Concise Synthesis of *Narcissus* Pyrrolophenanthridine Alkaloids: Vasconine, Assoanine and Oxoassoanine†

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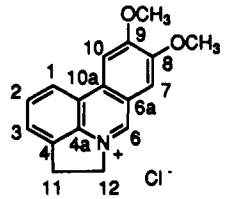
Introduction

Vasconine (1) is a pyrrolophenanthridinium salt recently identified by Codina, et al., as a minor constituent of Spanish *Narcissus vasconicus*.[4] Assoanine (**2a**) and oxoassoanine (**2b**) are structurally related pyrrolophenanthridine metabolites isolated from *Narcissus assoanus*.[5]



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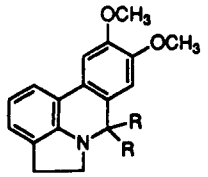
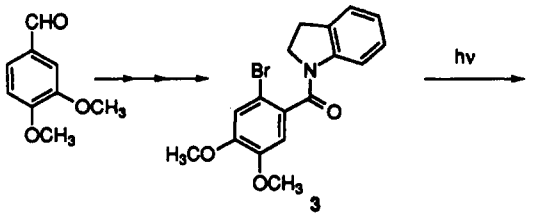


2a: R=H; **2b**: R + R = O

Interestingly, a synthetic scheme leading to 1 (via **2b** and **2a**) was reported by Cheng and co-workers long before the isolation of vasconine from its natural source.[6] In Cheng's approach the key C(10a)–C(10b) bond of the pyrrolophenanthridine skeleton was formed by photochemical cyclization of intermediate **3** to give oxoassoanine (**2b**) (Scheme 1); diborane reduction of **2b** presumably gave **2a**, which was not isolated but directly air-oxidized in acidic medium to give compound 1.

It is noteworthy that compound **2a** was apparently first reported in 1956 by Wildman *et al.* as a *Narcissus pseudonarcissus* metabolite called anhydromethylpseudolycorine.[7a] Wildman's laboratory also achieved the first synthesis of **2a** and, by air oxidation of **2a** under neutral conditions, compound **2b**. Several alternative methods are now available for construction of the pyrrolophenanthridine ring system; however, most of these appear to be attended by significant limitations in yield, generality, or directness.[7] We were intrigued by the emerging structure–activity relationship of various pyrrolophenanthridinium salts, including 1, against lymphocytic leukemia;[6,8] thus we set out to devise a new, concise synthesis of vasconine. We anticipated that a straightforward approach to vasconine would also provide convenient access to oxoassoanine via hydration–oxidation at C(6), or assoanine via borohydride reduction of the iminium C=N bond.

Scheme 1



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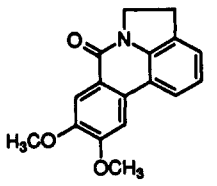

2b

Results and Discussion

In principle, the C(10a)–C(10b) bond of vasconine could be formed by nucleophilic aromatic substitution[9] of an N-protected 7-lithioindoline on either 2-methoxy- or 2-fluoro-4,5-dimethoxybenzaldehyde 2,4-dimethylpent-3-ylimine; however, this approach failed in our hands. 7-Lithio-*N*-BOC-indoline[10] did not appear to react with imine **4a** in ether solution; instead, imine **4a** was recovered unchanged nearly quantitatively from several attempts to effect this reaction. On the other hand, we were initially encouraged by an unoptimized S_NAr reaction of phenyllithium with benzaldimine **4b** to give, after hydrolysis and chromatographic isolation, biaryl carboxaldehyde **6** in 20% yield (Scheme 2).

In a concurrent, related study we also observed that dilithiated *N*-BOC-aniline derivatives react with 2-fluorobenzaldehyde 2,4-dimethylpent-3-ylimine to give fair to good yields of substituted phenanthridines after hydrolytic workup.[11] Nevertheless, several attempts to react imine **4b** with 7-lithio-*N*-BOC-indoline in ether solution gave only complex product mixtures. Mild hydrolytic removal of 2,4-dimethylpent-3-ylamine from these crude product mixtures using 1 M HCl (*N*-BOC-indoline was stable under the hydrolysis conditions)

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(1) Syntex Summer Research Intern.

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(3) Institute of Analytical Research.

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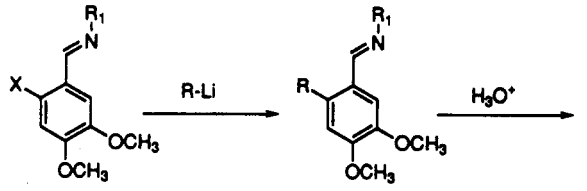
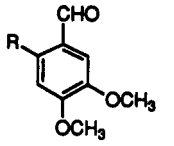
Scheme 2



4a: X = OCH_3
4b: X = F

5a: R = Ph
5b: R = N-BOC-indolin-7-yl

R_1 = 2,4-dimethylpent-3-yl



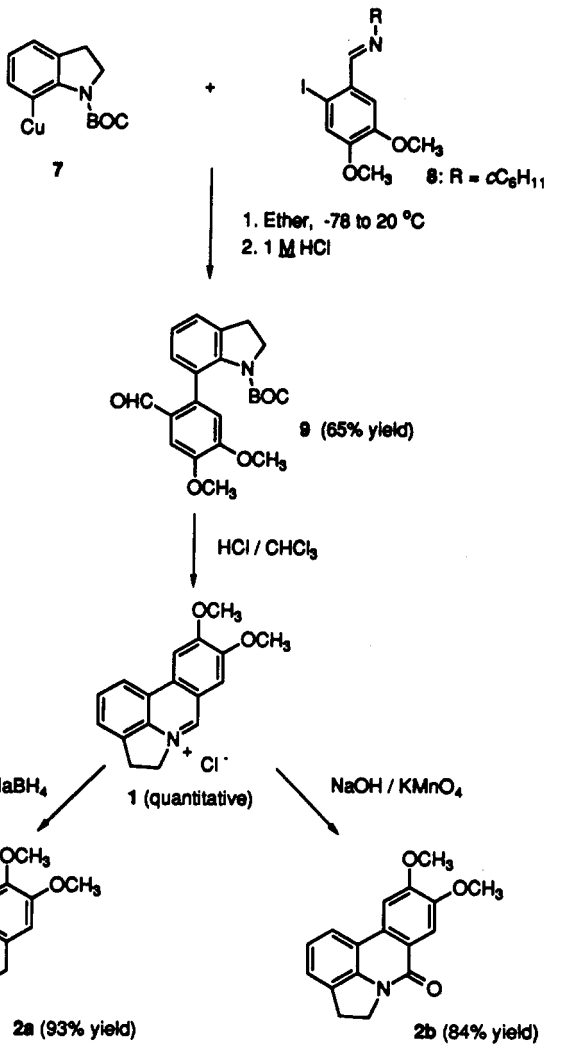
6: R = Ph (20% yield)
9: R = N-BOC-indolin-7-yl (≤2% yield)

resulted in a complex mixture of aldehydes which were later shown to contain ≤2% of the desired adduct **9**, by comparison with an authentic sample. Surprisingly, the major aldehydic product in these mixtures was identified as 3,4-dimethoxybenzaldehyde; however, we are presently unable to definitively explain the defluorination of imine **4b** under the reaction conditions that we used.

We next investigated Ziegler's room temperature Ullmann reaction conditions[12] for the construction of biaryl intermediate **9**. Thus, 7-lithio-*N*-BOC-indoline reacted with 1.0 equiv of CuI–$P(OEt)_3$ (ether, −45 °C) to give a red-brown slurry of (*N*-BOC-indolin-7-yl)copper; 2-iodo-4,5-dimethoxybenzaldehyde cyclohexylimine (**8**)[13] reacted with the organocopper reagent (−45 → 20 °C, 20 h) to give, after hydrolytic workup and chromatographic purification, aldehyde **9** in 65% yield. Deprotection and concomitant cyclization of **9** with anhydrous HCl in $CHCl_3$ solution gave a quantitative yield of pure vasconine (**1**) as a light yellow, amorphous solid. As expected, $NaBH_4$ reduction of **1** gave assoanine (93% yield) while brief treatment of **1** with aqueous NaOH–$KMnO_4$ gave oxoassoanine (**2b**) (84% yield) (Scheme 3).

Routine NMR spectral measurements on vasconine proved somewhat problematic, due in large part to the need for a mixed solvent system (24:1 $CDCl_3$–CD_3OD) to insure its adequate solubility. Even minute changes in the amount of CD_3OD or the concentration of the solute caused fairly large ^1H chemical shift changes; indeed, in our routine NMR samples the chemical shift values for all protons, and the chemical shift order for protons $H_{C(10)}$, $H_{C(2)}$ and $H_{C(7)}$, differed somewhat from the literature data recorded on a $CDCl_3$–CD_3OD solution of natural **1**.[4] In our hands, the ^1H NMR spectrum of **1** exhibited (a) a singlet at δ 9.89 belonging to the proton attached to C(6); (b) two singlets at δ 4.24 and 4.09 assignable to the 8- and 9-methoxy groups; (c) two singlets at δ 8.04 and 7.92 for the aromatic protons of ring A; (d) two triplets at δ 5.34 and 3.83 for the protons attached to C(12) and C(11),

Scheme 3



8: R = cC_6H_{11}
9 (65% yield)
2a (93% yield)
2b (84% yield)

respectively; and (e) doublets at δ 8.51 and 7.80 and a triplet at δ 7.93 belonging to a 1,2,3-trisubstituted aromatic ring. The six aromatic proton resonances were assigned on the basis of their ^1H–^1H connectivities from a 2-D COSY spectrum. The spatial proximity of the protons in rings A, B, and C were determined by 2-D NOESY and 1-D NOEDIFF experiments. The iminium-proton singlet (δ 9.89) showed an NOE with the $H_{C(7)}$ singlet (δ 7.92) and the $H_{C(12)}$ triplet (δ 5.34). Similarly, the $H_{C(10)}$ singlet (δ 8.04) showed an NOE with the $H_{C(1)}$ doublet (δ 8.51) and the methoxy group at δ 4.24. Thus, we were able to unambiguously assign the 9-methoxy resonance. The carbon spectrum of **1** showed 17 resonances; an APT experiment gave the number of protons attached to each carbon. The protonated carbons were assigned by their chemical shift values and their one-bond heteronuclear (^{13}C–^1H) correlations obtained from a 2-D HETCOR experiment. Unambiguous assignment of all the carbons, including the quaternary centers, was done by close inspection of a long-range 2-D HETCOR experiment optimized for three bonds. Long-range carbon correlations up to three bonds were observed for each proton resonance in the spectrum. For example, $H_{C(6)}$ was shown to correlate to C(6) (directly bonded), to C(4a), C(10a), and C(7) (all three bonds away), and to C(6a) (two bonds away). Assignment of the remaining correlations from the HETCOR spectrum confirmed the spectral assignments originally proposed for **1**.

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(13) 2-Iodo-4,5-dimethoxybenzaldehyde was prepared by the method described in Janssen, D. E.; Wilson, C. V. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 547. Imine **8** was coveniently prepared from this aldehyde and cyclohexylamine to give a product identical to that described in ref 12.

Experimental Section

^1H and ^{13}C NMR spectra of 1 in $CDCl_3$–CD_3OD were recorded at 500.13 MHz and 125.77 MHz, respectively. Routine spectra for all other compounds were measured on $CDCl_3$ solutions at 300.13 MHz for ^1H and 75.40 MHz for ^{13}C. All NMR spectra were recorded using internal tetramethylsilane as the internal standard.

2,4,5-Trimethoxybenzaldehyde 2,4-Dimethylpent-3-ylimine (4a). Imine **4a** was prepared from 2,4,5-trimethoxybenzaldehyde and 3-amino-2,4-dimethylpentane in 97% yield by a previously described procedure:[14] bp (0.3 Torr) 110–115 °C; mp 47–48 °C; ^1H NMR ($CDCl_3$) δ 8.43 (s, 1 H), 7.53 (s, 1 H), 6.50 (s, 1 H), 3.92 (s, 3 H), 3.90 (s, 1 H), 3.85 (s, 1 H), 2.47 (t, J = 6.0 Hz, 1 H), 2.03 (octet, J = 6.0 Hz, 2 H), 0.88 (d, J = 6.0 Hz, 6 H), 0.86 (d, J = 6.0 Hz, 6 H); ^{13}C NMR δ 154.6, 153.9, 151.7, 143.6, 117.5, 109.9, 97.1, 83.4, 56.8, 56.4, 56.1, 29.5, 20.5, 18.5. Anal. Calcd for $C_{17}H_{27}NO_3$: C, 69.59; H, 9.28; N, 4.77. Found: C, 69.88; H, 9.26; N, 4.89.

2-Fluoro-4,5-dimethoxybenzaldehyde 2,4-Dimethylpent-3-ylimine (4b). Imine **4b** was prepared as above from 2-fluoro-4,5-dimethoxybenzaldehyde[15] and 3-amino-2,4-dimethylpentane in 87% yield: bp (0.75 Torr) 90–100 °C; ^1H NMR ($CDCl_3$) δ 8.32 (s, 1 H), 7.46 (d, J = 6.8 Hz, 1 H), 6.60 (d, J = 11.6 Hz, 1 H), 3.92 (s, 3 H), 3.89 (s, 3 H), 2.48 (t, J = 6.0 Hz, 1 H), 2.05 (octet, J = 6.0 Hz, 2 H), 0.87 (d, J = 6.0 Hz, 6 H), 0.86 (d, J = 6.0 Hz, 6 H); ^{13}C NMR δ 157.2 (d, J = 245 Hz), 152.1 (d, J = 3.6 Hz), 151.8 (d, J = 10 Hz), 145.6, 115.6 (d, J = 10.4 Hz), 108.4 (d, J = 4.5 Hz), 99.4 (d, J = 27.7 Hz), 83.6, 56.4, 56.2, 29.4, 20.4, 18.4. Anal. Calcd for $C_{16}H_{24}FNO_2$: C, 68.30; H, 8.60; N, 4.98. Found: C, 68.45; H, 8.52; N, 5.24.

4,5-Dimethoxy-2-phenylbenzaldehyde (6). Bromobenzene (0.17 mL, 1.6 mmol) was dissolved in 5 mL of dry ether at 0 °C under a nitrogen atmosphere. *n*-BuLi (0.91 mL of a 1.6 M solution in hexanes; 1.5 mmol) was added dropwise over 3 min and the reaction mixture was maintained at 0 °C for 1.5 h. Imine **4b** (0.341 g, 1.2 mmol) in 1 mL of ether was added and the reaction mixture was allowed to warm to rt. After 14 h the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried ($MgSO_4$), filtered, and concentrated to give a syrupy residue. The residue was hydrolyzed with 0.33 mL of 4 M HCl in 3 mL of THF to give **6**: ^1H NMR ($CDCl_3$) δ 9.83 (s, 1 H), 7.54 (s, 1 H), 7.48–7.45 (m, 3 H), 7.40–7.37 (m, 2 H), 6.86 (s, 1 H), 3.99 (s, 3 H), 3.98 (s, 3 H). The 2,4-dinitrophenylhydrazone: mp 221.5–223 °C (ethanol). Anal. Calcd for $C_{21}H_{18}N_4O_6$: C, 59.72; H, 4.30; N, 13.26. Found: C, 59.74; H, 4.22; N, 13.14.

***tert*-Butyl 7-(2-Formyl-4,5-dimethoxyphenyl)-2,3-dihydroindole-1-carboxylate (9).** *N*-BOC-indoline (2.352 g; 10.7 mmol) and 1.8 mL of dry *N,N,N′,N′*-tetramethylethylenediamine were dissolved in 15 mL of dry ether at −40 °C (internal thermometer) under a nitrogen atmosphere. *sec*-BuLi (8.3 mL of a 1.3 M solution in cyclohexane) was added dropwise, and the reaction mixture was maintained at −40 to −50 °C for 2 h. Solid CuI–$P(EtO)_3$ complex (5.734 g; 16.1 mmol) was added in one portion to give a reddish-brown slurry. The reaction mixture was stirred vigorously at −45 °C for 30 min, and 2.002 g (5.4 mmol) of solid imine **8** was added in one portion. The reaction mixture was allowed to warm to rt over *ca.* 1 h (reaction mixture changed to green-black solution) and was stirred for 18 h at rt. The reaction mixture was poured into saturated NH_4Cl and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated with a rotary evaporator to give a pale yellow oil. The crude oil was dissolved in 50 mL of THF, 5.4 mL of 1 M HCl was added, and the reaction mixture was refluxed for 0.5 h. The reaction mixture was diluted with 150 mL of water and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated to give 2.06 g of a crude solid. Chromatography of the crude material on silica gel (95:5 hexane–EtOAc) gave 1.349 g (65% yield) of **9**: mp 139–140 °C; ^1H NMR ($CDCl_3$) δ 9.78 (s, 1 H), 7.48 (s, 1 H), 7.27–7.24 (m, 1 H), 7.15–7.09 (m, 2 H), 6.90 (s, 1 H), 4.10 (m, 2 H), 3.96 (s, 3 H), 3.95 (s, 3 H), 3.08 (t, J = 7.7 Hz, 2 H), 1.18 (s, 9 H); ^{13}C NMR δ 191.4, 153.7, 152.5, 148.2, 141.5, 140.7, 135.1, 131.1, 126.5, 125.8, 124.5, 124.2, 111.5, 108.4, 80.8, 56.2, 56.1, 50.5, 29.4, 27.9; MS *m/z* 383 (M, 10%), 282 (10%), 266 (100%), 57 (21%). Anal. Calcd for $C_{22}H_{25}NO_5$: C, 68.91; H, 6.57; N, 3.65. Found: C, 68.97; H, 6.82; N, 3.36.

Vasconine (1). Aldehyde **9** (0.8526 g, 2.22 mmol) was dissolved in 50 mL of $CHCl_3$. Anhydrous HCl was gently bubbled into the stirred solution at rt to give a thick yellow slurry. After 15 min the mixture was filtered and the precipitate was washed with dry ether to give, after drying, 0.667 g (quantitative yield) of amorphous vasconine, mp = 220–221 °C. This material was pure as judged by TLC (R_f = 0.2: silica gel; 9:1 CH_2Cl_2–CH_3OH) and ^1H NMR. An analytical sample of 1 was recrystallized from ethanol–ether to give yellow needles of vasconine sesquihydrate: mp 232–233 °C (lit.[4] mp 233–235 °C); ^1H NMR ($CDCl_3$–CD_3OD) δ 9.89 (s, 1 H), 8.51 (d, J = 7.3 Hz, 1 H), 8.04 (s, 1 H), 7.93 (t, J = 7.3 Hz, 1 H), 7.92 (s, 1 H), 7.80 (d, J = 7.3 Hz, 1 H), 5.34 (t, J = 7.2 Hz, 2 H), 4.24 (s, 3 H), 4.09 (s, 3 H), 3.83 (t, J = 7.2 Hz, 2 H); ^{13}C NMR δ 158.0 C(9), 151.9 C(8), 145.8 C(6), 136.2 C(4a), 131.2 C(2), 130.4 C(10a), 125.5 C(3), 123.4 C(10b), 121.6 C(6a), 120.0 C(1), 111.3 C(7), 102.4 C(10), 56.8 9-OCH_3, 56.7 8-OCH_3, 55.7 C(12), 27.6 C(11). EI-MS *m/z* 266 (M, 100%), 265 (11%), 264 (17%), 252 (6%), 251 (22%), 250 (34%), 222 (9%), 221 (5%), 220 (5%), 205 (10%), 193 (6%), 192 (5%), 190 (6%), 180 (4%), 178 (4%). Anal. Calcd for $C_{17}H_{16}ClNO_2(1.5\ H_2O)$: C, 62.10; H, 5.82; N, 4.26. Found: C, 61.73; H, 6.04; N, 4.37.

Assoanine (2a).[16] Vasconine (0.3613 g, 1.20 mmol) was dissolved in 35 mL of absolute ethanol. $NaBH_4$ (0.15 g) was added in portions to the stirred solution at room temperature. After 30 min, the reaction mixture was diluted with 200 mL of water and extracted with ethyl acetate. The ethyl acetate layer was washed with water, dried ($MgSO_4$), and concentrated to give 0.2977 g (93%) of assoanine: mp 175–176 °C; ^1H NMR δ 7.32 (dd, J = 7.4, 0.8 Hz, 1 H), 7.18 (s, 1 H), 7.00 (dt, J = 7.4, 0.8 Hz, 1 H), 6.76 (t, J = 7.4 Hz), 6.64 (s, 1 H), 4.09 (s, 1 H), 3.94 (s, 3 H), 3.88 (s, 3 H), 3.32 (t, J = 7.9 Hz, 2 H), 3.01 (t, J = 7.9 Hz, 2 H); ^{13}C NMR δ 149.6, 148.7, 148.4, 128.5, 124.8, 124.3, 123.4, 119.6, 119.4, 119.1, 110.3, 105.4, 56.1, 55.5, 53.2, 29.1; MS *m/z* (rel inten) 267 (60%) $[M]^{\bullet+}$, 266 (100%), 252 (4%), 251 (8%), 250 (19%), 222 (8%), 193 (5%), 180 (6%), 134 (16%). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.17; H, 6.43; N, 5.21.

Oxoassoanine (2b). Vasconine (0.1247 g, 0.41 mmol) was dissolved in 10 mL of water. At 20 °C under a nitrogen atmosphere 0.25 mL of 3 M NaOH were added 0.13 g of $KMnO_4$ and 20 mL of CH_2Cl_2 to the solution, and the mixture was stirred vigorously for 2 h. The reaction mixture was filtered through a Celite pad and the phases were separated. The aqueous layer was washed with 3 × 20 mL of CH_2Cl_2; the organic layers were combined, dried ($MgSO_4$), and concentrated to give 0.098 g (84%) of white solid oxoassoanine: mp 270–271 °C (lit.[9b] mp 268–269 °C); ^1H NMR δ 7.88 (s, 1 H), 7.83 (dd, J = 8.0, 1.0 Hz, 1 H), 7.54 (s, 1 H), 7.31 (dd, J = 8.0, 1.0 Hz, 1 H), 7.24 (t, J = 8.0 Hz, 1 H), 4.47 (t, J = 8.5 Hz, 2 H), 4.09 (s, 3 H), 4.04 (s, 3 H), 3.45 (t, J = 8.5 Hz, 2 H); ^{13}C NMR δ 159.7, 152.9, 149.5, 139.1, 131.0, 128.6, 123.6, 123.5, 120.7, 119.1, 116.7, 108.4, 102.9, 56.0 (2 O$\underline{C}H_3$), 46.5, 27.2.

Acknowledgment. We thank Mr. Jacob Berger for valuable contributions during the course of this work.

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(16) Our ^1H NMR and MS data for compound **2a** exactly match the corresponding data from ref 5 for natural assoanine; however, the ^{13}C NMR data given in ref 5 for assoanine is clearly incomplete (only 11 singlets are reported). In addition, the agreement between our ^{13}C NMR data for **2a** (16 distinct spectral lines) and the lines reported in ref 5 for natural assoanine is only fair. The extremely facile air oxidation of **2a** has been noted in both ref 7a and ref 5; we speculate that oxidative processes may have caused at least partial degradation of the small sample of natural assoanine reported in ref 5 during the measurement of its ^{13}C NMR spectrum. In our hands, synthetic **2a** was shown to be stable at rt under a nitrogen atmosphere during the course of a 2-h ^{13}C NMR experiment; however, several uncharacterized degradation products formed in $CDCl_3$ solutions of **2a** under an air atmosphere over the course of *ca.* 24 h.