<*Phyton-International Journal of Experimental Botany*>

Supporting Information

Rapid profiling and characterization of the multicomponents from the root and rhizome of *Salvia miltiorrhiza* by ultra-high performance liquid chromatography/ion mobility-quadrupole time-of-flight mass spectrometry in combination with computational peak annotation workflows

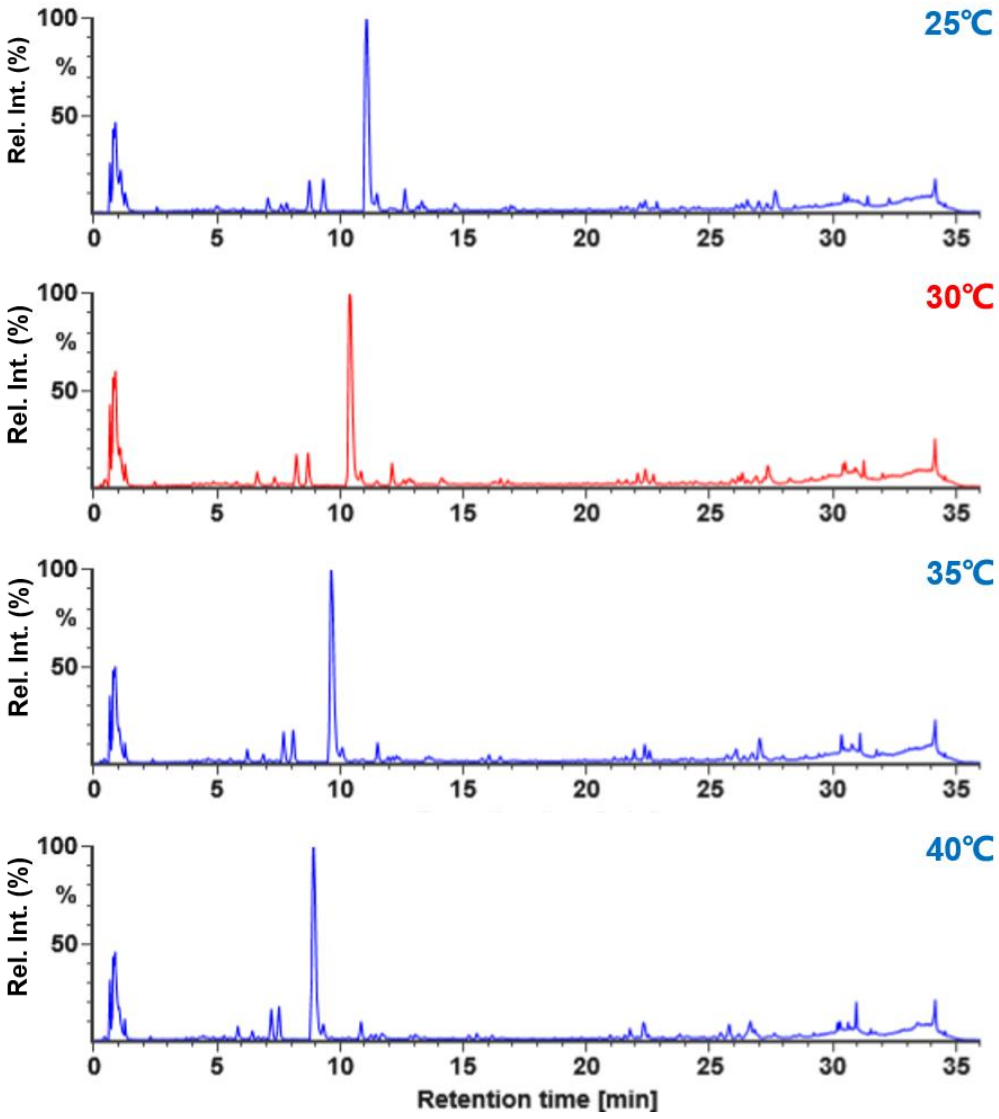

Figure S1 Comparison of the column temperature to improve the revolution of the various compounds of *Salvia miltiorrhiza* by using the HSS T3 column.

Table S1 Information of 10 UHPLC columns for stationary phases screening.

Stationary Phase	Type	Specification & Manufacturer	pH range	Separation Characteristics
HSS T3	RP	2.1 × 100 mm, 1.8 μm; Waters	2.0–8.0	Silica gel C18 column, triple bond to reduce carbon density; Enhance that retention of polar molecules; Compatible with 100% water phase.
BEH C18	RP	2.1 × 100 mm, 1.7 μm; Waters	1.0–12.0	The column used ethylene bridge hybrid particle technology, which Ethylene-bridged hybrid particles are bonded with C18, which is suitable for the retention of moderately or weakly polar compounds. Wide range of pH tolerance.
BEH Shield RP18	RP	2.1 × 100 mm, 1.6 μm; Waters	2.0–11.0	C18 single bond with embedded polar groups based on ethylene bridge hybrid particles, fully capped. Compared with the linear C18 bonded phase, it provides complementary separation selectivity. Especially suitable for phenolic acid analytes. Completely compatible with 100% aqueous mobile phase. The basic compound has good peak shape.
ZORBAX Extend C18	RP	2.1 × 100 mm, 1.8 μm; Agilent	2.0–11.5	. Spherical fully porous silica gel particles with double-ended octadecyl silane chemically bonded phase. Patented double tooth bonding technology, designed for high pH mobile phase. The pH range of the applicable mobile phase is wide, and the silica gel matrix and bimodal end ensure better peak shape.
ZORBAX SB C18	RP	2.1×100 mm, 1.8 μm/ Agilent	1.0–8.0	All empty silica gel particles with octadecyl silica gel chemical bonding phase with stereoprotective group on the side. Under low pH mobile phase conditions. It can provide the best stability.
ZORBAX Eclipse Plus C18	RP	2.1 × 100 mm, 1.8 μm; Agilent	2.0–9.0	Spherical fully porous silica gel particles of Double Terminated octadecyl silane chemical bonding phase; It can be used for the analysis of acidic and neutral samples, especially for the separation of alkaline compounds with poor peak shape on other chromatographic columns..
Stationary Phase	**Type**	**Specification & Manufacturer**	**pH range**	**Separation Characteristics**

Atlantis^{TM} Premier BEH C18 AX	RP/Anion Exchange mixed	2.1 × 100 mm, 1.7 μm; Waters	3.0–11.0	The column was packed with Reversed-Phase/Anion Exchange mixed Dedicated to retaining and separating polar analytes; It can improve the retention performance and sensitivity, and has excellent analytical performance, versatility and retention when used in polar compounds, and can also achieve balanced retention performance for various analytical mixtures.
ZORBAX SB-Aq	RP	2.1 × 100 mm, 1.8 μm; Agilent	1.0–8.0	Spherical fully porous silica gel particles of silica gel chemically bonded phase. It can be used for high acid mobile phase and high polarity samples, and is compatible with 100% pure water mobile phase.
CSH C18	RP	2.1 × 100 mm, 1.7 μm; Waters	1.0–11.0	On the basis of ethylene bridge hybrid particle (BEH), a small amount of charge is controlled on its surface. It is the first choice column for the analysis of alkaline drugs and peptides. And that chromatographic column balance is fast.
HSS C18 SB	RP	2.1 × 100 mm, 1.8 μm; Waters	2.0–8.0	Silica gel C18 column, unblocked; Strong retention of basic compounds; At the same time, it is convenient to speed up or convert HPLC method to UPLC.

Table S2 Detailed information of the 86 components characterized from *Salvia miltiorrhiza* in the current study.

No.	Observed t_R (min)	Observed m/z	Adducts	Formula	Mass error (ppm)	Observed drift (ms)	Observed CCS (Å^2)	ESI-MS/MS	Identification
1	0.77	503.1606	−H	$C_{18}H_{32}O_{16}$	−2.3	8.27	207.90	383.1196,263.0762,221.0657	raffitrinose
2	0.85	341.1082	−H	$C_{12}H_{22}O_{11}$	−2.3	6.67	171.24	235.0813,203.0557,195.0502,161.0447,145.0611	saccharose
3	0.98	377.0851	−H	$C_{18}H_{18}O_9$	−2.7	6.68	171.35	341.1081,232.8810	salvianic acid C
4	1.27	665.2122	−H	$C_{24}H_{42}O_{21}$	−3.5	9.49	236.97	665.2137,383.1197,341.1087,179.0552	stachyose
5*	2.51	197.0451	−H	$C_9H_{10}O_5$	2.5	6.90	179.41	179.0341,135.0447,123.0446	danshensu
6*	3.64	137.0240	−H	$C_7H_6O_3$	−2.3	4.02	116.68	137.0241,136.0156,109.0285	protocatechualdehyde
7*	4.24	193.0510	−H	$C_{10}H_{10}O_4$	1.7	5.15	139.40	134.0367	ferulic acid
8*	4.68	537.1038	−H	$C_{27}H_{22}O_{12}$	0.0	8.48	212.79	475.0377,453.0380,359.9737,295.0617	lithospermic acid
9	4.67	357.0618	−H	$C_{18}H_{14}O_8$	0.6	6.83	174.81	339.0517,322.0435,280.0347,253.0502	prolithospermic acid
10	5.9	521.1306	−H	$C_{24}H_{26}O_{13}$	1.0	8.41	211.26	367.9992,323.0781,179.0346,161.0243,135.0450	salviaflaside
11	6.75	339.0515	−H	$C_{18}H_{12}O_7$	1.5	8.62	174.33	321.9921,295.0617,280.0367,185.0243	miltiolignanolides C
12	6.78	535.1816	−H	$C_{26}H_{32}O_{12}$	−1.0	9.03	225.88	502.0347,366.9891,322.9986,280.0730,160.0563	1-hydroxy-pinoresinol-1-O-β-D-glucoside
13	8.2	179.0353	−H	$C_9H_8O_4$	2.0	6.72	176.16	133.0294,123.0451	caffeic acid
14*	8.34	359.0845	−H	$C_{18}H_{16}O_8$	1.4	9.79	245.24	325.0239,236.0544,161.0239,133.0290	rosmarinic acid
15*	8.84	493.1147	−H	$C_{26}H_{22}O_{10}$	1.3	8.37	210.34	295.0617,185.0243135.0451,123.0445,109.0292	salvianolic acid A
16*	8.86	313.0717	−H	$C_{17}H_{14}O_6$	0.0	8.27	209.05	295.0617,268.0681,239.0705,203.0346	salvianolic acid F
17	10.5	719.1612	+H	$C_{36}H_{30}O_{16}$	0.8	11.85	256.01	3223.0539,295.0588,279.0633	8',8'''-epi-Salvianolic acid Y
18*	10.62	717.1454	−H	$C_{36}H_{30}O_{16}$	−1.0	9.90	247.02	519.0952,339.0521,321.0413,295.0619	salvianolic acid B
19	11.04	295.0617	−H	$C_{17}H_{12}O_5$	1.9	8.29	209.86	295.0618,280.0363,249.0558,185.0244,135.0448	miltiolignanolides G
20	11.62	193.0508	−H	$C_{10}H_{10}O_4$	1.1	8.82	226.19	178.0263,175.0396,149.0614,134.0371	isoferulicacid
21	11.67	717.1448	−H	$C_{36}H_{30}O_{16}$	−1.9	9.78	244.17	519.0945,339.0517,321.0412,295.0614	lithospermic acid B or isomer
22	12.26	717.1451	−H	$C_{36}H_{30}O_{16}$	0.2	10.14	140.94	519.0949,339.0521,321.0412,295.0616	lithospermic acid B or isomer
23	12.47	373.0934	−H	$C_{19}H_{18}O_8$	1.3	7.05	179.92	324.0106,251.0704,233.0614,135.0449	methyl rosmarinate

24	12.92	551.1211	−H	$C_{28}H_{24}O_{12}$	3.0	8.77	219.60	520.1453,377.0877,305.0447,231.0283,200.0107	litherospermic acid monomethyl ester
25	12.96	731.1616	−H	$C_{37}H_{32}O_{16}$	−0.3	10.16	253.33	533.1113,353.0684,335.0575,309.0077,185.0246	8'''-epi-9'-methyl-Salvianolic acid B
26	13.08	551.1203	−H	$C_{28}H_{24}O_{12}$	1.5	8.76	219.53	371.0768,339.0517,321.0412,231.0306	monomethyl lithospermate
27	13.65	311.0928	−H	$C_{18}H_{16}O_5$	0.9	6.65	171.11	294.0776,279.0657,224.0467,199.0517	tanshindiol A
28*	14.65	731.1592	−H	$C_{37}H_{32}O_{16}$	−3.6	10.18	253.95	724.0494,645.3470,533.1098,203.1075	9'-methyl lithospermate B
29	16.21	281.1160	+H	$C_{18}H_{16}O_3$	−4.5	6.28	161.67	263.1057,235.1104,202.0763,191.0841,165.0688	1,2,5,6-tetrahydrotanshinone I
30*	16.23	491.0980	−H	$C_{26}H_{20}O_{10}$	2.0	8.35	209.82	371.1269,293.0463,269.0826,161.0231	salvianolic acid C
31	16.83	313.1423	+H	$C_{19}H_{20}O_4$	−3.8	6.76	172.50	253.0843,238.0607,223.0376,193.1002,153.0683	miltionone II
32	17.35	295.1320	+H	$C_{19}H_{18}O_3$	2.0	8.35	168.34	280.1071,262.0963,249.1278	isotanshinone IIA
33	17.98	283.0957	+H	$C_{17}H_{14}O_4$	−2.8	6.07	156.44	237.0898,189.0688,165.0687,152.0609,141.0688	dihydronortanshinone
34	19.33	293.0801	+H	$C_{18}H_{12}O_4$	−2.4	6.18	158.93	249.0900,219.0798,189.0690,178.0765,152.0610	tanshinol A
35	19.56	311.0933	−H	$C_{18}H_{16}O_5$	2.7	6.71	172.52	268.0685,239.0707,227.0330,209.0619	tanshindiol C
36	19.7	311.0932	−H	$C_{18}H_{16}O_5$	2.3	6.68	171.78	268.0721,221.0553,211.0756,195.0440	przewaquinone C
37	19.83	277.0849	+H	$C_{18}H_{12}O_3$	−3.7	6.02	155.51	249.0903,194.1058,178.0765,152.0608	isotanshinone I or isomer
38	20.22	294.1478	+H	$C_{19}H_{19}NO_2$	−3.4	6.50	166.62	278.1164,264.1007,236.1054,222.0551,191.0835	salviadione
39	20.69	295.0956	+H	$C_{18}H_{14}O_4$	−3.1	6.21	159.60	234.0953,221.0943,205.0638,115.0530	3-hydroxymethylenetanshinquinone
40	20.77	311.1271	+H	$C_{19}H_{18}O_4$	−2.3	6.64	169.72	293.1174,283.1323,250.0974	tanshinone IIB
41	20.91	293.0801	+H	$C_{18}H_{12}O_4$	−2.5	6.06	156.14	249.0904,231.0770,193.0997	hydroxytanshinone I
42	21.13	313.1068	+H	$C_{18}H_{16}O_5$	−0.8	6.42	164.46	271.1687,256.1448,241.1223,207.0793	tanshindiol B
43	21.18	311.0929	−H	$C_{18}H_{16}O_5$	1.3	6.77	173.97	295.0608,211.1041,199.0766,185.0623	purple danshen E
44	21.25	311.1271	+H	$C_{19}H_{18}O_4$	−2.2	6.62	169.34	253.0848,237.0895,223.0742,179.0834,165.0688	przewaquinone A
45	21.32	293.1165	+H	$C_{19}H_{16}O_3$	−2.5	6.37	163.60	278.0932,235.0741,203.0837,189.0689,178.0764	1-dehydrotanshinone Ⅱ A
46	21.64	485.3292	−H	$C_{30}H_{46}O_5$	3.9	9.14	228.69	485.3299,441.3393,377.2856,285.1502	urs-12,20(30)-dien-3β,7β,24-triol-28-oic acid
47	22.03	341.1379	+H	$C_{20}H_{20}O_5$	−1.4	6.99	177.65	321.0791,263.1058,235.1108,220.0867,192.0917	methyl dihydronortanshinonate
48	22.07	309.1116	+H	$C_{19}H_{16}O_4$	−1.6	6.45	165.17	265.0852,235.0744,178.0767,165.0687,152.0611	tanshinaldehyde
49	22.09	295.0984	−H	$C_{18}H_{16}O_4$	2.9	6.53	168.69	265.1472,263.010,249.0933,235.0770,222.0676,209.0607,165.0714	salmiltiorin A or isomer
50	22.48	281.1162	+H	$C_{18}H_{16}O_3$	3.9	9.14	160.77	265.0851,237.0897,152.0611,128.0610	salmiltiorin E
51	22.9	281.1526	+H	$C_{19}H_{20}O_2$	−3.6	6.37	163.84	266.1294,239.1054,205.0992,190.0748	dehydromiltirone

52	23.35	279.1009	+H	$C_{18}H_{14}O_3$	−2.5	6.02	155.45	218.0712,205.1001,189.0687,165.0685	dihydroisotanshinone II
53	23.56	281.1163	+H	$C_{19}H_{16}O_4$	−3.3	6.08	156.81	219.0791,191.0840,178.0767	danshenxinkun B
54	24.04	281.1169	+H	$C_{18}H_{16}O_3$	−1.3	6.12	157.81	235.1111,219.0795,202.0766,191.0844	trijuganone B
55	24.12	315.1587	+H	$C_{19}H_{22}O_4$	−0.8	6.87	173.97	282.1212,271.1689,254.0925,225.0903,204.0881	tanshinone Ⅴ
56	24.14	313.1457	−H	$C_{19}H_{22}O_4$	3.7	7.09	181.25	295.1355,283.1336,267.1019,255.1400,239.1080	neocryptotanshinone
57	24.18	299.2001	+H	$C_{20}H_{26}O_2$	−1.6	6.90	176.19	229.1213,201.0915,187.0746,159.0799,144.0563	microstegiol
58	24.42	271.1715	−H	$C_{18}H_{24}O_2$	4.2	7.07	181.44	267.1373,253.1208,237.0928,227.1076	miltiorolide A or isomer
59	24.49	339.1221	+H	$C_{20}H_{18}O_5$	−1.6	6.90	175.71	233.0951,218.0719,205.1002,190.0753,189.0689	methyl tanshinonate
60	24.6	279.0672	−H	$C_{17}H_{12}O_4$	3.1	6.25	162.42	251.0712,209.0606,165.0710,152.0632	nortanshinone
61	24.71	301.1796	+H	$C_{19}H_{24}O_3$	−0.8	6.72	171.76	301.1793,271.1684,256.1447,241.1214	miltipolone
62	24.98	269.1163	+H	$C_{17}H_{16}O_3$	−3.3	6.05	156.40	208.0872,203.0837,192.0909,179.0842,166.0741	danshenspiroketallactone
63	25.23	487.3419	+H	$C_{30}H_{46}O_5$	0.3	8.84	222.02	480.1428,435.1937,400.0974,296.1635,267.1385	2α,3α,23-trihydroxyurs-12,20 (30)-dien-28-oic acid
64*	25.41	277.0853	−H	$C_{18}H_{14}O_3$	−2.2	5.84	160.75	277.0873,253.0883,249.0910,233.0630,211.0763	dihydrotanshinone I
65	25.52	267.1371	+H	$C_{18}H_{18}O_2$	−3.2	7.01	179.41	249.1264,234.1029,215.0852,179.0828,131.049	4-methylenemiltirone
66	25.93	253.0849	+H	$C_{16}H_{12}O_3$	−4.2	5.68	147.80	190.0755,165.0686,152.0608	danshexinkun C
67	25.96	297.1109	+H	$C_{18}H_{16}O_4$	−4.1	6.56	168.13	268.1074,249.0898,235.0740,221.0948,207.0790,193.0998,179.0830,165.0743	salmiltiorin A or isomer
68	26.12	277.0853	+H	$C_{18}H_{12}O_3$	−2.3	5.86	151.67	249.0882,194.1034,178.0766,152.0608	isotanshinone I or isomer
69*	26.24	297.1479	+H	$C_{19}H_{20}O_3$	−2.2	6.60	169.03	237.0901,222.0666,203.0843,195.1157,181.0993	cryptotanshinone
70	26.26	301.2158	+H	$C_{20}H_{28}O_2$	−1.5	6.97	177.91	259.1688,213.1266,171.0792,163.0743,128.0606	sugiol
71	26.48	273.1839	+H	$C_{18}H_{24}O_2$	−1.0	6.42	165.02	257.1505,215.1056,203.1056,187.0746,141.0690	miltiorolide A or isomer
72	26.88	471.3501	−H	$C_{30}H_{48}O_4$	4.6	9.10	227.79	460.9930,423.3294,393.3180,377.2850,281.1179	psiguanin A
73	27.3	449.1066	+H	$C_{27}H_{30}O_{15}$	0.1	6.45	164.11	333.0058,263.0695,233.0948,191.0816,177.0681	kaempferol-3-O-β-D-glucopyranoside
74	27.64	299.1271	+H	$C_{18}H_{18}O_4$	−2.2	6.33	162.55	233.0953,205.1002,191.0836,178.0765,165.0688	tanshinol C
75	27.89	293.2135	−H	$C_{18}H_{30}O_3$	4.4	7.11	181.92	285.1856,271.0998,256.0787,241.1607,135.0496	2, 3-trans-4, 5-cis-diene-6-carbonyl stearic acid
76	27.96	287.1634	+H	$C_{18}H_{22}O_3$	−2.7	6.59	168.93	269.1529,239.1057,221.0954,195.0798,167.0844	epi-cryptoacetalide
77	28.19	315.1946	+H	$C_{20}H_{26}O_3$	−2.9	6.97	177.62	304.0096,267.1375,245.1164,233.0953,203.0826	6, 12-dihydroxyabieta-5, 8, 11, 13-tetraen-7-one
78	28.96	317.2105	+H	$C_{20}H_{28}O_3$	−1.9	7.00	178.23	229.1222,175.0748,147.0798,137.0589	7β-hydroxy-8, 13-abietadiene-11, 12-dione

79	29.08	265.0848	+H	$C_{17}H_{12}O_3$	−4.2	5.77	149.73	233.0950,215.0845,202.0765,189.0687,165.0686	1, 2-dihydortanshinquinone
80*	29.18	295.1321	+H	$C_{19}H_{18}O_3$	−2.5	6.41	164.43	280.5475,266.0917,262.0961,235.0752,207.0792	tanshinone IIA
81	29.42	299.1633	+H	$C_{19}H_{22}O_3$	−3.1	6.66	170.50	253.1584,223.1103,183.0794,153.0682,141.0688	neocryptotanshinone II or isomer
82	29.49	269.1530	+H	$C_{18}H_{20}O_2$	−2.1	6.33	163.06	253.1213,239.1057,193.0997,178.0768	salviolone
83	29.61	283.1688	+H	$C_{19}H_{22}O_2$	−1.8	6.55	168.14	235.1106,225.0901,207.0795,179.0838,165.0688	1, 2-didehydromiltirone
84	30.61	297.1505	−H	$C_{19}H_{22}O_3$	−2.5	6.41	178.84	270.1545,269.1554,253.1237	neocryptotanshinone II or isomer
85	30.65	557.1972	+H	$C_{36}H_{28}O_6$	2.5	9.58	240.16	511.1899,483.1598,455.1647,277.0861,235.0756	neo-przewaquinone A
86	31.2	279.2340	−H	$C_{18}H_{32}O_2$	3.8	13.36	338.50	251.1096,227.1081,197.0332,117.9291	linoleic acid

*: Identification by comparing with the reference standards

Table S3 Comparison between the experimental CCS values and their recordings in the AllCCS database for seven compounds characterized from *Salvia miltiorrhiza* in the current work.

No.	**Compound** (numbering in Table S2)	***m/z*** **$[M–H]^-$**	***m/z*** **$[M+H]^+$**	**CCS in ALLCCS database ($Å^2$)**	**Experimental CCS ($Å^2$)**	**Difference ($Å^2$)**	**Structure type**
1	tanshinone IIA (**80**#)	/	295.1321	168.73	164.43	4.30	Terpenoid
2	dihydrotanshinone I (**64**#)	277.0853	/	172.09	160.75	11.34	
3	isotanshinone IIA (**32**#)	/	295.1320	171.12	168.34	2.78	
4	miltipolone (**61**#)	/	301.1796	171.12	171.76	0.64	
5	salvianolic acid A (**15**#)	493.1147	/	209.90	210.34	0.44	Phenolic acid
6	salvianolic acid B (**18**#)	717.1454	/	247.30	247.02	0.28	
7	salviaflaside (**10**#)	521.1306	/	208.58	211.26	2.68	