

1 Supplementary information 2

2

No.	Time (min)	λ_{\max} (nm)	Negative ions (m/z)		Positive ions (m/z)		Identification	
			[M-H] ⁻	MS ²	[M+H] ⁺	MS ²		
1	4.28	270, 315	579	579→417 [M-H-glc] ⁻ , 255[M-H-2glc] ⁻	-	-	Glucoliquiritin (Liquiritigenin -7,4'-diglucoside) ^{38,39}	C ₂₇ H ₃₂ O ₁₄
2	4.48	272, 336	593	-	595	-	Vicenin-2 ^{40, 41}	C ₂₇ H ₃₀ O ₁₅
3	4.75	270, 336	563	-	565	-	Schaftoside ^{36, 43}	C ₂₆ H ₂₈ O ₁₄
4	4.93	270, 360	579	579→417 [M-H-glc] ⁻ , 255[M-H-2glc] ⁻	581	-	Glucosoliquiritin ³⁸	C ₂₇ H ₃₂ O ₁₄
5	5.00	225, 272, 335	577	577→485 [M-H-C ₆ H ₄ O] ⁻ , 473, 383	579	-	Isoviolanthin ^{36,44, 45}	C ₂₇ H ₃₀ O ₁₄
6	5.31	219, 275, 310	549	549→417 [M-H-api] ⁻ , 255 [M-H-api-glc] ⁻ , 135	573, 551, 419, 257,	551→257[M+H- api-glc] ⁺ , 137	Liquiritin apioside ^{37,44}	C ₂₆ H ₃₀ O ₁₃
7	5.45	219, 276, 310	417, 835	417→255 [M-H-glc] ⁻ , 135,119	837, 440, 419, 257	419→257 [M+H-glc] ⁺ , 239, 211, 163, 147, 137	Liquiritin* ^{38,44,43}	C ₂₁ H ₂₂ O ₉
8	5.53	190	723	-	340 [M+H], 679 [2M+H]	-	unassigned	
9	5.66	190	836	-	396, 792 [M+H]	-	unassigned	
10	5.78	287	949	-	453 [M+H]	-	unassigned	
11	5.98	288	433	433→271 [M-H-glc] ⁻ , 151	-	-	5-Hydroxylliquiritin ³⁷	C ₂₁ H ₂₂ O ₁₀
12	6.08	365	549	549→255 [M-H-api -glc] ⁻ , , 135	573, 551, 419, 257	551→257[M+H- api-glc] ⁺ , 239, 137, 115	Isoliquiritin apioside ^{36,38}	C ₂₆ H ₃₀ O ₁₃
13	6.29	280, 310	429+46	-	431	431→269 [M-H-glc] ⁺	Ononin ^{42,46}	C ₂₂ H ₂₂ O ₉
14	6.29	-	695	695→549 [M-H-C ₉ O ₂ H ₆] ⁻ , 531[M-H-C ₉ O ₂ H ₆ -H ₂ O] ⁻ , 399, 255	-	-	Licorice glycoside D ₂ /D ₁ ³⁸	C ₃₅ H ₃₆ O ₁₅
15	6.31	370	417, 835	417→255 [M-H-glc] ⁻ , 135,119	837, 419	419→257 [M+H-glc] ⁺ , 211, 147, 137	Isoliquiritin* ^{37,43}	C ₂₁ H ₂₂ O ₉

16	6.35	230, 325, 370	725	725→549 [M-H-C ₁₀ O ₃ H ₈] ⁻ , 531 [M-H-C ₁₀ O ₃ H ₈ -H ₂ O] ⁻ , 399[M-H- C ₁₀ O ₃ H ₈ -api-H ₂ O] ⁻ , 255 [M-H-C ₁₀ O ₃ H ₈ -api-glc] ⁻	-	-	Licorice glycoside A (C ₁ or C ₂) ⁴⁷	C ₃₆ H ₃₈ O ₁₆
17	6.59	278, 320	692	692→549[M-H-C ₉ NOH ₅] ⁻ , 255	694	-	Licorice glycoside E ³⁸	C ₃₅ H ₃₅ N O ₁₄
18	6.65	250	823	-	825	-	Licorice saponin J ₂ ^{37, 38, 46}	C ₄₂ H ₆₄ O ₁₆
19	6.78	250	984	-	986	-	Licoricesaponine A ₃ ⁴⁸	C ₄₈ H ₇₂ O ₂₁
20	6.99	236, 275, 315	255	255→135 (cleavage CO), 119	257	257→239, 211, 197, 165, 137, 119	Liquiritigenin* ³⁷	C ₁₅ H ₁₂ O ₄
21	7.29	-	983	-	985	-	Licorice saponin A ₃ ³⁸	C ₄₈ H ₇₂ O ₂₁
22	7.30	250	879	879→351 [2×C ₆ H ₈ O ₆ -H] ⁻	881	881→705 [M+H-C ₆ H ₈ O ₆] ⁺ , 511 [M+H-C ₆ H ₈ O ₆ - C ₆ H ₁₀ O ₇] ⁺	22β-Acetoxyglycyrrhizic acid ^{37, 49}	C ₄₄ H ₆₄ O ₁₈
23	7.35	250	837	-	839	839→487,469 [M+H-C ₆ H ₈ O ₆ - C ₆ H ₁₀ O ₇] ⁺	Yunganoside K ₂ ^{37,46}	C ₄₂ H ₆₂ O ₁₇
24	7.65	310, 370	269	-	271	-	Echinatin ^{47, 50}	C ₁₆ H ₁₄ O ₄
25	7.82	250	819	-	821	821→645 [M+H-C ₆ H ₈ O ₆] ⁺ , 451, 469	Licorice saponin E ₂ ³⁶	C ₄₂ H ₆₀ O ₁₆
26	7.96	250	837	837→351	839, 861	839→487,469	Licorice saponin G ₂ (24-hydroxyglycyrrhizin) ^{37,46}	C ₄₂ H ₆₂ O ₁₇
27	8.00	252	985	-	987	987→471	Yunganoside G ₁ ³⁸	C ₄₈ H ₇₄ O ₂₁
28	8.19	251	837	837→351	839	839→487,469	Isomer of Licorice saponin G ₂ ^{37,46}	C ₄₂ H ₆₂ O ₁₇
29	8.21	251	839	839→487, 469	841	841→489, 471	Yunganoside G ₂ ³⁸	C ₄₂ H ₆₄ O ₁₇
30	8.30	251	821	821→759 [M-H-CO ₂ -H ₂ O] ⁺ , 351 [2×C ₆ H ₈ O ₆ -H] ⁻ , 193	823, 453	823→647 [M+H-C ₆ H ₈ O ₆] ⁺ , 453 [M+H-C ₆ H ₈ O ₆ - C ₆ H ₁₀ O ₇] ⁺	Glycyrrhizin* ³⁷	C ₄₂ H ₆₂ O ₁₆
31	8.39	370	255	255→135, 119	257	257→137	Isoliquiritigenin* ³⁷	C ₁₅ H ₁₂ O ₄
32	8.45	251, 305	267	-	269, 291	-	Formononetin ^{37, 51, 52}	C ₁₆ H ₁₂ O ₄
33	8.62	252	821	821→759 [M-H-CO ₂ -H ₂ O] ⁺ , 351 [2×C ₆ H ₈ O ₆ -H] ⁻ , 193	823, 453	823→647 [M+H-glc] ⁺ , 453 [M+H-C ₆ H ₈ O ₆ - C ₆ H ₁₀ O ₇] ⁺	Glycyrrhizin isomer ³⁸	C ₄₂ H ₆₂ O ₁₆
34	8.69	-	955	-	957	-	Yunganoside A ₁ ³⁷	C ₄₈ H ₇₆ O ₁₉
35	9.00	230, 285	-	-	271	-	Medicarpin ^{53, 54}	C ₁₄ H ₁₄ O ₄

36	9.18	250	821	821→351 [2×C ₆ H ₈ O ₆ -H] ⁻	845, 823	-	Uralsaponin B ^{37,55}	C ₄₂ H ₆₂ O ₁₆
37	9.35	-	823	-	825	-	Licorice saponin J ₂ ³⁷	C ₄₂ H ₆₄ O ₁₆
38	9.38	350	367	367→309 [M-H-C ₄ H ₁₀] ⁻ , 297 [M-H-C ₅ H ₁₀] ⁻ , 281	369	369→313, 300, 283, 267, 165	Glycycomarin ³⁶	C ₂₁ H ₂₀ O ₆
39	9.45	283	354	-	356	-	Tetrahydropalmatine ⁴⁸	C ₂₁ H ₂₅ NO ₄
40	9.61	-	805	-	-	-	Licorice saponin C ₂ ³⁷	C ₄₂ H ₆₂ O ₁₅
41	9.69	-	353	353→323	-	-	Licochalcone D ⁵⁶	C ₂₁ H ₂₂ O ₅
42	9.72	262	351	351→335, 321, 295, 283	353	-	Licoisoflavone B ^{37, 57}	C ₂₀ H ₁₆ O ₆
43	9.82	262	353	353→297	-	-	Licoisoflavone A ⁵⁶	C ₂₁ H ₂₂ O ₅
44	9.98	250	483	-	485	-	Methylglycyrrhetate ⁴⁸	C ₃₁ H ₄₈ O ₄
45	10.06	228, 288	353	353→285	-	-	Gancaonin L ⁵⁶	C ₂₀ H ₁₈ O ₆
46	10.51	310, 370	337	337→281	339	-	Licochalcone C ³⁸	C ₂₁ H ₂₂ O ₄
47	10.55	280, 330	371	371→231, 109 [C ₆ O ₂ H ₅] ⁻	373	-	Licoleafol ³⁸	C ₂₁ H ₂₄ O ₆
48	10.58	-	365	-	367	-	Isoglycyrol ³⁶	C ₂₁ H ₁₈ O ₆
49	10.68	315, 368	337	337→305, 281 [M-H- C ₄ H ₈] ⁻	339	-	Licochalcone A ^{47, 58}	C ₂₁ H ₂₂ O ₄
50	10.90	262, 335	353	353→297	355	-	Licobenzofuran ⁵⁶	C ₂₁ H ₂₂ O ₅
51	10.94	265	351	351→321, 283, 263, 241	353	-	Gancaonin M ³⁷	C ₂₁ H ₂₀ O ₅
52	11.17	281	369	369→339, 295, 203, 177, 135	371	371→193, 181, 167, 137, 123	Glyasperin D ^{37, 58}	C ₂₂ H ₂₆ O ₅
53	11.25	-	335	-	337	337→293, 265, 153	Glabrone ³⁷	C ₂₀ H ₁₆ O ₅
54	11.46	285	423	-	425	425→369, 313, 221, 191, 165, 135	Licoricidin (Licorisoflavan B) ^{47, 44}	C ₂₆ H ₃₂ O ₅
55	11.65	295	423	-	425	425→313, 147, 135	Glisoflavanone ⁵⁹	C ₂₅ H ₂₈ O ₆
56	11.85	-	423	-	425	425→369, 191, 135	Kanzonol H ³⁸	C ₂₆ H ₃₂ O ₅
57	12.11	265	421	421→365, 351, 311	423	-	1-Methoxyficifolinol ^{37, 61}	C ₂₅ H ₂₆ O ₆
58	12.44	228, 292	421	421→365, 193 [C ₉ O ₅ H ₅] ⁻	423	-	Glyasperin A ^{37, 60}	C ₂₆ H ₃₀ O ₅
59	12.90	282	437	-	439	-	Licorisoflavan A ^{38, 61}	C ₂₇ H ₃₄ O ₅
60	12.96	250	469, 939	469→425 [M-H-CO ₂] ⁻	471, 941	-	18-β-Glycyrrhetic acid* ⁴⁴	C ₃₀ H ₄₆ O ₄

3 * The compounds has been identified using reference substance