Analytical and Bioanalytical Chemistry

Supplementary Information

An integrated strategy of MS-network- based offline 2DLC-QTOF-MS/MS coupled with UHPLC-QTRAP®-MS/MS for the characterization and quantification of the non-polysaccharides in Sijunzi Decoction

Bangjian Dong[1], Chongsheng Peng[1], Ping Ma, Xiaobo Li*

School of Pharmacy, Shanghai Jiao Tong University, No. 800 Dongchuan Road, Minhang District, Shanghai, 200240, China

Index of Contents

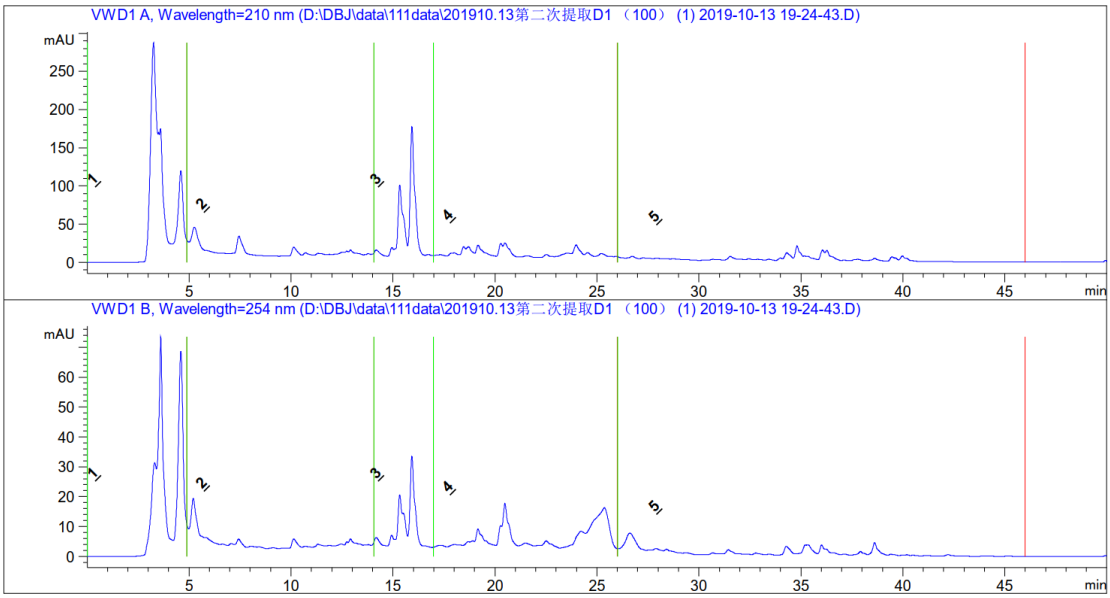


Fig. S1 The first dimensional separation: HPLC-DAD chromatograms of NPSs in SJZD (A) at 210 nm; (B) at 254 nm.

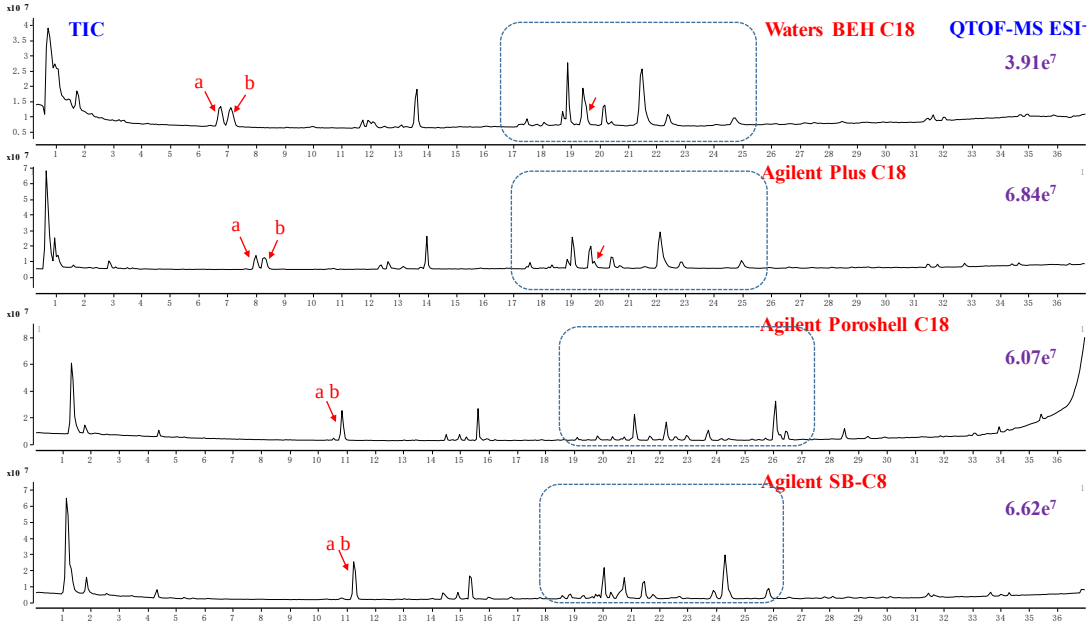
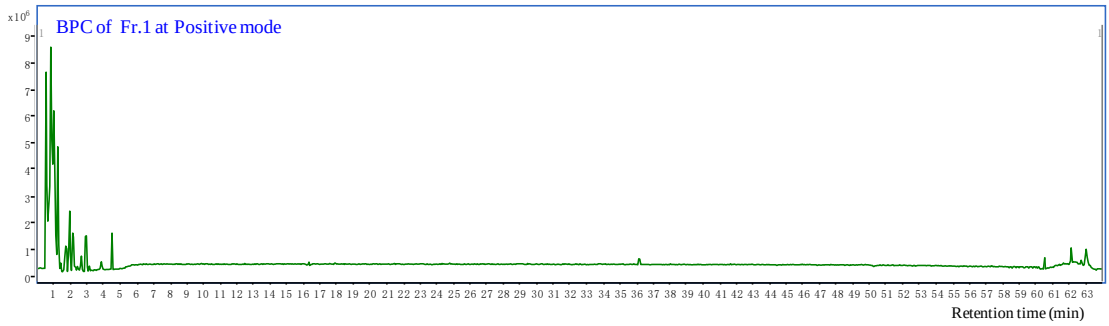
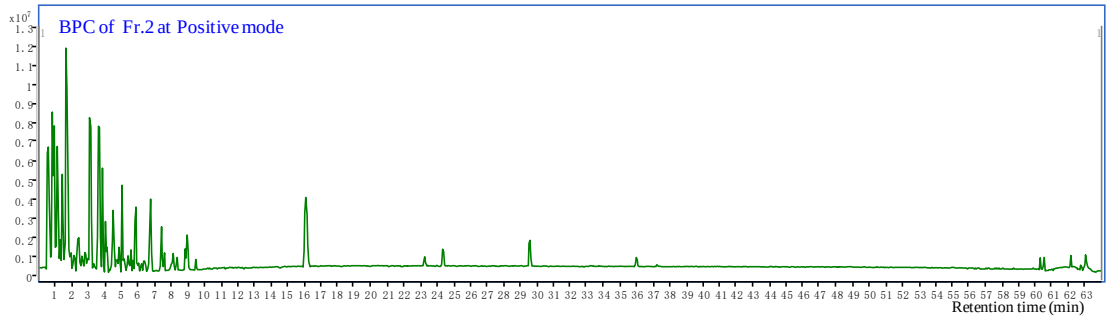
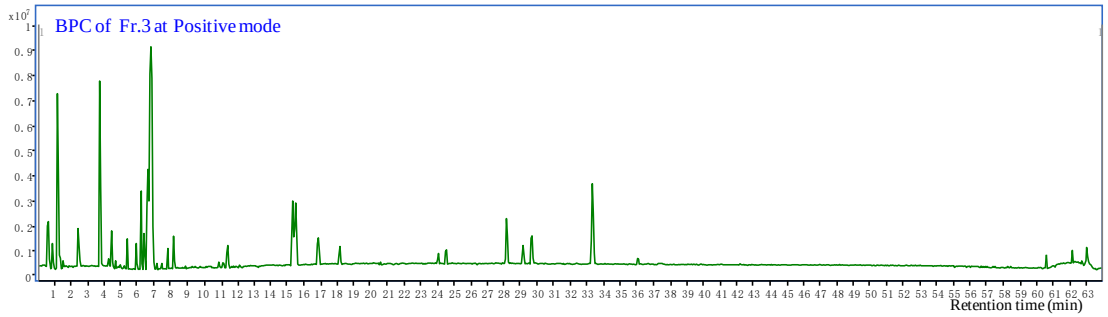
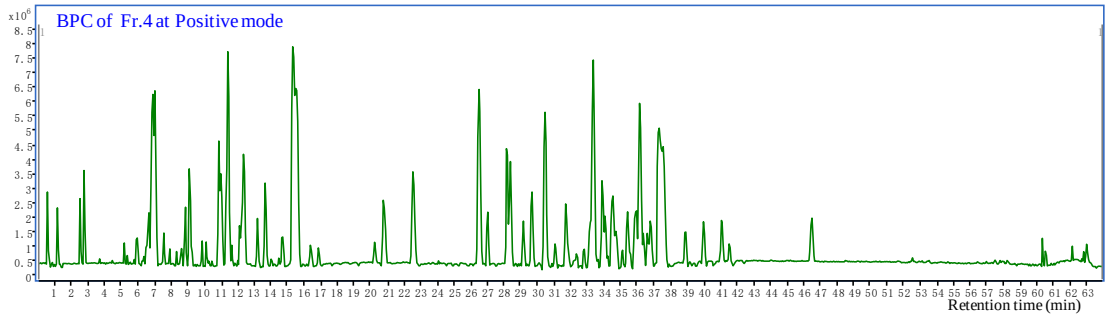


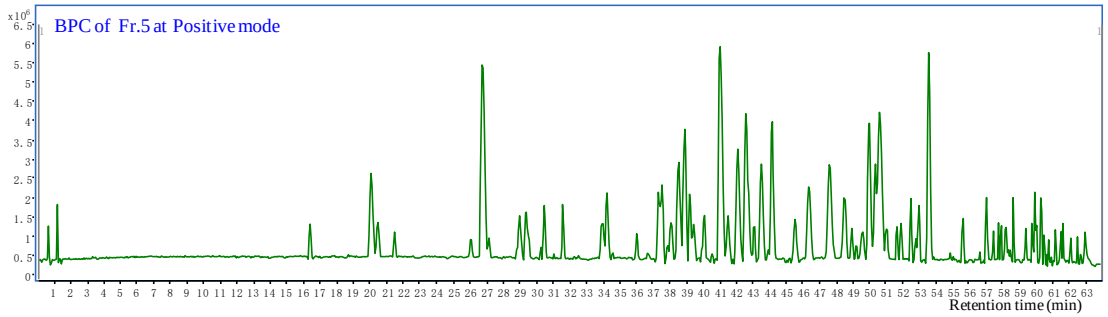
Fig. S2 Comparison of the separation selectivity of four RP columns for SJZD components using CH_3CN-0.1% water-containing formic acid for as the mobile phase (data was recorded on an Agilent UHPLC-QTOF-MS instrument. Sample A was used for optimization. a is liquiritin; b is liquiritin apioside).


BPC of Fr.1 at Positive mode
Retention time (min)


BPC of Fr.2 at Positive mode
Retention time (min)


BPC of Fr.3 at Positive mode
Retention time (min)


BPC of Fr.4 at Positive mode
Retention time (min)


BPC of Fr.5 at Positive mode
Retention time (min)

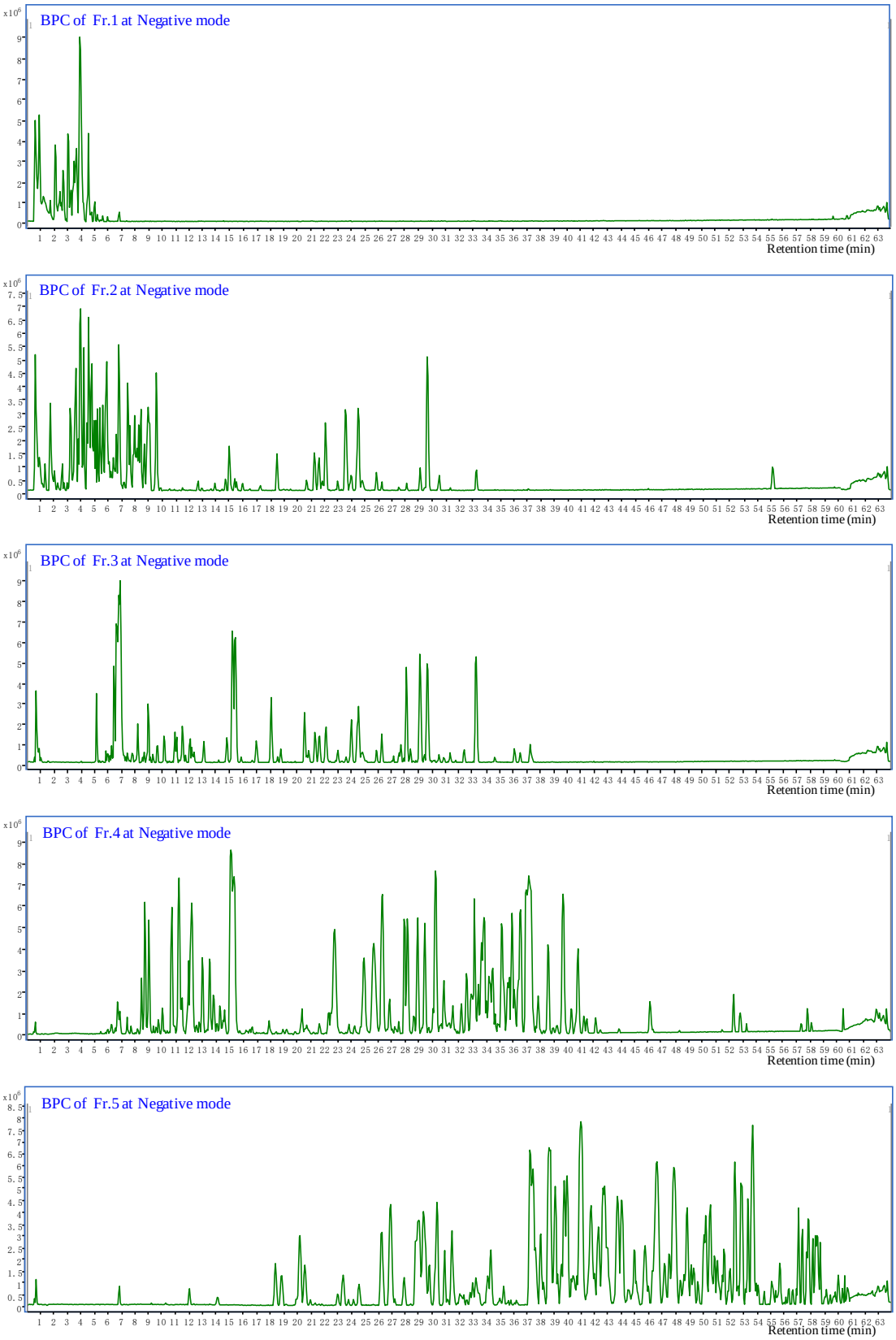
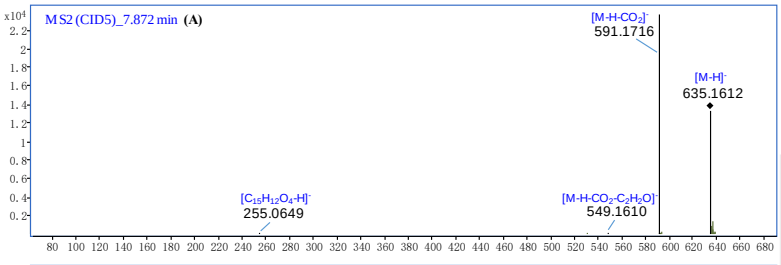
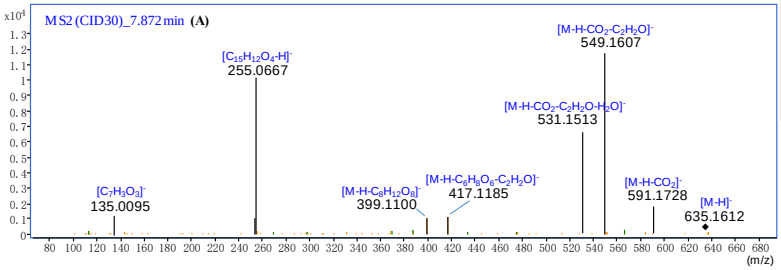
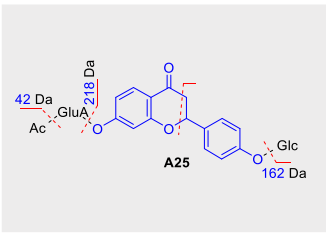
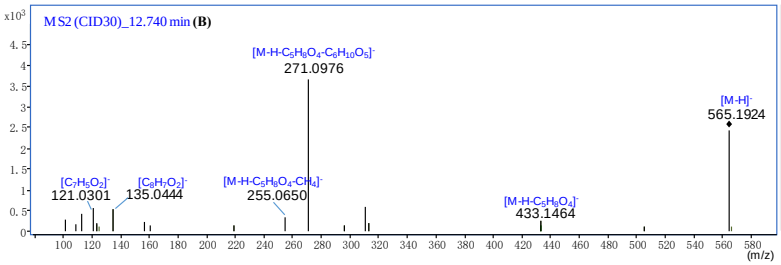


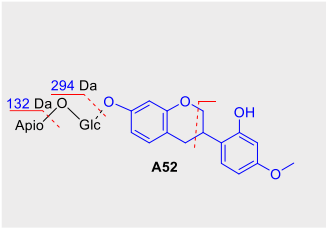
Fig. S3 Base peak intensity chromatograms (BPCs) in positive and negative ion mode of Fractions 1–5.

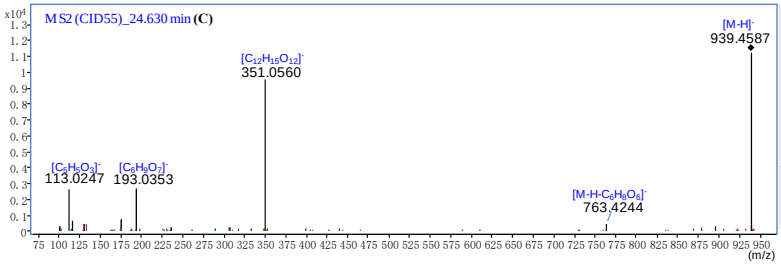

MS2 (CID5)_7.872 min (A)
[M-H-CO2]-
591.1716
[M-H]-
635.1612
[C15H12O4-H]-
255.0649
[M-H-CO2-C2H2O]-
549.1610

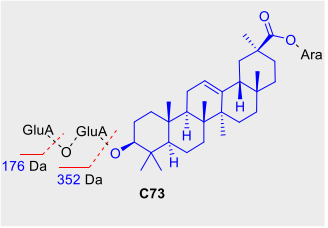

MS2 (CID30)_7.872 min (A)
[M-H-CO2-C2H2O]-
549.1607
[C15H12O4-H]-
255.0667
[M-H-CO2-C2H2O-H2O]-
531.1513
[C7H5O3]-
135.0095
[M-H-C6H12O6]-
399.1100
[M-H-C6H8O6-C2H2O]-
417.1185
[M-H-CO2]-
591.1728
[M-H]-
635.1612
(m/z)

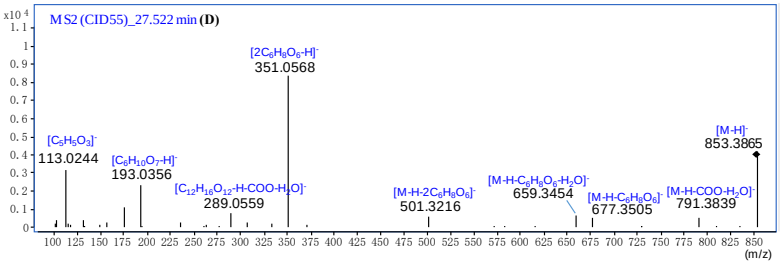

42 Da
218 Da
Ac
GluA
Glc
162 Da
A25

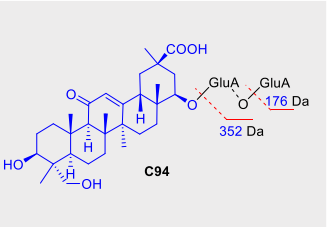

MS2 (CID30)_12.740 min (B)
[M-H-C5H8O4-C6H10O5]-
271.0976
[M-H]-
565.1924
[C7H5O2]-
121.0301
[C6H7O2]-
135.0444
[M-H-C5H8O4-CH4]-
255.0650
[M-H-C5H8O4]-
433.1464
(m/z)

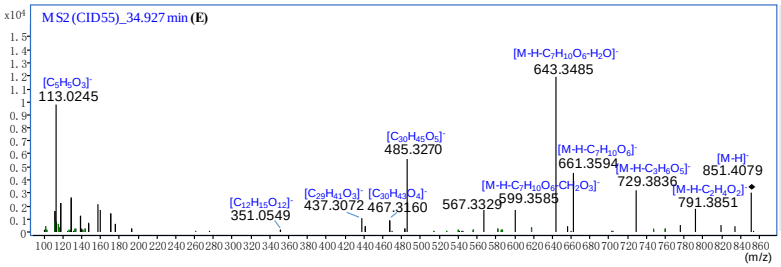

294 Da
132 Da
Apio
Glc
OH
A52

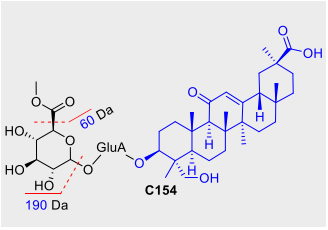

MS2 (CID55)_24.630 min (C)
[M-H]-
939.4587
[C12H15O12]-
351.0560
[C5H5O3]-
113.0247
[C6H5O7]-
193.0353
[M-H-C6H8O6]-
763.4244
(m/z)


Ara
GluA
GluA
176 Da
352 Da
C73


MS2 (CID55)_27.522 min (D)
[2C6H8O6-H]-
351.0568
[C5H5O3]-
113.0244
[C6H10O7-H]-
193.0356
[C12H16O12-H-COO-H2O]-
289.0559
[M-H-2C6H8O6]-
501.3216
[M-H-C6H8O6-H2O]-
659.3454
[M-H-C6H8O6]-
677.3505
[M-H-COO-H2O]-
791.3839
[M-H]-
853.3865
(m/z)


COOH
GluA
GluA
176 Da
352 Da
HO
OH
C94


MS2 (CID55)_34.927 min (E)
[M-H-C7H10O6-H2O]-
643.3485
[C5H5O3]-
113.0245
[C30H45O5]-
485.3270
[M-H-C7H10O6]-
661.3594
[M-H-C3H6O3]-
729.3836
[M-H]-
851.4079
[M-H-C7H10O6-CH2O3]-
599.3585
[M-H-C3H4O2]-
791.3851
[C12H15O12]-
351.0549
[C29H41O3]-
437.3072
[C30H43O4]-
467.3160
567.3329
(m/z)


OH
60 Da
HO
GluA
HO
HO
190 Da
C154

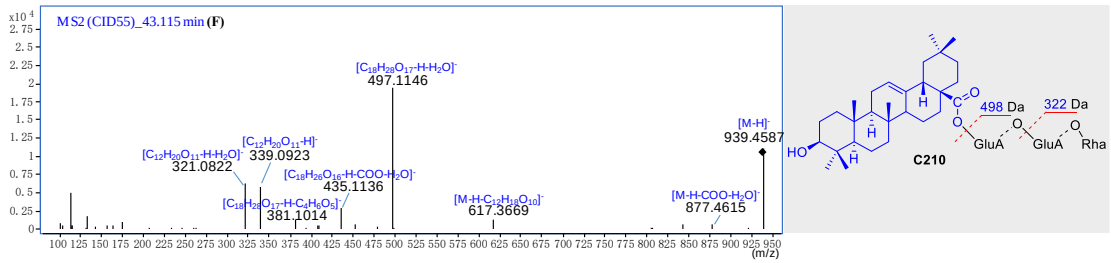


Fig. S4 Tandem mass spectra of six potential new compounds **A25** (A), **A52**(B), **C73** (C), **C94** (D), **C154** (E), and **C210** (F).

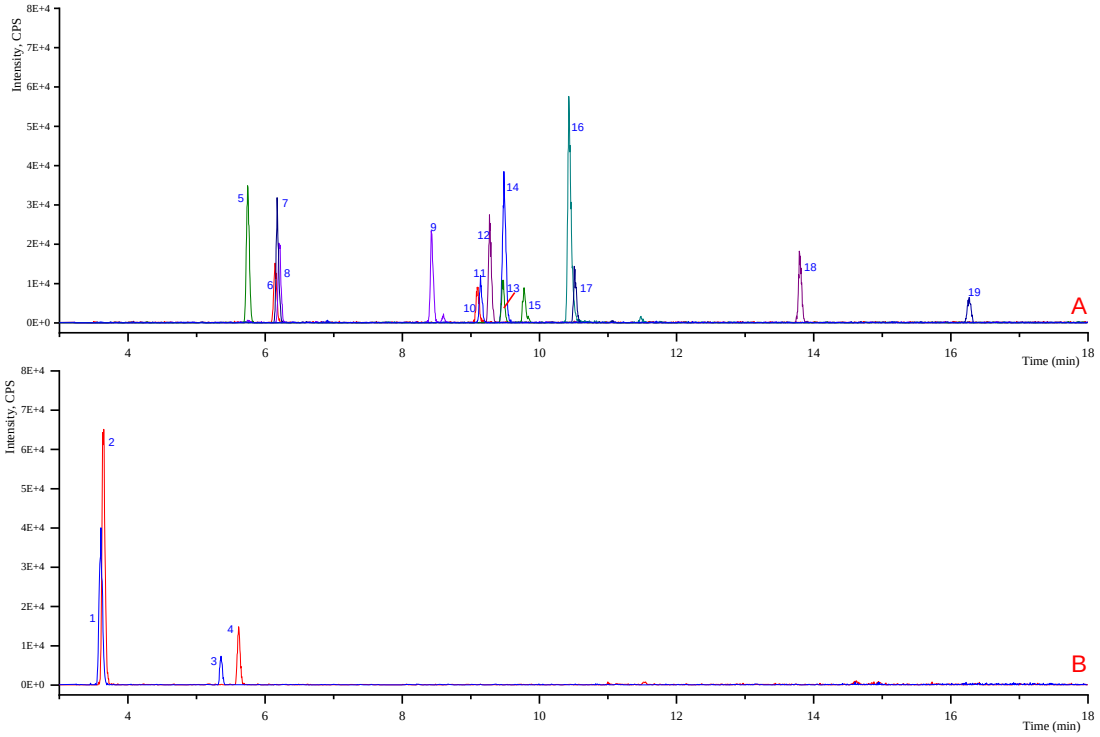


Fig. S5 Representative MRM chromatograms of 19 analytes from Sample B1 (A) and Sample B2 (B).

Table S1 UHPLC/QTRAP®-MS/MS parameters for the quantification.

NO.	Compound	Formula	RT (min)	Quantifier (*m/z*)	Qualifier (*m/z*)	CE[a] (eV)	DP (eV)	CXP (eV)
1	Liquiritin apioside	$C_{26}H_{30}O_{13}$	3.59	549.2→255.1	549.2→135.0	-50	-100	-15
2	Liquiritin	$C_{21}H_{22}O_9$	3.63	417.1→255.1	417.1→135.0	-28	-100	-15
3	Isoliquiritin apioside	$C_{26}H_{30}O_{13}$	5.35	549.2→255.1	549.2→135.0	-50	-100	-15
4	Isoliquiritin	$C_{21}H_{22}O_9$	5.60	417.1→255.1	417.1→135.0	-28	-100	-15
5	Ononin	$C_{22}H_{22}O_9$	5.75	475.1→267.1	475.1→252.0	-30	-100	-15
6	Liquiritigenin	$C_{15}H_{12}O_4$	6.15	255.1→135.0	255.1→119.2	-30	-100	-15
7	Ginsenoside Re	$C_{48}H_{82}O_{18}$	6.17	991.6→945.5	991.6→799.5	-30	-100	-15
8	Ginsenoside Rg1	$C_{42}H_{72}O_{14}$	6.20	845.5→799.5	845.5→637.6	-30	-100	-15
9	Ginsenoside Rf	$C_{42}H_{72}O_{14}$	8.42	845.5→799.5	845.5→637.6	-30	-100	-15
10	Isoliquiritigenin	$C_{15}H_{12}O_4$	9.10	255.1→135.0	255.1→119.2	-30	-100	-15
11	Ginsenoside Rb1	$C_{54}H_{92}O_{23}$	9.12	1153.6→1107.6	1153.6→945.5	-30	-100	-15
12	Ginsenoside Rg2	$C_{42}H_{72}O_{13}$	9.22	829.5→783.5	829.5→637.6	-30	-100	-15
13	Ginsenoside Rc	$C_{53}H_{90}O_{22}$	9.46	1123.6→1077.6	1123.6→945.5	-30	-100	-15
14	Formononetin	$C_{16}H_{12}O_4$	9.48	267.1→252.0	267.1→223.0	-30	-100	-15
15	Ginsenoside Rb2	$C_{53}H_{90}O_{22}$	9.76	1123.6→1077.6	1123.6→945.5	-30	-100	-15
16	Glycyrrhizic acid	$C_{42}H_{62}O_{16}$	10.43	821.4→351.1	821.4→193.1	-58	-100	-15
17	Ginsenoside Rd	$C_{48}H_{82}O_{18}$	10.51	991.6→945.5	991.6→783.5	-30	-100	-15
18	Ginsenoside Rg3	$C_{42}H_{72}O_{13}$	13.75	829.5→783.5	829.5→621.5	-30	-100	-15
19	Ginsenoside Rk1	$C_{42}H_{70}O_{12}$	16.26	811.5→765.5	811.5→161.3	-30	-100	-15

[a] the CE values was applied for quantifier ions