New Access to 7,17-*Seco* Norditerpenoid Alkaloids *via* Reduction of the Corresponding 8-Chloro Derivatives

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New access to the 7, 17-*seco* norditerpenoid alkaloids 9 (60%) from yunnaconitine (5), as well as 14 (46%) and 15 (22%) from isotalatizidine (10), *via* selective hydrolysis, chlorination and reduction with $NaBH_4$ is described.

Key words norditerpenoid alkaloid; 7,17-*seco* norditerpenoid alkaloid; yunnaconitine; isotalatizidine

The norditerpenoid alkaloids are a group of highly oxygenated and complex natural products. Apart from analgesic, local anesthetic, anti-inflammatory and antiarrhythmetic activities,[1)] these alkaloids afford novel derivatives.[2)] In order to search for more active, less toxic compounds, we have carried out structural modifications of the norditerpenoid alkaloids since 1986.[3)] One of the key reactions of the aconitine-type norditerpenoid alkaloid is cleavage of the C(7)–C(17) bond. The reactions of these type of alkaloids *via*: pyrolysis of *N*-oxides,[3b,4)] pyrolysis-reduction,[5a)] photolysis-reduction,[6)] rearrangement-reduction,[7)] oxidation-reduction[5b,8)] and neighboring group participation[9)] have been summarized. However, most of them led to complicated products with low yields[7)] or difficult purification.[3b)] Recently, we reported a new method for the preparation of the 7,17-*seco* norditerpenoid alkaloids *via* rearrangement of chloramine.[3k)] In this paper, we report in detail the cleavage of the C(7)–C(17) bond in the aconitine-type norditerpenoid alkaloids yunnaconitine (**5**) and isotalatizidine (**10**) by selective hydrolysis, chlorination and reduction with $NaBH_4$.

Results and Discussion

In 1987, Kulanthaivel and Pelletier[10)] reported a method for the cleavage of the C(11)–C(17) bond in the lycoctonine-type norditerpenoid alkaloid deltaline (**1**) (Fig. 1). Srivastava, *et al*. reported that an 11,17-*seco* compound **4** is obtained by the treatment of **2**, which has an anti-periplanar relationship between the lone pair of the nitrogen atom and the C(10)–Cl bond ($MeOH/H_2O$).[11)] Observation of the Dreiding model of the norditerpenoid alkaloids showed that both C(8)–Cl and C(10)–Cl bonds are located similarly to the lone electron pair of the nitrogen atom. We surmised that fragmentation of (**2**) gave (**3**) *via* pathway a (A_1). We have designed a method for the preparation of 7,17-*seco* compounds starting from yunnaconitine (**5**), probably proceeding by pathway b (B_1) (Fig. 2).

Heating yunnaconitine (**5**) with Ac_2O/TsOH afforded **6** (99% yield), and refluxing **6** in diglyme–H_2O (4 : 1) gave **7** (90% yield). The ^1H (^{13}C)-NMR spectra of **7** showed the non signal of the 8-OAc group. Reaction of **7** in dry benzene with freshly distilled $SOCl_2$ at room temperature afforded a major product (*Rf*, 0.15), which is probably an intermediate **8** (Fig. 3), followed by treatment with $NaBH_4$/MeOH, which gave a white powder in 60% yield in addition to other minor products. Its MS spectrum displayed a molecular ion peak at *m*/*z* 685, and the formula $C_{37}H_{51}NO_{11}$ was established by the HRFAB-MS spectrum. The ^1H- and ^{13}C-NMR spectra of the compound showed a characteristic trisubstituted double bond (δ_H 5.67, 1H, br s; δ_C 126.5 d, 132.4 s). Its structure was deduced to be **9** by careful analysis of its 2D-NMR data (^1H–^1H COSY, HMQC, HMBC) (Table 1). In addition, in the NOE experiments of **9**, enhancement of the signal at δ 2.64 ppm (H_2-15) was observed when the H-7 signal at δ 5.67 ppm was irradiated.

Similarly, acetylation of **10** with Ac_2O–TsOH gave the compound **11**, and selective hydrolysis of **11** afforded compound **12**, which was treated with $SOCl_2$; then the possible intermediate **13** formed (Fig. 4) was subsequently reduced with $NaBH_4$ to give a residue. Chromatographic separation of the reaction products on a Chromatotron gave compounds **14** and **15** (Fig. 4). Compound **14** was obtained as an amorphous powder, $C_{27}H_{41}NO_6$ (HRFAB-MS). The ^1H- and ^{13}C-NMR spectra of **14** showed a trisubstituted double bond (δ_H 5.37, 1H, d, J=6.8 Hz, H-7; δ_C 123.7 d, C-7; 135.2 s, C-8), and its structure was confirmed on the basis of 2D-NMR data (Table 2). Compound **15** was also obtained as a white amorphous powder, $C_{26}H_{37}NO_5$ (HRFAB-MS). Compared with compound **14**, the ^1H- and ^{13}C-NMR spectra of compound **15** are similar, except for a conjugated diene moiety (δ_H 5.54,

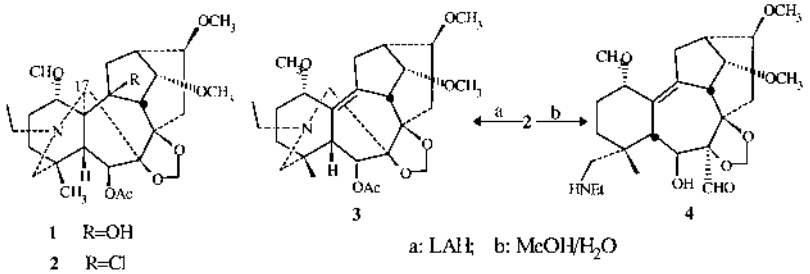

Fig. 1

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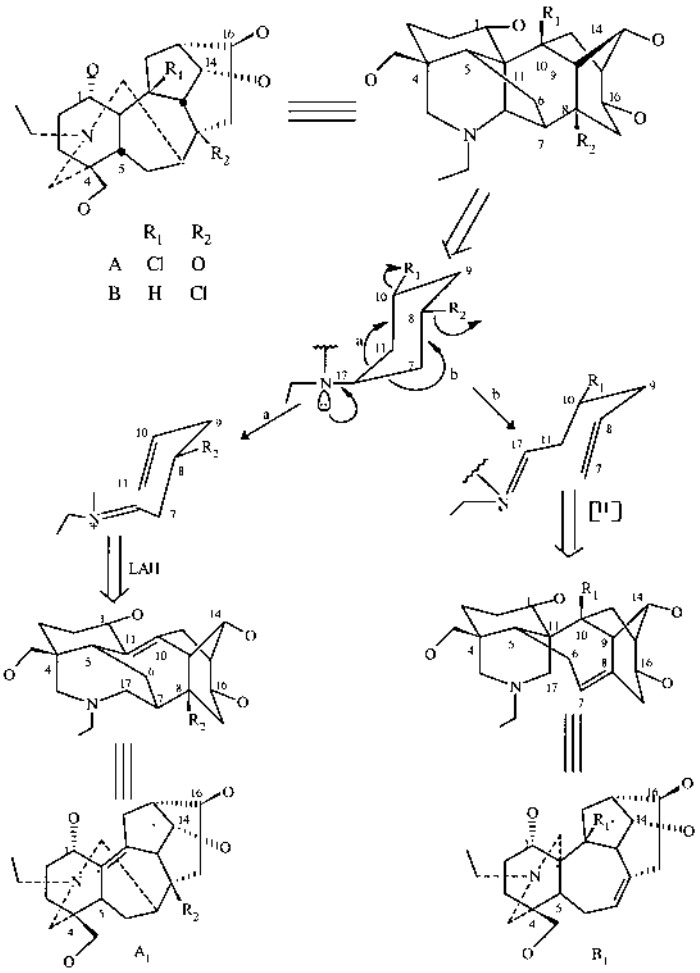

Fig. 2

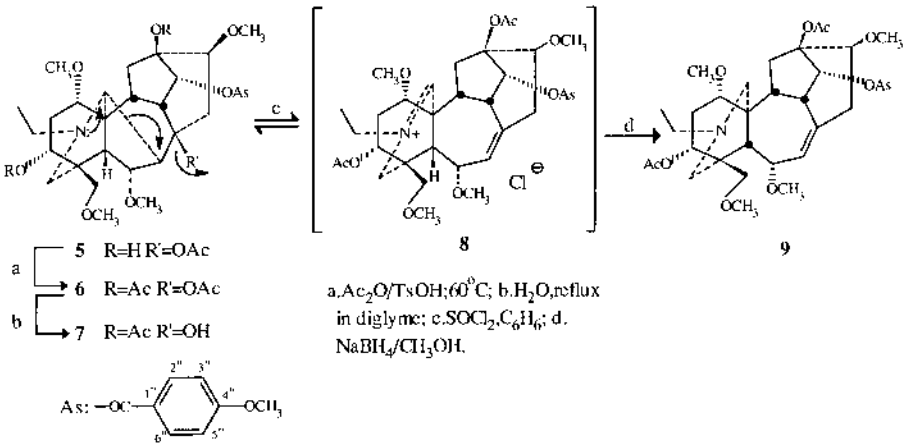

Fig. 3

1H, t, J=7.2 Hz, H-7; 6.24, 1H, d, J=7.2 Hz, H-15; 5.84, 1H, t, J=7.2 Hz, H-16; δ_C 125.5 d, C-7; 137.3 s, C-8; 129.2 d, C-15; 129.5 d, C-16) and only one methoxyl group (δ_H 3.29, 3H, s; δ_C 59.0 q), as well as some C-13 signals, such as C-12, C-14 and C-17. Finally, its structure **15** was confirmed based on its 2D-NMR data (Table 3) and NOE experiments.

Treatment of **12** with $SOCl_2$ (MeOH/H_2O, 40°C, 5 h)[12] or refluxing in 10% HCl solution gave the compound **16** (20% yield) and the starting material **10**, instead of the expected 7,17-*seco* products, respectively.

In summary, preparation of the 7,17-*seco* norditerpenoid alkaloids *via* reducing the corresponding probable 8-chloro derivatives with $NaBH_4$ in moderate yield is a novel method.

Experimental

General. Experimental Procedures ^{1}H- and ^{13}C-NMR spectra were acquired on a Bruker AC-E200 or a Varian INOVA-400/54 spectrometer. IR spectra were recorded on a Nicolet FT-IR 20BXB spectrometer. EIMS and FABMS were obtained with a VG Auto-spec 3000 mass spectrometer, and

Table 1. ^{1}H- and ^{13}C-NMR Data of Compound **9**

No.	δ_H	Mult (J=Hz)	δ_C	HMBC (H→C)
1	2.91	dd (7.2, 6.4)	84.3 d	17, 1′
2	2.50 (a)/2.80 (e)	m/m	31.4 t	1, 3, 11/1, 3
3	4.97	dd (11.6, 6.8)	72.0 d	4, 19
4	—	—	42.3 s	—
5	1.60	br s	40.8 d	1, 3, 4, 11
6	4.20	br s	79.3 d	
7	5.67	br s	126.5 d	5, 9
8	—	—	132.4 s	—
9	3.11	m	40.7 d	10, 11, 13
10	2.70	m	41.4 d	9, 11, 12
11	—	—	42.5 s	—
12	2.10 (a)/2.35 (e)	m/m	38.8 t	11, 16/11, 14, 16
13	—	—	83.7 s	—
14	5.20	br s	80.9 d	13
15	2.64 (a)/3.00 (e)	dd (12.0, 8.4)/ (hidden)	39.5 t	9, 13/9, 16
16	4.03	t (8.0)	82.6 d	12, 1, 14, 15, 16′
17	2.50	(hidden)	50.9 d	10, 11
18	3.10	(hidden)	71.9 t	3, 4
19	2.27/2.65	(hidden)	50.0 t	4′, 21/4, 5, 17, 18
$N\underline{CH_2}CH_3$	2.20/2.30	m/m	51.6 t	17, 19/22
$NCH_2\underline{CH_3}$	0.98	t (6.8)	11.8 q	17, 19, 21
1′	3.40	s	57.8 q	
6′	3.39	s	55.8 q	16
16′	3.35	s	57.5 q	
18′	3.20	s	58.8 q	18
3-OAc	2.05	s	170.1 s/21.3 q	
13-OAc	2.06	s	170.5 s/21.1 q	
COO	—	—	165.9 s	
1″	—	—	122.6 s	
2″, 6″	8.05	AA′BB′ (9.0)	131.8 d	3″, 4″, 5″, COO
3″, 5″	6.93	AA′BB′ (9.0)	113.5 d	1″, 4″
4″	—	—	163.3 s	
4″-OCH_3	3.85	s	55.3 q	

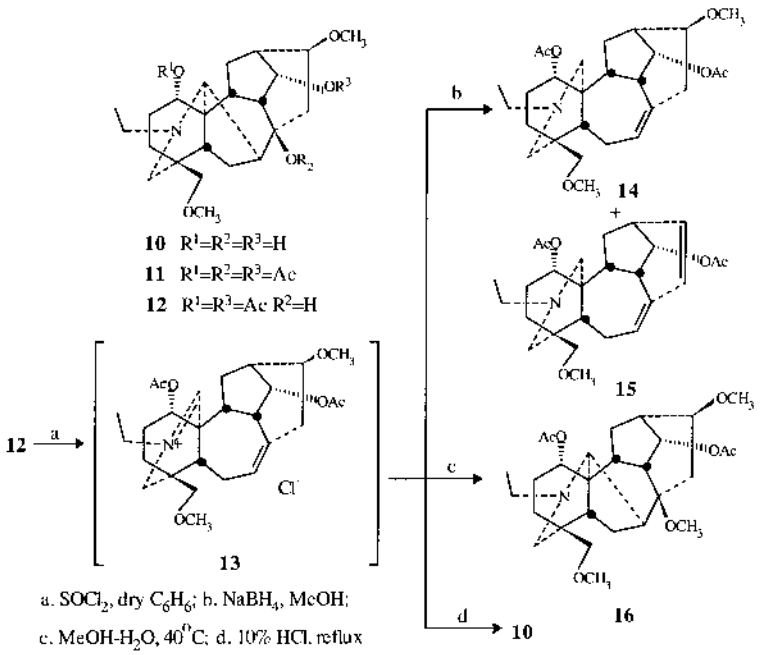

Fig. 4

TLC was performed on silica gel GF_{254} precoated plates sprayed with a modified Dragendorff's reagent for detection. Column chromatography was performed using silica gel H. Chromatographic separations on a Chromatotron were carried out on rotors coated with 1mm thick layers of silica gel H and 0.5% CMC. All of the silica gel GF_{254} and silica gel H in the experimental were purchased from Qingdao Sea Chemical Factor, People's Republic of China.

Compound 6 To a solution of yunnaconitine (**5**) (200 mg, 0.3 mmol) in

Table 2. ^{1}H- and ^{13}C-NMR Data of Compound **14**

No.	δ_H	Mult (J=Hz)	δ_C	HMBC (H→C)
1	4.53	dd (11.2, 5.6)	85.3 d	17, 1-O<u>C</u>OCH$_3$
2	1.72 (a)/2.69 (e)	m/m	27.1 t	1, 3
3	1.60	m	33.3 t	1, 2, 4, 5, 18
4	—	—	39.1 s	—
5	1.88	dd (10.4, 5.6)	38.6 d	1, 3, 4, 6, 7, 17
6	2.11 (a)/2.39 (e)	d (10.8)	24.1 t	5, 7, 8
7	5.37	d (6.8)	123.7 d	5, 9
8	—	—	135.2 s	—
9	3.03	m	42.2 d	14
10	1.64	m	43.4 d	5, 8, 9, 11, 12
11	—	—	40.6 s	—
12	1.13	m	29.4 t	10, 11, 13, 14, 16
13	2.57	m	35.7 d	9, 10, 12, 14, 15, 16
14	4.69	t (4.0)	76.2 d	8, 9, 13, 16, 14-O<u>CO</u>CH$_3$
15	*ca.* 1.80 (a)/2.47 (e)	m/m	34.0 t	8, 9, 13, 16/7, 8, 9,16
16	3.25	m	83.9 d	12, 14, 15, 16, 16′
17	2.1/2.79	ABq (11.2)	52.4 t	1, 11, 20/1, 5, 11, 20
18	2.95/3.15	ABq (9.2)	78.35 t	3, 4, 5, 18
19	2.16	(hidden)	52.2 t	17
N<u>CH$_2$</u>CH$_3$	2.29	q (7.2)	54.2 t	17, 19, 22
NCH$_2$<u>CH$_3$</u>	1.00	t (6.8)	12.0 q	17, 19 (^4J)
16′	3.23	s	55.6 q	16
18′	3.26	s	59.0 q	18
1-OAC	1.99	s	170.3 s, 21.3 q	
14-OAC	2.03	s	170.9 s, 21.0 q	

Table 3. ^{1}H- and ^{13}C-NMR Data of Compound **15**

No.	δ_H	Mult (J=Hz)	δ_C	HMBC (H→C)
1	4.60	dd (11.6, 6.0)	84.9 d	1′
2	1.70 (a)/2.60 (e)	m/m	27.0 t	1, 3, 4, /1, 3
3	1.63	m	33.6 t	1, 4, 5
4	—	—	39.6 s	—
5	1.95	m	41.6 d	4, 10, 17
6	2.75	m	23.3 t	7, 8
7	5.54	t (7.2)	125.5 d	15
8	—	—	137.3 s	—
9	3.25	m	42.8 d	8, 12
10	2.05	m	41.9 d	8, 9, 12
11	—	—	41.8 s	—
12	1.60	m	32.7 t	10, 13, 14, 16
13	2.65	m	36.2 d	15, 16
14	4.77	t (4.4)	73.7 d	8, 16, 14′
15	6.24	d (7.2)	129.2 d	7, 8
16	5.84	d (7.2)	129.5 d	8
17	2.16/2.78	ABq (11.6)	55.0 t	1, 10
18	2.96/3.25	ABq (9.2)	79.1 t	4, 19
19	2.18/2.48	ABq (10.4)	51.2 t	4, 5
N<u>CH$_2$</u>CH$_3$	2.29	q (6.8)	52.0 t	19
NCH$_2$<u>CH$_3$</u>	0.99	t (6.8)	11.9 q	21
18′	3.29	s	59.0 q	18
1-OAc	2.03	s	170.2 s, 21.5 q	
14-OAc	2.01	s	170.9 s, 21.0 q	

EtOAc (6 ml), TsOH (200 mg, 1.15 mmol) was added, and the solution was maintained at 60 °C for 3 h. After the work-up, compound **6** (210 mg, 99% yield) was obtained as an amorphous powder: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 1.09 (3H, t, J=7.0 Hz, <u>N</u>–CH$_2$<u>CH$_3$</u>), 1.29 (3H, s, 8-OAc), 2.02, 2.04 (each 3H, s, 2×OAc), 3.16, 3.17, 3.21, 3.36, 3.84 (each 3H, s, 5×OCH$_3$), 4.86 (1H, dd, J=10.0, 8.0 Hz, H-3β), 5.05 (1H, d, J=5.0 Hz, H-14β), 6.90, 8.02 (each 2H, AA′BB′ system, J=9.0 Hz, Ar-H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 81.4 (d, C-1), 31.7 (t, C-2), 71.3 (d, C-3), 42.2 (s, C-4), 46.0 (d, C-5), 79.8 (d, C-6), 43.5 (d, C-7), 85.1 (s, C-8), 48.9 (d, C-9), 40.9 (d, C-10), 49.8 (s, C-11), 35.1 (t, C-12), 81.8 (s, C-13), 76.6 (d, C-14), 39.4 (t, C-15), 83.2 (d, C-16), 61.0 (d, C-17), 71.5 (t, C-18), 48.8 (t, C-19), 55.9 (q, C-1′), 57.9 (q, C-6′), 57.9 (q, C-16′), 58.6 (q, C-18′), 47.4 (t, <u>N</u>CH$_2$), 13.2 (q, <u>N</u>–CH$_2$<u>CH$_3$</u>), 170.1 (s), 170.1 (s), 169.6 (s); 21.4 (q), 21.3 (q), 21.2 (q) (3×OAc); 165.8 (s, Ar–*COO*), 122.3 (s, C-1″), 131.7 (d, C-2″, 6″), 113.6 (d, C-3″, 5″), 163.3 (s, C-4″), 55.2 (q, 4″-OCH$_3$); EI-MS *m/z*: 743 [M$^+$] (5), 712 [M−OCH$_3$] (100), 684 (73), 652 (52), 135 (98); HREI-MS *m/z*: 743.3489 (Calcd for $C_{39}H_{53}NO_{13}$, 743.3514).

Compound 7 Compound **6** (380 mg, 0.51 mmol) was dissolved in diglyme–H_2O (4 : 1, 10 ml). The solution was refluxed for 6 h, then evaporated to dryness under reduced pressure to give a residue, which was chromatographed on a SiO_2 column (26 g) and eluted with $CHCl_3$–CH_3OH (95 : 5) to afford amorphous **7** (322 mg, 90% yield). ^{1}H-NMR ($CDCl_3$, 200

MHz) δ: 1.11 (3H, t, J=7.0 Hz, N–CH_2CH_3), 1.99, 2.05 (each 3H, s, 2×OAc), 3.19, 3.21, 3.26, 3.30, 3.84 (each 3H, s, 5×OCH_3), 4.88 (1H, t, J=7.0 Hz, H-3β), 5.44 (1H, d, J=5.0 Hz, H-14β), 6.92, 8.03 (each 2H, AA′BB′ system, J=9.0 Hz, Ar-H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 81.6 (d, C-1), 31.4 (t, C-2), 71.6 (d, C-3), 42.3 (s, C-4), 46.1 (d, C-5), 79.1 (d, C-6), 46.0 (d, C-7), 73.3 (s, C-8), 53.6 (d, C-9), 42.0 (d, C-10), 49.8 (s, C-11), 35.2 (t, C-12), 83.0 (s, C-13), 76.7 (d, C-14), 42.2 (t, C-15), 82.6 (d, C-16), 61.4 (d, C-17), 71.7 (t, C-18), 48.9 (t, C-19), 55.9 (q, C-1′), 57.5 (q, C-6′), 57.6 (q, C-16′), 58.7 (q, C-18′), 47.8 (q, N–CH_2), 14.0 (q, N–CH_2CH_3), 170.2 (s), 170.3 (s); 21.0 (q), 21.3 (q) (2×OAc); 165.5 (s, Ar–*COO*), 122.2 (s, C-1″), 131.8 (d, C-2″, 6″), 113.5 (d, C-3″, 5″), 163.3 (s, C-4″), 55.2 (q, 4″-OCH_3). EI-MS m/z: 701 $[M]^+$ (2), 670 $[M-OCH_3]^+$ (97), 610 (85), 135 (100); HREI-MS m/z: 701.3378 (Calcd for $C_{37}H_{51}NO_{12}$, 701.3411).

Compound 9 Compound **7** (200 mg, 0.28 mmol) was dissolved in benzene (10 ml). To the solution, $SOCl_2$ (2 ml, 2.8 mmol) was added, maintained for 10 h, and evaporated to dryness under reduced pressure to give a residue (210 mg) which was dissolved in methanol (5 ml). To the solution, $NaBH_4$ (200 mg) was added on an ice-bath, and the mixture was allowed to sit for 30 min. Evaporation under reduced pressure gave a residue. It was chromatographed on a SiO_2 (25 g) column and eluted with $CHCl_3$–MeOH (98 : 2) to afford amorphous **9** (112 mg, 60% yield). IR (KBr) ν_{max} 3000, 1740, 1730, 1620, 1260, 780 cm^{-1}; ^{1}H ($CDCl_3$, 400 MHz) and ^{13}C- ($CDCl_3$, 100 MHz) NMR spectra, see Table 1; The NOE experiments: the enhancement of the $H_{(a)}$-15 at δ 2.64 ppm was observed when irradiating the H-7 at δ 5.67 ppm; EI-MS m/z: 685 $[M]^+$ (29), 626 $[M-59]^+$ (23), 534 (45), 135 (100); HRFAB-MS m/z: 686.3590 (Calcd for $C_{37}H_{52}NO_{11}$ 686.3590).

Compound 11 Isotalatizidine (**10**) (1.2 g, 2.5 mmol) was dissolved in the mixture of Ac_2O (15 ml) and TsOH (1.2 g). The solution was kept at 60 °C for 6 h, and usual work-up gave **11** (1.28 g, 96%) as an amorphous powder; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 1.02, (3H, t, J=7.1 Hz, N–CH_2CH_3), 1.90, 1.95, 1.98 (each 3H, s, 3×OAc), 3.21, 3.24 (each 3H, s, 2×OCH_3), 4.67 (1H, t, J=4.8 Hz, H-14β), 4.83 (1H, dd, J=10.2, 6.8 Hz, H-1β); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 74.6 (d, C-1), 27.4 (t, C-2), 32.2 (t, C-3), 38.0 (s, C-4), 45.9 (d, C-5), 24.6 (t, C-6), 42.1 (d, C-7), 85.4 (s, C-8), 41.6 (d, C-9), 43.8 (d, C-10), 47.6 (s, C-11), 28.4 (t, C-12), 37.9 (d, C-13), 77.7 (d, C-14), 37.3 (t, C-15), 82.8 (d, C-16), 60.7 (d, C-17), 79.0 (t, C-18), 53.1 (t, C-19), 56.3 (q, C-16′), 59.2 (q, C-18′), 48.6 (t, NCH_2), 13.2 (q, NCH_2CH_3), 169.5 (s), 170.2 (s), 170.7 (s); 21.0 (q), 21.8 (q), 22.2 (q) (3×OAc); EI-MS m/z: 533 $[M]^+$ (5), 474 [M−59] (100), 432 (50), 414 (28), 400 (28); HREI-MS m/z: 533.2953 (Calcd for $C_{29}H_{43}NO_8$ 533.2988).

Compound 12 Compound **11** (535 mg, 1.0 mmol) was dissolved in diglyme–H_2O (4 : 1, 20 ml). The solution was refluxed for 6 h and evaporated to dryness under reduced pressure to give a residue which was chromatographed on a SiO_2 (20 g) column and eluted with $CHCl_3$–MeOH (98 : 2) to afford compound **12** (419 mg, 85% yield). Compound **12**: IR (KBr) ν_{max} 1742 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 1.07 (3H, t, J=7.2 Hz, NCH_2CH_3), 2.02, 2.03 (each 3H, s, 2×OAc), 3.21, 3.27 (each 3H, s, 2×OCH_3), 4.75 (1H, t, J=4.6 Hz, H-14β), 4.89 (1H, dd, J=10.1, 6.7 Hz, H-1β); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 76.2 (d, C-1), 27.2 (t, C-2), 32.2 (t, C-3), 38.2 (s, C-4), 45.0 (d, C-5), 24.8 (t, C-6), 46.0 (d, C-7), 73.3 (s, C-8), 45.9 (d, C-9), 43.8 (d, C-10), 47.4 (s, C-11), 27.9 (t, C-12), 34.9 (d, C-13), 78.0 (d, C-14), 40.6 (t, C-15), 81.5 (d, C-16), 61.1 (d, C-17), 79.1 (t, C-18), 53.2 (t, C-19), 56.0 (q, C-16′), 59.3 (q, C-18′), 48.7 (t, N–CH_2CH_3), 13.2 (q, N–CH_2CH_3), 170.3 (s), 170.4 (s); 21.2 (q), 21.8 (q) (2×OAc); EI-MS: m/z: 491 $[M]^+$ (5), 432 $[M-59]^+$ (100), 400 (45); HREI-MS m/z: 491.2832 (Calcd for $C_{27}H_{41}NO_7$ 491.2883).

Compounds 14 and 15 Compound **12** (400 mg, 0.81 mmol) was dissolved in benzene (10 ml). To the solution, $SOCl_2$ (2 ml, 8.1 mmol) was added; the mixture sat for 12 h, and was evaporated to dryness under reduced pressure to give a residue (408 mg) which was dissolved in MeOH (10 ml). To the solution, $NaBH_4$ (300 mg) was added in an ice bath, and it sat for 30 min. Work-up gave a residue, which was chromatographed on a Chromatotron (SiO_2 G) and eluted with petroleum ether–acetone (91 : 9) to give compounds **14** (212 mg, 46% yield) and **15** (95 mg, 22% yield). Compound **14**: IR (KBr) ν_{max} 3480, 3000, 1740, 1260 cm^{-1}; ^{1}H- ($CDCl_3$, 400 MHz) and ^{13}C- ($CDCl_3$, 100 MHz) NMR spectra, see Table 2; EIMS: m/z: 475 $[M]^+$ (15), 432 (11), 416 (100), 400 (10); HRFAB-MS m/z: 476.3012 (Calcd for $C_{27}H_{42}NO_6$, 476.3012). Compound **15**: IR (KBr) ν_{max} 3460, 3000, 1740, 1650, 1250 cm^{-1}; ^{1}H- ($CDCl_3$ 400 MHz) and ^{13}C- ($CDCl_3$ 100 MHz) NMR spectra, see in Table 3; The NOEDS (400 MHz) experiments: enhancement of H-15 (δ 6.24 ppm) and H-7 (δ 2.16 ppm) were observed in terms of irradiating the H-7 and H-15, respectively; EI-MS m/z: 443 $[M]^+$ (37), 400 (100); HRFAB-MS m/z: 444.2749 (Calcd for $C_{26}H_{38}NO_5$, 444.2749).

Compound 16 Treatment of **13** (200 mg, 0.4 mmol) with $SOCl_2$ for 30 min as the above mentioned method gave a residue (200 mg) which was treated with MeOH–H_2O (5 : 1, 12 ml) at 50 °C for 6 h to afford the complex mixture. This was chromatographed on a Chromatotron (SiO_2 G) and eluted with ether–acetone (2 : 1) to give **16** (40 mg, 20% yield). IR (KBr) ν_{max} 1734 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 1.07, (3H, t, J=7.1 Hz, N–CH_2CH_3), 1.99, 2.02 (each 3H, s, 2×OAc), 3.10, 3.26, 3.31 (each 3H, s, 3×OAc), 4.66 (1H, t, J=4.6 Hz, H-14β), 4.88 (1H, dd, J=10.0, 8.0 Hz, H-1β); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 75.2 (d, C-1), 27.6 (t, C-2), 31.3 (t, C-3), 38.2 (s, C-4), 42.9 (d, C-5), 23.9 (t, C-6), 46.1 (d, C-7), 77.5 (s, C-8), 44.2 (d, C-9), 40.0 (d, C-10), 47.9 (s, C-11), 29.2 (t, C-12), 37.7 (d, C-13), 78.0 (d, C-14), 37.3 (t, C-15), 83.4 (d, C-16), 60.6 (d, C-17), 79.5 (t, C-18), 53.4 (t, C-19), 48.1 (q, C-8′), 56.2 (q, C-16′), 59.4 (q, C-18′), 48.6 (t, N–CH_2), 13.4 (q, N–CH_2CH_3), 170.3 (s), 171.4 (s); 21.2 (q), 21.9 (q, 2×OAc); EI-MS m/z: 505 $[M]^+$ (19), 490 [M−15] (10), 474 [M−31] (30), 447 (100), 446 [M−59] (85), 430 (40), 414 (35), 402 (29), 372 (24); HREI-MS m/z: 505.2962 (Calcd for $C_{28}H_{43}NO_7$, 505.3039).

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