Pyranoquinolines. Part I. Syntheses and ultraviolet absorption characteristics of 6-chloro-4*H*-pyrano[3,2-*h*]quinoline-4-ones

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6-Chloro-2-phenyl and 2-*p*-anisyl-4*H*-pyrano[3,2-*h*]quinoline-4-ones, their 2,3-dihydro and 3-hydroxy derivatives, and 6-chloro-3-benzoyl-2-phenyl-4*H*-pyrano[3,2-*h*]quinoline-4-one are synthesized by the application of appropriate flavonoid syntheses to 5-chloro-7-acetyl-8-hydroxyquinoline (**5**). **5** was formed on Friedel–Crafts acetylation of 5-chloro-8-methoxy and -8-hydroxyquinolines. Ultraviolet spectra of **5** are studied at three different pH's in aqueous ethanol and those of the pyranoquinolines are studied in ethanolic solutions and compared with those of their corresponding simple flavonoids.

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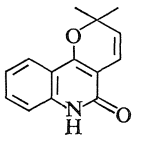
Survey of literature reveals that very few pyranoquinolines have been synthesized. Flindersine (1), isolated from *Flindersia australis* R.Br., is a pyrano[3,2-*c*]quinoline derivative (**1**) and



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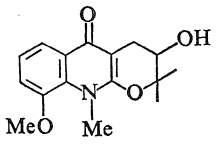

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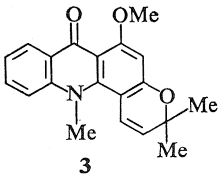

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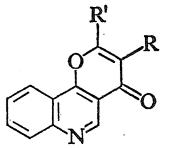

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isobalfourodine (**2**) (2) isolated from *Balfouradendron riedelianum* is a pyrano[2,3-*b*]quinoline derivative. Acronycine (**3**), isolated from *A. bauerii* (3) can be regarded as a pyrano[2,3-*h*]-quinoline derivative. Elliott and Tittensor (4) have reported syntheses of 2R′-3R-4*H*-pyrano-[3,2-*c*]quinoline derivatives. The fact that the pyranoquinolines are rare was the main consideration in the selection of the work described in the present communication dealing with the syntheses of 6-chloro-2-phenyl and 2-*p*-anisyl-4*H*-pyrano[3,2-*h*]quinoline-4-ones. This provided an opportunity of studying the application of some of the well known methods of flavonoid synthesis to an *o*-hydroxyquinolinone derivative (**5**). The ultraviolet spectra of the pyranoquinolines described in this communication are studied with a view to revealing their characteristic spectral trends and correlating them with those of their parent bicyclic quinoline and flavonoid derivatives.

The Friedel–Crafts acetylation of 5-chloro-8-hydroxyquinoline (**6**), formed on chlorination of 8-hydroxyquinoline (5), was studied using different proportions of the reactants in absence of any solvent and also in presence of solvents like carbon disulfide or nitrobenzene. The product viz., 5-chloro-7-acetyl-8-hydroxyquinoline (**5**) was formed in 40% yield when the reaction was carried out by heating a mixture of 5-chloro-8-hydroxyquinoline (1 part), acetyl chloride (2 parts), and anhydrous aluminium chloride (3 parts) at 120–130° for 12 h. When Friedel–Crafts acetylation of 5-chloro-8-methoxyquinoline (**7**) was effected under similar conditions, **5** was formed in about 50% yield. **7** was formed by the application of Skraup synthesis to 2-methoxy-5-chloroaniline following the method described by Weizmann and Bograchov (6) with the only modification that acetic acid was used as a diluent. It may be interesting to note that 8-hydroxyquinoline on Friedel–Crafts acylation affords 5-acyl-8-hydroxyquinoline in 52% yield (7). The hydroxyquinolinone (**5**) dissolved in dilute alkali solution but was almost insoluble in dilute acid solution. It developed a violet color with aqueous Fe^{+3} solution.

The condensation of **5** with benzaldehyde in presence of alcoholic alkali solution was carried out at room temperature and also at 80°. The product (**8**) obtained did not respond to the characteristic color reactions of a chalcone (8) and remained unchanged on prolonged refluxing with alcoholic acid solution. This suggested that

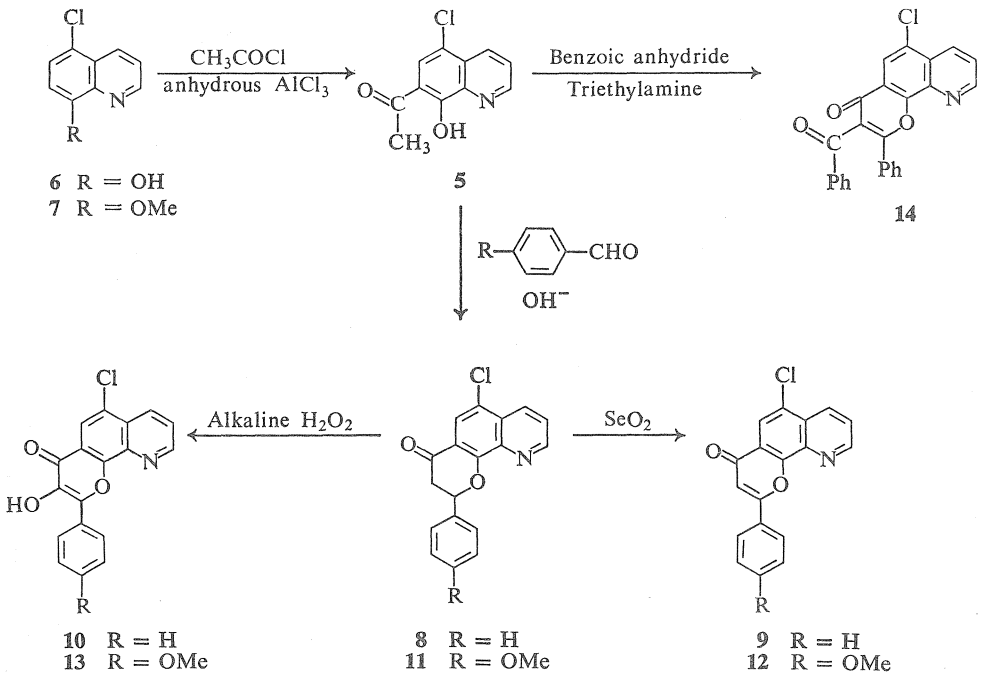


Chart I

the product **8** was not a chalcone but a flavanone derivative, 6-chloro-2-phenyl-4*H*-2,3-dihydropyrano[3,2-*h*]quinoline-4-one (**8**); this was also supported by the nature of its ultraviolet spectrum. The flavanone (**8**) was dehydrogenated on treatment with selenium dioxide (9) in dioxan solution to 6-chloro-2-phenyl-4*H*-pyrano[3,2-*h*]-quinoline-4-one (**9**). The Algar–Flynn oxidation (10) of **8** afforded 6-chloro-3-hydroxy-2-phenyl-4*H*-pyrano[3,2-*h*]quinoline-4-one (**10**). The latter compound (**10**) was also formed in very low yield when **8** was allowed to react with pentyl nitrite in alcoholic hydrochloric acid solution. These reactions have been summarized in Chart I.

6 - Chloro - 2 - *p* - anisyl - 4*H* - pyrano[3,2-*h*]-quinoline-4-ones **11**, **12**, and **13** (Chart I) were synthesized starting with **5** and anisaldehyde following the methods described for the synthesis of their corresponding desmethoxy analogues **8**, **9**, and **10** respectively. In this case too, the chalcone type of compound was not formed on condensing **5** with anisaldehyde but the flavanone derivative, 6-chloro-2-*p*-anisyl-4*H*-2,3-dihydropyrano[3,2-*h*]quinoline-4-one (**11**) was formed. All the reactions in this series ran much more smoothly giving better products than the corresponding reactions in the previous series.

Kostanecki–Robinson reaction of 5-chloro-7-acetyl-8-hydroxyquinoline (**5**) with benzoic anhydride in presence of triethylamine afforded 6-chloro-3-benzoyl-2-phenyl-4*H*-pyrano[3,2-*h*]-quinoline-4-one (**14**). The latter compound could not be deacylated when it was treated with hot 10% alkali solution. It is reported by Bhullar and Venkataraman (11) that 3-benzoyl-α-naphthoflavone having an angular structure analogous to that of **14** does not undergo deacylation on treatment with hot dilute alkali. A one-step Baker–Venkataraman transformation comprising a reaction between an *o*-hydroxyacetophenone derivative (12) with an acyl halide in presence of anhydrous potassium carbonate was applied to **5**. The latter (**5**) on treatment with benzoyl chloride in presence of anhydrous potassium carbonate in dry acetone afforded the flavone derivative (**9**). Some of these pyranoquinolines gave color reactions characteristic of flavonoids.

Thus all the above-mentioned flavonoid syntheses are applicable to 5-chloro-7-acetyl-8-hydroxyquinoline. The corresponding pyranoquinolines are formed in comparatively good yields. In this respect, **5** behaves like a simple *o*-hydroxyacetophenone derivative. This is not surprising as

TABLE I

Spectral data for 5-chloro-8-hydroxy and 5-chloro-7-acetyl-8-hydroxyquinolines

Compound	Medium	Band II λ_{max} (mμ) (log ε)	Band I λ_{max} (mμ) (log ε)
5	Acidic (pH = 1.2)	230* sh (4.10) 271 (4.49)	364 (3.50)
	Basic (pH = 14.0)	285 (4.39)	372–373 (3.95)
	Neutral (pH = 8.5)	230 In (4.10) 269 (4.41) 288 sh (3.87)	365–366 b (3.66)
6	Acidic (pH = 1.1)	226 In (3.98) 261 (4.66)	305 (3.34) 375–385 b (3.41)
	Basic (pH = 14.0)	258 (4.51)	346 (3.56) 380–385 (3.60)
	Neutral (pH = 8.4)	246 (4.56) 264 sh (3.70)	329 (3.56)

*Sh, shoulder; In, Inflection; b, broad.

the quinoline is a stable ring system and 8-hydroxyquinoline behaves like a true phenol (13). However, Pechmann condensation between 5-chloro-8-hydroxyquinoline and acetoacetic ester failed. The reaction was carried out both in presence of concentrated sulfuric acid and polyphosphoric acid. This seems to be due to absence of any activating group in a position para with respect to the point of cyclization (7-position) (14).

The ultraviolet spectra of 5-chloro-7-acetyl-8-hydroxyquinoline (**5**) were studied in aqueous alcoholic solution at three different pH's. The spectral curves are shown in Fig. 1 and the spectral data along with those of 5-chloro-8-hydroxyquinoline (**6**) are recorded in Table I. The ultraviolet spectrum of **6** was studied by Chakrabarty and co-workers (15) at different pH's for the determination of the acid dissociation constant. The ultraviolet spectrum of **5** in aqueous alcoholic solution at pH = 8.5 comprises two bands. The long wavelength band, designated as band I, forms a broad peak at 365 mμ (log ε = 3.66) and the short wavelength band, designated as band II, comprises an inflection at 230 mμ (log ε = 4.1), a sharp intense peak at 269 mμ (log ε = 4.41) and a shoulder at 288 mμ (log ε = 3.87). The spectrum of the compound **5** in the acidic medium (pH = 1.2) resembles very closely its spectrum at 8.5 pH. This suggested that the compound **5** exists mostly in the non-protonated form in acid solution and thereby indicating that it (**5**) is a very weak base. The spectrum of the compound **5** in the basic medium (pH = 14) however differs much from those in the acid and neutral media; the band II has suffered a bathochromic shift of 15 mμ and the band I has become broader and more intense than the corresponding bands in the spectra in the other two media. The bathochromic shift, broadening of the band and the increased intensity observed in the spectrum in the basic medium seems to be due to the anionic form in which the

TABLE II

Spectral data for pyranoquinoline derivatives and flavonoids

Compound	Band II λ_{max} (mμ) (log ε)	Band I λ_{max} (mμ) (log ε)
5	230* sh (4.10) 269 (4.40)	364–367 b (3.66)
8	224 In (4.19) 268 (4.43)	314 (3.93)
11	226 (4.45) 268 (4.51)	355–365 b (3.95)
9	241 (4.32) 282 (4.56)	
12	240 (4.30) 280–330 (4.2)	
10	235 (4.43) 280 (4.4)	335–338 sh (4.1)
13	236 (4.50) 284 (4.21)	340–370 b (3.63)
14	272 (4.58)	
15	220 (4.45) 246 sh (3.9) 284 In (3.4)	327 (3.62)
16	245 (4.22) 275–285 sh (3.76)	340–360 b (3.57)
17	255 (4.23)	298 (4.22)
18	275–280 (4.49)	

*Sh, shoulder; In, Inflection; b, broad.

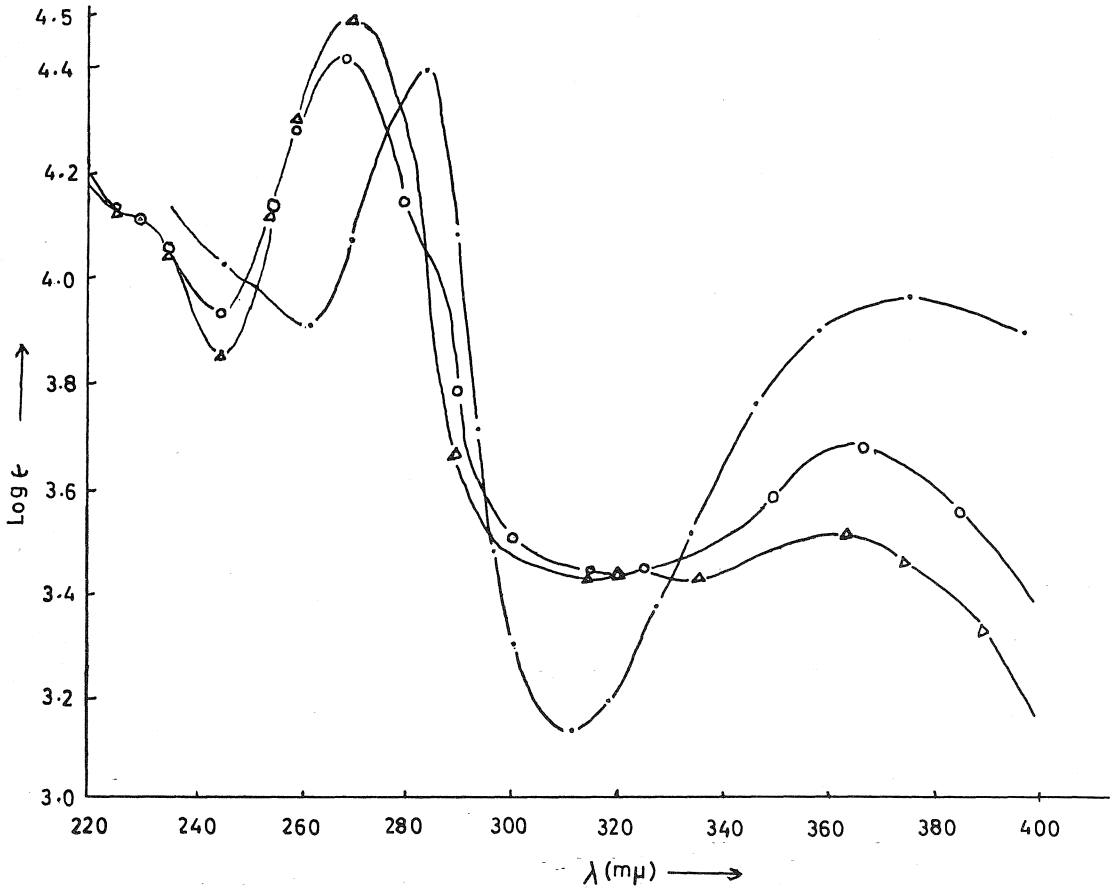
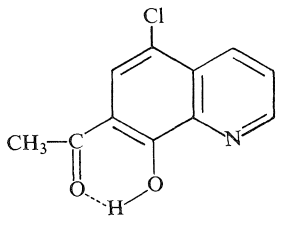


FIG. 1. The ultraviolet spectra of 5-chloro-7-acetyl-8-hydroxyquinoline (**5**) in acidic (—△—△—), basic (—•—•—), and neutral (—O—O—) media.

compound **5** would mostly exist in the basic medium. That the anionic form would prove a stronger chromophore than the neutral acid form has been observed in case of phenols and naphthols (16).

A comparative study of the spectrum of the compound **5** and its parent compound 5-chloro-8-hydroxyquinoline (**6**) reveals that all the bands in the spectrum of *o*-hydroxyquinolinone derivative (**5**) appear at longer wavelengths or are more intense than the corresponding bands in the spectrum of the compound **6**. This seems to be due to the strong hydrogen bond formation (chelation) between the hydroxy–hydrogen and the carbonyl–oxygen atoms (**5***a*).

The ultraviolet spectra of the pyranoquinolines (**8–14**) are studied in alcoholic solution. The



5*a*

spectral data are reported in Table II and the spectral curves are shown in Figs. 2 and 3.

It is reported that the spectrum of a flavanone comprises a strong absorption in 270–290 mμ region and a weak absorption in the form of inflection in the 320–330 mμ region; these bands have been designated as bands II and I respectively

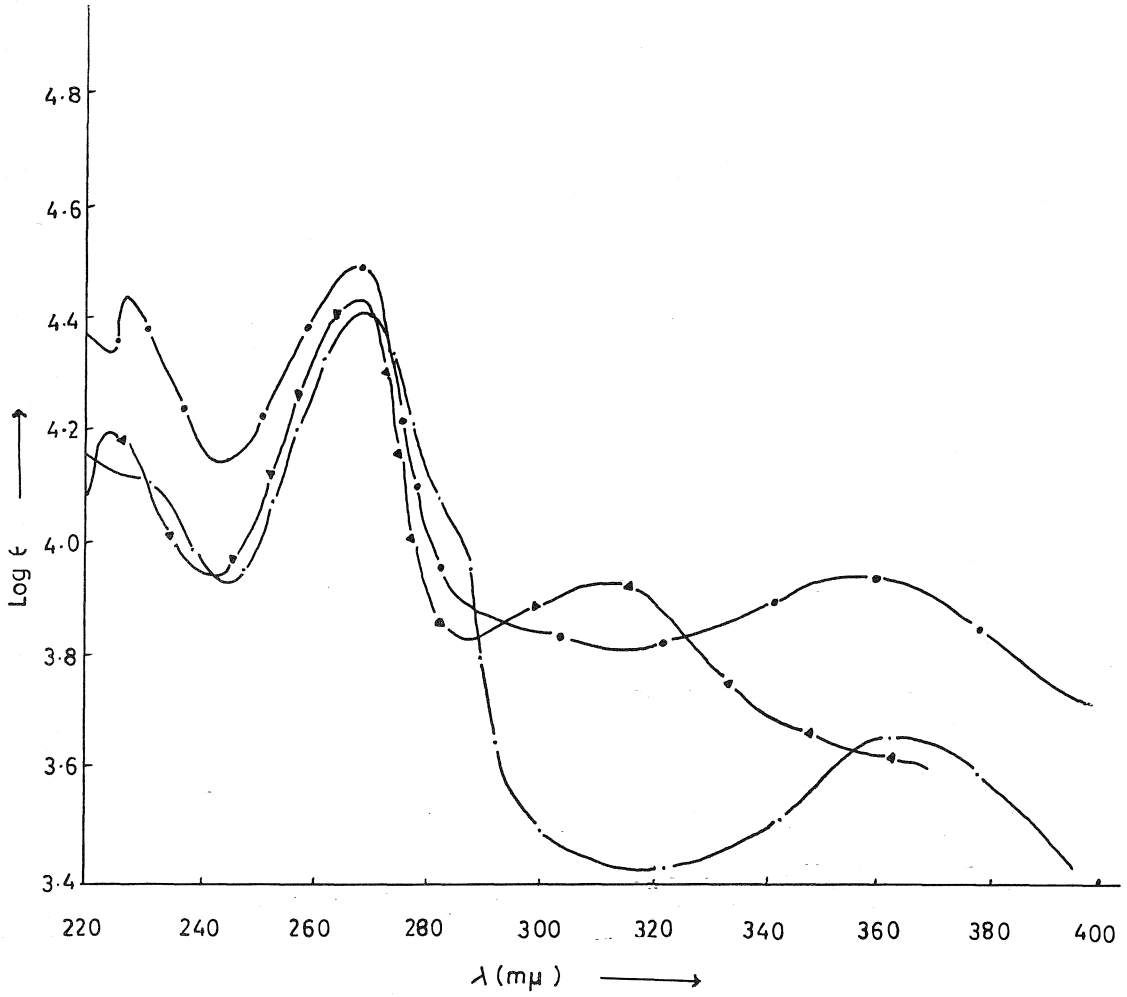


FIG. 2. The ultraviolet spectra of 5-chloro-7-acetyl-8-hydroxyquinoline (**5**) (—.—.—), 6-chloro-2-phenyl-4*H*-2,3-dihydropyrano[3,2-*h*]quinoline-4-one (**8**) (—▲—▲—), and 6-chloro-2-*p*-anisyl-4*H*-2,3-dihydropyrano[3,2-*h*]quinoline-4-one (**11**) (—.—.—).

(17). The spectrum of 6-chloro-2-phenyl-4*H*-2,3-dihydropyrano[3,2-*h*]quinoline-4-one (**8**) comprises two bands; band I appearing at 314 mμ ($\log \varepsilon = 3.93$) and band II comprising a sharp and more intense band at 268 mμ ($\log \varepsilon = 4.4$) and an inflection at 224 mμ ($\log \varepsilon = 4.19$). The band II in the spectrum of **8** resembles very closely the spectrum of the parent ketone 5-chloro-7-acetyl-8-hydroxyquinoline (**5**) (Fig. 2). This is not unexpected as in a flavanone there is no continuity of conjugation between the 2-phenyl and the carbonyl groups. The spectrum of 6-chloro-2-*p*-anisyl-4*H*-2,3-dihydropyrano[3,2-*h*]quinoline-4-one (**11**) also comprises two bands with the only difference that the band I in the spectrum of the compound **11** is more intense and appears at a longer wavelength than the corresponding band in the spectrum of its desmethoxy analogue (**8**).

The spectrum of 6-chloro-2-phenyl-4*H*-pyrano[3,2-*h*]quinoline-4-one (**9**) comprises a sharp inflection at 241 mμ and a prominent band of high intensity with a maxima near about 282 mμ. The low wavelength band II in the spectrum of a flavone has been attributed to the benzoyl grouping and any increase in conjugation in this grouping would result in a bathochromic shift and/or increase in the intensity of this band (18). In the flavone type pyranoquinoline **9**, the

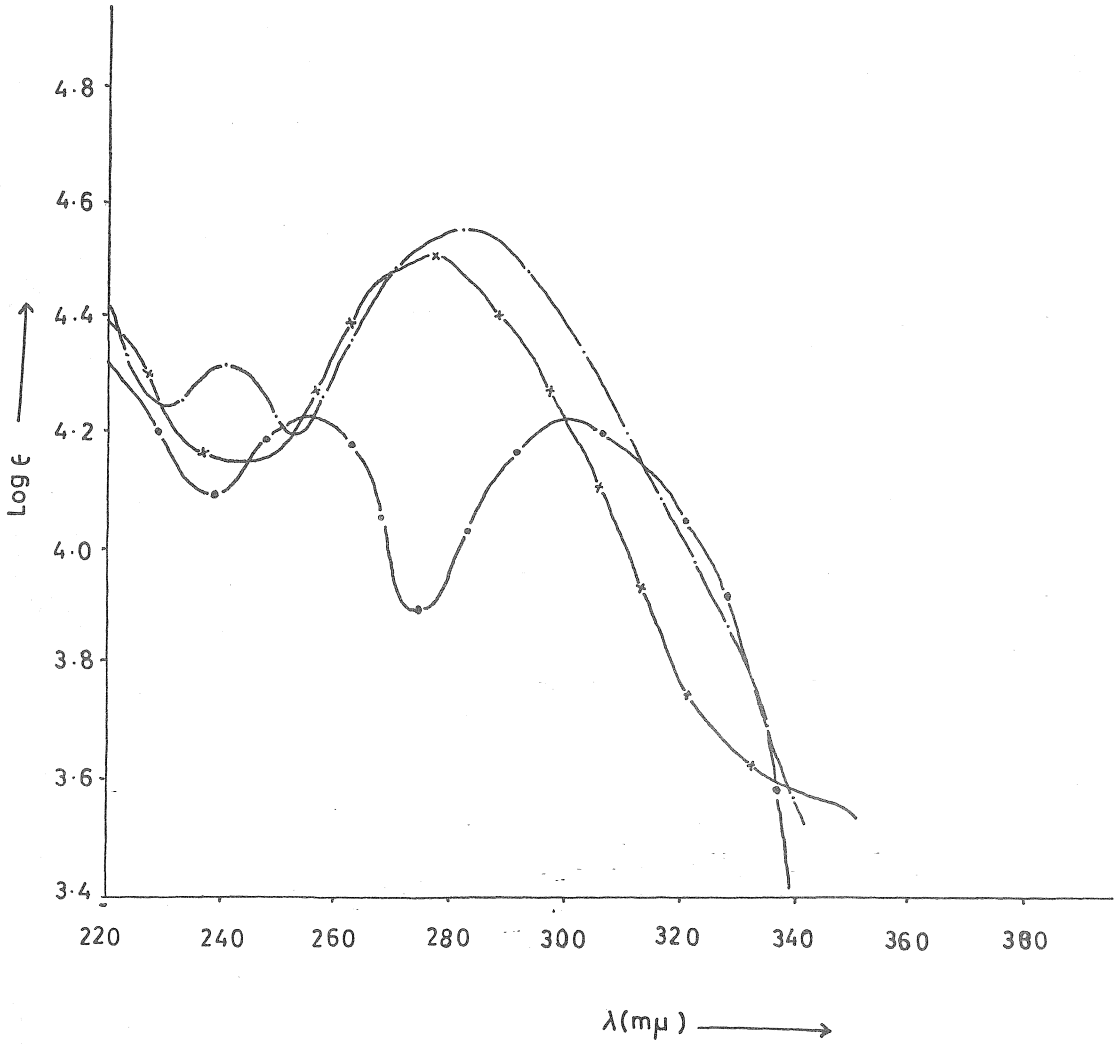


FIG. 3. The ultraviolet spectra of 6-chloroflavone (**17**) (—.—.—), 6-chloro-8-aminoflavone (**18**) (—×—×—), and 6-chloro-2-phenyl-4*H*-pyrano[3,2-*h*]quinoline-4-one (**9**) (—.—.—).

benzoyl grouping of a flavone is replaced by a quinonoyl grouping. This quinonoyl grouping being a stronger chromophore than the benzoyl grouping seems to be responsible for the prominent band II exhibited by the flavone type pyranoquinoline **9**. The long wavelength band which normally appears in the spectrum of a flavone in the region 320–380 mμ (19) is absent in the spectrum of **9**. It is likely that this band I has merged with the tail part of the intense band II and hence appears to have disappeared. The spectrum of 6-chloro-2-*p*-anisyl-4*H*-pyrano[3,2-*h*]quinoline-4-one (**12**) comprises a sharp inflection at 240 mμ and a very broad band ranging from 280 to 330 mμ with the log ε varying from 4.3 to 4.1. Due to the presence of the *p*-methoxy group in the cinnamoyl grouping, the band I in the spectrum of **12** would be more intense and would have undergone a red shift. Hence the broad 280–330 mμ band in the spectrum of **12** seems to be a continuous band comprising the end-part of the band II and whole of band I.

The spectra of the flavonol type of pyranoquinolines **10** and **13** comprise two bands. The band II in the spectra of each of these two compounds consists of an inflection at 235 mμ and a small peak at 280 mμ. The band I appears in the form of shoulder in the spectrum of **10** near

about 335 mμ and in the form of a broad band in the spectrum of **13**.

The spectrum of 6-chloro-3-benzoyl-2-phenyl-4*H*-pyrano[3,2-*h*]quinoline-4-one (**14**) comprises only one intense band appearing at 272 mμ (log ε = 4.58). The disappearance of one of the bands and the high intensity of the constituent band in the spectrum seems to be due to the additional —C—Ph group in 3-position.

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In order to bring forth the characteristics of the ultraviolet spectra of flavone and flavanone type pyranoquinolines which might distinguish them from their simple analogues, the ultraviolet spectra of 6-chloro, 6-chloro-8-aminoflavones, and flavanones and the corresponding pyrano-[3,2-*h*]quinoline derivatives are compared. The spectral data are given in Table II and spectral curves of only the flavone type of compounds are shown in Fig. 3. Comparative study of these spectral data reveals that in the flavanone type of compounds a continuous bathochromic shift and hyperchromic change is discernible as one passes from spectra of 6-chloro-2:3-dihydroflavone (**15**) to that of 6-chloro-2:3-dihydro-8-aminoflavone (**16**) and to that of 6-chloro-2-phenyl-4*H*-2,3-dihydropyrano[3,2-*h*]quinoline-4-one (**8**). In the flavone type of compounds, 6-chloroflavone (**17**) exhibits a two band spectrum—255 mμ (log ε = 4.23); 298 mμ (log ε = 4.22). The spectrum of 6-chloro-8-aminoflavone (**18**) comprises only one prominent and a comparatively more intense band at 275–280 mμ (log ε = 4.49). The spectrum of 6-chloro-2-phenyl-4*H*-pyrano[3,2-*h*]quinoline-4-one (**9**) comprises a similar but slightly more intense band appearing at a slightly longer wavelength and a characteristic distinguishing small peak at 241 mμ (log ε = 4.32).

This spectral analysis of pyranoquinoline derivatives thus reveals that the spectra do not exhibit any outstandingly distinguishing characteristics, except the ones which arise due to increased conjugation.

Experimental

The ultraviolet spectra of the compounds described in this communication are studied in ethanolic or aqueous ethanolic solution on Beckmann DU spectrophotometer. The ultraviolet spectra of 5-chloro-8-hydroxyquinoline and 5-chloro-7-acetyl-8-hydroxyquinoline are studied at three different pH's. The solvent composition was maintained constant in all the three media. The nearly neutral, acidic or basic solution of **5** (or **6**) was prepared by adding 20 ml of distilled water, 20 ml of 0.1 *M* HCl or 20 ml of 0.1 *M* NaOH to 80 ml of the pure ethanolic solution of the compound respectively. The ultraviolet spectra of other compounds were studied in pure ethanolic solution. In all these cases the concentrations of the reagent in solution were maintained accurately around 3×10^{-5} *M*.

5-Chloro-8-methoxyquinoline (7)

To a mixture of 2-methoxy-5-chloroaniline (20 g), arsenic oxide (18 g), glycerine (36 g), and acetic acid (40 ml) cooled in an ice-bath, concentrated sulfuric acid (50 g) was added in small lots over a period of 2 h. The reaction mixture was heated at 160–170° for 8 h, cooled, poured in ice-water, and filtered. The solid product obtained on rendering the filtrate alkaline was collected, washed, dried, and extracted in benzene. The solid product left on removal of benzene was purified by distillation under reduced pressure at 210–215° at 20 mm, m.p. 60–61° (6); yield 43%.

5-Chloro-7-acetyl-8-hydroxyquinoline (5)

A mixture of 5-chloro-8-hydroxyquinoline (1 g), acetyl chloride (2 g), and finely powdered anhydrous aluminium chloride (3 g) was left overnight at 0° and heated at 120–130° for 12 h, cooled, and decomposed with crushed ice and concentrated hydrochloric acid (2 ml). The solid product was collected, washed with water, dried in air and crystallized from aqueous ethanol (1:1) in yellow needles, m.p. 160–161°; yield 0.5 g.

5 was formed in about 50% yield when the reaction was carried out as described above using 5-chloro-8-methoxyquinoline in place of 5-chloro-8-hydroxyquinoline.

Anal. Calcd. for $C_{11}H_8O_2NCl$: C, 59.5; H, 3.6; N, 6.3; Cl, 16.0. Found: C, 59.3; H, 3.8; N, 6.0; Cl, 16.3.

6-Chloro-2-phenyl-4H-2,3-dihydropyrano[3,2-h]-quinoline-4-one (8)

A solution of **5** (0.5 g) and benzaldehyde (0.4 ml) in ethanol (15 ml) was mixed with sodium hydroxide solution (10 ml, 30%) with stirring and left at room temperature for 24 h. It was then decomposed with crushed ice and acidified with hydrochloric acid. The solid product was filtered, washed with bicarbonate solution, and then with water. It was crystallized from aqueous acetic acid (1:1) in yellow light needles, m.p. 191–192°; yield 0.3 g.

This product remained unchanged when it was refluxed with alcoholic hydrochloric acid solution for 48 h.

Anal. Calcd. for $C_{18}H_{12}O_2NCl$: C, 69.7; H, 3.87; N, 4.5; Cl, 11.5. Found: C, 69.6; H, 3.95; N, 4.7; Cl, 11.2.

6-Chloro-2-p-anisyl-4H-2,3-dihydro-pyrano[3,2-h]quinoline-4-one (11)

It was formed on condensing **5** (0.5 g) with anisaldehyde (0.4 ml) following the method described above. The product was crystallized from glacial acetic acid in yellow granules, m.p. 201–202°; yield 0.2 g.

This product remained unchanged on prolonged treatment with hot alcoholic hydrochloric acid.

Anal. Calcd. for $C_{19}H_{14}O_3NCl$: C, 67.1; H, 4.12; N, 4.1; Cl, 10.4. Found: C, 67.3; H, 4.35; N, 4.0; Cl, 10.2.

6-Chloro-2-phenyl-4H-pyrano[3,2-h]quinoline-4-one (9)

A suspension of **8** (0.25 g) and selenium dioxide (0.3 g) in dioxan (8 ml) was refluxed at 110–120° for 18 h, diluted with acetic acid (10) and refltouxed. The reac-mlatedlytion mixture was repefilte,red (thrice) remove

suspended selenium and concentrated on a water bath. The product which separated was collected and crystallized from acetic acid in pinkish white needles, m.p. 273–274°; yield 0.1 g.

Anal. Calcd. for $C_{18}H_{10}O_2NCl$: C, 70.2; H, 3.25; N, 4.5; Cl, 11.5. Found: C, 70.1; H, 3.0; N, 4.3; Cl, 11.8.

*6-Chloro-2-p-anisyl-4H-pyrano[3,2-h]quinoline-4-one (**12**)*

It was formed on treating **11** (0.25 g) with selenium dioxide (0.3 g) in dioxan (10 ml) as described above. It was crystallized from acetic acid in light-yellow needles, m.p. 303–304°; yield 0.08 g.

Anal. Calcd. for $C_{19}H_{12}O_3NCl$: C, 67.5; H, 3.55; N, 4.1; Cl, 10.5. Found: C, 67.8; H, 3.7; N, 4.0; Cl, 10.9.

*6-Chloro-3-hydroxy-2-phenyl-4H-pyrano[3,2-h]quinoline-4-one (**10**)*

It was synthesized by two methods.

*By Algar–Flynn Oxidation of **8** (Method a)*

A solution of **8** (0.2 g) in a mixture of methanol (10 ml) and 10% sodium hydroxide solution (6 ml) was cooled to 0° and mixed with hydrogen peroxide (5 ml, 20%). The reaction mixture was kept initially at 0° for 6 h and then at room temperature for 24 h. The product obtained on acidification was crystallized from acetic acid in light-yellow shining needles, m.p. 267–268°; yield 0.05 g.

*By the Action of Pentyl Nitrite on **8** (Method b)*

To a suspension of **8** (0.2 g) and pentyl nitrite (0.5 ml) in ethanol (5 ml), concentrated hydrochloric acid (5 ml) was added dropwise at room temperature and the mixture was left at room temperature for 6 h. More pentyl nitrite (0.5 ml) was added to the mixture and the reaction mixture was allowed to stand at room temperature for 6 h more. It was then diluted with water (10 ml), refluxed on a water-bath for 2 h, cooled, and neutralized with ammonia. The product was repeatedly crystallized from acetic acid in light-yellow shining needles, m.p. 267–268°; yield 0.02 g.

Anal. Calcd. for $C_{18}H_{10}O_3NCl$: C, 66.7; H, 3.09; N, 4.3; Cl, 10.9. Found: C, 66.5; H, 3.2; N, 4.3; Cl, 11.2.

*6-Chloro-3-hydroxy-2-p-anisyl-pyrano-[3,2-h]quinoline-4-one (**13**)*

It was formed on treatment of **11** (0.2 g) with hydrogen peroxide (5 ml, 20%) as described above in method *a*. It was crystallized from acetic acid in yellow powder, m.p. 295–296° (decomp.); yield 0.05 g.

Anal. Calcd. for $C_{19}H_{12}O_4NCl$: C, 64.4; H, 3.39; N, 3.9; Cl, 10.0. Found: C, 64.6; H, 3.5; N, 3.7; Cl, 10.3.

*6-Chloro-3-benzoyl-2-phenyl-4H-pyrano-[3,2-h]quinoline-4-one (**14**)*

A mixture of **5** (0.2 g), benzoic anhydride (0.8 g), and triethylamine (2 ml) was refluxed at 170–180° for 6 h, cooled and diluted with ether (10 ml). The product which separated out was collected, washed, dried, and crystallized from acetic acid in white shining needles, m.p. 281–282°; yield 0.1 g. It remained unchanged when treated with hot 10% alkali solution.

Anal. Calcd. for $C_{25}H_{14}O_3NCl$: C, 72.9; H, 3.4; N, 3.4; Cl, 8.6. Found: C, 73.1; H, 3.2; N, 3.6; Cl, 8.8.

*Baker–Venkataraman Transformation Reaction of 5-Chloro-7-acetyl-8-hydroxyquinoline: Formation of 6-chloro-2-phenyl-4H-pyrano[3,2-h]quinoline-4-one (**9**)*

A mixture of **5** (0.5 g), benzoyl chloride (0.5 ml), and anhydrous potassium carbonate (1 g) in dry acetone (35 ml) was refluxed for 24 h and distilled to remove acetone. The product which separated on treating the reaction mixture with water (25 ml) was collected, treated with concentrated sulfuric acid (15 ml) and poured on crushed ice. The solid product was filtered, washed, dried, and crystallized from acetic acid in pinkish white needles, m.p. 273–274°; yield 0.2 g. Mixture m.p. with the product obtained by the selenium dioxide dehydrogenation of the flavanone type pyranoquinoline (**8**) showed no depression.

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