

Supporting Information

Table S1. LC-MS/MS methods: Ion parameters of test compounds.

Compound Name	Q1Mass (<i>m/z</i>)	Q3Mass (<i>m/z</i>)	DP (volts)	CE (volts)	CXP (volts)	#
Hamamelitannin	483.18	168.8	-105	-42	-11	1-1
1,2,3,6-Tetra- <i>O</i> -galloyl glucose	787.213	168.9	-155	-70	-13	1-1
1,2,3,4,6-Penta- <i>O</i> -galloyl glucose	939.262	769.1	-165	-44	-21	1-1
Eugenin	937.241	301	-175	-64	-17	1-1
1-Desgalloyl eugenin	785.268	300.7	-175	-56	-19	1-1
(+)-Catechin	288.917	109.1	-90	-32	-17	1-2
(-)-Epicatechin gallate	441.043	168.9	-80	-28	-13	1-2
(-)-Gallocatechin	305.057	125.1	-95	-30	-19	1-2
Luteolin	284.85	132.3	-90	-68	-23	1-2
Quercetin	300.98	150.7	-105	-30	-9	1-2
Genistin	431.012	269.1	-55	-16	-15	1-2
Genistein	268.919	132.7	-105	-42	-21	1-2
Gallic acid	168.79	125	-65	-22	-19	1-3
4- <i>O</i> -Methylgallic acid	182.851	123.9	-65	-30	-19	1-4
Liquiritin	417.007	254.8	-85	-28	-5	1-5
Liquiritin apioside	549.216	135	-145	-62	-23	1-5
Liquiritigenin	254.895	118.9	-80	-38	-1	1-5
Isoliquiritin	416.971	255	-100	-24	-15	1-5
Isoliquiritin apioside	549.213	254.9	-150	-40	-23	1-5
Isoliquiritigenin	254.868	119	-75	-42	-21	1-5
Sophoricoside	431.061	268	-110	-44	-15	1-6
Hesperidin	609.238	301.1	-120	-38	-19	1-6
Hesperetin	301.101	164.2	-105	-34	-9	1-6
Liquiritigenin 4'- <i>O</i> -glucuronide	431.02	113	-80	-28	-19	1-6
Liquiritigenin 7- <i>O</i> -glucuronide	431.049	113	-75	-28	-17	1-6
Isoliquiritigenin 2'- <i>O</i> -glucuronide	431.041	254.8	-80	-26	-23	1-6
Isoliquiritigenin 4'- <i>O</i> -glucuronide	431.031	254.7	-85	-28	-15	1-6
Isoliquiritigenin 4- <i>O</i> -glucuronide	431.1	135	-85	-30	-1	1-6
Genistein 4'- <i>O</i> -glucuronide	445.06	113.1	-90	-26	-17	1-6
Genistein 7- <i>O</i> -glucuronide	445.072	269.1	-85	-30	-19	1-6
Hesperetin 7- <i>O</i> -glucuronide	477.016	301.1	-85	-34	-19	1-6
Luteolin 7- <i>O</i> -glucuronide	461.029	284.8	-90	-34	-15	1-6
Quercetin 3- <i>O</i> -glucuronide	477.029	301	-75	-32	-17	1-6
Castalagin	935.025	468.9	181	39	22	2-7
Niflumic acid (IS)	280.826	236.8	-55 -20	-24 -30	-11 -15	1-1, 1-2, 1-3, 1-4, 1-5 1-6
Vincamine (IS)	355.257	337.1	96	29	18	2-7

#: LC-MS/MS system and HPLC method ID are described in Table S2. Q1: quadrupole 1, Q3: quadrupole 3, DP: declustering potential, CE: collision energy, CXP: collision cell exit potential.

Table S2. LC-MS/MS methods: HPLC conditions.

LC-MS/MS System	HPLC Method	HPLC Condition
1	1	Column: Ascentis Express RP-amide column (100 × 2.1 mm I.D., 2.7-μm particle size; Supelco Analytical, Inc., Tokyo, Japan) Mobile phase (A) 0.2 vol % acetic acid, (B) acetonitrile containing 0.2 vol % acetic acid Gradient elution program (% B in A): 0–8 min, 22%; 8–8.01 min, 22% → 90%; 8.01–13 min, 90%; 13–13.01 min, 90% → 22%; 13.01–18 min, 22% Other conditions were: flow rate, 0.2 mL/min; column temperature, 40 °C
	2	Column: Ascentis Express RP-amide column Mobile phase (A) 0.2 vol % acetic acid, (B) acetonitrile containing 0.2 vol % acetic acid Gradient elution program (% B in A): 0–5 min, 22%; 5–10 min, 22% → 90%; 10–15 min, 90%; 15–15.1 min, 90% → 22%; 15.1–25 min, 22% Other conditions were: flow rate, 0.2 mL/min; column temperature, 40 °C
	3	Column: Ascentis Express RP-amide column Mobile phase (A) 0.2 vol % acetic acid, (B) acetonitrile containing 0.2 vol % acetic acid Gradient elution program (% B in A): 0–2 min, 22%; 2–10 min, 22% → 80%; 10–15 min, 80%; 15–15.1 min, 80% → 22%; 15.1–20 min, 22% Other conditions were: flow rate, 0.2 mL/min; column temperature, 40 °C
	4	Column: Ascentis Express RP-amide column Mobile phase (A) 0.2 vol % acetic acid, (B) acetonitrile containing 0.2 vol % acetic acid Gradient elution program (% B in A): 0–10 min, 10%; 10–10.1 min, 10% → 80%; 10.1–16 min, 80%; 16–16.01 min, 80% → 10%; 16.01–21 min, 10% Other conditions were: flow rate, 0.2 mL/min; column temperature, 40 °C
	5	Column: Inertsil Ph-3 column (100 × 2.1 mm I.D., 3-μm particle size; GL Sciences, Tokyo, Japan) Mobile phase (A) 10 mM ammonium acetate, (B) acetonitrile Gradient elution program (% B in A): 0–1 min, 20%; 1–13 min, 20% → 65%; 13–13.01 min, 65% → 20%; 13.01–18 min, 20% Other conditions were: flow rate, 0.3 mL/min; column temperature, 40 °C
	6	Column: Kinetex PFP column (100 × 2.1 mm I.D., 2.6-μm particle size; Phenomenex, Torrance, CA, USA) Mobile phase (A) 0.2 vol % acetic acid, (B) acetonitrile containing 0.2 vol % acetic acid Gradient elution program (% B in A): 0–10 min, 11%; 10–30 min, 11% → 40%; 30–30.01 min, 40% → 90%; 30.01–35 min, 90%; 35–35.01 min, 90% → 11%; 35.01–40 min, 11% Other conditions were: flow rate, 0.35 mL/min; column temperature, 40 °C
2	7	Column: Ascentis Express RP-amide column Mobile phase (A) 0.2 vol % formic acid, (B) acetonitrile Gradient elution program (% B in A): 0–1 min, 10%; 1–8 min, 10% → 30%; 8–10 min, 30% → 90%; 10–12 min, 90%; 12–12.01 min, 90% → 10%; 12.01–17 min, 10% Other conditions were: flow rate, 0.3 mL/min; column temperature, 40 °C

LC-MS/MS system: system 1, an API4000 triple quadrupole mass spectrometer (AB SCIEX, Tokyo, Japan) equipped with an Agilent 1100 system (Agilent Technologies, Tokyo, Japan); system 2, a TripleQuad6500 (AB SCIEX) equipped with an Agilent 1290 system (Agilent Technologies).