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STRUCTURE ELUCIDATION OF SIX NEW NON-PHENOLIC ALKALOIDS ISOLATED FROM CORYDALIS OCHOTENSIS VAR. RADDEANA

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Six new alkaloids, raddeanamine (1), raddeanine (2), raddeanidine (3), raddeanone (4), aobamine (5) and aobamidine (6), were isolated from the non-phenolic alkaloidal fraction of Corydalis ochotensis var. raddeana in addition to the known alkaloids, protopine, adlumidine (7) and ochotensimine (8).

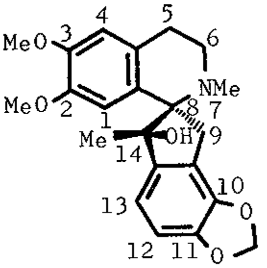
In connection with the previous study of the alkaloids from Corydalis ochotensis (Turcz) in Taiwan,[1] the alkaloidal fraction of C. ochotensis var. raddeana, which was collected in Sendai in September, 1975, has been investigated. We now wish to report the isolation and structural elucidation of six new alkaloids from the non-phenolic fraction.

The non-phenolic bases from C. ochotensis var. raddeana were characterised after separation by silica gel column chromatography followed by further purification using reverse phase high pressure liquid chromatography. In addition to the known alkaloids, protopine, adlumidine (7) and ochotensimine (8), six new alkaloids which we named, raddeanamine (1), raddeanine (2), raddeanidine (3), raddeanone (4), aobamine (5) and aobamidine (6) were isolated and their structures assigned by spectroscopic analyses as follows.

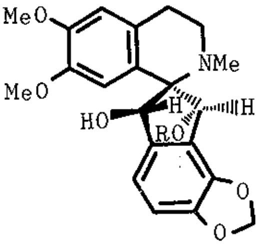
Raddeanamine (1), which was isolated as a syrup, $[\alpha]_D^{20}$ + 166° (c = 0.68, methanol), m/e 383 (M^+), 368, 365 and 206, showed a hydroxyl group at 3240 cm^{-1} in the i.r. spectrum ($CHCl_3$) and a quaternary methyl group at 1.23 ppm (3H, s) in addition to an N-methyl group at 2.56 (3H, s), two O-methyl groups at 3.43 (3H, s) and 3.81 (3H, s), a hydroxyl group at 5.23 br (1H, s, disappeared with D_2O), a methylenedioxy group at 5.94 (2H, s) and four aromatic protons at 6.19 (1H, s, 1 - H), 6.54 (1H, s, 4 - H), 6.67 and 6.83 (each 1H, each d, J 8 Hz, 12- and 13 - H) in the n.m.r. spectrum (δ $CDCl_3$), indicating the hydroxyl group to be syn to the nitrogen.

Raddeanine (2), m.p. 200 - 202° (from acetone), $[\alpha]_D$ + 79.4° (c = 0.11, methanol), m/e 385 (M^+), 370, 367, 352, 338, 324, 308 and 206, exhibited the hydroxyl group at 3590 cm^{-1} in the i.r. spectrum ($CHCl_3$) and two methine protons at 5.21 br (1H, s, 14 - H) and 5.42 br (1H, s, 9 - H), together with two hydroxyl groups at 2.10 br (2H, s, disappeared with D_2O), an N-methyl group at 2.60 (3H, s), two O-methyl groups at 3.40 and 3.81 (each 3H, each s), a methylenedioxy group at 5.97 (2H, s) and four aromatic protons at 6.16 (1H, s, 1 - H), 6.65 (1H, s, 4 - H), 6.76 and 6.80 (each 1H, each d, J 8 Hz, 12- and 13 - H) in the n.m.r. spectrum (δ $CDCl_3$), suggesting that the two hydroxyl groups are anti to the nitrogen.

Raddeanidine (3), which was isolated as a syrup, $[\alpha]_D^{20}$ + 82.7°

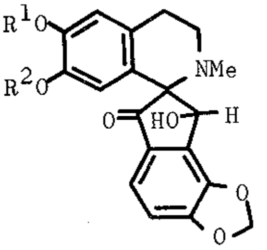


(1)



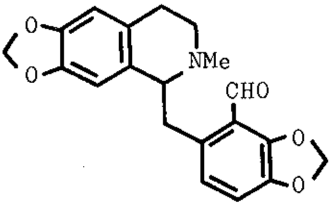
(2) R=H

(3) R=Ac

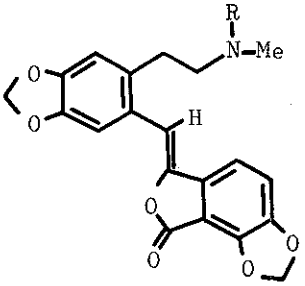


(4) $R^1=R^2=Me$

(9) $R^1+R^2=CH_2$

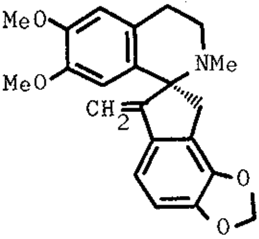


(5)

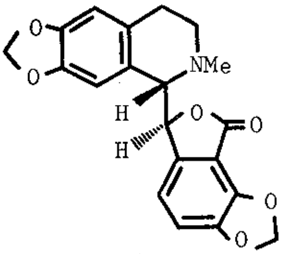


(6) R=Me

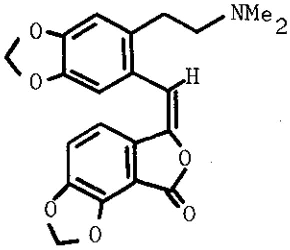
(10) R=COO  Br



(8)



(7)



(11)

(c = 0.52, methanol), *m/e* 427 (M^+), 384, 367, 352, 338, 324, 322, 308 and 206, showed absorptions for the hydroxyl at 3580 and for the carbonyl in the acetoxy group at 1740 cm^{-1} in the i.r. spectrum ($CHCl_3$) and two methine protons at 5.15 br (1H, s, 14 - H) and 6.57 (1H, s, 9 - H) in the n.m.r. spectrum [(δ $CDCl_3$) as well as 1.93 (3H, s, Ac), 2.50 (3H, s, NMe), 3.42 and 3.81 (each 3H, each s, 2 x OMe), 5.94 (2H, s, OCH_2O), 6.18 (1H, s, 1 - H), 6.55 (1H, s, 4 - H) and 6.81 (2H, s, 12 - and 13 - H)], indicating that the 14-hydroxyl and the 9-acetoxy groups are *anti* to the nitrogen.

Raddeanone (4), m.p. 132 - 133° (from acetone), $[\alpha]_D^{20}$ 0° (c = 0.085, methanol), λmax (EtOH) (log ε) 238 (4.58), 289 (4.12) and 313 nm (4.06), *m/e* 383 (M^+), 368, 352, 338, 324, 308, and 206, displayed a hydroxyl group at 3570 and a carbonyl group at 1720 cm^{-1} in the i.r. spectrum ($CHCl_3$) and a methine proton at 5.56 br (1H, s) and two aromatic protons at C_{12} and C_{13} positions at 7.01 (1H, d, *J* 8 Hz) and 7.51 (1H, d, *J* 8 Hz), respectively, in the n.m.r. spectrum [(δ $CDCl_3$) along with 2.37 (3H, s, NMe), 3.53 and 3.84 (each 3H, each s, 2 x OMe), 6.05 (1H, s, 1 - H), 6.15 and 6.20 (each 1H, each d, *J* 1 Hz, OCH_2O) and 6.66 (1H, s, 4 - H)], which are similar to those of sibiricine (9).[2] This supports the assignment of the carbonyl group to the C_{14} position[3] and confirms that the hydroxyl group at the C_9 position is *anti* to the nitrogen.

The i.r. [νmax ($CHCl_3$) 1680 cm^{-1} (C=O)] and n.m.r. [(δ $CDCl_3$) 2.35 (3H, s, NMe), 5.87 and 6.07 (each 2H, each s, 2 x OCH_2O), 6.48 (2H, s, 5 and 8 - H), 6.50 and 6.80 (each 1H, each d, *J* 8 Hz, 5' - and 6' - H) and 10.06 (1H, s, CHO)] spectra of aobamine, which was obtained as a syrup, *m/e* 353 (M^+) and 190, unstable on standing, indicated the structure (5).

On the basis of spectral analysis of aobamidine [λmax (EtOH) (log ε) 227 (4.38), 240 sh (4.32), 308 (4.10), 337 sh (3.94) and 390 nm (4.28); νmax ($CHCl_3$) 1760 cm^{-1} (C=O); δ ($CDCl_3$) 2.32 (6H, s, NMe), 5.94 and 6.20 (each 2H, each s, 2 x OCH_2O), 6.45, 6.68 and 7.61 (each 1H, each s, 2 x ArH and olefinic H) and 7.07 and 7.25 (each 1H, each d, J 8 Hz, 2 x ArH); m/e 381 (M^+), 336, 204, 177 and 58)], the structure of aobamidine, m.p. 195 - 197° (from ether), was the lactone (6). The stereochemistry, Z-form, was indicated by the similarity of its u.v. spectrum with that of the urethane (10) whose structure has been determined by X-ray analysis.[4] This assignment was further confirmed as follows. The methiodide of adlumidine (7) was treated with dilute aqueous sodium hydroxide solution to give the E-oriented derivative (11), λmax (EtOH) 362, 290, 268 sh, 240 sh and 226 nm, δ ($CDCl_3$) 2.20 (6H, s, NMe_2), 5.98 and 6.18 (each 2H, each s, 2 x OCH_2O), 6.65 (1H, s) and 6.80 (2H, s) (2 x ArH and olefinic H), 6.68 and 6.91 (each 1H, each d, J 8 Hz, 2 x ArH). This n.m.r. spectrum is consistent with that of adlumidicein enol lactone.[5] Irradiation of 11 in chloroform gave a mixture of E- and Z-compounds (11 and 6). The latter compound (6) was identical by i.r. and n.m.r. with aobamidine.

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