FOUR NEW DITERPENOID ALKALOIDS FROM
DELPHINIUM PENTAGYNUM

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Abstract—Four new diterpenoid alkaloids, dihydorgadesine, 14-acetyldihydorgadesine, pentagynine and dihydropentagynine, were isolated and identified in Delphinium pentagynum.

INTRODUCTION

We wish to report the structure determination of dihydorgadesine (1), 14-acetyldihydorgadesine (2), pentagynine (3) and dihydropentagynine (4), four new C19 diterpenoid alkaloids found in Delphinium pentagynum Lam.

Dihydorgadesine, C23H35NO6, mp 136–138°, crystallized from petrol ether–ethyl acetate, [α]D +54° (EtOH; c 1.0), IR (KBr), 3500, 3280 (OH) and 1080 cm⁻¹ (ether). 1H-NMR (90 MHz, CDCl₃), 81.10 (3H, s, C-CH₃), 1.10 (3H, t, J = 7 Hz, N-CH₂-CH₂), 3.37 (6H, s, two OCH₃), 3.65 (1H, m, W₁/₂ = 6 Hz, H-β), 3.98 (1H, s, H-6α) and 4.12 (1H, dd, J₁ = J₂ = 4.5 Hz, H-14β) [1]. This alkaloid proved to be identical (mp, IR, 1H-NMR and MS) with the LiAlH₄ reduction product of gadesine (5) [2] and therefore its structure was established.

14-Acetyldihydorgadesine was isolated as a resin, M⁺ 465.2733, C₂₃H₃₉N₂O₇ (calc. 465.2740). IR (KBr), 3440 (OH), 1275 and 1240 cm⁻¹ (acetate). The 1H-NMR (90 MHz, CDCl₃) displayed signals at 82.08 (3H, s) and 4.82 (1H, dd, J₁ = J₂ = 4.5 Hz) which confirmed the acetyl group to be situated on C-14α [1]. Its alkaline hydrolysis yielded dihydorgadesine allowing structure 2 to be assigned to this base.

Pentagynine, C₂₃H₃₅NO₆, mp 198–201°, [α]D +72° (EtOH; c 0.12), IR (KBr), 3480 (OH), 1000, 1085 (ether), 880 and 1000 cm⁻¹ (carboximidine inner ether [4]); 1H-NMR (90 MHz, CDCl₃), 80.75 (3H, s, C-CH₃), 0.96 (3H, t, J = 7 Hz, N-CH₂-CH₂), 2.90 and 3.15 (3H each, s, two OCH₃), 3.62 (1H, s, H-19), 3.64 (1H, m, W₁/₂ = 7 Hz, H-β), 3.94 (1H, d, J = 7 Hz, H-6β), 4.13 (1H, dd, J₁ = J₂ = 4.5 Hz, H-14β). The MS exhibited a peak at m/z 349[M – 56]⁺ (18), caused by loss of acrolein from ring A owing to the carboximidine inner ether [5].

LiAlH₄ reduction of pentagynine gave the aminoalcohol (4). Its IR did not show the absorptions of the inner ether. The 1H-NMR gave a signal at δ3.78 (1H, m, W₁/₂ = 6 Hz, H-β) and the MS a base peak at 390[M – OH]⁺ from loss of C-1αOH 6, thus confirming the presence of C-1αOH in 4 and the C-1-β-1-ether in pentagynine. By benzyolation with C₆H₅OCl-pyridine 4 was converted into the dibenzoate (6), mp 178–181°, 615 M⁺, IR (KBr), 1715 and 715 cm⁻¹ (benzoate). 1H-NMR (90 MHz, CDCl₃), 84.93 (1H, dd, J₁ = J₂ = 4.5 Hz, H-14β), and 5.20 (1H, q, J₁ = 7 Hz, J₂ = 10 Hz, H-1β) [1]. Treatment of 6 with Ac₂O and catalytic amounts of p-toluenesulfonic acid at room temp. yielded the 1,14-dibenzyol-8-acetyl derivative (7) as a resin, m/z 657 M⁺. The 1H-NMR gave a highly shielded 3-proton signal at δ8.43 due to the acetoxy-protons, characteristic of a C-14 benzoyl-C-8 acetyl substitution pattern [7].

The 1C-NMR (20.1 MHz, CDCl₃) of pentagynine: 891.19 (d, C-1), 22.96 (t, C-2), 30.22 (t, C-3), 38.32 (s, C-4), 37.34 (d, C-5), 84.30 (d, C-6), 56.88 (d, C-7), 73.57 (s, C-8), 52.63 (d, C-9), 39.04 (d, C-10), 47.50 (s, C-11), 28.65 (t, C-12), 45.72 (d, C-13), 75.50 (d, C-14), 39.04 (t, C-15), 82.17 (d, C-16), 61.72 (d, C-17), 20.20 (q, C-18), 68.75 (d, C-19), 47.84 (t, N-CH₂-CH₂), 14.35 (q, N-CH₂-CH₂), 58.00 (q, C-6'), 56.35 (q, C-16'), is consistent with structure 3. The chemical shifts

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1781
have been assigned by comparison with the $^{13}$C-NMR spectra of the related alkaloids chasmanine and neoline [8].

Dihydropentagynine, C$_{22}$H$_{37}$NO$_5$, mp 150–154$^\circ$, [$\alpha$]$_D$ + 43$^\circ$ (EtOH; c, 0.12). IR (KBr), 3460 (OH) and 1090 cm$^{-1}$ (ether). $^1$H-NMR (90 MHz, CDCl$_3$), $\delta$1.08 (3H, s, C–CH$_3$), 1.12 (3H, t, J = 7 Hz, N–CH$_2$–CH$_3$), 3.38 (6H, s, two OCH$_3$), 3.78 (1H, m, W$_{1/2}$ = 6 Hz, H-1$\beta$), 3.97 (1H, d, J = 8 Hz, H-6$\beta$) and 4.12 (1H, dd, $J_1$ = $J_2$ = 4.5 Hz, H-14$\beta$). This base was identical with the amino-alcohol (4).

The co-occurrence in the same plant of gadesine-dihydragadesine, pentagynine-dihydropentagynine, together with songoramine-songorine [9], suggests the possible existence of other such pairs in nature. They also form a redox system which may play a significant role in plant metabolism.

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REFERENCES