Table S1. All the identified or tentatively identified components from *Bolbostemma paniculatum* extracts and their UPLC-MS^n data.

No.	t_R (min)	Positive ESI mode			Negative ESI mode			Molecular mass	Formula	Identification	Confidence level of identity[a]
		Adduct ions	Mass error (ppm)	MS^n fragment ions	Adduct ions	Mass error (ppm)	MS^n fragment ions				
1	1.64	-	-	-	341.1092 $[M-H]^-$ 683.2264 $[2M-H]^-$	-0.68	MS^2: 179(100)	342.1162	$C_{12}H_{22}O_{11}$	sucrose	III
2	1.73	110.0602 $[M+H]^+$	-0.72	MS^2: 68(100)	108.0453 $[M-H]^-$	1.73	MS^2: 66(100)	109.0528	C_6H_7NO	2-acetylpyrrole	III
3	1.91	667.2277 $[M+H]^+$	2.15	-	665.2128 $[M-H]^-$	2.68	MS^2: 647(3.8), 503(12.7), **341**(100)[b] MS^3: 179(100)	666.2219	$C_{24}H_{42}O_{21}$	stachyose	III
4	2.25	237.0966 $[M+H]^+$	1.31	-	235.0821 $[M-H]^-$	1.02	MS^2: 179(100)	236.0896	$C_9H_{16}O_7$	α-hydroxyacetone glucoside	III
5	2.45	268.1042 [M+H]+	-0.63	-	266.0889 $[M-H]^-$	2.18	MS^2: 248(50.6), 238(100), 222(63.1), 134(33.8)	267.0968	$C_{10}H_{13}N_5O_4$	adenosine (**1**)[c]	I
6	3.13	-	-	-	289.0725 $[M-H]^-$	-2.55	MS^2:179(100), 125(76.5), 109(39.8)	290.0790	$C_{15}H_{14}O_6$	catechin	III
7	3.53	-	-	-	125.0243 $[M-H]^-$	1.06	MS^2: 81(100)	126.0317	$C_6H_6O_3$	maltol	III
8	4.18	127.0393 $[M+H]^+$	-2.59		125.0242 $[M-H]^-$	1.74	MS^2: 83(100)	126.0317	$C_6H_6O_3$	pyrogallol	III
9	4.21	-	-	-	235.1183 $[M-H]^-$	1.55	MS^2: 179(100)	236.1260	$C_{10}H_{20}O_6$	n-butyl-β-D-fructopyranoside	III
10	4.39	-	-	-	353.0854 $[M-H]^-$ 707.1791 $[2M-H]^-$	-1.32	MS^2: 335(100), 309(71.2), **191**(86.3) MS^3: 173(100), 127(69.2), 85(23.9)	354.0951	$C_{16}H_{18}O_9$	chlorogenic acid (**2**)	I
11	4.43	240.1235 $[M+H]^+$	-1.94	MS^2: **212**(100), 140(30.1) MS^3:112(100)	-	-	-	239.1158	$C_{12}H_{17}NO_4$	4-(2-formyl-5-methoxymethylpyrrol-1-yl)butyric acid methyl ester	III
12	4.66	-	-	-	595.1292 $[M-H]^-$	2.11	MS^2: 433(100), **285**(85.2) MS^3: 241(100), 161(25.4)	596.1377	$C_{26}H_{28}O_{16}$	3-O-[β-D-pyranrham-nose-(1-6)-β-D-galactopyranose]-5,7,4'-trihydroxyl flavone	III
13	4.74	391.1002	-0.63	-	367.1035 $[M-H]^-$	-0.12	MS^2: 353(85.6), 335(100),	368.1107	$C_{17}H_{20}O_9$	5-O-feruloylquinic acid	III

No.	t_R (min)	Positive ESI mode			Negative ESI mode			Molecular mass	Formula	Identification	Confidence level of identity[a]
		Adduct ions	Mass error (ppm)	MS^n fragment ions	Adduct ions	Mass error (ppm)	MS^n fragment ions				
		$[M+Na]^+$					**317**(38.5) MS^3: 179(100)				
14	4.81	449.1081 $[M+H]^+$	-0.58	-	447.0912 $[M-H]^-$ 895.1896 $[2M-H]^-$	-0.97	MS^2: 419(10.1), 327(24.8), **301**(44.5), 284(100), 257(8.81) MS^3: 179(100), 151(81.2)	448.1006	$C_{21}H_{20}O_{11}$	quercitrin (**3**)	I
15	5.18	-	-	-	191.0335 $[M-H]^-$	-0.41	MS^2: **176**(100) MS^3: 148(100), 120(26.7), 104(15.2)	192.0423	$C_{10}H_8O_4$	scopoletin (**4**)	I
16	5.22	-	-	-	433.0765 $[M-H]^-$	2.7	MS^2: 313(54.5), **301**(100), 182(11.8) MS^3: 273(100), 257(87.4), 193(41.3), 178(17.2), 165(10.3)	434.0849	$C_{20}H_{18}O_{11}$	quercetin-3-O-α-L-arabinopyranoside	III
17	5.53	415.3940 $[M+H]^+$	-1.34	MS^2: **397**(89.2), 273(100), 233(13.5) MS^3: 255(100), 215(35.1)	-	-	-	414.3862	$C_{29}H_{50}O$	β-sitosterol (**5**)	I
18	5.77	-	-	-	1333.6039 $[M-H]^-$	2.34	MS^2: 1249(100), 1189(51.4), 797(86.1)	1334.6143	$C_{63}H_{98}O_{30}$	tubeimoside Ⅱ	III
19	5.80	-	-	-	785.4691 $[M-H]^-$	1.17	MS^2: 653(80.6), 635(100), 553(27.5), 535(35.2), 491(70.7), 391(67.8), 343(40.4)	786.4766	$C_{41}H_{70}O_{14}$	tubeimoside Ⅳ	III
20	5.80	411.3610 $[M+H]^+$	2.78	MS^2: **393**(81.3), 271(100), 233(26.8) MS^3: 253(100), 215(65.2)	-	-	-	410.3549	$C_{29}H_{46}O$	stigmasta-7,16,25-triene-3-o1	III
21	5.82	787.4815 $[M+H]^+$	2.96	-	785.4689 $[M-H]^-$	1.14	MS^2: 653(80.6), 635(100),	786.4766	$C_{41}H_{70}O_{14}$	actinostemmoside F	III

No.	t_R (min)	Positive ESI mode			Negative ESI mode			Molecular mass	Formula	Identification	Confidence level of identity[a]
		Adduct ions	Mass error (ppm)	MS^n fragment ions	Adduct ions	Mass error (ppm)	MS^n fragment ions				
							553(27.5), 535(35.2), 491(70.7), 391(67.8), 343(40.4)				
22	6.00	787.4822 $[M+H]^+$	2.07	-	785.4689 $[M-H]^-$	1.14	MS^2: 653(80.6), 635(100), 553(27.5), 535(35.2), 491(70.7), 391(67.8), 343(40.4)	786.4766	$C_{41}H_{70}O_{14}$	7β,18,20,26-tetrahydroxy-(20S)-dammar-24E-en-3-O-α-L-(3-acetyl)arabinopyranosyl-(1→2)-β-D-glucopyranoside	III
23	6.05	411.3614 $[M+H]^+$	1.81	MS^2: **393**(100), 273(47.5), 233(40.1) MS^3: 255(100), 215(18.2)	-	-	-	410.3549	$C_{29}H_{46}O$	stigmasta-7,22,25-triene-3-ol	III
24	6.10	-	-	-	827.4776 $[M-H]^-$	2.71	MS^2: 827(56.1), 679(100), 621(12.6) **473**(87.2) MS^3: 455(100)	828.4871	$C_{43}H_{72}O_{15}$	7β,18,20,26-tetrahydroxy-(20S)-dammar-24E-en-3-O-α-L-arabinopyranosyl-(1→2)-β-D-(6-acetyl)-glucopyranoside	III
25	7.01	1349.6392 $[M+H]^+$	-1.49	-	1347.6194 $[M-H]^-$	2.42	MS^2: **1263**(100) MS^3: 1221(93.6), 1203(100), 1131(18.1) 811(14.2)	1348.6299	$C_{64}H_{100}O_{30}$	lobatoside D	III
26	7.26	-	-	-	1363.6154 $[M-H]^-$	-1.81	MS^2: 1279(100), 1219(5.93), 1147(1.0), 1057(5.6), 827(9.63)	1364.6249	$C_{64}H_{100}O_{31}$	tubeimoside III	III
27	7.39	-	-	-	1317.6083 $[M-H]^-$	2.88	MS^2: 1233(100), 1173(47.3), 781(38.5), 649(11.3)	1318.6194	$C_{63}H_{98}O_{29}$	tubeimoside Ⅰ(**6**)	Ⅰ

No.	t_R (min)	Positive ESI mode			Negative ESI mode			Molecular mass	Formula	Identification	Confidence level of identity[a]
		Adduct ions	Mass error (ppm)	MS^n fragment ions	Adduct ions	Mass error (ppm)	MS^n fragment ions				
28	7.44	1217.5969	-1.06	-	1215.5778 $[M-H]^-$	2.14	MS^2: 1041(66.2), **749**(100), MS^3: 587(100), 457(19.3)	1216.5877	$C_{59}H_{92}O_{26}$	lobatoside B	III
29	7.51	-	-	-	1231.5735 $[M-H]^-$	1.48	MS^2: 1189(7.9), 1159(13.6) 1147(100), 1105(5.6), 881(9.1), 821(17.0)	1232.5826	$C_{59}H_{92}O_{27}$	dexylosyltubeimoside Ⅲ	III
30	7.52	-	-	-	1185.5667 $[M-H]^-$	2.65	MS^2: 1101(100), 1059(14.3), 1041(10.1), 1023(1.2)	1186.5771	$C_{58}H_{90}O_{25}$	lobatoside C	III
31	7.67	1217.5915 $[M+H]^+$	2.84		1215.5773 $[M-H]^-$	2.56	MS^2: 1041(66.8), **749(100)** MS^3: 587(100), 457(23.1)	1216.5877	$C_{59}H_{92}O_{26}$	lobatoside G	III
32	7.92	-	-	-	1347.6189 $[M-H]^-$	2.79	MS^2: **1263**(100) MS^3: 1221(93.6), 1203(100), 1131((18.1), 811(14.2)	1348.6299	$C_{64}H_{100}O_{30}$	tubeimoside Ⅴ	III
33	8.42	1379.6439 $[M+H]^+$	2.81		1377.6297 $[M-H]^-$	2.56	MS^2: **1217**(100) MS^3: 895(100), 733(25.8),455(17.2), 137(11.3)	1378.6405	$C_{65}H_{102}O_{31}$	lobatoside F	III
34	8.89	817.4951 $[M+H]^+$	-0.86	-	815.4788 $[M-H]^-$	1.88	MS^2: 797(1.3) **769**(100), 635(1.0), 559(1.6) MS^3: 701(33.2), 637(100), 619(32.8)	816.4871	$C_{42}H_{72}O_{15}$	actinostemmoside H	III
35	9.71	771.4891 $[M+H]^+$	-0.23	-	769.4722 $[M-H]^-$	2.81	MS^2: 637(62.2), 619(100), 589(7.4), 571(9.3),	770.4816	$C_{41}H_{70}O_{13}$	7β,20,26-trihydroxy-(20S)-dammar-24E-en-3-O-α-L-	III

No.	t_R (min)	Positive ESI mode			Negative ESI mode			Molecular mass	Formula	Identification	Confidence level of identity[a]
		Adduct ions	Mass error (ppm)	MS^n fragment ions	Adduct ions	Mass error (ppm)	MS^n fragment ions				
							475(67.9), 427(8.0), 343(24.4)			arabinopyranosyl-(1→2)-β-D-glucopyranoside	
36	9.76	-	-	-	781.4365 $[M-H]^-$	1.89	MS^2: 649 469	782.4453	$C_{41}H_{66}O_{14}$	lobatoside A	III
37	10.87	-	-	-	811.4829 $[M-H]^-$ 1623.9679 $[2M-H]^-$	2.50	MS^2: 769(100), 751(4.6) 619(11.2), 571(6.7)	812.4922	$C_{43}H_{72}O_{14}$	7β,20,26-trihydroxy-(20S)-dammar-24E-en-3-O-α-L-(3-acetyl)arabinopyranosyl-(1→2)-β-D-glucopyranoside	III
38	11.68	-	-	-	799.4831 $[M-H]^-$	2.29	MS^2: 637(33.7), **475**(100), 457(14.7) MS^3: 439(100)	800.4922	$C_{42}H_{72}O_{14}$	actinostemmoside E	III
39	13.19	271.0589 $[M+H]^+$	-1.230	-	269.0457 $[M-H]^-$	0.77	MS^2: 241(32.2), 225(100), 197(3.98)	270.0528	$C_{15}H_{10}O_5$	emodin (**7**)	I
40	13.67	-	-	-	559.3260 $[M-H]^-$	2.94	MS^2: 541(26.9), 499(38.9), **481**(100) MS^3: 463(46.3), 439(27.0), 301(100), 283(24.5)	560.3349	$C_{32}H_{48}O_8$	23,24-dihydroisocucurbitacin B	III
41	13.76	285.0746 $[M+H]^+$	-0.92		283.0605 $[M-H]^-$	2.43	MS^2: 269 241 225 197	284.0685	$C_{16}H_{12}O_5$	emodinmonomethylether	III
42	14.48	-	-	-	559.3266 $[M-H]^-$	1.86	MS^2: 541(26.9), 499(38.9), **481**(100) MS^3: 463(46.3), 439(27.0), 301(100), 283(24.5)	560.3349	$C_{32}H_{48}O_8$	cucurbitacin E	III
43	15.03	699.3602 $[M+H]^+$	-1.43	MS^2: 615(54.2), 575(15.6), **521**(100), 437(34.8), 397(19.7) MS^3: 357(100), 273(21.5), 233(17.6)	697.3450 $[M-H]^-$	-1.32	-	698.3514	$C_{35}H_{54}O_{14}$	uzarigenin-3-β-sophoroside	III
44	15.27	581.3100	-2.60	-	557.3102 $[M-H]^-$	2.85	MS^2: 539(100), 515(30.8),	558.3193	$C_{32}H_{46}O_8$	cucurbitacin B (**8**)	I

No.	t_R (min)	Positive ESI mode			Negative ESI mode			Molecular mass	Formula	Identification	Confidence level of identity[a]
		Adduct ions	Mass error (ppm)	MS^n fragment ions	Adduct ions	Mass error (ppm)	MS^n fragment ions				
		$[M+Na]^+$					497(90.1) 479(10.2)				
45	16.57	701.3750 $[M+H]^+$	-0.67	MS^2: 701(51.2), **683**(89.3), 523(100), 335(35.9), 317(24.6), 277(12.3) MS^3: 665(100), 487(32.6), 299(33.7), 259(19.4)	699.3602 $[M-H]^-$	-0.67	-	700.3670	$C_{35}H_{56}O_{14}$	sileneoside H	III
46	16.94	577.4455 $[M+H]^+$	1.33	MS^2: 435(63.5), **397**(100), MS^3: 255(100),215(29.7)	575.4308 $[M-H]^-$	1.59	-	576.4390	$C_{35}H_{60}O_6$	daucosterol	III
47	17.56	537.3066 $[M+H]^+$	-0.75	MS^2: 453(56.3), 413(33.2), 395(21.4), **373**(100) MS^3: 289(100), 249(45.8), 231(39.7)	535.2900 $[M-H]^-$	2.35	-	536.2985	$C_{29}H_{44}O_9$	frugoside	III
48	17.96	573.4139 $[M+H]^+$	1.86	MS^2: 435(100), **393**(86.3) MS^3: 255(100), 215(37.2)	571.3995 $[M-H]^-$	1.60	-	572.4077	$C_{35}H_{56}O_6$	stigmasta-7,22,25-triene-3-O-β-D-glucopyranoside	III
49	18.77	-	-	-	1191.5806 $[M-H]^-$	0.77	MS^2: 1059(71.4), 897(36.7), 765(15.1) **487**(100) MS^3: 469(100)	1192.5877	$C_{57}H_{92}O_{26}$	3-O-α-L-arabinopyranosyl(1→2)-β-D-glucopyranosyl-bayogenin-28-O-β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranoside	III
50	19.32	539.3218 $[M+H]^+$	-0.10	MS^2: **521**(93.1), 335(100), 295(25.9), 277(63.3) MS^3: 503(100), 285(72.3), 245(61.3), 227(27.1)	537.3055 $[M-H]^-$	2.62	-	538.3142	$C_{29}H_{46}O_9$	integristerone A-25-acetate	III
51	19.96	493.3160 $[M+H]^+$	0.48	MS^2: **475**(100), 319(89.8), 279(54.7), 261(39.1) MS^3: 457(100), 269(39.3),	-	-	-	492.3087	$C_{28}H_{44}O_7$	24(28)-dehydromakisterone A	III

No.	t_R (min)	Positive ESI mode			Negative ESI mode			Molecular mass	Formula	Identification	Confidence level of identity[a]
		Adduct ions	Mass error (ppm)	MS^n fragment ions	Adduct ions	Mass error (ppm)	MS^n fragment ions				
				229(38.4), 211(15.2)							
52	20.99	279.1595 $[M+H]^+$	-1.24	MS^2: 279(100), 223(59.8), 167(65.3)	-	-	-	278.1518	$C_{16}H_{22}O_4$	di-butyl phthalate	III
53	22.96	653.6215 $[M+H]^+$	2.46	MS^2: 511(78.2), **397**(100) MS^3: 255(100), 215(67.2)	-	-	-	652.6158	$C_{45}H_{80}O_2$	β-sitosterol palmitate	III
54	23.67	811.6425 $[M+H]^+$	2.63	MS^2: 573(100), 435(56.1), **393**(79.2) MS^3: 255(100), 215(63.7)	809.6290 $[M-H]^-$	1.33	-	810.6374	$C_{51}H_{86}O_7$	stigmasta-7,22,25-triene-3-O-β-D-(6′-palmitoyl) glucopyranoside	III
55	24.24	691.6377 $[M+H]^+$	1.53	MS^2: 553(59.9), **393**(100) MS^3: 255(100), 215(55.4)	-	-	-	690.6315	$C_{48}H_{82}O_2$	stigmasta-7,22,25-triene-3-O-nonadecanoic acid ester	III
56	24.91	282.2799 $[M+H]^+$ 563.5530 $[2M+H]^+$	-2.69	MS^2: 237(100)	280.2640 $[M-H]^-$	2.10	-	281.2719	$C_{18}H_{35}NO$	9-octadecenamide	III
57	25.25	314.1379 $[M+H]^+$	2.50	-	312.1249 $[M-H]^-$	-2.46	MS^2: 193136	313.1314	$C_{18}H_{19}NO_4$	(E)-N-hydroxy phenylethyl-3-(4-hy-droxy-3-methoxy phenyl) acrylamide	III
58	26.51	-	-	-	255.2328 $[M-H]^-$	0.66	MS^2: 209(100)	256.2402	$C_{16}H_{32}O_2$	hexadecanoic acid	III
59	27.17	595.3974 $[M+Na]^+$	-0.91	MS^2: 435(70.8), 395(100), **393**(94.2) MS^3: 255(100), 215(36.9)	-	-	-	572.4077	$C_{35}H_{56}O_6$	(3β,22E)-stigmasta-7,22,25-trien-3-yl-β-D-glucopyranoside	III
60	27.62	327.1958 $[M+H]^+$	-1.01	MS^2: 255(100) MS^3: 215(100)	325.1818 $[M-H]^-$	-2.66	-	326.1882	$C_{21}H_{26}O_3$	3-oxo-androsta-1,4-dien-17a′-spiro-2′-3′-oxo-oxetane	III

[a] The confidence level of identity of all the identified components were determined following the four levels defined by the Metabolomics Standards Initiative. Level Ⅰ: confidently identified compounds; Level Ⅱ: Putatively annotated compounds; Level Ⅲ: putatively annotated compound classes; Level Ⅳ: unknown compounds.

[b] The bold m/z values and bracketed relative peak intensities showed the targeted MS^2 fragment ions for further MS^3 fragmentation.

[c] The bracketed bold figures showed the serial number of corresponding reference compounds.

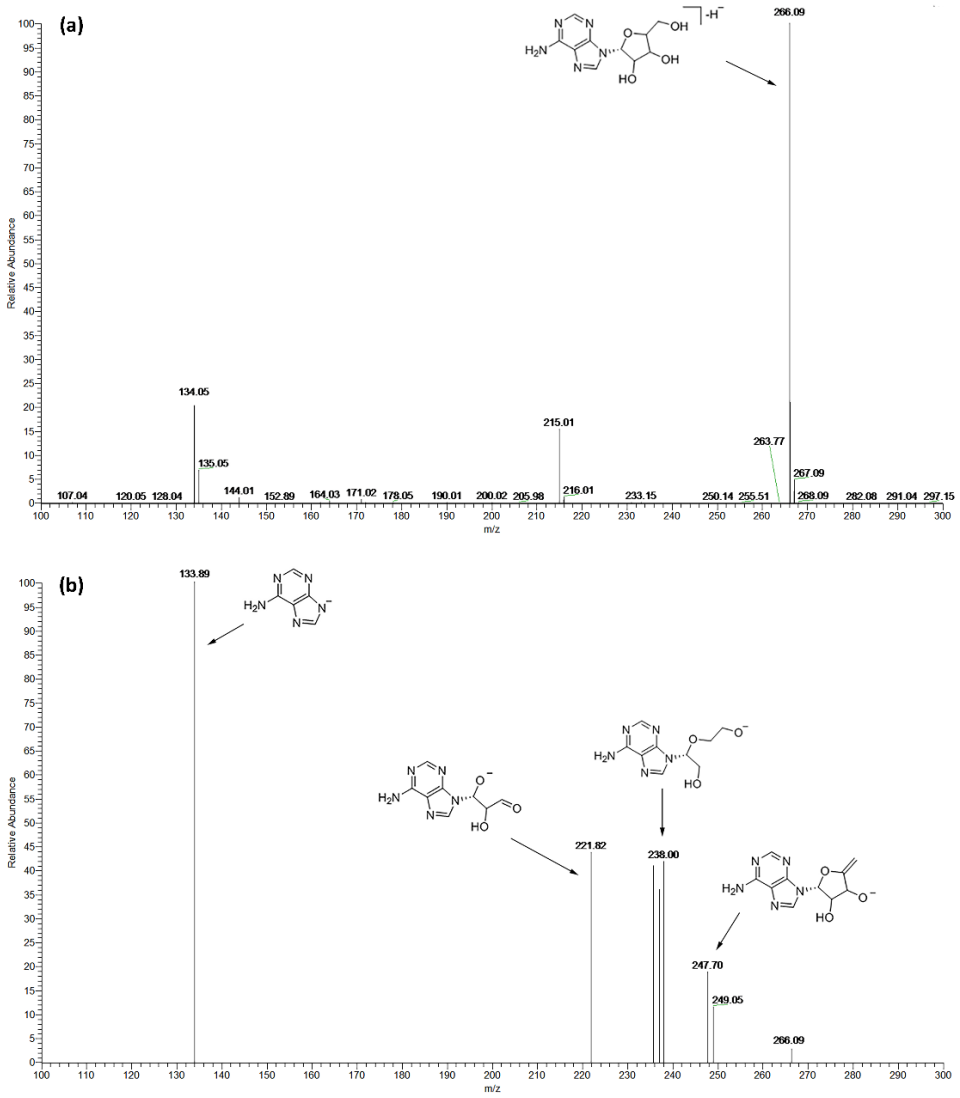

Figure S1. MS^n spectra and proposed fragment ions of adenosine (**1**) in negative ion mode: (**a**) MS spectrum; (**b**) MS^2 spectrum (precursor ion was m/z 266).

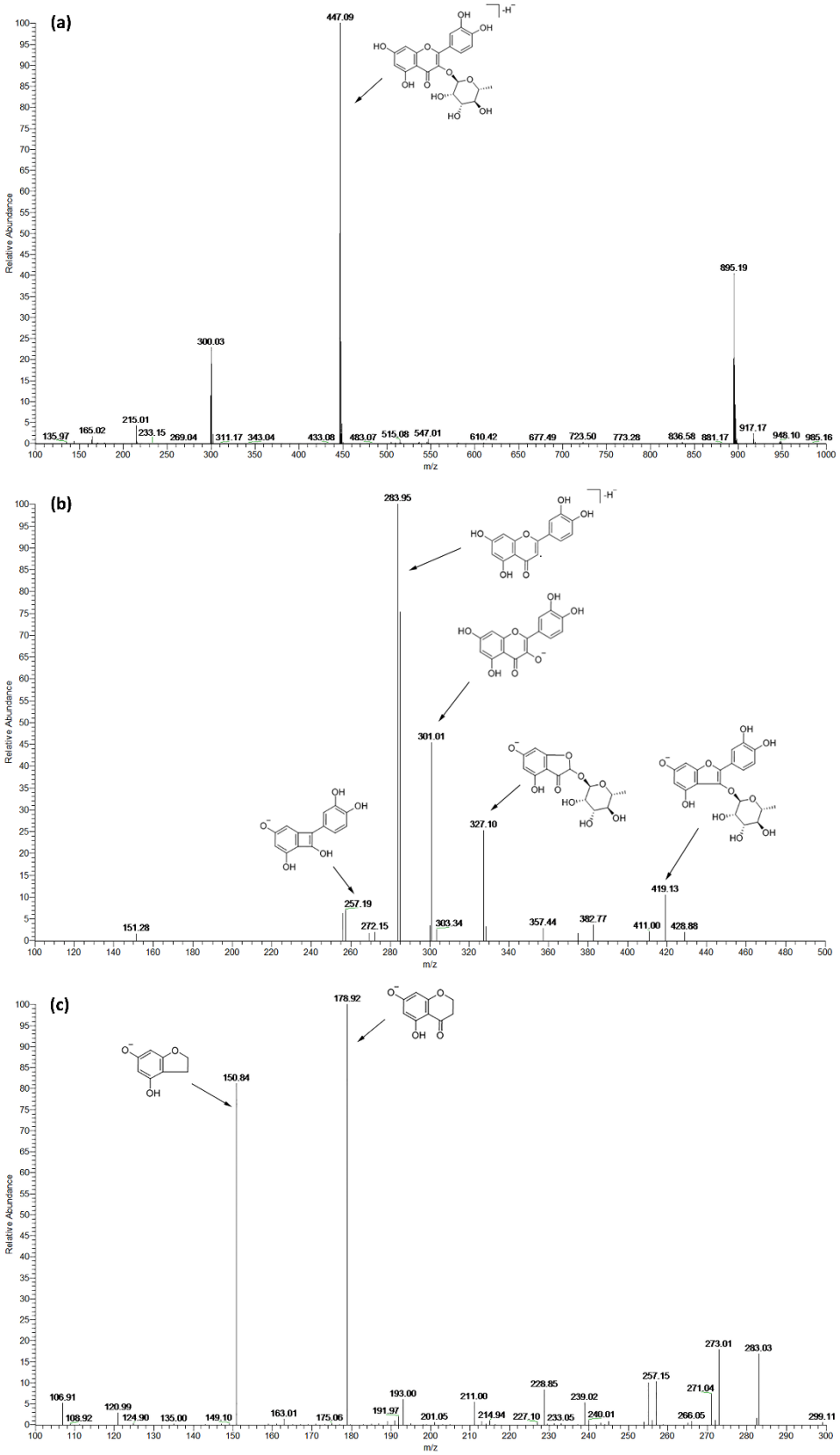

Figure S2. MS^n spectra and proposed fragment ions of quercitrin (**3**) in negative ion mode: (**a**) MS spectrum; (**b**) MS^2 spectrum (precursor ion was m/z 447); (**c**) MS^3 spectrum (precursor ion was m/z 301).

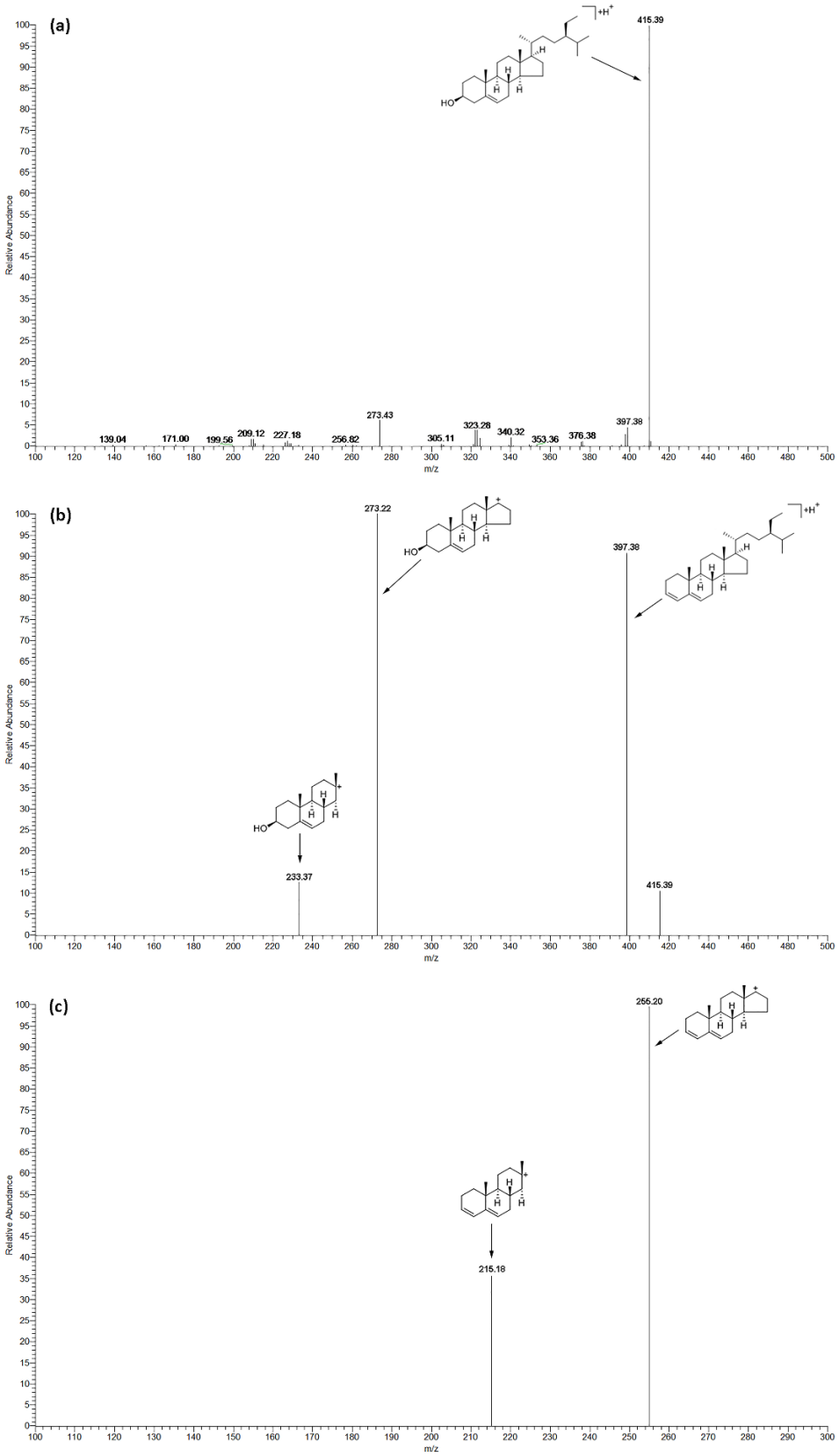

Figure S3. MS^n spectra and proposed fragment ions of β-sitosterol (**5**) in positive ion mode: (**a**) MS spectrum; (**b**) MS^2 spectrum (precursor ion was m/z 415); (**c**) MS^3 spectrum (precursor ion was m/z 397).

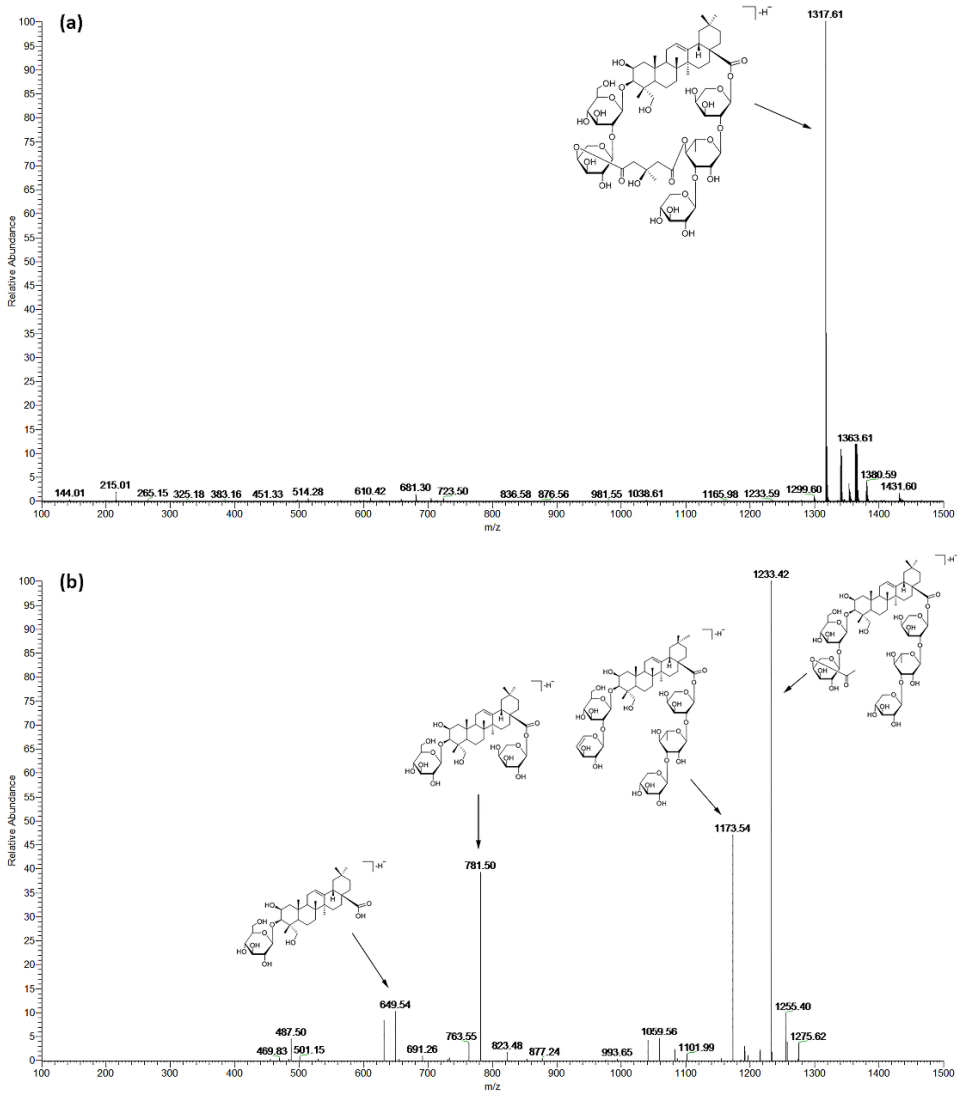

Figure S4. MS^n spectra and proposed fragment ions of tubeimoside Ⅰ (**6**) in negative ion mode: (**a**) MS spectrum; (**b**) MS^2 spectrum (precursor ion was m/z 1317).

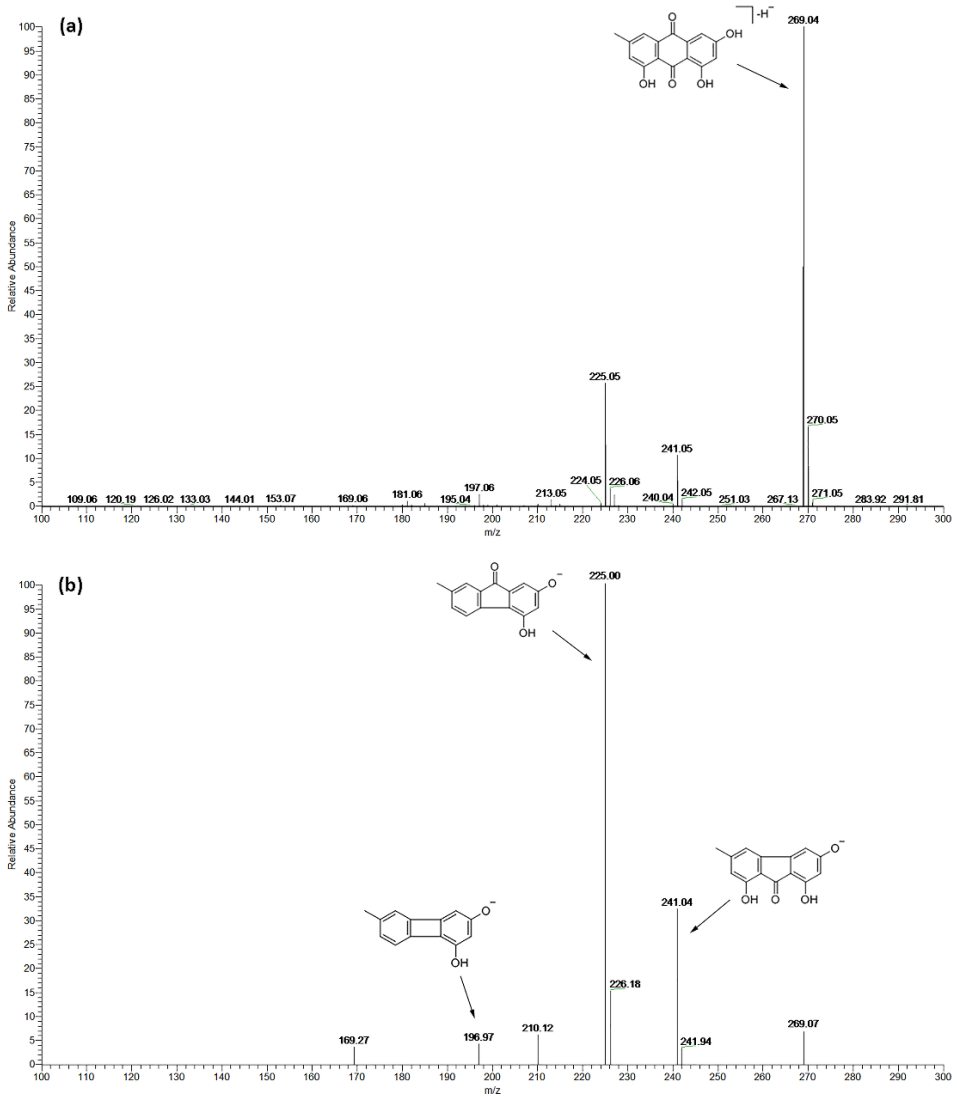

Figure S5. MS^n spectra and proposed fragment ions of emodin (**7**) in negative ion mode: (**a**) MS spectrum; (**b**) MS^2 spectrum (precursor ion was m/z 269).

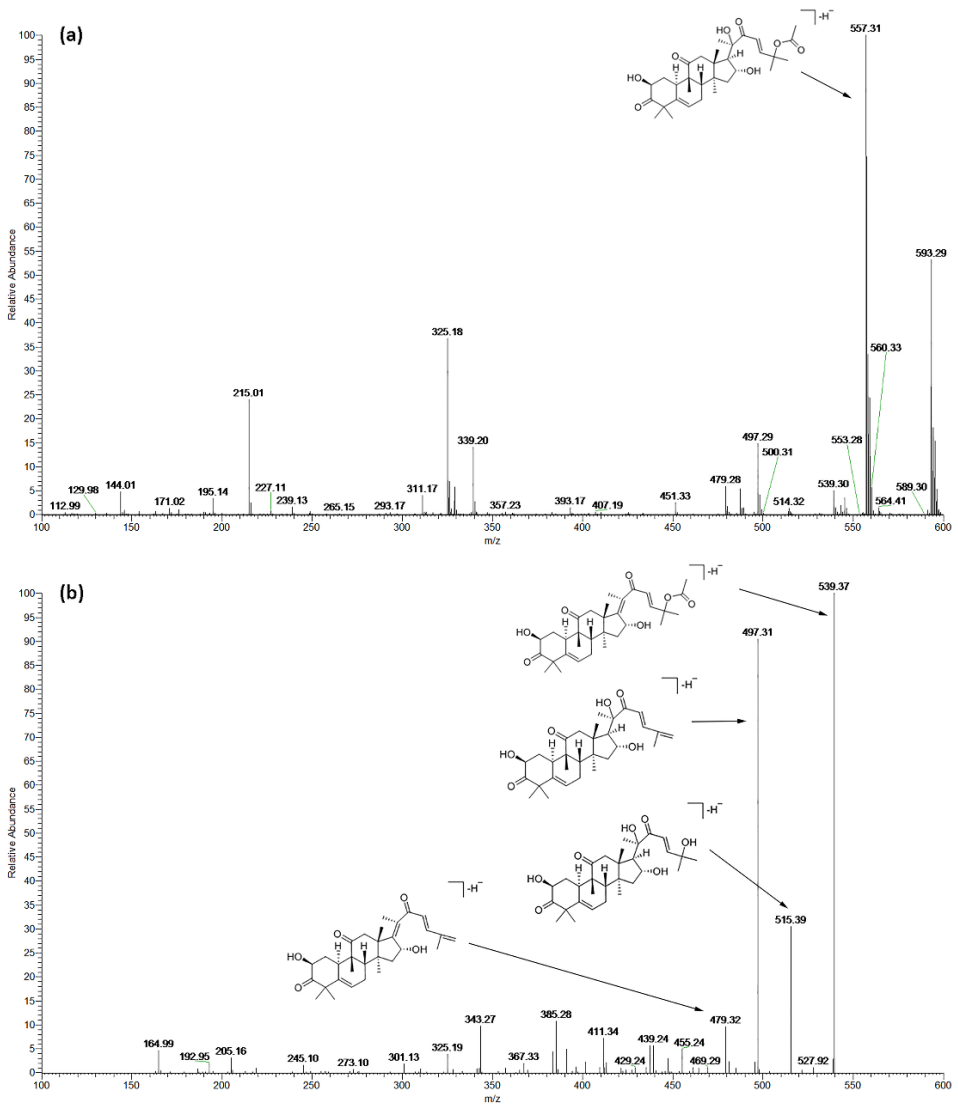

Figure S6. MS^n spectra and proposed fragment ions of cucurbitacin B (**8**) in negative ion mode: (**a**) MS spectrum; (**b**) MS^2 spectrum (precursor ion was m/z 557).

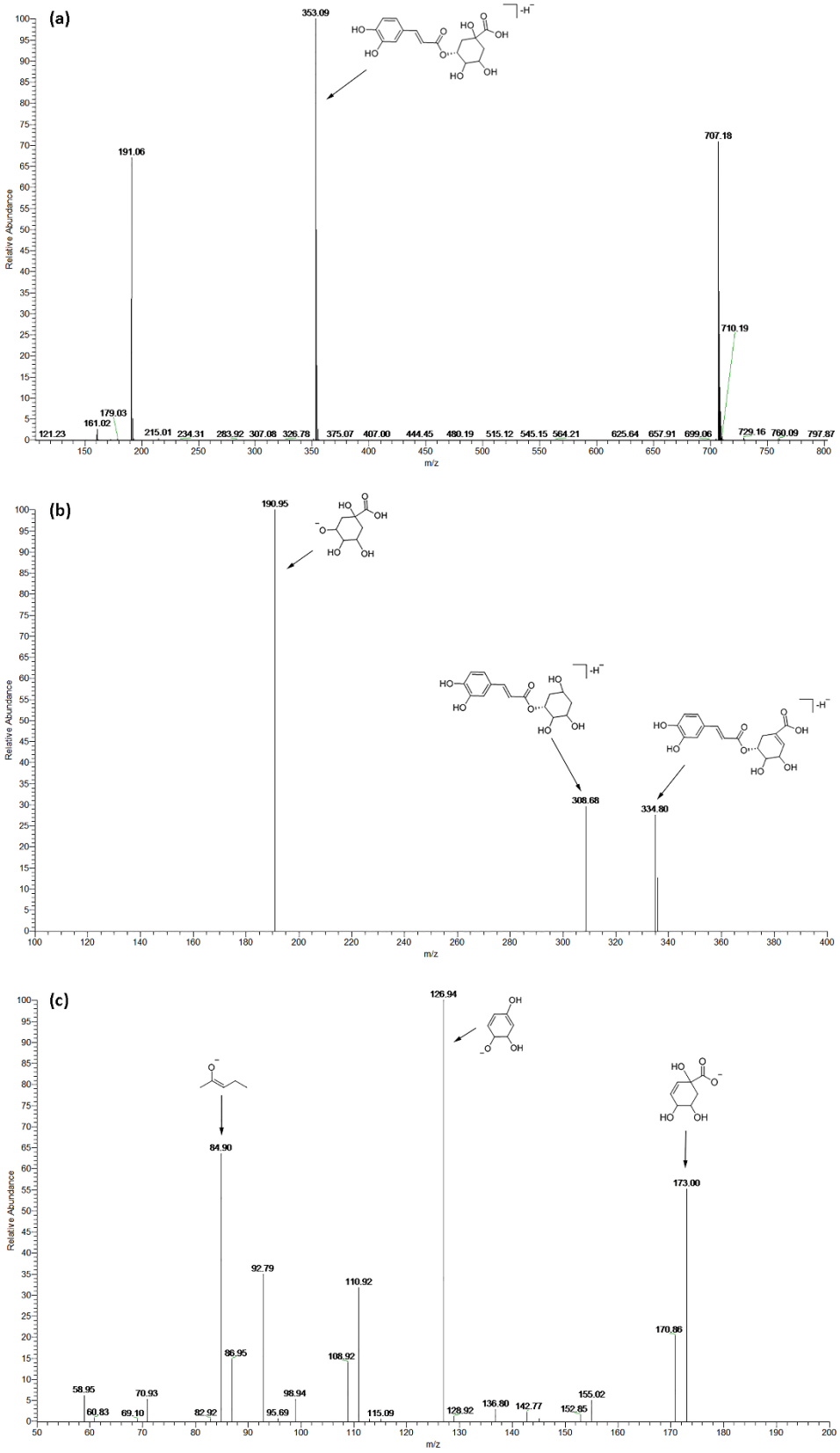

Figure S7. MS^n spectra and proposed fragment ions of chlorogenic acid (**2**) in negative ion mode: (**a**) MS spectrum; (**b**) MS^2 spectrum (precursor ion was m/z 353); (**c**) MS^3 spectrum (precursor ion was m/z 191).

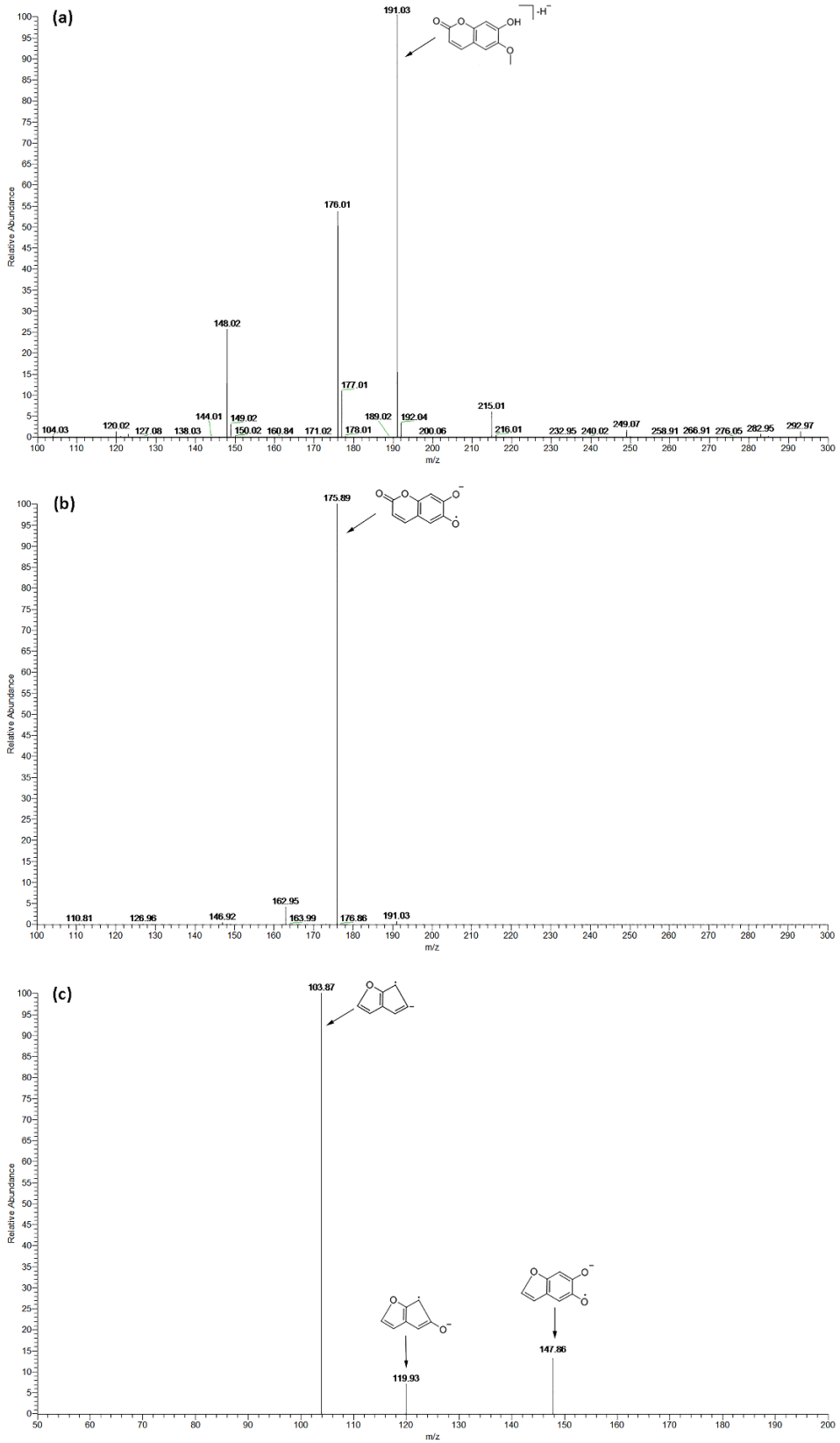

Figure S8. MS^n spectra and proposed fragment ions of scopoletin (**4**) in negative ion mode: (**a**) MS spectrum; (**b**) MS^2 spectrum (precursor ion was m/z 191); (**c**) MS^3 spectrum (precursor ion was m/z 176).