

# Non-Steroidal Antiinflammatory Agents. VI. Synthesis of 10-Oxo-5*H*-pyrrolo[1,2-*b*]isoquinoline-3-acetic Acid, A Conformationally Restricted Analogue of Tolmetin

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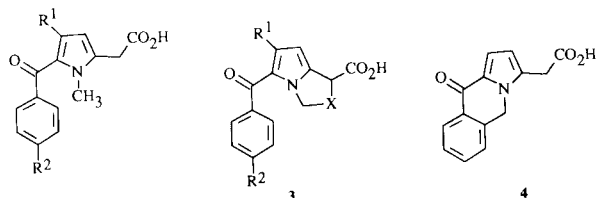
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The synthesis of 10-oxo-5*H*-pyrrolo[1,2-*b*]isoquinoline-3-acetic acid **4**, a tricyclic analogue of tolmetin which might show significant analgesic-antiinflammatory activity, has been accomplished in four steps. Alkylation of ethyl 2-pyrrolylglyoxylate (**15**) with 2-cyanobenzyl bromide afforded derivative **16**, which was transformed by the Huang-Minlon reaction into the dicarboxylic acid **6**. Cyclization of this key intermediate to **17**, followed by alkaline hydrolysis, afforded 10-oxo-5*H*-pyrrolo[1,2-*b*]isoquinoline-3-acetic acid (**4**). Various attempted syntheses of **6** are also discussed.

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Many synthetic efforts have been devoted in recent years to the preparation of cyclic analogs of the non-steroidal antiinflammatory drugs tolmetin (**1**) and zomepirac (**2**), in order to develop new high-potency compounds that elicit lower gastric irritancy than those in clinical use [1a-d]. The synthesis and pharmacological evaluation of various 5-*aroyl*-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]pyrrole-1-carboxylic acids **3** have been reported by Muchowski *et al.* [2a-d]. Some members of this class of compounds show potent analgesic or antiinflammatory activities comparable to that of morphine sulfate or indomethacin, respectively.

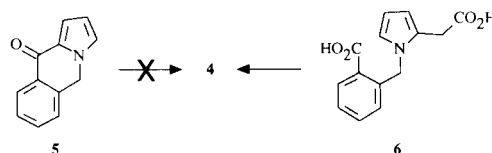


- 1** R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>  
**2** R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = Cl

In the early 1980's, we started a research program devoted to identify new, pyrrole-containing, non-steroidal antiinflammatory agents [3a-g]. Pursuing this research program we describe herein the synthesis of 10-oxo-5*H*-pyrrolo[1,2-*b*]isoquinoline-3-acetic acid (**4**), a novel conformationally restricted analogue of tolmetin (**1**), which might possess interesting pharmacological and toxicological profiles.

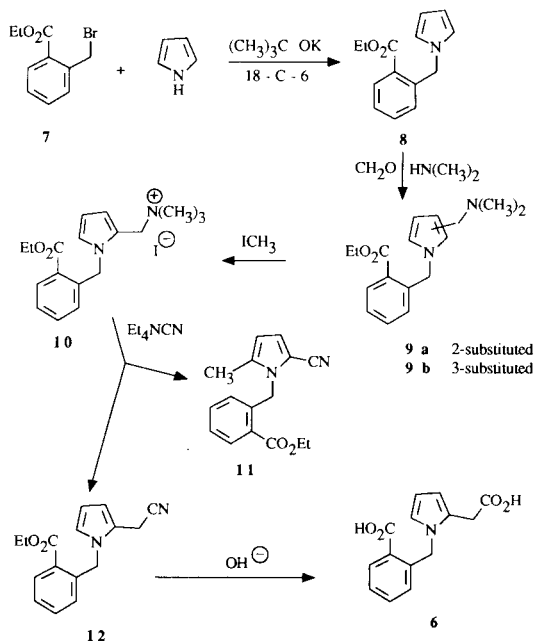
We previously reported [4] the preparation of 10-oxo-5*H*-pyrrolo[1,2-*b*]isoquinoline (**5**), but initial attempts to use it as a starting material for **4** failed, due to its poor reactivity towards electrophilic reagents (Scheme 1). We therefore planned to obtain **4** by intramolecular cyclization of 1-(2-carboxybenzyl)pyrrole-2-acetic acid (**6**).

Scheme 1



For this purpose, pyrrole was alkylated with 2-ethoxycarbonylbenzyl bromide (**7**) [5] in the presence of potassium *t*-butoxide and 18-crown-6 to give a 71% yield of **8**, which was subjected to the Mannich reaction using dimethylamine hydrochloride and aqueous formaldehyde to afford a mixture of isomers **9a** and **9b** in the ratio 2.7:1 respec-

Scheme 2



- 9a** 2-substituted  
**9b** 3-substituted

12

6

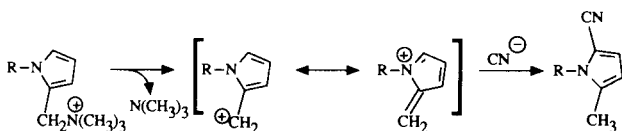
tively (63% total yield). The mixture was readily separated by column chromatography and **9a** was transformed into **10** with methyl iodide. Reaction of **10** with tetraethylammonium cyanide in refluxing acetonitrile led to an isomeric mixture of **11** and **12** in 67% total yield (Scheme 2).

A brief study of the effects of solvent and temperature on the yield and ratio of compounds **11** and **12** was carried out. As shown in Table 1, the reaction between **10** and tetraethylammonium cyanide did not proceed at room temperature, whereas at 80°, with the substitution of DMSO or 1,4-dioxane for acetonitrile, a lower total yield and an enhanced **11/12** ratio were observed. The predominant

Table 1

Solvent	Reaction Time (hours)	Temperature (°C)	Yield (%)	11/12 ratio
CH <sub>3</sub> CN	16	25	0	-
CH <sub>3</sub> CN	16	80	67	1.3
DMSO	16	25	0	-
DMSO	16	80	51	2.8
Dioxane	110	80	64	2.9

formation of the undesired isomer **11** can be easily explained by a preferred S<sub>N</sub>1 mechanism for the reaction pathway, as outlined in Equation 1 [6]. Although compound **12** could be separated from the isomeric mixture

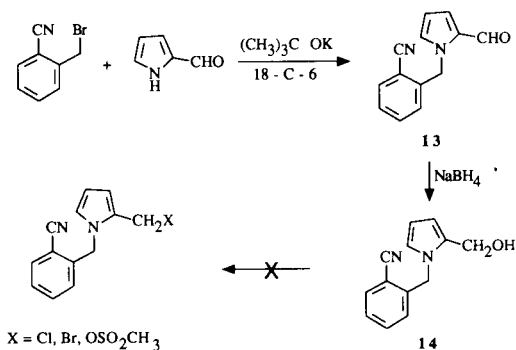


Eq. 1

and hydrolyzed to 1-(2-carboxybenzyl)pyrrole-2-acetic acid (**6**), the synthetic approach described above did not appear satisfactory and different routes to **6** were therefore investigated.

Alkylation of pyrrole-2-carboxaldehyde (Scheme 3) with the commercially available 2-cyanobenzyl bromide

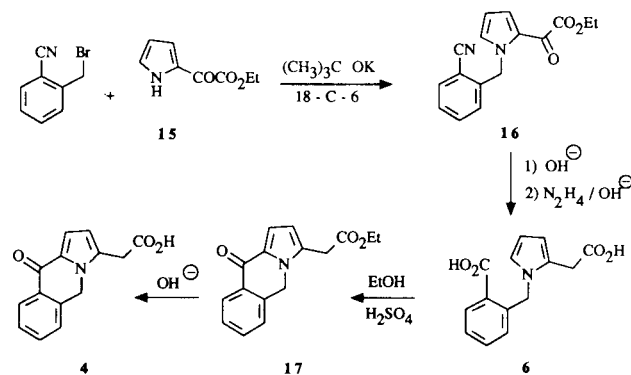
Scheme 3



smoothly afforded 1-(2-cyanobenzyl)pyrrole-2-carboxaldehyde (**13**), which was reduced quantitatively to the corresponding alcohol **14** using sodium borohydride. Unfortunately, all attempted transformations of the hydroxy function of **14** into a good leaving group (halides and sulfonates) furnished black intractable tars.

Thus, it appeared clear that the insertion of the 2-cyanobenzyl group had to be carried out on a pyrrole moiety already bearing an acetic chain. As the 2-cyanomethylpyrrole proved to be unsuitable for alkylation reactions [7], 2-cyanobenzyl bromide was reacted with ethyl 2-pyrrolylglyoxylate (**15**) [8] (Scheme 4) to give the derivative **16**. The elaboration of **16** into the dicarboxylic acid **6** was performed using a one-pot procedure following a previous report for similar alkyl 2-pyrrolylglyoxylate [9].

Scheme 4



We attempted the cyclization of **6** to **17** via a Friedel-Crafts reaction and by the use of strong dehydrating agents (polyphosphoric acid and phosphorus pentoxide), but **17** was best obtained by simply heating **6** in anhydrous ethanol in the presence of a catalytic amount of sulfuric acid. Final alkaline hydrolysis of **17** led to the desired 10-oxo-5H-pyrrolo[1,2-b]isoquinoline-3-acetic acid (**4**). The synthetic approach depicted in Scheme 4, therefore, allowed the preparation of our target **4** to be accomplished in an experimentally simple and profitable way.

## EXPERIMENTAL

Melting points were taken on a Büchi 530 apparatus and are uncorrected. Infrared spectra (Nujol mulls) were run on a Perkin-Elmer 297 spectrophotometer. The pmr spectra (TMS as the internal standard) were recorded on a Varian EM-390 or a Varian XL-200 instrument. Mass spectra were measured on a VG-70/250S instrument. Merck silica gel and alumina (70-230 mesh ASTM) were used for chromatographic purifications. Thin layer chromatography (tlc) was performed by using aluminum baked silica gel plates (C. Erba Stratocrom SIF-254). Developed plates were visualized by uv light. Solvents were reagent grade and when necessary were purified and dried by standard methods. Concentration of solutions after reactions and extractions involved the use of a rotary evaporator operating at re-

duced pressure of approximately 20 torr. Organic solutions were dried over anhydrous sodium sulfate. Elemental analyses were performed by Professor A. Pietrogrande, University of Padova, and Dr. G. Corbini, University of Siena, Italy.

#### 1-(2-Ethoxycarbonylbenzyl)pyrrole (8)

To a well-stirred mixture of 18-crown-6 (2.30 g, 8.7 mmoles) and 95% potassium *t*-butoxide (10.23 g, 87 mmoles) in dry diethyl ether (100 ml) a solution of pyrrole (5.83 g, 87 mmoles) in the same solvent (50 ml) was added slowly under a nitrogen atmosphere. After 30 minutes, a solution of 2-ethoxycarbonylbenzyl bromide **7** [5] (21.14 g, 87 mmoles) in dry diethyl ether (50 ml) was added dropwise into the above suspension and stirring was maintained for 16 hours at room temperature. Water (100 ml) was added and the organic layer was separated, washed with water and dried. Removal of the solvent furnished an oily residue, which was purified by column chromatography on silica gel, eluting with benzene:hexane (1:1). Evaporation of the appropriate eluates afforded 1-(2-ethoxycarbonylbenzyl)pyrrole **8** (14.14 g, 71%) as a yellowish oil; ir:  $\nu$  1715 (COOEt)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.38 (t, 3H,  $\text{COOCH}_2\text{CH}_3$ ), 4.40 (q, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 5.55 (s, 2H,  $\text{CH}_2\text{N}$ ), 6.23 (m, 2H, pyrrole  $\beta$ -protons), 6.72 (m, 3H, pyrrole  $\alpha$ -protons and benzene *H*-6), 7.3-7.6 (m, 2H, benzene *H*-4,5), 8.10 ppm (dd, 1H, benzene *H*-3).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{15}\text{NO}_2$ : C, 73.34; H, 6.59; N, 6.11. Found: C, 73.60; H, 6.55; N, 5.97.

#### Mannich Reaction of 1-(2-Ethoxycarbonylbenzyl)pyrrole.

A solution of dimethylamine hydrochloride (4.26 g, 52 mmoles) in 40% aqueous formaldehyde (3.92 g, 52 mmoles) was slowly added to 1-(2-ethoxycarbonylbenzyl)pyrrole **8** (11.46 g, 50 mmoles) and this mixture was warmed at 60° for 2 hours. The clear solution so obtained was poured into 25% aqueous sodium hydroxide (100 ml). Extraction with chloroform, followed by usual work-up of the organic layer, gave an oily residue which was chromatographed on an alumina column. Elution with chloroform:hexane (1:1) afforded 1.5 g of the starting material **8**, followed by **9a** (6.60 g, 46%) as a colorless oil; ir:  $\nu$  1750 (COOEt)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.38 (t, 3H,  $\text{COOCH}_2\text{CH}_3$ ), 2.06 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ), 3.13 (s, 2H,  $\text{CH}_2\text{N}(\text{CH}_3)_2$ ), 4.40 (q, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 5.45 (s, 2H,  $\text{Ph-CH}_2$ ), 6.08 (m, 2H, pyrrole  $\beta$ -protons), 6.45 (dd, 1H, benzene *H*-6), 6.63 (m, 1H, pyrrole  $\alpha$ -proton), 7.1-7.4 (m, 2H, benzene *H*-4,5), 8.02 ppm (dd, 1H, benzene *H*-3).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$ : C, 71.30; H, 7.75; N, 9.78. Found: C, 71.45; H, 7.68; N, 9.55.

Further elution of the above column with chloroform gave **9b** (2.46 g, 17%).

#### Preparation of Methiodide 10.

Iodomethane (3 ml, 48 mmoles) was added dropwise into a solution of **9a** (5.63 g, 19.6 mmoles) in dry diethyl ether (100 ml). After stirring overnight at room temperature, the precipitate was filtered and dried to give **10** (5.82 g, 69%), which was used in the next step without further purification.

#### Cyanation of Methiodide 10.

Tetraethylammonium cyanide (0.39 g, 2.5 mmoles) was added in one portion to a solution of **10** (1.07 g, 2.5 mmoles) in acetonitrile (30 ml). After refluxing for 16 hours, the solution was diluted with a saturated solution of sodium bicarbonate (50 ml) and diethyl ether (50 ml). The organic layer was separated, washed with

water and dried. The mixture obtained after evaporation of the solvent was separated by column chromatography on silica gel eluting with chloroform. The first eluted product was 2-cyano-1-(2-ethoxycarbonylbenzyl)-5-methylpyrrole **11** (0.25 g, 37%), which, after recrystallization from benzene/light petroleum ether, melted at 85-87°; ir:  $\nu$  2200 (CN), 1705 (COOEt)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.38 (t, 3H,  $\text{COOCH}_2\text{CH}_3$ ), 2.07 (s, 3H,  $\text{CH}_3$ ), 4.42 (q, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 5.67 (s, 2H,  $\text{CH}_2\text{N}$ ), 6.03 (d,  $J = 4.5$  Hz, 1H, pyrrole *H*-4), 6.25 (dd, 1H, benzene *H*-6), 6.82 (d,  $J = 4.5$  Hz, 1H, pyrrole *H*-3), 6.9-7.2 (m, 2H, benzene *H*-4,5), 8.15 ppm (dd, 1H, benzene *H*-3).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ : C, 71.62; H, 6.01; N, 10.44. Found: C, 71.69; H, 5.96; N, 10.50.

Further elution of the above chromatographic column with the same solvent gave 2-cyanomethyl-1-(2-ethoxycarbonylbenzyl)pyrrole **12** (0.20 g, 30%), mp 89-91° (from benzene/light petroleum ether); ir:  $\nu$  2240 (CN), 1695 (COOEt)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.35 (t, 3H,  $\text{COOCH}_2\text{CH}_3$ ), 3.50 (s, 2H,  $\text{CH}_2\text{CN}$ ), 4.35 (q, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 5.47 (s, 2H,  $\text{CH}_2\text{N}$ ), 6.22 (m, 2H, pyrrole  $\beta$ -protons), 6.45 (dd, 1H, benzene *H*-6), 6.65 (t, 1H, pyrrole  $\alpha$ -proton), 7.3-7.6 (m, 2H, benzene *H*-4,5), 8.07 ppm (dd, 1H, benzene *H*-3).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ : C, 71.62; H, 6.01; N, 10.44. Found: C, 71.57; H, 6.05; N, 10.53.

#### 1-(2-Cyanobenzyl)pyrrole-2-carboxaldehyde (13)

Prepared in 83% yield by alkylation of pyrrole-2-carboxaldehyde with 2-cyanobenzyl bromide following the procedure described for **8** with slight modifications (reaction time: 4 hours; solvent: tetrahydrofuran, **13** melted at 140-141° (from ethanol); ir:  $\nu$  2220 (CN), 1650 (CHO)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  5.77 (s, 2H,  $\text{CH}_2$ ), 6.32 (m, 1H, pyrrole *H*-4), 6.96-7.09 (superimposed signals, 3H, pyrrole *H*-3,5 and benzene *H*-6), 7.31-7.52 (m, 2H, benzene *H*-4,5), 7.65 (dd, 1H, benzene *H*-3), 9.54 ppm (s, 1H, CHO).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$ : C, 74.26; H, 4.80; N, 13.33. Found: C, 74.35; H, 4.81; N, 13.23.

#### 1-(2-Cyanobenzyl)-2-hydroxymethylpyrrole (14)

Sodium borohydride (0.38 g, 10 mmoles) was added in three portions to a solution of aldehyde **13** (2.10 g, 10 mmoles) in tetrahydrofuran (50 ml) containing water (0.5 ml). The mixture was refluxed for 2 hours, then concentrated to a small volume. Water (50 ml) and chloroform (50 ml) were added to the residue, the organic layer was separated, washed with water and finally dried. Evaporation of the solvent afforded in quantitative yield (2.12 g) the alcohol **14** as a yellowish oil homogeneous by tlc; ir:  $\nu$  3400 (OH), 2220 (CN)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.56 (br s, 1H, OH, exchangeable with deuterium oxide), 4.54 (s, 2H,  $\text{CH}_2\text{OH}$ ), 5.41 (s, 2H,  $\text{CH}_2\text{N}$ ), 6.14-6.21 (m, 2H, pyrrole  $\beta$ -protons), 6.68 (m, 1H, pyrrole  $\alpha$ -proton), 6.80 (dd, 1H, benzene *H*-6), 7.32-7.54 (m, 2H, benzene *H*-4,5), 7.67 ppm (dd, 1H, benzene *H*-3).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 73.55; H, 5.71; N, 13.20. Found: C, 73.25; H, 5.73; N, 13.10.

#### Ethyl 1-(2-Cyanobenzyl)pyrrole-2-glyoxylate (16)

Prepared in 95% yield as described for **13** starting from 2-cyanobenzyl bromide and ethyl 2-pyrrolylglyoxylate **15** [8]. Ethyl 1-(2-cyanobenzyl)pyrrole-2-glyoxylate **16** was a yellowish oil after chromatographic purification (silica gel-benzene); ir:  $\nu$  2230 (CN), 1740 (COOEt), 1650 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$

1.36 (t, 3H, COOCH<sub>2</sub>CH<sub>3</sub>), 4.35 (q, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 5.78 (s, 2H, CH<sub>2</sub>N), 6.33 (m, 1H, pyrrole *H*-4), 6.92 (d, 1H, benzene *H*-6), 7.19 (m, 1H, pyrrole *H*-3), 7.30-7.55 (m, 3H, pyrrole *H*-5 and benzene *H*-4,5), 7.65 ppm (dd, 1H, benzene *H*-3).

*Anal.* Calcd. for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 68.07; H, 5.00; N, 9.93. Found: C, 68.21; H, 4.98; N, 9.76.

#### 1-(2-Carboxybenzyl)pyrrole-2-acetic Acid (**6**).

##### Procedure 1.

A solution of 85% potassium hydroxide (7.54 g, 0.114 mole) in water (13 ml) was added to a stirred and cooled (0°) solution of **16** (14.96 g, 0.053 mole) in methanol (50 ml) at a rate such that temperature did not exceed 15°. The solution was stirred at room temperature for 2 hours, the volatiles were then removed *in vacuo* and the residue was azeotroped with benzene (4 × 50 ml) in order to achieve complete removal of water. Diethylene glycol (44 ml) and 85% hydrazine hydrate (18.6 ml) were added and the mixture was heated at 100-110° for 2 hours under a nitrogen atmosphere. To the cooled (40-50°) solution, solid 85% potassium hydroxide (25 g) was carefully added. The apparatus was set up for distillation and the mixture was gradually heated to 170-180°. This temperature was maintained for 70 minutes, during which time a distillate (about 27 ml) was collected. A further portion of diethylene glycol (30 ml) was added and the mixture was refluxed for 2 hours. After cooling to room temperature, the solution was diluted with water (130 ml), acidified (pH 4) with concentrated hydrochloric acid and extracted with ethyl acetate (2 × 100 ml). The organic layers were combined and washed with water, then brine, and dried. Evaporation of the solvent gave a solid residue, which was dissolved in methanol and cooled to -20° to afford 1-(2-carboxybenzyl)pyrrole-2-acetic acid (**6**) (8.20 g, 59%), mp 150-154°. A further recrystallization from methanol yielded an analytical sample, mp 157° (dec); ir: ν 1700 (COOH) cm<sup>-1</sup>; <sup>1</sup>H nmr (DMSO-d<sub>6</sub>): δ 3.32 (s, 2H, CH<sub>2</sub>COOH), 5.42 (s, 2H, CH<sub>2</sub>N), 5.99 (m, 2H, pyrrole β-protons), 6.25 (d, 1H, benzene *H*-6), 6.70 (m, 1H, pyrrole α-proton), 7.30-7.50 (m, 2H, benzene *H*-4,5), 7.90 (dd, 1H, benzene *H*-3), 12.7 ppm (br s, 2H, COOH, exchangeable with deuterium oxide).

*Anal.* Calcd. for C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.98; H, 5.15; N, 5.29.

##### Procedure 2.

To a suspension of 2-cyanomethyl-1-(2-ethoxycarbonylbenzyl)pyrrole **12** (0.34 g, 1.27 mmoles) in ethanol (5 ml) was added 10% aqueous potassium hydroxide (5 ml, 7.5 mmoles) and the mixture was refluxed for 75 minutes. After cooling, some undissolved material was filtered and the clear solution was made acidic by adding concentrated hydrochloric acid. The precipitate was extracted with ethyl acetate and the organic layer was washed with water and dried. Removal of the solvent yielded the dicarboxylic acid **6** (0.28 g, 85%) identical with a sample obtained by the alternate procedure.

#### Ethyl 10-Oxo-5*H*-pyrrolo[1,2-*b*]isoquinoline-3-acetate (**17**).

A mixture of dicarboxylic acid **6** (7.77 g, 0.03 mole), absolute ethanol (200 ml) and 96% sulfuric acid (1.5 ml) was refluxed in a Soxhlet apparatus charged with 3 Å molecular sieves (35 g) for 15 hours. After cooling, the solution was concentrated to a small volume, then poured onto crushed ice. Solid sodium carbonate decahydrate was added to pH 9 and the precipitate was taken up in chloroform. The organic layer was sequentially washed with sat-

urated sodium bicarbonate solution, water, brine, and water again, then dried and evaporated to give a solid residue. Chromatography on silica gel (chloroform as eluent) furnished ethyl 10-oxo-5*H*-pyrrolo[1,2-*b*]isoquinoline-3-acetate (**17**) (5.80 g, 72%) as a brownish solid. Recrystallization from ethanol afforded an analytical sample, mp 149-150°; ir: ν 1730 (COOEt), 1645 (C=O) cm<sup>-1</sup>; <sup>1</sup>H nmr (DMSO-d<sub>6</sub>): δ 1.20 (t, 3H, COOCH<sub>2</sub>CH<sub>3</sub>), 3.97 (s, 2H, CH<sub>2</sub>COOEt), 4.13 (q, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 5.41 (s, 2H, CH<sub>2</sub>N), 6.37 (d, J = 4 Hz, 1H, *H*-2), 7.02 (d, J = 4 Hz, 1H, *H*-1), 7.48-7.75 (m, 3H, *H*-6,7,8), 8.12 ppm (d, 1H, *H*-9); ms: m/e 269 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub>: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.24; H, 5.68; N, 5.10.

#### 10-Oxo-5*H*-pyrrolo[1,2-*b*]isoquinoline-3-acetic Acid (**4**).

A mixture of ester **17** (5.38 g, 20 mmoles) and 10% sodium hydroxide in 50% ethanol (25 ml, 60 mmoles) was refluxed for 70 minutes. The cooled solution was diluted with water (100 ml) and extracted with chloroform (3 × 15 ml). The aqueous layer was acidified with concentrated hydrochloric acid and the precipitate which formed was taken up in ethyl acetate. After usual work-up, the desired acid **4** was obtained (4.50 g, 94%), mp 178-179° dec (from ethanol); ir: ν 1710 (COOH), 1630 (C=O) cm<sup>-1</sup>; <sup>1</sup>H nmr (DMSO-d<sub>6</sub>): δ 3.89 (s, 2H, CH<sub>2</sub>COOH), 5.42 (s, 2H, CH<sub>2</sub>N), 6.37 (d, J = 4 Hz, 1H, *H*-2), 7.02 (d, J = 4 Hz, 1H, *H*-1), 7.45-7.75 (m, 3H, *H*-6,7,8), 8.12 (d, 1H, *H*-9), 12.74 ppm (s, 1H, COOH, exchangeable with deuterium oxide); ms: m/e 241 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>14</sub>H<sub>11</sub>NO<sub>3</sub>: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.83; H, 4.62; N, 5.64.

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