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Note

Preparation of imine alkaloids from norditerpenoids alkaloids

Liming Gao[†], Shangzhen Zheng*[†], Xiaojiang Hao[‡], Xiaoxiong Wang[†] & Xuwei Shen[†]

[†]Department of Chemistry, Northwest Normal University, Lanzhou 730 070, P.R. China
[‡]Kunming Institute of Botany, Academia Sinica, Kunming 650 204, P.R. China

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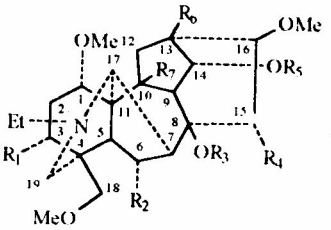
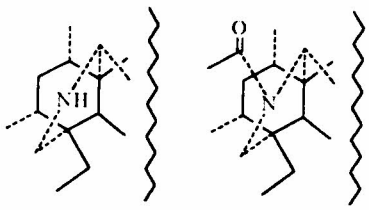
Oxidation of norditerpenoid alkaloids (yunconitine, crassiculine-A, talatisamine and 14-acetyltalatisamine) with $KMnO_4$ yields imine alkaloids **11–14**. Formation of the compounds **11–14** from norditerpenoid alkaloids is being reported for the first time.

Oxidation of norditerpenoid alkaloids with neutral $KMnO_4$, investigated by earlier workers[1-3], reveals the formation of different products. For examples, oxidation of indaconitine **1** with $KMnO_4$ in 80% aq. acetone yield the *N*-deethylation of secondary amines **8** (80%)[1]; as above, oxidation of aconitine **2** in CD_3COCD_3-D_2O(95:5) yield the acetamides **9** (13.8%)[2] and oxidation of aconifine **3** in 50% aq. acetone leads to the formation of lactams **10**[3]. But preparation of imines-type compounds have not been reported previously.

Unlike the earlier observation, oxidation of yunaconitine **4** with $KMnO_4$ (15 mol) gave compound **11** (34%), oxidation of crassiculine- A **5**, talatisamine **6** and 14-acetyltalatisamine **7** with the same $KMnO_4$ (10 mol) gave compounds **12** (82%), **13** (55%) and **14** (60%).

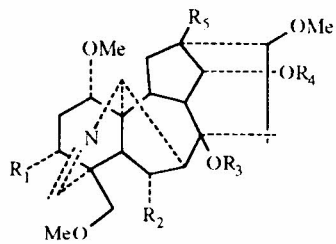
The absence of N-Et and the presence of N=CH moiety in the NMR spectra of above compounds indicated that they were imine alkaloids, just like bulleyanitine[4]. The method reported in this paper for obtaining imine alkaloids is a new method. The structures of imine alkaloids were determined on the basis of spectral data and compared with correlative compounds.

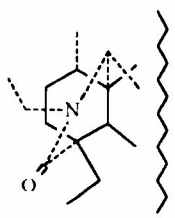




8 **9**

	R_1	R_2	R_3	R_4	R_5	R_6	R_7
1	OH	OCH_3	Ac	H	Bz	OH	H
2	OH	OCH_3	Ac	OH	Bz	OH	H
3	OH	OCH_3	Ac	OH	Bz	OH	OH
4	OH	OCH_3	Ac	H	As	OH	H
5	H	OCH_3	Ac	H	As	OH	H
6	H	H	H	H	H	H	H
7	H	H	H	H	Ac	H	H





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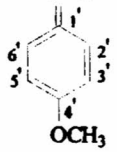
	R_1	R_2	R_3	R_4	R_5
11	OH	OCH_3	Ac	As	OH
12	H	OCH_3	Ac	As	OH
13	H	H	H	H	H
14	H	H	H	H	H

Experimental Section

Melting points are uncorrected. ^1H and ^{13}CNMR were recorded on Bruker AM-400 spectrometer using TMS as internal reference (chemical shifts in δ, ppm), mass spectra on a VG Auto SPEC- 3000 spectrometer and IR spectra on a Perkin-Elmer 577 spectrometer.

Reaction of yunaconitine with $KMnO_4$. To yunaconitine (1.2 g) in 50% aq. acetone (15 mL) was added $KMnO_4$ (4.5 g) portion wise and allowed the reaction to proceed at room temperature for 6 h, while stirring. The reaction mixture was then washed with

Table I—^{13}CNMR data of compounds **11-14** (in $CDCl_3$, 400 MHz, TMS)

C	**11**	12	**13**	**14**
1	83.36(CH)	81.73(CH)	83.05(CH)	83.36(CH)
2	33.12(CH_2)	24.83(CH_2)	25.25(CH_2)	25.11(CH_2)
3	71.27(CH)	34.22(CH_2)	27.18(CH_2)	27.04(CH_2)
4	50.22(C)	48.92(C)	48.53(C)	48.66(C)
5	43.40(CH)	37.84(CH)	37.72(CH)	36.0(CH)
6	80.13(CH)	82.64(CH)	23.71(CH_2)	24.42(CH_2)
7	43.40(CH)	43.82(CH)	45.79(CH)	44.95(CH)
8	84.14(C)	84.24(C)	72.06(C)	73.14(C)
9	53.45(CH)	54.13(CH)	45.11(CH)	44.25(CH)
10	40.90(CH)	40.76(CH)	41.67(CH)	41.72(CH)
11	51.69(C)	51.56(C)	49.51(C)	49.37(C)
12	34.75(CH_2)	32.98(CH_2)	27.30(CH_2)	28.30(CH_2)
13	76.68(C)	74.81(C)	52.83(CH)	53.26(CH)
14	78.50(CH)	77.97(CH)	75.18(CH)	76.69(CH)
15	38.25(CH_2)	38.89(CH_2)	38.05(CH_2)	40.41(CH_2)
16	83.36(CH)	83.44(CH)	81.68(CH)	81.49(CH)
17	61.56(CH)	59.14(CH)	62.09(CH)	62.19(CH)
18	77.86(CH_2)	79.56(CH_2)	75.18(CH_2)	75.78(CH_2)
19	165.48(CH)	162.33(CH)	169.11(CH)	164.40(CH)
C=O	169.54(C)	169.65(C)	—	170.57(C)
CH_3	21.51(CH_3)	21.49(CH_3)	—	21.23(CH_3)
1-OCH_3	55.74(CH_3)	55.38(CH_3)	56.13(CH_3)	56.03(CH_3)
6-OCH_3	58.76(CH_3)	58.67(CH_3)		
16-OCH_3	57.02(CH_3)	57.57(CH_3)	56.44(CH_3)	56.17(CH_3)
18-OCH_3	59.23(CH_3)	59.14(CH_3)	59.42(CH_3)	59.47(CH_3)
C=O	166.01(C)	165.93(C)		
	122.67(C)	122.52(C)		
	131.72(CH)	131.69(CH)		
OCH_3	113.80(CH)	113.60(CH)		
	163.55(C)	163.25(C)		
	113.80(CH)	113.60(CH)		
	131.72(CH)	131.69(CH)		
	55.40(CH_3)	55.59(CH_3)		

Multiplicities were determined from the DEPT experiments

$CHCl_3$ and H_2O. The solid that separated out was filtered. The remaining solution was extracted with $CHCl_3$ (3×10 mL) and dried over anhyd. Na_2SO_4 for 24 h. Crude extract was chromatographed on a column of silica H using pet.-acetone- diethylamine as eluent to give compound **11**.

Reaction of 5, 6 and 7 with $KMnO_4$. These reactions was carried out under similar conditions as above. Work-up of these reactions mixture followed by column chromatography gave compounds **12, 13** and **14**. All these compounds were white in colour and crystallised from pet.-acetone.

Compound 11. Yield 34%, $C_{33}H_{43}NO_{11}$, m.p. 227-28°; IR(KBr): 3460, 3385 (N=CH); MS: *m/z* 629(M^+), 614 (M^+-CH_3); ^{1}HNMR (400 MHz, $CDCl_3$): 1.27 (s, 3H,–CO–CH_3), 3.03, 3.17, 3.32, 3.50 and 3.82 (s, each 3H, 5×OCH_3), 4.08 (d, 1H, *J*=5 Hz, 6-βH), 4.86 (d, 1H, *J*=5.0 Hz, 14-βH), 7.44 (d, 1H, *J*=1 Hz, 19-H), 6.68, 7.96 (dd, 4H, J_1=J_2=9 Hz, Ar-H). For ^{13}CNMR see Table I.

Compound 12. Yield 82%, $C_{33}H_{43}NO_{10}$, m.p. 250-52°; IR (KBr): 3449, 3342 (N=CH); MS: *m/z* 613 (M^+), 135; ^{1}HNMR (400 MHz, $CDCl_3$): 1.36 (s, 3H, –CO–CH_3), 3.10, 3.18, 3.26, 3.53 and 3.85 (s, each 3 H, 5×OCH_3), 4.04 (d, 1H, *J*=6.5 Hz, 6-βH), 4.85 (d, 1H, *J*=4.5 Hz, 14-βH), 7.30 (d, 1H, *J*=1 Hz, 19- H),6.89, 7.97 (dd, 4H, J_1=J_2=9 Hz, Ar-H). For ^{13}CNMR see Table I.

Compound 13. Yield 55%, $C_{22}H_{33}NO_5$, m.p. 170-71°; IR (KBr): 3410, 3360 (N=CH); MS: m/z 391(M^+), 360 (M^+–OCH_3); ^{1}HNMR (400 MHz, $CDCl_3$): 3.16, 3.30, 3.30 (s, each 3H, 3×OCH_3), 4.11 (t, 1H, *J*=4.5 Hz, 14-βH), 7.55 (d, 1H, *J*=1 Hz, 19-H). For ^{13}CNMR see Table I.

Compound 14. Yield 60%, $C_{24}H_{35}NO_6$, m.p. 165-66°; IR (KBr): 3415, 3350 (N=CH); MS: *m/z* 433 (M^+), 418 (M^1-CH_3), 404, 388; ^{1}HNMR (400 MHz, $CDCl_3$): 2.05 (s, 3H, –CO–CH_3), 3.22, 3.24, 3.34 (s, each 3H, 3×OCH_3), 4.86 (t, 1H, *J*=5 Hz, 14- βH), 7.23 (d, 1H, *J*=1 Hz, 19-H). For ^{13}CNMR see Table I.

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