Synthesis and Spectroscopy of $LiClO_4$ Complexes of (–)-Sparteine, 2-Methyl- and 2-Oxosparteine, and 2-Cyano-2-methylsparteine

Beata Jasiewicz[a], Tomasz Rafałowicz[a], Ewa Sikorska[b], Igor Khmelinskii[c], Jacek Koput[a], Marek Sikorski[a], and Władysław Boczoń[a]

[a] Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
[b] Faculty of Commodity Science, Poznań University of Economics, al. Niepodległości 10, 60-967 Poznań, Poland
[c] Universidade do Algarve, FCT, 8000-117 Faro, Portugal

Reprint requests to Dr. M. Sikorski. Tel: +48 61 8291309. Fax: +48 61 8658008.
E-mail: Sikorski@amu.edu.pl

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Complexes formed between (–)-sparteine, 2-methyl- and 2-oxosparteine and 2-cyano-2-methylsparteine with lithium perchlorate ($LiClO_4$) were obtained in the solid state. The complexes, $C_{15}H_{26}N_2LiClO_4$, $C_{16}H_{28}N_2LiClO_4$, $C_{15}H_{24}N_2OLiClO_4$, and $C_{17}H_{27}N_3Li_2Cl_2O_8$ have been isolated and characterised by UV/vis, NMR, and IR, spectroscopy and by their mass spectra. Three of the four complexes present the 1:1 stoichiometry, while the 2-cyano-2-methylsparteine complex has the 1:2 stoichiometry.

Key words: Sparteine Derivatives, Lithium Complexes, UV/vis-NIR, NMR Spectra

Introduction

Considerable research effort has been devoted to different types of proton sponges. Sparteine, a naturally occurring member of the lupine alkaloid family, is a representative of one class of such compounds. Different types of studies covered various aspects of possible applications of such proton sponges, including sparteine and its derivatives. The interest in sparteine is possibly a never ending story; to name just a few of the numerous applications, we may recall analytical usage in determination of cations and identification of amines, through its role in living organisms, and finish with the applications in asymmetric synthesis [1 – 3]. Sparteine is a naturally occurring chiral diamine and has a widespread use as a chiral ligand in asymmetric synthesis. The structure of sparteine, with two nitrogen atoms specifically placed in space, makes it an excellent ligand for metal complexes [4 – 7]. The interest in complexes of lithium has been rather limited, however. Skolik and others have synthesised and studied the sparteine and α-isosparteine complexes with lithium salts by IR and ^{1}H NMR spectroscopy [8]. The results presented by these authors show that sparteine is present in an all-*chair* conformation in all the lithium complexes, see Fig. 1a. The complex formation of lactams and thiolactams derived from sparteine with the Cu(II) cation in ethanol was studied by theoretical, kinetic and MS methods [9]. Over a few decades, several crystal structures of protonated sparteine and sparteine metal complexes have been reported [6, 7, 10 – 17], among others, those of (+)-lupanine perchlorate monohydrate [16], 2-cyano-2-methylsparteine perchlorate [17] and 2-methylsparteine perchlorate [18]. We have now undertaken a research project aimed at characterising the spectral and photophysical properties of complexes between (–)-sparteine **(1)**, 2-methylsparteine **(2)**, 2-cyano-2-methylsparteine **(3)** and 2-oxosparteine **(4)** (as supporting ligands) with lithium perchlorate ($LiClO_4$).

Results and Discussion

The results show that the complexes of (–)-sparteine, 2-methylsparteine and 2-oxosparteine with lithium perchlorate ($LiClO_4$) exhibit the 1:1 stoichiometry. An exception is the 2-cyano-2-methylsparteine-$(LiClO_4)_2$ complex, which exhibits the 1:2 stoi_chiometry.

In the electronic absorption spectra recorded in acetonitrile, (–)-sparteine, and also 2-methylsparteine and 2-oxosparteine display a single intense transition in the

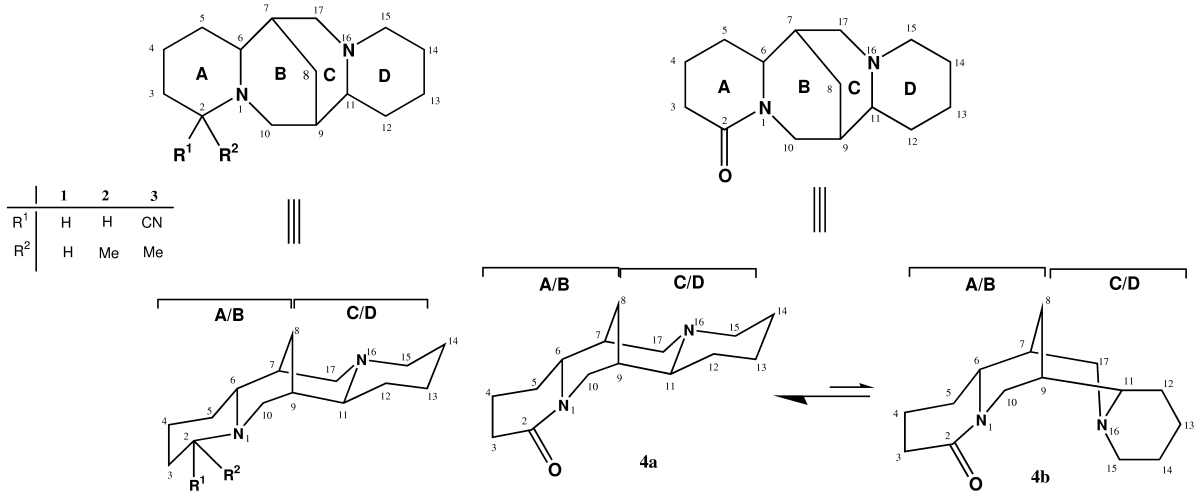

Fig. 1. (–)-Sparteine, 2-methylsparteine and 2-cyano-2-methylsparteine and their conformation-configuration arrangement (left part). 2-Oxosparteine and its conformation-configuration arrangement (right part).

UV region, tentatively assigned to a π, π^* transition. The corresponding maxima and molar extinction coefficients are presented in Table 1. The UV spectra of the complexes have their maxima blue-shifted and with lower molar extinction coefficients. We were interested in the feasibility of applying diffuse reflectance spectroscopy to the analysis of the $LiClO_4$ complexes with sparteine derivatives. A simple and successful approach quantitatively describing the interaction of light with a diffusing sample was proposed by Kubelka and Munk in 1931 [19]. In this formulation the remission function, $F(R)$, for an ideal diffuse scatterer, which is optically thick at the wavelength of choice, and for a homogeneous distribution of absorbers throughout the sample, is given by the Kubelka-Munk function *i. e.* $F(R) = (1-R)^2/2R = K/S$ where R represents the observed diffuse reflectance from the surface of the sample, K and S being the absorption and scattering coefficients, respectively. The corresponding diffuse reflectance absorption spectra of sparteine derivatives on KBr exhibit a single absorption band with the maximum at about 205 nm. For all the sparteine derivatives examined in this study the complexation with $LiClO_4$ caused the appearance of a broad, very low-intensity band lying in the 230 – 380 nm range.

In the IR spectra, the single band derived from ν_{Cl-O} of the ClO_4^- group is situated in its normal position at 1100 cm^{-1}. Fig. 2 shows the region of the IR spectra, containing the carbon-hydrogen vibrational bands [11, 20]. (–)-Sparteine and 2-methylsparteine have a

Table 1. UV spectral data of the $LiClO_4$ complexes studied, band maximum (nm) and extinction ($M^{-1}cm^{-1}$).

	Free ligand $\lambda_{max}(\varepsilon)$	$LiClO_4$ complex $\lambda_{max}(\varepsilon)$
(–)-Sparteine	202 (9800)	197 (2500)
2-Methylsparteine	202 (7400)	196 (3500)
2-Oxosparteine	206 (9500)	205 (1900)

number of carbon-hydrogen vibrational bands in the 2800 – 3000 cm^{-1} region, and of the low-frequency C–H stretching bands extending down to 2500 cm^{-1}, the so-called Bohlman "*trans*-band". It is well known that the nature of the "*trans*-band" depends on the conformational and configurational arrangement of sparteine and its derivatives [21]. The "*trans*-band" of the ligands consists, above all, of two absorption maxima at about 2794 and 2756 cm^{-1}, which result from the superposition of the oscillations of *trans*-axial hydrogen atoms at C-2, C-6, C-10 and C-11, C-15, C-17, respectively, in relation to the lone pairs on the nitrogen atoms at the N-1 and N-16 positions. The complexes between (–)-sparteine and 2-methylsparteine with lithium perchlorate ($LiClO_4$) only display bands in the 2800 – 3000 cm^{-1} region. Thus, the attachment of the metal ion to the N atom results in the disappearance of the "*trans*-band" [11, 12]. The absence of the "*trans*-band" in the complex suggests that both of the nitrogen atoms are coordinated. The absorption bands in the 400 – 600 cm^{-1} region have been assigned to N^+–Li vibrations. Some further features of the IR spectra were observed in the region of *ca.* 1150 cm^{-1} on the high-

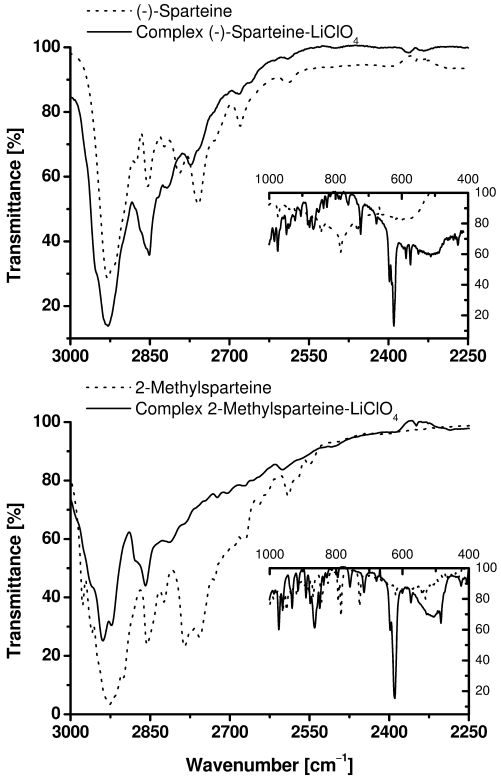

Fig. 2. IR spectra of (–)-sparteine and 2-methylsparteine together with corresponding spectra of their $LiClO_4$ complexes.

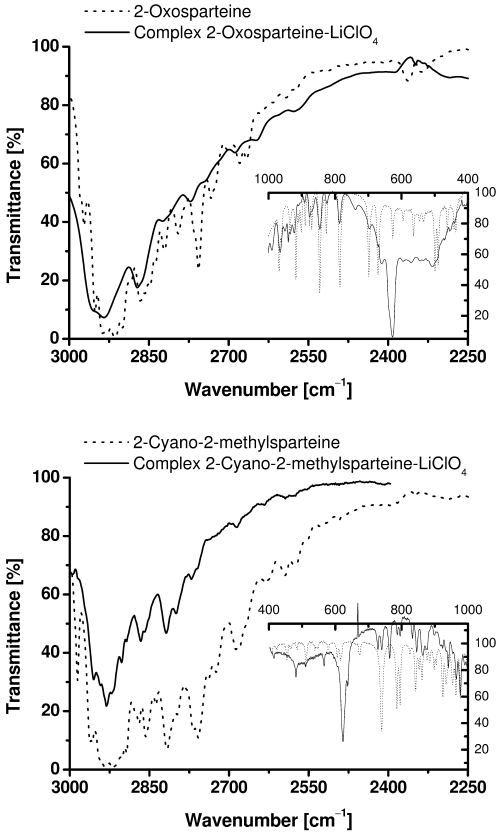

Fig. 3. IR spectra of 2-oxosparteine and 2-cyano-2-methylsparteine together with corresponding spectra of their $LiClO_4$ complexes.

frequency side of the broad ClO_4^- band [8]. However, the perturbations of the 2500 – 2800 cm^{-1} region are quite evident. As has been shown by Boczoń and others [21, 22], 2-methylsparteine assumes an all-*chair* conformation with *trans* A–B and *cis* C–D in the solid phase, which is also the case for complexes between (–)-sparteine and 2-methylsparteine with lithium perchlorate.

As follows from X-ray and spectroscopic data, the proton in crystalline (–)-sparteine-H^+ and in 2-methylsparteine-H^+ is located exclusively on N-1 [18, 23]. In the case of (–)-sparteine-H^+, it was proved that the passage from solid to a solution (CD_3CN) is accompanied by prototropy, giving rise to tautomeric equilibrium, in which the form with a proton located on N-16 predominates. The change of the proton location in the solution of (–)-sparteine–H^+ is manifested by drastic changes in the "*trans*-band" region of the IR spectrum, and by a hypsochromic shift of the ν_{N+-H} band by about 20 cm^{-1} (from 3030 cm^{-1} in the solid to 3050 cm^{-1} in solution) [23]. In the spectrum of 2-methylsparteine-H^+ in solution, the "*trans*-band" has only one maximum (near 2815 cm^{-1}), and the spectrum differs significantly from that measured for the solid compound [21]. Its similarity to the IR spectrum of (–)-sparteine-H^+ in solution allows one to assume the existence of a tautomeric equilibrium between the N-1-protonated and N-16-protonated forms in the solution of 2-methylsparteine-H^+. The ν_{N+-H} absorption band in the IR spectrum of 2-methylsparteine-H^+ in CD_3CN solution, similarly as for sparteine-H^+, appears as a hump at about 3040 cm^{-1}.

Similar to sparteine and 2-methylsparteine, 2-oxosparteine (lupanine), the most common of the sparteine lactams, occurs in two conformations, of which the *sofa/chair – boat/chair* form (**4a**) is favoured. The free electron pair on the N-1 nitrogen atom takes part in the lactim-lactam prototropy, therefore, there is no strong nucleophilic centre in the *sofa/chair – chair/chair* conformation of lupanine

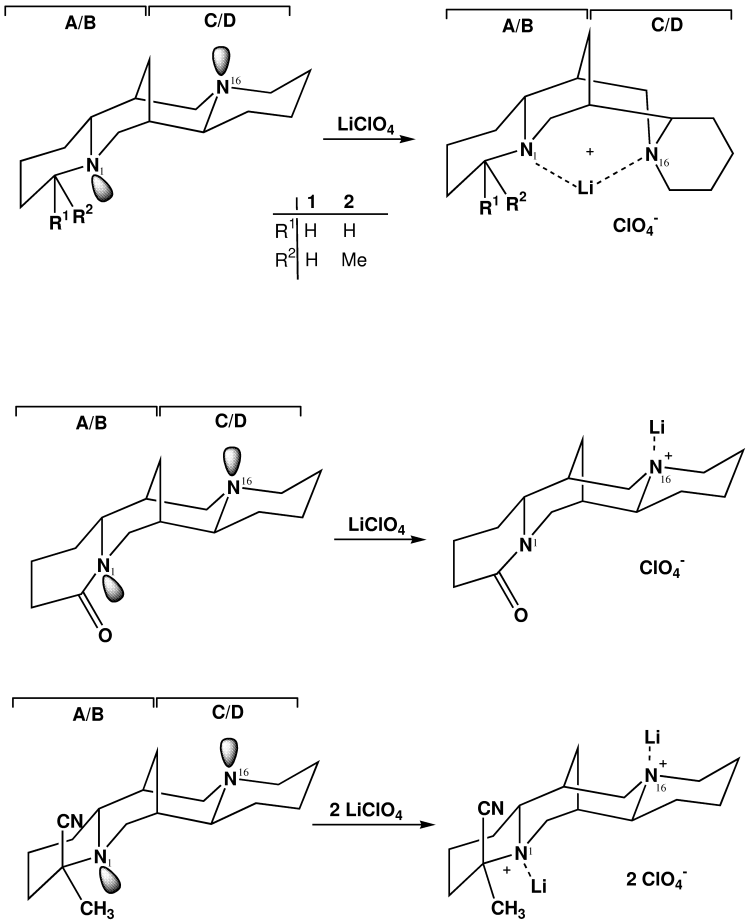

Fig. 4. (–)-Sparteine, 2-methylsparteine, 2-oxosparteine and 2-cyano-2-methylsparteine and their conformation-configuration arrangement as free ligands and $LiClO_4$ complexes.

(**4b**), which is a characteristic feature of sparteine and 2-methylsparteine in this conformation. Fig. 3 shows the region of the IR spectra, where the carbon-hydrogen vibrational bands occur. The spectrum of the 2-oxosparteine-$LiClO_4$ complex demonstrates disappearance of the Bohlman "*trans*-band" in the vicinity of the $2840-2600$ cm^{-1}, as was the case for the sparteine and 2-methylsparteine complexes with $LiClO_4$. However, the reason for that is now entirely clear. For the complexation of $LiClO_4$ with 2-oxosparteine at N-16 further information about the conformation of the ligand may be obtained from selected infrared bands. As a result, we suggest that the complex between lupanine and $LiClO_4$ can be formed by complexation of the lupanine molecule in the unchanged configuration, with the ring C remaining in the boat conformation. These results are confirmed by the analysis of the lupanine perchlorate monohydrate spectrum, showing that the N-16 protonation does not change the conformation of ring C, thus the *sofa/chair – boat/chair* conformation with *trans* C–D system exists in the solid state [16, 24].

The IR spectrum of 2-cyano-2-methylsparteine on KBr is generally very similar to those of the other sparteine derivatives, complemented by the vibrations of the CN bond of the newly introduced nitrile group, visible in the region of 2212 cm^{-1}. There are differences in the spectra of free 2-cyano-2-methylsparteine and its $LiClO_4$ complex in the "*trans*-band" region. As a result of the complexation of $LiClO_4$ with 2-cyano-2-methylsparteine at N-1 and at N-16 atoms the disappearance of two bands from the *trans* region, namely the bands at 2758 and 2682 cm^{-1} is observed. We suggest that the product is formed by complexation of the 2-cyano-2-methylsparteine molecule in its unchanged configuration, with the ring C remaining in the *boat* conformation. Interestingly, previously reported results on the 2-cyano-2-methylsparteine-$HClO_4$ system

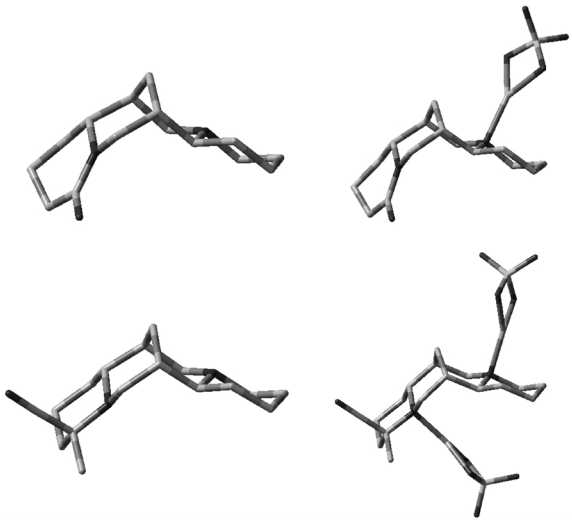

Fig. 5. 2-Oxosparteine and 2-cyano-2-methylsparteine and their conformation-configuration arrangement as free ligands and $LiClO_4$ complexes obtained at the theoretical level using density functional theory.

show the 1:1 complex in the all-*chair* form with the *trans-cis* system, independent of the solvent used in the synthesis [25]. The spectroscopic findings are also confirmed by the X-ray analysis, showing that protonation that takes place at the N-16 atom and subsequent formation of an intramolecular N^+-16-H-16···N-1 hydrogen bond is accompanied by inversion of the N-16 configuration compared with that in the free sparteine [17]. This intramolecular hydrogen bond is significantly weaker in 2-cyano-2-methylsparteine-$HClO_4$ as compared to 2-methylsparteine-$HClO_4$.

Further evidence for the solution structure of the complexes was derived from their NMR spectra. NMR data of (–)-sparteine, 2-methylsparteine, 2-cyano-2-methylsparteine and 2-oxosparteine complexes with lithium perchlorate ($LiClO_4$) in $CDCl_3$ or DMSO-d_6 are presented in Table 2. The NMR analysis involved a comparison of the complex spectrum with the corresponding spectrum of the free base, which allowed calculation of the complexation effect. The chemical shift changes resulting from complexation were determined by subtracting the chemical shifts of the individual carbon atoms of the free bases from those of the corresponding atoms of the complexes [26, 27]. Because of the solubility problems, two different solvents were used, $CDCl_3$ and DMSO-d_6 (for the 2-oxosparteine-$LiClO_4$ and 2-cyano-2-methylsparteine-$LiClO_4$ complexes). The signal attributed to the methyl group in 2-methylsparteine-$LiClO_4$ occurring at 20.1 ppm, indicates that this group is an equatorial substituent, the same as in the free base [26]. The results presented in Table 2 for 2-cyano-2-methylsparteine (in $CDCl_3$) and its complex with $LiClO_4$ (in DMSO-d_6) suggest that the solvent effect on the chemical shifts is small.

When analysing the complexation effects, it is necessary to account for the fact that for sparteine and 2-methylsparteine a change of the configurational-conformational system occurs upon conversion from the free base to the complex: from the *trans* C/D *boat/chair* into the *trans-cis* all-*chair* configuration. In the ^{13}C NMR spectra of the complexes, the chemical shifts of the carbon atoms are similar to those reported for sparteine and 2-methylsparteine monoperchlorate [28]. This means that in these compounds the reaction with $LiClO_4$ happens in the same way as in the reaction with acid and is accompanied by inversion at N-16. Most indicative of the all-chair sparteine skeleton in the complexes are the large upfield shifts observed on C-12, C-14 and C-17, in the range of 5.9 to 11.4 ppm. The values taken into account in the stereochemical studies are those of the chemical shifts at the carbon atoms mentioned, as well as that of the H-7-H-17β coupling constant, large in the boat conformation and small in the chair conformation [29]. The difference is evident if we compare the H-7-H-17β coupling constant of less than 3 Hz in sparteine and 2-methylsparteine complexes with lithium perchlorate, suggested to be in the all-*chair* conformation, to that of 9.2 Hz in 2-oxosparteine with lithium perchlorate or to that of 10.0 Hz for the 2-cyano-2-methylsparteine-$LiClO_4$ complex, suggested to be both in the *boat* conformation.

Additional information about complexes formed between 2-oxosparteine and 2-cyano-2-methylsparteine with lithium perchlorate ($LiClO_4$) were obtained at the theoretical level. The electronic structure of the complexes has been studied by means of the density functional theory (DFT). The DFT calculations were performed using the hybrid method B3LYP [30] in conjunction with the modest split-valence polarized basis set 6-31G** [31], employing the Gaussian 98 package of *ab initio* programs [32]. The results are presented in Fig. 5. The Li···N distances were found to be ~ 2.03 Å, with the Li atom located in the direction of the nitrogen lone-pair and on the bisector of the OClO angle. The binding energy of $LiClO_4$ with 2-oxosparteine was calculated to be 27 kcal/mol. The binding energy of two $LiClO_4$ molecules with 2-cyano-

Carbon atom	Sparteine x $LiClO_4$ **1-$LiClO_4$**		2-Methylsparteine x $LiClO_4$ **2-$LiClO_4$**		2-Cyano-2-methylsparteine x 2 $LiClO_4$ **3-2 $LiClO_4$**		2-Oxosparteine x $LiClO_4$ **4-$LiClO_4$**	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
2	55.6	*2.14	60.1	2.26	58.0	–	170.8	–
	−0.4	*3.24	*+2.1*	–	*−0.4*	–	*−0.6*	–
3	24.5	*1.72	33.8	*1.52	37.5	1.44	32.9[a]	*2.24
	−1.1	*1.72	*−1.5*	*1.68	*−0.9*	1.84	*−0.2*	*2.24
4	23.0	*1.92	22.9	*1.56	20.9	*1.40	19.4	*1.15
	−1.5	*1.98	*−1.6*	*1.64	*−0.4*	*1.62	*−0.3*	*1.30
5	29.3	*1.60	30.0	*1.58	28.5	*1.32	26.9	*1.10
	+0.2	*1.60	*−0.2*	*1.58	*−0.6*	*1.32	*+0.1*	*1.32
6	65.9	2.60	66.5	2.65	61.4	2.08	60.1	2.74
	−0.4		*+0.3*		*−0.3*		*−0.9*	
7	32.7	*1.88	32.9	1.98	32.5	1.88	31.5	1.55
	−0.2		*−0.9*		*−0.7*		*−0.9*	
8	26.6	*1.70	26.6	*1.70	26.7	*1.01	26.9	*1.88
	−0.8	*2.14	*−0.9*	*2.10	*−0.2*	*1.96	*−0.6*	*2.14
9	32.7	*1.88	33.2	1.93	35.3	1.52	34.2	1.32
	−3.2		*−3.2*		*−0.5*		*−0.7*	
10	60.9	2.70	57.4	2.55	53.3	2.02	46.2	2.31
	−0.9	3.32	*+0.1*	3.64	*−0.5*	2.86	*−0.6*	4.80
11	62.3	3.66	63.4	3.60	63.8	1.76	63.8	1.70
	−1.9		*−1.0*		*−0.9*		*−0.4*	
12	23.2	*1.84	23.3	*1.82	33.8	*1.52	32.1[a]	*1.32
	−11.3	*1.84	*−11.4*	*1.96	*−0.8*	*1.20	*−1.4*	*1.34
13	22.6	*1.46	22.8	*1.90	24.4	*1.20	24.1	*1.12
	−2.0	*1.56	*−2.1*	*2.00	*−0.5*	*1.64	*−0.4*	*1.54
14	18.0	*1.56	18.1	*1.65	25.4	*1.40	25.9	*1.42
	−7.8	*1.56	*−7.9*	*1.65	*−0.4*	*1.40	*+0.7*	*1.54
15	52.7	3.10	52.9	3.26	54.7	1.84	54.9	1.85
	−2.5	3.50	*−2.4*	3.46	*−0.8*	2.70	*−0.7*	1.66
17	47.3	3.12	47.6	3.22	52.7	2.165	51.7	1.83
	−6.1	3.60	*−5.9*	3.60	*−0.8*	2.62	*−1.2*	2.55
$-CH_3$	–	–	20.1	1.27	25.9	1.40	–	–
			−1.2		*−0.8*			
−CN	–	–	–	–	119.3	–	–	–
					−0.1			

Table 2. NMR data of sparteine (**1**), 2-methylsparteine (**2**), in $CDCl_3$ and 2-cyano-2-methylsparteine (**3**) and 2-oxosparteine (**4**) complexes with lithium salt in DMSO-d_6; δ values in ppm are given. Numbers given in italics represent the complexation effect.[a]

[a] Atom numbering is shown in Fig. 1; + upfield shift, – downfield shift; * δ_H values extracted from the HET-COR spectrum.

2-methylsparteine was calculated to be 49 kcal/mol, being nearly twice larger than that of the $LiClO_4$ – 2-oxosparteine complex. These binding energies are comparable to that predicted for the LiH – sparteine complex by Wiberg and Bailey to be 24 kcal/mol [33].

Conclusions

Complexes between (–)-sparteine, 2-methyl- and 2-oxosparteine with $LiClO_4$ have been synthesised. The 1:1 stoichiometry has been confirmed by elemental analysis and the MS spectral results. The proposed complex configuration, involving an all-*chair trans* A–B and *cis* C–D conformation of the (–)-sparteine and 2-methylsparteine ligands has been confirmed by the IR and NMR spectral data, being similar to that obtained in other metal complexes with the same ligands. A different, *sofa/chair – boat/chair* conformation, is proposed for the 2-oxosparteine complex, where complexation obviously does not affect the ligand configuration. 2-Cyano-2-methylsparteine·$2LiClO_4$ exhibits a 1:2 stoichiometry, with the complexation preserving the conformational-configurational structure of the free ligand, namely the *chair/chair – boat/chair* conformation with *trans* A–B and *trans* C–D systems.

Experimental Section

General techniques

Elemental analyses were carried out by means of a Perkin-Elmer 2400 CHN automatic analyser. IR spectra were recorded from KBr pellets with a Bruker FTIR 113v spectrometer. Low-resolution mass spectra were recorded using the fast atom bombardment (FAB) mode on an AMD-

Intectra Gmbh Model (604) two-sector mass spectrometer. Mass spectral data are reported in mass-to-charge units (*m/z*). NMR measurements were carried out on a Varian 300 Gemini spectrometer at 300 MHz at ambient temperature, using $\sim$ 0.5 M solutions in $CDCl_3$ or DMSO-d_6 (in the case of the complexes 2-oxosparteine-$LiClO_4$ and 2-cyano-2-methylsparteine-$LiClO_4$), TMS as internal reference, and 10 mm tubes. Ground-state absorption spectra were recorded on a Cary 5E Varian spectrophotometer. Ground-state diffuse reflectance absorption spectra were recorded on a Cary 5E Varian spectrophotometer equipped with an integrating sphere.

(–)-Sparteine was derived from commercial sparteine sulphate, $C_{15}H_{26}N_2 \times H_2SO_4 \times 5H_2O$, supplied by Aldrich. 2-Methylsparteine was synthesised by addition of methyllithium to the lactam carbonyl group of lupanine followed by reduction with $NaBH_4$ [21]. $LiClO_4$ was supplied by Pierce Inorganics B. V. (Holland). 2-Oxosparteine (lupanine) was isolated from *Lupinus albus* seeds according to methods described previously [34]. 2-Cyano-2-methylsparteine was synthesised by addition of KCN to 2-methyl-2,3-didehydrosparteine diperchlorate [25].

Complexes were prepared by mixing acetone solutions of $LiClO_4$ and the alkaloid ((–)-sparteine, 2-methylsparteine, 2-oxosparteine, 2-cyano-2-methylsparteine) in stoichiometric millimolar quantities. The solvent was evaporated from the combined solution under reduced pressure to dryness and the residue recrystallised from dry benzene, yielding white crystals.

(–)-Sparteine-$LiClO_4$: White crystals (92%), m.p. 165 – 169 °C. – MS: *m/z* (%) = 241 (21) [M + Li], 235 (100) [M + H]$^+$. –$C_{15}H_{26}N_2LiClO_4$ (340): calcd. C 53.09, H 8.25, N 8.25; found C 53.73, H 8.26, N 8.30.

2-Methylsparteine-$LiClO_4$: White crystals (78%), m.p. 190 – 193 °C. – MS: *m/z* (%) = 255 (25) [M + Li], 249 (100) [M + H]$^+$. –$C_{16}H_{28}N_2LiClO_4 \times H_2O$ (372): calcd. C 51.70, H 8.08, N 7.54; found C 51.34, H 7.88, N, 6.95.

2-Oxosparteine-$LiClO_4$: White crystals (60%), m.p. 190 – 195 °C. – MS: *m/z* (%) = 255 (22) [M + Li], 249 (100) [M + H]$^+$. –$C_{15}H_{24}N_2O_1LiClO_4$ x H_2O (372): calcd. C 48.39, H 6.99, N 7.52; found C 48.54, H 7.05, N 7.42.

2-Cyano-2-methylsparteine-$(LiClO_4)_2$: White crystals (84%), m.p. 195 – 197 °C. – MS: *m/z* (%) = 287 (18) [M + 2Li], 274 (100) [M + H]$^+$. –$C_{17}H_{27}N_3Li_2Cl_2O_8 \times H_2O$ (503): calcd. C 40.50, H 5.80, N 8.33; found C 40.93, H 5.05, N 8.16.

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[1] D. J. Pippel, G. A. Weisenburger, S. R. Wilson, P. Beak, Angew. Chem. Int. Ed. **37**, 2522 (1998).
[2] J. F. Remenar, B. L. Lucht, D. B. Collum, J. Am. Chem. Soc. **119**, 5567 (1997).
[3] J. F. Remenar, B. L. Lucht, D. Kruglyak, F. E. Romesberg, J. H. Gilchirst, D. B. Collum, J. Org. Chem. **62**, 5748 (1997).
[4] F. Toda, K. Tanaka, H. Ueda, T. Oshima, J. Chem. Soc. Chem. Commun. 743 (1983).
[5] K. B. Wiberg, W. F. Bailey, J. Mol. Struct. **556**, 239 (2000).
[6] R. Kuroda, S. F. Mason, J. Chem. Soc. Dalton Trans. 371 (1977).
[7] S. Lopez, I. Muravyov, S. R. Pulley, S. W. Keller, Acta Crystallogr. C **54**, 355 (1998).
[8] J. Skolik, U. Majchrzak-Kuczyńska, M. Wiewiórowski, Bull. Pol. Acad. Chem. **24**, 741 (1978).
[9] G. Schroeder, W. Wysocka, B. Łęska, R. Kolanoś, K. Eitner, J. K. Przybylak, J. Mol. Struct. **616**, 193 (2002).
[10] S. F. Mason, R. D. Peacock, J. Chem. Soc. Dalton Trans. 226 (1973).
[11] J. T. Wróblewski, G. J. Long, Inorg. Chem. **16**, 704 (1977).
[12] E. Boschmann, L. M. Weinstock, M. Carmack, Inorg. Chem. **13**, 1297 (1974).
[13] Y. M. Lee, M. J. Oh, S. N. Choi, I. H. Suh, J. H. Lee, J. R. Park, Bull. Korean Chem. Soc. **19**, 1382 (1998).
[14] Y. M. Lee, S. N. Choi, I. H. Suh, R. D. Bereman, Acta Crystallogr. C **54**, 1582 (1998).
[15] Y. M. Lee, G. W. Chung, M. A. Kwon, S. N. Choi, Acta Crystallogr. C **56**, 67 (2000).
[16] H. Małuszyńska, A. Hoser, Z. Kałuski, Acta Crystallogr. B **35**, 970 (1979).
[17] M. Kubicki, T. Borowiak, W. Boczoń, Acta Crystallogr. C **52**, 226 (1996).
[18] A. Katrusiak, A. Hoser, Z. Kałuski, W. Boczoń, Acta Crystallogr. B **36**, 1688 (1980).
[19] P. Kubelka, F. Munk, Z. Tech. Phys. **12**, 593 (1931).
[20] P. Bour, J. McCann, H. Wieser, J. Phys. Chem. **101**, 9783 (1997).
[21] W. Boczoń, Pol. J. Chem. **55**, 339 (1981).
[22] G. Schroeder, W. Boczoń, B. Łęska, K. Eitner, B. Kozioł, B. Brzezinski, J. Mol. Struct. **597**, 93 (2001).
[23] J. Skolik, P. J. Krueger, M. Wiewiórowski, J. Mol. Struct. **5**, 461 (1970).
[24] A. Perkowska, G. Pieczonka, M. Wiewiórowski, Bull. Pol. Acad. Chem. **27**, 637 (1979).
[25] W. Boczoń, Bull. Pol. Acad. Chem. **36**, 45 (1988).
[26] W. Boczoń, J. Skolik, Bull. Pol. Acad. Chem. **37**, 35 (1989).

[27] W. M. Gołębiewski, J. D. Spencer, Can. J. Chem. **63**, 716 (1985).
[28] W. Boczoń, J. Skolik, B. Kozioł, J. Mol. Struct. **328**, 1 (1994).
[29] T. Brukwicki, W. Wysocka, B. Nowak-Wydra, Can. J. Chem. **72**, 193 (1994).
[30] A. Becke, J. Chem. Phys. **98**, 5648 (1993).
[31] R. Ditchfield, W. J. Hehre, J. A. Pople, J. Chem. Phys. **54**, 724 (1971).
[32] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, A. J. Jr. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian 98, revision A.11.3. Gaussian, Inc., Pittsburg, PA. (2002).
[33] K. B. Wilberg, W. F. Bailey, J. Mol. Struct. **556**, 239 (2000).
[34] W. Wysocka, A. Przybył, Sci. Legumes **1**, 37 (1994).