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Mass Spectrometry of Bisquinolizidine Alkaloids: 2- and 15-Substituted Derivatives of Sparteine and 2- (or 14)-Dehydrosparteine

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The mass spectral fragmentations of 2-phenylsparteine, 2-(*p*-tolyl)sparteine, 15-phenylsparteine, 2-phenyl-2-dehydrosparteine, 2-(*p*-tolyl)-2-dehydrosparteine and 15-phenyl-14-dehydrosparteine were investigated. Fragmentation pathways, elucidation of which was assisted by accurate mass measurements and correlation between the abundances of the $M^{+\cdot}$ and the selected fragment ions of investigated compounds, are discussed. The data obtained create the basis for distinguishing structural isomers. © **1998 John Wiley & Sons, Ltd.**

KEYWORDS: bisquinolizidines; sparteines; dehydrosparteine; phenylsparteines; *p*-tolylsparteines structural isomers

INTRODUCTION

The quinolizidine alkaloids have interested chemists for several decades. The abundance differences in the electron ionization (EI) mass spectra of sparteine and α-isosparteine and their oxo- and hydroxy-substituted derivatives indicate a dependence of their fragmentation on the stereochemistry of the ring junctions.[1–6] The basic bisquinolizidine 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 of rings (C–D) is much more susceptible to inversion on the N-16 nitrogen atom and it may to occur in a *trans* boat-chair or *cis* double-chair conformation. A detailed EI mass spectrometric (MS) study of deuterated analogs of sparteine[1] indicated stereoisomeric effects of the main fragment ions. Ions at *m/z* 98 ($C_6H_{12}N$) were found to originate mainly by cleavage of ring B (i.e. containing A), whereas *m/z* 137 ions ($C_9H_{16}N$) were predominantly formed by cleavage of ring C (i.e. containing rings A and B). Similar effects were not obtained from analogous deuterated derivatives of α-isosparteine, in accordance with their entirely symmetric structures.[7]

This work is a continuation of our earlier reinvestigation of the mass fragmentation of lactams of sparteine and α-isosparteine,[3,4] multiflorine and its derivatives[5] and 13-keto- and hydroxy-substituted derivatives of sparteine and lupanine.[6]

The purpose of this study was to explain the mass fragmentation of 2-phenylsparteine (**1**), 2-(*p*-tolyl)sparteine (**2**) 15-phenylsparteine (**3**) 2-phenyl-2-dehydrosparteine (**4**), 2-(*p*-tolyl)-2-dehydrosparteine (**5**) and 15-phenyl-14-dehydrosparteine (**6**). We wished to determine the role of the phenyl and *p*-tolyl substituents in the cleavage reactions and to establish whether it is possible to determine the positions of these groups in the sparteine (or dehydrosparteine) skeleton on the basis of differences in the values of μ, defined as the ratio of the intensity of the selected fragment ions peaks to that of the parent ion peak. In **1**,[8] **2**,[9] **4**[10] and **5**,[11] the phenyl (or *p*-tolyl) substituent is localized at C-2 in the *trans* fused A and B ring system. In **3**,[12] the phenyl substituent is localized at C-15 in the *trans* fused C and D rings system, and in **6**,[12] the phenyl substituent is localized at C-15 in the *cis* fused C and D ring system. C/D *trans* fused rings of **1**–**5** have a boat-chair conformations. In contrast, C/D *cis* fused rings of **6** have a double chair conformation (Fig. 1).

EXPERIMENTAL

Low- and high-resolution EI mass spectra were recorded on an AMD-402 two-sector mass spectrometer (ionizing voltage 70 eV, accelerating voltage 8 kV, resolution 10 000). Samples were introduced by a direct insertion probe at a source temperature of ~180 °C. The elemental compositions of the ions were determined by a peak matching method relative to perfluorokerosene, using the same instrument. All masses measured agreed with those of the composition listed in the third column of Tables 1 and 2 within ±2 ppm. The collisionally activated decomposition (CAD) *B/E* linked scan spectra in the first field-free region were investigated using helium as the collision gas at a pressure of 1.73×10^{-5} with an ion source temperature of 180 °C,

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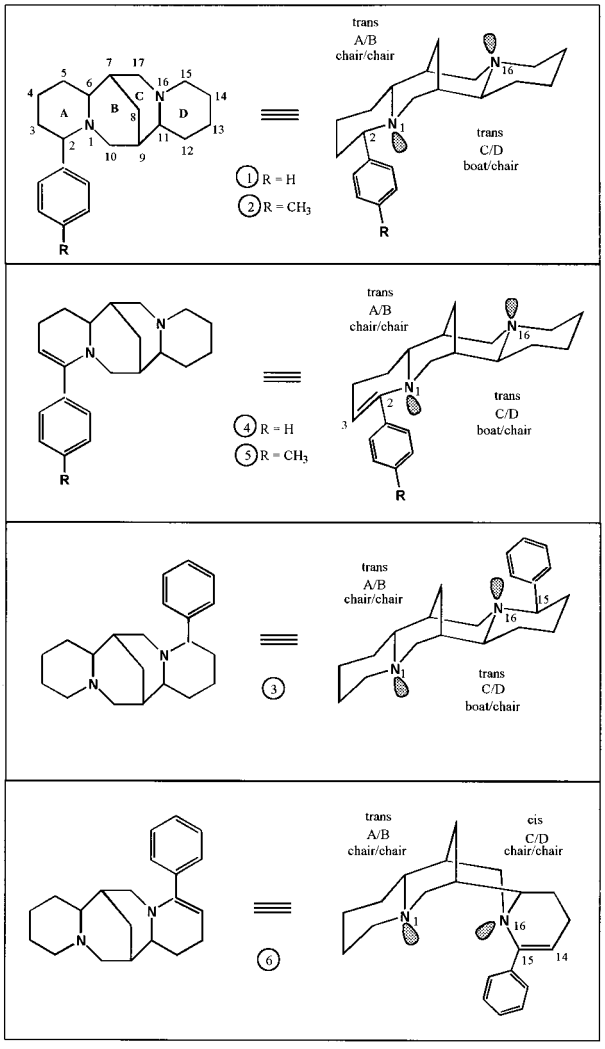


Figure 1. The structures of 2- and 15-substituted Derivatives of Sparteines (1,2,3) and 2-(or 14-)-Dehydrosparteines (4,5,6).

an ionization energy of 70 eV and an accelerating voltage of 8 kV.

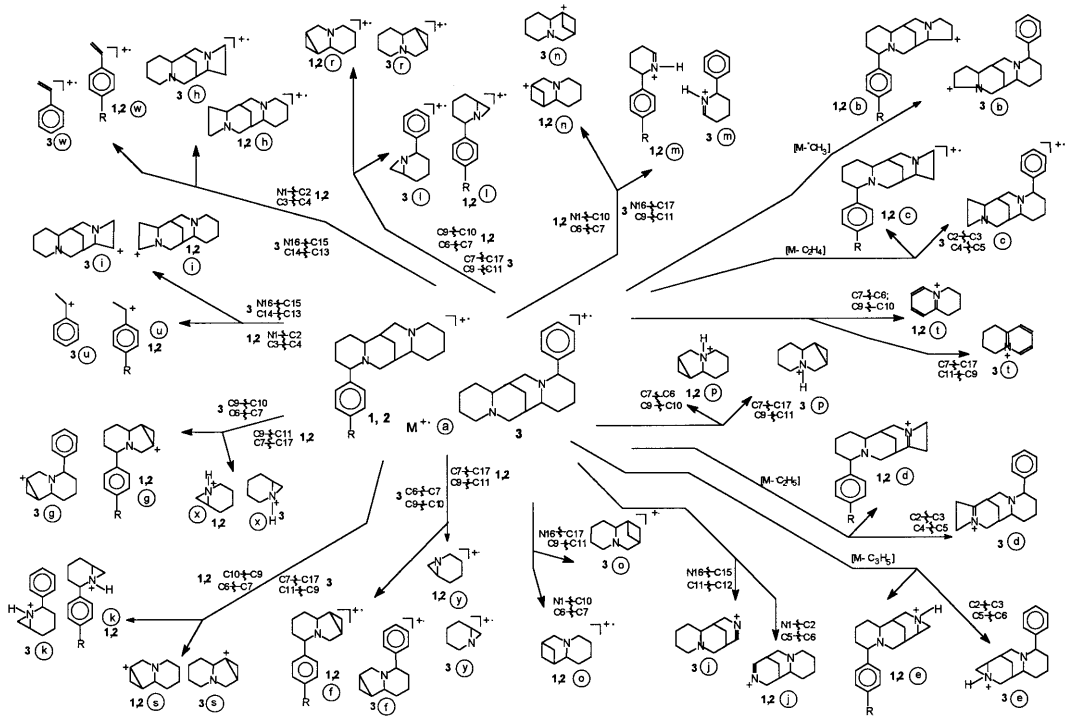
Compounds **1**,[8] **2**,[9] **3**,[12] **4**,[10] **5**[11] and **6**[12] were obtained in the form of the free bases according to the literature. The spectral characteristic were consistent with the literature data.[8–12]

RESULTS AND DISCUSSION

On the basis of the low-resolution EI mass spectra and exact mass determinations (Tables 1 and 2) and also CAD *B/E* linked scan spectra, the principal mass spectral fragmentation routes of compounds **1**, **2** and **3** are interpreted as shown in Scheme 1 and those of **4**, **5**, **6** as in Scheme 2.

As can be seen from Schemes 1 and 2 and Tables 1 and 2, the principal mass fragmentation pathways of 2-substituted sparteines and dehydrosparteines (**1**, **2**, **4**, **5**) are similar to those of the isomeric 15-substituted sparteine **3** and dehydrosparteine **6**, but show differences in the abundances of the important fragment ions. It is also seen that the presence of the methyl group in the *para* position of the phenyl ring of the molecules of **2** and **5** has no influence on the main routes of the mass fragmentation of the molecular ions of these compounds, in comparison with the mass fragmentation of molecular ions of **1** and **4**. It should be pointed out that only the fragmentation pathways have been confirmed by *B/E* linked scan spectra and that many of the cyclic ion structures shown in Schemes 1 and 2 are conjectural, similarly to those discussed previously in the literature.[1,2,7,13–15]

The common features of the mass spectral fragmentation of molecular ions of **1**, **2**, **4** and **5** are the cleavages of N1—C2, N1—C10, C3—C4, C6—C7, C7—C17,



Scheme 1. The pathways of the EI-mass fragmentation of the molecular ions of 1,2,3.

Table 1. Elemental compositions and relative intensities of the ion peaks in the EI mass spectra of 1–3 according to high-resolution data

Ion	*m/z*	Elemental composition	Relative peak intensity (%) 1	2	3
$M^{+\cdot}$ *a*	310	$C_{21}H_{30}N_2$	100		78
	324	$C_{22}H_{32}N_2$		100	
b	295	$C_{20}H_{27}N_2$	6		3
	309	$C_{21}H_{29}N_2$		6	
c	282	$C_{19}H_{26}N_2$	5		3
	296	$C_{20}H_{28}N_2$		5	
d	281	$C_{19}H_{25}N_2$	5		8
	295	$C_{20}H_{27}N_2$		5	
e	269	$C_{18}H_{25}N_2$	28		17
	283	$C_{19}H_{27}N_2$		26	
f	213	$C_{15}H_{19}N$	99		10
	227	$C_{16}H_{21}N$		92	
g	212	$C_{15}H_{18}N$	10		26
	226	$C_{16}H_{20}N$		10	
h	206	$C_{13}H_{22}N_2$	6	7	14
i	205	$C_{13}H_{21}N_2$	3	4	30
j	177	$C_{11}H_{17}N_2$	12	14	10
k	174	$C_{12}H_{16}N$	25		14
	188	$C_{13}H_{18}N$		22	
l	173	$C_{12}H_{15}N$	4		12
	187	$C_{13}H_{17}N$		5	
m	160	$C_{11}H_{14}N$	11		4
	174	$C_{12}H_{16}N$		12	
n	150	$C_{10}H_{16}N$	15	16	13
o	151	$C_{10}H_{17}N$	22	23	10
p	138	$C_9H_{16}N$	20	8	18
r	137	$C_9H_{15}N$	14	17	100
s	136	$C_9H_{14}N$	46	56	21
t	134	$C_9H_{12}N$	34	44	13
u	105	C_8H_9	2		7
	119	C_9H_{11}		2	
w	104	C_8H_8	7		7
	118	C_9H_{10}		6	
x	98	$C_6H_{12}N$	20	23	98
y	97	$C_6H_{11}N$	12	13	35

Table 2. Elemental compositions and relative intensities of the ion peaks in the EI mass spectra of 4–6 according to high-resolution data

Ion	*m/z*	Elemental composition	Relative peak intensity (%) 4	5	6
$M^{+\cdot}$ *a*	308	$C_{21}H_{28}N_2$	72		100
	322	$C_{22}H_{30}N_2$		74	
b	293	$C_{20}H_{25}N_2$	1		1
	307	$C_{21}H_{27}N_2$		1	
c	280	$C_{19}H_{24}N_2$	1		1
	294	$C_{20}H_{26}N_2$		1	
d	279	$C_{19}H_{23}N_2$	1		1
	293	$C_{20}H_{25}N_2$		1	
e	267	$C_{18}H_{23}N_2$	1		4
	281	$C_{19}H_{25}N_2$		1	
f	211	$C_{15}H_{17}N$	4		3
	225	$C_{16}H_{19}N$		3	
g	210	$C_{15}H_{16}N$	4		11
	224	$C_{16}H_{18}N$		3	
h	206	$C_{13}H_{22}N_2$	1	1	1
i	205	$C_{13}H_{21}N_2$	1	1	1
j	177	$C_{11}H_{17}N_2$	2	2	17
k	172	$C_{12}H_{14}N$	100		7
	186	$C_{13}H_{16}N$		100	
l	171	$C_{12}H_{13}N$	2		6
	185	$C_{13}H_{15}N$		2	
m	158	$C_{11}H_{12}N$	3		2
	172	$C_{12}H_{14}N$		7	
n	150	$C_{10}H_{16}N$	9	7	5
o	149	$C_{10}H_{15}N$	19	16	2
p	137	$C_9H_{15}N$	1	1	14
r	136	$C_9H_{14}N$	4	4	7
s	134	$C_9H_{12}N$	29	18	6
t	103	C_8H_7	2		1
	117	C_9H_9		2	
u	102	C_8H_6	1		1
	116	C_9H_8		2	
w	98	$C_6H_{12}N$	4	3	26
x	97	$C_6H_{11}N$	2	1	6

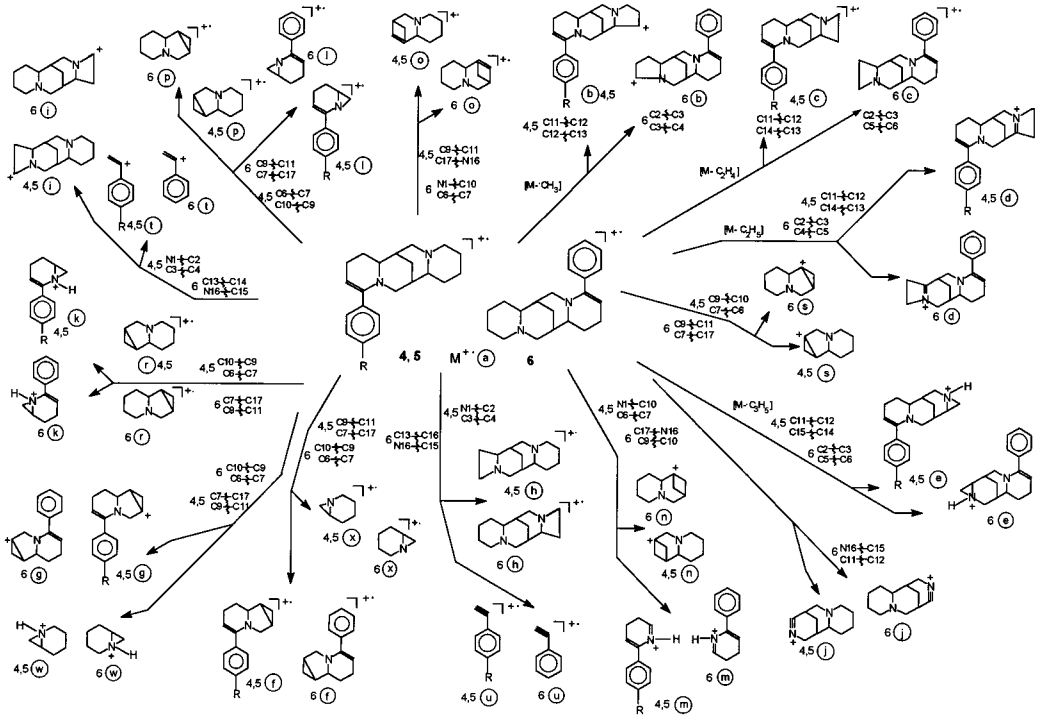
C9—C10, C9—C11 bonds of rings A, B and C of these compounds. In constrast, in **3** and **6** the cleavages of N16—C15, N16—C17, C6—C7, C7—C17, C9—C10, C9—C11 and C13—C14 bonds of rings D, C and B of the skeleton of sparteine or dehydrosparteine occur.

It should be pointed out that the basic peaks in the mass spectra of **1**, **2** and **6** are the molecular ions *a*, the odd-electron fragment ion *r* is the base peak of **3** and the even-electron fragment ions *k* are the base peaks of **4** and **5**.

Mass decomposition of the cyclic skeleton of molecular ions of **1**, **2** and **3** (Scheme 1, Table 1) proceeds by the cleavage of two or three bonds of rings A, B, C and D of the skeleton of sparteine. The two-bond cleavage of odd-electron molecular ion leads to odd-electron fragment ions *c*, *f*, *h*, *l*, *o*, *r*, *w* and *y* (Scheme 1, Table 1). In the mass decomposition of molecular ions of **1** and **2** (Scheme 1, Table 1), the odd-electron fragment ions *w* plus *h*, *f* plus *y* and *r* plus *l* were obtained by the cleavages of N1—C2/C3—C4 (ring A), C9—C11/C7—C17 (ring C) and C6—C7/C9—C10 (ring B) bonds, respectively. The cleavages of N1—C10/C6—C7 bonds of ring B in **1** and **2** lead to the odd-electron fragment ion *o*. The elimination of the neutral molecules of ethylene (odd-electron fragment ion *c*) from the molecular ions **1** and **2** can be explained on the basis of initial ionization at the C_{sp^3}—C_{sp^3} sigma bond of ring D. Decomposition of molecular ion of **3** leads to *w* plus *h*, *f* plus *y* and *r* plus *l* odd-electron fragment ions by the cleavages of N16—C15/C14—C13 (ring D), C6—C7/C9—C10 (ring B) and C7—C17/C9—C11 (ring C) bonds, respectively. The cleavages of N16—C17/C9—C11 (ring C) bonds of the molecular ion of **3** lead to the odd-electron fragment ion *o*. The elimination of the neutral molecule of ethylene (odd-electron fragment ion *c*) from the molecular ion of **3** can be explained as above in the case of **1** and **2**) on the basis of initial ionization at the C_{sp^3}—C_{sp^3} sigma bonds of ring A.

The three-bond cleavage with a neighbouring H-rearrangement reaction leads to even-electron fragment ions *b* ($M - {}^{\cdot}CH_3$), *d* ($M - {}^{\cdot}C_2H_5$), *e* ($M - {}^{\cdot}C_3H_5$), *g*, *i*, *j*, *k*, *m*, *n*, *p*, *s*, *t*, *u* and *x* (Scheme 1 and Table 1).

In the cases of the molecular ions of **1** and **2**, *k* and *s* even-electron fragment ions were obtained by the cleavages of C6—C7/C9—C10 (ring B) bonds, in addition to



Scheme 2. The pathways of the EI-mass fragmentation of the molecular ions of 4,5,6.

u and *i*, *g* and *x* and *n* and *m* even-electron fragment ions by the cleavages of N1—C2/C3—C4 (ring A), C9—C11/C7—C17 (ring C) and N1—C10/C6—C7 (ring B) bonds, respectively.

The same ions were obtained in the mass fragmentation of the molecular ion of **3** by the cleavages of C7—C17/C9—C11 (ring C, ions *k* and *s*), N16—C15/C14—C13 (ring D, ions *u* and *i*), C6—C7/C9—C10 (ring B, ions *g* and *x*) and N16—C17/C9—C11 (ring C, ions *m* and *n*) bonds of the skeleton of sparteine (Scheme 1, Table 1). It should be pointed out that methyl (ion *b*), ethyl (ion *d*) and allyl (ion *e*) radicals were probably eliminated from rings A (**3**) and D (**1**, **2**) of the skeleton of sparteine. Hydrogen transfer to a radical site at annular nitrogen atom occurs in the cases of *k*, *e*, *m*, *p* and *x* even-electron fragment ions (Scheme 1, Table 1). The charge is probably also situated on an annular nitrogen atom of the even-electron fragment ions *d* ($M - {}^{\cdot}C_2H_5$), *j* ($M - {}^{\cdot}C_{10}H_{12}R$) and *t* ($M - {}^{\cdot}C_{12}H_{18}RN$). In compounds **1** and **2** it is located at N-16 (ions *d* and *t*) or N—1 (ion *j*), but in constrast, in **3** at N—1 (ions *d* and *t*) or N—16 (ion *j*).

Decomposition of the cyclic skeleton of molecular ions of **4**, **5** and **6** (Scheme 2, Table 2) also proceeds by the cleavage of two and three bonds of rings A, B, C and D of the skeleton of sparteine.

The two-bond cleavage of the odd-electron molecular ion leads to odd-electron fragment ions *c*, *f*, *h*, *l*, *o*, *p*, *u* and *x* (Scheme 2, Table 2). Decomposition of the molecular ions of **4** and **5** (Scheme 2, Table 2) leads to the odd-electron fragment ions *u* plus *h*, *f* plus *x* and *p* plus *l* by cleavages of N1—C2/C3—C4 (ring A) C9—C11/C7—C17 (ring C) and C6—C7/C9—C10 (ring B) bonds, respectively. The cleavages of N1—C10/C6—C7 bonds of ring B of **4** and **5** lead to odd-electron fragment ion *o*. Elimination of the neutral molecules of ethylene (odd-electron fragment ion *c*) from molecular ions of **4** and **5** can be explained on the basis of initial ionization at the C_{sp^3}—C_{sp^3} sigma bond of ring D. Fragmentation of the molecular ion of **6** leads to *u* plus *h*, *f* plus *x* and *p* plus *l* odd-electron ions by the cleavages of N16—C15/C14—C13 (ring D), C6—C7/C9—C10 (ring B) and C7—C17/C9—C11 (ring C) bonds, respectively. The cleavages of N16—C17/C9—C11 (ring C) bonds of the molecular ion of **6** lead to the odd-electron fragment ion. Elimination of the neutral molecule of ethylene from **6** (odd-electron fragment ion *c*) can be rationalized (as above in the case of **3**) on the basis of initial ionization at the C_{sp^3}—C_{sp^3} sigma bonds of ring A.

Three-bond cleavage with a neighbouring H-rearrangement reaction leads to even-electron fragment ions *b* ($M - {}^{\cdot}CH_3$), *d* ($M - {}^{\cdot}C_2H_5$), *e* ($M - {}^{\cdot}C_3H_5$), *g*, *i*, *j*, *k*, *m*, *n*, *p*, *r*, *s*, *t* and *w* (Scheme 2 and Table 2).

In the cases of the molecular ions of **4** and **5**, *k* and *r* even-electron fragment ions were obtained by the cleavages of N1—C2/C3—C4 (ring A), C9—C11/C7—C17 (ring C) and N1—C10/C6—C7 (ring B) bonds, respectively. The same ions were obtained in the fragmentation processes of the molecular ion of **6** by the cleavages of C7—C17/C9—C11 (ring C, ions *k* plus *r*), N16—C15/C14—C13 (ring D, ions *t* plus *i*), C6—C7/C9—C10 (ring B, ions *g* plus *w*) and N16—C17/C9—C11 (ring C, ions *m* plus *n*) bonds of the skeleton of sparteine (Scheme 2, Table 1). Methyl (ion *b*), ethyl (ion *d*) and allyl (ion *e*) radicals were probably eliminated from rings A (**6**) and D (**4** and **5**). Hydrogen transfer to a radical site at an annular nitrogen atom is seen in the cases of *k*, *e*, *m*, *p* and *w* even-electron fragment ions (Scheme 2, Table 2). The charge is probably localized on an annular nitrogen atom of the even-electron fragment ions *d* ($M - {}^{\cdot}C_2H_5$), *j* ($M - {}^{\cdot}C_{10}H_{12}R$) and *t* ($M - {}^{\cdot}C_{12}H_8NR$). In the cases of compounds **4** and **5**, it is at N—16 (ions *d* and *s*) or at N—1 (ion *j*), but in the case of **6** it is at N—1 (ions *d* and *s*) or at N—16 (ion *j*).

Table 3 presents, for all the compounds investigated (**1**–**6**), the ratios of the intensities (int) of the *x* (**1**–**3**), *w*

Table 3. Values of μ_1–μ_6 calculated from the EI mass spectra of 1–6 recorded at 75 eV

Compound	μ_1	μ_2	μ_3	μ_4	μ_5	μ_6
1	0.20	0.14	0.25	0.99	0.46	0.12
2	0.23	0.17	0.22	0.92	0.56	0.13
3	1.25	1.28	0.17	0.12	0.26	0.44
4	0.05	0.01	1.38	0.05	0.05	0.02
5	0.04	0.01	1.35	0.04	0.05	0.01
6	0.26	0.14	0.07	0.03	0.07	0.06

(**4–6**), *r* (**1–3**), *p* (**4–6**), *k* (**1–6**), *f* (**1–6**), *s* (**1–3**), *r* (**4–6**), *y* (**1–3**) and *x* (**4–6**) ion peaks to those of the parent ion peaks, i.e.

$$\mu_1 = r \text{ int } x^+/r \text{ int } M^{+\cdot} \text{ (1–3)}$$
$$\mu_2 = r \text{ int } r^{+\cdot}/r \text{ int } M^{+\cdot} \text{(1–3)}$$
$$\mu_3 = r \text{ int } k^+/r \text{ int } M^{+\cdot} \text{ (1–6)}$$
$$\mu_5 = r \text{ int } s^+/r \text{ int } M^{+\cdot} \text{ (1–3)}$$
$$\mu_6 = r \text{ int } y^{+\cdot}/r \text{ int } M^{+\cdot} \text{ (1–3)}$$
$$\mu_1 = r \text{ int } w^+/r \text{ int } M^{+\cdot} \text{ (4–6)}$$
$$\mu_2 = r \text{ int } p^{+\cdot}/r \text{ int } M^{+\cdot} \text{ (4–6)}$$
$$\mu_4 = r \text{ int } f^{+\cdot}/r \text{ int } M^{+\cdot} \text{ (1–6)}$$
$$\mu_5 = r \text{ int } r_+/r \text{ int } M^{+\cdot} \text{ (4–6)}$$
$$\mu_6 = r \text{ int } x^+/r \text{ int } M^{+\cdot} \text{ (4–6)}$$

As can be seen from the data in Table 3, the differences between the relative intensities of the peaks of the selected fragment ions *f*, *k*, *p*, *r*, *s*, *w*, *x*, *y* and $M^{+\cdot}a$ ions, i.e. the values of μ_1–μ_6 for **1**, **2**, **4**, **5** and also **3** and **6** may be sufficient to differentiate isomers. It is possible to distinguish isomeric 2- and 15-phenyl-substituted sparteines and dehydrosparteines. This problem has not been tackled previously. According to Neuer-Jehle *et al.*,[13,14] the EI mass spectra of sparteine and α-isosparteine reveal a dependence of the fragmentation of the molecular ions on the stereochemistry of ring junctions of the bisquinolizidine skeleton. The same dependence has been also confirmed in the processes of mass decomposition of the molecular ions of **1**, **2**, **4** and **5**. The coefficients μ_3 and μ_4 (Table 3) discussed in this paper are the counterparts of the coefficients of $\mu = r$ int m/z 98/*r*. int $M^{+\cdot}$ and $\mu = r$ int m/z 137/*r* int $M^{+\cdot}$ considered by Neuer-Jehle *et al.*[13,14] The values of μ_4 for **1** and **2** (0.99 and 0.92, respectively) and of μ_3 for **4** and **5** (1.38 and 1.35, respectively) are almost the same as those obtained by Neuer-Jehle *et al.*[13,14] for α-isosparteine (0.93 and 1.50, respectively). Hence the information on *trans* A/B–*trans* C/D junctions of the bisquinolizidine skeleton of **1**, **2**, **4** and **5** may be obtained from the analysis of the mass spectra of these compounds with the values of μ_4 (**1** and **2**) and μ_3 (**4** and **5**). For **3** and **6**, the values of μ_3 and μ_4 are different from those obtained from sparteine and α-isosparteine by Neuer-Jehle *et al.*[13,14] For **3**, this may be interpreted as the influence of the substituent in the C—15 position. It ought to be pointed out that according to Neuer-Jehle *et al.*,[13,14] the value of $\mu_1 = 1.25$ for **3** allows one to establish the junction of A/B *trans* rings of the bisquinolizidine skeleton of this compound, on the basis of the structure of the even-electron fragment ion *x* of **3** containing ring A.

CONCLUSION

The EI-induced mass fragmentation of the molecular ions of **1–6** proceeds by the cleavages of C_{sp^3}—C_{sp^3}, C_{sp^3}—C_{sp^2}, C_{sp^3}—N and C_{sp^2}—N bonds of the A, B, C and D rings of the sparteine or dehydrosparteine skeleton. The fission of these bonds depends mainly on the location of the phenyl (or *p*-tolyl) group in the bisquinolizidine skeleton, but in some respect also on the stereochemistry of the ring junctions.

In the processes of the EI-induced mass fragmentation of the molecular ions of **1–6** the elimination of the phenyl (or *p*-tolyl) substituent has not been observed.

The presence of a methyl substituent in the *para* position of the phenyl ring of **2** and **5** does not influence the fragmentation routes of the molecular ions of these compounds, in comparison with **1** and **4**.

15-Phenyl-substituted sparteine (**3**) may be distinguished from the isomeric 2-phenyl-substituted sparteine (**1**) on the basis of the higher values of μ_1, μ_2 and μ_6 and the lower values of μ_3, μ_4 and μ_5 (Table 3).

15-Phenyl-substituted 14-dehydrosparteine (**6**) may be distinguished from the isomeric 2-phenyl-substituted 2-dehydrosparteine (**4**) on the basis of the higher values of μ_1 and μ_2 and the lower value of μ_3 (Table 3).

The values of μ_4 of **1** and **2** and μ_3 of **4** and **5** confirm according to the literature,[13,14] the *trans* A/B–*trans* C/D junction of the rings of the bisquinolizidine system of these compounds.

REFERENCES

1. N. Neuer-Jehle, H. Nesvadba and G. Spiteller, *Monatsh. Chem.* **95**, 687 (1964).
2. D. Schumann, G. Spiteller and N. Neuer-Jehle, *Monatsh. Chem.* **99**, 390 (1968).
3. U. Majchrzak-Kuczyńska, M. Wiewiórowski and E. Wyrzykiewicz, *Org. Mass Spectrom.* **19**, 600 (1984).
4. U. Majchrzak-Kuczyńska, M. Wiewiórowski and E. Wyrzykiewicz, *Bull. Pol. Acad. Sci. Chem.* **33**, 1 (1985).
5. E. Wyrzykiewicz, W. Wysocka and M. Wiewiórowski, *Org. Mass Spectrom.* **23**, 700 (1988).
6. E. Wyrzykiewicz and W. Wysocka, *Org. Mass Spectrom.* **25**, 453 (1990).
7. N. S. Wulfson and V. G. Zaikin, *Usp. Khim.* **45**, 1780 (1976).
8. W. Boczoń, *Pol. J. Chem.* **55**, 339 (1981).
9. W. Boczoń and B. Kozioł, *J. Mol. Struct.* **403**, 171 (1997).
10. W. Boczoń, *J. Mol. Struct.* **158**, 127 (1987).
11. W. Boczoń, *Bull. Pol. Acad. Sci. Chem.* **36**, 21 (1988).
12. W. Boczoń, *Bull. Pol. Acad. Sci. Chem.* **36**, 37 (1988).
13. N. Neuer-Jehle, H. Nesvadba and G. Spiteller, *Monatsh. Chem.* **98**, 836 (1967).
14. J. Tamas, in *Applications of Mass Spectrometry to Organic Stereochemistry*, edited by J. S. Splitter and F. Turecek, p. 628. VCH, New York (1994).
15. S. D. Sastry and C. R. Waller, *Biochem. Appl. Mass Spectrom.* 655 (1972), and references cited therein.