

## CHIROPTICAL PROPERTIES OF THE 5,16-CYCLOCORYNANE TYPE ALKALOIDS\*

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As shown by measurement of optical rotatory dispersion and circular dichroism, the chiroptical properties of pentacyclic alkaloids of the 5,16-cyclocorynane type are analogous to those of the yohimbane and eburnane alkaloids. The alkaloids (+)-lochnerine (*Id*), (+)-šarpagine (*If*), (+)-pericyclivine (*Ig*), (-)-polyneuridine (*Ih*), (+)-akuammidine (*Ii*), (-)-voachalotine (*Ij*) and some ajmaline degradation products *Ia*–*Ic* are of the same absolute configuration (*S*) at the C<sub>(3)</sub> atom.

In connection with investigations on chiroptical properties of compounds with an indole chromophore<sup>1–8</sup> it appeared of interest to compare a group of substances with the pentacyclic structure *I* (i.e., alkaloids and alkaloid derivatives with the parent 5,16-cyclocorynane<sup>9</sup> ring system) with other indole compounds containing the same basic tetracyclic skeleton A–D. With compounds of the type *I*, the closure of the fifth ring by means of a substituted methylene bridge between the C<sub>(5)</sub> and C<sub>(15)</sub> atoms necessarily increases the rigidity of the whole system and might thus affect the chiroptical behaviour of the substances in comparison with the less rigid compounds of the yohimbane *II* (ref.<sup>1,10,11</sup>) or eburnane *III* (ref.<sup>2</sup>) type where the fifth ring is *ortho* or *ortho-peri* annelated to the parent tetracyclic ring system.

The UV spectra of compounds *Ia*–*Ik* (Table I) do not exhibit such differences which would make possible correlation with respect to the substitution at the C<sub>(16)</sub> atom or on the aromatic ring or with respect to the presence of a C<sub>(19)</sub>=C<sub>(20)</sub> double bond and also are not considerably different from the UV spectra of compounds of the *II* or *III* type (cf.<sup>1,2</sup>). In the region of longer wavelength transitions of the aromatic chromophore (an analogy of the benzene B<sub>2u</sub> ← A<sub>1g</sub> band<sup>17</sup>), all the curves form a multiple Cotton effect of the same sign (positive in the case of the configuration according to formula *I*) which corresponds with UV maxima. On CD curves, there are located positive dichroic bands (Fig. 1) at 300–270 nm. There may be observed a difference between compounds substituted on the indole ring and com-

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TABLE I  
 Ultraviolet Spectra of Alkaloids and their Derivatives in Methanol

Compound	$\lambda_{\max}$ , nm (log $\epsilon$ )			Ref.	
<i>Ia</i>	289 (3.69)	282 (3.73)	—	225 (4.41)	<sup>a</sup>
<i>Ib</i>	291 (3.82)	284 (3.87)	—	228 (4.54)	12
<i>Ic</i>	291 (3.81)	284 (3.85)	276 (3.67) <sup>a</sup>	228 (4.56)	12
<i>Id</i>	292 (3.84)	—	278 (3.92)	226 (4.41)	13
<i>Ie</i>	—	285 (3.65)	280 (3.65)	226 (4.20)	<sup>a</sup>
<i>If</i>	294 (3.92)	—	278 (3.92)	226 (4.36)	14
<i>Ig</i>	289 (3.79)	281 (3.88)	—	225 (4.51)	15
<i>Ih</i>	289 (3.71)	281 (3.82)	—	228 (4.51)	16
<i>Ii</i>	290 (3.82)	280 (3.83)	—	227 (4.51)	14
<i>Ij</i>	291 (3.79)	284 (3.84)	275 (3.88)	230 (4.56)	<sup>a</sup>
<i>Ik</i>	290 (3.71)	284 (3.75)	277 (3.70)	230 (4.47)	<sup>a</sup>

<sup>a</sup> This paper.

pounds without these substituents (Fig. 1). Compounds without substituents on the aromatic nucleus exhibit fine structure of the long wavelength band with all maxima in the positive region. On the other hand, lochnerine (*Id*), N-methyllochnerine (*Ie*), and sarpagine (*If*) exhibit two long wavelength bands lacking the fine structure; the longest wavelength band (bathochromically shifted when compared with the first group) is of a negative sign. The short wavelength electronic transition of the indole chromophore (probably an analogy of the  $B_{1u} \leftarrow A_{1g}$  band) is also optically active and manifests itself by a negative Cotton effect at about 230 nm. Another

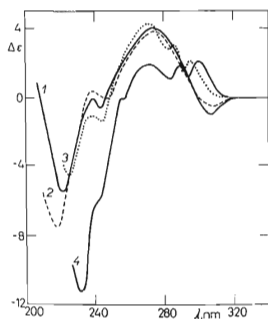
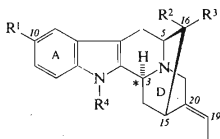


FIG. 1  
 Circular Dichroism Curves in Methanol  
 1 Lochnerine (*Id*), 2 sarpagine (*If*), 3 pericyclivine (*Ig*), 4 voachalotine (*Ij*).

band of the positive dichroic absorption is situated at 205 nm. It may be encountered only with compounds lacking the carboxyl chromophore but also with difficulty because of the unfavourable  $\Delta\epsilon/\epsilon$  ratio. Even in this case, the existence of this band undoubtedly depends on the electronic transitions in the indole chromophore (the  $E_1$  band). With compounds *Ig*–*Ij*, the curve is complicated by dichroic absorption of the  $n-\pi^*$  transition in the carboxylic group. On all CD curves there may be observed two insignificant maxima of opposite signs (the negative one at longer wavelengths and the positive one at shorter wavelengths) in the 245–235 nm region. The electronic origin of these maxima is obscure; they do not correspond to any maxima in UV spectra.



I

	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
<i>Ia</i> ,	H	H	CH <sub>3</sub>	CH <sub>3</sub> (19,20 $\alpha$ -dihydro)
<i>Ib</i> ,	H	H	CH <sub>2</sub> OH	CH <sub>3</sub> (19,20 $\alpha$ -dihydro)
<i>Ic</i> ,	H	CH <sub>2</sub> OH	H	CH <sub>3</sub> (19,20 $\alpha$ -dihydro)
<i>Id</i> ,	OCH <sub>3</sub>	H	CH <sub>2</sub> OH	H
<i>Ie</i> ,	OCH <sub>3</sub>	H	CH <sub>2</sub> OH	CH <sub>3</sub>
<i>If</i> ,	OH	H	CH <sub>2</sub> OH	H
<i>Ig</i> ,	H	COOCH <sub>3</sub>	H	H
<i>Ih</i> ,	H	CH <sub>2</sub> OH	COOCH <sub>3</sub>	H
<i>Ii</i> ,	H	COOCH <sub>3</sub>	CH <sub>2</sub> OH	H
<i>Ij</i> ,	H	CH <sub>2</sub> OH	COOCH <sub>3</sub>	CH <sub>3</sub>
<i>Ik</i> ,	H	CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>3</sub>

In the whole series, the absolute configuration on the C<sub>(3)</sub> atom is the same (*S*), as it may be inferred from the significant resemblance of the curves. This assignment is in accordance with chemical intercorrelations<sup>12,18–23</sup> (direct or indirect) between the absolute configuration of compounds *Ib*–*Ik* and that of corynantheine<sup>24,25</sup> and corynantheidine<sup>26</sup>, as well as with relations to the alkaloid akuammidine (*Ii*) the absolute configuration of which was unequivocally determined by the anomalous X-ray diffraction<sup>27,28</sup>.

As shown by comparison of the compound *Ia* curve with that of the tetracyclic base<sup>5</sup> *IV*, the closure of an additional ring manifests itself only by an increased rotatory

strength of dichroic bands at longer wavelengths (the Kautzmann-Eyring effect<sup>29</sup>) but not by a substantial change in position or sign of these bands. The ring closure has no effect on the short wavelength region. Identical results have been obtained in comparisons of the remaining compounds *I* with yohimbane alkaloids<sup>1</sup> *II* and eburnane alkaloids<sup>2</sup> *III* (Fig. 2). An analogous situation has been encountered<sup>5</sup> when

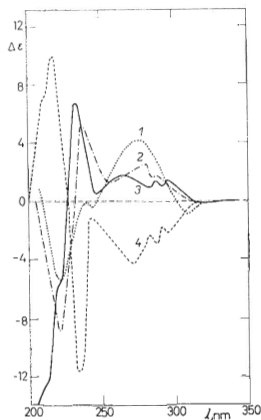
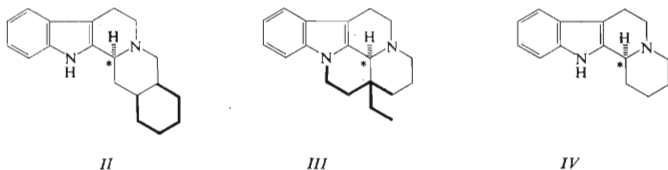


FIG. 2  
Comparison of Circular Dichroism Curves of Various Types of Indole Alkaloids in Methanol

1 Lochnerine (*Id*), 2 vincamine (type *III*), 3 yohimbine (type *II*), 4 pseudoyohimbine (type *II*).

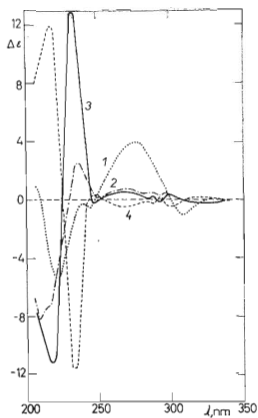
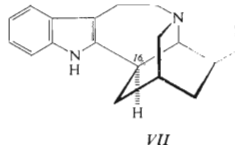
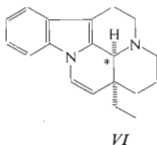
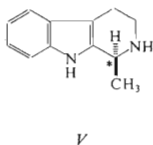


FIG. 3  
Comparison of Circular Dichroism of Lochnerine with Those of Simpler Cyclic Systems in Methanol

1 Lochnerine (*Id*), 2 tetracyclic base *IV*, 3 (+)-1-methyl-1,2,3,4-tetrahydro- $\beta$ -carboline (*V*, 3 $\alpha$ H), 4 (-)-1-methyl-1,2,3,4-tetrahydro- $\beta$ -carboline (*V*, 3 $\beta$ H).

comparing the tricyclic 1,2,3,4-tetrahydroharmane\* (*V*) and the tetracyclic base *IV* curves (Fig. 3). The chiroptical properties of all the present substances thus markedly depend on the chirality at the  $C_{(3)}$  atom while the influence of other centers is farly lower. It appears therefore acceptable to generalise that the (*S*) configuration at the  $C_{(3)}$  chiral center shown in formulae *I*–*V* is in accord with the positive dichroic absorption at 300–270 nm, the negative one at 230–220 nm, and the positive one in the short wavelength region at about 205 nm in all compounds containing the original 1,2,3,4-tetrahydro- $\beta$ -carboline ring system. The chiroptical properties of compounds with a changed chromophoric system such as eburnamenine<sup>3</sup> (*VI*) and the ibogamine (*VII*) type alkaloids<sup>7,8</sup> are quite different.



As indicated by comparison of curves of compounds *Ib* and *Ic*, the configuration at the  $C_{(16)}$  carbon atom does not exert any marked influence on the shape of the curve. The magnitude of this influence undoubtedly depends on the nature of substituents attached to this carbon atom but even with the methoxycarbonyl group there was not observed any correlation (for a different situation with NMR spectra see for example ref.<sup>23</sup>).

## EXPERIMENTAL

Melting points were taken on a heated microscope stage (Boetius microblock) and were not corrected. The UV spectra were measured in methanolic solutions on a Specord UV-VIS (Zeiss, Jena, German Democratic Republic) apparatus. The sign of optical rotation of the present compounds refers to values and conditions given in quoted papers.

### Starting Materials

(+)-Lochnerine<sup>13</sup> (*Id*), (+)-sarpagine<sup>14</sup> (*If*), (+)-N-methyllochnerine<sup>20</sup> (*Ie*), (+)-pericyclivine<sup>15</sup> (*Ig*), (–)-polyneuridine<sup>16</sup> (*Ih*), and (+)-akuammidine<sup>14</sup> (*Ii*) were authentic samples and their physical constants were identical with those reported in the literature. (–)-Deoxyajmalol B (*Ib*)

\* The earlier<sup>5</sup> prepared samples of 1,2,3,4-tetrahydroharmane (*V*) were optically impure as suggested by chiroptical properties. A novel resolution procedure using N-protected amino acids as resolution agents has now afforded samples of a higher specific rotation value; these samples are believed to be pure enantiomers. Noteworthy, the use of N-benzyloxycarbonyl-L-alanine leads to the levorotatory enantiomer *V* while the dextrarotatory enantiomer is obtained with the use of N-benzyloxycarbonyl-L-valine. In view of the accessibility of N-protected amino acid derivatives and their variety, the choice of a suitable resolving acid is considerably extended.

TABLE II  
Optical Rotatory Dispersion Data of Alkaloids in Methanol

Com- pound	$\lambda$ , nm ( $[\phi]$ ) <sup>a</sup>									
<i>Id</i>	325	310	300 sh	291 pk	—	273	—	253 tr	236	220 pk
	(+1 700°)	(+1 880°)	(+7 500°)	(+9 800°)	—	(0°)	—	(-10 800°)	(0°)	(+26 000°)
<i>Id</i> <sup>b</sup>	325	307	300 sh	290 sh	283 pk	267	—	248 tr	—	—
	(+1 800°)	(+1 300°)	(+4 370°)	(+8 740°)	(+9 400°)	(0°)	—	(-8 000°)	—	—
<i>Ie</i>	325	312	—	292 pk	—	276	—	257 tr	238	—
	(+1 000°)	(+1 000°)	—	(+7 400°)	—	(0°)	—	(-9 100°)	(0°)	—
<i>If</i>	325	310	303 sh	290 pk	280 sh	275	—	252 tr	234	—
	(+1 980°)	(+3 090°)	(+6 400°)	(+8 570°)	(+4 900°)	(0°)	—	(-9 000°)	(0°)	—
<i>Ig</i>	325	308	299 pk	292 tr	289 pk	278	—	250 tr	226	—
	(+800°)	(+3 200°)	(+7 000°)	(+2 950°)	(+6 450°)	(0°)	—	(-19 000°)	(0°)	—
<i>Ih</i>	325	—	300 pk	292 tr	287 pk	284 tr	282pk	253 sh	244 sh	235 sh <sup>c</sup>
	(+350°)	—	(+2 600°)	(-400°)	(+650°)	(-1 620°)	(-350°)	(-17 000°)	(-22 000°)	(33 000°) <sup>c</sup>
<i>Ii</i>	325	313	299 pk	293 tr	290 pk	279	—	250 sh	240 <sup>c</sup>	—
	(+2 000°)	(+3 100°)	(+7 260°)	(+5 060°)	(+7 980°)	(0°)	—	(-22 000°)	(-28 000°)	—

<sup>a</sup> sh shoulder, pk peak, tr trough; <sup>b</sup> in trifluoroethanol; <sup>c</sup> end value.

and (–)-deoxyajmalol A (*Ic*) were obtained from deoxyajmaline *via* the corresponding deoxyajmalals by hydrogenation on the Adams catalyst in ethanol according to Bartlett and coworkers<sup>12</sup>.

17,21-Dideoxyajmalol B (*Ia*) was obtained by the lithium aluminium hydride reduction of deoxyajmalol B *p*-toluenesulfonate<sup>12</sup> in tetrahydrofuran; m.p. 166–167°C (acetone). For C<sub>20</sub>H<sub>26</sub>N<sub>2</sub> (294.4) calculated: 81.58% C, 8.90% H, 9.52% N; found: 81.04% C, 9.17% H, 9.36% N. IR spectrum (CHCl<sub>3</sub>) lacks either OH or >C=O vibrational bands.

(–)-Voachalotine (*Ij*) was prepared by the lead tetraacetate oxidation of (–)-vincamajine<sup>30</sup> in glacial acetic acid and reduction of the thus-obtained ester aldehyde with potassium hydroborate in ethanol; m.p. 222–224°C (reported<sup>31</sup>, m.p. 223–224°C); the spectra were identical with those of the authentic specimen. The lithium aluminium hydride reduction of compound *Ij* in tetrahydrofuran afforded voachalotinol (*Ik*), m.p. 289–290°C (ethanol); reported<sup>32</sup>, m.p. 294°C. IR spectrum (nujol): OH, 3350 and 3430 cm<sup>-1</sup>; 1,2-disubstituted benzene, 745 cm<sup>-1</sup>.

#### (–)-1,2,3,4-Tetrahydroharmine (*V*, 3 $\alpha$ H)

To a solution of ( $\pm$ )-1,2,3,4-tetrahydroharmine (1.3 g) in ethanol (20 ml) there was added N-benzoyloxycarbonyl-L-alanine (1.4 g) in ethanol (8 ml) and the mixture kept at room temperature for 30 h. Yield, 886 mg of crystals which were recrystallised three times from ethanol to afford 475 mg of a salt, m.p. 194–200°C,  $[\alpha]_D^{20}$  –40° (c 0.5 in ethanol). For C<sub>23</sub>H<sub>27</sub>N<sub>3</sub>O<sub>4</sub> (409.5) calculated: 67.46% C, 6.65% H, 10.26% N; found: 67.37% C, 7.13% H, 10.30% N. The base was liberated with dilute aqueous ammonia, extracted with ether, the extract dried, and evaporated under diminished pressure to afford 226 mg of a foam. Crystallisation from acetone yielded prisms, m.p. 146–148°C,  $[\alpha]_D^{20}$  –81.6° (c 1 in ethanol). Molecular weight C<sub>12</sub>H<sub>14</sub>N<sub>2</sub> 186.1157 (calculated), 186.1148 (determined by mass spectrometry).

#### (+)-1,2,3,4-Tetrahydroharmine (*V*, 3 $\beta$ H)

A solution of ( $\pm$ )-1,2,3,4-tetrahydroharmine (1.6 g) in ethanol (20 ml) was treated with N-benzoyloxycarbonyl-L-valine (1.95 g) and kept at room temperature overnight to deposit crystals (1.9 g) which were recrystallised three times from ethanol. M.p. 176–180°C;  $[\alpha]_D^{20}$  +20° (c 1, ethanol). Yield, 980 mg. For C<sub>25</sub>H<sub>31</sub>N<sub>3</sub>O<sub>4</sub> · 1/2 C<sub>2</sub>H<sub>5</sub>OH (460.5) calculated: 67.80% C, 7.44% H, 9.12% N; found: 68.08% C, 7.97% H, 9.03% N. From 900 mg of the salt, the base was liberated with dilute aqueous ammonia, extracted with ether, the extract dried, and evaporated under diminished pressure to afford 390 mg of a substance, m.p. 144–148°C (acetone),  $[\alpha]_D^{20}$  +82° (c 1 in ethanol). The mass spectrum was identical with that of the (–)-isomer.

#### Spectropolarimetric Measurements

Optical rotatory dispersion was measured in methanol unless stated otherwise in Table II on a JASCO UV/ORD-5 apparatus in 0.1–1.0 mm thick cells (concentrations, 0.05–0.01 g of the substance per 100 ml of the solution).

Circular dichroism was measured in methanol on Roussel Jouan 185 Model II and Cary 60-CD dichrographs in 0.5–2.0 mm thick cells (concentrations, 0.002–0.100 g per 100 ml of the solution). The following  $\lambda$  values are expressed in nm ( $\Delta\epsilon$ ).

17,21-Dideoxyajmalol B (*Ia*): 320 (0), max. 297 (+1.2), min. 292 (+0.7), max. 286 (+0.9), min. 281 (+0.4), max. 275 (+1.0), 255 (0), max. 230 (–8), 218 (0), max. 206 (+4.5), 195 (0).

(–)-Deoxyajmalol B (*Ib*): 320 (0), max. 298 (+1.55), min. 293.5 (+0.7), max. 288 (+1.2), min. 285 (+0.7), max. 272 (+1.5), 257 (0), max. 233.5 (–6.6), 216 (0), max. 205 (+3.6).

(-)-*Deoxyajmalol* A (Ic): 320 (0), max. 298 (+1.4), min. 293 (+0.6), max. 288 (+1.05), min. 284 (+0.55), max. 272 (+1.2), 258 (0), max. 232.5 (-7.6), 215 (0), max. 206 (+1.8), 198 (0).

(+)-*Lochnerine* (Id): 320 (0), max. 307 (-0.86), 299 (0), max. 274.5 (+4.14), 247 (0), max. 244 (-0.52), max. 238.5 (0), max. 222 (-5.45), 209.5 (0), max. 205 (+2.3).

(+)-*Sarpagine* (If): 320 (0), max. 309 (-0.57), 300 (0), max. 275 (+3.89), 248 (+0.29), 242 (+0.29), max. 240 (+0.47), 237 (0), 230 (-2.86), max. 217 (-7.45), 208 (0), rise to positive values.

(+)-*Pericyclivine* (Ig): 310 (0), max. 294 (+2.2), min. 291 (+1.5), max. 286 (+3.15), min 283 (+2.82), max. 270 (+4.29), 248 (0), max. 243.5 (-1.35), min. 236 (-1.10), max. 224.5 (-4.59), end value 220 nm (-4).

(+)-*Akuammidine* (Ii): 310 (0), max. 292 (+1.15), max. 283 (+3.4), max. 268 (+5.3), 243 (0), 240 (-0.9), max. 225 (-7.5), 210 (0), rise to negative values.

(-)-*Voachalotine* (Ij): 320 (0), max. 299 (+2.25), min. 293.5 (+1.20), max. 289.5 (+1.95), min. 285 (+1.20), max. 274 (+1.95), 259 (0), 243 (-5.9), 240 (-6.7), max. 232 (-11.5), 212 (0), rise to positive values.

*Voachalotinol* (Ik) 320 (0), max. 299 (+1.7), min. 293 (+1.0), max. 288 (+1.1), min. 280 (+0.8), max. 271 (+1.5), 250 (0), max. 232 (-4.0), 218 (0), max. 207 (+3.5), 198 (0).

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