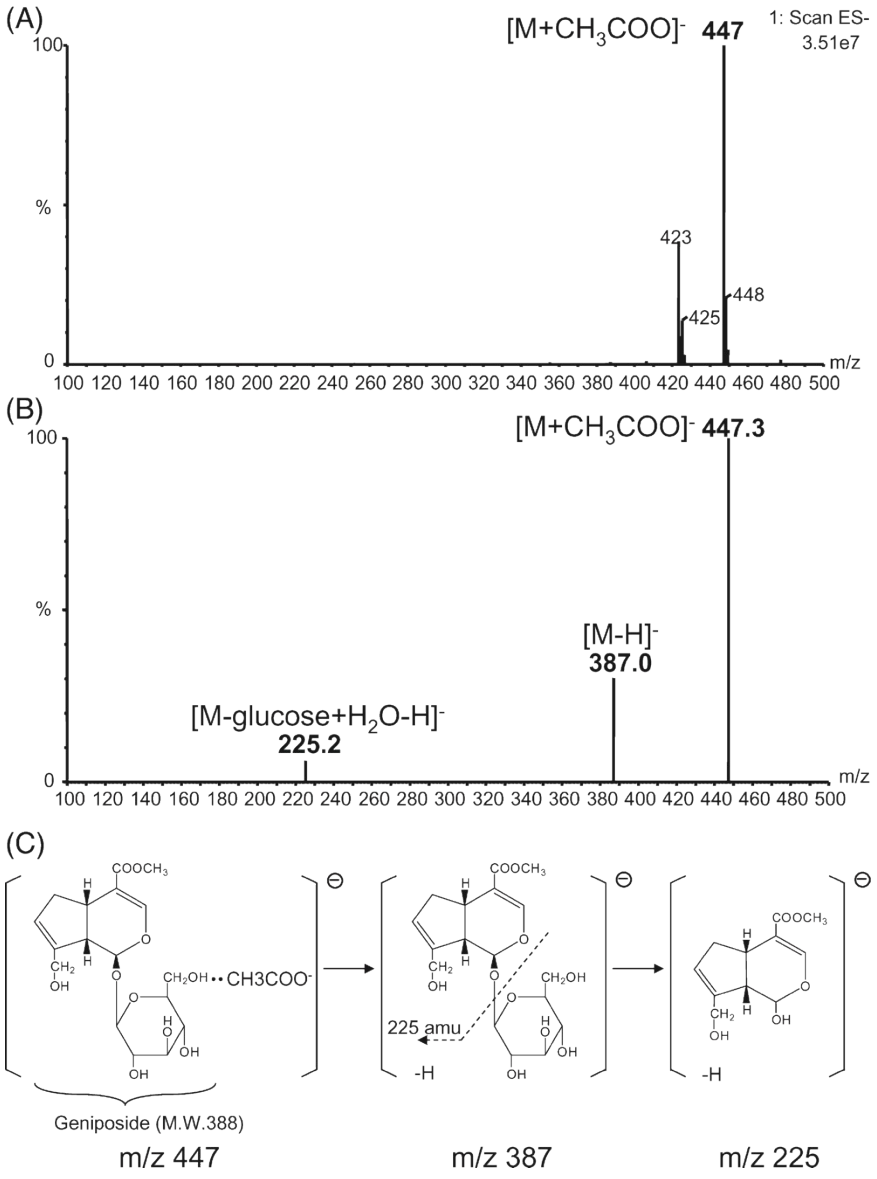
Electronic Supplementary Material (ESI) for Analytical Methods.

MS^2 spectrum of Geniposide in reference



MS^2 fragmentation ions of Mussaenosidic acid in reference

Table 1 Chemical constituents identified in an extract of YCHD by HPLC-Q/TOF-MS/MS in negative ion mode

Peak no.	t_R (min)	Molecular formula	Theoretical $[M-H]^-$	Measured $[M-H]^-$	Error[a] (ppm)	Characteristic MS/MS fragmentation ions (% base peak) (*m/z*)	Proposed compounds
1	0.803	$C_{12}H_{22}O_{11}$	377.0856[b]	377.0857	0.27	341 (100), 215 (11.1), 179 (20.5), 119 (18.1), 89 (49.6), 59 (34.1)	Gentiobiose
2	0.972	$C_5H_7NO_3$	128.0353	128.0364	8.59	101.0257 (17.8), 88.0426 (54.1), 85.0308 (100)	Pyroglutamic acid
3	1.309	$C_7H_6O_5$	169.0137	169.0136	−0.59	125.0238 (100), 107.0133 (2.2), 79.0193 (12.2)	Gallic acid
4	1.646	$C_{19}H_{26}O_{15}$	493.1199	493.1189	−2.03	313.0564 (63.2), 271.0455 (66.2), 211.0240 (21.9), 169.0137 (100), 125.0237 (30.7)	6-*O*-Galloylsucrose
5	1.815	$C_{16}H_{22}O_{10}$	373.1140	373.1146	1.61	211.0612 (27.4), 193.0502 (5.8), 167.0712 (13.6), 149.0604 (78.9), 123.0453 (100)	Geniposidic acid[c]
6	2.068	$C_{13}H_{16}O_9$	315.0722	315.0722	0.00	153.0190 (32.4), 152.0115 (47.9), 109.0291 (34.4), 108.0227 (100)	Protocatechuic acid-3-glucoside
7	2.237	$C_{16}H_{26}O_9$	397.1271[b]	397.1265	−1.51	361.1496 (100), 317.1589 (1.9), 181.0862 (31.7), 137.0964 (11.2), 89.0245 (12.4), 59.0144 (20.6)	Villosolside
8	2.405	$C_{16}H_{18}O_9$	353.0878	353.0878	0.00	191.0538 (100), 85.0284 (7.9)	1-CQA
9	2.405	$C_{16}H_{24}O_{11}$	391.1246	391.1250	1.02	229.0713 (24.5), 211.0611 (17.1), 185.0823 (75.2), 167.0712 (93.1), 149.0616 (100), 141.0549 (42.5), 123.0449 (57.9)	Shanzhiside
10	3.401	$C_{16}H_{18}O_9$	353.0878	353.0878	0.00	191.0538 (100), 179.0326 (51.1), 135.0429 (62.5)	Neochlorogenic acid (5-COA)
11	3.67	$C_{17}H_{24}O_{11}$	439.1013[b]	439.1007	−1.37	403.1247 (8.9), 241.0719 (100), 223.0610 (12.3), 139.0397 (43.7), 101.0239 (31.8)	Scandoside methyl ester
12	3.754	$C_{16}H_{26}O_8$	381.1322[b]	381.1319	−0.79	345.1548 (50.6), 179.0547 (15.9), 165.0913 (100), 121.1017 (12.9), 119.0345 (19.0), 89.0245 (56.9)	Picrocrocinic acid
13	3.754	$C_{16}H_{22}O_{11}$	389.1089	389.1088	−0.26	227.0566 (24.3), 209.0450 (48.9), 183.0667 (51.1), 165.0551 (100), 139.0395 (53.9)	Deacetylasperulosidic acid
14	4.344	$C_{16}H_{24}O_9$	395.1114[b]	395.1111	−0.76	359.1346 (95.4), 197.0813 (100), 125.0612 (62.4), 107.0492 (28.9)	Ixoroside
15	4.85	$C_{17}H_{26}O_{11}$	405.1402	405.1395	−1.73	225.0766 (29.3), 179.0566 (57.6), 141.0555 (82.2), 123.0447 (48.5), 119.0349 (30.4), 101.0239 (100)	Shanzhiside methyl ester
16	4.934	$C_{17}H_{24}O_{11}$	439.1013[b]	439.1015	0.46	403.1249 (30.5), 241.0714 (100), 223.0615 (14.1), 139.0399 (87.3), 121.0299 (46.8), 101.0242 (24.1)	Gardenoside
17	5.778	$C_{17}H_{24}O_{11}$	439.1013[b]	439.1005	−1.82	403.1246 (12.6), 241.0710 (100), 223.0617 (40.8), 139.0394 (71.9), 101.0248 (52.6)	Deacetylasperulosidic acid methyl ester
18	6.368	$C_{15}H_{14}O_6$	289.0718	289.0710	−2.77	245.0816 (45.1), 203.0706 (35.3), 137.0242 (30.25), 123.0450 (78.6), 109.0294 (100)	Catechin
19	6.436	$C_{16}H_{18}O_9$	353.0878	353.0878	0.00	191.0547 (100), 85.0294 (6.1)	Chlorogenic acid (3-CQA)[c]
20	6.874	$C_9H_8O_4$	179.0350	179.0350	0.00	135.0437 (100), 89.0395 (5.7)	Caffeic acid[c]
21	7.632	$C_{16}H_{18}O_9$	353.0878	353.0878	0.00	191.0535 (60.7), 179.0324 (70.3), 173.0426 (100), 135.0431 (80.9), 93.0335 (27.6)	Cryptochlorogenic acid (4-CQA)
22	7.885	$C_{16}H_{24}O_{10}$	375.1297	375.1303	1.60	213.0764 (39.1), 195.0660 (38.4), 169.0877 (47.9), 151.0770 (95.2), 125.0605 (80.7), 107.0510 (100)	Mussaenosidic acid
23	8.307	$C_{23}H_{34}O_{15}$	585.1592[b]	585.1584	−1.37	549.1815 (12.3), 225.0769 (69.3), 207.0657 (13.4), 123.0449 (100), 101.0243 (64.9)	Genipin gentiobioside[c]
24	8.56	$C_8H_8O_2$	135.0452	135.0453	0.74	120.0244 (5.5), 108.0206 (10.8), 92.0279 (100)	4′-Hydroxyacetophenone
25	9.487	$C_{17}H_{24}O_{10}$	423.1063[b]	423.1070	1.65	387.1282 (5.5), 225.0762 (100), 207.0653 (13.5), 123.0447 (85.3), 101.0243 (74.5)	Geniposide[c]

MS^2 fragmentation ions of Jasminoside B in reference

Table 2 Chromatographic and mass spectral data of the fifty-five compounds in Zhi-Zi-Da-Huang decoction[a]

No.	t_R (min)	Formula	Quasi-molecular (+/−)	ppm (+/−)	UV (nm)	Fragment ions (+/−)	Assignment
1	12.794	$C_{16}H_{22}O_{11}$	— 389.1097	— −1.96	225	— 227, 209, 183, 165, 147, 139	Deacetylasperulosidic acid
2	13.345	$C_{16}H_{22}O_{11}$	— 389.1104	— −3.76	225	— 227, 209, 183, 165, 147, 139, 119, 191	Scandoside
3	16.629	$C_{16}H_{24}O_{11}$	415.1224 391.1228	−3.36 4.55	235	— 229, 211, 192, 185, 167, 149	Caryoptosidic acid
4	16.979	$C_7H_6O_4$	— 153.0197	— −2.39	220, 255	— 153, 134, 124, 109	Gentisic acid
5	16.996	$C_{16}H_{24}O_{11}$	415.1222 391.1232	−2.85 3.53	235	253, 235 229, 211, 193, 185, 167, 149, 127, 119	Shanzhiside
6	17.229	$C_{17}H_{24}O_{11}$	427.1231 463.1438	−3.51 4.12	240	— 403, 241, 223, 193	6α-Hydroxygeniposide
8	19.280	$C_{16}H_{26}O_8$	369.1526 345.1536	−1.77 4.31	230, 280	324, 207, 203, 185, 153 179, 165, 161, 121, 119, 101, 89	Picrocrocinic acid
9	19.330	$C_{21}H_{24}O_{11}$	475.1231 451.1224	−4.46 4.83	—	427, 367, 343, 271, 253, 235 289, 271, 245, 227, 203, 179	Catechin-*O*-glucoside
10	20.964	$C_{17}H_{24}O_{11}$	427.1204 463.1436	1.69 4.56	240	409, 265, 233, 203 403, 241, 223, 193, 179, 127, 101	6β-Hydroxygeniposide
11	22.231	$C_{16}H_{26}O_8$	369.1533 405.1751	−3.79 3.74	240	— 345, 327, 183, 165, 161, 119, 113, 101	Jasminoside B
12	22.298	$C_{15}H_{16}O_9$	341.0857 339.0723	2.97 −0.42	—	179, 151, 135, 123, 107 321, 177	Esculin
13	23.315	$C_{15}H_{14}O_6$	291.0860 289.0719	1.08 −0.48	280	273, 207, 165, 147, 139, 123 271, 245, 203, 187, 151, 109	Catechin
14	23.348	$C_{16}H_{18}O_9$	355.1033 353.0861	−2.66 4.82	234, 280, 330	163, 145, 135, 117 221, 205, 191, 179, 173, 161, 134,	3-Caffeoylquinic acid
15	24.266	$C_{10}H_{16}O_3$	— 243.1241	— −1.24	245	— 183, 165, 153, 139, 59	Jasminodiol
17	27.717	$C_{21}H_{26}O_{13}$	487.1456 485.1320	−2.02 −3.98	228, 255, 290	355, 341, 193, 179 177	5,7-Dihydroxychromone-7-rutinoside
19	29.217	$C_{16}H_{18}O_9$	— 353.0863	— 4.25	234, 280, 330	— 191, 179, 173, 135	4-Caffeoylquinic acid
20	29.984	$C_{17}H_{22}O_{10}$	409.1118 385.1121	−3.32 4.97	240, 285, 330	247, 185 223, 205, 190, 175	Sinapylglucoside
21	30.451	$C_{21}H_{26}O_{13}$	487.1437 485.1320	1.89 −3.98	228, 255, 290	341, 179, 147, 129 219, 177	5,7-Dihydroxychromone - 7-neohesperidoside
22	30.818	$C_{16}H_{24}O_{10}$	399.1262 375.1315	−0.08 −4.85	243	355, 237, 219 357, 315, 227, 213, 195, 169, 161, 151	Dihydrocornic acid
23	32.185	$C_{16}H_{26}O_8$	369.1533 405.1780	−3.79 −3.40	241	— 345, 327, 315, 165, 161, 113, 101	Jasminoside G
25	33.436	$C_{15}H_{14}O_6$	291.087 289.0729	−2.36 −3.92	280	273, 165, 147, 139, 123 271, 245, 227, 203, 179, 151, 125, 109	Epicatechin
26	36.654	$C_{16}H_{26}O_8$	369.1514 345.1538	1.70 4.89	238	— 301, 285, 183, 179, 165, 161, 149	Jasminoside D
27	37.271	$C_{16}H_{26}O_7$	331.1762 389.1798	−3.24 4.89	245	169, 151, 139, 123, 109, 85 329, 224, 179, 161, 119, 113, 101, 89	Jasminoside A/E
28	38.504	$C_{16}H_{26}O_7$	331.1758 389.1802	−2.03 3.86	244	169, 151, 139, 123, 109, 85 227, 179, 161, 131, 119, 113, 101	Jasminoside A/E

MS^2 fragmentation ions of 6α-hydroxygeniposide in reference

Table 1. Characterization of the Components of the *P. scandens* decoction by HPLC/DAD/ESI-MS^n

Peak	t_R (min)	$[M-H]^-$ (*m/z*)	HPLC/ESI-MS^n	Identification
1	15.1	445	MS^2 [445]: 283, 191, 147; MS^3 [147]: 119	Paederosid
2	13.6	463	MS^2 [463]: 415, 371, 283; MS^3 [415]: 371, 191; MS^4 [191]: 147, 119	Paederosidic acid
3	15.7	477	MS^2 [477]: 429, 385, 353; MS^3 [385]: 353, 325	Paederosidic acid methyl ester
4	10.8	403	MS^2 [403]: 241; MS^3 [241]: 223, 193; MS^4 [223]: 205	6-Hydroxy geniposide
5	12.8	413	MS^2 [413]: 251, 191, 147; MS^3 [147]: 79	Asperuloside
6	9.0	371	MS^2 [371]: 209, 165; MS^3 [165]: 147, 135	Deacetyl asperuloside