The Absolute Configuration of Ushinsunine and the Synthesis of *dl*-Michelalbine

Ushinsunine (**1**) and michelalbine (**2**), isolated from *Michelia* species (Magnoliaceae), are members of aporphine alkaloids having a unique structural feature with an alcoholic hydroxyl group at C-7. The absolute stereochemistry of the bases has been left undetermined through *trans*-configuration of the hydroxyl group with respect to 6a-hydrogen was assigned.¹⁾ Recent paper²⁾ on the stereospecific synthesis of 7-hydroxy aporphine has prompted us to report our results on the absolute configuration of the alkaloids and synthesis of racemic michelalbine (**7**).

Catalytic hydrogenation of ushinsunine (**1**) over platinum black in 48% hydrobromic acid gave a non-phenolic base. This product was found to be identical with *D*-roemerine (**3**)³⁾ by comparison of their infrared (IR) (CHCl₃), ultraviolet (UV), thin-layer chromatography (TLC) and specific rotation; $[\alpha]_D^{25}$: -67.5° (CHCl₃) with an authentic specimen of *D*-roemerine. Consequently, the absolute configuration of ushinsunine and michelalbine was established corresponding to the formula (**1**) and (**2**) [6a:S, 7:R] respectively by the chemical correlation with *D*-roemerine (**3**).

Catalytic hydrogenation of 1-(2-nitrobenzoyl)-6,7-methylenedioxy-3,4-dihydroisoquinoline (**4**)⁴⁾ with Raney nickel yielded a product (**5**), which gave positive test on diazo-coupling. Subsequently, reduction of (**5**) with sodium borohydride in aqueous methanol afforded 1-(α -hydroxy-2-aminobenzyl)-6,7-methylenedioxy-1,2,3,4-tetrahydroisoquinoline (**6**). Pschorr reaction of this product **6** gave a base, mp 210–212°. This base was characterized as *dl*-

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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: Cho-ujisou; 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 CHCl₃, and in KBr) and no depression of mixture melting point with optically active amide (IIc), [α]_D—18.3° (in CHCl₃), mp 178—179°, which was synthesized using (—)-3-ethylpiperidine.

On reduction with LiAlH₄, the glyoxamides (IIa,b) gave rise to bases (IIIa,b). [IIIa: UV $\lambda_{\text{max}}^{\text{MeOH}}$ m μ (log ϵ): 284 (4.22), 291 (4.17 sh), IIIb: 284 (4.14), 291 (4.09 sh)]. The base

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