

Chiroptical Studies. Part LXXXVII.¹ Circular Dichroism of Some Sparteine Alkaloids

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C.d. data have been recorded for seventeen compounds of the sparteine series related to 11 β -sparteine (α -isosparteine) and 11 α -sparteine. The chromophores involved are the tertiary amine and *NN*-dialkyl-lactam systems; the compounds studied include eight amines, eight amino-lactams, and one dilactam.

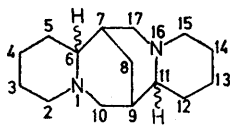
THE sparteine alkaloids are of considerable interest for chiroptical studies because they contain chromophores of two different types (*NN*-dialkyl-lactam and tertiary amine) in a rather rigid system of four fused six-membered rings (1). The skeleton may be considered

¹ Preceding paper in the Westfield series, hitherto entitled 'Optical Rotatory Dispersion and Circular Dichroism,' Part LXXXVI, L. Bartlett, D. N. Kirk, and P. M. Scopes, *J.C.S. Perkin I*, 1974, 2219.

as two quinolizidine systems fused together, or as a diazabicyclo[3.3.1]nonane which has been extended by one six-membered ring at each end (for general references see ref. 2). The chiroptical properties of the amide

² 'The Alkaloids,' ed. R. H. F. Manske, Academic Press, New York and London: N. J. Leonard in vol. 3, 1953, p. 119, and vol. 6, 1960, p. 253; F. Bohlmann and D. Schumann in vol. 9, 1967, p. 191; R. K. Hill in 'Chemistry of the Alkaloids,' ed. S. W. Pelletier, Van Nostrand, New York, 1970, pp. 418—422.

chromophore have been much studied, though not in the substitution pattern found here; few chiroptical studies on tertiary amines are available. Some o.r.d.



(1)

measurements on sparteine derivatives have been reported.³

Configuration and Nomenclature.—The absolute configurations of compounds in the group are known from studies by Okuda.⁴ Most of the known naturally occurring compounds have the configurations at C-6, C-7, and C-9 shown in formula (2); in particular, they have the $6\beta(H)$ -configuration (in terms of steroid conventions). The configuration at C-11 is variable, and we suggest that for semisystematic nomenclature the stem-name 'sparteine' should imply the configurations at C-6, C-7, and C-9 shown in (2), *i.e.* (6*R*,7*S*,9*S*), and that the configuration of the hydrogen atom (or any group replacing hydrogen) at C-11 should be stated as α or β , following the pattern employed for steroids.⁵ Thus compound (3), hitherto known simply as 'sparteine,' becomes 11 α -sparteine; ' α '-isosparteine (2) becomes 11 β -sparteine.

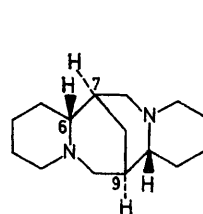
Conformation and Symmetry.—11 β -Sparteine (2) is a rigid molecule with an all-chair conformation in all circumstances (2A); its skeleton shows C_2 symmetry, and may be represented as part of a diamond network. The 11 α -sparteine system (3) can exist either in an 'all-chair' conformation (3A) or in a conformation in which ring c is a boat, and the remaining three rings are chairs (3B). Extensive studies on the conformations of the sparteine alkaloids by i.r. and n.m.r.^{6,7} spectroscopy have been carried out.

The conformation of any particular 11 α -compound depends on the nature and position of ring substituents, on the state (crystalline or in solution), and on the character of the solvent. For many 11 α -compounds n.m.r. and i.r. measurements indicate the all-chair conformation in polar solvents, but the 'c-boat' conformation in non-polar solvents; in certain cases, however, the 'c-boat' conformation may occur also in

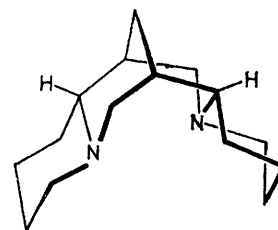
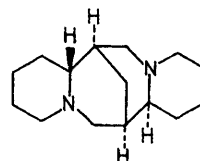
polar solvents as a result of intramolecular hydrogen bonding (*cf.* p. 2567).

It had been hoped that c.d. measurements in a range of solvents would provide further evidence regarding conformations; the c.d. results, however, show no clear correlation with the i.r. studies. In the present state of knowledge of the c.d. behaviour of amides and of tertiary amines, our c.d. results are therefore presented on their own in an empirical fashion.

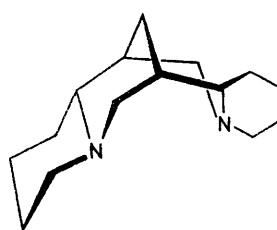
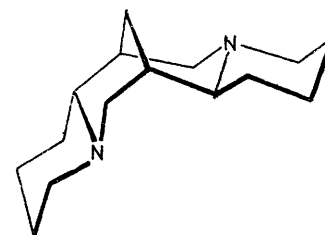
The Bis-(tertiary amines).—These compounds include 11 α -sparteine, 11 β -sparteine, and their hydroxy-derivatives, in which the only chromophores are the tertiary nitrogen atoms at the bridgeheads of the quinolizidine systems. Earlier data on the u.v. absorption of tertiary



(2)

(2A) all-chair, 11 β -H

(3)

(3A) all-chair, 11 α -H(3B) chair, chair, boat, chair, 11 α -H

³ S. Iskanderov and S. Yu. Yunusov, *Khim. prirod. Soedinenii*, 1970, **6**, 494 (*Chem. Nat. Compounds*, 1970, **6**, 519); S. Iskanderov, R. A. Shaimardanov, and S. Yu. Yunusov, *ibid.*, 1971, **7**, 636 (*Chem. Nat. Compounds*, 1971, **7**, 615).

⁴ S. Okuda, K. Tsuda, and H. Kataoka, *Chem. and Ind.*, 1961, 1115, 1751; *cf.* W. Klyne and J. Buckingham, 'An Atlas of Stereochemistry,' Chapman and Hall, London 1974, p. K21.

⁵ I.U.P.A.C.-I.U.B. Rules of Steroid Nomenclature, *Pure Appl. Chem.*, 1972, **31**, 285.

⁶ (a) P. Baranowski, P. Skolik, and M. Wiewiorowski, *Tetrahedron*, 1964, **20**, 2383; (b) M. Wiewiorowski, O. E. Edwards, and M. D. Bratek-Wiewiorowska, *Canad. J. Chem.*, 1967, **45**, 1447; (c) J. Skolik, P. J. Krueger, and M. Wiewiorowski, *Tetrahedron*, 1968, **24**, 5439; (d) J. Skolik, M. Wiewiorowski, and K. Jedrzyczak, *Bull. Acad. polon. Sci. Sér. chim.*, 1969, **17**, 201; (e) J. Skolik, M. Wiewiorowski, and P. J. Krueger, *J. Mol. Structure*, 1970, **5**, 461.

amines are summarised by Scott⁸ (*cf.* Leonard⁹ and Mason¹⁰) and some recent examples are listed in a valuable brief communication by Parello and Picot,¹¹ together with c.d. data for six compounds including 11 α -sparteine; a comparison of simple secondary and

⁷ (a) F. Bohlmann and D. Schumann, *Tetrahedron Letters*, 1965, 2433, 2435; (b) F. Bohlmann, D. Schumann, and C. Arndt, *ibid.*, p. 2705; (c) F. Bohlmann, H. Overwien, and D. Schumann, *Chem. Ber.*, 1965, **98**, 659.

⁸ A. I. Scott, 'Interpretation of the Ultraviolet Spectra of Natural Products,' Pergamon, Oxford, 1964, p. 17.

⁹ N. J. Leonard and D. M. Locke, *J. Amer. Chem. Soc.*, 1955, **77**, 437.

¹⁰ S. F. Mason, *Quart. Rev.*, 1961 **15**, 287.

¹¹ J. Parello and F. Picot, *Tetrahedron Letters*, 1968, 5083.

tertiary amines is given by Kostyanovsky *et al.*¹² The longest wavelength band which is generally recognisable is at about 200–210 nm (ϵ ca. 3000 per tertiary nitrogen atom). In addition, a shoulder at 230 nm is apparent in the unpolarised u.v. absorption for a few compounds. Most compounds however show a c.d. band at 220–230 nm. In many cases the change from a hydrocarbon to an alcohol as solvent is accompanied by a blue-shift (due to association of the alcohol with lone pairs of tertiary nitrogen atoms, *cf.* ref. 11). The band at ca. 200 nm, which is presumably of n - σ^* character, disappears completely on protonation.¹³

Table I presents u.v. and c.d. data for the two unsubstituted compounds, 11 β - and 11 α -sparteine, and for

Previous scattered work on c.d. of tertiary amines includes studies on piperidine derivatives;^{14,15} other monocyclic and bicyclic compounds, including a comparison between the behaviour of secondary and tertiary amines;¹² pyrrolizidine alkaloids;¹⁶ and steroid alkaloids and amines.^{11,17} Extensive studies of the o.r.d. curves of sparteine and related alkaloids have been reported by Iskanderov *et al.*;³ the greater simplicity of the c.d. curves discussed in the present paper exemplifies the advantages of c.d. over o.r.d. when a choice of techniques is available.

Our c.d. measurements were made for each compound in hexane, in methanol, and in methanol with an excess of acid present. For all compounds in Table I, the c.d.

TABLE I
C.d. of sparteines and their hydroxy-derivatives, and of lupinines

Compound	Hexane				Methanol *			
	Absorption		C.d.		Absorption		C.d.	
	ϵ	λ /nm	$\Delta\epsilon$ †	λ /nm	ϵ	λ /nm	$\Delta\epsilon$ †	λ /nm
11 β -Sparteine (‘ α' -Isosparteine)	3680	240	+2.79	245	1880	225	+1.22	230
	8180	210	-8.89	217	4800!	202	-3.55	206
11 α -Sparteine (Sparteine)			+6.1!	194			-0.06	242
			-0.39	236			+0.59	208
	7300	205	+3.12	202–208	3600	199	+1.6!	195
			+2.11	189				
4 α (<i>eq</i>)-Hydroxy-11 α -sparteine			-0.17	238				
12 β (<i>ax</i>)-Hydroxy-11 α -sparteine	5200	198	+0.78	220	3500	205	+0.46	200
			+0.12	234				
			-0.40	213			-1.06	202
	8100	198	+1.98	198				
13 α (<i>eq</i>)-Hydroxy-11 α -sparteine			-2.8!	186				
			-0.36	237				
13 β (<i>ax</i>)-Hydroxy-11 α -sparteine	7300	201	+3.98	208	3850	203	+1.68	197
			-0.54	237				
Lupinine	7100	201	+3.61	208	3300	203	+1.92	201
	4600	198	+0.29	209			+0.11	211
Epilupinine			-1.2!	195				
	4300	205	+0.05	225				
			-0.35	204				
			+0.4!	185				

* None of the compounds listed in this Table showed any c.d. in acidic methanol. † All $\Delta\epsilon$ values are maxima except those marked ! (lowest wavelength measured).

six of their hydroxy-derivatives. We find for 11 β -sparteine an absorption maximum in hexane at 210 nm (ϵ ca. 8180) with a shoulder at 240 nm (ϵ 3680); other members of the series with and without hydroxy-groups show similar absorption bands at about 200–205 nm, but in most cases the shoulder at 240 nm cannot be detected. Lupinine and epilupinine (4), which are useful models for one-half of the sparteine skeleton, show absorption at about 200 nm with ϵ ca. 4000.

¹² R. G. Kostyanovsky, I. M. Gella, V. I. Markov, and Z. E. Samojlova, *Tetrahedron*, 1974, **30**, 39.

¹³ E. Tannenbaum, E. M. Coffin, and H. Harrison, *J. Chem. Phys.*, 1953, **21**, 311; L. W. Pickett, M. E. Corning, G. M. Wieder, D. A. Semenov, and J. M. Buckley, *J. Amer. Chem. Soc.*, 1953, **75**, 1618.

¹⁴ J. C. Craig and S. K. Roy, *Tetrahedron*, 1965, **21**, 401; J. C. Craig, ‘Some Newer Physical Methods in Structural Chemistry,’ ed. R. Bonnett, London, 1967, p. 170; H. C. Beyerman, L. Maat, J. P. Visser, J. C. Craig, and R. P. K. Chan, *Rec. Trav. chim.*, 1969, **88**, 1012; G. Fodor, E. Bauerschmidt, and J. C. Craig, *Canad. J. Chem.*, 1969, **47**, 4393; H. C. Beyerman, S. van den Bosch, and J. H. Brenker, *Rec. Trav. chim.*, 1971, **90**, 755; H. C. Beyerman, B. S. L. Bordes, L. Maat, and F. M. Varnaar, *ibid.*, 1972, **91**, 1441.

bands disappeared, as expected, on acidification of a methanolic solution. 11 β -Sparteine is considered first because of its inherent C_2 symmetry; it shows in hexane a moderate positive c.d. band at 245 nm, and two strong bands at 217 and <194 nm.

The effects of ‘non-chromophoric’ substituents on the c.d. of compounds such as the sparteines may be direct (involving perturbation of an essentially symmetrical chromophore) or indirect (involving stabilisation of a conformation other than that which is favoured in the parent compound). The c.d. results for 4 α -, 13 α -, and 13 β -hydroxy-derivatives of 11 α -sparteine all show

¹⁵ A. Guggisberg, M. M. Badawi, M. Hesse, and H. Schmid, *Helv. Chim. Acta*, 1974, **57**, 414.

¹⁶ C. C. J. Culvenor, D. H. G. Crout, W. Klyne, W. P. Mose, J. D. Renwick, and P. M. Scopes, *J. Chem. Soc. (C)*, 1971, 3653; J. Hrbek, L. Hruban, A. Klásek, N. K. Kochetkov, A. M. Likhoshesterov, F. Šantavý, and G. Snatzke, *Coll. Czech. Chem. Comm.*, 1972, **37**, 3918.

¹⁷ J. P. Alazard and X. Lusinchi, *Bull. Soc. chim. France*, 1972, 3267; *cf.* for a simple pyrrolidine derivative, L. Blomqvist, K. Leander, B. Luning, and J. Rosenblom, *Acta Chem. Scand.*, 1972, **26**, 3203.

patterns roughly similar to those for the unsubstituted alkaloid itself. 12 β -Hydroxy-11 α -sparteine, however, shows a curve of reversed signs. I.r. studies⁶ show internal hydrogen-bonding between the axial 12 β -hydroxy-group and the lone pair of N-16; this probably stabilises the boat-chair conformation of rings c and d,

portant alkaloids are mono-oxosparteines in which, by virtue of formal substitution of :O for H₂ at a methylene group adjacent to one of the tertiary nitrogen atoms, an NV-disubstituted lactam group is present. The other tertiary nitrogen system remains unchanged. The amide carbonyl group is found in the 11 α -sparteine

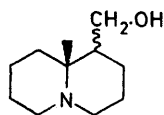
TABLE 2
C.d. of sparteine lactams and their derivatives

Compound	Free base in hexane				Free base in methanol				Salt in methanol ^a			
	Absorption		C.d.		Absorption		C.d.		Absorption		C.d.	
	ϵ	λ/nm	$\Delta\epsilon$ †	λ/nm	ϵ	λ/nm	$\Delta\epsilon$ †	λ/nm	ϵ	λ/nm	$\Delta\epsilon$ †	λ/nm
Monolactams												
2-Oxo-11 β -sparteine (2-Oxo- α' -isosparteine; α -isolupanine)	17,800	215	+5.30 -4.37 -4.68	236 215 193	16,200	210	+6.96 -6.96	229 198	12,500	207	+8.35 -17.0	227 202
2-Oxo-11 α -sparteine (Lupanine)	17,250	209	+4.32 -9.28 +6.95	235 208 190	18,000	205	+5.83 -6.17	224 200	15,400	205	+6.52 -9.26	224 200
13 α -Hydroxy-2-oxo-11 α -sparteine ^b (13-Hydroxylupanine)			+0.80sh +1.16 -2.67	245 235 208	6100	211	+4.80 -4.45	223 200			+5.55 -8.9!	222 197
13 β -Hydroxy-2-oxo-11 α -sparteine (13- <i>epi</i> -Hydroxylupanine)			+1.05sh +3.03 -7.20	254 235 208	6900	211	+5.49 -7.45	224 197			+6.28 -8.63	224 197
17 β -Hydroxy-2-oxo-11 α -sparteine (17-Hydroxylupanine)	7700	207	+3.31 -7.34 +8.44	241 ^c 210 190	8500	205	+1.48 -2.09	225 207			+1.89 -23.0	229 203
13 β ,17 β -Dihydroxy-2-oxo-11 α -sparteine	600sh 2200	250 208	+0.53 -1.05 -1.42	233 209 298 ^d	800sh 2100	255 211	+0.62 -0.56 -1.47	225 206 293 ^d			-2.18 -21.0	254* 201
2,13-Dioxo-11 α -sparteine (13-Oxolupanine)	530sh 5700	255 211	+4.25 -7.98 +5.0!	243 211 194	1200sh 6200	260 209	+1.33 -1.95 +3.3!	246 212 195			+5.90 -7.2!	255 200
10-Oxo-11 α -sparteine (Aphylline)	18,000	206	+0.88 -10.2 +11.7!	244 220 185	18,700	205	-6.95 +6.04	220 202	16,900	207	+4.83 -12.4	227 203
15-Oxo-11 α -sparteine	10,600	210	-3.32 +2.37sh +5.7!	233 215 207	11,900	206	-5.24 +5.4!	226 206			-1.22 +3.4!	255 206
17-Oxo-11 α -sparteine	770sh 13,400	241 209	+3.82 -7.14 +7.90 -5.10	236 218 205 193	7400	211	+2.45 -1.43 +2.7!	223 210 197			-0.82 +4.08	228 205
Dilactam												
2,17-Dioxo-11 α -sparteine (17-Oxolupanine)	12,900	207	-0.26 +3.64 -10.2 +22.8	264 232 216 204	13,200	209	-0.04 +7.92 +7.7!	262 220 206			-0.05 +8.13 +7.68	264 219 206

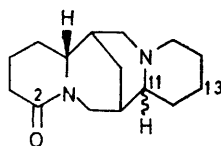
† All $\Delta\epsilon$ values are maxima except those marked sh (shoulder) or ! (lowest wavelength measured).

^a Salts were formed by adding an excess of HCl to the methanolic solution of the base, except in two cases marked * where the crystalline perchlorate was used. ^b 13 α -Hydroxy-15 β -(5-hydroxymethyl-2-furyl)-2-oxo-11 α -sparteine was also examined in methanol [$\Delta\epsilon$ + 7.94 (228 nm), -3.97 (201 nm), -6.2! (195 nm)] and in acidic methanol [$\Delta\epsilon$ + 10.8 (225 nm), -8.5 (201 nm)]; the compound was insoluble in hexane. ^c Measured on base liberated from the perchlorate. ^d Ketonic $\pi \rightarrow \pi^*$ band.

even in hydroxylic solvents. Lupanine (4; β -CH₂OH) and epilupanine (4; α -CH₂OH) show c.d. bands which



(4)



(5)

are much less intense than those given by the bis-(tertiary amine) skeleton in 11 α - and 11 β -sparteine.

Lactam-Tertiary Amines (Oxosparteines).—Several im-

series at all four possible positions (2, 10, 15, and 17), but in the more symmetrical 11 β -sparteine series only the 2-oxo-compound is available. Various hydroxy-2-oxo-11 α -sparteines have been studied, and also 2,13-dioxo-11 α -sparteine, in which the 13-oxo-group is of normal ketonic character.

There is no reason to suppose that the c.d. behaviour of the substituted amide group would be significantly altered in acidic methanol; the c.d. bands of amines at about 200 nm are obliterated by acid,¹³ and the observed c.d. of the monolactam monoamino-compounds in acid is presumably essentially that of the lactam chromophore alone (perturbed by quaternary nitrogen).

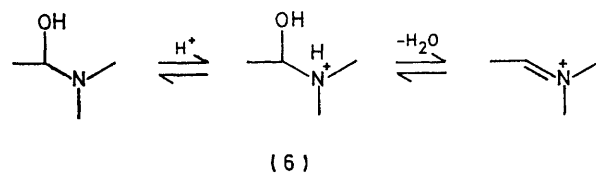
Literature data on the u.v. absorption of lactams are sparse.^{18,19} We found for three of the lactams studied u.v. maxima at 205–207 nm (ϵ_{max} 12,000–17,000) in acidic methanol, and rather more intense maxima at similar wavelengths in (neutral) methanol and in hexane.

No extensive collection of c.d. data for lactams is available; some recent papers, in which references to earlier work may be found are given as refs. 20–25 (as well as 18 and 19); very few of the compounds considered in these references are *NN*-dialkyl-lactams of the kind found in the sparteine series. C.d. studies on acetamido-derivatives¹ of chiral amines, which appear to show a surprising measure of conformational rigidity, are also noted.

2-Oxo-compounds. We consider first the 2-oxo-11 α - and 11 β -sparteines (5) carrying no other substituents; each compound gives, down to about 200 nm, the same c.d. pattern in hexane, in methanol, and in acidic methanol; *viz.* a strong positive band at about 225–230 nm and a strong negative band at about 200–215 nm. A further band at about 190 nm is negative for the 11 β - and positive for the 11 α -compound. It would be tempting to consider the first two bands as a couplet due to interaction between two chromophores the transitions of which are of approximately the same energy. However, such a hypothesis is untenable because the apparent couplet is present with even greater intensity in acidic methanol, in which the tertiary amine group has been quaternised and shows no absorption in the region of 200 nm. The coupled oscillator or exciton chirality treatment has been applied primarily to compounds containing a pair of identical or almost identical chromophores, by, for example, Mason²⁶ (*cf.* refs. 27 and 28); it has recently been applied to pairs of chromophores, the members of which are of significantly different character although the energies of the transitions involved are similar.^{29,30}

The 13 α - and 13 β -hydroxy-2-oxo-11 α -sparteines show c.d. curves generally similar to those of the parent oxo-compound. The two 17 β -hydroxy-substituted 2-oxo-11 α -sparteines (6) as salts have an additional Cotton effect at about 255 nm which is not present for the other 2-oxosparteines; the short-wavelength negative maxima near 200 nm are very much more intense ($\Delta\epsilon$ –20) than those for the rest of the series. The

maximum near 255 nm presumably arises from the protonated carbinolamine structure [N-16, C(17)-OH], which exists as an iminium salt ($\text{N}^+=\text{C}$) in the presence of strong acid (for chiroptical properties of C=N groups see ref. 31a).



2,13-Dioxo-11 α -sparteine (7) has,^{*} in addition to the lactam group and the tertiary nitrogen, a ketonic carbonyl chromophore at C-13 which gives rise to a moderate negative Cotton effect near 295 nm ($n \rightarrow \pi^*$ transition). The molecule is believed⁶ to exist in a conformational equilibrium containing equal proportions of the all-chair and 'c-boat' conformers; for either conformation the observed negative Cotton effect is in accordance with the prediction of the Octant Rule, as refined recently.³² (O.r.d. measurements for a 4-oxo-sparteine have been reported.³³) On addition of acid to the methanolic solution the ketonic Cotton effect for compound (7) disappears, owing to hemiacetal formation;³⁴ the form of the c.d. curve is then the same as that for 2-oxo-11 α -sparteine and its hydroxy-derivatives.

Other oxosparteines. 10-Oxo-11 α -sparteine (8) gives a strong apparent c.d. couplet of opposite sign to that of the 2-oxo-analogue in hexane and methanol; this may be a reflection of the fact that the surroundings of the amide chromophores in the two compounds (*i.e.* rings A and B) are quasi-enantiomeric. However, the c.d. curve for 10-oxo-11 α -sparteine in acidic methanol is of the same sign as for the 2-oxo-analogue. The c.d. curves for 15-oxo-11 α -sparteine are of opposite sign to those for the 2-oxo-analogue; the amide chromophore here is part of the CD ring fragment of the molecule and (if we disregard possible conformational differences) is of a type quasi-enantiomeric to that in the 2-oxo-compound. The c.d. results for 17-oxo-11 α -sparteine are distinguished from those of the 2-oxo-analogue by the smaller magnitudes of the Cotton effects; the signs are the same as those of the bands for the 2-oxo-compound in hexane and in methanol; in acidic methanol the signs are reversed.

¹⁸ H. Basch, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, 1968, **49**, 5007.

¹⁹ C. G. Overberger, G. Montando, J. Šebenda, and R. A. Veneski, *J. Amer. Chem. Soc.*, 1969, **91**, 1256.

²⁰ J. A. Schellman, *Accounts Chem. Res.*, 1968, **1**, 144.

²¹ D. W. Urry, *Ann. Rev. Phys. Chem.*, 1968, **19**, 477.

²² H. Wolf, *Tetrahedron Letters*, 1965, 1075; O. Červinka, L. Hub, F. Snatzke, and G. Snatzke, *Coll. Czech. Chem. Comm.*, 1973, **38**, 897.

²³ W. Klyne and P. M. Scopes in 'Fundamental Aspects and Recent Developments in O.R.D. and C.D.', ed. F. Ciardelli and P. P. Salvadori, Heyden, London, 1973, p. 126.

²⁴ M. Goodman, C. Toniolo, and J. Falcetta, *J. Amer. Chem. Soc.*, 1969, **91**, 1816.

²⁵ H. Rehling and H. Jensen, *Tetrahedron Letters*, 1972, 2793; H. Ogura, H. Takayanagi, K. Kubo, and K. Furuhashi, *J. Amer. Chem. Soc.*, 1973, **95**, 8056; H. Ogura, H. Takayanagi, and K. Furuhashi, *Chem. Letters*, 1973, 387.

²⁶ S. F. Mason and G. W. Vane, *J. Chem. Soc. (B)*, 1966, 370; for a list of applications and correlations with the Bijvoet X-ray technique, see S. F. Mason, *J.C.S. Chem. Comm.*, 1973, 239.

²⁷ O. E. Weigang, jun., and M. J. Nugent, *J. Amer. Chem. Soc.*, 1969, **91**, 4555.

²⁸ N. Harada and K. Nakanishi, *Accounts Chem. Res.*, 1972, **5**, 257.

²⁹ N. Harada, *J. Amer. Chem. Soc.*, 1973, **95**, 240; M. Koreeda, N. Harada, and K. Nakanishi, *ibid.*, 1974, **96**, 266.

³⁰ G. Ohloff, E. Otto, V. Rautenstrauch, and G. Snatzke, *Helv. Chim. Acta*, 1973, **56**, 1874.

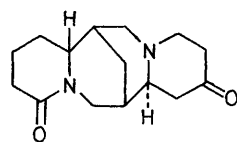
³¹ P. Crabbé, 'An Introduction to the Chiroptical Methods in Chemistry,' Mexico 1971, (a) p. 64; (b) pp. 54–56.

³² D. N. Kirk and W. Klyne, *J.C.S. Perkin I*, 1974, 1076.

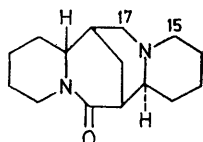
³³ S. I. Goldberg and R. F. Moates, *J. Org. Chem.*, 1967, **32**, 1832.

³⁴ C. Djerassi, L. A. Mitscher, and B. J. Mitscher, *J. Amer. Chem. Soc.*, 1959, **81**, 947.

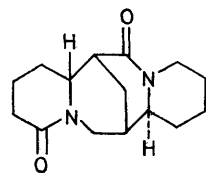
Dilactam. The only dilactam available is 2,17-dioxo-11 α -sparteine (9). The c.d. curve in methanol is unusual in showing two maxima of the same sign (positive) at about 220 and 206 nm; as expected it is virtually unchanged by addition of acid. In contrast, the c.d.



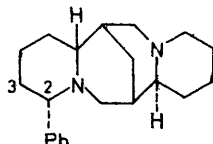
(7)



(8)



(9)



(10)

curve in hexane shows a very strong 'couplet' ($\Delta\epsilon$ -10 , 216 nm; $+22$, 204 nm).

Data for this compound (described as 'D-oxo-lupanine') in other solvents have been published.³⁵

2-Arylsparteines.—C.d. data for 2 α -phenyl-11 α -sparteine (10) and the corresponding 2,3-didehydro-compound (which are insoluble in hexane) are presented for methanolic and acidic methanolic solutions (Table 3). 2 α -Phenyl-11 α -sparteine shows a small positive Cotton effect centred at 261 nm, with the vibrational fine structure characteristic of the aromatic nucleus. The sign of this 1L_b Cotton effect, is as expected, unaffected by protonation. Maxima below 220 nm arise from the superposition of Cotton effects due to the aromatic nucleus (1L_a transition) and the tertiary nitrogen.

The 2,3-didehydro-compound exhibits in methanol a series of overlapping Cotton effects with positive maxima at 277 and 246 nm (styrene chromophore)^{31b} and a shoulder at 219 nm. On addition of acid there is a

³⁵ F. A. Bovey, *Pure Appl. Chem.*, 1968, **16**, 417.

marked change in the c.d. curve; the first two maxima are negative (at 267 and 255 nm) and the next is positive at 213 nm with a shoulder at 222 nm. This inversion

TABLE 3
C.d. of arylsparteines

	Free base (MeOH)		Salt (MeOH)	
	$\Delta\epsilon$	λ /nm	$\Delta\epsilon$	λ /nm
2-Phenyl-11 α -sparteine (10)	+0.23	268	+0.17	268
	+0.24	261	+0.19	261
	+0.23	255	+0.13	255
	+0.17	248	+0.09	248
	+1.07	219	-0.80	215
	-5.62sh	202		
2,3-Didehydro-2-phenyl-11 α -sparteine	-8.04!	195		
	+6.04	277	-1.89	267
	+7.81	246	-1.30sh	255
	+2.84sh	219	+2.37sh	222
	-4.26!	203	+3.20	213

of sign is presumably associated partly with the isomerisation of the double bond from 2,3- to 1,2- (which is known to occur on protonation of 2,3-didehydro-2-phenylsparteine), and also with the related change in conformation from CD boat-chair to all-chair.

EXPERIMENTAL

All compounds examined were available from the collection of M. W. in Poznań. Compounds available as the free base were examined in hexane and in methanol; they were converted into salts by the addition of aqueous 10M-hydrochloric acid (1 drop) to the methanolic solution of the base (*ca.* 5 ml); two compounds available only as the perchlorate were converted into the free base by dissolving the salt in water, adding alkali, and extracting the base into ether.

C.d. curves were recorded on a Jouan Dichrographe 185 with solutions of concentration 1 mg ml⁻¹ or less and path lengths 10 mm or less. U.v. absorption data were recorded for the same solutions on a Unicam SP 800 spectrometer.

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