

# A NOTE ON THE CHIROPTICAL PROPERTIES OF UNSATURATED DERIVATIVES OF LYSERGIC ACID

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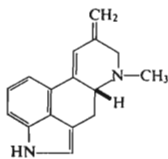
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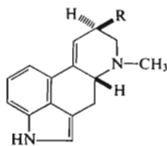
Circular dichroism of ergolene derivatives, containing aromatic ring conjugated with one or two double bonds, was studied. The results indicate the inherently chiral arrangement of chromophore in a left-handed helical system.

It has been known<sup>1</sup> that conjugated unsaturated systems — when nonplanar — constitute a chiral element which may exert a considerably greater influence on the optical activity than the presence of an asymmetric atom. This phenomenon may be exemplified on *cis*- and *trans*-dienes<sup>2-6</sup>, styrene-like substances<sup>7</sup> and biphenyls<sup>8</sup>. However, there are lacking data on analogous compounds containing a larger conjugated system. In the present paper, we wish to report the chiroptical properties of (5*R*)-6-methyl-8-methylene-9-ergolene (*I*), the diene system of which is conjugated with the aromatic ring.

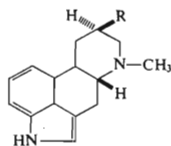
Compound *I* displays a strong long-wavelength Cotton effect at 343 nm ( $\Delta\epsilon$  8.45), the positive sign of which corresponds to a left-handed helix system of the aromatic ring and the double bonds (Fig. 1), the same as that established by Crabbé<sup>7</sup> for the styrene chromophore in 1,3,5(10),8- and 1,3,5(10),9(11)-estratetraene derivatives. Examination of Dreiding models indicates that only a left-handed helical arrangement is possible for *I* possessing the absolute configuration<sup>9,10</sup> 5*R*.



*I*



*II*, R = CH<sub>2</sub>OH  
*III*, R = CH<sub>2</sub>CH<sub>2</sub>OH  
*IV*, R = COOH

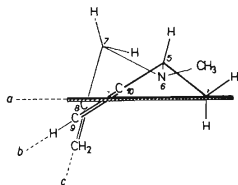


*V*

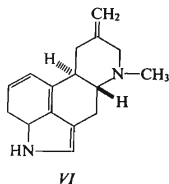
The location of the observed dichroic bands of compound *I* corresponds to the ultra-violet maxima (in methanol:  $\lambda_{\max}$  338 nm,  $\log \epsilon$  3.84; sh 259 nm;  $\lambda_{\max}$  244 nm,  $\log \epsilon$  4.00). Conjugated systems containing one double bond less (compounds *II–IV*) produce a hypsochromic shift of the longest-wavelength Cotton effect towards 316 nm (compound *III*). The positive sign, however, does not change. All compounds *I–IV* display a strong negative Cotton effect at about 250 nm. We did not observe any Cotton effect on the optical rotatory dispersion curve of compound *V* (both

FIG. 1  
Conformation of (5*R*)-6-Methyl-8-methylene-9-ergolene (*I*)

*a* Direction of the rings A, B; *b* direction of the double bond  $C_{(9)}=C_{(10)}$ ; *c* direction of the double bond  $C_{(8)}=CH_2$ .



conjugated double bonds are saturated in this compound); only poorly distinct irregularities on the negative plain curve at about 275 nm were seen. In the longer-wavelength region, the circular dichroism band has a low intensity and its location corresponds to the absorption bands in the ultraviolet spectra of compound *V* and other indole derivatives<sup>11</sup>. A somewhat more intensive dichroic band is located at 232 nm. An analogous circular dichroism spectrum has been observed with compound *VI* (in this compound, the double bond at position 9, 10 is saturated and the methylene double bond at the carbon atom  $C_{(8)}$  is isolated from the indole nucleus).



After disappearance of the inherently chiral unsaturated chromophore, the only source of optical activity with compounds *V* and *VI* in the near ultraviolet region is the induced chirality of electron transitions of the indole nucleus. Chirality of this kind is poorly effective in general and especially in our case because of the great distance of the chirality center from the chromophoric system.

The validity of findings on the chiral styrene derivatives<sup>7</sup> may be thus extended on larger conjugated systems. Also in this case, the left-handed helix type of conformation leads to a positive sign of the longest-wavelength dichroic band. Furthermore, similar to the styrene derivatives, the circular dichroism and optical rotatory dispersion data of compound I (and III) may be correlated with the use of the equation<sup>7</sup>  $a = 0.122 [\Theta]$ .

## EXPERIMENTAL

The optical rotatory dispersion measurements were performed in methanol on a Jasco ORD/UV-5 apparatus in 0.01–0.1 dm cells. The circular dichroism was measured on Jouan Model 185 apparatus in a 0.001 dm cell.

(5*R*)-6-Methyl-8-methylen-9-ergolene<sup>12</sup> (I). ORD: 400 nm,  $[\Phi] + 6000^\circ$ ; max. 369 nm,  $+17000^\circ$ ; 340 nm,  $0^\circ$ ; plateau 322–290 nm,  $-17000^\circ$ ; min. 268 nm,  $-39000^\circ$ ; 258 nm,  $0^\circ$ ; max. 249 nm,  $+34000$ ; 240 nm,  $0^\circ$ ; 225 nm,  $-60000^\circ$ . CD: 400 nm,  $\Delta\epsilon 0$ ; 343 nm,  $+8.45$ ; 270 nm,  $0$ ; 258 nm,  $-8.05$ ; 252 nm,  $0$ ; 237.5 nm,  $+14.1$ ; 208 nm,  $0$ ; end value 190 nm,  $-39.8$ .

(5*R*, 8*R*)-6-Methyl-8-hydroxymethyl-9-ergolene<sup>13</sup> (II). ORD: 400 nm,  $+950^\circ$ ; 345 nm,  $+8300^\circ$ ; max. 337 nm,  $+9200^\circ$ ; 329 nm,  $+9000^\circ$ ; 316 nm,  $0^\circ$ ; sh 306 nm,  $-7500^\circ$ ; min. 284 nm,  $-13200^\circ$ ; max. 262 nm,  $-11000^\circ$ ; sh 242 nm,  $+4600^\circ$ ; max. 227 nm,  $+29000^\circ$ ; 217 nm,  $0^\circ$ ; 215 nm,  $-25000^\circ$ .

(5*R*, 8*R*)-6-Methyl-8-( $\beta$ -hydroxyethyl)-9-ergolene<sup>14</sup> (III). ORD: 400 nm,  $+1400^\circ$ ; max. 336 nm,  $+12000^\circ$ ; 315 nm,  $0^\circ$ ; sh 295 nm,  $-11200^\circ$ ; min. 285 nm,  $-14500^\circ$ ; max. 262 nm,  $-10500^\circ$ ; min 257 nm,  $-12000^\circ$ ; sh 242 nm,  $-6000^\circ$ ; 235 nm,  $0^\circ$ ; 225 nm,  $+45000^\circ$ . CD: 350 nm,  $\Delta\epsilon 0$ ; 316 nm,  $+5.29$ ; sh 294 nm,  $+3.23$ ; 258 nm,  $+0.65$ ; 248 nm,  $-1.65$ ; 236 nm,  $-0.82$ ; 214 nm,  $+14.8$ ; 195 nm,  $0$ .

D-Lysergic acid<sup>15</sup> (IV) (5*R*, 8*R*). ORD: 400 nm,  $+1900^\circ$ ; max. 340 nm,  $+15000^\circ$ ; 315 nm,  $0^\circ$ ; min. 290 nm,  $-25000^\circ$ ; 265 nm,  $-24000^\circ$ ; max. 243 nm,  $-2500^\circ$ ; min. 236 nm,  $-11700^\circ$ ; max. 227 nm,  $-5000^\circ$ ; 216 nm,  $-22000^\circ$ .

(5*R*, 8*R*, 10*R*)-6-Methyl-8-hydroxymethylergolane<sup>13</sup> (V). ORD: 400 nm,  $-350^\circ$ ; 250 nm,  $-2300^\circ$ ; min. 227 nm,  $-14000^\circ$ . CD: 305 nm,  $\Delta\epsilon 0$ ; 297 nm,  $+0.15$ ; 291 nm,  $-0.55$ ; 270 nm,  $+0.49$ ; 235 nm,  $+2.75$ ; end value 225 nm,  $-1.22$ .

(5*R*, 10*R*)-6-Methyl-8-methylen-ergolane<sup>14</sup> (VI). CD: 305 nm,  $\Delta\epsilon 0$ ; 296 nm,  $+0.20$ ; 292 nm,  $-0.15$ ; 287 nm,  $+0.30$ ; 271 nm,  $+0.61$ ; 241 nm,  $+0.40$ ; 232 nm,  $-1.07$ ; end value 225 nm,  $-0.50$ .

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