Electronic Supplementary Material (ESI) for Analyst

Rapid screening for synthetic antidiabetic drug adulteration in herbal dietary supplements using direct analysis in real time mass spectrometry

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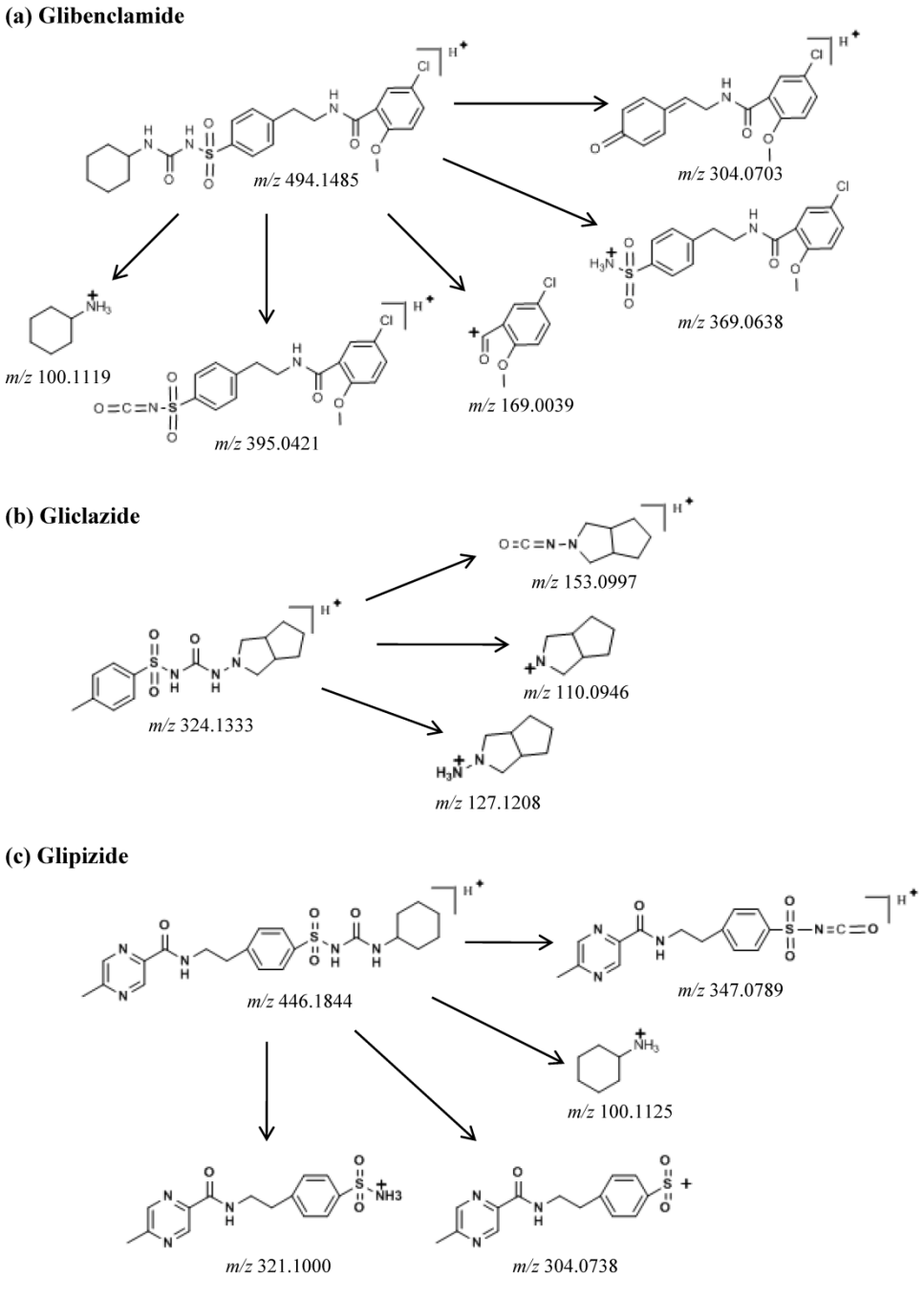

Fig. S1 The proposed fragmentation pathways of seven synthetic antidiabetic drugs.

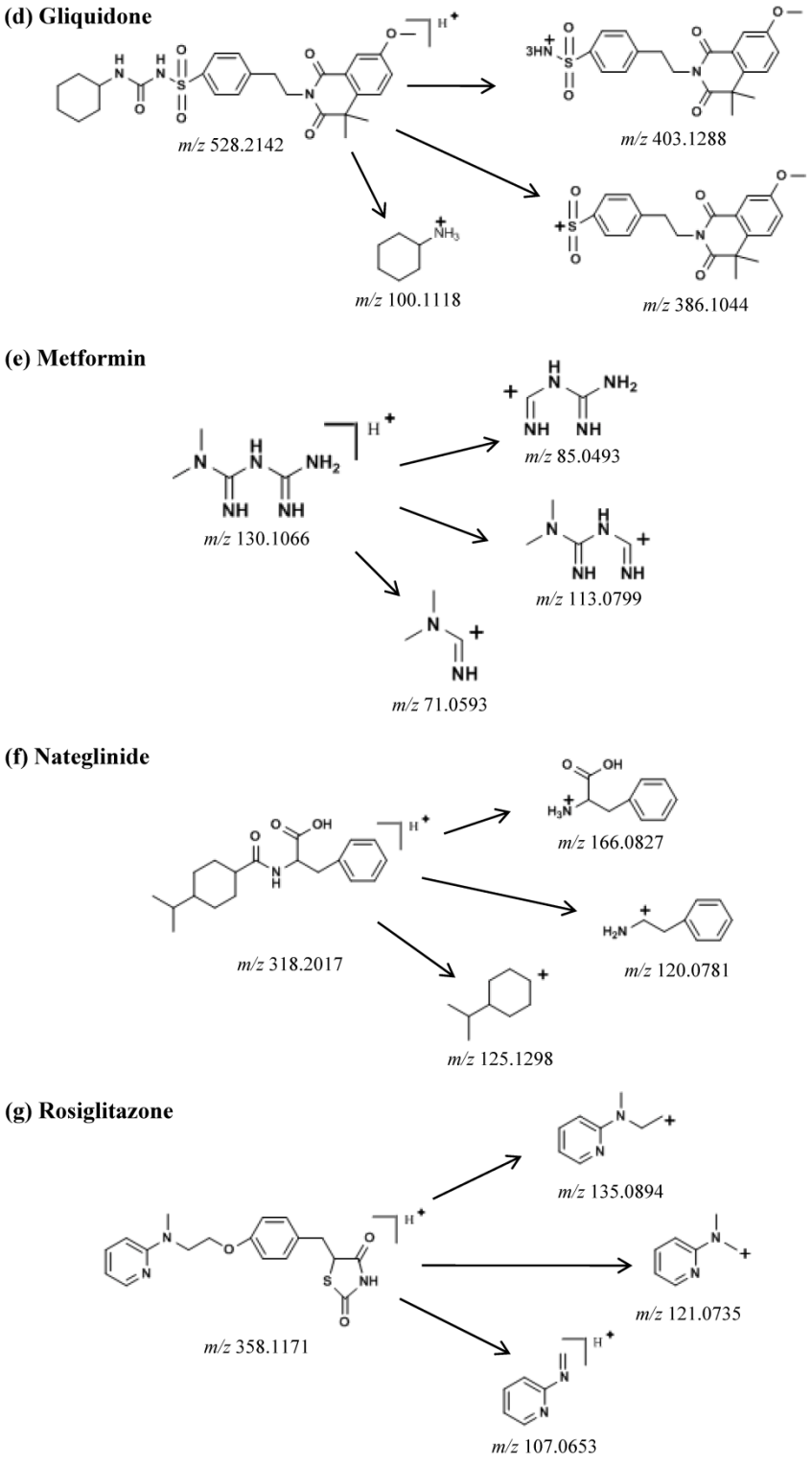

Fig. S1 (continued)

Table S1 MS and MS/MS data of the seven synthetic antidiabetic drugs in methanol/water (50/50, v/v) at the LOD concentrations

Compounds	$[M + H]^+$			Product ions			
	Observed m/z	Calculated m/z	Error ppm*	Observed m/z	Calculated m/z	Error ppm*	Abundance
Metformin	130.1072	130.1093	-16	85.0492	85.0514	-26	346
				71.0601	71.0609	-11	1501
				113.0820	113.0827	-6	301
Nateglinide	318.2050	318.2069	-6	125.1310	125.1330	-16	166
				166.0858	166.0868	-6	220
				120.0816	120.0813	2	356
Gliclazide	324.1372	324.1382	-3	110.0963	110.0970	-6	269
				127.1208	127.1235	-21	327
				153.1013	153.1028	-10	148
Rosiglitazone	358.1220	358.1225	-1	107.0620	107.0609	10	60
				121.0742	121.0766	-20	113
				135.0916	135.0922	-4	1711
Glipizide	446.1820	446.1862	-9	100.1113	100.1126	-13	53
				347.0748	347.0814	-19	111
				321.0988	321.1021	-10	211
Glibenclamide	494.1486	494.1516	-6	169.0051	169.0056	-3	1508
				304.0731	304.0740	-3	470
				369.0645	369.0676	-8	2486
				395.0469	395.0468	0	230
Gliquidone	528.2139	528.2168	-5	386.1067	386.1062	1	384
				100.1122	100.1126	-4	316
				403.1307	403.1328	-5	718

*Relatively high mass errors were observed due to lack of reference solutions introduced during the entire analysis to correct the m/z values, but the combination of m/z values and relative intensities of multiple product ions could make sure the detection of synthetic drug adulterant was reliable.

Table S2 MS and MS/MS data of the seven synthetic antidiabetic drugs adulterated in matrix 1 at the LOD concentrations

Compounds	$[M + H]^+$			Product ions			
	Observed m/z	Calculated m/z	Error ppm*	Observed m/z	Calculated m/z	Error ppm*	Abundance
Metformin	130.1060	130.1093	-25	85.0498	85.0514	-19	461
				71.0607	71.0609	-3	2813
				113.0825	113.0827	-2	220
Nateglinide	318.2050	318.2069	-6	125.1310	125.1330	-16	1324
				166.0847	166.0868	-13	1502
				120.0804	120.0813	-7	2665
Gliclazide	324.14**	324.1382	-	110.0974	110.0970	4	306
				127.1203	127.1235	-25	598
				153.0984	153.1028	-29	239
Rosiglitazone	358.1220	358.1225	-1	107.0590	107.0609	-18	175
				121.0766	121.0766	0	394
				135.0905	135.0922	-13	3168
Glipizide	446.19**	446.1862	-	100.1124	100.1126	-2	1980
				347.0825	347.0814	3	287
				321.1000	321.1021	-7	1114
				304.0731	304.0756	-8	52
Glibenclamide	494.15**	494.1516	-	169.0039	169.0056	-10	135
				304.0707	304.0740	-11	39
				369.0627	369.0676	-13	372
Gliquidone	528.22**	528.2168	-	386.0949	386.1062	-29	61
				100.1112	100.1126	-14	1038
				403.1266	403.1328	-15	196

*Relatively high mass errors were observed due to lack of reference solutions introduced during the entire analysis to correct the m/z values, but the combination of m/z values and relative intensities of multiple product ions could make sure the detection of synthetic drug adulterant was reliable.

**The m/z valves of target synthetic drugs were overlaid by those of interfering compounds from supplementary matrix.

Table S3 MS and MS/MS data of the seven synthetic antidiabetic drugs adulterated in matrix 2 at the LOD concentrations

Compounds	$[M + H]^+$			Product ions			
	Observed m/z	Calculated m/z	Error ppm*	Observed m/z	Calculated m/z	Error ppm*	Abundance
Metformin	130.11**	130.1093	-	85.0500	85.0514	-16	210
				71.0597	71.0609	-17	595
				113.0815	113.0827	-11	157
Nateglinide	318.2059	318.2069	-3	125.1342	125.1330	10	101
				166.0911	166.0868	26	587
				120.0832	120.0813	16	892
Gliclazide	324.1315	324.1382	-21	110.0952	110.0970	-16	579
				127.1212	127.1235	-18	654
				153.1010	153.1028	-12	160
Rosiglitazone	358.12**	358.1225	-	107.0590	107.0609	-18	225
				121.0750	121.0766	-13	450
				135.0920	135.0922	-1	2929
Glipizide	446.1846	446.1862	-4	100.1114	100.1126	-12	991
				347.0783	347.0814	-9	102
				321.1010	321.1021	-3	304
				304.0706	304.0756	-16	47
Glibenclamide	494.1482	494.1516	-7	169.0032	169.0056	-14	1223
				304.0700	304.0740	-13	342
				369.0650	369.0676	-7	2116
				395.0448	395.0468	-5	83
Gliquidone	528.22**	528.2168	-	386.1011	386.1062	-13	155
				100.1117	100.1126	-9	2834
				403.1288	403.1328	-10	399

*Relatively high mass errors were observed due to lack of reference solutions introduced during the entire analysis to correct the m/z values, but the combination of m/z values and relative intensities of multiple product ions could make sure the detection of synthetic drug adulterant was reliable.

**The m/z valves of target synthetic drugs were overlaid by those of interfering compounds from supplementary matrix.

Table S4 MS and MS/MS data of the seven synthetic antidiabetic drugs adulterated in matrix 3 at the LOD concentrations

Compounds	$[M + H]^+$			Product ions			
	Observed m/z	Calculated m/z	Error ppm*	Observed m/z	Calculated m/z	Error ppm*	Abundance
Metformin	130.11**	130.1093	-	85.0503	85.0514	-13	1560
				71.0603	71.0609	-8	6206
				113.0820	113.0827	-6	550
Nateglinide	318.2052	318.2069	-5	125.1311	125.1330	-15	299
				166.0875	166.0868	4	456
				120.0801	120.0813	-10	963
Gliclazide	324.14**	324.1382	-	110.0979	110.0970	8	292
				127.1206	127.1235	-23	601
				153.1004	153.1028	-16	74
Rosiglitazone	358.1220	358.1225	-1	107.0603	107.0609	-6	200
				121.0760	121.0766	-5	223
				135.0913	135.0922	-7	2577
Glipizide	446.1881	446.1862	4	100.1112	100.1126	-14	2539
				347.0795	347.0814	-5	265
				321.0986	321.1021	-11	1746
				304.0735	304.0756	-7	42
Glibenclamide	494.1501	494.1516	-3	169.0059	169.0056	2	247
				304.0716	304.0740	-8	95
				369.0644	369.0676	-9	404
				395.0388	395.0468	-20	41
Gliquidone	528.2168	528.2168	0	386.1000	386.1062	-16	55
				100.1113	100.1126	-13	1877
				403.1297	403.1328	-8	105

*Relatively high mass errors were observed due to lack of reference solutions introduced during the entire analysis to correct the m/z values, but the combination of m/z values and relative intensities of multiple product ions could make sure the detection of synthetic drug adulterant was reliable.

**The m/z valves of target synthetic drugs were overlaid by those of interfering compounds from supplementary matrix.