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THREE STEROIDAL ALKALOIDS FROM *BUXUS HILDEBRANDTII*

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Key Word Index—*Buxus hildebrandtii*; Buxaceae; steroidal alkaloids; *O*(30)-benzoyl-16-deoxybuxidienine-C; 30-hydroxybuxamine-A; 30-norbuxamine-A; cyclomicrobuxamine; buxamine-A; buxamine-C; cyclobuxoviridine; moenjodaramine; cyclorolfeine.

Abstract—From the leaves of *Buxus hildebrandtii* three new steroidal alkaloids have been isolated and their structures determined by spectroscopic analysis. The following derived names have been suggested for these new alkaloids: *O*(30)-benzoyl-16-deoxybuxidienine-C, 30-hydroxybuxamine-A and 30-norbuxamine-A. In addition the known alkaloids cyclomicrobuxamine, buxamine-A, cyclobuxoviridine, moenjodaramine, buxamine-C and cyclorolfeine were also isolated.

INTRODUCTION

The family Buxaceae is known to contain several species occurring in temperate regions of both hemispheres and at only higher elevations in the tropics. Hutchinson in his most recent work merged the purely African genus *Notobuxus* Oliv. containing eight species with *Buxus* [1]. *Buxus hildebrandtii* Baill. is the only indigenous member of the family known to occur in Ethiopia.

Chemical studies on *Buxus* species occurring in Asia, in particular *B. papilosa* Schneider and *B. sempervirens* L. have resulted in the isolation and characterization of several but closely related series of steroidal alkaloids [2]. Some of these alkaloids are known to exhibit antimalarial and antituberculosis properties [2].

Except for a report on *B. madagascarica* [2], it appears that none of the African species belonging to the genus *Buxus* have been subjected to a phytochemical study. Our investigation of the leaves of *B. hildebrandtii*, collected from Ethiopia, has resulted in the isolation and structure elucidation of several steroidal alkaloids. We report here three novel and some known steroidal alkaloids. The type of alkaloids present indicate the close relationship of this African species with other members of the genus *Buxus*.

RESULTS AND DISCUSSION

An ethanol extract of the leaves of *B. hildebrandtii* proved to be a rich source of alkaloids, which after separation by chromatographic techniques yielded several known as well as some hitherto undescribed *Buxus* alkaloids.

It was possible by means of spectroscopic methods and comparison of physical data with literature reports [3–8] to identify the following known alkaloids: cyclomicrobuxamine (**1**), buxamine-A (**2**), buxamine-C (**3**), cyclobuxoviridine (**4**), moenjodaramine (**5**) and cyclorolfeine (**6**). We describe below the structure elucidation of three novel steroidal alkaloids isolated from *B. hildebrandtii*.

O(30)-Benzoyl-16-deoxybuxidienine-C (**7**) gave by HR mass spectrometric analysis a $[M]^+$ at 518.3860 which suggested the molecular formula $C_{34}H_{50}N_2O_2$. The UV spectrum showed absorption maxima at 238 and 246 nm with shoulders at 225 and 254 nm, characteristic of a 9(10→19)*abeo*-diene system [9]. The presence in the mass spectrum of a base peak at *m/z* 72 due to $[C_4H_{10}N]^+$ clearly indicated that the dimethylamino group is located at C-20. Furthermore, a peak at *m/z* 105 $[C_7H_4O]^+$ suggested the presence of a benzoyl substituent.

The ^{1}H NMR ($CDCl_3$, 400 MHz) showed three C-methyl singlets at δ0.67, 0.69 and 0.72 corresponding to the tertiary methyl protons at C-32, C-31 and C-18, respectively. A doublet integrating for three protons at δ0.85 was due to the C-21 secondary methyl protons. A multiplet at δ5.52 and a broad singlet at δ6.00 were assigned to the vinylic protons at C-11 and C-19, respectively, and the two AB doublets centred at δ4.11 and 4.56 (J = 11.4 Hz) were due to the geminal methylene protons at C-30. The N_a-methyl protons resonated at δ2.37 while the N_b-dimethyl protons appeared as 6H singlet at δ2.19. Three sets of multiplets centred at δ7.43, 7.54 and 8.03 resulted from C-3′/C-5′, C-4′ and C-2′/C-6′ protons of the benzoyl group, respectively. The assignments of the remaining protons, established by means of ^{1}H–^{1}H COSY and hetero-COSY are given in the Experimental section.

The benzoyl group in the compound was placed at position 30 based on the following observations. The IR spectrum suggested the presence of a secondary amine (3400 cm^{-1}) and an ester carbonyl (1710 cm^{-1}) ruling out an alternative structure in which the benzoyl group would be attached to N_a and a hydroxyl group at C-30. Further the ^{1}H NMR spectrum of compound **7a**, the product obtained upon cleavage of the benzoyl moiety, showed an upfield shift of 0.48 and 0.82 ppm for each of the methylene protons of C-30, respectively, clearly indicating the attachment of the benzoyl moiety on the

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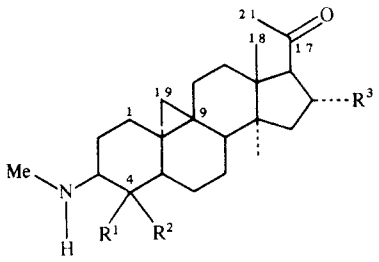
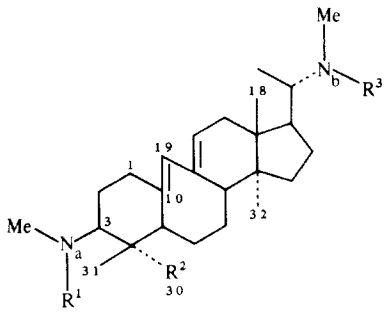
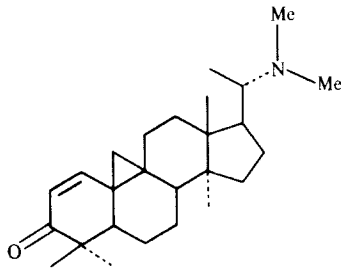


1 R^1,R^2 = $=CH_2$, R^3 = H
6 R^1 = R^2 = Me, R^3 = OH



2 R^1 = R^2 = R^3 = Me
3 R^1 = H, R^2 = R^3 = Me
7 R^1 = H, R^2 = —CH_2OCOPh, R^3 = Me
7a R^1 = H, R^2 = —CH_2OH, R^3 = Me
8 R^1 = R^3 = Me, R^2 = —CH_2OH
9 R^1 = R^3 = Me, R^2 = H



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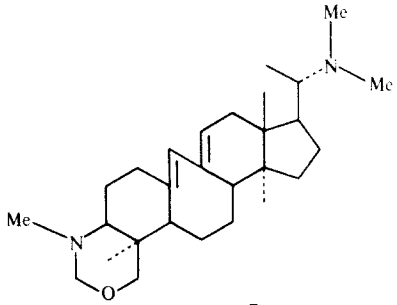

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oxygen of C-30 consistent with earlier observations on C-30 hydroxy [10] and acetoxy [11] *Buxus* alkaloids. Furthermore the derivative compound **7a** exhibited identical ^{1}H NMR and mass spectral data to that reported for 16-deoxybuxidienine-C [4]. The ^{13}C NMR assignments confirmed by the use of DEPT and hetero-COSY experiments are shown in Table 1. Compound **7** is the first example of a naturally occurring *O*-benzoylated steroidal alkaloid.

It is worthwhile to discuss the stereochemistry at C-4 of this compound. It is to be noted that for *Buxus* alkaloids with a hydroxymethylene substituent attached to C-4, the β configuration had been earlier assigned to this centre based on ^{1}H NMR and chemical evidence [11]. However, Sangare *et al.* [12], relying mainly on ^{13}C NMR data, pointed out that this substituent should be placed at the α orientation and consequently indicated the need to revise previous β stereochemical assignment of the hydroxymethylene group attached to C-4, an observation that later received support from X-ray analysis [13]. Assignments in the literature [10] that still represent substituents such as hydroxymethylene or derivatives attached to C-4 as β, need therefore to be reversed and the hydroxymethylene group should be represented with an α configuration unless evidence to the contrary is available in individual cases.

Thus, the ^{13}C NMR spectral data shown in Table 1 for **7** gave a chemical shift value of *ca* 11 ppm for the C-4 Me substituent, that is for C-31, a value consistent, following arguments developed previously [12], to an α orientation for the hydroxymethylene group or its benzoyl ester derivative.

The presence of a 9(10→19)*abeo*-diene system was likewise established by the UV spectrum of 30-hydroxybuxamine-A (**8**). HR mass spectrometry showed a $[M]^+$ peak at *m/z* 428.3766 corresponding to $C_{28}H_{48}N_2O$. In addition peaks at *m/z* 72, representing a trimethyliminium side chain fragment from ring D, and a peak at *m/z* 71 $[C_4H_9]^+$ from ring A, indicated dimethyl substitution at both N_a and N_b. This observation was substantiated by the ^{1}H NMR spectrum, which furthermore shows the presence of a hydroxymethylene group attached to C-4. As for **7**, particularly taking into account the chemical shift of C-31 in the ^{13}C NMR spectrum (Table 1), the α configuration can be assigned to the C-4 hydroxymethylene group.

30-Norbuxamine-A (**9**), isolated as an amorphous solid, gave by HR mass spectrometry the molecular formula $C_{27}H_{46}N_2$. The UV spectrum indicated the presence of a 9(10→19) *abeo*-diene moiety. The mass spectrum in addition to the $[M]^+$ showed fragments at *m/z* 71 and 72, indicative of dimethyl substitution at both N_a and N_b. The ^{1}H NMR spectrum showed the presence of two tertiary, and interestingly, two secondary methyl protons. One of the secondary methyl groups was readily assigned to C-21 while the other was placed on C-4, an assignment further supported by ^{1}H–^{1}H COSY experiments. As discussed above for **7** and **8** the β configuration could be assigned to the secondary methyl group (C-30) attached to C-4.

Table 1. ^{13}C NMR data on compounds isolated from *B. hildebrandtii*

C	2	7	8	9
1	37.3	40.3	40.8	40.8
2	31.6[a]	29.6	29.1	29.6
3	71.8	61.6	73.5	73.5
4	42.3	42.9	43.0	43.0
5	140.7	49.1	49.2[a]	49.2
6	121.6	25.4	21.2	21.2
7	31.8[a]	27.0	25.3	25.3
8	31.8	49.7	49.5[a]	49.5
9	50.1	138.3	138.3	138.3
10	36.5	134.9	134.1	134.1
11	21.1	129.5	129.4	129.4
12	39.6	38.5	38.5	38.5
13	41.9	48.6	48.6	43.8
14	54.2	44.3	43.8	48.6
15	27.5	33.0	33.0	33.0
16	24.3	28.8	27.0	27.0
17	56.7	45.7	48.0	48.0
18	19.4	15.8	15.8	15.8
19	12.1	130.1	129.7	129.7
20	62.1	61.7	57.1	57.1
21	10.7	9.7	9.9	9.9
30	—	65.9	73.2	—
31	—	11.3	11.1	11.1
32	—	17.1	17.1	17.1
N_a-Me	—	35.6	39.8	39.8
N_b-Me	39.7	39.9	39.8	39.8
1′	—	130.5	—	—
2′	—	128.4	—	—
3′	—	129.5	—	—
4′	—	132.8	—	—
5′	—	129.5	—	—
6′	—	128.4	—	—
C=O	—	166.2	—	—

[a,b] Assignments in a column may be interchanged.

EXPERIMENTAL

General. Mps: uncorr. ^{1}H NMR in $CDCl_3$ at 400 MHz with TMS as int. standard; ^{13}C NMR also in $CDCl_3$ at 100 MHz. IR in $CHCl_3$. UV in MeOH. MS direct inlet 70 eV. Optical rotation unless otherwise stated in CH_2Cl_2. The purity of the samples were checked on TLC (silica gel Merck precoated plates).

Plant material. Leaves of *Buxus hildebrandtii* were collected in April 1988 from Bale province, Ethiopia, at a locality 2 km towards Ginir from Sof Omar Bridge in an *Acacia-Buxus* woodland at an altitude of 1350 m. The plant was identified by Dr Sebsebe Demissew (National Herbarium, Addis Ababa University) where a voucher specimen Sebsebe 2121 has been deposited.

Extraction and isolation. Air-dried leaves (10 kg) were extracted by cold percolation with EtOH (Ext. I) followed by extraction using a Soxhlet apparatus with the same solvent (Ext. II). Removal of solvent gave 1.5 and 0.5 kg of crude extracts, respectively. Total alkaloids were isolated from Ext. I by treatment with 5% HCl (pH 3.5), which was successively washed with *n*-hexane (5 × 1 l) and CH_2Cl_2 (5 × 1 l). The aq. layer was basified to pH 9.0 (NH_3) and extracted into CH_2Cl_2 (8 × 1 l) and EtOAc (5 × 1 l), successively. The basic CH_2Cl_2 and EtOAc exts were combined (48 g) and loaded on to a silica gel column (1.5 kg), eluting with petrol (60–80°) containing increasing amounts of EtOAc–Et_2NH mixts. The fr. obtained by elution with 10% EtOAc and 1% Et_2NH, after rechromatography on silica gel (100 g) eluting with petrol–EtOAc–Et_2NH (500:10:1) and subsequent sepn on prep. TLC (petrol–EtOAc–Et_2NH, 50:2:1) yielded **2** (13 mg), **7** (30 mg) and **9** (10 mg). Work on substances isolated from other more polar fractions is in progress.

Total alkaloids obtained from Ext. II were likewise sepd. The weakly basic alkaloid fr. obtained by extraction at pH 3.5 (20 g) was loaded on silica gel (300 g) and eluted with $CHCl_3$ containing increasing amounts of MeOH. The fr. obtained by elution with 15% MeOH (4 g) was again rechromatographed over silica gel (100 g) eluting with petrol–EtOAc–Et_2NH (200:10:1). Subsequent prep. TLC sepn petrol–EtOAc–Et_2NH (200:5:1) and crystallization (Me_2CO) gave **1** (140 mg) and **4** (410 mg). The basic ext. from Ext. II (10 g) was applied to a silica gel column (300 g) and eluted with petrol containing various proportions of Me_2CO and Et_2NH. The fr. obtained by elution with 1% Me_2CO and 0.2% Et_2NH in petrol yielded **5** (300 mg). The fr. obtained by elution with 10% Me_2CO and 1% Et_2NH in petrol was subjected to prep. TLC petrol–EtOAc–Et_2NH (80:6:1) to give **6** (4 mg), **8** (3 mg) and other as yet unidentified alkaloids.

(+)-*Cyclomicrobuxamine* (**1**). Needles from Me_2CO, mp 131–133° (lit. [3] amorphous). $[\alpha]_D$ +106° (*c* 2.8) (lit. [3] +140°). Found: $[M^+]$ 355.2870; $C_{24}H_{37}NO$ requires 355.2875. UV λ_{max} nm: 203. IR ν_{max} cm^{-1}: 3650 (N–H), 1690 (C=O), 1650, 1600 (C=C), 1440, 1380, 1360. ^{1}H NMR: δ2.90 (1H, *dd*, J=4.5, 12.8 Hz, H-3α), 2.94 (1H, *dd*, $J_{17\alpha/16\alpha}=J_{17\alpha/16\beta}=9$ Hz, H-17α), 0.99 (3H, *s*, Me-18), 0.06 (1H, *d*, J_{gem}=4.5 Hz, H-19), 0.32 (1H, *d*, J_{gem}=4.5 Hz, H-19), 2.09 (3H, *s*, Me-21), 4.59 (1H, *br s*, H-30), 4.83 (1H, *br s*, H-30), 0.89 (3H, *s*, Me-32), 2.50 (3H, *s*, N-Me). ^{13}C NMR [see Table 1]. EIMS *m/z* (rel. int.): 355 $[M]^+$ (25), 340 $[M-Me]^+$ (100), 326 $[M-Ac]^+$ (12), 216 (10), 137 (11), 136 (20), 107 (18), 91 (38), 79 (36), 73 (81).

Buxamine-A (**2**). Amorphous. $[\alpha]_D$ +66° (lit. [4] +40). ^{1}H NMR: δ5.50 (1H, *m*, H-11), 5.91 (1H, *br s*, H-19), 2.51 (1H, *m*, H-20), 0.86 (3H, *d*, $J_{21/20}$=6.4 Hz, Me-21), 0.70 (3H, *s*, Me), 0.72 (3H, *s*, Me), 0.74 (3H, *s*, Me), 1.01 (3H, *s*, Me), 2.23 (6H, *s*, N-$(Me)_2$ 2.21 (6H, *s*, N-$(Me)_2$). EIMS *m/z* (rel. int.): 412 $[M]^+$ (6), 397, 369, 367, 98, 73 (8), 72 (100).

Buxamine-C (**3**). Amorphous. $[\alpha]_D$ +22.4° (*c* 0.3) (lit. [5] +24). UV λ_{max} nm: 225, 238, 246, 254. IR ν_{max} cm^{-1}: 3400 (N–H), 2850. ^{1}H NMR: δ5.51 (1H, *m*, H-11), 5.94 (1H, *m*, H-19), 0.86 (3H, *d*, $J_{21/20}$=6.3 Hz), 0.67 (3H, *s*, Me), 0.72 (3H, *s*, Me), 0.75 (3H, *s*, Me), 1.07 (3H, *s*, Me), 2.50 (3H, *s*, N_a-Me), 2.21 (6H, *s*, N_b-$(Me)_2$).

Cyclobuxoviridine (**4**). Amorphous (lit. [6] 182°). UV λ_{max} nm: 262. IR ν_{max} cm^{-1}: 2820, 1660 (C=O). ^{1}H NMR: δ5.93 (1H, *d*, $J_{1/2}$ = 10 Hz, H-1), 6.76 (1H, *d*, $J_{2/1}$ = 10 Hz, H-2), 0.76 (1H, *d*, J_{gem} =4.7 Hz, H-19), 2.43 (1H, *m*, H-20), 0.82 (3H, *d*, $J_{21/20}$=6.5 Hz, Me-21), 0.91 (3H, *s*, Me), 0.93 (3H, *s*, Me), 0.95 (3H, *s*, Me), 1.08 (3H, *s*, Me), 2.17 (6H, *s*, N-$(Me)_2$). EIMS *m/z* 383 $[M]^+$, 370, 369, 354, 326, 287, 286, 232, 218, 167, 159, 135, 121, 119, 107.

Moenjodaramine (**5**). White powder mp 158–160° (lit. [7] 177°. $[\alpha]_D$ +65° (*c* 0.2) (lit. [7] +61 and +33°). UV λ_{max} nm: 225, 238, 246, 254. IR ν_{max} cm^{-1}: 2850, 1450, 1360. ^{1}H NMR: δ5.53 (1H, *m*, H-11), 5.96 (1H, *br s*, H-19), 2.44 (1H, *m*, H-20), 0.82 (3H, *d*, *J* 21/20=6.4 Hz, Me-21), 3.22 (1H, *d*, J_{gem}=10.8 Hz, H-31β), 3.80 (1H, *d*, J_{gem}=10.8 Hz, H-31α), 3.55 (1H, *d*, J_{gem}=7.6 Hz, H-33β), 4.40 (1H, *d*, J_{gem}=7.6 Hz), 0.69 (3H, *s*, Me), 0.73 (3H, *s*, Me), 1.02 (3H, *s*, Me), 2.16 (3H, *s*, N_a- Me), 2.02 (6H, *s*, N_b-$(Me)_2$). EIMS *m/z* (rel. int.): 426 $[M]^+$, 411, 398, 85 (64), 83 (100), 72 (82).

(+)-*Cyclorolfeine* (**6**). Amorphous (lit. [8] 253°). [α] +48° ($CHCl_3$) (lit. [8] +119]. Found: $[M]^+$ 387.3128; $C_{25}H_{41}NO_2$ requires 387.3137. IR ν_{max} cm^{-1}: 1690, 3350. ^{1}H NMR: δ0.31 (1H, *d*, $J_{19\alpha,19\beta}$=4.3 Hz, H-19α), 0.55 (1H, *d*, $J_{19\beta,19\alpha}$=4.3 Hz, H-19β), 0.74 (3H, *s*, Me), 0.91 (3H, *s*, Me), 0.95 (3H, *s*, Me), 1.17 (3H,

s, Me), 2.14 (3H, s, 21-Me), 2.43 (3H, s, N-Me), 3.00 (1H, d, $J_{17\alpha,16\beta}$ = 6.6 Hz, H-17α), 4.88 (1H, m, H-16β). ^{13}C NMR: δ31.5 (C-1), 26.9 (C-2), 68.6 (C-3), 39.9 (C-4), 47.5 (C-5), 21.2 (C-6), 26.1 (C-7), 48.4 (C-8), 19.2 (C-9), 26.2 (C-11), 32.6 (C-12), 47.7 (C-13), 45.9 (C-15), 72.0 (C-16), 70.6 (C-17), 15.0 (C-18), 30.1 (C-19), 209.9 (C-20), 31.2 (C-21), 25.8 (C-30), 20.7 (C-31), 20.7 (C-32), 35.6 (N_a-Me). EIMS *m/z* (rel. int.) 387 (40), 372.2899 ($C_{24}H_{38}NO_2$) (50).

30 (O)-*Benzoyl-16-deoxybuxidienine-C* (**7**). Gum $[\alpha]_D$ −75° ($CHCl_3$). Found: $[M]^+$ 518.3860; $C_{34}H_{50}N_2O_2$ requires 518.3872. UV λ_{max} nm (log ε): 225sh (4.49), 238 (4.53), 248 (4.49), 254sh (4.23). IR ν_{max} cm^{-1}: 3400 (N–H), 2900, 1710 (ester C=O), 1600 (C=C). ^{1}H NMR: δ2.24 (1H, m, H-1β), 2.28 (1H, m, H-1α), 1.42 (1H, m, H-2β), 2.17 (1H, m, H-2α), 2.54 (1H, dd, $J_{3\alpha/2\alpha}$ = 11.8 Hz, $J_{3\alpha/2\beta}$ = 4.2 Hz, H-3α) 1.84 (1H, m, H-5α) 1.28 (1H, m, H-6β), 1.54 (1H, m, H-6α), 1.56 (1H, m, H-7β), 1.89 (1H, m, H-7α), 2.13 (1H, m, H-8β), 5.52 (1H, m, H-11), 2.00 (1H, m, H-12β), 2.09 (1H, m, H-12α) 1.27 (1H, m, H-15β), 1.39 (1H, m, H-15α), 1.45 (1H, m, H-16β), 2.05 (1H, m, H-16α), 2.47 (1H, m, H-17α), 0.72 (3H, s, Me-18), 6.00 (1H, br s, H-19), 2.49 (1H, m, H-20), 0.85 (3H, d, $J_{20/21}$ = 6.7 Hz, Me-21), 4.11 (1H, d, J_{gem} = 11.4 Hz H-30), 4.56 (1H, d, J_{gem} = 11.4 Hz, H-30), 0.69 (3H, s, Me-31), 0.67 (3H, s, Me-32), 2.37 (3H, s, N_a-Me), 2.19 (6H, s, N_b-$(Me)_2$), 8.03 (2H, m, H-2′/6′), 7.43 (2H, m, H-3′/5′), 7.54 (1H, m, H-4′). ^{13}C NMR [see Table 1]. EIMS *m/z*: 518 $[M]^+$ 497, 447, 396, 369, 367, 354, 326, 268, 211, 185, 183, 171, 119, 105, 84, 73, 72.

Hydrolysis of compound **7**. Compound **7** (6 mg) was dissolved in 3 ml of methanolic NaOH (1%) and the soln allowed to stand for 12 hr at room temp. Solvent was removed and the product partitioned between H_2O and CH_2Cl_2. The debenzoyl product **7a** (4 mg) was obtained from the CH_2Cl_2 layer. **7a**: amorphous, $[\alpha]_D$ +84 ($CHCl_3$). Found: $[M]^+$ 414.3611; $C_{27}H_{46}N_2O$ requires 414.3610. UV λ_{max}^{MeOH} nm: 238, 246, with shoulders at 228 and 254. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3650 (OH) and 3400 (NH). ^{1}H NMR: 5.53 (1H, m, H-11), 5.99 (1H, br s, H-19), 0.86 (3H, d, $J_{20/21}$ = 6.4 Hz, H-21), 0.69 (3H, s, Me), 0.74 (3H, s, Me), 0.88 (3H, s, Me), 3.74 (1H, d, J_{gem} = 9.4 Hz, H-30) 3.63 (1H, d, J_{gem} = 9.4 Hz, H-30), 2.21 (6H, s, N_b-$(Me)_2$), 2.45 (3H, s, N_a-Me). EIMS *m/z* (rel. int.): 414 $[M]^+$ (100), 399 (10), 344 (5), 343 (15), 328 (5), 268 (5), 253 (3), 95 (38), 91 (44).

30-*Hydroxybuxamine-A* (**8**). Amorphous, $[\alpha]_D$ +61 ($CHCl_3$). Found: $[M]^+$ 428.3766; $C_{28}H_{48}N_2O$ requires 428.3767. UV λ_{max} nm: 225 (sh), 238, 248, 254 (sh). IR ν_{max} cm^{-1}: 3345 (OH). ^{1}H NMR: δ2.16 (1H, m, H-1β), 2.28 (1H, m, H-1α), 1.59 (1H, m, H-2β), 1.73 (1H, m, H-2α), 2.62 (1H, dd, J = 3.7, 12.5 Hz, H-3α), 5.52 (1H, m, H-11), 2.00 (1H, m, H-12β), 2.10 (1H, m, H-12α), 2.56 (1H, m, H-20β), 0.89 (3H, d, $J_{21/20}$ = 6.4 Hz, Me-21), 3.60 (1H, d, J_{gem} = 10.4 Hz, H-30), 3.71 (1H, d, J_{gem} = 10.4 Hz, H-30), 0.74 (3H, s, Me), 1.00 (3H, s, Me), 0.68 (3H, s, Me), 2.25 (6H, s, N_a-$(Me)_2$), 2.30 (6H, s, N_b-$(Me)_2$). ^{13}C NMR (see Table 1). EIMS *m/z* (rel. int.): 428 $[M]^+$ (4), 413.3551 ($C_{27}H_{45}N_2O$), 369, 357, 344, 342, 314, 282, 183, 157, 143, 91, 73, 72.0814 ($C_4H_{10}N$) (100).

30-*Norbuxamine-A* (**9**). $C_{27}H_{46}N_2$. Amorphous. $[\alpha]_D$ −13° ($CHCl_3$). Found: $[M]^+$ 398.3666; $C_{27}H_{46}N_2$ 398.3661. UV λ_{max} nm: 238, 246 with shoulders at 228 and 254. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1596 (C=C). ^{1}H NMR: δ2.52 (1H, m, H-3α), 5.54 (1H, m, H-11), 5.88 (1H, br s, H-19), 2.40 (1H, m, H-20), 0.87 (3H, d, $J_{21/20}$ = 6.4 Hz, Me-21), 0.72 (3H, s, Me), 0.75 (3H, s, Me), 1.02 (3H, d, J = 6.4 Hz), 2.23 (6H, s, N_a-$(Me)_2$), 2.21 (6H, s, N_b-$(Me)_2$). EIMS *m/z* (rel. int.): 398 $[M]^+$, 383.3405 ($C_{27}H_{43}N_2$), 369, 356, 354, 308, 279, 239, 225, 183, 169, 167, 157, 129, 119, 91, 83, 72.0813 ($C_4H_{10}N$).

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