

Supplementary material

Table S1. LC–MS/MS conditions for quantification of detected compounds by negative/positive ion MRM

Compound	Selected transitions	Dwell (msec)	DP	EP	CE	CXP
isoquercetin	463/299.9	20	-115	-3.76	-40	-17.5
quercetin 3- <i>O</i> -rhamnoside	447/300	20	-97.15	-14	-34	-18
phloridzin	435/273	20	-89	-3.9	-22.2	-47.8
robinin	739/593	20	-126	-10.7	-42.6	-32.2
rutin	609/300	20	-125	-10.5	-60	-13.6
isorhamnetin 3- <i>O</i> -rutinoside	623/315	20	-90.8	-10.8	-46.7	-17.7
quercetin 3- <i>O</i> -galactoside	463/300	20	-104.7	-10.6	-40.2	-15
myricitrin	463/316	20	-97.8	-10.7	-40.6	-17.7
myricetin 3- <i>O</i> -galactoside	479/316	20	-95.6	-15	-37.7	-16.1
neohesperidin	609/301	20	-94	-15	-38.8	-14.2
luteolin	285/133	20	-97.6	-10.7	-50.6	-16.6
kaempferol	285/186.9	20	-113	-8.7	-39.2	-9.7
quercetin	301/151	20	-94.6	-15	-30.6	-7
isorhamnetin	315/300	20	-111.4	-15	-31.9	-17.9
myricetin	317/151	20	-60	-10	-40	-15
apigenin	269/117	20	-107.8	-15	-45.1	-4.7
ellagic acid	301/283	20	-101	-13	-44.7	-15.2
epicatechin	289/245	20	-93	-9	-21.7	-14.6
catechin	289/245	20	-93	-9	-21.7	-14.6
epigallocatechin	305/125	20	-87.3	-10.7	-29	-4.9
epigallocatechin gallate	457/169	20	-89	-10.8	-22.1	-8.2
procyanidin B1	577/289	20	-99.8	-3.5	-22.3	-7.9
procyanidin B2	577/289	20	-99.2	-3	-35	-17.7
chlorogenic acid	353/191	20	-71.1	-5.1	-21.1	-10.7
<i>p</i> -coumaric acid	163/119	20	-56.3	-2	-20.04	-8
ferulic acid	193/134	20	-58.2	-11	-20	-5.8
sinapic acid	223/164	20	-53.9	-11	-18.3	-8.2
gallic acid	169/125	20	-58.9	-6	-19.7	-4.9
caffeic acid	179/135	20	-69.6	-13.9	-19.1	-23
quinic acid	191/85	20	-84.1	-15	-32	-13.9
syringic acid	197/121	20	-52	-10.7	-24.8	-4.5
cyanidin 3,5-di- <i>O</i> -glucoside	611/287	100	177	14	55	19
cyanidin 3- <i>O</i> -glucoside	449/287	100	192	12	27.2	20.5
cyanidin 3- <i>O</i> -arabinoside	419/287	100	194	11.5	24	19.7
delphinidin 3- <i>O</i> -glucoside	465/303	100	181	14	30	21

malvidin 3- <i>O</i> -glucoside	493/331	100	94	12	29	21
pelargonidin 3- <i>O</i> -glucoside	433/271	100	76.9	10.1	28.8	18.8
pelargonidin 3- <i>O</i> - rutinoside	579/271	100	98	13	40	18.4

DP= declustering potential; EP=entrance potential; CE= collision energy; CXP = cell exit potential.

Table S2. Accuracy, precision, linearity, LOQ and LOD of LC-ESI-QqQ-MS/MS MRM method for the analysis of standard compounds.

Compound	Calibration curve	r ²	Intra-day (CV%)	Inter-day (CV%)	LOQ (µg/mL)	LOD (µg/mL)
isoquercetin	y=7.05 ^{e5} x-5.69 ^{e3}	0.999	1.03	3.56	0.008	0.003
quercetin 3- <i>O</i> -rhamnoside	y=2.1 ^{e6} x-1.4 ^{e4}	0.999	1.99	2.52	0.006	0.002
phloridzin	y=2.14 ^{e6} x+1.22 ^{e3}	0.999	2.96	3.36	0.008	0.003
robinin	y=1.29 ^{e6} x-1.28 ^{e4}	0.999	3.55	6.73	0.012	0.004
rutin	y=8.09 ^{e5} x+1.08 ^{e3}	0.999	4.24	5.03	0.009	0.003
isorhamnetin 3- <i>O</i> - rutinoside	y=1.81 ^{e6} x+1.17 ^{e3}	0.999	4.64	7.61	0.007	0.002
quercetin 3- <i>O</i> -galactoside	y=2.74 ^{e6} x+1.32 ^{e4}	0.999	1.71	2.85	0.005	0.001
myricitrin	y=1.78 ^{e6} x-7.27 ^{e3}	0.999	5.14	6.03	0.004	0.001
myricetin 3- <i>O</i> -galactoside	y=1.6 ^{e6} x-1.54 ^{e4}	0.998	2.57	4.35	0.008	0.002
neohesperidin	y=1.79 ^{e6} x+2.95 ^{e3}	0.999	1.55	3.76	0.006	0.002
luteolin	y=1.85 ^{e6} x-9.48 ^{e3}	0.999	3.99	4.48	0.005	0.001
kaempferol	y=9.95 ^{e4} x-935	0.999	2.59	4.22	0.009	0.004
quercetin	y=3.91 ^{e5} x+2.28 ^{e4}	0.999	4.39	6.47	0.041	0.013
isorhamnetin	y=2.52 ^{e6} x+1.16 ^{e4}	0.998	5.23	7.09	0.007	0.003
myricetin	y=2.33 ^{e5} x-396	0.999	0.58	2.16	0.006	0.002
apigenin	y=1.56 ^{e6} x-1.75 ^{e3}	0.997	1.91	3.22	0.002	0.001
ellagic acid	y=2.35 ^{e4} x-2.04 ^{e4}	0.993	6.34	7.33	0.085	0.026
epicatechin	y=6.95 ^{e5} x-8.29 ^{e3}	0.999	5.65	7.12	0.009	0.003
catechin	y=6.42 ^{e5} x-352	0.999	3.87	5.52	0.004	0.001
epigallocatechin	y=7.83 ^{e5} x-7.68 ^{e3}	0.999	7.93	8.72	0.009	0.003
epigallocatechin gallate	y=2.45 ^{e6} x-1.96 ^{e4}	0.998	8.29	9.33	0.008	0.002
procyanidin B1	y=7.5 ^{e5} x-5.69 ^{e3}	0.999	6.67	8.05	0.008	0.002
procyanidin B2	y=7.26 ^{e5} x-6.69 ^{e3}	0.999	1.27	3.23	0.009	0.003
chlorogenic acid	y=1.71 ^{e6} x-5.28 ^{e4}	0.998	4.19	5.67	0.035	0.011
<i>p</i> -coumaric acid	y=3.69 ^{e6} x+2.38 ^{e4}	0.999	1.24	4.55	0.008	0.002
ferulic acid	y=1.28 ^{e6} x-3.63 ^{e3}	0.999	4.53	5.03	0.008	0.003
sinapic acid	y=3.85 ^{e5} x-2.12 ^{e3}	0.997	1.47	2.87	0.007	0.002
gallic acid	y=2.35 ^{e5} x-8.33 ^{e3}	0.999	0.61	2.11	0.021	0.006
caffeic acid	y=2.31 ^{e6} x+4.55 ^{e3}	0.998	1.24	3.15	0.042	0.013
quinic acid	y=3.75 ^{e5} x-3.65 ^{e3}	0.999	7.65	8.95	0.011	0.003
syringic acid	y=6.64 ^{e4} x+350	0.999	3.85	5.25	0.027	0.008

cyanidin glucoside	3,5-di-O-	$y=5,98e^5x+4,31e^5$	0.993	1.97	4.06	0.008	0.002
cyanidin 3-O-glucoside		$y=6,14e^4x-2,03e^4$	0.994	3.42	6.72	0.010	0.003
cyanidin 3-O-arabinoside		$y=1,5e^6x+4,38e^6$	0.993	0.76	4.24	0.090	0.020
delphinidin 3-O-glucoside		$y=2,01e^6x+5,46e^4$	0.998	1.59	2.95	0.050	0.012
malvidin 3-O-glucoside		$y=1,56e^6x+3,29e^6$	0.994	4.31	5.56	0.007	0.0003
pelargonidin glucoside	3-O-	$y=1.53e^7x+4.4e^4$	0.999	4.5	6.01	0.004	0.001
pelargonidin rutinoside	3-O-	$y=7.47e^6x-1.26e^4$	0.999	4.95	5.48	0.007	0.003
