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FOUR NEW DITERPENOID ALKALOIDS FROM *DELPHINIUM PENTAGYNUM*

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

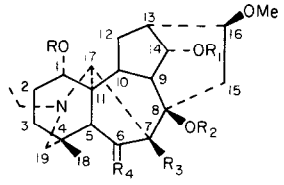
Abstract—Four new diterpenoid alkaloids, dihydrogadesine, 14-acetyldihydrogadesine, pentagynine and dihydropentagynine, were isolated and identified in *Delphinium pentagynum*.

INTRODUCTION

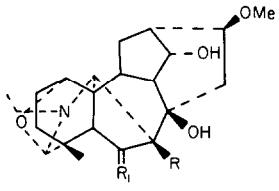
We wish to report the structure determination of dihydrogadesine (**1**), 14-acetyldihydrogadesine (**2**), pentagynine (**3**) and dihydropentagynine (**4**), four new C_{19} diterpenoid alkaloids found in *Delphinium pentagynum* Lam.

Dihydrogadesine, $C_{23}H_{37}NO_6$, mp 136–138°, crystallized from petrol ether–ethyl acetate, $[\alpha]_D + 54°$ (EtOH; *c*, 0.1). IR (KBr), 3500, 3280 (OH) and 1080 cm^{-1} (ether); ^{1}H-NMR (90 MHz, $CDCl_3$), δ1.10 (3H, *s*, C-CH_3), 1.10 (3H, *t*, $J = 7$ Hz, N-CH_2-CH_3), 3.37 (6H, *s*, two OCH_3), 3.65 (1H, *m*, $W_{1/2} = 6$ Hz, H-1β), 3.98 (1H, *s*, H-6α) and 4.12 (1H, *dd*, $J_1 = J_2 = 4.5$ Hz, H-14β) [1]. This alkaloid proved to be identical (mp, IR, ^{1}H-NMR and MS) with the $LiAlH_4$ reduction product of gadesine (**5**) [2] and therefore its structure was established.

14-Acetyldihydrogadesine was isolated as a resin, M^+ 465.2733, $C_{25}H_{39}NO_7$ (calc. 465.2740). IR (KBr),



1 R = R_1 = R_2 = H, R_3 = OH, R_4 = β-OMe, α-H
2 R = R_2 = H, R_1 = Ac, R_3 = OH, R_4 = β-OMe, α-H
4 R = R_1 = R_2 = R_3 = H, R_4 = β-H, α-OMe
6 R = R_1 = B_z, R_2 = R_3 = H, R_4 = β-H, α-OMe
7 R = R_1 = B_z, R_2 = Ac, R_3 = H, R_4 = β-H, α-OMe



3 R = H, R_1 = β-H, α-OMe
5 R = OH, R_1 = β-OMe, α-H

3440 (OH), 1275 and 1240 cm^{-1} (acetate). The ^{1}H-NMR (90 MHz, $CDCl_3$) displayed signals at δ2.08 (3H, *s*) and 4.82 (1H, *dd*, $J_1 = J_2 = 4.5$ Hz) which confirmed the acetate group to be situated on C-14α [1]. Its alkaline hydrolysis yielded dihydrogadesine allowing structure **2** to be assigned to this base.

Pentagynine, $C_{23}H_{35}NO_5$, mp 198–201°, $[\alpha]_D + 72°$ (EtOH, *c* 0.12); IR (KBr), 3480 (OH), 1000, 1085 (ether), 880 and 1000 cm^{-1} (carbinolamine inner ether [4]); ^{1}H-NMR (90 MHz, C_6D_6), δ0.75 (3H, *s*, C-CH_3), 0.96 (3H, *t*, $J = 7$ Hz, N-CH_2-CH_3), 2.90 and 3.15 (3H each, *s*, two OCH_3), 3.62 (1H, *s*, H-19), 3.64 (1H, *m*, $W_{1/2} = 7$ Hz, H-1β), 3.94 (1H, *d*, $J = 7$ Hz, H-6β), 4.13 (1H, *dd*, $J_1 = J_2 = 4.5$ Hz, H-14β). The MS exhibited a peak at *m/z* 349[M − 56]$^+$ (**18**), caused by loss of acroleine from ring A owing to the carbinolamine inner ether [5].

$LiAlH_4$ reduction of pentagynine gave the amino-alcohol (**4**). Its IR did not show the absorptions of the inner ether. The ^{1}H-NMR gave a signal at δ3.78 (1H, *m*, $W_{1/2} = 6$ Hz, H-1β) 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–C-19 ether in pentagynine. By benzoylation with C_6H_5OCl–pyridine **4** was converted into the dibenzoate (**6**), mp 178–181°, 615 M^+, IR (KBr), 1715 and 715 cm^{-1} (benzoate). ^{1}H-NMR (90 MHz, $CDCl_3$), δ4.93 (1H, *dd*, $J_1 = J_2 = 4.5$ Hz, H-14β), and 5.20 (1H, *q*, $J_1 = 7$ Hz, $J_2 = 10$ Hz, H-1β) [1]. Treatment of **6** with Ac_2O 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 ^{1}H-NMR gave a highly shielded 3-proton signal at δ1.43 due to the acetoxy-protons, characteristic of a C-14 benzoyl-C-8 acetyl substitution pattern [7].

The ^{13}C-NMR (20.1 MHz, $CDCl_3$) of pentagynine: δ91.19 (*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-CH_2-CH_3), 14.35 (*q*, N-CH_2-CH_3), 58.00 (*q*, C-6′), 56.35 (*q*, C-16′), is consistent with structure **3**. The chemical shifts

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

Dihydropentagynine, $C_{23}H_{37}NO_5$, mp 150–154°, $[\alpha]_D + 43°$ (EtOH; *c*, 0.12). IR (KBr), 3460 (OH) and 1090 cm^{-1} (ether). ^{1}H-NMR (90 MHz, $CDCl_3$), δ1.08 (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-1β), 3.97 (1H, *d*, $J = 8$ Hz, H-6β) and 4.12 (1H, *dd*, $J_1 = J_2 = 4.5$ Hz, H-14β). 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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