Table S1

Chromatographic parameters for simultaneous quantitation of the two markers in *Z. schinifolium* seeds by HPLC–PDA.

Chromatographic parameter	
Analytical column	XBridge reverse-phase C_{18} (250 mm length × 4.6 mm ID, 5 μm particle size)
Detector	PDA[1] (235 and 310 nm)
Flow rate	1.0 mL/min
Injection volume	10.0 μL
Column temperature	40.0 °C
Mobile phase	1.0% (v/v) distilled water solution of acetic acid : 1.0% (v/v) solution of acetic acid in acetonitrile (1 : 1)

[1] PDA: photo-diode array

Table S2

Repeatability of retention time and peak area of the two markers (n = 6).

No.	Retention time (min)		Peak area (mAU)	
	Bergapten	**Schinifoline**	**Bergapten**	**Schinifoline**
1	5.631	8.149	2,409,851	1,395,099
2	5.628	8.146	2,412,426	1,396,535
3	5.633	8.151	2,410,016	1,395,809
4	5.629	8.146	2,404,693	1,391,498
5	5.637	8.152	2,401,711	1,391,360
6	5.634	8.150	2,400,370	1,390,291
Mean	5.632	8.149	2,406,511.167	1,393,432.000
SD	0.003	0.003	4,949.441	2,681.680
RSD (%)	0.059	0.031	0.206	0.192

The concentration of the analyzed standard solution was both 50 μg/mL.

Table S3

Stability (%) of the two markers measured at room temperature and under refrigeration using standard and sample solutions.

Day	Standard solution[1]				Sample solution[2]			
	Room temperature[3]		Refrigeration[4]		Room temperature		Refrigeration	
	Bergapten	Schinifoline	Bergapten	Schinifoline	Bergapten	Schinifoline	Bergapten	Schinifoline
0	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
1	99.82	100.09	99.21	99.44	99.54	99.55	100.34	98.37
2	102.13	102.42	98.51	98.40	99.33	99.24	100.29	98.26
3	100.05	99.69	98.30	100.21	99.52	99.84	100.30	98.38
4	99.81	101.05	100.49	100.63	98.69	99.02	100.19	98.36
7	102.72	102.55	101.49	101.32	97.58	99.79	100.17	98.19
10	97.98	98.59	102.95	103.39	97.65	99.75	100.03	98.13
Mean	100.19	100.43	99.95	100.31	98.90	99.60	100.19	98.53
SD	1.55	1.46	1.63	1.54	0.96	0.35	0.13	0.66
RSD (%)	1.55	1.46	1.63	1.53	0.97	0.35	0.13	0.67

[1] Concentration of standard solution was 6.25 μg/mL (bergapten) and 1.25 μg/mL (schinifoline). [2] Concentration of sample solution was 10.0 mg/mL. [3] Room temperature: 23 ± 1 °C. [4] Refrigeration: approximately 4 °C.

Table S4

Parameters for simultaneous quantitation of the two markers in *Z. schinifolium* seeds by the UPLC–MS/MS MRM method.

UPLC conditions				**MS conditions**	
UPLC system	Acquity UPLC I-Class			MS detector	TQD[1]
Column	Acquity UPLC BEH C_{18} analytical column (2.1 mm × 100 mm, 1.7 μm)			MS software	MassLynx v4.2
Column temp.	45 °C			Ion source	ESI[2] positive
Sample temp.	5 °C			Acquisition mode	MRM[3]
Injection volume	2.0 μL			Capillary voltage	3.0 kV
Flow rate	0.3 mL/min			Cone gas flow	50 L/h
Mobile phase A	0.1% (v/v) formic acid in distilled water			Desolvation gas flow	500 L/h
Mobile phase B	Acetonitrile			Desolvation temp.	300 °C
Gradient	Time (min)	A (%)	B (%)	Source temp.	120 °C
	Initial	80	20		
	0.1	80	20		
	14.0	5	95		
	15.0	0	100		
	15.1	80	20		
	18.0	80	20		

[1] TQD: triple quadrupole detector. [2] ESI: electrospray ionization. [3] MRM: multiple reaction monitoring.

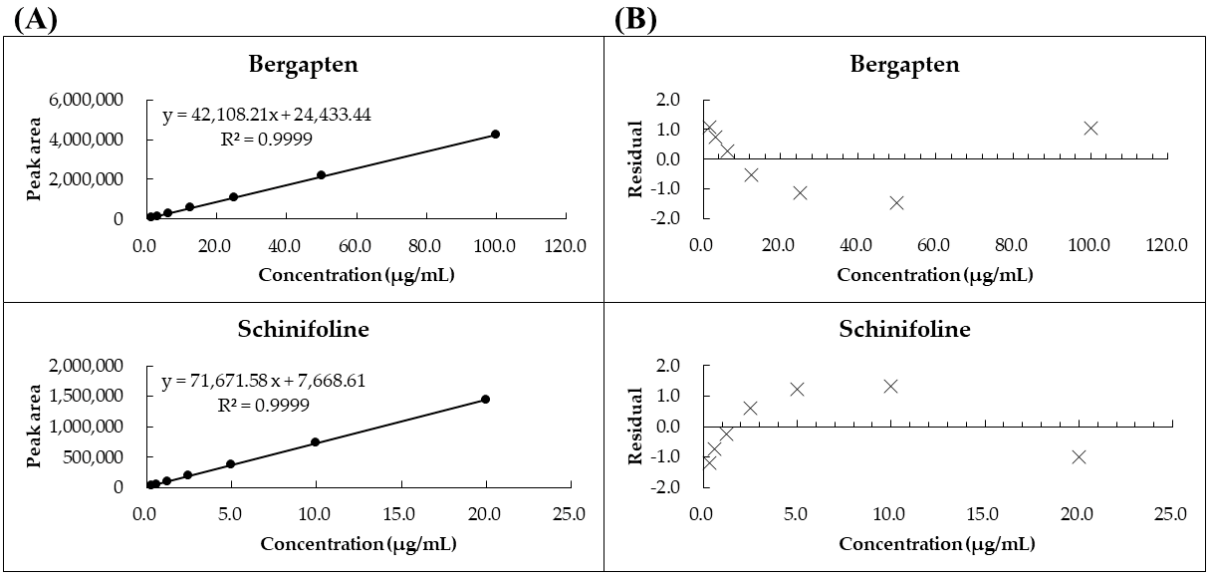


Figure S1. Calibration curves (A) and residual plots (B) for evaluating the linearity of the two marker substances in HPLC–PDA method.

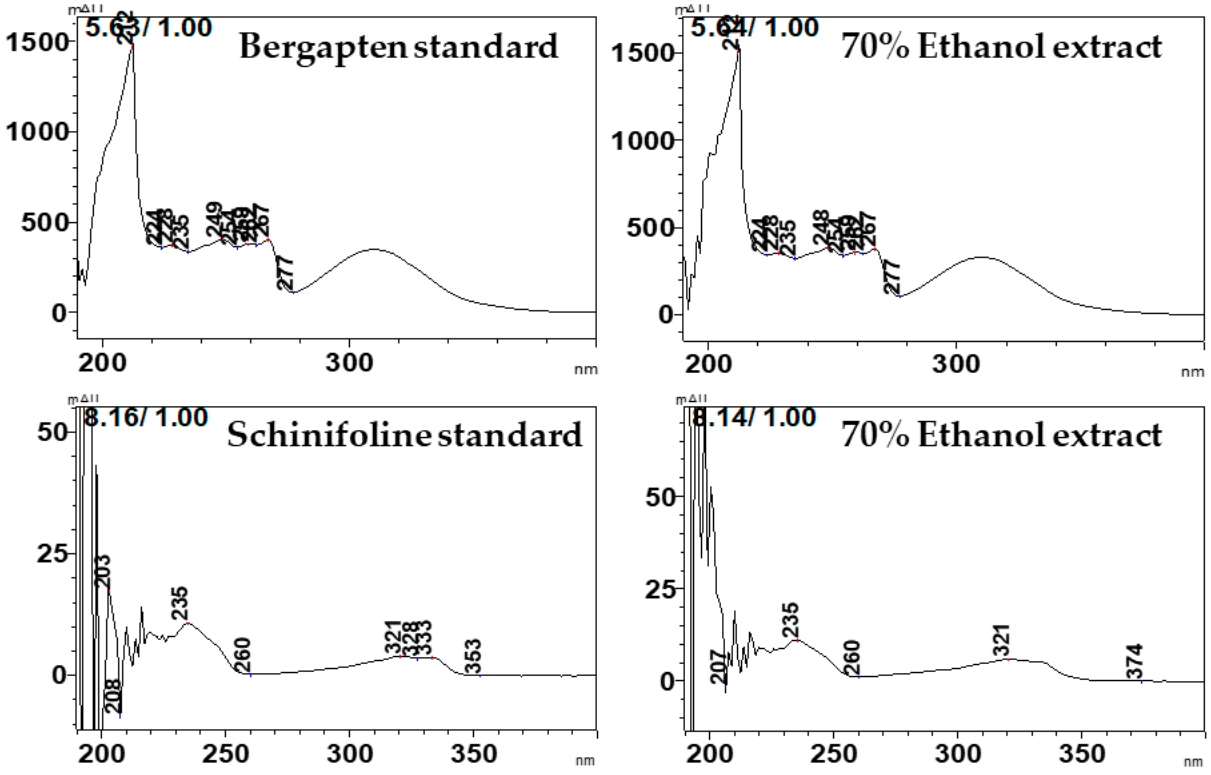
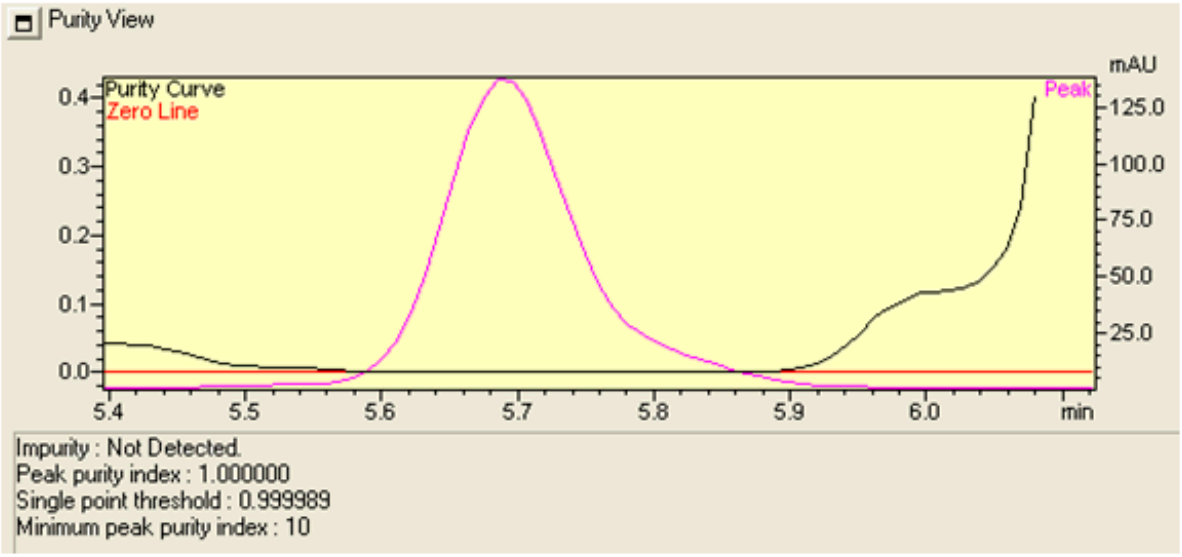


Figure S2. Validation of selectivity through UV spectra comparison.

Bergapten



Schinifoline

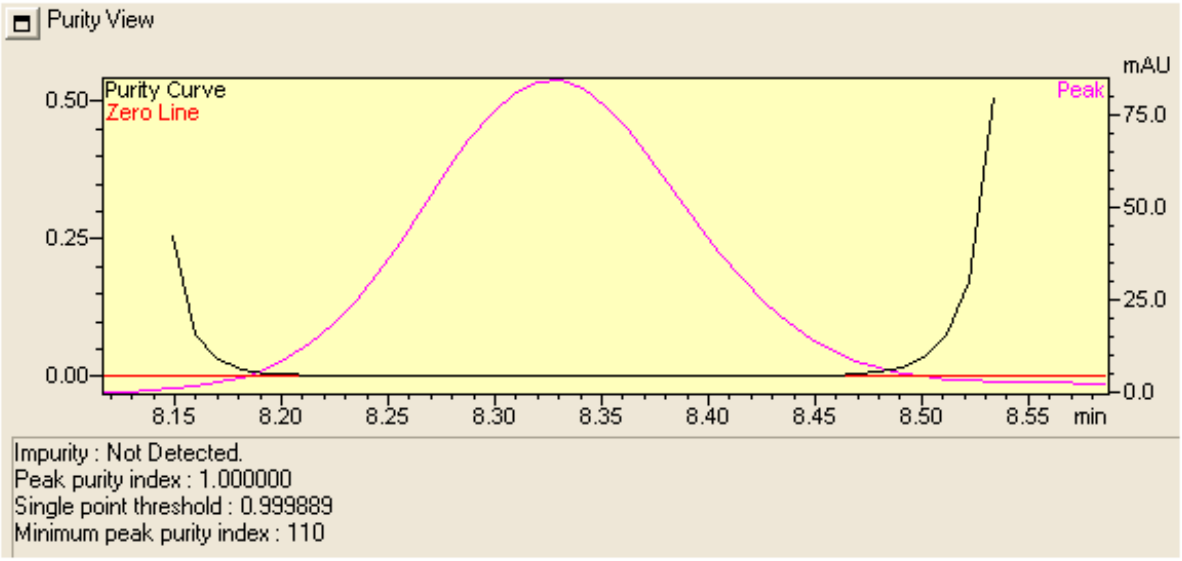
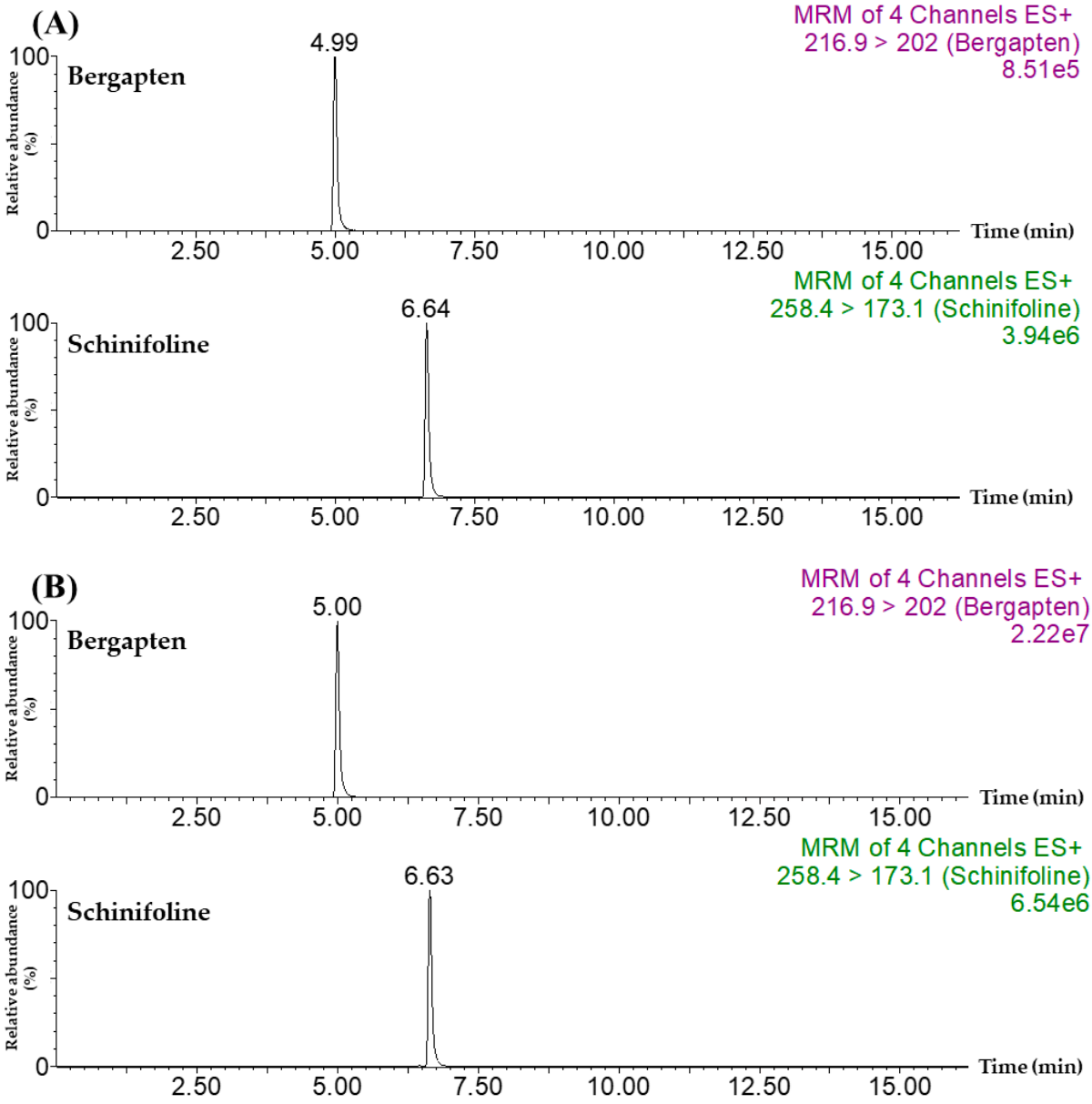


Figure S3. Peak purity evaluation to demonstrate the selectivity of two components in a sample.


(A)
Bergapten
4.99
MRM of 4 Channels ES+
216.9 > 202 (Bergapten)
8.51e5
Schinifoline
6.64
MRM of 4 Channels ES+
258.4 > 173.1 (Schinifoline)
3.94e6
(B)
Bergapten
5.00
MRM of 4 Channels ES+
216.9 > 202 (Bergapten)
2.22e7
Schinifoline
6.63
MRM of 4 Channels ES+
258.4 > 173.1 (Schinifoline)
6.54e6
Relative abundance (%)
Time (min)
100
0
2.50
5.00
7.50
10.00
12.50
15.00

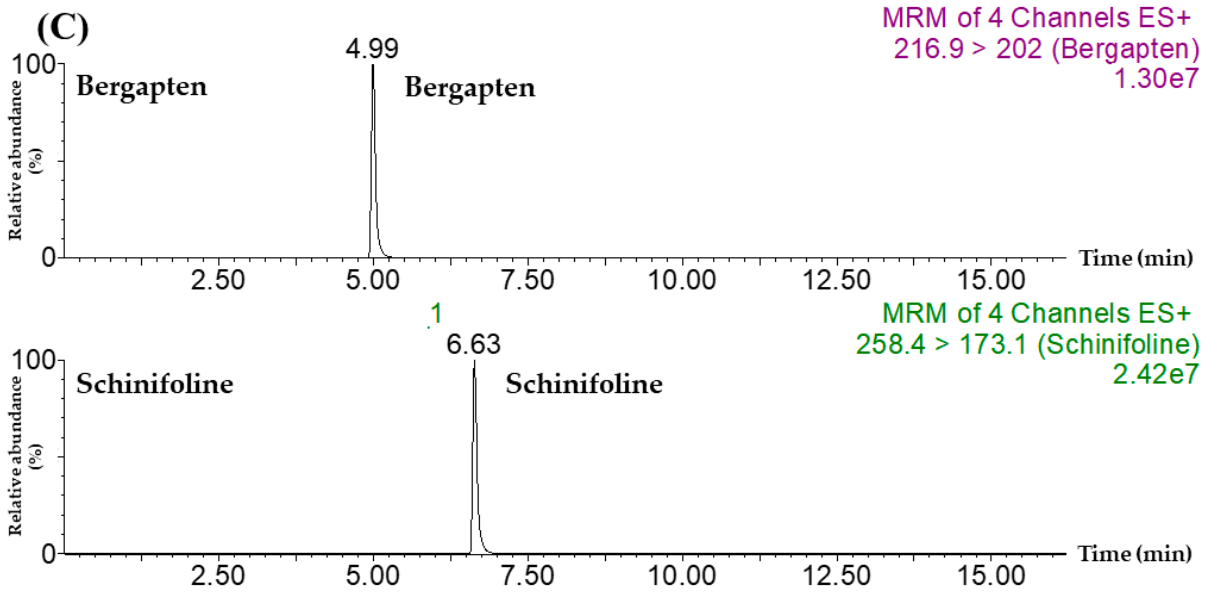


Figure S4. Extracted ion chromatograms for each standard marker (A), 2018ZSS sample (B), and 2021ZSS sample (C) measured by LC–MS/MS MRM mode.

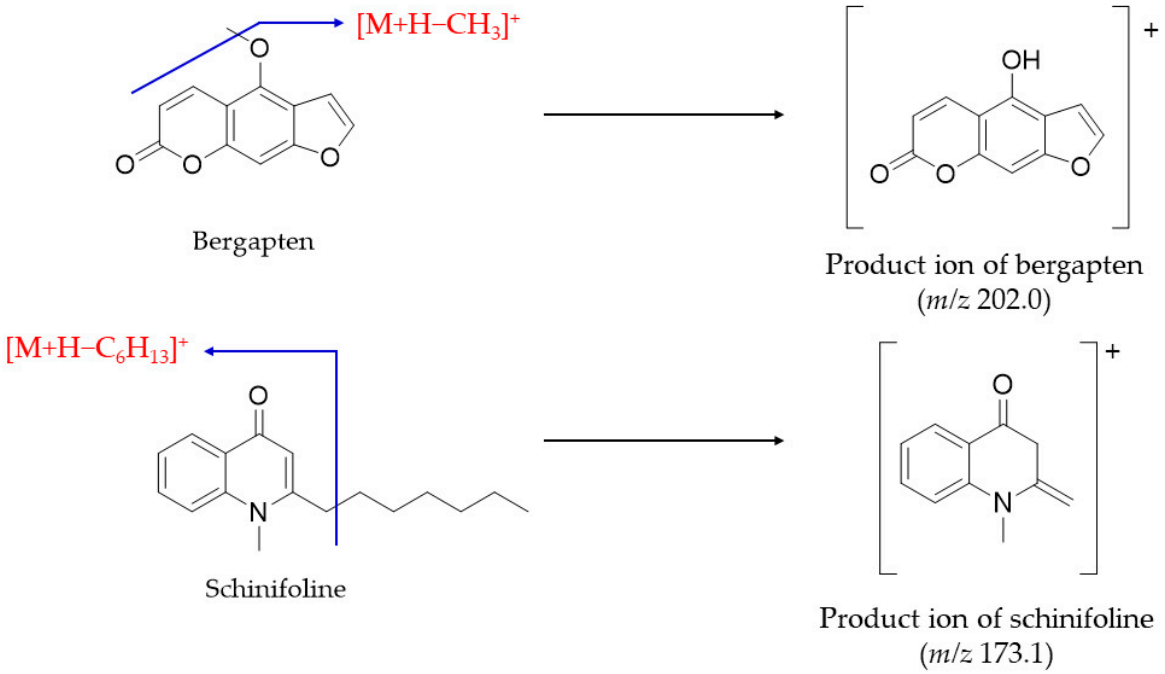


Figure S5. Fragmentation of the two markers by the UPLC–MS/MS MRM method.

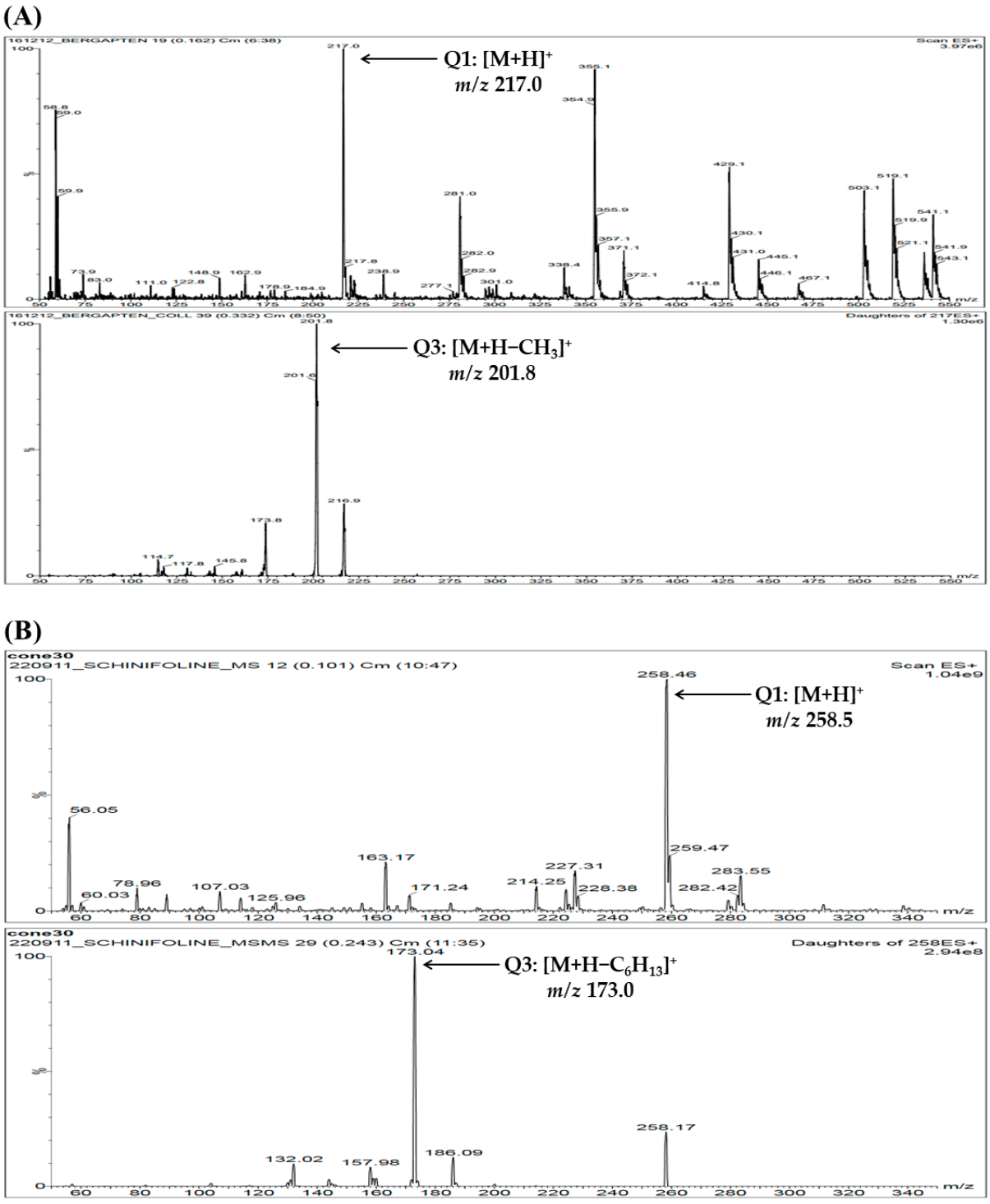


Figure S6. Precursor ion (Q1) and product ion (Q3) peaks of bergapten (A) and schinifoline (B) by the UPLC–MS/MS MRM method.

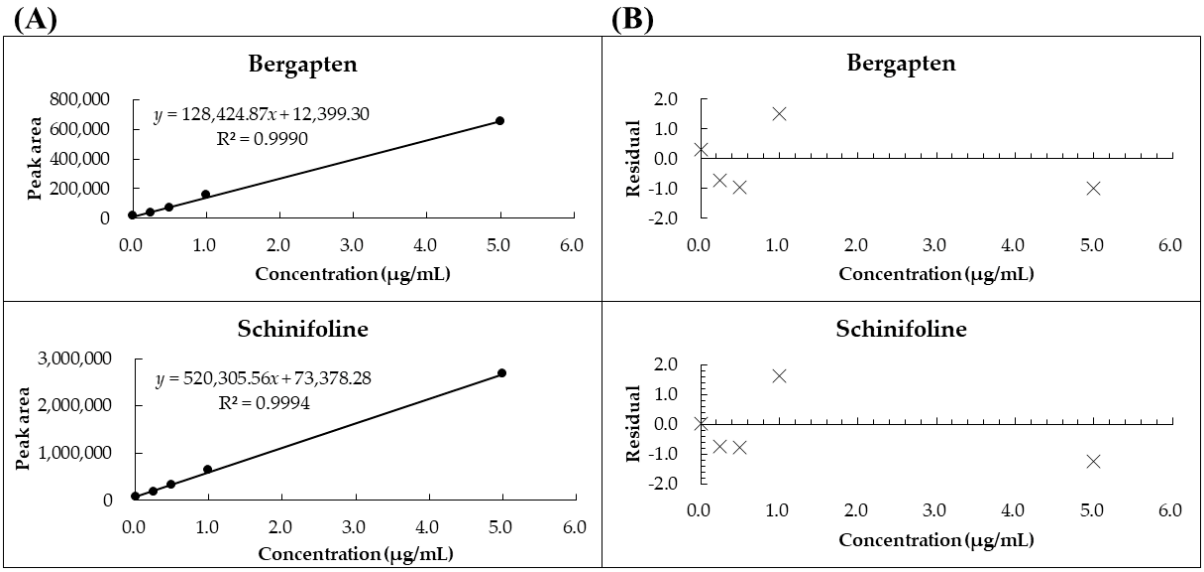


Figure S7. Calibration curves (A) and residual plots (B) of the two markers in UPLC–MS/MS MRM method.