FOUR NEW DITERPENOID ALKALOIDS FROM *DELPHINIUM PENTAGYNUM*

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Key Word Index—*Delphinium pentagynum*; Ranunculaceae; diterpenoid alkaloids; dihydrogadesine; 14-acetyldihydrogadesine; pentagynine; dihydropentagynine.

Abstract—Four new diterpenoid alkaloids, dihydrogadesine, 14-acetyldihydrogadesine, pentagynine and dihydropentagynine, were isolated and identified in *Delphinium pentagynum*.

INTRODUCTION

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

Dihydrogadesine, C₂₃H₃₇NO₆, mp 136–138°, crystallized from petrol ether–ethyl acetate, $[\alpha]_D^{25} + 54^\circ$ (EtOH; c, 0.1). IR (KBr), 3500, 3280 (OH) and 1080 cm⁻¹ (ether); ¹H-NMR (90 MHz, CDCl₃), δ 1.10 (3H, s, C-CH₃), 1.10 (3H, t, J = 7 Hz, N-CH₂-CH₃), 3.37 (6H, s, two OCH₃), 3.65 (1H, m, W_{1/2} = 6 Hz, H-1 β), 3.98 (1H, s, H-6 α) and 4.12 (1H, dd, J₁ = J₂ = 4.5 Hz, H-14 β) [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-Acetyldihydrogadesine was isolated as a resin, M⁺ 465.2733, C₂₅H₃₉NO₇ (calc. 465.2740). IR (KBr),

3440 (OH), 1275 and 1240 cm⁻¹ (acetate). The ¹H-NMR (90 MHz, CDCl₃) displayed signals at δ 2.08 (3H, s) and 4.82 (1H, dd, J₁ = J₂ = 4.5 Hz) which confirmed the acetate group to be situated on C-14 α [1]. Its alkaline hydrolysis yielded dihydrogadesine allowing structure 2 to be assigned to this base.

Pentagynine, C₂₃H₃₅NO₅, mp 198–201°, $[\alpha]_D^{25} + 72^\circ$ (EtOH, c 0.12); IR (KBr), 3480 (OH), 1000, 1085 (ether), 880 and 1000 cm⁻¹ (carbinolamine inner ether [4]); ¹H-NMR (90 MHz, C₆D₆), δ 0.75 (3H, s, C-CH₃), 0.96 (3H, t, J = 7 Hz, N-CH₂-CH₃), 2.90 and 3.15 (3H each, s, two OCH₃), 3.62 (1H, s, H-19), 3.64 (1H, m, W_{1/2} = 7 Hz, H-1 β), 3.94 (1H, d, J = 7 Hz, H-6 β), 4.13 (1H, dd, J₁ = J₂ = 4.5 Hz, H-14 β). The MS exhibited a peak at m/z 349[M – 56]⁺ (18), caused by loss of acrolein from ring A owing to the carbinolamine inner ether [5].

LiAlH₄ reduction of pentagynine gave the amino-alcohol (4). Its IR did not show the absorptions of the inner ether. The ¹H-NMR gave a signal at δ 3.78 (1H, m, W_{1/2} = 6 Hz, H-1 β) and the MS a base peak at 390[M – OH]⁺ from loss of C-1 α OH 6, thus confirming the presence of C-1 α OH in 4 and the C-1–C-19 ether in pentagynine. By benzylation 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), δ 4.93 (1H, dd, J₁ = J₂ = 4.5 Hz, H-14 β), and 5.20 (1H, q, J₁ = 7 Hz, J₂ = 10 Hz, H-1 β) [1]. Treatment of 6 with Ac₂O and catalytic amounts of p-toluenesulfonic acid at room temp. yielded the 1,14-dibenzoyl-8-acetyl derivative (7) as a resin, m/z 657 M⁺. The ¹H-NMR gave a highly shielded 3-proton signal at δ 1.43 due to the acetoxy-protons, characteristic of a C-14 benzoyl-C-8 acetyl substitution pattern [7].

The ¹³C-NMR (20.1 MHz, CDCl₃) of pentagynine: δ 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-CH₃), 14.35 (q, N-CH₂-CH₃), 58.00 (q, C-6'), 56.35 (q, C-16'), is consistent with structure 3. The chemical shifts

- 1 R = R₁ = R₂ = H, R₃ = OH, R₄ = β -OMe, α -H
- 2 R = R₂ = H, R₁ = Ac, R₃ = OH, R₄ = β -OMe, α -H
- 4 R = R₁ = R₂ = R₃ = H, R₄ = β -H, α -OMe
- 6 R = R₁ = B₂, R₂ = R₃ = H, R₄ = β -H, α -OMe
- 7 R = R₁ = B₂, R₂ = Ac, R₃ = H, R₄ = β -H, α -OMe

- 3 R = H, R₁ = β -H, α -OMe
- 5 R = OH, R₁ = β -OMe, α -H

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

Dihydropentagynine, $\text{C}_{23}\text{H}_{37}\text{NO}_5$, mp 150–154°, $[\alpha]_{\text{D}} + 43^\circ$ (EtOH; c , 0.12). IR (KBr), 3460 (OH) and 1090 cm^{-1} (ether). ^1H -NMR (90 MHz, CDCl_3), δ 1.08 (3H, s , C- CH_3), 1.12 (3H, t , $J = 7\text{ Hz}$, N- $\text{CH}_2\text{-CH}_3$), 3.38 (6H, s , two OCH_3), 3.78 (1H, m , $W_{1/2} = 6\text{ Hz}$, H-1 β), 3.97 (1H, d , $J = 8\text{ Hz}$, H-6 β) and 4.12 (1H, dd , $J_1 = J_2 = 4.5\text{ Hz}$, H-14 β). This base was identical with the amino-alcohol (4).

The co-occurrence in the same plant of gadesine-dihydrogadesine, 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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