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Structure elucidation of a new designer benzylpiperazine: 4-Bromo-2,5-dimethoxybenzylpiperazine

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ABSTRACT

A new designer benzylpiperazine was seized in Germany for the first time. Interpreting the results of gas chromatography–mass spectroscopy (GC–MS), product ion spectroscopy (GC–MS/MS), and nuclear magnetic resonance (NMR) spectroscopy the compound was 4-bromo-2,5-dimethoxybenzylpiperazine. The structure of the new benzylpiperazine was finally proved by two-dimensional NMR correlations and by GC–MS after synthesis of two of the possible isomers from commercially available starting materials. Additionally mass spectroscopic data after liquid chromatography–mass spectroscopy (LC–MS/MS) using electrospray ionization (ESI) as well as ultraviolet (UV) spectral data of the new compound are presented. A small quantity of the new benzylpiperazine was seized in very high purity along with other also very pure designer drugs in Hamburg, Germany.

1. Introduction

In a set of seized compounds with 56 substances a great number of vessels with partly small amounts of, however highly pure, compounds were seized at a suspect premises in 2006 by the Landeskriminalamt (LKA) Hamburg. These compounds represented some interesting designer tryptamines and the first seizures of the dihydrofuran annelated phenethylamine Fly (**1**) and the difuran annelated amphetamine Bromodragon-Fly (**2**) in Germany (Fig. 1). The compounds **1** and **2** have already been described [1–3]. The handwritten labels of any of the vessels were correct in almost all cases in regard to the results of the analyses.

Among the confiscated objects a small vial containing approximately 60 mg of a grey powder was found labeled "Br-BZP" indicating a benzylpiperazine containing bromine (compound **3**). The structure elucidation of **3** by means of GC–MS, GC–MS/MS, and NMR-spectroscopy is described and some analytical data of one of its isomers and some derivatives as well as UV data and mass spectroscopic data after liquid chromatography (LC–ESI/MS/MS) are presented in the following.

From the piperazines benzylpiperazine (BZP), 1-(4-fluorophenyl)piperazine (pFPP), 1-(3-trifluoromethyl)piperazine (TFMPP), 1-(2-methylphenyl)piperazine (oMePP), 1-(3-methylphenyl)piperazine (mMePP), 1-(4-methylphenyl)piperazine (pMePP), 1-(2-chlorophenyl)piperazine (oCPP), 1-(3-chlorophenyl)piperazine (mCPP), 1-(4-chlorophenyl)piperazine (pCPP), 1-(2-methoxyphenyl)piperazine (oMeOPP), 1-(4-methoxyphenyl)piperazine (pMeOPP), 1,4-dibenzylpiperazine (DBZP) (Fig. 2) only BZP and mCPP are scheduled in Germany at present. Benzyl- and phenylpiperazines, and especially combinations of them act physiologically like the ecstasy amphetamines [4,5].

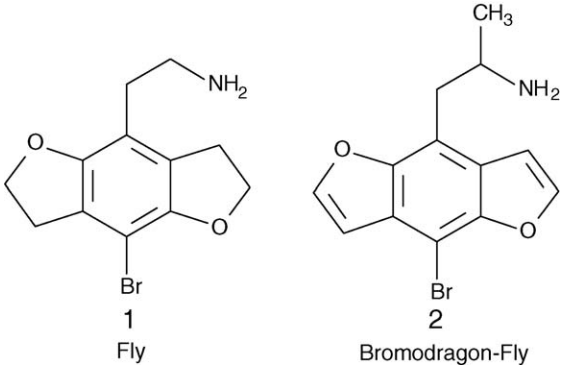

Fig. 1. Structures of Fly (**1**) and Bromodragon-Fly (**2**).

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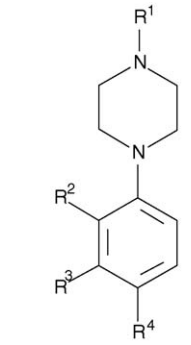
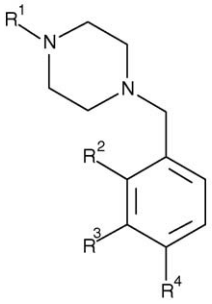


Compound	R^1	R^2	R^3	R^4
pFPP	H	H	H	F
TFMPP	H	H	CF_3	H
oMePP	H	CH_3	H	H
mMePP	H	H	CH_3	H
pMePP	H	H	H	CH_3
oCPP	H	Cl	H	H
mCPP	H	H	Cl	H
pCPP	H	H	H	Cl
oMeOPP	H	OCH_3		
pMeOPP	H	H	H	OCH_3



Compound	R^1	R^2	R^3	R^4
BZP	H	H	H	H
DBZP	Benzyl	H	H	H

Fig. 2. Structures of already known phenyl- and benzyl-piperazines.

2. Materials and methods

A sample of approximately 20 mg of the seized grey powder was provided for the analysis by the LKA Hamburg. All chemicals and solvents were purchased in a p.a. quality.

2.1. GC–MS-analysis

2.1.1. 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.

2.1.2. 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.

2.1.3. 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

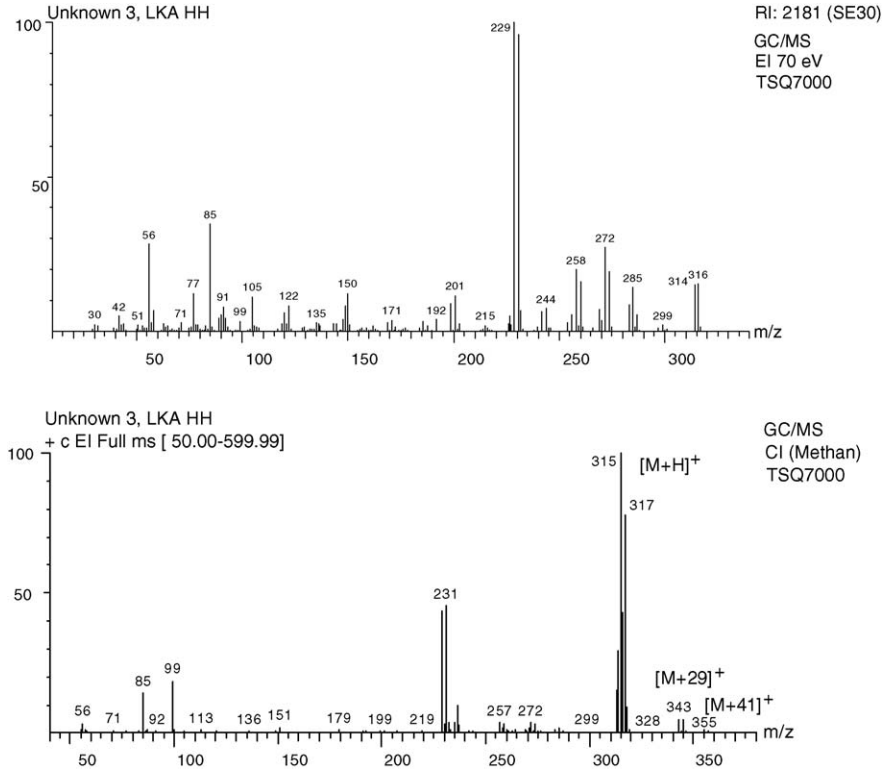


Fig. 3. GC–MS spectra of compound **3** after EI (top) and CI (bottom).

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.

2.1.4. MS parameters

The electron ionization 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 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 [6] was set using *n*-butyl benzene and adjusting the 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. This ensured the reproducibility of the product ion mass spectra and the usability of a product ion mass spectra library for the identification of the product ions structure [7].

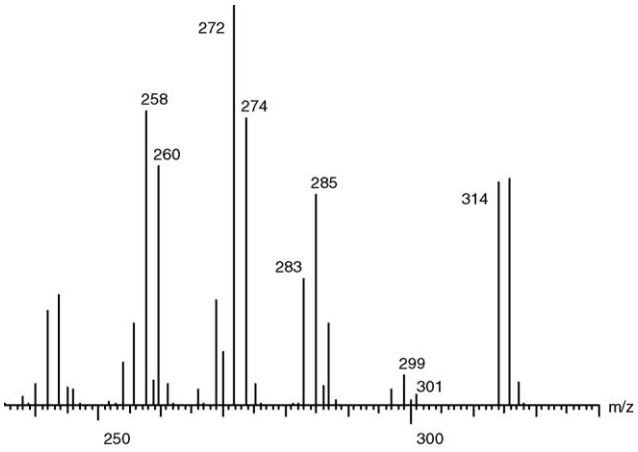


Fig. 4. Extended molecular mass region of the EI spectrum of compound **3**.

2.2. ^{1}H and ^{13}C NMR analysis

NMR-spectra were recorded with an Avance III 300 NMR spectrometer (Bruker) at a resonance frequency of 300.13 MHz protons and 75.47 MHz for ^{13}C-atoms 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 dimethylsulfoxide was used with a concentration of 2.3 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). The samples were measured at 300 K.

For structure elucidation gradient selected C,H-correlations (HMQC (Heteronuclear Multiple Quantum Coherence) and HMBC (Heteronuclear Multiple Bond

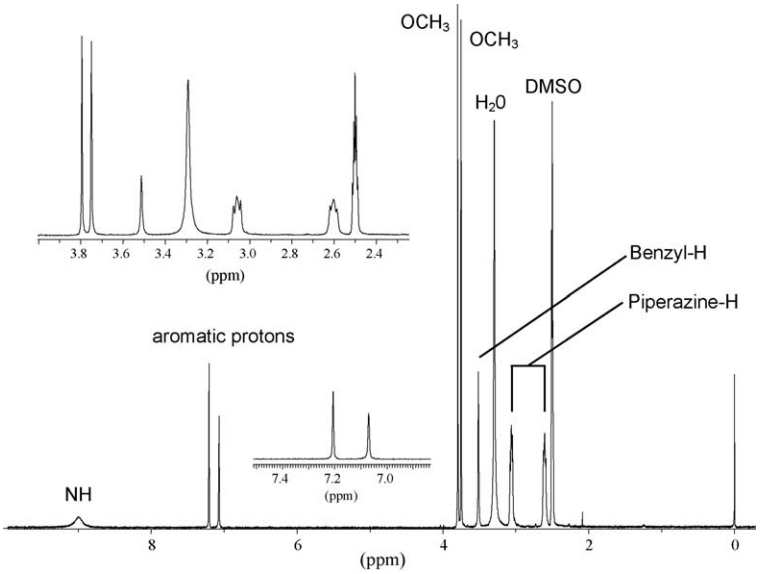


Fig. 5. ^{1}H NMR spectrum of compound **3** and extended parts of it.

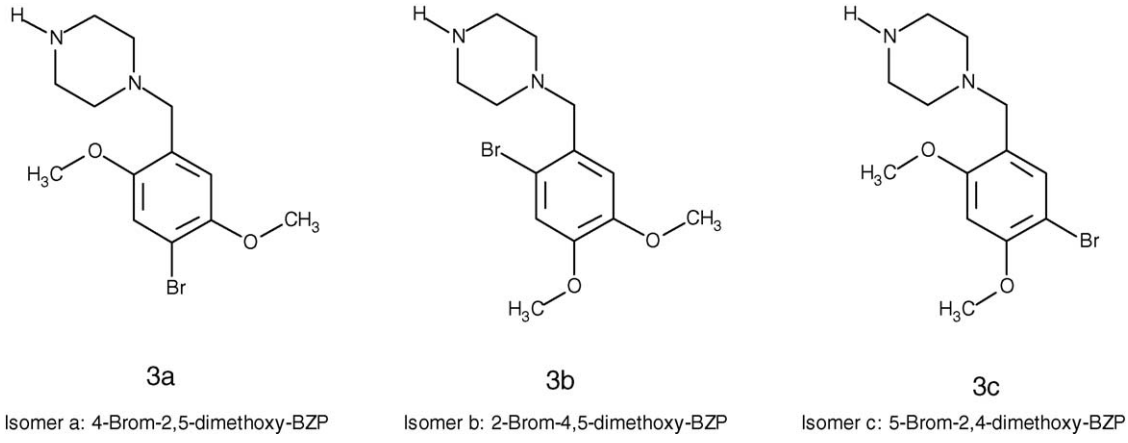


Fig. 6. Possible structures for compound **3** (BZP = benzylpiperazine).

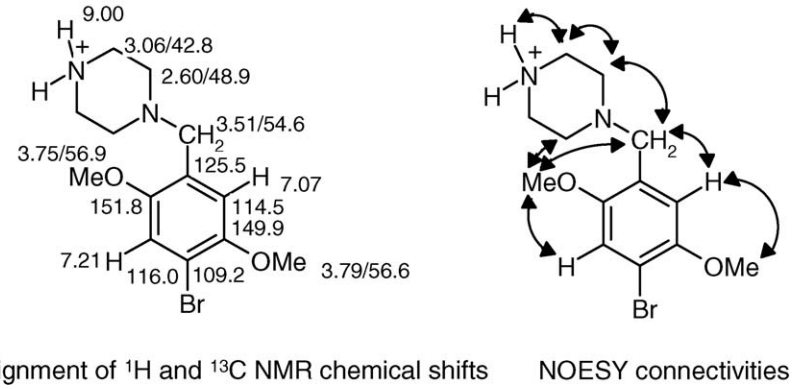


Fig. 7. Assignment of ^{1}H and ^{11}C NMR data and important cross signals in the two-dimensional $^{1}H,^{1}H$-NOESY spectrum of **3a**.

Correlation)) as well as H,H-long-range correlations (by Correlated Spectroscopy (COSY), delay 250 ms) and dipole–dipole-interactions through space (by Nuclear Overhauser Effect Spectroscopy (NOESY), delay 1.8 s) were recorded using the manufacturer's pulse programs.

2.3. LC–MS/MS analysis

2.3.1. Sample preparation

A solution of the powder with a concentration of 9.55 μg/mL in methanol was prepared. This was used to optimize the ionization and detection conditions for mass spectrometric measurement. For analysis after chromatographic separation a diluted solution of 95.5 ng/mL was used. Five microlitres of this extract were injected by partial loop technique on the column.

2.3.2. Equipment

The mass spectra were obtained with a LC–MS-system consisting of a Surveyor HPLC with a Surveyor Autosampler Plus coupled with a Surveyor PDA Plus detector and a LCQ Deca XP Max ion trap mass spectrometer (each produced by Thermo-Finnigan).

2.3.3. LC parameters

For separation an AQUA C18-column (Phenomenex, length 150 mm × 2 mm, particle size 3 μm, pore volume 125 Å) with an AQUA precolumn (Phenomenex, 4 mm × 2 mm) was used. The column temperature was held at 30 °C. The mobile phase was an isocratic solution consisting of 30% A (50 mM ammonium acetate buffer, pH 5) and 70% B (methanol) with a flow rate of 100 μL/min. Under these conditions 4-bromo-2,5-dimethoxybenzylpiperazine elutes at 6.54 min.

2.3.4. Photodiode array (PDA) parameters

The scan range was 200–600 nm with a scan bandwidth of 1 nm and a scan rate of 5 Hz.

2.3.5. MS parameters

To generate the protonated molecular ion (pseudo molecular ion) electrospray ionization (ESI) was used in the positive mode with following parameters: sheath gas flow rate 80 au (arbitrary units), aux gas flow rate 15 au, spray voltage 5 kV, capillary temperature 230 °C, capillary voltage 15 V. The gas used was nitrogen.

Five scan events were processed continuously: a full ms scan with a scan range of m/z = 50–500, a full ms scan with a scan range of m/z = 90–500 after collision induced dissociation (CID) of the fragment with m/z = 314.9 (MS^2 of the pseudo molecular ion of **3**), a full ms scan with a scan range of m/z = 60–500 after CID of the fragment with m/z = 228.9 from m/z = 314.9 (MS^3 of the pseudo molecular ion of **3**), a full ms scan with a scan range of m/z 55–500 after CID of the fragment with m/z = 200.8 from m/z = 228.9 from m/z = 314.9 (MS^4 of the pseudo molecular ion of **3**), and a full ms scan with a scan range of m/z 50–500 after CID of the fragment with $m/$

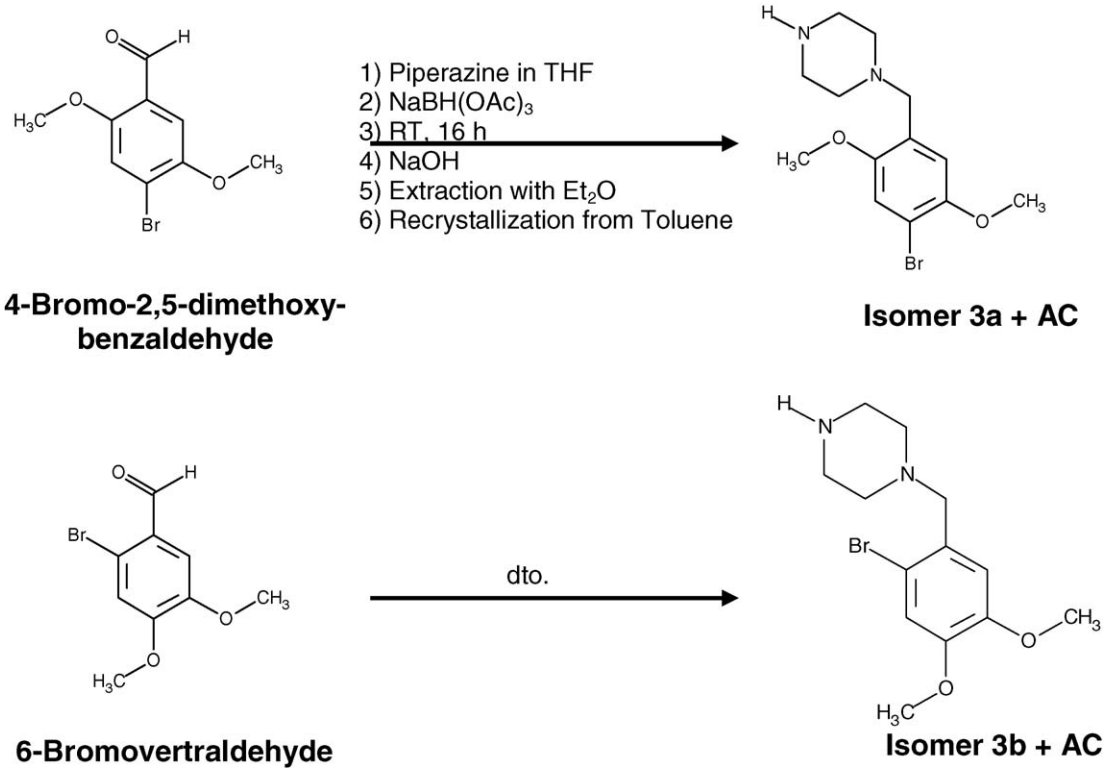


Fig. 8. Synthetic routes for the isomers **3a** and **3b**, AC = acetate.

z = 149.9 from m/z = 228.9 from m/z = 314.9 (MS^4 of the pseudo molecular ion of **3**). The collision energies used for the MS^n experiments were adjusted in that way that the parent ion in the product ion spectra had an intensity of $\leq$10% relative to the base fragment. The collision energies ranged from 25 to 29% of the normalized collision energy. The isolation width was set to 1.0–1.2 amu. The collision gas was helium.

2.4. Synthesis of the two isomers 3a and 3b

For the synthesis of the two isomeric benzylpiperazines 4-bromo-2,5-dimethoxybenzylpiperazine (**3a**) and 2-bromo-4,5-dimethoxybenzylpiperazine (**3b**) the aldehydes 4-bromo-2,5-dimethoxybenzaldehyde (Apollo Scientific Intermediates for Research and Development, Bredbury, UK) and 6-bromoveratraldehyde (Sigma–Aldrich) were stirred at room temperature under nitrogen with piperazine and sodium triacetoxyborohydride in THF analogous to Abdel-Magid et al. [8]. After an alkaline hydrolysis the free bases as well as the acetates and the dimers arising as by-products were extracted with diethyl ether. The evaporation residue was purified by recrystallization from toluene. The recrystallization product was subjected to GC–MS analysis. The yields of the products were not determined.

MS data and UV data processing, analysis and visualization were made with Chemograph Plus [9].

3. Results and discussion

3.1. First results of GC–MS and GC–MS/MS analyses

In Fig. 3 the GC–MS spectra of compound **3** after electron ionization (EI) (at the top) and after chemical ionization (CI) (at the

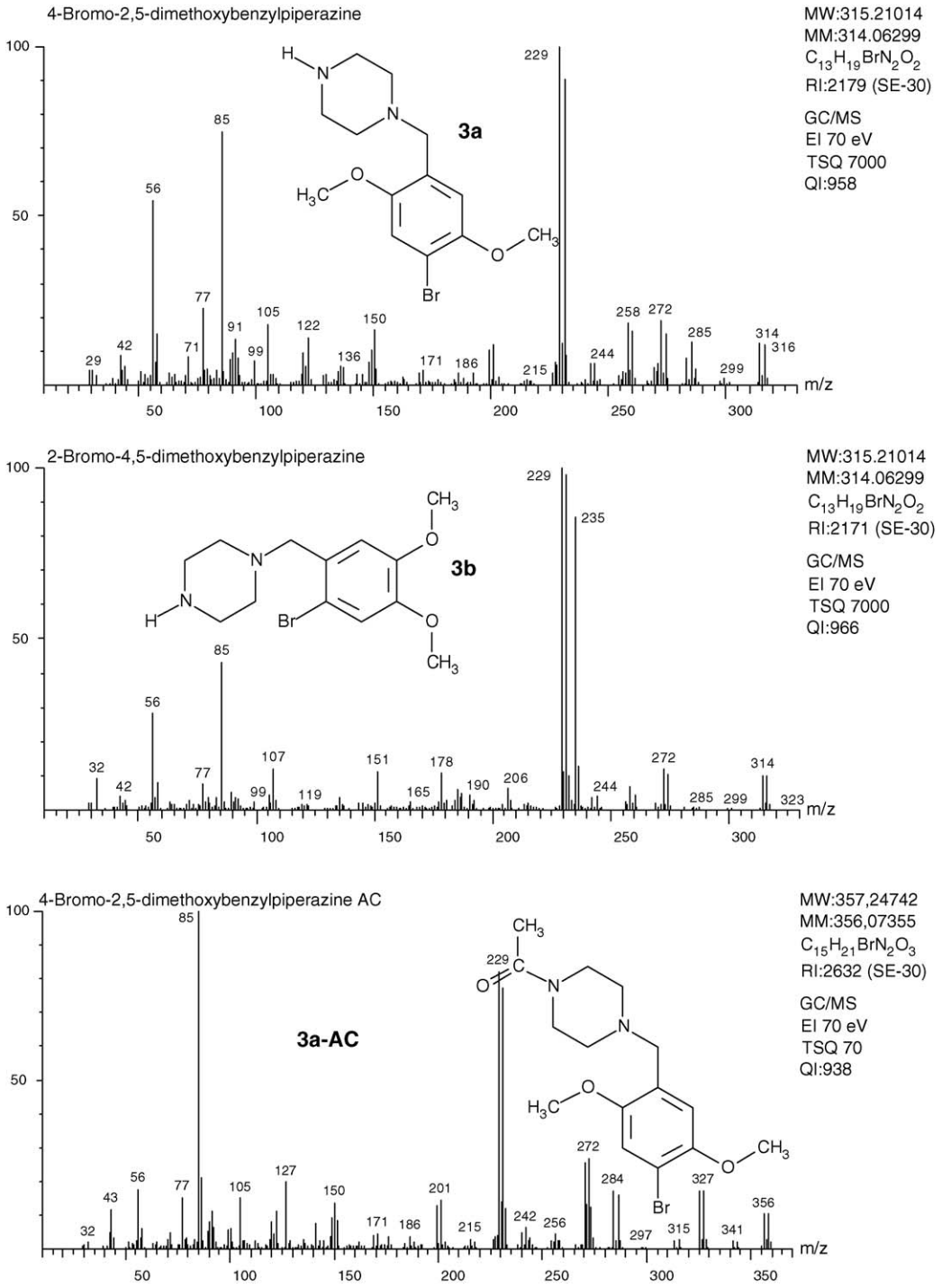


Fig. 9. GC–MS spectra (EI, 70 eV) of the isomers **3a** and **3b**, their acetates (**3a-AC** and **3b-AC**), and both of the bis(bromodimethoxybenzyl)piperazines (**Bis-3a** and **Bis-3b**).

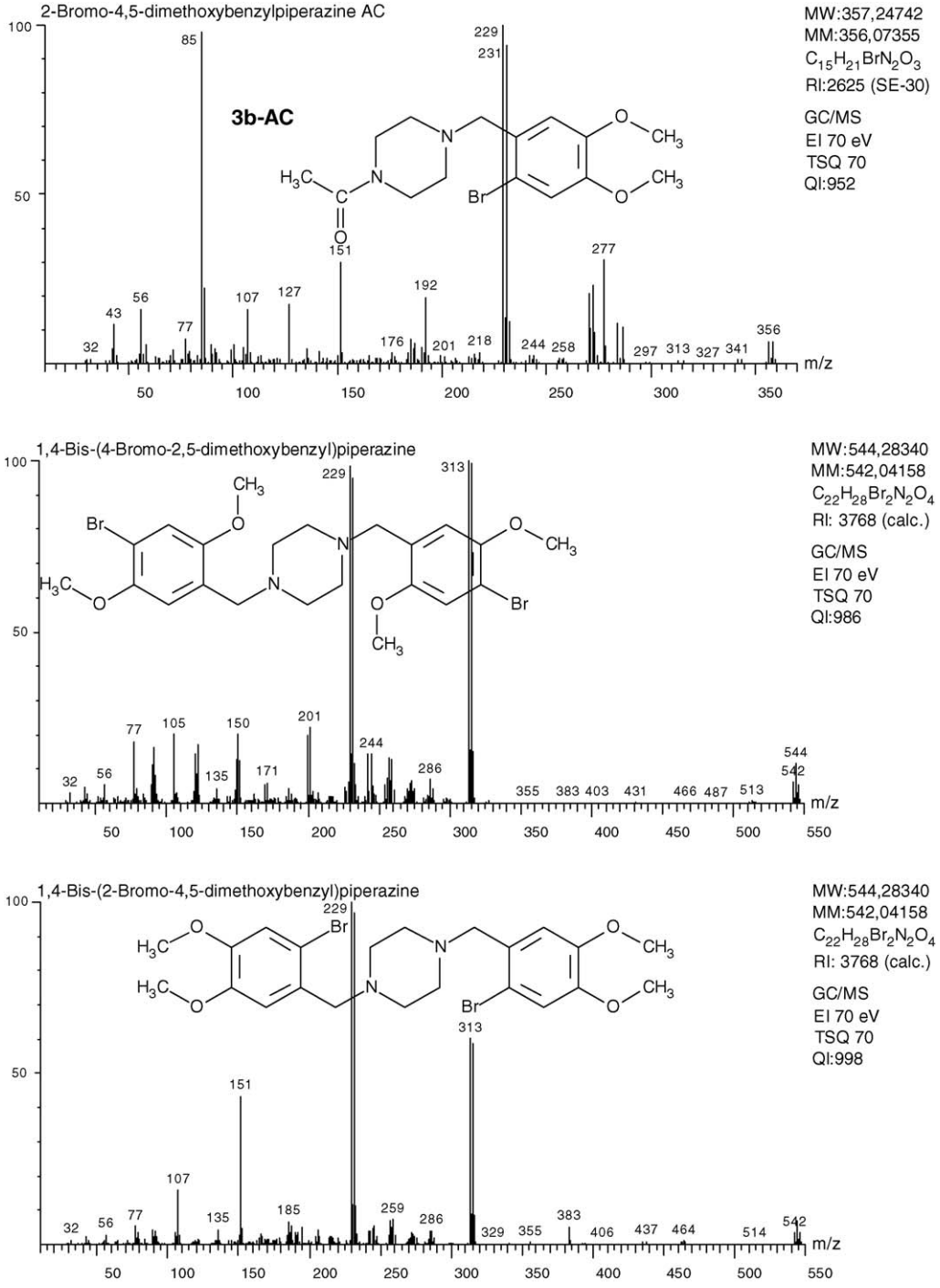


Fig. 9. (*Continued*).

bottom) are shown. The isotope cluster of the highest mass fragments confirmed the presence of a bromine atom in the compound. The CI spectrum confirmed a molecular weight of 315 Da. Concerning the presence of one bromine atom an even number of nitrogen atoms in the molecule therefore had to be concluded.

After electron ionization (Fig. 3 at the top) the molecule loses a part with the mass of 85 Da and forms intensive fragments at $m/z = 229$ and 231 preserving the bromine atom in the fragments. The complementary fragment with $m/z = 85$ with a loss of the bromine containing part of the molecule is also formed. This fragment and the fragment split off could probably be a piperazine ring. A product ion spectroscopic examination of this fragment confirmed this assumption. The product ion spectrum of the fragment with $m/z = 85$ of compound **3** was identical with that of the mass $m/z = 85$ of piperazine after electron ionization. Furthermore fragments with $m/z = 99$ are present in the EI and CI spectra – probably caused by a piperazinyl cation with an additional methylene group. This indicated the presence of a benzylpiperazine moiety. This was consistent with the hint given by the label of the vessel. A mass balance yielded a difference of 60 Da (molecular mass = 315 Da, bromine = 80 Da, piperazinyl moiety = 85 Da, benzyl moiety with one substituent = 90 Da).

In Fig. 4 the molecular mass region of the EI spectrum of compound **3** is presented in extended format.

One recognizes a loss of 15 Da (methyl radical) forming bromine containing fragments with $m/z = 299$ and 301 as well as losses of a molecule with $m/z = 29$ Da (forming bromine containing fragments with $m/z = 285$ and 287) and 31 Da (forming bromine containing fragments with $m/z = 283$ and 285) respectively. The loss of $m/z = 29$ can be assigned to a formaldehyde radical. The loss of $m/z = 31$ can be assigned to a methoxy radical. In summary, these fragmentation pathways indicate the presence of one or more methoxy group(s) in the unknown compound. Two methoxy groups would fit to the above mentioned mass deficit of 60 Da. Therefore a trisubstituted bromobenzylpiperazine had to be considered as a possible structure for the unknown compound **3**.

3.2. NMR spectroscopic results

According to the ^{1}H NMR spectrum compound **3** actually is a bromodimethoxybenzylpiperazine (Fig. 5). The following signals were detected: The protons of the piperazine ring at 2.60 ppm (4H, triplet (t)) and 3.06 ppm (4H, t), the benzylic protons at 3.51 ppm (2H, singlet (s)), the protons of the methoxy groups at 3.75 ppm (3H, s) and 3.79 ppm (3H, s), the two aromatic protons at 7.07 ppm (1H, s) and 7.21 ppm (1H, s), and the protons of the protonated amino group of the piperazine ring at 9.00 ppm (2H, broad s). The benzylpiperazine contains obviously two hydrogen atoms in para-position in the aromatic ring, since no coupling can be seen between the two aromatic proton signals.

The ^{13}C NMR spectrum and the DEPT spectrum of compound **3** were also compatible with a bromodimethoxybenzylpiperazine. The following signals were measured: The carbon atoms of the piperazine ring at 42.8 ppm and 48.9 ppm, the benzylic carbon atom at 54.6 ppm, the carbon atoms of the methoxy groups at 56.3 ppm and 56.6 ppm, the carbon atoms of the aromatic ring at 109.2 ppm, 114.5 ppm, 116.0 ppm, 125.5 ppm, 149.4 ppm, and 151.8 ppm.

Following these results three possibilities arose for the structure of the unknown compound **3** (Fig. 6).

Several NMR experiments were carried out to determine the distribution of the substituents in the aromatic ring by far distant couplings. A preliminary H,H-long-range spectrum and a NOESY spectrum showed cross signals for each of the two aromatic protons with one of the different methoxy groups, respectively. This is only possible for the isomers **3a** and **3b**. In isomer **3c** one aromatic proton should show cross signals to both of the different methoxy groups. Isomer **3c** was therefore ruled out for the structure of the seized compound. Before the NMR HMQC and HMBC experiments could be recorded, additionally a synthesis of both isomers (**3a** and **3b**) and their mass spectroscopic comparison was done to clear the structure of compound **3**.

Later the relative position of the methoxy groups to each other (in para-position in isomer **3a** or neighbouring in isomer **3b**) was also identified with a gradient selected NOESY experiment as cross peaks of the benzylic protons with one aromatic proton and one methoxy group were detected. So isomer **3b** was clearly ruled out. Furthermore a gradient selected HMQC and gradient selected HMBC experiment allowed complete assignment of all the signals with either ^{1}J(C,H), or ^{2}J(C,H), and ^{3}J(C,H) correlations confirming again **3a**. The results of the identified NOESY cross signals are given in Fig. 7, showing also the complete assignment of the chemical shift for ^{1}H and ^{13}C data [10].

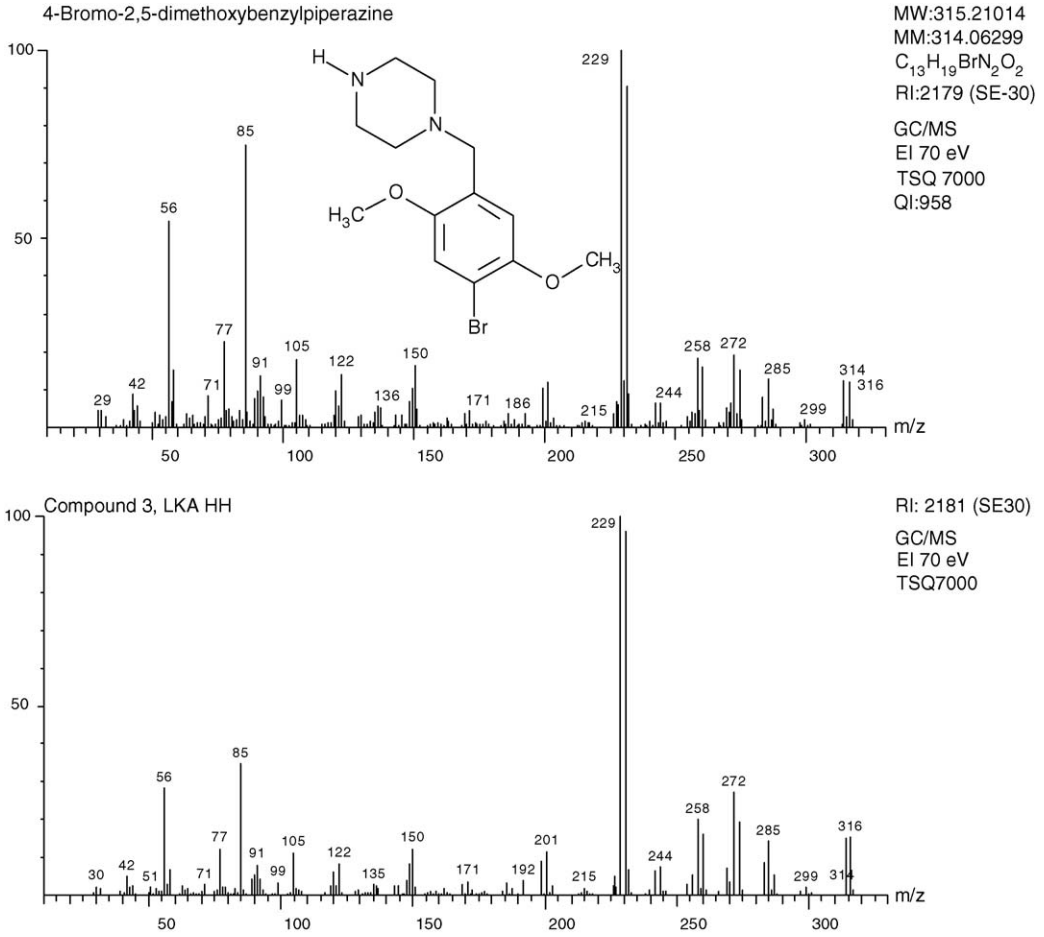


Fig. 10. GC–MS spectra (EI, 70 eV) of the isomer **3a** (top) and the unknown **3** (bottom).

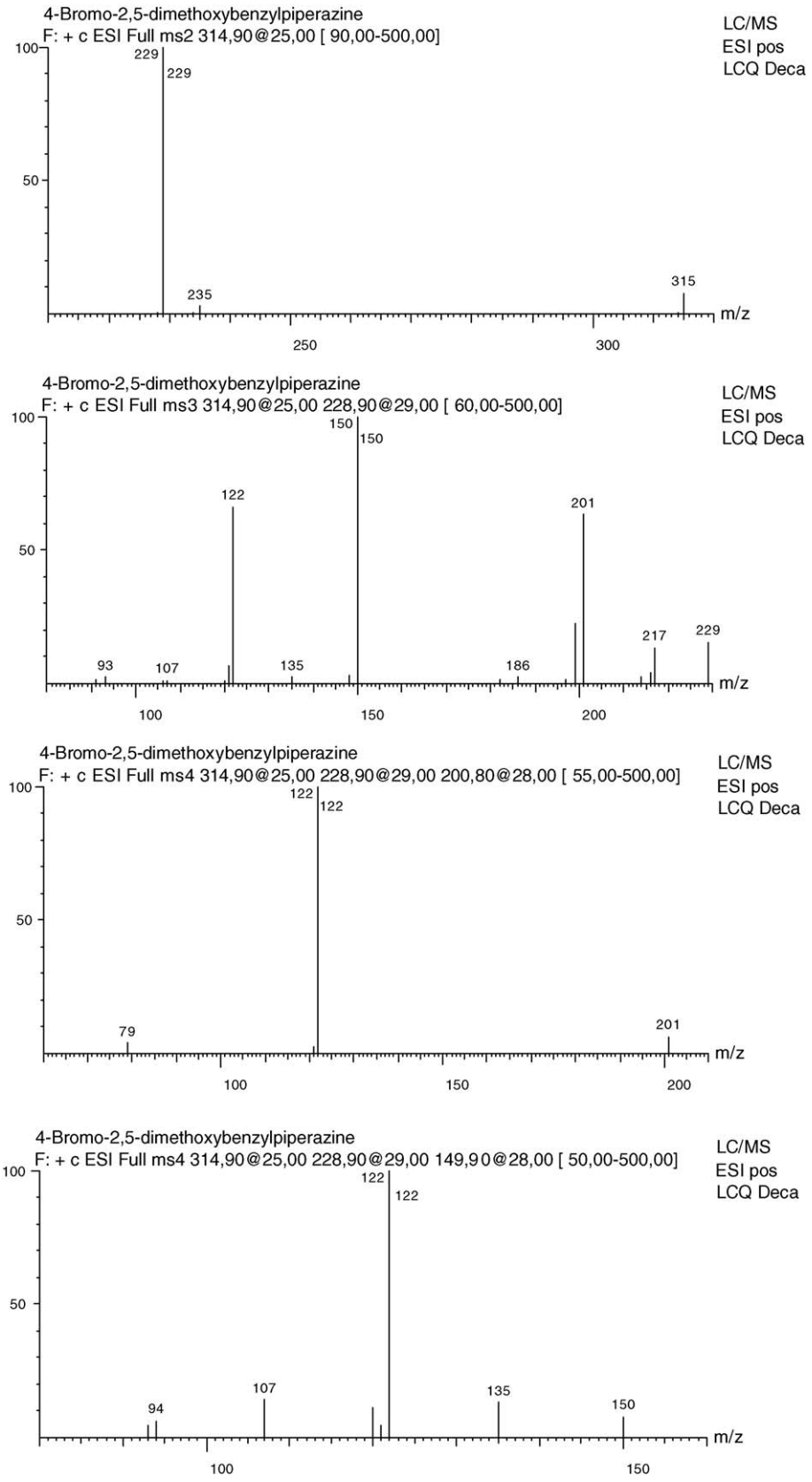


Fig. 11. MS–MS data of 4-bromo-2,5-dimethoxybenzylpiperazine after ESI ionization.

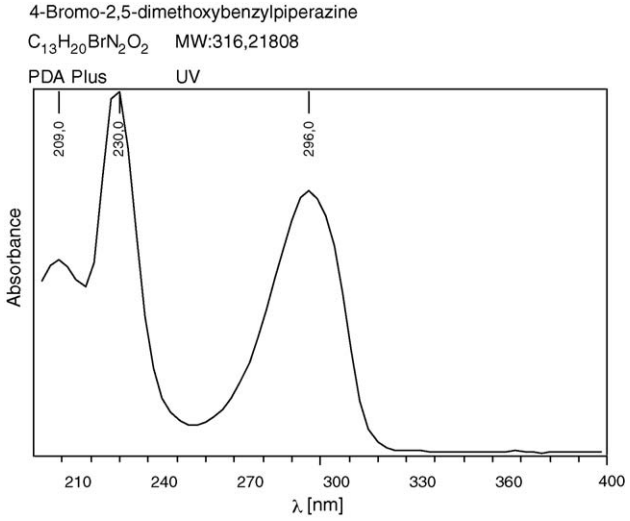


Fig. 12. UV-spectrum of 4-bromo-2,5-dimethoxybenzylpiperazine.

3.3. Synthesis of the isomers 3a and 3b

Fig. 8 shows the synthetic routes for the isomers **3a** and **3b**. The two aldehydes 4-bromo-2,5-dimethoxybenzaldehyde and 6-bromovertraldehyde were added to a solution of piperazine in THF in the presence of sodium triacetoxyborohydride at room temperature according to a publication of Abdel-Magid et al. [8] to give the corresponding isomers (**3a** and **3b**) and their acetates (**3a-AC** and **3b-AC**). In addition, the corresponding bis(bromodimethoxybenzyl)piperazines (**Bis-3a** and **Bis-3b**) were formed.

In Fig. 9 the GC–MS spectra of the products after recrystallization from toluene as well as the spectra of some by-products are presented.

The GC–MS spectra of the isomers **3a** and **3b** after electron ionization are characteristically different from each other: The isomer **3a** shows a relatively strong fragment at $m/z = 285$ (loss of a methoxy radical with $m/z = 31$) opposite to isomer **3b** that shows an intensive fragment at $m/z = 235$ (loss of a bromine atom). These different fragmentation pathways can easily be explained by the losses of the substituents ortho to the benzyl moiety and the following stabilization of the positive charge by mesomerism.

In Fig. 10 the comparison of the GC–MS spectra of the synthetic isomer **3a** and the unknown compound **3** is depicted. The spectrum of the unknown contains a relatively intense fragment cluster at $m/z = 285$ and lacks the fragment with $m/z = 235$. The two compounds additionally show almost identical retention indices (RI). Therefore the structure elucidation of compound **3** as 4-bromo-2,5-dimethoxybenzylpiperazine has been verified by synthesis, too.

3.4. Mass spectral and UV data after liquid chromatography

In Fig. 11 MS^2-, MS^3-, and MS^4-spectra after chromatographic separation and positive electrospray ionization (ESI) and of a solution containing 95.5 ng/mL of the new benzylpiperazine are presented. Starting from the pseudomolecular ion isotope with $m/z = 315$ collision induced dissociation (CID) experiments were performed. Under the conditions applied the MS^2-spectrum is dominated by a fragment with $m/z = 229$ after loss of piperazine besides a fragment with $m/z = 235$ with low intensity. Fragment rich spectra are produced after CID of the fragment with $m/z = 229$ (MS^3 of the pseudomolecular ion with $m/z = 315$) including loss of CO (fragment $m/z = 201$) followed by loss of bromine (fragment $m/z = 122$) or loss of bromine (fragment $m/z = 150$) followed by loss of CO (fragment $m/z = 122$). CID of fragments from MS^3 with $m/z = 201$ and 150 (MS^4 of the pseudomolecular ion with $m/z = 315$) result in mass spectra with much less fragmentation: only one intense fragment with $m/z = 122$ by loss of bromine from $m/z = 201$ and fragments with $m/z = 135$ (loss of methyl radical) and 122 (loss of CO) from $m/z = 150$, respectively.

In Fig. 12 the UV-spectrum acquired after chromatographic separation of a standard containing 9.55 μg/mL 4-bromo-2,5-dimethoxybenzylpiperazine is depicted. The UV maxima are somewhat shifted comparing to the UV-spectrum of Pragst and Bakdash [11] due to the differing pH of the buffers and the different mobile phases used. Pragst and Bakdash used an acetonitrile/phosphate-buffer with a pH of 2.3 and registered two shoulders at 210 nm and 230 nm as well as one maximum at 300 nm. Under the conditions used here strong maxima at 230 nm and 296 nm as well as a maximum at 209 nm are measured.

4. Conclusion

The structure of the new designer benzylpiperazine 4-bromo-2,5-dimethoxybenzylpiperazine has been elucidated by gas chromatography–mass spectrometry, NMR-spectroscopy, and synthesis of two possible isomers. NMR spectroscopic data, mass spectral data including MS–MS data after liquid chromatography, and UV data have been reported as well as mass spectral data of some by-products of its synthesis and the synthesis of one of its isomers.

To our knowledge 4-bromo-2,5-dimethoxybenzylpiperazine is not yet described and represents a new benzylpiperazine on the illegal designer drug market. Meanwhile this new benzylpiperazine has been seized in Saxony, Germany, too. Until now nothing is known yet about the pharmacological action of this compound. Probably it combines the amphetamine-like acting benzylpiperazine with hallucinogenic actions caused by the 4-bromo-2,5-dimethoxy substitution pattern. However, this is only a hypothesis that has to be examined by further investigations.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.forsciint.2009.03.003.

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