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Mass and NMR spectroscopic characterization of 3,4-methylenedioxypyrovalerone: A designer drug with α-pyrrolidinophenone structure

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ABSTRACT

This study presents and discusses the nuclear magnetic resonance (NMR) spectroscopic and mass spectroscopic data of the designer drug 3,4-methylenedioxypyrovalerone (MDPV), a drug variant of pyrovalerone. MDPV was first seized in Germany in the year 2007. The structure elucidation of the aliphatic part of MDPV was carried out by product ion spectroscopy of the immonium ion with *m/z* 126 formed after electron ionization, and by 1D ^{1}H and ^{13}C NMR spectroscopy. Additional two-dimensional NMR spectroscopy was used to verify the structure of the alkyl side chain, and to determine the methylenedioxy position in the aromatic ring.

1. Introduction

In 2007 we reported the appearance of 4′-methyl-α-pyrrolidinohexanophenone (MPHP [1,2]) and of 4′-methyl-α-pyrrolidinobutyrophenone (MPBP [1,3]) on the German illegal drug market. These compounds are part of a series of clandestinely produced α-pyrrolidinophenones, such as α-pyrrolidinopropiophenone (PPP [4]), 4′-methyl-α-pyrrolidinopropiophenone (MPPP [1,5]), 4′-methoxy-α-pyrrolidinopropiophenone (MOPPP [6]), and 3,4-methylenedioxy-α-pyrrolidinopropiophenone (MDPPP [7]) (Fig. 1). The α-pyrrolidinophenones are structurally closely related to the central stimulatory 1-phenyl-2-pyrrolidinopentane (prolintane) [8] and α-aminophenones like cathinone, methcathinone, 2-methylamino-1-phenylpropane-1-one (Jeff) [9], bupropion [10], amfepramone, metamfepramone, 3,4-methylenedioxycathinone homologs [11] or 1-(4-methylphenyl)-2-(pyrrolidin-1-yl)pentan-1-one (pyrovalerone) [12–15].

In June 2007 customs officers from Saxony (a federal state of Germany) investigated against a person who was the addressee of a drug mail shipment from China. During the police raid of the person's working room a suitcase was found containing a lot of small plastic containers (each of 2 mL volume) among other things. Three of these containers were labeled with "MDPV". In two of these containers 1.3 g of grey coloured substances with a granular consistence were found. This material later analysed to be MDPV (1, Fig. 2) occurred in the chemical form of its free base. The third vial contained 0.9 g of a white powder, later identified as the hydrochloride salt of MDPV. All seized compounds were found to be nearly pure.

Analytical data of MDPV (1) have not been published yet. The nuclear magnetic resonance (NMR) spectroscopic and mass spectroscopic data of MDPV are presented and discussed. In addition to common GC–MS methods the structural identification of the seized compound was achieved by product ion mass spectrometry [16,17] and one- and two-dimensional NMR spectroscopy.

2. Methods

2.1. Chemicals

MDPV·HCl was provided by the Landeskriminalamt Sachsen, Dresden (Germany) for research purposes and was part of the originally seized compound. Sodium hydroxide and diethyl ether were purchased from Merck. DMSO-d_6 was obtained from Deutero, Kastellaun. All solvents and reagents used were of analytical grade.

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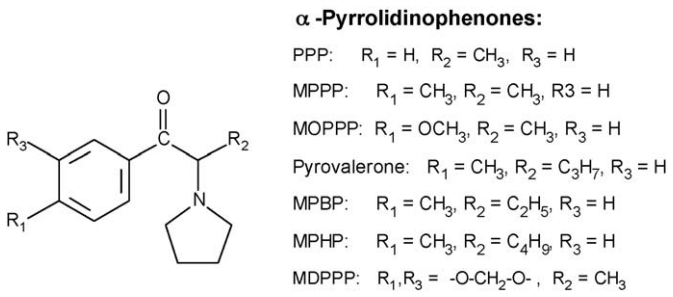

Fig. 1. Structures of some α-pyrrolidinophenones.

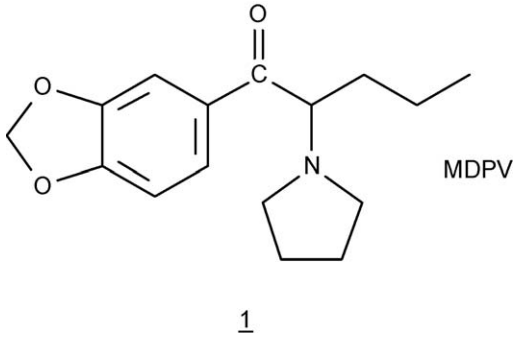

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Fig. 2. 1-(3,4-Methylenedioxyphenyl)-2-pyrrolidinylpentan-1-one (methylenedioxypyrovalerone, MDPV).

2.2. Mass spectrometry (GC–MS and GC–MS–MS)

2.2.1. Sample preparation

Approximately 2 mg of the powder were suspended in 1 mL of de-ionized water, alkalized with an aqueous sodium hydroxide solution (5%, w/w) and extracted with 2 mL of diethyl ether. For analysis 1 μL of this extract was injected into the GC–MS system.

2.2.2. Equipment

The electron ionization (EI) mass spectra were obtained with a Finnigan TSQ 7000 triple stage quadrupole mass spectrometer coupled to a gas chromatograph (Trace GC Ultra, Thermo Electron) with an autosampler CTC CombiPAL (CTC Analytics, Switzerland).

2.2.3. GC parameters

The samples were introduced via the gas chromatograph with splittless injection using a fused silica capillary column DB-1 (30 m × 0.32 mm, film thickness 0.25 μm). The temperature program used consisted of an initial temperature of 80 °C, held for 1 min, followed by a ramp to 280 °C with 15 °C/min. The final temperature was held for 20 min. The injector temperature was 220 °C. The transfer line temperature was maintained at 280 °C. The carrier gas was helium in constant flow modus at a flow rate of 1.0 mL/min.

2.2.4. MS parameters

The electron ionization (EI) energy was 70 eV with an emission current of 400 μA. The scan time was 1 s and the scan range was m/z 29–600. The ion source temperature was maintained at 175 °C.

The chemical ionization (CI) energy was 70 eV with an emission current of 400 μA and a source temperature of 175 °C. The reactant gas was methane and the source pressure was 1.5 mTorr (0.2 Pa). The scan time was 1 s and the scan range was m/z 50–600.

In the EI-MS/MS-product-ion-mode the ionization energy was 70 eV with an emission current of 400 μA and a source temperature of 175 °C. The scan time was 1 s and the scan range was m/z 10–130. The collision gas was Argon. The collision energy was approximately 20 eV and the collision gas pressure was approximately 1.5 mTorr (0.2 Pa). The exact target-thickness [18] was set using n-butyl benzene and adjusting intensity ratios m/z 92/91 to 0.2 and m/z 65/91 to 0.02 by variation of collision energy and collision gas pressure [18]. This ensures the reproducibility of the product ion mass spectra and the use of a product ion mass spectra library for the identification of the structure of the product ions [19].

2.3. NMR spectroscopy

NMR spectra were recorded with a Bruker Avance NMR spectrometer operating at a resonance frequency of 600.13 MHz for ^{1}H NMR spectra and 150.92 MHz for ^{13}C NMR spectra, respectively. Compound 1 was dissolved in perdeuterated dimethylsulfoxide at a concentration of 2 mg/0.6 mL. The following ^{1}H NMR spectra were recorded using standard pulse programs at 300 K: one-dimensional (1D) ^{1}H NMR, a CPD-decoupled ^{13}C NMR- and a ^{13}C NMR-DEPT-experiment with ^{1}H-decoupling using GARP, were acquired to obtain resonance frequencies of all proton- and carbon-atoms in compound 1. 2D-gradient selected COSY [20], ^{1}H,^{13}C-HSQC [21] and HMBC [22] were also acquired, which correlate geminal and vicinal protons, carbon atoms with their directly attached proton, and carbon and proton atoms generally separated by three or two bonds, respectively [23]. All spectra were referenced to the solvent (^{1}H: DMSO-d_5, at 2.50 ppm, ^{13}C: DMSO-d_6 at 39.5 ppm). H/D-exchange was performed to determine the position of N–H resonance by adding one drop of D_2O to the sample followed by vigorous shaking.

3. Results and discussion

Figs. 3 and 4 show the CI and EI mass spectra of MDPV (1) in the form of its free base. The molecular weight was confirmed by chemical ionization mass spectrometry with methane as reagent gas. The CI spectrum shows a signal of the protonated molecule at m/z 276 with the typical adduct ions at m/z 304 ($[M+C_2H_5]^+$) and 316 ($[M+C_3H_5]^+$) indicating a molecular mass of 275 Da and an odd number of nitrogen atoms.

The EI spectrum of compound 1 shows analogous fragmentation characteristics as other α-pyrrolidinophenones [1] (Scheme 1): the

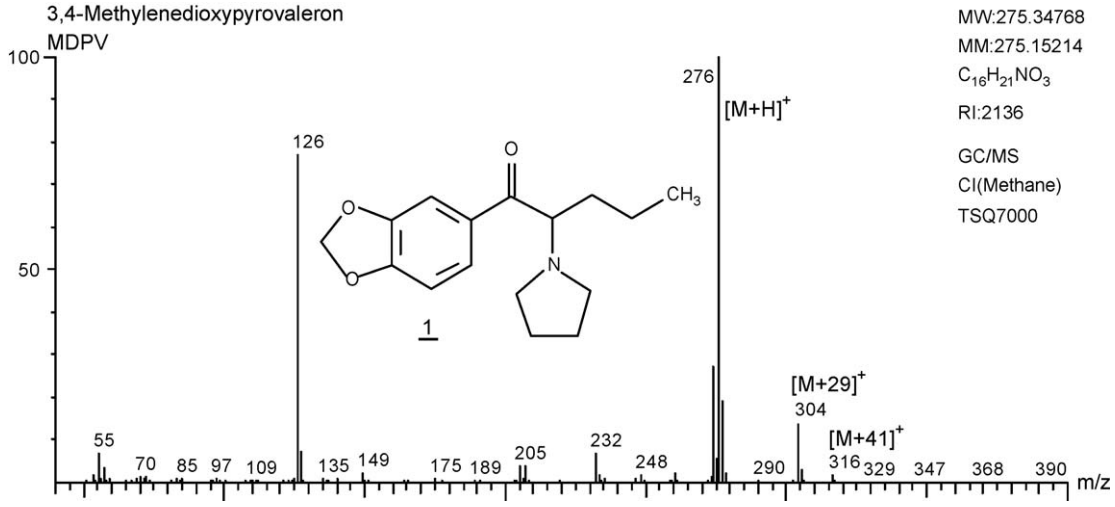
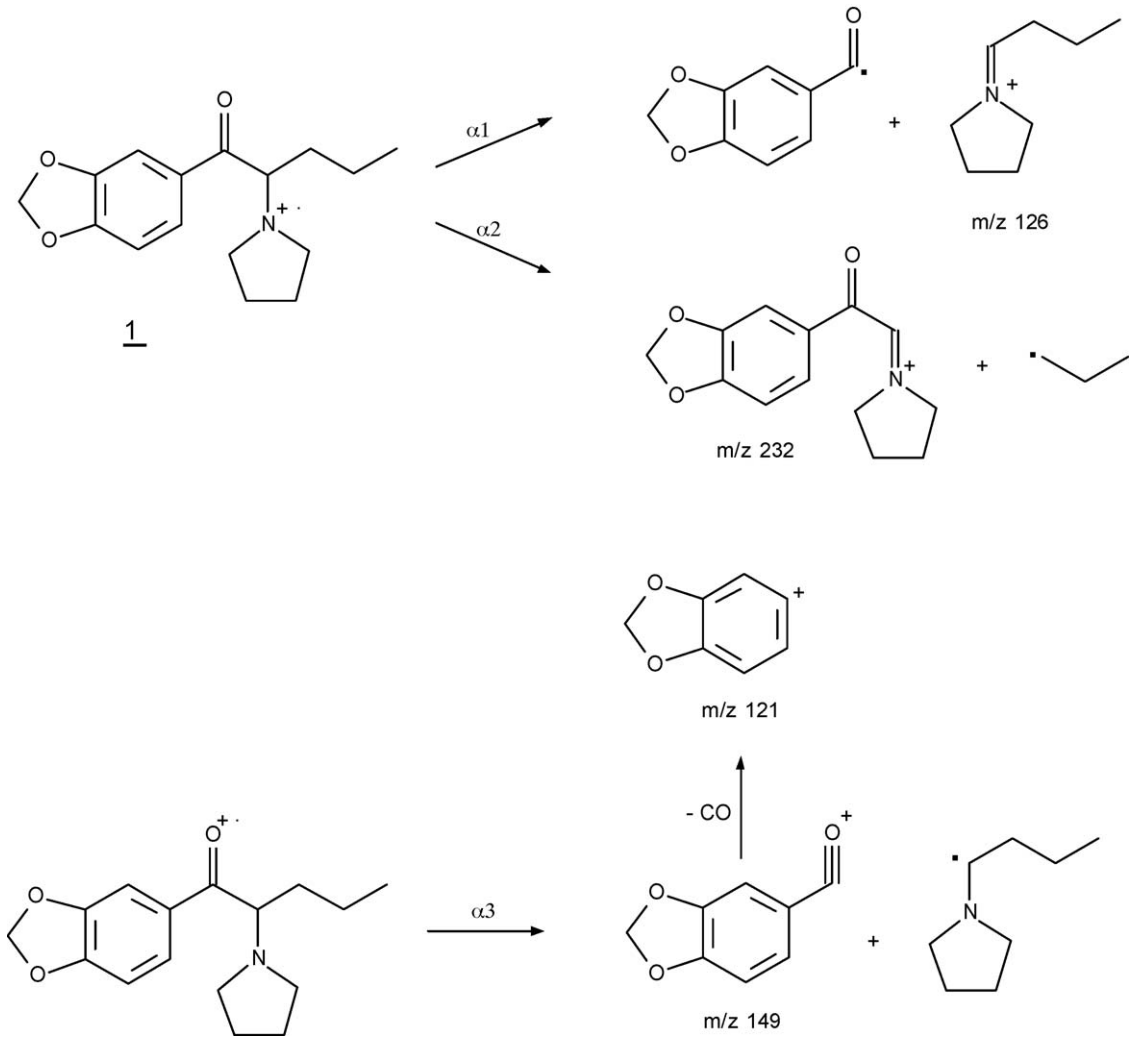


Fig. 3. CI spectrum (70 eV, methane) of MDPV (1).



Scheme 1. Main electron ionization fragmentations of MDPV (1).

radical electron of the nitrogen atom induces a fast α-cleavage reaction (α1) of the benzyl bond and produces a base peak immonium ion at *m*/*z* 126. The alternative α-cleavage reaction (α2) produces an immonium ion at *m*/*z* 232 with low intensity by the loss of a propyl radical. M-15 and M-29 α-cleavage fragments are found with low intensities at *m*/*z* 260 and *m*/*z* 246, respectively. Ionization at the carbonyl oxygen atom and α-cleavage reaction (α3) yields a methylenedioxybenzoyl cation at *m*/*z* 149, and a subsequent CO loss may be responsible for the ion at *m*/*z* 121 (Scheme 1). Therefore, all fragments were in good agreement with the structure of 1 proposed to be MDPV.

The distinction between structure 1 as an n-alkyl-derivative and other possible isobaric branched alkyl-derivatives was achieved by product ion mass spectrometry and NMR spectroscopy. Product ion mass spectrometry of immonium ions formed by electron ionization has successfully been applied for structure elucidation of immonium ions up to *m*/*z* 72 [16], and of even larger masses [1,19]. For a number of new designer drugs this method has distinguished structure isomers of the alkyl-amino moiety as well as unambiguously established the ring substitution patterns of methylenedioxyamphetamines by the examination of the CI-generated homobenzyl cations [1,16,17,24–28].

Fig. 5 shows the product ion mass spectrum of the immonium ion with *m*/*z* 126 originating from compound 1 during electron ionization (Fig. 5, I) and compares it with the product ion mass spectra of isomeric immonium ions (Fig. 5, II–V) from our database [19] that exhibit the best similarity values. The product ion spectrum of compound 1 shows a very good agreement with the product ion spectrum of the immonium ion prepared from 1-(3,4-dimethylphenyl)-2-pyrrolidinopentan-1-one (Fig. 5, II). The subtle intensity differences in the product ion spectra I and II can by explained by small differences in the internal energies of the respective precursor immonium ions, as they were generated from different precursor compounds.

The product ion spectrum of the butylidenepyrrolidinium ion at *m*/*z* 126 (Fig. 5, I) shows fragments analogous to the corresponding ion of MPBP [1].

An inductively (i) driven rearrangement (*r*) of a tautomeric immonium ion generated by a hydrogen shift with loss of propene and charge retention at the nitrogen generates a pyrrolidinium cation with an exocyclic double bond at *m*/*z* 84 (Scheme 2). Sigma cleavage (σ) of the immonium ion following the hydrogen shift may result in the intense radical cation at *m*/*z* 69 violating the even electron rule [29] (Scheme 2).

A loss of a terminal ethyl radical generates an intense radical immonium ion at *m*/*z* 97 that also violates the even electron rule. A protonated ethylnitrile may account for the ion at *m*/*z* 42. Loss of the pyrrolidine ring leads to a homoallylic cation at *m*/*z* 55. As in the MPBP-derivative, the fragment at *m*/*z* 55 can also be built by the fragmentation of the pyrrolidine ring.

The high similarity between the product ion spectrum of the unknown (Fig. 5, I) and the product ion spectrum of the immonium

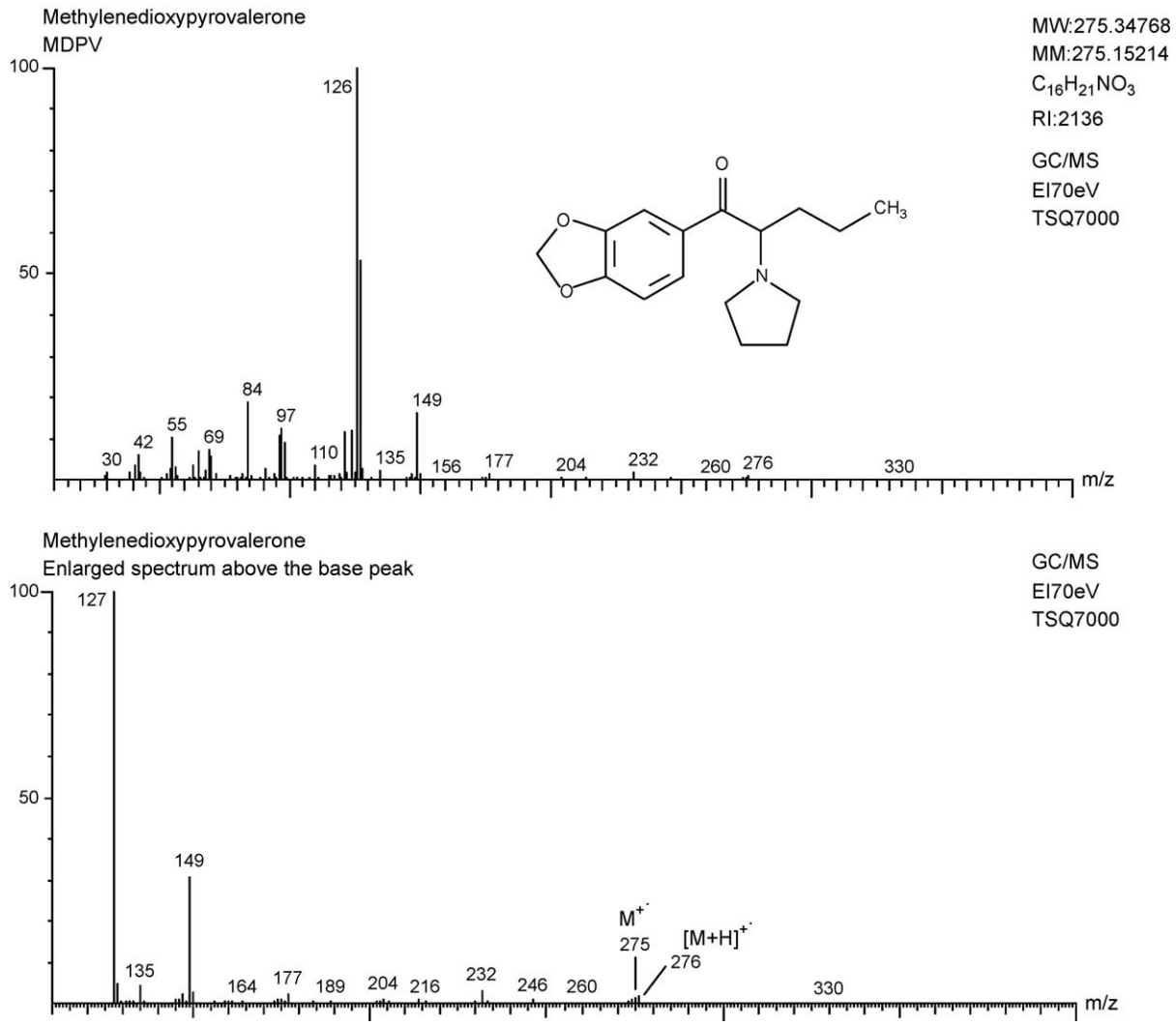
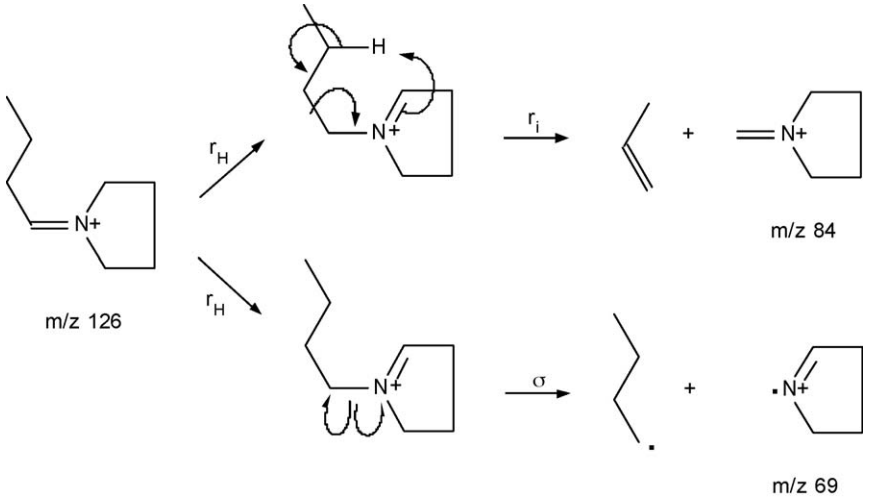


Fig. 4. EI spectrum (70 eV) of MDPV (1) (at the top) and enlarged spectrum above the base peak (at the bottom).

ion generated from 1-(3,4-dimethylphenyl)-2-pyrrolidinopentan-1-one (Fig. 5, II) as well as the logical explanation of the endo- and exocyclic fragments suggest the unknown immonium ion at *m*/*z* 126 (Fig. 5, I) to have an unbranched alkyl chain.

It is obvious that the immonium ion of the seized compound cannot originate from the branched N-pyrrolidinyl- (Fig. 5, III + IV) or homologous N-piperidinyl-derivatives (Fig. 5, V) because of their different product ion mass spectra. Because our product ion



Scheme 2. Possible ways for the formation of the cations at *m*/*z* 84 and *m*/*z* 69.

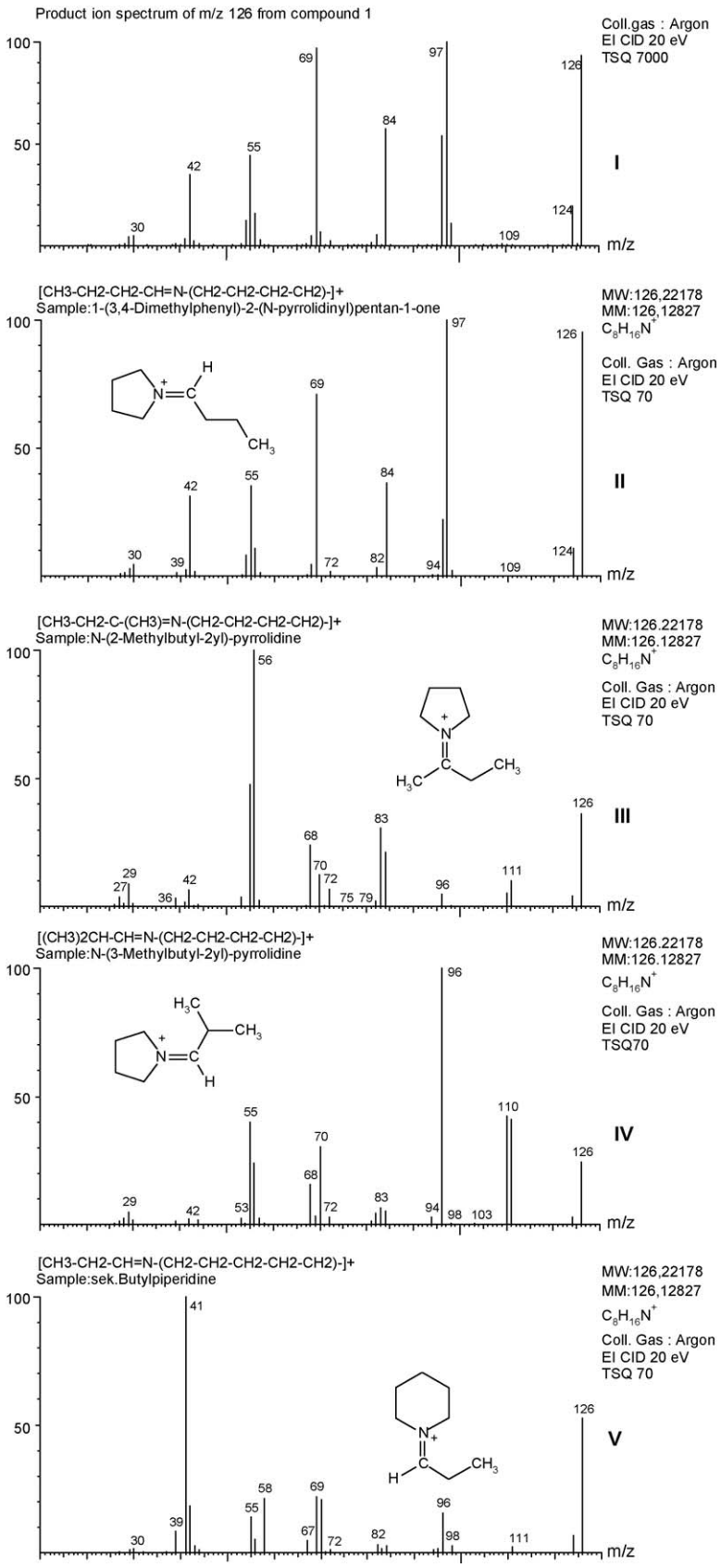


Fig. 5. Product ion mass spectra of the immonium ion from 1 and best similarity library product ion spectra.

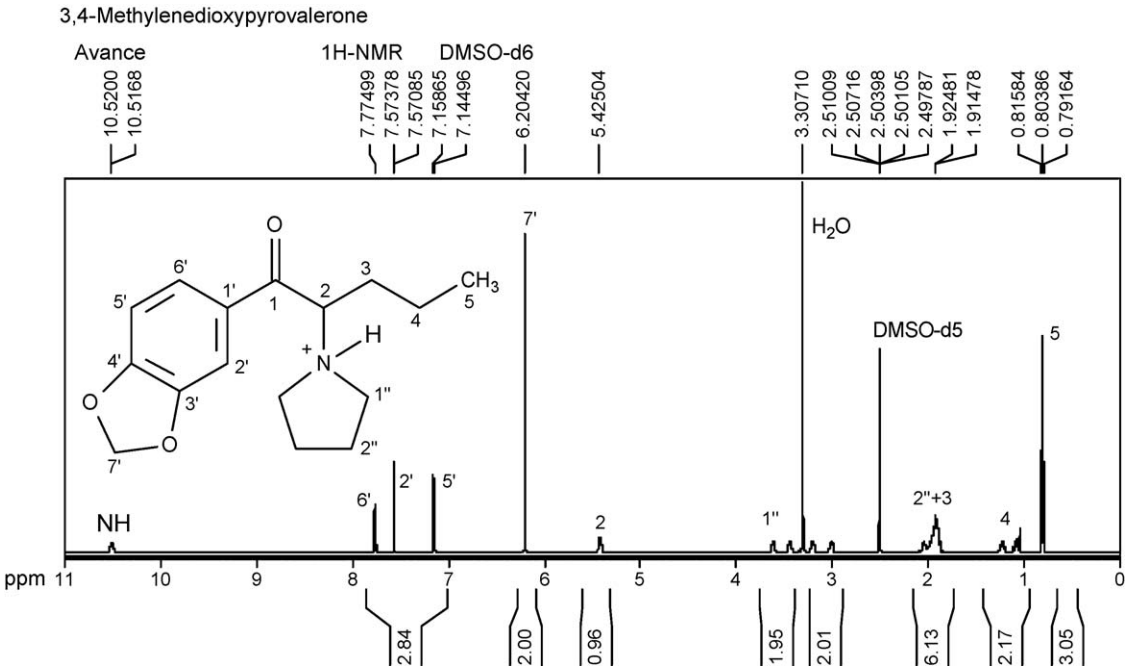


Fig. 6. ^{1}H NMR spectrum of protonated MDPV.

spectra database [19] does not yet contain any isomeric immonium ions with 126 Da and in order to locate the position of the methylenedioxy group the application of NMR spectroscopy became necessary (Figs. 6 and 7).

^{1}H NMR spectrum of the protonated compound 1 (Fig. 6) demonstrates its very high purity, as all observed peaks except for those of DMSO solvent and water can be related to the substance. The protonated amine shows a resonance at 10.52 ppm, which exchanges upon addition of D_2O (not shown). The methinic proton H-2 (integral: 1H) resonates at 5.42 ppm, and the other protons of the alkyl chain appear centred at 1.97 (multiplet for H-3), 1.22 and 1.07 (multiplets for the diastereotopic protons on C-4), and 0.80 ppm (3H, triplet of the methyl group C-5). The aromatic protons H-5′ and H-6′ are coupled (^{3}J = 8.3 Hz); and H-5′ appears as doublet at 7.15 ppm (1H). H-6′ yields a characteristic doublet of doublets at 7.77 ppm (1H), owing to the additional ^{4}J-coupling (1.8 Hz) to H-2′. Expectedly, H-2′ is a doublet, resonating at 7.57 ppm (1H). This coupling pattern unambiguously establishes the 3,4-methylenedioxy substitution. The methylene group of the methylenedioxy substructure gives a singlet (2H) at 6.20 ppm.

The multiplets of the methylene protons H-1″ of the pyrrolidine-ring appear as separated signals for each single proton at 3.64 ppm, 3.44 ppm, 3.21 ppm, and 3.01 ppm (1H each), while the methylene protons H-2″ of the pyrrolidine-ring resonate at 1.87–2.07 ppm, and partially overlap with the methylene protons H-3 of the alkyl side chain (6H). The wide separation of the H-1″ methylene protons is remarkable, and establishes a strong diasterotopic character of the protons that neighbour the nitrogen atom in the pyrrolidine ring. This phenomenon was previously detected in the ^{1}H NMR spectrum of MPHP [1]. There the signals

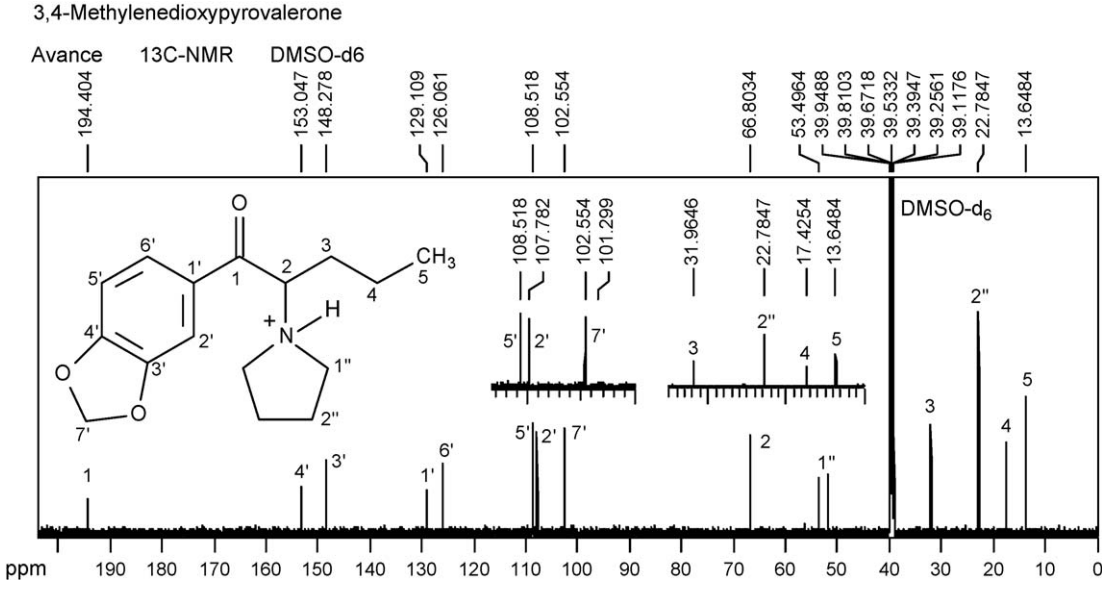


Fig. 7. ^{13}C NMR-spectrum of protonated MDPV.

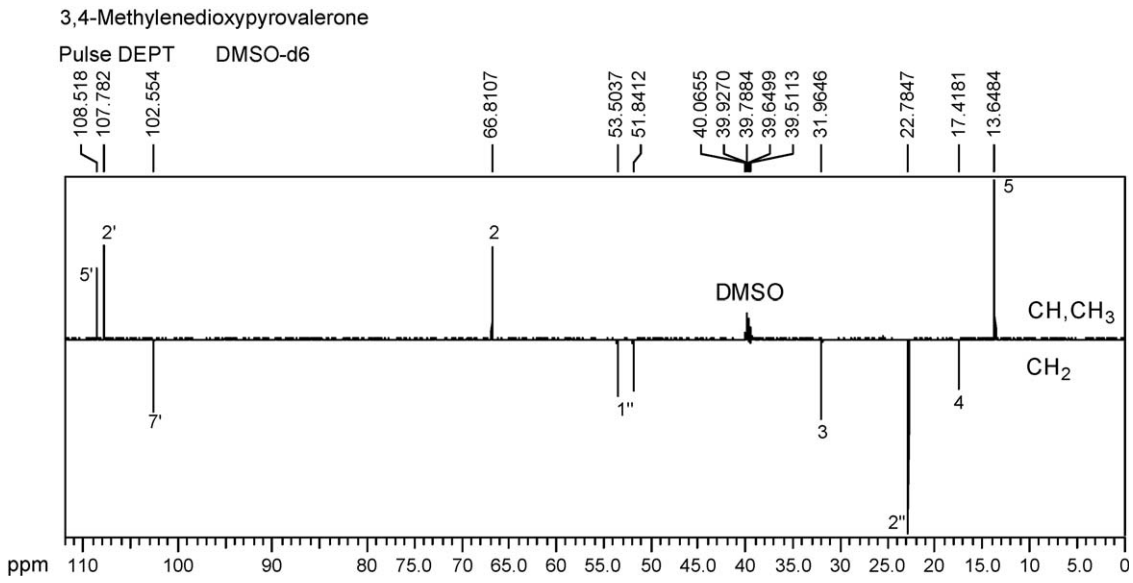


Fig. 8. DEPT-spectrum of protonated MDPV.

confluence at higher temperature, which showed that a higher flexibility of the molecule at raised temperature suspends the diasterotopic property of the methylene protons H-1″. Here, the diasterotopic character, or the energetic barriers for rotation and nitrogen inversion, are even larger, as elevated temperatures were insufficient to significantly increase the dynamic broadening (not shown). However, alkalization easily abolishes the observation, and yields average signals for all H-1″ and H-2″ signals (not shown).

In the ^{13}C NMR spectrum of protonated 1 (Fig. 7) the signals of the carbon atoms can be related as follows using the chemical shifts and the results of a DEPT-spectrum (Fig. 8): Carbonyl-carbon C-1 at 194.4 ppm, aromatic carbons C-1′, C-2′, C-3′, C-4′, C-5′, and C-6′ at 129.1 ppm, 107.8 ppm, 148.3 ppm, 153.0 ppm, 108.5 ppm, and 126.1 ppm, respectively; carbon of the methylene group C-7′ of the methylenedioxy ring at 102.6 ppm. The carbons C-1″ of pyrrolidine moiety resonate at 53.5 ppm and 51.8 ppm, as the chiral centre at C-2 combined with decelerated inversion at the protonated pyrrolidine-nitrogen and steric hindrance leads to two non-degenerate C-1″ signals. The two C-2″ signals nevertheless overlap at 22.8 ppm. The secondary carbon C-2 resonates at 66.8 ppm and the carbon atoms of the aliphatic side chain C-3, C-4, and C-5 are observed at 31.9 ppm, 17.4 ppm, and 13.6 ppm, respectively.

Proton and ^{13}C resonances were unambiguously correlated in an HSQC experiment. The coupling patterns of H-2, H-3, H-4, and H-5, and the results of the HMBC experiments as well as the identification of carbon atoms C-2, C-3, C-4, and C-5 via the ^{13}C-DEPT-spectrum (Fig. 8) clearly prove the unbranched aliphatic side chain of compound 1 [30].

4. Conclusion

The structure of the designer drug MDPV has been elucidated by mass spectrometry and NMR spectroscopy. Again product ion mass spectrometry of immonium ions proved to be a powerful tool to distinguish between isobaric structures of the alkyl-amino moiety of designer drugs. The substitution pattern of the aromatic ring was cleared by NMR spectroscopy which also confirmed the product ion mass spectrometry result of an unbranched aliphatic side chain. Furthermore an interesting signal splitting effect in the NMR spectrum was detected. In contrast to previously detected effects in a protonated α-pyrrolidinophenone, it could not be abolished by rising of the temperature but by alkalization.

All seized phenethylamine derivatives with an α-aminophenone substructure having appeared as designer drugs [1,31–33] on the illegal market in Germany so far could be related to one offender living in the German State of Hesse. The identical origin was supported by hints of criminal investigation, the individuality of this substance-class and the occurrence of the compounds in the rare salt form of nitrate in every case. In contrast this pyrrolidinophenone MDPV occurred as its free base and in the salt form MDPV·HCl. Furthermore the criminal investigation showed connections to China. So another origin of this α-pyrrolidinophenone has to be mentioned.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.forsciint.2009.05.001.

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