Synthesis of Some Pyrrolo[4,3,2-*de*]quinolines

Piotr Balczewski and John A. Joule*

Chemistry Department, University of Manchester, Manchester M13 9PL, U.K.

Carlos Estévez and Mercedes Alvarez*

Laboratori de Química Orgànica, Facultat de Farmàcia, Universitat de Barcelona, 08028 Barcelona, Spain

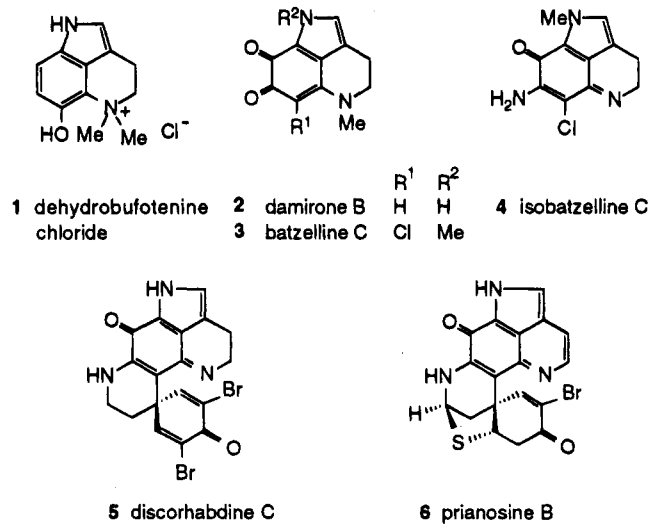
Received January 28, 1994®

The selenium dioxide oxidation of the methyl group in 5-acetamido-6-methoxy-4-methylquinoline produced 1,2-dihydro-8-methoxy-2-oxopyrrolo[4,3,2-*de*]quinoline, **8b**. Halogenation and nitration of **8b** gave 6-substituted derivatives **8c–e**. 6-Halo-1,2-dihydro-8-methoxy-2-oxopyrrolo[4,3,2-*de*]-quinolines were *O*-demethylated, giving phenols **8g** and **8h**. Reaction of **8b**, and its *N*-methyl derivative **8i**, with iodomethane resulted in quaternization of the quinoline ring nitrogen; borohydride reduction of the salts thus produced, and then aerial oxidation, led to dioxindoles **12a,b** and **13a,b**. Lithium aluminum hydride reduction of **12a** produced indole **10b**.

Introduction

The 1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline ring system was first recognized as a component of a natural product when the structure of the toad poison, dehydrobufotenine, **1**, was elucidated.[1] Much more recently, several marine alkaloids[2] such as the tricyclic batzellines,[3] isobatzellines,[4] and damirones[5] and more complex structures such as the discorhabdines[6] and prianosines[7] have been described which are also based on a 1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline nucleus. The simplest examples from each of these groups are **2–6**.

In most synthetic work relating to these natural products, so far described, including preparations of the unsubstituted[8,9] and 1-methyl[10] tricyclic systems of *O*-methylnordehydrobufotenine,[11] of dehydrobufotenine itself,[12] and then later of batzelline C and isobatzelline C,[13] discorhabdin C,[14] and damirones A and B,[15] the tricyclic heterocycle has been constructed *from an indole*, i.e., by forming the six-membered nitrogen-containing ring as a late step, by cyclization either of a 4-aminoindole carrying a two-carbon chain at its C-3[8–14] or of a tryptamine quinone.[15]



		R¹	R²	
1 dehydrobufotenine chloride	**2** damirone B	H	H	**4** isobatzelline C
	3 batzelline C	Cl	Me	

5 discorhabdine C **6** prianosine B

We have been examining an alternative strategy, namely the construction of such structures *starting from a quinoline*, and have given a preliminary report[16] of a synthesis of 8-methoxy-1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline using this approach. We describe here other investigations, using 6-methoxy-4-methylquinoline as starting material, aimed at the production of pyrroloquinolines carrying functionality on the benzene ring suitable for further elaboration into the natural products described above.

Results and Discussion

Nitration of 6-methoxy-4-methylquinoline[17] gave its 5-nitro derivative, **7a**, cleanly.[18] Reduction of the nitro

® Abstract published in *Advance ACS Abstracts,* July 1, 1994.

(1) Märki, F.; Robertson, A. V.; Witkop, B. *J. Am. Chem. Soc.* **1961**, *83*, 3341–3342. Robinson, B.; Smith, G. F.; Jackson, A. H.; Shaw, D.; Frydman, B.; Deulofeu, V. *Proc. Chem. Soc. (London)* **1961**, 310–311.

(2) Salas, M.; Alvarez, M; Joule, J. A. Marine Nitrogen-Containing Heterocyclic Natural Products. 1. Structures and Syntheses of Compounds Containing Quinoline and/or Isoquinoline Units. *Heterocycles* **1991**, *32*, 759–794; Marine Nitrogen-Containing Heterocyclic Natural Products. 2. Structures and Syntheses of Compounds Containing Indole Units. **1991**, *32*, 1391–1429.

(3) Sakemi, S.; Sun, H. H.; Jefford, C. W.; Bernardinelli, G. *Tetrahedron Lett.* **1989**, *30*, 2517–2520.

(4) Sun, H. H.; Sakemi, S.; Burres, N.; McCarthy, P. *J. Org. Chem.* **1990**, *55*, 4964–4966.

(5) Stierle, D. B.; Faulkner, D. J. *J. Nat. Prod.* **1991**, *54*, 1131–1133.

(6) Perry, N. B.; Blunt, J. W.; McCombs, J. D.; Munro, M. H. G. *J. Org. Chem.* **1986**, *51*, 5476–5478. Perry, N. B.; Blunt, J. W.; Munro, M. H. G. *Tetrahedron* **1988**, *44*, 1727–1734. Perry, N. B.; Blunt, J. W.; Munro, M. H. G.; Higa, T.; Sakai, R. *J. Org. Chem.* **1988**, *53*, 4127–4128.

(7) Kobayashi, J.; Cheng, J.-F.; Ishibashi, M.; Nakamura, H.; Ohizumi, Y.; Hirata, Y.; Sasaki, T.; Lu, H.; Clardy, J. *Tetrahedron Lett.* **1987**, *28*, 4939–4942. Cheng, J.-F.; Ohizumi, Y.; Wälchli, M. R.; Nakamura, H.; Hirata, Y.; Sasaki, T.; Kobayashi, J. *J. Org. Chem.* **1988**, *53*, 4621–4624.

(8) Hester, J. B. *J. Org. Chem.* **1964**, *29*, 1158–1160.

(9) Hamabuchi, S.; Hamada, H.; Hironaka, A.; Somei, M. *Heterocycles* **1991**, *32*, 443–448.

(10) Julia, M.; Huang, Y.; Igolen, J. *C. R. Hebd. Seances Acad. Sci.* **1967**, *265*, 110–112.

(11) Lee, F. G. H.; Daly, J. W.; Manian, A. A. *J. Med. Chem.* **1969**, *12*, 321–324.

(12) Gannon, W. F.; Benigni, J. D.; Suzuki, J.; Daly, J. W. *Tetrahedron Lett.* **1967**, 1531–1533.

(13) Tao, X. L.; Nishiyama, S.; Yamamura, S. *Chem. Lett.* **1991**, 1785–1786.

(14) Nishiyama, S.; Cheng, J.-F.; Yamamura, S.; Tao, X. L. *Tetrahedron Lett.* **1991**, *32*, 4151–4154.

(15) Sadanandan, E. V.; Cava, M. P. *Tetrahedron Lett.* **1993**, *34*, 2405–2408.

(16) Venemalm, L.; Estévez, C.; Alvarez, M.; Joule, J. A. *Tetrahedron Lett.* **1993**, *34*, 5495–5496.

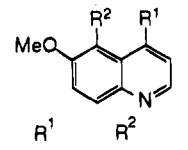
(17) Campbell, K. N.; Schaffner, I. J. *J. Am. Chem. Soc.* **1945**, *67*, 86–89.

0022-3263/94/1959-4571$04.50/0

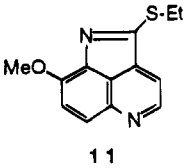
group was achieved efficiently using ammonium formate in the presence of palladium on charcoal, giving 5-amino-6-methoxy-4-methylquinoline, **7b**, though care was necessary because excess reagent led to saturation of the heterocyclic ring.[19] Subsequent acetylation of **7b** at room temperature afforded the acetamide **7c**, but heating amine **7b** in acetic anhydride produced imide **7d**, which could be subsequently converted into the amide with sodium hydroxide in refluxing methanol.

It was now the plan to establish the five-membered heterocyclic ring by oxidation of the methyl, then lactam formation. In the event, selenium dioxide[20] in hot dioxane produced a mixture of the anticipated amide–acid **7e**, together with two compounds already having the desired third ring—the imide **8a** and the amide **8b**. Although it was possible to separate and characterize each of these compounds, in practice it was simpler to treat the crude oxidation mixture with hot methanolic hydrogen chloride, thus converting all into amide **8b** only. As an alternative, use of Vismara's procedure[21] produced a mixture of **8a** and **8b**. During a search for a suitable solvent for recrystallization, it was found that tricyclic imide **8a** reacted easily with hot methanol with ring opening giving amide–ester **7f**.

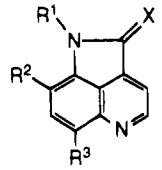
Tricyclic amide **8b** was utilized for various objectives: (i) to introduce halogen at quinoline C-8, both because some of the natural products carry chlorine at that position and also as a means to facilitate the formation of the spirocyclic system of the discorhabdins, and a nitrogen substituent at quinoline C-7, again because some of the alkaloids have this feature; (ii) to modify the oxidation level of the five- and six-membered heterocyclic rings, to approach that in the natural products.



	R^1	R^2
7a	Me	NO_2
7b	Me	NH_2
7c	Me	NHAc
7d	Me	NAc_2
7e	CO_2H	NHAc
7f	CO_2Me	NHAc

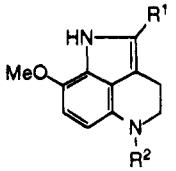


11



	R^1	R^2	R^3	X
8a	Ac	MeO	H	O
8b	H	MeO	H	O
8c	H	MeO	Br	O
8d	H	MeO	Cl	O
8e	H	MeO	NO_2	O
8f	Ac	MeO	Br	O
8g	H	HO	Br	O
8h	H	HO	Cl	O
8i	Me	MeO	H	O
8j	H	MeO	H	S

9



	R^1	R^2
10a	SH	Et
10b	H	Me

Bromination and chlorination of tricyclic amide **8b** took place, as desired, in the benzene ring *para* to the amide nitrogen, *i.e.*, at the quinoline C-8 (NOE was observed betwee H-7 and the MeO group), giving **8c** and **8d**, respectively. Nitration also took place regioselectively at quinoline C-8, producing **8e**. The further development of the halo derivatives was prevented by the finding that exposure to nitrating conditions simply resulted in *ipso* substitution and the formation of **8e**. With the plan that nitrosation or diazo coupling might allow the desired introduction of a 7-nitrogen substituent, the halo compounds **8d** and **8f** (the *N*-acetyl derivative of **8c**) were demethylated, using boron tribromide, giving phenols **8h** and **8g**, respectively; however, all attempts to utilize these for the introduction of a nitrogen group at quinoline C-7 failed. In other experiments aimed at the functionalization of quinoline C-7, attempts were made to lithiate chloro amide **8d** and *N*-methylated amide **8i** (obtained by reaction of **8b** with sodium hydride and iodomethane), but again with no success, some nucleophilic addition to the pyridine ring being the only discernible result.

It was our original belief that reduction of the lactam carbonyl group in amide **8b** would be straightforward, but this proved *not* to be the case: for example, starting material was recovered from treatment with either diborane or lithium aluminum hydride in THF at reflux for a short time; prolonged exposure to either reductant resulted in total loss of organic-soluble material. We believe now that the formation of a saturated five-membered ring in this situation is difficult while the six-membered ring is aromatic and planar.

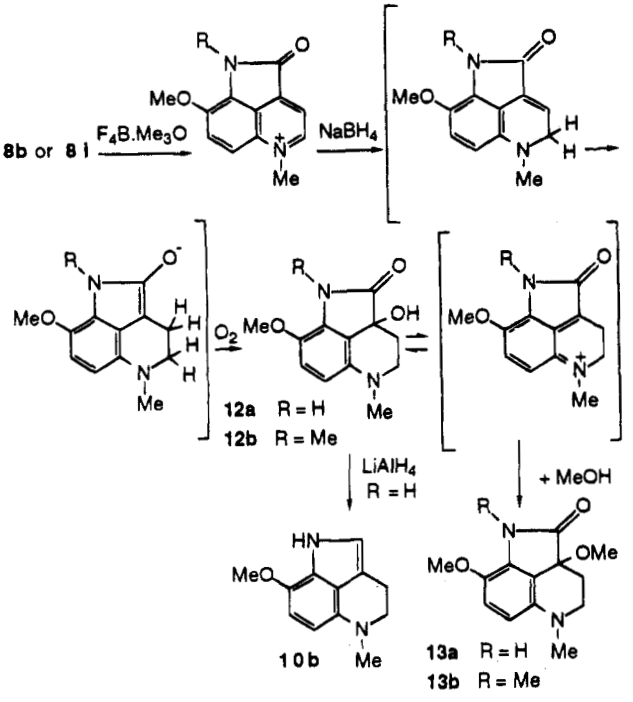
The amide was converted into the thioamide **8j** which could not be fully characterized, since it was easily reconverted into **8b**, but gave a satisfactory MS analysis. Attempted hydrogenolysis with Raney nickel led only to the original amide **8b**. Reaction of the thioamide with triethyloxonium borofluoride and then reduction with sodium borohydride produced different products, depending on the times of reaction, but none of these was the desired fully reduced material. Alkylation took place at both sulfur and nitrogen, as the structures of the products demonstrated: *N*-ethyldihydro- and -tetrahydro derivatives **9** and **10a** and *S*-ethyl unreduced derivative **11** were isolated.

In the hope that a protocol involving alkylation and then reduction might be simpler in the absence of competing *S*-alkylation, the amides **8b** and **8i** were reacted with iodomethane, or better trimethyloxonium borofluoride, and then reduced with borohydride. From each lactam, two comparable products were isolated: all four compounds retained the amide carbonyl group (IR and ^{13}C) and all four compounds had an additional *N*-methyl; *i.e.*, the pyridine nitrogen had been alkylated, as desired, but in one compound from each starting material there was also an additional *O*-methyl group. It was also clear from mass spectroscopy that in all four products four hydrogen atoms had been added but, as well, that an additional oxygen atom had been incorporated. These data, taken with the observation of ^1H NMR signals for just four saturated hydrogen atoms, located in a chiral environment, led to dioxindole and dioxindole methyl ether structures **12a,b** and **13a,b** for the compounds derived from amides **8b** and **8i**.

The formation of these products must involve a sequence (Scheme 1) in which *N*-alkylation is followed by two hydride additions, one to the pyridinium α-position then a second conjugate addition to the unsaturated amide thus produced. We envisage an aerial oxidation of the anion of the oxindole[22] as the means by which the extra oxygen is introduced and that the methoxyl groups in **13a,b** are introduced subsequently by an elimination/addition sequence, as shown.

(18) Balczewski, P.; Morris, G. A.; Joule, J. A. *J. Chem. Res., Synop.* **1992**, 308; *J. Chem. Res., Miniprint* **1992**, 2514–2523.
(19) Balczewski, P; Joule, J. A. *Synth. Commun.* **1990**, *20*, 2815–2819.
(20) Jerchel, D.; Heider, J.; Wagner, H. *Liebigs Ann. Chem.* **1958**, *613*, 153–170.
(21) Vismara, E.; Fontana, F.; Minisci, F. *Gazz. Chim. Ital.* **1987**, *117*, 135–136.
(22) Aeberli, P.; Houlihan, W. J. *J. Org. Chem.* **1968**, *33*, 1640–1643.

Scheme 1



Reduction of dioxindole **12a** with lithium aluminum hydride in hot dioxane gave the target indole **10b**; this presumably involves reduction of amide to amine and then loss of water.

Experimental Section

Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO_2 (silica Gel 60 F254, Merck 0.063–0.200 mm); the spots were located with iodoplatinate reagent or UV light. Column chromatography was carried out on SiO_2 (silica gel 60, SDS 0.060–0.2 mm). Flash chromatography was carried out on SiO_2 (silica gel 60, SDS 0.040–0.060 mm). Drying of organic extracts during the workup of reaction was performed over anhydrous Na_2SO_4, and solutions were evaporated under reduced pressure with a rotatory evaporator. IR data are given in cm^{-1}; NMR data are given in δ.

6-Methoxy-4-methyl-5-nitroquinoline (7a). 6-Methoxy-4-methylquinoline[17] (3.13 g, 18 mmol) was added in portions to fumic nitric acid (30 mL) during 15 min at −40 °C, and the mixture was allowed to rise to 0 °C. The reaction mixture was poured onto ice, basified with NaOH, and extracted with CH_2Cl_2. The organic layer was washed with H_2O. The organic extracts were dried and evaporated to give 3.52 g (90%) of **7a**. IR (KBr): 1509, 1347. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.58 (s, 3H); 4.04 (s, 3H); 7.27 (d, J = 4.4 Hz, 1H); 7.55 (d, J = 9.4 Hz, 1H); 8.24 (d, J = 9.4 Hz, 1H); 8.70 (d, J = 4.4 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.2 (q); 56.9 (q); 115.3 (d); 120.1 (s); 125.5 (d); 133.6 (d); 134.6 (s); 139.9 (s); 142.5 (s); 148.8 (d); 149.1(s). MS (EI): 218 (M, 100); 201 (69); 157 (36); 142 (51); 129 (41); 115 (64); 102 (31). MS (CI, NH_3): 219 (M + 1). HRMS: calcd for $C_{11}H_{10}N_2O_3$ 218.0691, found, 218.0692.

5-Amino-6-methoxy-4-methylquinoline (7b). A mixture of **7a** (8.0 g, 36 mmol), Pd/C (10%, 0.72 g), and NH_4HCO_2 (10.20 g, 155 mmol) in MeOH (300 mL) was refluxed for 2 h and filtered through Celite. The organic solution was evaporated and the residue basified with aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic solution was dried and evaporated to give 6.5 g (96%) of **7b**. Mp: 98–101 °C (MeOH, lit.[23] mp 98–100 °C). IR (KBr): 3423, 3342 . ^{1}H-NMR (300 MHz, $CDCl_3$): 2.98 (s, 3H); 3.98 (s, 3H); 4.52 (br, 2H); 6.97 (d, J = 4.3 Hz, 1H); 7.39 (d, J = 9.1 Hz, 1H); 7.57 (d, J = 9.1 Hz, 1H); 8.52 (d, J = 4.3 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.1 (q); 56.5 (q); 115.22 (d); 119.6 (s); 119.7 (d); 122.3 (d); 132.0 (s); 143.0 (s); 143.2 (s); 144.9 (s); 147.9 (d). MS (EI): 188 (M, 76), 173 (100), 145 (53). MS (CI, NH_3): 189 (M + 1, 100). HRMS: calcd for $C_{11}H_{12}N_2O$ 188.0949, found 188.0951.

5-(Acetylamino)-6-methoxy-4-methylquinoline (7c). The compound **7b** (3.0 g, 16 mmol) was added to Ac_2O (15 mL), and the resulting mixture was stirred for 20 h at rt. The reaction mixture was poured onto ice and basified with aqueous NaOH. The solid was filtered, washed with H_2O, and dried in vacuum over P_2O_5 at 50 °C during 14 h to give 2.1 g (80%) of **7c**. IR (KBr): 3450, 1657, 1560, 1577. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.74, 2.27 (2s, 3H); 2.79, 2.81 (2s, 3H); 3.95, 3.99 (2s, 3H); 6.98, 7.15 (2 bs, 1H); 7.11, 7.19 (2d, J = 4.3 Hz, 1H); 7.48, 7.53 (2d, J = 9.3 Hz, 1H); 8.10, 8.16 (2d, J = 9.3 Hz, 1H); 8.57, 8.63 (2d, J = 4.3 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.3, 22.6 (2q); 23.5, 24.3 (2q); 56.2 , 56.4 (2q); 115.3, 115.4 (2d); 118.9, 119.5 (2s); 124.6, 125.5 (2d); 127.3, 127.7 (2s); 131.3 (d); 132.2 (d); 142.9, 143.2 (2s); 144.1, 144.3 (2s); 147.6, 148.4 (2d); 153.2, 154.4 (2s); 171.3, 174.2 (2s). MS (EI): 230 (M, 40); 188 (35); 173 (100); 145 (39); 43 (28). MS (CI, NH_3): 231 (M + 1, 100). HRMS: calcd for $C_{13}H_{14}N_2O_2$ 230.1054, found, 230.1051. The aqueous filtrate was extracted with CH_2Cl_2, and the organic layer was dried and evaporated to give a residue which was purified by column chromatography on SiO_2 (95:5 CH_2Cl_2–MeOH) to give an additional amount of **7c** (0.8 g).

5-(Diacetylamino)-6-methoxy-4-methylquinoline (7d). A mixture of **7b** (0.52 g, 2.77 mmol) and acetic anhydride (1.05 g, 10.36 mmol) was stirred at reflux temperature during 30 min, H_2O was added to the reaction mixture, and the resulting solution was basified with $NaHCO_3$ and extracted with $CHCl_3$. The organic layers were washed with brine, dried, and evaporated to give a residue which was purified by flash vacuum chromatography on SiO_2 with Et_2O–$CHCl_3$ (1:1) as eluent to yield 0.46 g (61%) of **7d**. Mp: 139–141 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.26 (s, 6H); 2.59 (s, 3H); 3.98 (s, 3H); 7.20 (d, J = 4.4 Hz, 1H); 7.57 (d, J = 9.4 Hz, 1H); 8.27 (d, J = 9.4 Hz, 1H); 8.66 (d, J = 4,4 Hz, 1H). ^{13}C-NMR (75 Mz, $CDCl_3$): 22.3 (q); 26.3 (q); 56.5 (q); 115.4 (d); 121.5 (s); 125.6 (d); 126.7 (s); 133.3 (d); 141.2 (s); 144.5 (s); 148.3 (d); 153.0 (s); 173.4 (s). MS (EI): 272 (M, 42); 230 (70); 215 (24); 188 (72); 173 (74); 145 (22); 43 (100). HRMS calcd for $C_{15}H_{16}O_3N_2$ 272.1161, found 272.1163.

5-(Acetylamino)-6-methoxyquinoline-4-carboxylic Acid (7e), 1-Acetyl-1,2-dihydro-8-methoxy-2-oxopyrrolo[4,3,2-*de*]quinoline (8a), and 1,2-Dihydro-8-methoxy-2-oxopyrrolo[4,3,2-*de*]quinoline (8b). The compound **7c** (10.9 g, 47.3 mmol) was added in portions to a suspension of SeO_2 (7.9 g, 70.9 mmol) in dry dioxane (650 mL) at 80 °C under nitrogen. The reaction mixture was refluxed for 2 h and then allowed to cool to 50 °C and filtered through Celite. The combined filtrates were evaporated to give a residue which was separated by column chromatography; on elution with $CHCl_3$, in the first fractions were obtained 126 mg (17%) of **8a**. Mp: 136–139 °C ($CHCl_3$–Et_2O). IR (KBr): 2850, 1630. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.83 (s, 3H); 4.08 (s, 3H); 7.64 (d, J = 9.3 Hz, 1H); 7.90 (d, J = 4.5 Hz, 1H); 8.01 (d, J = 9.3 Hz, 1H); 9.15 (d, J = 4.5 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.4 (q); 57.9 (q); 117.9 (d); 120.1 (s); 122.6 (s); 123.6 (d); 126.7 (d); 131.6 (s); 142.6 (s); 144.8 (s); 150.5 (d); 166.9 (s); 169.2 (s). MS (EI): 242 (M, 13); 240 (45); 200 (100); 185 (73); 125 (37). MS (CI, NH_3): 243 (M + 1, 100). HRMS: calcd for $C_{13}H_{10}N_2O_3$ 242.0691, found 242.0693. The following fractions gave 74.5 mg (12%) of **8b**. Mp: 261–263 °C ($CHCl_3$–Et_2O). IR ($CHCl_3$): 3000, 1712, 1229. ^{1}H-NMR (500 MHz, $CDCl_3$–DMSO-d_6): 3.97 (s, 3H); 7.34 (d, J = 9.5 Hz, 1H); 7.64 (d, J = 9.5 Hz, 1H); 7.75 (d, J = 4.5 Hz, 1H); 8.98 (d, J = 4.5 Hz, 1H); 10.45 (br, 1H). ^{13}C-NMR (300 MHz, DMSO-d_6): 57.2 (q); 117.5 (d); 121.0 (s); 121.9 (s); 122.8 (d); 123.1 (d); 133.3 (s); 140.4 (s); 141.9 (s); 150.7 (d); 167.8 (s). MS (EI): 200 (M, 8); 120 (41); 92 (42); 91 (100). MS (CI, NH_3): 201 (M + 1). HRMS: calcd for $C_{11}H_8N_2O_2$ 200.0585, found 200.0586. Finally, on elution with $CHCl_3$–MeOH (9:1–9:5) was obtained 318 mg (40%) of compound **7e**. Mp: 259–261 °C (MeOH). IR (KBr): 3045, 2893. ^{1}H-NMR (300 MHz, DMSO-d_6): 3.91 (s, 3H); 7.40 (d, J = 4.3 Hz, 1H); 7.78 (d, J = 9.4 Hz, 1H); 8.09 (d, J = 9.4 Hz, 1H); 8.77 (d, J = 4.3 Hz, 1H); 9.19 (br, 1H). ^{13}C-NMR (75 MHz, DMSO-d_6): 22.6 (q); 56.6 (q); 117.9 (d); 118.9 (s); 119.8 (d);

(23) Weber, R. W.; Cook, J. M. *Heterocycles* **1982**, *19*, 2089–2092.

123.6 (s); 130.3 (d); 138.8 (s); 143.9 (s); 147.9 (d); 154.5 (s); 170.4 (s); 170.2 (s). MS (EI): 260 (M, 2); 201 (14); 200 (100); 186 (10); 185 (77); 171 (10); 130 (17). HRMS: calcd for $C_{13}H_{12}N_2O_4$ 260.0797, found 260.0791] and 84.5 mg (12%) of the starting material **7c**.

Methyl 5-(Acetylamino)-6-methoxyquinoline-4-carboxylate (7f). A solution of **8a** (24 mg, 0.10 mmol) in MeOH (3 mL) was refluxed for 15 min. Evaporation of the solvent gave 27 mg (98%) of **7f**. Mp dec.: 90 °C (Me_2CO). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.72, 2.21 (2s, 3H); 2.73, 3.70 (2s, 3H); 3.99, 4.00, 4.01, 4.02 (4s, 6H); 6.57, 7.10 (2 br, 1H); 7.37, 7.44 (2d, J = 4.3 Hz, 1H); 7.60, 7.62 (2d, J = 9.4, 1H); 8.18, 8.23 (2d, J = 9.4 Hz, 1H); 8.81, 8.85 (2d, J = 4.3 Hz, 1H). MS(EI): 274 (M, 26); 232 (33); 217 (35); 200 (27); 185 (87). MS (CI, NH_3): 275 (M + 1, 100). HRMS: calcd for $C_{14}H_{14}N_2O_4$ 274.0953, found 274.0962.

1,2-Dihydro-8-methoxy-2-oxopyrrolo[4,3,2-*de*]quinoline (8b). Method A. The compound **7c** (10.9 g, 47.3 mmol) was added in portions to a suspension of SeO_2 (7.9 g, 70.9 mmol) in dry dioxane (650 mL) at 80 °C under nitrogen. The reaction mixture was refluxed for 3.5 h and then cooled to 50 °C and filtered through Celite. Evaporation left a residue which was treated with 2 N HCl/MeOH at reflux temperature for 12 h. The solvent was removed under reduced pressure, an aqueous solution of $NaHCO_3$ added, and the resulting solution extracted with CH_2Cl_2. The organic layer was dried and evaporated to give a residue which was purified by column chromatography over SiO_2. Elution with CH_2Cl_2–MeOH (99:1) gave **8b** (4.32 g, 46%). **Method B.** To a solution of **7c** (800 mg, 3.48 mmol) in dry DMSO (40 mL) were added CF_3CO_2H (932 mg, 8.16 mmol), I_2 (884 mg, 3.48 mmol), *t*-BuI (128 mg, 0.68 mmol), and $FeCl_2{\cdot}4H_2O$ (catalytic amount) under nitrogen. The mixture was stirred for 6 h at 80 °C and for 15 min at 130 °C and after this time was diluted with H_2O (25 mL) and a saturated aqueous solution of $Na_2S_2O_3$ (8 mL) added. The resulting solution was basified with $NaHCO_3$ and extracted with AcOEt. The organic solution was washed with H_2O, dried, and evaporated to give 545 mg of a residue which was purified by column chromatography over SiO_2. On elution with CH_2Cl_2, 145 mg (18%) of **8a** was obtained, and with CH_2Cl_2–MeOH (99:1) 160 mg (23%) of **8b**.

6-Bromo-1,2-dihydro-8-methoxy-2-oxopyrrolo[4,3,2-*de*]quinoline (8c). To a stirred solution of **8b** (685 mg, 3.43 mmol) in $CHCl_3$ (350 mL) was added a solution of bromine (4.38 g, 27.4 mmol) in $CHCl_3$ (80 mL) dropwise at room temperature during 1 h. The resulting reaction mixture was stirred for 18 h. After this time the precipitate was separated by filtration, washed with $CHCl_3$, basified with an aqueous solution of Na_2CO_3, and extracted with $CHCl_3$. The organic solution was dried and evaporated to give a residue which was purified by flash column chromatography with $CHCl_3$ giving 0.67 g (70%) of **8c**. Mp: 273–275 °C. IR (KBr): 3200, 1720, 1480. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.05 (s, 3H); 7.72 (s, 1H); 7.91 (d, J = 4.4 Hz, 1H); 8.02 (br, 1 H); 9.21 (d, J = 4.4 Hz 1H). MS (EI): 280, 278 (6), 265 (4), 263 (4), 230 (17), 188 (13), 173 (36). HRMS calcd for $C_{11}H_7N_2O_2Br$ 277.9691, found 277.9702.

6-Chloro-1,2-dihydro-8-methoxy-2-oxopyrrolo[4,3,2-*de*]quinoline (8d). To a stirred solution of **8b** (340 mg, 1.7 mmol) in glacial acetic acid (40 mL) was added aqueous NaClO (5%, 2.8 mL, 1.9 mmol) dropwise at 25 °C and the resulting solution stirred for 3.5 h. The reaction mixture was poured onto H_2O, basified with aqueous NaOH, and extracted with $CHCl_3$. The organic solution was dried and evaporated to give 232 mg (58%) of **8d**. Mp: 261–263 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.04 (s, 3H); 7.52 (s, 1H); 7.92 (d, J = 4.4 Hz, 1H); 9.20 (d, J = 4.4 Hz, 1H); 8.02 (br, 1H). MS (EI): 236 (30); 234 (9); 221 (3); 219 (10); 86 (61); 84 (100). MS (CI, NH_3): 237 (14), 235 (37). HRMS: calcd for $C_{11}H_7O_2N_2Cl$ 234.0202, found 234.0196.

1,2-Dihydro-8-methoxy-6-nitro-2-oxopyrrolo[4,3,2-*de*]quinoline (8e). To a solution of fuming HNO_3 (2.5 mL) cooled to −35 °C was added **8b** (7 mg, 0.035 mmol) in portions. The reaction mixture was warmed during 30 min to 5 °C and then poured onto ice, basified with aqueous NaOH, and extracted with $CHCl_3$. The organic extracts were dried and evaporated to give 7.2 mg (84%) of **8e**. Mp: 283 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.14 (s, 3H); 7.97 (br, 1H); 7.98 (d, J = 4.4 Hz, 1H); 8.40 (s, 1 H); 9.43 (d, J = 4.4 Hz, 1H). MS (EI): 245 (M, 100); 215 (74); 128 (65); 101 (34). HRMS: calcd for $C_{11}H_7O_4N_3$ 245.0437, found 245.0438.

1-Acetyl-6-bromo-1,2-dihydro-8-methoxy-2-oxopyrrolo[4,3,2-*de*]quinoline (8f). A suspension of **8c** (600 mg, 2.2 mmol) in Ac_2O (170 mL) was refluxed for 4 h and then left overnight at room temperature. The reaction mixture was poured onto ice, stirred vigorously for 1 h, basified with aqueous NaOH, and extracted with $CHCl_3$. The organic layer was dried and evaporated to give 637 mg (92%) of **8f**. Mp: 204–207 °C. ^{1}H-NMR (80 MHz, $CDCl_3$): 2.79 (s, 3H); 4.07 (s, 3H); 7.87 (s, 1H); 7.92 (d, J = 4.5 Hz, 1H); 9.21 (d, J = 4.5 Hz, 1H). MS (EI): 280 (54); 278 (62); 265 (28); 263 (32). MS (CI, NH_3): 323 (98); 321 (100); 281 (37); 279 (39); 280 (23); 278 (19). HRMS: calcd for $C_{13}H_9O_3N_2Br$ 319.9797, found 319.9799.

6-Bromo-1,2-dihydro-8-hydroxy-2-oxopyrrolo[4,3,2-*de*]quinoline (8g). To a solution of **8f** (610 mg, 1.9 mmol) in CH_2Cl_2 (120 mL) was added $BBr_3{\cdot}Me_2S$ (4.2 g, 13.3 mmol) in CH_2Cl_2 (150 mL) during a period of 10 min at room temperature and under nitrogen. The resulting solution was stirred at reflux temperature for 4 h, cooled, and washed with aqueous NaOH. The aqueous solution was acidified with HCl and extracted with EtOAc. The organic extract, dried and evaporated, gave 200 mg (40%) of a powdered solid identified as **8g**. Mp: >335 °C. ^{1}H-NMR (80 MHz, DMSO-d_6): 7.67 (s, 1H); 7.96 (d, J = 4.5 Hz, 1H); 9.10 (d, J = 4.5 Hz, 1H); 10.79 (s, 1H); 10.96 (s, 1H). MS (EI): 264 (37); 266 (30); 199 (46); 155 (30); 129 (55). MS (CI, NH_3): 267 (M + 1, 62); 265 (M, 50); 187 (100). HRMS: calcd for $C_{10}H_5N_2O_2Br$ 263.9535, found 263.9544 .

6-Chloro-1,2-dihydro-8-hydroxy-2-oxopyrrolo[4,3,2-*de*]quinoline (8h). To a stirred solution of **8d** (153.4 mg, 0.65 mmol) in CH_2Cl_2 (250 mL) was added a solution of NaI (98.1 mg, 0.65 mmol) and 18-crown-6 (34 mg, 0.13 mmol), BBr_3 (3.277 g, 13 mmol) in CH_2Cl_2 (100 mL) was added, and the reaction mixture was refluxed for 2 weeks. The solution was extracted with H_2O, washed with aqueous $NaHCO_3$, dried, and evaporated to give 50 mg of starting material. The aqueous layer was acidified with 2 N HCl to pH 4.5 and extracted with EtOAc. The organic layer, dried and evaporated, gave 109 mg (75%) of **8h**. Mp: >340 °C. ^{1}H-NMR (300 MHz, DMSO-d_6): 7.89 (s, 1H); 8.38 (d, J = 4.4 Hz, 1H); 9.50 (d, J = 4.4 Hz, 1H); 11.25 (s, 1H); 11.42 (s, 1H). FABMS: 221 (M + 1, 10). MS (EI): 222 (32); 220 (M, 100); 194 (6); 192 (18); 164 (39); 130 (22); 129 (79); 102 (14). HRMS: calcd for $C_{16}H_5N_2O_2Cl$ 220.0039, found 220.0030.

1,2-Dihydro-8-methoxy-1-methyl-2-oxopyrrolo[4,3,2-*de*]quinoline (8i). To a solution of **8b** (100 mg, 0.50 mmol) in dry THF (15 mL) was added NaH (40 mg, 1.01 mmol) at 0 °C under nitrogen. The temperature of the reaction mixture was allowed to rise to 10 °C and then stirred for 30 min. Iodomethane (705 mg, 5.0 mmol) was then added to the refluxing reaction mixture in three portions at intervals of 15 min, under nitrogen. To the resulting solution was added H_2O (5 mL), the solution was stirred for 30 min, and the THF was removed in vacuum. The aqueous solution was extracted with AcOEt. The organic layer was dried and evaporated to leave 117 mg (quantitative yield) of **8i**. Mp: 151–153 °C (CH_2Cl_2–Me_2CO). IR (KBr): 1680. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.63 (s, 3H); 4.04 (s, 3H); 7.47 (d, J = 9.1 Hz, 1H); 7.78 (d, J = 9.1 Hz, 1H); 7.86 (d, J = 4.1 Hz, 1H); 9.09 (d, J = 4.1 Hz, 1H). ^{13}C-NMR (200 MHz, $CDCl_3$): 29.7 (q); 56.9 (q); 117.7 (d); 121.2 (d); 124.1 (d); 133.5 (s); 141.7 (s); 141.8 (s); 146.8 (s); 150.6 (d); 166.8 (s). MS (EI): 214 (M, 78); 199 (100); 171 (30); 144 (16); 116 (36); 101 (17). HRMS: calcd for $C_{12}H_{10}N_2O_2$ 214.0742, found 214.0748.

1,5-Dihydro-5-ethyl-2-mercapto-8-methoxypyrrolo[4,3,2-*de*]quinoline (9). A solution of **8b** (144 mg, 0.72 mmol) and Lawesson's reagent (174 mg, 0.43 mmol) in dry toluene (11 mL) was maintained at 100 °C for 2 h under Ar. The solvent was removed, and the residue was purified by column chromatography on SiO_2. Elution with CH_2Cl_2–MeOH (99:1) gave compound **8j** (146 mg, 94%). To a solution of **8j** (70 mg, 0.32 mmol) in dry CH_2Cl_2 (1 mL) was added $BF_4{\cdot}Et_3O$ (0.38 mL of 1 M CH_2Cl_2 solution) at 0 °C under Ar. The mixture was stirred for 5 min at 0 °C and 45 min at rt. The solvent was removed at reduced pressure, the residue was dissolved in dry

MeOH (1 mL), the solution was cooled at 0 °C, and $NaBH_4$ (31 mg, 0.82 mmol) was added. The reaction mixture was stirred for 5 min at 0 °C and 2 h at rt under nitrogen. HCl (2 N, 1 mL) was added to the reaction solution, and the stirring was maintained for 5 min; after that it was basified with 2 N NaOH, the MeOH was removed under reduced pressure, and the residue was diluted with H_2O and extracted with Et_2O. The organic extract was washed with brine, dried, and evaporated to give 29 mg of a residue which was purified by column chromatography on SiO_2. Elution with *n*-hexane–CH_2Cl_2 (20:80) gave 21 mg (25%) of **9**. IR ($CHCl_3$): 3400; 3018; 2850; 1599. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.21 (t, J = 8 Hz, 3H); 1.65 (br, 1H); 2.70 (q, J = 8 Hz, 2H); 3.83 (s, 3H); 6.91 (d, J = 2.6 Hz, 1H); 6.98 (d, J = 2.6 Hz, 1H); 7.75 (d, J = 8.1 Hz, 1H); 7.82 (d, J = 8.1 Hz, 1H). ^{13}C (200 MHz, $CDCl_3$): 16.0 (q); 24.7 (t); 55.3 (q); 114.0 (d); 114.3 (d); 133.3 (d); 133.1 (d). MS (EI): 247 (M + 1, 2); 246 (M, 13); 186 (35); 185 (100); 171 (31).

5-Ethyl-1,3,4,5-tetrahydro-2-mercapto-8-methoxypyrrolo[4,3,2-*de*]quinoline (10a). A similar procedure as described for the preparation of **9** from **8j** (76 mg, 0.35 mmol) using solid $F_4B{\cdot}Et_3O$ (85 mg, 0.45 mmol) maintaining 2 h of stirring at rt for the alkylation step and similar workup as described before gave 8 mg (9%) of **10a**. IR ($CHCl_3$): 1599, 1504. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.28 (t, J = 6.0 Hz, 3H); 2.75 (q, J = 6.0 Hz, 2H); 3.00 (t, J = 6.0 Hz, 2H); 3.50 (t, J = 6.0 Hz, 2H); 3.91 (s, 3H); 6.19 (d, J = 7.5 Hz, 1H); 6.50 (d, J = 7.5 Hz, 1H). MS (CI, NH_3): 266 (M + 1 + NH_3, 24); 249 (M + 1, 100); 248 (M, 2).

1,3,4,5-Tetrahydro-8-methoxy-5-methylpyrrolo[4,3,2-*de*]quinoline (10b). $LiAlH_4$ (15 mg, 0.39 mmol) was added to a solution of **12a** (24 mg, 0.11 mmol) in dry dioxane (8 mL), and the mixture was stirred at reflux temperature under nitrogen for 3 h. The reaction mixture was cooled at 0 °C, and H_2O was added. The organic solvent was removed and the aqueous residue was extracted with Et_2O. The organic layer was dried and evaporated leave 21 mg (95%) of **10b** as an oil. IR (film): 1603, 1519, 1453, 1380, 1344, 1259, 1210. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.96 (s, 3H); 3.09 (t, J = 5.4 Hz, 2H); 3.27 (t, J = 5.4 Hz, 2H); 3.93 (s, 3H); 6.14 (d, J = 8.0 Hz, 2H); 6.56 (d, J = 8.0 Hz, 1H); 6.77 (s, 1H); 8.05 (sa, 1H). ^{13}C-NMR (200 MHz, $CDCl_3$): 23.5 (t); 38.6 (c); 53.1 (t); 55.9 (c); 97.6 (d); 103.7 (d); 115.2 (d). MS (EI): 202 (M, 87), 187 (100); 91 (66).

2-(Ethylthio)-8-methoxypyrrolo[4,3,2-*de*]quinoline (11). A similar procedure as described for the preparation of **9** from **8j** (123 mg, 0.57 mmol) using solid $BF_4{\cdot}Et_3O$ (129 mg, 0.68 mmol) and 1 h of stirring at rt for the alkylation step and similar workup as described before gave 12 mg (9%) of **11**. IR (KBr): 2860, 1448. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.53 (t, J = 7.3 Hz, 3H); 3.46 (c, J = 7.3 Hz, 2H); 4.50 (s, 3H); 7.28 (d, J = 9.2 Hz, 1H); 7.70 (d, J = 4.5 Hz, 1H); 7.78 (d, J = 9.2 Hz, 1H); 9.98 (d, J = 4.5 Hz, 1H). ^{13}C-NMR (200 MHz, $CDCl_3$): 14.3 (q); 25.4 (t); 60.4 (q); 116.0 (d); 127.6 (d); 128.6 (d); 134.0 (s); 140.0 (s); 142.6 (s); 148.8 (s); 148.8 (d); 150.2 (s); 164.8 (s). MS (EI): 246 (M + 2, 6); 245 (M + 1, 17); 244 (M, 100); 229 (88); 216 (35); 201 (48).

1,2,2a,3,4,5-Hexahydro-2a-hydroxy-8-methoxy-5-methyl-2-oxopyrrolo[4,3,2-*de*]quinoline (12a) and 1,2,2a,3,4,5-Hexahydro-2a,8-dimethoxy-5-methyl-2-oxopyrrolo[4,3,2-*de*] quinoline (13a). Method A. To a solution of **8b** (100 mg, 0.50 mmol) in THF (20 mL) was added MeI (1.14 g, 8.03 mmol) in four portions and the mixture refluxed for 26 h under nitrogen. The solvent was removed, the resulting residue was dissolved in dry MeOH (20 mL), the solution was cooled to 0 °C, and $NaBH_4$ (56 mg, 1.48 mmol) was added. The reaction mixture was stirred for 5 min at 0 °C and 20 h at rt. The solvent was eliminated under vacuum, H_2O was added to the residue, and the mixture was stirred 30 min and extracted with AcOEt. The organic solution was dried and evaporated to give 207 mg of a mixture which was purified by column chromatography on silica gel. Elution with *n*-hexane–CH_2Cl_2 (1:1) gave 12 mg (12%) of **13a**. IR ($CHCl_3$): 3440, 3010, 2940, 1725. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.47 (ddd, J = 13.4, 13.3 and 5.6 Hz, 1H); 2.25 (ddd, J = 13.4, 4.0 and 1.8 Hz, 1H); 2.94 (s, 3H); 3.17 (ddd, J = 12.0, 5.6 and 1.8 Hz, 1H); 3.25 (s, 3H); 3.57 (ddd, J = 13.3, 12.0 and 4.0 Hz, 1H); 3.79 (s, 3H); 6.27 (d, J = 8.9 Hz, 1H); 6.83 (d, J = 8.9 Hz, 1H). ^{13}C-NMR (200 MHz, $CDCl_3$): 27.7 (t); 36.6 (q); 45.9 (t); 50.8 (q); 57.0 (q); 105.2 (d); 117.2 (d). MS (CI, NH_3): 250 (5); 249 (39); 232 (10); 217 (100). MS (EI): 249 (12); 248 (97); 218 (29); 217 (100); 205 (25); 201 (20). MS (CI, NH_3): 267 (12); 249 (30); 217 (100); 203 (44). HRMS: calcd for $C_{13}H_{16}O_3N_2$ 248.1161, found 248.1165. Elution with CH_2Cl_2–MeOH (99:1) gave 14 mg of starting material **8b** and 29 mg (30%) of **12a**. Mp: 260–262 °C ($CHCl_3$–Me_2CO). IR (KBr): 3400, 3200, 2928, 1698, 1615. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.58 (ddd, J = 13.4, 12.7 and 5.3 Hz, 1H); 2.19 (ddd, J = 13.4, 3.4 and 1.8 Hz, 1H); 2.98 (s, 3H); 3.27 (ddd, J = 12.1, 5.3 and 1.8 Hz, 1H); 3.71 (m, 2H); 3.81 (s, 3H); 6.30 (d, J = 8.9 Hz, 1H); 6.85 (d, J = 8.9 Hz, 1H); 7.10 (br, 1H). ^{13}C-NMR (200 MHz, $CDCl_3$): 27.3 (t); 37.0 (q); 46.1 (t); 57.3 (q); 70.1 (d); 105.4 (d); 117.1 (d); 117.9 (s); 124.1 (s); 135.7 (s); 139.6 (s); 179.3 (s). MS (EI): 235 (30); 234 (80); 218 (82); 203 (64); 191 (100); 175 (48). MS (CI, NH_3): 235 (100); 219 (86); 217 (38); 203 (32). HRMS: calcd for $C_{12}H_{14}N_2O_3$ 234.1004, found 234.1009. **Method B.** To a solution of **8b** (100 mg, 0.50 mmol) in dry CH_2Cl_2 (20 mL) was added $BF_4{\cdot}Et_3O$ (81 mg, 0.55 mmol) at 0 °C under nitrogen. The mixture was stirred for 5 min at 0 °C and 16 h at rt. The solvent was evaporated under vacuum, the resulting residue was dissolved in dry MeOH (10 mL), the solution was cooled at 0 °C, and $NaBH_4$ (45 mg, 1.21 mmol) was added. The reaction mixture was stirred for 5 min at 0 °C and 22 h at rt. The solvent was removed, H_2O was added to the residue, and the mixture was stirred 30 min and extracted with AcOEt. The organic solution was dried and evaporated to give 100 mg of a mixture which was purified by column chromatography on SiO_2. On elution with *n*-hexane–CH_2Cl_2 (50:50) **13a** (30 mg, 28%) and with CH_2Cl_2 **12a** (28 mg, 27%) were obtained.

1,2,2a,3,4,5-Hexahydro-2a-hydroxy-8-methoxy-1,5-dimethyl-2-oxopyrrolo[4,3,2-*de*]quinoline (12b) and 1,2,-2a,3,4,5-Hexahydro-2a,8-dimethoxy-1,5-dimethyl-2-oxopyrrolo[4,3,2-*de*] quinoline (13b). Method A. A similar procedure as described in method A for preparation of compounds **12a** and **13a** starting from **8i** (134 mg, 0.63 mmol) yielded a crude reaction mixture which was purified by column chromatography on SiO_2. Elution with *n*-hexane–CH_2Cl_2 (40–60) yielded 10 mg (7%) of **13b**. IR (film): 2870, 1606, 1520. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.45 (ddd, J = 13.4, 13.3 and 5.6 Hz, 1H); 2.27 (ddd, = 13.4, 4.0 and 1.8 Hz, 1H); 2.95 (s, 3H); 3.11–3.22 (m, 1H); 3.18 (s, 3H); 3.43 (s, 3H); 3.46–3.68 (m, 1H); 3.80 (s, 3H); 6.30 (d, J = 8.9 Hz, 1H); 6.87 (d, J = 8.9 Hz, 1H). ^{13}C-NMR (200 MHz, $CDCl_3$): 25.8 (t); 29.52 (q); 36.8 (q); 46.0 (t); 51.0 (q); 57.9 (q); 105.6 (d); 118.7 (d). MS (EI): 246 (M, 2); 232 (12); 200 (26); 186 (12); 185 (100); 171 (19); 170 (11). Elution with CH_2Cl_2 gave 65 mg (48% conversion) of starting material **8i** and 65 mg (44%) of **12b**. IR ($CHCl_3$): 1709, 1608, 1519, 1364. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.53 (ddd, J = 13.4, 13.3 and 5.3 Hz, 1H); 2.17 (ddd, J = 13.3, 3.7 and 1.7 Hz, 1H); 2.98 (s, 3H); 3.24 (ddd, J = 12.0, 5.3 and 1.7 Hz, 1H); 3.42 (s, 3H); 3.65 (m, 2H); 3.80 (s, 3H); 6.32 (d, J = 8.9 Hz, 1H); 6.88 (d, J = 8.9 Hz, 1H). ^{13}C-NMR (200 MHz, $CDCl_3$): 27.4 (t); 28.9 (q); 37.0 (q); 46.0 (t); 58.2 (q); 69.4 (d); 105.7 (d); 118.8 (d); 176.0 (s). MS (EI): 249 (25); 248 (100); 233 (50); 232 (52); 217 (50); 205 (51). MS (CI): 249 (100); 233 (62); 231 (30). HRMS: calcd for $C_{13}H_{16}N_2O_3$ 248.1161, found 248.1163. **Method B.** A similar procedure as described in method A for preparation of compounds **12a** and **13a** starting from **8i** (207 mg, 0.97 mmol) gave, after column chromatographic purification, the compounds **13b** (25 mg, 10%) and **12b** (97 mg, 43%).

Acknowledgment. P.B. was on leave from the Polish Academy of Sciences in Lódz, Poland. We thank the SERC, UK, the British Council and Ministerio de Educación y Ciencia of Spain (Acciones Integradas 1991-92, MDR/980/2, HB-119-A), and CIRIT, Generalitat de Catalunya (QF N 92-4315), for generous financial support.

Supplementary Material Available: Copies of ^{1}H NMR spectra of all compounds and NMR data complete with peak assignments (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.