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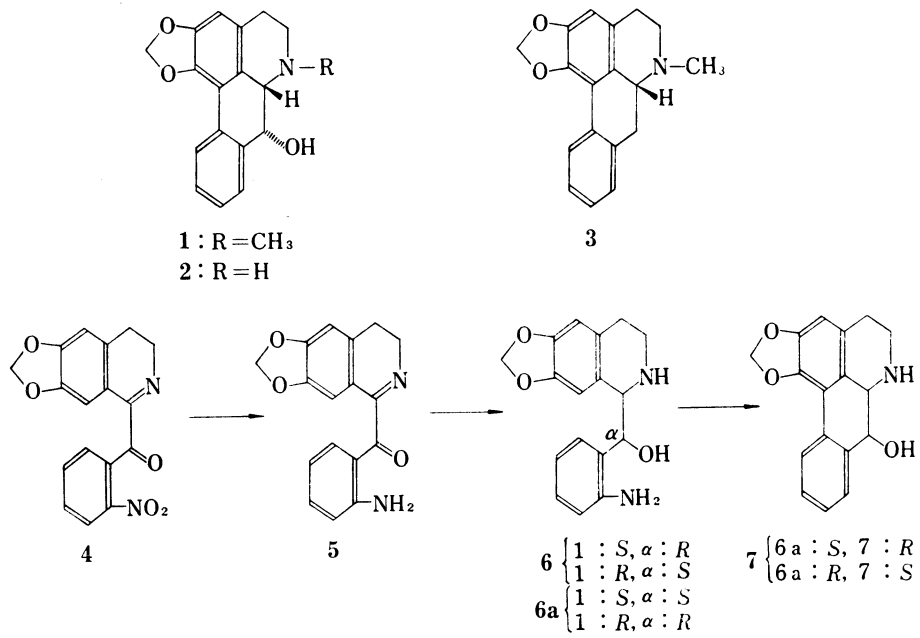
The Absolute Configuration of Ushinsunine and the Synthesis of *dl*-Michelalbine

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 paper[2] on the stereospecific synthesis of 7-hydroxy aporphine has promted 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) ($CHCl_3$), ultraviolet (UV), thin-layer chromatography (TLC) and specific rotation; $[\alpha]_D$: $-67.5°$ ($CHCl_3$) 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*-

1) T-H. Yang. *Yakugaku Zasshi*, **82**, 794, 798, 811 (1962); M. Tomita and H. Furukawa, *ibid.*, **82**, 925 (1962).
2) J.L. Neumeyer and F.E. Granchelli, *Tetrahedron Letters*, **1970**, 5261.
3) T. Nakasato and S. Asada, *Yakugaku Zasshi*, **86**, 1205 (1966); M. P. Cava, K. Nomura, R.H. Schlessinger, and K.T. Buck, *Chem. Ind.* (London), **1964**, 282.
4) W.I. Taylor, *Tetrahedron*, **14**, 42 (1961).

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.