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STRUCTURAL ELUCIDATION OF TWO NEW SPIROBENZYLISOQUINOLINE ALKALOIDS, YENHUSOMINE AND YENHUSOMIDINE†

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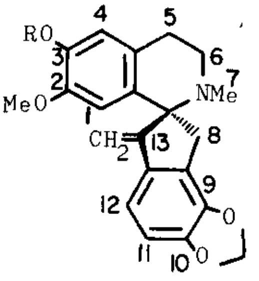
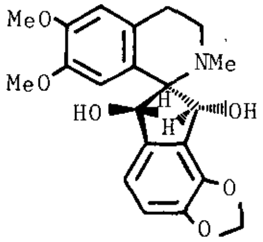
Yenhusomine and yenhusomidine, isolated from Corydalis ochotensis Turcz. (Papaveraceae) together with protopine, ochotensimine, and adlumidine, were assigned structures (3) and (4), respectively.

Corydalis ochotensis Turcz. (Papaveraceae) is a biennial herb which distributes mainly in northern China, Siberia, Korea and Japan. In 1940, Manske isolated from this plant aurotensine belonging to the protoberberine series, protopine and cryptopine of the protopine series, and ochotensine (Alkaloid F 17), ochotensimine (Alkaloid F 48), and Alkaloid F 49.[1] The spirobenzylisoquinoline structures 1 and 2 were assigned at a later date to ochotensine and ochotensimine, respectively.[2] Impelled by a desire to further investigate the alkaloidal components of this plant growing on Mt. Nengkao, Tienchih, in Taiwan's Central Mountains, we wish to describe the structural elucidation of two further spirobenzylisoquinolines,

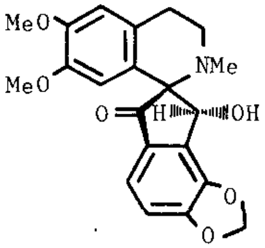


(1) R=H

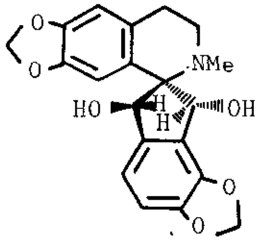
(2) R=Me



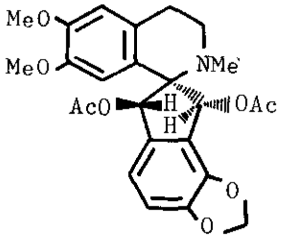
(3)



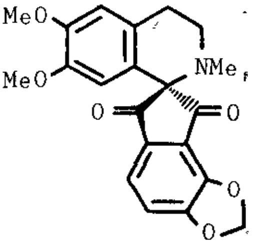
(4)



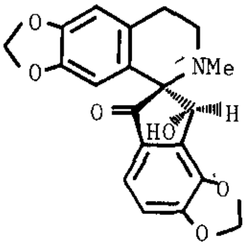
(5)



(6)



(7)



(8)

yenhusomine (3) and yenhusomidine (4).

Yenhusomine (3), $C_{21}H_{23}NO_6$, colourless prisms, mp 127 - 128° (MeOH), $[\alpha]_D^{19}$ + 48° (c = 1.0, MeOH), exhibits a methylenedioxylated 1,2,3,4-tetrahydroisoquinoline system, λ_{max}^{EtOH} 241 and 288 nm (log ε 4.11 and 3.85), ν_{max} (Nujol) 3480 and 3300 (2 x OH), 1030 and 935 cm^{-1} (OCH_2O), m/e 385 (M^+). In the nmr spectrum δ ($CDCl_3$), the chemical shifts of the N-methyl group at 2.71 (3H, s), the protons due to 8 - H and 13 - H at 4.91 (1H, s) and 5.52 (1H, broad s), respectively, the methylenedioxy group at 5.99 and 6.02 (each 1H, d, J = 1.3 Hz) and four aromatic protons of C - 1, 4, 11 and 12 position at 6.10 (1H, s), 6.70 (1H, s), and 6.94 ppm (2H, s), respectively, are similar to those of ochrobirine (5).[3] The protons of one methoxyl group appeared at an unusually shielded position at 3.39 and another one at 3.83 ppm, suggesting that the methoxyl groups are located at the C - 2 and 3 positions in the spirobenzylisoquinoline skeleton. Acetylation of yenhusomine (3) with acetic anhydride and pyridine gave the diacetate (6), δ ($CDCl_3$) 1.84 and 2.12 (each 3H, each s, 2 x OAc). Oxidation of 3 with Jones reagent furnished oxoyenhusomine (7) as yellowish orange prisms, mp 174 - 175° (EtOH), $[\alpha]_D^{26}$ + 286° (c = 0.4, MeOH), ν_{max} (Nujol) 1733 and 1700 cm^{-1} (2 x CO). The nmr spectrum showed the methylenedioxy group at 6.34 (2H, s) and aromatic protons at 6.00 (1H, s, 1 - H), 6.70 (1H, s, 4 - H), 7.32 (1H, d, J = 8 Hz, 11 - H) and 7.72 ppm (1H, d, J = 8 Hz, 12 - H). Furthermore, the cd curve of yenhusomine at 294, 275, and 241 nm ($\Delta\varepsilon$ + 14.6, - 3.4, and + 11.6) resembles that of ochrobirine (5)[4] so that the absolute configuration of yenhusomine is as indicated in expression 3.

Yenhusomidine (4), $C_{21}H_{21}NO_6$, colourless prisms, mp 240 - 241°, $[\alpha]_D^{29}$ 0° (c = 0.41, $CHCl_3$),[5] whose picrate forms yellow prisms, mp 214 - 215°, shows λ_{max}^{EtOH} 207, 238, 290, and 314 nm (logε 4.40, 4.21, 3.74, and 3.72), ν_{max} (Nujol) 3275 (OH), 1706 (C = O), 1041 and 931 cm^{-1} (OCH_2O). The nmr spectrum showed one N-methyl group at 2.33 (3H, s), two methoxyl group at 3.66 and 3.88 (each 3H, each s), one methylenedioxy group at 6.24 ppm (2H, s). An AB quartet

(J = 8 Hz) at 7.51 and 7.02 ppm was assigned for the signals due to 12 - H and 11 - H protons, respectively, which suggested the existence of a carbonyl group at C - 13. Other aromatic protons at the C - 1 and C - 4 positions appeared at 6.11 and 6.64 ppm, respectively. The proton geminal to the hydroxyl group at C - 8 was observed at 5.14 ppm as a sharp singlet, suggesting that the hydroxyl group is oriented syn to the nitrogen. In the case of sibiricine (8), the proton at C - 8, oriented syn to the nitrogen, appeared at 5.57 ppm as a broad singlet.[6] This conclusion was also supported by the observation of a hydroxyl band in the ir spectrum at 3275 cm^{-1}.[7]

Among the isolated bases, protopine, ochotensimine (2) and adlumidine have been characterised.

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