

Supplementary material

Rapid On-site Identification of Pyrrolizidine Alkaloids in Herbal Medicines Using Miniature Mass Spectrometry

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23 Table S1 Sample information of herbs.

Sample	Source	Batch number
<i>Panax notoginseng</i> -1	Yunnan	WS2022120754
<i>Panax notoginseng</i> -2	Yunnan	WS2022120739
<i>Panax notoginseng</i> -3	Yunnan	LX2023102003
<i>Panax notoginseng</i> -4	Yunnan	GX2023072601
<i>Panax notoginseng</i> -5	Yunnan	HCT202310201
<i>Gynura japonica</i> -1	Jiangsu	YZ201810081
<i>Gynura japonica</i> -2	Jiangsu	YZ201810082
<i>Gynura japonica</i> -3	Shanghai	SH202305151
<i>Gynura japonica</i> -4	Zhejiang	YW201109251
<i>Gynura japonica</i> -5	Zhejiang	XJ201109251
<i>Senecio scandens</i> -1	Anhui	SH201508011
<i>Senecio scandens</i> -2	Guizhou	GZ201512251
<i>Senecio scandens</i> -3	Guangdong	GZ202004291
<i>Senecio scandens</i> -4	Henan	HN201512261
<i>Senecio scandens</i> -5	Jiangsu	JS202209161
<i>Senecio vulgaris</i> -1	Yunnan	LJ202207051
<i>Senecio vulgaris</i> -2	Sichuan	MG202007115
<i>Senecio vulgaris</i> -3	Xinjiang	WLMQ202207081
<i>Senecio vulgaris</i> -4	Heilongjiang	MDJ202007311
<i>Senecio vulgaris</i> -5	Jilin	TH202209161
<i>Ligularia duciformis</i>	Sichuan	KD200008
<i>Tussilago farfara</i>	Anhui	AH202412041
Qianbai Biyan tablets	Guangdong	231210
Zhisou Huatan pills	Guizhou	15417003
Medicinal liquor	Shanghai	2023HSOS02

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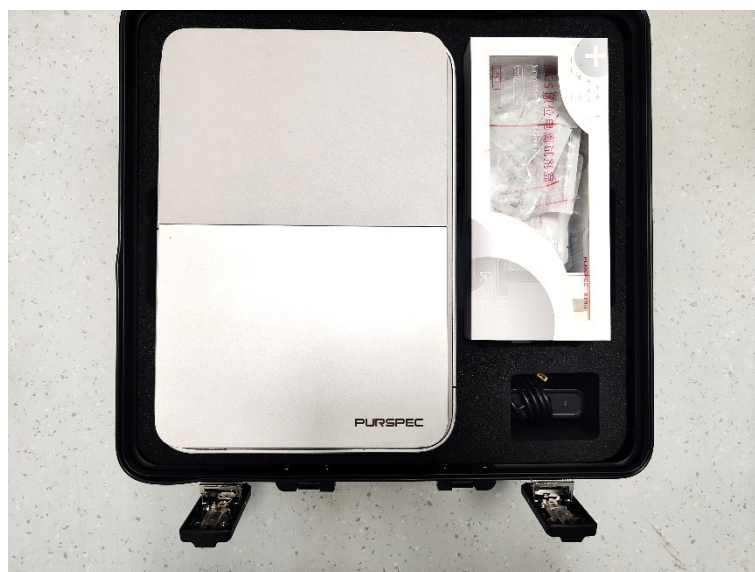
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NO.	Precursor ion (<i>m/z</i>)	MW	Product ion (<i>m/z</i>)	Type	Predicted compounds	Source	Ref.
1	334	333	306; 138; 120	RET	Seneciphylline	GJ; SV; ML	1, 2
2	336	335	308; 138; 120	RET	Senecionine	GJ; SV; ML	1, 2
3	350	349	138; 120; 118	RETNO	Seneciphylline N-oxide	GJ; SV; ML	1, 2
4	352	351	138; 120; 118	RETNO	Jacobine or Retrorsine or Senecionine N-oxide	GJ; SV; ML	2, 3
5	354	353	138; 120; 118	RETNO	Rosmarinine or Isorosmarinine	GJ; SV	3, 4
6	354	353	140; 122	PLA	Hadiensine	GJ	3
7	356	355	138; 136; 120	RETNO	2-Acety-heliotrine	GJ	3
8	366	365	338; 138; 120	RET	Adonifoline	SS; QBT	5
9	366	365	168; 150	OTO	Senkirkine	TF; ZHP	6
10	368	367	138; 136	RETNO	Jacobine N-oxide or Retrorsine N-oxide	GJ; SV	2, 3
11	370	369	352; 138	RET	Othonnine N-oxide	GJ; SV	3, 4
12	376	375	316; 138	RETNO	Seneciphyllinine	GJ	3
13	392	391	154; 136	RETNO	Seneciphyllinine N-oxide	GJ	3
14	396	395	336; 308; 138	RET	Isoline	LD	7

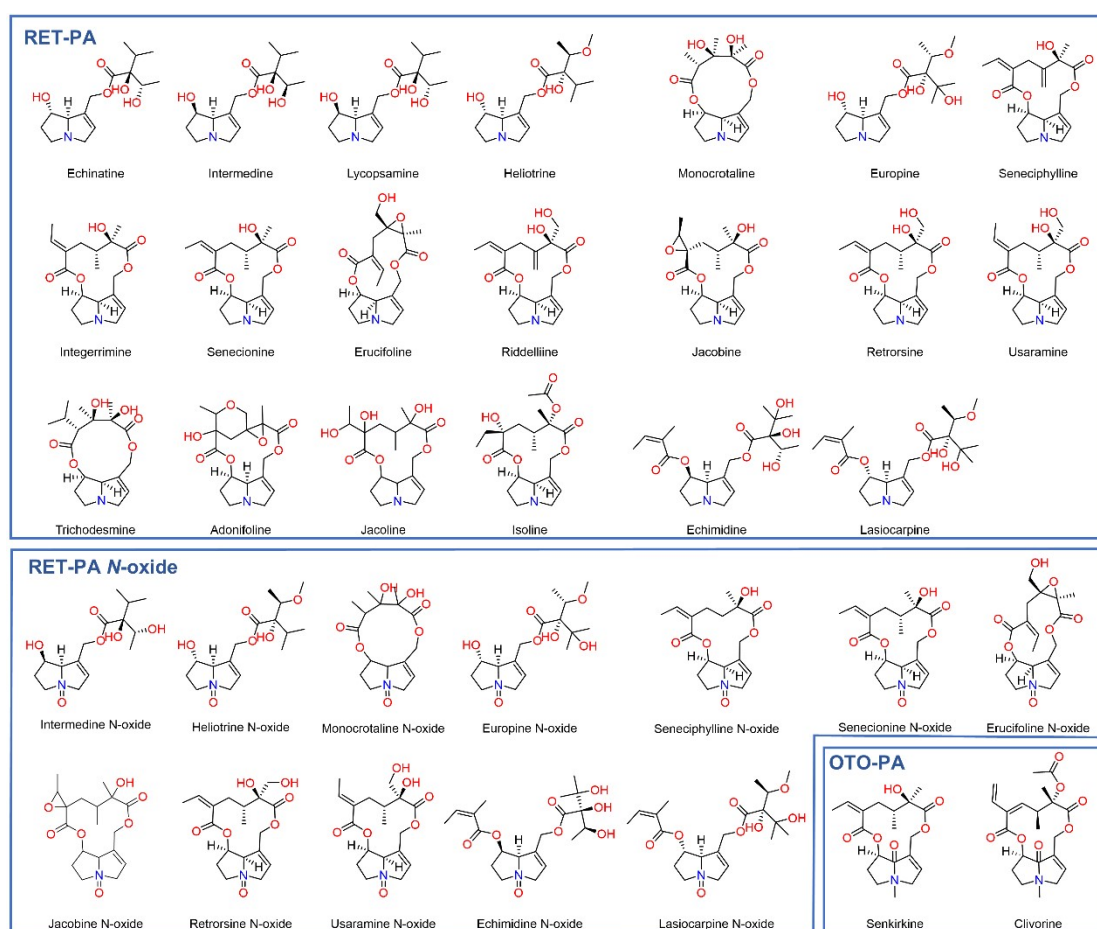
28 **Table S2** Representative PAs in herb samples were detected by PCS-Mini MS.

29 GJ: *Gynura japonica*; SV: *Senecio vulgaris*; ML, Medicinal liquor; SS: *Senecio*
30 *scandens*; QBT: Qianbai Biyan tablets; TF: *Tussilago farfara*; ZHP: Zhisou Huatan
31 pills; LD, *Ligularia duciformis*.

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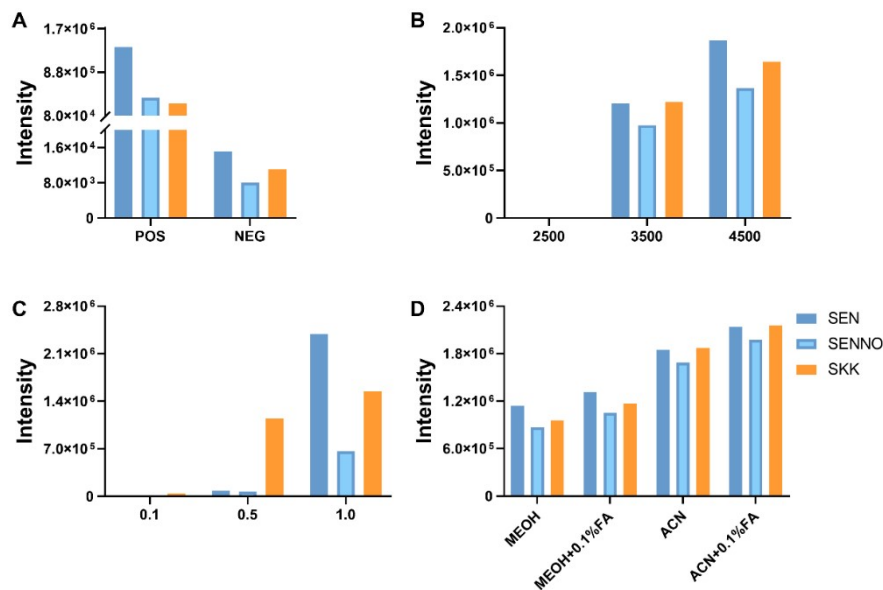
33 **Fig. S1** Mini MS in a suitcase.



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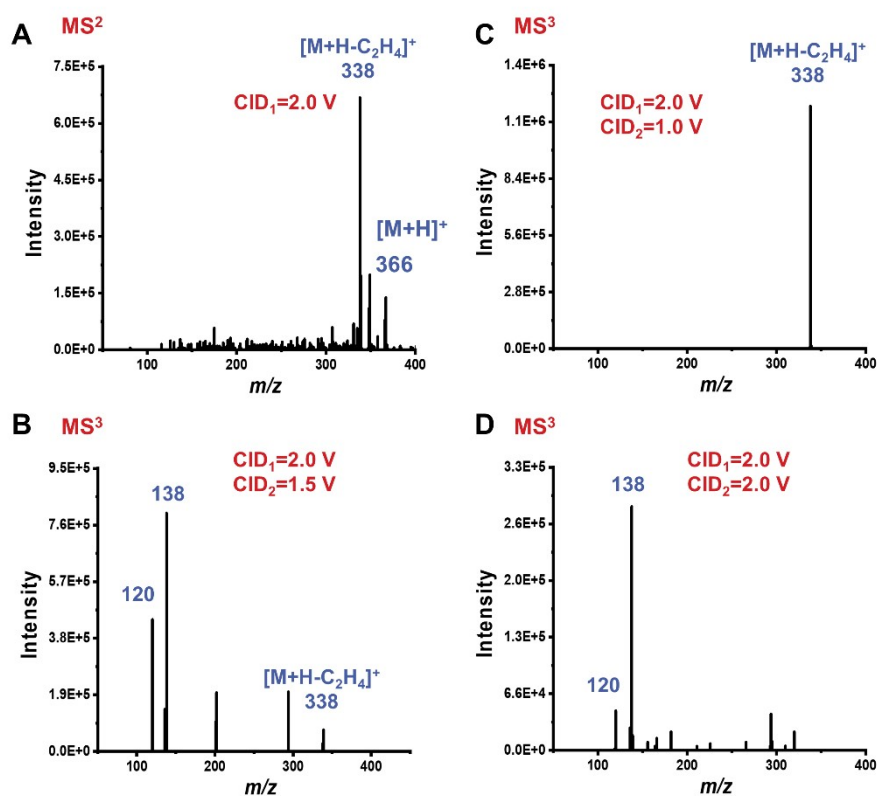
35 **Fig. S2** Structures of 34 PAs.

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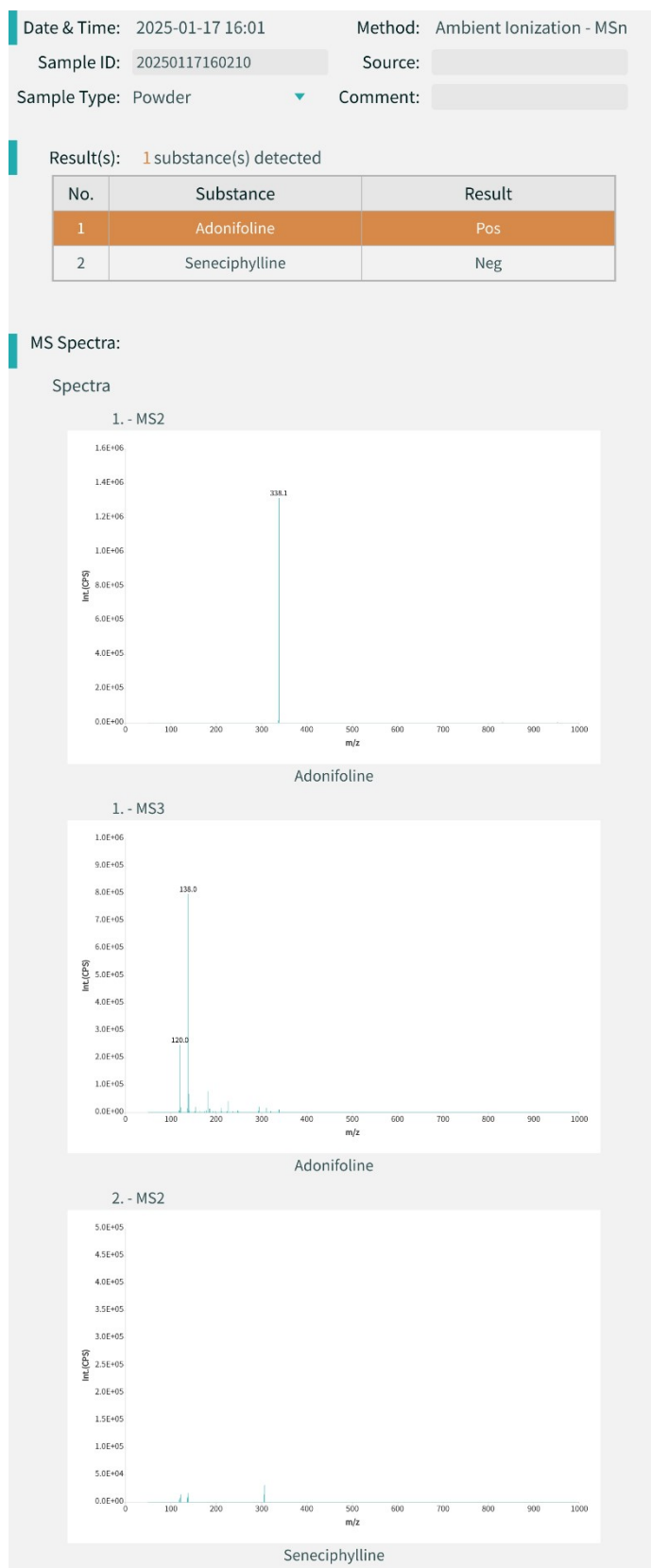
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38 **Fig. S3** Optimization results for polarity (A), spray voltage (B), scan speed (C), and
 39 extraction solvent (D). SEN: senecionine; SENNO: senecionine N-oxide; SKK:
 40 senkirkine.



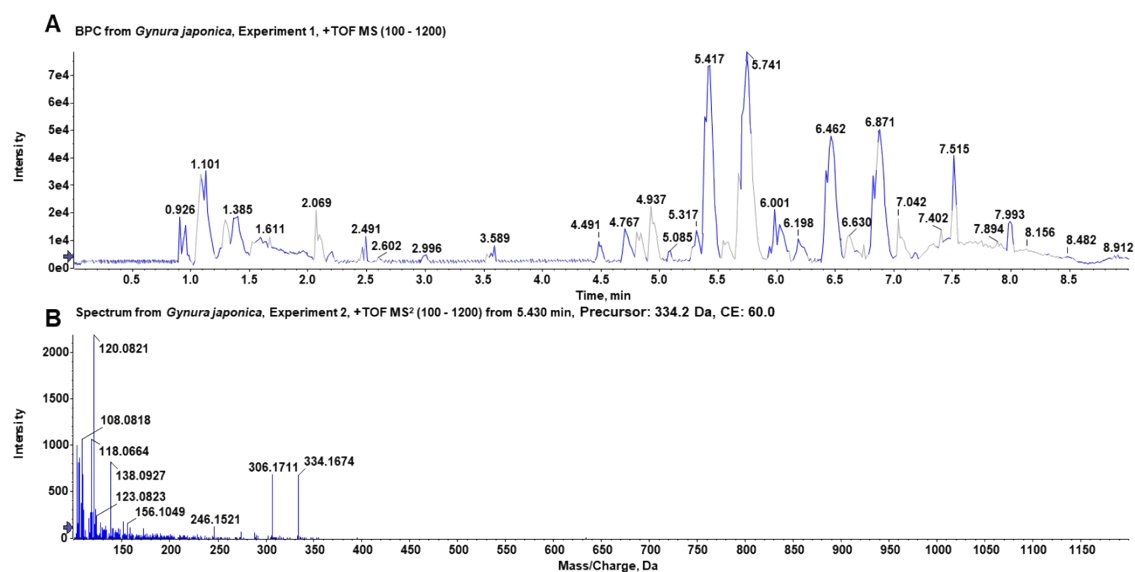
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42 **Fig. S4** Optimization of CID energy and scanning modes. CID₁ refers to the CID
 43 energy of MS² mode, while CID₂ refers to the CID energy of MS³ mode.



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45 **Fig. S5** Analytical report section of the PAs database.



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 47 **Fig. S6** The base peak chromatograms (A) and MS² spectrum of seneciophylline (B) of
 48 *Gynura japonica* by HPLC-MS.
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50 References

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