

Supporting Information

Rapid detection of adulterated drugs in herbal dietary supplements by wooden-tip electrospray ionization mass spectrometry

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Table S1. Detection results of the tranquilizer samples

Sample No.	Drugs detected by HPLC-DAD	Drugs detected by WT-ESI-MS
A01	Doxepin, Clonazepam	Doxepin, Clonazepam
A02	Melatonin	Melatonin
A03	Zopiclone	Zopiclone
A04	Diazepam	Diazepam
A05	Zopiclone	Zopiclone
A06	Zopiclone, Melatonin	Zopiclone, Melatonin
A07	Zopiclone, Melatonin	Zopiclone, Melatonin
A08	Diazepam	Diazepam
A09	Diazepam	Diazepam
A10	Melatonin	Melatonin
A11	Doxepin	Doxepin
A12	Doxepin	Doxepin
A13	Doxepin	Doxepin
A14	Doxepin, Nitrazepam	Doxepin, Nitrazepam
A15	Doxepin	Doxepin
A16	Doxepin	Doxepin
A17	Melatonin	Melatonin
A18	Doxepin, Nitrazepam	Doxepin, Nitrazepam
A19	Chlorpheniramine	Chlorpheniramine
A20	Chlordiazepoxide	Chlordiazepoxide
A21	Chlorpheniramine	Chlorpheniramine
A22	Melatonin, Zaleplon	Melatonin, Zaleplon
A23	Melatonin, Zaleplon	Melatonin, Zaleplon
A24	Melatonin	Melatonin
A25	Melatonin	Melatonin, <i>Chlorpheniramine</i>
A26	Doxepin, Nitrazepam	Doxepin, Nitrazepam
A27	Melatonin	Melatonin
A28	Diazepam	Diazepam
A29	Melatonin	Melatonin
A30	Melatonin	Melatonin
A31	Alprazolam	Alprazolam
A32	Diazepam	Diazepam
A33	Not Detected	Not Detected
A34	Not Detected	<i>Melatonin</i>
A35	Not Detected	Not Detected
A36	Not Detected	Not Detected
A37	Not Detected	Not Detected
A38	Not Detected	<i>Melatonin</i>
A39	Diazepam	Diazepam
A40	Melatonin	Melatonin
A41	Melatonin	Melatonin
A42	Melatonin	Melatonin
A43	Chlorpheniramine	Chlorpheniramine

Table S2. Detection results of the aphrodisiac samples

Sample No.	Drugs detected by HPLC-DAD	Drugs detected by WT-ESI-MS
Z01	Sildenafil, Vardenafil	Sildenafil, Vardenafil
Z02	Sildenafil	Sildenafil
Z03	Sildenafil	Sildenafil
Z04	Sildenafil, Tadalafil	Sildenafil, Tadalafil
Z05	Sildenafil	Sildenafil
Z06	Sildenafil	Sildenafil
Z07	Tadalafil, Sildenafil	Tadalafil, Sildenafil
Z08	Sildenafil	Sildenafil
Z09	Sildenafil, Tadalafil	Sildenafil, Tadalafil
Z10	Sildenafil	Sildenafil
Z11	Sildenafil	Sildenafil
Z12	Sildenafil, Tadalafil	Sildenafil, Tadalafil
Z13	Sildenafil	Sildenafil
Z14	Tadalafil	Tadalafil
Z15	Vardenafil, Sildenafil, Tadalafil	Vardenafil, Sildenafil, Tadalafil
Z16	Vardenafil, Sildenafil, Tadalafil	Vardenafil, Sildenafil, Tadalafil
Z17	Sildenafil, Tadalafil	Sildenafil, Tadalafil
Z18	Sildenafil	Sildenafil
Z19	Sildenafil, Tadalafil	Sildenafil, Tadalafil
Z20	Sildenafil, Tadalafil	Sildenafil, Tadalafil
Z21	Sildenafil	Sildenafil
Z22	Sildenafil	Sildenafil
Z23	Sildenafil	Sildenafil
Z24	Sildenafil	Sildenafil
Z25	Amino-tadalafil	Amino-tadalafil, <i>Sildenafil</i> , <i>Hydroxyhomosildenafil</i>
Z26	Not Detected	Not Detected
Z27	Not Detected	Not Detected
Z28	Not Detected	Not Detected
Z29	Not Detected	Not Detected
Z30	Not Detected	Not Detected
Z31	Not Detected	Not Detected
Z32	Not Detected	Not Detected
Z33	Not Detected	Not Detected
Z34	Not Detected	Not Detected
Z35	Sildenafil	Sildenafil
Z36	Not Detected	Not Detected
Z37	Not Detected	Sildenafil
Z38	Not Detected	Not Detected
Z39	Sildenafil	Sildenafil
Z40	Sildenafil	Sildenafil
Z41	Sildenafil	Sildenafil
Z42	Sildenafil	Sildenafil
Z43	Sildenafil	Sildenafil
Z44	Sildenafil	Sildenafil
Z45	Sildenafil	Sildenafil
Z46	Sildenafil	Sildenafil
Z47	Sildenafil	Sildenafil
Z48	Sildenafil	Sildenafil
Z49	Sildenafil	Sildenafil
Z50	Sildenafil	Sildenafil
Z51	Sildenafil	Sildenafil
Z52	Sildenafil	Sildenafil
Z53	Sildenafil	Sildenafil
Z54	Sildenafil	Sildenafil
Z55	Sildenafil	Sildenafil
Z56	Sildenafil	Sildenafil
Z57	Sildenafil	Sildenafil

Table S3. Detection results of the weight-loss samples

Sample No.	Drugs detected by HPLC-DAD	Drugs detected by WT-ESI-MS
J01	Sibutramine, Phenolphthalein	Sibutramine, Phenolphthalein
J02	Sibutramine, Phenolphthalein	Sibutramine, Phenolphthalein
J03	Not Detected	Not Detected
J04	Not Detected	Not Detected
J05	Not Detected	Not Detected
J06	Not Detected	Not Detected
J07	Not Detected	Not Detected
J08	Not Detected	Not Detected
J09	Phenolphthalein	Phenolphthalein
J10	Sibutramine, Phenolphthalein	Sibutramine, Phenolphthalein
J11	Not Detected	Not Detected
J12	Sibutramine, Phenolphthalein	Sibutramine, Phenolphthalein
J13	Not Detected	Not Detected
J14	Sibutramine	Sibutramine
J15	Not Detected	Not Detected
J16	Phenolphthalein	Phenolphthalein
J17	Not Detected	Not Detected
J18	Sibutramine	Sibutramine
J19	Not Detected	<i>Sibutramine</i>
J20	Not Detected	Not Detected
J21	Not Detected	Not Detected
J22	Not Detected	Not Detected
J23	Not Detected	Not Detected
J24	Sibutramine	Sibutramine
J25	Not Detected	Not Detected
J26	Not Detected	Not Detected
J27	Not Detected	Not Detected
J28	Not Detected	Not Detected
J29	Not Detected	Not Detected
J30	Not Detected	Not Detected
J31	Not Detected	Not Detected
J32	Phenolphthalein	Phenolphthalein
J33	Sibutramine, Phenolphthalein	Sibutramine, Phenolphthalein
J34	Sildenafil, Phenolphthalein	Sildenafil, <i>Sibutramine</i> , Phenolphthalein
J35	Phenolphthalein	Phenolphthalein
J36	Not Detected	Not Detected
J37	Not Detected	Not Detected
J38	Not Detected	Not Detected
J39	Not Detected	Not Detected
J40	Not Detected	Not Detected
J41	Not Detected	Not Detected
J42	Phenolphthalein	<i>Sibutramine</i> , Phenolphthalein
J43	Not Detected	Not Detected
J44	Not Detected	Not Detected

Table S4. MS/MS data of 17 standard tranquilizer drugs

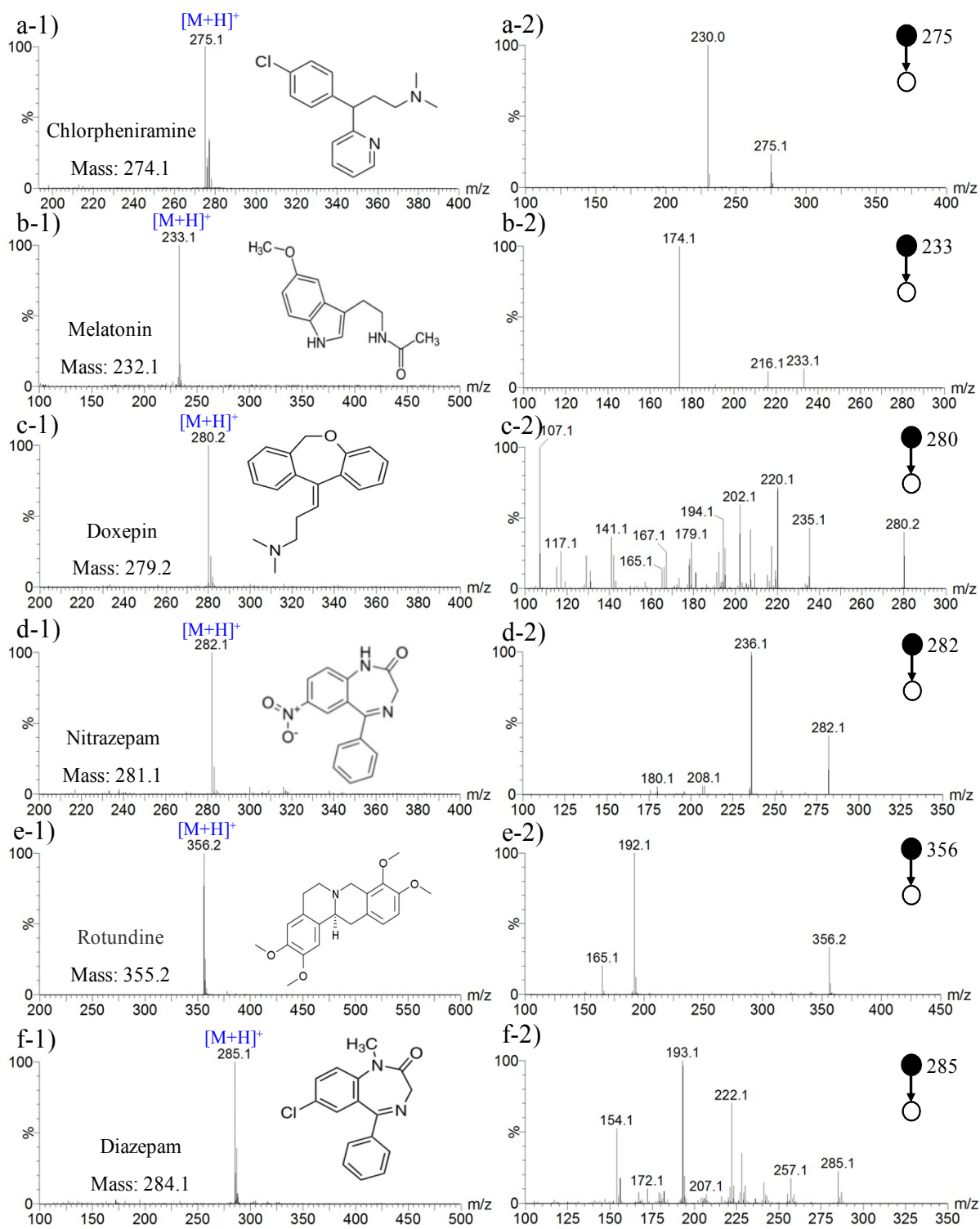
No	Drug	Monoisotopic mass (Da)	CE (eV)	Major product ions of [M+H] ⁺ (%)	Figure
1	Alprazolam	308.1	30	165.0(10), 205.1(20), 241.1(15), 274.1(25), 281.1(100)	S1n
2	Amobarbital	226.1	25	141.3(12), 157.3(100), 185.3(20)	S1o
3	Clonazepam	315.0	25	207.1(12), 214.1(12), 270.0(100)	S1i
4	Cocculine	329.2	35	137.1 (10), 153.1(25), 181.1(100), 195.1(45), 207.1(95), 223.1(50), 239.1(50), 255.1(10)	S1q
5	Chlordiazepoxide	299.1	25	227.3(60), 241.3(40), 255.3(25), 266.3(15), 283.3(100)	S1g
6	Chlorpheniramine	274.1	25	230.0(100)	S1a
7	Diazepam	284.1	25	154.1(50), 172.1(10), 193.1(100), 207.1(10), 222.1(65), 228.1(40), 257.1(20)	S1f
8	Doxepin	279.2	35	107.1(100), 117.1(30), 141.1(40), 167.1(30), 179.1(40), 194.1(50), 202.1(65), 220.1(80), 235.3(100)	S1c
9	Melatonin	232.1	25	174.1(100), 216.1(10)	S1b
10	Midazolam	325.1	30	209.1(10), 244.0(20), 291.1(100)	S1k
11	Nitrazepam	281.1	25	180.1(10), 208.1(10), 236.1(100)	S1d
12	Oxazepam	286.1	20	231.4(10), 241.1(100), 269.1(50)	S1m
13	Rotundine	355.0	25	165.1(20), 192.1(100)	S1e
14	Triazolam	343.0	30	165.0(15), 206.0(10), 239.0(25), 282.0(20), 308.0(100), 315.0(70),	S1l
15	Venlafaxine	277.2	20	121.1 (35), 147.1(70), 159.1(20), 173.1(30), 215.1(100), 260.2(90)	S1h
16	Zaleplon	305.1	25	209.1(10), 219.1(25), 236.1(100), 260.1(30), 264.1(60)	S1p
17	Zopiclone	388.1	15	143.1(10), 245.1(100), 345.1(55)	S1j

Table S5. MS/MS data of 11 standard aphrodisiac drugs

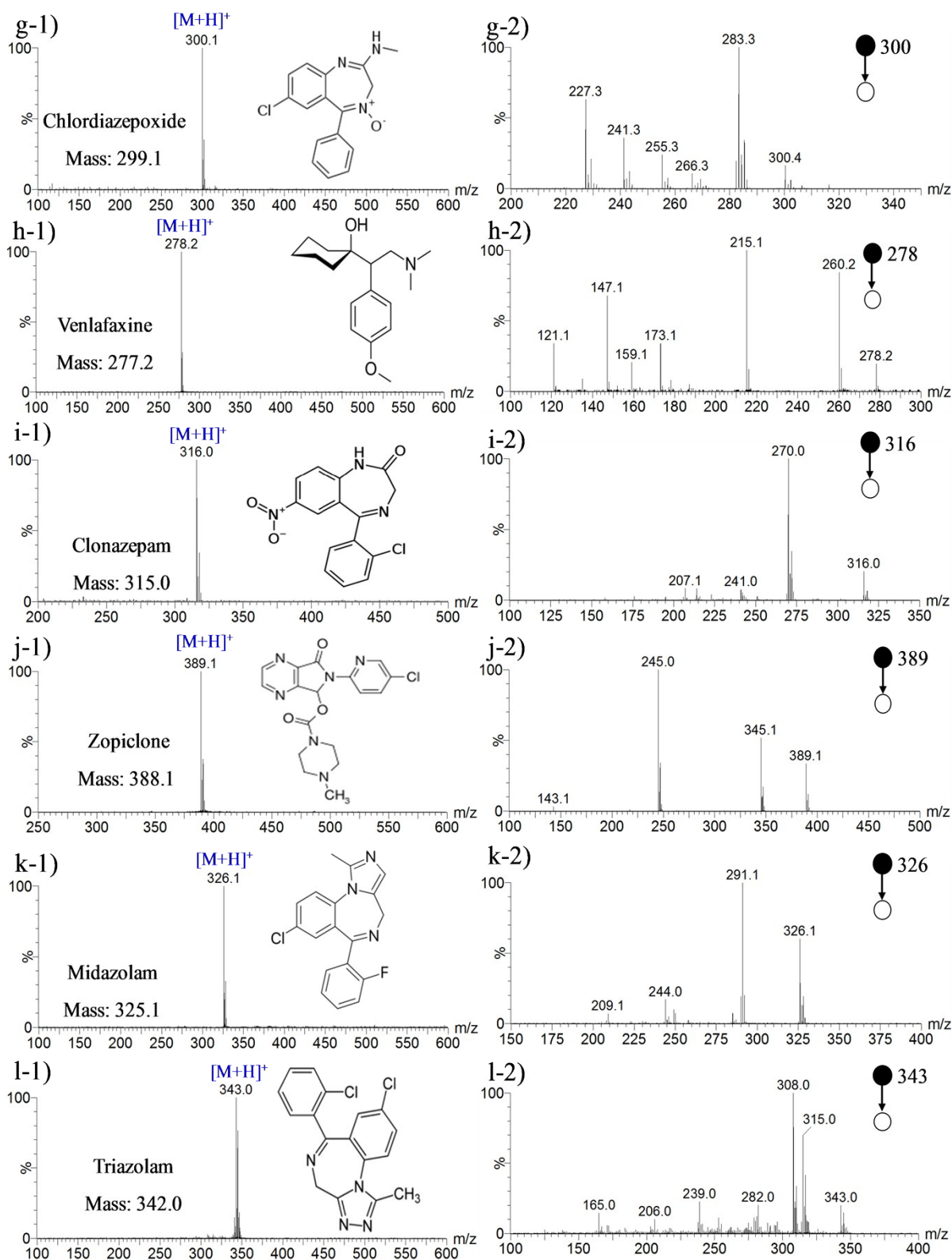
No	Drug	Monoisotopic mass (Da)	CE (eV)	Major product ions of [M+H] ⁺ (%)	Figure
1	Acetildenafil	466.3	50	111.1 (30), 127.1(50), 166.1(20), 297.1(100), 311.1(35), 325.1(50), 341.2(35), 353.2(20), 396.2(15), 439.2(10)	S2a
2	Amino-tadalafil	390.1	20	135.2(40), 169.1(10), 241.1(10), 250.1(20), 263.1(30), 269.1(100), 322.1(25), 359.1(20)	S2d
3	Homosildenafil	488.2	40	113.1(30), 254.1(5), 283.2(100), 299.2(20), 311.2(45), 377.2(10), 461.2(10)	S2k
4	Hydroxyhomosildenafil	504.2	40	112.1(30), 129.1(25), 283.1(100), 299.1(20), 311.1(75), 377.1(50), 461.2(20), 487.2(65)	S2h
5	Noracetildenafil	452.3	40	113.1 (15), 166.1(20), 285.2(10),297.2(100), 311.2(30), 325.2(50), 341.2(30), 353.2(10), 396.2(10),	S2b
6	Norneosildenafil	459.2	35	256.1(20), 283.1(100), 299.(60), 312.2(35), 329.2(15) 349.2(10), 403.2(10), 432.2(20)	S2f
7	Pseudo-varденаfil	459.2	35	151.1(100), 256.1(15), 284.1(50), 299.2(40), 312.2(60), 329.2(10), 377.2(5), 432.2(15)	S2i
8	Sildenafil	474.2	35	255.1(10), 283.1(100), 299.1(25), 311.1(50), 377.1(10)	S2e
9	Sulfoaildenafil	504.2	30	113.1 (20), 271.1(10), 299.1(100), 313.1(10), 327.1(90), 343.1(5), 393.1(30), 438.1(10)	S2g
10	Tadalafil	389.1	20	135.2(20), 240.1(10), 250.4(15), 262.1(20), 268.5(100), 302.5(10), 325.5(15)	S2c
11	Vardenafil	488.2	35	151.1(100), 284.1(25), 299.1(35), 312.1(85), 376.1(20)	S2j

Table S6. MS/MS data of 5 standard weight-loss drugs

No	Drug	Monoisotopic mass (Da)	CE (eV)	Major product ions of [M+H] ⁺ (%)	Figure
1	N-Desmethysibutramine	265.2	15	109.1(10), 125.1(80), 139.1(100), 153.1(60), 165.1(10), 179.2(30)	S3d
2	N,N-Didesmethysibutramine	251.2	15	109.1(10), 125.0(80), 139.0(100), 153.0(55), 165.0(10), 179.1(30)	S3e
3	Ephedrine	165.1	15	117.1(15), 133.1(20), 148.2(100)	S3a
4	Phenolphthalein	318.1	15	225.1(100)	S3b
5	Sibutramine	279.2	15	109.1(10), 125.0(95), 139.0(100), 153.0(60), 165.0(15), 179.1(40)	S3c



(Figure S1, continued)



(Figure S1, continued)

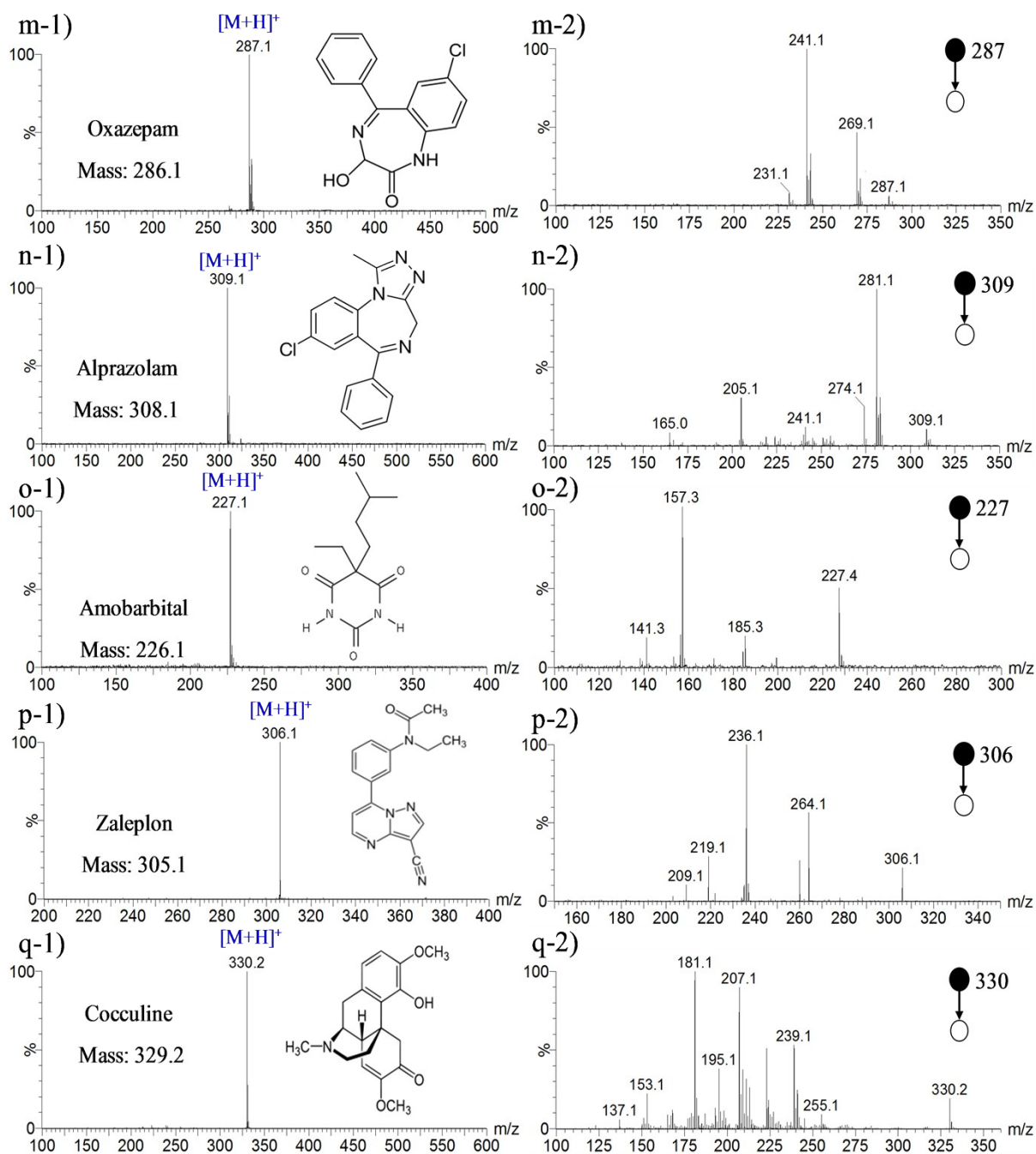
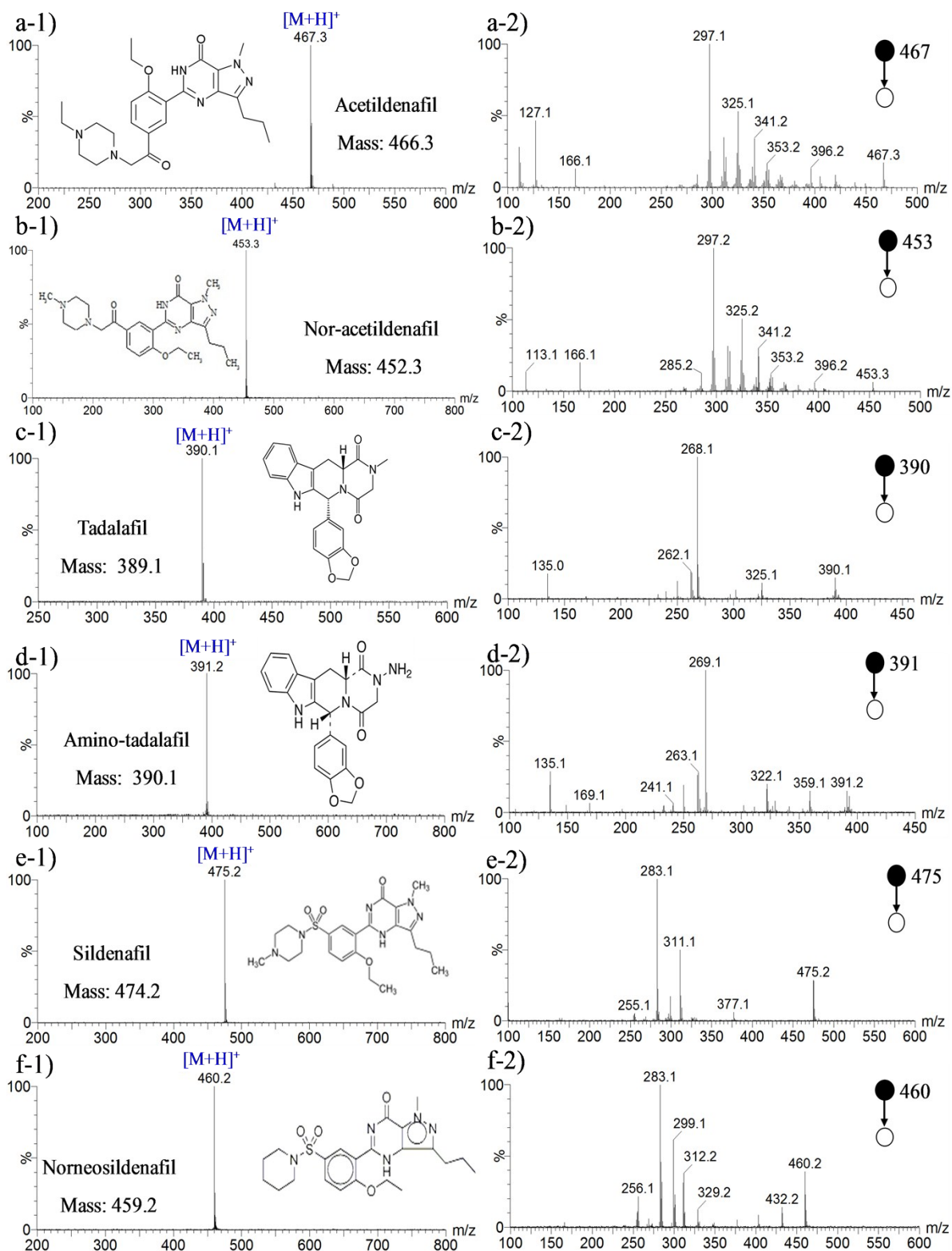


Figure S1. ESI-MS and MS/MS spectra of 17 standard tranquilizer drugs: a) chlorpheniramine, b) miltanone, c) doxepin, d) nitrazepam, e) rotundine, f) diazepam, g) chlordiazepoxide, h) venlafaxine, i) clonazepam, j) zopiclone, k) midazolam, l) triazolam, m) oxazepam, n) alprazolam, o) amobarbital, p) zaleplon, q) cocculine.



(Figure S2, continued)

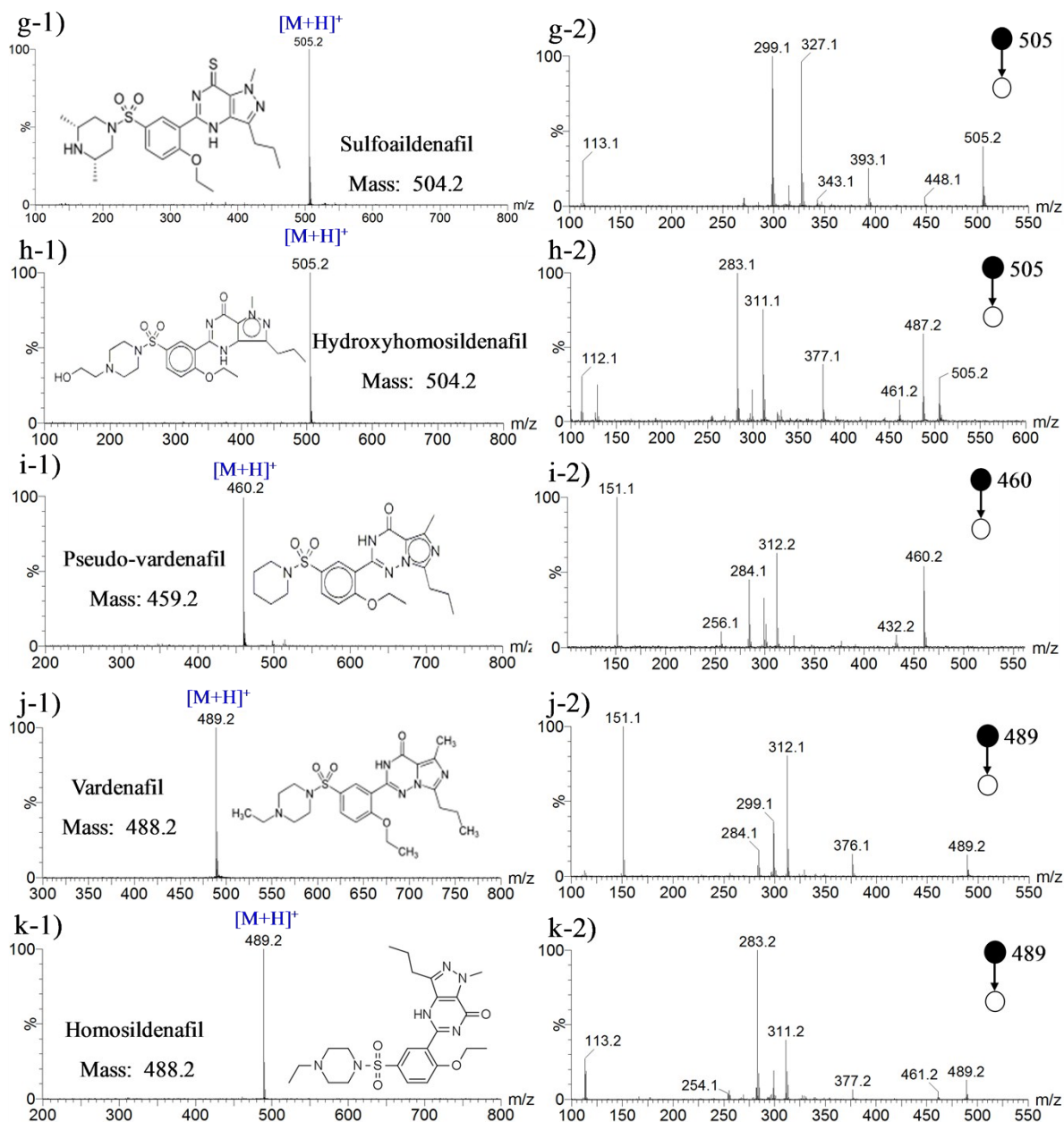


Figure S2. ESI-MS and MS/MS spectra of 11 standard aphrodisiac drugs: a) acetildenafil, b) nor-acetildenafil, c) tadalafil, d) amino-tadalafil, e) sildenafil, f) norneosildenafil, g) sulfoildenafil, h) hydroxyhomosildenafil, i) pseudo-varденаfil, j) vardenafil, k) homosildenafil.

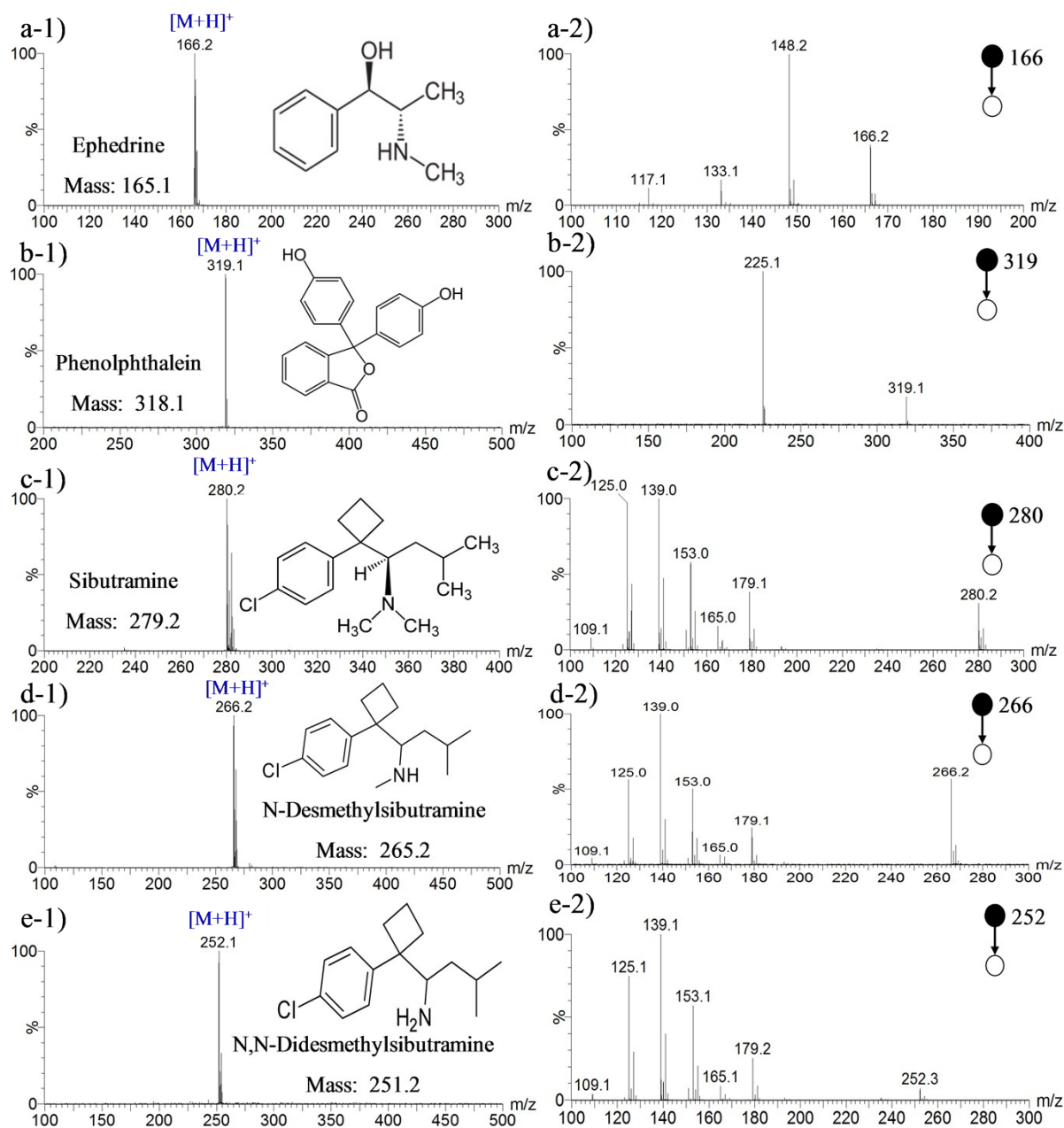


Figure S3. ESI-MS and MS/MS spectra of 5 standard weight-loss drugs: a) ephedrine, b) phenolphthalein, c) sibutramine, d) N-desmethyisibutramine, e) N, N-didesmethyisibutramine.