III. Thioanalogs of Sparteine Lactams. (+)-17-Thionosparteine and its Perchlorate Salt

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Sparteine Thiolactams, (+)-17-Thionosparteine, (+)-17-Thionosparteinium Perchlorate

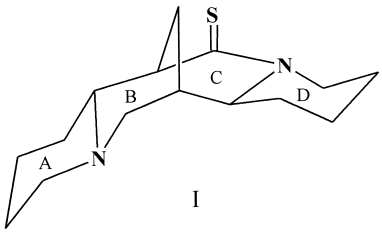
(+)-17-Thionosparteine and its perchlorate have been obtained and characterized by IR and NMR spectroscopy as well as by X-ray diffraction analysis. Introduction of the thiolactam group into the *cis*-quinolizidine system causes conformational rigidity of this fragment. Moreover, the conformations in solution and in the solid state are the same.

Introduction

The present work is a continuation of our studies on sparteine thiolactams. Structural information from X-ray diffraction as well as IR and NMR spectra has been obtained previously for (+)-2-thionosparteine [1] and its perchlorate [2], both of them having the thioamide group located in ring A of the sparteine skeleton. The thioamide group has been recognized as a useful synthon in numerous organic syntheses [3], in particular, it transforms easily to a variety of functional groups and shows high affinity to organometallic compounds. These properties make it a perfect substrate for the production of a series of new, biologically active substances [4].

Among the factors that determine the biological activity of potential receptor ligands, their conformational flexibility plays a significant role. Among the thiono-derivatives of sparteine which are known so far, these requirements of flexibility have been met in (+)-2-thionosparteine. Its conformational preferences have been determined both in solution and in the solid state [1]. The flexibility of the C/D *cis*-quinolizidine fragment in (+)-2-thionosparteine is higher than that in 2-oxosparteine [5]. In solution the conformational equilibrium $C_{boat} \rightleftharpoons C_{chair}$ has been reached at room temperature with the C_{boat} conformer contribution of 81% and that of C_{chair} conformer of 19%, whereas in the crystal there are two molecules in the asymmetric unit, one being in the boat conformation and the other in the chair conformation [1].

(+)-17-Thionosparteine (hereafter **I**) and its perchlorate salt (hereafter **I**·$\mathbf{HClO_4}$) have the thioamide group in ring C of the flexible *cis*-quinolizidine system and these derivatives have been obtained in order to compare the thioamide group influence on the conformation of the C/D fragment of sparteine skeleton in both the free base and the cation.



I

Results and Discussion

NMR spectra of **I** *and* **I**·$\mathbf{HClO_4}$

The ^{13}C NMR spectra of **I** were tentatively assigned by a comparison with the spectra of 17-oxosparteine [6] and the assignment was corroborated by the $^{13}C-^{1}H$ COSY spectra in $CDCl_3$ (Table 1). The signal of C(17) in the spectrum of **I** in $CDCl_3$ is shifted downfield by 28.3 ppm when compared to the analogous carbon atom of 17-oxosparteine. Downfield shifts are also observed for carbon atoms in α position relative to the thiolactam

Table 1. ^{13}C NMR shifts of carbon atoms of **(+)**17-thionosparteine (**I**) and (+)17-thionosparteinium perchlorate (**I·HClO$_4$**).

Atoms	**I**, C_6D_6 δ [ppm][a]	**I**, $CDCl_3$ δ [ppm][a]	**I·HClO$_4$**, $CDCl_3$ δ [ppm][a]	Protonation effect $\Delta = \delta_{I\cdot HClO_4} - \delta_I$ $CDCl_3$, δ [ppm][a]
C(2)	57.68 t	56.96	57.80	+0.84
C(3)	26.15 t	25.39	22.76[c]	–2.63
C(4)	25.66 t[b]	24.70	23.94	–0.76
C(5)	32.10 t	31.25	29.30	–1.95
C(6)	66.06 d	66.44	66.38	–0.06
C(7)	52.88 d	52.11	49.71	–2.40
C(8)	27.46 t	26.99	24.43[d]	–2.56
C(9)	36.09 d	35.49	33.07	–2.42
C(10)	63.66 t	63.00	59.72	–3.28
C(11)	66.34 d	65.41	64.67	–0.74
C(12)	34.56 t	34.32	33.75	–0.57
C(13)	25.63 t[b]	25.09	22.47[c]	–2.62
C(14)	25.15 t	24.92	24.43[d]	–0.49
C(15)	52.09 t	56.06	52.42	–3.64
C(17)	198.72 s	198.04	192.93	–5.11

[a] From TMS; [b] signals can be interchanged; [c] signals can be interchanged; [d] signals overlapping.

group: C(7) (7.9 ppm), C(11) (4 ppm) and C(15) (9.6 ppm). Similar shifts have been observed for analogous systems [2]. Protonation effect is similar to that observed for similar quinolizidine alkaloids [7].

Complete analysis of the ^1H NMR spectra of **I** in C_6D_6 (Table 2) was accomplished using 2D ^1H–^1H and ^{13}C–^1H COSY spectra. Some of the ^1H–^1H coupling constants were read out directly from the spectra (Table 2). They were used to calculate the H–C–C–H torsion angles (by means of the generalized Karplus equation [8]), which were then compared with those obtained from X-ray diffraction analysis (Table 3). The majority of H–C–C–H angles determined by the two methods are in agreement.

The H(9)–C(9)–C(11)–H(11) angle was calculated as the minimum value obtainable from the generalized Karplus equation, since J_{9-11} could not be read out from the spectra. The 11-H signal is a doublet of doublets instead of ddd because one of the coupling constants is smaller then the

Table 2. ^1H NMR chemical shifts and coupling constants of (+)17-thionosparteine (**I**).

H Atoms	Chemical shifts δ [ppm][a] C_6D_6	Coupling constants J [Hz]
2b eq	2.60	J_{2b-2a} = 11.0, J_{2b-3a} = 3.7, J_{2b-3b} = 2.3, J_{2b-4a} = 1.8
2a ax	1.74	
3a ax	1.46	J_{3a-3b} = 12.8, J_{3a-2a} = 12.8, J_{3a-4b} = 12.8, J_{3a-2b} = 3.7, J_{3a-4a} = 3.7
3b eq	1.31	
4a eq	1.66	
4b ax	1.15	
5a ax	2.29	J_{5a-5b}=13.7, J_{5a-4b} = 13.5, J_{5a-6a} = 11.4, J_{5a-4a} = 3.9
5b eq	1.81	J_{5b-5a} = 13.7, J_{5b-4a} = 2.7, J_{5b-4b} = 2.7, J_{5b-6a} = 2.7, J_{5b-3b} = 2.7
6a ax	1.64	J_{6a-5a} = 11.4, J_{6a-5b} = 2.7, J_{6a-7a} = 2.7
7a eq	3.30	J_{7a-6a} = 2.7, J_{7a-8a} = 2.7, J_{7a-8b} = 2.7, J_{7a-9a} = 2.7
8a eq[b]	1.72	
8b ax[b]	1.16	
9a eq	1.15	
10a eq	2.43	$J_{10a-10b}$ = 11.0, J_{10a-9a} = 2.5, J_{10a-8a} = 2.5
10b ax	1.87	$J_{10b-10a}$ = 11.4, J_{10b-9a} = 2.3
11a[c]	3.00	$J_{11a-12a}$ = 11.4, $J_{11a-12b}$ = 2.7
12b eq	1.10	
12a ax	0.93	
13b ax	1.04	
13a eq	1.38	
14b eq	1.21	
14a ax	1.43	
15b ax	2.41	$J_{15b-15a}$ = 12.8, $J_{15b-14a}$ = 12.8, $J_{14b-15b}$ = 3.0
15a eq	6.15	$J_{15a-15b}$ = 12.8, $J_{15a-14b}$ = 2.7, $J_{15a-14a}$ = 2.7, $J_{15a-13a}$ = 2.7

[a] From TMS; [b] in ring B; [c] axial in the more abundant conformer.

Table 3. H–C–C–H torsion angles in **I** [deg].

	Calculated by Haasnoot's equation	Calculated from X-ray data Molecule A	Molecule B
H(2b)–C(2)–C(3)–H(3a)	–58	–56	–56
H(2b)–C(2)–C(3)–H(3b)	63	62	62
H(2a)–C(2)–C(3)–H(3a)	–178	–174	–174
H(3a)–C(3)–C(4)–H(4a)	57	53	53
H(3a)–C(3)–C(4)–H(4b)	164	172	172
H(4a)–C(4)–C(5)–H(5a)	–56	–55	–55
H(4a)–C(4)–C(5)–H(5b)	62	62	62
H(4b)–C(4)–C(5)–H(5a)	–169	–173	–174
H(4b)–C(4)–C(5)–H(5b)	–62	–55	–56
H(5a)–C(5)–C(6)–H(6a)	–172	–179	–179
H(5b)–C(5)–C(6)–H(6a)	61	66	65
H(6a)–C(6)–C(7)–H(7a)	–59	–58	–59
H(7a)–C(7)–C(8)–H(8a)	–62	–62	–60
H(7a)–C(7)–C(8)–H(8b)	64	58	60
H(8a)–C(8)–C(9)–H(9a)	58	62	61
H(9a)–C(9)–C(10)–H(10a)	–61	–62	–64
H(9a)–C(9)–C(10)–H(10b)	63	56	53
H(9a)–C(9)–C(11)–H(11a)	85	86	83
H(11a)–C(11)–C(12)–H(12b)	–59	–60	–59
H(11a)–C(11)–C(12)–H(12a)	–165	–178	–176
H(14b)–C(14)–C(15)–H(15b)	59	61	64
H(14b)–C(14)–C(15)–H(15a)	–60	–61	–60
H(14a)–C(14)–C(15)–H(15b)	173	179	178
H(14a)–C(14)–C(15)–H(15a)	65	58	58

spectrometer resolution. According to the Haasnoot equation, the minimum value of the relevant H–C–C–H torsion angle is 0.71 for 85.6° but for the region between 80° and 91° the value is less than 0.8.

The NMR spectra corroborate that (+)-17-thionosparteine and its cation have very similar conformations in solution.

X-ray crystal structure of **I** *and* $\mathbf{I \cdot HClO_4}$

Selected bond distances and bond angles for **I** and $\mathbf{I \cdot HClO_4}$ are given in Table 4. Fig. 1 shows the molecular structure and atom numbering of **I**. As the conformation of the cation of **I** is the same as the one of the free base, it has not been presented. Moreover **I** crystallizes with two molecules in the asymmetric unit and the differences between them are not statistically relevant. For that reason only one molecule is shown in Fig. 1. Fig. 2 shows intermolecular hydrogen bonding in $\mathbf{I \cdot HClO_4}$.

The configuration of both the free base **I** and the cation of $\mathbf{I \cdot HClO_4}$ is *trans/quasi-cis* for the A/B and C/D quinolizidine systems, respectively;

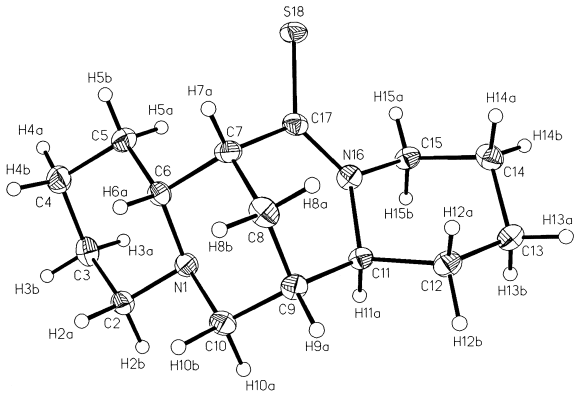


Fig. 1. Displacement ellipsoid representation (at the 50% probability level) of (+)-17-thionosparteine (**I**) together with the numbering scheme [18]. The hydrogen atoms are drawn as spheres with arbitrary radii.

the torsion angles which define the configurations are given in Table 5.

Due to the resonance in the thioamide group, the N(16) atom lost its basicity and only the N(1) atom is accessible to protonation. The protonation of N(1) in $\mathbf{I \cdot HClO_4}$ causes a small but significant elongation of the bonds to N(1). As the proto-

nation ocurred in the rigid *trans*-quinolizidine part, both the free base and the cation have the same conformation of their C/D fragments. The flattening of the thioamide group causes the ring C to adopt a *sofa* conformation with its non-crystallographic plane of symmetry passing through C(8) and N(16) atoms; the asymmetry parameters $\Delta C_s^{8,16}$ are 1.3°, 3.8° and 0.6° for molecules A and B of **I** and for the cation of **I·HClO$_4$**, respectively [9]. They clearly indicate that molecule B of **I** has some deviation towards a *half-chair* conformation. The other rings, A, B and D, have *chair* conformations in both **I** and **I·HClO$_4$**.

As in (+)-2-thionosparteine [1] and its perchlorate [2], also in **I** and in the cation of **I·HClO$_4$** resonance induced intramolecular hydrogen bonds to S(18) are found; their parameters are given in Tables 6 and 7, respectively. Small differences are statistically unrelevant. The intramolecular hydrogen bonds are accompanied by the enlargement of the exo bond angles: S(18)–C(17)–N(16) are as large as 124.4(4)° and 124.1(3)° in molecules A and B of **I**, respectively and 124.4(2)° in the cation of **I**. Similar values have been observed in (+)-2-thionosparteine [1] and in its cation [2].

In the crystal structure packing of **I**, only weak van der Waals interactions are observed, whereas in that of **I·HClO$_4$** the cations are linked with the perchlorate anions through $N(1)^+$–H···O(2) hydrogen bonds (Table 7, Fig. 2). No intermolecular hydrogen bonds have been found in which the thiolactam sulfur atom is involved as it was the case for the crystal packing in the structure of (+)-2-thionosparteinium perchlorate [2]. In this aspect, the crystal packing of **I·HClO$_4$** is the same as that of (+)-17-oxosparteinium perchlorate [10],

Table 4. Selected bond lengths [Å] and angles [deg] for **I** and **I·HClO$_4$**.

I	Molecule A		Molecule B	
N(1)–C(2)	1.456(5)		N(1A)–C(2A)	1.461(5)
N(1)–C(6)	1.459(5)		N(1A)–C(6A)	1.463(5)
N(1)–C(10)	1.457(5)		N(1A)–C(10A)	1.466(5)
N(16)–C(11)	1.488(5)		N(16A)–C(11A)	1.481(5)
N(16)–C(15)	1.464(5)		N(16A)–C(15A)	1.472(5)
N(16)–C(17)	1.329(5)		N(16A)–C(17A)	1.329(5)
C(17)-S(18)	1.674(4)		C(17A)-S(18A)	1.675(4)
C(2)–N(1)–C(6)		111.1(3)	C(2A)–N(1A)–C(6A)	109.7(3)
C(2)–N(1)–C(10)		108.3(3)	C(2A)–N(1A)–C(10A)	108.2(3)
C(10)–N(1)–C(6)		111.2(3)	C(6A)–N(1A)–C(10A)	112.2(3)
C(17)–N(16)–C(15)		121.5(3)	C(17A)–N(16A)–C(15A)	121.5(3)
C(17)–N(16)–C(11)		126.1(3)	C(17A)–N(16A)–C(11A)	125.7(3)
C(15)–N(16)–C(11)		112.2(3)	C(15A)–N(16A)–C(11A)	112.1(3)
N(16)–C(17)–C(7)		116.9(3)	N(16A(–C(17A)–C(7A)	117.1(3)
N(16)–C(17)-S(18)		124.4(3)	N(16A)–C(17A)-S(18A)	124.0(3)
C(7)–C(17)-S(18)		118.7(3)	C(7A)–C(17A)-S(18A)	118.9(3)
I·HClO$_4$				
N(1)–C(2)	1.506(4			
N(1)–C(6)	1.513(4)			
N(1)–C(10)	1.501(4)			
N(16)–C(11)	1.485(4)			
N(16)–C(15)	1.474(4)			
N(16)–C(17)	1.333(4)			
C(17)-S(18)	1.675(3)			
C(2)–N(1)–C(6)		111.2(3)		
C(2)–N(1)–C(10)		109.2(2)		
C(6)–N(1)–C(10)		112.0(3)		
C(17)–N(16)–C(15)		121.5(3)		
C(17)–N(16)–C(11)		125.6(2)		
C(15)–N(16)–C(11)		112.7(3)		
N(16)–C(17)–C(7)		116.9(3)		
N(16)–C(17)-S(18)		124.2(2)		
C(7)–C(17)-S(18)		118.9(2)		

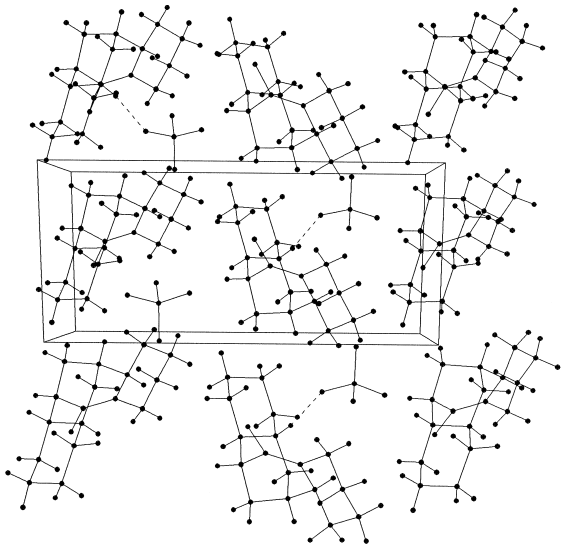


Fig. 2. Packing diagram of **I·HClO$_4$** seen along the [001] direction [18].

although there is no isostructurality of these two crystals. This observation gives rise to a further discussion on a comparison between lactam and thiolactam groups in 17-oxo/thiono derivatives. In [2] we postulated the lone pairs on the sulfur atom in 2-thionosparteine and its cation to be more diffuse as compared with those on oxygen in lupanine and its cation. Our observation confirmed in any case the findings derived by Allen [11]. In the case of **I** and **I·HClO$_4$** the sulfur atom S(18) accepts also more than one intramolecular hydrogen bond of the C–···S type (Table 6). A further argument for the diffuse character of the lone pairs on the thiono sulfur atom is supplied by the directionality of the weak C–H···S hydrogen bonds to sulfur atoms in both **I** and **I·HClO$_4$**.

Probably the diffuse character of the sulfur lone pairs causes also the more "regular" *sofa* conformation of the rings C in **I** and **I·HClO$_4$**. Their aforementioned asymmetry parameters are much lower than those for the ring C in 17-oxosparteine ($\Delta C_s^{8,16}$ = 7.80°) [12] and 17-oxosparteinium cation ($\Delta C_s^{8,16}$ = 6.3°) [10]. This indicates distortions to a *half-chair* form and as a consequence, to higher deviations from planarity.

The X-ray and spectroscopic results clearly indicate that the 17-thionosparteine free base (**I**) and its perchlorate are conformationally rigid and due to that the application of 17-thionosparteine as a receptor ligand or in asymmetric synthesis seems to be doubtful.

Table 7. Hydrogen-bonds for **I·HClO$_4$** [Å and deg.].

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(1)···O(2)$^{(i)}$	0.85(3)	2.06(2)	2.890(4)	169(2)
C(15)–H(15A)···S(18)	0.92(4)	2.46(4)	3.046(5)	121(3)
C(5)–H(5A)···S(18)	0.94(4)	3.02(4)	3.473(5)	111(3)

Symmetry codes: (i) $-x + 2$, $½ + y$, $-z + 2$.

Table 5. Torsion angles in **I** and **I·HClO$_4$**.

Torsion angle	**I** – Molecule A	**I** – Molecule B	**I**$^+$	Configuration of piperidine ring fusion
C(5)–N(6)–N(1)–C(2)	–58.7(4)°	–61.2(4)°	–58.5(3)°	
C(7)–C(6)–N(1)–C(10)	+53.9(4)°	+52.2(4)°	+49.9(3)°	A/B *trans*
C(17)–N(16)–C(11)–C(9)	+6.5(5)°	+14.8(5)°	+7.0(4)°	
C(15)–N(16)–C(11)–C(12)	+58.4(4)°	+60.7(4)°	+55.8(3)°	C/D *quasi-cis*

Table 6. Hydrogen bonds for **I** [Å and deg.].

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
C(15)–H(15A)···S(18)	0.90(5)	2.53(4)	3.043(4)	117(3)
C(15A)–H(15C)···S(18A)	0.91(5)	2.55(4)	3.039(4)	114(3)
C(5)–H(5A)···S(18)	0.93(5)	2.96(4)	3.465(4)	115(3)
C(5A)–H(5C)···S(18)	0.98(5)	2.89(4)	3.425(4)	115(3)

Experimental Section

General techniques

Melting points were determined on a Boetius apparatus (PHMK 05 VEB Wägetechnik Rapido, Radebeul). The IR spectra were recorded by means of a FT-IR Bruker IFS 113v spectrometer (KBr pellets technique). Electron-impact mass spectra were taken on an AMD 402 spectrometer at standard parameters. The ^{1}H NMR, ^{13}C NMR, ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY and DEPT spectra (in C_6D_6, c = 0.06 M) were measured on a Varian Gemini 300 spectrometer at a frequency of 75.462 MHz for ^{13}C NMR and 300 MHz for ^{1}H). Thin layer chromatography (TLC) was carried out on silica gel sheets (Merck) in the system acetone–methanol–ammonia (4:1:0.05).

(–)-17-Oxosparteine

420 mg of (–)-sparteine sulfate pentahydrate (Aldrich Chemical Company) were dissolved in 3 ml of a water-dioxane mixture (1:2). To the solution were added 7 ml of alkaline potassium ferricyanide (5 ml of 1 N aqueous solution of potassium ferricyanide in 2 ml of 20% aq. NaOH) and 10 g of diatomaceous earth. The mixture was settled in a column and eluated with ethyl ether. After evaporation 210 mg of white crystalline powder of (–)-17-oxosparteine were obtained. Recrystallization from hexane (5 ml) afforded 189 mg (77%) of (–)-17-oxosparteine, m.p. 86–87 °C, $[\alpha]_D^{20} = -11.6°$ (c 0.5, C_2H_5OH). – IR (KBr): ν = 2795–2700, 1632 cm^{-1}. – MS: *m/z* (%) = 248 (60) [M$^+$], 220 (58), 97 (100). – $C_{15}H_{24}N_2O$ (248.4): calcd. C 72.54, H 9.74, N 11.28; found C 71.97, H 9.58, N 11.06.

(+)-17-Thionosparteine (**I**)

124 mg of (–)-17-oxosparteine were dissolved in 5 ml of toluene and 162 mg of solid Lawesson's reagent were added. The reaction mixture was stirred continuously at 100 °C for 13 h. The excess of Lawesson's reagent was removed on a column filled with neutral alumina oxide (Woelm, activity II, 11 g) using dichloromethane. Subsequent elution of **I** and crystallization from hexane gave 92 mg (70%) of (+)-17-thionosparteine, m.p. 89–91 °C, $[\alpha]^{20} = +85.8°$ (c 0.5, C_2H_5OH). – IR (KBr): ν = 2805–2650, 1491, 1140 cm^{-1}. – MS: *m/z* (%) = 264 (74) [M$^+$], 265 (15) [M+1], 266 (4) [M+2], 231 (100). – $C_{15}H_{24}N_2S$ (264.4): calcd. C 68.13, H 9.15, N 10.59; found C 68.16, H 9.02, N 10.60.

(+)-17-Thionosparteinium perchlorate (**I·HClO$_4$**)

52.8 mg (0.2 mmol) of **I** were dissolved in 1.5 ml of methanol and 0.96 ml (0.22 mmol) of 60% perchloric acid solution in methanol (1:39 v/v) were added. A white powder was precipitated. Recrystallization from ethanol gave 55 mg (75%) of transparent crystals, m.p. 231 °C. – IR (KBr): ν = 1494, 2954–2783 cm^{-1}.

X-ray crystal structure determination of **I**

Single crystals were obtained by slow evaporation of saturated hexane solution. A colourless transparent crystal was selected for the X-ray investigation. To check the possibility of phase transitions, the unit cell parameters were measured as a function of decreasing temperature down to 100(2) K. No phase transition was observed in the temperature range of 293–100 K and the data collection was carried out at 100(2) K on a KUMA KM4 diffractometer [13] using Mo–K$_\alpha$ radiation. The accurate unit cell parameters were obtained by the least-square fit of setting angles of 26 reflections (2Θ range 6.3°–31.3°). In the data collection the 2Θ–Θ scan method was applied with a variable scan rate ranging from 0.02°/s to 0.25°/s, depending on reflection intensity. One control reflection (2 1 3) was measured every 100 current measurements. The data were corrected for Lorentz and polarization effects, but not for absorption [13]. The structure was solved by direct methods using SHELXS-97 program [14] and refined by full-matrix least-squares method with SHELXL-97 [15]. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o^2) + (0.036P)^2 + 1.27P]$ where $P = (F_o^2 + 2F_c^2)/3$.

All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms at C15 and C15A were refined. The remaining H atoms were calculated in their theoretical positions and refined as a "riding model". The isotropic displacement parameters U_i of all hydrogen atoms were set at 1.2 times of their carrier atoms. The absolute configuration was assigned according to the previous determination of the naturally occurring sparteine derivatives [16].

X-ray structure determination of **I·HClO$_4$**

Single crystals were obtained by slow evaporation of saturated ethanol solution. A colourless transparent crystal was selected for the X-ray investigation. The data collection was carried out on a KUMA KM4 CCD diffractometer [17] using Mo–K$_\alpha$ radiation at 293(2) K. The intensity data

Table 8. Crystal data and structure refinement for **I** and **I·HClO$_4$**

	I	**I·HClO$_4$**
Empirical formula	$C_{15}H_{24}N_2S$	$C_{15}H_{24}N_2S \cdot HClO_4$
Formula weight	264.42	364.88
Temperature	100(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1$	monoclinic, $P2_1$
Unit cell dimensions	a = 8.614(2) Å b = 12.612(3) Å; β = 96.16(3) deg c = 12.931(3) Å	a = 6.996(1) Å b = 14.768(3) Å; β= 106.88(3) deg c = 9.045(2) Å
Volume	1396.7(6) Å^{-3}	894.2(3) Å^{-3}
Z, calculated density	4, 1.257 mg/m^3	2, 1.355 mg/m^3
Absorption coefficient	0.217 mm^{-1}	0.351 mm^{-1}
F(000)	576	388
Crystal size	0.70 × 0.35 × 0.30 mm	0.1 × 0.1 × 0.5 mm
Theta range for data collection	1.58 to 25.05 deg	2.73 to 24.98 deg
Index ranges	$0 \le h \le 10, 0 \le k \le 15, -15 \le l \le 15$	$-8 \le h \le 7, -17 \le k \le 15, -10 \le l \le 10$
Reflections collected/unique	2787/2606 [R(int) = 0.0134]	4671/2491 [R(int) = 0.0210]
Completeness to theta = 25.05	100.0%	99.5%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2606/1/363	2491/1/236
Goodness-of-fit on F^2	1.132	1.021
Final R indices [I > 2sigma(I)]	R1 = 0.0348, wR2 = 0.0908	R1 = 0.0365, wR2 = 0.0901
R Indices (all data)	R1 = 0.0399, wR2 = 0.0937	R1 = 0.0446, wR2 = 0.0937
Absolute structure parameter	0.04(10)	-0.07(7)
Largest diff. peak and hole	0.362 and −0.222 e · Å^{-3}	0.196 and −0.230 e · Å^{-3}
Extinction coefficient		0.021(4)

were corrected for Lorentz and polarization effects, but not for absorption [17]. The structure was solved by direct methods using SHELXS-97 program [14] and refined by full-matrix least-squares method with SHELXL-97 [15]. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized with $w^{-1} = [\sigma^2(F_o^2) + (0.06P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined anisotropically. The positional parameters and isotropic displacement parameters of hydrogen atoms at N(1), C(6), C(9) and C(15) were refined. The remaining H atoms were located at their theoretical positions and refined as a "riding model". Their isotropic displacement parameters U_i were set at 1.2 of U_{eq} of their carrier atoms. The absolute configuration was assigned according to the previous determination of the naturally occurring sparteine derivatives [16].

The crystallographic data, together with data collection and structure refinement details for **I** and **I·HClO$_4$** are listed in Table 8. Additional crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 177864 and 177865. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB 1EZ, U. K. [Fax: +44 12 23 33 60 33. E-mail: deposit@ccdc.cam.ac.uk].

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