yield by a method analogous to the preparation of compound **9d**: mp 141-142 °C; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 3 H), 1.71 (s, 3 H), 2.39 (s, 3 H), 2.88 (s, 6 H), 5.68 (s, 1 H), 7.20 (d, J = 8 Hz, 2 H), 7.27 (s, 1 H), and 7.62 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.28, 21.64, 24.93, 42.16, 104.10, 115.47, 127.72, 129.42, 140.26, 142.46, 143.82, and 146.46; IR ($CHCl_3$) 1625, 1390, 1135, and 810 cm^{-1}; mass spectrum, m/z 279 (EI, M$^+$). Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.47; H, 7.59; N, 5.01. Found: C, 64.35; H, 7.72; N, 4.99.

(*E*,*E*)-1-(Dimethylamino)-2-[(4-methylphenyl)-sulfonyl]-1,3-heptadiene (9h). This material was prepared in 88% yield by a method analogous to the preparation of compound **9d**: mp 45-46 °C; ^{1}H NMR ($CDCl_3$) δ 0.71 (t, J = 7 Hz, 3 H), 1.22 (hex, J = 7 Hz, 2 H), 1.92 (q, J = 7 Hz, 2 H), 2.32 (s, 3 H), 2.91 (s, 6 H), 5.51 (dt, J = 16 Hz, J = 7 Hz, 1 H), 5.85 (d, J = 16 Hz, 1 H), 7.16 (d, J = 8 Hz, 2 H), 7.22 (s, 1 H), and 7.60 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.76, 21.63, 22.52, 35.56, 43.48, 104.82, 119.45, 127.76, 129.48, 138.18, 140.26, 142.62, and 146.58; IR ($CHCl_3$) 1625, 1400, and 1140 cm1-^{1}; mass spectrum, m/z 293 (EI, M$^+$). Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.48; H, 7.92; N, 4.77. Found: C, 65.62; H, 8.02; N, 4.65.

(*E*,*E*)-1-(Dimethylamino)-2-[(4-methylphenyl)-sulfonyl]-1,3-octadiene (9i). This material was prepared in 92% yield by a method analogous to the preparation of compound **9d**: mp 58-59 °C; ^{1}H NMR ($CDCl_3$) δ 0.77 (t, J = 7 Hz, 3 H), 1.15 (m, 4 H), 1.95 (q, J = 7 Hz, 2 H), 2.35 (s, 3 H), 2.93 (s, 6 H), 5.12 (dt, J = 16 Hz, J = 7 Hz, 1 H), 5.87 (d, J = 16 Hz, 1 H), 7.18 (d, J = 8 Hz, 2 H), 7.24 (s, 1 H), and 7.62 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.05, 21.64, 31.48, 33.14, 43.49, 104.84, 119.32, 127.79, 129.48, 138.41, 140,24, 142.61, and 146.54; IR ($CHCl_3$) 1630, 1400, and 1140 cm^{-1}; mass spectrum, m/z 307 (EI, M$^+$). Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.40; H, 8.21; N, 4.56. Found: C, 66.15; H, 8.22; N, 4.52.

(*E*,*E*)-1-(Dimethylamino)-2-[(4-methylphenyl)-sulfonyl]-1,3-undecadiene (9j). This material was prepared in 94% yield by a method analogous to the preparation of compound **9d**: mp 61-62 °C; ^{1}H NMR ($CDCl_3$) δ 1.82 (t, J = 7 Hz, 3 H), 1.15 (m, 10 H), 1.92 (q, J = 7 Hz, 2 H), 2.32 (s, 3 H), 2.92 (s, 6 H), 5.53 (dt, J = 16 Hz, J = 7 Hz, 1 H), 5.88 (d, J = 16 Hz, 1 H), 7.16 (d, J = 9 Hz, 2 H), 7.26 (s, 1 H), and 7.62 (d, J = 9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.29, 21.64, 22.87, 29.22, 29.36, 32.03, 33.47, 43.49, 104.85, 119.27, 127.79, 129.48, 138.42, 140.27, 142.58, and 146.55; IR ($CHCl_3$) 1630, 1405, and 1145 cm^{-1}; mass spectrum, m/z 349 (EI, M$^+$). Anal. Calcd for $C_{20}H_{31}NO_2S$: C, 68.71; H, 8.96; N, 4.01. Found: C, 69.00; H, 9.01; N, 3.95.

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New Synthesis of Pyrrolo[3,2,1-*ij*]quinolin-4-one Derivatives

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A new convenient synthesis of pyrrolo[3,2,1-*ij*]quinolin-4-one derivatives is described. In this method, methyl-7-hydroxyquinoline-2-ones are the starting materials onto which the third pyrrolo ring is condensed directly, yielding dehydrogenated methyl-9-hydroxypyrrolo[3,2,1-*ij*]quinolin-4-ones.

Introduction

The tricyclic 4*H*-pyrrolo[3,2,1-*ij*]quinoline system has been known for a long time. In fact, the so-called methyldiketolilolidine (i.e. 2-methyl-1,2,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinoline-4,6-dione) was first obtained by Knorr quinoline synthesis from 2-methylindoline.[1]

More recently, polyfluorohydroxyisopropyl derivatives of 1,2-dihydropyrrolo[3,2,1-*ij*]quinolin-4-one have been synthesized and tested for antihypertensive activity,[2] and 1,2,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinolin-4-one and some analogues have been prepared as systemic fungicides of agricultural interest.[3a,b]

All previous synthetic pathways to obtain pyrroloquinolinones used indoline or its derivatives as the starting materials.[2,3a,4-7]

We now report a new, less expensive method for obtaining pyrrolo[3,2,1-*ij*]quinolin-4-one derivatives, which consists of building a pyrrole ring at the appropriate position of the quinolinone nucleus. In this way dehydrogenated methyl 9-hydroxy derivatives of the title tricyclic system may be directly synthesized. Useful intermediates are 8-allyl derivatives of 7-hydroxyquinolin-2-

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ones, which are readily obtained by Claisen rearrangement of the corresponding 7-*O*-allyl ethers. Bromination of the allyl moiety, followed by cyclization in alkaline medium, gives the desired pyrrolo[3,2,1-*ij*]quinolin-4-one derivatives.

Results and Discussion

Starting materials for the synthesis of the title compounds are the appropriately methylated 7-hydroxyquinolin-2-ones **4–6**. These compounds can be prepared through pathway A or B. Following the previously reported method A,[9] a mixture of *m*-phenylenediamine, or its 4-methyl derivative, and ethyl acetoacetate, or its 2-methyl derivative, were reacted, giving methyl-7-aminoquinolin-2-ones **1–3**. These compounds were diazotized and hydrolyzed, yielding methyl-7-hydroxyquinolin-4-ones **4–6**.

Using method B, 3-aminophenol was condensed with ethyl acetoacetate or its 2-methyl derivative, the main condensation products being methyl-7-hydroxyquinolin-2-ones **4–6**. However, these compounds are not the only products, as previously reported.[8] They are accompanied by minor amount of the structural isomer 4-methyl-7-aminocoumarin (**7**), or its 3,4-dimethyl analogue **9**, as well as by 4-methyl-5-hydroxyquinolin-4-one (**8**), or its 3,4-dimethyl analogue **10**. These byproducts were isolated in pure form by column chromatography.

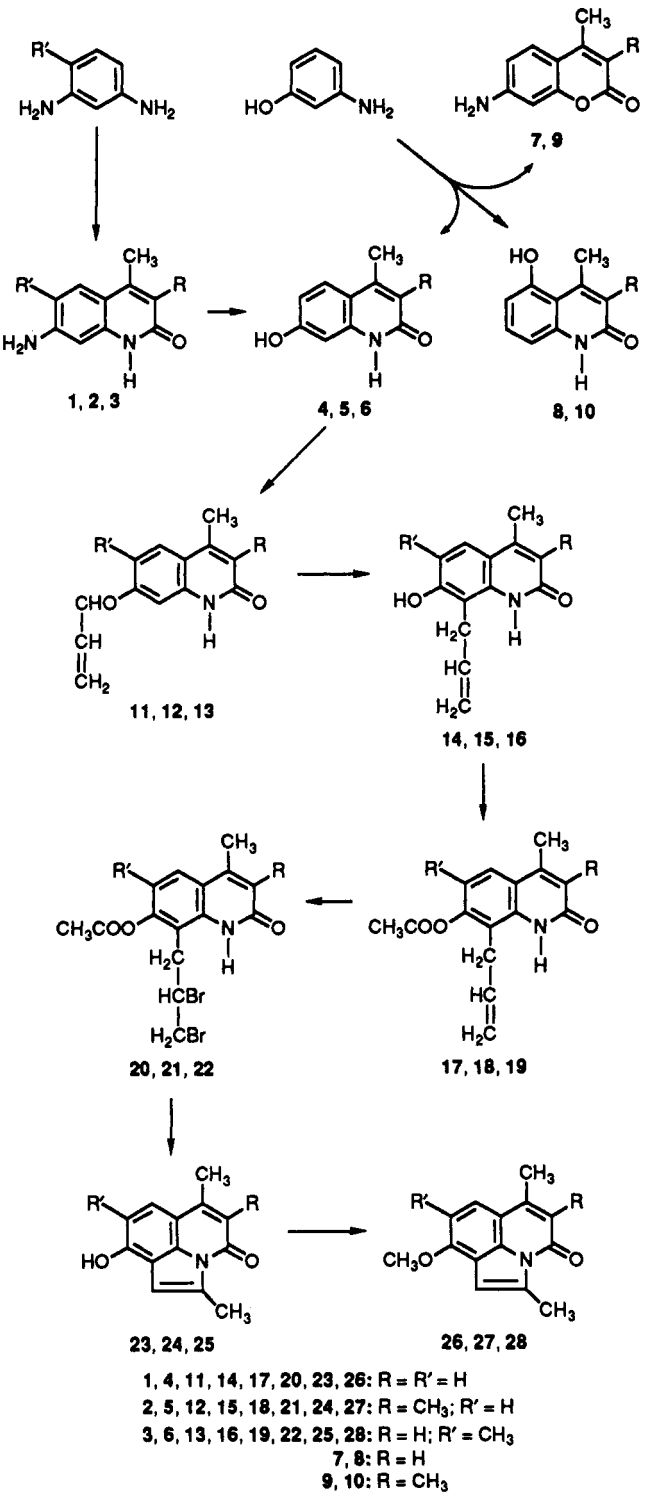
Both methods A and B are suitable for preparing the desired synthons in acceptable yields. However, method A is less time consuming, since it does not require chromatographic separation.

According to Scheme I, methyl-7-hydroxyquinolin-2-ones **4–6** were condensed with allyl bromide to give the corresponding 7-*O*-allyl ethers **11–13**, which underwent Claisen rearrangement. This reaction furnishes 8-allyl derivatives **14–16** exclusively, even when the other ortho position (i.e. 6) is free (unlike the case of coumarin isosteres[10]). The 8-position of 7-hydroxyquinolin-2-ones is more activated than the 6-position.

Methyl-7-hydroxy-8-allylquinolin-2-ones **14–16** were then acetylated and brominated at room temperature to afford 8-(dibromopropyl) derivatives **20–22**, which on cyclization in alkaline medium gave unexpectedly only methyl-9-hydroxypyrrolo[3,2,1-*ij*]quinolin-4-one derivatives **23–25**. It was expected, in fact, that the oxygen atom of the 7-acetoxy group might also have been competitively involved in the cyclization, as happens in coumarin isosteres, and lead to the formation of a 7,8-condensed furan ring.[10] The formation in alkaline medium of the enolate form which results from the tautomeric lactam–lactim equilibrium in quinolin-2-ones derivatives[11] probably causes cyclization to proceed, to give the condensed pyrrole ring exclusively.

This synthetic pathway constitutes a new approach to interesting methyl-9-hydroxypyrrolo[3,2,1-*ij*]quinolin-4-one derivatives.

Scheme I



Experimental Section

Melting points were determined on an open-capillary melting point apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel plates 60-F-254 (Merck, 0.25 mm) with an ethyl acetate–cyclohexane mixture (35:65). Column chromatography was performed by using 70–230-mesh silica gel (Merck) and eluting with dichloromethane. NMR spectra were recorded on a 200-MHz spectrometer and are referenced to the deuterium lock signal from the sample solvent. Elemental analyses were carried out by the Microanalytical Laboratory of the Department of Pharmaceutical Sciences of Padova University under the direction of A. Pietrogrande.

Methyl-7-hydroxyquinolin-2-ones 4–6. Method A. 4-Methyl-7-aminoquinolin-2-one (1). A mixture of *m*-phenylenediamine (20.0 g, 184.9 mmol) and ethyl acetoacetate (23.6 mL, 184.9 mmol) was heated at 150 °C for 48 h. The cooled reaction mixture was suspended in 40 mL of methanol, and the undissolved solid was collected. The crude product was crystallized from ethanol, giving 1 (43%): mp 279 °C; ^{1}H NMR

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(acetone-d_6) δ 7.48 (d, J = 8.8 Hz, 1 H, H-5), 6.64 (dd, J = 8.8 and 2.2 Hz, 1 H, H-6), 6.49 (d, J = 2.2 Hz, 1 H, H-8), 6.14 (q, J = 1.0 Hz, 1 H, H-3), 2.39 (d, J = 1.0 Hz, 3 H, Me-4). Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N. 16.08. Found: C, 68.79; H, 5.75; N, 15.99.

3,4-Dimethyl-7-aminoquinolin-2-one (2). This compound was prepared from *m*-phenylenediamine and ethyl 2-methylacetoacetate in an analogous manner to **1**. The crude product was crystallized from methanol (22%): mp 300 °C; ^{1}H NMR (acetone-d_6) δ 7.52 (d, J = 8.8 Hz, 1 H, H-5), 6.63 (dd, J = 8.8 and 2.2 Hz, 1 H, H-6), 6.48 (d, J = 2.2 Hz, 1 H, H-8), 2.39 (q, J = 0.7 Hz, 3 H, Me-4), 2.13 (q, J = 0.7 Hz, 3 H, Me-3). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.11; H, 6.42; N, 14.73.

4,6-Dimethyl-7-aminoquinolin-2-one (3). This compound was prepared from 2,4-diaminotoluene and ethyl acetoacetate in an analogous manner to **1**. The crude product was crystallized from methanol (22%): mp 300 °C; ^{1}H NMR (acetone-d_6) δ 7.39 (br s, 1 H, H-5), 6.54 (s, 1 H, H-8), 6.14 (q, J = 1.1 Hz, 1 H, H-3), 2.41 (d, J = 1.1 Hz, 3 H, Me-4), 2.20 (br s, 3 H, Me-6). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 69.99; H, 6.38; N, 14.66.

4-Methyl-7-hydroxyquinolin-2-one (4). A mixture of **1** (6.7 g, 38.6 mmol), water (50 mL), concentrated sulfuric acid (40 mL), and ice (60 g) was cooled to 0 °C. An aqueous solution (10 mL) of sodium nitrite (3.0 g, 43.4 mmol) was added dropwise with stirring. The mixture was cautiously poured into 150 mL of boiling 10 M sulfuric acid. The boiling was continued for 10 min, and the mixture was diluted with water and cooled to give a precipitate, which was crystallized from methanol, to give **4** (95%): mp 300 °C (lit. mp.[8] 300 °C); ^{1}H NMR (acetone-d_6) δ 7.62 (d, J = 8.6 Hz, 1 H, H-5), 6.77 (dd, J = 8.6 and 2.6 Hz, 1 H, H-6), 6.73 (d, J = 2.6 Hz, 1 H, H-8), 6.28 (q, J = 1.1 Hz, 1 H, H-3), 2.45 (d, J = 1.1 Hz, 3 H, Me-4). Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.42; H, 5.11; N, 7.87.

3,4-Dimethyl-7-hydroxyquinolin-2-one (5). This compound was prepared from **2** in an analogous manner to **4**. The crude product was crystallized from methanol, giving **5** (94%): mp 300 °C; ^{1}H NMR (methanol-d_4) δ 7.62 (d, J = 8.8 Hz, 1 H, H-5), 6.74 (dd, J = 8.8 and 2.4 Hz, 1 H, H-6), 6.69 (d, J = 2.4 Hz, 1 H, H-8), 2.42 (br s, 3 H, Me-4), 2.15 (br s, 3 H, Me-3). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.81; H, 5.75; N, 7.29.

4,6-Dimethyl-7-hydroxyquinolin-2-one (6). This compound was prepared from **3** in an analogous manner to **4**. The crude product was crystallized from methanol, giving **6** (90%): mp 300 °C; ^{1}H NMR (acetone-d_6) δ 7.48 (br s, 1 H, H-5), 6.73 (s, 1 H, H-8), 6.25 (q, J = 1.1 Hz, 1 H, H-3), 2.44 (d, J = 1.1 Hz, 3 H, Me-4), 2.24 (br s, 3 H, Me-6). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.73; H, 5.79; N, 7.18.

Methyl-7-hydroxyquinolin-2-ones 4, 5. Method B. 4-Methyl-7-hydroxyquinolin-2-one (4). A mixture of 3-aminophenol (20.0 g, 183.3 mmol) and ethyl acetoacetate (23.3 mL, 183.3 mmol) was heated at 150 °C for 20 h to give a yellow sticky mass which after cooling solidified upon treatment with methanol (30 mL). The solid was chromatographed on silica gel, eluting with dichloromethane to yield the following, in order of elution. (i) 4-Methyl-7-aminocoumarin (**7**) (7%; EtOH): mp 222 °C, ^{1}H NMR (acetone-d_6) δ 7.45 (d, J = 8.6 Hz, 1 H, H-5), 6.65 (dd, J = 8.6 and 2.2 Hz, 1 H, H-6), 6.50 (d, J = 2.2 Hz, 1 H, H-8), 5.94 (q, J = 1.1 Hz, 1 H, H-3), 2.38 (d, J = 1.1 Hz, 3 H, Me-4). Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.33; H, 5.19; N, 7.93. (ii) 4-Methyl-5-hydroxyquinolin-2-one (**8**) (16%; MeOH): mp 300 °C; ^{1}H NMR (acetone-d_6) δ 7.28 (dd, J = 8.1 and 8.0 Hz, 1 H, H-7), 6.80 (dd, J = 8.1 and 1.1 Hz, 1 H, H-6 or H-8), 6.61 (dd, J = 8.0 and 1.1 Hz, 1 H, H-6 or H-8), 6.28 (q, J = 1.2 Hz, 1 H, H-3), 2.72 (d, J = 1.2 Hz, 3 H, Me-4). Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.26; H, 5.15; N, 7.91. (iii) **4** (55%; MeOH).

3,4-Dimethyl-7-hydroxyquinolin-2-one (5). This compound was prepared from 3-aminophenol in an analogous manner to **4**. The crude product gave the following after chromatography by eluting with dichloromethane. (i) 3,4-Dimethyl-7-aminocoumarin (**9**) (6%, MeOH): mp 278 °C; ^{1}H NMR (methanol-d_4) δ 7.46 (d, J = 8.7 Hz, 1 H, H-5), 6.65 (dd, J = 8.7 and 2.3 Hz, 1 H, H-6), 6.50 (d, J = 2.3 Hz, 1 H, H-8), 2.37 (q, J = 0.7 Hz, 3 H, Me-4), 2.11 (q, J = 0.7 Hz, 3 H, Me-3). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.78; H, 5.83; N, 7.31. (ii) 3,4-Dimethyl-5-hydroxyquinolin-2-one (**10**) (11%, MeOH): mp 288 °C; ^{1}H NMR (methanol-d_4) δ 7.20 (dd, J = 8.1 and 8.0 Hz, 1 H, H-7), 6.76 (dd, J = 8.1 and 1.2 Hz, 1 H, H-6 or H-8), 6.59 (dd, J = 8.0 and 1.2 Hz, 1 H, H-6 or H-8), 2.74 (q, J = 0.7 Hz, 3 H, Me-4), 2.17 (q, J = 0.7 Hz, 3 H, Me-3). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.75; H, 5.81; N, 7.33. (iii) **5** (36%, MeOH).

Methyl-7-(allyloxy)quinolin-2-ones 11–13. 4-Methyl-7-(allyloxy)quinolin-2-one (11). To a solution of **4** (17.5 g, 100 mmol) in acetone (1800 mL) were added 12.9 mL (149.8 mmol) of allyl bromide and 50.0 g of anhydrous potassium carbonate. The mixture was refluxed until **4** disappeared (5 h; TLC). After cooling, the solid was filtered off and washed with fresh acetone. The solvent was evaporated from the pooled filtrate and washings, and the residue was crystallized from methanol to give **11** (72%): mp 179 °C; ^{1}H NMR ($CDCl_3$) δ 12.43 (br s, 1 H, H-1), 7.58 (d, J = 8.9 Hz, 1 H, H-5), 6.88 (d, J = 2.4 Hz, 1 H, H-8), 6.85 (dd, J = 8.9, 2.4 Hz, 1 H, H-6), 6.45 (q, J = 1.0 Hz, 1 H, H-3), 6.18–5.99 (m, 1 H, H-2′), 5.53–5.31 (m, 2 H, H-3′), 4.64 (dt, J = 5.3, 1.6 Hz, 2 H, H-1′), 2.47 (d, J = 1.0 Hz, 3 H, Me-4). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.36; H, 5.99; N, 6.50.

3,4-Dimethyl-7-(allyloxy)quinolin-2-one (12). This compound was prepared from **5** in an analogous manner to **11**. The crude product was crystallized from methanol to afford **12** (76%): mp 168 °C; ^{1}H NMR ($CDCl_3$) δ 12.36 (br s, 1 H, H-1), 7.59 (d, J = 8.9 Hz, 1 H, H-5), 6.91 (d, J = 2.6 Hz, 1 H, H-8), 6.83 (dd, J = 8.9, 2.6 Hz, 1 H, H-6), 6.20–6.01 (m, 1 H, H-2′), 5.55–5.31 (m, 2 H, H-3′), 4.65 (dt, J = 5.4, 1.5 Hz, 2 H, H-1′), 2.44 (br s, 3 H, Me-4), 2.29 (br s, 3 H, Me-3). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.29; H, 6.54; N, 6.06.

4,6-Dimethyl-7-(allyloxy)quinolin-2-one (13). This compound was prepared from **6** in an analogous manner to **11**. The crude product was crystallized from methanol to yield **13** (55%): mp 231 °C; ^{1}H NMR ($CDCl_3$) δ 12.46 (br s, 1 H, H-1), 7.40 (br s, 1 H, H-5), 6.80 (s, 1 H, H-8), 6.44 (q, J = 1.0 Hz, 1 H, H-3), 6.20–6.01 (m, 1 H, H-2′), 5.56–5.29 (m, 2 H, H-3′), 4.65 (dt, J = 5.1, 1.5 Hz, 2 H, H-1′), 2.46 (d, J = 1.0 Hz, 3 H, Me-4), 2.31 (br s, 3 H, Me-6). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.20; H, 6.49; N, 6.08.

Methyl-8-allylquinolin-2-ones 14–16. 4-Methyl-7-hydroxy-8-allylquinolin-2-one (14). A solution of **11** (9.5 g, 44.1 mmol) in *N*,*N*-diethylaniline (30 mL) was refluxed for 3 h. On cooling the mixture, a precipitate was obtained, which was washed with cyclohexane and crystallized from ethyl acetate to give **14** (70%): mp 231 °C; ^{1}H NMR (acetone-d_6) δ 7.58 (d, J = 8.9 Hz, 1 H, H-5), 6.85 (d, J = 8.9 Hz, 1 H, H-6), 6.29 (q, J = 1.1 Hz, 1 H, H-3), 6.04–5.85 (m, 1 H, H-2′), 5.04–4.89 (m, 2 H, H-3′), 3.63 (dt, J = 5.7, 1.7 Hz, 2 H, H-1′), 2.46 (d, J = 1.1 Hz, 3 H, Me-4). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.30; H, 5.94; N. 6.46.

3,4-Dimethyl-7-hydroxy-8-allylquinolin-2-one (15). This compound was prepared from **12** in an analogous manner to **14**. The crude product was crystallized from methanol to give **15** (83%): mp 220 °C; ^{1}H NMR (acetone-d_6) δ 7.58 (d, J = 8.9 Hz, 1 H, H-5), 6.83 (d, J = 8.9 Hz, 1 H, H-6), 6.05–5.86 (m, 1 H, H-2′), 5.05–4.89 (m, 2 H, H-3′), 3.63 (dt, J = 5.7, 1.7 Hz, 2 H, H-1′), 2.45 (q, J = 0.7 Hz, 3 H, Me-4), 2.17 (q, J = 0.7 Hz, 3 H, Me-3). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.23; H, 6.51; N, 6.02.

4,6-Dimethyl-7-hydroxy-8-allylquinolin-2-one (16). This compound was prepared from **13** in an analogous manner to **14**. The crude product was crystallized from ethyl acetate to give **16** (75%): mp 223 °C; ^{1}H NMR (acetone-d_6) δ 9.53 (br s, 1 H, H-1 or OH), 8.09 (br s, 1 H, H-1 or OH), 7.46 (q, J = 0.8 Hz, 1 H; H-5), 6.21 (q, J = 1.1 Hz, 1 H, H-3), 6.09–5.90 (m, 1 H, H-2′), 5.12–4.96 (m, 2 H, H-3′), 3.89 (dt, J = 5.7, 1.8 Hz, 2 H, H-1′), 2.43 (d, J = 1.1 Hz, 3 H, Me-4), 2.36 (d, J = 0.8 Hz, 3 H, Me-6). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.24; H, 6.46; N, 6.06.

Methyl-7-acetoxy-8-allylquinolin-2-ones 17–19. 4-Methyl-7-acetoxy-8-allylquinolin-2-one (17). A mixture of **14** (6.5 g, 30.2 mmol), sodium acetate (1.0 g), and acetic anhydride (40 mL) was refluxed for 1 h. The reaction mixture was cautiously

diluted with 40 mL of water, refluxed for 10 min, and poured into water (600 mL). The precipitate was collected, washed with abundant water, and crystallized from methanol to give **17** (90%): mp 211 °C; ^{1}H NMR ($CDCl_3$) δ 8.93 (br s, 1 H, 1-H), 7.63 (d, J = 8.8 Hz, 1 H, H-5), 7.00 (d, J = 8.8 Hz, 1 H, H-6), 6.51 (q, J = 1.1 Hz, 1 H, H-3), 5.98–5.79 (m, 1 H, H-2′), 5.21–5.05 (m, 2 H, H-3′), 3.51 (dt, J = 5.7, 1.8 Hz, 2 H, H-1′), 2.48 (d, J = 1.1 Hz, 3 H, Me-4), 2.37 (s, 3 H, Ac). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.88; H, 5.78; N, 5.21.

3,4-Dimethyl-7-acetoxy-8-allylquinolin-2-one (18). This compound was prepared from **15** in the same manner as **17**. The crude product was crystallized from methanol to give **18** (96%): mp 225 °C; ^{1}H NMR ($CDCl_3$) δ 9.75 (br s, 1 H, 1-H), 7.65 (d, J = 8.8 Hz, 1 H, H-5), 6.97 (d, J = 8.8 Hz, 1 H, H-6), 6.01–5.81 (m, 1 H, H-2′), 5.14–5.02 (m, 2 H, H-3′), 3.59 (dt, J = 5.7, 1.5 Hz, 2 H, H-1′), 2.46 (br s, 3 H, Me-4), 2.35 (s, 3 H, Ac), 2.26 (br s, 3 H, Me-3). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.58; H, 6.19; N, 5.08.

4,6-Dimethyl-7-acetoxy-8-allylquinolin-2-one (19). This compound was prepared from **16** in an analogous manner to **17**. The crude product was crystallized from methanol to give **19** (83%): mp 237 °C; ^{1}H NMR ($CDCl_3$) δ 9.08 (br s, 1 H, H-1), 7.47 (q, J = 0.8 Hz, 1 H, H-5), 6.49 (q, J = 1.1 Hz, 1 H, H-3), 5.96–5.77 (m, 1 H, H-2′), 5.18–5.05 (m, 2 H, H-3′), 3.49 (d, J = 5.5 Hz, 2 H, H-1′), 2.46 (d, J = 1.1 Hz, 3 H, Me-4), 2.38 (s, 3 H, Ac), 2.24 (d, J = 0.8 Hz, 3 H, Me-6). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.61; H, 6.30; N, 5.09.

Methyl-7-acetoxy-8-(2,3-dibromopropyl)quinolin-2-ones 20–22. 4-Methyl-7-acetoxy-8-(2,3-dibromopropyl)quinolin-2-one (20). A solution of bromine (1.3 mL, 25.3 mmol) in 20 mL of acetic acid was added dropwise to a solution of **17** (6.5 g, 25.3 mmol) in 150 mL of acetic acid at room temperature. After the addition was complete, the solution was stirred for 30 min. The solvent was evaporated, and the residue was crystallized from methanol to give **20** (70%): mp 165 °C; ^{1}H NMR ($CDCl_3$) δ 7.69 (d, J = 8.9 Hz, 1 H, H-5), 7.06 (d, J = 8.9 Hz, 1 H, H-6), 6.54 (q, J = 0.8 Hz, 1 H, H-3), 4.53–4.39 (m, 1 H, H-2′), 4.11–3.90 (m, 2 H, H-3′), 3.82–3.48 (m, 2 H, H-1′), 2.51 (d, J = 0.8 Hz, 3 H, Me-4), 2.42 (s, 3 H, Ac). Anal. Calcd for $C_{15}H_{15}Br_2NO_3$: C, 43.19; H, 3.62; N, 3.36; Br, 38.32. Found: C, 43.01; H, 3.47; N, 3.28; Br, 38.19.

3,4-Dimethyl-7-acetoxy-8-(2,3-dibromopropyl)quinolin-2-one (21). This compound was prepared from **18** in an analogous manner to **20**. The crude product was crystallized from methanol (60%): mp 189 °C; ^{1}H NMR ($CDCl_3$) δ 10.65 (br s, 1 H, H-1), 7.71 (d, J = 8.9 Hz, 1 H, H-5), 7.03 (d, J = 8.9 Hz, 1 H, H-6), 4.49–4.38 (m, 1 H, H-2′), 4.08–3.80 (m, 2 H, H-3′), 3.55–3.42 (m, 2 H, H-1′), 2.49 (br s, 3 H, Me-4), 2.42 (s, 3 H, Ac), 2.31 (br s, 3 H, Me-3). Anal. Calcd for $C_{16}H_{17}Br_2NO_3$: C, 44.58; H, 3.97; N, 3.25; Br, 37.07. Found: C, 44.39; H, 3.84; N, 3.11; Br, 36.88.

4,6-Dimethyl-7-acetoxy-8-(2,3-dibromopropyl)quinolin-2-one (22). This compound was prepared from **19** in an analogous manner to **20**. The crude product was crystallized from methanol to give **16** (64%): mp 153 °C; ^{1}H NMR ($CDCl_3$) δ 10.21 (br s, 1 H, H-1), 7.53 (br s, 1 H, H-5), 6.54 (q, J = 1.0 Hz, 1 H, H-3), 4.49–4.36 (m, 1 H, H-2′), 4.06–3.22 (m, 4 H, H-3′ and H-1′), 2.49 (d, J = 1.0 Hz, 3 H, Me-4), 2.45 (s, 3 H, Ac), 2.25 (br s, 3 H, Me-6). Anal. Calcd for $C_{16}H_{17}Br_2NO_3$: C, 44.58; H, 3.97; N, 3.25; Br, 37.07. Found: C, 44.41; H, 3.87; N, 3.05; Br, 36.96.

Methyl-9-hydroxypyrrolo[3,2,1-*ij*]quinolin-4-ones 23–25. 2,6-Dimethyl-9-hydroxypyrrolo[3,2,1-*ij*]quinolin-4-one (23). A solution of 5% potassium hydroxide in 100 mL of absolute ethanol was added to a solution of **20** (2.1 g, 50 mmol) in 150 mL of absolute ethanol, and the mixture was refluxed in the dark for 2 h. After cooling, the mixture was acidified with dilute hydrochloric acid and diluted with water, and the precipitate was collected. The solid was crystallized from methanol to give **23** (43%): mp 282 °C; ^{1}H NMR (methanol-d_4) δ 7.58 (d, J = 8.4 Hz, 1 H, H-7), 6.83 (d, J = 8.4 Hz, 1 H, H-8), 6.66 (q, J = 1.4 Hz, 1 H, H-1), 6.27 (q, J = 0.9 Hz, 1 H, H-5), 2.74 (d, J = 1.4 Hz, 3 H, Me-2), 2.52 (d, J = 0.9, 3 H, Me-6). Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 72.96; H, 5.15; N, 6.50.

2,5,6-Trimethyl-9-hydroxypyrrolo[3,2,1-*ij*]quinolin-4-one (24). This compound was prepared from **21** in the same manner as **23**. The crude product was crystallized from methanol to give **24** (55%): mp 276 °C; ^{1}H NMR (methanol-d_4) δ 7.53 (d, J = 8.5 Hz, 1 H, H-7), 6.80 (d, J = 8.5 Hz, 1 H, H-8), 6.62 (q, J = 1.3 Hz, 1 H, H-1), 2.75 (d, J = 1.3 Hz, 3 H, Me-2), 2.46 (q, J = 0.7 Hz, 3 H, Me-6), 2.18 (q, J = 0.7, 3 H, Me-5). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.74; H, 5.69; N, 6.13.

2,6,8-Trimethyl-9-hydroxypyrrolo[3,2,1-*ij*]quinolin-4-one (25). mhis compound was prepared from **22** in the same manner as **23**. The crude product was crystallized from methanol to give **25** (50%): mp 265 °C; ^{1}H NMR (methanol-d_4) δ 7.48 (q, J = 0.7 Hz, 1 H, H-7), 6.70 (q, J = 1.3 Hz, 1 H, H-1), 6.25 (q, J = 1.1 Hz, 1 H, H-5), 2.74 (d, J = 1.3 Hz, 3 H, Me-2), 2.51 (d, J = 1.1 Hz, 3 H, Me-6), 2.36 (d, J = 0.7 Hz, 3 H, Me-8). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.69; H, 5.64; N, 6.09.

Methyl-9-methoxypyrrolo[3,2,1-*ij*]quinolin-4-ones 26–28. 2,6-Dimethyl-9-methoxypyrrolo[3,2,1-*ij*]quinolin-4-one (26). Dimethyl sulfate (0.17 mL, 1.8 mmol) and potassium carbonate (3.0 g) were added to a solution of **23** (0.25 g, 1.2 mmol) in acetone (100 mL), and the suspension was refluxed for 3 h. The mixture was cooled, and the solid was filtered off and washed with acetone. The filtrate and the acetone washings were evaporated under reduced pressure, and the residue was crystallized from methanol to give **26** (56%): mp 106 °C; ^{1}H NMR ($CDCl_3$) δ 7.50 (d, J = 8.5 Hz, 1 H, H-7), 6.83 (d, J = 8.5 Hz, 1 H, H-8), 6.55 (q, J = 1.3 Hz, 1 H, H-1), 6.33 (q, J = 1.0 Hz, 1 H, H-5), 4.02 (s, 3 H, OMe), 2.79 (d, J = 1.3 Hz, 3 H, Me-2), 2.49 (d, J = 1.0 Hz, 3 H, Me-6). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.71; H, 5.72; N, 6.03.

2,5,6-Trimethyl-9-methoxypyrrolo[3,2,1-*ij*]quinolin-4-one (27). This compound was prepared from **24** in an analogous manner to **26**. The crude product was crystallized from methanol to give **27** (94%): mp 150 °C; ^{1}H NMR ($CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 1 H, H-7), 6.86 (d, J = 8.5 Hz, 1 H, H-8), 6.59 (q, J = 1.3 Hz, 1 H, H-1), 4.04 (s, 3 H, OMe), 2.83 (d, J = 1.3 Hz, 3 H, Me-2), 2.49 (q, J = 0.8 Hz, 3 H, Me-6), 2.26 (q, J = 0.8 Hz, 3 H, Me-5). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.49; H, 6.24; N, 5.69.

2,6,8-Trimethyl-9-methoxypyrrolo[3,2,1-*ij*]quinolin-4-one (28). This compound was prepared from **25** in the same manner as **26**. The crude product was crystallized from methanol to give **28** (75%): mp 181 °C; ^{1}H NMR ($CDCl_3$) δ 7.40 (q, J = 0.7 Hz, 1 H, H-7), 6.71 (q, J = 1.3 Hz, 1 H, H-1), 6.40 (q, J = 1.1 Hz, 1 H, H-5), 4.27 (s, 3 H, OMe), 2.82 (d, J = 1.3 Hz, 3 H, Me-2), 2.51 (d, J = 1.1 Hz, 3 H, Me-6), 2.36 (d, J = 0.7, 3 H, Me-8). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.41; H, 6.11; N, 5.65.