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Studies on the Synthesis of Some Pyrrolocoumarins and Furoquinolones

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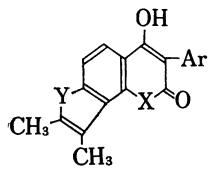
Treatment of 4-aminobenzofuran derivatives with hydrochloric acid led to the formation of 4-hydroxyindole derivatives in good yields, wheras alkaline hydrolysis of 4-acylaminobenzofurans gave 4-aminobenzofurans normally. Synthesis of pyrrolocoumarins and furoquinolones by thermal condensation of those above mentioned compounds with phenylmalonates are also described.

Several derivatives of furocoumarins[2,3] and benzofurocoumarins[2,3] were obtained from natural sources; some of them possess biological activities.



I: X=Y=O
II: X=O, Y=NH
III: X=NH, Y=O

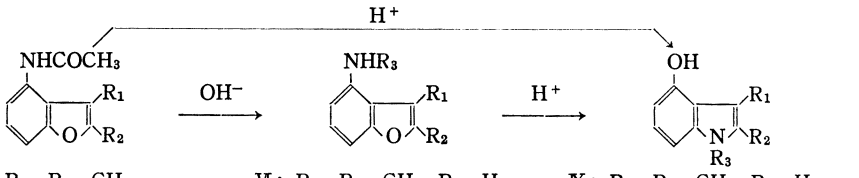
Based upon these observations, the synthesis of 4-hydroxyfuro[2,3-*h*]coumarins (I) and furoquinolines have been reported by Royer, *et al.*[4-8] and Kawase, *et al.*[9-11]

Synthesis of pyrrolo-derivatives of 4-hydroxy-coumarins (II) and furo-derivatives of 4-hydroxy-carbostyrils (III) and their biological properties are of interest for us, since those compounds are analogs (stated above) in which one of the oxygens is replaced to the nitrogen.

Here we wish to report the synthesis of pyrrolocoumarins (II), furoquinolones (III) and the starting materials.

Preparation of 4-Hydroxyindoles

Royer and co-workers[8] failed to obtain 4-amino-2,3-dimethylbenzofuran (VI) by the hydrolysis of 4-acetamido-2,3-dimethylbenzofuran (IV) with mineral acid. Our interest in preparing 4-aminobenzofuran (VI) led us to reinvestigate the deacetylation of IV.



IV: $R_1=R_2=CH_3$
V: $R_1+R_2=-(CH_2)_4-$

VI: $R_1=R_2=CH_3$, $R_3=H$
VII: $R_1=R_2=CH_3$, $R_3=C_2H_5$
VIII: $R_1+R_2=-(CH_2)_4-$, $R_3=H$

IX: $R_1=R_2=CH_3$, $R_3=H$
X: $R_1=R_2=CH_3$, $R_3=C_2H_5$
XI: $R_1+R_2=-(CH_2)_4-$, $R_3=H$

Chart 1

1) Location: *Kawagishi, 2-2-50, Toda-shi, Saitama.*
2) F.M. Dean, "Naturally-occuring Oxygen-ring Compounds," Butterworths, London, 1963, p. 135, 176.
3) A. Mustafa, "Furopyrans and Furopyrones," ed. by A. Weissberger, Interscience Publishers, London, 1967, p. 14, 243.
4) R. Royer, E. Bisagni, A.-M. Laval-Jeantet and J.-P. Marquet, *Bull. Soc. Chim. France*, **1965**, 2607.
5) J.-P. Lechartier, P. Demerseman, A. Cheutin and R. Royer, *Bull. Soc. Chim. France*, **1966**, 1716.
6) R. Royer, P. Demerseman, A.-M. Laval-Jeantet, J.-F. Rossignol and A. Cheutin, *Bull. Soc. Chim. France*, **1968**, 1026.
7) C. Pene, P. Demerseman, A. Cheutin and R. Royer, *Bull. Soc. Chim. France*, **1966**, 586.
8) R. Royer, P. Demerseman, C. Pène and G. Colin, *Bull. Soc. Chim. France*, **1967**, 915.
9) Y. Kawase, M. Nanbu and H. Yanagihara, *Bull. Chem. Soc. Japan*, **41**, 1201 (1968).
10) Y. Kawase, M. Nanbu, F. Miyoshi and H. Kawamura, *Bull. Chem. Soc. Japan*, **41**, 2683 (1968).
11) Y. Kawase and S. Kondo, *Bull. Chem. Soc. Japan*, **43**, 3268 (1970).

The hydrolysis of IV with hydrochloric acid did not afford the 4-aminobenzofuran (VI), but gave the compound of mp 103—105°,[12] which was confirmed as 4-hydroxyindole derivative (IX) on the basis of the following spectral data. The infrared (IR) spectrum shows absorption bands at 3560, 3400 cm^{-1}, and the ultraviolet (UV) spectrum shows absorption maxima at 273.5, 288.5 and 297 mμ. On the other hand, an alkaline hydrolysis of the amide (IV) afforded the 4-aminobenzofuran (VI)[13] normally, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 3340, UV λ_{max}^{EtOH} mμ: 263, 296.

This acid catalized rearrangement from 4-aminobenzofuran into 4-hydroxyindole was also observed in the case of its derivatives such as 4-ethylaminobenzofuran (VII) and its analogs. For example, the compound (VII), which was synthesized by the reduction of amide (IV) using $LiAlH_4$ in THF, could be converted to the 1-ethyl-4-hydroxyindole derivative (X). Furthermore 5-hydroxy-1,2,3,4-tetrahydrocarbazole (XI) was obtained from 9-acetamido-1,2,3,4-tetrahydrodibenzofuran (V), which was prepared by the Beckmann rearrangement of the oxime (XVI) of 9-acetyl-1,2,3,4-tetrahydrodibenzofuran (XV). The structure of X and XI were established with their spectral data. The IR and UV spectra revealed these products to possess the 4-hydroxyindole system.

On the other hand, the hydrolysis of V under basic conditions gave the 9-amino-1,2,-3,4-tetrahydrodibenzofuran (VIII).

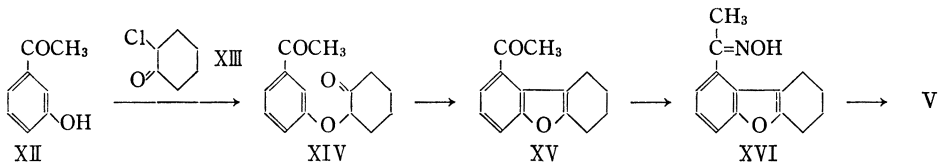


Chart 2

The starting material (XV) was synthesized as follows; the reaction of *m*-hydroxyacetophenone[14] with 2-chlorocyclohexanone[15] in the presence of potassium carbonate gave the ether (XIV), which was cyclized to dibenzofuran (XV) with conc. H_2SO_4.

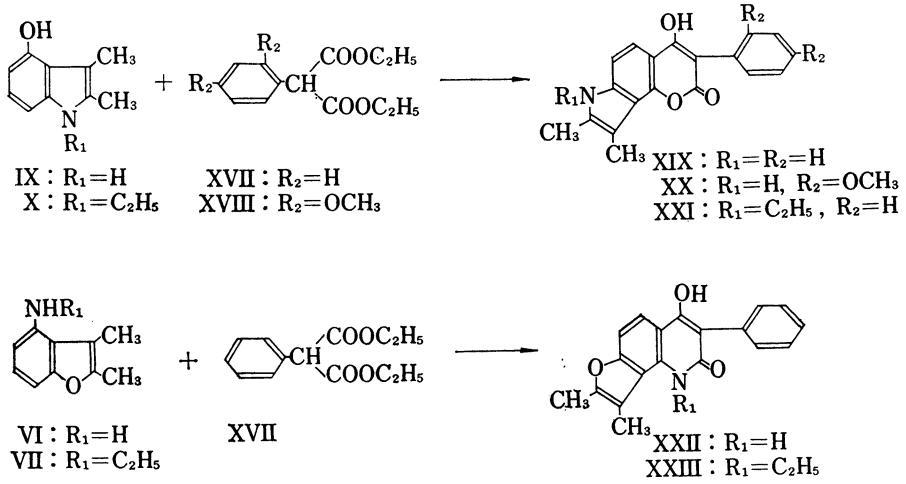


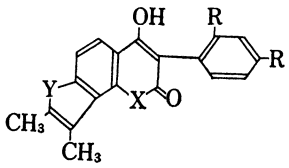
Chart 3

12) S. Hauptmann, H. Blume, G. Hartmann, D. Haendel and P. Franke, *Z. Chem.*, **6**, 183 (1966).
13) Y. Kawase, *Chem. Ind.* (London), **1970**, 688.
14) L.C. King, M. McMhirter and D.M. Barton, *J. Am. Chem. Soc.*, **67**, 2089 (1945).
15) A. Rècsei, *Chim. Ber.*, **60**, 1420 (1927).

Preparation of Pyrrolocoumarins and Furoquinolones

The pyrrolocoumarin derivatives (XIX, XX, XXI) were prepared by the thermal condensation, which is similar to the method of Mentzer for the synthesis of 3-phenylcoumarin derivatives (I),[16,17] of 4-hydroxyindole derivatives with ethyl phenylmalonate or ethyl 2,4-dimethoxyphenylmalonate. Structures of the compounds (XIX, XX, XXI) were elucidated with their spectral data as shown in Table I.

TABLE I. The NMR Spectra [δ (ppm) values]



	X	Y	R	Solvent	9-CH_3	8-CH_3	6-H or 5-H		ar-H	Other		
										OCH_3	CH_2CH_3	CH_2CH_3
XIX	O	NH	H	*d*-DMSO	2.58[s]	2.71[s]	7.08[d]	7.52[d]	7.68[bs]	—	—	—
XX	O	NH	OMe	*d*-DMSO	2.32[s]	2.43[s]	7.23[d]	7.54[d]	6.5—7.3[m]	3.71[s](3H) 3.80[s](3H)	—	—
XXI	O	NEt	H	$CDCl_3$-TFA	2.31[s]	2.41[s]	7.11[d]	7.48[d]	7.34[bs]	—	1.30[t]	4.09[q]
XXII	NH	O	H	$CDCl_3$-TFA	2.60[s]	2.60[s]	7.38[d]	7.41[d]	7.41[bs]	—	—	—
XXIII	NEt	O	H	$CDCl_3$-TFA	2.41[s]	2.48[s]	7.49[d]	8.01[d]	7.46[bs]	—	1.24[t]	4.74[q]

s=singlet, d=doublet (J=9cps), t=triplet (J=7 cps), q=quartet (J=7cps), m=multiplet, bs=broad singlet

The furoquinolones (XXII, XXIII) were synthesized by the thermal condensation, similar to the method for the synthesis of 3-substituted-4-hydroxycarbostyrils developed by Baker, Lappin and Riegel,[18] of 4-aminobenzofuran derivatives (VI, VII) with ethyl phenylmalonate (XVII). The structure of XXII and XXIII were proved with their analytical and spectral data (Table I).

The biological activity of the furoquinolones and pyrrolocoumarins stated above will be reported in a forthcoming paper.

Experimental[19]

4-Amino-2,3-dimethylbenzofuran (VI)——A mixture of 4-acetamido-2,3-dimethylbenzofuran[8] (IV) (1.27 g), 30% NaOH (40 ml) and EtOH (8 ml) was refluxed for 23 hr. After removal of the solvent, the residue was extracted with benzene. The extract was washed with H_2O, dried over Na_2SO_4, and evaporated to give the amine (VI) as an oil. Fractional distillation of this oil afforded a pale brown viscous oil (825 mg), bp 141—142° (1 mmHg). Recrystallization from ligroin gave VI as colorless needles, mp 40—42°[12]. UV λ_{max}^{EtOH} mμ (log ε): 263.0 (4.08), 296 (3.53). IR ν_{max}^{film} cm^{-1}: 3420, 3340 (NH_2). NMR ($CDCl_3$) ppm: 2.21 (6H, singlet, $2\times CH_3$), 3.82 (2H, broad singlet, NH_2), 6.30 (1H, quartet, J=6.0 and 2.0 cps, C_5-H or C_7-H), 6.81 (1H, quartet, J=8.0 and 6.0 cps, C_6-H), 6.89 (1H, quartet, J=8.0 and 2.0 cps, C_7-H or C_5-H).

4-Hydroxy-2,3-dimethylindole (IX)——a) A mixture of the amide (IV) (6.4 g), conc. HCl (5 ml) and EtOH (50 ml) was refluxed for 1.5 hr. After removal of the solvent, the residue was basified with 10% NH_4OH and extracted with benzene. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated to give a dark reddish viscous oil (IX) (4.35 g), whose distillation afforded pale reddish crystals, bp 153—155°

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17) C. Mentzer, *Compt. Rend.*, **232**, 1674 (1951).
18) R.H. Baker, G.R. Lappin and B. Riegel, *J. Am. Chem. Soc.*, **68**, 1284 (1946).
19) All melting points are uncorrected. The IR and UV spectra were recorded on type EPS-2U Hitachi and Nippon Bunko Model IR-E spectrometer respectively. Nuclear magnetic resonance (NMR) spectra were taken with recording JNM C-60 spectrometer with tetramethylsilane as an internal standard.

(1 mmHg), mp 101—103°. Recrystallization from ligroin gave IX (2.68 g) as pale reddish prisms, mp 103—105°.[12] UV λ_{max}^{EtOH} mμ (log ε): 273.5 (3.60), 288.5 (3.55) and 297 (3.51). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3560, 3440 (OH), 3380 (NH). NMR ($CDCl_3$) ppm: 2.18 (3H, singlet, CH_3), 2.38 (3H, singlet, CH_3), 4.7—5.2 (1H, broad, OH), 6.30 (1H, quartet, J=6.0 and 2.0 cps, C_5-H or C_7-H), 6.84 (1H, quartet, J=8.0 and 2.0 cps, C_7-H or C_5-H), 7.78 (1H, quartet, J=6.0 and 8.0 cps, C_6-H), 7.46 (1H, broad singlet, NH).

b) By the similar procedure described above for IX from the amide (IV), IX was obtained from VI in 60% yield and recrystallized from ligroin to afford reddish prisms, mp 101—103°, which was identified with IX described above by virtue of its IR, NMR spectra and the mixed melting point.

4-Ethylamino-2,3-dimethylbenzofuran (VII)——A solution of the amide (IV) (5.0 g) in THF (30 ml) was added to a solution of $LiAlH_4$ (2.5 g) in THF (300 ml) and heated to reflux for 5 hr with stirring. After cooling, the excess of reagent was decomposed by addition of H_2O. The inorganic substances were filtered off. The filtrate was evaporated to give the amine (VII) (3.14 g), bp 125—127° (1 mmHg), which was rapidly crystallized on standing. Recrystallization from EtOH–H_2O gave VII as colorless needles, mp 52—53°. *Anal.* Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99; N, 7.44. Found: C, 76.04; H, 8.13; N, 7.29. UV λ_{max}^{EtOH} mμ (log ε): 269 (3.22) and 300 (2.82). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3395 (NH). NMR ($CDCl_3$) ppm: 1.23 (3H, triplet, J=7.0 cps, CH_2CH_3), 2.21 (6H, singlet, 2×CH_3), 3.12 (2H, quartet, J=7.0 cps, CH_2CH_3), 3.85 (1H, broad singlet, NH), 6.26 (1H, quartet, J=7.5 and 1.5 cps, C_5-H or C_7-H), 6.73 (1H, quartet, J=8.5 and 1.5 cps, C_7-H or C_5-H), 7.02 (1H, quartet, J=7.5 and 8.0 cps, C_6-H).

1-Ethyl-4-hydroxy-2,3-dimethylindole (X)——A mixture of the preceding amine (VII) (1.0 g), conc. HCl (8.0 ml) and EtOH (10 ml) was refluxed for 4 hr. After distillation of the solvent, the residue was basified with 10% NH_4OH and extracted with benzene. The extract was washed with water, dried over Na_2SO_4 and evaporated to give the hydroxyindole (X) (720 mg) as a pale brown viscous syrup, bp 155—157° (3 mmHg). This oil was solidified soon on standing and recrystallization from benzene gave X as colorless prisms, mp 119—120°. *Anal.* Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99; N, 7.44. Found: C, 76.61; H, 8.04; N, 7.61. UV λ_{max}^{EtOH} mμ (log ε): 274.5 (3.48), 294 (3.74), 302.5 (3.81). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3560, 3350 (OH). NMR ($CDCl_3$) ppm: 1.23 (3H, triplet, J=7.5 cps, $CH_2\underline{CH_3}$), 2.24 (3H, singlet, 3-CH_3), 2.43 (3H, singlet, 2-CH_3), 4.03 (2H, quartet, J=7.5 cps, $\underline{CH_2}CH_3$), 4.5—5.3 (1H, broad singlet, OH), 6.34 (1H, quartet, J=7.0 and 2.5 cps, C_5-H or C_7-H), 6.1—7.2 (2H, multiplet, C_6-H and C_7-H or C_5-H).

3-Acetylphenoxy-2-cyclohexanone (XIV)——A mixture of 3-hydroxyacetophenone[14] (XII) (12.9 g), 2-chlorocyclohexanone[15] (XIII) (15 g), potassium carbonate (19.6 g) and acetone (100 ml) was heated at 60° with stirring for 16 hr. The inorganic substances were filtered off. The filtrate was evaporated to give an oily residue, which was extracted with ether. The extract was washed with 3% NaOH and water, dried over Na_2SO_4 and evaporated to give crude XIV. Distillation of this product gave a pure XIV (10.89 g), bp 177—178° (1 mmHg). IR ν_{max}^{film} cm^{-1}: 1725 (C=O), 1685 (C=O).

9-Acetyl-1,2,3,4-tetrahydrodibenzofuran (XV)——To a conc. H_2SO_4 (104 g), the preceding ether (XIV) (20.7 g) was added dropwise with stirring at 10° during 30 min; stirring was continued for a futher 4 hr at room temperature. The mixture was poured into ice-water and then extracted with ether. The extract was washed with 5% NaOH and water, dried over Na_2SO_4 and evaporated to leave an oil. A viscous oil (5.5 g) which was distilled fractionally, bp 170—173° (4 mmHg), was purified by silica gel chromatography (200 g) using benzene–*n*-hexane (1:1) as eluant. After removal of the solvent 9-acetyl-1,2,3,4-tetrahydrodibenzofuran (XV) (3.54 g) was obtained as a viscous syrup, bp 138—140° (2 mmHg). IR ν_{max}^{film} cm^{-1}: 1690 (C=O). NMR ($CDCl_3$) ppm: 1.6—2.1 (4H, multiplet, 2×CH_2), 2.5—2.9 (4H, multiplet, 2×CH_2), 2.57 (3H, singlet, CH_3), 6.95—7.6 (3H, multiplet, 3×ar-H).

9-Acetyl-1,2,3,4-tetrahydrodibenzofuran Oxime (XVI)——A mixture of 9-acetyl-1,2,3,4-tetrahydrodibenzofuran (XV) (2.7 g), hydroxylamine hydrochloride (1.05 g), anhydrous sodium acetate (1.29 g) and ethanol (30 ml) was refluxed for 50 min, and then allowed to stand overnight at room temperature. After removal of the solvent, the residue was extracted with benzene. The extract was washed with water, dried over Na_2SO_4 and distilled off. The crystalline residue was recrystallized from benzen–*n*-hexane to afford the oxime (XVI) (1.70 g) as colorless prisms, mp 139—140°. *Anal.* Calcd. for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.47; H, 6.65; N, 5.89. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (OH), 3480—3000 (OH), 1626 (C=N).

9-Acetamido-1,2,3,4-tetrahydrodibenzofuran (V)——A mixture of the preceding oxime (XVI) (2.8 g) and polyphosphoric acid (45 g) was heated at 100° with stirring for 3 hr. The reaction mixture was poured into ice-water, then pale brown crystals were collected. This product was chromatographied on alumina. Elution with benzene–ethyl acetate (2:1) gave the amide (V) (1.0 g), which yielded colorless needles, mp 199—201°, (from EtOH). *Anal.* Calcd. for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.32; H, 6.66; N, 6.03. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (NH), 1675 (C=O).

9-Amino-1,2,3,4-tetrahydrodibenzofuran (VIII)——The amide (V) (700 mg) was allowed to react with 30% NaOH (3 ml) in EtOH (6 ml) in a similar manner as described above for VI from the amide (IV) to obtain the amine (VIII) (544 mg) as a brown viscous syrup, which was charactarized as the hydrochloride (290 mg), mp 221—222° (decomp.) (fine colorless prisms from EtOH–ether). *Anal.* Calcd. for $C_{12}H_{13}ON \cdot HCl$: C, 64.41; H, 6.31; N, 6.26; Cl, 15.85. Found: C, 64.18; H, 6.50; N, 5.93; Cl, 15.50. UV λ_{max}^{EtOH} mμ (log ε) (Hydrochloride): 261 (4.13), 286 (3.57). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 3360 (NH_2). NMR ($CDCl_3$-TFA) ppm: 1.7—2.2 (4H, multiplet, 2×CH_2), 7.12—7.57 (3H, multiplet, ar-H).

5-Hydroxy-1,2,3,4-tetrahydrocarbazole (XI)——By the similar precedure described above for IX from the amide (IV), XI was obtained from V and recrystallized from ligroin to give fine colorless prisms (133 mg), mp 162—165°. *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.09; H, 7.00; N, 7.32. UV λ_{max}^{EtOH} mμ (log ε): 274 (3.87), 288.5 (3.83), 296.5 (3.81). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3560 (OH), 3440 (NH). NMR ($CDCl_3$) ppm: 1.7—2.1 (4H, multiplet, $2\times CH_2$), 2.5—3.1 (4H, multiplet, $2\times CH_2$), 4.3 (1H, broad, OH), 6.32 (1H, quartet, $J=3$ and 6 cps, C_8-H or C_6-H), 6.77 (1H, triplet, $J=6.0$ cps, C_7-H), 6.83 (1H, quartet, $J=3$ and 6 cps, C_6-H or C_8-H).

3-Phenyl-4-hydroxy-8,9-dimethyl-7H-pyrrolo[2,3-*h*]coumarin (XIX)——A mixture of the hydroxyindole (IX) (1.0 g) and diethyl phenylmalonate (XVII) (1.47 g) was heated at 240—270° for 40 min in a current of N_2. After cooling, the product was precipitated by adding benzene–EtOH (3: 1, 5 ml), collected by filtration, and washed with benzene. Recrystallization from THF gave pale yellow needles (XIX, 965 mg), mp 286—289° (decomp.). *Anal.* Calcd. for $C_{19}H_{15}O_3N$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.50; H, 5.01; N, 4.49. UV λ_{max}^{EtOH} mμ (log ε): 273 (4.54), 326 (4.23). IR ν_{max}^{Nujol} cm^{-1}: 3320 (NH), 1640 (C=O).

3-(2,3-Dimethyoxyphenyl)-4-hydroxy-8,9-dimethyl-7H-pyrrolo[2,3-*h*]coumarin (XX)——A mixture of the the hydroxy indole (IX) (1.23 g) and diethyl 2,4-dimethoxypheuylamlonate (XVIII) (2.5 g) was heated at 260—270° for 50 min in a current of N_2. After cooling , the residual crystals were recrystallized from ethyl acetate to give the pyrrolocoumarin (XX) (1.7 g) as pale brown prisms, mp 240—242°. *Anal.* Calcd. for $C_{21}H_{19}O_5N$: C, 69.03; H, 5.24; N, 3.83. Found: C, 68.52; H, 5.44; N, 3.56. UV λ_{max}^{EtOH} mμ (log ε): 270 (4.45), 322 (4.15). IR ν_{max}^{Nujol} cm^{-1}: 3320 (NH), 1645 (C=O).

3-Phenyl-4-hydroxy-7-ethyl-8,9-dimethylpyrrolo[2,3-*h*]coumarin (XXI)——A mixture of 1-ethyl-4-hydroxyindole (X) (1.0 g) and diethyl phenylmalonate (XVII) (1.32 g) was heated at 250—300° for 40 min in a current of N_2. The residue was recrystallized from ethyl acetate to give XXI (640 mg) as pale brown prisms, mp 249—251° (decomp.). *Anal.* Calcd. for $C_{21}H_{19}O_3N$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.28; H, 6.00; N, 3.98. UV λ_{max}^{EtOH} mμ (log ε): 273,5 (4.46), 328 (4.16). IR ν_{max}^{Nujol} cm^{-1}: 1630 (C=O).

3-Phenyl-2,4-dihydroxy-8,9-dimethylfuro[2,3-*h*]quinoline (XXII)——A mixture of the 4-aminobenzofuran (VI) (680 mg) and diethyl malonate (XVII) (1.0 g) was heated at 270° for 15 min in a current of N_2. After cooling, the residual crystals were washed with ether and recrystallized from THF to give XXII (900 mg) as colorless needles, mp 300—301° (decomp.). *Anal.* Calcd. for $C_{19}H_{15}O_3N$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.92; H, 4.98; N, 4.51. UV λ_{max}^{EtOH} mμ (log ε): 263.5 (4.31), 300 sh (3.77). IR ν_{max}^{Nujol} cm^{-1}: 3360 (NH), 1621 (C=O).

1-Ethyl-3-phenyl-2,4-dihydroxy-8,9-dimethylfuro[2,3-*h*]quinoline (XXIII)——A mixture of N-ethylaminobenzofuran (VII) (568 mg) and diethyl phenylmalonate (XVII) (710 mg) was heated at 240—300° for 25 min in a current of N_2. The residue was recrystallized from ethyl acetate to give XXIII (403 mg) as pale brown needles, mp 218—220° (decomp.). *Anal.* Calcd. for $C_{21}H_{19}O_3N$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.24; H, 5.77; N, 4.19. UV λ_{max}^{EtOH} mμ (log ε): 267 (4.68), 306sh(3.97), 335sh (3.89). IR ν_{max}^{Nujol} cm^{-1}: 1608 (C=O).

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