A Synthetic Route to Dehydrosecodine Analogues[1]

Paul D. Leeson†
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Pyridinium salts (**21**) and (**22**) were synthesised and their reductions to analogues of the postulated biosynthetic intermediate dehydrosecodine (**1**) investigated. From (**22**) the isomeric 1-methyl-19-oxodehydrosecodines (**5**)—(**7**) were isolated. Wittig reaction of the 2-methoxalylindoles (**14**) and (**15**) with methylenetriphenylphosphorane led to the dihydro-oxepino[4,5-*b*]indole derivative (**19**).

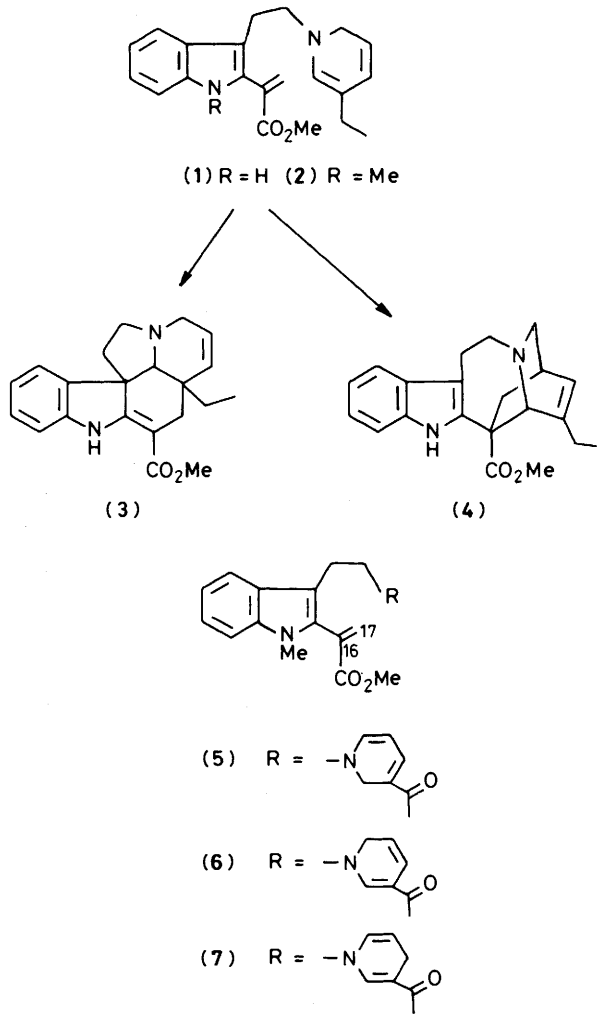
The suggested intermediacy of dehydrosecodine (**1**)[2,3] in the biosynthesis of the monoterpenoid indole alkaloids tabersonine (**3**) and catharanthine (**4**) (Scheme 1) has stimulated intensive efforts to mimic these biogenetic proposals.[4–9] We describe here a short and flexible synthesis of (**1**) derivatives which complements the existing methods.[6,7] The key step is reduction of a pyridinium salt to generate the dihydropyridine functionality. The approach is exemplified by the synthesis of the 1-methyl-19-oxodehydrosecodines (**5**)—(**7**), and an attempted synthesis of 1-methyldehydrosecodine (**2**). Compounds (**2**) and (**5**)—(**7**) are stabilised derivatives of (**1**) in which the N(1)-methyl group prevents the easy dimerisation of the indole-2-acrylate moiety.[10] Additionally, in (**5**)—(**7**) the electron-withdrawing keto group at C-19 stabilises and permits ready isolation of the dihydropyridines.[11]

The route used to synthesise the required pyridinium salts (**21**) and (**22**) is shown in Scheme 2. An important step is the introduction of the acrylate by a Wittig reaction of a 2-alkoxalylindole with methylenetriphenylphosphorane.[4] The course of the reaction was found to depend upon the nature of the R^1 substituent in the glyoxalates (**12**)—(**15**). With the acetate (**12**) and the chloride (**13**) the expected acrylates (**16**) and (**17**) were obtained but with the bromo- (**14**)‡ and iodo- (**15**) compounds the only isolated products were triphenylphosphine and the dihydro-oxepine (**19**). Structure (**19**) was confirmed by degradation to the diol (**20**) with $LiAlH_4$; this material was identical with that obtained from $LiAlH_4$ treatment of (**17**). The formation of (**19**) is likely to involve initial intramolecular alkylation of a betaine or oxaphosphetane intermediate to give (**18**). The cation (**18**) could yield (**19**) by a number of pathways. The net process, shown in (**18**; arrows), is ring expansion by a 1,2-shift of oxygen with elimination of triphenylphosphine, then deprotonation.

The pyridinium iodide (**22**) upon treatment with $NaCNBH_3$[7a] or with $NaBH(OMe)_3$ in *N*-methylpyrrolidone gave a mixture of the isomeric 1-methyl-19-oxodehydrosecodines (**5**)—(**7**). Separation of these compounds was achieved by preparative layer chromatography on alumina, and the structures were assigned on the basis of their characteristic u.v. spectra.[11] The mass spectra[10] of (**5**)—(**7**) indicated partial reduction of the 16,17-(acrylate) double bond had occurred. In common with other stabilized 1,4-dihydropyridine analogues[7] of (**1**), compounds (**5**)—(**7**) could not be induced to undergo intramolecular cyclisations according to Scheme 1.

1-Methyldehydrosecodine (**2**) and its isomers were expected to be intermediates in metal hydride reductions of the pyridinium iodide (**21**). Controlled treatment of (**21**) with $NaBH(OMe)_3$ in protic solvents gave the tetrahydropyridines (**23**) and (**24**);[12] (**23**) was the major product (90% by n.m.r.). In non-protic solvents, reductions of (**21**) with several metal hydride reagents resulted in complex mixtures containing low yields of (**23**). Neither (**2**) nor the 1-methyl derivatives of (**3**) and (**4**) were detectable in these mixtures. The dihydropyridine in (**2**) could, in agreement with other evidence,[3c,9,11] function as a reducing agent for the 16,17-double bond.

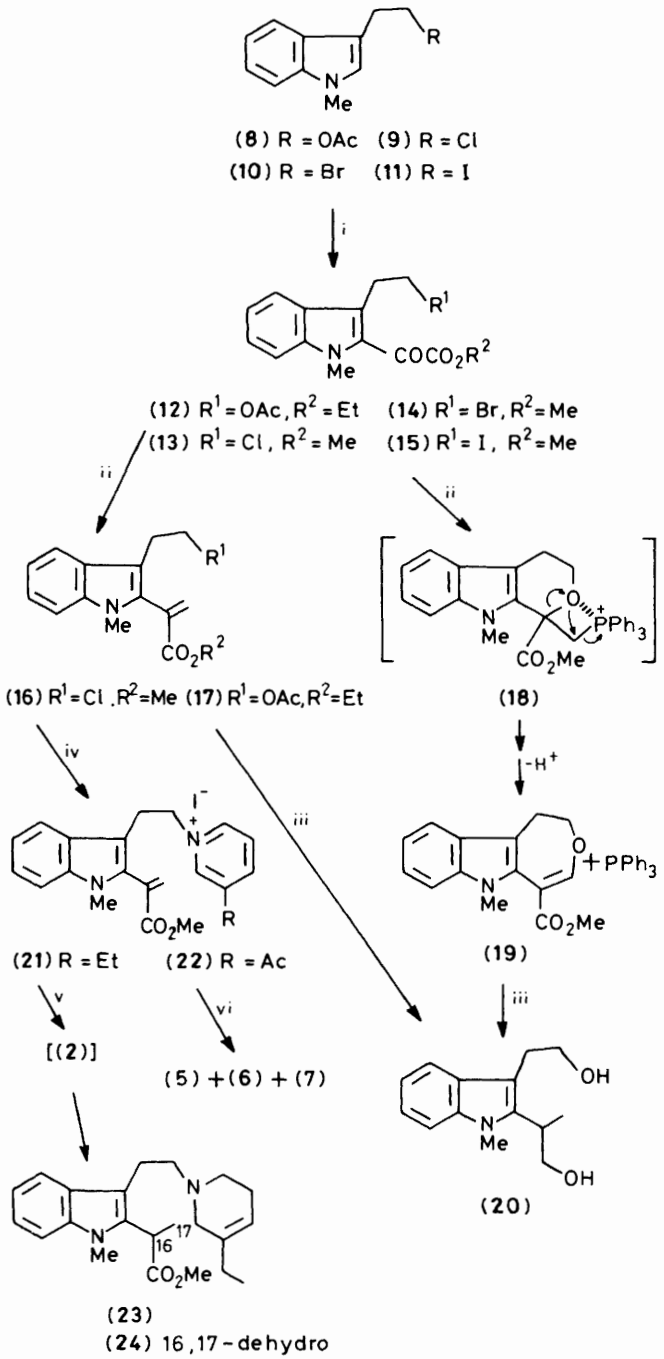
The synthesis reported here provides a simpler alternative to present methods[6,7] for construction of the dehydrosecodine (**1**)



Scheme 1.

† *Current address:* Smith Kline and French Research Limited, The Frythe, Welwyn, Herts, AL6 9AR.

‡ After completion of the work described here,[1] the synthesis of compound (**14**) by a similar route and its use in secodine alkaloid synthesis was described.[12a]



Scheme 2. *Reagents:* i, $ClCOCO_2R^2$, $AlCl_3$; ii, $CH_2{=}PPh_3$; iii, $LiAlH_4$; iv, 3-R-pyridine, NaI; v, $NaBH(OMe)_3$, MeOH; vi, $NaBH(OMe)_3$ or $NaCNBH_3$.

alkaloid system, and is capable of extension to other N-1 and dihydropyridine analogues of (**1**).

Experimental

Column chromatography was carried out with Fisons silica gel, 100—200 mesh, or Woelm neutral alumina (activity III). Preparative layer chromatography (p.l.c.) was performed using plates coated to a thickness of 1 mm in silica gel F-254 or commercially prepared plates pre-coated to a thickness of 1 mm in alumina F-254. Organic solutions were dried over anhydrous sodium sulphate.

3-(2-Acetoxyethyl)-2-ethoxalyl-1-methylindole (**12**).—3-(2-Hydroxyethyl)indole (44.8 g, 0.278 mol) was dissolved in AnalaR pyridine (50 ml) and to the cooled (0 °C) stirred solution was added acetic anhydride (50 ml). The solution was warmed to room temperature and after 1 h evaporated to dryness. The residue was dissolved in EtOAc, and the solution washed with saturated aqueous $NaHCO_3$, saturated aqueous NaCl, and then dried and evaporated to give 3-(2-acetoxyethyl)-indole (55.3 g, 0.273 mol), which was divided into three and each portion *N*-methylated as follows. To a stirred slurry of sodium hydride (from 4.60 g of a 50% dispersion in oil) in dry tetrahydrofuran (THF) (40 ml) under nitrogen was slowly added 3-(2-acetoxyethyl)indole (18.0 g) in dry THF (100 ml). The mixture was refluxed for 5 min, cooled to 0 °C and then methyl iodide (11.0 ml) was added to it. After 0.5 h at room temperature, saturated aqueous NH_4Cl was added to the mixture and the whole extracted with EtOAc. The organic solution was dried and evaporated. The yield of 3-(2-acetoxyethyl)-1-methylindole (**8**) from three reactions was 58.2 g (0.269 mol); δ($CDCl_3$) 2.04 (3 H, s, $OCOCH_3$), 3.07 (2 H, t, $ArCH_2$), 3.70 (3 H, s, NCH_3), 4.32 (2 H, t, CH_2O) and 6.8—7.7 (5 H, m, ArH); *m/z* 217 (M^+). Compound (**8**) (0.50 g, 2.3 mmol) was dissolved in ethoxalyl chloride (6.11 g, 0.0217 mol) and to the cold (−15 °C) stirred solution was added aluminium chloride (0.50 g, 3.75 mmol). The mixture was stirred at room temperature for 24 h, cooled to 0 °C, decomposed with crushed ice, and extracted with EtOAc. The organic solution was washed with saturated aqueous $NaHCO_3$, dried, and chromatographed on silica gel (35 g). Elution with CH_2Cl_2 gave (**12**) (0.45 g, 1.42 mmol, 62%), m.p. 50—51 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 64.5; H, 6.1; N, 4.2; M^+, 317. $C_{17}H_{19}NO_5$ requires C, 64.3; H, 6.0; N, 4.4%; *M*, 317); $\lambda_{max.}$(EtOH) 225, 243, and 324 nm; $\nu_{max.}$ 1 730 (ester CO) and 1 645 cm^{-1} (ketone CO); δ($CDCl_3$) 1.46 (3 H, t, OCH_2CH_3), 2.04 (3 H, s, $OCOCH_3$), 3.24 (2 H, t, $ArCH_2$), 4.00 (3 H, s, NCH_3), 4.29 (2 H, t, CH_2O), and 4.48 (2 H, q, OCH_2CH_3).

3-(2-Chloroethyl)-2-methoxalyl-1-methylindole (**13**).—Compound (**8**) (58.2 g, 0.269 mol) was dissolved in MeOH (750 ml) and KOH (17.0 g) in water (100 ml) was added to the solution. Additional MeOH was added to homogenise the mixture, and after 1 h water was added (total volume 2 l) and the mixture extracted with EtOAc. The dried solution was evaporated and the residue chromatographed on alumina (1.4 kg). Elution with Et_2O–EtOAc–MeOH (10:10:1) gave 3-(2-hydroxyethyl)-1-methylindole (38.0 g, 0.217 mol); δ($CDCl_3$) 2.12 (1 H, s, OH), 2.93 (2 H, t, $ArCH_2$), 3.60 (3 H, s, NCH_3), 3.79 (2 H, t, CH_2O) and 6.8—7.6 (5 H, m, ArH); *m/z* 175 (M^+). This alcohol (5.22 g, 0.0298 mol) was dissolved in dry Et_2O (50 ml) and thionyl chloride (3.73 g, 0.0313 mol) added dropwise to the cooled (0 °C) stirred solution. After 2 h at room temperature saturated aqueous $NaHCO_3$ was added and the mixture extracted with EtOAc. The organic solution was dried and evaporated to give the chloride (**9**) (5.60 g) which was dissolved in methoxalyl chloride (26.6 g, 0.217 mol) and aluminium chloride (5.2 g, 0.039 mol) added with stirring. The mixture was stirred at 65—70 °C for 0.5 h after which time the reaction was complete as monitored by the appearance in the u.v. spectrum of the mixture of the characteristic 2-acylindole chromophore, $\lambda_{max.}$ 323 nm. The reaction was worked up and the product purified as described for (**12**) to give (**13**) (4.70 g, 16.8 mmol, 56%), m.p. 79—80 °C (Found: C, 60.1; H, 4.9; Cl, 12.7; N, 4.9; M^+, 279 and 281. $C_{14}H_{14}ClNO_3$ requires C, 60.1; H, 5.0; Cl, 12.7; N, 5.0%; *M*, 279 and 281; $\lambda_{max.}$(EtOH) 225, 243, and 323 nm; $\nu_{max.}$ 1 730 (ester CO) and 1 645 cm^{-1} (ketone CO); δ($CDCl_3$) 3.22—3.78 (4 H, m, $ArCH_2CH_2Cl$), 3.97 and 4.01 (2 × 3 H, 2 × s, NCH_3 and OCH_3) and 7.1—7.8 (4 H, m, ArH).

3-(2-*Bromoethyl*)-2-*methoxalyl*-1-*methylindole* (**14**).—This compound was prepared from (**10**) [from 3-(2-hydroxyethyl)-1-methylindole and PBr_3 [13]] as described for (**13**) in 42% yield, m.p. 80—81 °C (Found: C, 52.0; H, 4.3; Br, 24.7; N, 4.3; M^+, 325 and 323. $C_{14}H_{14}BrNO_3$ requires C, 51.8; H, 4.4; Br, 24.7; N, 4.3%; *M*, 325 and 323); $\lambda_{max.}$(EtOH) 224, 243, and 323 nm; $\nu_{max.}$ 1 730 (ester CO) and 1 645 cm^{-1} (ketone CO); δ($CDCl_3$) 3.27—3.64 (4 H, m, ArCH_2CH_2Br), 3.94 and 4.00 (2 × 3 H, 2 × s, NCH_3 and OCH_3) and 7.0—7.8 (4 H, m, Ar*H*).

3-(2-*Iodoethyl*)-2-*methoxalyl*-1-*methylindole* (**15**).—3-(2-Hydroxyethyl)-1-methylindole (0.30 g, 1.71 mmol) was dissolved in dry pyridine (2 ml) and treated at 0 °C with methanesulphonyl chloride (0.3 ml). After 0.5 h at room temperature the solution was evaporated and the residue dissolved in EtOAc; the solution was washed with dilute HCl, water, and saturated aqueous NaCl. The dried solution was evaporated and the residue refluxed in dry acetone (20 ml) with sodium iodide (2.0 g) for 0.5 h. After evaporation the residue was partitioned between water and EtOAc, and the organic layer dried and evaporated to give the iodide (**11**) (0.46 g). The latter was treated with methoxalyl chloride and aluminium chloride as described above to give (**15**) (0.158 g, 0.43 mmol, 25%), m.p. 82—83 °C (Found: C, 46.1; H, 3.9; N, 3.7; M^+, 371. $C_{14}H_{14}INO_3$ requires C, 45.3; H, 3.9; N, 3.7%; *M*, 371); $\lambda_{max.}$(EtOH) 224, 244, and 323 nm; $\nu_{max.}$ 1 730 (ester CO) and 1 645 cm^{-1} (ketone CO); δ($CDCl_3$) 3.23—3.60 (4 H, m, ArCH_2CH_2I), 4.00 and 4.04 (2 × 3 H, 2 × s, NCH_3 and OCH_3), and 7.1—7.8 (4 H, m, ArH).

3-(2-*Chloroethyl*)-2-(1-*methoxycarbonylvinyl*)-1-*methylindole* (**16**).—To a stirred slurry of methyltriphenylphosphonium bromide (4.64 g, 0.013 mol) in dry THF under nitrogen was added n-butyl-lithium (5.90 ml of a 1.84M solution in hexane, 10.8 mmol). After 5 min, the orange solution was cooled to −50 °C and a solution of (**13**) (2.79 g, 10 mmol) in dry THF (15 ml) was added to it. The reaction mixture was warmed to 0 °C over 0.5 h and then to room temperature; after 2 h excess of saturated NH_4Cl was added to the mixture. The mixture was extracted with EtOAc and the organic extract dried and evaporated; the residue was chromatographed on silica gel (200 g). Elution with CH_2Cl_2 gave (**16**) (1.91 g, 6.9 mmol, 69%), m.p. 55—56 °C (Found: C, 64.7; H, 5.8; Cl, 12.9; N, 4.9; M^+, 277 and 279. $C_{15}H_{16}ClNO_2$ requires C, 64.8; H, 5.8; Cl, 12.8; N, 5.0%; *M*, 277 and 279); $\lambda_{max.}$(EtOH) 229 and 280 nm; $\nu_{max.}$ 1 715 (CO) and 1 625 cm^{-1} (C=C); δ($CDCl_3$) 3.17 and 3.60 (2 H, m, ArCH_2CH_2Cl), 3.54 and 3.76 (3 × 3 H, 3 × s, OCH_3 and NCH_3), 5.96 and 6.84 (1 H, d, =CH_2), and 7.0—7.7 (4 H, m, ArH).

Similarly prepared, from (**12**), was (**17**) (83%); $\lambda_{max.}$(EtOH) 229 and 282 nm; $\nu_{max.}$ 1 720 (CO), and 1 620 cm^{-1} (C=C); δ($CDCl_3$) 1.27 (3 H, t, OCH_2CH_3), 2.01 (3 H, s, $OCOCH_3$), 3.03 and 4.24 (2 H, t, ArCH_2CH_2O), 3.58 (3 H, s, NCH_3), 4.26 (2 H, q, OCH_2CH_3), 5.95 and 6.82 (1 H, d, =CH_2), and 7.0—7.7 (4 H, m, ArH); *m/z* 315 (M^+).

1,2-*Dihydro*-5-*methoxycarbonyl*-6-*methyl*-6H-*oxepino*[4,5-b]*indole* (**19**).—Reaction of (**14**) (0.324 g, 1.0 mmol) with methylenetriphenylphosphorane was performed as described for (**16**) above. Purification of the crude product by p.l.c. on silica [eluant Et_2O–light petroleum (b.p. 60—80 °C), 3:2] gave triphenylphosphine, identical in all respects with authentic material, and (**19**) (0.060 g, 0.23 mmol, 22%), m.p. 137—138 °C [from CH_2Cl_2–light petroleum (b.p. 60—80 °C] (Found: C, 69.9; H, 5.9; N, 5.4; M^+, 257.1051. $C_{15}H_{15}NO_3$ requires C, 70.0; H, 5.8; N, 5.5%; *M*, 257.1057); $\lambda_{max.}$(EtOH) 235 and 308 nm; $\nu_{max.}$ 1 705 (CO) and 1 605 cm^{-1} (C=C); δ($CDCl_3$) 3.12 (2 H, t, $ArCH_2$), 3.49 (3 H, s, NCH_3), 3.76 (3 H, s, OCH_3), 4.40 (2 H, t, CH_2O), 6.9—7.5 (4 H, m, ArH), and 7.62 (1 H, s, =CHO).

Similar treatment of (**15**) with methylenetriphenylphosphorane gave (**19**) (47%).

3-(2-*Hydroxyethyl*)-2-(1-*methyl*-2-*hydroxyethyl*)-1-*methylindole* (**20**).—Compound (**19**) (0.050 g, 0.20 mmol) was dissolved in dry THF (3 ml) under nitrogen and to the stirred solution at room temperature was added an excess of $LiAlH_4$ in portions over 3 h. Saturated aqueous Rochelle salt (5 ml) was cautiously added to the mixture which was then extracted with EtOAc; the extract was dried and evaporated and the residue purified by p.l.c. on silica (eluant $CHCl_3$–MeOH, 10:1) to give (**20**) (0.025 g, 55%); $\lambda_{max.}$(EtOH) 229 and 281 nm; $\nu_{max.}$ 3 500 cm^{-1} (OH); δ($CDCl_3$) 1.34 (3 H, d, $CHCH_3$), 3.69 (3 H, s, NCH_3), and 7.0—7.5 (4 H, m, Ar*H*); *m/z* 233 (M^+).

Treatment of (**17**) with $LiAlH_4$ under the same conditions also gave (**20**), identical in all respects (t.l.c., u.v., i.r., n.m.r., and mass spectroscopy) with the sample obtained from (**19**).

Preparation of the Pyridinium Salts (**21**) *and* (**22**).—Compound (**16**) (1.00 g, 3.6 mmol), sodium iodide (2.70 g, 18 mmol) and 3-ethylpyridine (1.94 g, 18 mmol) were stirred in dry acetonitrile (10 ml) in the dark in a sealed flask under nitrogen at 75—80 °C for 54 h. The cooled mixture was evaporated to dryness, dissolved in CH_2Cl_2, filtered, and evaporated. The residue was dissolved in hot water, cooled, and extracted with Et_2O. The aqueous layer was evaporated and the residue dissolved in CH_2Cl_2 and the solution dried. Evaporation gave the crude product, which was recrystallised from CH_2Cl_2–light petroleum (b.p. 40—60 °C) to give 3-[2-(3-*ethylpyridin*-1-*io*)*ethyl*]-2-(1-*methoxycarbonylvinyl*)-1-*methylindole iodide* (**21**) (1.53 g, 3.2 mmol, 89%), m.p. 186 °C (decomp.) (Found C, 55.5; H, 5.5; I, 26.7; N, 5.6. $C_{22}H_{25}IN_2O_2$ requires C, 55.5; H, 5.3; I, 26.7; N, 5.9%); $\lambda_{max.}$(EtOH) 227 and 269 nm; $\nu_{max.}$ 1 725 (CO) and 1 630 cm^{-1} (C=C); δ($CDCl_3$) 0.83 (3 H, t, CH_2CH_3), 2.46 (2 H, q, CH_2CH_3), 3.41 (3 H, s, NCH_3), 3.71 (3 H, s, OCH_3), 3.75 (2 H, t, $ArCH_2$), 4.88 (2 H, t, CH_2N^+), 6.01 and 6.79 (1 H, d, =CH_2) and 6.7—8.9 (8 H, m, ArH).

Use of 3-acetylpyridine in the above procedure gave 3-[2-(3-acetylpyridin-1-io)ethyl]-2-(1-methoxycarbonylvinyl)-1-methylindole iodide (**22**) (86%), m.p. 159-160 °C (decomp.), $\lambda_{max.}$(EtOH) 227, 275, 293infl. $\lambda_{min.}$ 247 nm; $\nu_{max.}$ 1 720 (ester CO), 1 700 (ketone CO) and 1 630 cm^{-1} (C=C); δ($CDCl_3$) 2.37 (3 H, s, $COCH_3$), 3.47 (3 H, s, NCH_3), 3.77 (3 H, s, OCH_3), 5.10 (2 H, t, CH_2N^+), 6.13 and 6.79 (1 H, d, =CH_2), 6.8—7.3 (4 H, m, ArH), 7.90 (1 H, m, Py-5H), 8.59 (1 H, d, Py-4H), 8.93 (1 H, s, Py-2H), and 9.33 (1 H, d, Py-6H).

3-[2-(3-*Ethyl*-1,2,5,6-*tetrahydro*-1-*pyridyl*)*ethyl*]-2-(1-*methoxycarbonylethyl*)-1-*methylindole* (1-*Methyl*-16,17-*dihydrosecodine*) (**23**).—Compound (**21**) (0.060 g) was dissolved in dry MeOH (5 ml) and $NaBH(OMe)_3$ added in small portions to the stirred cooled (−20 °C) solution under nitrogen. The reaction was quenched by water (10 ml) when t.l.c. (silica, $CHCl_3$–MeOH, 10:1) showed that all of (**21**) had been consumed. The mixture was extracted with EtOAc and the extract was dried and evaporated. The residue was purified by p.l.c. (silica, eluant $CHCl_3$–MeOH, 15:1) to give (**23**) (0.033 g, 74%) (Found: M^+, 354.2307. $C_{22}H_{30}N_2O_2$ requires *M*, 354.2308); $\lambda_{max.}$(EtOH) 229 and 286 nm; δ($CDCl_3$) 1.04 (3 H, t, CH_2CH_3), 1.59 (3 H, d, $CHCH_3$), 3.74, 3.76 (6 H, s, OCH_3, NCH_3), 4.17 (1 H, d, $CHCH_3$), 5.50 (1 H, m, =CH), and 7.0—7.7 (4 H, m, ArH). The presence of 1-methylsecodine (**24**) to the extent of 10% was apparent in the n.m.r. spectrum; δ 5.99 and 6.85 (0.1 H, d, =CH_2). When performed at a range of temperatures from −70 to 25 °C, this reaction led to similar (**23**):(**24**) product ratios. Use of an excess of reducing agent gave (**23**) only.

1-*Methyl*-19-*oxodehydrosecodines* (**5**)—(**7**). (*a*) Compound (**22**) (0.20 g) was dissolved in dry *N*-methylpyrrolidone (3 ml) and to the stirred solution under nitrogen was added $NaBH(OMe)_3$ over 1 h, when the reaction was complete as deduced by the disappearance of (**22**) on t.l.c. (silica, $CHCl_3$–*MeOH*–Et_3N, 20:1:0.1; 1.2 molar equivalents of the reducing agent were generally required). The reaction mixture was diluted with water and extracted with EtOAc; the organic extract was then washed with water, dried, and evaporated to yield a reddish gum.

(*b*) Compound (**22**) was treated with $NaCNBH_3$ in water–CH_2Cl_2 using the reported[7a] method. The crude product from both reduction procedures consisted of the same three major components according to t.l.c. and had: $\nu_{max.}$ 1 720 (COs) and 1 640 cm^{-1} (C=C); $\delta(CDCl_3)$ 1.85 (3 H, s, $COCH_3$), 3.54 (3 H, s, NCH_3), 3.76 (3 H, s, OCH_3), and 5.93 and 6.79 (1 H, d, $=CH_2$). Separation of the mixture was accomplished by p.l.c. on alumina, under nitrogen with $CHCl_3$ as the eluant. The three major bands were removed as rapidly as possible from the alumina with EtOAc. In order of decreasing R_F, these components were: (i) 3-[2-(3-*acetyl*-1,2-*dihydro*-1-*pyridyl*)-*ethyl*]-2-(1-*methoxycarbonylvinyl*)-1-*methylindole* (1-methyl-19-oxodehydrosecodine A*) (**5**) (0.050 g, 34%), $\lambda_{max.}$(EtOH) 281, 290infl, 350infl, and 455; $\lambda_{min.}$ 408 nm; *m/z* 364 (M^+, 26%), 241 (21), 228 (58), 184 (33), 149 (100), and 136 (13); (ii) 3-[2-(3-acetyl-1,4-dihydro-1-pyridyl)ethyl]-2-(1-methoxycarbonylvinyl)-1-methylindole (1-methyl-19-oxodehydrosecodine C†) (**7**) (0.020 g, 13%), $\lambda_{max.}$(EtOH) 291 and 375; $\lambda_{min.}$ 328 nm; *m/z* 364 (M^+, 44%), 241 (31), 228 (100), 184 (54), 149 (28), and 136 (13); (iii) 3-[2-(5-acetyl-1,2-dihydro-1-pyridyl)ethyl]-2-(1-methoxycarbonylvinyl)-1-methylindole (1-methyl-19-oxodehydrosecodine B*) (**6**) (0.055 g, 37%), $\lambda_{max.}$(EtOH) 274infl, 282, 294infl, and 358; $\lambda_{min.}$ 320 nm; *m/z* 364 (M^+), 241, 228, 184, 149, and 136. In the mass spectra of (**5**)—(**7**), low abundance signals at *m/z* 366, 243 and 230 were indicative[10] of the 16,17-dihydro compounds.

* Nomenclature from ref. 3.

† Proposed nomenclature.

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