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Norditerpenoid Alkaloids from the Roots of *Delphinium stapeliosum*

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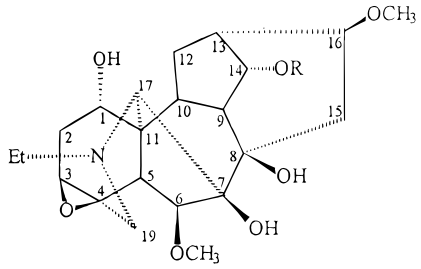
From the roots of *Delphinium stapeliosum* three new norditerpenoid alkaloids, 14-demethyltuguaconitine (**1**), 14-deacetyl-14-isobutyrylnudicauline (**2**), and 14-deacetyl-14-isobutyrylajadine (**3**), and nine known norditerpenoid alkaloids, delbonine (**4**), methyllycaconitine (**5**), 14-deacetylnudicauline (**6**), ajacine (**7**), deltatsine (**8**), delcosine (**9**), 14-deacetylajadine (**10**), nudicauline (**11**), and ajadine (**12**), were isolated. Structure elucidation and identification were based on NMR and mass spectra.

The genus *Delphinium* is, like the genus *Aconitum*, a rich source of diterpenoid alkaloids.[1,2] The roots of various *Delphinium* plants are used in Nepalese folklore for the treatment of rheumatism, cough, fever, toothache, and as an adulterant of aconite.[3]

In the course of our continuing investigation of diterpenoid alkaloids of vegetable origin, we investigated the Nepalese species *Delphinium stapeliosum* Brühl (Ranunculaceae), which hitherto has not been explored as to its alkaloidal content. We have isolated three new (**1**−**3**) and nine known (**4**−**12**) norditerpenoid alkaloids from its roots. All compounds were identified by ^{1}H and ^{13}C NMR, DEPT, and LC quadrupole mass spectra.

Results and Discussion

To the new alkaloid 14-demethyltuguaconitine (**1**), the molecular formula $C_{22}H_{33}NO_7$ was assigned by LCQ mass spectrometry (*m*/*z* 424 [M + H]$^+$) and ^{13}C NMR studies. The ^{1}H and ^{13}C NMR spectra indicated the presence of two methoxyl groups (δ_H 3.38 and 3.42, 3H each, s) and an *N*-ethyl group (δ_H 1.08, 3H, t, J = 7.2 Hz). The ^{13}C NMR spectrum displayed 22 carbon signals. The DEPT spectrum showed the signals for four quaternary, 10 methine, five methylene, and three methyl carbons. The downfield quaternary signals at δ_C 89.6 and 78.1 were assigned to the oxygenated carbons C-7 and C-8, respectively. The signals at δ_C 53.5 and 58.6 were attributed to the nonoxygenated carbons C-11 and C-4, respectively. Four of the 10 methine carbons were oxygenated (δ_C 77.9, 90.0, 75.6, and 81.9). The ^{13}C NMR chemical shifts were quite comparable with those of tuguaconitine[4] (**13**) except for C-14. The molecular ion peak *m*/*z* of **1** was found to be 14 amu less than that of tuguaconitine (**13**), indicating that it contains one methylene group less. This was supported by the presence of only two methoxyl signals in the ^{13}C NMR spectrum. No signal was observed at δ_C 83.5−85.0 for a methoxy substituent at C-14,[1] but a signal for a H-14 in the ^{1}H NMR spectrum was observed at δ_H 4.13. Hence, the locations of the methoxyl groups at C-6 and C-16 were established by comparison of the ^{13}C NMR values of **1** with those of **13**.[4] Two signals at δ_C 58.7 for the methine carbon (C-3) and at δ_C 58.6 for the quaternary carbon (C-4) suggested an epoxy bridge between C-3 and C-4. A doublet at δ_C 77.9 in the ^{13}C NMR spectrum of **1** was assigned to OH-1α. This also indicated the presence of a C-3,C-4 epoxy group, because the general range of the ^{13}C NMR chemical shift of a OH-1α substituent combined with a C-3,C-4 epoxy group is reported to be 77.0−77.5 ppm.[1]



14-demethyltuguaconitine (**1**) R = H
Tuguaconitine (**13**) R = CH_3

The molecular formula of 14-deacetyl-14-isobutyrylnudicauline (**2**) was assigned as $C_{40}H_{54}N_2O_{11}$, based on LCQ mass spectrometry (*m*/*z* 739 [M + H]$^+$) and the ^{13}C NMR spectrum. The ^{1}H NMR spectrum exhibited the signals for an *N*-ethyl group methyl at δ_H 1.08 (3H, t, J = 6.9 Hz) and for 3 × OCH_3 at 3.28, 3.30, and 3.35 (3H each, s). Further assignments were δ_H 4.09 (1H, s) for H-6α, 3.84 (2H, d, J = 14.9 Hz) for H_2-18, 4.76 (1H, br t, J = 4.7 Hz) for H-14β, and 1.18 (6H, d, J = 7.0 Hz) for two CH_3 of $CH(CH_3)_2$. The DEPT experiment showed 10 quaternary, 15 methine, eight methylene, and seven methyl signals. Of 10 quaternary carbons, four could be assigned to the ester carbonyls at δ_C 164.0 (benzoyl), 177.2 (isobutyryl), 175.7 (C-1″), and 179.7 (C-4″). The oxygenated quaternary carbons at δ_C 88.5 and 77.2 were assigned to C-7 and C-8, whereas the nonoxygenated quaternary carbons at δ_C 49.0 and 37.5 were attributed to C-11 and C-4. Comparison of the ^{13}C NMR spectral data of **2** with those of the known alkaloids 14-deacetylnudicauline[5] (**6**), occidentalidine,[6] and 14-isobutyrylnudicaulidine[7] suggested that the three methoxyl signals at δ_C 55.8, 58.2, and 55.9 could be assigned to methoxyls at C-1, C-6, and C-16, respectively. Similarly, the methine signals at δ_C 83.9, 90.6, and 82.2 were ascribed to the methoxyl-bearing carbons C-1, C-6, and C-16, respectively. The ^{13}C NMR chemical shifts were in good

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agreement with those of 14-deacetylnudicauline[5] (**6**) except for the isobutyryl group. The molecular ion peak (*m*/*z* 739 $[M + H]^+$) of **2** was found to represent 70 amu more than that of 14-deacetylnudicauline (**6**) (*m*/*z* 669 $[M + H]^+$), indicating the presence of an extra isobutyryl group. This group was placed at C-14, inasmuch as no signal for a C-14-bearing methoxyl group was observed. The C-14 isobutyryl group was assigned an α-configuration based on the following analysis. The general range of the chemical shift of C-14 with an α-hydroxyl and α-acetyl group in lycoctonine-type norditerpenoid alkaloids with no substituent at C-9, C-10, or C-13 is 74.5−77.0 ppm.[1] There is no example in the literature of any diterpenoid alkaloid having a C-14 substituent in the *β*-configuration.[1,2] The presence of an isobutyryl group at C-14 was also supported by a signal at δ_H 4.76 (1H, br t, $J = 4.7$ Hz) in the ^{1}H NMR spectrum. This value agrees with that found for occidentalidine,[6] 14-isobutyrylnudicaulidine,[7] and glaucerine,[8] which have a 14α-isobutyryl group.

The molecular formula $C_{37}H_{52}N_2O_{10}$ of 14-deacetyl-14-isobutyrylajadine (**3**) was derived from the LCQ mass spectrum (*m*/*z* 685 $[M + H]^+$) and from the ^{13}C NMR data. The ^{1}H NMR spectrum gave signals at δ_H 1.08 (1H, t, $J =$ 7.0 Hz, *N*-Et), 3.28, 3.32, 3.38 (3H each, s, 3 × OCH_3), 3.91 (1H, s, H-6α), and 4.77 (1H, br t, $J = 4.7$ Hz, H-14*β*) and resonances typical of an aromatic group at 7.13, 7.57 (1H each, t, $J = 7.6$, 7.7 Hz) and 7.97, 8.72 ppm (1H each, d, J = 7.8, 8.5 Hz), such as found in 14-deacetylajadine (**10**) and ajacine (**7**). Comparison of the above shifts with those of 14-isobutyrylnudicaulidine[7] showed significant differences in the C-18 ester moiety. The ^{13}C NMR spectrum displayed 36 peaks for 37 carbons, because the signals for the two isobutyryl CH_3 groups coincided. The patterns of the ^{1}H and ^{13}C NMR spectra indicated that compound **3** is also a lycoctonine-type norditerpenoid alkaloid. Multiplicities were determined from the DEPT spectrum, which revealed the presence of nine quaternary, 14 methine, seven methylene, and seven methyl carbons. Of the nine quaternary carbons, five were oxygenated (δ_C 177.3, 169.0, 168.1, 88.5, and 76.4) and four were nonoxygenated (δ_C 142.0, 114.6, 49.1, and 37.7). Two of the oxygenated quaternary carbons could be assigned to C-7 (δ_C 88.5) and C-8 (δ_C 76.4), and three were ester carbons. The nonoxygenated quaternary carbon signals at δ_C 49.1 and 37.7 were assigned to C-11 and C-4, respectively. The basic lycoctonine-type skeleton usually has four quaternary carbons (C-4, C-7, C-8, and C-11) and no substitution at C-10 or C-13. The ^{13}C NMR spectral data of **3** showed close similarities with those of 14-deacetylajadine[9] (**10**), except for the C-14 isobutyryl group. This fact is consistent with the mass spectrum, which showed the molecular ion at *m*/*z* 684, that is, 70 amu more than that of 14-deacetylajadine (**10**). Thus, 14-deacetyl-14-isobutyrylajadine (**3**) is the C-14 isobutyryl derivative of 14-deacetylajadine (**10**). That the isobutyryl function was located at C-14 was evident by the presence of a characteristic H-14*β* signal at δ_H 4.77 (1H, br t, $J =$ 4.7 Hz) and the chemical shift δ_C 75.6 for a C-14 bearing an isobutyryl group, as found for 14-isobutyrylnudicaulidine,[7] occidentalidine,[6] glaucerine,[8] and 14-deacetyl-14-isobutyrylnudicauline (**2**). The three methoxyl groups at δ_C 55.8, 58.2, and 56.0 (all q) were assigned to C-1 (δ_C 83.9, d), C-6 (δ_C 90.9, d), and C-16 (δ_C 82.3, d), respectively, by comparison of the ^{13}C NMR chemical shifts with those of 14-deacetylajadine (**10**),[9] occidentalidine,[6] and 14-isobutyrylnudicaulidine.[7]

Delbonine (**4**), a noncrystalline alkaloid, was previously isolated from *Delphinium bonvalotti* Franch by Jiang and Sung.[10] The detailed ^{13}C NMR spectral assignments that we present here have not been reported previously. The assignments given in Table 1 were made by comparison with the spectral data of deltatsine[11] and other reported spectral values for related alkaloids.[1,2]

Table 1. ^{13}C NMR Chemical Shifts and Assignments for Alkaloids **1**−**4**

carbon	1	2	3	4
1	77.9	83.9	83.9	72.3
2	31.5	26.9	26.1	27.1
3	58.7	31.9	32.3	29.4
4	58.6	37.5	37.7	37.2
5	45.4	42.9	50.4	38.2
6	90.0	90.6	90.9	90.9
7	89.6	88.5	88.5	91.1
8	78.1	77.2	76.4	81.8
9	48.7	50.0	43.1	48.7
10	39.7	45.7	45.8	44.6
11	53.5	49.0	49.1	49.2
12	29.6	28.3	28.2	29.4
13	42.8	37.7	37.9	36.8
14	75.6	75.5	75.6	75.4
15	34.4	33.7	33.9	30.4
16	81.9	82.2	82.3	82.4
17	67.5	64.4	64.4	66.2
18		69.3	69.8	78.7
19	54.3	52.3	52.5	57.4
20	50.1	51.0	51.0	50.4
21	14.0	14.0	14.1	13.7
CH_3O-1		55.8	55.8	
CH_3O-6	58.9	58.2	58.2	59.2
CH_3O-8				50.7
CH_3O-14				
CH_3O-16	56.4	55.9	56.0	56.2
CH_3O-18				59.4
$NHCOCH_3$			169.0	
			25.5	
$COCH_3$				170.5
				21.4
C═O		177.2	177.3	
CH		34.2	34.3	
$(CH_3)_2$		18.9	18.9	
		18.8	18.9	
C═O		164.0	168.1	
1′		126.9	114.6	
2′		133.0	142.0	
3′		129.4	120.7	
4′		133.7	135.0	
5′		131.0	122.6	
6′		130.0	130.3	
1″		175.7		
2″		35.3		
3″		37.0		
4″		179.7		
5″		16.4		

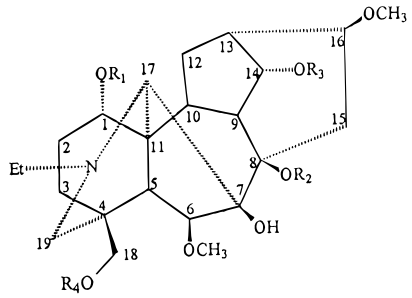
Experimental Section

General Experimental Procedures. Melting points were determined on a Kofler hot stage and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. Chemical shifts are given in parts per million (ppm) downfield to TMS. Optical rotations were determined on a Perkin−Elmer 341 polarimeter. LCQ mass spectra were recorded on a Finnigan LCQ G-2 mass spectrometer. Chromatographic separations were carried out by column chromatography on Merck Kieselgel 0.02−0.2 mm and TLC on Merck Si gel 60 F_{254} plates (0.2 mm and 0.25 mm) and neutral aluminum oxide 60 F_{254} plates (0.25 mm). TLC spots were visualized by exposure to iodine vapor and/or by spraying with Dragendorff's reagent.

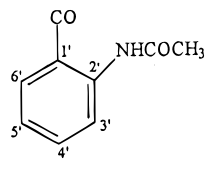
Plant Material. Plants were collected by one of us (P.M.S.) at Phulchoki Hill, Kathmandu Valley, Nepal, in September

1996, and identified by comparison with the authentic herbarium specimens at the National Herbarium Laboratory, Plant Research Division, Department of Plant Resources, Kathmandu, Nepal. Voucher specimens (PMS 96−1) of the plant are deposited in the herbarium of the Natural Products Research Laboratory, Dr. A. Katz, Basel.

Extraction and Isolation. Air-dried and powdered roots (60 g) were percolated with ether (250 mL) and then extracted three times with $CHCl_3$ (250 mL each) at pH 9 by adding 25% aqueous NH_4OH solution. The $CHCl_3$ extracts were concentrated in vacuo to give 1.3 g of dark brown crude alkaloidal mixture, which was dissolved in 25 mL $CHCl_3$ and treated with a few drops of NaOH (0.5 N). The $CHCl_3$ layer was washed with demineralized water, dried over anhydrous K_2CO_3, filtered, and evaporated in vacuo to give a crude alkaloidal mixture (1.18 g). This residue was subjected to column chromatography on Si gel (35 g) eluting with a gradient system of cyclohexane, chloroform, methanol, and diethylamine (5%), starting with cyclohexane−chloroform−diethylamine (18:2:1). In all, 31 fractions of 50 mL each were collected. Preparative TLC on Si gel [cyclohexane−chloroform−diethylamine (5:4:1)] was carried out for each of fractions 8−17, which were eluted with chloroform−diethylamine (20:1) to chloroform−methanol−diethylamine (19:1:1). Fractions showing the same spots were combined for further separation. Fractions 15−17 yielded pure compound **9** (16 mg). Repeated preparative TLC of fractions 12−17 on aluminum oxide plates [cyclohexane−chloroform−ethanol (24:75:1)] gave **5** (90 mg), **6** (12 mg), and **7** (15 mg). Alkaloids **8** (16 mg), **11** (9 mg), and **10** (6 mg) were isolated by repeated preparative TLC of fractions 10−14 on Si gel and aluminum oxide plates [cyclohexanes−ethyl acetate−ethanol (6:3:1)]. Similarly, alkaloids **4** (5 mg), **3** (3.3 mg), **2** (2.9 mg), **1** (5 mg), and **12** (1.7 mg) were isolated by repeated preparative TLC of fractions 8−10 and 15−17 on Si gel and aluminum oxide plates.



	R_1	R_2	R_3	R_4
2	CH_3	H	$COCH(CH_3)_2$	A
3	CH_3	H	$COCH(CH_3)_2$	B
4	H	CH_3	Ac	CH_3
5	CH_3	H	CH_3	A
6	CH_3	H	H	A
7	CH_3	H	CH_3	B
8	H	CH_3	H	CH_3
9	H	H	H	CH_3
10	CH_3	H	H	B
11	CH_3	H	Ac	A
12	CH_3	H	Ac	B



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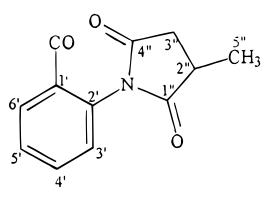

A

14-Demethyltuguaconitine (1): crystals (acetone−ether), mp 208−210 °C; $[\alpha]^{20}_D$ +59.5° (*c* 0.337, $CHCl_3$); ^{1}H NMR δ 1.08 (3H, t, *J* = 7.2 Hz, *N*-Et), 3.38, 3.42 (3H each, s, 2 × OCH_3), 3.87 (1H, s, H-1β), 3.94 (1H, br s, H-6α), 4.13 (1H, m, H-14β), 2.87 (1H, s, H-17), 2.55, 2.76 (2H, d, *J* = 10 Hz, H-19); ^{13}C NMR, see Table 1; LCQ MS *m*/*z* 446.3 $[M + Na]^+$ (7), 424.3 $[M + H]^+$ (62), 406 (4), 392 (100), 374 (26), 360 (16), 356 (17), 346 (33), 342 (16), 324 (10), 314 (39), 306 (4).

14-Deacetyl-14-isobutyrylnudicauline (2): amorphous; $[\alpha]^{20}_D$ +26.7° (*c* 0.235, $CHCl_3$); ^{1}H NMR δ 1.08 (3H, t, *J* = 6.9 Hz, *N*-Et), 3.28, 3.30, 3.35 (3H each, s, 3 × OCH_3), 1.46 (3H, br, H-5″), 2.54 (1H, m, isobutyryl group), 1.18 [6H, d, *J* = 7.0 Hz, $CH(CH_3)_2$], 2.46, 2.62 (2H, d, *J* = 11.9 Hz, H-19), 3.84 (2H, d, *J* = 14.9 Hz, H-18), 4.76 (1H, br t, *J* = 4.7 Hz, H-14β), 4.09 (1H, s, H-6α); ^{13}C NMR, see Table 1; LCQ MS *m*/*z* 761.7 $[M + Na]^+$ (17), 739.8 $[M + H]^+$ (100), 707 (9), 689 (6), 675 (5), 456 (5).

14-Deacetyl-14-isobutyrylajadine (3): amorphous; $[\alpha]^{20}_D$ +22.9° (*c* 0.314, $CHCl_3$); ^{1}H NMR δ 1.08 (3H, t, *J* = 7.0 Hz, *N*-Et), 1.18 [6H, d, *J* = 7.0 Hz, $CH(CH_3)_2$], 2.24 (3H, s, *N*$HCOCH_3$), 2.47, 2.75 (2H, d, *J* = 12.8 Hz, H-19), 2.54 (1H, m, isobutyryl group), 3.28, 3.32, 3.38 (each 3H, s, 3 × OCH_3), 3.91 (1H, s, H-6α), 4.18 (2H, dd, *J* = 11.3, 17.5 Hz, H-18), 4.77 (1H, br t, *J* = 4.7 Hz, H-14β), 10.98 (1H, br s, *N*H), ^{13}C NMR, see Table 1; LCQ MS *m*/*z* 685 $[M + H]^+$ (100), 653 (100), 621 (43), 603 (25), 575 (17), 442 (27).

Delbonine (4): amorphous; ^{1}H NMR δ 1.09 (3H, t, *J* = 7.2 Hz, *N*-Et), 2.07 (3H, s, OAc), 3.33 (3H, s, OCH_3), 3.37 (9H, s, 3 × OCH_3), 3.67 (1H, br s, H-1β), 3.15 (1H, d, *J* = 8.9 Hz, H-18α), 4.80 (1H, br t, *J* = 4.6 Hz, H-14β), 2.92 (2H, m, H-20), 3.83 (1H, s, H-6α), 2.81 (1H, s, H-17); ^{13}C NMR, see Table 1; LCQ MS *m*/*z* 510.4 $[M + H]^+$ (66), 492 (30), 478 (50), 460 (100), 428 (73), 400 (57), 368 (49).

Methyllycaconitine (5): amorphous; ^{1}H NMR δ 1.07 (3H, t, *J* = 7.2 Hz, *N*-Et), 3.25, 3.34, 3.35, and 3.40 (each 3H, s, 4 × OCH_3), 1.47 (3H, br, H-5″), 3.60 (1H, br t, *J* = 4.6 Hz, H-14β), 3.87 (1H, s, H-6α), 4.08 (2H, d, *J* = 4.5 Hz, H-18); ^{13}C NMR data were identical with those published in the literature;[12] LCQ MS *m*/*z* 683.4 $[M + H]^+$ (100), 665 (20), 651 (100), 633 (18), 619 (54), 587 (14), 354 (8).

14-Deacetylnudicauline (6): amorphous; ^{1}H NMR δ 1.06 (3H, t, *J* = 7.1 Hz, *N*-Et), 3.25 (3H, s, OCH_3), 3.36 (6H, s, 2 × OCH_3), 3.85 (1H, s, H-6α), 1.46 (3H, br, H-5″), 2.86 (2H, m, H-20), 4.0 (1H, m, H-14β), 7.28−8.05 (aromatic hydrogens); ^{13}C NMR data, identical with previous published data;[5] LCQ MS *m*/*z* 669.4 $[M + H]^+$ (100), 651 (28), 637 (100), 619 (18), 605 (60), 573 (10), 372 (18).

Ajacine (7): crystals (acetone−ether), mp 143−144 °C (lit.[13] 142−143 °C); ^{1}H NMR δ 1.09 (3H, t, *J* = 7.0 Hz, *N*-Et), 2.24 (3H, s, *N*$HCOCH_3$), 3.27, 3.35, 3.39, 3.44 (each 3H, s, 4 × OCH_3), 3.64 (1H, br t, H-14β), 2.84 (2H, m, H-20), 3.91 (1H, s, H-6α), 10.99 (1H, br s, *N*H); ^{13}C NMR data, identical with published data;[12] LCQ MS *m*/*z* 629.3 $[M + H]^+$ (100), 611 (12), 597 (100), 579 (22), 565 (48), 547 (32), 386 (22).

Deltatsine (8): amorphous; ^{1}H NMR δ 1.09 (3H, t, *J* = 7.1 Hz, *N*-Et), 2.64 (2H, d, *J* = 8.8 Hz, H-19), 3.36 (3H, s, OCH_3), 3.40 (6H, s, 2 × OCH_3), 3.47 (3H, s, OCH_3), 3.66 (1H, br s, H-1β), 3.85 (1H, s, H-6α), 4.0 (1H, m, H-14β), 2.83 (1H, s, H-17), 2.92 (2H, m, H-20); ^{13}C NMR data were identical with published data;[11] LCQ MS *m*/*z* 468.5 $[M + H]^+$ (100), 450 (25), 436 (50), 418 (100), 404 (18), 386 (75), 354 (18).

Delcosine (9): crystals (acetone−ether), mp 204−206 °C (lit.[13] 203−204 °C); ^{1}H NMR δ 1.11 (3H, t, *J* = 7.2 Hz, *N*-Et), 3.33 (3H, s, OCH_3), 3.37 (6H, s, 2 × OCH_3), 3.68 (1H, br s, H-1β), 4.02 (1H, s, H-6α), 2.94 (2H, m, H-20), 4.12 (1H, m, H-14β); ^{13}C NMR data, identical with published data;[12] LCQ MS *m*/*z* 476.4 $[M + Na]^+$ (25), 454.4 $[M + H]^+$ (50), 436 (30), 422 (22), 404 (100), 372 (35), 354 (10).

14-Deacetylajadine (10): crystals (acetone−ether), mp 106−110 °C (lit.[9] 121.3−122.2 °C); ^{1}H NMR δ 1.1 (3H, t, *J* = 7.1 Hz, *N*-Et), 2.24 (3H, s, *N*$HCOCH_3$), 3.30, 3.39, 3.40 (each 3H, s, 3 × OCH_3), 3.89 (1H, s, H-6α), 4.0 (1H, m, H-14β), 10.99 (1H, br s, *N*H); ^{13}C NMR data, identical with reported data;[9] LCQ MS *m*/*z* 637.4 $[M + Na]^+$ (8), 615.4 $[M + H]^+$ (100), 597 (10), 583 (100), 565 (38), 551 (60), 372 (48).

Nudicauline (11): amorphous; ^{1}H NMR δ 1.06 (3H, t, *J* = 6.9 Hz, *N*-Et), 2.06 (3H, s, OAc), 3.26, 3.33, 3.35 (each 3H, s, 3 × OCH_3), 4.75 (1H, br t, *J* = 4.5 Hz, H-14β), 4.09 (1H, s,

H-6α); ^{13}C NMR data, identical with published data;[14] LCQ MS *m*/*z* 733.3 $[M + Na]^+$ (100), 711.4 $[M + H]^+$ (55), 693 (13), 679 (100), 661 (20), 647 (50), 414 (19).

Ajadine (12): crystals (acetone−ether), mp 126−128 °C (lit.[13] 134−136 °C); ^{1}H NMR δ 1.08 (3H, t, J = 7.1 Hz, *N*-Et), 2.07 (3H, s, OAc), 3.27, 3.34, 3.37 (3H each, s, 3 × OCH_3), 2.24 (3H, s, *N*H$COCH_3$), 2.47, 2.70 (2H, d, J = 11.9 Hz, H-19), 2.97 (1H, br s, H-1β), 3.91 (1H, s, H-6α), 4.18 (2H, dd, J = 11.33, 16.7 Hz, H-18), 4.76 (1H, br t, J = 4.85 Hz, H-14β), 10.99 (1H, br s, *N*H); ^{13}C NMR data, identical with reported data;[15] LCQ MS *m*/*z* 657.3 $[M + H]^+$ (100), 639 (3), 625 (100), 607 (19), 593 (41), 579 (23), 575 (32), 565 (3), 533 (6), 519 (5), 501 (2), 414 (24).

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