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Mass spectral and NMR spectral data of two new designer drugs with an α-aminophenone structure: 4′-Methyl-α-pyrrolidinohexanophenone and 4′-methyl-α-pyrrolidinobutyrophenone

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Abstract

This study presents and discusses the nuclear magnetic resonance (NMR) spectroscopic and mass spectroscopic data of the new designer drug 4′-methyl-α-pyrrolidinobutyrophenone (MPBP) and its homolog 4′-methyl-α-pyrrolidinohexanophenone (MPHP) which were seized in 2004 and 2000 in Germany for the first time. The structure elucidation of the aliphatic part of MPBP was carried out by product ion spectroscopy of the immonium ion formed after electron ionization as well as with ^{1}H and ^{13}C NMR. Product ion spectroscopy of immonium ions again proved to be a powerful tool to determine the structure of designer drugs and to distinguish between isobaric structures of the alkyl-amino moiety.

Keywords: Designer drugs; α-Pyrrolidinophenone substructure; Structure elucidation; Mass spectral data; Product ion mass spectrometry; NMR spectroscopy

1. Introduction

A series of clandestinely produced phenethylamine derivatives with α-pyrrolidinophenone substructures have appeared on the German illegal market in recent years, e.g. α-pyrrolidinopropiophenone (PPP), 4′-methyl-α-pyrrolidinopropiophenone (MPPP), 4′-methoxy-α-pyrrolidinopropio-phenone (MOPPP), 3,4-methylenedioxy-α-pyrrolidinopropiophenone (MDPPP), and 4′-methyl-α-pyrrolidinohexanophenone (MPHP, **2**) (Fig. 1). These compounds are closely related to the central stimulating 1-phenyl-pyrrolidino-pentane (prolintane) [1] and α-aminophenones like cathinone, methcathinone, 2-methylamino-1-phenylpropane-1-one (Jeff) [2], bupropion [3], amfepramone, metamfepramone, 3,4-methylenedioxycathinone homologs [4] or 4′-methyl-α-pyrrolidinovalerophenone (pyrovalerone) [5–8]. Information about the dosage [1], pharmacology [1,5] and toxicology [1,3] is available only for some of these compounds. The metabolism of pyrovalerone, PPP, MPPP, MOPPP, MDPPP, and MPHP in rats as well as of bupropion has been described in literature [3,7–13].

During an automobile inspection in the year of 2004 in Hesse (a federal state of Germany) 260 g of a white crystalline material were seized. First results of the analysis with gas chromatography–mass spectrometry (GC–MS) indicated that the unknown compound in the material was a new designer drug of the phenethylamine-type with an α-aminophenone moiety. Possible structures were a 4′-**m**ethyl-α-**p**yrrolidino**bu**tyro**p**henone with the acronym MPBP (**1**) (IUPAC: 2-pyrrolidine-1-yl-1-*p*-tolyl-butane-1-one) or its possible isobaric isomer **3** (Fig. 1). The material was found to be nearly pure. The amine occurred in the form of its nitrate salt, a rare salt form on the designer drug market.

Compounds **1** and **3** are homologs of 4′-**m**ethyl-α-**p**yrrolidino**h**exano-**p**henone with the acronym MPHP (**2**) (IUPAC: 2-pyrrolidine-1-yl-1-*p*-tolyl-hexane-1-one) which was already seized in 2000 and was presented partially on the XII Symposium of the German Society of Toxicological and Forensic Chemistry in 2001 [14].

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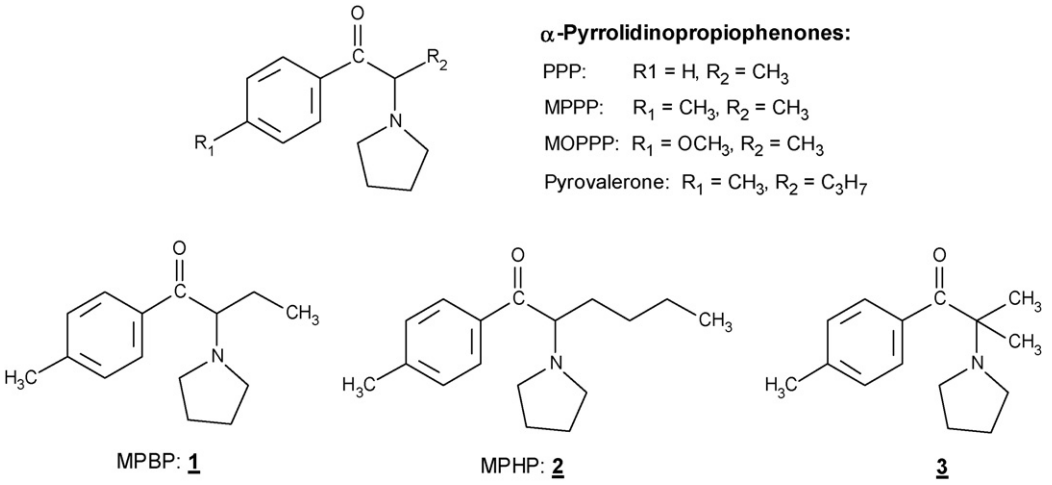


Fig. 1. Structures of some α-pyrrolidinophenones.

The nuclear magnetic resonance (NMR) spectroscopic and mass spectroscopic data of MPBP and MPHP which have not been completely published 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 [15–17] and NMR spectroscopy. Meanwhile the metabolism of MPBP in rats has also been cleared and presented [18].

2. Methods

2.1. Chemicals

MPBP·HNO_3 and MPHP·HNO_3 were provided by the Hessisches Landeskriminalamt, Wiesbaden (Germany) for research purposes and were parts of the originally seized compounds. 2-Pyrrolidinoalkanes and 2-piperidinoheptane were synthesised to get appropriate precursors for the corresponding immonium

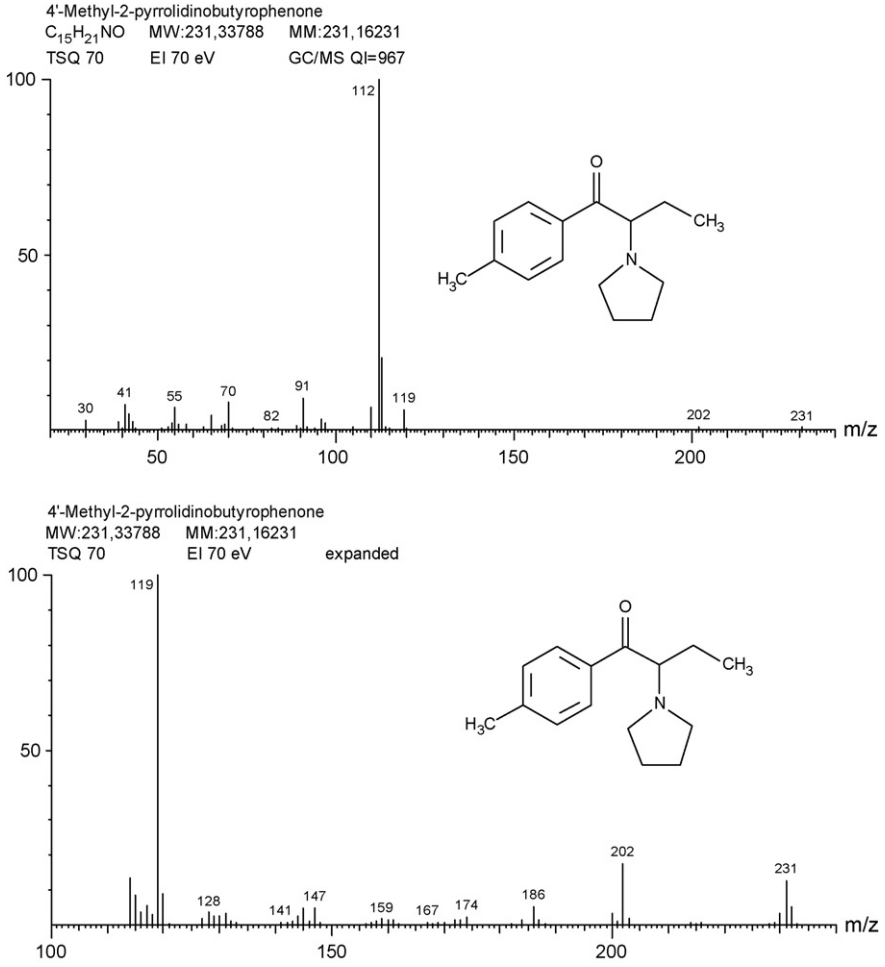


Fig. 2. EI spectra (70 eV) of MPBP (**1**).

ions. They were prepared by adding pyrrolidine or piperidine to a diethyl ether solution of the corresponding 2-bromoalkane (length of the alkyl chain more than C_3). All solvents and reagents used were of analytical grade.

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

The electron ionization (EI) mass spectra were obtained with a Finnigan TSQ 70 triple stage quadrupole mass spectrometer with a DEC-Station 2100 coupled to a Varian 3400 CX gas chromatograph.

The samples were introduced via the gas chromatograph with splitless injection using a fused silica capillary column DB1 (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 at 15 °C/min. The final temperature was held for 15 min. The injector temperature and detector temperature were 280 °C. The ion source temperature was 150 °C and carrier gas was helium.

The electron ionization energy was 70 eV with an emission current of 200 μA. The scan time was 1 s and the scan range was 30–600 Da.

The chemical ionization (CI) energy was 70 eV with an emission current of 200 μA and a source temperature of 150 °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 30–600 Da.

In the EI-MS/MS-product-ion-mode the ionization energy was 70 eV with an emission current of 200 μA. The collision gas was Argon. The collision energy was approx. 20 eV and the collision gas pressure was approx. 1.5 mTorr (0.2 Pa). The exact target-thickness [19] 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 [19].

For all mass spectrometric measurements 1 ml diluted NaOH (5% in water) and 4 ml diethyl ether were added to approx. 2 mg of the compound in a screw capped glass vial. The vial was closed and shaken for a few seconds. After separation an aliquot of the ether layer was transferred into an auto sampler vial. 1 μl was injected in the GC–MS system.

2.3. NMR spectroscopy

NMR spectra were recorded with an ARX 300 NMR (Bruker) at a resonance frequency of 300.13 MHz for ^{1}H NMR spectra and 75.47 MHz for ^{13}C NMR spectra, respectively. The ^{1}H NMR spectra were recorded using standard pulse programs. The ^{13}C NMR spectra were recorded with ^{1}H decoupling using composite pulse decoupling. Additionally ^{13}C NMR-DEPT spectra (DEPT, distortionless enhancement by polarization transfer) were recorded. As solvent perdeuterated dimethylsulfoxid was used, the concentration of substances was adjusted to approx. 10 mg/0.6 ml. Calibration of spectra was done by tetramethylsilane as internal standard or by signal of 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 absorption. For H/D-exchange one to two drops of D_2O were added to the samples followed by vigorous shaking. Samples were measured at 300 K if not stated otherwise.

3. Results and discussion

Molecular weights were confirmed by mass spectrometry after chemical ionization with methane as reagent gas. Compound **1** as well as most of all α-aminophenones analyzed so far [20,21] showed little amounts of impurities having molecular weights 2 and 4 Da lower compared to the molecular weight of the respective aminophenone.

Indirectly the α-aminophenone moiety was indicated by detection of characteristic EI mass spectra of didehydro- and

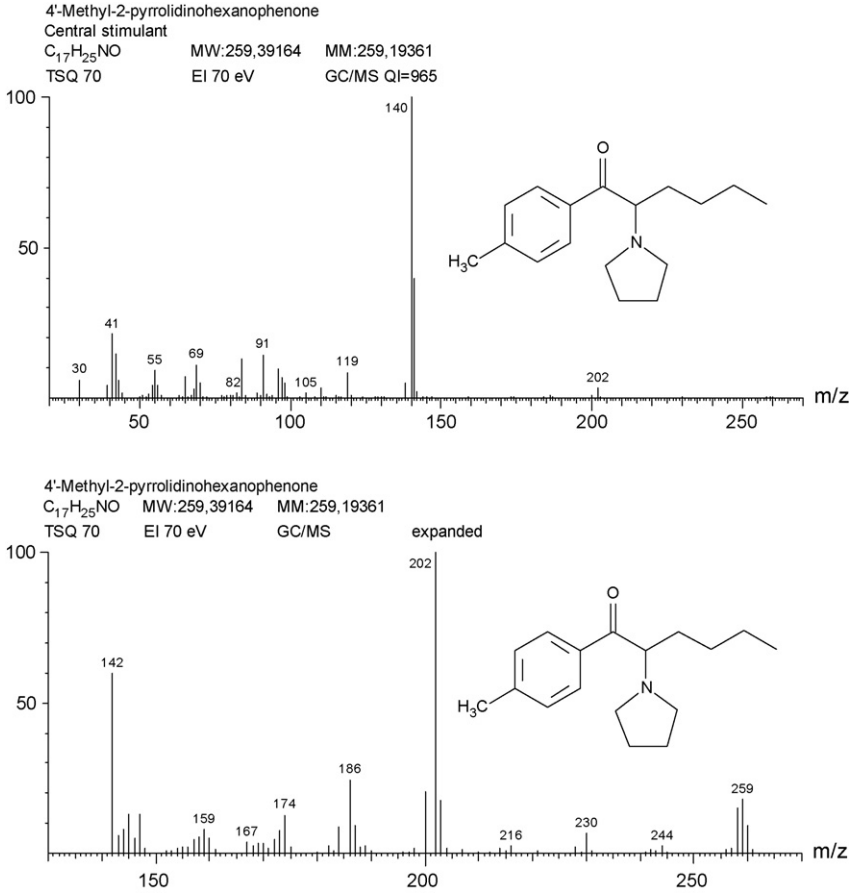
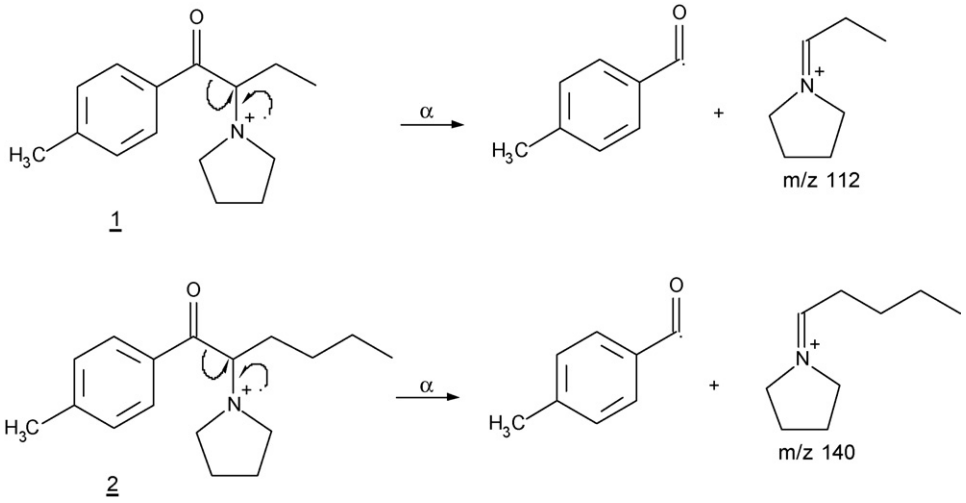


Fig. 3. EI spectra (70 eV) of MPHP (**2**).



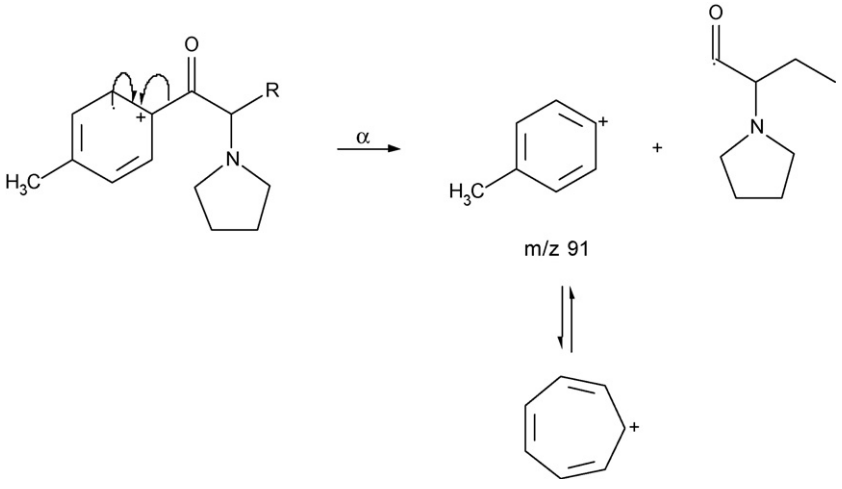
Scheme 1. Formation of the base peak in mass spectra of MPBP (**1**) and MPHP (**2**).

tetradehydro-compounds as typical by-products as well as by identification of aromatic and aliphatic fragments after hydrolysis and thermolysis. Typically, additional isobaric compounds (position isomers of the *p*-methylphenyl moiety) can be observed due to impurity of the precursor phenones. Impurities could sufficiently be separated from the respective aminophenone by chromatography.

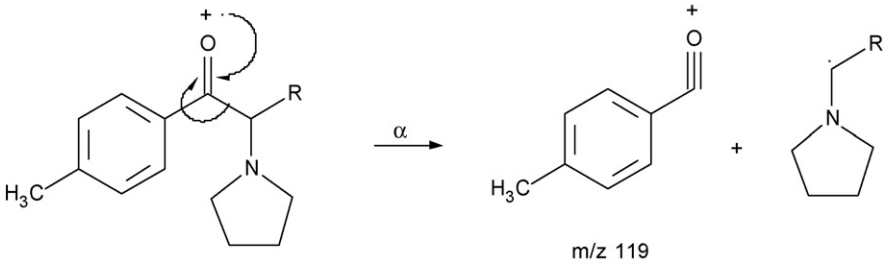
Figs. 2 and 3 show the EI mass spectra of compounds **1** and **2** as free bases and the enlarged segments of each spectrum above the base peaks.

The electron-donating ability of the nitrogen atoms in compounds **1** and **2** induce fast α-cleavage reactions (α) of the benzyl bond (Scheme 1) and produce intense immonium ions. The EI mass spectra of **1** and **2** show these immonium ions as base peaks at *m/z* 112 (**1**) and 140 (**2**).

The alternative α-cleavage reaction breaking stable alkyl bonds produces immonium ions at *m/z* 202 with low intensities by loss of an ethyl or butyl radical, respectively. Both EI spectra show M-15 σ-cleavage fragments with low intensities at *m/z* 216 and 244.



Scheme 2. Formation of fragment *m/z* 91.



Scheme 3. Formation of *p*-methylbenzoyl cations.

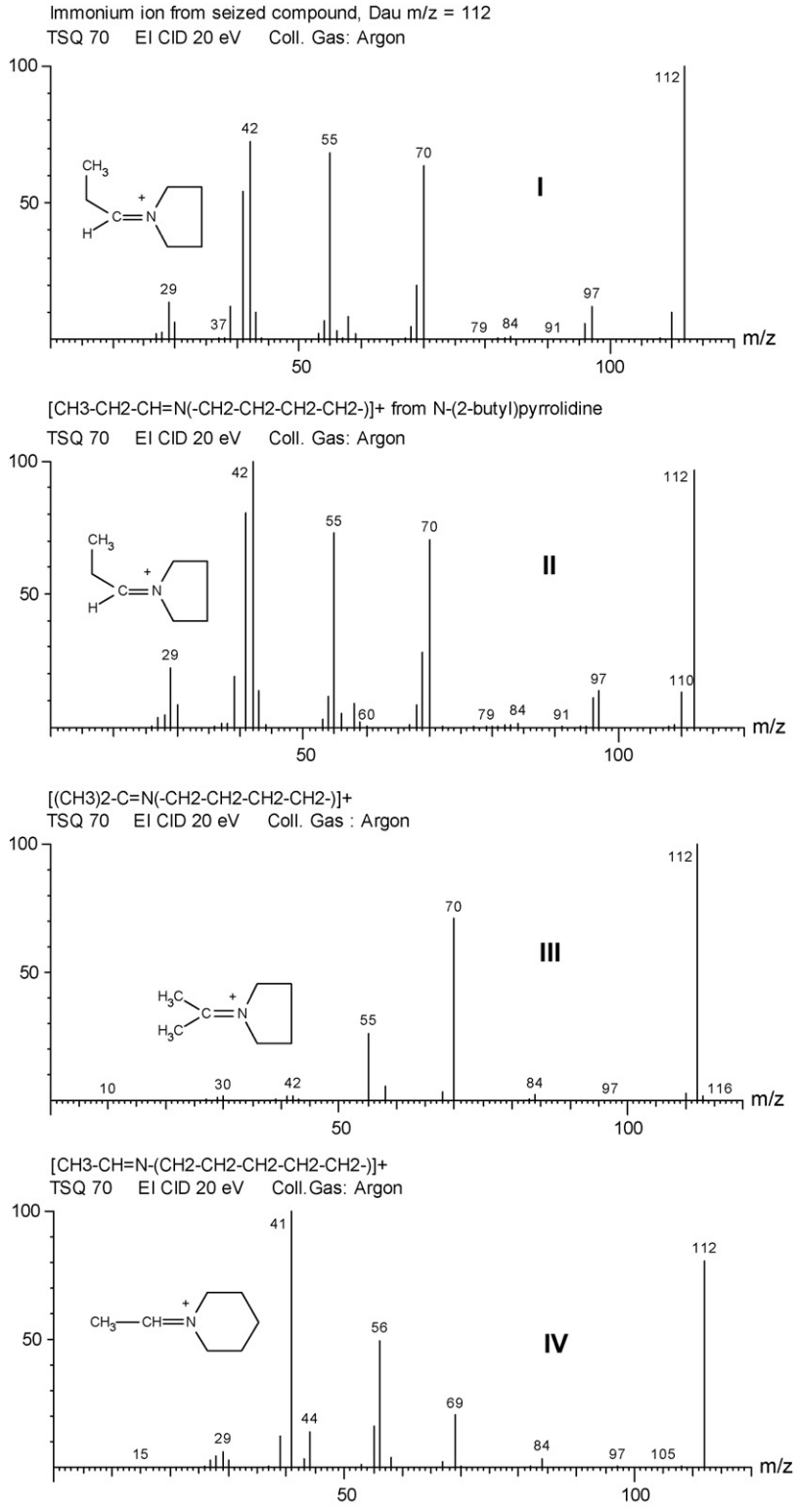
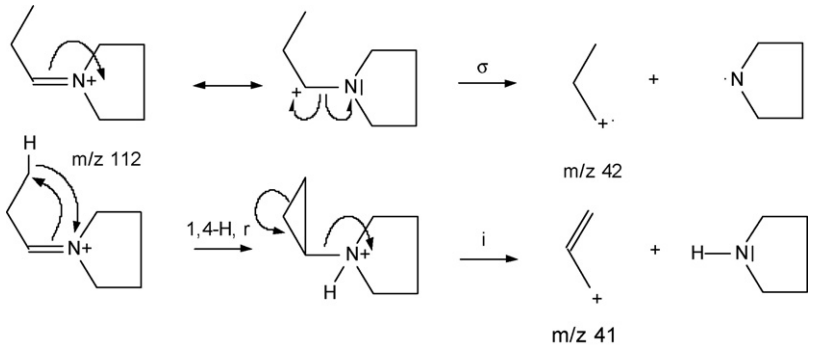


Fig. 4. Product ion mass spectra of the immonium ion from **1** and product ion library spectra.

Ionization of an aromatic π-bond with α-cleavage gives an ion at *m*/*z* 91 which arranges to the tropylium cation (Scheme 2).

Ionization at the carbonyl oxygen atom and α-cleavage reaction gives *p*-methylbenzoyl cations at *m*/*z* 119 (Scheme 3).

Discrimination between structure **1** (as an *n*-alkyl-derivative) and **3** (as a branched alkyl-derivative) was maintained by product ion mass spectrometry and NMR spectroscopy. Immonium ions up to *m*/*z* 72 can unambiguously be identified by product ion mass spectrometry [15]. Our further experiments

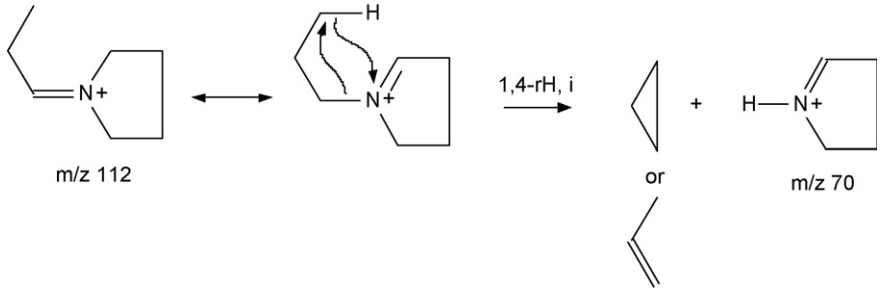


Scheme 4. Possible way for formation of exocyclic alkyl ions.

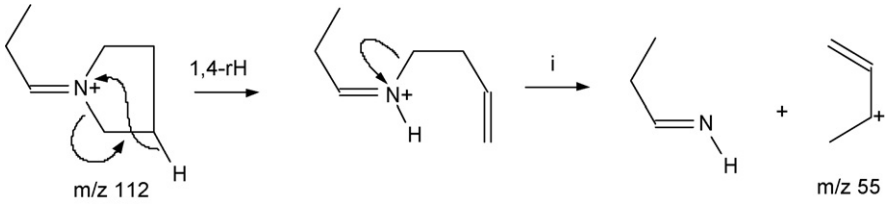
have suggested that immonium ions with greater masses can also be distinguished properly. Product ion mass spectrometry of immonium ions formed by electron ionization has successfully been applied to a number of new designer drugs to determine and differenciate structure isomerism of the alkylamino moiety of designer drugs as well as to determine the ring substitution pattern of methylenedioxy-amphetamines by examination of the homobenzyl cations formed after chemical ionization [15–17,22–26].

Fig. 4 shows the product ion mass spectrum of the immonium ion with *m/z* 112 originating from compound **1** (Fig. 4, I) and some isomeric product ion mass spectra from our database. The product ion spectrum of the suspect compound shows a very good agreement with the product ion spectrum of the immonium ion prepared from 2-pyrrolidinobutane (Fig. 4, II). Little differences in internal energies of the identical immonium ions generated from different precursor compounds may explain the small intensity differences in the product ion spectra I and II (Fig. 4).

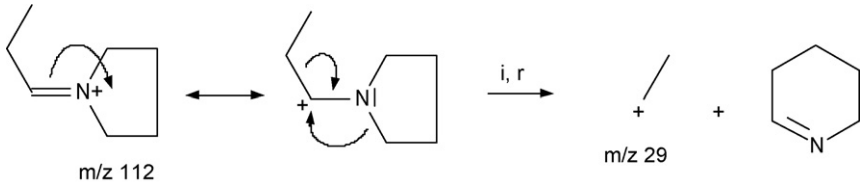
Product ion spectrum of the suspect compound (Fig. 4, I) and product ion spectrum of the immonium ion prepared from 2-pyrrolidinobutane (Fig. 4, II) show a base peak product ion with the mass of an propyl radical cation at *m/z* 42 by loss of a pyrrolidino radical violating the even electron rule [27]



Scheme 5. Possible way for formation of the pyrrolidinium cation at *m/z* 70.



Scheme 6. Possible way for formation of the homoallylic cation at *m/z* 55.



Scheme 7. Possible way of ethyl loss by inductive cleavage with charge migration.

(Scheme 4). During the CID process internal energies of about 2–5 eV are added to the immonium ion leading to reaction pathways that are not so common in conventional mass spectrometry [15–17]. Loss of pyrrolidine leads to an intense allylic cation at *m/z* 41 by a rearrangement (r) via 1,4-hydrogene-shift (1,4-rH) followed by an inductive cleavage (i). These inductively driven charge migration processes represent the exocyclic alkyl moiety of the immonium ions (Fig. 4, I and II).

The inductively driven loss of propene (or the isobaric cyclopropane) with charge retention at the nitrogen on the other hand generates a pyrrolidinium cation at *m/z* 70 (Scheme 5).

This ion can also be found in other isobaric pyrroloimmonium ions like the dimethyl pyrroloimmonium ion (Fig. 4, III) and seems to be an indicator of the pyrrolidino partial structure.

The elimination of the exocyclic substituent including the nitrogen atom generates an ion with the mass of a homoallylic cation at *m/z* 55 (Scheme 6) which represents the endocyclic carbon chain of the pyrrolidine-ring.

A loss of a methyl radical generates a radicalic immonium ion at *m/z* 97 violating the even electron rule. The ethyl ion at *m/z* 29 can be generated by an inductive cleavage process (i) with carbon framework rearrangement (r) and charge migration (Scheme 7) and seems to be an indicator of an ethyl group. Isobaric immonium ions with an isopropyl pyrrolidino structure (Fig. 4, III) do not show this fragment.

The similarity between the product ion spectrum of the unknown (Fig. 4, I) and the product ion spectrum of the immonium ion generated from *N*-(2-butyl) pyrrolidine (Fig. 4,

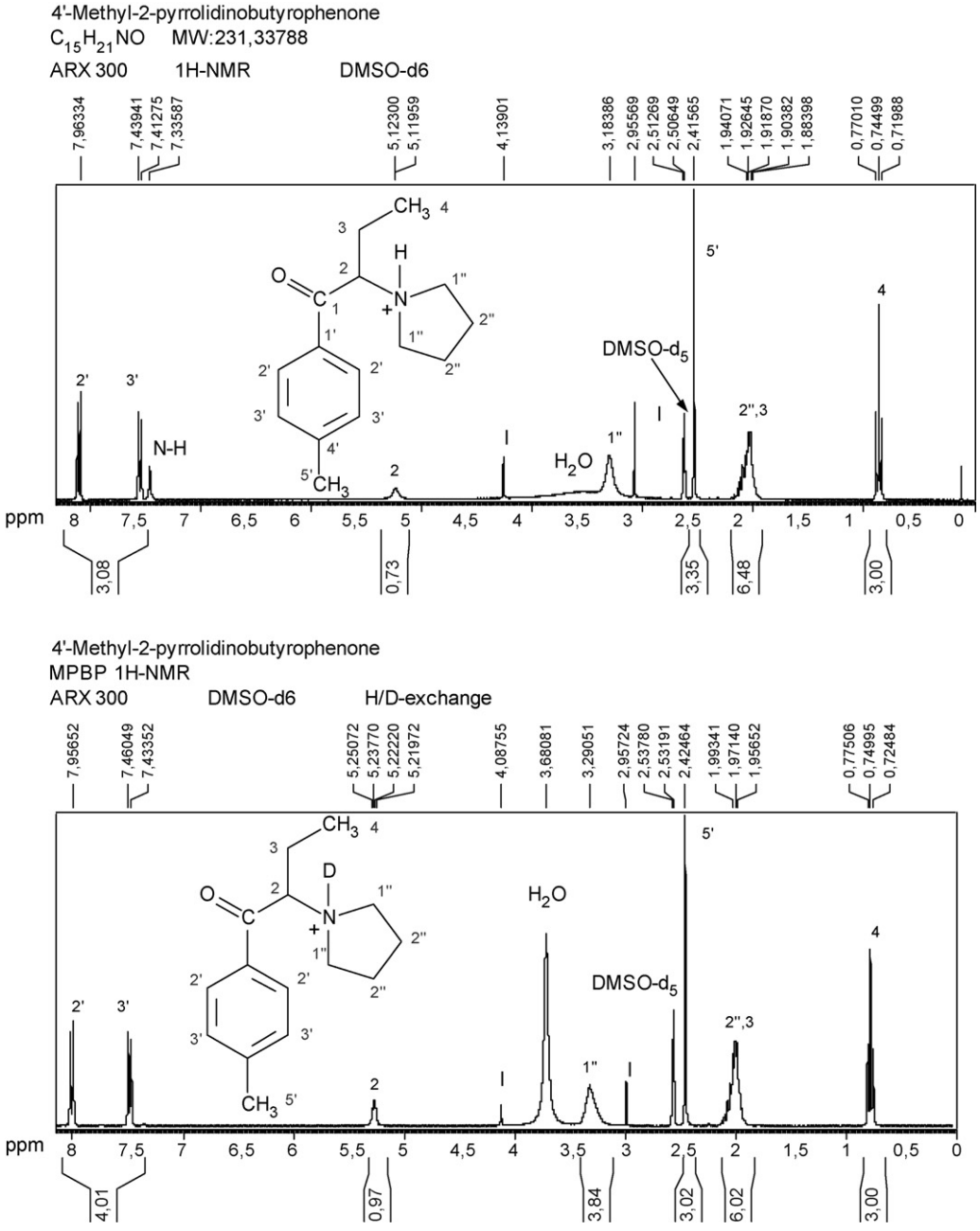


Fig. 5. ^{1}H NMR spectra (inferior: after D_2O exchange) of MPBP in the existing salt form.

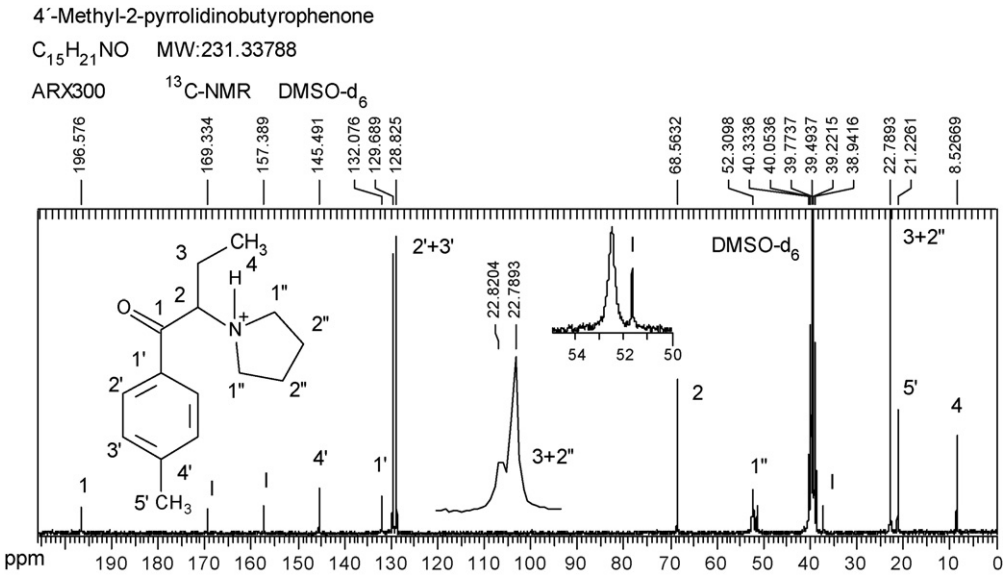


Fig. 6. ^{13}C NMR spectrum of MPBP in the existing salt form.

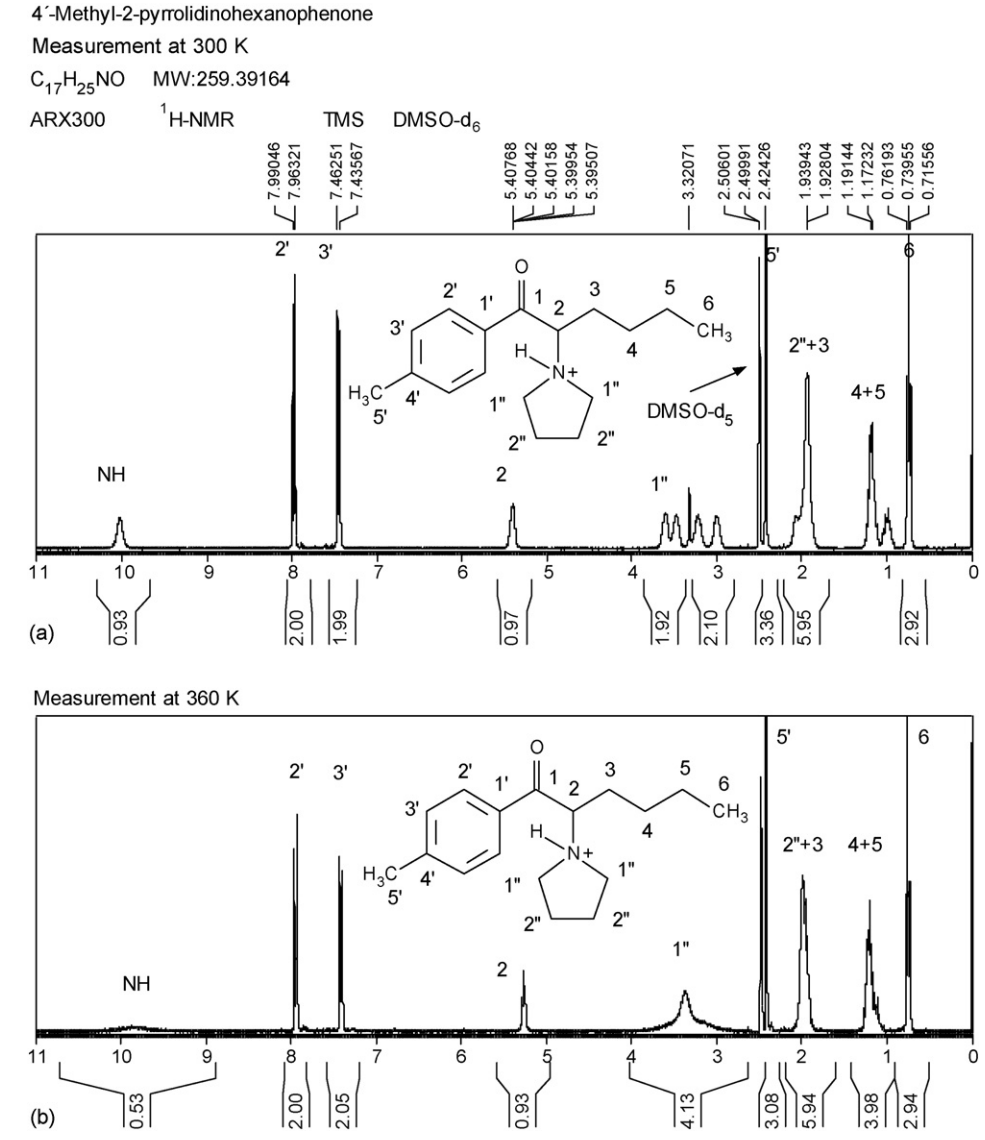


Fig. 7. (a and b) ^{1}H NMR spectra of MPHP at 300 and 360 K in the existing salt form.

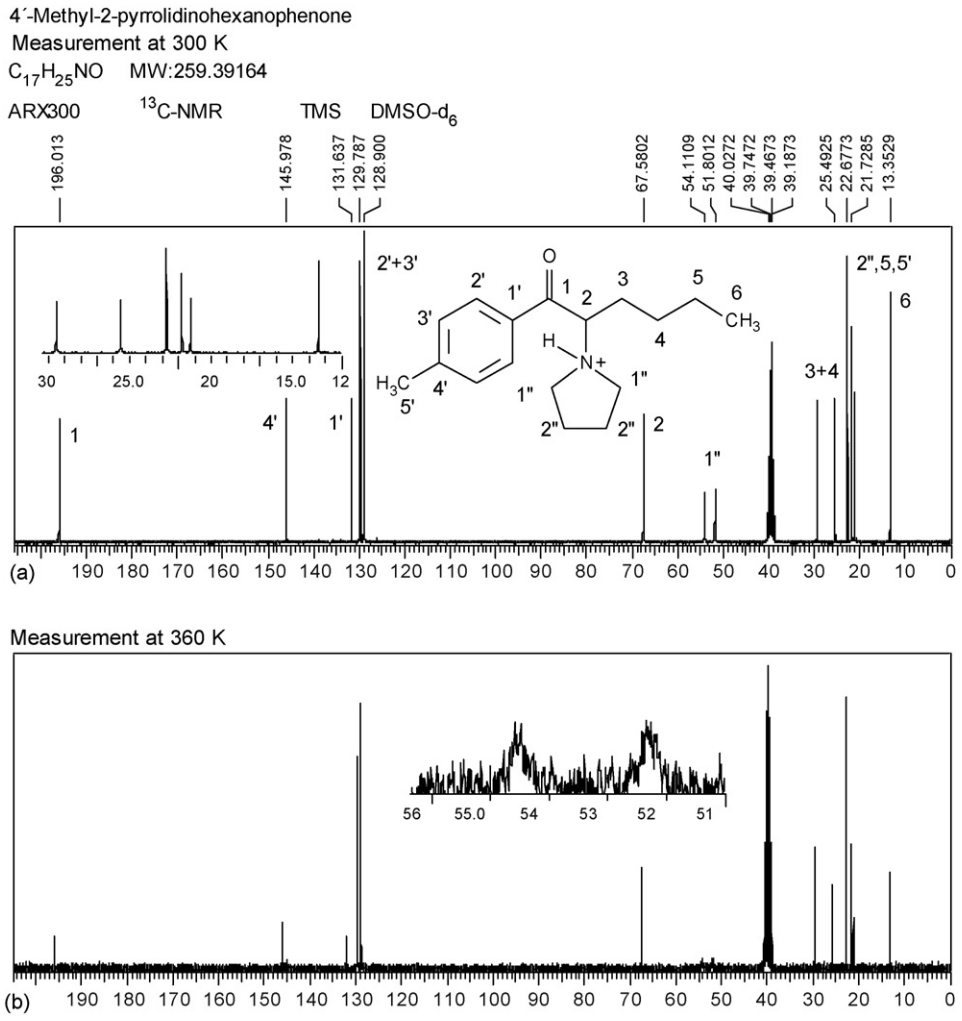


Fig. 8. (a and b) ^{13}C NMR spectra of MPHP at 300 and 360 K in the existing salt form.

II) as well as the finding of all logical endo- and exocyclic fragments recommend the unknown immonium ion at *m/z* 112 (Fig. 4, I) to have the structure of an ethylpyrroloimmonium ion (Fig. 4, II). This originates from the *n*-propylpyrrolidino partial structure of **1**. It is obvious that the immonium ion of the seized compound cannot originate from the branched *N*-pyrrolidinyl- (Fig. 4, III) or from the homologous *N*-piperidinyl-derivative (Fig. 4, IV) because the product ion mass spectra are very different compared to that of the seized compound.

Because not all product ion mass spectra of the isomeric immonium ions with 112 Thomson exist in our database [28] yet additional NMR spectroscopy has been carried out (Figs. 5 and 6). Although spectra showed little signals of impurities (I) [originating from by-products] the structure of **1** could nevertheless be deduced properly.

^{1}H NMR of compound **1** in the existing salt form after D_2O exchange (Fig. 5 inferior) shows the broad signal of the methinic proton on C-2 (1H) at 5.23 ppm and the triplet of the methyl group on C-4 at 0.745 ppm (3H). The multiplet of methyleneprotons H-1″ of the pyrrolidine-ring appears at 3.29 ppm (4H). The multiplet at 1.97 ppm (6H) can be related to methyleneprotons H-2″ of pyrrolidine-ring and the methyleneprotons H-3 of the alkyl side chain. Aromatic protons H-2′ and H-3′ appear as characteristic doublets at 7.96 and 7.45 ppm (4H), respectively and clearly confirm the *para*-substitution pattern in the aromatic ring. The *p*-methyl group of the aromatic substructure gives a singlet (3H) at 2.42 ppm.

In ^{13}C NMR of **1** in the existing salt form (Fig. 6) signals of carbon atoms can be related as follows using the chemical shifts and the results of a DEPT spectrum: carbonyl-carbon C-1 at 196.6 ppm, aromatic carbons C-1′, C-2′/C-3′, and C-4′ at 132.1, 129.7/128.8, and 145.5 ppm, respectively; carbon of the methyl group C-5′ at the aromatic ring at 21.2 ppm; carbons C-1″ and C-2″ of pyrrolidine moiety at 52.3 ppm (broadened signal effected by diastereotopy of carbons 1″, perhaps this phenomenon is due to decelerated inversion at the protonated pyrrolidine-nitrogen) and 22.8 ppm, respectively; the secondary carbon C-2 at 68.6 ppm and carbon atoms of the aliphatic side chain C-3 and C-4 at 22.8 and 8.53 ppm, respectively.

The coupling-pattern of H-2 and H-4 as well as the identification of carbon atoms C-2, C-3 and C-4 via the ^{13}C DEPT spectrum clearly prove the unbranched aliphatic side chain of compound **1**.

Fig. 7 shows ^{1}H NMR spectra of 4′-methyl-pyrrolidinohexanophenone **2** at 300 and 360 K. Besides the doublets of the aromatic protons H-2′ and H-3′ at 7.98 and 7.45 ppm,

respectively, the triplet of the methinic proton H-2 at 5.40 ppm, the singlet of the 5′-methyl group at 2.42 ppm, the pyrrolidine protons H-2″, and the methylene protons H-3 at 1.93 ppm as broad multiplet additionally two signals of the methylene protons H-4 and H-5 from the aliphatic side chain appear at 1.17–1.01 ppm as broadened signals. Remarkable is the widely separated signal group of the methylene protons H-1″ neighbouring the nitrogen atom in the pyrrolidine ring at 3.63–3.01 ppm caused by the diastereotopic properties of these protons (Fig. 7a). These separated signals confluence to a broad signal at a temperature of 360 K (Fig. 7b), showing that a higher flexibility of the molecule at raised temperature suspends the diasterotopic property of the methylene protons H-1″.

The higher degree of diasterotopic property of methylene protons in the pyrrolidine ring of compound **2** compared to MPBP (**1**) becomes obvious too considering the signals of carbon atoms C-1″ in the ^{13}C NMR spectrum of MPHP (**2**) (Fig. 8): in contrast to MPBP (**1**) signals of the two carbons C-1″ at 54.1 and 51.8 ppm are well separated (Fig. 8). The reasons for this phenomenon may be steric effects caused by the longer aliphatic side chain in compound **2**. All other carbon atoms can be related as shown in Fig. 8 comparing the values of the chemical shifts and the results of a DEPT spectrum.

4. Conclusion

The structures of two new designer drugs MPBP and MPHP have been elucidated by mass spectrometry and NMR spectroscopy. Some interesting aspects in the NMR spectra of MPHP due to possible diastereotopic effects have been reported. The structure elucidation of the aliphatic side chain of MPBP has been carried out by product ion spectrometry of the immonium ion formed after electron ionization assisted by NMR spectroscopy. Again product ion spectroscopy of immonium ions proved to be a powerful tool to determine the structure of designer drugs and to distinguish between isobaric structures of the alkyl-amino moiety.

All seized phenethylamine derivatives with an α-aminophenone substructure having appeared as designer drugs [14,20,21] on the illegal German market so far can be related to one offender living in Hesse. The identical origin was supported by hints of criminal investigation, the individuality of this substance-class and their occurrence in the rare salt form of nitrate. Another portion of the designer drug **1** (obviously MPBP·HNO_3) combined with amphetamine and caffeine was seized almost at the same time in Northern Bavaria at a drug dealer living in the nearby state of Hesse.

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