michelalbine (**7**) by TLC and spectral [UV(EtOH), IR (KBr), nuclear magnetic resonance (DMSO)] comparisons with natural base (**2**). Sodium borohydride reduction of **5** seems to have proceeded in a highly stereoselective manner to give only **6** which eventually was converted to *dl*-michelalbine. Diastereoisomer (**6a**) was not detected in the reduction product.

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The Synthesis of Secamine and Presecamine Skeletons and the Isolation of Tetrahydrosecamine from *Amsonia elliptica* ROEM et SCHULT.

Recently, biogenetically-interesting indole alkaloids, secamine, presecamine and the corresponding dihydro and tetrahydro (VId, Vd) homologues were isolated from *Rhazya stricta* DECAISNE and *R. orientalis* A. DC. (Apocynaceae).[1a,b] The structure determination and the synthesis of these alkaloids have been accomplished by Smith and his co-workers.[1b,c]

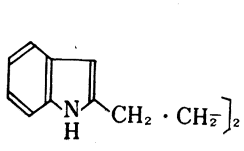
We wish to report the isolation of tetrahydrosecamine (VId) and several other indole alkaloids from *Amsonia elliptica* ROEM. et SCHULT. (Apocynaceae, Japanese name: Choujisou; taxonomically, the *Amsonia* sp. is closely related with *Rhazya* sp.[2]), and a new synthesis of crystalline *dl*-didemethoxycarbonyltetrahydropresecamine (Vb) and amorphous *dl*-didemethoxycarbonyltetrahydrosecamine (VIb). At the same time, *dl*-bisnorethyl-didemethoxycarbonyltetrahydropresecamine (Va) and its secamine type derivative (VIa) were synthesized through a similar route as shown in the Scheme. A mixture of racemic and meso forms of compound (IIIb) has been previously synthesized.[1a] The same reaction gave us pure IIa and IIb from compound (I)[3]: Amide (IIb) showed the same infrared (IR) spectrum (in $CHCl_3$, and in KBr) and no depression of mixture melting point with optically active amide (IIc), $[\alpha]_D$—18.3° (in $CHCl_3$), mp 178—179°, which was synthesized using (−)-3-ethylpiperidine.

On reduction with $LiAlH_4$, the glyoxamides (IIa,b) gave rise to bases (IIIa,b). [IIIa: UV λ_{max}^{MeOH} mμ (log ε): 284 (4.22), 291 (4.17 sh), IIIb: 284 (4.14), 291 (4.09 sh)]. The base

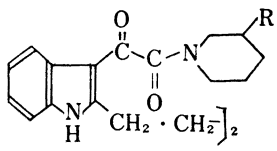
1) *a*) D.A. Evans, G.F. Smith, G.N. Smith, and K.S.J. Stapleford, *Chem. Comm.*, **1968**, 859; *b*) G.A. Cordell, G.F. Smith, and G.N. Smith, *Chem. Comm.*, **1970**, 191; *c*) G.A. Cordell, G.F. Smith, and G.N. Smith, *Chem. Comm.*, **1970**, 189.

2) A. Engler and K. Prantl, "Die Natürlichen Pflanzenfamilien," Verlag von Wilhelm Engelmann (Leipzig), IV-2 1897, p. 109.

3) M. Julia and P. Manoury, *Bull. Soc. Chim. France*, **1964**, 1953.



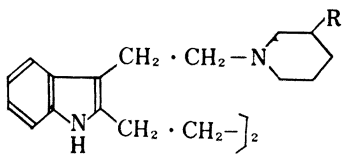
I



II

IIa : R=H(58% in the yield)
mp 218–219°
IIb : R=C_2H_5(44% in the yield)
mp 185–185.5°
IIc : R=C_2H_5(optically active)
mp 178–179°

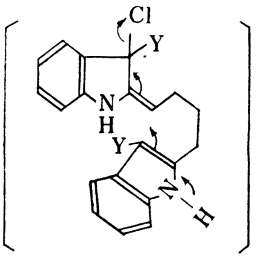
$LiAlH_4$ in THF
quantitative yield



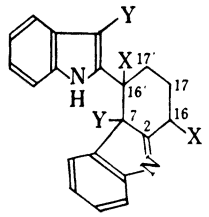
III

IIIa : R=H
IIIb : R=C_2H_5
λ_{max}^{MeOH} mμ (log ε); 225(4.81), 275(4.09 sh), 284(4.14), 291(4.09 sh)

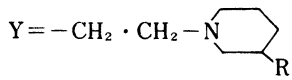
t–BuOCl
$N(C_2H_5)_3$
in CH_2Cl_2



IV



V[a)]



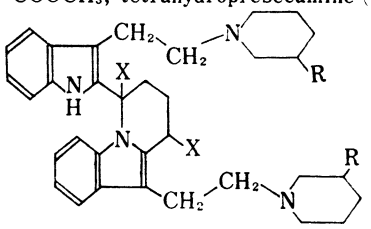
Va : R=H, X=H; mp 170–171° (30% in the yield), $\nu_{C=N}^{CHCl_3}$ 1580cm^{-1}

Vb : R=C_2H_5, X=H; mp 139.5–140°(7% in the yield), $\nu_{C=N}^{CHCl_3}$ 1580cm^{-1}
λ_{max}^{MeOH} mμ (log ε); 220(4.59), 275(4.00), 283(3.98 sh), 291(3.88 sh)

Vc : R=C_2H_5, X=H; mp 122–123° (optically active)

Vd : R=C_2H_5, X=$COOCH_3$; tetrahydropresecamine ($\Delta^{1,2} \rightarrow \Delta^{2,16}$)

2N HCl
room temp.



VI

VIa : R=H, X=H
VIb : R=C_2H_5, X=H
λ_{max}^{MeOH} mμ (log ε); 224(4.89), 275(4.16 sh), 285(4.28), 292(4.26)
VId : R=C_2H_5, X=$COOCH_3$; tetrahydrosecamine

a) The numbering follows ref. 1*a*.

(IIIa) gave a crystalline HBr salt, mp 301—303° (decomp.) and a picrate mp 216—219° (decomp.). These amorphous free bases (IIIa,b) were oxidized with a molar equivalent of *t*-BuOCl in CH_2Cl_2 at room temperature[4)] to give compounds of the presecamine type. The oxidation products were purified by column chromatography on alumina to give crystalline bases (Va,b). The IR spectrum (in $CHCl_3$) showed peak of $\nu_{C=N}$ in both compounds (Va, b)

4) N. Finch and W.I. Taylor; *J. Am. Chem. Soc.*, **84**, 3871 (1962).

and the ε values of the UV spectrum showed the presence of only one indolic chromophore in the molecule (Va, b). [Va: UV λ_{max}^{MeOH} (log ε): 283 (3.92 sh), 291 (3.83 sh); Vb: 283 (3.98 sh), 291 (3.88 sh)]. The nuclear magnetic resonance (NMR) spectra of Va, b showed one proton quartet (at 4.08 ppm in Va and 4.10 ppm in Vb), which was the X portion of ABX type (J_{AX}=0—1 Hz, J_{BX}=5 Hz) and this system was proved by decoupling experiments (A at 1.80 ppm and B at 2.46 ppm in compound (Vb)). Using the same route, optically active compound (Vc), mp 122—123° was synthesized and the base (Vc) showed the same IR spectrum (in KBr) as Vb. The presecamine type compounds (Va, b) rearranged to the secamine type compounds (VIa, b) in 2N HCl at room temp. as previously observed.[1b] The products of this interesting rearrangement were supported by their NMR spectra which showed a dramatic downfield shift of the C-16′ hydrogen to 5.74 ppm (VIa) and 5.72 ppm (VIb) (triplet, J=5 Hz; the triplet was decoupled to singlet by irradiation at 2.24 ppm). The ε values of the ultraviolet (UV) spectra (in MeOH) showed the presence of two indolic chromophores in the molecules (VIa, b). The base (VIa) gave a crystalline HCl salt, mp 257—258° although both free bases were amorphous.

The base (VIb) was homogeneous by thin-layer chromatography (TLC)[5] after purification by column chromatography on alumina.

The crude secamine type base (0.87%) obtained from the roots of *Amsonia elliptica* Roem et Schult. was subjected to column chromatography on alumina to yield tetrahydrosecamine (VId) (0.028%), $[\alpha]_D$=+9.7° (in 95% EtOH). The UV spectrum showed an indolic chromophore and the IR spectrum (in $CHCl_3$) showed peaks at 3420 (NH), 1730 (C=O) cm^{-1}. The NMR spectrum showed signals at 0.91 ppm (t, 6H), 3.59 ppm (s, 3H) and 3.70 ppm (s, 3H). The mass spectrum showed presence of *m/e*: 680 (M^+) and a strong base peak ion at *m/e*: 126. The alkaloid was amorphous and not completely pure since its NMR spectrum exhibited a signal at 4.25 ppm (broad) and the signal due to methoxycarbonyl group at 3.59 ppm was slightly split. The alkaloid was demethoxycarbonylated according to the procedure of Smith[1a] to yield didemethoxycarbonyltetrahydrosecamine. This base was identified by comparison of TLC and UV, IR, NMR and mass spectra with those of the synthetic base (VIb). Although the natural base was amorphous, it showed as in the case of the synthetic base, the presence of a characteristic signal at 5.66 ppm (t, 1H) for C-16′ hydrogen which was decoupled to give rise to a singlet by irradiation at 2.28 ppm.

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5) The solvent system for TLC was benzene: EtOH: $HN(Et)_2$ (8.5:1.0:0.5).