

Supplementary Information

Table S1. ESI–MS/MS Parameters and analytical characteristics for the Analysis of target analytes by MRM Negative and Positive Ionization Mode.

Target compounds	Rt (min)	Precursor ion	MRM1 (CE, V)	MRM2 (CE, V)
<i>Compounds analyzed by NI mode</i>				
Gallic acid	8.891	168.9 [M – H]–	125.0 (10)	–
Protocatechuic acid	10.818	152.9 [M – H]–	108.9 (12)	–
3,4-Dihydroxyphenylacetic acid	11.224	167.0 [M – H]–	123.0 (2)	–
(+)-Catechin	11.369	289.0 [M – H]–	245.0 (6)	202.9 (12)
Pyrocatechol	11.506	109.0 [M – H]–	90.6 (18)	52.9 (16)
2,5-Dihydroxybenzoic acid	12.412	152.9 [M – H]–	109.0 (10)	–
4-Hydroxybenzoic acid	12.439	136.9 [M – H]–	93.1 (14)	–
Caffeic acid	12.841	179.0 [M – H]–	135.0 (12)	–
Vanillic acid	12.843	166.9 [M – H]–	151.8 (10)	122.6 (6)
Syringic acid	12.963	196.9 [M – H]–	181.9 (8)	152.8 (6)
3-Hydroxybenzoic acid	13.259	137.0 [M – H]–	93.0 (6)	–
Vanillin	13.397	151.0 [M – H]–	136.0 (10)	–
Verbascoside	13.589	623.0 [M – H]–	461.0 (26)	160.8 (36)
Taxifolin	13.909	303.0 [M – H]–	285.1 (2)	125.0 (14)
Sinapic acid	13.992	222.9 [M – H]–	207.9 (6)	163.8 (6)
p-Coumaric acid	14.022	162.9 [M – H]–	119.0 (12)	–
Ferulic acid	14.120	193.0 [M – H]–	177.8 (8)	134.0 (12)
Luteolin 7-glucoside	14.266	447.1 [M – H]–	285.0 (24)	–
Rosmarinic acid	14.600	359.0 [M – H]–	196.9 (10)	160.9 (10)
2-Hydroxycinnamic acid	15.031	162.9 [M – H]–	119.1 (10)	–
Pinoresinol	15.118	357.0 [M – H]–	151.0 (12)	135.7 (34)
Eriodictyol	15.247	287.0 [M – H]–	151.0 (4)	134.9 (22)
Quercetin	15.668	301.0 [M – H]–	178.6 (10)	151.0 (16)
Kaempferol	16.236	285.0 [M – H]–	242.8 (16)	229.1 (18)
<i>Compounds analyzed by PI mode</i>				
Chlorogenic acid	11.802	355.0 [M + H]+	163.0 (10)	–
(–)-Epicatechin	12.458	291.0 [M + H]+	139.1 (12)	122.9 (36)
Hesperidin	14.412	611.1 [M + H]+	449.2 (4)	303.0 (20)
Hyperoside	14.506	465.1 [M + H]+	303.1 (8)	–
Apigenin 7-glucoside	14.781	433.1 [M + H]+	271.0 (18)	–
Luteolin	15.923	287.0 [M + H]+	153.1 (34)	135.1 (36)
Apigenin	16.382	271.0 [M + H]+	153.0 (34)	119.1 (36)

Rt, retention time; NI, negative ion; and PI, positive ion.

Table S2. Calibration curves and sensitivity properties of the method

Compounds	Linearity and sensitivity characteristics				
	Range ($\mu\text{g/L}$)	Linear equation	R^2	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
Gallic acid	5–500	$y = 4.82x - 26.48$	0.9988	1.46	4.88
Protocatechuic acid	2.5– 500	$y = 5.65x - 9.99$	0.9990	1.17	3.88
3,4-Dihydroxyphenylacetic acid	5–500	$y = 5.13x - 12.39$	0.9990	1.35	4.51
(+)-Catechin	10–500	$y = 1.45x + 1.95$	0.9974	3.96	13.20
Pyrocatechol	25–400	$y = 0.11x - 0.52$	0.9916	9.62	32.08
Chlorogenic acid	1–500	$y = 12.14x + 32.34$	0.9995	0.55	1.82
2,5-Dihydroxybenzoic acid	5–500	$y = 3.79x - 14.12$	0.9980	2.12	7.08
4-Hydroxybenzoic acid	5–500	$y = 7.62x + 22.79$	0.9996	1.72	5.72
(-)-Epicatechin	5–500	$y = 9.11x - 9.99$	0.9971	1.85	6.18
Caffeic acid	5–500	$y = 11.09x + 16.73$	0.9997	3.15	10.50
Vanillic acid	10–500	$y = 0.49x - 1.61$	0.9968	2.56	8.54
Syringic acid	10–500	$y = 0.74x - 1.54$	0.9975	3.75	12.50
3-Hydroxybenzoic acid	5–500	$y = 3.69x - 12.29$	0.9991	1.86	6.20
Vanillin	50–500	$y = 2.02x + 135.49$	0.9926	15.23	50.77
Verbascoside	2.5– 500	$y = 8.59x - 28.05$	0.9988	0.82	2.75
Taxifolin	5–500	$y = 12.32x + 9.98$	0.9993	1.82	6.05
Sinapic acid	5–500	$y = 2.09x - 6.79$	0.9974	2.64	8.78
p-Coumaric acid	5–500	$y = 17.51x + 53.73$	0.9997	1.93	6.44
Ferulic acid	5–500	$y = 3.32x - 4.30$	0.9992	1.43	4.76
Luteolin 7-glucoside	1–500	$y = 45.25x + 156.48$	0.9996	0.45	1.51
Hesperidin	5–500	$y = 5.98x + 0.42$	0.9993	1.73	5.77
Hyperoside	2.5– 500	$y = 16.32x - 1.26$	0.9998	0.99	3.31

Rosmarinic acid	1–500	$y = 9.82x - 17.98$	0.9989	0.57	1.89
Apigenin 7-glucoside	1–500	$y = 21.33x - 31.69$	0.9983	0.41	1.35
2-Hydroxycinnamic acid	1–500	$y = 16.72x - 26.94$	0.9996	0.61	2.03
Pinoresinol	10–500	$y = 0.80x - 2.69$	0.9966	3.94	13.12
Eriodictyol	2.5– 500	$y = 14.24x - 0.50$	0.9998	0.80	2.68
Quercetin	5–500	$y = 14.68x - 18.25$	0.9997	1.23	4.10
Luteolin	5–500	$y = 8.96x + 26.80$	0.9992	1.34	4.46
Kaempferol	10–500	$y = 0.82x - 3.06$	0.9959	3.30	10.99
Apigenin	2.5– 500	$y = 11.29x + 38.05$	0.9987	0.96	3.20

LOD and LOQ: limit of detection and limit of quantification, respectively.