Supporting information

Applying target data screening followed by characteristic fragment filtering for the comprehensive screening and identification of alkaloids in *Corydalis yanhusuo* W.T. Wang by UPLC-Q-TOF/MS^E

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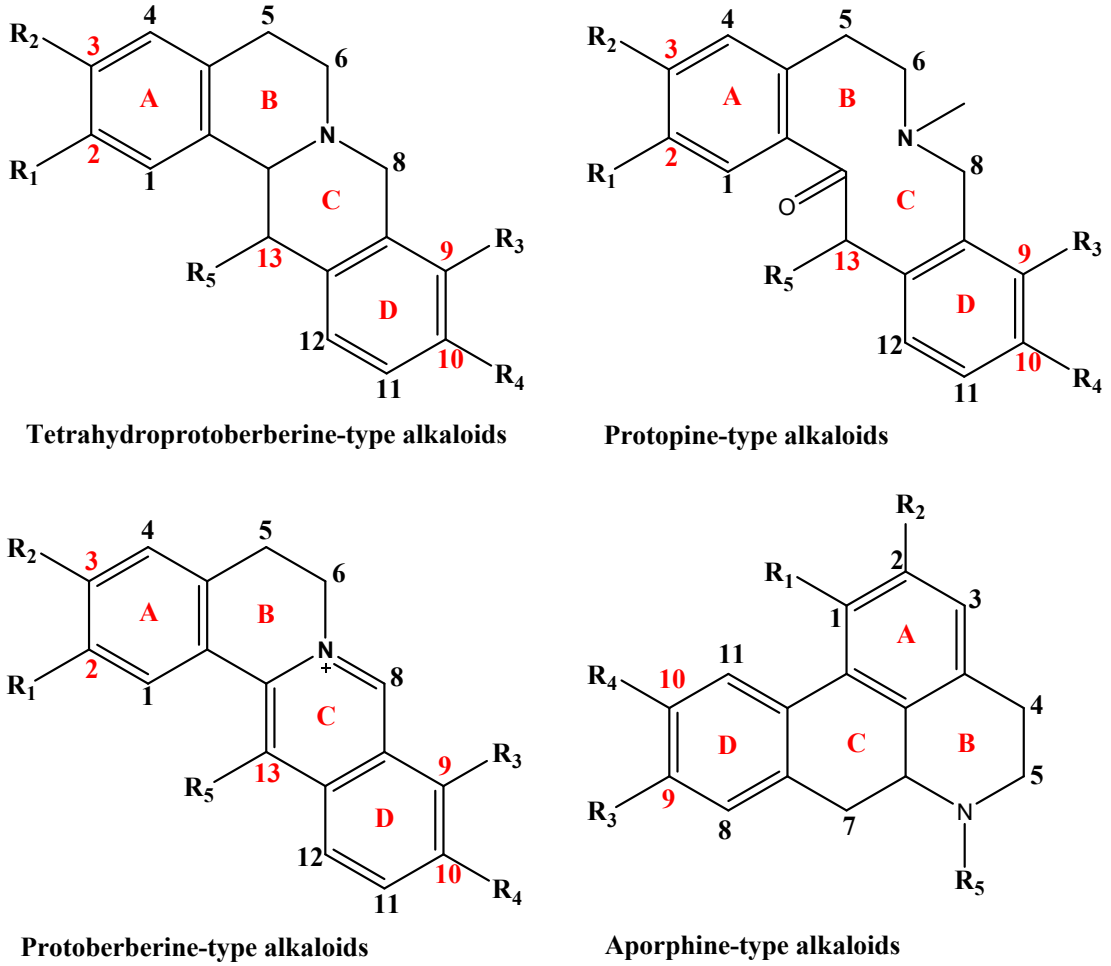

Fig. S1. The chemical structures of the four types of alkaloids in yanhusuo

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Abbreviations: **UPLC Q-TOF/MS**, ultra-performance liquid chromatography quadrupole time-of-flight mass spectrometry; **TCM**, traditional Chinese medicine; **BPI**, Base peak ion chromatogram; **ESI**, electro spray ionization;

3.1 Optimization of UPLC-MS conditions

The LC conditions and MS conditions were optimized. LC conditions including the mobile phase system (methanol/water, acetonitrile/water, acetonitrile/0.1% formic acid in water), column temperature (30°C, 40°C), flow rate (0.2 mL/min, 0.3 mL/min, 0.4 mL/min) and injection volume (2 μL, 3 μL, 5 μL) were examined in the gradient program. The LC conditions were optimized as described in Section 2.3, and the chromatographic peaks were well separated. MS conditions, including ionization mode, capillary voltage, cone voltage, source temperature, desolvation gas temperature and collision energy were optimized. The results showed that the alkaloids had a higher response in the positive ion mode than the negative ion mode. The major alkaloids in yanhusuo were well detected. Meanwhile, in order to obtain abundant fragmentation ion information, the collision energy of the 10-40 V ramp trap collision was selected.

3.2 Alkaloid fragmentation pattern analysis and characteristic ion determination

3.2.1 Fragmentation patterns and characteristic ions of tetrahydroprotoberberine alkaloids

Tetrahydroprotoberberine-type alkaloids easily underwent RDA cleavage with complementary fragment ions in MS, since the C-ring was saturated[1-3]. The largest difference occurred between tetrahydroprotoberberine-type alkaloids and other types of alkaloids in the electrospray ionization mass spectrometry. The abundant fragment ions information of the tetrahydroprotoberberine and tetrahydroberberine alkaloids is shown in Fig. S2. According to the fragmentation pathways of tetrahydropalmatine

(Fig. S3) and tetrahydroberberine (Fig. S4), and the related literature, fragments above *m/z* 280 were predominantly cleaved by substituents and fragment ions below *m/z* 200 were produced by RDA cleavage. RDA cleavage produced the highest intensity of nitrogen-containing fragments as characteristic fragments of the tetrahydroprotoberberine-type alkaloids, and the characteristic ions were related to the type of substituents at the C2-C3 positions. When the C2-C3 positions possessed two methoxyl, methylenedioxyl, a methoxyl and a hydroxyl, respectively, the characteristic ions were *m/z* 192.1019, *m/z* 176.0706 and *m/z* 178.0869, respectively, which were used to rapidly identify the tetrahydroprotoberberine-type alkaloid compounds.

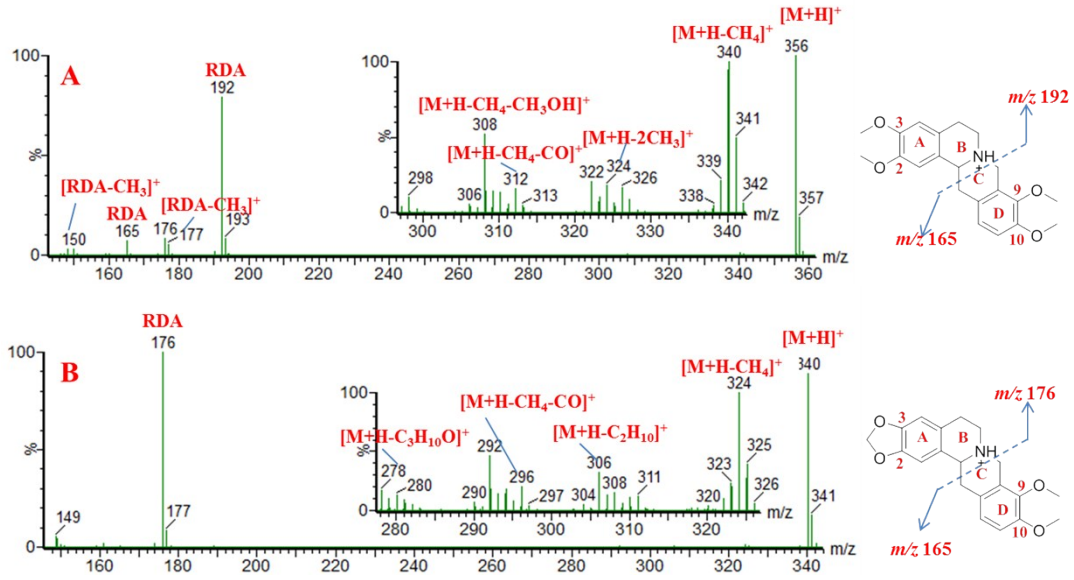

Fig. S2 The MS spectra in high energy scan of A (tetrahydropalmatine) and B (tetrahydroberberine) in positive ion

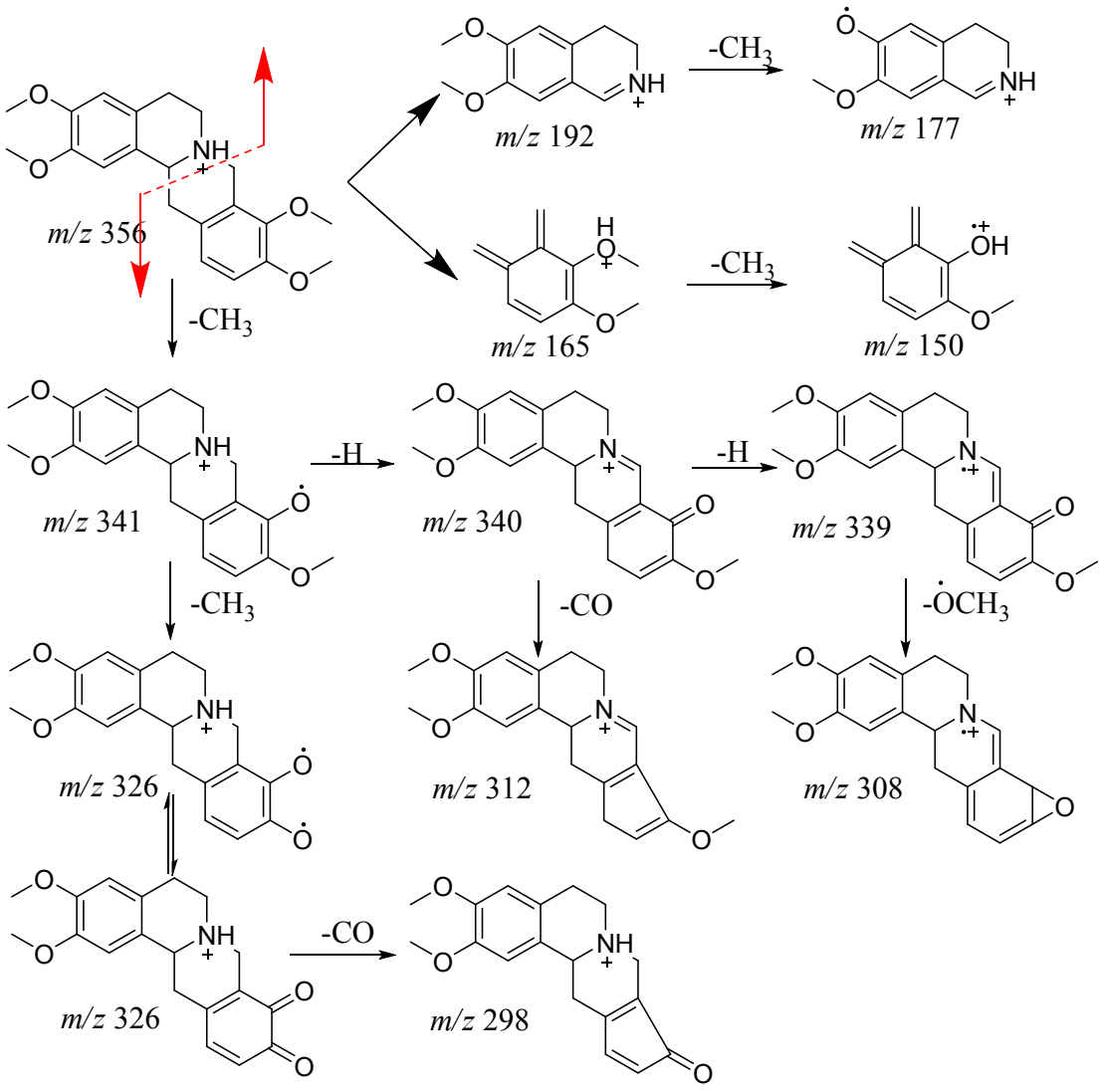

Fig. S3 The possible fragmentation pathway of tetrahydropalmatine

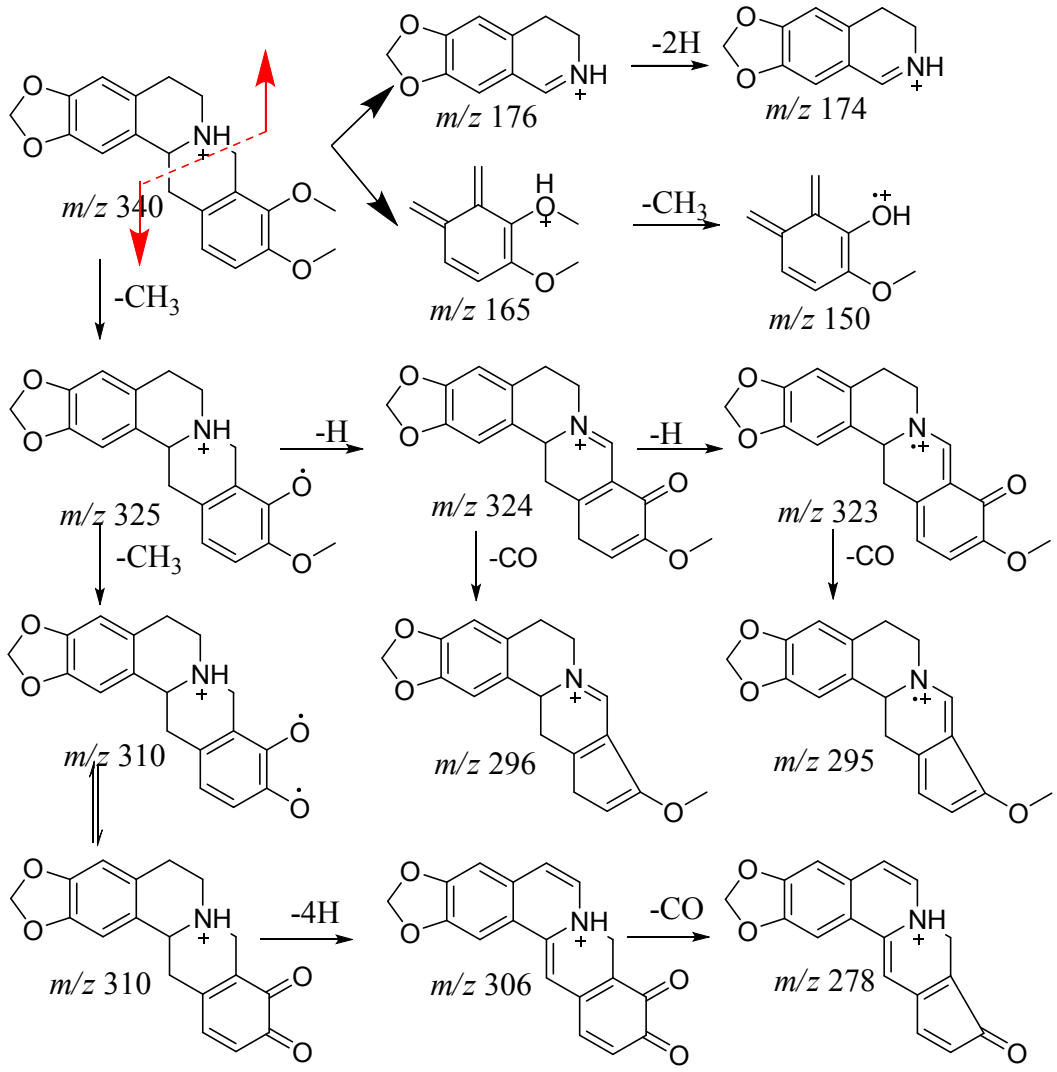

Fig. S4 The possible fragmentation pathway of tetrahydroberberine

3.2.2 Fragmentation patterns and characteristic ions of protoberberine alkaloids

The C-ring structure of Protoberberine-type alkaloid was not saturated, so it was difficult for the alkaloid to experience RDA cleavage. The principal cleavage was of the substituents[4, 5]. In this study, according to references of palmatine, berberine and dehydrocorydaline and related literature, the possible fragmentation pathways were summarized to obtain characteristic ions. The abundant fragment ion information of palmatine, dehydrocorydaline and berberine are shown in Fig. S5. Summarizing the fragmentation pathway of palmatine (Fig. S6), dehydrocorydaline (Fig. S7) and

berberine (Fig. S8) and related literature, it was easy to determine that the fragment ion information was linked to the substituent cleavage on the A- and D-rings. When the substituents contained two or more methoxy groups, the characteristic fragment ions were $[M - CH_3]^+$, $[M - CH_4]^+$, $[M - CH_4 - CO]^+$, $[M - 2CH_3]^+$ and $[M - CH_3OH]^+$. When the substituent contained a methylenedioxyl group, the characteristic fragment ion exhibited $[M - CO]^+$. These characteristic fragment ions were used to rapidly identify the protoberberine-type alkaloid compounds.

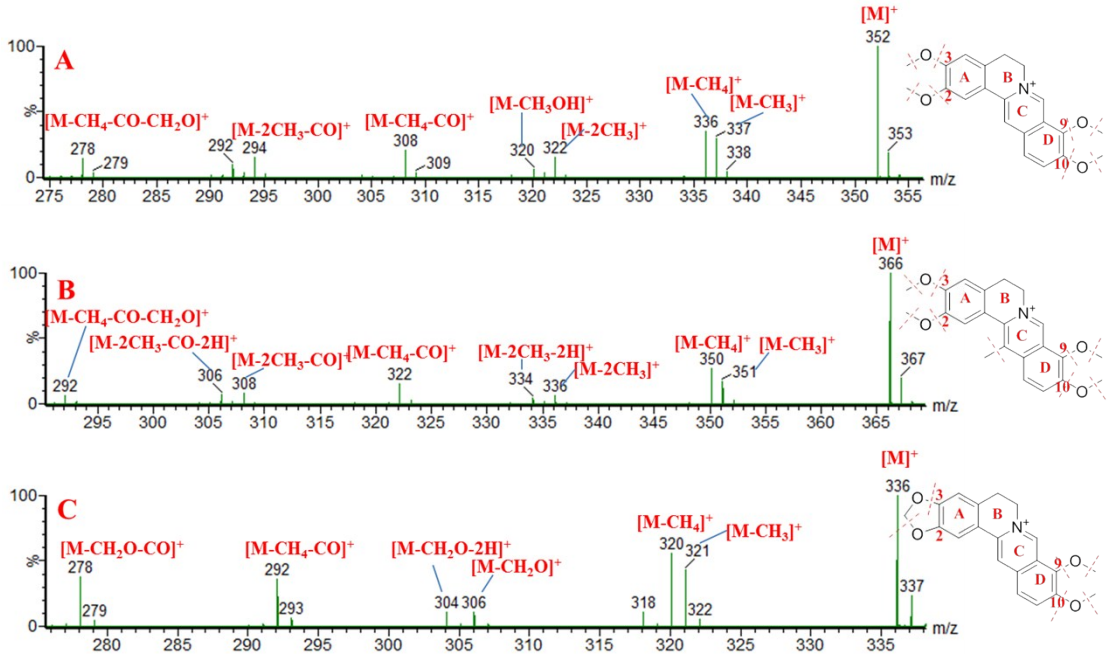

Fig. S5 The MS spectra in high energy scan of A (palmatine), B(dehydrocorydaline) and C (berberine) in positive ion

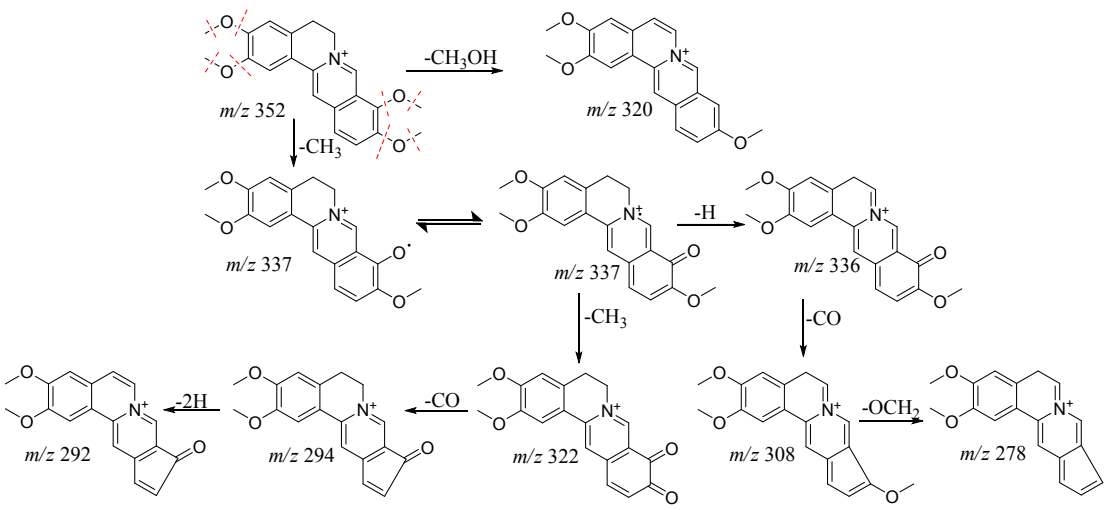

Fig. S6 The possible fragmentation pathway of palmatine

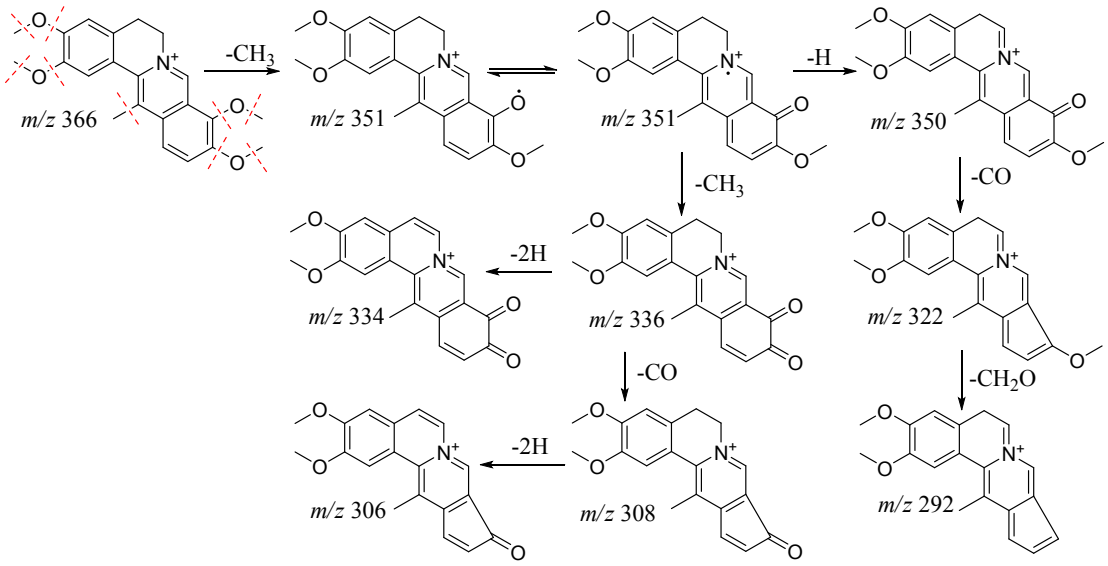

Fig. S7 The possible fragmentation pathway of dehydrocorydaline

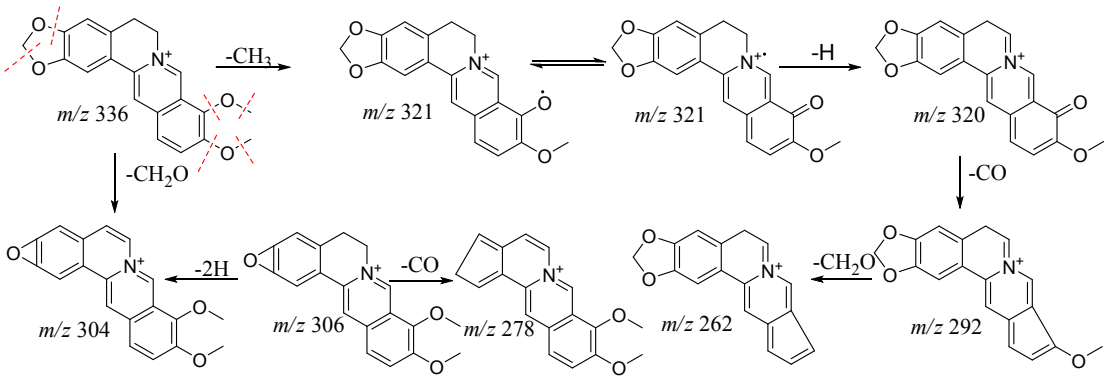

Fig. S8 The possible fragmentation pathway of berberine

3.2.3 Fragmentation patterns and characteristic ions of protopine alkaloids

The skeleton and substituents of protonine-type alkaloids were similar to the tetrahydroprotoberberine-type alkaloids. Therefore, the two types of alkaloids were also similar to the fragmentation pathway, which both easily undergo RDA cleavage to produce complementary fragment ions[1, 2]. However, there were some differences between protopine-type alkaloids and tetrahydroprotoberberine-type alkaloids in the structure. Specifically, protopine-type alkaloids were linked to oxygen to form a carbonyl group at the C14 position. The abundant fragment ion information of protopine and allocryptopine is shown in Fig. S9. Summarizing the fragmentation pathways of protopine (Fig. S10) and allocryptopine (Fig. S11) and related literature, it was found that the fragment ions with higher relative abundance in mass spectra were produced by the further dehydrated after RDA cleavage, instead of being directly produced by RDA cleavage. According to the fragmentation pathway of the reference substances to obtain the characteristic ions, the characteristic ions were related to the type of substituents at the C2-C3 positions. When the C2-C3 positions possessed two methoxyl, methylenedioxyl, a methoxyl and a hydroxyl, respectively, the characteristic ions were *m/z* 222.1125, *m/z* 206.0812 and *m/z* 208.0968, respectively. Furthermore, corresponding dehydration fragments *m/z* 204.1019, *m/z* 188.0712 and *m/z* 190.0868 were also as characteristic ions, respectively, which were used to rapidly identify the compounds of protopine-type alkaloids.

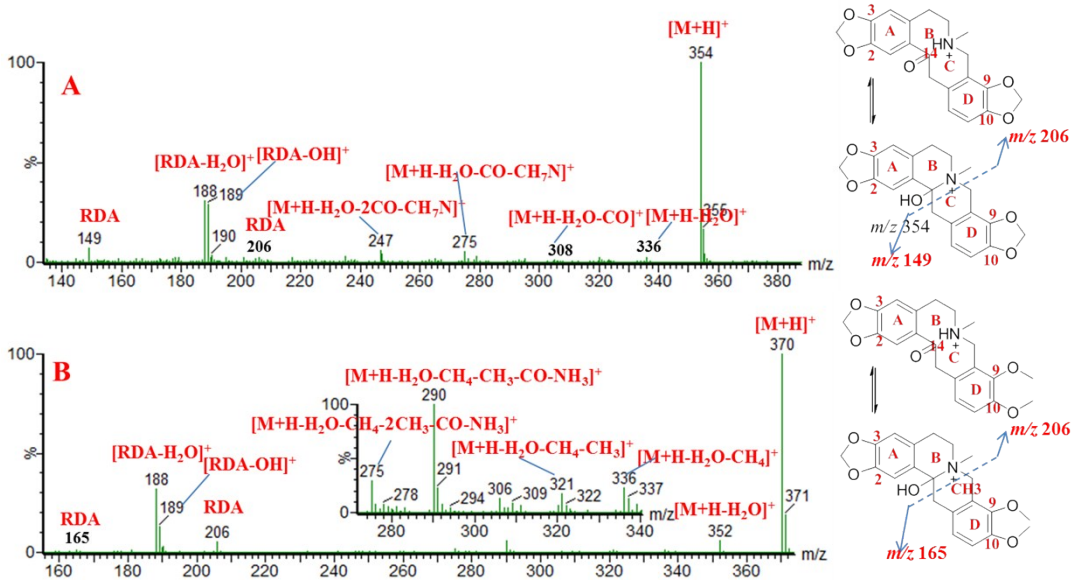

Fig. S9 The MS spectra in high energy scan of A (protopine) and B (allocryptopine) in positive ion

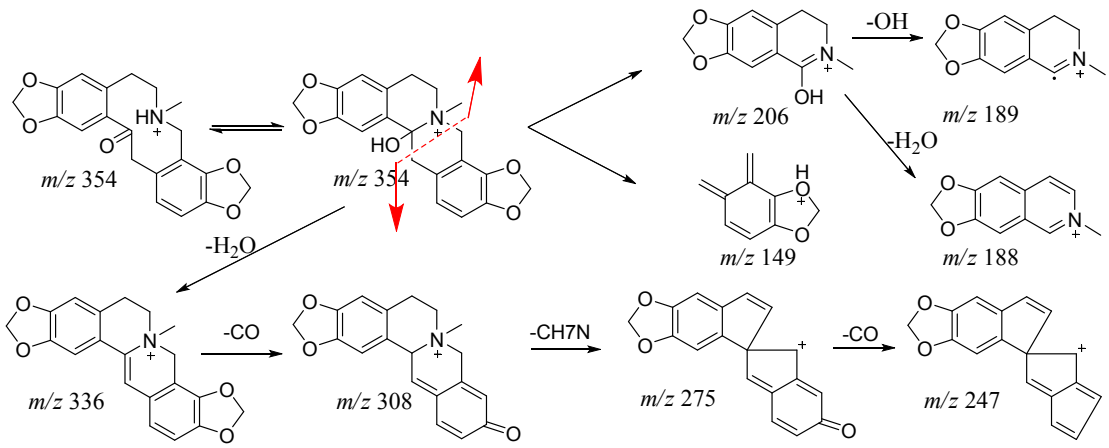

Fig. S10 The possible fragmentation pathway of protopine

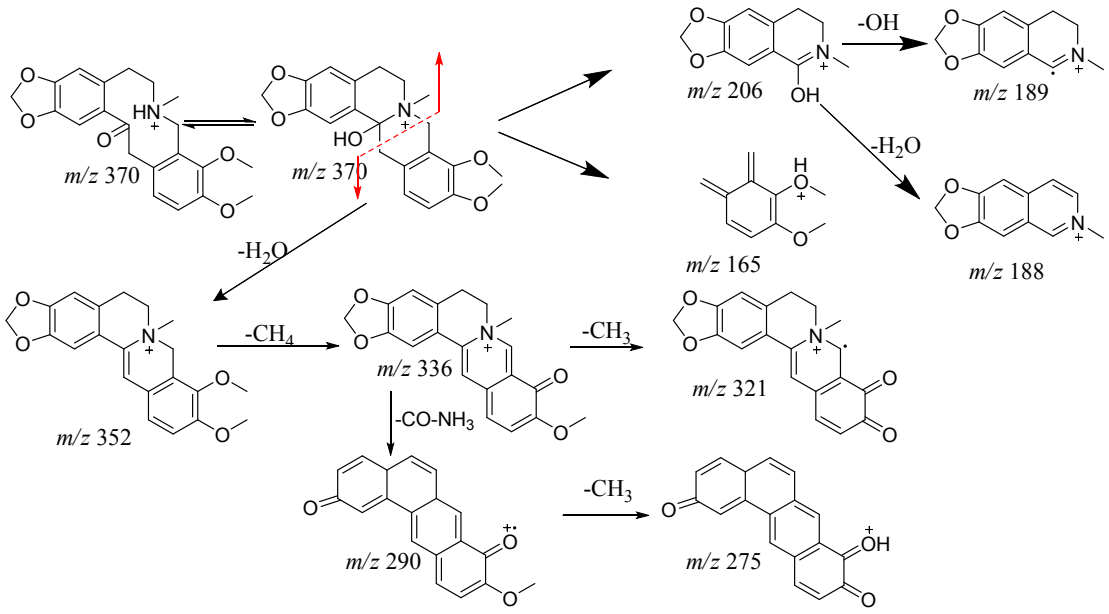

Fig. S11 The possible fragmentation pathway of allocryptopine

3.2.4 Fragmentation patterns and characteristic ions of aporphine alkaloids

There were considerable differences in the structural framework and fragmentation pathway between the aporphine-type alkaloids and the other alkaloids. Owing to the lack of the corresponding reference substance, the cleavage path was summed up by the related literature to determine the characteristic fragment ions. A weak bond existed in the amide group, so aporphine-type alkaloids very easily lost $(CH_3)_2NH$ or CH_3NH_2 substituents to produce the most abundant fragment of $[M - 45]^+$ or $[M - 31]^+$ as the characteristic fragment ions, which was used to characterize the aporphine-type alkaloids. Peak 49 displayed a molecular ion at *m/z* 356.1861$[M + H]^+$ with a molecular formula of $C_{21}H_{25}NO_4$. The abundant fragment ion information of peak 49 is shown in Fig. S12. Peak 49 produced the higher intensity ion at *m/z* 325.1439$[M + H - CH_3NH_2]^+$, as well as other fragment ions at *m/z* 294.1255$[M + H - CH_3NH_2 - OCH_3]^+$, *m/z* 279.1019$[M + H - CH_3NH_2 - OCH_3 - CH_3]^+$, *m/z* 251.1$[M + H - CH_3NH_2 - CH_3OH - CH_3 - CO]^+$, *m/z* 310.1205$[M + H - CH_3NH_2 - CH_3]^+$ and so on. Based on

its retention times and fragment ions and compared with the reference literature, peak 49 was tentatively identified as glaucine or its isomer. The possible glaucine fragmentation pathway is shown in Fig. S13.

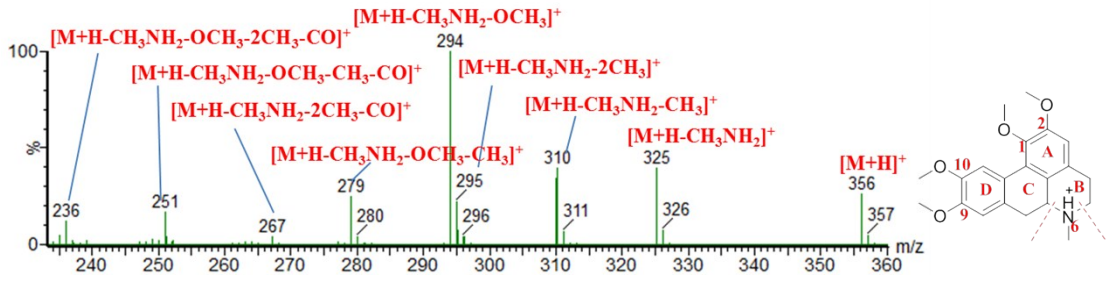

Fig. S12 The MS spectra in high energy scan of peak 49 in positive ion

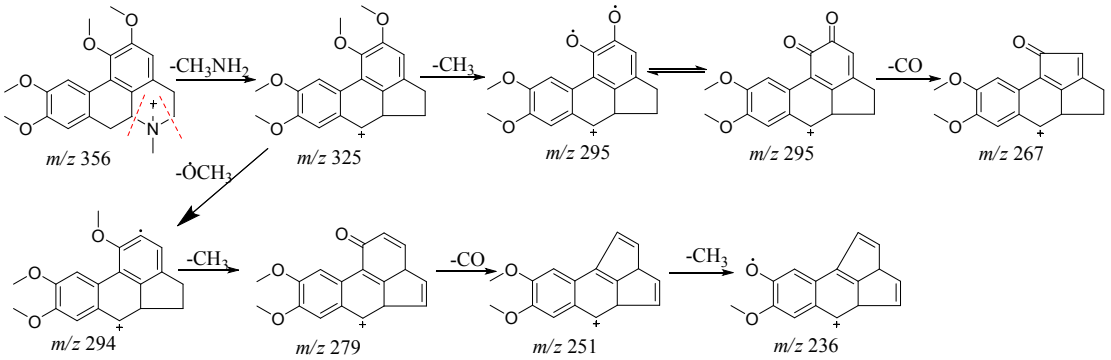

Fig. S13 The possible fragmentation pathway of glaucine

3.4.5 Other compounds

In addition to the above four types of alkaloids, 22 other alkaloids were tentatively identified based on the accurate mass and MS/MSE data, previous reports[1, 2, 6, 7] and online databases. The mass error of the quasi-molecular ions of these 22 compounds was lower than 10 ppm. Detailed identification of the other alkaloids was given in Table S5.

Table S1 The data screening table of tetrahydroprotoberberine alkaloids

[M+H]+	C-2	C-3	C-9	C-10	C-13
356.1862	**OCH_3**	**OCH_3**	**OCH_3**	**OCH_3**	**H**
370.2018	**OCH_3**	**OCH_3**	**OCH_3**	**OCH_3**	**CH_3**
340.1543	**OCH_3**	**OCH_3**	**-OCH_2O-**		**H**

354.1705	OCH_3	OCH_3	-OCH_2O-		CH_3
342.1705	**OCH_3**	**OCH_3**	**OCH_3**	**OH**	**H**
356.1862	**OCH_3**	**OCH_3**	**OCH_3**	**OH**	**CH_3**
342.1705	**OCH_3**	**OCH_3**	**OH**	**OCH_3**	**H**
356.1862	**OCH_3**	**OCH_3**	**OH**	**OCH_3**	**CH_3**
328.1543	**OCH_3**	**OCH_3**	**OH**	**OH**	**H**
342.1705	**OCH_3**	**OCH_3**	**OH**	**OH**	**CH_3**
342.1705	**OCH_3**	**OH**	**OCH_3**	**OCH_3**	**H**
356.1862	**OCH_3**	**OH**	**OCH_3**	**OCH_3**	**CH_3**
342.1705	**OH**	**OCH_3**	**OCH_3**	**OCH_3**	**H**
356.1862	**OH**	**OCH_3**	**OCH_3**	**OCH_3**	**CH_3**
326.1392	**OCH_3**	**OH**	**-OCH_2O-**		**H**
340.1543	OCH_3	OH	-OCH_2O-		CH_3
326.1392	**OH**	**OCH_3**	**-OCH_2O-**		**H**
340.1543	OH	OCH_3	-OCH_2O-		CH_3
328.1549	**OCH_3**	**OH**	**OH**	**OCH_3**	**H**
342.1705	**OCH_3**	**OH**	**OH**	**OCH_3**	**CH_3**
328.1549	**OCH_3**	**OH**	**OCH_3**	**OH**	**H**
342.1705	**OCH_3**	**OH**	**OCH_3**	**OH**	**CH_3**
328.1549	**OH**	**OCH_3**	**OH**	**OCH_3**	**H**
342.1705	**OH**	**OCH_3**	**OH**	**OCH_3**	**CH_3**
328.1549	**OH**	**OCH_3**	**OCH_3**	**OH**	**H**
342.1705	**OH**	**OCH_3**	**OCH_3**	**OH**	**CH_3**
314.1392	OCH_3	OH	OH	OH	H
328.1549	**OCH_3**	**OH**	**OH**	**OH**	**CH_3**
314.1392	OH	OCH_3	OH	OH	H
328.1549	**OH**	**OCH_3**	**OH**	**OH**	**CH_3**
340.1543	**-OCH_2O-**		**OCH_3**	**OCH_3**	**H**
354.17	-OCH_2O-		OCH_3	OCH_3	CH_3
324.123	**-OCH_2O-**		**-OCH_2O-**		**H**
338.1387	**-OCH_2O-**		**-OCH_2O-**		**CH_3**
326.1387	**-OCH_2O-**		**OCH_3**	**OH**	**H**
340.1543	**-OCH_2O-**		**OCH_3**	**OH**	**CH_3**
326.1387	**-OCH_2O-**		**OH**	**OCH_3**	**H**
340.1543	**-OCH_2O-**		**OH**	**OCH_3**	**CH_3**
312.1236	-OCH_2O-		OH	OH	H
326.1392	**-OCH_2O-**		**OH**	**OH**	**CH_3**

Table S2 The data screening table of protonine alkaloids

[M+H]+	C-2	C-3	C-9	C-10	C-13
386.1967	OCH_3	OCH_3	OCH_3	OCH_3	H
400.2124	OCH_3	OCH_3	OCH_3	OCH_3	CH_3
370.1654	OCH_3	OCH_3	-OCH_2O-		H

384.1811	OCH_3	OCH_3	-OCH_2O-		CH_3
372.1811	OCH_3	OCH_3	OCH_3	OH	H
386.1967	OCH_3	OCH_3	OCH_3	OH	CH_3
372.1811	OCH_3	OCH_3	OH	OCH_3	H
386.1967	OCH_3	OCH_3	OH	OCH_3	CH_3
358.1694	OCH_3	OCH_3	OH	OH	H
372.1811	OCH_3	OCH_3	OH	OH	CH_3
372.1811	**OCH_3**	**OH**	**OCH_3**	**OCH_3**	**H**
386.1967	OCH_3	OH	OCH_3	OCH_3	CH_3
372.1811	**OH**	**OCH_3**	**OCH_3**	**OCH_3**	**H**
386.1967	OH	OCH_3	OCH_3	OCH_3	CH_3
356.1498	OCH_3	OH	-OCH_2O-		H
370.1654	**OCH_3**	**OH**	**-OCH_2O-**		**CH_3**
356.1498	OH	OCH_3	-OCH_2O-		H
370.1654	**OH**	**OCH_3**	**-OCH_2O-**		**CH_3**
358.1654	OCH_3	OH	OH	OCH_3	H
372.1811	**OCH_3**	**OH**	**OH**	**OCH_3**	**CH_3**
358.1654	OCH_3	OH	OCH_3	OH	H
372.1811	**OCH_3**	**OH**	**OCH_3**	**OH**	**CH_3**
358.1654	OH	OCH_3	OH	OCH_3	H
372.1811	**OH**	**OCH_3**	**OH**	**OCH_3**	**CH_3**
358.1654	OH	OCH_3	OCH_3	OH	H
372.1811	**OH**	**OCH_3**	**OCH_3**	**OH**	**CH_3**
344.1498	OCH_3	OH	OH	OH	H
358.1654	OCH_3	OH	OH	OH	CH_3
344.1498	OH	OCH_3	OH	OH	H
358.1654	OH	OCH_3	OH	OH	CH_3
370.1654	**-OCH_2O-**		**OCH_3**	**OCH_3**	**H**
384.1811	-OCH_2O-		OCH_3	OCH_3	CH_3
354.1341	**-OCH_2O-**		**-OCH_2O-**		**H**
368.1498	-OCH_2O-		-OCH_2O-		CH_3
356.1498	-OCH_2O-		OCH_3	OH	H
370.1654	-OCH_2O-		OCH_3	OH	CH_3
356.1498	-OCH_2O-		OH	OCH_3	H
370.1654	-OCH_2O-		OH	OCH_3	CH_3
342.1341	-OCH_2O-		OH	OH	H
356.1498	-OCH_2O-		OH	OH	CH_3

Table S3 The data screening table of protoberberine alkaloids

m/z	n(OCH_3)	n(OH)	n(-OCH_2O-)	C-13
320.0917	**0**	**0**	**2**	**H**
334.1074	**0**	**0**	**2**	**CH_3**
308.0917	0	2	1	H

322.1074	**0**	**2**	**1**	**CH_3**
296.0917	0	4	0	H
310.1074	0	4	0	CH_3
310.1074	1	3	0	H
324.1230	**1**	**3**	**0**	**CH_3**
322.1074	1	1	1	H
336.1230	**1**	**1**	**1**	**CH_3**
324.1230	**2**	**2**	**0**	**H**
338.1387	2	2	0	CH_3
336.1230	**2**	**0**	**1**	**H**
350.1387	2	0	1	CH_3
338.1387	3	1	0	H
352.1543	**3**	**1**	**0**	**CH_3**
352.1543	**4**	**0**	**0**	**H**
366.1705	**4**	**0**	**0**	**CH_3**

Table S4 The data screening table of aporphine alkaloids

m/z	n(OCH_3)	n(OH)	n(-CH_2O-)	N-(CH_3)n	n(-2H)
310.1074	0	0	2	0	0
308.0923	0	0	2	0	1
324.1236	0	0	2	1	0
322.1079	0	0	2	1	1
338.1387	0	0	2	2	0
336.1230	0	0	2	2	1
298.1079	0	2	1	0	0
296.0923	0	2	1	0	1
312.1236	0	2	1	1	0
310.1079	0	2	1	1	1
326.1387	0	2	1	2	0
324.1230	0	2	1	2	1
286.1079	0	4	0	0	0
284.0923	0	4	0	0	1
300.1236	0	4	0	1	0
298.1079	0	4	0	1	1
314.1387	0	4	0	2	0
312.1230	0	4	0	2	1
300.1236	1	3	0	0	0
298.1079	1	3	0	0	1
314.1392	1	3	0	1	0
312.1236	1	3	0	1	1
328.1543	1	3	0	2	0
326.1387	1	3	0	2	1
312.1230	1	1	1	0	0

310.1079	1	1	1	0	1
326.1230	1	1	1	1	0
324.1236	1	1	1	1	1
340.1543	1	1	1	2	0
338.1387	1	1	1	2	1
314.1392	2	2	0	0	0
312.1236	2	2	0	0	1
328.1549	**2**	**2**	**0**	**1**	**0**
326.1392	**2**	**2**	**0**	**1**	**1**
342.1700	2	2	0	2	0
340.1543	2	2	0	2	1
326.1392	2	0	1	0	0
324.1236	2	0	1	0	1
340.1549	2	0	1	1	0
338.1392	**2**	**0**	**1**	**1**	**1**
354.1700	2	0	1	2	0
352.1543	2	0	1	2	1
328.1549	3	1	0	0	0
326.1392	3	1	0	0	1
342.1700	3	1	0	1	0
340.1549	3	1	0	1	1
356.1856	3	1	0	2	0
354.1700	3	1	0	2	1
342.1705	4	0	0	0	0
340.1549	4	0	0	0	1
356.1862	**4**	**0**	**0**	**1**	**0**
354.1705	**4**	**0**	**0**	**1**	**1**
370.2073	4	0	0	2	0
368.1856	4	0	0	2	1

Red numbers indicate quasi-molecular ions matched with yanhusuo compounds

References

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Table S5 86 alkaloid compounds identified from Yanhusuo by UPLC-Q-TOF/MS^{E}

NO.	**RT (min)**	**Formula**	**Measured mass (m/z)**	**Mass Error (ppm)**	**Response**	**Adducts**	**MS/MS^{E}**	**Identification**
1	3.6	$C_{19}H_{21}NO_4$	328.1548	1.46	9208	+H	328.1545$[M + H]^+$, **297.1134$[M + H - CH_3NH_2]^+$,** 265.0863$[M + H - CH_3NH_2 - CH_3OH]^+$, 222.0686$[M+H - CH_3NH_2 - CH_3OH - CH_3 - CO]^+$, 282.0880$[M + H - CH_3NH_2 - CH_3]^+$	(+)-isoboldine or boldine
2[a]	3.88	$C_{19}H_{24}NO_3$	314.1752	0.42	12250	-e	314.1753 $[M]^+$, 269.1172 $[M - (CH_3)_2NH]^+$, 147.0448 $[M - C_{10}H_{18}NO]^+$	magnocurarine
3	4.5	$C_{19}H_{21}NO_4$	328.1544	0.27	4265	+H	328.1538$[M + H]^+$, **192.1024$[M + H - C_8H_8O_2]^+$,** 177.0544$[M + H - C_8H_8O_2 - CH_3]^+$, 313.1305$[M + H - CH_3]^+$, 312.1244$[M + H - CH_4]^+$, 296.1286$[M + H - CH_3OH]^+$,	demethylcorydalmine
4[b]	4.81	$C_{18}H_{17}NO_4$	312.1236	1.66	3354	+H	312.1234$[M + H]^+$, 294.0766$[M + H - CH_3 - 2H]^+$, 279.0516$[M + H - 2CH_3]^+$	unknow

5	4.9	$C_{19}H_{21}NO_4$	328.1547	1.19	10473	+H	328.1554$[M + H]^+$, **297.1126$[M + H - CH_3NH_2]^+$,** 265.0863$[M + H - CH_3NH_2 - CH_3OH]^+$, 222.0674$[M + H - CH_3NH_2 - CH_3OH - CH_3 - CO]^+$, 282.0890$[M + H - CH_3NH_2 - CH_3]^+$	(+)-isoboldine or boldine
6	5.07	$C_{19}H_{21}NO_4$	328.1548	1.51	6892	+H	328.1546$[M + H]^+$, **178.0869$[M + H - C_9H_{10}O_2]^+$,** 176.0706$[M + H - C_9H_{10}O_2 - 2H]^+$, 298.1459$[M + H - 2CH_3]^+$, 313.1305$[M + H - CH_3]^+$, 312.1226$[M + H - CH_4]^+$, 296.1286$[M + H - CH_3OH]^+$, 163.0631$[M + H - C_9H_{10}O_2 - CH_3]^+$, 280.09770$[M + H - CH_3 - 2H - OCH_3]^+$,	(S)-scoulerine
7	5.98	$C_{20}H_{23}NO_4$	342.1694	0.97	7158	+H	342.1694$[M + H]^+$, **192.1020$[M + H - C_9H_{10}O_2]^+$,** 177.0789$[M + H - C_9H_{10}O_2 - CH_3]^+$, 151.0760$[M + H - C_{11}H_{13}NO_2]^+$	corydalmine
8	6.33	$C_{19}H_{19}NO_4$	326.1387	0.15	8565	+H	326.1383$[M + H]^+$, **295.0923$[M + H - CH_3NH_2]^+$,** 263.0704$[M + H - CH_3NH_2 - CH_3OH]^+$, 280.07490$[M + H - CH_3NH_2 - CH_3]^+$	bulbocapnine
9[a]	6.4	$C_{19}H_{24}NO_3$	314.1753	0.64	225179	-e	314.1753 $[M]^+$, 269.1172$[M - C_2H_7N]^+$, 192.1016$[M - C_8H_{10}O]^+$,	magnocurarine

10	6.75	$C_{19}H_{21}NO_4$	328.1547	1.2	147286	+H	328.1547$[M + H]^+$, **178.0870$[M + H - C_9H_{10}O_2]^+$,** 163.0634$[M + H - C_9H_{10}O_2 - CH_3]^+$, 151.0761$[M + H - C_{10}H_{11}NO_2]^+$, 176.0711$[M + H - C_9H_{10}O_2 - 2H]^+$, 313.1305$[M + H - CH_3]^+$, 312.1244$[M + H - CH_4]^+$, 296.1286$[M + H - CH_3OH]^+$, 298.10713$[M + H - 2CH_3]^+$, 280.09770$[M + H - CH_3 - 2H - OCH_3]^+$, 148.0761$[M + H - C_9H_{10}O_2 - CH_3OH]^+$, 119.0500$[M + H - C_{10}H_{11}NO_2 - CH_3OH]^+$	(S)-scoulerine
11	6.97	$C_{20}H_{23}NO_4$	342.1703	0.95	31719	+H	342.1705$[M + H]^+$, **178.0865$[M + H - C_{10}H_{12}O_2]^+$,** 163.0632$[M + H - C_{10}H_{12}O_2 - CH_3]^+$, 165.0918$[M + H - C_{10}H_{11}NO_2]^+$, 176.0700$[M + H - C_{10}H_{12}O_2 - 2H]^+$, 326.1393$[M - CH_4]^+$, 294.1131$[M - CH_3 - 2H - OCH_3]^+$, 312.1242$[M + H - 2CH_3]^+$	tetrahydrojatrorrhizine or tetrahydrocolumbamine
12	7.08	$C_{19}H_{13}NO_5$	336.0869	0.84	5577	+H	336.0865$[M + H]^+$, 308.0927$[M + H - CO]^+$, 306.0777$[M + H – CO - 2H]^+$, 278.0827$[M + H - 2CO - 2H]^+$,	8-oxocoptisine

13[b]	7.3	$C_{21}H_{25}NO_5$	372.1806	0.23	3191	+H	372.1808$[M + H]^+$, 354.1696$[M + H - H_20]^+$, 340.1541$[M + H - CH_3OH]^+$, **208.0966$[M + H - C_{10}H_{12}O_2]^+$,** **190.0864$[M + H - C_{10}H_{12}O_2 - H_2O]^+$,** 165.0919$[M + H - C_{11}H_{14}NO_3]^+$,	protopine-type alkaloid
14	7.53	$C_{19}H_{19}NO_4$	326.1391	1.14	23219	+H	326.139$[M + H]^+$, **178.0867$[M + H - C_9H_8O_2]^+$,** 163.0631$[M + H - C_9H_8O_2 - CH_3]^+$, 149.0603$[M + H - C_{10}H_{12}NO_2]^+$ 176.0709$[M + H - C_9H_8O_2 - 2H]^+$,	(S)-cheilanthifoline or isochelianthifoline
15	7.86	$C_{20}H_{23}NO_4$	342.1703	0.97	78963	+H	342.1702$[M + H]^+$, **192.1021$[M + H - C_9H_{10}O_2]^+$,** 177.0784$[M + H - C_9H_{10}O_2 - CH_3]^+$, 151.0760$[M + H - C_{11}H_{13}NO_2]^+$, 149.0592$[M + H - C_{11}H_{13}NO_2 - 2H]^+$, 190.0845$[M + H - C_9H_{10}O_2 - 2H]^+$	corydalmine
16	7.87	$C_{10}H_9NO_3$	192.0656	0.4	8185	+H	192.0656$[M + H]^+$, 148.0762$[M + H - COO]^+$, 176.0668$[M + H - O]^+$	noroxyhydrastinine
17	8.04	$C_{20}H_{23}NO_4$	342.17	0.01	35111	+H	342.1705$[M + H]^+$, **192.1027$[M + H - C_9H_{10}O_2]^+$,** 151.0746$[M + H - C_{11}H_{13}NO_2]^+$, 326.1383$[M + H - CH_4]^+$, 310.1441$[M + H - CH_3OH]^+$, 328.1533$[M + H - CH_2]^+$,	corydalmine

							190.1851[M + H - $C_9H_{10}O_2$ - 2H]$^+$	
18[b]	8.56	$C_{21}H_{25}NO_5$	372.1806	0.25	27131	+H	372.1807[M + H]$^+$, 354.1696[M + H - H_2O]$^+$, **208.0973[M + H - $C_{10}H_{12}O_2$]$^+$,** **190.0866[M + H - $C_{10}H_{12}O_2$ - H_2O]$^+$,** 165.0919[M + H - $C_{11}H_{14}NO_3$]$^+$,	protopine-type alkaloid
19	8.85	$C_{19}H_{16}NO_4^+$	322.1079	1.57	30389	-e	**322.1077[M]$^+$,** 307.0842[M - CH_3]$^+$, 306.0769[M - CH_4]$^+$, 279.0897[M - CH_3 - CO]$^+$, 278.0813[M - CH_4 - CO]$^+$,	berberrubine or dehydrocheilanthifoline
20	8.9	$C_{19}H_{18}NO_4^+$	324.1227	-1.01	5356	-e	**324.1222[M]$^+$,** 322.1078[M - 2H]$^+$, 309.1005[M - CH_3]$^+$, 294.0768[M - $2CH_3$]$^+$, 292.0980[M - CH_3OH]$^+$, 308.0918[M - CH_4]$^+$, 280.0974[M - CH_4 - CO]$^+$,	demethyleneberberine or stepharanine

21	9.08	$C_{20}H_{23}NO_4$	342.1704	1.35	1052483	+H	342.1704$[M + H]^+$, **178.0870$[M + H - C_{10}H_{12}O_2]^+$,** 163.0635$[M + H - C_{10}H_{12}O_2 - CH_3]^+$, 326.1393$[M - CH_4]^+$, 176.0712$[M + H - C_{10}H_{10}O_2]^+$ 312.1234$[M + H - 2CH_3]^+$	(R)-(+)-corypalmine or tetrahydrocolumbamine
22	9.26[b]	$C_{21}H_{25}NO_4$	356.1862	1.6	533293	+H	356.1863$[M + H]^+$, **192.1026$[M + H - C_{10}H_{12}O_2]^+$,** 177.0790$[M + H - C_{10}H_{12}O_2 - CH_3]^+$, 340.1548$[M + H - CH_4]^+$, 341.1622$[M + H - CH_3]^+$, 308.1285$[M + H - CH_3 - 2H - OCH_3]^+$, 190.0859$[M + H - C_{10}H_{12}O_2 - 2H]^+$, 324.1628$[M + H - CH_3OH]^+$, 326.1392$[M + H - 2CH_3]^+$, 165.0919$[M + H - C_{11}H_{13}NO_2]^+$, 150.0667$[M + H - C_{11}H_{13}NO_2 - CH_3]^+$, 135.0447$[M + H - C_{11}H_{13}NO_2 - 2CH_3]^+$	tetrahydropalmatine isomer or yuanhunine
23	9.66	$C_{19}H_{18}NO_4^+$	324.1222	1.31	3885	-e	**324.1228$[M]^+$,** 292.0980$[M - CH_3OH]^+$, 308.0916$[M - CH_4]^+$, 280.0975$[M - CH_4 - CO]^+$,	demethyleneberberine or stepharanine
24	9.85	$C_{19}H_{18}NO_4^+$	324.1236	1.81	20559	-e	**324.1237$[M]^+$,** 309.1004$[M - CH_3]^+$, 294.0769$[M - 2CH_3]^+$, 292.0977$[M - CH_3OH]^+$,	demethyleneberberine

25	9.85	$C_{20}H_{23}NO_4$	342.1703	1.01	120853	+H	342.1703$[M + H]^+$, **178.0867$[M + H - C_{10}H_{12}O_2]^+$,** 163.0635$[M + H - C_{10}H_{12}O_2 - CH_3]^+$, 176.0707$[M + H - C_{10}H_{12}O_2 - 2H]^+$, 326.1393$[M - CH_4]^+$, 312.1242$[M + H - 2CH_3]^+$	demethyleneberberine or stepharanine
26	9.91[b]	$C_{21}H_{25}NO_4$	356.1857	0.15	169456	+H	356.1858$[M + H]^+$, **192.1023$[M + H - C_{10}H_{12}O_2]^+$,** 165.0914$[M + H - C_{11}H_{13}NO_2]^+$, 326.1390$[M + H - 2CH_3]^+$, 341.1623$[M + H - CH_3]^+$, 308.1358$[M + H - CH_3 - 2H - OCH_3]^+$, 324.1629$[M + H - CH_3OH]^+$, 190.0863$[M + H - C_{10}H_{12}O_2 - 2H]^+$, 150.0682$[M + H - C_{11}H_{13}NO_2 - CH_3]^+$, 135.04475$[M + H - C_{11}H_{13}NO_2 - 2CH_3]^+$	tetrahydropalmatine isomer
27	10.08[b]	$C_{21}H_{25}NO_4$	356.1858	0.51	367569	+H	356.1859$[M + H]^+$, **192.1029$[M + H - C_{10}H_{12}O_2]^+$,** 177.0794$[M + H - C_{10}H_{12}O_2 - CH_3]^+$, 340.1549$[M + H - CH_4]^+$, 308.1281$[M + H - CH_3 - 2H - OCH_3]^+$, 326.1390$[M + H - 2CH_3]^+$, 190.0858$[M + H - C_{10}H_{12}O_2 - 2H]^+$, 162.0554$[M + H - C_{10}H_{12}O_2 - 2CH_3]^+$	tetrahydropalmatine isomer

28*	10.42	$C_{20}H_{19}NO_5$	354.1341	1.51	819976	+H	354.1341$[M + H]^+$,	protopine
							188.0713$[M + H - C_9H_8O_2 - H_2O]^+$,	
							149.0605$[M + H - C_{11}H_{11}NO_3]^+$,	
							206.0813$[M + H - C_9H_8O_2]^+$,	
							189.0772$[M + H - C_9H_8O_2 - OH]^+$,	
							336.1235$[M + H - H_2O]^+$,	
29	10.84	$C_{21}H_{21}NO_5$	368.1493	0.16	10827	+H	368.149$[M + H]^+$,	corycavine
							352.1185$[M + H - CH_4]^+$,	
							338.1009$[M + H - 2H - CO]^+$,	
							336.1238$[M + H - 2H – CO - 2H]^+$,	
30	11.01	$C_{20}H_{20}NO_4^+$	338.1391	1.21	16873	-e	**338.1389$[M]^+$,**	jatrorrhizine or
							323.1153$[M - CH_3]^+$,	columbamine
							294.1134$[M - CH_4 - CO]^+$,	
							291.08958$[M - CH_3 - CH_3OH]^+$,	
							306.11318$[M - CH_3OH]^+$,	
							308.0921$[M - 2CH_3]^+$	
31	11.02	$C_{21}H_{23}NO_4$	354.1695	-1.44	10871	+H	354.1693$[M + H]^+$,	dehydroglaucine isomer
							338.1390$[M + H - CH_4]^+$,	
							323.1153$[M + H - CH_3NH_2]^+$,	
							265.0863$[M + H - CH_3NH_2 - CH_3OH]^+$,	
							280.0967$[M + H - CH_3NH_2 - CH_3OH - CH_3 - CO]^+$,	
							308.0921$[M + H - CH_3NH_2 - CH_3]^+$	
32[a]	11.23	$C_{20}H_{21}NO_4$	340.1546	0.81	22174	+H	340.1548$[M + H]^+$,	tetrahydroprotoberberine-
							192.1023$[M + H - C_9H_8O_2]^+$,	type alkaloid
							324.1209$[M + H - CH_4]^+$	

33	11.41	$C_{19}H_{14}NO_4^+$	320.0921	1.12	80618	-e	**320.0921[M]$^+$,** **318.0772[M - 2H]$^+$** 292.0971[M - CO]$^+$, 290.0815[M – CO - 2H]$^+$ 264.1018[M – CO - CO]$^+$, 262.0807[M – CO – CO - 2H]$^+$, 277.0743[M- CO - CH_3]$^+$	coptisine or pseudocoptisine
34	11.56	$C_{20}H_{20}NO_4^+$	338.1381	-1.66	17973	-e	**338.1382[M]$^+$,** 323.1132[M - CH_3]$^+$, 294.1134[M - CH_4 - CO]$^+$, 291.0896[M - CH_3 - CH_3OH]$^+$, 306.1132[M - CH_3OH]$^+$, 308.0926[M - 2CH_3]$^+$	jatrorrhizine or columbamine
35	11.65	$C_{21}H_{25}NO_4$	356.186	1.04	397941	+H	356.1859[M + H]$^+$, **178.0870[M + H - $C_{11}H_{14}O_2$]$^+$,** 163.0642[M + H - $C_{11}H_{14}O_2$ - CH_3]$^+$, 340.1543[M + H - CH_4]$^+$, 326.1390[M + H - 2CH_3]$^+$, 308.1297[M + H - CH_3OH - CH_3]$^+$	corybulbine or Isocorybulbine
36[a]	11.78	$C_{19}H_{19}NO_4$	326.1391	1.25	4317	+H	326.139[M + H]$^+$, **176.0715[M + H - $C_9H_{10}O_2$]$^+$**	nandinine
37	12.05	$C_{19}H_{14}NO_4^+$	320.0925	2.28	1437278	-e	**320.0925[M]$^+$,** **318.0772[M - 2H]$^+$** 292.0976[M - CO]$^+$, 290.0818[M – CO - 2H]$^+$ 264.1018[M – CO - CO]$^+$,	coptisine or pseudocoptisine

							262.0867[M – CO – CO - 2H]$^+$, 277.0743[M – CO - CH_3]$^+$	
38*	12.08	$C_{21}H_{23}NO_5$	370.1655	1.54	447391	+H	370.1654[M + H]$^+$, **188.072[M + H - $C_{10}H_{12}O_2$ - H_2O]$^+$,** **206.08232[M + H - $C_{10}H_{12}O_2$]$^+$,** 165.0911[M + H - $C_{11}H_{11}NO_3$]$^+$, 352.15492[M + H - H_2O]$^+$, 354.13161[M + H - CH_4]$^+$, 340.12416[M + H - 2CH_3]$^+$	allocryptopine
39	12.24	$C_{19}H_{17}NO_4$	324.1237	1.95	463292	+H	324.1236[M + H]$^+$, **176.0714[M + H - $C_9H_8O_2$]$^+$,** 149.0607[M + H - $C_{10}H_9NO_2$]$^+$, 310.1086[M + H - CH_2]$^+$, 174.0556[M + H - $C_9H_8O_2$ - 2H]$^+$, 161.0486[M+H - $C_9H_8O_2$ - CH_3]$^+$	tetrahydrocoptisine
40	12.48	$C_{20}H_{20}NO_4^+$	338.139	0.85	845403	+H	**338.1394[M]$^+$,** **336.1236[M - 2H]$^+$,** 323.1161[M - CH_3]$^+$, 322.1079[M - CH_4]$^+$, 307.0852[M - C_2H_7]$^+$, 294.1131[M - CH_4 - CO]$^+$, 291.08958[M - CH_3 - CH_3OH]$^+$, 306.1128[M - CH_3OH]$^+$,	jatrorrhizine or columbamine

							308.0918[M - $2CH_3$]$^+$	
41	12.6	$C_{19}H_{14}NO_4^+$	320.092	0.73	16351	-e	**320.0925[M]$^+$,** 292.0976[M - CO]$^+$, 290.0818[M – CO - 2H]$^+$ 264.1018[M - 2CO]$^+$, 262.0867[M - 2CO - 2H]$^+$,	coptisine or pseudocoptisine
42*	12.73	$C_{21}H_{25}NO_4$	356.1859	0.73	1644391	+H	356.1859[M + H]$^+$, **192.1023[M + H - $C_{10}H_{12}O_2$]$^+$,** 165.0912[M + H - $C_{11}H_{13}NO_2$]$^+$, 340.1549[M + H - CH_4]$^+$, 341.16288[M + H - CH_3]$^+$, 339.15806[M + H - CH_3 - 2H]$^+$, 150.0680[M + H - $C_{11}H_{13}NO_2$ - CH_3]$^+$, 308.1358[M + H - CH_3 - 2H - OCH_3]$^+$, 190.0856[M + H - $C_{10}H_{12}O_2$ - 2H]$^+$, 324.1629[M + H - CH_3OH]$^+$, 326.1364[M + H - $2CH_3$]$^+$, 298.1440[M + H - $2CH_3$ - CO]$^+$, 135.0447[M + H - $C_{11}H_{13}NO_2$ - $2CH_3$]$^+$, 177.0791[M + H - $C_{10}H_{12}O_2$ - CH_3]$^+$,	tetrahydropalmatine

							162.0552[M + H -$C_{10}H_{12}O_2$ - 2CH_3]$^+$, 134.0728[M + H - $C_{10}H_{12}O_2$ - CH_3 - 2CO]$^+$, 159.0685[M + H - $C_{10}H_{12}O_2$ - CH_3OH]$^+$	
43	12.75	$C_{22}H_{23}NO_5$	382.165	0.25	19124	+H	382.165[M + H]$^+$, 366.1338[M + H - CH_4]$^+$, 354.1702[M + H - CO]$^+$ 350.1386[M + H - CH_3OH]$^+$, 340.1549[M + H – CO - CH_2]$^+$ 324.1239[M + H – CO - 2CH_3]$^+$ 308.1358[M + H – CO - CH_3 - CH_3O]$^+$	7-aldehyde dehydroglaucine
44	12.83	$C_{20}H_{25}NO_3$	328.191	0.72	347521	+H	328.1910[M + H]$^+$, 283.1327[M + H - C_2H_6N]$^+$, 251.1055[M + H - $C_3H_{10}NO$]$^+$,	leonticine

45	12.93	$C_{20}H_{20}NO_4^+$	338.139	1.02	84316	-e	**338.1392[M]$^+$,** 322.1081[M - CH_4]$^+$, 294.1134[M - CH_4 - CO]$^+$, 291.0896[M - CH_3 - CH_3OH]$^+$, 306.1123[M - CH_3OH]$^+$, 308.0926[M - $2CH_3$]$^+$	jatrorrhizine or columbamine
46	12.93	$C_{20}H_{25}NO_3$	328.1915	2.29	398967	+H	328.1915[M + H]$^+$, 298.14467[M + H - $2CH_3$]$^+$, 296.16725[M + H - CH_3OH]$^+$, 121.0651[M + H - $C_{12}H_{16}NO_2$]$^+$, 175.0750[M + H - $C_9H_{14}NO$]$^+$,	leonticine
47	12.97	$C_{22}H_{28}NO_4^+$	370.2016	0.89	179649	-e	370.2015[M]$^+$, **206.1183[M - $C_{10}H_{12}O_2$]$^+$,** 190.0864[M - $C_{10}H_{12}O_2$ - CH_3 - 2H]$^+$, 191.0934[M - $C_{10}H_{12}O_2$ - CH_3]$^+$, 354.1687[M - CH_4]$^+$, 340.1488[M - $2CH_3$]$^+$	N- methyltetrahydropalmatine
48	13.08	$C_{21}H_{25}NO_4$	356.1862	1.46	1281448	+H	356.1861[M + H]$^+$, **325.1439[M + H - CH_3NH_2]$^+$,** 294.1255[M + H - CH_3NH_2 - CH_3O]$^+$, 279.1019[M + H - CH_3NH_2 - CH_3O - CH_3]$^+$, 251.1068[M + H - CH_3NH_2 - CH_3OH - CH_3 - CO]$^+$, 310.12054[M + H - CH_3NH_2 - CH_3]$^+$	Glaucine

49	13.54	$C_{20}H_{17}NO_5$	352.1182	0.82	76455	+H, -e	352.1183$[M + H]^+$, 322.0717$[M + H - 2CH_3]^+$, 336.0864$[M + H - CH_3]^+$, 320.0916$[M + H - CH_3OH]^+$, 308.0923$[M + H – CO - CH_3]^+$, 294.0766$[M + H – CO - 2CH_3]^+$, 292.0974$[M + H – CO - CH_3O]^+$,	oxoglaucine
50	13.6	$C_{22}H_{28}NO_4^+$	370.2009	1.76	179649	-e	370.2019$[M]^+$, **206.1184$[M - C_{10}H_{12}O_2]^+$,** 190.0862$[M - C_{10}H_{12}O_2 - CH_3 - 2H]^+$, 191.0934$[M - C_{10}H_{12}O_2 - CH_3]^+$, 354.1681$[M - CH_4]^+$, 340.1486$[M - 2CH_3]^+$	N-methyltetrahydropalmatine
51	13.61	$C_{21}H_{24}NO_4$	354.1696	-1.08	15630	-e	**354.1698$[M]^+$,** **352.1221$[M - 2H]^+$,** 339.1445$[M - CH_3]^+$, 322.0686$[M - 2H - 2CH_3]^+$,	8,9- dihydropalmatine
52*	13.83	$C_{20}H_{21}NO_4$	340.1547	1.09	558282	+H	340.1548$[M + H]^+$, **176.0714$[M + H - C_{10}H_{12}O_2]^+$,** 324.1231$[M - CH_4]^+$, 174.0556$[M + H - C_{10}H_{14}O_2]^+$, 161.0483$[M + H - C_{10}H_{14}O_2 - CH_3]^+$, 308.1285$[M - CH_3OH]^+$, 292.10203$[M + H - CH_3 - 2H - OCH_3]^+$, 165.0915$[M + H - C_{10}H_9NO_2]^+$, 150.0668$[M + H - C_{10}H_9NO_2 - CH_3]^+$,	tetrahydroberberine

							325.13568[M + H - CH_3]$^+$	
53[b]	14.27	$C_{21}H_{23}NO_5$	370.1654	1.25	61086	+H	370.1654[M + H]$^+$, **190.0868[M + H - $C_{10}H_{10}O_2$ - H_2O]$^+$,** 352.1538[M + H - H_2O]$^+$, **208.0968[M + H - $C_{10}H_{10}O_2$]$^+$,** 163.0761[M + H - $C_{11}H_{14}NO_3$]$^+$,	protopine-type alkaloid
54[b]	14.41	$C_{21}H_{23}NO_4$	354.1705	0.6	194877	+H	354.1705[M + H]$^+$, **190.0873[M + H - $C_{10}H_{12}O_2$]$^+$** 188.0714[M + H - $C_{10}H_{14}O_2$]$^+$ 175.0634[M + H - $C_{10}H_{14}O_2$ - CH_3]$^+$ 160.0762[M + H - $C_{10}H_{10}O_2$ - CH_3OH]$^+$,	tetrahydroprotoberberine-type alkaloid
55	14.57	$C_{21}H_{22}NO_4^+$	352.1545	0.57	36130	-e	**352.1546[M]$^+$,** 337.1313[M - CH_3]$^+$, 336.1238[M - CH_4]$^+$, 308.1280[M - CH_4 - CO]$^+$, 320.1287[M - CH_3OH]$^+$, 322.1079[M - 2CH_3]$^+$, 294.1126[M - 2CH_3 - CO]$^+$ 292.0968[M - 2CH_3 – CO - 2H]$^+$	dehydrocorybulbine or palmatine or 13-methyldehydrocorydalmine or 13-methylpalmatrubine or yanhusuine or 13-methylcolumbamine

56[b]	14.58	$C_{21}H_{25}NO_5$	372.1808	0.55	36963	+H	372.1809$[M + H]^+$, 354.1730$[M + H - H_2O]^+$, **208.0968$[M + H - C_{10}H_{12}O_2]^+$,** **190.0868$[M + H - C_{10}H_{12}O_2 - H_2O]^+$,** 165.09153$[M + H - C_{11}H_{14}NO_3]^+$, 322.1073$[M + H - C_2H_{10}O]^+$,	protopine-type alkaloid
57	14.59	$C_{20}H_{15}NO_4$	334.1078	1.15	6345	+H	334.1074$[M + H]^+$, 306.1118$[M + H - CO]^+$, 304.0983$[M + H - 2H - CO]^+$	dihydrosanguinarine
58	14.76	$C_{21}H_{22}NO_4^+$	352.1548	1.37	254426	-e	**352.1548$[M]^+$,** 337.1313$[M - CH_3]^+$, 336.1238$[M - CH_4]^+$, 308.1293$[M - CH_4 - CO]^+$, 320.1287$[M - CH_3OH]^+$, 322.1079$[M - 2CH_3]^+$, 294.1132[M - 2CH3 - CO]$^+$ 292.0976$[M - 2CH_3 – CO - 2H]^+$	dehydrocorybulbine or palmatine or 13- methyldehydrocorydalmine or 13-methylpalmatrubine or yanhusuine or 13-methylcolumbamine
59	14.79	$C_{20}H_{16}NO_4^+$	334.1079	9.58	107925	-e	**334.1079$[M]^+$,** 306.1118$[M - CO]^+$, 304.0968$[M – CO - 2H]^+$, 292.0980$[M – CO - CH_2]^+$, 278.0810$[M - 2CO]^+$,	corysamine

60	14.86	$C_{22}H_{27}NO_4$	370.2018	1.5	2650842	+H	370.2018$[M + H]^+$,	corydaline
							192.1025$[M + H - C_{11}H_{14}O_2]^+$,	
							165.0919$[M + H - C_{12}H_{15}NO_2]^+$,	
							179.1074$[M + H - C_{11}H_{13}NO_2]^+$,	
							354.1679$[M + H - CH_4]^+$,	
							355.1765$[M + H - CH_3]^+$,	
							338.1789$[M + H - CH_3OH]^+$,	
							177.0797$[M + H - C_{11}H_{14}O_2 - CH_3]^+$,	
							162.05431$[M + H - C_{11}H_{14}O_2 - 2CH_3]^+$,	
							134.07218$[M + H - C_{11}H_{14}O_2 - 2CH_3 - CO]^+$,	
							153.08749$[M + H - C_{12}H_{16}NO_2]^+$,	
							218.11835$[M + H - C_9H_{12}O_2]^+$,	
							322.14987$[M + H - CH_3 - 2H - OCH_3]^+$,	
							150.0682$[M + H - C_{12}H_{15}NO_2 - CH_3]^+$,	
							206.11758$[M + H - C_{10}H_{12}O_2]^+$	
61	14.98	$C_{21}H_{22}NO_4^+$	352.1548	1.3	803986	-e	**352.1553$[M]^+$,**	dehydrocorybulbine
							337.1310$[M - CH_3]^+$,	or palmatine
							336.1238$[M - CH_4]^+$,	or 13-methyldehydrocorydalmine
							308.1293$[M - CH_4 - CO]^+$,	or 13-methylpalmatrubine
							320.1287$[M - CH_3OH]^+$,	or yanhusuine
							322.1079$[M - 2CH_3]^+$,	or 13-methylcolumbamine
							294.1132$[M - 2CH_3 - CO]^+$	
							292.0983$[M - 2CH_3 – CO - 2H]^+$	

62	15.24	$C_{20}H_{21}NO_4$	340.155	1.83	36554	+H	**309.1129[M + H - CH_3NH_2]$^+$,** 278.1180[M + H - CH_3NH_2 - OCH_3]$^+$, 340.15467[M + H]$^+$, 294.0893[M + H - CH_3NH_2 - CH_3]$^+$, 266.09375[M + H - CH_3NH_2 - CH_3 - CO]$^+$, 263.0708[M+H - CH_3NH_2 - OCH_3 - CH_3]$^+$, 235.0787[M + H - CH_3NH_2 - OCH_3 - CH_3 - CO]$^+$,	nantenine or dicentrine
63	15.58	$C_{20}H_{19}NO_4$	338.1389	0.49	10581	+H	338.1387[M + H]$^+$, **176.0710[M + H - $C_{10}H_{10}O_2$]$^+$,** 191.0934[M + H - $C_9H_8O_2$]$^+$, 149.0600[M + H - $C_{11}H_{11}NO_2$]$^+$,	tetrahydrocorysamine
64	15.65	$C_{21}H_{21}NO_5$	368.1496	0.87	8596	+H	368.1493[M + H]$^+$, 352.1185[M + H - CH_4]$^+$, 338.1009[M + H - 2H - CO]$^+$, 336.1238[M + H - 2H – CO - 2H]$^+$,	corycavine
65*	15.88	$C_{20}H_{18}NO_4$	336.1231	0.15	403600	-e	**336.1236[M]$^+$,** 320.0923[M - CH_4]$^+$, 292.0973[M - CH_4 - CO]$^+$, 290.0808[M - CH_4 – CO - 2H]$^+$, 321.0997[M - CH_3]$^+$, 306.0767[M - 2CH_3]$^+$, 304.0973[M - CH_3OH]$^+$, 278.0817[M-2CH_3-CO]$^+$	berberine

66*	16.14	$C_{21}H_{22}NO_4^+$	352.1544	0.31	1179308	-e	**352.1554[M]$^+$,** 337.1310[M - CH_3]$^+$, 336.12367[M - CH_4]$^+$, 308.12860[M - CH_4 - CO]$^+$, 278.0815[M - CH_4 – CO - CH_2O]$^+$, 320.0941[M - CH_3OH]$^+$, 322.1079[M - 2CH_3]$^+$, 294.1132[M - 2CH_3 - CO]$^+$	palmatine
67	16.49	$C_{21}H_{19}NO_5$	366.134	0.98	73564	+H	366.1341[M + H]$^+$, 320.0921[M + H - C_2H_6O]$^+$, 336.0841[M + H - 2CH_3]$^+$, 351.1101[M + H - CH_3]$^+$,	8-hydroxyldihydrochelerythrine
68	16.63	$C_{21}H_{22}NO_4^+$	352.1546	0.83	100363	-e	**352.1545[M]$^+$,** 337.1306[M - CH_3]$^+$, 336.1230[M - CH_4]$^+$, 308.1277[M - CH_4 - CO]$^+$, 320.0941[M - CH_3OH]$^+$, 322.1079[M - 2CH_3]$^+$, 294.1132[M - 2CH_3 - CO]$^+$ 292.0968[M - 2CH_3 – CO - 2H]$^+$	dehydrocorybulbine or palmatine or 13-methyldehydrocorydalmine or 13-methylpalmatrubine or yanhusuine or 13-methylcolumbamine
69[b]	17.25	$C_{22}H_{26}NO_4^+$	368.1857	0.14	16200	-e	368.1858[M]$^+$, 352.1539[M - CH_4]$^+$, 324.1593[M - CH_4 - CO]$^+$, 336.1200[M - CH_3OH]$^+$, 338.1387[M - 2CH_3]$^+$,	unknow
70	17.34	$C_{20}H_{25}NO_3$	328.191	0.83	6807	+H	328.1908[M+H]$^+$,	leonticine

							283.1337[M + H - $(CH_3)_2N$]$^+$,	
71[a]	17.88	$C_{22}H_{27}NO_5$	386.196	-0.6	3745	+H	386.1963[M + H]$^+$, 354.1685[M + H - CH_3OH]$^+$, 338.1391[M + H - C_2H_8O]$^+$,	muramine
72[*]	18.03	$C_{22}H_{24}NO_4^+$	366.1707	1.87	3759312	+H	**366.1706[M]$^+$,** 350.1390[M - CH_4]$^+$, 351.1468[M - CH_3]$^+$, 322.1442[M - CH_4 - CO]$^+$, 292.0972[M - CH_4 – CO - CH_2O]$^+$, 336.1238[M - 2CH_3]$^+$, 319.1186[M - CH_3 - CH_3OH]$^+$, 334.1079[M - 2CH_3 - 2H]$^+$, 308.1289[M - 2CH_3 - CO]$^+$, 306.0647[M - 2CH_3 – CO - 2H]$^+$	dehydrocorydaline
73[b]	18.86	$C_{22}H_{24}NO_4^+$	366.17	0.17	174182	+H	**366.1700[M]$^+$,** 350.1381[M - CH_4]$^+$, 351.1459[M - CH_3]$^+$, 321.0997[M - 3CH_3]$^+$, 322.1442[M - CH_4 - CO]$^+$, 320.0921[M-CH_4-CO-2H]$^+$, 292.0972[M - CH_4 – CO - CH_2O]$^+$, 336.1231[M - 2CH_3]$^+$, 319.1186[M - CH_3 - CH_3OH]$^+$, 334.1076[M - 2CH_3 - 2H]$^+$, 308.1289[M-2CH_3-CO]$^+$, 306.0647[M - 2CH_3 – CO - 2H]$^+$	dehydrocorydaline

74	19.13	$C_{20}H_{17}NO_5$	352.1183	1.04	221806	+H, +Na	352.1184$[M + H]^+$, 306.0764$[M + H - CH_3OH]^+$, 322.0712$[M + H - 2CH_3]^+$, 337.0946$[M + H - CH_3]^+$, 336.0868$[M + H - CH_4]^+$, 304.0612$[M + H - CH_3 - COOH]^+$	oxoglaucine
75	19.28	$C_{19}H_{16}NO_4^+$	322.1069	-1.41	4640	-e	**322.1081$[M]^+$,** 320.0893$[M - 2H]^+$, 307.0842$[M - CH_3]^+$, 306.0769$[M - CH_4]^+$, 279.0897$[M - CH_3 - CO]^+$, 278.0807$[M - CH_4 - CO]^+$,	berberrubine or dehydrocheilanthifoline
76	23.72	$C_{21}H_{21}NO_5$	368.1492	-0.05	5356	+H	368.1487$[M + H]^+$, 353.1255$[M + H - CH_3]^+$, 338.1408$[M + H - 2H - CO]^+$, 336.1217$[M + H - 2H – CO - 2H]^+$,	corycavine
77	24.25	$C_{21}H_{21}NO_5$	368.1496	0.9	16181	+H, -e	368.1492$[M + H]^+$, 353.1255$[M + H - CH_3]^+$, 338.1038$[M + H - 2H - CO]^+$, 336.1238$[M + H - 2H – CO - 2H]^+$,	corycavine
78	24.3	$C_{21}H_{19}NO_6$	382.1276	4.61	25705	-e	382.1285$[M + H]^+$, 338.1391$[M + H - COO]^+$, 350.0661$[M + H - C_2H_8]^+$,	oxychelidonine
79	24.38	$C_{22}H_{25}NO_5$	384.1806	0.26	5028	+H	384.1806$[M + H]^+$, 352.1539$[M + H - CH_3OH]^+$, 320.0920$[M + H - C_3H_{12}O]^+$,	7-aldehyde glaucine

80	24.76	$C_{19}H_{13}NO_5$	336.0874	2.22	39448	+H, e, +Na	336.0875$[M + H]^+$, 308.0925$[M + H - CO]^+$, 306.0769$[M + H – CO - 2H]^+$,	8-oxocoptisine
81[a]	25.19	$C_{20}H_{13}NO_5$	348.0878	3.36	11474	+H, -e	348.0875$[M + H]^+$, 333.0644$[M + H - CH_3]^+$, 332.0923$[M + H - CH_3 - H]^+$, 337.09453$[M + H - CH_3]^+$, 336.0868$[M + H - CH_4]^+$ 304.06115$[M + H - CH_3 - COOH]^+$	oxysanguinarine
82	25.99	$C_{21}H_{23}NO_4$	354.1695	-1.44	10871	+H	354.1693$[M + H]^+$, **323.1153$[M + H - CH_3NH_2]^+$,** 280.0967$[M + H - CH_3NH_2 - CH_3OH - CH_3 - CO]^+$, 308.0921$[M + H - CH_3NH_2 - CH_3]^+$	dehydroglaucine
83	26	$C_{20}H_{19}NO_4$	338.1389	0.76	28554	+H	338.1388$[M + H]^+$, **307.1201$[M + H - CH_3NH_2]^+$,** 292.0969$[M + H - CH_3NH_2 - CH_3]^+$, 324.1232$[M + H - CH_2]^+$, 322.1075$[M + H - CH_3]^+$, 280.0973$[M + H - C_3H_6O]^+$,	dehydronantenine
84	26.49	$C_{20}H_{15}NO_4$	334.1077	0.86	8441	+H	334.1076$[M + H]^+$, 332.0807$[M + H - 2H]^+$, 304.0950$[M + H - 2H - CO]^+$, 318.0764$[M + H - CH_3]^+$,	dihydrosanguinarine

85	26.77	$C_{21}H_{19}NO_4$	350.1392	1.52	63104	+H	350.1392$[M + H]^+$, 348.1272$[M + H - 2H]^+$, 318.0774$[M + H - 2H - 2CH_3]^+$, 290.0819$[M + H - 2H - 2CH_3 - CO]^+$, 335.1148$[M + H - CH_3]^+$, 334.1081$[M + H - CH_4]^+$, 332.0887$[M + H - 2H - CH_3 - H]^+$, 302.0818$[M + H - 2H - CH_3 – H – CO - 2H]^+$,	dihydrochelerythrine
86	26.97	$C_{20}H_{15}NO_4$	334.1078	1.12	72976	+H	334.1076$[M + H]^+$, 332.0887$[M + H - 2H]^+$, 304.0950$[M + H - 2H - CO]^+$, 318.0765$[M + H - CH_3]^+$,	dihydrosanguinarine

*: Compared with a standard substance;

a:Reported for the first time in yanhusuo

b: Potential new compounds