

Electronic Supplementary Information

Direct mass spectrometry fingerprinting: A simple and efficient method for pharmaceutical product analysis

Jiewei Deng,^{§^a} Chunlin Fan,^{§^b} Zhengjin Jiang,^c Wencai Ye,^{*^b} Yunyun Yang^{*^a}

^a *Guangdong Provincial Public Laboratory of Analysis and Testing Technology, China National Analytical Center Guangzhou, China. Fax: +86 20 8768 1384; Tel: +86 20 3765 6885 823; E-mail: yy_yang@vip.126.com*

^b *Institute of Traditional Chinese Medicine and Natural Products, Jinan University, Guangzhou, China. Fax: +86 20 8522 1559; Tel: +86 20 8522 0936; E-mail: chywc@yahoo.com.cn*

^c *Department of Pharmacy and Guangdong Province Key Laboratory of Pharmacodynamic Constituents of Traditional Chinese Medicine and New Drug Research, Jinan University, Guangzhou, China.*

§ These authors contributed equally to this work.

Table S-1

A summary of the tested samples

Samples no.	Brand	Type	Origins	Batch no.
A01	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	100203
A02	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	100401
A03	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	100611
A04	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	100706
A05	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	100801
A06	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	100804
A07	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	100810
A08	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	101103
A09	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	101112
A10	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	110307
A11	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	110508
A12	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	110601
A13	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	110609
A14	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	110705
A15	Wanglaoji	Sugarless	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	110719
B01	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1012003
B02	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1012006
B03	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1102106
B04	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1103201
B05	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1103207
B06	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1104120
B07	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1104145
B08	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1105012
B09	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1105141
B10	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1105147
B11	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1106061
B12	Wanglaoji	Sugar	Wanglaoji Pharmaceutical Co. Ltd., Guangdong, China	1107101
C01	Xiangxue	Sugar	Huazhou Chinese Medicine Co. Ltd., Guangdong, China	20100905
C02	Xiangxue	Sugar	Huazhou Chinese Medicine Co. Ltd., Guangdong, China	20110302
C03	Xiangxue	Sugar	Huazhou Chinese Medicine Co. Ltd., Guangdong, China	20110304
C04	Xiangxue	Sugar	Huazhou Chinese Medicine Co. Ltd., Guangdong, China	20110401
C05	Xiangxue	Sugar	Huazhou Chinese Medicine Co. Ltd., Guangdong, China	20110501
C06	Xiangxue	Sugar	Huazhou Chinese Medicine Co. Ltd., Guangdong, China	20110502
C07	Xiangxue	Sugar	Huazhou Chinese Medicine Co. Ltd., Guangdong, China	20110503
C08	Xiangxue	Sugar	Huazhou Chinese Medicine Co. Ltd., Guangdong, China	20110904
D01	Guanhe	Sugar	Luofushan Baihe Pharmaceutical Co. Ltd., Guangdong,	1011010
D02	Guanhe	Sugar	Luofushan Baihe Pharmaceutical Co. Ltd., Guangdong,	1106005
D03	Guanhe	Sugar	Luofushan Baihe Pharmaceutical Co. Ltd., Guangdong,	1107008
D04	Guanhe	Sugar	Luofushan Baihe Pharmaceutical Co. Ltd., Guangdong,	1107009
D05	Guanhe	Sugar	Luofushan Baihe Pharmaceutical Co. Ltd., Guangdong,	1107010
D06	Guanhe	Sugar	Luofushan Baihe Pharmaceutical Co. Ltd., Guangdong,	1108011
E01	Longma	Sugar	Yikang Pharmaceutical Co. Ltd., Guangdong, China	101110
E02	Longma	Sugar	Yikang Pharmaceutical Co. Ltd., Guangdong, China	110205
F01	Suyongkang	Sugar	Guoyitang Pharmaceutical Co. Ltd., Guangdong, China	100801
F02	Suyongkang	Sugar	Guoyitang Pharmaceutical Co. Ltd., Guangdong, China	100802

Table S-2

The major constituents detected in GLG by HPLC–ESI–TOF/IT–MS and direct ESI–TOF–MS in negative-ion mode.

Peaks of HPLC	t_R of HPLC (min)	Deduced molecular formula	Theoretical molecular weight	Experimental mass of deprotonated molecule by ESI–TOF–MS (m/z) / error (ppm)	Negative ESI–IT–MS (m/z) parent ion/ fragmental ions	Identification
1	1.57	C ₆ H ₁₂ O ₇	196.0538	195.0511 [M–H] [–] /–0.38	195/129, 177, 159, 99	gluconic acid ^{a)}
2	1.79	C ₇ H ₁₂ O ₆	192.0634	191.0566 [M–H] [–] /–2.70	191/85, 173, 127, 93, 111	quinic acid ^{a)}
3	2.23	C ₄ H ₆ O ₅	134.0215	133.0144 [M–H] [–] /–1.14	133/115	malic acid ^{a)}
4	4.01	C ₇ H ₁₂ O ₆	192.0634	191.0566 [M–H] [–] /–2.7	191/111, 173	citric acid ^{a)}
5	4.21	C ₅ H ₇ NO ₃	129.0426	128.0354 [M–H] [–] /–0.88	128/84, 99	–
6	4.74	C ₇ H ₁₁ NO ₅	189.0637	188.0561 [M–H] [–] /–2.04	188/170,128	–
7	5.41	C ₈ H ₁₀ O ₇	218.0427	217.0349 [M–H] [–] /2.23	217/199, 155	–
8	6.05	C ₇ H ₈ O ₆	188.0321	187.0251 [M–H] [–] /–1.69	187/169, 127, 142	–
9	6.31	C ₆ H ₁₀ O ₅	162.0528	161.0451 [M–H] [–] /2.51	161/99	–
10	7.63	C ₈ H ₁₁ NO ₅	201.0637	200.0568 [M–H] [–] /–1.66	200/156	–
11	8.39	C ₇ H ₆ O ₅	170.0215	169.0140 [M–H] [–] /1.46	169/125	gallic acid ^{a)}
12	8.68	C ₈ H ₆ O ₆	198.0164	197.0088 [M–H] [–] /1.88	197/153,109	–
13	9.93	C ₉ H ₁₄ O ₅	202.0841	201.0769 [M–H] [–] /–0.11	201/139, 109, 127, 159	–
14	10.35	C ₁₂ H ₂₂ O ₉	310.1264	309.1187 [M–H] [–] /1.18	309/263, 179	–
15	12.22	C ₇ H ₁₀ O ₆	190.0477	189.0399 [M–H] [–] /2.64	189/171	–
16	12.54	C ₂₃ H ₁₇ O	310.1264	309.1294 [M–H] [–] /–0.95	309/263, 179	–
17	12.96	C ₂₃ H ₁₇ O	310.1264	309.1297 [M–H] [–] /–1.92	309/263, 179	–
18	13.23	C ₂₃ H ₁₇ O	310.1264	309.1294 [M–H] [–] /–0.95	309/263, 179	–
19	13.67	C ₂₃ H ₁₇ O	310.1264	309.1287 [M–H] [–] /–0.68	309/263, 179	–
20	14.58	C ₇ H ₈ O ₆	188.0321	187.0249 [M–H] [–] /–0.63	187/143, 99, 125	–
21	15.42	C ₇ H ₆ O ₄	154.0266	153.1958 [M–H] [–] /–1.62	153/109	protocatechuic acid ^{a)}
22	15.73	C ₉ H ₁₄ O ₈	250.0689	249.0613 [M–H] [–] /1.00	249/231, 217, 199, 155	–
23	16.72	C ₁₅ H ₁₈ O ₉	342.0951	341.0880 [M–H] [–] /–0.57	341/203, 323	–
24	16.89	C ₉ H ₁₂ O ₇	232.0583	231.0501 [M–H] [–] /–0.74	231/185, 203,199,155	–
25	17.89	C ₁₅ H ₁₈ O ₉	342.0951	341.0877 [M–H] [–] /0.31	341/203, 323	–
26	18.48	C ₁₅ H ₁₈ O ₉	342.0951	341.0876 [M–H] [–] /0.60	341/203, 323	–
27	20.03	C ₇ H ₆ O ₃	138.0317	137.0243 [M–H] [–] /0.86	137/109, 91	–
28	20.19	C ₁₅ H ₁₈ O ₉	342.0951	341.0874 [M–H] [–] /1.19	341/203, 179, 233, 281, 323	–
29	20.55	C ₁₆ H ₁₈ O ₉	354.0951	353.0884 [M–H] [–] /–1.68	353/191, 179, 135	5- <i>O</i> -caffeoylquinic acid ^{a)}
30	20.84	C ₇ H ₆ O ₃	138.0317	137.0242 [M–H] [–] /1.59	137/93	4-hydroxybenzoic acid ^{a)}
31	22.03	C ₁₄ H ₁₆ O ₈	312.0845	311.0771 [M–H] [–] /0.61	311/191	–
32	22.21	C ₁₀ H ₁₆ O ₈	264.0845	263.0768 [M–H] [–] /1.67	263/231	abscisic acid
33	22.62	C ₁₄ H ₁₆ O ₈	312.0845	311.0768 [M–H] [–] /1.35	311/173, 137	–
34	23.03	C ₁₅ H ₁₈ O ₉	342.0951	341.0877 [M–H] [–] /0.31	341/281, 251, 179, 321, 221	–
35	24.63	C ₁₅ H ₁₈ O ₉	342.0951	341.0873 [M–H] [–] /1.48	341/281, 251, 179, 321, 221	–
36	25.35	C ₁₆ H ₁₈ O ₉	354.0951	353.0882 [M–H] [–] /–1.12	353/191, 179, 135	3- <i>O</i> -caffeoylquinic acid ^{a)}
37	26.11	C ₉ H ₈ O ₄	180.0423	179.0347 [M–H] [–] /1.58	179/135	caffeic acid ^{a)}
38	26.28	C ₁₆ H ₁₈ O ₉	354.0951	353.0882 [M–H] [–] /–1.12	353/173, 179, 191	4- <i>O</i> -caffeoylquinic acid ^{a)}
39	27.02	C ₁₃ H ₈ O ₈	292.0219	291.0148 [M–H] [–] /–0.61	291/247	–
40	28.12	C ₁₅ H ₁₈ O ₈	326.1002	325.0926 [M–H] [–] /1.05	325/265, 237	–
41	28.57	C ₁₈ H ₂₈ O ₉	388.1733	387.1665 [M–H] [–] /–1.14	387/207, 163, 369	–
42	29.33	C ₂₇ H ₂₂ O ₁₈	634.0806	633.0741 [M–H] [–] /–1.20	633/301, 463, 275	–
43	30.36	C ₂₇ H ₃₀ O ₁₅	594.1585	593.1501 [M–H] [–] /1.84	593/473, 503, 353, 575, 503	multiflorin
44	30.71	C ₁₂ H ₁₈ O ₄	226.1205	225.1128 [M–H] [–] /1.91	255/181, 207, 147, 165,135	–
45	31.71	C ₉ H ₈ O ₃	164.0473	163.0399 [M–H] [–] /0.90	163/119	p-coumaric acid ^{a)}
46	31.98	C ₁₂ H ₈ O ₆	248.0321	247.0245 [M–H] [–] /1.14	247/191, 219, 203	–
47	32.67	C ₂₆ H ₂₈ O ₁₄	564.1479	563.1396 [M–H] [–] /1.08	563/443, 473, 383, 353, 545	–

48	33.93	C ₂₁ H ₂₀ O ₁₁	448.1006	447.0937 [M-H] ⁻ /-0.93	447/357, 327, 429	isoorientin
49	35.19	C ₂₂ H ₂₆ O ₁₁	466.1475	465.1408 [M-H] ⁻ /-1.22	465/285, 303, 137, 241	-
50	36.84	C ₂₆ H ₂₈ O ₁₄	564.1479	563.1397 [M-H] ⁻ //1.65	563/473, 443, 353, 383, 455	-
51	37.81	C ₂₃ H ₂₈ O ₁₂	496.1581	495.1510 [M-H] ⁻ /-0.38	495/281, 451, 375, 357, 151	-
52	38.23	C ₂₃ H ₂₈ O ₁₂	496.1581	431.0993 [M-H] ⁻ /-2.16	431/311, 341, 413	apigenin-8-C-glucoside ^{a)}
53	39.43	C ₂₁ H ₂₀ O ₁₀	432.1056	431.0989 [M-H] ⁻ /-1.23	431/311, 341, 413	-
54	40.23	C ₂₅ H ₃₀ O ₁₃	538.1686	537.1620 [M-H] ⁻ /-1.09	537/493, 161, 323	-
55	41.18	C ₂₁ H ₂₀ O ₁₂	464.0955	463.0877 [M-H] ⁻ /1.08	463/301	qercetin-3-O-β-D-glucoside ^{a)}
56	43.84	C ₉ H ₁₂ O ₄	184.0736	183.0666 [M-H] ⁻ /-1.73	183/137	-
57	45.55	C ₉ H ₁₆ O ₄	188.1049	187.0973 [M-H] ⁻ /1.71	187/125	-
58	46.57	C ₂₅ H ₂₄ O ₁₂	516.1268	515.1201 [M-H] ⁻ /-1.17	515/353	4,5-di-O- caffeoylquinic acid ^{a)}
59	46.95	C ₂₆ H ₂₈ O ₁₅	580.1428	579.1364 [M-H] ⁻ /-1.48	579/417, 541	-
60	48.45	C ₂₅ H ₂₄ O ₁₂	516.1268	515.1202 [M-H] ⁻ /-1.36	515/353	3,5-di-O- caffeoylquinic acid ^{a)}
61	54.87	C ₂₅ H ₂₄ O ₁₂	516.1268	515.1199 [M-H] ⁻ /-0.78	515/353	3,4-di-O- caffeoylquinic acid ^{a)}
62	55.81	C ₃₆ H ₃₄ O ₁₆	722.1847	721.1782 [M-H] ⁻ /-1.08	721/541	-
63	57.41	C ₂₁ H ₁₈ O ₁₂	462.0798	461.0736 [M-H] ⁻ /-2.19	461/285	-
64	59.69	C ₂₁ H ₂₀ O ₁₀	432.1056	431.0977 [M-H] ⁻ /1.55	431/269	vitexin/isovitexin
65	62.33	C ₂₅ H ₃₀ O ₁₂	522.1737	521.1672 [M-H] ⁻ /-1.36	521/315, 163, 297, 357	-
66	63.38	C ₃₆ H ₅₈ O ₁₁	666.3979	711.3965[M+HCOO] ⁻ /-0.61	711/503	-
67	66.18	C ₁₅ H ₁₀ O ₆	286.0477	285.0410 [M-H] ⁻ /-1.88	285/241, 199, 175, 151	-
68	69.04	C ₃₆ H ₅₈ O ₁₁	666.3979	711.3963 [M+HCOO] ⁻ /-0.29	711/503	-
69	77.51	C ₃₆ H ₅₈ O ₁₁	666.3979	711.3964 [M+HCOO] ⁻ /-0.43	711/503	-
70	84.35	C ₃₆ H ₅₈ O ₁₀	650.4030	695.4016 [M+HCOO] ⁻ /-0.58	695/487	-
71	85.06	C ₃₆ H ₅₈ O ₁₀	650.4030	695.4019 [M+HCOO] ⁻ /-1.01	695/487	-
72	85.46	C ₃₆ H ₅₆ O ₁₄ S	744.3391	743.3336 [M-H] ⁻ /-2.42	743/663, 255	-
73	85.98	C ₄₂ H ₆₆ O ₁₈ S	890.3970	889.3902 [M-H] ⁻ /-0.55	889/809, 727, 647, 255	-
74	86.42	C ₃₆ H ₅₈ O ₁₀	650.4030	695.4020 [M+HCOO] ⁻ /-1.15	695/487	-
75	87.62	C ₄₁ H ₆₆ O ₁₆ S	846.4072	845.4015 [M-H] ⁻ /-1.91	845/683	-
76	88.31	C ₁₈ H ₃₄ O ₅	330.2406	329.2339 [M-H] ⁻ /-1.76	329/311, 293, 229, 211	tricin
77	91.77	C ₄₁ H ₆₆ O ₁₆ S	846.4072	845.4013 [M-H] ⁻ /-1.68	845/683	-
78	94.38	C ₃₆ H ₅₆ O ₁₄ S	744.3391	743.3330 [M-H] ⁻ /-1.61	743/663, 255	-
79	94.56	C ₄₂ H ₆₄ O ₁₇ S	872.3864	871.3808 [M-H] ⁻ /-1.90	871/791, 709, 629, 255	-
80	94.87	C ₄₂ H ₆₄ O ₁₈ S	888.3813	887.3758 [M-H] ⁻ /-1.96	887/725, 827, 665	-
81	95.19	C ₄₂ H ₆₄ O ₁₇ S	872.3864	871.3804 [M-H] ⁻ /-1.44	871/791, 709, 629, 255	-
82	96.57	C ₃₄ H ₆₈ O ₂₀ S	828.4025	827.3935 [M-H] ⁻ /2.04	827/665, 621	-
83	99.82	C ₃₇ H ₅₈ O ₁₂ S	726.3649	725.3589 [M-H] ⁻ /-1.76	725/645, 255, 681,549, 601	-
84	101.93	C ₃₆ H ₅₆ O ₁₃ S	728.3442	727.3381 [M-H] ⁻ /-1.67	727/647, 255	-
85	102.76	C ₃₅ H ₅₆ O ₁₁ S	684.3543	683.3481 [M-H] ⁻ /-1.52	683/639, 603, 569, 513, 433	-
86	102.86	C ₃₆ H ₅₆ O ₁₃ S	728.3442	727.3378 [M-H] ⁻ /-1.25	727/647, 255	-
87	102.93	C ₃₅ H ₅₆ O ₁₁ S	684.3543	683.3478 [M-H] ⁻ /-1.09	683/639, 603, 569, 513, 433	-
88	103.91	C ₃₆ H ₅₆ O ₁₃ S	728.3442	727.3375 [M-H] ⁻ /-0.84	727/647, 255, 551	-
89	104.78	C ₃₄ H ₆₈ O ₂₀ S	828.4025	827.3942 [M-H] ⁻ /1.19	827/783	-
90	107.21	C ₃₅ H ₅₆ O ₁₁ S	684.3543	683.3485 [M-H] ⁻ /-2.11	683/639, 603, 569, 513, 433	-
91	109.84	C ₃₆ H ₅₄ O ₁₂ S	710.3336	709.3274 [M-H] ⁻ /-1.52	709/629, 255, 665	-
92	110.95	C ₃₆ H ₅₄ O ₁₂ S	710.3336	709.3271 [M-H] ⁻ /-1.10	709/629, 255, 665	-
93	111.56	C ₃₆ H ₅₄ O ₁₂ S	710.3336	709.3273 [M-H] ⁻ /-1.38	709/629, 255, 665	-
94	112.19	C ₃₇ H ₅₈ O ₁₂ S	726.3649	725.3586 [M-H] ⁻ /-1.35	725/665, 621, 647, 585	-
95	113.31	C ₃₅ H ₅₄ O ₁₀ S	666.3438	665.3378 [M-H] ⁻ /-1.69	665/621	-
96	114.13	C ₃₆ H ₅₆ O ₁₂ S	712.3518	711.3432 [M-H] ⁻ /-1.72	711/631, 255, 667	-
97	114.91	C ₃₆ H ₅₄ O ₁₂ S	710.3336	709.3280 [M-H] ⁻ /-2.36	709/629, 255, 665	-
98	117.81	C ₃₉ H ₄₀ O ₃	556.2977	555.2898 [M-H] ⁻ /1.2	555/225, 299, 255, 165	-

^{a)} The identity was confirmed by comparing its *t_R*, UV spectra, ESI-TOF-MS and ESI-IT-MS data with those of the reference substances.