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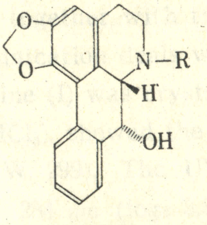
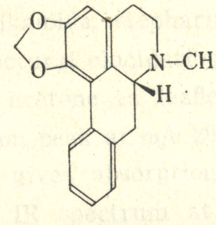
The Absolute Configuration of Ushinsunine and the Synthesis of *dl*-Michelalbine

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**).

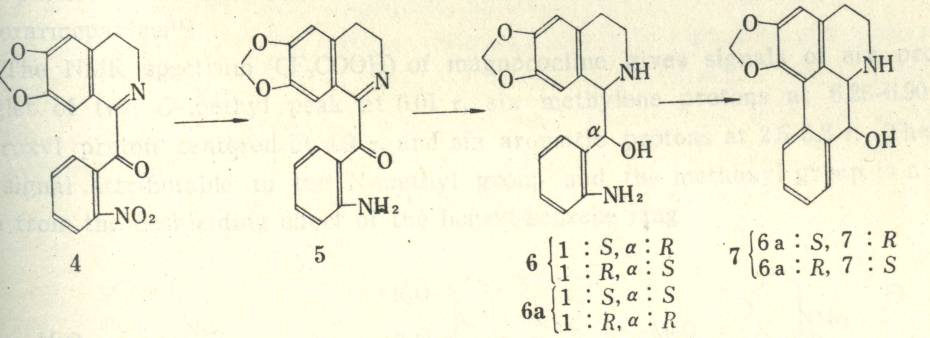
Catalytic hydrogenation of ushinsunine (**1**) over platinum black in 48% hydrobromic acid gave a non-phenolic base. This product was found to be identical with D-roemerine (**3**)[3] by comparison of their infrared (IR) ($CHCl_3$), ultraviolet (UV), thin-layer chromatography (TLC) and specific rotation; $[\alpha]_D$: $-67.5°$ ($CHCl_3$) 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**).



1 : R=CH_3
2 : R=H



3



6 {1 : *S*, α : *R*; 1 : *R*, α : *S*}
6a {1 : *S*, α : *S*; 1 : *R*, α : *R*}
7 {6a : *S*, 7 : *R*; 6a : *R*, 7 : *S*}

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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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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