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ALKALOIDS OF *RAUWOLFIA NITIDA* ROOT BARK

MOHAMMED A. AMER and WILLIAM E. COURT

Postgraduate School of Studies in Pharmacy, University of Bradford, West Yorkshire BD7 1DP, U.K.

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Key Word Index—*Rauwolfia nitida*; Apocynaceae; root indole alkaloids; sarpagan; dihydroindole; peraksine; indolenine; heteroyohimbine; yohimbine; 18-hydroxy-yohimbine esters; anhydronium and macroline bases.

Abstract—Thirty-three indole alkaloids were isolated from the root bark of *Rauwolfia nitida*. Sarpagan, dihydroindole, indolenine, yohimbine, 18-hydroxy-yohimbine ester, heteroyohimbine and anhydronium base types were isolated. The principal alkaloids were reserpine (0.034%), serpentinine (0.033%), pseudoreserpine (0.013%) and reserpiline (0.012%).

INTRODUCTION

The West Indian species *Rauwolfia nitida* is a large shrub or small tree 2–15 m tall occurring on hills, in forests and in pastures at altitudes below 600 m in the Bahamas, Cuba, Jamaica, Dominica, Puerto Rico and some other Caribbean islands [1, 2]. The roots have been used in indigenous medicine as an emetic and cathartic [1]. The weakly basic alkaloids reserpine, rescinnamine and reserpiline were detected by PC of root extracts [3]. Subsequently, deserpidine and deserpideine were isolated [4, 5]. The leaves yielded the heteroyohimbine alkaloids ajmalicine, isoreserpiline, isoreserpinine, rauniticine, raunitidine, reserpiline and reserpinine [6].

The roots have now been reinvestigated and 33 alkaloids isolated and identified.

RESULTS

Known *Rauwolfia* alkaloids were characterized by analytical methods as shown in Table 1 together with chromogenic reactions as described earlier [7] and identified either by comparison with authentic compounds or published data [8].

Alkaloid NRB6 produced a typical yohimbinoid UV spectrum with a well-defined minimum at 248 nm. Peaks in the IR spectrum at 1730 and 740 cm^{-1} indicated carbonyl ester absorption and a non-substituted *ar* indole ring, respectively. The EIMS peak at *m/z* 396 was 42 u greater than that for yohimbine but fragment ions representing the β-carboline nucleus occurred at *m/z* 184, 170, 169 and 156, confirming the presence of a non-substituted aromatic ring. Mass fragments at *m/z* 337 ($M^+ - 59$) and *m/z* 336 ($M^+ - 60$) indicated loss of COOMe and COOMe + H groups, respectively. Such groups were confirmed by ^1H NMR at δ 3.64 (3 H, *s*) and 2.13 (3 H, *s*), respectively. NRB6 was therefore an acetyl yohimbine, data agreeing with published data [9] except for the $[\alpha]_D$ value. EIMS peaks at *m/z* 267 (25%) and 266 (72%) corresponded with *m/z* 225 (17%) and 224 (34%) in NRB28. NRB6 was found to be identical with the acetyl derivative of NRB28 ($[\alpha]_D$, UV, IR, EIMS, co-TLC) and was identified as acetyl-alloyohimbine.

Compound NRB8 demonstrated an indole chromophore with a well-defined UV minimum at 250 nm and the IR spectrum indicated a non-substituted aromatic ring (740 cm^{-1} *s*) and an aldehyde or ketone group (1720 cm^{-1} *w*). The mass spectrum was of the sarpagan type with β-carboline fragments at *m/z* 196, 183, 182 and 168, i.e. 14 u more than that for non-substituted indole compounds. Fragment ions at *m/z* 291 ($M^+ - 15$), 277 ($M^+ - 29$) and 263 ($M^+ - 43$) suggested loss of Me, CHO and C-16 together with its substituents and an additional hydrogen atom, respectively. ^1H NMR signals at δ 9.52 (1 H, *s*) and 2.52 (3 H, *s*) indicated CHO and N_a – Me, respectively, and signals at δ 5.45 (1 H, *q*) and 1.65 (3 H, *d*) were attributed to an exocyclic ethylidene side-chain. Comparison of NRB8 with vellosimine [10] revealed a similarity except for Me substitution of the indole nitrogen atom. Thus, NRB8 was identified as N_a-methylvellosimine.

The UV spectrum of alkaloid NRB15 suggested a dihydroindole chromophore but the chromogenic reactions and EIMS confirmed a nordihydroindole structure with fragment ions of the β-carboline nucleus occurring at *m/z* 169, 168, 144 and 130. Compared with nortetraphyllicine [11] NRB15 showed a M^+ at *m/z* 336 which was 42 u greater and suggested the presence of an acetyl group, the peak at *m/z* 294 confirming loss of the acetyl group. The IR spectrum showed the presence of a carbonyl group (1740 cm^{-1}) and the absence of OH. An acetyl derivative was prepared by the method described for NRB6 from an authentic sample of nortetraphyllicine and was found to be identical (UV, EIMS, co-TLC). NRB15 was therefore identified as 17-*O*-acetyl-nortetraphyllicine.

DISCUSSION

Earlier work on 10 African *Rauwolfia* species [12] when related to published data on other species indicated that the African species might be classified as *allo* (C-3Hα, C-20Hα) configuration or *normal* (C-3Hα, C-20Hβ) configuration dominated groups on the basis of the stereochemistry of the principal heteroyohimbine alkaloids present in the plants. Close examination of the occurrence of alkaloids in the American *R. nitida* roots revealed that such a division cannot readily be applied to this species because, although the *allo* configuration is

Table 1. Known *Rauwolfia* alkaloids isolated from *R. nitida* roots (2 kg)

	Alkaloid identified	Analytical methods	Yield (mg)
Weakly basic fraction			
NRB1	Tetraphylline	mp, mmp $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR	65
NRB2	Isoreserpiline	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, co-TLC	10
NRB3	Ajmalicine	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, co-TLC	12
NRB4	Isoreserpinine	mp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR	30
NRB5	Reserpiline	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, co-TLC	240
NRB7	Reserpinine	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, co-TLC	135
NRB9	Reserpine	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, co-TLC	685
NRB10	Lochnerine	mp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, acetyl derivative	10
NRB11	3-Isoajmalicine	$[\alpha]_D$, UV, IR, EIMS	10
NRB12	Pseudoreserpine	$[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR	270
NRB13	Serpentinine	mp, $[\alpha]_D$, UV, IR, EIMS	670
NRB14	Deserpidine	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, co-TLC	75
Intermediate base fraction			
NRB16	Tetraphyllicine	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, co-TLC	120
NRB17	Nortetraphyllicine	mp, $[\alpha]_D$, UV, IR, EIMS, co-TLC	10
NRB18	Normacusine B	$[\alpha]_D$, UV, IR, EIMS, co-TLC	8
NRB19	Ajmaline	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, co-TLC	135
NRB20	Suaveoline	$[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, co-TLC	43
NRB21	Ajmalidine	$[\alpha]_D$, UV, IR, EIMS	4
NRB22	Norajmaline	$[\alpha]_D$, UV, IR, EIMS, co-TLC	8
NRB23	Raucaffrinoline	$[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, co-TLC	120
NRB24	Yohimbine	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, co-TLC	45
NRB25	Vellosimine	mp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR	10
NRB26	α-Yohimbine	mp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR	32
NRB27	11-Methoxyyohimbine	mp, $[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR	15
NRB28	Alloyohimbine	$[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR	25
NRB29	18-Hydroxyyohimbine	$[\alpha]_D$, UV, IR, EIMS, ^{1}H NMR, co-TLC	18
Strongly basic fraction			
NRB30	Peraksine	$[\alpha]_D$, UV, IR, EIMS, co-TLC	8
NRB31	Sarpagine	mp, mmp, $[\alpha]_D$, UV, IR, EIMS, co-TLC	12
NRB32	Alstonine	$[\alpha]_D$, UV, EIMS, co-TLC	10
NRB33	Serpentine	mp, $[\alpha]_D$, UV, IR, EIMS, co-TLC	23

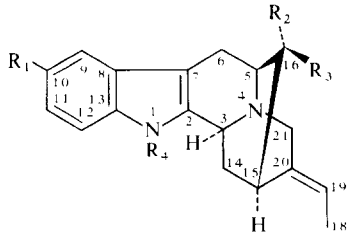
dominant, there is greater representation of the *normal* configuration compounds. Also, we have previously observed that when *allo* configuration heteroyohimbines are dominant oxindole alkaloids co-occur [13]. This co-occurrence has not been observed in *R. nitida* roots during this investigation or in reports published by other workers [3, 6].

The alkaloids isolated show a systematic relationship. Thus, the sarpagans normacusine B **1**, vellosimine **2**, N_a-methyl-vellosimine **3**, lochnerine **4** and sarpagine **5** form a closely allied group and such compounds can be readily converted to the N_a-demethyl-dihydroindoles nortetraphyllicine **6**, its 17-*O*-acetyl derivative **7** and norajmaline **8** and, by further methylation, to the N_a-methyl-dihydroindoles tetraphyllicine **9** and ajmaline **10** and its 17-keto variant ajmalidine **11**. The dihydroindoles comprised *ca* 5% of the total alkaloids present and no *ar*-substituted dihydroindoles, which occur in some other *Rauwolfia* species [12, 14, 15], were found. Peraksine **12**, a trace compound, is also probably sarpagan derived but its role in the biosynthetic pathway is not established. Likewise the function of the indolenine alkaloid raucaffrinoline **13** is not easily comprehended although such a compound is intermediate between the sarpagan and ajmalan alkaloids [16].

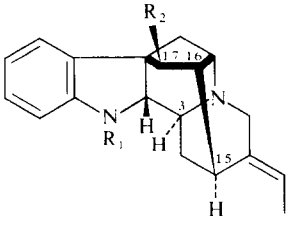
The yohimbine group was represented by the *normal* configuration compounds yohimbine **14** and its 11-methoxy congener **15**, and the *allo* configuration relatives α-yohimbine **16**, alloyohimbine **17** and acetylalloyohimbine **18**, alkaloids of the two configurations occurring in *ca* equal amounts.

Compounds of the 18-hydroxy-yohimbine group were characteristically of the more stable *epi-allo* (C-3Hβ, C-20Hα) configuration and comprised 18-hydroxy-yohimbine **19** and its esters deserpidine (demethoxy-reserpine) **20**, pseudoreserpine (17-demethyl-reserpine) **21** and reserpine **22**. Significantly, although reserpine occurred in large amount, rescinnamine **23**, its trimethoxycinnamoyl relative which occurred in many other *Rauwolfia* species [17], was not detected.

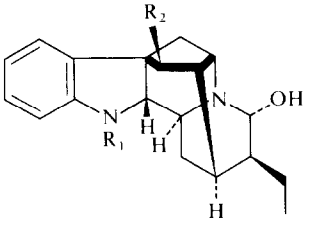
The heteroyohimbine group alkaloids also occurred in fair yield comprising 22% of the total alkaloids isolated. Ajmalicine **24** and its 11-methoxy congener tetraphylline **25** represented the *normal* configuration compounds in small yield together with a trace amount of isoajmalicine **26**, the *pseudo* (C-3Hβ, C-20Hβ) isomer of ajmalicine. The *allo* configuration compounds present were reserpinine (11-methoxy-tetrahydroalstonine) **27** and isoreserpiline (10,11-dimethoxy-tetrahydroalstonine) **28** and were accompanied by the more stable *epi–allo* congeners



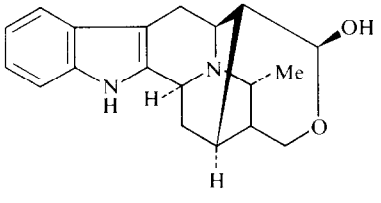
1 $R_1 = R_2 = R_4 = H$; $R_3 = CH_2OH$
2 $R_1 = R_2 = R_4 = H$; $R_3 = CHO$
3 $R_1 = R_2 = H$; $R_3 = CHO$; $R_4 = Me$
4 $R_1 = OMe$; $R_2 = R_4 = H$; $R_3 = CH_2OH$
5 $R_1 = OH$; $R_2 = R_4 = H$; $R_3 = CH_2OH$



6 $R_1 = H$; $R_2 = OH$
7 $R_1 = H$; $R_2 = OAc$
9 $R_1 = Me$; $R_2 = OH$



8 $R_1 = H$; $R_2 = OH$
10 $R_1 = Me$; $R_2 = OH$
11 $R_1 = Me$; $R_2 = =O$



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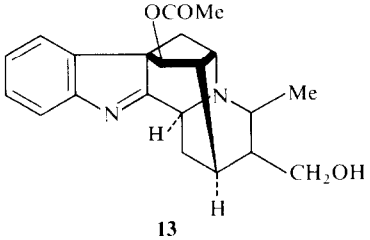

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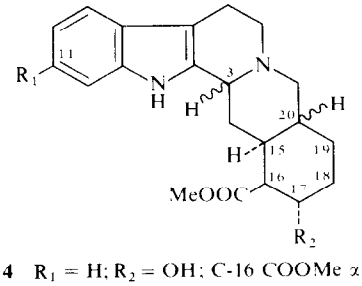
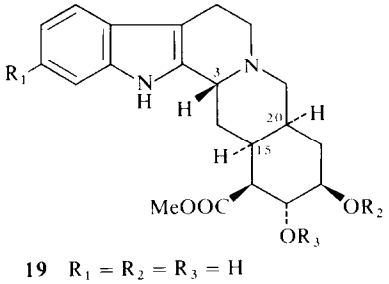
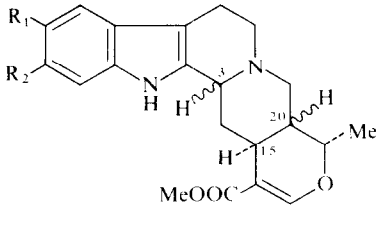


14 $R_1 = H$; $R_2 = OH$; C-16 COOMe α; *normal*
15 $R_1 = MeO$; $R_2 = OH$; C-16 COOMe α; *normal*
16 $R_1 = H$; $R_2 = OH$; C-16 COOMe β; *allo*
17 $R_1 = H$; $R_2 = OH$; C-16 COOMe α; *allo*
18 $R_1 = H$; $R_2 = OAc$; C-16 COOMe α; *allo*



19 $R_1 = R_2 = R_3 = H$
20 $R_1 = H$; $R_2 = TMB$; $R_3 = Me$
21 $R_1 = OMe$; $R_2 = TMB$; $R_3 = H$
22 $R = OMe$; $R_2 = TMB$; $R_3 = Me$
23 $R_1 = OMe$; $R_2 = TMC$; $R_3 = Me$



24 $R_1 = R_2 = H$; *normal*
25 $R_1 = H$; $R_2 = OMe$; *normal*
26 $R_1 = R_2 = H$; *pseudo*
27 $R_1 = H$; $R_2 = OMe$; *allo*
28 $R_1 = R_2 = OMe$; *allo*
29 $R_1 = H$; $R_2 = OMe$; *epi-allo*
30 $R_1 = R_2 = OMe$; *epi-allo*

isoreserpinine **29** and reserpiline **30**, respectively. Reserpiline was the principal heteroyohimbine alkaloid isolated and formed 8.2% of the total alkaloid content but the *ar*-unsubstituted tetrahydroalstonine was conspicuously absent.

The anhydronium bases derived from the heteroyohimbines demonstrated a similar division to yield the *normal* configuration compounds serpentine **31** and serpentinine **32** and the *allo* configuration alkaloid alstonine **33**. Serpentinine may be formed by the degradation of serpentine and formed 23.6% of the total alkaloids of *R. nitida* roots. It has not been detected in African *Rauwolfia* roots. Alstonine is derived from the undetected tetrahydroalstonine.

The presence of the macroline compound suaveoline **34** is contentious although evidence is accumulating to suggest that it is a natural compound probably derived from ajmaline [18].

The absence of compounds such as the E-*seco* alkaloids geissoschizol, corynantheol and geissoschizine suggests that the root stores the end products of biosynthesis. Therefore, the N_a-demethyl-dihydroindoles and the sarpagans occurred in low yields (0.5% and 2% of the total alkaloids, respectively).

Pharmaceutically the roots are interesting because of the high yield of the hypotensive and tranquillizing drug reserpine (24% of the total alkaloids isolated).

EXPERIMENTAL

Mps are uncorr. IR spectra were measured in KBr discs or $CHCl_3$. ^1H NMR spectra were determined in $CDCl_3$ or CD_3OD at 60 MHz. EIMS were obtained by direct inlet, 70 eV, 100 μA, 200–250°.

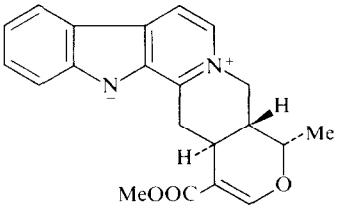
Plant material. Roots of *R. nitida* Jacq. were collected in Jamaica in 1960 and supplied by Brome & Schimmer Ltd. Reference sample No. RAU 112-601 is deposited with the Collection of Materia Medica and Herbaria, University of Bradford.

Extraction and fractionation. Coarsely powdered root bark (2 kg) was extrd and fractionated as described earlier [19] to yield 25 g weakly basic fraction, 16.5 g intermediate base fraction and 10 g strongly basic fraction.

Separation. The weakly basic fraction was adsorbed on a column (55 × 3.5 cm) of Al_2O_3 (500 g) and successively eluted with 500-ml vol. of C_6H_{14}–EtOAc (4:1, 7:3, 3:2, 11:9, 2:3, 3:7, 1:4, 1:9); EtOAc; EtOAc–MeOH (49:1, 19:1, 9:1, 4:1, 3:1, 1:1). Successive eluate samples (100 ml) were collected, screened by TLC and samples of similar composition bulked to yield fractions A–H.

Further separation was performed on Si gel layers. Fraction A analysed by prep. TLC [Me_2CO–petrol–CCl_4–*iso*-octane, 7:6:4:3) yielded NRB1 (65 mg) and NRB2 (10 mg). Fractions B and C were similarly separated by prep. TLC (BuOH–EtOAc–$C_2H_4Cl_2$, 1:3:7) to give NRB3 (12 mg), NRB4 (30 mg) and NRB5 (240 mg). Fraction D purified by prep. TLC (Et_2O–MeOH, 19:1) produced NRB6 (8 mg). Fraction E sepd by prep. TLC [$CHCl_3$–petrol–MeOH-*iso*octane, 7:1:1:1) yielded NRB7 (135 mg) and NRB8 (15 mg). Fraction F on concn yielded a crystalline deposit which on recryst. from MeOH–EtOAc (1:1) gave NRB9 (685 mg). The residual mother liquor on prep. TLC ($CHCl_3$–EtOAc–MeOH, 8:1:1) produced NRB10 (10 mg). Fraction G on prep. TLC separation ($CHCl_3$–Me_2CO–*iso*octane–MeOH, 7:1:1:1) yielded NRB11 (10 mg), NRB12 (270 mg) and NRB13 (670 mg). Fraction H purified by prep. TLC ($CHCl_3$–Me_2CO–EtOAc–MeOH, 6:2:1:1) yielded NRB14 (75 mg).

The intermediate base fraction was adsorbed on a column (50 × 3.5 cm) of Al_2O_3 and successively eluted with 500-ml vol. of EtOAc; EtOAc–MeOH (99:1, 49:1, 19:1, 9:1, 17:3, 4:1, 7:3, 3:2, 1:1); MeOH. Successive eluate samples (100 ml) were collected, screened by TLC and similar samples bulked to yield fractions I–VIII. Fraction I separated by prep. TLC ($CHCl_3$–EtOAc–Me_2CO–MeOH, 4:3:2:1) yielded on further purification NRB15 (5 mg) and NRB16 (120 mg). Similarly, Fraction II after prep. TLC separation ($CHCl_3$–EtOAc–Me_2CO–MeOH, 8:7:3:1, in an atmosphere of NH_3) gave NRB17 (10 mg) and NRB18 (8 mg). Fraction III by prep. TLC (EtOAc–*iso*PrOH–NH_3, 16:3:1) yielded NRB19 (135 g), NRB20 (42 mg) and NRB21 (4 mg). Fraction IV



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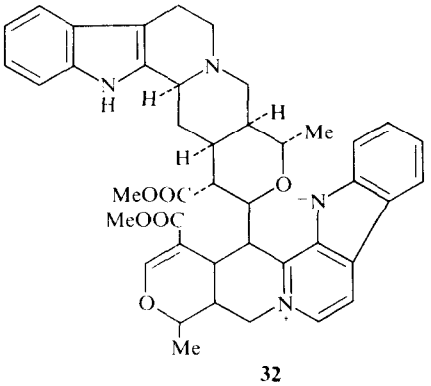

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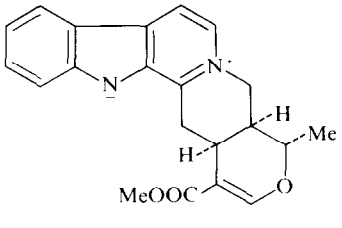

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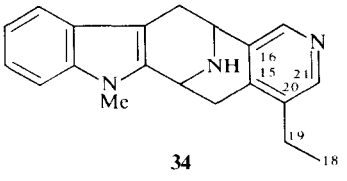

34

refractionated by prep. TLC (EtOAc–Et_2O–MeOH, 3:5:2) produced NRB22 (8 mg) and NRB23 (120 mg). Fraction V purified by prep. TLC (EtOAc–Et_2O *iso*octane, 9:10:1) yielded NRB24 (45 mg) and NRB25 (10 mg). Fraction VI by prep. TLC ($CHCl_3$–EtOAc–*iso*PrOH–Me_2CO–NH_3, 10:3:2:4:1) gave NRB26 (32 mg). Fraction VII yielded by prep. TLC (Me_2CO–$CHCl_3$–petrol–MeOH–NH_3, 8:4:6:1:1) NRB27 (15 mg) and NRB28 (25 mg). Fraction VIII on prep. TLC (Me_2CO petrol EtOAc–NH_3, 6:2:1:1) produced NRB29 (18 mg).

Prep. TLC (Me_2CO–petrol–EtOAc–NH_3, 6:2:1:1) of the strong base fraction yielded two compounds which were repurified by prep. TLC ($CHCl_3$–MeOH, 3:1, NH_3 atm) to produce NRB30 (8 mg) and NRB31 (12 mg). The base-line streaks of the plates were collected, eluted with MeOH and the resultant concd eluate purified by prep. TLC (Me_2CO–MeOH–Et_2NH, 7:2:1) to yield NRB32 (10 mg) and NRB33 (23 mg).

Identification of alkaloids. Known *Rauwolfia* alkaloids were characterized and identified as indicated in Table 1.

NRB6, acetyl-alloyohimbine, off-white amorphous powder; $[\alpha]_D^{22}$ −89° ($CHCl_3$, $c = 0.01$); UV λ_{max}^{MeOH} nm (log ε) 225 (4.58), 284 (3.77), 290 (3.65); λ_{min}^{MeOH} nm 248; IR ν_{max}^{KBr} cm^{-1} 3400*w*, 2940*m*, 1730*s*, 1620*m*, 1440*m*, 1370*m*, 1240*s*, 1160*m*, 1080*m*, 1020*m*, 960*w*, 740*s*; EIMS (probe) 70 eV, *m/z* (rel. int.); 396 $[M]^+$ (36), 395 $[M - H]^+$ (82), 379 $[M - OH]^+$ (7), 337 $[M - COOMe]^+$ (25), 336 $[M - OCOMe + H]^+$ (13), 335 (36), 267 (25), 266 (72), 184 (38), 170 (62), 169 (52), 156 (45), 144 (27), 143 (23), 130 (13); ^1H NMR (60 MHz, $CDCl_3$): δ 7.52–7.14 (4 H, *m*, *ar*), 5.24 (1 H, *m*), 3.64 (3 H, *s*, C-16 COOMe), 2.13 (3 H, *s*, C-17 OCOMe), 1.84 (2 H, *m*); chromogenic reactions, greenish grey with $FeCl_3$–$HClO_4$, yellow with Ce $(SO_4)_2$ reagent. Preparation of acetylyohimbine: 15 mg NRB28 was treated with Ac_2O–pyridine (2:1) for 2 hr at room temp.; the mixture was poured into ice-cold H_2O and extrd with $CHCl_3$; the $CHCl_3$ ext was concd under red. pres. and the acetyl derivative recovered by prep. TLC (Si gel: $CHCl_3$–EtOAc–Me_2CO–MeOH, 4:3:2:1).

NRB8, N_a-methyl-vellosimine, colourless, crystalline plates; mp 255–260°; $[\alpha]_D^{22}$ +23° ($CHCl_3$, $c = 0.01$); UV λ_{max}^{MeOH} nm (log ε) 230 (4.21) 285 (3.85), 294 (3.82); λ_{min}^{MeOH} nm 250; IR ν_{max}^{KBr} cm^{-1} 3420*s*, 2930*s*, 1720*w*, 1620*w*, 1590*w*, 1470*s*, 1380*s*, 1335*m*, 1310*m*, 1250*m*, 1190*m*, 1130*s*, 1100*s*, 1070*s*, 950*m*, 740*s*, EIMS (probe) 70 eV, *m/z* (rel. int.): 306 $[M]^+$ (73), 305 $[M - H]^+$ (33), 291 $[M - Me]^+$ (13), 278 $[M - CO]^+$ (23), 277 $[M - CHO]^+$ (100), 263 $[M - CH.CHO + H]^+$ (23), 249 (16), 235 (8), 196 (20), 183 (83), 182 (50), 181 (11), 170 (13), 168 (30), 144 (12); ^1H NMR (60 MHz, DMSO): δ 9.52 (1 H, *s*, CHO), 7.65–7.01 (4 H, *m*, *ar*), 5.45 (1 H, *q*, C-19 H), 2.52 (3 H, *s*, N_a – Me), 1.65 (3 H, *d*, C-18 Me); chromogenic reactions, grey with $FeCl_3$–$HClO_4$, yellow with 2, 4-DNPH.

NRB15, 17-*O*-acetyl-nortetraphyllicine, white amorphous powder; $[\alpha]_D^{22}$ +41° (MeOH, $c = 0.01$), UV λ_{max}^{MeOH} nm (log ε) 215 (4.31), 246 (4.50), 292 (3.63); λ_{min}^{MeOH} nm 225, 270; IR ν_{max}^{KBr} cm^{-1} 2925*s*, 1740*s*, 1605*s*, 1460*s*, 1240*s*, 1120*m*, 1080*m*, 1030*m*, 760*m*, 740*s*; EIMS (probe) 70 eV, *m/z* (rel. int.): 336 $[M]^+$ (100), 321 $[M - Me]^+$ (8), 294 $[M + H - COMe]^+$ (15); 293 $[M - COMe]^+$ (22), 278 $[M + H - OCOMe]^+$ (14), 277 $[M - OCOMe]^+$ (55), 169 (95), 168 (55), 167 (20), 144 (12), 143 (27), 130 (37); chromogenic reactions, orange with $FeCl_3$–$HClO_4$, orange with Ce $(SO_4)_2$; acetyl derivative of nortetraphyllicine prepared as for NRB6 and compared (UV, EIMS, co-TLC).

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