

Supplementary Information

UHPLC-ESI-Q-TOF-MS/MS analysis, antioxidant activity combined fingerprints for quality consistency evaluation of Compound Liquorice Tablets

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Table S1 Identification of the chemical constituents in CLT by HPLC-Q-TOF-MS/MS.

No.	t _R (min)	Identification	λ _{max} (nm)	Formula	selected ions	Experimental (m/z)	Theoretical (m/z)	Error (ppm)	MS ² (m/z)	Source
1 ^a	1.942	Morphine	192sh, 209, 284	C ₁₇ H ₁₉ NO ₃	[M+H] ⁺	286.1440	286.1438	0.7	286 [M+H] ⁺ , 268 [M+H-H ₂ O] ⁺ , 252 [M+H-H ₂ O-CH ₄] ⁺ , 229 [M+H-C ₃ H ₇ N] ⁺ , 227 [M+H-C ₃ H ₇ N-H ₂] ⁺ , 211 [M+H-C ₃ H ₇ N-H ₂ O] ⁺ , 201 [M+H-C ₃ H ₇ N-CO] ⁺ , 187 [M+H-C ₃ H ₇ N-H ₂ O-C ₂ H ₂] ⁺ , 183 [M+H-C ₃ H ₇ N-CO-H ₂ O] ⁺ , 181 [M+H-C ₃ H ₇ N-CO-H ₂ O-H ₂] ⁺ , 165 [M+H-C ₃ H ₇ N-CO-H ₂ O-H ₂ O] ⁺ , 153 [M+H-C ₃ H ₇ N-CO-H ₂ O-CO-H ₂] ⁺	P
2 ^a	2.537	Codeine	215, 239sh, 284	C ₁₈ H ₂₁ NO ₃	[M+H] ⁺	300.1601	300.1594	2.3	300 [M+H] ⁺ , 282 [M+H-H ₂ O] ⁺ , 266 [M+H-H ₂ O-CH ₄] ⁺ , 243 [M+H-C ₃ H ₇ N] ⁺ , 241 [M+H-C ₃ H ₇ N-H ₂] ⁺ , 225 [M+H-C ₃ H ₇ N-H ₂ O] ⁺ , 215 [M+H-C ₃ H ₇ N-CO] ⁺ , 199 [M+H-C ₃ H ₇ N-H ₂ O-C ₂ H ₂] ⁺ , 183 [M+H-C ₃ H ₇ N-CO-CH ₄ O] ⁺ , 181 [M+H-C ₃ H ₇ N-CO-CH ₄ O-H ₂] ⁺ , 165 [M+H-C ₃ H ₇ N-CO-CH ₄ O-H ₂ O] ⁺ , 153 [M+H-C ₃ H ₇ N-CO-CH ₄ O-CO-H ₂] ⁺	P
3	3.010	Isoschaftoside	220, 273	C ₂₆ H ₂₈ O ₁₄	[M-H] ⁻	563.1399	563.1401	-0.4	563 [M-H] ⁻ , 473 [M-H-C ₃ H ₆ O ₃] ⁻ , 443 [M-H-C ₃ H ₆ O ₃ -CH ₂ O] ⁻ , 383 [M-H-C ₆ H ₁₂ O ₆] ⁻ , 353 [M-H-C ₃ H ₆ O ₃ -CH ₂ O-C ₃ H ₆ O ₃] ⁻ , 151 [M-H-ara-glu-C ₈ H ₈ O] ⁻	L
4	3.205	Isoviolanthin	227, 276	C ₂₆ H ₃₀ O ₁₄	[M-H] ⁻	577.1559	577.1557	0.3	577 [M-H] ⁻ , 457 [M-H-C ₃ H ₆ O ₃ -CH ₂ O] ⁻ , 383 [M-H-C ₇ H ₁₅ O ₆] ⁻ , 353 [M-H-C ₃ H ₆ O ₃ -CH ₂ O-C ₄ H ₈ O ₃] ⁻ , 135 [M-H-rha-glu-C ₈ H ₈ O] ⁻	L
5	3.351	Isoliquiritigenin-4'-apiosyl (1→2) glucoside	227, 271, 310sh	C ₂₆ H ₃₀ O ₁₃	[M-H] ⁻	549.1628	549.1608	3.6	549 [M-H] ⁻ , 429 [M-H-C ₇ H ₄ O ₂] ⁻ , 417 [M-H-api] ⁻ , 255 [M-H-api-glu] ⁻ , 135 [M-H-api-glu-C ₈ H ₈ O] ⁻ , 119 [M-H-api-glu-C ₇ H ₄ O ₃] ⁻	L
6 ^a	3.460	Liquiritigenin-4'-apiosyl (1→2) glucoside	231, 276, 310sh	C ₂₆ H ₃₀ O ₁₃	[M-H] ⁻	549.1635	549.1608	4.9	549 [M-H] ⁻ , 417 [M-H-api] ⁻ , 255 [M-H-api-glu] ⁻ , 135 [M-H-api-glu-C ₈ H ₈ O] ⁻ , 119 [M-H-api-glu-C ₇ H ₄ O ₄] ⁻	L
7 ^a	3.606	Liquiritin	219, 231, 275, 310	C ₂₁ H ₂₂ O ₉	[M-H] ⁻	417.1186	417.1186	0.0	417 [M-H] ⁻ , 255 [M-H-glu] ⁻ , 135 [M-H-glu-C ₈ H ₈ O] ⁻ , 119 [M-H-glu-C ₇ H ₄ O ₄] ⁻	L
8 ^a	4.499	Sodium benzoate	228, 272	C ₇ H ₅ O ₂ Na	[M-H] ⁻	121.0287	121.029	-2.5	121 [M-H] ⁻ , 77 [M-H-CO ₂] ⁻	B
9	4.642	Isoliquiritigenin-4'-apiosyl (1→2) glucoside	199, 230, 361	C ₂₆ H ₃₀ O ₁₃	[M-H] ⁻	549.1603	549.1608	-0.9	549 [M-H] ⁻ , 429 [M-H-C ₇ H ₄ O ₂] ⁻ , 417 [M-H-api] ⁻ , 255 [M-H-api-glu] ⁻ , 135 [M-H-api-glu-C ₈ H ₈ O] ⁻ , 119 [M-H-api-glu-C ₇ H ₄ O ₄] ⁻	L
10	4.878	Isoliquiritigenin-4'-apiosyl (1→2) glucoside	238, 286, 369	C ₂₆ H ₃₀ O ₁₃	[M-H] ⁻	549.1611	549.1608	0.5	549 [M-H] ⁻ , 429 [M-H-C ₇ H ₄ O ₂] ⁻ , 417 [M-H-api] ⁻ , 255 [M-H-api-glu] ⁻ , 135 [M-H-api-glu-C ₈ H ₈ O] ⁻ , 119 [M-H-api-glu-C ₇ H ₄ O ₃] ⁻	L

Table 2 (*continued*)

11*	5.131	Isoliquiritoside	200, 231, 361	C ₂₁ H ₃₂ O ₉	[M-H] ⁻	417.1178	417.1168	2.4	417 [M-H] ⁻ , 255 [M-H-glu] ⁻ , 148 [M-H-glu-C6H6O2] ⁻ , 135 [M-H-glu-C8H8O] ⁻ , 119 [M-H-glu-C7H4O3] ⁻	L
12	5.376	Neoisoliquiritin	235, 280, 323	C ₂₁ H ₃₂ O ₉	[M-H] ⁻	417.1176	417.1186	-2.4	417 [M-H] ⁻ , 255 [M-H-glu] ⁻ , 135 [M-H-glu-C8H8O] ⁻ , 119 [M-H-glu-C7H4O3] ⁻	L
13	5.584	4',7-Dihydroxyflavone	236, 285, 325	C ₁₅ H ₁₀ O ₄	[M-H] ⁻	253.0499	253.0501	-0.8	253 [M-H] ⁻ , 135 [M-H-C8H6O] ⁻ , 117 [M-H-C7H4O3] ⁻	L
14	5.933	Licochalcone B	236, 262, 355	C ₁₆ H ₁₄ O ₅	[M-H] ⁻	285.0755	285.0763	-2.8	285 [M-H] ⁻ , 270 [M-H-CH3] ⁻ , 177 [M-H-C6H5O-CH3] ⁻ , 150 [M-H-C7H6O2-CH3] ⁻ , 121 [M-H-C9H10O3] ⁻	L
15*	6.431	Liquiritigenin	219, 232, 274, 310	C ₁₅ H ₁₂ O ₄	[M-H] ⁻	255.0653	255.0657	-1.6	255 [M-H] ⁻ , 135 [M-H-C8H8O] ⁻ , 119 [M-H-C7H4O3] ⁻	L
16	7.665	Licorice saponin G2	252	C ₄₂ H ₆₂ O ₁₇	[M-H] ⁻	837.3914	837.3909	0.6	837 [M-H] ⁻ , 661 [M-H-GlcA] ⁻ , 485 [M-H-2GlcA] ⁻ , 351 [2GlcA-H] ⁻ , 193 [GlcA-H] ⁻	L
17	8.321	Yunganoside K2 or its isomer	248, 369	C ₄₂ H ₆₂ O ₁₇	[M-H] ⁻	837.3928	837.3909	2.3	837 [M-H] ⁻ , 661 [M-H-GlcA] ⁻ , 485 [M-H-2GlcA] ⁻ , 351 [2GlcA-H] ⁻ , 193 [GlcA-H] ⁻	L
18	8.401	Yunganoside K3 or its isomer	247, 368	C ₄₂ H ₆₂ O ₁₇	[M-H] ⁻	837.391	837.3909	0.1	837 [M-H] ⁻ , 661 [M-H-GlcA] ⁻ , 485 [M-H-2GlcA] ⁻ , 351 [2GlcA-2H2O-H] ⁻	L
19*	8.780	Glycyrrhizic acid	251	C ₄₂ H ₆₂ O ₁₆	[M-H] ⁻	821.3976	821.396	1.9	821 [M-H] ⁻ , 645 [M-H-GlcA] ⁻ , 469 [M-H-2GlcA] ⁻ , 351 [2GlcA-2H2O-H] ⁻ , 193 [GlcA-H] ⁻	L
20	9.582	Isomer of licorice saponin B2	252	C ₄₂ H ₆₄ O ₁₅	[M+H] ⁺	809.4348	809.4323	3.1	809 [M+H] ⁺ , 633 [M+H-GlcA] ⁺ , 439 [M+H-2GlcA-H2O] ⁺	L
21	9.750	Licorice saponin K2	254	C ₄₂ H ₆₂ O ₁₆	[M-H] ⁻	821.3966	821.396	0.7	821 [M-H] ⁻ , 645 [M-H-GlcA] ⁻ , 469 [M-H-2GlcA] ⁻ , 351 [2GlcA-2H2O-H] ⁻ , 193 [GlcA-H] ⁻	L
22	10.162	Licorice saponin H2	247	C ₄₂ H ₆₂ O ₁₆	[M-H] ⁻	821.3948	821.396	-1.5	821 [M-H] ⁻ , 645 [M-H-GlcA] ⁻ , 351 [2GlcA-2H2O-H] ⁻ , 193 [GlcA-H] ⁻	L
23*	10.410	Isoliquiritigenin	240, 305sh, 370	C ₁₅ H ₁₂ O ₄	[M-H] ⁻	255.0659	255.0657	0.8	255 [M-H] ⁻ , 135 [M-H-C8H8O] ⁻ , 119 [M-H-C7H4O3] ⁻	L
24	10.715	Formononetin	249, 305	C ₁₆ H ₁₂ O ₄	[M-H] ⁻	267.0657	267.0653	1.5	267 [M-H] ⁻ , 252 [M-H-CH3] ⁻ , 223 [M-H-CO2] ⁻ , 195 [M-H-CO2-CO] ⁻ , 135 [M-H-C9H9O] ⁻	L
25	11.374	Licorice saponin C2	249	C ₄₂ H ₆₂ O ₁₅	[M+H] ⁺	807.4183	807.4167	2.0	807 [M+H] ⁺ , 631 [M+H-GlcA] ⁺ , 437 [M+H-2GlcA-H2O] ⁺	L
26	11.589	Apioglycyrrhizin or araboglycyrrhizin	247	C ₄₁ H ₆₂ O ₁₄	[M-H] ⁻	777.4055	777.4061	-0.8	777 [M-H] ⁻ , 645 [M-H-Api] ⁻ , 469 [M-H-Api-GlcA] ⁻	L
27	11.704	Licorice saponin B2	253	C ₄₂ H ₆₄ O ₁₅	[M-H] ⁻	807.418	807.4167	1.6	807 [M-H] ⁻ , 631 [M-H-GlcA] ⁻ , 455 [M-H-2GlcA] ⁻ , 351 [2GlcA-2H2O-H] ⁻ , 193 [GlcA-H] ⁻	L
28	11.935	Apioglycyrrhizin or araboglycyrrhizin	253	C ₄₁ H ₆₂ O ₁₄	[M-H] ⁻	777.4063	777.4061	0.3	777 [M-H] ⁻ , 645 [M-H-Api] ⁻ , 469 [M-H-Api-GlcA] ⁻	L
29	12.891	Isomer of licorice saponin B2	255, 319	C ₄₂ H ₆₄ O ₁₅	[M-H] ⁻	807.415	807.4167	-2.1	807 [M-H] ⁻ , 351 [2GlcA-2H2O-H] ⁻	L
30	13.100	Licochalcone D	247, 254	C ₂₁ H ₂₂ O ₅	[M-H] ⁻	353.1384	353.1389	-1.4	353 [M-H] ⁻ , 338 [M-H-CH3] ⁻ , 177 [M-H-C11H13O-CH3] ⁻ , 150 [M-H-C12H14O2-CH3] ⁻ , 121 [M-H-C9H10O3-C5H8] ⁻	L
31	13.243	Glycyrrhetic acid glucuronide	253	C ₃₆ H ₃₄ O ₁₀	[M-H] ⁻	645.3659	645.3639	3.1	645 [M-H] ⁻ , 469 [M-H-GlcA] ⁻	L

Table 2 (*continued*)

32	13.968	Isomer of glycyrrhetic acid glucuronide	249, 349	C ₃₆ H ₅₄ O ₁₀	[M-H] ⁻	645.3661	645.3639	3.4	645 [M-H] ⁻ , 469 [M-H-GlcA] ⁻	L
33	14.507	Licochalcone C	255, 262, 369	C ₂₁ H ₂₂ O ₄	[M-H] ⁻	337.1433	337.1440	-2.1	337 [M-H] ⁻ , 305 [M-H-CH ₃ OH] ⁻ , 243 [M-H-C ₆ H ₅ O] ⁻ , 229 [M-H-C ₆ H ₅ O-CH ₃] ⁻ , 201 [M-H-C ₇ H ₅ O ₂ -CH ₃] ⁻ , 187 [M-H-C ₇ H ₅ O ₂ -CH ₃ -CH ₂] ⁻ , 146 [M-H-C ₇ H ₅ O ₂ -CH ₃ -CH ₂ -C ₃ H ₅] ⁻ , 120 [M-H-C ₁₄ H ₁₇ O ₂] ⁻	L
34	14.834	Licochalcone E	254, 355	C ₂₁ H ₂₂ O ₄	[M-H] ⁻	337.1435	337.1440	-1.5	337 [M-H] ⁻ , 305 [M-H-CH ₃ OH] ⁻ , 279 [M-H-C ₄ H ₁₁] ⁻ , 267 [M-H-C ₅ H ₁₀] ⁻ , 243 [M-H-C ₆ H ₅ O] ⁻ , 229 [M-H-C ₆ H ₅ O-CH ₃] ⁻ , 201 [M-H-C ₇ H ₅ O ₂ -CH ₃] ⁻ , 185 [M-H-C ₇ H ₅ O ₂ -CH ₃ -CH ₄] ⁻ , 159 [M-H-C ₇ H ₅ O ₂ -CH ₃ -CH ₄ -C ₂ H ₄] ⁻ , 146 [M-H-C ₇ H ₅ O ₂ -CH ₃ -CH ₄ -C ₃ H ₃] ⁻ , 120 [M-H-C ₁₄ H ₁₇ O ₂] ⁻ , 109 [M-H-C ₇ H ₅ O ₂ -CH ₃ -CH ₄ -C ₄ H ₄ -C ₄ H ₂] ⁻	L
35	15.002	Licochalcone A	253, 311, 376	C ₂₁ H ₂₂ O ₄	[M-H] ⁻	337.1436	337.1440	-1.2	337 [M-H] ⁻ , 305 [M-H-CH ₃ OH] ⁻ , 281 [M-H-C ₄ H ₈] ⁻ , 229 [M-H-C ₆ H ₅ O-CH ₃] ⁻ , 201 [M-H-C ₇ H ₅ O ₂ -CH ₃] ⁻ , 187 [M-H-C ₇ H ₅ O ₂ -CH ₃ -CH ₂] ⁻ , 120 [M-H-C ₁₄ H ₁₇ O ₂] ⁻	L
36	15.793	Glycyrrhetic acid hydroxylate	238, 276	C ₃₀ H ₄₆ O ₅	[M-H] ⁻	485.3252	485.3267	-3.1	485 [M-H] ⁻ , 441 [M-H-CO ₂] ⁻	L
37	16.859	Glabrol	280	C ₂₅ H ₂₈ O ₄	[M-H] ⁻	391.1900	391.1909	-2.3	391 [M-H] ⁻ , 203 [M-H-C ₁₃ H ₁₆ O] ⁻ , 187 [M-H-C ₁₂ H ₁₂ O ₃] ⁻	L
38	18.476	18- α -glycyrrhetic acid	253	C ₃₀ H ₄₆ O ₄	[M-H] ⁻	469.3341	469.3318	4.9	469 [M-H] ⁻ , 425 [M-H-CO ₂] ⁻	L
39	18.612	18- β -glycyrrhetic acid	253	C ₃₀ H ₄₆ O ₄	[M-H] ⁻	469.3321	469.3318	0.6	469 [M-H] ⁻ , 425 [M-H-CO ₂] ⁻	L
40	19.105	3-oxoglycyrrhetic acid	260	C ₃₀ H ₄₄ O ₄	[M-H] ⁻	467.3146	467.3161	-3.2	467 [M-H] ⁻ , 423 [M-H-CO ₂] ⁻	L
41	19.890	11-deoxoglycyrrhetic acid	252	C ₃₀ H ₄₈ O ₃	[M-H] ⁻	455.3511	455.3525	-3.1	455 [M-H] ⁻ , 397 [M-H-CO ₂ -CH ₂] ⁻	L

^a Further confirmed with reference compounds. P: Powdered Poppy Capsule Extractive; B: Sodium Benzoate; L: Licorice Root (Extract) Concrete.

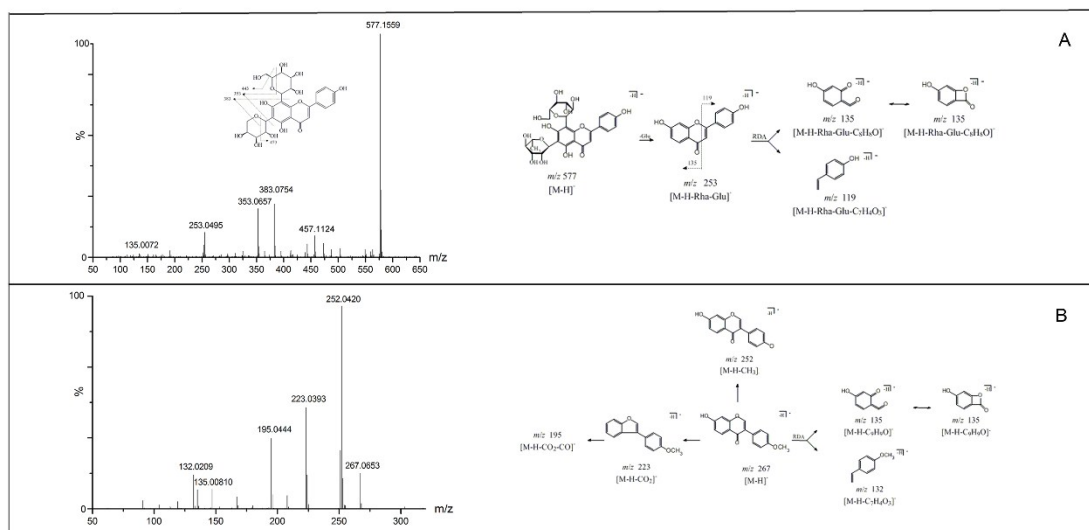


Figure S1 The ESI-MS/MS spectrum and proposed fragmentation pathways of isoviolanthin (A) and formononetin (B) in negative ion mode.