

Table S1. Optimized parameters for the LC-ESI-MS/MS qualitative analysis of phenolic acids and flavonoids.

Compound	Retention time [min]	[M-H] ⁻ [m/z]	Fragment ions [m/z]	Collision energy [eV]
Phenolic acids				
Gallic acid	5.16	168.7	78.9	-36
			124.9	-14
Homogentisic acid	6.34	166.8	123	-12
			108	-36
α -Resorcylic acid	7.87	152.8	109	-12
			64.9	-20
Protocatechuic acid	8.42	152.9	80.9	-26
			107.8	-38
4-Hydroxybenzoic acid	10.84	136.8	93	-18
			80.9	-110
Gentisic acid	11.45	152.9	107.8	-52
			107.9	-18
Vanillic acid	11.49	166.8	123	-12
			122.8	-24
Syringic acid	11.44	196.9	181.9	-12
			88.9	-30
Caffeic acid	11.69	178.7	134.9	-30
			108.9	-14
γ -Resorcylic acid	12.04	152.8	65	-30
			93	-16
3-hydroxybenzoic acid	12.10	136.9	75	-48
			119	-14
4-Hydroxycinnamic acid (<i>p</i> -coumaric acid)	14.10	162.7	93	-44
			121	-36
Sinapic acid	14.47	222.8	148.9	-20
			133.9	-16
Ferulic acid	14.87	192.8	177.9	-12
			121.9	-18
3,4-Dimethoxybenzoic acid (Veratric acid)	15.26	180.7	136.9	-12
			160.8	-20
Rosmarinic acid	15.91	358.7	196.8	-22
			119	-14
3-Hydroxycinnamic acid (<i>m</i> -Coumaric acid)	16.05	162.8	91	-36
			119	-14
2-Hydroxycinnamic acid (<i>o</i> -Coumaric acid)	17.15	162.8	91	-36
			93	-16
Salicylic acid	17.91	136.8	75	-48
			136.9	-12
3,5-Dimethoxybenzoic acid	18.25	180.8	122	-20
			148	-16
2,5-Dimethoxycinnamic acid	18.50	206.9	132.9	-14
	19.06			
Flavonoid aglycones				
Catechin	9.64	288.8	244.9	-16
			109	-32
Taxifolin	15.15	302.7	124.9	-26
			284.8	-14

Myricetin	16.57	316.7	136.9	-32
			150.9	-26
Luteolin	17.82	284.7	132.9	-38
			150.9	-26
Eriodictyol	17.89	286.7	134.9	-32
			150.9	-18
Quercetin	17.94	300.7	150.9	-26
			178.8	-20
Kaempferol	18.58	284.7	116.8	-46
			93	-52
Apigenin	18.64	268.8	117	-44
			106.8	-34
Flavonoid glycosides				
Rutin			299.6	-46
(Quercetin 3-O-rutinoside)	11.99	608.7	270.9	-60
Hyperoside			299.7	-28
(Quercetin 3-O-galactoside)	12.80	462.7	254.7	-42
			284.8	-30
Luteolin-7-O-glucoside	12.87	446.8	132.9	-78
			299.7	-30
Isoquercetin	13.00	462.7	270.7	-44
			284.8	-38
Kaempferol – 3-O-rutinoside	13.31	592.7	226.7	-68
Isorhamnetin-3-O-rutinoside (Narcissoside)	13.52	622.8	314.9	-40
			298.8	-52
			226.8	-54
Astragalin	14.66	446.7	254.8	-40
			313.9	-30
Isorhamnetin-3-O-glucoside	14.76	476.8	270.9	-44
			299.7	-30
Quercitrin	14.83	446.7	270.7	-40
			267.7	-38
Apigenin 7-O-glucoside	14.91	430.7	116.9	-84
			270.8	-22
Naringenin 7-O-glucoside	15.12	432.7	118.9	-64
			284.8	-38
Tiliroside	17.39	592.8	254.7	-56

Table S2. Analytical parameters applied for LC-MS/MS quantitative method.

Compound	LOD [ng/mL]	LOQ [ng/mL]	R ²	Linearity range [ng/mL]
Phenolic acids				
Gallic acid	500	750	0.9989	750-15000
Homogentisic acid	250	450	0.9991	450-9000
α -Resorcylic acid	200	250	0.9994	750-38500
Protocatechuic acid	300	500	0.9988	1000-20000
4-Hydroxybenzoic acid	200	400	0.9993	500-15000
Gentisic acid	150	300	0.9990	500-15000
Vanilic acid	1000	1900	0.9983	1900-19000
Syringic acid	500	750	0.9991	750-17500
γ -Resorcylic acid	250	450	0.9995	450-9000
Caffeic acid	70	180	0.9994	180-4000
3-hydroxybenzoic acid	400	700	0.9996	1650-33000
4-Hydroxycinnamic acid (<i>p</i> -coumaric acid)	20	50	0.9995	100-3500
Sinapic acid	400	750	0.9989	750-25000
Ferulic acid	20	45	0.9994	75-12500
3,4-Dimethoxybenzoic acid (Veratric acid)	500	750	0.9995	750-36000
3-Hydroxycinnamic acid (<i>m</i> -Coumaric acid)	20	50	0.9993	100-15000
2-Hydroxycinnamic acid (<i>o</i> -Coumaric acid)	20	50	0.9996	100-3000
Salicylic acid	5	15	0.9992	15-1750
3,5-Dimethoxybenzoic acid	200	400	0.9992	600-12000
2,5- Dimethoxycinnamic acid	700	1700	0.9989	1700-34000
Flavonoid aglycones				
Catechin	25	50	0.9987	250-20000
Taxifolin	20	50	0.9986	50-5000
Myricetin	3	5	0.9992	10-3300
Luteolin	20	40	0.9980	40-4000
Eriodictyol	5	15	0.9982	15-5000
Quercetin	2	3	0.9985	30-3000
Kaempferol	20	40	0.9984	40-10000
Apigenin	3	4	0.9987	12-6000
Flavonoid glycosides				
Rutin (Quercetin 3- <i>O</i> -rutinoside)	120	300	0.9990	300-6000
Hyperoside (Quercetin 3- <i>O</i> -galactoside)	150	200	0.9988	500 - 15000
Luteolin-7- <i>O</i> -glucoside	50	80	0.9990	150-15000
Isoquercetin	150	275	0.9989	400 - 16000
Kaempferol – 3- <i>O</i> - rutinoside	60	125	0.9990	125-50000
Isorhamnetin-3- <i>O</i> - rutinoside (Narcissoside)	100	200	0.9993	400-16000
Astragalin	100	200	0.9987	400 - 12000

Isorhamnetin-3-O-glucoside	80	150	0.9996	250-10000
Quercitrin	75	150	0.9989	250-20000
Apigenin 7-O-glucoside	20	40	0.9987	100-5000
Naringenin 7-O-glucoside	100	175	0.9992	250-25000
Tiliroside	100	200	0.9989	300-20000
