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STUDIES ON ANTIANAPHYLACTIC AGENTS—III[1]

A NOVEL CONVERSION REACTION OF 4-OXO-4*H*-1-BENZOPYRAN-3-CARBOXALDEHYDES TO 3-HALOGENOCHROMONES[2]

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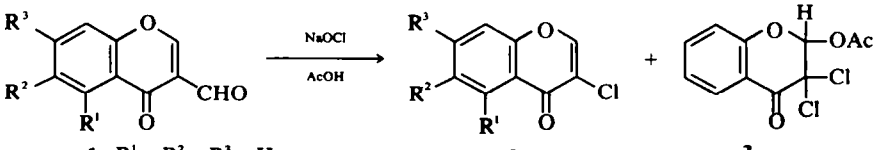
Abstract—4-Oxo-4*H*-1-benzopyran-3-carboxaldehydes in acetic acid react with sodium hypochlorite (aqueous solution) to yield 3-chlorochromones. The reaction of sodium hypobromite with **1** yields 3-bromochromone **15** and other compounds depending on the conditions. Under the normal laboratory lighting hydroxyacetophenone **14**, **15** and hydroxychromanone **16** were obtained, whereas **15** and acetoxychromanone **17** were produced by the reaction in the dark. The addition-elimination mechanism described is the most likely in these reactions.

The synthesis of chromones bearing halogen at C-3 position has been investigated for a long time. The well known method is halogenation of C_2-substituted chromones with a variety of halogenating agents.[3-6] The Allan-Robinson chromone synthesis is rarely employed.[7,8] In the case of C_3-halogenation of C_2-unsubstituted chromones, the desired compounds must be synthesized by halogen addition followed by dehydrohalogenation[9-11] or Friedel-Crafts reaction of α,β-dihalogenoacrylic acid derivatives with a phenol ether derivative.[12]

During an investigation of the oxidation of 4 - oxo - 4*H* - 1 - benzopyran - 3 - carboxaldehyde **1**[13,14] it was found that addition of aqueous sodium hypochlorite into the acetic acid solution of **1** afforded 3-chlorochromone **2** in 86% yield. The structure of **2** was confirmed by the comparison with an authentic sample.[5] The mother liquor, subjected to silica gel column chromatography, yielded 2 - acetoxy - 3, 3 - dichlorochromanone **3**.

By applying this reaction to 4 - oxo - 4*H* - 1 - benzopyran - 3 - carboxaldehydes[14,15] bearing ethyl, nitro, acetoxy, or diacetoxy groups (**4**, **6**, **8**, **10** and **12**), the following results were obtained. (Scheme 1, Table 1). The characteristic spectra of some 3-chlorochromones are as follows; in IR spectra (Table 2) all show a strong CO band of the pyrone ring at 1655 ± 5 cm^{-1} and in the NMR spectra (Table 3) C-2 protons occur at δ $8{\cdot}12 \pm 0{\cdot}10$ in $CDCl_3$. The mass spectra show the usual chromone degradation pathways,[16] differing from 4 - oxo - 4*H* - 1 - benzopyran - 3 - carboxaldehydes[14,15] and -3-carboxylic acids.[1,14]

When **1** was treated with aqueous sodium hypobromite under the normal laboratory lighting, three products were obtained. The first crystal separating out was found to be 2,2,3',5' - tetrabromo - 2' - hydroxy - acetophenone (**14**; 30%).[17] The second and third components were isolated from the mother liquor by silica gel PLC. The second compound was the expected 3-bromochromone (**15**; 8%).[10] The structure of **14** and **15** were



1: $R^1 = R^2 = R^3 = H$ — **2**
4: $R^1 = R^3 = H$, $R^2 = Et$ — **5**
6: $R^1 = R^3 = H$, $R^2 = NO_2$ — **7**
8: $R^1 = R^2 = H$, $R^3 = OAc$ — **9**
10: $R^1 = R^3 = OAc$, $R^2 = H$ — **11**
12: $R^1 = H$, $R^2 = R^3 = OAc$ — **13**

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SCHEME 1.

Table 1. Synthesis of 3-chlorochromones from corresponding 4-oxo-4*H*-1-benzopyran-3-carboxaldehydes

Compound	M.p. (°C)	Yield (%)	Solv[a]	Formula	Analysis (%) Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
5	48–49	43	A	$C_{11}H_9ClO_2$	63·32	4·35		63·19	4·38	
7	148–148·5	68	B	$C_9H_4ClNO_4$	47·92	1·79	6·21	47·87	1·71	6·21
9	151–152	69	B	$C_{11}H_7ClO_4$	55·37	2·96		55·27	2·90	
11	123–124	69	C	$C_{13}H_9ClO_6$	52·63	3·06		52·69	2·97	
13	139–140	82	B	$C_{13}H_9ClO_6$	52·63	3·06		52·50	3·04	

[a] Solvent for recrystallization: A = EtOAc-Petroleum ether, B = EtOH, C = MeOH.

Table 2. IR Absorption data (KBr discs) of some 3-chlorochromones between 1800 and 1600 cm^{-1}

Compound	C=O and C=C			OAc
2	1655	1615(sh)	1605	
5	1655		1610	
7	1660	1630	1610	
9	1650	1620	1610	1775
11	1650	1630	1615	1770
13	1660		1620	1790, 1775
15	1655	1615(sh)	1605	

Table 3. NMR Spectral data of some 3-chlorochromones

Compound	Solv[a]	H_2[b]	Other protons
2	A	8·13	*c*
5	B	8·02	*d*
7	A	8·22	*e*
9	A	8·13	*f*
11	A	8·05	*g*
13	A	8·10	*h*
15	A	8·25	*i*

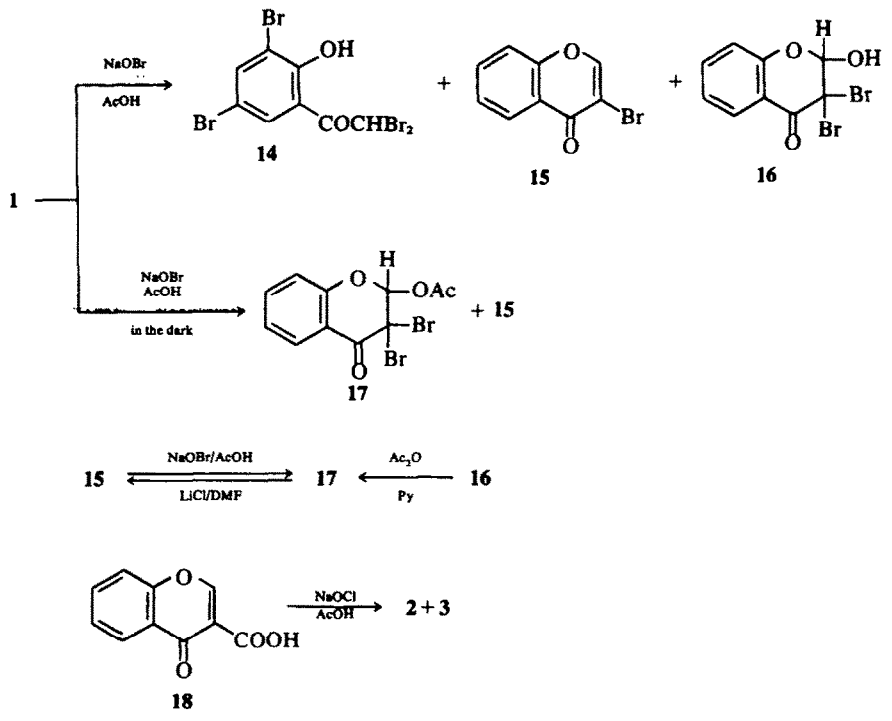
[a] A = $CDCl_3$, B = CCl_4.
[b] All signals are singlet.
[c] 8·3 (H_5, dd, J = 2 and 8), 7·3–7·9 ($H_{6,7,8}$, m).
[d] 7·92 (H_5, d, J = 2), 7·47 (H_7, dd, J = 8 and 2), 7·25 (H_8, d, J = 8), 2·77 (CH_2, q, J = 7), 1·30 (CH_3, t, J = 7).
[e] 9·02 (H_5, d, J = 3), 8·50 (H_7, dd, J = 9 and 3), 7·68 (H_8, d, J = 9).
[f] 8·28 (H_5, d, J = 9), *ca* 7·18 (H_6, dd), *ca* 7·27 (H_8, d, J = 2), 2·33 (OAc, s).
[g] 7·23 (H_6, d, J = 2), 6·88 (H_8, J = 2), 2·32 (OAc, s), 2·42 (OAc,s).
[h] 7·98 (H_5, s), 7·38 (H_8, s), 2·30 (OAc × 2, s).
[i] 8·2–8·4 (H_5), 7·3–7·8 ($H_{6,7,8}$, m).

confirmed by analytical and spectral properties and also by a comparison of m.ps with those reported. The third compound was assigned as 2 - hydroxy - 3,3 - dibromochromanone (**16**; 12%) on the basis of elemental, IR, NMR and mass spectral analyses.

In an attempt to make sure whether or not **14** was produced from **15** or **16**, they were treated with sodium hypobromite under similar reaction conditions. However the production of **14** was not observed. This fact suggests that two different reactions occurred spontaneously. As the chromone ring is usually stable in acidic solutions, the formation of **14** from **1** is probably caused by a radical reaction, that is to say, the loss of two carbons will occur after the radical ring opening. In the reaction of **1** with sodium hypobromite in the dark, two compounds were separated by silica gel column chromatography. The first compound was 2 - acetoxy - 3,3 - dibromochromanone **17** (yield; 28·5%) and **15** as the second compound was obtained in 32% yield. Thus the yield of **15** increased, and **14** and **16** were scarcely found. To ascertain whether or not **17** was produced by the addition of an acetoxy group and a Br atom to **15**, the latter was treated in the dark, when **17** was produced. On the contrary, **17** was transformed to **15** by treatment with anhydrous lithium chloride in dimethyl formamide (used to eliminate hydrogen bromide from α-bromoketosteroids).[18] The structure of **16** was also confirmed by converting it with acetic anhydride and pyridine to **17**.

On the other hand, the reaction between 4 - oxo - 4*H* - 1 - benzopyran - 3 - carboxylic acid **18**[1,14] in acetic acid and aqueous sodium hypochlorite gave **2** and **3** in 41 and 29% yields respectively. From this fact, **18** was presumed as the intermediate in the conversion of **1** to **2**, but not detected on TLC during the reaction. This reaction though similar to the Hunsdiecker reaction (for the degradation of a heavy metal salt of a carboxylic acid in anhydrous media by means of halogens to a halide with one less C atom) differs in that the formation of **2** from **18** is achieved in the presence of water.

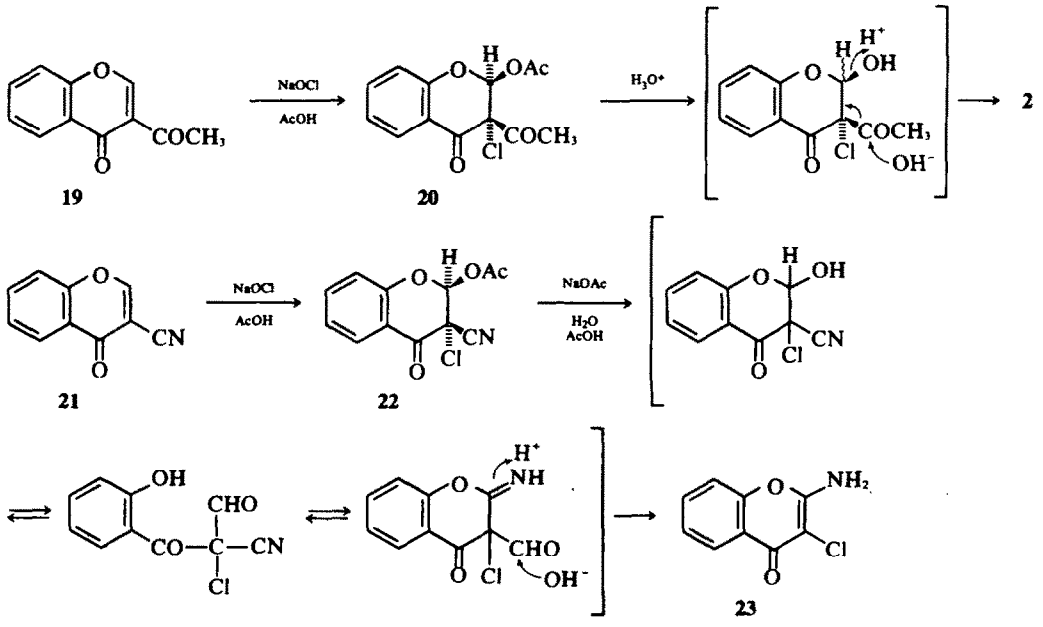
The halogenation mechanism was investigated by using 3 - substituted - 4 - oxo - 4*H* - 1 - benzopyrans whose substituents cannot be eliminated easily. The reaction of aqueous sodium hypochlorite with 3-acetylchromone **19**[13] in acetic acid afforded only 2 - acetoxy - 3 - acetyl - 3 - chlorochromanone **20** in 55% yield, probably because of the trans addition of the acetoxy anion and chloronium cation to the C-2 and C-3 double bond of the chromone nucleus. Its structure was supported by the hydrolysis of **20** with 1N HCl to **2**. On the other hand, 4 - oxo - 4*H* - 1 - benzopyran - 3 - carbonitrile **21**[19] was treated similarly with aqueous sodium hypochlorite to afford 2 - acetoxy - 3 - chloro - 3 - cyano-



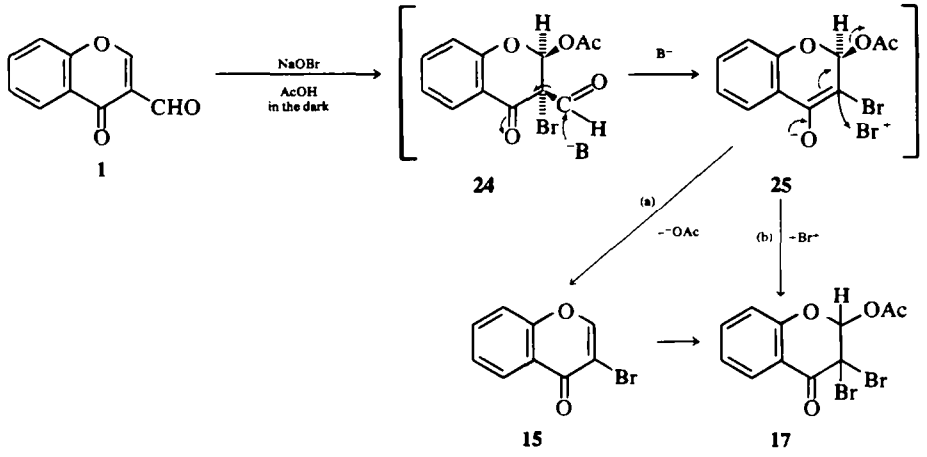
SCHEME 2.

chromanone **22** in 62% yield, which could be hydrolyzed with aqueous acetic acid in the presence of sodium acetate to 2 - amino - 3 - chlorochromone **23**. The reaction mechanisms of **20** to **2** and **22** to **23** are shown in the Scheme 3.

The Hunsdiecker reaction proceeds through a radical mechanism in anhydrous media, whereas **18** reacts with hypochlorite in the presence of water to afford **2**. Therefore the radical mechanism is very unlikely in the conversion of 4 - oxo - 4*H* - 1 -



SCHEME 3.



SCHEME 4.

benzopyran - 3 - carboxaldehydes and **18** to 3-halogenochromones. As the addition of an acetoxy anion and halogenium cation to the C-2 and C-3 double bond of C_2 unsubstituted chromones (e.g. **19** or **21**) occurs readily, the following halogenation mechanism which involves the addition-elimination reaction is reasonable. As a representative example, the conversion of **1** to **15** in the dark is given in Scheme 4. The initial step is the addition of an acetoxy anion and bromonium ion (or acetyl hypobromite) to chromone nucleus. The formyl group of **24** so produced may be attacked by base (e.g. acetoxy anion) to afford **25** which will be followed by (a) elimination of an acetoxy group at C-2 to produce **15** or (b) an attack of bromonium ion at C-3 to produce **17**. **17** is also produced from **15** at the same time. The proposed pathways involves 2 - acetoxy - 3 - formyl - 3 - bromochromanone **24** as an intermediate but the detection of **24** was unsuccessful.

EXPERIMENTAL

M.ps were taken with micro melting point apparatus (Yanagimoto) and are uncorrected. IR spectra were recorded on a Hitachi Infrared Spectrophotometer EPI-S2. NMR spectra were measured on Varian Associates T-60 instrument, and are given parts per million (δ) downfield from an internal TMS standard. Mass spectra were recorded with Hitachi RMU-6D or Hitachi RMS-4 instruments. TLC-sheets Woelm pre-coated Silica gel F 254/366 were used for TLC. PLC-plate Silica'gel F_{254} (Merck) was used for preparative layer chromatography.

3-Chlorochromone (**2**) *and 2-acetoxy-3,3-dichlorochromanone* (**3**). To a stirred soln of **1**[13,14] (5·22 g; 30 mmole) in 90 ml AcOH, 30 ml of NaOCl aq (active chlorine; *ca* 10%) was added at room temp during 10 min. After 20 min, the solvent was evaporated *in vacuo* and EtOAc and H_2O were added. The organic solvent layer was separated, dried (Na_2SO_4), treated with active carbon, and evaporated *in vacuo*. The residual crystals were recrystallized from EtOH to afford **2** (4·69 g; 86%) as colorless needles, m.p. 114–115° (lit.[5] 112–113°). This material was identical with an authentic sample prepared by the method of Zagorevskii.[5]

The mother liquor was evaporated *in vacuo*, and the residual oil was chromatographed on a silica gel dry column (42 g) using (1) benzene (100 ml) (2) $CHCl_3$ (100 ml) and (3) $CHCl_3$-acetone-HCO_2H (9 : 1 : 0·1) (200 ml). The third of the six eluates gave **3** (108 mg, 1% yield) as colorless crystals, m.p. 86·5–87·5°. IR (KBr) cm^{-1}: 1780 (CO), 1720 (chromanone CO), NMR ($CDCl_3$): 8·0 (1H, dd, J = 8 and 2 Hz, H_5), 7·4–7·8 (1H, m, H_7), 6·9–7·3 (2H, m, $H_{6,8}$), 6·72 (1H, s, H_2), 2·10 (3H, s, OAc). Mass spectrum: *m/e* 274, 276, 278 (ratio 8 : 5 : 1, M^+), 232, 234, 236 (ratio 10 : 6 : 1, M^+–CH_2CO), 215, 217, 219 (ratio 9 : 6 : 1, *m/e* 232–OH), 180, 182 (ratio 2 : 1, *m/e* 215-Cl), 163, 121, 120, 92. (Found: C, 47·80; H, 2·71. Calcd for $C_{11}H_8Cl_2O_4$: C, 48·03; H, 2·93%).

2,2,3',5' - Tetrabromo - 2' - hydroxyacetophenone (**14**), *3 - bromochromone* (**15**) *and 2 - hydroxy - 3,3 - dibromochromanone* (**16**). A mixture of **1** (1·74 g; 10 mmole) and 30 ml AcOH was heated and the resulting soln cooled to room temp, and 15 ml of 38% NaOBr aq was added at room temp during 1 hr and stirring was continued for 1 hr. The separated yellow crystals were collected and recrystallized from EtOH to afford **14** (1·37 g; 30%) as yellow needles, m.p. 121–122° (lit.[17] m.p. 120–121°). IR (KBr) cm^{-1}: 1655 (CO). NMR ($CDCl_3$): 11·88 (1H, s, OH), 8·02 (1H, d, J = 2 Hz, $H_{6'}$), 7·95 (1H, d, J = 2 Hz, $H_{4'}$), 6·66 (1H, s, H_2). Mass spectrum: *m/e* 448, 450, 452, 454, 456 (ratio 2 : 8 : 11 : 8 : 2, M^+). (Found: C, 21·50; H, 0·96. Calcd for $C_8H_4Br_4O_2$: C, 21·27; H, 0·89%).

The filtrate was evaporated to dryness *in vacuo*, and EtOAc and H_2O were added. The organic layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. TLC showed two compounds (R_f 0·80 and 0·57) which were separated by a PLC (silica gel in $CHCl_3$-acetone-HCO_2H (9 : 1 : 0·1)). The corresponding portions of silica gel on the plate were removed and eluted with acetone. The first fraction (R_f 0·80) was crystallized from EtOH to afford **15** (170 mg; 8%) as colorless needles, m.p. 96–97° (lit.[10] m.p. 93°). The second fraction (R_f 0·57) gave **16** (270 mg; 8%) as a colorless oil. Mass spectrum: *m/e* 320, 322, 324 (1 : 2 : 1, M^+). IR (neat) cm^{-1}: 3400 (OH), 1710, 1695, 1610. NMR ($CDCl_3$): 7·97 (1H, dd, J = 2 and 8 Hz, H_5), 7·60 (1H,

dt, J = 2 and 8 Hz, H_7), 6·92–7·30 (2H, m, $H_{6,8}$), 5·43 (1H, s, H_2), 4·08 (1H, mound, OH). (Found: C, 33·52; H, 1·60. Calcd for $C_9H_6Br_2O_3$: C, 33·57; H, 1·88%).

Compound **15** *and* 2 - *acetoxy* - 3,3 - *dibromochromanone* (**17**). To a warm soln of **1** (870 mg; 5 mmole) in 15 ml AcOH, protected from normal laboratory lighting, 7 ml of 38% NaOBr aq was added during 5 min, and stirring was continued for 1 hr at room temp. The solvent was evaporated *in vacuo*, and EtOAc and H_2O were added and the organic layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residual oil was chromatographed on 50 g of silica gel (benzene and next benzene-acetone (1:1)). Evaporation of the first eluate *in vacuo* gave a solid which was recrystallized from EtOH to afford **17** (525 mg; 28·5%) as colorless prisms, m.p. 101–102°. IR (KBr) cm^{-1}: 1775 (OAc), 1710 (CO), NMR ($CDCl_3$): 7·95 (1H, dd, J = 7 and 2 Hz, H_5), 7·55 (1H, dt, J = 7 and 2 Hz, H_7), 6·9–7·27 (2H, m, $H_{6,8}$), 6·67 (1H, s, H_2), 2·10 (3H, s, OAc). (Found: C, 36·54; H, 2·22. Calcd for $C_{11}H_8Br_2O_4$: C, 36·30; H, 2·21%).

Evaporation of the second eluate *in vacuo* gave crystals which were recrystallized from EtOH to afford **15** (398 mg; 32%) as colorless plates, m.p. 93–95°.

Production of **17** *from* **15**. To a soln of **15** (50 mg; 0·222 mmole) in 1 ml AcOH, 0·5 ml of 38% NaOBr aq was added and the vessel stoppered and protected from light at room temp for 3 days. The separated crystals were collected by filtration and recrystallized from EtOH to afford **17** (42 mg, 52%).

Production of **15** *from* **17**. A soln of **17** (182 mg; 0·5 mmole), anhyd LiCl (63 mg; 1·5 mmole) in 1 ml dimethylformamide was heated at 100° for 1·5 hr, and extracted with EtOAc after diluting with 20 ml of H_2O. The EtOAc phase was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was recrystallized from EtOH to give 16 mg (14%) of light yellow needles, m.p. 94·5–95·5. This material was identical with an authentic sample.

Production of **17** *by the acetylation of* **16**. A soln of **16** (100 mg; 0·31 mmole), 1 ml Ac_2O and 0·5 ml pyridine was kept at room temp for 2 hr, and extracted 3 times with EtOAc after diluting with 20 ml 1N HCl. The EtOAc phase was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was dissolved in EtOH and cooled when colorless prisms of **17** separated out, (56 mg; 50%), m.p. 101–102°. This material was identical with the sample prepared by the above method.

Reaction of 4 - *oxo* - 4*H* - 1 - *benzopyran* - 3 - *carboxylic acid* (**18**[1,14]) *with* NaOCl. To a soln of **18** (190 mg; 1 mmole) in 10 ml AcOH, 1 ml of NaOCl aq (active chlorine; *ca* 10%) was added at room temp with stirring for 30 min. The solvent was evaporated *in vacuo* and EtOAc and H_2O were added. The organic solvent layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was chromatographed on a silica gel column in chloroform. The first component consisted of **3** (80 mg; 29%), m.p. 85–86°. The second component, **2** (74 mg; 41%) was recrystallized from EtOH: as colorless needles, m.p. 110–111°. Both meterials were identical with samples obtained before.

2 *Acetoxy* - 3 - *acetyl* - 3 - *chlorochromanone* (**20**). To a soln of **19**[13] (188 mg; 1 mmole) in 4 ml AcOH, 1·2 ml of NaOCl aq (active Cl; *ca* 10%) was added at room temp during 30 min. The solvent was evaporated *in vacuo*, and EtOAc and H_2O were added. The organic solvent layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residual oil was crystallized by cooling, affording 150 mg (55%) of colorless crystals, m.p. 71·5–72·5°. IR (KBr) cm^{-1}: 1775 (OAc), 1730 (Ac), 1705 (CO). NMR (CCl_4): 7·93 (1H, dd, J = 8 and 2 Hz, H_5), 7·45–7·75 (1H, m, H_7), 6·9–7·3 (2H, m, $H_{6,8}$), 6·66 (1H, s, H_2), 2·57 (3H, s, Ac), 1·98 (3H, s, OAc). Mass spectrum: *m/e* 282, 284 (ratio 3:1, M^+), 240, 242 (ratio 3:1, M^+–CH_2CO), 205 (240-Cl). (Found: C, 55·10; H, 3·67. Calcd for $C_{13}H_{11}ClO_5$: C, 55·24; H, 3·92%).

Production of **2** *by the hydrolysis of* **20**. A mixture of **20** (100 mg; 0·355 mmole), 2 ml 1N HCl and 2 ml MeOH was heated at 80° for 1 hr and then evaporated *in vacuo*, H_2O and EtOAc were added and the organic solvent layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. Crystallization of resulting oil from EtOH afforded 15 mg (23%) of colorless prisms, m.p. 111–112°. This material was identical with an authentic sample.

2 - *Acetoxy* - 3 - *chloro* - 3 - *cyanochromanone* (**22**). Compound **21**[19] (1·71 g; 10 mmole) was dissolved in 40 ml AcOH by heating and the soln was cooled to room temp and 18 ml of NaOCl aq soln (active Cl; *ca* 10%) was added during 1 hr. The mixture was evaporated *in vacuo*, and EtOAc and H_2O were added to the residue. The organic layer was separated, washed with H_2O, dried (Na_2SO_4), treated with active carbon and evaporated *in vacuo*. EtOH was added to the resulting syrup and the soln was cooled till crystals separated out. Recrystallization from EtOH afforded 1·64 g (62%) of colorless tablets, m.p. 92·5–93·5°. IR (KBr) cm^{-1}: 1788 (OAc), 1710 (CO). NMR ($CDCl_3$): 7·95 (1H, dd, J = 2 and 8 Hz, H_5), 7·63 (1H, dt, *J* = 2 and 8 Hz, H_7), 6·93–7·33 (2H, m, $H_{6,8}$), 6·72 (1H, s, H_2), 2·13 (3H, s, OAc). (Found: C, 54·36; H, 2·78; N, 5·36. Calcd for $C_{12}H_8ClNO_4$: C, 54·26; H, 3·03; N, 5·27%).

2 - *Amino* - 3 - *chlorochromone* (**23**). A mixture of **22** (1·06 g; 4 mmole) and anhyd NaOAc (1·64 g; 20 mmole) in 40 ml AcOH and 4 ml H_2O was refluxed for 7 hr. The soln was evaporated *in vacuo*, and H_2O was added. Insoluble material was collected by filtration and recrystallized from acetone (charcoal) to afford 420 mg (54%) of yellow tablets, m.p. 277–279° (decomp). IR (KBr) cm^{-1}: 3520, 3325, 1677, 1652, 1610, 1540. NMR (CF_3COOD): 7·55–8·42 (only aromatic protons). Mass spectrum: *m/e* 195, 197 (ratio 3:1, M^+). (Found: C, 55·45; H, 2·79; Cl, 17·77; N, 7·20. Calcd for $C_9H_6ClNO_2$: C, 55·26; H, 3·09; Cl, 18·12; N, 7·16%).

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