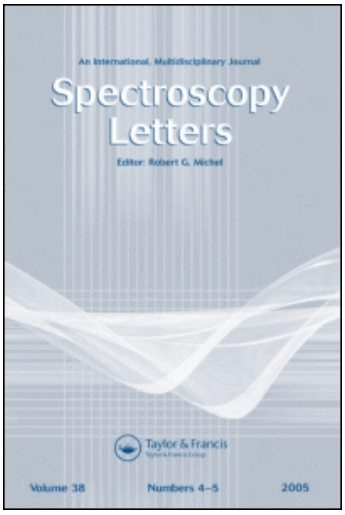

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Mass Spectrometry of Bis-quinolizidine Alkaloids: Differentiation of Stereoisomers and Metamers Using ESI and FAB Mass Spectrometry

Beata Jasiewicz[a]; Elżbieta Wyrzykiewicz[a]
[a] Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland

To cite this Article Jasiewicz, Beata and Wyrzykiewicz, Elżbieta(2009) 'Mass Spectrometry of Bis-quinolizidine Alkaloids: Differentiation of Stereoisomers and Metamers Using ESI and FAB Mass Spectrometry', Spectroscopy Letters, 42: 1, 49 — 57
To link to this Article: DOI: 10.1080/00387010802428435
URL: http://dx.doi.org/10.1080/00387010802428435

Spectroscopy Letters, 42:49–57, 2009

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010802428435

Taylor & Francis
Taylor & Francis Group

Mass Spectrometry of Bis-quinolizidine Alkaloids: Differentiation of Stereoisomers and Metamers Using ESI and FAB Mass Spectrometry

Beata Jasiewicz, and Elżbieta Wyrzykiewicz

Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland

ABSTRACT The ESI and FAB mass spectral fragmentations of seven bis-quinolizidine alkaloids were investigated. Fragmentation pathways, elucidation of which was assisted by FAB/CID mass spectra measurements, are discussed. The data create the basis for distinguishing stereoisomers and metamers.

KEYWORDS bis-quinolizidine alkaloids, ESI mass spectra, FAB mass spectra, lupanine, sparteine

INTRODUCTION

A study of Bis-quinolizidine alkaloids by the EIMS method has been stimulated by the evidence of its suitability for distinction of their stereoisomers, metamers, and positional isomers.[1–6] The stereochemical effects that are encountered with dissociations of stereoisomers incorporating saturated heterocyclic rings are due to the spatial relationship of chemical bonds to be broken or formed. The basic bis-quinolizidine system sparteine consists of four rings, two of which (A/B) form a double-chair system of *trans*-quinolizidine that is relatively resistant (for thermodynamic reasons) to conformational–configurational changes. The second system (C/D) is much more susceptible to inversion at the N16 nitrogen atom and it can attain a *trans* boat/chair or a *cis* double/chair conformation. According to Haasnoot,[7] sparteine adopts exclusively a C-boat conformer. Theoretical calculations have confirmed that the free base of sparteine has one most favorable conformer with chair-chair *trans*-quinolizidine A/B system and boat/chair *trans*-quinolizidine C/D system.[8] The main characteristic of the Electron impact (EI) mass fragmentation of molecular ions of Bis-quinolizidine alkaloids is the dependence of the fragmentation pathway of the bis-quinolizidine skeleton on the stereochemistry of the A/B and C/D ring junctions. However, Electrospray ionization (ESI) and Fast atom bombardment (FAB) mass spectral behavior of these compounds has not been reported to our knowledge. This lack of information should

Received 4 January 2008; accepted 27 May 2008.

Address correspondence to Beata Jasiewicz, Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland. E-mail: beatakoz@amu.edu.pl

be overcome because ESI-MS and FAB-MS give very useful information for the chemical characterization of other types of alkaloids.[9–12]

It should be pointed out that the study of the differences in the mass spectra of stereoisomeric compounds with known structure can help to elucidate stereochemical problems in the asymmetric syntheses.[9] The current work involves the results of the ESI and FAB mass spectrometric study of 2-phenyl-2,3-didehydrosparteine (**1**), 15-phenyl-14, 15-didehydrosparteine (**2**), 2-cyano-2-methylsparteine (**3**), 17-cyanolupanine (**4**), 17-methyllupanine (**5**), 2,17-dimethylsparteine (**6**) and 2-methyl-17-oxosparteine (**7**) (Fig. 1). We wanted to determine the cleavage reactions for the fragmentation processes of **1–7** in the ESI and FAB conditions and to establish whether it would be possible to distinguish the positional isomers (**1**, **2**, **5**, **7**) and metamers (**3**, **4**; **5**, **6**, **7**) on the basis of differences in the mass spectra (i.e., the presence or absence of relevant ions) between these compounds. The derivatives of sparteine (**1–3**, **6**) studied have A/B *trans*-fused rings with double-chair conformations and C/D *trans*-fused rings with boat/chair conformations (**1, 3**, **6**). 15-Phenyl-14,15-didehydrosparteine (**2**) has C/D *cis*-fused rings with double-chair conformations. In contrast, 17-cyano-(or 17-methyl) lupanines (**4**, **5**) have A/B *trans*-fused rings with sofa/chair conformations and C/D *trans*-fused rings with boat/chair conformations. 2-Methyl-17-oxosparteine (**7**) has A/B *trans*-fused rings with double-chair conformations and C/D *trans*-fused rings with sofa/chair conformations.

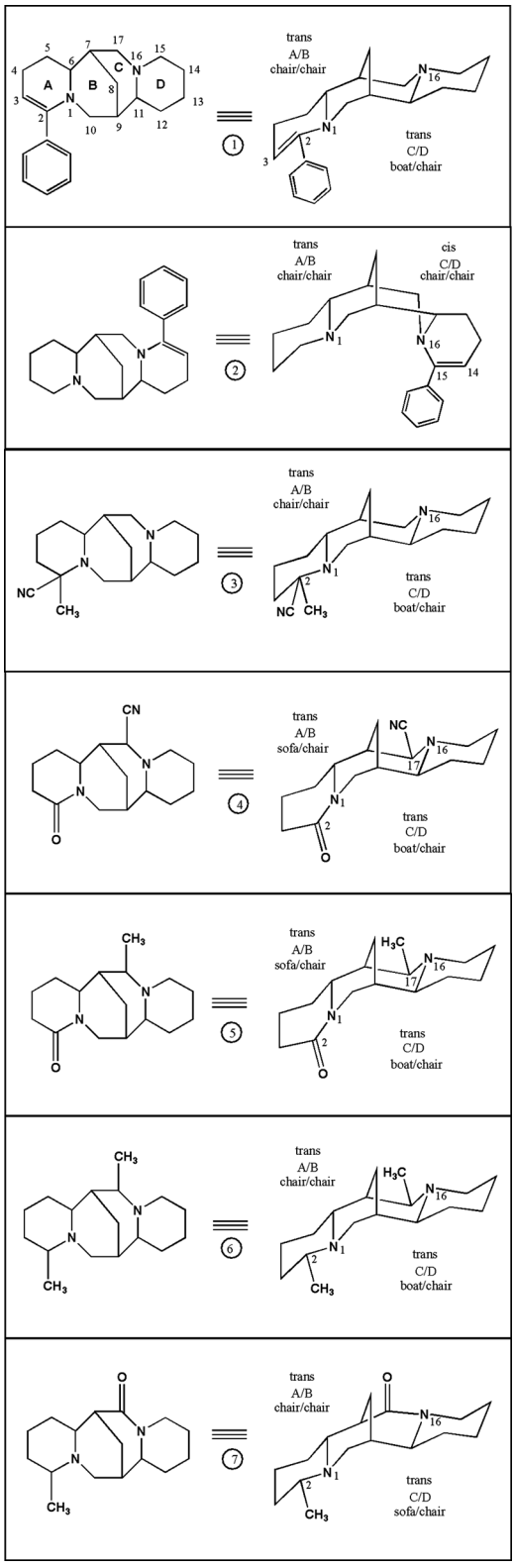

FIGURE 1 **Structures of compounds 1–7.**

MATERIALS AND METHODS

The compounds **1–7** were obtained and their structures confirmed according to the literature methods.[13–19] The positive mode ESI mass spectra of **1–7** were recorded on a ZQ mass spectrometer (Waters/Micromass, Manchester, UK) equipped with a Harvard Apparatus syringe pump. The sample solutions were prepared in methanol in a concentration 5×10^{-5} M, which is typical for ESI. The samples were infused into the ESI source using a Harvard multipump at a flow rate of 40 μL min^{-1}. The ESI source potential was 3 kV on the capillary, 0.5 kV on the lens, 4 V on the extractor, and the cone voltage was 30 V. The source and desolvation temperatures were 120°C and 300°C, respectively. Nitrogen was used as neutralizing and desolvation gas at flow rates of 100 and 300 L h^{-1}, respectively. The

TABLE 1 Relative Abundances of Characteristic Ions in the Positive-Mode ESI Spectra of Compounds 1–7

	$M+H^+$		
	Elemental composition m/z (%)		
Compound	(a)	(b)	(c)
1	$C_{21}H_{28}N_2+H^+$ 309 (100)	$C_{12}H_{15}N+H^+$ 174 (38)	—
2	$C_{21}H_{28}N_2+H^+$ 309 (100)	$C_{17}H_{18}N_2+H^+$ 251 (7)	—
3	$C_{17}H_{27}N_3+H^+$ 274 (100)	$C_{16}H_{26}N_2+H^+$ 247 (99)	$C_7H_{13}N+H^+$112 (20)
4	—	$C_{15}H_{22}N_2O+H^+$ 247 (100)	$C_9H_9NO+H^+$ 148 (6)
5	$C_{16}H_{26}N_2O+H^+$ 263 (100)	$C_9H_9NO+H^+$ 148 (5)	$C_7H_{13}N+H^+$ 112 (28)
6	$C_{17}H_{30}N_2+H^+$ 263 (100)	—	—
7	$C_{16}H_{26}N_2O+H^+$ 263 (57)	$C_{15}H_{24}N_2O+H^+$ 249 (100)	—

FAB spectra were produced by liquid secondary ions mass spectrometry (LSIMS) ionization (Cs^+ ion bombardment) using 3-nitrobenzyl alcohol (NBA) as matrix. These spectra were recorded on positive mode on an AMD-Intectra GmBH-Harpstedt D-27243 Model 604 two-sector spectrometer. For Cedrin-induced discution (CID) experiments, helium was used as a collision gas in the first field-free region (1FFR) at a pressure corresponding with 50% attenuation of the precursor ion signal.

RESULTS AND DISCUSSION

The relative abundances of characteristic ions in the positive-ion ESI mass spectra of **1–7** are summarized in Table 1, and the pathways of the ESI mass fragmentation of the compounds **1–4** are described in Fig. 2 and those of **5–7** in Fig. 3. In the mass spectrum of **6** only the protonated molecule $[M+H]^+$, $[C_{17}H_{30}N_2+H]^+$, m/z 263, was observed, whereas in the mass spectra of **1–3**, **5**, and **7**, the protonated molecules $[M+H]^-$ together with the even-electron fragment ions were found. It should be pointed out that from the mass spectrum of **4**, the protonated molecule $[M-H]^+$ is missing and only two even-electron fragment ions **b** $[M+H\text{-}HCN]^+$, $C_{15}H_{22}N_2O^+$ m/z 247, and **c**, $[C_9H_9NO+H]^+$ m/z 148, were observed. The latter of these ions was obtained by the cleavages of the C7–C17 and C9–C11 bonds of ring C (Table 1, Fig. 2).

In the ESI fragmentation of protonated molecule $[M+H]^+$ of **1**, simple cleavages of Csp^3–Csp^3 bonds (C9–C10, C6–C7) of ring B gave the even-electron ion **b**, $[C_{12}H_{15}N+H]^+$, m/z 174 (Table 1, Fig. 2). The positive mode ESI spectrum of **2** showed the even-electron fragment ion **b**, $[C_{17}H_{18}N_2+H]^+$ at m/z 251. This ion was obtained by the cleavages of C6–C5 and N1–C2 bonds of ring A. The structure of **2** (i.e., *cis*-fused C/D rings in chair/chair conformations) implies that N1 and N16 annular nitrogen atoms are close enough to each other for an intra-annular H bridging to occur and enable the formation of an additional six-membered ring (Fig. 2, Table 1). In the ESI fragmentation of protonated molecule $[M+H]^+$ of **3**, the cleavages of C6–C7 and C9–C10 bonds of ring B with simultaneous elimination of HCN molecule were observed. The even-electron fragment ion **c**, $[C_{17}H_{13}N_2+H]^+$ at m/z 112, was obtained in the fragmentation processes. In the mass spectrum of **3**, the even-electron fragment ion $[(M+H)-HCN]^+$, $[C_{16}H_{26}N_2+H]^+$, m/z 247, was present (Fig. 2, Table 1). It ought to be pointed out that in the mass spectrum of **4**, the protonated molecule $[M+H]^+$ was absent. In this spectrum, only two even-electron fragment ions **b** $[(M+H)^+ -HCN]^+$ ($C_{15}H_{22}N_2O$ m/z 247) and **c**$[(C_9H_9NO+H)^+$ m/z 148] were observed. The latter of these ions was obtained by the cleavages of the C7–C17 and C9–C11 bonds of ring C (Table 1, Fig. 2). The differences in the dissociation pathways are probably due to the different substituents on the rings A and C (i.e., the position of substituents in the bis-quinolizidine skeleton), and as well as the stereochemistry of the ring junctions of this skeleton are sufficient to differentiate the isomeric sparteine and lupanine derivatives (**1–2**; **3–4**). On the basis of the presence (or absence) of the characteristic even-electron fragment ions in the positive ESI mode (Table 1, Fig. 2) at m/z 174 (**1**), m/z 251 (**2**), m/z 148 (**4**), m/z 112 (**3**) together with the fragment ions at m/z 247 (**3**), it is possible to distinguish isomers **1** from **2** and metamers **3** from **4**. In the ESI mass

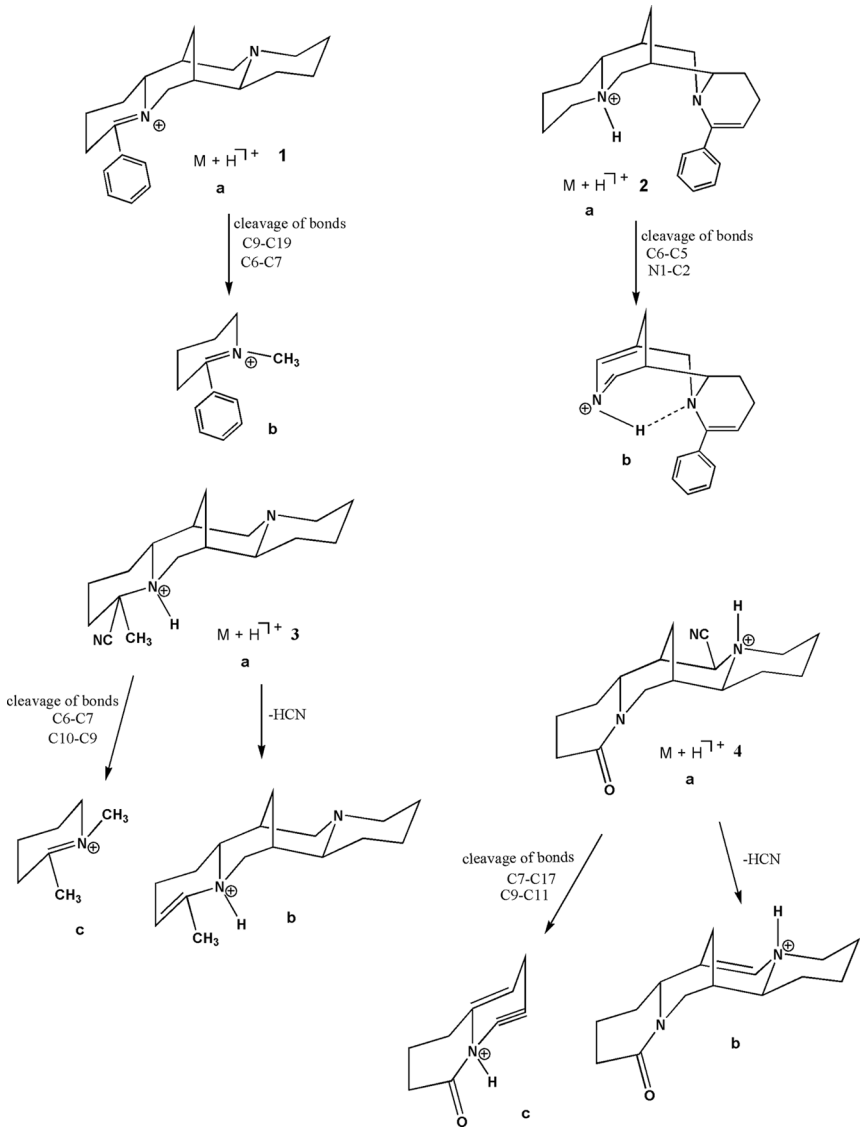

FIGURE 2 **The fragmentation pathways in the ESI spectra of compounds 1–4.**

spectrum of **6**, only the protonated molecule $[M+H]^+$ was observed, but in the ESI mass spectra of **5** and **7**, instead of this ion, the even-electron fragment ions were observed (Table 1, Fig. 3). The ESI mass spectrum of compound **5** revealed the even-electron fragment ions **b**, $[C_9H_9NO+H]^+$ m/z 148, and **c**, $[C_7H_{13}N+H]^+$ m/z 112, obtained by the cleavages of C7–C17 and C9–C11 bonds of ring C with retention and migration of charge, respectively. Compound **7** only eliminated a neutral methylene group leading to the even-electron ion **b**, $[C_{15}H_{24}N_2O+H]^+$ at m/z 249 (Table 1, Fig. 3). The differences in the ESI mass fragmentation of compounds **5**, **6**, and **7** depends on the location of the alkyl and carbonyl functions in the bis-quinolizidine skeleton as well as the differences in the conformations of the A/B and C/D rings. On the basis of the presence (or absence) as well as the differences in the abundances of the characteristic protonated molecule $M+H^+$ **a** (m/z 309, **1**,**2**; m/z 274, **3**,**4**; m/z 263, **5**–**7**), **b** (m/z 174, **1**; m/z 251, **2;** m/z 247, **3**,**4**; m/z 148, **5;** m/z 249, **7**), and **c** (m/z 112, **3**–**5**) in the positive-mode ESI mass spectra, it is possible to distinguish between isomeric **1**,**2**; **5**,**7** and metameric **3**,**4**; **5**,**6**; **6**,**7** (Table 1).

The mass spectrometric behavior of isomeric **1**–**7** was also investigated in detail by positive FAB mass spectrometry combined with CID. The relative abundances of characteristic peaks of even-electron ions are presented in Table 2. The characteristic product ions obtained from protonated molecule $[M+H]^+$ for compounds **1**–**7** are presented in Table 3. On

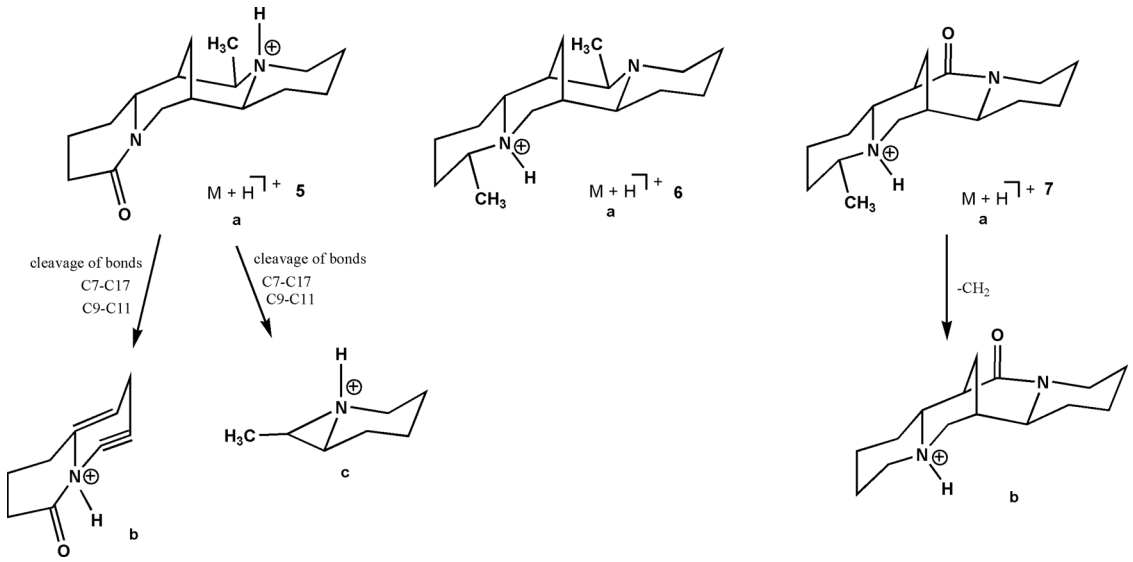

FIGURE 3 **The fragmentation pathways in the ESI spectra of compounds 5–7.**

the basis of FAB and FAB/CID mass spectra of **1–7**, the postulated structures of fragment ions from isomeric **1** and **2** are shown in Fig. 4, those of **3** and **4** in Fig. 5, and those of **5–7** in Fig. 6. In the FAB spectra of **1** and **2** apart from the expected protonated molecule $[M+H]^+$ **a** at m/z 309, there are also $M^{+\bullet}$ and $[M\text{-}H]^+$ ions as well as fragment ions. Fragmentation of the cyclic $[M+H]^+$ of **1**, **2** (Fig. 4, Table 2) proceeds by the cleavages of two bonds of rings B or C of the sparteine skeleton. The cleavages of bonds C6–C7 and C9–C10 of ring B (for **1**) or C9–C11 and C7–C17 of ring D (for **2**) lead to the even-electron fragment ions **f** $[C_{12}H_{15}N+H]^+$, m/z 174, and the cleavages of bonds N1–C2 and C4–C5 of ring A (for **1**) or N16–C15, C13–C12 of ring D (for **2**) lead to the even-electron fragment ions **e** $[C_{12}H_{19}N_2+H]^+$, m/z 192. The cleavages of bonds C6–C7 and N1–C10 of ring B (for **1**) or C7–C17, C9–C11 of ring C (for **2**) lead to the even-electron fragment ion **g1** $[C_{11}H_7N+H]^+$, m/z 154. It should be pointed out that the origin of the even-electron fragment ions **g1** and **h1** has been confirmed by the FAB/CID mass spectra of **1** and **2** (Table 3). Ions **g1** and **h1** are the product ions of the precursor $[M+H]^+$ **a** of **1** and **2** (Table 3). It should also be mentioned that even-electron fragment ions at m/z 154 (**g2**) and at m/z 136 (**h2**) have different elemental composition connected with the fragmentation of liquid matrix (*m*-nitrobenzyl alcohol; NBA) (Table 2); for example, **g2** $[C_7H_7NO_3+H]^+$; $[NBA+H]^+$ at m/z 154 and **h2** $[C_7H_7NO_3+H\text{–}H_2O]^+$; $[NBA+H\text{–}H_2O]^+$ at m/z 136. The even-electron ions **g** form the basic peaks for the spectra of **1** and **2**. The differences in the relative abundances of even-electron ions **e** $[C_{12}H_{19}N_2+H]^+$, m/z 192, and **f** $[C_{12}H_{15}N+H]^+$, m/z 174 (Table 2), in the FAB spectra of **1** and **2** allow the differentiation of these positional isomers. The differences in the relative abundances of ions **e** and **f** in the spectra of **1** and **2** depends clearly on the location of the phenyl substituent in the skeleton of bis-quinolizidine and the differences in the conformations of C/D rings (*trans* C/D boat-chair for **1**; *cis* C/D chair-chair for **2**). In the FAB spectra of **3** and **4** apart from the expected protonated molecules $[M+H]^+$ **a** at m/z 274, there are also peaks of $M^{+\bullet}$ and $[M\text{–}H]^+$ ions, as well as those of fragment ions (Table 2).

Fragmentation of the cyclic protonated molecule $[M+H]^+$ of **3** (Table 2) proceeds by the cleavages of C6–C7 and C9–C10 bonds of ring C and leads to the even-electron fragment ion **h1** $[C_9H_{13}N+H]^+$, m/z 136. Elimination of the HCN molecules from the protonated molecule $[M+H]^+$ **a** of **3** and **4** leads to the even-electron ions **d** $[C_{16}H_{26}N_2+H]^+$, m/z 247, for **3** and $[C_{15}H_{22}N_2O+H]^+$, m/z 247, for **4**, respectively. Metameric compounds **3** and **4** may be distinguished from each other based on the differences in the relative abundance of ions **a** and **d** (Table 2, Fig. 5) as well as the different elemental composition of ions **d**, m/z 247. In the FAB

TABLE 2 **Relative Abundances of Characteristic Ions in the Positive-Mode FAB spectra of Compounds 1–7**

	$M+H^+$								
	Elemental composition m/z (%)								
Compound	(a)	(b)	(c)	(d)	(e)	(f)	(g1/g2)	(h1/h2)	(i)
1	$C_{21}H_{28}N_2+H^+$ 309 (30)	$C_{19}H_{13}N+NBA^+$ 289 (13)			$C_{12}H_{19}N_2+H^+$ 192 (4)	$C_{12}H_{15}N+H^+$ 174 (8)	**g1** $C_{11}H_7N+H^+$ **g2** NBA $+H^+$ 154 (100)	**h1** $C_9H_{13}N+H^+$ **h2** NBA $+H\text{-}H_2O^+$ 136 (80)	
2	$C_{21}H_{28}N_2+H^+$ 309 (6)	$C_{19}H_{13}N+NBA^+$ 289 (12)			$C_{12}H_{19}N_2+H^+$ 192 (68)	$C_{12}H_{15}N+H^+$ 174 (4)	**g1**$C_{11}H_7N+H^+$ **g2** NBA $+H^+$ 154 (100)	**h1** $C_9H_{13}N+H^+$ **h2** NBA $+H\text{-}H_2O^+$ 136 (75)	
3	$C_{17}H_{27}N_3+H^+$ 274 (100)			$C_{16}H_{26}N_2+H^+$ 247 (28)			**g2** NBA $+H^+$ 154 (5)	**h1** $C_9H_{13}N+H^+$ **h2** NBA $+H\text{-}H_2O^+$ 136 (15)	
4	$C_{16}H_{23}N_3O+H^+$ 274 (16)			$C_{15}H_{22}N_2O+H^+$ 247 (100)			**g2** NBA $+H^+$ 154 (35)	**h1** $C_9H_{13}N+H^+$ **h2** NBA $+H\text{-}H_2O^+$ 136 (38)	
5	$C_{16}H_{26}N_2O+H^+$ 263 (62)			$C_{15}H_{22}N_2O+H^+$ 247 (15)			**g2** NBA $+H^+$ 154 (3)	**h1** $C_9H_{13}N+H^+$ **h2** NBA $+H\text{-}H_2O^+$ 136 (18)	$C_7H_{13}N+H^+$ 112 (100)
6	$C_{17}H_{30}N_2+H^+$ 263 (100)			$C_{16}H_{26}N_2+H^+$ 247 (5)			**g2** NBA $+H^+$ 154 (5)	**h1** $C_9H_{13}N+H^+$ **h2** NBA $+H\text{-}H_2O^+$ 136 (8)	$C_7H_{13}N+H^+$ 112 (36)
7	$C_{16}H_{26}N_2O+H^+$ 263 (73)		$C_{15}H_{24}N_2O+H^+$ 249 (100)	$C_{15}H_{22}N_2O+H^+$ 247 (38)			**g2** NBA $+H^+$ 154 (25)	**h1** $C_9H_{13}N+H^+$ **h2** NBA $+H\text{-}H_2O^+$ 136 (48)}	$C_7H_{13}N+H^+$ 112 (47)

NBA, $[C_7H_7NO_3]$ nitrobenzyl alcohol.

TABLE 3 **Product Ions Obtained from the Protonated Molecule $[M+H]^+$ Ions Generated from Compounds 1–7 Under FAB Conditions**

Compound	$M+H^+$ m/z	Product ions m/z
1	309	289, 192, 174, 154, 136
2	309	289, 192, 174, 154, 136
3	274	247, 136
4	274	247, 136
5	263	247, 136
6	263	247, 136, 112
7	263	249, 247, 136, 112

spectra of **5–7** (Table 2) apart from the expected protonated molecules $[M+H]^+$ at m/z 263, there are also $M^{+\bullet}$ and $[M–H]^+$ ions, as well as fragment ions. The common characteristic features of the FAB fragmentation of the protonated molecules $[M+H]^+$ **a** of the lupanine skeleton of **5**, as well as those of the sparteine skeleton of **6** and **7** are cleavages of bonds in rings B and C, and simultaneous elimination of methyl and hydrogen radicals. The even-electron fragment ions **d**, $[C_{15}H_{22}N_2O+H]^+$ for **5** and **7** and $[C_{16}H_{26}N_2+H]^+$ for **6** at m/z 247 were obtained in this way by FAB fragmentation (Table 2).

It should be pointed out that the characteristic elimination of neutral methylene group from protonated molecules $[M+H]^+$ **a** of **7** leads to the basic peak **c**, $[C_{15}H_{24}N_2O+H]^+$ at m/z 249, in the FAB spectrum of this compound (Table 2) and that the even-electron fragment ions **h1**, $[C_9H_{13}N+H]^+$ at m/z 136, can be obtained from the even-electron fragment ions **d** of **5–7** by the C7–C17 and C9–C11 bonds cleavages in ring C (compound **5** and **7**) and those of C6–C7 and C10–C9 bonds in ring B (compound **6**) (Fig. 6). The presence of the abundant ion **d** in the FAB spectrum of **7** allows its differentiation from metameric **6** and isomeric **5**. Metameric **5** and **6** may be distinguished by the different relative abundances of ions **i**, $[C_7H_{13}N+H]^+$ at m/z 112 (Table 2). These ions have been obtained from protonated molecules $[M+H]^+$ **a** of **5–7** by the cleavages of bonds C6–C7 and N1–C9 in ring B for **6** and **7** and bonds C7–C17, C9–C10 in ring C for **5** and **6** (Table 3).

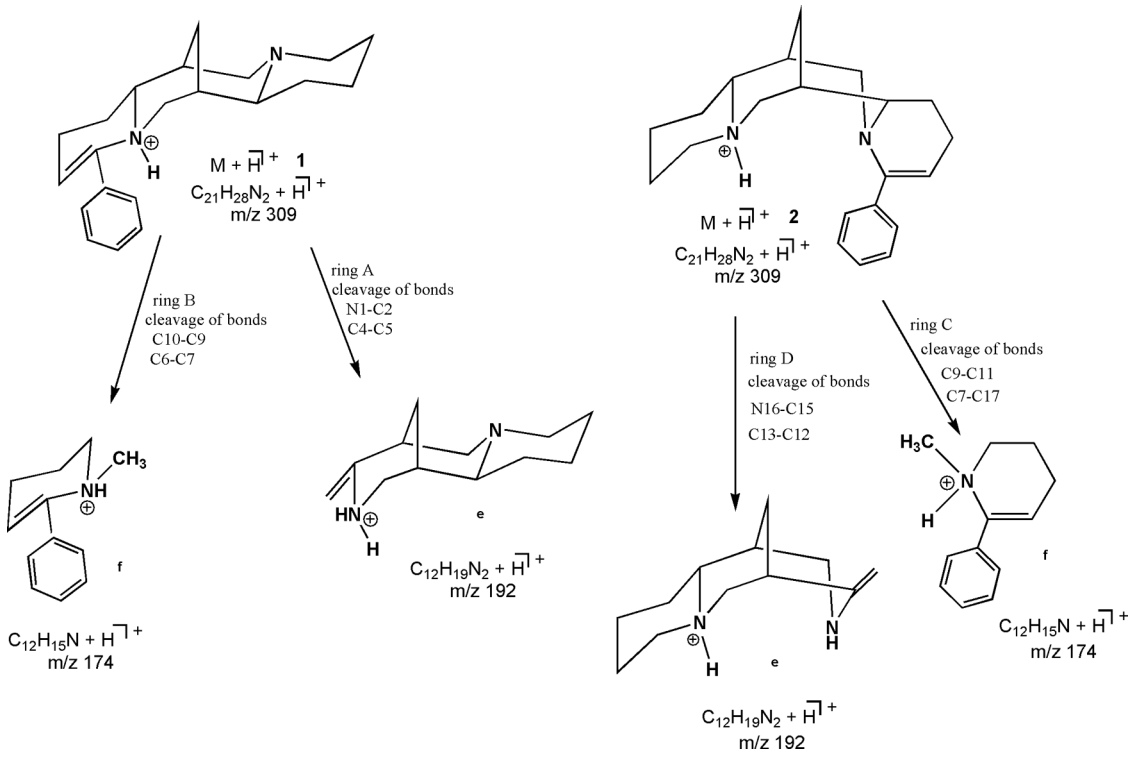

FIGURE 4 **The postulated structures of the fragment ions in the FAB spectra of isomeric 1 and 2.**

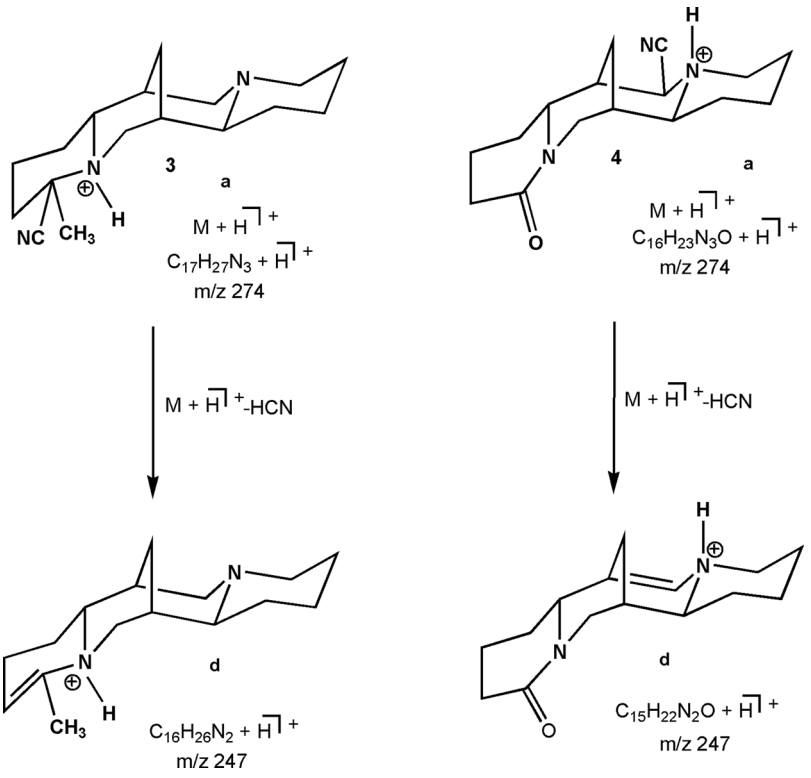

FIGURE 5 **The postulated structures of the fragment ions in the FAB spectra of metameric 3 and 4.**

CONCLUSIONS

The current study demonstrates that positional isomers and metamers of sparteine and lupanine derivatives **1**–**7** can be differentiated on the basis of their ESI and FAB mass spectra. The ESI and FAB mass fragmentation of the protonated molecules $[M+H]^+$ of **1**–**7** proceeds by the cleavages of bonds in the B, C, and D rings of the bis-quinolizidine skeleton. The

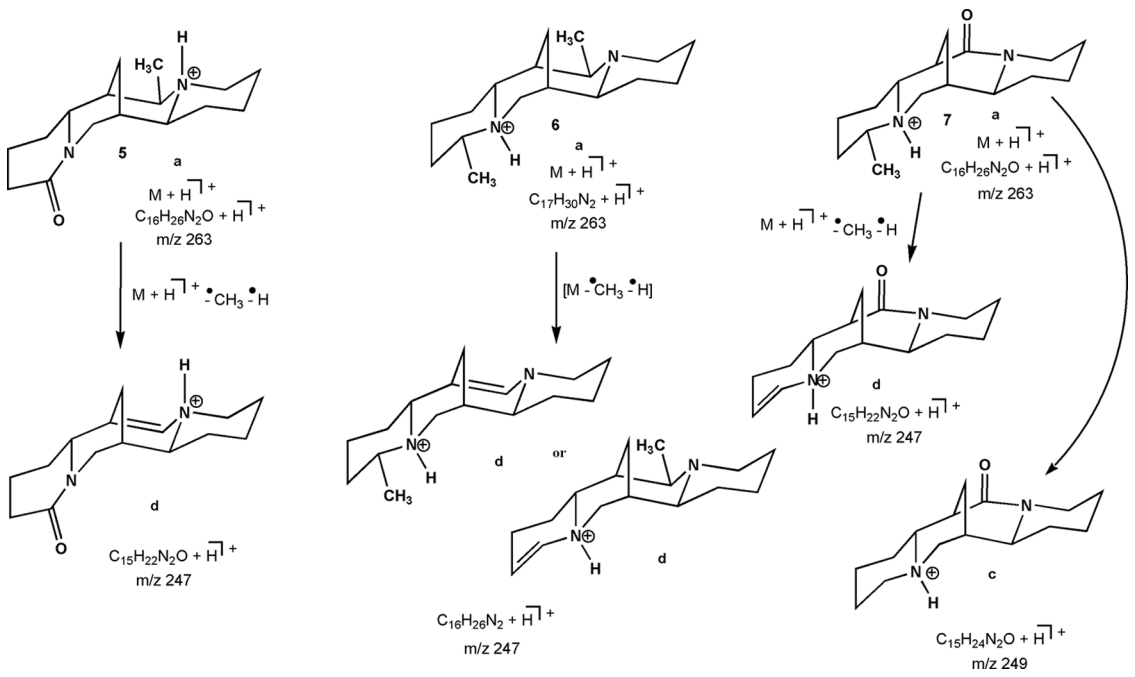

FIGURE 6 **The postulated structures of the fragment ions in the FAB spectra of metameric 5–7.**

fission of these bonds depends mainly on the location of the alkyl, phenyl, and carbonyl functions in the bis-quinolizidine skeleton but to some extent also on the stereochemistry of C/D ring junctions.

REFERENCES

1. Tamas, J. Stereochemical effects in the mass spectra of quinolozidine and indole alkaloids In *Applications of Mass Spectrometry to Organic Stereochemistry*; Splitter, J. S.; Turecek, F., Eds.; VCH: New York, 1994; 625–626.
2. Majchrzak-Kuczyńska, U.; Wiewiórowski, M.; Wyrzykiewicz, E. Mass spectrometry of bis-quinolizidine alkaloids: Lactams of sparteine and α-isosparteine. *Org. Mass Spectrom.* **1984**, *19*, 600–604.
3. Wyrzykiewicz, E.; Wysocka, W. Mass spectrometry of bisquinolizidine alkaloids: Multiflorine and its derivatives. *Org. Mass Spectrom.* **1990**, *25*, 453–456.
4. Wyrzykiewicz, E.; Boczoń, W.; Kozioł, B. Mass spectrometry of bisquinolizidine alkaloids: 2- and 15-substituted derivatives of sparteine and 2- (or 14)-dehydrosparteine. *J. Mass Spectrom.* **1998**, *33*, 971–975.
5. Wyrzykiewicz, E.; Boczoń, W.; Kozioł, B. Mass spectrometry of bis-quinolizidine alkaloids: 2- and 17-alkyl-substituted derivatives of sparteine and lupanine. *J. Mass Spectrom.* **2000**, *35*, 1271–1277.
6. Jasiewicz, B.; Boczoń, W.; Wyrzykiewicz, E. Mass spectrometry of bisquinolizidine alkaloids: 2- and 17-cyano-substituted derivatives of sparteine and lupanine. *J. Mass. Spectrom.* **2004**, *39*, 541–547.
7. Haasnoot, C. A. G. Conformational analysis of six-membered rings in solution: Ring puckering coordinates derived from vicinal NMR proton-proton coupling constants. *J. Am. Chem. Soc.* **1993**, *115*, 1460–1468.
8. Galasso, V.; Asaro, F.; Berti, F.; Kovač, B.; Habuš, I.; Sacchetti, A. On the structure and spectroscopic properties of sparteine and its diastereoisomers. *Chem. Phys.* **2003**, *294*, 155–169.
9. Bartok, T.; Felföldi, K.; Szöllösi, G.; Bartok, M.; Dega-Szafran, Z.; Thiel, J. Mass spectra of iso-cinchona – and halogenated cinchona alkaloids. *Eur. J. Mass Spectrom*. **2000**, *6*, 347–355.
10. Xiang, Y.; Abliz, Z.; Li, L. J.; Huang, X. S.; Yu, S. S. Study of structural characteristic features of phenanthriondolizidine alkaloids by fast atom bombardment with tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 1668–1674.
11. Bartok, M.; Szabó, P. T.; Bartok, T.; Szöllösi, G. Identification of ethyl pyruvate and dihydrocinchonidine adducts by electrospray ionization mass spectrometry. *Rapid Commun. Mass Spectrom.* **2000**, *14*, 509–514.
12. Wang, Y.; Song, F.; Xu, Q.; Liu, Z.; Liu, S. Characterization of aconitine-type alkaloids in the flowers of *Aconitum kusnezoffii* by electrospray ionization tandem mass spectrometry. *J. Mass Spectrom.* **2003**, *38*, 962–970.
13. Boczoń, W. Further studies on the stereochemistry of sparteine, its isomers and derivatives. Part XIV. Synthesis, structure and spectroscopic properties of the 2-phenyl-2-dehydrosparteine and its diprotonated salts (chloride, bromide and perchlorate). *J. Mol. Struct.* **1987**, *158*, 127–139.
14. Boczoń, W. Further studies on the stereochemistry of sparteine, its isomers and derivatives. XVI. Synthesis, structure and spectroscopic properties of 14-dehydro-15-phenylsparteine, 15-phenylsparteine and their salts. *Bull. Acad. Pol. Chim.* **1988**, *36*, 37–43.
15. Boczoń, W. Further studies on the stereochemistry of sparteine, its isomers and derivatives. XVII. Synthesis, structure and spectroscopic properties of the cyano-derivatives of 2-methyl- and 2-phenyl-sparteines and their salts. *Bull. Acad. Pol. Chim.* **1988**, *36*, 45–58.
16. Skolik, J.; Stopa, Wł. Synthesis and spatial analysis of cyano-derivatives of sparteine. *Zesz. Nauk. WSE, Ser. I.* **1972**, *46*, 193–202.
17. Wiewiórowski, M.; Pieczonka, G.; Skolik, J. Further studies on the stereochemistry of sparteine, its isomers and derivatives. Part I. Synthesis, structure and properties of 16,17-endo-methylene-lupaninium perchlorate, 17-β-methyllupanine and 17-β-methylsparteine. *J. Mol. Struct.* **1977**, *40*, 233–246.
18. Boczoń, W.; Jasiewicz, B. Synthesis and conformational analysis of disubstituted sparteine derivatives. *Collect. Czech. Chem. Commun.* **2003**, *68*, 696–710.
19. Jasiewicz, B.; Boczoń, W. Oxidation reaction of bis-quinolizidine system: Synthesis of new 2-methyl-17-oxosparteine and 2-methyl-α-isosparteine. *Lett. Org. Chem.* **2007**, *4*, 27–31.