

Article

Comparison of the Characteristic Mass Fragmentations of Phenethylamines and Tryptamines by Electron Ionization Gas Chromatography Mass Spectrometry, Electrospray and Matrix-Assisted Laser Desorption Ionization Mass Spectrometry

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Abstract: Characteristic mass fragmentation of 20 phenethylamine/tryptamine standards were investigated and compared by means of matrix assisted laser desorption/time-of-flight mass spectrometry (MALDI/TOFM), gas chromatography–electron ionization–mass spectrometry (GC-EI/MS) and liquid chromatography–electrospray ionization/mass spectrometry (LC-ESI/MS) methods. As a result, three characteristic peaks ($[M]^+$ and fragments from the C_β - C_α bond breakage) were found to be unique and contained information useful in identifying 2C series compounds based on the GC-EI/MS method. We found that the protonated molecular ion ($[M+H]^+$) and two types of fragments produced from the α -cleavage and β -cleavage processes were useful mass spectral information in the rapid screening and confirmation of phenethylamine and tryptamine derivatives when ESI/MS and MALDI/TOFMS methods were applied. This assay was successfully used to determine samples that contain illicit drugs.

Keywords: phenethylamine; tryptamine; MALDI/TOFMS; GC-EI/MS; LC-ESI/MS

1. Introduction

Thus far, gas chromatography/mass spectrometry (GC/MS) is the officially prescribed and most popular technique for the analysis of illicit drugs such as phenethylamines, tryptamines and their analogs [1–9]. 2C series compounds, invented by Alexander Shulgin, are general names for the family of psychedelic phenethylamines containing methoxy groups on the 2 and 5 positions of a benzene ring. The increased availability of 2C-series of phenethylamine derivatives on the illicit market has become a serious social problem. However, little mass spectrum information is available concerning their detection. Because of this, GC/MS analysis has dominated the field of drug screening for many years, and a huge database is typically available in commercial libraries. However, the sample preparation for GC/MS analysis is still complicated and time consuming. Typically, various samples (such as clandestine tablets, hair, urine, etc.) must be pretreated to extract the analytes by either liquid–liquid or solid-phase extraction methods. Each analyte has unique properties for extraction, and the conditions required for the subsequent individual derivatization, prior to their injection into the GC/MS system, are also different. Thus, thousands of samples, especially those that contain multiple components, are frequently involved in routine testing. Due to the large number of samples, a rapid and soft-ionization method, which is also reliable and complementary to GC/MS for use in

forensic analysis, would be highly desirable. Two types of soft ionization methods—electrospray ionization/mass spectrometry (ESI/MS) and matrix-assisted laser desorption ionization/time-of-flight mass spectrometry (MALDI/TOFMS)—have become more popular and have widespread use in many fields. In this paper, we report on the characteristic mass fragmentations of 11 phenethylamine and 9 tryptamine standards, including 2C series compounds, which were obtained by GC-EI/MS, LC-ESI/MS and MALDI/TOFMS.

2. Materials and Methods

2.1. Apparatus

A gas chromatograph (GC 6890 Hewlett-Packard, Avondale, PA, USA) equipped with a mass spectrometer (Hewlett-Packard 5973 mass selective detector) was used. Herein, a capillary column (30 m × 0.25 µm I.D.) with an HP-5MS (cross-linked 5% PH ME siloxane) bonded stationary phase film, 0.25 µm in thickness (Agilent Technologies, Santa Clara, CA, USA) was used. For the MALDI/TOFMS experiments, a linear type of time-of-flight mass spectrometer (TOFMS), the modified Wiley–McLaren design (R. M. Jordan Co., Grass Valley, CA, USA), the laser source (Nd:YAG laser; 355 nm) and the data acquisition system used were similar to those used in previously described methods [10,11]. In this case, the inlet temperature was maintained at 250 °C and the column oven was held at 70 °C for 1 min; programmed from 70 to 200 °C at 15 °C/min; held for 2 min; programmed from 200 to 260 °C at 20 °C/min; and, finally, held for 8.84 min (carrier gas: helium, flow-rate 1 mL/min). The mass spectrometry conditions were as follows: ionization energy, 70 eV; ion source temperature, 230 °C. For the ESI-MS experiments, a LC/MS system (Finnigan LCQ Classic LC/MS/MS) consisting of an electrospray ionization probe operated in the positive ion mode and an Xcalibur data system was used. Infusion into the mass spectrometer was performed by a built-in syringe pump at a flow rate of 0.01 mL/min. The tube lens offset was set at −5 V; sheath gas and auxiliary gas flow rates were 60 and 10 (arb), respectively. Scan mode used was full scan; the capillary temperature and spray voltage were set to 150 °C and 4.5 kV, respectively [12].

2.2. Reagents

The procedures for the synthesis of these drugs have been described previously by Ann and Alexander Shulgin in publications titled *PiHKAL* (Phenethylamines I Have Known and Loved) and *TiHKAL* (Tryptamines I Have Known and Loved) [13,14]. Shulgin also invented the term 2C, being an abbreviation for the 2 carbon atoms between the benzene ring and the amino group, as described below. The following drugs were generously donated by the Military Police Command, Forensic Science Center, Taipei city, Taiwan, including methamphetamine (MA), 2,4-dimethoxy-5-bromoamphetamine (2,4-DOB), 3,4-methylenedioxyamphetamine (3,4-MDA), 3,4-benzodioxol-5-yl-2-butylamine (3,4-BDB), 3,4-methylenedioxymethamphetamine (3,4-MDMA), *N*-methyl-1-(1,3-benzodioxol-5-yl)-2-butylamine (MBDB), 4-chloro-2,5-dimethoxy-β-phenethylamine (2C-C), 4-ethylthio-2,5-dimethoxy-β-phenethylamine (2C-T-2), 4-propylthio-2,5-dimethoxy-β-phenethylamine (2C-T-7), 4-bromo-2,5-dimethoxy-β-phenethylamine (2C-B), 4-iodo-2,5-dimethoxy-β-phenethylamine (2C-I), α-methyltryptamine (AMT), *N,N*-dimethyltryptamine (DMT), 5-methoxy-α-methyltryptamine (5-MeO-AMT), *N,N*-diethyltryptamine (DET), *N,N*-dipropyltryptamine (DPT), *N,N*-dibutyltryptamine (DBT), *N,N*-diisopropyltryptamine (DIPT), 5-methoxy-*N,N*-dimethyltryptamine (5-MeO-DMT) and 5-methoxy-*N,N*-diisopropyltryptamine (5-MeO-DIPT). Following synthesis, the final products were identified by NMR and IR and verified by GC-MS. LSD (lysergic acid diethylamide) was acquired from Radian International (Austin, TX, USA). α-Cyano-4-hydroxycinnamic acid (CHCA) and 2,5-dihydroxybenzoic acid (2,5-DHB) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals were of analytical grade and were obtained from commercial sources.

2.3. Sample Preparation

Matrices: In the case of 2,5-DHB, 10.0 mg were dissolved in a 1.0 mL aliquot of water/acetonitrile (*v/v*, 50/50), which also contained 0.1% trifluoroacetic acid. In contrast to this, 10 mg of CHCA were dissolved in a 1.0 mL aliquot of a water/acetonitrile (*v/v*, 50/50) solution that contained 0.1% trifluoroacetic acid.

Standards: The preparation of analytes for GC/MS and LC/MS was the same as described below, but without any matrix. Solutions for each of the analogs were prepared by dissolving the appropriate amount in methanol to obtain a final concentration. A drop of the aqueous (0.001 mL) matrix compound solution was mixed with the analyte solution (0.01 mg mL⁻¹ methanol) and dried, resulting in a solid deposit of analyte-doped matrix crystals, which was used in the MALDI/TOFMS for analysis.

Tablet: The tablets were ground into a fine powder, and approximately 1.0 mg was dissolved in 1.0 mL methanol. After 2 min of sonication and a 1 min centrifugation at 5000 rpm at room temperature, the upper layer was collected and used directly in the analysis by MALDI/TOFMS.

Hair: The blank hair samples (black and white hair) were collected from two adult male volunteers, respectively. After a rinsing, the hair samples were immersed in a methanol stock solution containing a 3,4-MDMA standard (0.2 mg mL⁻¹) for making 3,4-MDMA spiked samples. Two days later, the hair samples were moved to the substrate for drying. Then, 0.001 mL of CHCA-solution was loaded on the hair substrate, and the samples were directly used for the subsequent MALDI/TOFMS experiments.

Urine: The blank urine sample was collected from an adult male volunteer. A 0.9 mL filtered aliquot of urine was spiked with the 0.1 mL LSD standard solution (0.01 mg mL⁻¹ methanol) to make an LSD-spiked urine solution. Then, 0.001 mL aliquot of the LSD-spiked urine solution was mixed with 0.001 mL of 2,5-DHB-solution and loaded on the MALDI substrate for drying.

3. Results and Discussion

The abbreviations of the 11 phenethylamine and 9 tryptamine standards (tabulated by structure) used in this study are shown in Table 1. In fact, 55 tryptamine and 179 phenethylamine compounds were synthesized and described by Ann and Alexander Shulgin in *TiHKAL* and *PiHKAL*, respectively [13,14]. These compounds have been abused since the mid-1980s. Hence, more detailed information about the characteristic mass fragments, produced under different types of ionization methods, is highly desirable for the screening and confirmation of phenethylamine and tryptamine derivatives. Figure 1a shows the basic structures of primary (1°), secondary (2°), and tertiary (3°) amines, respectively; the chemical structures of phenethylamine, tryptamine and their derivatives of various substituents are shown in Figure 1b. Figure 2 shows a general schematic outline for the α -cleavage and β -cleavage based on ESI and MALDI modes, respectively, when *N,N*-dimethyltryptamine (DMT; Mw: 188) was selected as the model compound. This scheme shows that, if a tryptamine (or phenethylamine) acquires a proton, it will form a $[M+H]^+$ ion. The α -cleavage would progress at the C $_{\alpha}$ -N bond, and, as a result, a cation (indole-containing group) and small neutral amine (NHR_{N1}R_{N2}) are formed. In this case, $[M+H]^+$ ion (m/z : 189) and the cation (m/z : 58) can be observed. However, the proton also could be donated to the C $_{\beta}$ atom, leading to a C $_{\alpha}$ -C $_{\beta}$ bond breakage (i.e., β -cleavage). As a result, an iminium ion (CH₂=N⁺R_{N1}R_{N2}) and a neutral fragment would form.

Table 1. Abbreviations used for the phenethylamine and tryptamine standards (tabulated structure) in this study.

A. Phenethylamines									
Abbrev.	R	R ₂	R ₃	R ^a	R ₄	R ₅	R ₆	R _{N1}	Full Name
MA	CH ₃	H	H		H	H	H	CH ₃	methamphetamine
2,4-DOB	CH ₃	OCH ₃	H		OCH ₃	Br	H	H	2,4-dimethoxy-5-bromoamphetamine
3,4-MDA	H	H		-OCH ₂ O-	H		H	H	3,4-methylenedioxyamphetamine
3,4-BDB	CH ₂ CH ₃	H		-OCH ₂ O-	H		H	H	3,4-benzodioxol-5-yl-2-butylamine
3,4-MDMA	CH ₃	H		-OCH ₂ O-	H		H	CH ₃	3,4-methylenedioxymethamphetamine
MBDB	CH ₂ CH ₃	H		-OCH ₂ O-	H		H	CH ₃	N-methyl-1-(1,3-benzodioxol-5-yl)-2-butylamine
2C-T-7	H	H	OCH ₃		SCH ₂ CH ₂ CH ₃	H	OCH ₃	H	4-propylthio-2,5-dimethoxy-β-phenethylamine
2C-T-2	H	H	OCH ₃		SCH ₂ CH ₃	H	OCH ₃	H	4-ethylthio-2,5-dimethoxy-β-phenethylamine
2C-C	H	H	OCH ₃		Cl	H	OCH ₃	H	4-chloro-2,5-dimethoxy-β-phenethylamine
2C-B	H	H	OCH ₃		Br	H	OCH ₃	H	4-bromo-2,5-dimethoxy-β-phenethylamine
2C-I	H	H	OCH ₃		I	H	OCH ₃	H	4-iodo-2,5-dimethoxy-β-phenethylamine
B. Tryptamines									
Abbrev.	R ₅	R	R _{N1}	R _{N2}	Full Name				
AMT	H	CH ₃	H	H	α-methyltryptamine				
DMT	H	H	CH ₃	CH ₃	N,N-dimethyltryptamine				
5-MeO-AMT	OCH ₃	CH ₃	H	H	5-methoxy-α-methyltryptamine				
DET	H	H	CH ₂ CH ₃	CH ₂ CH ₃	N,N-diethyltryptamine				
DPT	H	H	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	N,N-dipropyltryptamine				
DBT	H	H	CH ₂ CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₂ CH ₃	N,N-dibutyltryptamine				
5-MeO-DMT	OCH ₃	H	CH ₃	CH ₃	5-methoxy-N,N-dimethyltryptamine				
DIPT	H	H	CH(CH ₃) ₂	CH(CH ₃) ₂	N,N-diisopropyltryptamine				
5-MeO-DIPT	OCH ₃	H	CH(CH ₃) ₂	CH(CH ₃) ₂	5-methoxy-N,N-diisopropyltryptamine				

a: A ring formed with both R₃ and R₄.

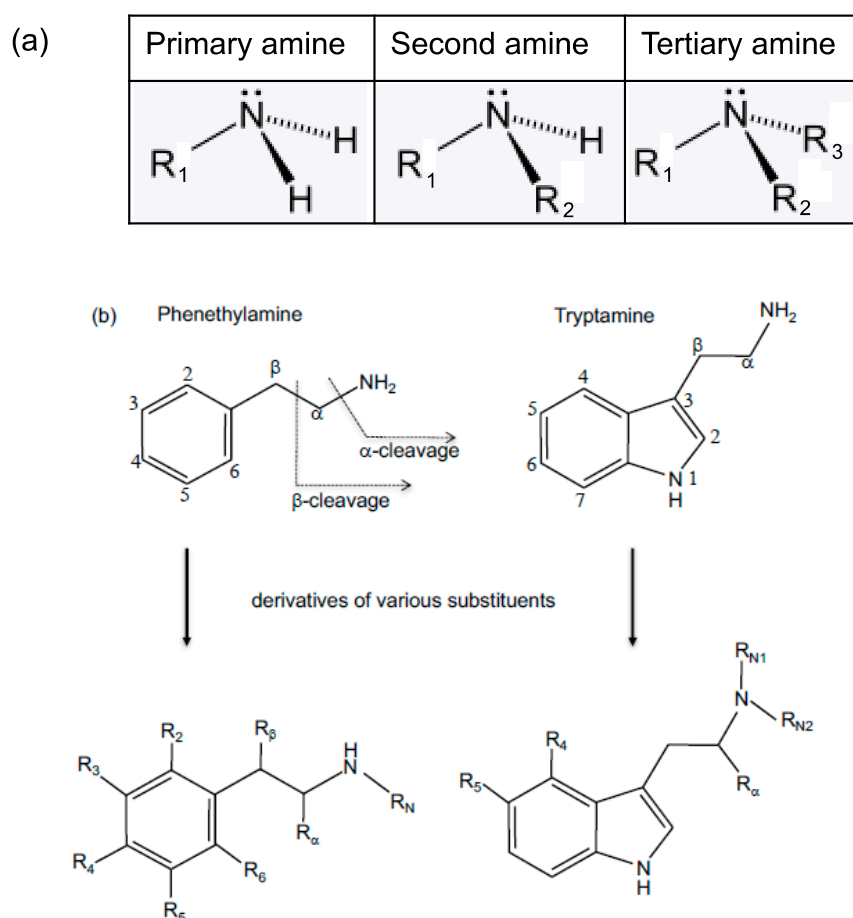


Figure 1. (a) basic structure of primary (1°), secondary (2°), and tertiary (3°) amines; and (b) chemical structures of phenethylamine, tryptamine and their derivatives of various substituents.

Table 2 shows the differences and similarities in the mass spectra of these phenethylamine/tryptamine compounds when different ionization methods are applied, including EI-MS, ESI-MS and MALDI/TOFMS. It can be found that, in the case of ESI/MS, the ions of $m/z = 58$, 144 and 189 come from β -cleavage, α -cleavage and $[M+H]^+$, respectively. In the case of MALDI/TOFMS, only α -cleavage and $[M+H]^+$ can be found. In contrast, different fragments are found when EI mode was used. All of these characteristic peaks are very important to identify tryptamine and phenethylamine. Among these data, our group selected 2C-T-7 (a primary amine), 3,4-MBDB (a secondary amine), and DET (a tertiary amine) as the model compounds for comparison, as described below. Figure 3 shows the EI/MS, ESI/MS and MALDI/TOFMS spectra of the three model compounds. As shown in Figure 3a (the upper mass spectrum; based on the EI mode), a parent ion of 2C-T-7, at $m/z = 255$, can be clearly observed. The other 2C series compounds also show similar consequences, as shown in Table 2, i.e., the parent ions obviously can be obtained. This is not a common phenomenon because, when the EI mode is used, in general, the energy of the electron makes it too difficult to obtain the parent ion. The reason for this could be that the functional groups ($-OCH_3$ at R_3/R_5 and halogens at R_4) attach at the benzene ring, resulting in stronger $C_\beta-C_\alpha$ and $C_\alpha-N$ bonds. In fact, the $C_\alpha-N$ bond does not break for any compound investigated in this study when the EI mode was used. Two fragment ions ($m/z = 30$, 225) clearly form because of the $C_\beta-C_\alpha$ bond breakage; the $C_\alpha-N$ bond seems very difficult to break. The three characteristic peaks ($[M]^+$ and fragments from the $C_\beta-C_\alpha$ bond breakage) are very unique and provide useful information for identifying 2C series compounds in actual forensic cases using the SIM (select ion monitoring) mode [12]. In the cases of the ESI and MALDI methods (the middle and bottom mass spectra of Frame 3a, respectively), a stable

protonated parent ion ($[M+H]^+$, $m/z = 256$) can be clearly observed. The α -cleavage process would produce a major fragment at $m/z = 239$, indicating the loss of a neutral fragment, $256 - 239 = 17$ (NH_3). In the β -cleavage process, a peak at $m/z = 30$ ($H_2C=N^+H_2$) should be observed, indicating the loss of a larger neutral fragment, $256 - 30 = 226$. However, the peak of $m/z = 30$ cannot be seen on the ESI-spectrum because the detection range of the instrument (Finnigan LCQ Classic) is limited to m/z above 50. Our group used the MALDI method to examine this and found that the fragment of $m/z = 30$ does indeed exist, although its intensity is very weak. Figure 3b shows the EI/MS, ESI/MS and MALDI/TOFMS spectra of 3,4-MBMB. As shown in the upper mass spectrum (EI), the parent ion ($m/z = 208$) is not formed, whereas two fragment ions ($m/z = 58, 177$) are produced from the C_β - C_α bond breakage. No peak can be observed from the C_α -N bond breakage again. The peak at $m/z = 58$ is the major fragment of 3,4-MBMB, suggesting that this is the most stable fragment ion that forms after electron impact. It is obvious in this case, the EI mode is not suited for rapid screening if it is dependent only on the major peak at $m/z = 58$. 3,4-MDMA shows similar pattern with 3,4-MBMB. In traditional method, 3,4-MDMA can be performed via reaction with acetic anhydride, which provides specific fragments ($m/z = 58, 100$ and 162), permitted its characterization [15]. However, while such a specific derivative-reagent is suitable for one compound, it may not be suitable for others. In contrast, stable protonated parent ions ($[M+H]^+$, $m/z = 208$) can be clearly observed by means of ESI and MALDI modes (the middle and bottom mass spectra of Frame B, respectively). In the case of ESI/MS, α -cleavage is the major process that would produce a fragment at $m/z = 177$, indicating the loss of a neutral fragment, $208 - 177 = 31$ [$NH_2(CH_3)$], but the peak from β -cleavage cannot be found. It should be noted that, in the case of MALDI/TOFMS, fragment ions from both α -cleavage and β -cleavage could be observed, even though the fragment from α -cleavage is insignificant. Figure 3c shows the EI/MS, ESI/MS and MALDI/TOFMS spectra of DET. A parent ion ($m/z = 217$) is formed by the EI mode even though its intensity is insignificant, and two fragment ions ($m/z = 86, 144$) are produced from the C_β - C_α bond breakage. In the case of ESI/MS, stable protonated parent ions ($[M+H]^+$, $m/z = 217$) and two fragments ($m/z = 86, 144$), which are formed through α -cleavage and β -cleavage processes, can be clearly observed. The α -cleavage is the major process that would produce a fragment at $m/z = 144$, indicating the loss of a neutral fragment, $217 - 144 = 73$ [$NH(CH_2CH_3)_2$]. Meanwhile, the β -cleavage process also occurs, in which a peak at $m/z = 58$ [$H_2C=N^+(CH_3)_2$] was observed, indicating the loss of a larger neutral fragment, $217 - 86 = 131$. The ion intensity order of DMT is as follows: $[M+H]^+ \gg$ fragment formed by the α -cleavage process $>$ fragment formed by the β -cleavage process. In the case of MALDI/TOFMS, the ion intensity of $[M+H]^+$ is greater than the fragment from the β -cleavage process, but the fragment ($m/z = 144$) from α -cleavage is missing. Thus, our group concludes that the three characteristic peaks, ($[M+H]^+$ and the peaks from the α -cleavage and β -cleavage processes) are very unique and provide useful information in identifying phenethylamines and tryptamines in actual forensic cases based on the ESI/MS or MALDI/TOFMS methods. Although a direct sample injection is possible based on some LC-ESI/MS methods, which would be an ideal method for rapid screening, thus far, such studies also can be performed by means of MALDI/TOFMS since the sample substrate used in MALDI/TOFMS can be much easily inserted and changed. Our group selected MALDI/TOFMS as the rapid screening tool for the following studies, including actual clandestine tablet, hair and urine samples.

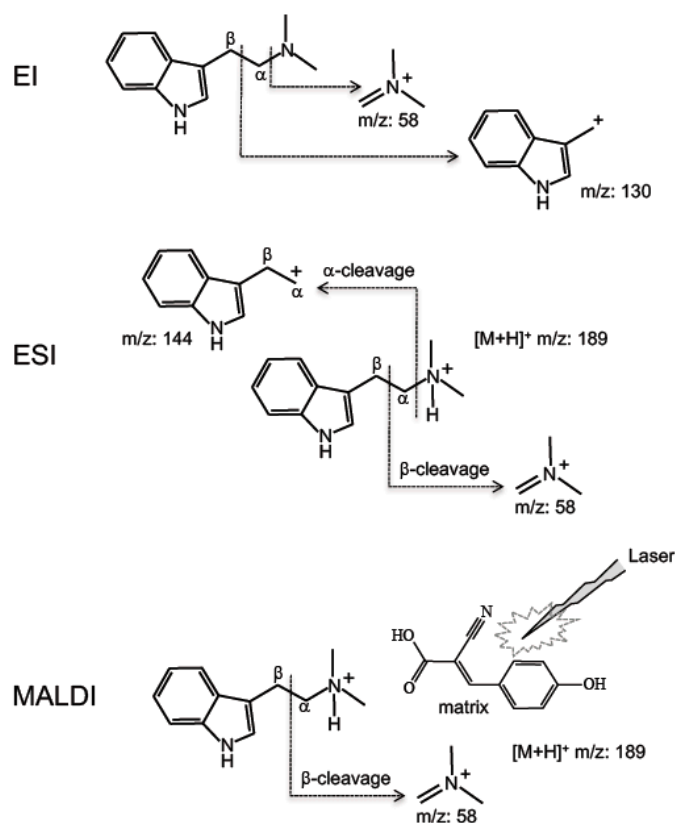


Figure 2. A general schematic outline for α -cleavage and β -cleavage when the EI/MS (electron ionization–mass spectrometry), ESI/MS (electrospray ionization/mass spectrometry) and MALDI/TOFMS (matrix assisted laser desorption/time-of-flight mass spectrometry) methods were used, respectively. *N,N*-dimethyltryptamine (DMT; Mw: 188) was selected as the model compound.

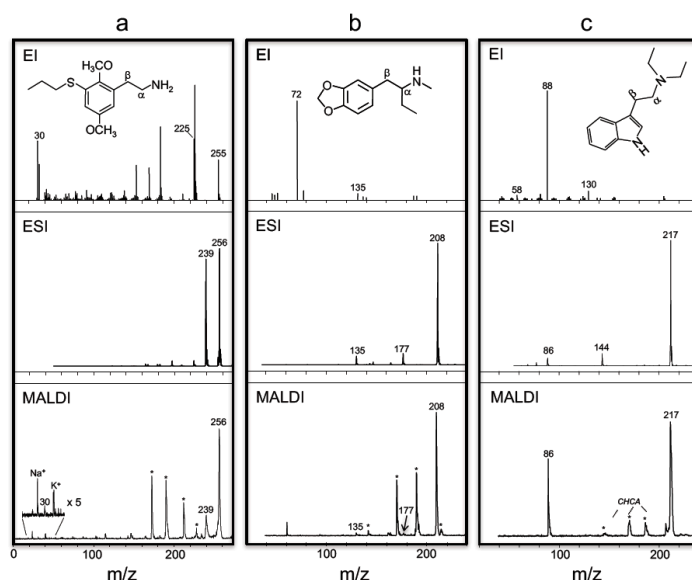


Figure 3. EI/MS; ESI/MS; and MALDI/TOFMS spectra of (a) 2C-T-7, (b) 3,4-MBMB and (c) DET (each sample, 0.1 mg mL^{-1} methanol), respectively. The major fragments of CHCA are indicated as “*”.

Table 2. Mass fragmentations (m/z values) of phenethylamines and tryptamines based on EI/MS, ESI/MS and MALDI/TOFMS, respectively. The three types of amines show different characteristic mass fragments. The symbols of 1°, 2° and 3° are abbreviations of primary, secondary and tertiary amines, respectively.

Abbrev.	EI/MS			ESI/MS			MALDI/TOFMS			
	$C_{\beta} \cdots C_{\alpha}$	$C_{\alpha} \cdots N$	M^+	β -Cleavage	α -Cleavage	$[M+H]^+$	β -Cleavage	α -Cleavage	$[M+H]^+$	
1°	2C-T-7	30, 225	–	255	–	239	256	30	239	256
1°	2C-T-2	30, 211	–	241	–	225	242	30	225	242
1°	2C-C	30, 185	–	215	–	199	216	30	199	216
1°	2C-B	30, 229	–	259	–	243	260	30	243	260
1°	2C-I	30, 277	–	307	–	291	308	30	291	308
1°	AMT	44, 130	–	174	–	158	175	44	158	175
1°	5-MeO-AMT	44, 160	–	–	–	188	205	44	188	205
1°	2,4-DOB	44, 230	–	–	–	257	274	44	257	274
1°	3,4-MDA	44, 135	–	–	–	163	180	44	163	180
1°	3,4-BDB	58, 135	–	–	–	177	194	58	177	194
2°	3,4-MDMA	58, 135	–	–	–	163	194	58	163	194
2°	3,4-MBDB	72, 135	–	–	–	177	208	72	177	208
2°	MA	58, 91	–	–	–	119	150	58	119	150
3°	DMT	58, 130	–	188	58	144	189	58	–	189
3°	DET	86, 130	–	–	86	144	217	86	–	217
3°	DPT	114, 130	–	–	114	144	245	114	–	245
3°	DBT	130, 142	–	–	142	144	273	142	–	273
3°	5-MeO-DMT	58, 160	–	218	58	174	219	58	–	219
3°	DIPT	114, 130	–	–	114	144	245	114	–	245
3°	5-MeO-DIPT	114, 160	–	–	114	174	275	114	–	275

Figure 4a shows a typical mass spectrum obtained by the MALDI/TOFMS method from an actual clandestine tablet, which was seized from the illicit market. CHCA and Nd:YAG laser (355 nm) were used as the matrix and excitation source, respectively. As can be seen from the mass spectrum in Figure 4a, the ion peaks at $m/z = 194$ and $m/z = 58/163$ correspond to the protonated parent ion and the fragments from β -cleavage and α -cleavage, respectively, indicating that the tablet could contain 3,4-MDMA. The ion peaks at $m/z = 150$ and $m/z = 58/119$ correspond to the protonated parent ion and the fragments from the β -/ α -cleavage, respectively, indicating that the tablet also contains methamphetamine. Furthermore, the ion peaks belong to norephedrine ($m/z = 152$) and ephedrine ($m/z = 166$), raw materials for the synthesis of methamphetamine. The fragment ($m/z = 136$) from α -cleavage also was found. Peaks corresponding to caffeine and ketamine also were found, showing that this was a tablet with multiple components. Herein, it should be noted that 3,4-BDB (3,4-benzodioxol-5-yl-2-butylamine) can provide similar pattern with 3,4-MDMA. Hence, in this case, the clandestine tablet should be examined in detail if ion peaks at $m/z = 194$ and $m/z = 58$ were found. In other words, a rapid screening method is important and useful for saving time. Figure 4b shows a typical MALDI-TOF mass spectrum for a 3,4-MDMA spiked hair (black color). The inset shows a 3,4-MDMA spiked white hair. The results indicate that the MALDI/TOFMS method is also useful for rapid screening of hair samples without any pretreatment; however, a black hair absorbs laser emission better than a white hair. Finally, a 0.01 mg mL⁻¹ DMT standard was spiked to a blank urine sample. The findings show that ion peaks at $m/z = 189$ and $m/z = 58$ can be found (data not shown). The limit of detection of DMT in urine is about 0.001 mg mL⁻¹. Instead, Figure 4c shows the mass spectrum of a LSD (a tertiary amine with a tryptamine-like structure) spiked urine sample, since LSD is very difficult to detect by GC/MS without derivatization process. As seen in the mass spectrum, several peaks appear, but the peak of the spiked LSD urine sample (0.001 mg mL⁻¹) can be clearly observed. The matrix used was 2,5-DHB, since it works better than CHCA. The inset shows the same urine sample before spiking. In Taiwan, if the concentration of amphetamines or related metabolites exceeds 0.0005 g mL⁻¹, a suspect is judged guilty. The method proposed here provides sufficient sensitivity to permit identification at such a low level of LSD.

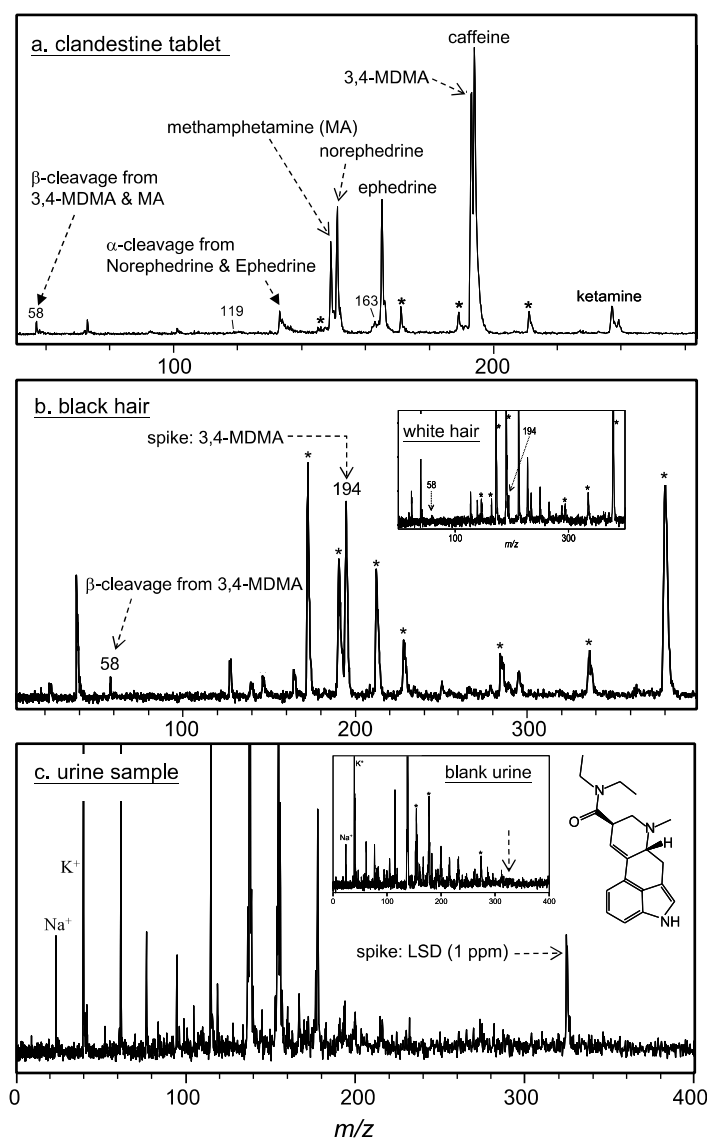


Figure 4. (a) MALDI-TOF mass spectrum obtained from an actual clandestine tablet, which was seized from the illicit market in 2001, using CHCA and Nd:YAG laser (355 nm) as the matrix and excitation source, respectively. (b) MALDI-TOF mass spectrum for a 3,4-MDMA spiked hair (black color); inset, a 3,4-MDMA spiked white hair. (c) MALDI-TOF mass spectrum obtained from of LSD spiked urine sample, using DHB as the matrix. The major fragments of matrix (CHCA) are indicated as “*”.

4. Conclusions

Our group demonstrated that a MALDI/TOFMS method can be used successfully for rapid screening of tablet, hair and urine samples. This is because the protonated parent ion and the fragments from β -cleavage and α -cleavage are unique and useful for the identification of phenethylamines and tryptamines. The results from this study show that MALDI/TOFMS is accurate, sensitive and quick, which makes it a viable method for use in rapid drug screening. The MALDI/TOFMS method is sufficiently reliable to serve as a complementary alternative to the officially prescribed method, GC/MS, for use in this field.

Author Contributions: C.-H.L. conceived and designed the experiments; B.-H.C., H.-M.C., and W.-X.C. performed the experiments and analyzed the data; J.-T.L. contributed reagents/materials/analysis tools; and C.-H.L. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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