CHIROPTICAL INVESTIGATIONS ON THE IBOGA AND VOACANGA ALKALOIDS* **

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Circular dichroic spectra of thirteen ibogane-type alkaloids have been measured in the 400—200 nm region. As inferred from comparison of the curve parameters, (—)-coronaridine (*I*), (—)-conopharyngine (*II*), (—)-isovoacristine (*III*), (—)-isovoacangine (*IV*), (—)-voacangine (*V*), (—)-ibogamine (*VIII*), (—)-ibogaine (*IX*), (—)-tabernanthine (*X*), and (—)-iboxygaine (*XI*) possess the same absolute configuration (16*S* with substances *I*—*V* and 16*R* with *VIII*—*XI*). On the other hand, the absolute configuration of (+)-catharanthine (*VI*) is reversed, *i.e.* 16*R*. The reversed absolute configuration with respect to (—)-ibogamine (*VIII*) is also shown by the enantiomer *XIII* obtained by degradation of the alkaloid *VI*. Consequences of these observations for the biogenesis of indole alkaloids are discussed.

Investigations on stereochemistry of indole alkaloids are important in elucidation of the biosynthesis of these substances[2]. The use of chemical intercorrelation between the particular types of indole alkaloids is limited or, in some cases, made impossible by their wide structural variety and their marked polycyclic character. An unequivocal route in this respect consists in determination of the absolute configuration by means of the anomalous X-ray diffraction for the particular group of indole alkaloids[3]. However, such a type of structural analysis is rather laborious and is therefore mainly used in the case of key problems only. It is consequently suitable to correlate structurally similar alkaloids by means of physical and chemical methods, especially in examinations aiming to detect the corresponding enantiomeric structures (if any). In this respect, the chiroptical methods prove as the most potent.

In our previous work, optical rotatory dispersion (ORD) and circular dichroism (CD) of some groups of indole alkaloids has been investigated, namely, of the yohimbane[4], eburnane[5,6], and 5,16-cyclo-3,4-secocorynane[7] group, the indolo[2,3-*a*]-quinolizidine derivatives[4,8], and the lysergic acid[9] group. In the present work, we have extended our examinations on the alkaloids derived from the parent ibogane skeleton[10]. The stereochemistry of the ibogane-type alkaloids has been object of

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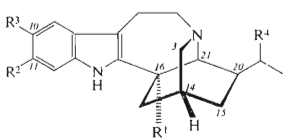
** Preliminary communication: ref.[1].

considerable interest[11] and its elucidation has been approached by chemical as well as physical means. From the present standpoint, the most important contributions are structural analyses (anomalous X-ray diffraction) of cleavamine methiodide[12,13], obtained by degradation[14,15] of (+)-catharanthine (*VI*), and of the dimeric alkaloid (+)-leurocristine[16]. The results indicate the same absolute configuration for (+)-catharanthine (*VI*) and for the cleavamine portion of the leurocristine molecule. The chemical correlation of coronaridine and ibogamine with (+)-catharanthine (*VI*) has been attempted by Kutney and coworkers[17,18]. Curiously enough, the comparison was stopped at the stage of the mere constitution, the optical activity of the substances not being taken into consideration. In spite of the clear insufficiency of such a chemical correlation for the determination of absolute configuration, the whole series of iboga alkaloids[18,19,20] was finally ascribed[21] (after correction of the previous erroneous interpretation[18,19]; *cf.* the note in ref.[20]) the absolute configuration identical with that of (+)-cleavamine[12,13]. Furthermore, it must have been known at the time of the above proposal that some types of indole alkaloids occur in the plant material in both enantiomeric forms even when they are closely related with respect to the structure and when they contain a greater number of asymmetric centers (*e.g.*, alkaloids of the eburnane[22,23] or aspidospermane[24] type). Our aim was to gather chiroptical data of a great number of the ibogane-type alkaloids and their confrontation with known facts.

The following alkaloids* were used in our investigations: (−)-coronaridine

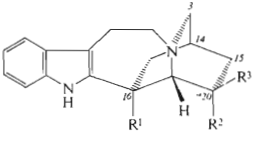


I, $R^1 = COOCH_3$, $R^2 = R^3 = R^4 = H$, (16*S*, 20*S*)
II, $R^1 = COOCH_3$, $R^2 = R^3 = OCH_3$, $R^4 = H$,, (16*S*, 20*S*)
III, $R^1 = COOCH_3$, $R^2 = OCH_3$, $R^3 = H$, $R^4 = OH$, (16*S*, 20*R*)
IV, $R^1 = COOCH_3$, $R^2 = OCH_3$, $R^3 = R^4 = H$, (16*S*, 20*S*)
V, $R^1 = COOCH_3$, $R^2 = R^4 = H$, $R^3 = OCH_3$, (16*S*, 20*S*)
VIII, $R^1 = R^2 = R^3 = R^4 = H$, (16*R*, 20*S*)
IX, $R^1 = R^2 = R^4 = H$, $R^3 = OCH_3$, (16*R*, 20*S*)
X, $R^1 = R^3 = R^4 = H$, $R^2 = OCH_3$, (16*R*, 20*S*)
XI, $R^1 = R^2 = H$, $R^3 = OCH_3$, $R^4 = OH$, (16*R*, 20*R*)
XIV, $R^1 = COCH_3$, $R^2 = R^3 = H$, $R^4 = OH$, (16*S*, 20*R*)

* The sign of optical rotation refers to values and measurement conditions as given in the respective papers.

(*I*, as the hydrochloride, from *Tabernaemontana psychotrifolia* H.B. et K., ref.[25]), (−)-conopharyngine (*II*, from *Tabernaemontana pachysiphon* STAPF, ref.[26]), (−)-isovoacristine (*III*, as adduct with dimethyl sulfoxide, from *Tabernaemontana laurifolia* BLANCO, ref.[27]), (−)-isovoacangine (*IV*, from *Tabernaemontana laurifolia* BLANCO, ref.[27]), (−)-voacangine (*V*, plant source unknown, from collections of Smith, Kline & French Laboratories, Philadelphia, U.S.A.), and (+)-catharanthine (*VI*, as the hydrochloride, from *Catharanthus roseus* G. DON., ref.[28]), all belonging to a group of substances bearing a methoxycarbonyl on the $C_{(16)}$ carbon atom of the ibogane skeleton. From the group of substances lacking this substituent, the following alkaloids have been studied: (−)-ibogamine (*VIII*, from *Tabernanthe iboga* BAILL., ref.[29]), (−)-ibogaine (*IX*, from *Tabernanthe iboga* BAILL., ref.[29]), (−)-tabernanthine (*X*, from *Tabernaemontana laurifolia* BLANCO, ref.[27]), and (−)-iboxygaine (*XI*, from *Tabernanthe iboga* BAILL., ref.[29]). (+)-Dihydrocatharanthine (*VII*) was obtained by catalytic hydrogenation[15,30] of (+)-catharanthine (*VI*); (+)-epiibogamine (*XII*) was prepared by the decarbomethoxylation[15,30] of *VII*; (+)-ibogamine (*XIII*) resulted from the reaction of (+)-dihydrocatharanthine (*VII*) with conc. hydrochloric acid[15].

Results of CD spectral measurements are summarised in Table I. On the curves, three types of Cotton effects may be in principle distinguished, namely, *1*) long-wavelength dichroic bands with a significant fine structure between 270 and 320 nm, *2*) dichroic bands between 230 and 250 nm, and *3*) a dichroic band at about 220 nm. Their positions correspond to a certain extent with the appropriate absorption bands in ultraviolet spectra of particular substances (Table II). No differences are observed between the curves of substances containing a methoxycarbonyl group on the $C_{(16)}$ carbon atom and those of substances lacking this substituent. In the spectral region examined, the electronic transitions in the ester group do not assert themselves to a considerable extent; all the dichroic bands present must be therefore connected with electronic transitions in the aromatic indole ring system. The electronic transitions may be assigned in analogy with those in naphthalene[31].



VI, $R^1 = COOCH_3$, $R^2, R^3 = CH_2CH_3$, $\Delta^{15,20}$, (16*R*)
VII, $R^1 = COOCH_3$, $R^2 = CH_2CH_3$, $R^3 = H$, (16*R*, 20*S*)
XII, $R^1 = R^3 = H$, $R^2 = CH_2CH_3$, (16*S*, 20*S*)
XIII, $R^1 = R^2 = H$, $R^3 = CH_2CH_3$, (16*S*, 20*R*)
XV, $R^1 = COOCH_3$, $R^2 = H$, $R^3 = CH_2CH_3$ (16*R*, 20*R*)

The multiple Cotton effect in the long-wavelength region comprises two groups of maxima. The first group with maxima at about 300 nm and above this value obviously corresponds to the ^1L_b band in the naphthalene spectrum (312 nm, ref.[32]) while the position of the second group is in accordance with the ^1L_a band (in naphthalene at 289 nm). The signs of both bands are identical in all substances examined except for the bases *V*, *IX*, and *XI*. The sign of both Cotton effect types obviously depends on the substitution of the indole ring system (Fig. 1). Unequal signs occur in the case of compounds bearing the methoxyl group at position R^3 only (substances *V*, *IX*, and *XI* of our set). The signs are equal when the methoxyl group is situated at position R^2 or simultaneously at positions R^2 and R^3. The sign reversal due to the change in substituent positions obviously occurs in the longer-wavelength dichroic band since that at shorter wavelengths may be unequivocally correlated with the absolute configuration at $C_{(16)}$. The different response of the two bands towards substitution is obviously connected with the different polarisation[31]. The ^1L_b band is associated

TABLE I

CD Spectral Parameters of Substances *I*—*XII* in Methanol

Alkaloid	λ_{max}, nm ($\Delta\varepsilon$)			
I	296 (−2·1)	288 (−5·6)	242 (+5·0)	215 (−2·6)
		277 (−8·1)	231 (+2·4)	
		272 (−9·3)	227 (+3·3)	
II	311 (−1·6), 293 (−2·5)	280 (−4·0)	244 (+3·8)	225 (−2·4)
III	298 (−4·0)	285 (−2·6)	249 (+3·0)	219 (−1·4)
		276 (−3·8)	236 (+5·7)	
IV	320 (−0·4), 316 (−1·2)	286 (−2·5)	250 (+4·5)	217 (−1·5)
	307 (−3·7), 301 (−4·4)	277 (−2·9)	239 (+5·7)	
V	312 (+0·7)	281 (−5·0)	251 (+2·5)	225 (−1·5)
VI	293 (+0·8)	286 (+1·9)	242 (−0·25)	219 (+3·3)
		278 (+2·8)		
		270 (+3·2)		
VII	295 (+2·3)	281 (+3·5)	240 (−1·6)	217 (+1·5)
		275 (+3·7)	229 (−2·9)	
			221 (−0·7)	
VIII	—	288 (−0·4)	238 (+7·5)	218 (−8·9)
IX	308 (+0·75)	280 (−1·9)	242 (+13·8)	220 (−6·5)
X	297 (−1·4)	—	239 (+5·7)	221 (+5·8)
XI	308 (+0·25)	279 (−1·0)	238 (+6·0)	217 (−6·6)
XII	292 (+0·25)	—	245 (−2·3)	220 (+5·0)
		—	236 (−6·2)	
XIII	—	288 (+0·45)	238 (−7·8)	218 (+9·2)

TABLE II

UV Spectra of Substances *I*—*XIII* in Methanol

Substance	λ_{max} nm (log ε)			Reference
I (HCl)[a]	294 (3·82)	284 (3·88)	226 (4·54)	33
II	303 (4·08)	281sh (3·85)	223 (4·46)	34
III	298 (3·88)	278 (3·74)	226 (4·54)	35
IV	298 (3·88)	278 (3·74)	227 (4·53)	35
V	300 (3·93)	287 (3·97)	225 (4·43)	36
VI[a]	292 (3·88)	284 (3·92)	226 (4·56)	36
VII	295 (3·91)	286 (3·96)	226 (4·56)	[b]
VIII	291 (3·94)	283 (3·96)	225 (4·56)	36
IX	290 (4·00)	282sh (3·98)	225 (4·43)	37
X	299 (3·78)	270 (3·62)	228 (4·52)	35
XI	—	288 (3·99)	227 (4·46)	38
XIII	291 (3·80)	284 (3·85)	226 (4·49)	[b]

[a] In ethanol; [b] this paper.

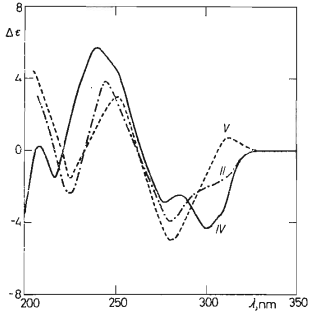


FIG. 1

CD Curves of Alkaloids with Methoxyl Substituents on the Indole Ring System ——— (—)-Isovoacangine (*IV*), 11-methoxy substituted; —·—·— (—)-conopharyngine (*II*), 10,11-dimethoxy substituted; - - - - - (—)-voacangine (*V*), 10-methoxy substituted. Measured in methanol.

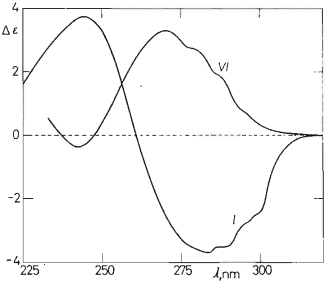


FIG. 2

CD Curves of Native Alkaloids (—)-Coronaridine (*I*) and (+)-Catharanthine (*VI*), Measured in Methanol

with the electronic transition which is longitudinally polarised (*i.e.* parallel to the long pseudo-axis of the bicyclic indole system). On the contrary, the ^1L_a band is transversely polarised (*i.e.*, perpendicular to the long pseudo-axis of the molecule). The substituents at positions R^2 and R^3 lie on different sides of the nodal plane from the standpoint of the ^1L_b transition but not from the standpoint of the ^1L_a. The wider validity of this interpretation must be of course verified by examination of selected models. The electronic nature of other dichroic bands is less obvious but the short-wavelength dichroic band at 220 nm probably corresponds to the ^1B_b band of naphthalene (at 221 nm, see ref.[32]).

In determinations of the absolute configuration, the overall resemblance of CD spectra of bases in the particular set of alkaloids is of course more important. With compounds *I – V* and *VIII – XI*, the dichroic band at about 280 nm (Cotton effect attributable to the ^1L_a band) is negative, the next Cotton effect (2^{nd}) at shorter wavelenghts is positive, and the further one (3^{rd}) is negative again. Such an agreement undoubtedly indicates the same absolute configuration of all the above substances at least on the $C_{(16)}$ carbon atom, *i.e.*, on the chirality center nearest to the aromatic chromophore. On the other hand, bases *VI*, *VII*, *XII*, and *XIII* exhibit reversed dichroic characteristics and obviously possess an opposite configuration. Since the absolute configuration of (+)-catharanthine (*VI*) is unequivocally determined from the anomalous X-ray diffraction on the molecule of cleavamine methiodide[12,13], we may infer for all the alkaloids examined and also for all the alkaloids which are chemically correlated with the examined ones, *e.g.*, for (–)-heyneanine[39] (*XIV*),

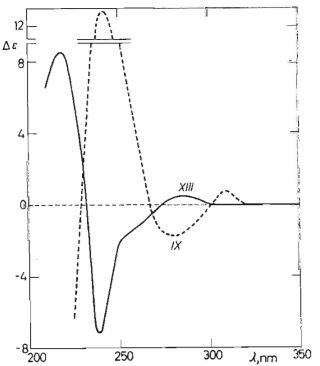


FIG. 3

CD Curves of Native Alkaloids (–)-Ibogaine (*IX*) and of (+)-Ibogamine (*XIII*) Obtained by Degradation of (+)-Catharanthine (*VI*), Measured in Methanol

the absolute configurations as expressed by formulae shown in the present paper. The enantiomeric character of (+)-catharanthine (*VI*) and (−)-coronaridine (*I*) may be clearly seen from Fig. 2, and that of (−)-ibogaine (*IX*) and (+)-ibogamine (*XIII*) from Fig. 3.

In this connection it is of interest to mention the earlier report[40] concerning (−)-ibogaine (*IX*), (−)-ibogamine (*VIII*), and (−)-tabernanthine (*X*, from *Tabernanthe iboga* BAILL, ref.[29]) which were ascribed the same absolute configuration as inferred in the present work. The assignment citted[40] was based on a comparison of ORD curves of (−)-*cis*-10-methyl-1-decalone[41] and (−)-*cis*-1-cyano-6-bromomethyl-8-ethyl-4-quinolone, the common degradation product of the alkaloids *VIII*—*X*. However the thus-inferred absolute configuration[40] was desregarded because it was opposite[18,19] to that (seemingly) following from the correlation with cleavamine[14]. Now it is clear that the motive for the disregard was not justified.

As convincingly indicated by data of the present work, alkaloids of the ibogane type examined belong to two enantiomeric series. This observation has also been confirmed by reproduction[15] of the degradation of (+)-catharanthine (*VI*) to ibogamine (*XIII*). Compound *XIII* was shown to be dextrorotatory and to exhibit a strictly enantiomeric behaviour when compared with (−)-ibogamine (*VIII*) from the plant *Tabernanthe iboga* BAILL.[29] (Table I). Dr R. T. Brown (Department of Chemistry, The University of Manchester) was kind enough to inform us in a letter from April 13th, 1973 that the CD spectrum of coronaridine obtained by a transformation from (+)-catharanthine (*VI*) corresponds to that of the enantiomer of the naturally occurring (−)-coronaridine (*I*). Another confirmation consists in the structural analysis of (+)-coronaridine hydrobromide with the use of the anomalous X-ray diffraction[42]. Two consequences may be inferred from the observed existence of two enantiomeric series in the group of the ibogane type alkaloids. *1.* In Nature there may in principle occur alkaloids of the same constitution but belonging to different enantiomeric series. It is therefore necessary to characterise carefully the optical activity of the isolated substances. The importance of this requirement might be exemplified by the discovery[43] of (±)-ibogamine in the species *Tabernaemontana retusa* (LAM.) PICHON. *2.* In view of the existence of natural racemates and enantiomeric forms with the above type alkaloids, it is essential for the biosynthesis of ibogane bases to postulate an intermediary stage which could lead to the potential formation of both enantiomeric series, *i.e.*, to postulate a structure with at most one center of chirality.

EXPERIMENTAL

Melting points were taken on a heated microscope stage (Boetius microblock). The CD spectra were measured on a Roussel-Jouan Dichrograph CD 185 Model II apparatus in 0·01—0·2 cm cells at 22—25°C. The concentration of methanolic solutions was about 0·5 mg/ml. The UV spectra were recorded on a Specord UV-VIS spectrophotometer (Jena, German Democratic Republic). The IR spectra were taken on a UR 10 apparatus (Jena, German Democratic Republic).

(+)-*Dihydrocatharanthine* VII. A solution of dried (+)-catharanthine (*VI*; 450 mg) in ethanol (35 ml) was hydrogenated over the Adams catalyst. Two crystallisations from methanol afforded 260 mg of the dihydro compound *VII*, m.p. 66–70°C (resolidification and remelting at 150 to 151°C), $[\alpha]_D^{20}$ +31·2° (*c* 1, chloroform). The IR spectrum was identical with that of an authentic specimen.

(+)-*Ibogamine* (XIII). A solution of dihydrocatharanthine *VII* (200 mg) in conc. hydrochloric acid (20 ml) was refluxed under nitrogen for 15 h, evaporated under diminished pressure, the base liberated with aqueous ammonia, and extracted with ether to afford 175 mg of a substance which was chromatographed on alumina (Brockmann activity II–III; 15 g). Elution with 1 : 1 benzene–light petroleum led to 35 mg of (+)-ibogamine (*XIII*). Crystallisation from methanol afforded 11·3 mg of a substance, m.p. 159–162°C, $[\alpha]_D^{20}$ +52·7° (*c* 0·9, ethanol).

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