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Simultaneous determination of nineteen hallucinogenic tryptamines/β-calbolines and phenethylamines using gas chromatography–mass spectrometry and liquid chromatography–electrospray ionisation-mass spectrometry

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Abstract

To investigate the trend of non-controlled drugs of abuse, simultaneous analytical methods were developed using GC–MS and LC–ESI-MS for 8 tryptamines/β-carbolines, 6 phenethylamines of typically non-controlled substances in Japan, and, additionally, five legally controlled tryptamines and phenethylamines originally found in fungi or plants. Moreover, the proposed methods were applied to analyses of these drugs in 99 kinds of products (a total number of 123 products purchased at adult shops or via the Internet over the past 2 years in Japan), which potentially advertised psychotropic/psychoactive effects. The samples were extracted with methanol under ultrasonication. After centrifugation, the extracts were filtered prior to injections. GC–MS analysis was performed using a DB-5MS capillary column. Regarding the LC–ESI-MS analysis; the separation of the target drugs was optimized on an ODS column in acetonitrile/MeOH (7:3)–10 mM ammonium formate buffer (pH 3.5)/acetonitrile (95:5) by a linear gradient program and a quantitative analysis was carried out by the monitoring of each $[M+H]^+$ in the positive ion mode of ESI-MS. As a result of the analyses using GC–MS and LC–ESI-MS, 5-MeO-DIPT (the synthetic substance known by the street name "Foxy") was found in 8 out of the 99 kinds of products. Additionally, AMT (from brown powder), DMT (from dried plant), harmine and harmaline (from dried plant) were also found in some of the 99 products. These analytical methods could be useful for the investigation of the distribution of the non-controlled psychotropic tryptamines/β-carbolines and phenethylamines in the market.
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Keywords: Tryptamines; Phenethylamines; Non-controlled substances; GC–MS; LC–ESI-MS

1. Introduction

Many analogs of tryptamines/β-carbolines and phenethylamines are hallucinogenic substances that exist naturally in some plants, fungi and animals, but can also be produced synthetically [1–8]. Some of these drugs are strictly controlled by the Narcotics and Psychotropic Control Law in Japan but many non-controlled analogs have been widely distributed as easily available psychotropic substances, especially via the Internet.

N,*N*-Dimethyltryptamine (DMT) is a typical psychoactive compound (5-HT agonist) in the tryptamine derivatives and existed in thousands of species of plants [4]. Its structurally related compounds, *N*,*N*-dimethyl-5-methoxytryptamine (5-MeO-DMT), bufotenine, psilocybin and psilocin are also naturally occurring chemicals [4]. Three of them, DMT, psilocybin and psilocin are controlled by the Narcotics and Psychotropic Control Law in Japan and every fungi, including psilocin and/or psilocybin, has been strictly controlled since 2002. However, the source plants of DMT are uncontrolled. Ayahuasca, a South American psychotropic plant mixture, is prepared with some plants and/or chemicals, usually consisting of at least some harmala alkaloids (β-carboline alka-

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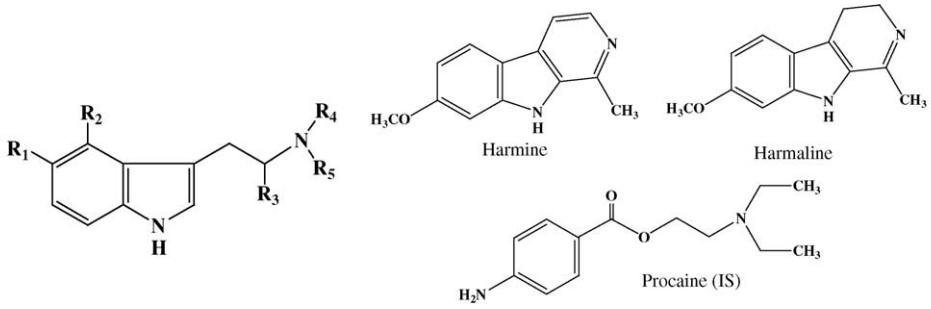

Compounds		R_1	R_2	R_3	R_4	R_5
Chemicals	α-Methyltryptamine (AMT)	H	H	CH_3	H	H
	5-Methoxy-α-methyltryptamine (5-MeO-AMT)	OCH_3	H	CH_3	H	H
	N,N-Diisopropyl-5-methoxytryptamine (5-MeO-DIPT)	OCH_3	H	H	$CH(CH_3)_2$	$CH(CH_3)_2$
	N,N-Diisopropyl-4-hydroxytryptamine (4-OH-DIPT)	H	OH	H	$CH(CH_3)_2$	$CH(CH_3)_2$
Natural products	*N,N*-Dimethyltryptamine (DMT)*	H	H	H	CH_3	CH_3
	5-Methoxy-*N,N*-dimethyltryptamine (5-MeO-DMT)	OCH_3	H	H	CH_3	CH_3
	Bufotenine	OH	H	H	CH_3	CH_3
	Psilocin*	H	OH	H	CH_3	CH_3
	Psilocybin*	H	OH_2PO_3	H	CH_3	CH_3
	Harmine					
	Harmaline					

Fig. 1. Chemical structures of tryptamine-type compounds studied in this study and the internal standard (IS). (Asterisks represent the compounds controlled by the Narcotics and Psychotropic Control Law in Japan).

loids showing monoamine oxidase [MAO]-inhibiting properties) and DMT [9–13]. This combination is important because DMT is metabolized quickly in the body by MAO enzyme and so it is not orally psychoactive unless combined with MAO-inhibitor [12,13], such as the harmala alkaloids, for example, harmine and harmaline. *N,N*-Diisopropyl-5-methoxytryptamine (5-MeO-DIPT) also produces pharmacological effects similar to those of DMT while 5-MeO-DIPT is an orally active hallucinogen [14]. In 2004, the Deputy Administrator of the Drug Enforcement Administration issued a final rule to place 5-MeO-DIPT and α-methyltryptamine (AMT) into Schedule I of the Controlled Substances Act.

As regards hallucinogenic phenethylamines; mescaline is one of the classic hallucinogens, which is known as the major alkaloid of cactus peyote [15–17]. It is used as the potency standard against which all other phenethylamine bases have been compared [5,18]. On the other hand, 3,4,5-trimethoxyamphetmine (TMA) was the very first totally synthetic psychedelic hallucinogen, structurally related to mescaline [19]. Both compounds are strictly controlled by law in Japan and in most countries but the source plants of mescaline are not controlled. 2,4,5-Trimethoxyamphetmine (TMA-2) is also a synthetic chemical that is one of the isomers of TMA, but more potent than TMA and mescaline [5,20]. 2,5-Dimethoxy-4-iodophenethylamine (2C-I), 4-ethylthio-2,5-dimethoxyphenethylamine (2C-T-2), 2,5-dimethoxy-4-isopropylthiophenethylamine (2C-T-4), 2,5-dimethoxy-4-n-propylthiophenethylamine (2C-T-7) and 2-methylamino-1-(3,4-methylenedioxyphenethyl) butane (MBDB) are typical hallucinogenic phenethylamines that have recently appeared on the market [21–26]. Although the legal statuses of the above tryptamines/phenethylamines and their related compounds vary between countries, some are still available as non-controlled drugs, especially on the Internet market.

In this study, to investigate the trend of these drugs of abuse in Japan, simultaneous analytical methods were developed using gas chromatograph-mass spectrometry (GC–MS) and liquid chromatography–electrospray ionization–mass spectrometry (LC–ESI-MS) for 19 hallucinogenic compounds, 8 tryptamines/β-carbolines (AMT, 5-methoxy-α-methyltryptamine [5-MeO-AMT], 5-MeO-DMT, 5-MeO-DIPT, *N,N*-diisopropyl-4-hydroxytryptamine [4-OH-DIPT], bufotenine, harmine and harmaline), 6 phenethylamines (TMA-2, 2C-I, 2C-T-2, 2C-T-4, 2C-T-7 and MBDB) of typical substances non-controlled as narcotics in Japan, and, additionally, five legally controlled tryptamines (psilocybin, psilocin, DMT) and phenethylamines (mescaline and TMA) originally found in fungi or plants except TMA. Moreover, the proposed methods were applied to analyses of these drugs in 99 kinds of products (123 products) that advertised psychotrophic/psychoactive effects. The chemical structures of tryptamines/β-carbolines and phenethylamines investigated in this study are shown in Figs. 1 and 2.

2. Experimental

2.1. Chemicals and reagents

Ninety-nine kinds of products (123 products in all) that advertised psychotropic/psychoactive effects were purchased at adult shops or via the Internet over the past 2 years in Japan (from October in 2002 to March in 2004). These products contained 14 tablet forms, 3 capsule forms, 11 powdered

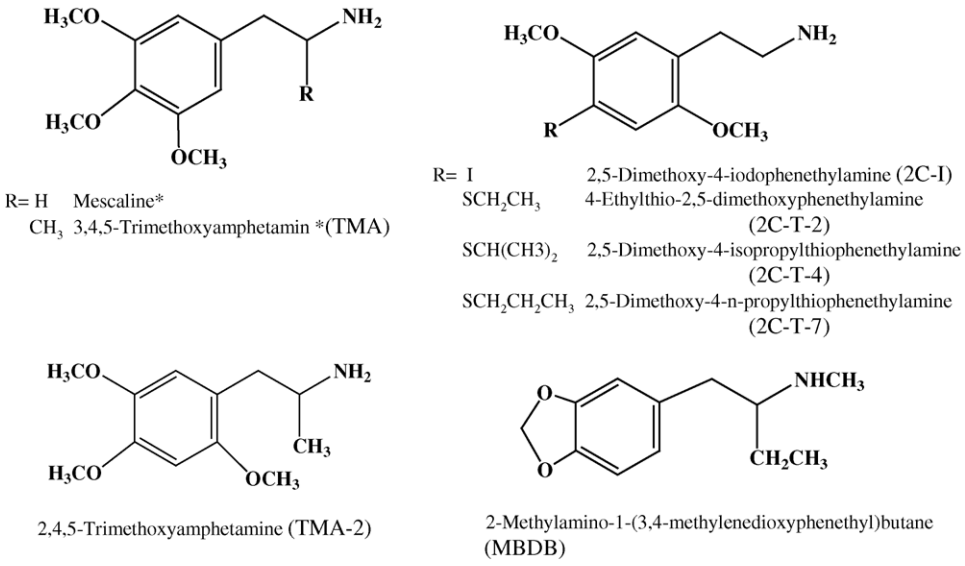

Fig. 2. Chemical structures of phenethylamine-type compounds studied in this study. (Asterisks represent the compounds controlled by the Narcotics and Psychotropic Control Law in Japan).

forms, 56 liquid forms, 3 other forms (brown resin, a small piece of paper and a spray) and 12 dried plants/mushrooms. The products sold as "chemical reagents" via the Internet were excluded in this study. AMT hydrochloride was supplied from Acros Organics (Geel, Belgium). Bufotenine (1 mg/mL methanol solution), harmine, harmaline and procaine hydrochloride (used as an internal standard) were purchased from Wako Pure Chemical Industries (Osaka, Japan). MBDB hydrochloride (1 mg/mL methanol solution) was provided from Cerilliant (TX, USA). DMT [27], psilocin [28], psilocybin [28], mescaline sulfate [29] and TMA sulfate [30] were prepared by our reported methods. 5-MeO-AMT, 5-MeO-DIPT, 4-OH-DIPT, 5-MeO-DMT, TMA-2, 2C-I, 2C-T-2, 2C-T-4 and 2C-T-7 (all of which were sold as chemical reagents) were obtained via the Internet. Their structures and purities were confirmed by HPLC, GC–MS and ^{1}H nuclear magnetic

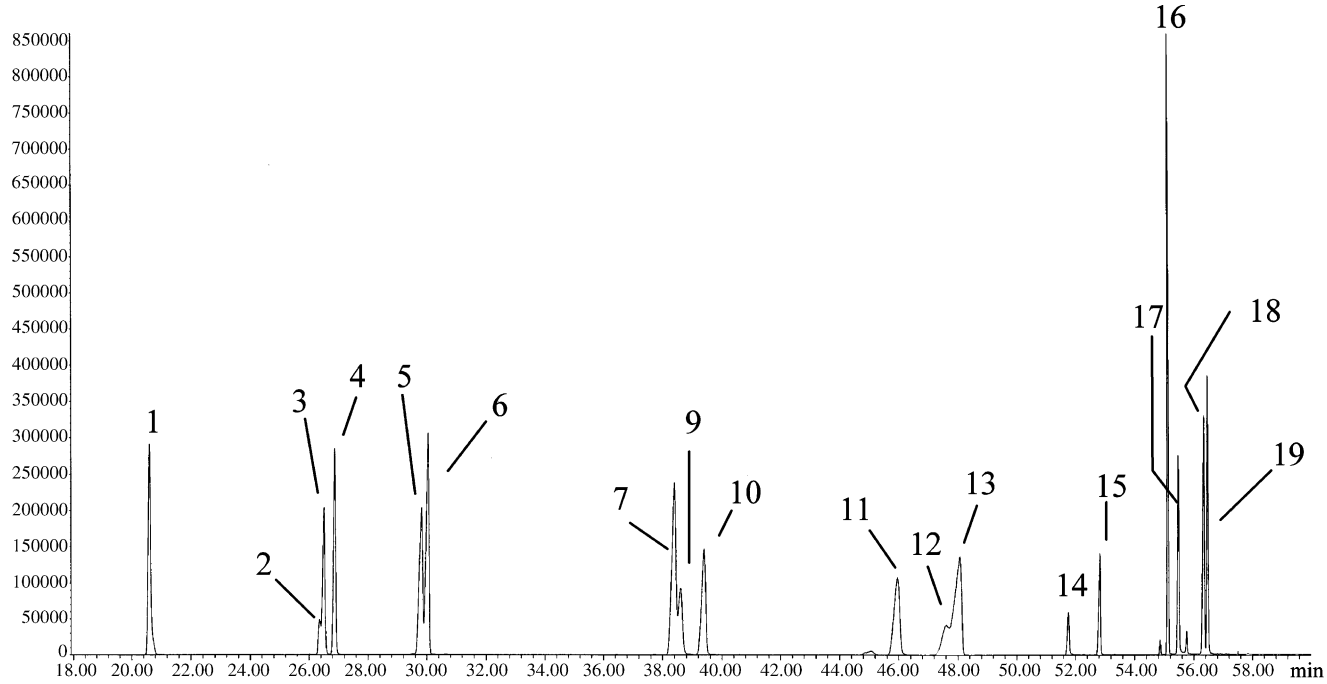

Fig. 3. Total ion chromatogram obtained with the GC–MS analysis of a mixed standard solution of 18 drugs except psilocybin (50 μg/mL). (1) = MBDB; (2) = TMA; (3) = mescaline; (4) = TMA-2; (5) = AMT; (6) = DMT; (7) = 2C-T-4; (8) = 2C-I; (9) = 2C-T-2; (10) = 2C-T-7; (11) = 5-MeO-AMT; (12) = 5-MeO-DMT; (13) = Psilocin; (14) = bufotenine; (15) = 5-MeO-DIPT; (16) = harmaline; (17) = harmine and (18) = 4-OH-DIPT.

resonance after their recrystallizations. Centrifugal filter devices (Ultrafree-MC, 0.45 μm filter unit) were from Millipore Corporation (Bedford, MA, USA). All other chemicals and solvents were of an analytical reagent grade or a HPLC grade (Wako Pure Chemical Industries).

2.2. Instrumentation

For the qualitative analysis of the 19 compounds, GC–MS in the electron impact (EI) mode at 70 eV of electron energy was used. The instrument consisted of a Hewlett-Packard 5890 series II plus GC with a 5972 mass selective detector. Helium was used as the carrier gas through the fused silica capillary column (DB5-MS capillary, 30 m × 0.25 mm i.d., 0.25 μm film thickness) at 1 mL/min. The injector temperature was 200 °C and splitless injection was employed with a split valve on-time of 1.0 min. The oven temperature was started at 120 °C (held for 1.0 min), followed by a 2.5 °C/min ramp to 190 °C (held for 20 min) and a second 15 °C/min ramp to 280 °C (held for 5 min). The mass selective detector was kept at 280 °C. To confirm the mass fragment of each compound, data was obtained in a full scan mode with a scan range of *m*/*z* 40–550.

For the qualitative and quantitative analysis of the compounds, the LC–ESI-MS consisting of an Agilent 1100 series HPLC system equipped with a 1100 series LC/MSD SL (Agilent Technology, Palo Alto, CA, USA) was used. Chromatographic separation was performed in a gradient mode using an Atlantis dC18 column (2.0 mm i.d. × 50 mm, 5 μm) protected by a Sentry guard column (2.0 mm i.d. × 10 mm, 5 μm) (Waters, MA, USA) at 40 °C. The following gradient system was used with a mobile phase A (10 mM ammonium formate (pH 3.5)/acetonitrile (95:5, v/v)) and a mobile phase B (acetonitrile/methanol, (7:3, v/v)) delivered at 0.3 mL/min; A:B 100:0(0 min)-95:5(15 min)-90:10(35 min)-73:27(52 min)-30:70(60 min). The mobile phase composition was then brought back to the starting point in 1 min and the column re-equilibrated in 10 min. The injection volume was 1 μL. For the detection system, a tandem setting of photo diode array detector (PDA) and a mass detector (MSD)

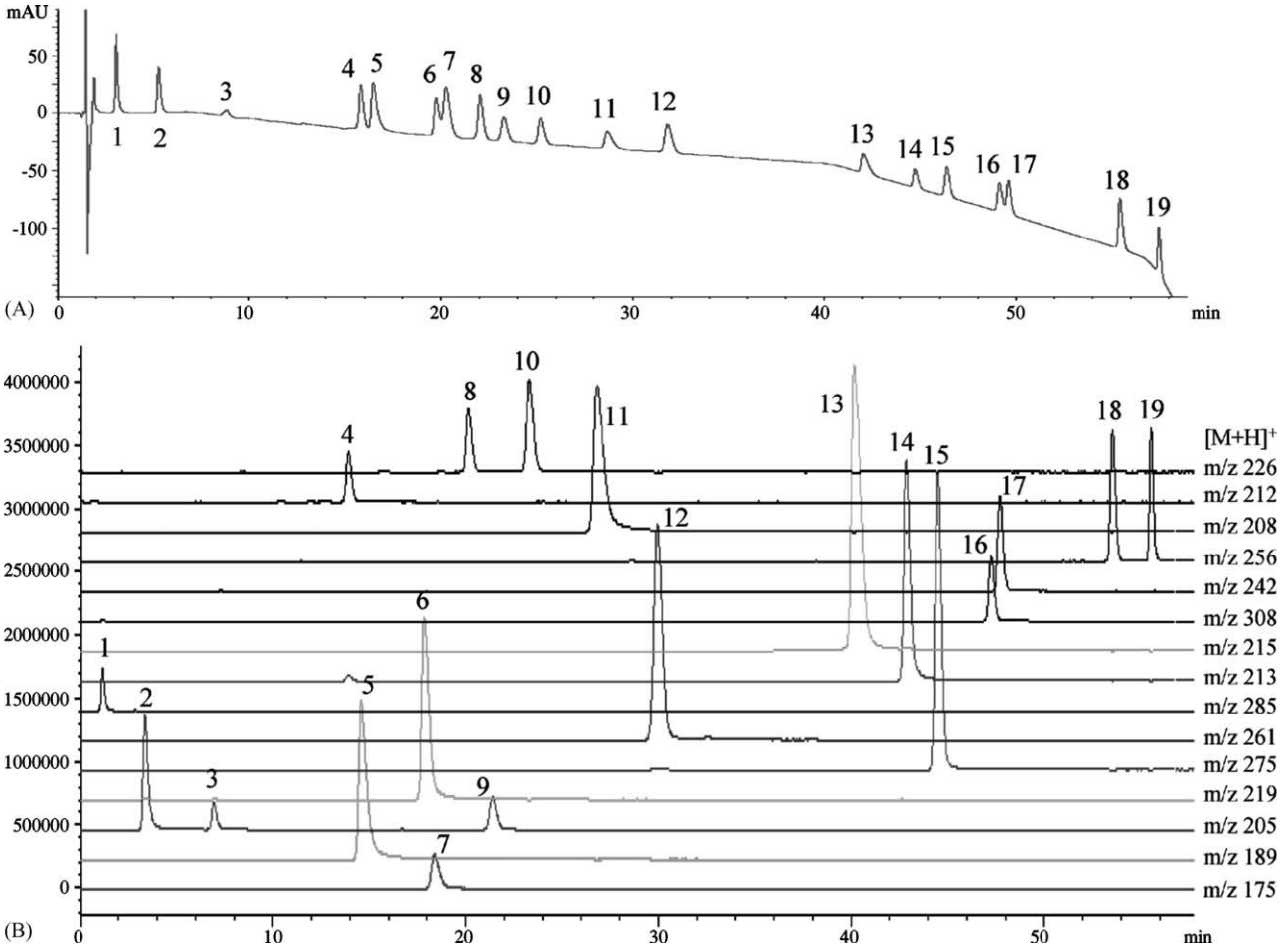

Fig. 4. HPLC-UV (A) and –MS (B) chromatograms of a mixed standard solution of 18 drugs (50 μg/mL). (1) = Psilocybin; (2) = bufotenine; (3) = psilocin; (4) = mescaline; (5) = DMT; (6) = 5-MeO-DMT; (7) = AMT; (8) = TMA; (9) = 5-MeO-AMT; (10) = TMA-2; (11) = MBDB; (12) = 4-OH-DIPT; (13) = harmaline; (14) = harmine; (15) = 5-MeO-DIPT; (16) = 2C-I; (17) = 2C-T-2; (18) = 2C-T-4 and (19) = 2C-T-7.

was adopted. Mass analysis by the ESI was used in a positive mode. Nitrogen gas was used as the nebulization and was delivered at a flow rate of 13 L/min at 350 °C. The nebulizer pressure was 50 psig, the vaporizer temperature was 350 °C, the capillary voltage was 3500 V and the fragmentation voltage was 80 V. MS data were recorded in the full scan mode (*m*/*z* 50–400). A quantitative analysis was carried out by the monitoring of each protonated molecular ion ($[M+H]^+$) in the positive ion mode of ESI-MS. The monitoring ions were as follows: Bufotenine (*m*/*z* 205), psilocin (*m*/*z* 205), psilocybin (*m*/*z* 285), harmine (*m*/*z* 213), harmaline (*m*/*z* 215), AMT (*m*/*z* 175), DMT (*m*/*z* 189), 5-MeO-AMT (*m*/*z* 205), 5-MeO-DMT (*m*/*z* 219), 5-MeO-DIPT (*m*/*z* 275), 4-OH-DIPT (*m*/*z* 261), mescaline (*m*/*z* 212), TMA (*m*/*z* 26), TMA-2 (*m*/*z* 226), 2C-I (*m*/*z* 308), 2C-T-2 (*m*/*z* 242), 2C-T-4 (*m*/*z* 256), 2C-T-7 (*m*/*z* 256), MBDB (*m*/*z* 208) and procaine (IS) (*m*/*z* 237). Detection and integration of chromatographic peaks were performed by the Agilent Chemistation data analysis system (Agilent Technology, Palo Alto, CA, USA).

2.3. Standard solutions

An individual standard solution of 1.0 mg/mL of each drug, Bufotenine, psilocin, psilocybin, harmine, harmaline, AMT, DMT, 5-MeO-AMT, 5-MeO-DMT, 5-MeO-DIPT, 4-OH-DIPT, mescaline, TMA, TMA-2, 2C-I, 2C-T-2, 2C-T-4, 2C-T-7 and MBDB was prepared in methanol and stored in the dark at −20 °C. Mixed standard solutions, ranging from 0.1 to 50.0 μg/mL of all 19 drugs, were prepared by mixing an aliquot of each stock solution. These solutions were freshly prepared for each analysis. Solution of 0.2 mg/mL of the IS (procaine) in methanol was also prepared.

2.4. Sample extraction methods

Finely powdered samples of the products of powders, resin, contents of capsules, tablets (each 20 mg), small pieces of papers (100 mg) or dried plant/mushroom materials (100 mg) were extracted with 2 mL of methanol by ultrasonication for 10 min. For liquid samples (including a spray sample), each 200-μL solution was diluted to 2 mL with methanol. For the quantitative analyses, each methanol solution was spiked with 50 μL of the IS solution (0.2 mg/mL). After centrifugation (5 min at 3000 rpm), the solutions were filtered though a centrifugal filter device prior to the injection. If it was necessary, each solution was diluted with methanol to the adequate concentration. As far as possible, all extraction procedures were performed under protection from daylight, and amber glass utensils were used.

2.5. Calibration curves

The drug concentrations in the samples were calculated using the peak-area ratios of the protonated molecular ions ($[M+H]^+$) of the target compounds versus the IS. Calibration samples containing 0.1, 0.25, 0.5, 1.0, 5.0, 10.0 and 50.0 μg/mL of each were prepared just before the analysis. The limit of quantitation (LOQ) of each drug was chosen to be the concentration of the lowest calibration standard with an acceptable limit of variance.

2.6. Precision and accuracy of the method

The precision and accuracy of the method were evaluated by assaying triplicates of the mixed standard solution,

Table 1
The precisions and accuracies of the method using mixed standard solutions by LC–ESI-MS

Compounds	$[M+H]^+$	Precision (%)			Accuracy (%)		
		0.5 μg	5.0 μg	25.0 μg	0.5 μg	5.0 μg	25.0 μg
AMT	175	8.3	0.7	1.6	−8.1	−5.6	12.2
DMT	189	5.0	2.0	2.5	−4.7	−1.0	10.1
5-MeO-AMT	205	10.8	1.7	2.3	−18.1	−10.2	3.5
5-MeO-DMT	219	2.0	1.2	1.3	−0.2	−5.8	12.4
5-MeO-DIPT	275	3.1	4.0	0.9	1.8	−2.8	8.0
4-OH-DIPT	261	2.7	1.0	0.3	−1.9	−5.8	9.7
Bufotenine	205	1.3	1.8	1.7	−5.6	−8.2	15.0
Psilocin	205	2.7	1.2	1.2	−2.5	−4.0	6.0
Psilocybin	285	3.0	5.8	0.8	−0.4	−3.8	6.3
Harmine	213	2.7	2.6	1.4	−4.2	−5.7	10.6
Harmaline	215	4.6	1.7	0.7	3.9	−8.4	10.6
2-C-I	308	5.4	6.6	2.0	−1.9	−2.1	6.8
2-C-T-2	242	3.6	0.5	1.4	−7.8	−8.4	6.8
2-C-T-4	256	1.3	0.9	0.2	−8.4	−9.7	8.2
2-C-T-7	256	2.8	0.5	0.3	−8.3	−7.5	8.2
TMA	226	4.7	1.0	1.0	−2.6	−2.9	1.6
TMA-2	226	1.8	1.0	0.9	−3.9	−6.4	9.0
MBDB	208	5.9	4.1	2.6	−3.4	−12.2	10.3
Mescaline	212	4.9	0.6	0.4	−17.9	−2.1	1.3

*Linear range: 0.1–50 ug/mL ($r > 0.9773$).

containing 0.5, 5.0 and 25.0 μg/mL of each drug. Accuracy, expressed as bias, was calculated as the difference between the amount of each drug added and recovered.

3. Results and discussion

3.1. Qualitative analysis by GC–MS

Chromatographic separation of the 19 tryptamines and phenethylamines was studied by GC–MS for qualitative analysis. With the analytical condition described in Experimental, a good separation of all drugs (except psilocybin) was confirmed in 60 min although pscilocybin was not able to be detected by EI-MS. It is thought that pcilocybin decomposed into psilocin at high temperature [31]. Fig. 3 shows a total ion chromatogram obtained with the GC–MS analysis of a mixed standard solution of 18 drugs (each 50 μg/mL), except psilocybin. The retention time of each compound is as follows: MBDB (20.6 min), TMA (22.4 min), mescaline (26.5 min), TMA-2 (26.9 min), AMT (29.8 min), DMT (30.1 min), 2C-T-4 (38.4 min), 2C-I (38.6 min), 2C-T-2 (39.4 min), 2C-T-7 (46.0 min), 5-MeO-AMT (47.6 min), 5-MeO-DMT (48.1 min), psilocin (51.8 min), bufotenine (52.8 min), 5-MeO-DIPT (55.1 min), harmaline (55.5 min), harmine (56.4 min) and 4-OH-DIPT (56.5 min).

3.2. Qualitative and quantitative analysis of tryptamines and phenethylamines by LC–ESI-MS

For a successful chromatographic separation of the 19 compounds (11 tryptamines/β-carbolines and 8 phenethylamines) and procaine (IS), stationary phases of different manufacturers have been screened. Developing a LC separation in one run was challenging because some compounds investigated in this study show extremely similar chemical properties. The best result was obtained with an Atlantis dC18 column which was a difunctionally-bonded and silica-based reversed-phase HPLC column. With PDA (monitored at UV 210 nm), a relatively good separation was confirmed in 60 min when a gradient elution with 10 mM ammonium acetate (pH 3.5)/acetonitrile (95:5, v/v) and acetonitrile/MeOH (7:3, v/v) was adopted on the analytical column. Mass detection was carried out by the ESI in the positive mode. The conditions for ionization of each drug, such as the nebulizer pressure, drying gas flow rate, drying gas temperature, vaporizer temperature, capillary voltage, and fragmentation voltage were investigated using flow-injection analysis and the optimum conditions were determined, as described in the experimental section. The protonated molecule ions ($[M + H]^+$) were observed as base peak ions according to all compounds investigated in this study and the quantitative analysis was done using these ions as selected monitoring ions. Fig. 4 shows LC-PAD (UV 210 nm) (A) and LC–ESI-MS (B) chromatograms of the standard mixed solution (each 50 μg/mL). The linearity of the response for all compounds was confirmed between 0.1 and 50.0 μg/mL ($r < 0.9773$). Table 1 shows the precisions and accuracies of the method using the mixed standard solutions by LC–ESI-MS.

3.3. Analyses of the products obtained from the Japanese market

The proposed methods were applied to analyses of these drugs in 99 kinds of products (a total number of 123 products purchased at adult shops or via the Internet over the past 2 years in Japan), which potentially advertised psychotropic/psychoactive effects. The forms of these products were varied, such as tablets, powder, liquid (drinks or colored aroma liquid), resin, a spray and some pieces of dried plants/mushrooms. The products sold as “chemical reagents” via the Internet were excluded in this study.

Table 2
The compounds detected in the 99 kinds of products in this study

Samples		Compounds (μg/mg sample)
No. 14-104	A small piece of paper	5-MeO-DIPT 18.4 μg/g paper
No. 14-138	Liquid	5-MeO-DIPT 550.8 μg/mL, (1-benzylpiperazine)
No. 14-162	White powder	5-MeO-DIPT 808.7
No. 15-218	Brown powder	5-MeO-DIPT >0.1 Harmine 41.1 Harmaline 36.5 (1,2,3,4-Tetrahydroharmine)
No. 15-219	Brown resin	5-MeO-DIPT 129.3 AMT 14.5
No. 15-am6	Brown powder	5-MeO-DIPT 26.2, Harmine 7.5, Harmaline 8.0 (Atropine/Hyoscyamine, 1,2,3,4-Tetrahydroharmine)
No. 15-am10	Brown powder	5-MeO-DIPT 100.7
No. 15-am14	Brown powder	5-MeO-DIPT 58.9
No. 15-am16	Brown powder	AMT 80.7
No. 15-am19	Brown powder	Harmine 4.0, Harmaline 4.1
No. 15-am20	Dark green powder	Harmine 7.6, Harmaline 8.1 (Scopolamine, 1,2,3,4-Tetrahydroharmine)
No.15-am21-1	Dried plant (seeds)	Harmine 29.7, Harmaline 32.3 (1,2,3,4-Tetrahydroharmine)
No.15-am21-2	Smoky pink powder	DMT 11.8
No. 15-am22	Dried plant (seeds)	Harmine 20.2, Harmaline 24.2 (1,2,3,4-Tetrahydroharmine)
No. 15-am23	Dried plant (vines)	Harmine 2.7, Harmaline 0.1 (1,2,3,4-Tetrahydroharmine)

As a result of the analyses using GC–MS and LC–ESI-MS, 5-MeO-DIPT (the synthetic substance known by the street name “Foxy”) was found in 8 out of the 99 kinds of products, and AMT, DMT, harmine and harmaline were also found in some of the 99 products as shown in Table 2. No phenethylamines investigated in this study were detected in the products. The samples of 15-218 (brown powder), 15-219 (brown resin), 15-am6 (brown powder), 15-am10 (brown powder), 15-am14 (brown powder) and 15-am16 (brown powder) were sold as “mixture of mushrooms/plants” at adult shops or via the Internet. However, the chemical compounds, 5-MeO-DIPT and/or AMT, were detected. Fig. 5 shows GC–MS and LC-MS analyses of the extract of the sample 15-am16, in which AMT was detected. Moreover, in the sample of 15–218, 15–219 and 15-am6, the compounds that have MAO inhibiting properties (harmine and harmaline) were also detected. It is possible that some plants (including these compounds) were added to the samples for the purpose of strengthening a potential psychotropic effect of 5-MeO-DITP. The results of the analyses of the extract of the sample 15-am6 were shown in Fig. 6. The largest amount of 5-MeO-DIPT was determined in the sample 14–138 (white powder, sold at an adult shop) and its concentration was more than 80%. The synthesis and preliminary human psychopharmacology study on 5-MeO-DIPT was first published in 1980 [14]. 5-MeO-DIPT produces pharmacological effects similar to those of DMT while it is an orally active hallucinogen [14]. It is controlled in the United States (Schedule 1) and Germany (Schedule 1). The samples of 15-am21-1 (smoky pink powder, described as “mimosa”) and 15-am21-2 (small seeds, described as “harmala”) were sold as a set of “Ayahuasca” via the Internet, in which DMT (15-am21-1), harmine and harmaline (15-am21-2) were determined. In the other dried plant samples, 15-am22 (seeds, described

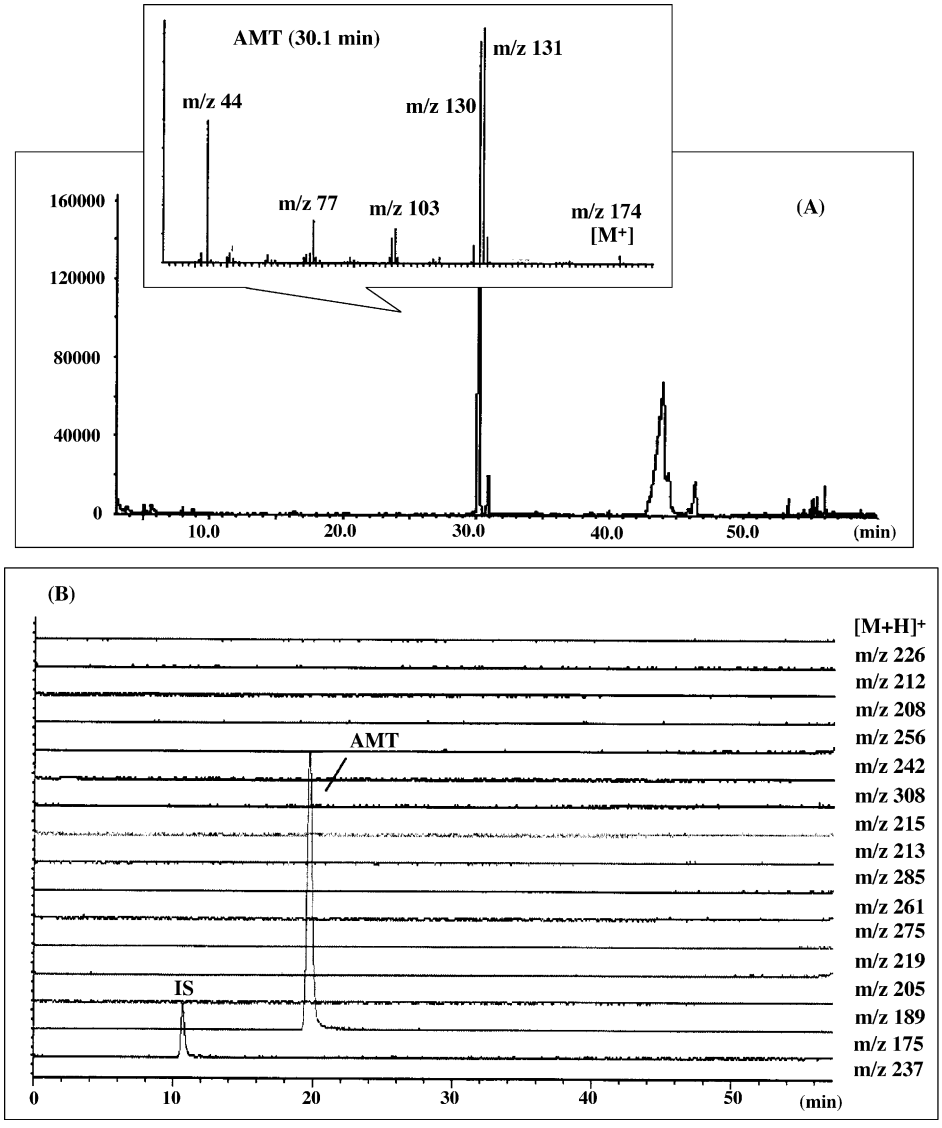

Fig. 5. GC–MS (A) and LC-MS (B) analyses of the extract of the sample 15-am16.

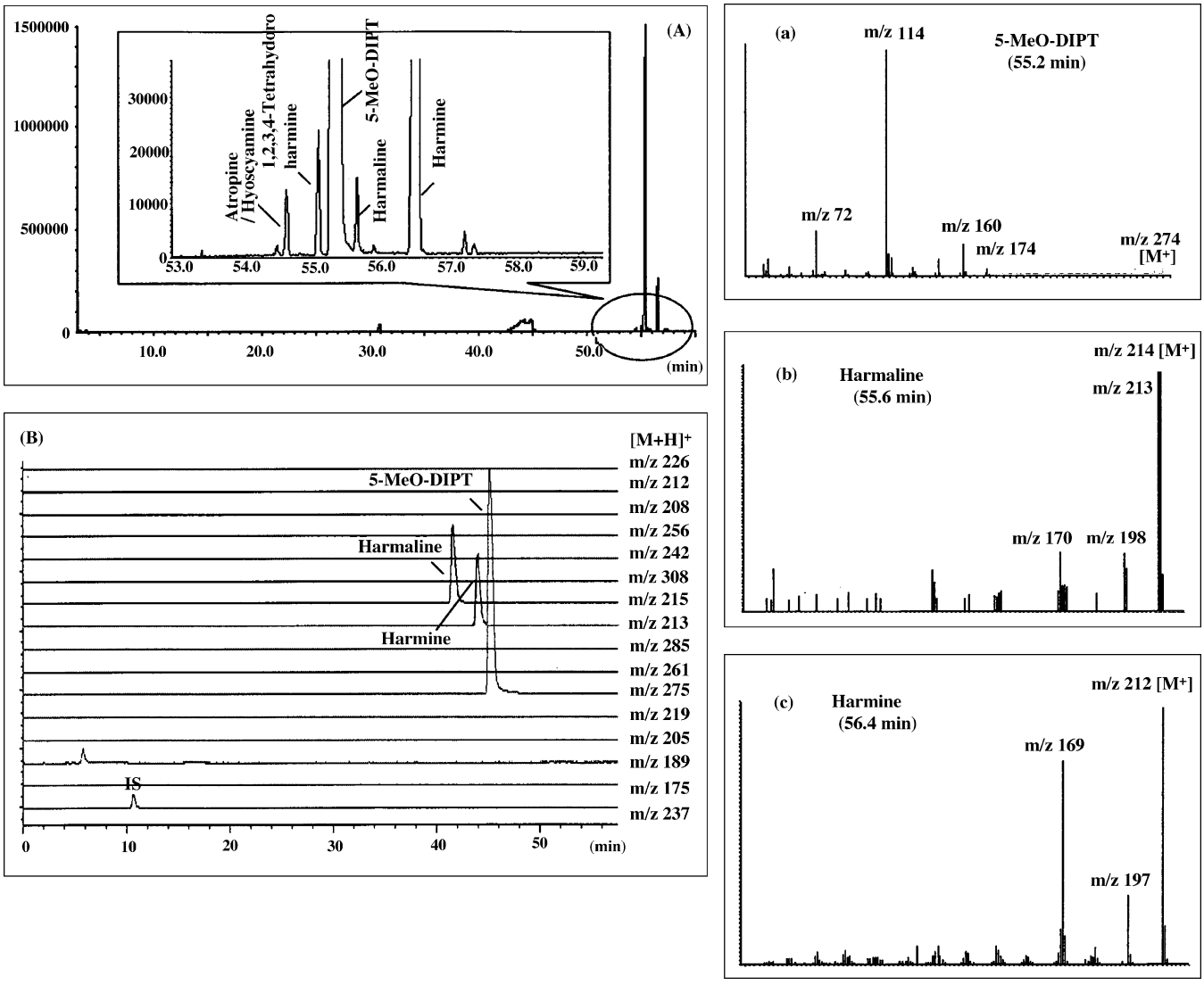

Fig. 6. GC–MS (A) and LC-MS (B) analyses of the extract of the sample 15-am6. EI mass spectra of the GC–MS peaks of 55.2 min (5-MeO-DIPT) (a), 55.6 min (harmaline) (b) and 56.4 min (harmine) (c) were also shown.

as "harmala") and 15-am23 (veins, described as "caapi"), harmine and harmaline were also detected. The other compounds detected in this study, although not target compounds (1,2,3,4-Tetrahydroharmine, atropine/hyoscyamine and scopolamine), were identified by the comparison of GC retention times and EI-mass fragmentation patterns between the peaks of the samples and their standard compounds.

4. Conclusions

The simultaneous analytical methods of 19 hallucinogenic tryptamines/β-calbolines and phenethylamines using GC–MS and LC–ESI-MS have been developed. Moreover, the proposed methods were applied to analyses of these drugs in 99 kinds of products (123 products) that advertised psychotropic/psychoactive effects. The synthesized compounds, 5-MeO-DIPT and AMT were found in 8 out of the 99 kinds of products for 5-MeO-DIPT and in 2 for AMT, although these samples were mostly sold as "mixtures of mushrooms/plants". DMT, harmine and harmaline were also found in some samples of dried plants. These analytical methods could be useful for the investigation of the distribution of the non-controlled psychotropic tryptamines and phenethylamines in the market.

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