

From this result, the structure of digiprolactone was established as 2,4-dihydroxy-2,6,6-trimethyl-4^{1,2}-cyclohexaneacetic acid γ -lactone (I).

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Received June 26, 1964

[Chem. Pharm. Bull.]
12 (9) 1118 ~ 1121

UDC 547.94.02 : 543.4 [535.563]

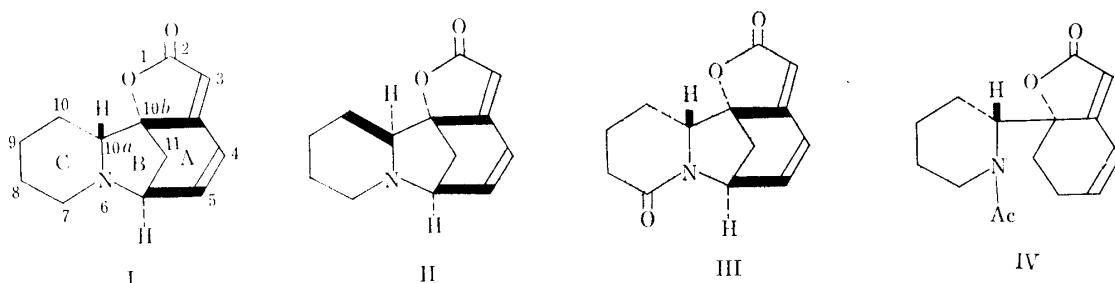
Optical Rotatory Dispersion and Circular Dichroism of Securinine and Allosecurinine

The absolute stereochemistry of securinine has recently been established as I by the chemical and optical rotatory dispersion (ORD) proofs¹⁾ as well as by the X-ray crystallography.²⁾ Since it has been shown that allosecurinine is an epimer of securinine at C_{10a},³⁾ absolute configuration of allosecurinine should be assigned II. The present communication is concerning the ORD and circular dichroism (CD) studies on both alkaloids,

*¹ UV absorption spectra, ORD curves and CD curves were measured with a Hitachi spectrophotometer, a Rudolph automatic recording spectropolarimeter and a Baird-Atomic/Jouan Dichrograph (Model JO-1), respectively.

- 1) Z. Horii, M. Ikeda, Y. Yamawaki, Y. Tamura, S. Saito, K. Kotera : Tetrahedron, 19, 2101 (1963).
- 2) S. Imado, M. Shiro, Z. Horii : Chem. & Ind. (London), in press.
- 3) I. Satoda, M. Murayama, J. Tsuji, E. Yoshii : Tetrahedron letters, 1962, 1199.

which provides examples of a new type of inherently dissymmetric transoid diene chromophore and also further confirmation of the absolute configuration of allosecurinine.



Dreiding models of the alkaloids show that both compounds contain a rigid and skewed diene conjugated with a five-membered lactone. Thus, the chirality of the conjugated diene system or the absolute configuration at C_{10b} can be correlated with the ORD and CD of the alkaloids.

In Figs. 1~4 are shown the results of the ultraviolet (UV), ORD, and CD measurements*¹ of I~N in dioxane solution. Securinine (I) shows two absorption maxima at 255 $m\mu$ ($\log \varepsilon$ 4.20) (a $\pi \rightarrow \pi^*$ transition) and 333 $m\mu$ ($\log \varepsilon$ 3.35), which correspond in positions to those of the two negative CD maxima at 250 $m\mu$ ($[\theta]$ -80480) and 328 $m\mu$ ($[\theta]$ -52300), or to the midpoints of the two negative ORD Cotton effects ($c=0.0017$, $[\alpha]_{367} -11840^\circ$, $[\alpha]_{298} +17280^\circ$, $[\alpha]_{262} 0^\circ$, $[\alpha]_{240} +13500^\circ$), respectively. The high molecular ellipticities of the CD maxima or the high amplitudes of the ORD Cotton effects are no doubt evidence for the inherently dissymmetric chromophore. Further, it is conceivable that the short wave length CD maximum or ORD Cotton effect arises from the transoid diene chromophore and the long wave length one does from the new type of inherently dissymmetric chromophore, in which homoconjugation of the nitrogen with the conjugated diene system*^{2,1)} is involved. This view is supported by the observation that compounds (III)*⁴ and (IV)*⁴ show only one negative CD maximum of high molecular ellipticity ($[\theta]_{265} -586500^\circ$ for III and $[\theta]_{276} -68000$ for IV) or ORD Cotton effect of high amplitude ($c=0.0028$, $[\alpha]_{298} -17800^\circ$ for III and $c=0.0032$, $[\alpha]_{285} -19000^\circ$, $[\alpha]_{267} +55000^\circ$ for IV), but lack the maximum or Cotton effect due to the long wave length absorption.*⁴

The negative sign of the short wave length CD maxima or ORD Cotton effects of I, III, and IV accords with that anticipated from the helicity rule*^{5,6)} of the transoid diene. The result, together with the observation that the corresponding dihydro and tetrahydro derivatives of I, III, and IV exhibit merely weak ORD curves, indicates that the introduction of the lactone ring to the diene system does not affect the sign.

The similar situation is also noted on the UV, CD, and ORD curves of allosecurinine (II)*^{6,7} as shown in Fig. 2 (UV λ_{\max} $m\mu$ ($\log \varepsilon$) : 257 (4.19), 345 (3.22); $[\theta]_{240} -77000$, $[\theta]_{335} -45300$; $c=0.0016$, $[\alpha]_{380} -11100^\circ$, $[\alpha]_{293} +19000^\circ$, $[\alpha]_{255} +11000^\circ$, $[\alpha]_{240} +28000^\circ$). The result gives an alternative proof for the absolute configuration of allosecurinine at C_{10b} .

*² The unusually high optical rotations at β -line of securinine and allosecurinine (-1042° and -1059° in ethanol, respectively) are also explained from the same basis.

*³ This value is of no quantitative significance since the measurement was made in a highly diluted solution ($c=0.00004$).

*⁴ Securinine hydrochloride also shows a single ORD Cotton effect ($c=0.0025$, $[\alpha]_{300} -4000^\circ$, $[\alpha]_{273} -13500^\circ$, $[\alpha]_{232} +23000^\circ$) in methanol solution.

*⁵ It has recently been reported that the application of the helicity rule to β -erythroidine gives the opposite conclusion from that by the X-ray crystallography and chemical evidence. (V. Boekelheide, G. R. Wenzinger : J. Org. Chem., 29, 1307 (1964)).

4) S. Saito, K. Kotera, N. Shigematsu, A. Ide, N. Sugimoto, Z. Horii, M. Hanaoka, Y. Yamawaki, Y. Tamura : Tetrahedron, 19, 2085 (1963).

5) U. Weiss, H. Ziffer : Experientia, 19, 108 (1963).

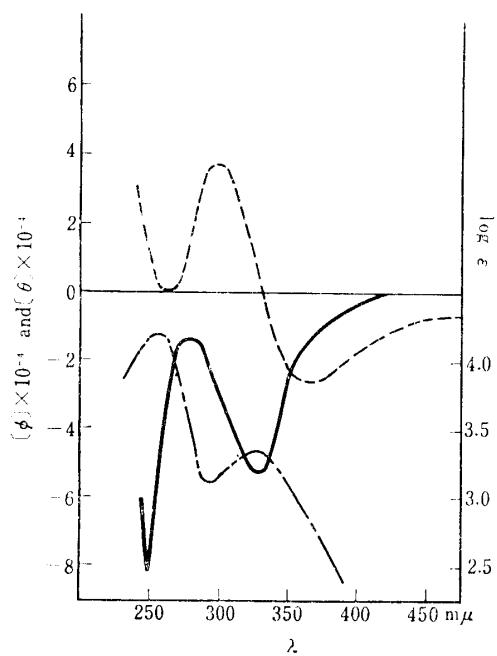


Fig. 1. Securinine (I)

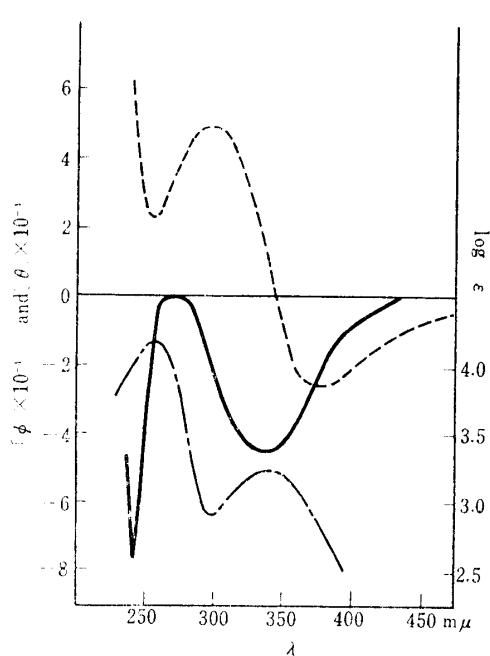


Fig. 2. Allosecurinine (II)

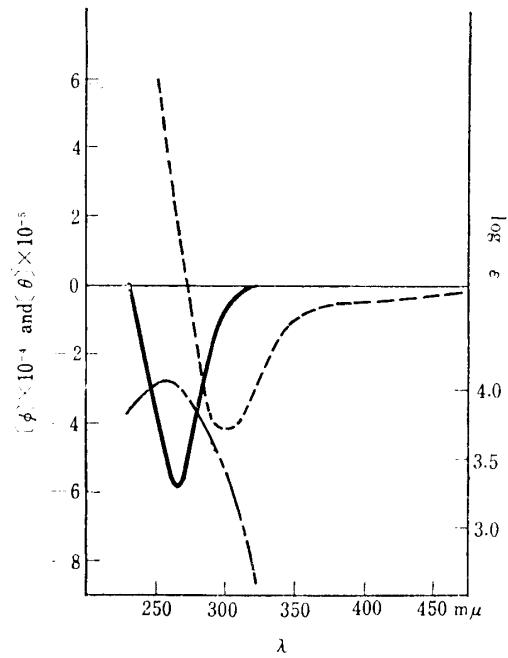


Fig. 3. Compound (III)

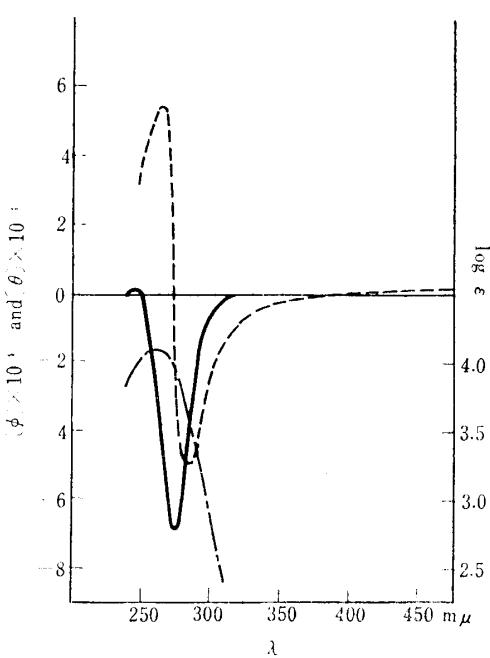


Fig. 4. Compound (IV)

UV absorption spectra (—·—·—), ORD curves (-----), and CD curves (—·—·—) in dioxane solution.

*⁶ Phyllochrisine isolated from *Phyllanthus discoides* Muell. Arg. by Pareollo, *et al.*⁶⁾ was identified by the mixed melting points, the infrared spectra and the thin-layer chromatography with allosecurinine. The authors thank Dr. Pareollo for providing a sample of phyllochrisine.

*⁷ Allosecurinine hydrochloride also shows a single ORD Cotton effect ($c=0.00241$, $[\alpha]_{300}=4850^\circ$, $[\alpha]_{265}=12500^\circ$, $[\alpha]_{233}+8300^\circ$) in methanol solution.

6) J. Pareollo, A. Melera, R. Goutarel: Bull. soc. chim. France, 1963, 898.

is the same as that of securinine. Further, it is of interest to find that in protonic solvents as methanol or ethanol the long wave length absorption maximum of allosecurinine occurs at 300~302 m μ as Parelo, *et al.*⁶⁾ reported, while in non-protonic solvents as hexane or dioxane it shifts toward the red by ca. 40 m μ . The corresponding absorption maximum of securinine is almost unchanged in both kinds of solvents (Table I).

TABLE I. The Long Wave Length Absorption Band of Securinine and Allosecurinine in Various Solvents

Solvent	Securinine		Allosecurinine	
	m μ	(log ϵ)	m μ	(log ϵ)
MeOH	325	(3.23)	300	(3.26)
EtOH	330	(3.24)	302	(3.27)
Dioxane	333	(3.35)	345	(3.22)
Hexane	328	(3.11)	342	(3.17)

The authors are indebted to Prof. C. Djerassi, Stanford University, California, U.S.A., for the helpful suggestions and the measurements of the CD curves. The authors also thank Dr. M. Murayama, Nippon Shinyaku Co., for providing a sample of allosecurinine.

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Received June 30, 1964

[Chem. Pharm. Bull.
12 (9) 1121 ~ 1124]

UDC 547.913.6.02

Study on the Chemical Shifts for the Methyl Groups of Deoxypodocarpic Acid (Enantiomer) Type Compounds and Syntheses
of their 10 β -15 or 10 α -17 Epoxy Derivatives^{*1~3}

In our previous paper,¹⁾ the syntheses of two kinds of isomeric 10-hydroxypodocarpa-5,7,13-trien-16-oic acid enantiomers (X) and (XIV) as well as the selective oxidation reaction of C₁- and C₁₂-CH₃ of their esters (X) and (XII) were reported. Throughout the above

*1 This communication will be published in detail as diterpenoids (V).

*2 A part of this work was presented at the International Symposium on the Chemistry of Natural Products held at Kyoto, Japan, on April 16, 1964 (Symposium Abstracts, p. 41~42).

*3 All analytical values of new compounds were in good agreement with molecular formula shown. All melting point (except m.m.p.) were measured on the Kofler block and were uncorrected. All NMR spectra were measured at 60 Mc. (Varian Model A-60 for esters, acids and alcohols and Japan Electron Optics Lab. Co., Ltd. JNM 3H-60 for amides and nitrils) in CDCl₃ (5~10% solution) vs. (CH₃)₄Si as internal reference (Authors thank to Dr. K. Takeda, Dr. K. Tori, Shionogi & Co., Ltd., Osaka and Prof. T. Okamoto, Tokyo Univ., Tokyo, for the NMR measurements and also to Dr. N. Nakagawa, the Univ. of Electron-communication, Tokyo, for his discussion on them).

1) A. Tahara, K. Hirao: This Bulletin, 12, 984 (1964).