<RSC Advances>

Electronic Supplementary Information (ESI)

A strategy for establishment of practical identification methods for Chinese patent medicine from systematic multi-component characterization to selective ion monitoring of chemical markers: Shuxiong Tablet as a case study

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Fig. S11 The MS and MS^2 spectra of representative ginsenosides **162** (PPT type), **180** (malonyl substituted) and **156** (C17-side chain varied).

Fig. S12 The MS and MS^2 spectra of a representative unknown FOG compound **27**.

Fig. S13 Enlarged CID-MS/MS spectra of four FOG reference standards: 6-hydroxy kaempferol-3,6-di-*O*-*β*-D-glucoside (**59**), 6-hydroxykaempferol-3-*O*-*β*-D-glucoside (**77**), quercetin-7-*O*-*β*-D-glucoside (**83**), and quercetin-3-*O*-*β*-D-glucoside (**84**).

Fig. S14 The MS and MS^2 spectra of representative QCG (**61)**, phenolic acid (**22**), and phthalide (**89**) compounds in SXT.

Fig. S15 The MS^2 spectra of four mono-*O*-caffeorylquinic acids, including comounds **9**, **14**, **33** and **37**. Abundant product ions at *m/z* 173.04 were only observed in **37**, in consistent with the reported spetrum of 4-*O*-caffeorylquinic acid. The intensity ratio of product ions *m/z* 179.04 to *m/z* 191.06 was larger in **14** (5-*O*- caffeorylquinic acid) than **33** (3-*O*- caffeorylquinic acid).

Fig. S16 A 2D plot of retention time (t_R) versus mass-to-charge (*m/z*) of the precursor ions of 250 compounds characterized from SXT based on the structure subclasses.

Fig. S17 The MS fingerprint of 20 batches of Carthamus tinctoris samples: showing the presence of hydroxysafflor yellow A (HSYA), anhydrosafflor yellow B (AnHSYB) and kaempferol-3-*O*-rutinoside. These data have been reported in our recent study in literature [7].

Fig. S18 The base-peak chromatograms of a home-made SXT sample and three compositional drugs: showing the presence of 11 selected chemical markers for

authentication of SXT. FA: ferulic acid; KR: kaempferol-3-*O*-rutinoside; ZL: *Z*-ligustilide; LA: levistolide A.

Fig. S19 Exacted ion chromatograms (EIC) of eleven chemical markers determined with the home-made SXT sample on the QTOF mass spectrometer under the SIM chromatographic condition (**A**) and fingerprinting conditions of a Notoginseng total saponins preparation, CF, or CR (**B**). EIC of each individual drug under the corresponding fingerprinting condition (NRR, CF, or CR) is shown as (**C**). The gradient elution programs were by reference to literature [7,37,46].

Fig. S20 Comparison of the signal to noise ratio (S/N) of six reference standards (ferulic acid, kaempferol-3-*O*-rutinoside, noto-R1, Rb1, HSYA, and AnHSYB) at three concentration levels on UPLC-QTOF and UPLC-QDa by the individual SIM.

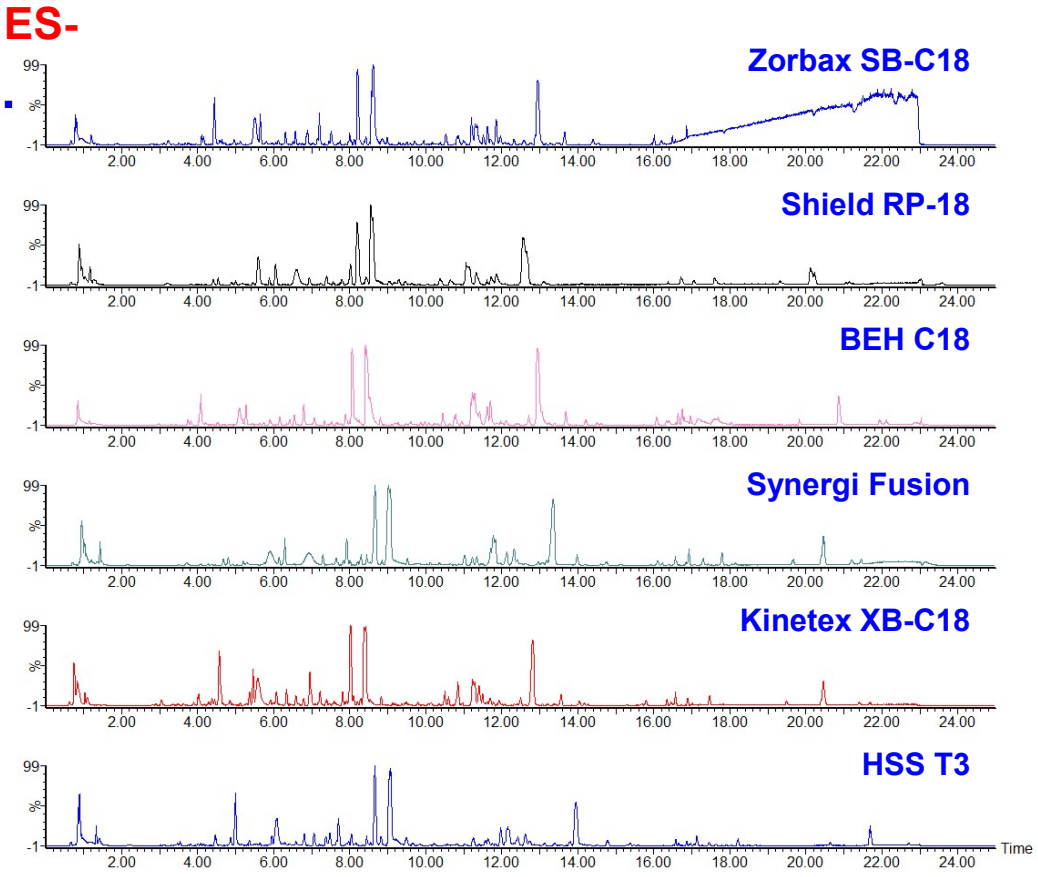
Fig. S21 The SIM spectra of ten batches of commercial SXT samples (S1−S4, S6−S8, and S10−S12) determined on both UPLC-QTOF and UPLC-QDa.

Table S1 Detailed information of the 251 compounds characterized from SXT by UHPLC/QTOF-Fast DDA.

Detailed information of 73 reference standards

A total of 73 reference standards were used for characterization of multi-components in SXT. Amongst them, malonyl ginsenoside-Rb1 (**176**) and -Rd (**198**) were isolated from the root of *P. ginseng*. The other saponin compounds, including notoginsenoside-R_1 (**118**), -R_2 (**166**), -R_3 (**104**), -R_4 (**161**), -G (**136**), -K (**202**), -M (**109**), -T (**158**), -T_5 (**210**), 20(*R*)-noto-R_2 (**170**), ginsenoside-Ra_3 (**167**), -Rb_1 (**173**), -Rb_2 (**184**), -Rc (**178**), -Rd (**196**), -Re (**127**), -Re_3 (**107**), -Rf (**160**), -Rg_1 (**126**), -Rg_2 (**172**), -Ro (**181**), -F_2 (**217**), -Rk_3 (**213**), 20(*S*)-Rg_3 (**223**), 20(*R*)-Rg_3 (**227**), 20-*O*-Glc-Rf (**115**), 20(*S*)-Rh_1 (**174**), 20(*R*)-Rh_1 (**179**), 20(*S*)-Rh_2 (**247**), 20(*R*)-Rh_2 (**248**), 20(*S*)-sanchirhinoside-A_3 (**145**), -A_4 (**137**), -A_5 (**122**), vinaginsenoside-R_4 (**151**), 5,6-didehydroginsenoside-Rb_1 (**169**), compound K (**245**), and 20(*S*)-PPT (**234**), were isolated from the root of *P. notoginseng*. Cis-*p*-coumaric acid-4-*O*-*β*-D-glucoside (**32**), trans-*p*-coumaric acid-4-*O*-*β*-D-glucoside (**15**), syringin (**31**), saffloquinoside A (**95**), hydroxysafflor yellow A (**39**, HSYA), isosafflomin C (**119**), safflomin C (**125**), anhydrosafflor yellow B (**91**, AnHSYB), quercetin (**140**), quercetin-7-*O*-*β*-D-glucoside (**83**), quercetin-3-*O*-*β*-D-glucoside (**84**), kaempferol-3-*O*-*β*-D-glucoside (**99**), (2*S*)-4',5,6,7-tetrahydroxy-flavanone-6-*O*-*β*-D-glucoside (**88**), 5,7,4'-trihydroxy-6-methoxyflavonol-3-*O*-*β*-D-rutinoside (**93**), 6-hydroxykaempferol-3-*O*-*β*-D-glucoside (**77**), kaempferol-3-*O*-rutinoside (**90**, KR), kaempferol-3-*O*-*β*-D-glucosyl-(1→2)-*β*-D-glucoside (**75**), rutin (**81**), 6-hydroxyapigenin-6-*O*-*β*-D-glucoside-7-*O*-*β*-D-glucuronide (**63**), 6-hydroxykaempferol-3,6-di-*O*-*β*-D-glucoside (**59**), 6-hydroxykaempferol-3-*O*-*β*-D-rutinoside-6-*O*-*β*-D-glucoside (**58**), 6-hydroxy kaempferol-3,6,7-tri-*O*-*β*-D-glucoside (**25**), and (2*E*,8*E*,10*E*)-12*R*-tridecatriene-4,6-diyne-1,12,13-triol-1-*O*-*β*-D-glucoside (**71**), were isolated from the floret of *C. tinctorius*. Four phthalides, including *Z*-ligustilide (**230**, ZL), senkyunolide I (**114**), senkyunolide H (**124**), and levistolide A (**250**, LA), were isolated from *L. chuanxiong*. Neochlorogenic acid (**14**), chlorogenic acid (**33**), 3,5-di-*O*-caffeoylquinic acid (**100**), ferulic acid (**80**, FA), kaempferol (**163**), luteolin (**139**), and luteolin-7-*O*-*β*-D-glucoside (**85**), were purchased from National Institute for the Control of

Pharmaceutical and Biological Products (Beijing, China) or Shanghai U-sea Biotech Co., Ltd. (Shanghai, China).


ES-
Zorbax SB-C18
Shield RP-18
BEH C18
Synergi Fusion
Kinetex XB-C18
HSS T3
99
%
-1
2.00
4.00
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18.00
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Time

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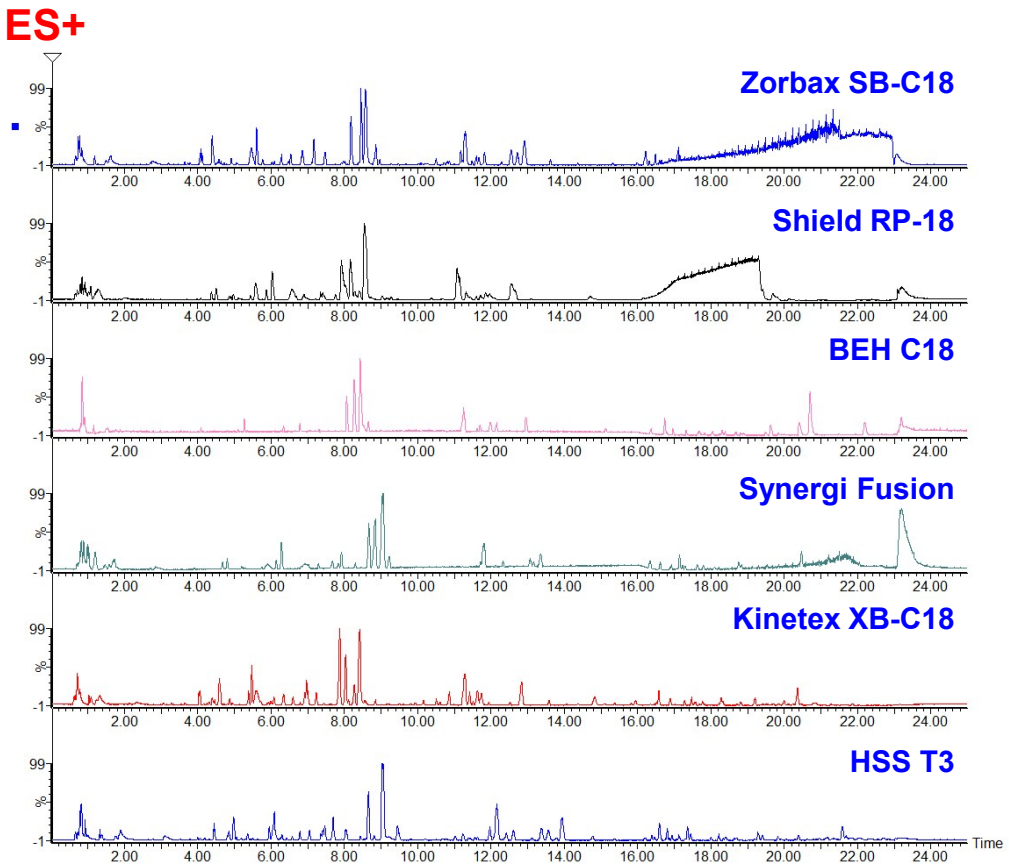


Fig. S1 Comparison of six different UHPLC columns for the separation of multi-components from SXT in the negative (ES-) and positive (ES+) ion modes, respectively.

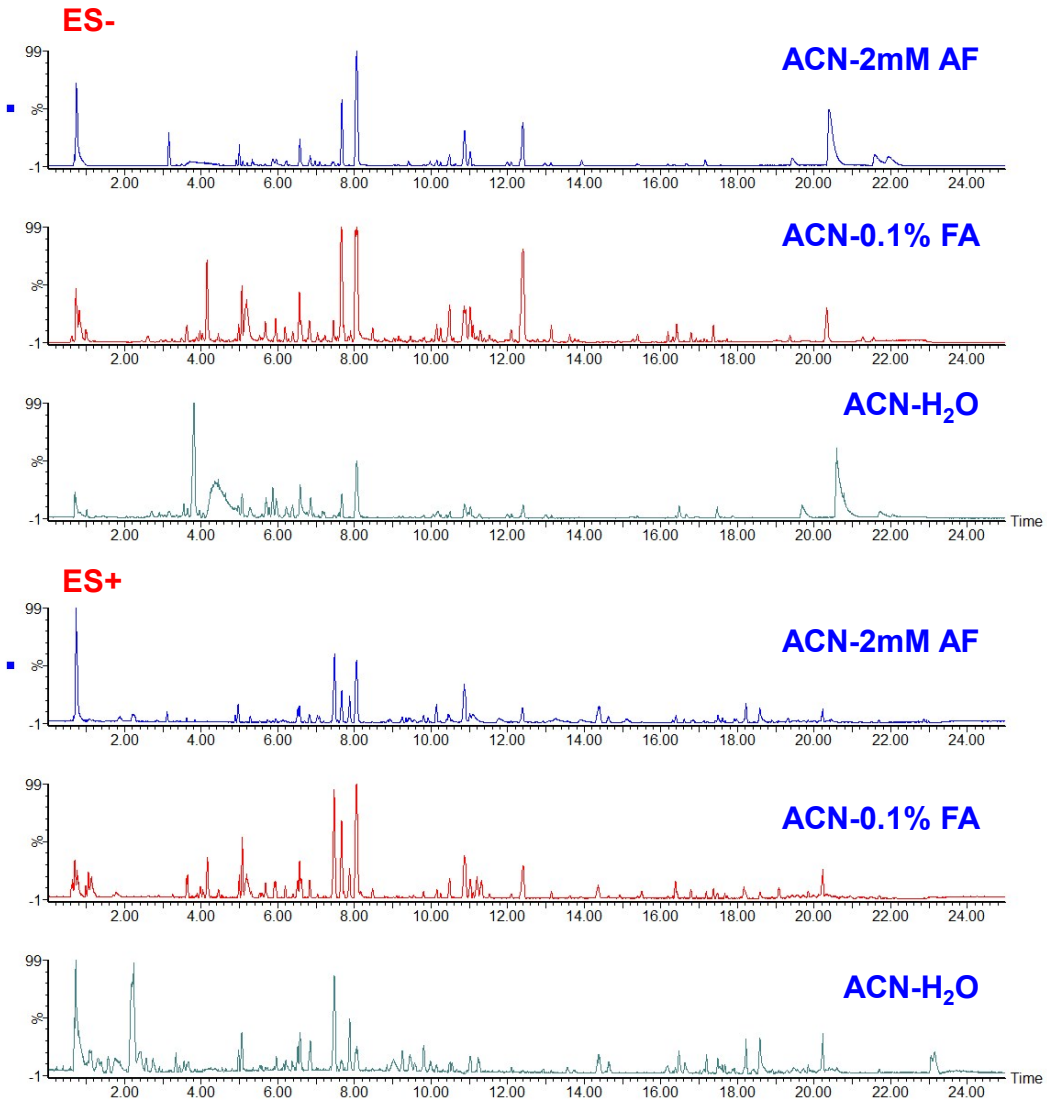


Fig. S2 Comparison of the effluence of different compositions of mobile phase on the resolution and ion response of SXT componnets in the both modes. **ACN:** acetonitrile; **FA**: formic acid; **AF**: ammonium formate.

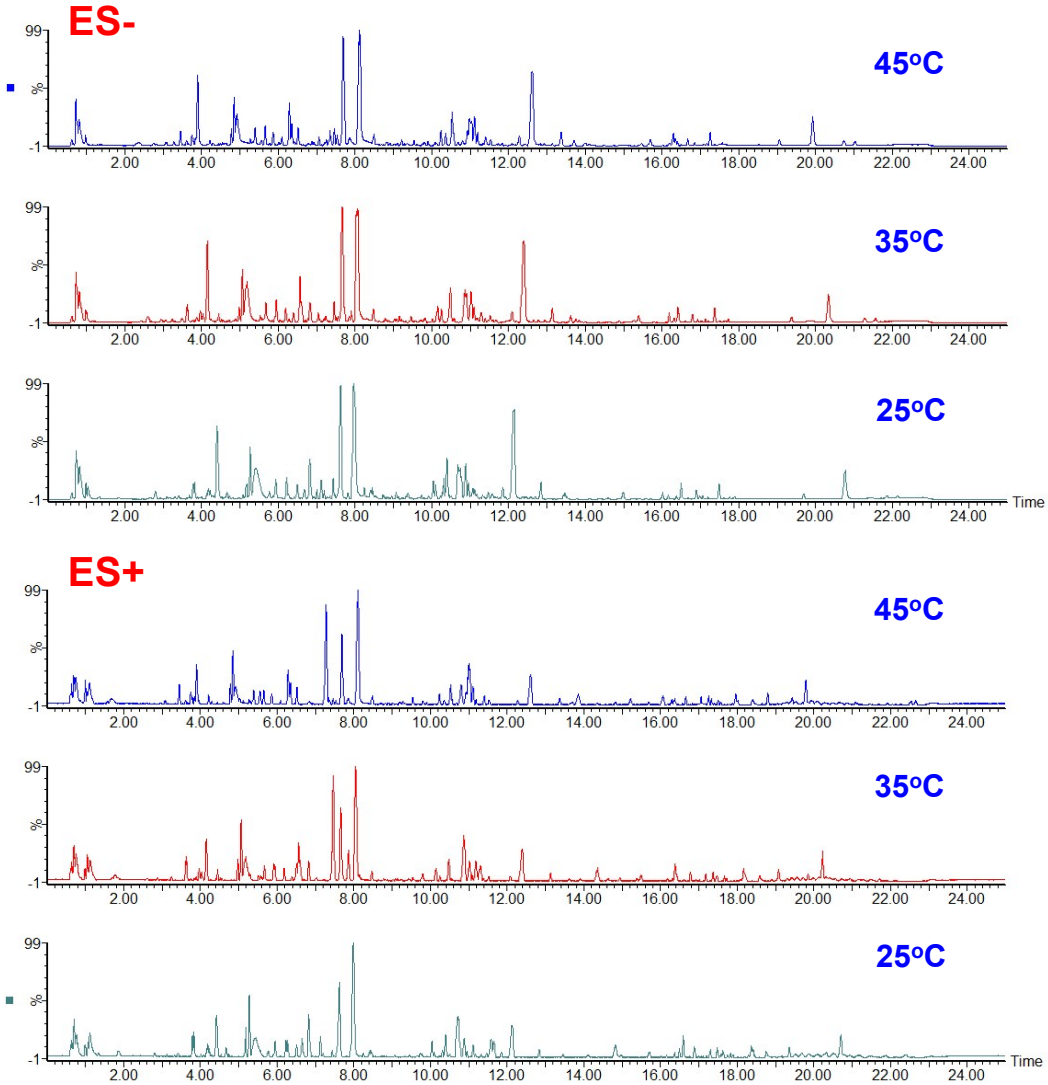


Fig. S3 Comparison of the influence of different column temperatrue on the separation of compounds from SXT in both ionization modes.

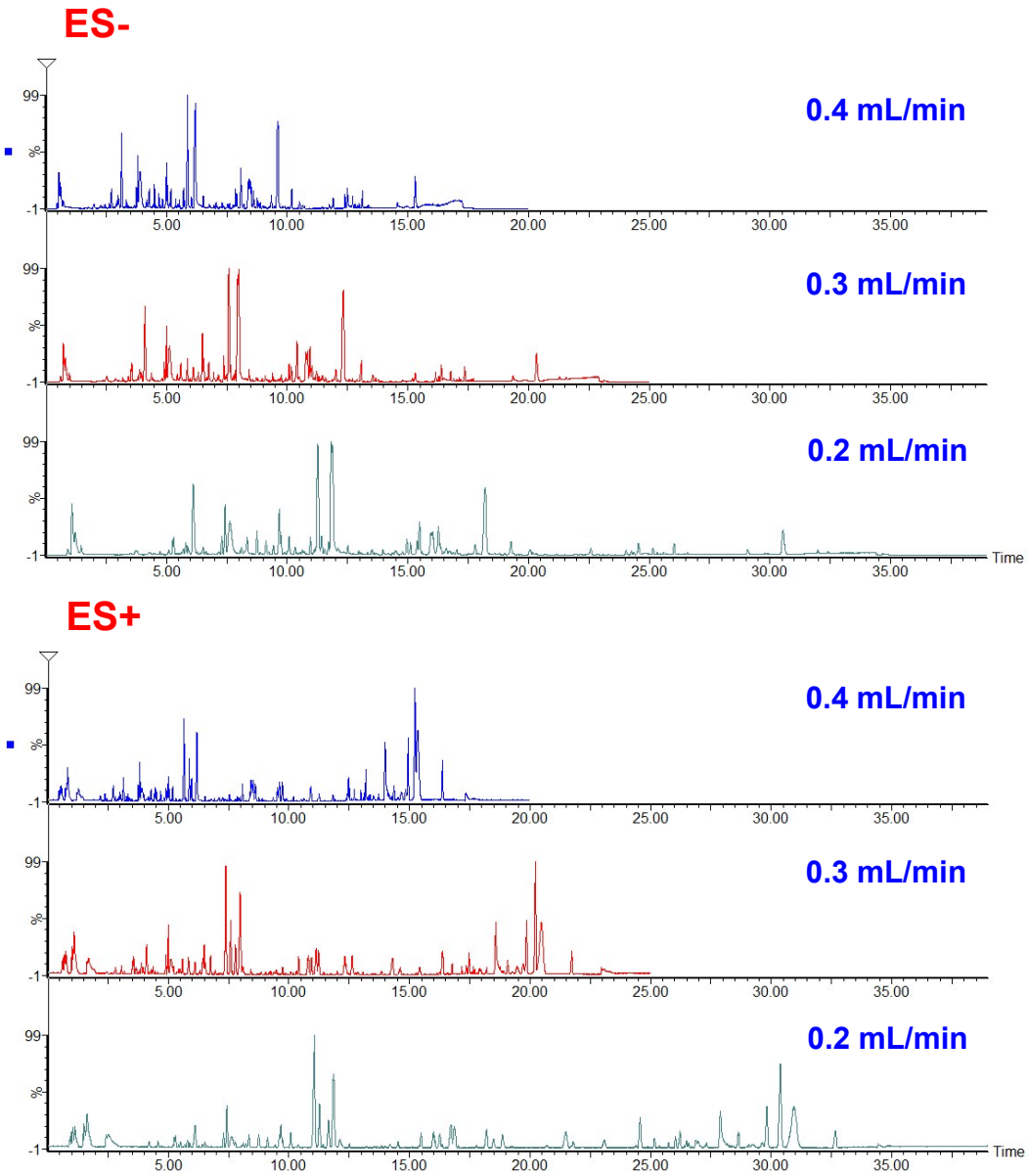


Fig. S4 Comparison of the influence of different flow rates on the separation of compounds from SXT in both ionization modes.

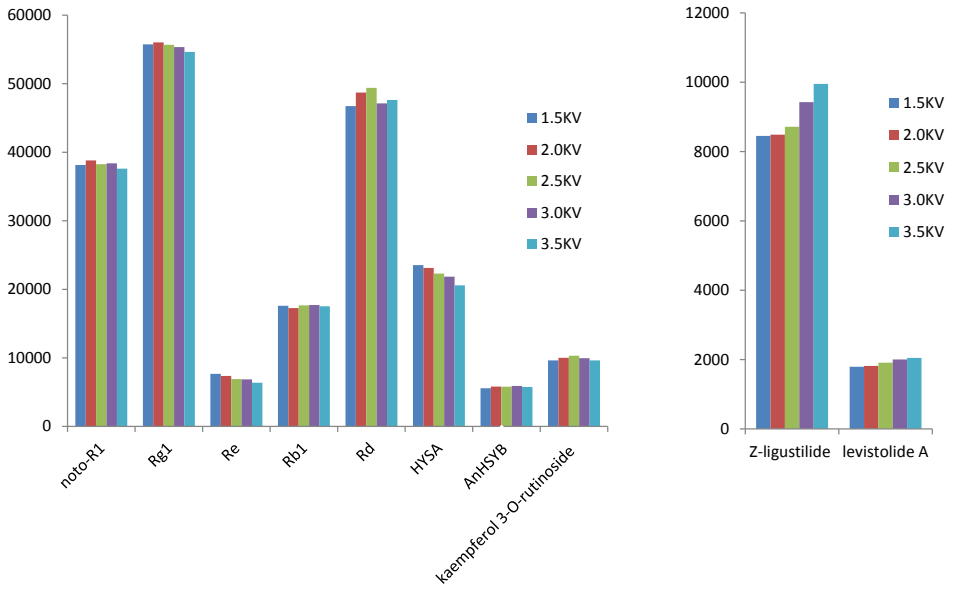


Fig. S5 Comparison of the peak areas of ten index compounds obtained under five different spray voltages (1.5 kV to 3.5 kV).

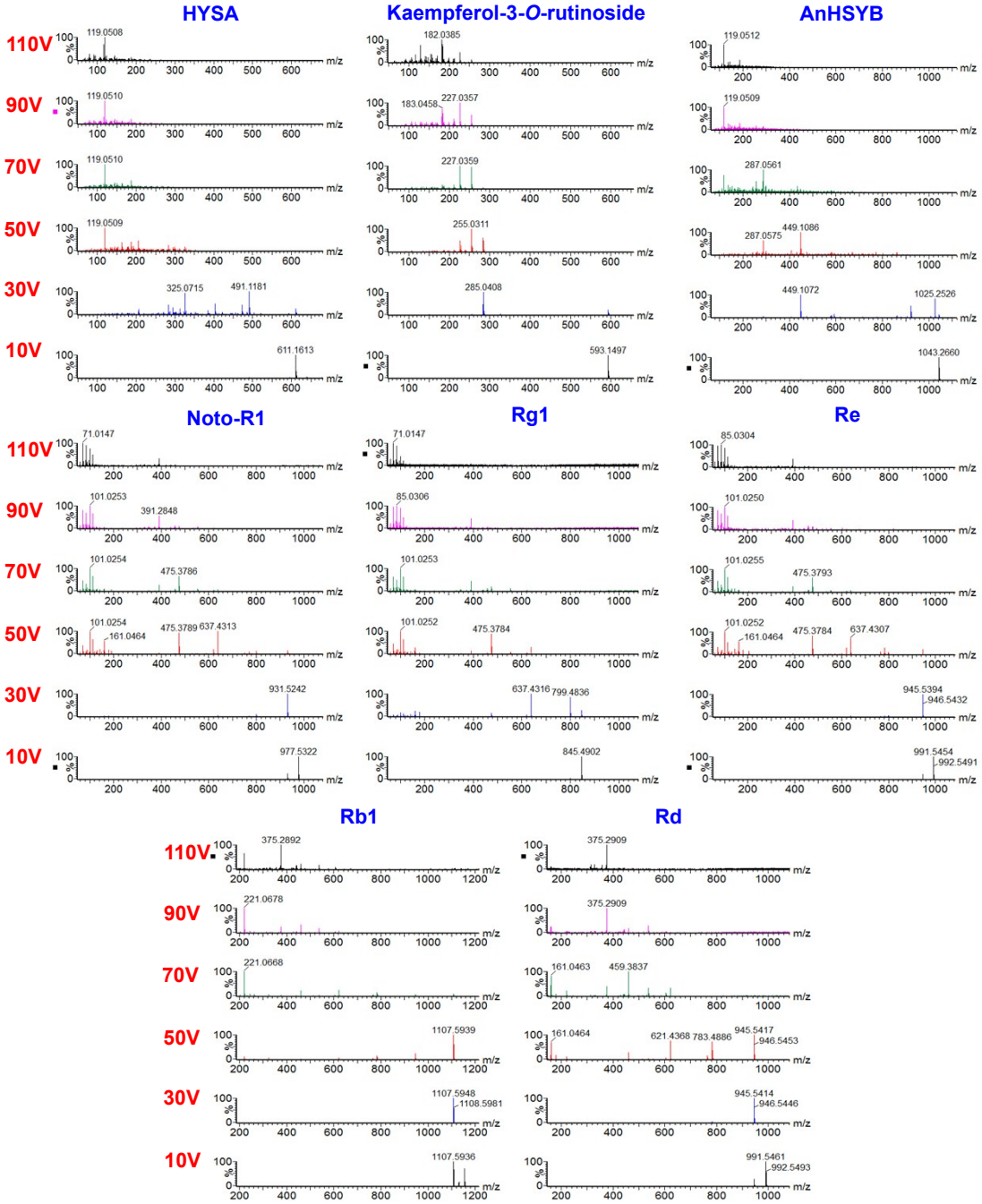


Fig. S6 The Fast DDA-MS^2 spectra of 8 representative compounds (noto-R1, Rg1, Re, Rb1, Rd, HSYA, AnHSYB and kaempferol 3-*O*-rutinoside) obtained in negative mode under constant collision energies rangeing from 10 V to 110 V.

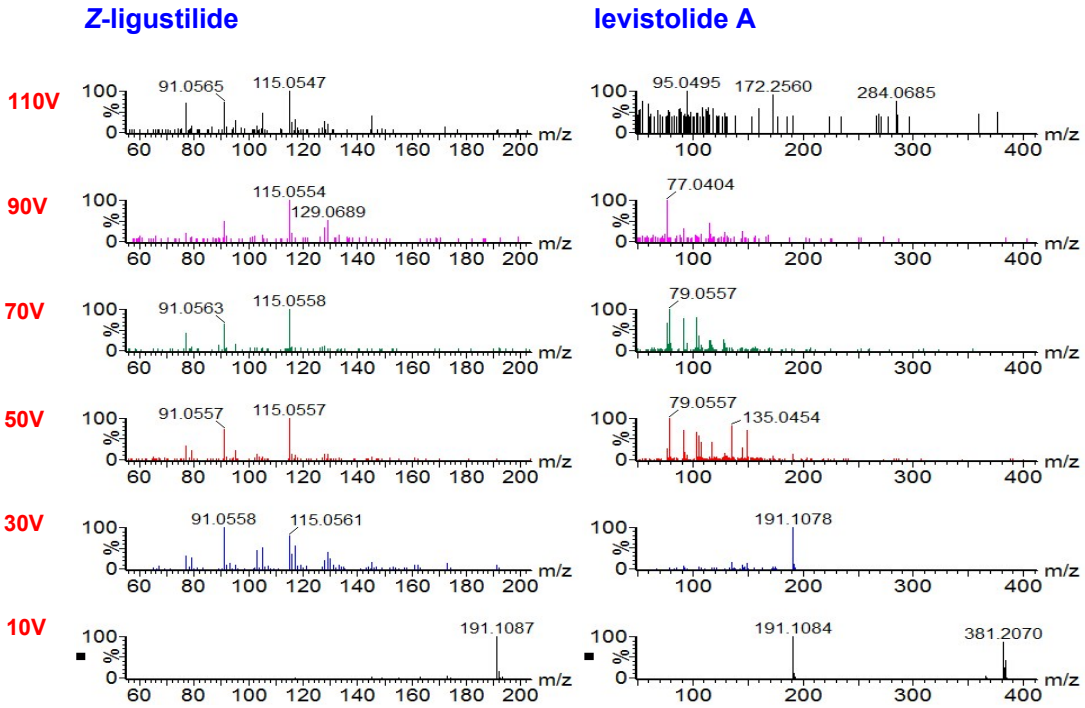


Fig. S7 The Fast DDA-MS^2 spectra of 2 representative compounds (*Z*-ligustilide and levistolide A) obtained in ES+ under constant collision energies ranging from 10 V to 110 V.

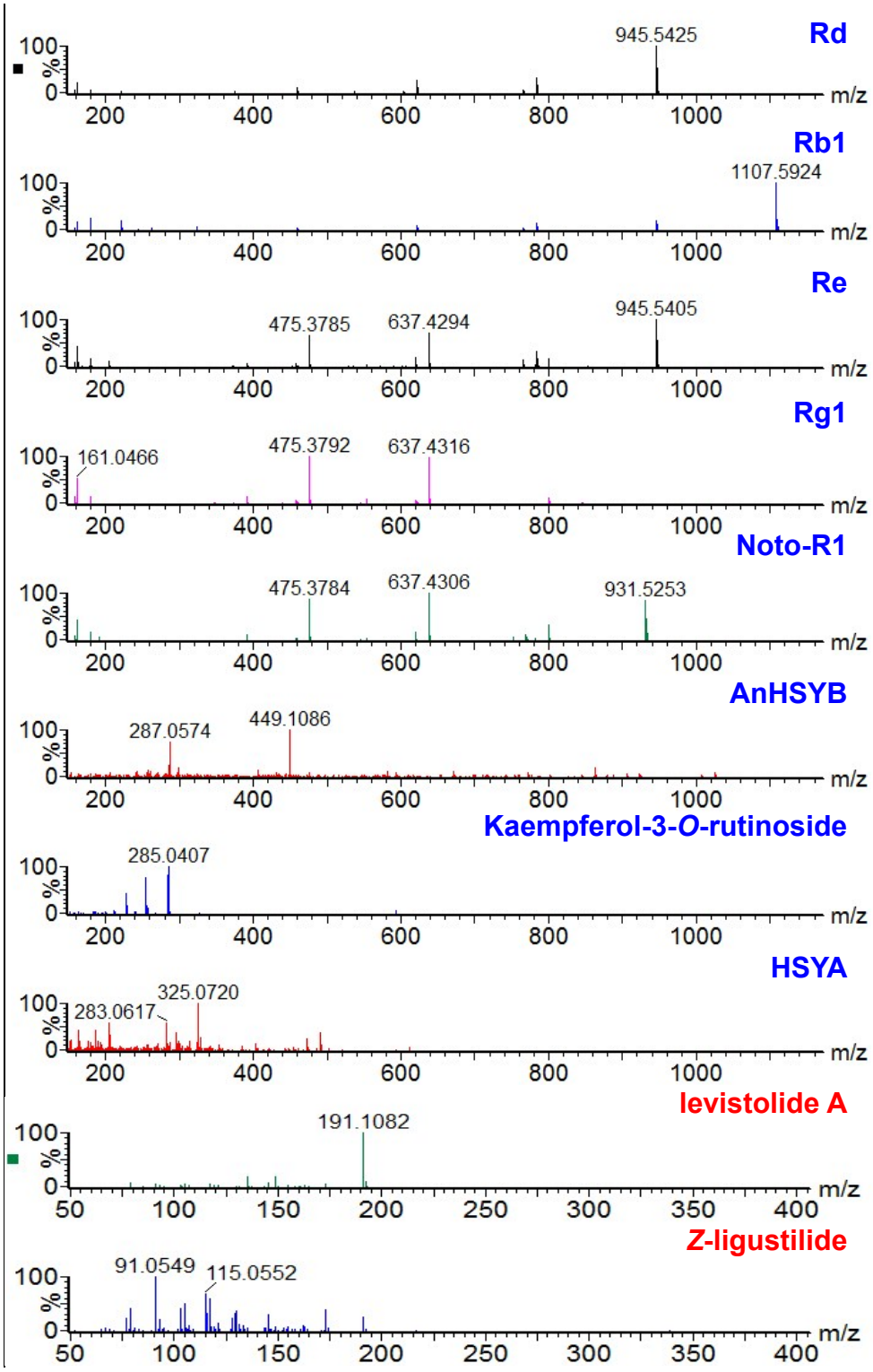
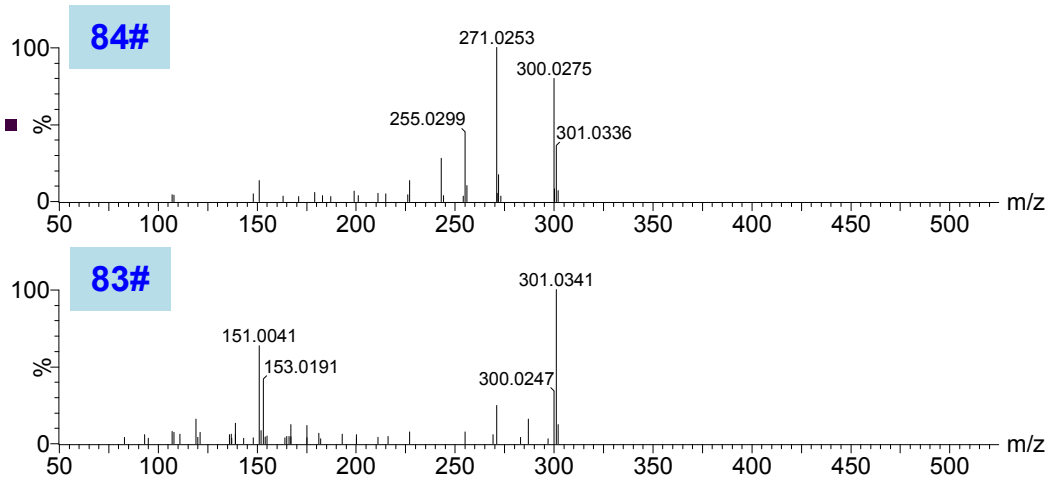


Fig. S8 The Fast DDA-MS^2 spectra of representative compounds in optimzied CE Noto-R1, Rg1, Re, Rb1, Rd, HSYA, AnHSYB, and kaempferol 3-*O*-rutinoside, in ES-; *Z*-ligustilide and levistolide A in ES+.



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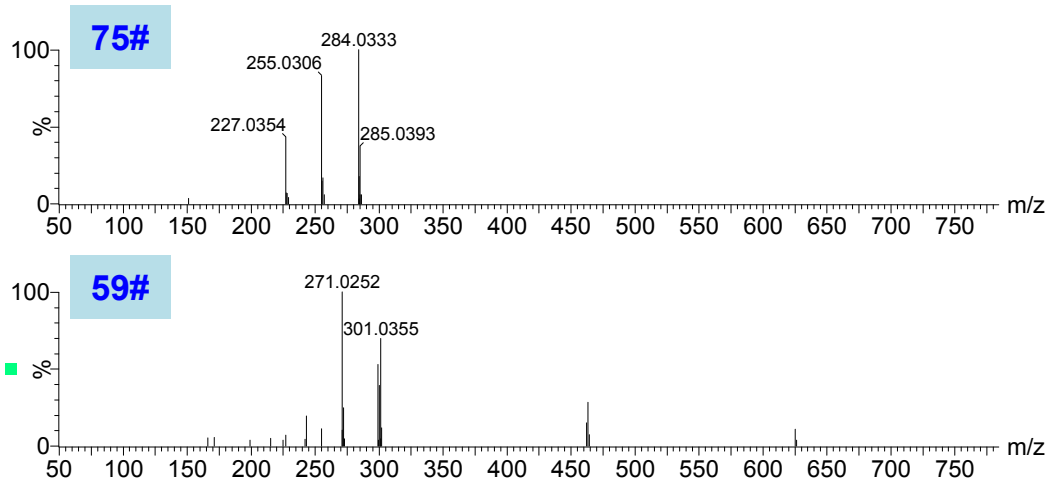
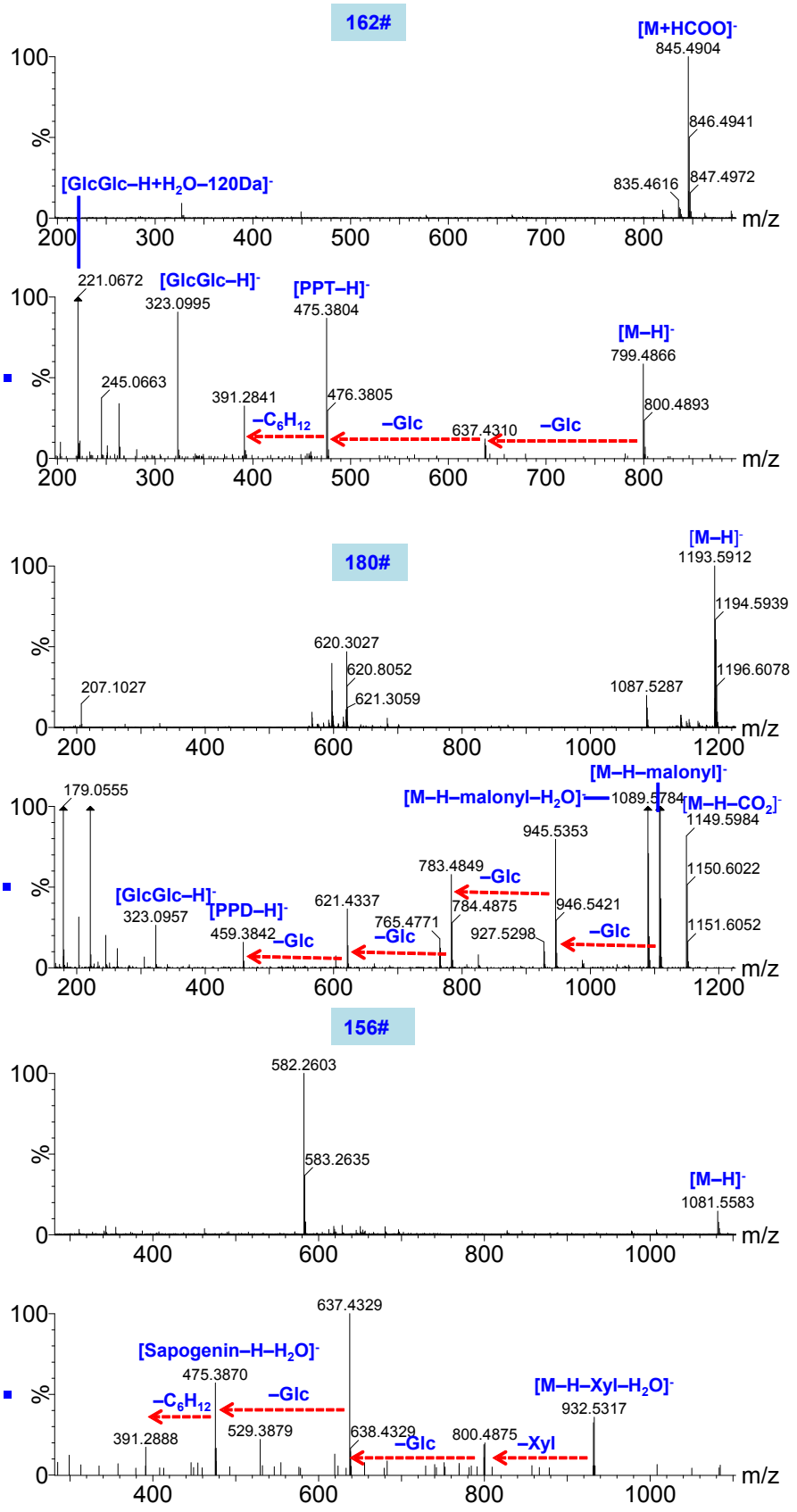


Fig. S10 The MS^2 spectra of kaempferol-3-*O*-*β*-D-glucosyl(1→2)-*β*-D-glucoside (**75**) and 6-hydroxykaempferol-3,6-di-*O*-*β*-*D*-glucoside (**59**).



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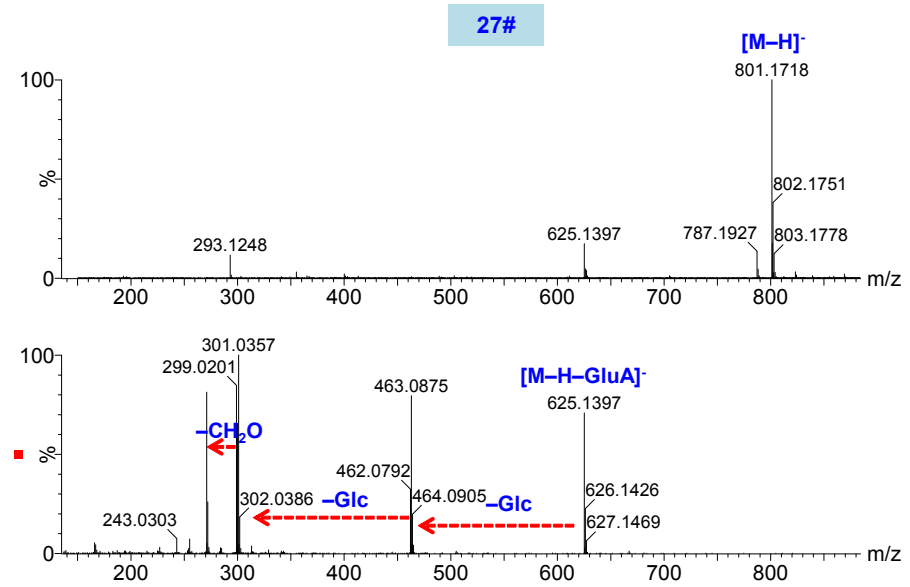

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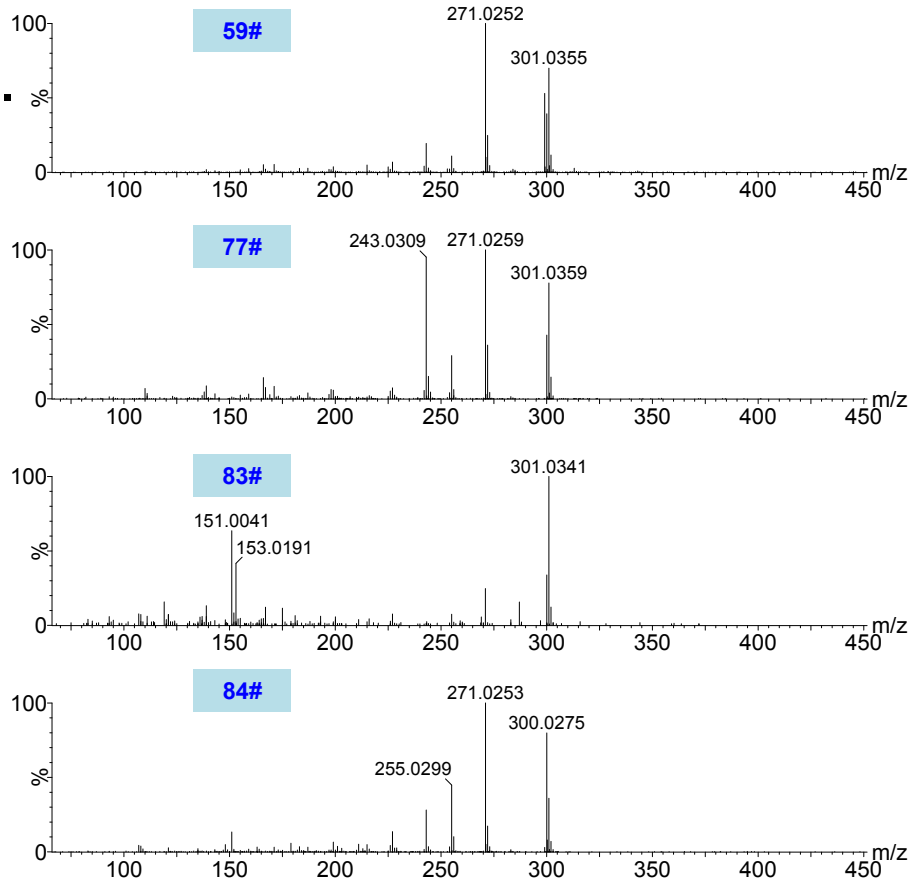

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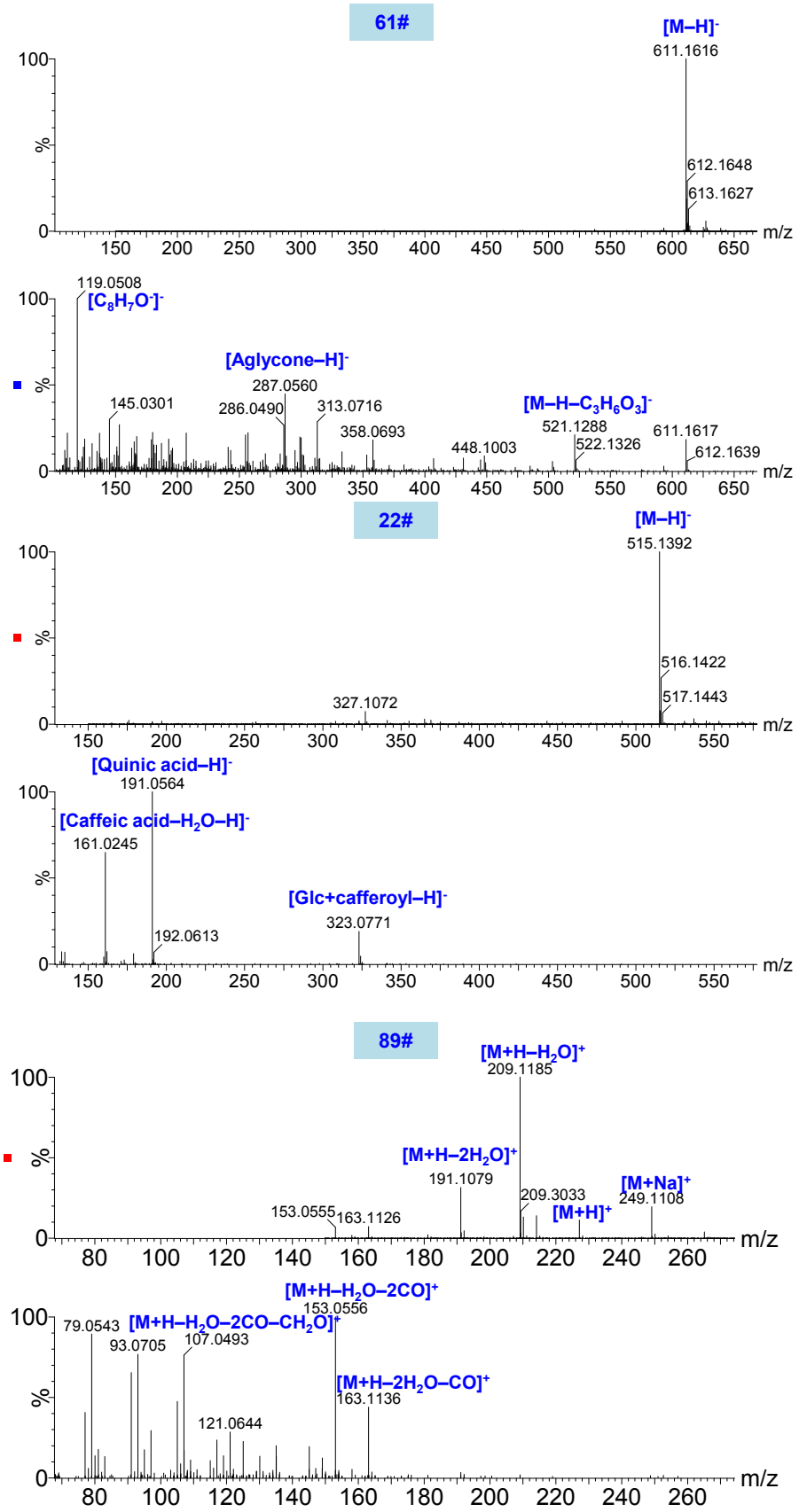

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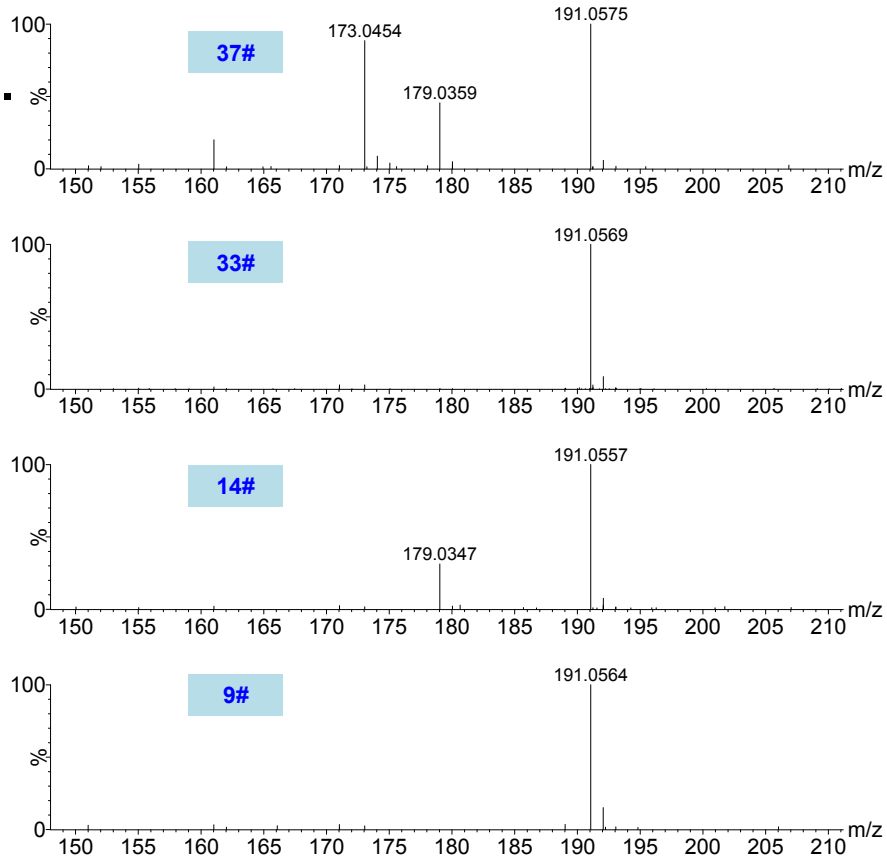

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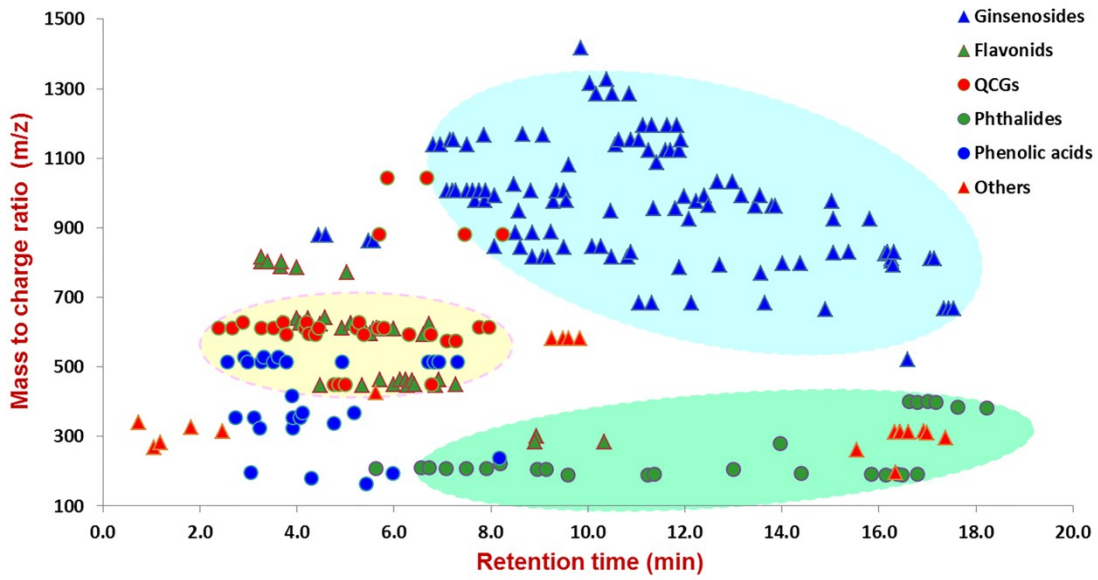

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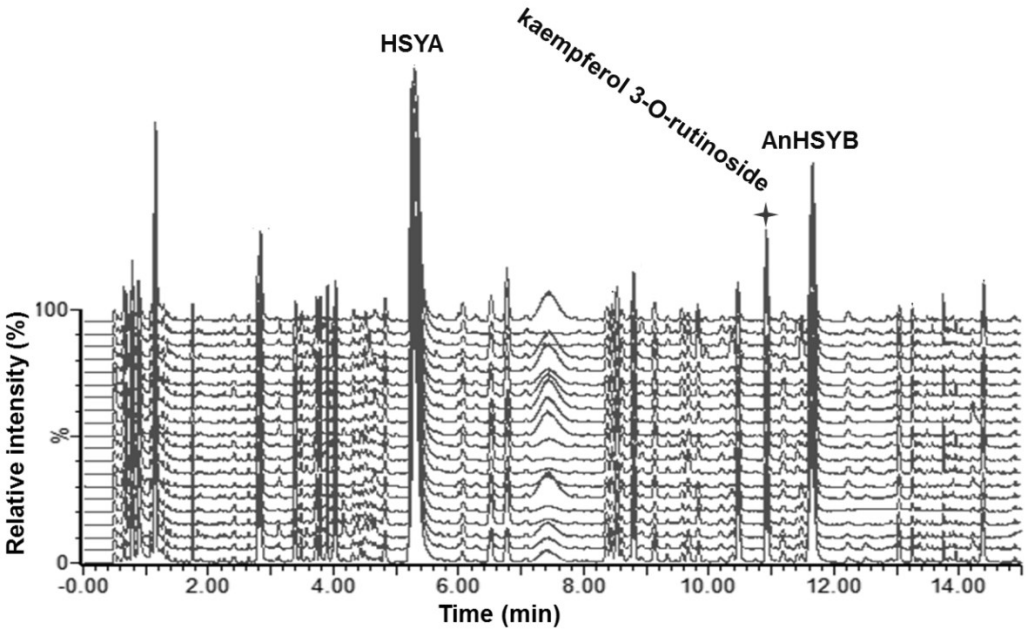

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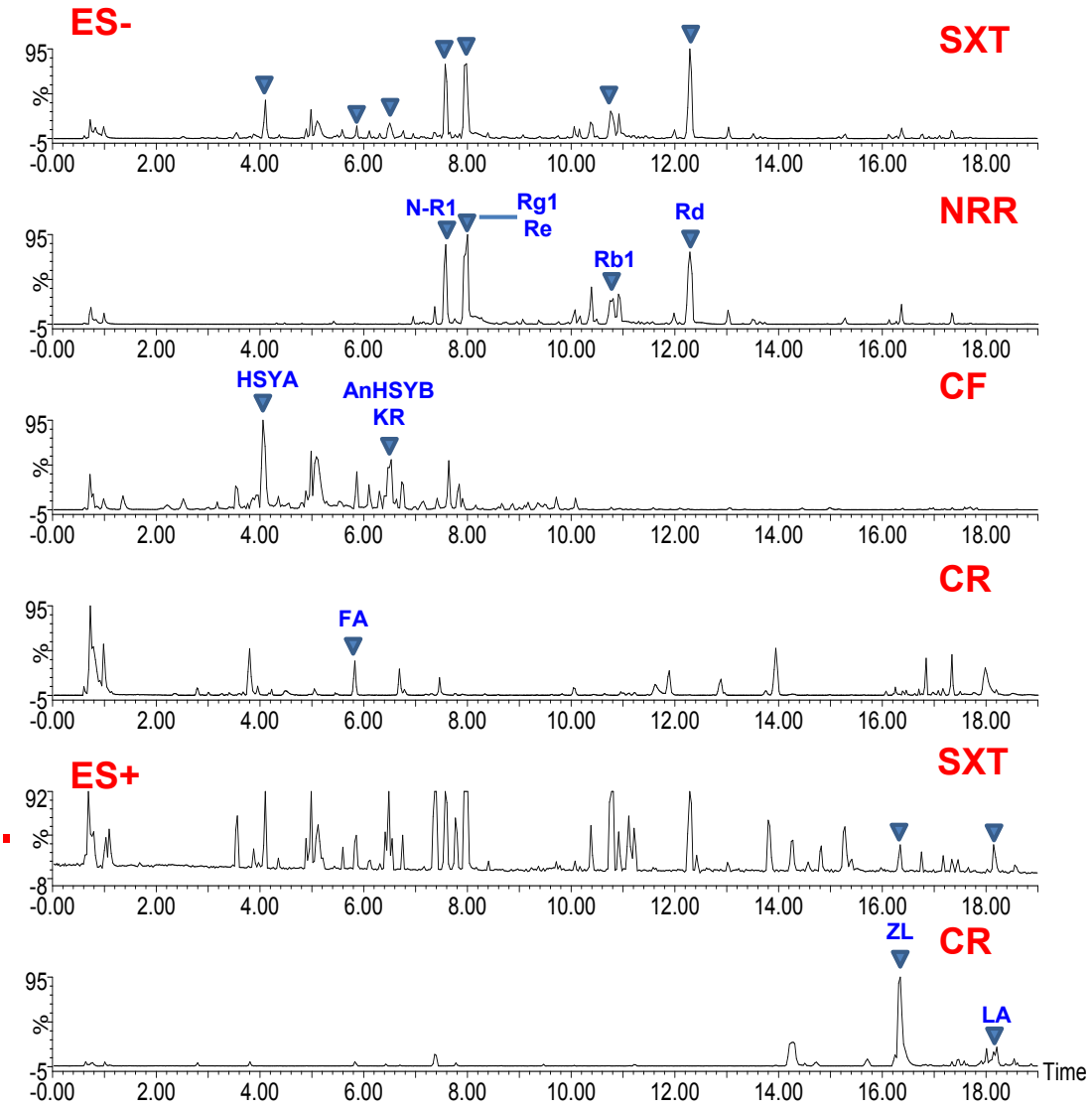

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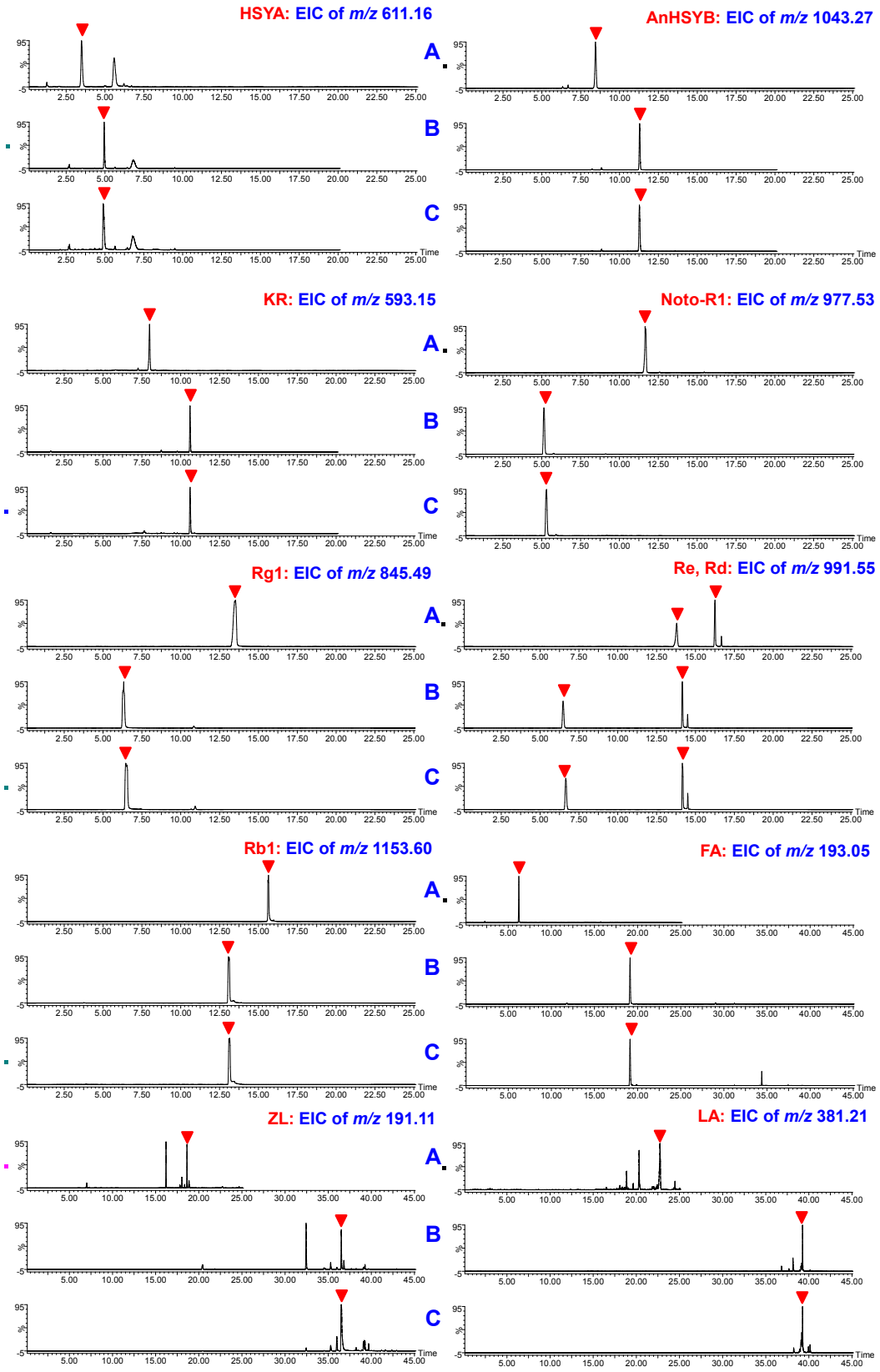

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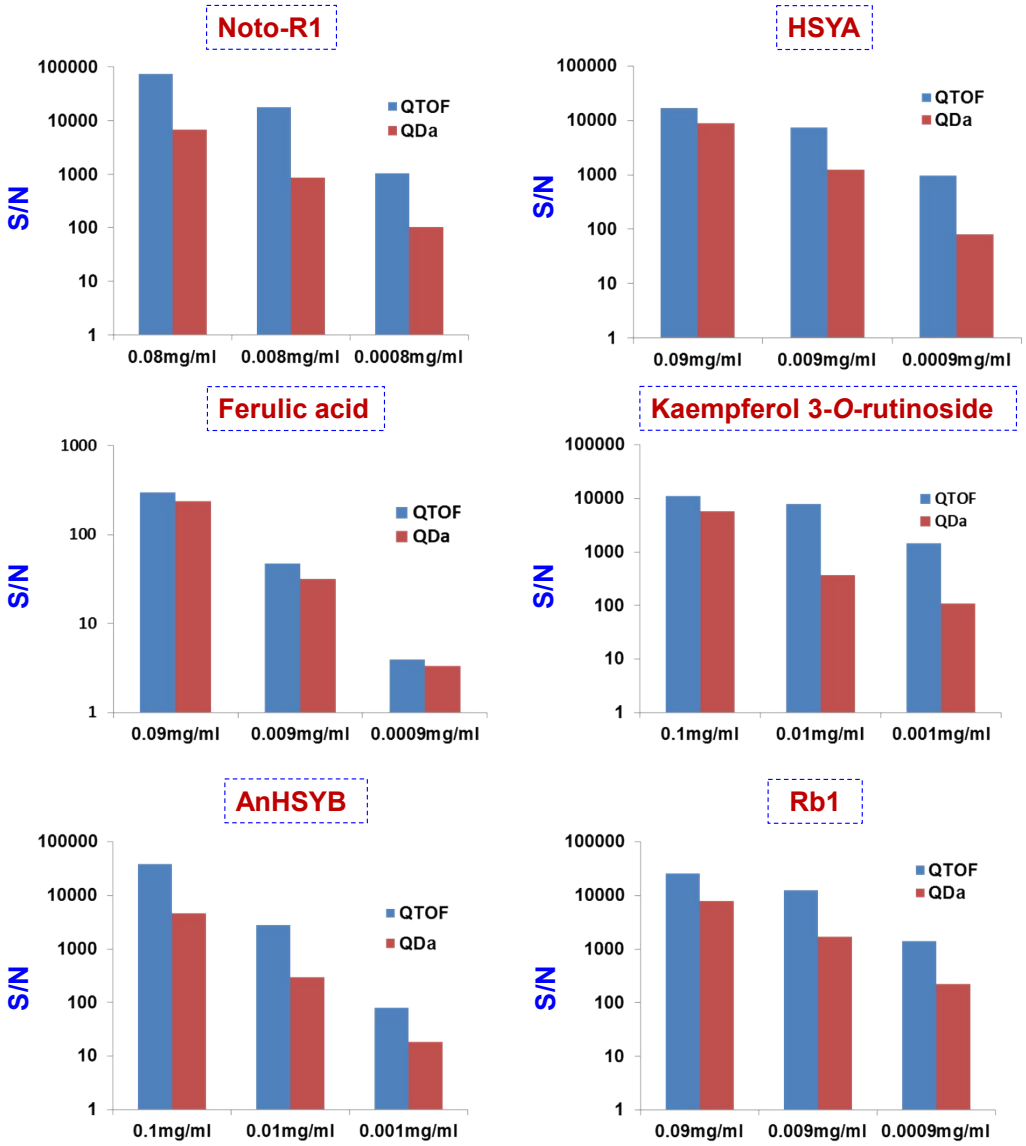

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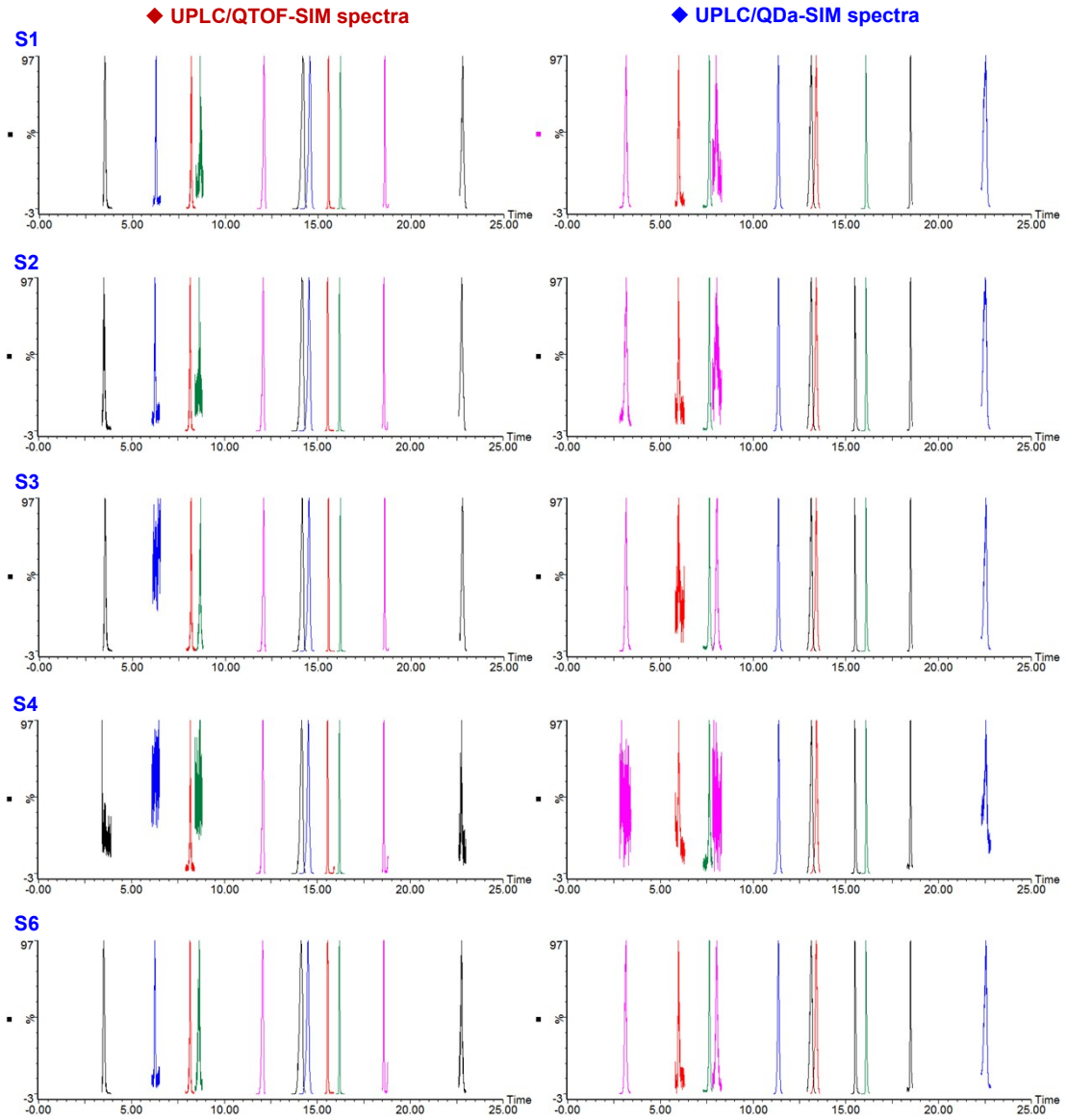
◆ UPLC/QTOF-SIM spectra
◆ UPLC/QDa-SIM spectra
S1
S2
S3
S4
S6
97
%
-3
-0.00
5.00
10.00
15.00
20.00
25.00
Time

(**Continnued**)

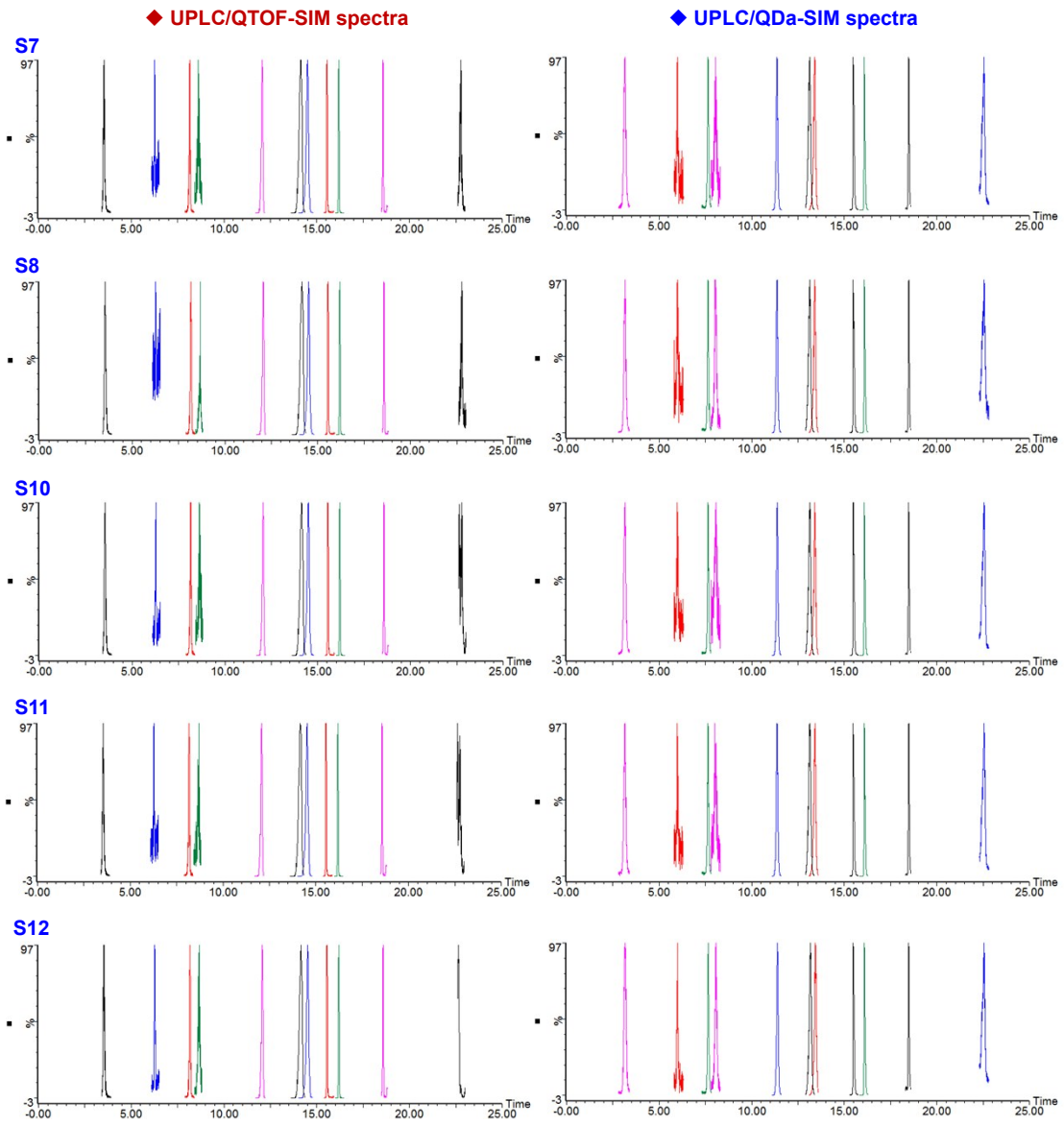

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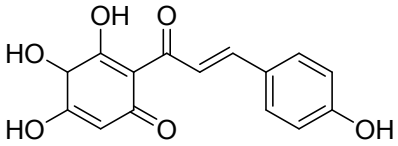
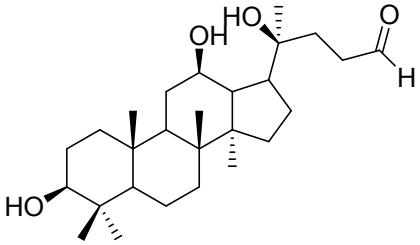
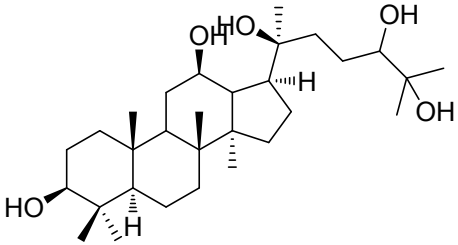
Table S1 Detailed information of the 250 compounds characterized from SXT by UHPLC/QTOF-Fast DDA.



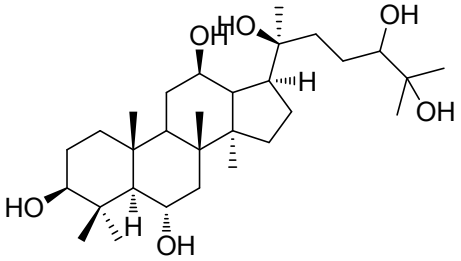
X



E-1



F-1



G-1

No.	t_R (min)	m/z	Precursor ions	Mass error (ppm)	Formula	MS/MS ions	Identification	Subclass	Source
1	0.73	341.1089	$[M-H]^-$	1.5	C12H22O11	113-101-71	lactose or isomer	others	LC/CT/PN
2	1.05	268.1053	$[M+H]^+$	2.6	C10H13N5O4	136- 119	adenosine	others	LC/CT/PN
3	1.19	282.0846	$[M-H]^-$	2.8	C10H13N5O5	150-133-108	guanosine	others	LC/CT/PN
4	1.82	326.1249	$[M-H]^-$	2.8	C15H21NO7	164-147	N-D-fructose-1-yl-L-phenylalanine or isomer	others	LC/CT
5	2.38	611.1593	$[M-H]^-$	-3.1	C27H32O16	593-491-473	hydroxysafflor yellow B/C or safflomin A or isomer	QCGs	CT
6	2.47	315.0732	$[M-H]^-$	5.1	C13H16O9	152-108	protocatechuic acid 4-glucoside or isomer	others	LC
7	2.57	515.1398	$[M-H]^-$	-0.6	C22H28O14	191-179-135	caffeoylquinic acid glycoside	phenolic acids	LC
8	2.67	611.1622	$[M-H]^-$	1.6	C27H32O16	491-328-283-119	hydroxysafflor yellow B/C or safflomin A or isomer	QCGs	CT
9	2.73	353.0877	$[M-H]^-$	1.1	C16H18O9	191-135-85	1-*O*-caffeoylquinic acid	phenolic acids	LC
10	2.88	627.1542	$[M-H]^-$	-3	C27H32O17	627-463-343-153	methylsafflomin C/methylisosafflomin C or isomer	QCGs	CT
11	2.91	529.1523	$[M-H]^-$	-6.4	C23H30O14	193-178-149-134	5-*O*-(4'-[*β*-D-glucopyranosyl]-trans-feruloyl) quinic acid or isomer	phenolic acids	LC

12	2.98	515.1388	$[M-H]^-$	-2.5	$C_{22}H_{28}O_{14}$	191-179-135	caffeoylquinic acid glycoside	phenolic acids	LC
13	3.04	197.0092	$[M-H]^-$	3	$C_8H_6O_6$	109-	terephthalic acid or isomer	phenolic acids	LC
14[a]	3.11	353.0873	$[M-H]^-$	0	$C_{16}H_{18}O_9$	191-135-85	5-*O*-caffeoylquinic acid (neochlorogenic acid)	phenolic acids	LC/CT
15[a]	3.23	325.0938	$[M-H]^-$	4.6	$C_{15}H_{18}O_8$	163-119-93	trans-*p*-coumaric acid-4-*O*-*β*-D-glucopyranoside	phenolic acids	CT
16	3.26	803.1865	$[M-H]^-$	-2.1	$C_{33}H_{40}O_{23}$	641- 478- 317- 286- 258- 202	6-Hydroxyquercetin-3,6,7-tri-*O*-*β*-D-glucoside (6-Hydroxyquercetin -Glc-Glc-Glc)	FOGs	CT
17	3.26	817.1658	$[M-H]^-$	-2.1	$C_{33}H_{38}O_{24}$	641-478-315-287-271	6-Hydroxyquercetin-3,6-di-*O*-*β*-glucoside-7-*O*-*β*-glucuronide (6-Hydroxyquercetin -Glc-Glc-GluA)	FOGs	CT
18	3.26	515.1394	$[M-H]^-$	-1.4	$C_{22}H_{28}O_{14}$	179-173-135-93	caffeoylquinic acid glycoside	phenolic acids	CT
19	3.26	611.1605	$[M-H]^-$	-1.1	$C_{27}H_{32}O_{16}$	299-287-183-153-119	hydroxysafflor yellow B/C or isomer	QCGs	CT
20	3.32	529.1558	$[M-H]^-$	0.2	$C_{23}H_{30}O_{14}$	193-191-173-134-93	5-O-(4'-[*β*-D-glucopyranosyl]-trans-feruloyl) quinic acid or isomer	phenolic acids	LC
21	3.39	801.1688	$[M-H]^-$	-4.7	$C_{33}H_{38}O_{23}$	625-463-301-271	6-hydroxykaempferol-3,6-di-*O*-*β*-glucoside-7-*O*-*β*-glucuronide or isomer (6-hydroxykaempferol -Glc-Glc-GluA)	FOGs	CT
22	3.52	515.1392	$[M-H]^-$	-1.7	$C_{22}H_{28}O_{14}$	323-191-161-135-133-93-85	caffeoylquinic acid glycoside	phenolic acids	LC
23	3.52	611.1588	$[M-H]^-$	-3.9	$C_{27}H_{32}O_{16}$	521-300-191-119	hydroxysafflor yellow B/C or safflomin A or isomer	QCGs	CT
24	3.62	529.1566	$[M-H]^-$	-0.2	$C_{23}H_{30}O_{14}$	173-93	5-O-(4'-[β-D-glucopyranosyl]-trans-feruloyl) quinic acid or isomer	phenolic acids	LC
25[a]	3.66	787.1920	$[M-H]^-$	-1.7	$C_{33}H_{40}O_{22}$	625-463-301-299-271	6-Hydroxykaempferol-3,6,7-tri-*O*-*β*-D-glucoside	FOGs	CT
26	3.68	625.1397	$[M-H]^-$	-1.3	$C_{27}H_{30}O_{17}$	625-463-301-271	quercetin (or 6-hydroxykaempferol)-Glc-Glc	FOGs	CT
27	3.68	801.1718	$[M-H]^-$	-1.0	$C_{33}H_{38}O_{23}$	625-463-301-299-271	6-hydroxykaempferol-3,6-di-O-β-glucoside-7-O-β-glucuronide or isomer (6-hydroxykaempferol-Glc-Glc-GluA)	FOGs	CT
28	3.71	627.1562	$[M-H]^-$	0.2	$C_{27}H_{32}O_{17}$	623-507-419-299-205-135	methylsafflomin C/methylisosafflomin C or isomer	QCGs	CT
29	3.78	515.1401	$[M-H]^-$	0.0	$C_{22}H_{28}O_{14}$	341-191-179-173-135-93	caffeoylquinic acid glycoside	phenolic acids	LC

30	3.78	593.1506	$[M-H]^-$	0.0	C27H30O15	575-483-119	saffloquinoside C or safflow yellow A	QCGs	CT
31[a]	3.90	417.1404	$[M+HCOO]^-$	1.7	C17H24O9	191-135-119	syringin	phenolic acids	CT
32[a]	3.91	325.0911	$[M-H]^-$	-3.7	C15H18O8	no	cis-*p*-coumaric acid-4-*O*-*β*-D-glucopyranoside	phenolic acids	CT
33[a]	3.92	353.0874	$[M-H]^-$	0.3	C16H18O9	191-85	3-*O*-caffeoylquinic acid (chlorogenic acid)	phenolic acids	LC/CT
34	4.00	639.1201	$[M-H]^-$	0.6	C27H28O18	463-300-271-255-243	quercetin (or 6-hydroxykaempferol)-Glc-GluA	FOGs	CT
35	4.00	785.1776	$[M-H]^-$	0.0	C33H38O22	609-463-447-301-271-255-243	quercetin (or 6-hydroxykaempferol)-Rha-Glc-GluA	FOGs	CT
36	4.06	625.1420	$[M-H]^-$	2.4	C27H30O17	462-299-271-151	quercetin (or 6-hydroxykaempferol)-Glc-Glc	FOGs	LC/CT
37	4.06	353.0889	$[M-H]^-$	4.5	C16H18O9	191-173-135-93	4-*O*-caffeoylquinic acid	phenolic acids	CT
38	4.12	367.1031	$[M-H]^-$	0.5	C17H20O9	119-	3-feruloylquinic acid or isomer	phenolic acids	LC
39[a]	4.17	611.1609	$[M-H]^-$	-0.5	C27H32O16	491-471-325-283-205-163-119	hydroxysafflor yellow A	QCGs	CT
40	4.17	625.1407	$[M-H]^-$	0.3	C27H30O17	463-301-271-255-243-178	quercetin (or 6-hydroxykaempferol)-Glc-Glc	FOGs	CT
41	4.20	627.1551	$[M-H]^-$	-1.6	C27H32O17	627-419-299-207-178-119	methylsafflomin C/methylisosafflomin C or isomer	QCGs	CT
42	4.23	639.1192	$[M-H]^-$	-0.8	C27H28O18	463-301-271-255-243-165-139	quercetin (or 6-hydroxykaempferol)-Glc-GluA	FOGs	CT
43	4.25	595.1657	$[M-H]^-$	-1.0	C27H32O15	385-355-313-119	dihydrosaffloquinoside A or isomer	QCGs	CT
44	4.29	179.0354	$[M-H]^-$	5.6	C9H8O4	135-	caffeic acid	phenolic acids	LC/CT
45	4.38	593.1505	$[M-H]^-$	-0.2	C27H30O15	447-299-119	saffloquinoside C or safflow yellow A	QCGs	CT
46	4.44	611.1606	$[M-H]^-$	-1.0	C27H32O16	521-491-328-119	hydroxysafflor yellow B/C or safflomin A or isomer	QCGs	CT
47	4.44	879.4934	$[M+HCOO]^-$	-2.2	C42H74O16	671-653-510-496	notoginsenoside J or isomer ((G-1)-Glc-Glc)	saponins	PN
48	4.47	447.0922	$[M-H]^-$	-1.1	C21H20O11	284-255-227	kaempferol-Glc	FOGs	CT
49	4.47	623.1249	$[M-H]^-$	0.2	C27H28O17	447-284-255-227	kaempferol-Glc-GluA	FOGs	CT
50	4.57	641.1358	$[M-H]^-$	0.6	C27H30O18	641-479-317-287	6-hydroxyquercetin-Glc-Glc	FOGs	CT
51	4.60	879.4927	$[M+HCOO]^-$	-3.0	C42H74O16	671-653-509-367	notoginsenoside J or isomer ((G-1)-Glc-Glc)	saponins	PN
52	4.76	337.0935	$[M-H]^-$	3.6	C16H17O8	247-191	*p*-coumaroylquinic acid or isomer	phenolic acids	CT
53	4.76	449.1089	$[M-H]^-$	1.1	C21H22O11	329-287-259-195-181-167-128-119	X+Glc	QCGs	CT

54	4.86	449.1080	$[M-H]^-$	-0.9	$C_{21}H_{22}O_{11}$	329-301-287-223-195-167-119	X+Glc	QCGs	CT
55	4.92	611.1606	$[M-H]^-$	-1.0	$C_{27}H_{32}O_{16}$	449-287-166-119-109	4',5,6,7-tetrahydroxy-flavanone -di-glucoside	FOGs	LC
56	4.92	515.1188	$[M-H]^-$	-0.4	$C_{25}H_{24}O_{12}$	191-179-161-135	di-O-caffeoylquinic acid	phenolic acids	CT
57	4.99	449.1079	$[M-H]^-$	-1.1	$C_{21}H_{22}O_{11}$	329-301-287-195-167-119	X+Glc	QCGs	CT
58[a]	5.03	771.1981	$[M-H]^-$	-0.4	$C_{33}H_{40}O_{21}$	771-609-462-301-271-243-165	6-hydroxykaempferol-3-*O*-*β*-rutinoside-6-*O*-*β*-D-glucoside	FOGs	CT
59[a]	5.11	625.1420	$[M-H]^-$	2.4	$C_{27}H_{30}O_{17}$	625-463-301-271-255-243	6-hydroxykaempferol 3,6- *O*-*β*-diglucoside	FOGs	CT
60	5.18	367.1017	$[M-H]^-$	-3.3	$C_{17}H_{20}O_9$	191-134-93	3-feruloylquinic acid or isomer	phenolic acids	LC
61	5.22	611.1616	$[M-H]^-$	0.7	$C_{27}H_{32}O_{16}$	611-521-287-119	hydroxysafflor yellow B/C or isomer	QCGs	CT
62	5.27	627.1567	$[M-H]^-$	1.0	$C_{27}H_{32}O_{17}$	627-419-299-178-119	methylsafflomin C/methylisosafflomin C or isomer	QCGs	CT
63[a]	5.34	623.1243	$[M-H]^-$	-0.8	$C_{27}H_{28}O_{17}$	623-447-285	6-hydroxyapigenin-6-*O*-*β*-D-glucoside-7-*O*-*β*-D-glucuronide	FOGs	CT
64	5.35	447.0932	$[M-H]^-$	1.1	$C_{21}H_{20}O_{11}$	no	kaempferol-Glc	FOGs	CT
65	5.38	593.1497	$[M-H]^-$	-1.5	$C_{27}H_{30}O_{15}$	119-	saffloquinoside C or isomer	QCGs	CT
66	5.43	163.0404	$[M-H]^-$	5.5	$C_9H_8O_3$	119-93	(*Z*)-3-(4-hydroxyphenyl) acrylic acid	phenolic acids	LC/CT
67	5.48	861.4824	$[M+HCOO]^-$	-2.8	$C_{42}H_{72}O_{15}$	653-491-403	notoginsenoside M/vinaginsenoside R15 (491-Glc-Glc)	saponins	PN
68	5.51	595.1294	$[M-H]^-$	-0.8	$C_{26}H_{28}O_{16}$	300-271-255-243	quercetin (or 6-hydroxykaempferol)-Xyl-Glc	FOGs	CT
69	5.57	609.1448	$[M-H]^-$	-1.3	$C_{27}H_{30}O_{16}$	301-271-243-165-110	quercetin (or 6-hydroxykaempferol)-rutinoside	FOGs	CT
70	5.57	861.4836	$[M+HCOO]^-$	-1.4	$C_{42}H_{72}O_{15}$	653-553-491-403	notoginsenoside M/vinaginsenoside R15 (491-Glc-Glc)	saponins	PN
71[a]	5.62	425.1464	$[M+HCOO]^-$	3.8	$C_{19}H_{24}O_8$	157-143-129	(2*E*,8*E*,10*E*)-12*R*-tridecatriene-4,6-diyne-1,12,13-triol-1-*O*-*β*-D-glucopyranoside	others	CT
72	5.63	207.1024	$[M+H-H2O]^+$	1.4	$C_{12}H_{16}O_4$	207-189-165-153-123-91-79	chuanxiongnolide R2 or isomer	phthalides	LC
73	5.64	611.1610	$[M-H]^-$	-0.3	$C_{27}H_{32}O_{16}$	449-287-164-153-136-119	4',5,6,7-tetrahydroxy-flavanone -di- *O*-*β*-glucoside	FOGs	CT
74	5.67	611.1602	$[M-H]^-$	-1.6	$C_{27}H_{32}O_{16}$	611-449-287-285-256-119	hydroxysafflor yellow B/C or isomer	QCGs	CT
75[a]	5.69	609.1462	$[M-H]^-$	1.0	$C_{27}H_{30}O_{16}$	429-284-255-227	kaempferol-3-O-β-D-glucosyl (1→2)-β-D-glucoside	FOGs	CT

76	5.70	881.2153	$[M-H]^-$	1.5	$C_{42}H_{42}O_{21}$	761-593-449-287	2(X+Glc)-H_2O	QCGs	CT
77[a]	5.71	463.0889	$[M-H]^-$	2.6	$C_{21}H_{20}O_{12}$	301-271-243	6-hydroxykaempferol-3- *O*-*β*-D-glucopyranoside	FOGs	CT
78	5.80	611.1614	$[M-H]^-$	0.3	$C_{27}H_{32}O_{16}$	521-287-119	hydroxysafflor yellow B/C or isomer	QCGs	CT
79	5.86	1043.2675	$[M-H]^-$	0.6	$C_{48}H_{52}O_{26}$	923-449-287-119	anhydrosafflor yellow B isomer	QCGs	CT
80[a]	5.97	193.0517	$[M-H]^-$	8.3	$C_{10}H_{10}O_4$	178-134-133-106	ferulic acid	phenolic acids	LC
81[a]	5.99	609.1469	$[M-H]^-$	2.1	$C_{27}H_{30}O_{16}$	301-271-255-243-227	rutin	FOGs	CT
82	5.99	449.1093	$[M-H]^-$	2.0	$C_{21}H_{22}O_{11}$	287-166-153-119	(2*S*)-4',5,6,7-tetrahydroxy-flavanone -D-glucoside	FOGs	CT
83[a]	6.12	463.0872	$[M-H]^-$	-1.1	$C_{21}H_{20}O_{12}$	301-287-271-151	quercetin-7- *O*-*β*-D-glucoside	FOGs	CT
84	6.25	463.0878	$[M-H]^-$	0.2	$C_{21}H_{20}O_{12}$	300-271-255-243	quercetin-3- *O*-*β*-D-glucoside	FOGs	CT
85[a]	6.28	447.0926	$[M-H]^-$	-0.2	$C_{21}H_{20}O_{11}$	285-151-133-107	luteolin-7-O- *O*-*β*-glucopyranoside	FOGs	CT
86	6.31	593.1498	$[M-H]^-$	-1.3	$C_{27}H_{30}O_{15}$	310-177-119	saffloquinoside C or safflow yellow A	QCGs	CT
87	6.37	461.0711	$[M-H]^-$	-2.0	$C_{21}H_{18}O_{12}$	285-271-255	Kaempferol-GluA	FOGs	CT
88[a]	6.43	449.1077	$[M-H]^-$	-1.6	$C_{21}H_{22}O_{11}$	287-166-153-139-110	(2*S*)-4',5,6,7-tetrahydroxy-flavanone 6-O- *O*-*β*-glucoside	FOGs	CT
89	6.56	209.1178	$[M+H-H2O]^+$	3.3	$C_{12}H_{18}O_4$	163-153-107-93-79-77	senkyunolide J/N	phthalides	LC
90[a]	6.6	593.1497	$[M-H]^-$	-1.5	$C_{27}H_{30}O_{15}$	285-255-227	kaempferol 3- *O*-*β*-rutinoside	FOGs	CT
91[a]	6.67	1043.2654	$[M-H]^-$	-1.4	$C_{48}H_{52}O_{26}$	923-862-593-449-287-119	anhydrosafflor yellow B	QCGs	CT
92	6.7	515.1184	$[M-H]^-$	-1.2	$C_{25}H_{24}O_{12}$	191-179-161-135	di-O-caffeoylquinic acid	phenolic acids	LC
93[a]	6.73	623.1619	$[M-H]^-$	1.1	$C_{28}H_{32}O_{16}$	315-300-299-271-243-215	5,7,4'-trihydroxy-6-methoxyflavone-3- *O*-*β*-D-rutinoside	FOGs	LC
94	6.73	209.1182	$[M+H-H2O]^+$	1.9	$C_{12}H_{18}O_4$	153-79	senkyunolide J/N	phthalides	CT
95[a]	6.76	593.1509	$[M-H]^-$	0.5	$C_{27}H_{30}O_{15}$	430-297-119	saffloquinoside A	QCGs	CT
96	6.77	449.1084	$[M-H]^-$	0	$C_{21}H_{22}O_{11}$	119-	X+Glc	QCGs	CT
97	6.80	1139.5850	$[M+HCOO]^-$	0.1	$C_{53}H_{90}O_{23}$	1093-961-799-637-475-221	gypenoside LXXI or isomer (PPT-(Glc-Glc)-Glc-Xyl)	saponins	PN
98	6.83	515.1183	$[M-H]^-$	-1.4	$C_{25}H_{24}O_{12}$	191-179-161-135-85	di-O-caffeoylquinic acid	phenolic acids	LC

99[a]	6.86	447.0931	$[M-H]^-$	0.9	C21H20O11	284-255-227	kaempferol-3- *O*-*β*-D-glucoside	FOGs	CT
100[a]	6.92	515.1185	$[M-H]^-$	-1.0	C25H24O12	191-179-135	3,5-di-O-caffeoylquinic acid	phenolic acids	LC
101	6.93	463.0873	$[M-H]^-$	-0.9	C21H20O12	301-271-243	quercetin (or 6-hydroxykaempferol)-Glc	FOGs	CT
102	6.96	1139.5854	$[M+HCOO]^-$	0.4	C53H90O23	1094-961-637-475-221	gypenoside LXXI or isomer (PPT-(Glc-Glc)-Glc-Xyl)	saponins	PN
103	7.08	207.1030	$[M+H-H2O]^+$	4.3	C12H16O4	207-189-153-117-105-91-79	chuanxiongnolide R2 or isomer	phthalides	LC
104[a]	7.09	1007.5422	$[M+HCOO]^-$	-0.5	C48H82O19	961-799-637-475-323-263-221	noto-R3	saponins	PN
105	7.09	574.1562	$[M-H]^-$	0.2	C27H29NO13	364-338-244-232-119	cartormin or isomer	QCGs	
106	7.15	1153.5995	$[M+HCOO]^-$	-1.0	C54H92O23	1107-961-945-799-783-637-475-221	quinquenoside Ja or isomer (PPT-(Glc-Glc)-Rha-Glc)	saponins	PN
107[a]	7.21	1007.5428	$[M+HCOO]^-$	0.1	C48H82O19	961-799-781-637-619-475-391-221	ginsenoside Re3	saponins	PN
108	7.22	1153.5985	$[M+HCOO]^-$	-1.8	C54H92O23	1107-961-946-800-637-475-221	quinquenoside Ja or isomer (PPT-(Glc-Glc)-Rha-Glc)	saponins	PN
109[a]	7.28	1007.5426	$[M+HCOO]^-$	-0.1	C48H82O19	961-799-637-475-391-323-221	noto-M	saponins	CT
110	7.28	449.1088	$[M-H]^-$	0.9	C21H22O11	287-181-165-153-139-119-110	(2*S*)-4',5,6,7-tetrahydroxy-flavanone -D-glucoside	FOGs	CT
111	7.28	574.1561	$[M-H]^-$	0.0	C27H29NO13	364-338-244-232-119	cartormin or isomer	QCGs	PN
112	7.31	515.1199	$[M-H]^-$	1.7	C25H24O12	191-179-173-161-135-93	di-O-caffeoylquinic acid	phenolic acids	LC
113	7.46	881.2106	$[M-H]^-$	-3.9	C42H42O21	449-287-153-119	2(X+Glc)-H_2O	QCGs	CT
114[a]	7.49	207.1031	$[M+H-H2O]^+$	4.8	C12H16O4	207-189-161-133-119-105-91-79	senkyunolide I	phthalides	LC
115[a]	7.50	1007.5409	$[M+HCOO]^-$	-1.8	C48H82O19	961-799-637-475-391-221	20-O-glu-Rf	saponins	PN
116	7.50	1139.5862	$[M+HCOO]^-$	1.1	C53H90O23	1093-932-637-475-245	gypenoside LXXI or isomer (PPT-Glc-(Glc-Xyl)-Glc)	saponins	PN
117	7.63	1007.5431	$[M+HCOO]^-$	0.4	C48H82O19	961-799-637-475-245-221	notoginsenoside N/R6 or isomer (PPT-(Glc-Glc)-Glc)	saponins	PN
118[a]	7.68	977.5336	$[M+HCOO]^-$	1.5	C47H80O18	931-799-769-637-619-475-391-191	noto-R1	saponins	PN
119[a]	7.76	613.1555	$[M-H]^-$	-0.3	C30H30O14	407-361-287-241-119	isosafflomin C	QCGs	CT
120	7.76	1007.5403	$[M+HCOO]^-$	-2.4	C48H82O19	961-799-781-637-475	notoginsenoside N/R6 or isomer (PPT-Glc-Glc-GLc)	saponins	PN

121	7.85	1167.5790	$[M+HCOO]^-$	-0.8	C54H90O24	1121-959-797-637-473-263-221	notoginsenoside B or isomer (473-(Glc-Glc)-Glc-Glc)	saponins	PN
122[a]	7.88	977.5320	$[M+HCOO]^-$	-0.1	C47H80O18	931-799-637-620-475-391-191	20-(*S*)-Sanchi-A5	saponins	PN
123	7.89	1007.5423	$[M+HCOO]^-$	-0.4	C48H82O19	961-799-637-475-323	notoginsenoside N/R6 or isomer (PPT-Glc-Glc-GLc)	saponins	PN
124[a]	7.90	207.1032	$[M+H-H2O]^+$	5.3	C12H16O4	207-189-161-133-119-105-91-79	senkyunolide H	phthalides	LC
125[a]	7.95	613.1564	$[M-H]^-$	1.1	C30H30O14	407-361-287-241-119	safflomin C	QCGs	CT
126[a]	8.07	845.4901	$[M+HCOO]^-$	0.2	C42H72O14	799-637-553-475-391	ginsenoside Rg1	saponins	PN
127[a]	8.07	991.5463	$[M+HCOO]^-$	-1.5	C48H82O18	945-800-783-765-637-619-475-391-205	ginsenoside Re	saponins	PN
128	8.18	237.0781	$[M-H]^-$	7.6	C12H14O5	193-136-108	3,4,5-trimethoxycinnamylic acid or isomer	phenolic acids	LC
129	8.19	221.0821	$[M+H]^+$	3.2	C12H12O4	179-165-161-129-109-105-81	senkyunolide D	phthalides	LC
130	8.24	881.2138	$[M-H]^-$	-0.2	C42H42O21	700-593-473-449-311-287-119	2(X+Glc)-H_2O	QCGs	CT
131	8.47	1025.5465	$[M+HCOO]^-$	-6.5	C48H84O20	979-817-799-655-637-493-221	(F-1)-(Glc-Glc)-Glc	saponins	PN
132[b]	8.50	885.4827	$[M-H]^-$	-2.4	C45H74O17	799-781-637-619-475-391	malonyl ginsenoside Rg1 or isomer (PPT-Glc-Glc-mal)	saponins	PN
133	8.57	947.5204	$[M+HCOO]^-$	-1.3	C46H78O17	901-769-739-607-475-391	PPT-Xyl-Glc-Xyl	saponins	PN
134	8.60	843.4727	$[M+HCOO]^-$	-1.8	C42H70O14	635-473	pseudo ginsenoside G1/G2 or isomer (473-Glc-Glc)	saponins	PN
135	8.65	1169.5924	$[M+HCOO]^-$	-2.7	C54H92O24	1123-961-781-637-475-221	notoginsenoside A or isomer (PPT-Glc-Glc-Glc-Glc)	saponins	PN
136[a]	8.82	1005.5263	$[M+HCOO]^-$	-0.7	C48H80O19	959-797-635-473-221	noto-G	saponins	PN
137[a]	8.85	815.4794	$[M+HCOO]^-$	0.1	C41H70O13	769-609-475-391	20-(*S*)-Sanchi-A4	saponins	PN
138	8.85	885.4849	$[M-H]^-$	0.1	C45H74O17	637-619-475-391	malonyl ginsenoside Rg1 or isomer (PPT-Glc-Glc-mal)	saponins	PN
139[a]	8.91	285.0400	$[M-H]^-$	0.4	C15H10O6	151-133-107	luteolin	FOGs	LC
140[a]	8.93	301.0360	$[M-H]^-$	4.0	C15H10O7	151-121-107	Quercetin	FOGs	LC
141	8.95	205.0867	$[M+H]^+$	1.0	C12H12O3	149-145-115-105-91	senkyunolide B or isomer	phthalides	LC
142	9.07	815.4782	$[M+HCOO]^-$	-1.3	C41H70O13	637-619-475	pseudoginsenoside RT3 or isomer (PPT-Xyl-Glc)	saponins	PN
143	9.07	1167.5752	$[M+HCOO]^-$	-4.0	C54H90O24	1121-959-797-637-473-263-221	notoginsenoside B or isomer (473-(Glc-Glc)-Glc-Glc)	saponins	PN
144	9.13	205.0867	$[M+H]^+$	1.0	C12H12O3	163-149-145-115-107-91-89-65	senkyunolide B or isomer	phthalides	LC

145[a]	9.17	815.4785	$[M+HCOO]^-$	-1.0	C41H70O13	637-553-475-391	20-(*S*)-Sanchi-A3	saponins	PN
146	9.23	887.498	$[M-H]^-$	-2.7	C45H76O17	783-637-619-475-391	mal-PPT-Glc-Rha	saponins	PN
147	9.26	582.2595	$[M-H]^-$	-1.5	C34H37N3O6	342-316-145-119	N1, N5, N10-(*E*)-tri-*p*-coumaroylspermidine or isomer	others	CT
148	9.29	975.515	$[M+HCOO]^-$	-1.5	C47H78O18	929-797-635-475	PPT-Glc-Glc-Xyl	saponins	PN
149	9.36	1007.5383	$[M+HCOO]^-$	0.2	C48H82O19	961-781-621-537-221	notoginsenoside N/R6 or isomer ((F-1)-Rha-(Glc-Glc))	saponins	PN
150	9.48	582.2604	$[M-H]^-$	0.0	C34H37N3O6	462-342-316-299-145-119	N1, N5, N10-(*E*)-tri-*p*-coumaroylspermidine or isomer	others	CT
151[a]	9.50	1007.5413	$[M+HCOO]^-$	-1.4	C48H82O19	961-799-781-637-475-391-221	vinaginoside R4	saponins	PN
152	9.50	843.4726	$[M+HCOO]^-$	-1.9	C42H70O14	798-635-473	pseudo ginsenoside G1/G2 or isomer (473-Glc-Glc)	saponins	PN
153	9.55	977.5298	$[M+HCOO]^-$	-2.4	C47H80O18	931-799-637-353-221	noto-R1 isomer (PPT-(Glc-Glc)-Xyl)	saponins	PN
154	9.59	189.0923	$[M+H]^+$	3.7	C12H12O2	171-161-145-128-115-105-91-77	butylidenrphthalide isomer	phthalides	LC
155	9.61	582.2603	$[M-H]^-$	-0.2	C34H37N3O6	462-342-316-145-119	N1, N5, N10-(*E*)-tri-*p*-coumaroylspermidine or isomer	others	CT
156	9.61	1081.5583	$[M-H]^-$	0.0	C55H86O21	932-800-637-475-391	(H_2O-PPT)-Glc-Glc-Xyl-Xyl	saponins	PN
157	9.83	582.2599	$[M-H]^-$	-0.9	C34H37N3O6	462-342-316-299-273-145-119	N1, N5, N10-(*E*)-tri-*p*-coumaroylspermidine or isomer	others	CT
158[a]	9.85	1417.6823	$[M+HCOO]^-$	-2.0	C64H108O31	1240-1077-945-783-765-621-553-459-353-221	noto-T	saponins	PN
159	10.04	1315.6519	$[M+HCOO]^-$	-1.1	C60H102O28	1269-1107-945-783-621-383-221	quinquenoside V (PPT-(Glc-Glc)-Glc-Glc-Xyl)	saponins	PN
160[a]	10.09	845.4896	$[M+HCOO]^-$	-0.4	C42H72O14	799-637-475-391-221	ginsenoside Rf	saponins	PN
161[a]	10.17	1285.6405	$[M+HCOO]^-$	-1.9	C59H100O27	1239-1107-1077-945-783-621-353-221	noto-R4	saponins	PN
162	10.27	845.4904	$[M+HCOO]^-$	0.6	C42H72O14	799-637-475-391-323-221	notoginsenoside U (PPT-(Glc-Glc))	saponins	PN
163[a]	10.34	285.0414	$[M-H]^-$	5.3	C15H10O6	no	kaempferol	FOGs	LC
164	10.38	1325.6366	$[M-H]^-$	-0.9	C62H102O30	1281-1240-1221-1107-1089-1077-945-927-783-765-621-459	PPD-Glc-Glc-Glc-Glc-Xyl-mal	saponins	PN

165	10.47	947.5200	$[M+HCOO]^-$	-1.7	C46H78O17	901-769-475-323-203-191	notoginsenoside Rw1/chikusetsusaponin L5 (PPT-(Glc-Xyl)-Xyl)	saponins	PN
166[a]	10.49	815.4801	$[M+HCOO]^-$	1.0	C41H70O13	769-637-475-391-191	20(S)-noto R2	saponins	PN
167[a]	10.50	1285.6405	$[M+HCOO]^-$	-1.9	C59H100O27	1239-1107-945-783-621-459-323-263-221	ginsenoside Ra3	saponins	PN
168	10.57	1137.6011	$[M+HCOO]^-$	-4.0	C54H92O22	1091-929-767-605-221	notoginsenoside I (PPD-Xyl-Glc-Glc-Glc)	saponins	PN
169[a]	10.63	1151.5809	$[M+HCOO]^-$	-3.5	C54H90O23	1105-943-781-619-457-323-221	5,6-didehydroginsenoside Rb1	saponins	PN
170[a]	10.82	815.4793	$[M+HCOO]^-$	0.0	C41H70O13	769-637-475-391	20(*R*)-noto R2	saponins	PN
171	10.85	1285.6382	$[M+HCOO]^-$	-3.7	C59H100O27	1239-1107-1077-945-783-621-459-353-221	notoginsenoside Fa (PPD-(Glc-Glc)-Glc-Glc-Xyl)	saponins	PN
172[a]	10.89	829.4928	$[M+HCOO]^-$	-2.5	C42H72O13	783-637-619-475-391-205	20(*S*)-ginsenoside Rg2	saponins	PN
173[a]	10.89	1153.5977	$[M+HCOO]^-$	-2.5	C54H92O23	1107-945-783-621-459-323-263-221	Rb1	saponins	PN
174[a]	11.05	683.4360	$[M+HCOO]^-$	-1.5	C36H62O9	637-475-391	20(*S*)-Rh1	saponins	PN
175	11.05	1153.5979	$[M+HCOO]^-$	-2.3	C54H92O23	1107-945-783-621-459-323-221	Rb1 isomer (PPD-(Glc-Glc)-Glc-Glc)	saponins	PN
176[a]	11.14	1193.5925	$[M-H]^-$	-2.5	C57H94O26	1149-1107-1089-945-927-783-765-621-459-323-221	malonyl ginsenoside Rb1	saponins	PN
177	11.24	189.0928	$[M+H]^+$	6.3	C12H12O2	152-147-133-129-105-91-77	butylidenrphthalide isomer	phthalides	LC
178[a]	11.25	1123.5859	$[M+HCOO]^-$	-3.6	C53H90O22	1077-945-915-783-765-921-459-221-191	ginsenoside Rc	saponins	PN
179[a]	11.32	683.4348	$[M+HCOO]^-$	-3.2	C36H62O9	637-475-391	20(*R*)-Rh1	saponins	PN
180	11.32	1193.5912	$[M-H]^-$	-3.6	C57H94O26	1149-1107-1089-945-927-783-621-459-323-221	malonyl ginsenoside Rb1 isomer (PPD-(Glc-Glc)-Glc-Glc-mal)	saponins	PN
181[a]	11.35	955.4856	$[M-H]^-$	-4.9	C48H76O19	793-731-613-569-523-497-455	ginsenoside Ro	saponins	PN
182	11.37	191.1085	$[M+H]^+$	6.8	C12H14O2	191-149-135-107-103-91-79-77	3-butylphthalide or isomer	phthalides	LC
183	11.41	1087.5287	$[M-H]^-$	-3.5	C53H84O23	1087-925-745-731-569-551-455	OA-GluA-Glc-xyl-Glc	saponins	PN

184[a]	11.60	1123.5850	$[M+HCOO]^-$	-4.5	C53H90O22	1077-945-783-621-459-191	ginsenoside Rb2	saponins	PN
185	11.64	1193.5914	$[M-H]^-$	-3.4	C57H94O26	1149-1107-1089-945-927-783-621-459-221	malonyl ginsenoside Rb1 isomer (PPD-(Glc-Glc)-Glc-Glc-mal)	saponins	PN
186	11.70	1123.5853	$[M+HCOO]^-$	-4.2	C53H90O22	1077-945-783-621-459-293-221-191	notoginsenoside L/ginsenoside Rb3 (PPD-(Glc-Glc)-(Glc-Xyl))	saponins	PN
187	11.80	955.4944	$[M-H]^-$	4.3	C48H76O19	777-613-569-523-497-455	ginsenoside Ro isomer (OA-GluA-Glc-Glc)	saponins	PN
188	11.83	1193.5963	$[M-H]^-$	0.7	C57H94O26	1107-1089-945-783-621-459-221	malonyl ginsenoside Rb1 isomer (PPD-(Glc-Glc)-Glc-Glc-mal)	saponins	PN
189	11.88	785.4680	$[M+HCOO]^-$	-0.9	C40H68O12	739-607-475-391	PPT-Xyl-Xyl	saponins	PN
190	11.89	1123.5879	$[M+HCOO]^-$	-1.9	C53H90O22	1077-945-783-621-459-221-191	notoginsenoside L/ginsenoside Rb3 (PPD-(Glc-Glc)-(Glc-Xyl))	saponins	PN
191	11.92	1153.6007	$[M+HCOO]^-$	0.1	C54H92O23	1107-945-783-621-459-221	Rb1 isomer (PPD-(Glc-Glc)-Glc-Glc)	saponins	PN
192	11.98	989.5303	$[M+HCOO]^-$	-1.8	C48H80O18	943-781-619-457-221	5,6-didehydroginsenoside Rd (457-(Glc-Glc)-Glc)	saponins	PN
193	12.08	925.4765	$[M-H]^-$	-3.5	C47H74O18	793-719-613-569-497-455	OA-GluA-Glc-Xyl	saponins	PN
194	12.13	683.4348	$[M+HCOO]^-$	-3.2	C36H62O9	475-391	ginsenoside F1 or sanchinoside B1 (PPT-Glc)	saponins	PN
195	12.23	975.5510	$[M+HCOO]^-$	-1.9	C48H82O17	929-767-605	vinaginoside R3 or isomer (PPD-Rha-Glc-Glc)	saponins	PN
196[a]	12.40	991.5465	$[M+HCOO]^-$	-1.3	C48H82O18	945-783-621-459-375-221	ginsenoside Rd	saponins	PN
197	12.49	965.4940	$[M+HCOO]^-$	-1.8	C45H76O19	919-757-739-595-577-433	floraginsenoside Kb or isomer ((E-1)-Glc-Glc-Glc)	saponins	PN
198[a]	12.67	1031.5425	$[M-H]^-$	-0.2	C51H84O21	945-783-765-621-459	malonyl ginsenoside Rd	saponins	PN
199	12.72	793.4376	$[M-H]^-$	0.3	C42H66O14	793-631-569-455	OA-GluA-Glc	saponins	PN
200	12.99	1031.5367	$[M-H]^-$	-5.8	C51H84O21	987-945-825-783-621-459-221	malonyl ginsenoside Rd isomer (PPD-(Glc-Glc)-Glc-mal)	saponins	PN
201	13.00	205.087	$[M+H]^+$	2.4	C12H12O3	187-141-115-91	senkyunolide E or isomer	phthalides	LC
202[a]	13.16	991.5453	$[M+HCOO]^-$	-2.5	C48H82O18	945-621-459-323-221	noto-K	saponins	PN

203	13.45	961.5349	$[M+HCOO]^-$	-2.4	C47H80O17	915-783-753-621-459	notoginsenoside Fe/gypenoside IX/notoginsenoside L (PPD-(Glc-Glc)-Xyl)	saponins	PN
204	13.55	991.5468	$[M+HCOO]^-$	-1.0	C48H82O18	945-783-621-459	gypenoside XVII (PPD-Glc-Glc-Glc)	saponins	PN
205	13.57	769.4360	$[M-H]^-$	-1.8	C40H66O14	638-475-457	pseudoginsenoside Rt3 (PPT-Glc-Xyl)	saponins	PN
206	13.64	683.4366	$[M+HCOO]^-$	-0.6	C36H62O9	637-475-391	ginsenoside F1 or sanchinoside B1 (PPT-Glc)	saponins	PN
207	13.80	961.5361	$[M+HCOO]^-$	-1.1	C47H80O17	915-783-621-459-375	notoginsenoside Fe/gypenoside IX/notoginsenoside L (PPD-(Glc-Glc)-Xyl)	saponins	PN
208	13.86	961.5370	$[M+HCOO]^-$	-0.2	C47H80O17	915-783-621-459-375-221	PPD-(Glc-Glc)-Xyl	saponins	PN
209	13.96	279.1603	$[M+H]^+$	2.5	C16H22O4	233-205-201-191-149-123	senkyunolide M	phthalides	LC
210[a]	14.02	797.4680	$[M+HCOO]^-$	-0.9	C41H68O12	751-619-457	noto-T5	saponins	PN
211	14.38	797.4663	$[M+HCOO]^-$	-3.0	C41H68O12	751-619-457	noto-T5 isomer (457-Glc-Glc)	saponins	PN
212	14.40	193.1241	$[M+H]^+$	6.2	C12H16O2	147-137-119-105-91-77	senkyunolide A	phthalides	LC
213[a]	14.90	665.4264	$[M+HCOO]^-$	-0.2	C36H60O8	619-457	ginsenoside Rk3	saponins	PN
214	15.03	975.5515	$[M+HCOO]^-$	-1.4	C48H82O17	929-783-621-459-375	vinaginoside R3 isomer (PPD-Glc-Glc-Rha)	saponins	PN
215	15.07	827.4757	$[M+HCOO]^-$	-4.4	C42H70O13	781-619-439-221	sanchirhinoside B isomer (457-(Glc-Glc))	saponins	PN
216	15.07	925.4792	$[M-H]^-$	-0.5	C47H74O18	701-523-455	unknown	saponins	PN
217[a]	15.38	829.4938	$[M+HCOO]^-$	-1.3	C42H72O13	621-537-459	ginsenoside F2	saponins	PN
218	15.55	261.1864	$[M+H]^+$	3.4	C17H24O2	105-77	panaxydol	others	PN
219	15.81	925.4789	$[M-H]^-$	-0.9	C47H74O18	731-569-551-483-455	OA-GluA-Glc-Xyl	saponins	PN
220	15.84	191.1077	$[M+H]^+$	2.6	C12H14O2	173-145-129-115-103-91-77	(*E*)-ligustilide	phthalides	LC
221	16.12	825.4617	$[M-H]^-$	-2.3	C42H68O13	779-617-455	OA-Glc-Glc	saponins	PN
222	16.14	189.0907	$[M+H]^+$	-4.8	C12H12O2	171-152-128-115-91	E-butylidenrphthalide	phthalides	LC
223[a]	16.17	829.4933	$[M+HCOO]^-$	-1.9	C42H72O13	784-621-459-221	20(*S*)-Rg3	saponins	PN
224	16.26	803.4563	$[M+HCOO]^-$	-2.4	C43H66O11	757-595-433	(E-1)-Glc-Glc	saponins	PN
225	16.26	811.4824	$[M+HCOO]^-$	-2.5	C42H70O12	765-603	ginsenoside F4 or isomer	saponins	PN

226	16.29	793.4348	$[M-H]^-$	-3.3	C42H66O14	613-569-509-497-455	chikusetsusaponin Iva or isomer (OA-GluA-Glc)	saponins	PN
227[a]	16.31	829.4949	$[M+HCOO]^-$	0	C42H72O13	783-621-459-375-221	20(*R*)-Rg3	saponins	PN
228	16.32	313.2391	$[M-H]^-$	3.8	C18H34O4	183-129-99	1,18-octadecanedioic acid or isomer	others	LC/CT/PN
229	16.34	195.1387	$[M+H]^+$	1.0	C12H18O2	149-79	cnidilide or isomer	others	LC
230[a]	16.38	191.108	$[M+H]^+$	4.2	C12H14O2	173-145-129-117-115-105-91-79	*Z*-ligustilide	phthalides	LC
231	16.42	311.2239	$[M-H]^-$	5.5	C18H32O4	201-171	octadecanedioic acid or isomer	others	PN
232	16.45	313.2394	$[M-H]^-$	4.8	C18H34O4	201-171-165-155-127-125	1,18-octadecanedioic acid or isomer	others	LC/CT/PN
233	16.48	189.0922	$[M+H]^+$	3.2	C12H12O2	171-152-128-115-91	(*Z*)-butylidenrphthalide	phthalides	LC
234[a]	16.59	521.3850	$[M+HCOO]^-$	1.5	C30H52O4	no	20(*S*)-PPT	saponins	PN
235	16.61	311.2228	$[M-H]^-$	1.9	C18H32O4	171-	linoleic acid 13-hydroperoxide or isomer	others	LC
236	16.63	401.2326	$[M+H]^+$	-0.5	C24H32O5	383-191-149-145-135-105-91	chuanxiongdiolide B/R2	phthalides	LC
237	16.79	191.1077	$[M+H]^+$	2.6	C12H14O2	191-173-145-129-117-115-105-103-91-79	3-butylphthalide isomer	phthalides	LC
238	16.79	399.2168	$[M+H]^+$	-0.8	C24H30O5	241-191-173-149-135-117-105-91-79	chuanxiongnolide A/B	phthalides	LC
239	16.93	315.2553	$[M-H]^-$	5.7	C18H36O4	315-297-279-201-171-141-127	9,10-dihydroxyoctadecanoic acid or isomer	others	LC/CT/PN
240	16.99	309.2072	$[M-H]^-$	1.9	C18H30O4	171-	linoleic acid 9-hydroperoxide or isomer	others	PN
241	17.01	401.2325	$[M+H]^+$	-0.7	C24H32O5	383-191-175-149-135-117-105-91-79	chuanxiongdiolide B/R2	phthalides	LC
242	17.06	811.4841	$[M+HCOO]^-$	-0.4	C42H70O12	765-603-556	ginsenoside F4 or isomer	saponins	PN
243	17.15	811.4850	$[M+HCOO]^-$	0.7	C42H70O12	765-603	ginsenoside F4 or isomer	saponins	PN
244	17.18	399.2181	$[M+H]^+$	2.5	C24H30O5	191-173-149-145-135-117-105-91-79	chuanxiongnolide A/B	phthalides	LC
245[a]	17.34	667.4428	$[M+HCOO]^-$	1.0	C36H62O8	459-	compound K	saponins	PN
246	17.37	295.2287	$[M-H]^-$	4.7	C18H32O3	277-195-171	hydroxy-linoleic acid or isomer	others	LC/CT/PN

247[a]	17.44	667.4401	$[M+HCOO]^-$	-3.0	C36H62O8	459-375	20(*S*)-Rh2	saponins	PN
248[a]	17.54	667.4475	$[M+HCOO]^-$	8.1	C36H62O8	459-	20(*R*)-Rh2	saponins	PN
249	17.62	383.2221	$[M+H]^+$	-0.3	C24H30O4	191-149-135-105-91-79	senkyunolide P or isomer	phthalides	LC
250[a]	18.22	381.2067	$[M+H]^+$	0.3	C24H28O4	191-173-149-135-121-117-91-79	levistolide A	phthalides	LC

[a] the compounds unambiguously identified by comparison with reference standards;

[b] mal stands for the abbreviation of malonyl group.