



Contrasting chiroptical properties of sparteine lactams and thiolactams

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Received 20 April 2001; accepted 22 May 2001

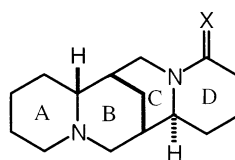
Abstract—The CD spectra of several mono- and dilactams and thiolactams of sparteine were measured with the purpose of clarifying spectra–structure relations. It is shown that the Cotton effects of lactams are predominantly of the opposite sign to those of the corresponding thiolactams. In bichromophoric molecules **7–9** the observed CD spectra are dominated by exciton type interactions. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

In spite of a number of studies conducted and the need for reliable correlations between the structure and the CD data, the chiroptical properties of lactams and thiolactams are not adequately understood in relation to their structure.¹ Unsurprisingly, a general rule relating the CD spectrum to the configuration and conformation of lactams and thiolactams is yet to emerge.² One of the underlying reasons is uncertainty about conformational equilibria in simple lactams and thiolactams. Oxo- and thiono-derivatives of sparteines are good candidates for spectra–structure correlations as their configuration and conformations are reasonably well established through a combination of X-ray diffraction, NMR spectroscopy and molecular mechanics studies. In addition, their tetracyclic structure means that the number of possible conformers is significantly reduced.

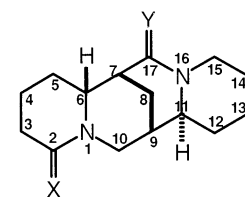
Some sparteine alkaloids, including lactam derivatives, were already studied by CD spectroscopy in hexane and methanol solutions³ but no decisive structural correlations were proposed. We investigated the lactams and thiolactams **1–9** by CD in acetonitrile solution, with the aim of revealing any structure–chiroptical data correlations.

Thionation of the lactam chromophore is known to bring about a red shift of the absorption bands.^{4–7} The presence of both $n\text{--}\pi^*$ and $\pi\text{--}\pi^*$ transitions is well documented for the thioamide chromophore.^{8,9} It has been established that the polarization direction of the $\pi\text{--}\pi^*$ transition is deflected from the direction of the C=S bond by an angle of 14–16°, according to single crystal spectroscopy¹⁰ and CNDO/S calculations.¹¹ Thus, the polarization directions of the $\pi\text{--}\pi^*$ transitions of both the amide¹² and the thioamide¹³ chromophores are similar and they are close to the line connecting the nitrogen and the oxygen (or sulfur) atoms. Additionally thiolactams exhibit a short-wavelength transition observed as a UV maximum at ca. 210 nm. The polarization direction of this transition is nearly orthogonal to the polarization direction of the long-wavelength $\pi\text{--}\pi^*$ band.¹⁰ The short-wavelength transition has been tentatively assigned as an $n_\sigma\text{--}\pi^*$ type transition.⁴



1 X=O

2 X=S



3 X=O, Y=H₂

4 X=S, Y=H₂

5 X=H₂, Y=O

6 X=H₂, Y=S

7 X=Y=O

8 X=S, Y=O

9 X=Y=S

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2. Results and discussion

Lactams and thiolactams display in the accessible UV region at least two transitions. The $n\text{--}\pi^*$ transition is demonstrated in the CD spectra as a Cotton effect at ca. 230 nm (lactams) and at 340–365 nm (thiolactams). The strong $\pi\text{--}\pi^*$ band is seen in the UV spectra at ca. 205 nm (*N*-alkylated lactams) and at 275–290 nm (*N*-alkylated thiolactams), as well as in the CD spectra. The position of the CD Cotton effect is frequently red-shifted with regard to the UV maximum ($\pi\text{--}\pi^*$). These data refer to the compounds studied here, in acetonitrile solution. Some lactams, such as **5** and **7**, show two Cotton effects of opposite sign in the region of the $\pi\text{--}\pi^*$ transition. All thiolactams exhibit a short-wavelength transition at 210–240 nm, observed as a Cotton effect in the CD spectra whose maximum is

usually shifted bathochromically with respect to the corresponding UV maximum.

Examples of the CD/UV spectra of 15-oxo-11 α -sparteine **1** and its 15-thio analog **2** are shown in Fig. 1 (see also Table 1). Lactam **1** shows a negative $n\text{--}\pi^*$ Cotton effect ($\Delta\epsilon$ -4.2 at 230 nm) and a positive $\pi\text{--}\pi^*$ Cotton effect ($\Delta\epsilon$ $+9.1$ at 195 nm). Opposite sign pattern holds for thiolactam **2**, i.e. a positive $n\text{--}\pi^*$ Cotton effect ($\Delta\epsilon$ $+0.9$ at 343 nm) and a negative $\pi\text{--}\pi^*$ Cotton effect ($\Delta\epsilon$ -2.4 at 289 nm). The 15-oxo compound **1** is known to exist in the solid state¹⁴ in a conformation characterized by a half-chair ($12\alpha,13\beta$) ring D, with a positive (O)C–N endocyclic torsion angle (ring C in a boat form). The 15-thiono analog **2** in the solid state displays ring D in a distorted sofa form, whereas ring C is a sofa (8β).¹⁵ It may appear that the opposite signs of

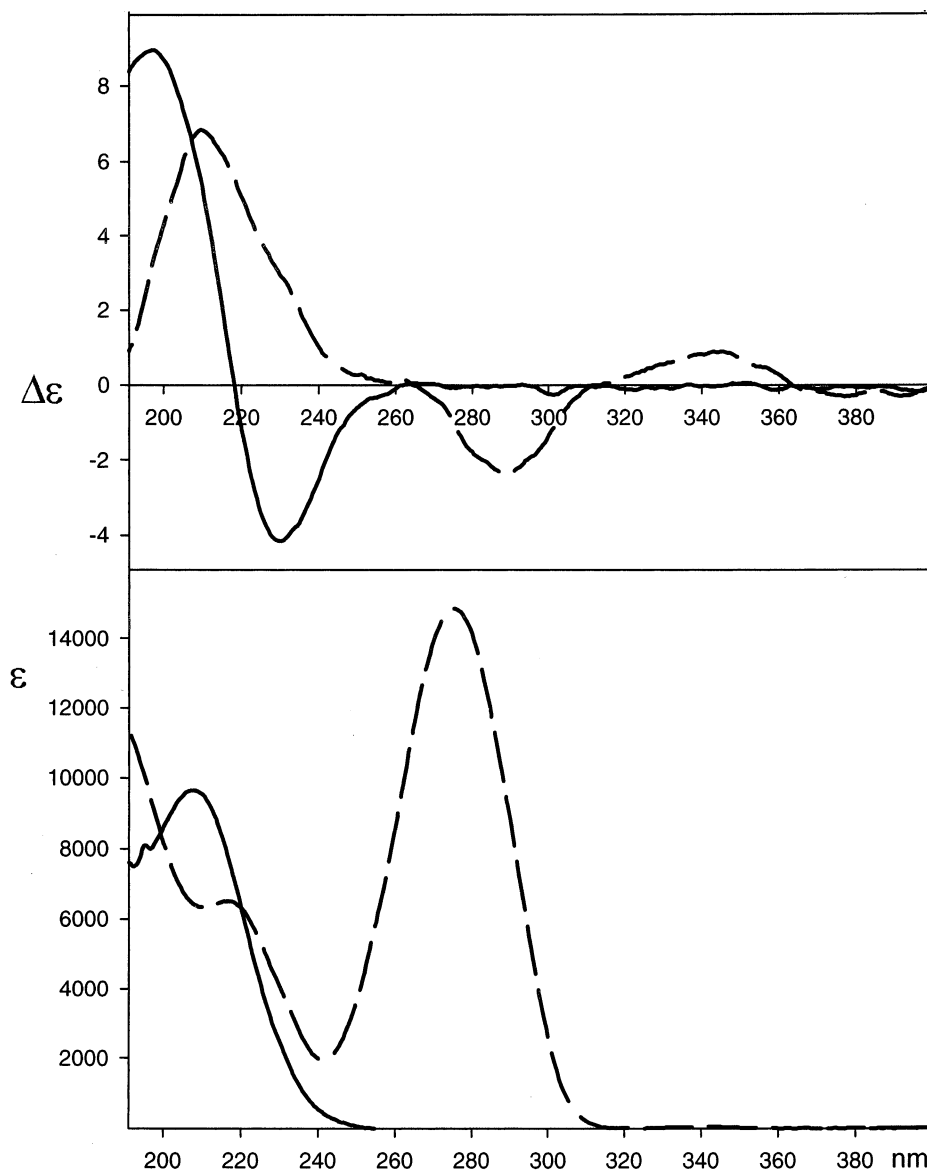


Figure 1. CD (top panel) and UV (bottom panel) spectra of **1** (—) and **2** (---).

Table 1. CD and UV data for **1–9** (solvent acetonitrile unless stated otherwise)

Compound	$n-\pi^*$	$\pi-\pi^*$		$n_\sigma-\pi^*$	
	$\Delta\epsilon$ (nm)	$\Delta\epsilon$ (nm)	ϵ (nm)	$\Delta\epsilon$ (nm)	ϵ (nm)
1	−4.2 (230)	+9.1 (195)	9800 (208)		
2	+0.89 (343)	−2.4 (289)	14900 (275)	+6.8 (209)	6500 (217)
3	+5.4 (231)	−7.3 (206)	8600 (206)		
4	+0.73 (363)	+9.6 (281)	13800 (280)	−1.5 (236)	6500 (210)
4^a	+1.4 (385)	+4.3 (290)	13800 (283)	−1.3 (231)	^b
				+3.6 (213)	
4^c	+0.6 (369)	+11.0 (278)	13600 (278)	−1.0 (225)	^b
5	+2.8 (231)	−3.6 (217), +3.2 (206)	11300 (203)		
6	−3.4 (355)	+20.8 (286), −2.3 (240)	14100 (283)	−5.2 (213)	5900 (210)
7	+5.5 (229)	−4.2 (215), +19.3 (203)	13900 (207)		
8	+0.23 (385), −0.59 (347)	+18.7 (284)	13600 (281)	^d	^d
	+2.2 (230)	−13.5 (218), +22.6 (206)	10400 (206)		
9	−1.9 (365)	+86.8 (294), −13.8 (270)	24200 (288)	−11.7 (229), −13.3 (208)	7800sh (213)

^a Solvent cyclohexane.^b Maximum not observed.^c Solvent methanol.^d These bands are hidden under short-wavelength $\pi-\pi^*$ bands.

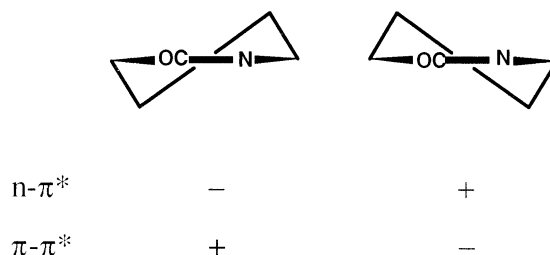
Cotton effects for **1** and **2** are due to conformational differences of the lactam and thiolactam rings in, respectively, **1** and **2**.

The CD data for lactams and thiolactams in positions 2 (**3** and **4**) and 17 (**5** and **6**) are shown in Table 1. Compounds **3**^{16,17} and **4**¹⁸ are known to exist in a ring A half-chair (4 β ,5 α)–sofa (4 β), ring C boat conformation. Despite the close conformational similarity, **3** and **4** show opposite sign $\pi-\pi^*$ Cotton effects; however, the $n-\pi^*$ Cotton effects are positive for both compounds regardless of the solvent used (see Table 1). There is a significant red shift and increased intensity of the $\pi-\pi^*$ Cotton effect as well as a blue shift of the $n-\pi^*$ Cotton effect of **4** in polar methanol solvent, compared to the data for nonpolar cyclohexane solution. When CD measurement was conducted in the solid state (KBr pellet), the $n-\pi^*$ Cotton effect of **4** was again positive. In the region of the $\pi-\pi^*$ transition, there were two observed Cotton effects: a negative one at longer wavelength (ca. 315 nm) and a positive one at ca. 285 nm. The origin of these two Cotton effects is probably extrinsic, i.e. due to the interaction of the two $\pi-\pi^*$ transition moments in the neighboring thiolactam molecules.

The case of ring C lactam **5** and thiolactam **6** is quite similar to that of **1** and **2**. The nearly planar lactam or thiolactam chromophore is a part of a distorted sofa (8 β) ring C conformer with the endocyclic C–N angle negative.^{15,19,20} The $n-\pi^*$ Cotton effect of **5** is positive, while the $\pi-\pi^*$ Cotton effect is bisignate. The corresponding Cotton effects for **6** are negative and bisignate. Again, despite conformational similarity thiolactam **6** displays Cotton effects of opposite sign to those of **5**.

The observed Cotton effects of monolactams and monothiolactams **1–6** are not simply correlated with any single structural parameter of the sparteine skele-

ton. Given the flexibility of the lactam or thiolactam ring, as follows from the X-ray data mentioned earlier and those for structurally related perhydropyrimidinones,²¹ the signs and magnitudes of the Cotton effects may reflect either (or both) the nonplanarity of the lactam/thiolactam chromophore (see related papers on CD of bicyclic lactams and thiolactams in which the internal strain is the cause of nonplanarity of the chromophore^{7,22}), or the conformation of the substituents (rings) in the vicinity of the chromophore. The empirical rule proposed earlier^{23,24} relates the sign of the $n-\pi^*$ transition in δ -lactam to the chirality of the half-chair conformation of the lactam ring (Scheme 1). This rule is apparently applicable to the present cases in a limited way (i.e. **1** and **3**, but not to **5**). It should be noted, however, that the signs of the $n-\pi^*$ and $\pi-\pi^*$ Cotton effects of structurally related lactams and thiolactams studied here are opposite, the exception being the same sign of the $n-\pi^*$ Cotton effect of **3** and **4**. While there is no obvious reason for the observed sign change, one of the possible explanations can be referred to subtle conformational differences between lactam and thiolactam rings in the same molecular environment, amply documented by X-ray diffraction studies. As expected, the short-wavelength (ca. 210 nm) Cotton effect for thiolactams **2**, **4** and **6** is of opposite sign to that of the $\pi-\pi^*$ transition at ca. 280 nm.

**Scheme 1.** An empirical correlation of the signs of the $n-\pi^*$ and $\pi-\pi^*$ Cotton effects with ring conformation of six-membered lactams.

The bichromophoric sparteine derivatives **7–9**, with oxo and/or thiono groups in positions 2 and 17, are known from the X-ray studies to exist in a sofa (4β) ring A and a distorted sofa (8β) ring C conformation.¹⁵ The chromophore in ring A is close to planarity whereas there is a deviation from planarity of the chromophore in ring C (negative endocyclic (X)C–N torsion angle). The conformations of rings A and C are not significantly different from those in the corresponding monochromophoric analogs **3–6**.

The analysis of the CD spectra of bichromophoric sparteine derivatives **7–9** was carried out by ‘synthesizing’ the CD curve from the CD curves of the component monochromophoric compounds and comparing the resultant spectrum with the experimental one. The difference is due to the interaction of the two chromophores. This interaction, if present, is primarily due to exciton coupling of the allowed π – π^* transitions, and it carries stereochemical information. The case of bis-lactam **7** is shown in Fig. 2. Bis-lactam **7** has two nearly planar amide chromophores, as determined by the X-ray diffraction study.²⁵ It is characterized by a positive n – π^* Cotton effect ($\Delta\epsilon$ +5.5 at 229 nm) and a pair of Cotton effects in the region of the π – π^* transition ($\Delta\epsilon$

–4.2 at 215 nm and +19.3 at 203 nm). The subtraction CD curve confirms the existence of a strong Cotton effect ($\Delta\epsilon$ +22.9 at 203 nm), apparently the first band of the positive exciton couplet. The interaction between the two chromophores is also seen in the case of lactam–thiolactam **8** (Fig. 3). The differential CD curve differs from the CD curve of **8** only by the magnitude of the Cotton effects. The main features of the differential CD curve are the presence of a strong positive Cotton effect in the region of the π – π^* thiolactam transition ($\Delta\epsilon$ +12.5 at 285 nm) and a pair of short-wavelength Cotton effects ($\Delta\epsilon$ –9.9 at 219 nm and +19.5 at 206 nm). The exciton interaction between the 17-lactam and 2-thiolactam chromophores is clearly visible, despite the energy gap (ca. 75 nm) between the π – π^* excitations of the two chromophores. The positive Cotton effect at 285 nm can be used for stereochemical correlation while interpretation of the short-wavelength Cotton effects is more problematic due to the possible involvement of the short-wavelength transition at ca. 210 nm in the thiolactam chromophore.

The case of bis(thiolactam) **9** (Fig. 4) is quite similar to that of **8**, i.e. the differential CD curve is different from

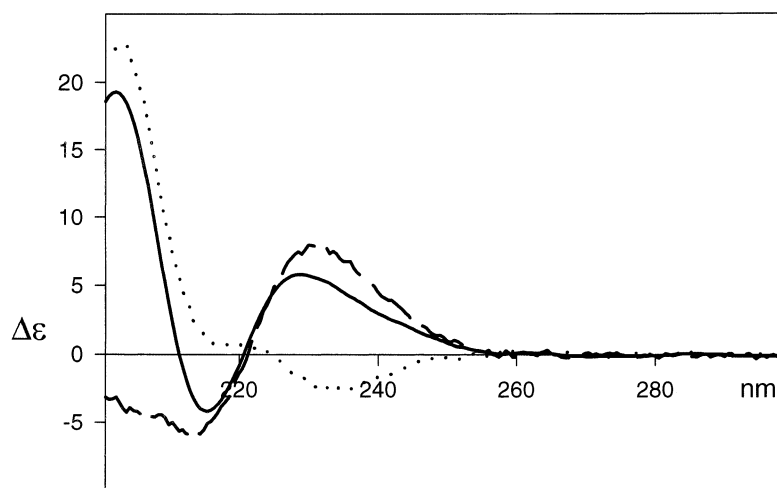


Figure 2. CD spectrum of **7** (—), a sum of the CD spectra of **3** and **5** (---) and a differential CD curve **7**–(**3**+**5**) (···).

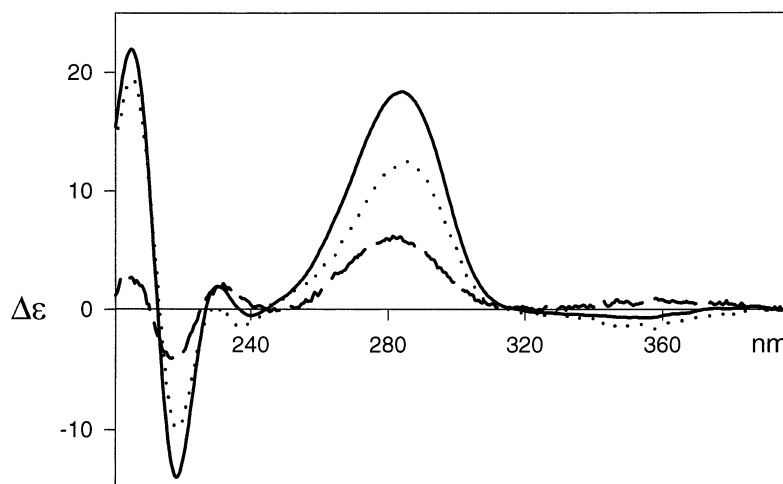


Figure 3. CD spectrum of **8** (—), a sum of the CD spectra of **4** and **5** (---) and a differential CD curve **8**–(**4**+**5**) (···).

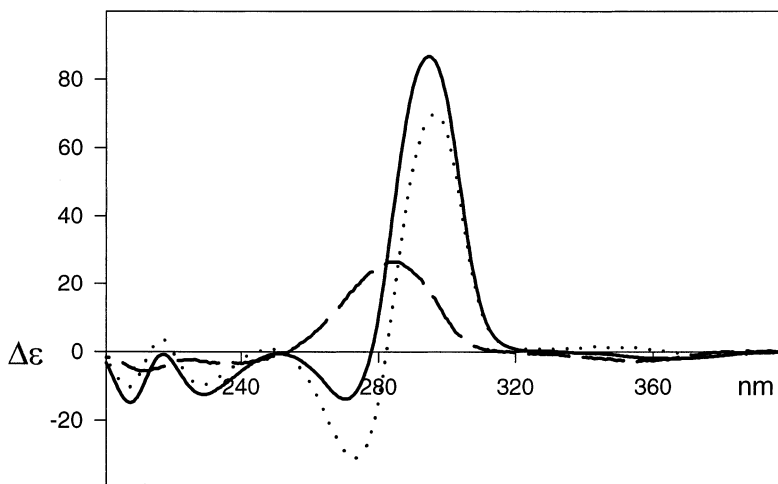
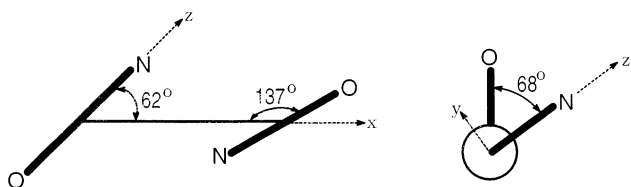


Figure 4. CD spectrum of **9** (—), a sum of the CD spectra of **4** and **6** (---) and a differential CD curve **9**–(**4**+**6**) (···).



Scheme 2. Geometry of the amide π – π^* electric dipole transition moments system (thick bars) in bis-lactam **7**.

that of **9** only by the magnitude of the Cotton effects. Exciton interaction between the two thiolactam chromophores in **2** and **17** positions produces a strong positive exciton couplet in the π – π^* absorption region ($\Delta\epsilon$ +69.9 at 296 nm and –13.8 at 270 nm), clearly indicating positive helicity of the interacting electric dipole transition moments of the two thiolactam chromophores. There is also seen significant red shift of the π – π^* absorption band of **9**, both in the UV and the CD spectrum (long-wavelength Cotton effect). This is typical for the longitudinal (as opposed to parallel) arrangements of the electric dipole transition moments (Scheme 2).

In the molecule **7**, the directions of the amide π – π^* electric dipole transition moments are approximated as the vectors connecting the nitrogen and the carbonyl oxygen atoms. The positions of the atoms were obtained from MM⁺ computed lowest-energy structure of **7**. Using a simple algorithm for a degenerate coupled-oscillator²⁶ one obtains readily a positive rotational strength for the lower-energy CD band and a negative rotational strength for the higher-energy CD band, which is exactly the result obtained experimentally.

3. Conclusion

We have shown that the CD spectra of sparteine lactams and thiolactams do not correlate uniformly with the chromophoric ring conformation. More importantly, the Cotton effects of lactams are mainly of

opposite sign to those of the corresponding thiolactams. This is in apparent contradiction to the published CD data for bicyclic lactams and thiolactams, for which in many cases the corresponding Cotton effects were of the same sign.⁷ In bichromophoric molecules **7**–**9** there is an observed exciton type interaction, most profoundly demonstrated in bis-thiolactam **9**, using the component subtraction analysis of the CD spectra.

4. Experimental

CD spectra of the solution were recorded on a Jasco J-810 polarimeter. Melting points were determined on a Boetius apparatus (PHMK 05 VEB Wagetechnik Rapido, Radebul). The IR spectra were recorded by means of an FT-IR Bruker IFS 113v spectrometer (KBr pellets). Electron impact mass spectra were taken on an AMD 402 spectrometer. The ¹³C NMR spectra (in CDCl₃ at room temperature) were measured on a Varian Gemini 300 spectrometer.

(–)-Sparteine was prepared from commercially available (–)-sparteine sulfate pentahydrate (Aldrich Chemical Company).

4.1. (–)-15-Oxosparteine **1**

(–)-15-Oxosparteine was obtained from sparteine according to the method described previously;²⁷ yield 32%; mp 51°C; $[\alpha]_D^{20}$ = –9.1 (*c* 0.5, C₂H₅OH); IR (KBr) 1629, 1144, 1348 cm^{–1}. ¹³C NMR (CDCl₃): δ 170.6, 65.8, 61.5, 58.6, 56.2, 40.2, 36.5, 32.7, 32.1, 32.1, 29.5, 27.3, 25.8, 24.6, 20.0; *m/z*: 248 (M⁺), *m/z*: 98 (100). Anal. calcd for C₁₅H₂₄N₂O (248): C, 72.54; H, 9.74; N, 11.28. Found: C, 72.42; H, 9.77; N, 11.26%.

4.2. (+)-15-Thionosparteine **2**

(+)-15-Thionosparteine was obtained from **1** according to the method described for 2-thionosparteine;¹⁸ yield 94%; mp 122°C; $[\alpha]_D^{20}$ = +49.0 (*c* 0.5, C₂H₅OH); IR (KBr) 1432, 1351, 1289 cm^{–1}. ¹³C NMR (CDCl₃): δ

200.1, 65.3, 61.2, 61.1, 56.0, 49.9, 42.2, 36.7, 32.5, 31.3, 29.5, 27.3, 25.5, 24.3, 18.3; m/z : 264 (M^+), m/z : 98 (100), m/z : 231 (20). Anal. calcd for $C_{15}H_{24}N_2S$ (264): C, 68.13; H, 9.15; N, 10.59. Found: C, 68.01; H, 9.12; N, 10.59%.

4.3. (+)-2-Oxosparteine 3

(+)-2-Oxosparteine was isolated from *Lupinus angustifolius* seeds according to the method described previously;²⁸ oil; $[\alpha]_D^{20} = +76.5$ (c 1, C_2H_5OH); IR (KBr) 2756–2700, 1632 cm^{-1} . ^{13}C NMR ($CDCl_3$):²⁷ δ 171.4, 64.2, 61.0, 55.6, 52.9, 46.8, 34.9, 33.5, 33.1, 32.4, 27.5, 26.8, 25.2, 24.5, 19.7; m/z : 248 (M^+), m/z : 136 (100). Anal. calcd for $C_{15}H_{24}N_2O \cdot 0.5H_2O$ (257): C, 71.00; H, 9.79; N, 10.88. Found: C, 71.10; H, 9.69; N, 10.93%.

4.4. (+)-2-Thionosparteine 4

(+)-2-Thionosparteine was obtained from **3** according to the method described previously;¹⁸ yield 74%, mp 79°C; $[\alpha]_D^{20} = +266.0$ (c 0.53, C_2H_5OH); IR (KBr) 1630, 1154, 1490 cm^{-1} . ^{13}C NMR ($CDCl_3$): δ 201.8, 64.2, 62.9, 55.2, 55.1, 52.23, 43.0, 36.1, 33.7, 32.4, 28.2, 27.0, 24.6, 24.6, 19.3; m/z : 264 (M^+ , 100), m/z : 231 (82). Anal. calcd for $C_{15}H_{24}N_2S$ (264): C, 68.13; H, 9.15; N, 10.59. Found: C, 68.01; H, 9.12; N, 10.59%.

4.5. (–)-17-Oxosparteine 5

(–)-17-Oxosparteine was obtained by oxidation of sparteinium sulfate pentahydrate salt according to the method described previously;²⁷ yield 86%; mp 87°C; $[\alpha]_D^{20} = -11.6$ (c 0.5, C_2H_5OH); IR (KBr) 2795–2700, 1632 cm^{-1} . ^{13}C NMR ($CDCl_3$):²⁷ δ 169.5, 64.8, 63.1, 61.3, 56.8, 44.1, 42.3, 35.0, 33.6, 30.3, 27.3, 25.5, 25.5, 25.5, 24.7; m/z : 248 (M^+), m/z : 97 (100). Anal. calcd for $C_{15}H_{24}N_2O$ (248): C, 72.54; H, 9.74; N, 11.28. Found: C, 71.97; H, 9.58; N, 11.06%.

4.6. (+)-17-Thionosparteine 6

(+)-17-Thionosparteine was obtained from **5** according to the method described for 2-thionosparteine;¹⁸ yield 79%; mp 91°C; $[\alpha]_D^{20} = +85.8$ (c 0.5, C_2H_5OH); IR (KBr) 2805–2650, 1491, 1140 cm^{-1} . ^{13}C NMR ($CDCl_3$): δ 198.0, 66.4, 65.4, 63.0, 57.0, 56.152.1, 35.5, 34.3, 31.3, 27.0, 25.4, 25.1, 24.9, 24.7; m/z : 264 (M^+ , 100), m/z : 231 (81). Anal. calcd for $C_{15}H_{24}N_2S$ (264): C, 68.13; H, 9.15; N, 10.59. Found: C, 68.16; H, 9.02; N, 10.60%.

4.7. (+)-2,17-Dioxosparteine 7

(+)-2,17-Dioxosparteine was obtained by oxidation of **3** according to the method described previously;²⁹ yield 86%; mp 147°C; $[\alpha]_D^{20} = +154.6$ (c 0.5, C_2H_5OH); IR (KBr) 1645, 1474–1445 cm^{-1} . ^{13}C NMR ($CDCl_3$):²⁶ δ 171.0, 167.0, 61.2, 59.0, 48.1, 43.7, 43.1, 33.9, 33.5, 33.2, 32.9, 27.1, 25.3, 25.1, 19.5; m/z : 262 (M^+), m/z : 150 (100). Anal. calcd for $C_{15}H_{22}N_2O_2$ (262): C, 68.67; H, 8.45; N, 10.68. Found: C, 68.30; H, 8.62; N, 10.54%.

4.8. (+)-2-Thiono-17-oxosparteine 8

(+)-2-Thiono-17-oxosparteine was obtained from **7** according to the method described for 2-thionosparteine;¹⁸ yield 75%; mp 219°C; $[\alpha]_D^{20} = +410.9$ (c 1, C_2H_5OH); IR (KBr) 1637, 1497, 1152 cm^{-1} . ^{13}C NMR ($CDCl_3$): δ 202.9, 166.3, 61.9, 60.3, 55.7, 44.4, 43.3, 42.6, 35.0, 33.2, 27.3, 27.0, 25.2, 24.9, 18.9; m/z : 278 (M^+), m/z : 150 (100), m/z : 245 (18). Anal. calcd for $C_{15}H_{22}N_2OS$ (278): C, 64.71; H, 7.96; N, 10.06. Found: C, 64.70; H, 7.82; N, 9.86%.

4.9. (+)-2,17-Dithionosparteine 9

(+)-2,17-Dithionosparteine was obtained from **7** according to the method described for 2-thionosparteine;¹⁸ yield 80%; mp 205°C; $[\alpha]_D^{20} = +812.0$ (c 0.5, CH_2Cl_2); IR (KBr) 1483, 1436, 1353, 1248, 1145 cm^{-1} . ^{13}C NMR ($CDCl_3$): δ 203.7, 194.3, 65.3, 62.5, 55.7, 53.0, 52.4, 42.7, 35.6, 33.9, 27.2, 26.7, 24.7, 24.3, 19.0; m/z : 294 (M^+), m/z : 261 (100). Anal. calcd for $C_{15}H_{22}N_2S_2$ (294): C, 61.18; H, 7.53; N, 9.51. Found: C, 61.13; H, 7.36; N, 9.50%.

Acknowledgements

We thank Professor T. Borowiak for providing us with the results of X-ray diffraction analysis prior to publication.

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