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Short communication

N,*N*-Dimethyltryptamine and dichloromethane: Rearrangement of quaternary ammonium salt product during GC–EI and CI-MS–MS analysis

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Abstract

N,*N*-Dimethyltryptamine (DMT) **1** is a simple tryptamine derivative with powerful psychoactive properties. It is abundant in nature and easily accessible through a variety of synthetic routes. Most work-up procedures require the use of organic solvents and halogenated representatives are often employed. DMT was found to be reactive towards dichloromethane, either during work-up or long term storage therein, which led to the formation of the quaternary ammonium salt *N*-chloromethyl-DMT chloride **2**. Analysis of this side-product by gas chromatography ion trap mass spectrometry (GC–MS), both in electron and chemical ionisation tandem MS modes, gave only degradation products. For example, **2** could not be detected but appeared to have rearranged to 3-(2-chloroethyl)indole **3** and 2-methyltetrahydro-β-carboline **4**, whereas HPLC analysis enabled the detection of **2**. GC–MS is a standard tool for the fingerprinting of drug products. The identification of a particular synthetic route is based on the analysis of impurities, provided these side products can be established to be route-specific. The *in situ* detection of both **3** and **4** within a DMT sample may have led to erroneous conclusions with regards to the identification of the synthetic route.

Keywords: Tryptamines; Hallucinogens; Forensic; Analysis; Mass spectrometry

1. Introduction

The tryptamine derivative *N*,*N*-dimethyltryptamine (DMT) **1** (Fig. 1) has significant psychoactive effects on the human mind when ingested parenterally [1,2].

It is often referred to as a hallucinogenic substance in an attempt to describe its neuroactive properties which also made it an attractive target for human clinical studies [3–9]. DMT, and some of its derivatives, are widely abundant in nature and mammalian systems [10,11] and are also easily accessible through a variety of synthetic routes. The extent of by-product formation, either as part of quality control procedures for materials prepared for clinical studies or during clandestine synthesis, is not well documented [12,13]. Identification of potentially toxic contaminants present in manufactured preparations of DMT and analogues and their characterisation is therefore required to assist clinical and forensic investigations.

DMT free base, when dissolved in dichloromethane (DCM), formed a quaternary ammonium salt by-product **2** (Fig. 1). This study reports on the observation that this side product, when subjected to gas chromatography mass spectrometry (GC–MS) analysis, formed two rearrangement products in the total ion chromatograms (TICs).

2. Experimental

2.1. Materials

Solvents and reagents were from Aldrich (UK) and were of HPLC-grade, analytical grade or equivalent.

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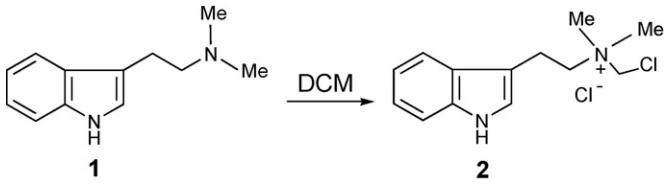

Fig. 1. *N,N*-Dimethyltryptamine **1**. *N*-chloromethyl-DMT chloride **2**.

2.2. Instrumentation

EI and CI mass spectra were obtained on a Varian Saturn 2200 ion trap MS equipped with a Varian CP-3800 gas chromatograph (Varian, USA) and a Combi Pal autosampler (CTC Analytics, Switzerland). Data handling was completed with Saturn GC/MS Workstation, Version 5.52 software. Chromatographic separation was achieved using a 5% phenyl, 30 m × 0.25 mm CP-Sil 8 CB Low Bleed/MS column with a film thickness of 0.25 μm. The carrier gas was helium at 1 ml/min (EFC constant flow mode). A CP-1177 injector (280 °C) was used in split mode (50:1). The transfer line, manifold and ion trap temperatures were set to 270, 95 and 200 °C, respectively. The column temperature was programmed as follows: 90 °C and held for 2 min, then heated at 20 °C/min to 260 °C and held at this temperature for 10.5 min; total run time was 21 min. HPLC-grade methanol was used as the liquid CI reagent. Ionisation parameters (0.5 s/scan): CI storage level: 19.0 *m/z*, ejection amplitude: 15.0 *m/z*, background mass: 55 *m/z*, maximum ionisation time: 2000 μs, maximum reaction time: 40 ms and target TIC: 5000 counts. CI-MS–MS spectra were obtained by collision induced dissociation of the protonated molecule $[M+H]^+$ within the ion trap, using helium, by application of a waveform excitation amplitude in the non-resonant mode. Excitation storage level was set to 48.0 *m/z*. The excitation amplitude was set to 20 V. The number of ions in the trap was controlled by an automatic gain control function.

NMR spectra were recorded using a Bruker DPX 300 or Avance 300 at 300.1 MHz (^{1}H NMR) or 75.5 MHz (^{13}C NMR). Chemical shifts are reported relative to TMS at $\delta = 0$ ppm. NMR spectra were obtained by ^{1}H, proton decoupled ^{13}C, DEPT-135 and DEPT-90, HSQC and HMBC experiments.

LC–MS analysis used a Waters Alliance 2695 HPLC separations module coupled to a Micromass LCT orthogonal acceleration time-of-flight (TOF) mass spectrometer (Waters, UK) equipped with an electrospray ionisation source in positive mode. Flow rate was set at 0.8 ml/min with a 9:1 post-column split. A flow of 80 μl/min was infused into the ESI source and the remaining flow was directed to a Waters 486 UV detector set at 280 nm. The column temperature was set by air-conditioned surroundings at 21 °C. The aqueous mobile phase A consisted of 40 mM ammonium formate and 0.1% formic acid (pH 3.80). The organic component B was 0.1% formic acid in methanol. The mobile phase composition was set to 30% B and linearly increased to 90% B within 15 min, held for 5 min and returned to 30% B over 3 min. The column was left to equilibrate before the next injection for 12 min. Total run time was 35 min; total acquisition time was 20 min. The column used was a Phenomenex Synergi Max-RP (80 Å 250 × 4.6 mm, 4 μm). The sample was prepared at 1 mg/ml and 20 μl was injected onto column. Mass drift calibration and determination of exact masses were carried out with a sodium formate solution. Operation settings were: capillary voltage: 3000 V, sample cone voltage: 30 V, RF lens: 200 V, desolvation temperature: 150 °C, source temperature: 100 °C, acceleration: 200 V, cone gas flow: 22 l/h, desolvation gas flow: 602 l/h.

Alternatively, HPLC-UV analysis was carried out on an Agilent (1100 & 1200 Series) system, consisting of a G1322A degasser, G1311A quaternary pump, G1313A autosampler, G1316A column at air-conditioned ambient temperature (21 °C) and a G1314 VWD set at 280 nm. Software control was by ChemStation, version Rev A. 10.02[1757].

2.3. Work-up procedure after DMT synthesis

The identities of all synthesised compounds were confirmed by direct infusion ESI-TOF-MS exact mass measurements and NMR spectroscopy.

N,N-Dimethyltryptamine **1** was synthesised by a microwave-accelerated reduction of indole-3-yl-*N,N*-dimethylglyoxalylamide (1.0 mmol) in tetrahydrofuran (6 ml) with lithium aluminium hydride (6.0 mmol) [14]. At the end of the reaction the mixture was transferred into a conical flask and cooled on ice. The tubes were then rinsed with 3 ml × 8 ml THF and the washings added to the flask. Excess lithium aluminium hydride was destroyed by the dropwise addition of 5 ml water, followed by 4 ml 20% NaOH and 5 ml water. The volume of THF was increased by the addition of 20 ml. The precipitated inorganic salts were removed by filtration and washed with 30 ml THF. The filtrate was evaporated under reduced pressure and the resulting oily residue was dissolved in 60 ml chloroform, 1 ml 20% NaOH and 10 ml water and thoroughly shaken in a separating funnel. The organic layer was separated and two additional chloroform extractions (20 ml) from the remaining alkaline aqueous phases were carried out. The combined organic fractions were washed with distilled water (2 ml × 40 ml) and saturated aqueous NaCl (40 ml). The organic phase was evaporated under reduced pressure and the resulting product was purified by flash chromatography ($CHCl_3$/MeOH/NH_4OH: 8/2/0.1). Yields and analytical data were in agreement with previously published work [15].

2.4. Synthesis of N-chloromethyl-DMT chloride 2

DMT (1.1 mmol) was dissolved in DCM at 10 mg/ml. This solution was left sealed and stored at ambient temperatures for 4 days until precipitation of the product was complete. The crystalline white needles were filtered, washed with the solvent and dried under vacuum over P_2O_5. Data for *N*-chloromethyl-DMT chloride **2** (189 mg, 0.69 mmol, 63%): ^{1}H NMR (d_4-MeOD): 7.61 (1H, d, H-4, *J* 8.0 Hz), 7.36 (1H, d, H-7, *J* 8.0 Hz), 7.22 (1H, s, H-2), 7.12 (1H, td, H-6, *J* 7.6, 1.1 Hz), 7.05 (1H, td, H-5, *J* 6.8, 1.1 Hz), 5.39 (2H, s, CH_2–Cl), 3.74–3.70 (2H, m, CH_2-α), 3.31 (6H, s, CH_3), 3.30–3.26 (2H, m, CH_2-β). ^{13}C NMR: 138.2 (C-7a), 128.0 (C-3a), 124.6 (C-2), 122.9 (C-6), 120.3 (C-5), 118.9 (C-4), 112.7 (C-7), 108.8 (C-3), 69.7 (CH_2–Cl), 64.4

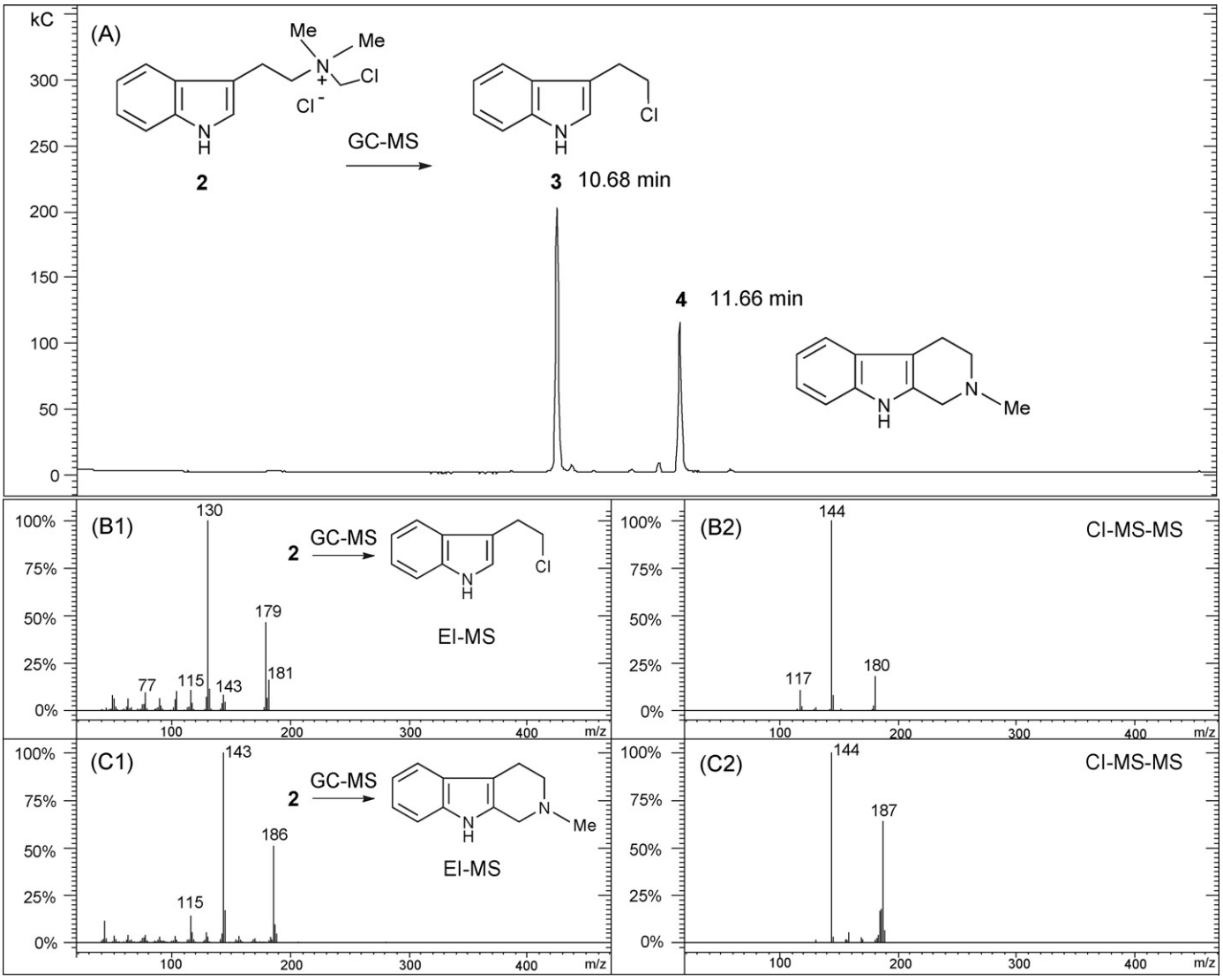

Fig. 2. Representative examples of formation of degradation products during GC-MS analysis of halogenated quaternary ammonium salt derivatives of DMT **1**. (A) *N*-Chloromethyl-DMT **2** forms two major rearrangement products which were identified as 3-(2-chloroethyl)-indole **3** and 2-methyl-tetrahydro-β-carboline **4**. Single stage electron ionisation mass spectra (EI-MS) B**1** & C**1** and chemical ionisation tandem mass spectra are shown (CI-MS-MS) B**2** & C**2** for compounds **3** and **4**.

(CH_2-α), 50.2 (CH_3), 19.9 (CH_2-β). HRESIMS-theory for ^{35}Cl isotope cation: 237.1159; observed: 237.1146.

3. Results and discussion

3.1. Exposure of DMT to halogenated solvents

Halogenated solvents such as dichloromethane are commonly used during work-up procedures, e.g. for acid–base extractions after synthesis or isolation from plant materials. Previous work involved the synthesis and analytical characterisation of a number of *N*,*N*-dialkylated "designer" tryptamine derivatives where DCM has been used as the organic solvent [15]. It was observed that when DMT free base was left in DCM over a period of up to several days, crystalline needles precipitated which were characterised as *N*-chloromethyl-DMT **2**. Interestingly, it has also recently been shown by Buchanan and co-workers that **2** was indeed present as a side-product during the isolation of tryptamines from the Chinese shrub *Acacia confusa*. In that case, DCM had been used during the purification of the plant extract [16]. A second example was found in the literature where the N^1-methyl derivative of **2** was detected when N^1-Me-DMT was dissolved in DCM and irradiated at 253.7 nm in the presence of pyridine *N*-oxide and benzophenone [17].

3.2. GC–MS analysis of N-chloromethyl-DMT chloride 2

Exposure of DMT free base **1** to DCM led to the precipitation of *N*-chloromethyl-DMT **2** as crystalline needles. Precipitation of **2** appeared to be concentration-dependent and preliminary results indicated that crystallisation of **2** occurred when **1** was dissolved in DCM at a concentration of about 10 mg/ml. The presence of **2** at lower concentrations, however, could conveniently be detected by LC-UV/MS without precipitation (not shown). Under GC–MS conditions the qua-

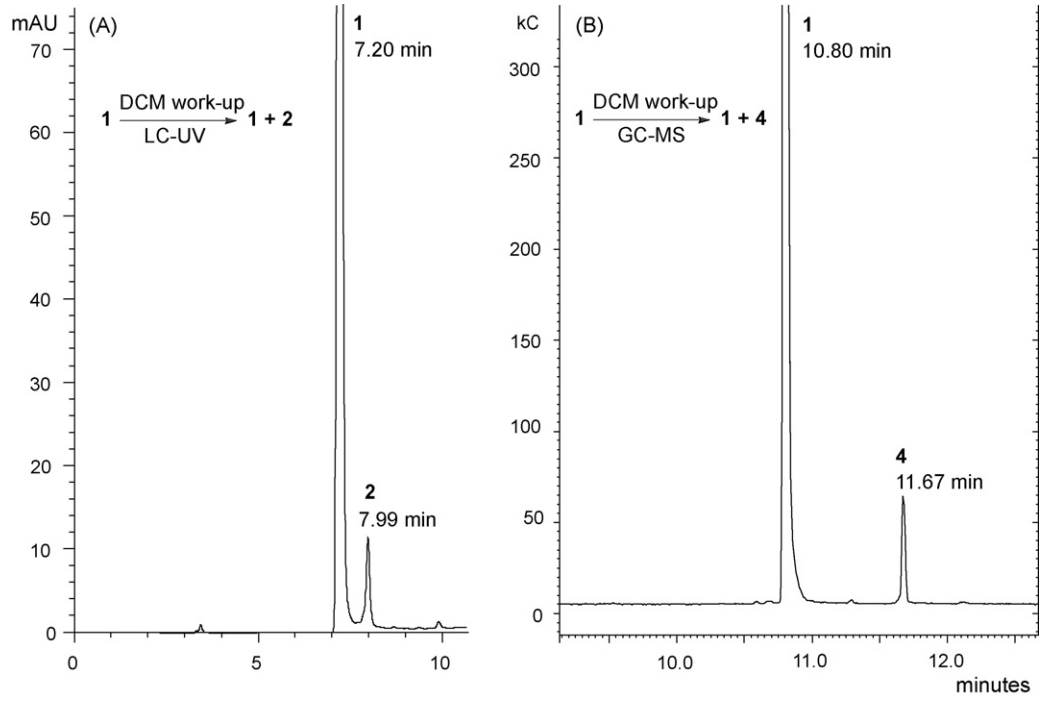

Fig. 3. Impact of two different analytical techniques on artefact formation from the same sample: DMT **1** work-up was carried out with dichloromethane (DCM) instead of chloroform. (A) HPLC-UV trace at 280 nm after 20 μg on column injection. A time-limited contact between DMT and DCM during work-up revealed the presence of the *N*-chloromethylated **2**. (B) A 20 ng on column injection of the same sample onto GC-MS where the presence of **2** led to detection of 2-Me-THBC **4**.

ternary ammonium salt **2** was observed to be converted into two different compounds, namely 3-(2-chloroethyl)indole **3** and 2-methyltetrahydro-β-carboline **4** (2-Me-THBC), Fig. 2(A).

Inspection of the EI mass spectrum of the first peak at 10.68 min indicated the possible presence of an ethylindole moiety with the corresponding quinolinium base peak at *m/z* 130 [18] as indicated in Fig. 2(B1). A *NIST* 2002 library search did not yield any hits but a chlorine pattern was observed at *m/z* 179/*m/z* 181 and the fact that the tryptamine-based mass spectral pattern remained unchanged pointed towards the presence of chlorine in the ethylamine side chain. Further support was obtained from CI-MS where a protonated molecule $[M+H]^+$ base peak appeared at *m/z* 180 and *m/z* 182 (ratio 3:1). Further fragmentation of the $[M+H]^+$ at *m/z* 180 (^{35}Cl isotope) yielded a species at *m/z* 144, Fig. 2(B2). This assignment was verified by the synthesis of **3** from tryptophol and thionyl chloride by an adapted procedure [19]. Retention time and mass spectra were found to be identical. The *NIST* 2002 library yielded a hit for the second peak at 11.66 min (Fig. 2(A)) and suggested 2-Me-THBC **4** as a possible candidate with a potential molecular ion at *m/z* 186. The corresponding EI and CI tandem mass spectra are shown in Fig. 2(C1 and C2), respectively. Under EI conditions, a characteristic base peak at *m/z* 143 was observed which is known to occur after *retro*-Diels-Alder fragmentation (RDA) [20]. The presence of this base peak ion can also provide some structural information because it points towards the absence of any substituent at position C-1. Indeed, tetrahydro-β-carboline (THBC) (M_w 172) itself also forms this particular base peak which disappears as soon as one or two particular substituents are present at position C-1. If this was the case, the dominating mechanism, i.e. base peak formation, would then be represented by alkyl cleavages [20–23]. CI-MS–MS confirmed the $[M+H]^+$ to occur at *m/z* 187 with further dissociation to *m/z* 144. A 2-Me-THBC standard **4** was then synthesised by an adapted procedure [24]. This was based on reductive alkylation of THBC with aqueous formaldehyde and $NaBH_3CN$ which confirmed its presence, as originally indicated by the mass spectral library.

The formation of both compounds **3** and **4** during analysis was somewhat surprising because a simple dequaternisation of **2** would have been expected under GC–MS conditions by methyl cleavage to leave the tertiary *N*-chloromethyl derivative. This would have been detected as a third peak in the total ion chromatogram which was not the case (Fig. 2(A)). This particular phenomenon of dequaternisation of ammonium salts subjected to GC–MS has been observed in this laboratory on several occasions. For example, *N*,*N*,*N*-trimethylammonium salts of DMT were observed to demethylate which resulted in their detection as the respective DMT derivatives (unpublished results).

3.3. Impact of dichloromethane work-up on product purity and detection

As discussed above, precipitation of quaternary ammonium derivative of DMT occurred after storage in the dichloromethane for a period of several days. Although it enabled convenient characterisation, it was of interest to investigate the extent of formation after a simple work-up using DCM as the organic solvent where contact time was more limited. DCM, instead of chloroform was employed during work-up after synthesis of DMT **1**. The free base product was subsequently subjected to

HPLC and GC–MS analysis. The results are depicted in Fig. 3 and indicate that differential pieces of data have been obtained.

Fig. 3(A) shows a magnified section of the LC-UV trace after injection of DMT **1** (10 μg on column), where **1** was observed to elute after 7.20 min. Interestingly, the *N*-chloromethylated by-product **2** was also detected at 7.99 min and corresponded to ~4% of the total area. The same free base product was then investigated by GC–MS. Fig. 3(B) shows a magnified section of the TIC in CI-MS mode and relates to a 20 ng injection on the column. Apart from the expected DMT at 10.80 min, 2-Me-THBC **4** was detected which accounted for ~0.7% of the total area. This demonstrated that degradation of **2** can still be observed by GC–MS even after DCM work-up where exposure of **1** to DCM was limited. Under these conditions, however, it appeared that 3-(2-chloroethyl)indole **3** was not detectable. This was only the case when pure **2** was analysed by GC–MS (Fig. 2(A)). The detection of 2-Me-THBC **4** during GC–MS analysis would provide misleading information if the analyst was aiming at the identification of route-specific impurities. For example, the presence of tetrahydro-β-carbolines such as 2-Me-THBC in DMT preparations could point towards a plant-based material. THBCs are also often found as a consequence of Pictet–Spengler cyclisations during reductive amination procedures (unpublished results and [13]). Fig. 3 highlights the complementary value of LC analysis. The presence of quaternary ammonium salt impurities in DMT preparations after exposure to halogenated solvents would have gone unnoticed if GC–MS had been the only method of analysis.

One of the inherent limitations of GC–MS analysis is encountered when the sample material is not volatile enough for the transfer to the gas phase. Under the conditions of a hot injection port, degradation of the analyte may then occur and consequently no detection is observed. Artefact formation and/or degradation during GC–MS analysis is not uncommon and requires particular attention when forensically relevant samples are subject to investigation. Ephedrine, for example, has been observed to be converted to methamphetamine (MA), particularly at elevated temperatures in the injector [25]. The combination of ephedrine, formaldehyde contamination in methanol and increased injection temperature has also led to the false identification of phenmetrazine [26] and injections of methanolic solutions of MA hydrochloride have been observed to form both methylated and demethylated artefacts. It was furthermore found that artefacts were not detected when new inlet liners were used, even at elevated temperatures [27]. Other examples were reported during the analysis of several 2,5-dimethoxyphenethylamine "designer" drugs (2C-T-7, 2C-T-2 and 2C-I) where injections of methanolic solutions resulted in the detection of methylene, $N{=}CH_2$, artefacts [28,29,30].

The occurrence of thermally induced degradation of impurities would also pose a question on their impact on human health. DMT itself is not orally active, i.e. it has to be injected, e.g. as a fumarate salt, or smoked. Smoking of the free base product requires evaporation and application of heat, e.g. by heating a glass pipe with a lighter. It is currently unknown whether this procedure could cause a similar conversion of impurity **2** into **3** and **4**, as it has been observed after submission to a heated GC injection port. Further studies, for example on temperature dependence, are warranted in order to assess this question. Any potential synergistic pharmacological or toxicological effects, which may arise after inhalation of these impurities, also remain to be investigated. Finally, it seems worth noting that the *N*,*N*-dimethylated tryptamine substitution pattern seems particularly vulnerable to DCM and impurity formation during work-up. Preliminary studies have indicated that a variety of other mono and dialkylated tryptamine derivatives may not display this behaviour to such an extent due to steric reasons, unless exposure is extended over a period of months. DMT was also observed to react with other halogenated solvents (unpublished).

4. Conclusions

This study has shown that generation of artificially formed by-products, either induced by solvent interactions or due to instrumentation, can increase the complexities often encountered during "fingerprint" analyses or impurity profiling procedures. *N*,*N*-Dimethyltryptamine free base has been found to form a chloromethylated quaternary ammonium salt when dissolved in dichloromethane. Under GC–MS conditions, this was not detectable but instead several rearrangement products have been identified. This not only underlines the value of using complementary analytical techniques as exemplified with the use of HPLC, but also raises awareness of the potential for misinterpretation of data such as the identification of a synthetic procedure used during illegal manufacturing of drugs.

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References

[1] A.T. Shulgin, J. Psychedelic Drugs 8 (1976) 167–168.
[2] R.J. Strassman, Behav. Brain Res. 73 (1996) 121–124.
[3] R.J. Strassman, C.R. Qualls, Arch. Gen. Psychiatry 51 (1994) 85–97.
[4] R.J. Strassman, C.R. Qualls, E.H. Uhlenhuth, R. Kellner, Arch. Gen. Psychiatry 51 (1994) 98–108.
[5] E. Gouzoulis-Mayfrank, K. Heekeren, A. Neukirch, M. Stoll, C. Stock, M. Obradovic, K.A. Kovar, Pharmacopsychiatry 38 (2005) 301–311.
[6] C.S. Grob, D.J. McKenna, J.C. Callaway, G.S. Brito, E.S. Neves, G. Oberlaender, O.L. Saide, E. Labigalini, C. Tacla, C.T. Miranda, R.J. Strassman, K.B. Boone, J. Nerv. Ment. Dis. 184 (1996) 86–94.
[7] J. Riba, A. Rodriguez-Fornells, G. Urbano, A. Morte, R. Antonijoan, M. Montero, J.C. Callaway, M.J. Barbanoj, Psychopharmacology 154 (2001) 85–95.
[8] J. Riba, M. Valle, G. Urbano, M. Yritia, A. Morte, M.J. Barbanoj, J. Pharmacol. Exp. Ther. 306 (2003) 73–83.
[9] J. Riba, S. Romero, E. Grasa, E. Mena, I. Carrio, M.J. Barbanoj, Psychopharmacolgy 186 (2006) 93–98.
[10] R.E. Schultes, A. Hofmann, in: C.C. Thomas (Ed.), The Botany and Chemistry of Hallucinogens, Springfield, Illinois, USA, 1980.
[11] C. Rätsch, The Encyclopedia of Psychoactive Plants: Ethnopharmacology and Its Applications, Park Street Press, Rochester, VT, 2005.

[12] S. Freeman, J.F. Alder, Eur. J. Med. Chem. 37 (2002) 527–539.
[13] S.D. Brandt, S. Freeman, P. McGagh, N. Abdul-Halim, J.F. Alder, J. Pharm. Biomed. Anal. 36 (2004) 675–691.
[14] M.E. Speeter, W.C. Anthony, J. Am. Chem. Soc. 76 (1954) 6208–6210.
[15] S.D. Brandt, S. Freeman, I.A. Fleet, P. McGagh, J.F. Alder, Analyst 130 (2005) 330–344.
[16] M.S. Buchanan, A.R. Carroll, D. Pass, R.J. Quinn, Magn. Reson. Chem. 45 (2007) 359–361.
[17] M. Nakagawa, T. Kaneko, H. Yamaguchi, T. Kawashima, T. Hino, Tetrahedron 30 (1974) 2591–2600.
[18] M.W. Couch, C.M. Williams, Anal. Biochem. 50 (1972) 612–622.
[19] P.G. Baraldi, B. Cacciari, R. Romagnoli, G. Spalluto, A. Monopoli, E. Ongini, K. Varani, P.A. Borea, J. Med. Chem. 45 (2002) 115–126.
[20] R.T. Coutts, R.A. Locock, G.W.A. Slywka, Org. Mass Spectrom. 3 (1970) 879–889.
[21] J. Gynther, Acta Chem. Scand. B B42 (1988) 433–441.
[22] T. Herraiz, Rapid Commun. Mass Spectrom. 11 (1997) 762–768.
[23] S.D. Brandt, D. Mansell, S. Freeman, I.A. Fleet, J.F. Alder, J. Pharm. Biomed. Anal. 41 (2006) 872–882.
[24] J.L. Castro, R. Baker, A.R. Guiblin, S.C. Hobbs, M.R. Jenkins, M.G.N. Russell, M.S. Beer, J.A. Stanton, K. Scholey, R.J. Hargreaves, M.I. Graham, V.G. Matassa, J. Med. Chem. 37 (1994) 3023–3032.
[25] A.H.B. Wu, S.S. Wong, K.G. Johnson, A. Ballatore, W.E. Seifert, Biol. Mass Spectrom. 21 (1992) 278–284.
[26] S.M.R. Wille, W.E.E. Lambert, J. Chromatogr. A 1045 (2004) 259–262.
[27] T.L. Li, Y.S. Giang, J.F. Hsu, S.G. Cheng, R.H. Liu, S.M. Wang, Forensic Sci. Int. 162 (2006) 113–120.
[28] D.S. Theobald, S. Fehn, H.H. Maurer, J. Mass Spectrom. 40 (2005) 105–116.
[29] D.S. Theobald, R.F. Staack, M. Puetz, H.H. Maurer, J. Mass Spectrom. 40 (2005) 1157–1172.
[30] D.S. Theobald, M. Putz, E. Schneider, H.H. Maurer, J. Mass Spectrom. 41 (2006) 872–886.