7-*O*-(3''-*O*-Glc)-Rha (=rhodioflavonoside)	traces	traces	traces	traces	n.d.
95	Herbacetin 7-*O*-(3''-*O*-Glc)-Rha (=rhodiosin)	n.d.	n.d.	traces	1.32 ± 0.02	n.d.
96	Gossypetin 7-*O*-Rha-8-*O*-Glc (=rhodiolgidin)	n.d.	n.d.	traces	17.62 ± 0.35	0.35 ± 0.00
97	Kaempferol *O*-Hex-*O*-dHex (S7)	n.d.	n.d.	traces	traces	n.d.
98	Herbacetin-8-*O*-Xyl (=rhodalin)	0.10 ± 0.00	0.02 ± 0.00	traces	traces	n.d.
99	Herbacetin 7-*O*-Rha-8-*O*-Glc (=rhodionidin)	traces	traces	traces	20.42 ± 0.41	1.39 ± 0.02
100	Quercetin 3,7-di-*O*-Glc	n.d.	n.d.	n.d.	traces	n.d.
101	Kaempferol 3,7-di-*O*-Glc	traces	traces	n.d.	traces	n.d.
102	Quercetin 3-*O*-Glc-7-*O*-Rha	n.d.	n.d.	traces	traces	n.d.
103	Kaempferol 3-*O*-Glc-7-*O*-Rha	traces	traces	traces	0.09 ± 0.00	n.d.
104	Gossypetin 8-*O*-Glc (=gossypin)	n.d.	n.d.	n.d.	traces	n.d.
105	Kaempferol 3,7-di-*O*-Rha (=kaempferitrin)	n.d.	n.d.	n.d.	traces	n.d.
106	Gossypetin 7-*O*-Rha (=rhodiolgin)	n.d.	n.d.	n.d.	traces	n.d.
107	Quercetin 3-*O*-Glc (=isoquercitrin)	traces	traces	traces	0.08 ± 0.00	n.d.
108	Quercetin 3-*O*-Rha (=quercitrin)	traces	traces	n.d.	traces	n.d.
109	Herbacetin 8-*O*-Glc (=herbacin)	traces	traces	traces	traces	n.d.
110	Herbacetin *O*-dHex (S8)	traces	traces	n.d.	1.46 ± 0.03	n.d.
111	Kaempferol 3-*O*-Rha (=afzelin)	0.36 ± 0.00	0.06 ± 0.00	n.d.	0.12 ± 0.00	n.d.
112	Herbacetin 7-*O*-Rha (=rhodionin)	traces	traces	n.d.	1.77 ± 0.04	n.d.
113	Herbacetin *O*-dHex (S3)	n.d.	n.d.	n.d.	traces	n.d.
114	Kaempferol 7-*O*-Rha	0.10 ± 0.00	traces	n.d.	traces	n.d.
115	Hibiscetin di-*O*-Hex-*O*-HexA (S38)	n.d.	n.d.	traces	traces	n.d.
116	Gossypetin di-*O*-Hex-*O*-HexA (S378)	n.d.	n.d.	0.55 ± 0.01	traces	n.d.
117	Gossypetin *O*-Ac-di-*O*-Hex-*O*-HexA (S378)	n.d.	n.d.	traces	n.d.	traces
118	Gossypetin *O*-Ac-di-*O*-Hex-*O*-HexA (S378)	n.d.	n.d.	traces	traces	n.d.
119	Herbacetin di-*O*-Hex-*O*-HexA (S38)	n.d.	n.d.	traces	traces	n.d.
120	Herbacetin di-*O*-Hex-*O*-HexA (S378)	traces	traces	10.35 ± 0.21	n.d.	traces
121	Herbacetin *O*-Mal-di-*O*-Hex-*O*-HexA (S378)	traces	traces	2.11 ± 0.04	traces	traces
122	Herbacetin *O*-Ac-di-*O*-Hex-*O*-HexA (S378)	n.d.	n.d.	traces	n.d.	traces
123	Hibiscetin *O*-Hex-*O*-HexA (S38)	traces	traces	0.89 ± 0.02	0.92 ± 0.02	0.07 ± 0.00
124	Hibiscetin *O*-Mal-*O*-Hex-*O*-HexA (S38)	n.d.	n.d.	traces	traces	traces
125	Hibiscetin *O*-Ac-*O*-Hex-*O*-HexA (S38)	n.d.	n.d.	traces	n.d.	traces
126	Gossypetin 3-*O*-Glc-8-*O*-GlcA	0.19 ± 0.00	0.08 ± 0.00	1.42 ± 0.03	2.33 ± 0.05	0.37 ± 0.00
127	Gossypetin 3-*O*-(3''-*O*-Ac)-Glc-8-*O*-GlcA (=rhodiquadrin B)	traces	traces	traces	traces	traces
128	5-*O*-Feruloylquinic acid	traces	traces	traces	traces	traces
129	Herbacetin 8-*O*-(2''-*O*-Glc)-GlcA (=rhodiquadrin C)	traces	traces	traces	traces	traces
130	Herbacetin 3-*O*-Glc-8-*O*-GlcA	traces	traces	10.52 ± 0.22	4.96 ± 0.10	1.14 ± 0.02
131	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA (S3,8)	n.d.	n.d.	traces	n.d.	n.d.
132	Herbacetin 3-*O*-(3''-*O*-Ac)-Glc-8-*O*-GlcA	0.16 ± 0.00	0.07 ± 0.00	0.38 ± 0.00	0.37 ± 0.00	traces
133	Gossypetin di-*O*-Ac-*O*-Hex-*O*-HexA (S3,8)	0.09 ± 0.00	0.03 ± 0.00	traces	n.d.	traces
134	Gossypetin di-*O*-Ac-*O*-Hex-*O*-HexA (S3,8)	traces	traces	traces	traces	traces
135	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA (S3,8)	traces	traces	traces	0.49 ± 0.01	0.95 ± 0.02
136	Herbacetin *O*-Ac-*O*-Hex-*O*-HexA (S3,8)	traces	traces	traces	traces	traces
137	Herbacetin di-*O*-Ac-*O*-Hex-*O*-HexA (S3,8)	traces	traces	0.63 ± 0.02	0.40 ± 0.01	traces
138	Gossypetin 8-*O*-GlcA (=hibifolin)	n.d.	n.d.	traces	n.d.	traces
139	Gossypetin *O*-Mal-*O*-HexA (S8)	n.d.	n.d.	traces	0.65 ± 0.02	n.d.
140	Gossypetin *O*-Mal-*O*-HexA (S8)	traces	traces	traces	n.d.	n.d.
141	Gossypetin *O*-Ac-*O*-HexA (S8)	traces	traces	traces	traces	n.d.
142	Gossypetin *O*-Ac-*O*-HexA (S8)	n.d.	n.d.	traces	traces	n.d.

Table S8. *Cont.*

No	Compound	Roots	Rhizome	Leaves	Flowers	Stems
143	Herbacetin 8-*O*-GlcA (=melocorin)	0.55 ± 0.01	0.19 ± 0.00	traces	2.55 ± 0.05	2.03 ± 0.04
144	Herbacetin *O*-Mal-*O*-HexA (S8)	0.14 ± 0.00	0.05 ± 0.00	traces	traces	n.d.
145	Herbacetin *O*-Ac-*O*-HexA (S8)	traces	traces	traces	n.d.	n.d.
146	Herbacetin *O*-Ac-*O*-HexA (S8)	n.d.	n.d.	traces	n.d.	n.d.
	Total galloyl glucoses	5.45	3.08	100.63	68.19	10.98
	incl. mono-galloyl glucoses	0.61	0.30	1.05	0.48	0.60
	di-galloyl glucoses	2.29	1.17	10.35	1.56	3.89
	tri-galloyl glucoses	0.83	0.42	1.95	0.00	1.04
	tetra-galloyl glucoses	0.00	0.00	4.77	7.99	1.42
	penta-galloyl glucoses	0.00	0.00	25.60	12.21	0.94
	hexa-galloyl glucoses	0.00	0.00	37.79	24.02	2.22
	hepta-galloyl glucoses	0.00	0.00	17.45	19.10	0.51
	octa-galloyl glucoses	0.00	0.00	0.00	1.31	0.09
	Total catechins	10.58	57.40	0.00	0.00	0.12
	Total procyanidins	8.77	34.81	0.00	3.02	0.23
	incl. dimers	3.50	15.48	0.00	0.19	0.15
	trimers	3.47	12.29	0.00	0.00	0.00
	tetramers	0.24	1.14	0.00	1.10	0.00
	pentamers	1.56	5.90	0.00	1.73	0.08
	Hydroquinone glucosides	4.64	8.87	16.62	24.04	2.67
	p-Hydroxyphenethyl alcohol glucosides	1.97	20.12	0.62	1.87	traces
	Hydroxynitrile glucosides	0.97	2.64	1.42	2.66	0.58
	Rosiridol glucosides	traces	5.18	0.53	6.45	traces
	Cinnamyl alcohols glucosides	19.89	55.76	0.58	1.26	0.39
	incl. *p*-hydroxycinnamyl alcohol glucosides	traces	6.30	0.58	1.26	0.39
	cinnamyl alcohol glucosides	19.89	47.42	0.00	0.00	0.00
	p-methoxycinnamyl alcohol glucosides	traces	2.04	0.00	0.00	0.00
	Total flavonol glucosides	1.69	0.50	26.85	55.55	6.30
	incl. neutral glucoside	0.56	0.08	traces	42.88	1.74
	acidic glucoside	1.13	0.42	26.85	12.67	4.56
	incl. herbacetin glucosides	0.95	0.33	23.99	33.74	5.51
	gossypetin glucosides	0.28	0.11	1.97	20.60	0.72
	hibiscetin glucosides	0.00	0.00	0.89	0.92	0.07
	kaempferol glucosides	0.46	0.06	traces	0.21	traces
	quercetin glucosides	traces	traces	traces	0.08	traces

[a] Traces—<0.01 mg/g; n.d.—not detected. [a] Abbreviation used: Ac—acetyl; Ara*f*—arabinofuranose; Ara*p*—arabinopyranose; Glc—glucose; GlcA—glucuronic acid; EGC—epigallocatechin unit; EGCG—epigallocatechin gallate unit; Hex—hexose; HexA—hexuronic acid; Mal—malonyl; Pent—pentose; Rha—rhamnose; Xyl—xylose. Substitution type of flavonol glycoside: S3—3-*O*-substituted; S8—8-*O*-substituted; S37—3,7-di-*O*-substituted; S78—7,8-di-*O*-substituted; S38—3,8-di-*O*-substituted; S378—3,7,8-tri-*O*-substituted; S?—unknown type of *O*-substitution. [c] As a sum of compounds **34** and **35**. [d] As a sum of compounds **37** and **38**.

Table S9. Content of selected compounds in three *R. rosea* extracts, mg/g dry extract weight ± S.D.

No	Compound	Rhizome extract	Leaves extract	Flowers extract
7	1,6-Di-*O*-galloyl glucose	traces	48.21 ± 0.98	traces
11	Procyanidin dimer (EGC-EGCG)	44.68 ± 0.87	n.d.	n.d.
16	Procyanidin trimer (EGC-EGC-EGCG)	32.75 ± 0.64	n.d.	n.d.
22	Epicatechin	57.14 ± 1.16	n.d.	n.d.
23	Epigallocatechin gallate	27.11 ± 0.55	n.d.	n.d.
24	Gallocatechin gallate	37.08 ± 0.73	n.d.	n.d.
30	Epicatechin gallate	14.93 ± 0.27	n.d.	n.d.
32	Penta-*O*-galloyl glucose	n.d.	35.73 ± 0.72	22.82 ± 0.46
33	1,2,3,4,6-Penta-*O*-galloyl glucose	n.d.	92.26 ± 1.87	24.93 ± 0.48
34+35	Hexa-*O*-galloyl glucoses	n.d.	188.92 ± 3.79	95.80 ± 1.97
37+38	Hepta-*O*-galloyl glucoses	n.d.	85.14 ± 1.73	75.42 ± 1.42
46	Hydroquinone *O*-Glc (=arbutin)	18.67 ± 0.35	53.11 ± 1.03	51.82 ± 1.04
48	Tyrosol *O*-Glc (=salidroside)	46.94 ± 0.92	traces	traces
70	Cinnamyl alcohol *O*-(6′-*O*-Ara*f*)-Glc (=rosarin)	42.79 ± 0.86	n.d.	n.d.
71	Cinnamyl alcohol *O*-(6′-*O*-Ara*p*)-Glc (=rosavin)	69.54 ± 1.38	n.d.	n.d.
73	Cinnamyl alcohol *O*-Glc (=rosin)	24.27 ± 0.47	n.d.	n.d.
96	Gossypetin 7-*O*-Rha-8-*O*-Glc (=rhodiolgidin)	n.d.	traces	71.42 ± 1.47
99	Herbacetin 7-*O*-Rha-8-*O*-Glc (=rhodionidin)	traces	traces	81.73 ± 1.62
120	Herbacetin di-*O*-Hex-*O*-HexA (S378)	traces	50.28 ± 1.02	n.d.
130	Herbacetin 3-*O*-Glc-8-*O*-GlcA	traces	53.67 ± 1.09	19.74 ± 0.37
	Total galloyl glucoses	traces	450.26	218.97
	Total procyanidins	77.43	n.d.	n.d.
	Total catechins	136.26	n.d.	n.d.
	Total hydroquinone glucosides	18.67	53.11	51.82
	Total *p*-hydroxyphenethyl alcohol glucosides	46.44	traces	traces
	Total cinnamyl alcohol glucosides	136.60	n.d.	n.d.
	Total flavonol glucosides	traces	103.95	172.89

n.d.—not detected.

Table S10. Content of selected compounds of *R. rosea* rhizome extract (whole probe) before and after *in vitro* treatment by the simulated gastric and intestinal media, mg/probe ± S.D.

No	Compound	Non-treated	After gastric phase	After intestinal phase
7	1,6-Di-*O*-galloyl glucose	traces	n.d.	n.d.
11	Procyanidin dimer (EGC-EGCG)	22.15 ± 0.42	18.63 ± 0.38	1.18 ± 0.02
16	Procyanidin trimer (EGC-EGC-EGCG)	16.30 ± 0.31	8.63 ± 0.15	0.94 ± 0.02
22	Epicatechin	27.94 ± 0.54	25.63 ± 0.52	1.22 ± 0.02
23	Epigallocatechin gallate	13.42 ± 0.25	5.42 ± 0.11	0.18 ± 0.00
24	Gallocatechin gallate	18.97 ± 0.38	4.73 ± 0.08	0.23 ± 0.00
30	Epicatechin gallate	7.45 ± 0.14	5.14 ± 0.12	0.58 ± 0.01
32	Penta-*O*-galloyl glucose	n.d.	n.d.	n.d.
33	1,2,3,4,6-Penta-*O*-galloyl glucose	n.d.	n.d.	n.d.
34+35	Hexa-*O*-galloyl glucoses	n.d.	n.d.	n.d.
37+38	Hepta-*O*-galloyl glucoses	n.d.	n.d.	n.d.
46	Hydroquinone *O*-Glc (=arbutin)	9.32 ± 0.17	8.64 ± 0.17	7.11 ± 0.15
48	Tyrosol *O*-Glc (=salidroside)	23.48 ± 0.45	22.76 ± 0.47	20.54 ± 0.41
70	Cinnamyl alcohol *O*-(6′-*O*-Ara*f*)-Glc (=rosarin)	21.18 ± 0.40	20.98 ± 0.42	25.35 ± 0.51
71	Cinnamyl alcohol *O*-(6′-*O*-Ara*p*)-Glc (=rosavin)	34.75 ± 0.67	33.86 ± 0.69	26.18 ± 0.52
73	Cinnamyl alcohol *O*-Glc (=rosin)	12.09 ± 0.22	12.93 ± 0.25	15.71 ± 0.31
96	Gossypetin 7-*O*-Rha-8-*O*-Glc (=rhodiolgidin)	n.d.	n.d.	n.d.
99	Herbacetin 7-*O*-Rha-8-*O*-Glc (=rhodionidin)	traces	n.d.	n.d.
120	Herbacetin di-*O*-Hex-*O*-HexA (S378)	traces	n.d.	n.d.
130	Herbacetin 3-*O*-Glc-8-*O*-GlcA	traces	n.d.	n.d.
	Total galloyl glucoses	traces	n.d.	n.d.
	Total procyanidins	38.45	27.26	2.12
	Total catechins	67.78	40.92	2.21
	Total hydroquinone glucosides	9.32	8.64	7.11
	Total *p*-hydroxyphenethyl alcohol glucosides	23.48	22.76	20.54
	Total cinnamyl alcohol glucosides	68.02	67.77	67.24
	Total flavonol glucosides	traces	n.d.	n.d.

n.d.—not detected.

Table S11. Content of selected compounds of *R. rosea* leaves extract (whole probe) before and after *in vitro* treatment by the simulated gastric and intestinal media, mg/probe ± S.D.

No	Compound	Non-treated	After gastric phase	After intestinal phase
7	1,6-Di-*O*-galloyl glucose	24.02 ± 0.49	22.83 ± 0.42	15.79 ± 0.31
11	Procyanidin dimer (EGC-EGCG)	n.d.	n.d.	n.d.
16	Procyanidin trimer (EGC-EGC-EGCG)	n.d.	n.d.	n.d.
22	Epicatechin	n.d.	n.d.	n.d.
23	Epigallocatechin gallate	n.d.	n.d.	n.d.
24	Gallocatechin gallate	n.d.	n.d.	n.d.
30	Epicatechin gallate	n.d.	n.d.	n.d.
32	Penta-*O*-galloyl glucose	17.53 ± 0.36	5.37 ± 0.11	0.92 ± 0.02
33	1,2,3,4,6-Penta-*O*-galloyl glucose	46.18 ± 0.90	12.78 ± 0.23	1.40 ± 0.03
34+35	Hexa-*O*-galloyl glucoses	94.27 ± 1.91	25.92 ± 0.51	3.18 ± 0.06
37+38	Hepta-*O*-galloyl glucoses	42.49 ± 0.86	11.37 ± 0.19	0.72 ± 0.02
46	Hydroquinone *O*-Glc (=arbutin)	26.59 ± 0.54	24.19 ± 0.47	19.14 ± 0.37
48	Tyrosol *O*-Glc (=salidroside)	traces	n.d.	n.d.
70	Cinnamyl alcohol *O*-(6′-*O*-Ara*f*)-Glc (=rosarin)	n.d.	n.d.	n.d.
71	Cinnamyl alcohol *O*-(6′-*O*-Ara*p*)-Glc (=rosavin)	n.d.	n.d.	n.d.
73	Cinnamyl alcohol *O*-Glc (=rosin)	n.d.	n.d.	n.d.
96	Gossypetin 7-*O*-Rha-8-*O*-Glc (=rhodiolgidin)	traces	n.d.	n.d.
99	Herbacetin 7-*O*-Rha-8-*O*-Glc (=rhodionidin)	traces	n.d.	n.d.
120	Herbacetin di-*O*-Hex-*O*-HexA (S378)	25.09 ± 0.48	24.98 ± 0.48	24.82 ± 0.49
130	Herbacetin 3-*O*-Glc-8-*O*-GlcA	26.82 ± 0.53	26.70 ± 0.51	26.61 ± 0.52
	Total galloyl glucoses	224.49	78.27	22.01
	Total procyanidins	n.d.	n.d.	n.d.
	Total catechins	n.d.	n.d.	n.d.
	Total hydroquinone glucosides	26.59	24.19	19.14
	Total *p*-hydroxyphenethyl alcohol glucosides	traces	n.d.	n.d.
	Total cinnamyl alcohol glucosides	n.d.	n.d.	n.d.
	Total flavonol glucosides	51.91	51.68	51.43

n.d.—not detected.

Table S12. Content of selected compounds of *R. rosea* flowers extract (whole probe) before and after *in vitro* treatment by the simulated gastric and intestinal media, mg/probe ± S.D.

No	Compound	Non-treated	After gastric phase	After intestinal phase
7	1,6-Di-*O*-galloyl glucose	traces	n.d.	n.d.
11	Procyanidin dimer (EGC-EGCG)	n.d.	n.d.	n.d.
16	Procyanidin trimer (EGC-EGC-EGCG)	n.d.	n.d.	n.d.
22	Epicatechin	n.d.	n.d.	n.d.
23	Epigallocatechin gallate	n.d.	n.d.	n.d.
24	Gallocatechin gallate	n.d.	n.d.	n.d.
30	Epicatechin gallate	n.d.	n.d.	n.d.
32	Penta-*O*-galloyl glucose	11.40 ± 0.22	3.06 ± 0.06	0.83 ± 0.02
33	1,2,3,4,6-Penta-*O*-galloyl glucose	12.37 ± 0.25	3.29 ± 0.06	0.86 ± 0.02
34+35	Hexa-*O*-galloyl glucoses	47.63 ± 0.94	12.53 ± 0.25	2.63 ± 0.05
37+38	Hepta-*O*-galloyl glucoses	37.75 ± 0.76	9.43 ± 0.19	2.04 ± 0.04
46	Hydroquinone *O*-Glc (=arbutin)	25.73 ± 0.49	24.18 ± 0.50	19.55 ± 0.39
48	Tyrosol *O*-Glc (=salidroside)	traces	n.d.	n.d.
70	Cinnamyl alcohol *O*-(6′-*O*-Ara*f*)-Glc (=rosarin)	n.d.	n.d.	n.d.
71	Cinnamyl alcohol *O*-(6′-*O*-Ara*p*)-Glc (=rosavin)	n.d.	n.d.	n.d.
73	Cinnamyl alcohol *O*-Glc (=rosin)	n.d.	n.d.	n.d.
96	Gossypetin 7-*O*-Rha-8-*O*-Glc (=rhodiolgidin)	35.67 ± 0.67	35.04 ± 0.72	34.81 ± 0.69
99	Herbacetin 7-*O*-Rha-8-*O*-Glc (=rhodionidin)	40.59 ± 0.82	40.11 ± 0.81	39.93 ± 0.77
120	Herbacetin di-*O*-Hex-*O*-HexA (S378)	n.d.	n.d.	n.d.
130	Herbacetin 3-*O*-Glc-8-*O*-GlcA	9.82 ± 0.19	9.73 ± 0.19	9.58 ± 0.19
	Total galloyl glucoses	109.15	28.31	6.36
	Total procyanidins	n.d.	n.d.	n.d.
	Total catechins	n.d.	n.d.	n.d.
	Total hydroquinone glucosides	25.73	24.18	19.55
	Total *p*-hydroxyphenethyl alcohol glucosides	traces	n.d.	n.d.
	Total cinnamyl alcohol glucosides	n.d.	n.d.	n.d.
	Total flavonol glucosides	86.08	84.88	84.32

n.d.—not detected.