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Aminocoumarin derivatives **3-10** were condensed with diethyl ethoxymethylenemalonate to give intermediates **11-18**. Thermal cyclizations of intermediates give benzopyranopyridinecarboxylates **19-26**. These esters were hydrolyzed to the corresponding benzopyranopyridine carboxylic acids **27-34**.

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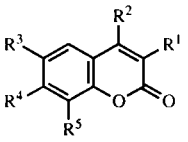
Recently, the chemistry of coumarins has aroused considerable interest because of their versatile practical applications [1-3]. Coumarins are widely distributed in nature and exhibit various physiological effects and some of them have been found to possess antibacterial properties [4-8]. Even a simple 3-aminocoumarin has been reported to act as an antibacterial agent [9]. In our attempts to synthesize new compounds with coumarinic skeleton, we have tried to condense the pyridinecarboxylic moiety onto the coumarinic system.

Table I

Aminocoumarins



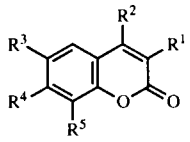
Compound	R^1	R^2	R^3	R^4	R^5
3	NH_2	H	H	H	F
4	H	NH_2	H	H	H
5	H	H	NH_2	H	H
6	OH	H	NH_2	H	H
7	H	CH_3	H	NH_2	H
8	H	CF_3	H	NH_2	H
9	OH	H	H	H	NH_2
10	NH_2	H	NH_2	H	H

Aminocoumarins and various substituted aminocoumarins are good starting materials from which target compounds can be synthesized by the routes generally shown in Scheme I. Aminocoumarin derivatives **3-10** used here are available either commercially or by literature procedures [10-12].

In one case (Scheme I) we have obtained the desired aminocoumarin **3** starting from salicylaldehyde **1** [13].

Table II

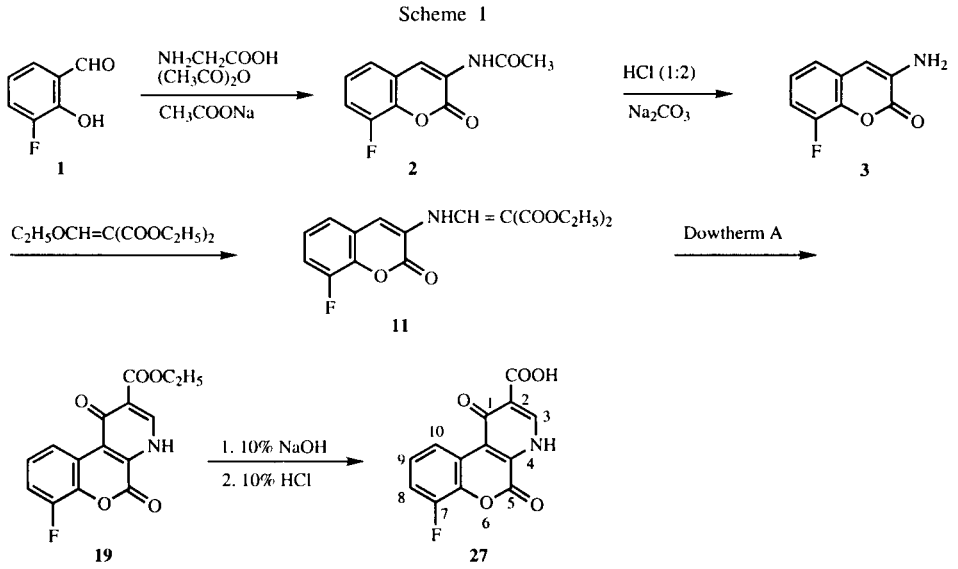
Condensed intermediates



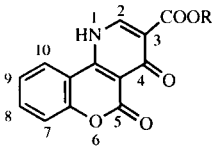
Compound	R^1	R^2	R^3	R^4	R^5
11	X	H	H	H	F
12	H	X	H	H	H
13	H	H	X	H	H
14	OH	H	X	H	H
15	H	CH_3	H	X	H
16	H	CF_3	H	X	H
17	OH	H	H	H	X
18	X	H	X	H	H

X stands for $-NHCH=C(COOC_2H_5)_2$.

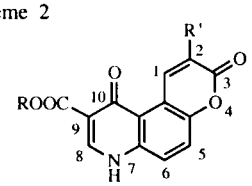
Scheme I



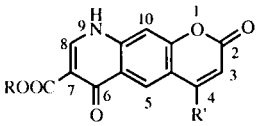
Scheme 2



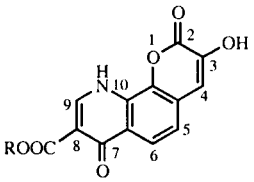
20 R = C_2H_5
28 R = H



21 R = C_2H_5; R' = H
22 R = C_2H_5; R' = OH
29 R = R' = H
30 R = H; R' = OH



23 R = C_2H_5; R' = CH_3
24 R = C_2H_5; R' = CF_3
31 R = H; R' = CH_3
32 R = H; R' = CF_3



25 R = C_2H_5
33 R = H

Compounds **11-17** were refluxed in Dowtherm A to give the desired tri- and tetracyclic mono- and diesters.

Esters **19-25** were hydrolyzed to the corresponding monocarboxylic acids **27-33** with 10% sodium hydroxide.

Up to now, coumarin-quinolone dicarboxylic acids have not been described in the literature. The reaction of 3,6-diaminocoumarin **10** with diethyl ethoxymethylenemalonate, followed by cyclization of the biscondensed product **18** with subsequent hydrolysis of that ester **26** gave benzopyranopyridine dicarboxylic acid **34**.

All the benzopyranopyridine carboxylic acids described above were prepared from aminocoumarins, by the procedure depicted in Scheme I.

Scheme 3

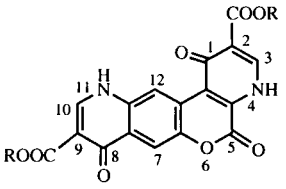


Table III

Products from the Condensation of Amines with Diethyl Ethoxymethylenemalonate

Compound	Reaction time	Mp/°C	Solvent	Yield %	Formula	Molecular Formula Analyses Calcd. C	H	N	Found C	H	N
11	5 hours	175-177	Ethanol	95	$C_{17}H_{16}FNO_6$	58.45	4.62	4.01	58.35	4.46	3.98
13	10 minutes	141-142	Ethanol	96	$C_{17}H_{17}NO_6$	61.62	5.17	4.23	61.87	4.99	4.17
14	60 minutes	250-253	Acetic acid	88	$C_{17}H_{17}NO_7$	58.79	4.93	4.03	58.64	4.64	4.25
15	30 minutes	139-140	Ethanol	98	$C_{18}H_{19}NO_6$	62.60	5.55	4.06	62.58	5.63	4.02
16	27 hours	125-126	Ethanol	92	$C_{18}H_{16}F_3NO_6$	54.14	4.04	3.51	54.12	4.17	3.46
17	4 hours	230-231	Acetic acid	89	$C_{17}H_{17}NO_7$	58.79	4.93	4.03	58.98	4.89	3.91
18	6 hours	131-134	Ethanol	87	$C_{25}H_{28}N_2O_{10}$	58.13	5.46	5.43	57.74	5.19	5.40

Table IV

Benzopyranopyridine Esters

Compound	Reaction time	Mp/°C	Solvent	Yield %	Formula	Molecular Formula Analyses Calcd. C	H	N	Found C	H	N
19	40 minutes	288-290	[a]	89	$C_{15}H_{10}FNO_5$	59.41	3.32	4.62	59.74	2.97	4.72
20	13 hours	>300	dimethyl sulfoxide	56	$C_{15}H_{11}NO_5$	63.16	3.89	4.91	62.98	3.92	5.07
21	15 minutes	>300	dimethyl formamide	84	$C_{15}H_{11}NO_5$	63.16	3.89	4.91	63.05	3.92	4.88
22	45 minutes	>300	[a]	95	$C_{15}H_{11}NO_6$	59.80	3.68	4.65	59.66	3.61	4.27
23	10 minutes	>300	[a]	69	$C_{16}H_{13}NO_5$	64.21	4.38	4.68	64.36	4.14	4.50
24	15 minutes	>300	[a]	94	$C_{16}H_{10}F_3NO_5$	54.40	2.85	3.97	54.41	2.97	3.86
25	40 minutes	>300	[a]	86	$C_{15}H_{11}NO_6$	59.80	3.68	4.65	59.45	3.29	4.28
26	50 minutes	175-177	Ethanol	87	$C_{21}H_{16}N_2O_8$	59.43	3.80	6.60	59.72	3.89	6.89

[a] These compounds were too insolubile for recrystallization.

The Gould-Jacobs reaction [14] starting with amino-compounds **3-10** in diethyl ethoxymethylenemalonate give condensation intermediates **11-18**. Reaction times ranged from 10 minutes to 27 hours at 120° (Table III). D. T. Connor and coworkers [15] described earlier 4-amino-coumarin condensed derivative **12**. Their attempt to obtain the desired ester **20** from this derivative in refluxing diphenyl ether was unsuccessful [15].

Antimicrobial Screening Results.

Benzopyranopyridine carboxylic acids described here were examined for their antimicrobial activity. We have obtained the best results in the case of 3-hydroxy-2,7-dioxo-7,10-dihydro-2*H*-pyrano[3,2-*h*]quinoline-8-carboxylic acid

Table V

Benzopyranopyridine Carboxylic Acids

Compound	Reaction time	Mp/°C	Solvent	Yield %	Formula	Molecular Formula Analyses Calcd. C	H	N	Found C	H	N
27	90 minutes	>300	dimethyl formamide	97	$C_{13}H_6FNO_5$	56.74	2.20	5.09	56.52	1.84	5.11
28	90 minutes	>300	dimethyl formamide	95	$C_{13}H_7NO_5$	60.70	2.74	5.45	60.37	2.43	5.51
29	3 hours	>300	dimethyl formamide	85	$C_{13}H_7NO_5$	60.70	2.74	5.45	60.37	2.80	5.76
30	3 hours	>300	dimethyl formamide	83	$C_{13}H_7NO_6$	57.15	2.58	5.13	57.45	2.98	5.05
31	20 minutes	>300	dimethyl formamide	75	$C_{14}H_9NO_5$	61.99	3.34	5.17	61.84	3.44	5.04
32	2 hours	>300	dimethyl formamide	99	$C_{14}H_6F_3NO_5$	51.70	1.86	4.31	51.48	1.82	4.27
33	3 hours	>300	dimethyl formamide	66	$C_{13}H_7NO_6$	57.15	2.58	5.13	57.10	2.60	4.97
34	45 minutes	>300	dimethyl formamide	58	$C_{17}H_8N_2O_8$	55.44	2.19	7.61	55.22	2.58	7.50

33. This compound was found to possess high antimicrobial activity against *Bacillus subtilis*, *Bacillus cereus*, *Bacillus pumilus* and *Salmonela panama* and was slightly less active against *Staphyloccocus aureus* and *Escherichia coli*. In case of 2-Hydroxy-3,10-dioxo-7,10-dihydro-3*H*-pyrano[3,2-*f*]-quinoline-9-carboxylic acid **30**, 4-(trifluoromethyl)- 2,6-dioxo-6,9-dihydro-2*H*-pyrano[3,2-*g*]quinoline-7-carboxylic acid **32**. and 1,5,8 Trioxo-1,5,8,11-tetrahydro-4*H*-pyrido[3',2':4,5-*b*]pyrano-[2,3-*g*]quinoline-2,9-dicarboxylic acid **34** we have foud them to have very veak activity against Gram-negative microorganisms, while the activity against Gram-positive microorganisms was comparabile with activity of compound **33**. Other benzopyranopyridine carboxylic acids described here were practically inactive towards all the tested microorganisms. In generall, all compounds that showed any activity were more active against Gram-positive than Gram-negative microorganisms.

A more detailed study of biological properties of these compounds and some of their derivatives are currently in progress and will be the subject of a forthcoming publication.

EXPERIMENTAL

Melting points were measured with a Fisher-Johns melting point apparatus without correction. Microanalyses for C, H and N were done on a Perkin-Elmer Analyser 2400. The nmr data were measured on a Varian Gemini 300 spectrometer (300 MHz) with TMS as internal standard. Infrared spectra were recorded on a Magna FTIR 760 Nicolet spectrometer in potassium bromide.

3-Amino-8-fluorocoumarin (**3**).

Starting from 3-fluorosalicylaldehyde **1**, by known procedure, we have prepared 3-acetylamino-8-fluorocoumarin **2** and 3-amino-8-fluorocoumarin **3**. We have used the known procedure

Table VI

IR and NMR Spectral Data

Compound	IR (potassium bromide)	^{1}H NMR (DMSO-d_6) δ (TMS)
3-Amino-8-fluorocoumarin (**3**)	3430, 3316 (NH_2), 1704 (C=O), 1644 (C=C) and 777 cm^{-1}	5.9 (s, 2H, NH_2), 6.7 (s, 1H, H4), 7.1-7.2 (m, 3H, H5-H7)
Diethyl{[(8-fluoro-2-oxo-2*H*-[1]-benzo-pyrano-3-yl)amino]methylene}malonate (**11**)	3227 (NH), 2977, 2906, 1724 (C=O),1689 (C=O), 1599 (C=C), 1236 and 767 cm^{-1}	1.2 (t, 3H, CH_3, J = 7.0 Hz), 1.3 (t, 3H, CH_3, J = 7.0 Hz), 4.1 (q, 2H, CH_2, J = 7.0 Hz), 4.2 (q, 2H, CH_2, J = 7.0 Hz), 7.3-7.5 (m, 3H, ArH), 8.0 (s, 1H, H4), 8.4 (d, 1H, N-CH, $J_{N\text{-}CH,NH}$ = 13.0 Hz), 10.7 (d,1H, NH, $J_{N\text{-}CH,NH}$ = 12.9 Hz)
Diethyl{[(2-oxo-2*H*-[1]-benzopyrano-6-yl)amino]methylene}malonate (**13**)	3140 (NH), 1710 (C=O), 1655 (C=C) and 760 cm^{-1}	1.2 (t, 3H, CH_3, J = 7.0 Hz), 1.3 (t, 3H, CH_3, J = 7.0 Hz), 4.2 (q, 2H, CH_2, J = 7.0 Hz), 4.3 (q, 2H, CH_2, J = 7.0 Hz), 6.5 (d, 1H, H3, $J_{3,4}$ = 9.5 Hz), 7.4 (d, 1H, H7, $J_{7,8}$ = 8.7 Hz), 7.6-7.8 (m, 2H, H8 and H5), 8.1 (d, 1H, H4, $J_{3,4}$ = 9.5 Hz), 8.4 (d, 1H, N-CH, $J_{N\text{-}CH,NH}$ = 13.6 Hz), 10.7 (d, 1H, NH, $J_{N\text{-}CH,NH}$ = 13.4 Hz)
Diethyl{[(3-hydroxy-2-oxo-2*H*-[1]-benzo-pyrano-6-yl)amino]methylene}malonate (**14**)	3331 (OH), 2995 (NH), 1697 (C=O), 1598 (C=C) and 770 cm^{-1}	1.2 (t, 3H, CH_3, J = 7.0 Hz), 1.3 (t, 3H, CH_3, J = 7.0 Hz), 4.1 (q, 2H, CH_2, J = 7.0 Hz), 4.2 (q, 2H, CH_2, J = 7.0 Hz), 7.1 (s, 1H, H7), 7.3-7.5 (m, 2H, H8 and H5), 7.6 (s, 1H, H4), 8.4 (d, 1H, N-CH, $J_{N\text{-}CH,NH}$ = 13.8 Hz), 10.7 (s, 1H, OH), 11.2 (d, 1H, NH, $J_{N\text{-}CH,NH}$ = 13.6 Hz)
Diethyl{[(4-methyl-2-oxo-2*H*-[1]-benzo-pyrano-7-yl)amino]methylene}malonate (**15**)	2990 and 2893 (NH), 1737 and 1689 (C=O), 1602 (C=C) and 776 cm^{-1}	1.2 (t, 3H, CH_3, J = 6.9 Hz), 1.3 (s, 3H, CH_3), 1.4 (t, 3H, CH_3, J = 6.9 Hz), 4.1 (q, 2H, CH_2, J = 7.0 Hz), 4.2 (q, 2H, CH_2, J = 6.9 Hz), 6.2 (s, 1H, H3), 7.2-7.6 (m, 3H, ArH), 8.3 (d, 1H, N-CH, $J_{N\text{-}CH,NH}$ = 11.1 Hz), 10.7 (d, 1H, NH, $J_{N\text{-}CH,NH}$ = 11.1 Hz)

Table VI (continued)

Compound	IR (potassium bromide)	^{1}H NMR (DMSO-d_6) δ (TMS)
Diethyl{[(4-(trifluoromethyl)-2-oxo-2*H*-[1]-benzopyrano-7-yl)amino]methylene}-malonate (**16**)	3531, 3094 and 2987 (NH), 1752 (C=O), 1602 (C=C), 1273 (CF_3) and 760 cm^{-1}	1.2 (t, 3H, CH_3, J = 7.0 Hz), 1.3 (t, 3H, CH_3, J = 7.0 Hz), 4.1 (q, 2H, CH_2, J = 7.0 Hz), 4.2 (q, 2H, CH_2, J = 7.0 Hz), 6.8 (s, 1H, H3), 7.4-7.6 (m, 3H, ArH), 8.4 (d, 1H, N-CH, $J_{N\text{-}CH,NH}$ = 11.7 Hz), 10.7 (d, 1H, NH, $J_{N\text{-}CH,NH}$ = 12.6 Hz)
Diethyl{[(3-hydroxy-2-oxo-2*H*-[1]-benzopyrano-8-yl)amino]methylene}-malonate (**17**)	3313 (OH), 2981 (NH), 1726 (C=O), 1677 (C=C) and 764 cm^{-1}	1.2 (t, 3H, CH_3, J = 7.0 Hz), 1.3 (t, 3H, CH_3, J = 7.0 Hz), 4.1 (q, 2H, CH_2, J = 7.0 Hz), 4.2 (q, 2H, CH_2, J = 7.0 Hz), 6.2 (s, 1H, H3), 7.2-7.6 (m, 3H, ArH), 8.6 (d, 1H, N-CH, $J_{N\text{-}CH,NH}$ = 13.5 Hz), 10.6 (s, 1H, OH), 11.2 (d, 1H, NH, $J_{N\text{-}CH,NH}$ = 13.7 Hz)
Tetraethyl{[(2-oxo-2*H*-[1]-benzopyrano-3,6-diyl)diamino]dimethylene}malonate (**18**)	2983 (NH), 1736 and 1692 (C=O), 1655 and 1595 (C=C) and 765 cm^{-1}	1.0 (t, 3H, CH_3, J = 7.0 Hz), 1.0 (t, 3H, CH_3, J = 7.1 Hz), 1.1 (t, 3H, CH_3, J = 7.1 Hz), 1.2 (t, 3H, CH_3, J = 7.0 Hz), 4.1 (q, 2H, CH_2,J = 7.0 Hz), 4.2 (q, 2H, CH_2, J = 7.1 Hz), 4.2 (q, 2H, CH_2, J = 7.0 Hz), 4.3 (q, 2H, CH_2, J = 7.0 Hz), 7.3-7.5 (m, 3H, ArH), 7.8 (s, 1H, H4), 8.2 (d, 1H, N-CH, $J_{N\text{-}CH,NH}$ = 13.8 Hz), 8.3 (d, 1H, N-CH, $J_{N\text{-}CH,NH}$ = 13.5 Hz), 10.7 (d, 1H, NH, $J_{N\text{-}CH,NH}$ = 13.9 Hz), 10.8 (d, 1H, NH, $J_{N\text{-}CH,NH}$ = 13.7 Hz)
Ethyl 7-fluoro-1,5-dioxo-1,4-dihydro-5*H*-benzopyrano[3,4-*b*]pyridine-2-carboxylate (**19**)	3086 (OH), 2991(NH), 1754, 1721 and 773 cm^{-1}	1.3 (t, 3H, CH_3, J = 7.1 Hz), 4.3 (q, 2H, CH_2, J = 7.1 Hz), 7.3-7.6 (m, 2H, H10 and H9), 8.3 (s, 1H, H8), 9.3 (s, 1H, H3), 12.9 (bs, 1H, NH)
Ethyl 4,5-dioxo-1,4-dihydro-5*H*-benzopyrano[4,3-*b*]pyridine-3-carboxylate (**20**)	3435 (OH), 2917 (NH), 1747 and 1711 (C=O), 1618 (C=C) and 767cm^{-1}	1.3 (t, 3H, CH_3, J = 7.1 Hz), 4.3 (q, 2H, CH_2, J = 7.1 Hz), 7.3-8.0 (m, 3H, ArH), 8.4 (s, 1H, H2), 12.3 (bs, 1H, NH,)
Ethyl 3,10-dioxo-7,10-dihydro-3*H*-pyrano-[3,2-*f*]quinoline-3-carboxylate (**21**)	3034 (NH), 1754 and 1704 (C=O), 1602 (C=C) and 760 cm^{-1}	1.3 (t, 3H, CH_3, J = 7.1 Hz), 4.2 (q, 2H, CH_2, J = 7.1 Hz), 6.5 (d,1H, H2, $J_{1,2}$ = 9.9 Hz), 7.7 (d, 1H, H5, $J_{5,6}$ = 9.0 Hz), 7.9 (d, 1H, H6, $J_{5,6}$ = 9.0 Hz), 8.5 (s, 1H, H8), 10.0 (d, 1H, H1, $J_{1,2}$ = 10.0 Hz), 12.4 (bs, 1, NH)
Ethyl 2-hydroxy-3,10-dioxo-7,10-dihydro-3*H*-pyrano[3,2-*f*]quinoline-3-carboxylate (**22**)	3362 (OH), 2970 NH), 1708 (C=O), 1621 (C=C) and 767 cm^{-1}	1.3 (t, 3H, CH_3, J = 7.1 Hz), 4.2 (q, 2H, CH_2, J = 7.0 Hz), 7.6 (d, 1H, H5, $J_{5,6}$ = 9.0 Hz), 7.7 (d, 1H, H6, $J_{5,6}$ = 8.9 Hz), 8.5 (s, 1H, H8), 9.3 (s, 1H, H1), 10.7 (s, 1H, OH), 12.5 (s, 1H, NH)
Ethyl 4-methyl-2,6-dioxo-6,9-dihydro-2*H*-pyrano[3,2-*g*]quinoline-7-carboxylate (**23**)	3442 (OH), 2927 (NH), 1707 (C=O), 1639 (C=C) and 746 cm^{-1}	1.2 (t, 3H, CH_3, J = 7.1 Hz), 1.3 (s, 3H, CH_3), 4.1 (q, 2H, CH_2, J = 7.1 Hz), 6.2 (s, 1H, H3), 7.4-7.8 (m, 2H, H5 and H10), 10.3 (s, 1H, H8), 12.4 (bs, 1H, NH)
Ethyl 4-(trifluoromethyl)-2,6-dioxo-6,9-dihydro-2*H*-pyrano[3,2-*g*]quinoline-7-carboxylate (**24**)	1746 and 1708 (C=O), 1602 (C=C) and 750 cm^{-1}	1.3 (t, 3H, CH_3, J = 7.1 Hz), 4.3 (q, 2H, CH_2, J = 7.1 Hz), 7.1 (s,1H, H3), 7.6-7.9 (m, 2H, H5 and H10), 8.5 (s, 1H, H8), 12.4 (bs, 1H, NH)
Ethyl 3-hydroxy-2,7-dioxo7,10-dihydro-2*H*-pyrano[3,2-*b*]quinoline-8-carboxylate (**25**)	3360 (OH), 2972 (NH), 1710 (C=O), 1625 (C=C) and 765 cm^{-1}	1.3 (t, 3H, CH_3, J = 7.1 Hz), 4.2 (q, 2H, CH_2, J = 7.1 Hz), 6.1 (s,1H, H4), 6.9-7.9 (m, 2H, H5 and H6), 8.3 (s. 1H, H9), 10.8 (s, 1H OH), 12.6 (s, 1H, NH)
Diethyl 1,5,8-trioxo-1,5,8,11-tetrahydro-4*H*-pyrido[3',2':4,5-*b*]pyrano-[2,3-*g*]quinoline-2,9-dicarboxylate (**26**)	3073 (NH), 1708 (C=O), 1618 (C=C) and 767 cm^{-1}	1.3 (t, 3H, CH_3, J = 7.1 Hz), 1.4 (t, 3H, CH_3, J = 7.1 Hz), 4.2 (q,2H, CH_2, J = 7.1 Hz), 4.3 (q, 2H, CH_2, J = 7.1 Hz), 7.0-8.2 (m,2H, H7 and H12), 8.8 (s, 1H, H3), 9.0 (s 1H, H10), 11.6 (s, 1H, NH), 12.3 (bs, 1H, NH)
7-Fluoro-1,5-dioxo-1,4-dihydro-5*H*-benzopyrano[3,4-*b*]pyridine-2-carboxylic acid (**27**)	3388 (OH), 3060 (NH), 1724 (C=O), 1624 (C=C) and 780 cm^{-1}	7.5-7.7 (m, 3H, ArH), 9.2 (s, 1H, H3), 11.3 (s, 1, NH), 13.4 (s,1H, COOH)
4,5-Dioxo-1,4-dihydro-5*H*-benzopyrano-[4,3-*b*]pyridine-3-carboxylic acid (**28**)	3227 (OH), 3073 (NH), 1766 and 1740 (C=O), 1618 (C=C) and 764 cm^{-1}	7.5-7.8 (m, 4H, ArH), 8.7 (s, 1H, H2), 11.8 (bs, 1H, NH), 13.1 (s, 1H, COOH)
3,10-Dioxo-7,10-dihydro-3*H*-pyrano[3,2-*g*]-quinoline-9-carboxylic acid (**29**)	3073 (OH), 2980 (NH), 1701 (C=O), 1605 (C=C) and 772 cm^{-1}	6.6 (d, 1H, H2, $J_{1,2}$ = 9.4 Hz), 7.7 (d, 1H, H5, $J_{5,6}$ = 9.0 Hz), 8.0 (s,1H, H8), 8.5 (d, 1H, H6, $J_{5,6}$ = 9.0 Hz), 8.9 (d, 1H, H1, $J_{1,2}$ = 9.6 Hz), 12.1 (s, 1H, NH), 13.5 (s, 1H, COOH)
2-Hydroxy-3,10-dioxo-7,10-dihydro-3*H*-pyrano[3,2-*f*]quinoline-9-carboxylic acid (**30**)	3422 (OH), 3081 (NH), 1702 (C=O), 1609 (C=C) and 766 cm^{-1}	7.3-7.8 (m, 2H, H5 and H6), 7.9 (s, 1H, H8), 9.1 (s, 1H, H1), 10.5 (bs, 1H, OH), 12.1 (s, 1H, NH), 15.0 (s, 1H, COOH)
4-Methyl-2,6-dioxo-6,9-dihydro-2*H*-pyrano-[3,2-*g*]quinoline-7-carboxylic acid (**31**)	3309 (OH), 3085 (NH), 1728 (C=O), 1625 (C=C) and 752 cm^{-1}	1.9 (s, 3H, CH_3), 6.6 (s, 1H, H3), 7.6-8.0 (m, 2H, H5 and H10), 9.0 (s, 1H, H8), 13.2 (bs, 1H, NH), 14.9 (s, 1H, COOH)
4-(Trifluoromethyl)- 2,6-dioxo-6,9-dihydro-2*H*-pyrano[3,2-*g*]quinoline-7-carboxylic acid (**32**)	3086 (OH), 2598 (NH), 1756 and 1711 (C=O), 1649 (C=C) and 751 cm^{-1}	7.2 (s, 1H, H3), 7.8 (s, 1H, H10), 8.6 (s, 1H, H5), 9.0 (s, 1H, H8), 13.4 (bs, 1H, NH), 14.5 (bs, 1H, COOH)
3-Hydroxy-2,7-dioxo-7,10-dihydro-2*H*-pyrano-[3,2-*h*]quinoline-8-carboxylic acid (**33**)	3067 (OH), 2922 (NH), 1719 (C=O), 1619 (C=C) and 777 cm^{-1}	6.3 (s, 1H, H4), 7.0-8.6 (m, 3H, ArH and H9), 10.8 (bs, 1H, OH), 13.0 (bs, 1H, NH), 15.3 (bs, 1H, COOH)
1,5,8 Trioxo-1,5,8,11-tetrahydro-4*H*-pyrido-[3',2':4,5-*b*]pyrano-[2,3-*g*]quinoline-2,9-dicarboxylic acid (**34**)	3067 (NH), 1719 (C=O), 1619 (C=C) and 777 cm^{-1}	8.0 (s, 1H, H7), 8.1 (s, 1H, H12), 8.6 (s, 1H, H3), 9.0 (s, 1H, H10), 12.5 (bs, 1H, NH), 13.5 (bs, 1H, NH), 14.9 (s, 1H, COOH), 15.5 (s, 1H, COOH)

for the preparation of 3-aminocoumarin starting from salicylaldehyde [13].

General Procedure for the Condensation of Amines with Diethyl Ethoxymethylenemalonate.

A mixture of amine (0.012 mole) and diethyl ethoxymethylenemalonate (0.014 mole) was heated at 120° from 10 minutes to 27 hours. The reaction mixture was cooled and filtered. Recrystallization gave analytically pure material. Data for reaction times, melting points, recrystallization solvents, yields and molecular formula analyses are given in Table III.

Tetraethyl{[(2-oxo-2*H*-[1]-benzopyrano-3,6-diyl]diamino-(dimethylene}malonate (**18**).

Title compound **18** was prepared from diamine **10** (0.006 mole) and diethyl ethoxymethylenemalonate (0.013 mole) according to the above general procedure.

General Procedure for Cyclization of the Condensed Amines.

A solution of substrate (0.001 mole) in Dowtherm A (50 ml) was refluxed from 10 minutes to 13 hours. The reaction mixture was cooled and then (30 ml) of low boiling petroleum ether was added. The product was filtered and washed with diethyl-ether. Recrystallization, necessary only in few cases, gave analytically pure material. Data for reaction times, melting points, recrystallization solvents, yields and molecular formula analyses are given in Table IV.

General Procedure for Hydrolysis of the Esters.

A suspension of the ester (0.006 mole) in 10% sodium hydroxyde solution (20 ml) was refluxed from 20 minutes to three hours followed by addition of charcoal and refluxed for additional five minutes. Solution was filtered, then cooled and precipitated with 10% hydrochloric acid solution (to pH 2-3). This solid product was filtered and washed with water, and recrystallization to give analytically pure material. Data for reaction times, melting points, recrystallization solvents, yields and molecular formula analyses are given in Table V.

Spectral data for all compounds prepared are given in Table VI.

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